

INTERNATIONAL TABLES
for CRYSTALLOGRAPHY

Volume

B

Reciprocal space

Edited by U. Shmueli

Second edition

INTERNATIONAL TABLES
FOR
CRYSTALLOGRAPHY

International Tables for Crystallography

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INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY

Volume B
RECIPROCAL SPACE

Edited by
U. SHMUELI

Second Edition

Published for
THE INTERNATIONAL UNION OF CRYSTALLOGRAPHY

by
KLUWER ACADEMIC PUBLISHERS

DORDRECHT/BOSTON/LONDON

2001

A C.I.P. Catalogue record for this book
is available from the Library of Congress
ISBN 0-7923-6592-5 (acid-free paper)

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, USA

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands

Technical Editor: N. J. Ashcroft

First published in 1993
Second edition 2001

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International Union of Crystallography

Printed in Great Britain by Alden Press, Oxford

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Preface

BY URI SHMUELI

The purpose of Volume B of *International Tables for Crystallography* is to provide the user or reader with accounts of some well established topics, of importance to the science of crystallography, which are related in one way or another to the concepts of reciprocal lattice and, more generally, reciprocal space. Efforts have been made to extend the treatment of the various topics to include X-ray, electron, and neutron diffraction techniques, and thereby do some justice to the inclusion of the present Volume in the new series of *International Tables for Crystallography*.

An important crystallographic aspect of symmetry in reciprocal space, space-group-dependent expressions of trigonometric structure factors, already appears in Volume I of *International Tables for X-ray Crystallography*, and preliminary plans for incorporating this and other crystallographic aspects of reciprocal space in the new edition of *International Tables* date back to 1972. However, work on a volume of *International Tables for Crystallography*, largely dedicated to the subject of reciprocal space, began over ten years later. The present structure of Volume B, as determined in the years preceding the 1984 Hamburg congress of the International Union of Crystallography (IUCr), is due to (i) computer-controlled production of concise structure-factor tables, (ii) the ability to introduce many more aspects of reciprocal space – as a result of reducing the effort of producing the above tables, as well as their volume, and (iii) suggestions by the National Committees and individual crystallographers of some additional interesting topics. It should be pointed out that the initial plans for the present Volume and Volume C (*Mathematical, Physical and Chemical Tables*, edited by Professor A. J. C. Wilson), were formulated and approved during the same period.

The obviously delayed publication of Volume B is due to several reasons. Some minor delays were caused by a requirement that potential contributors should be approved by the Executive Committee prior to issuing relevant invitations. Much more serious delays were caused by authors who failed to deliver their contributions. In fact, some invited contributions had to be excluded from this first edition of Volume B. Some of the topics here treated are greatly extended, considerably updated or modern versions of similar topics previously treated in the old Volumes I, II, and IV. Most of the subjects treated in Volume B are new to *International Tables*.

I gratefully thank Professor A. J. C. Wilson, for suggesting that I edit this Volume and for sharing with me his rich editorial experience. I am indebted to those authors of Volume B who took my requests and deadlines seriously, and to the Computing Center of Tel Aviv University for computing facilities and time. Special thanks are due to Mrs Z. Stein (Tel Aviv University) for skilful assistance in numeric and symbolic programming, involved in my contributions to this Volume.

I am most grateful to many colleagues—crystallographers for encouragement, advice, and suggestions. In particular, thanks are due to Professors J. M. Cowley, P. Goodman and C. J. Humphreys, who served as Chairmen of the Commission on Electron Diffraction during the preparation of this Volume, for prompt and expert help at all stages of the editing. The kind assistance of Dr J. N. King, the Executive Secretary of the IUCr, is also gratefully acknowledged. Last, but certainly not least, I wish to thank Mr M. H. Dacombe, the Technical Editor of the IUCr, and his staff for the skilful and competent treatment of the variety of drafts and proofs out of which this Volume arose.

Preface to the second edition

BY URI SHMUELI

The first edition of Volume B appeared in 1993, and was followed by a corrected reprint in 1996. Although practically all the material for the second edition was available in early 1997, its publication was delayed by the decision to translate all of Volume B, and indeed all the other volumes of *International Tables for Crystallography*, to Standard Generalized Markup Language (SGML) and thus make them available also in an electronic form suitable for modern publishing procedures.

During the preparation of the second edition, most chapters that appeared in the first edition have been corrected and/or revised, some were rather extensively updated, and five new chapters were added. The overall structure of the second edition is outlined below.

After an introductory chapter, Part 1 presents the reader with an account of structure-factor formalisms, an extensive treatment of the theory, algorithms and crystallographic applications of Fourier methods, and treatments of symmetry in reciprocal space. These are here enriched with more advanced aspects of representations of space groups in reciprocal space.

In Part 2, these general accounts are followed by detailed expositions of crystallographic statistics, the theory of direct methods, Patterson techniques, isomorphous replacement and anomalous scattering, and treatments of the role of electron

microscopy and diffraction in crystal structure determination. The latter topic is here enhanced by applications of direct methods to electron crystallography.

Part 3, *Dual Bases in Crystallographic Computing*, deals with applications of reciprocal space to molecular geometry and ‘best’-plane calculations, and contains a treatment of the principles of molecular graphics and modelling and their applications; it concludes with the presentation of a convergence-acceleration method, of importance in the computation of approximate lattice sums.

Part 4 contains treatments of various diffuse-scattering phenomena arising from crystal dynamics, disorder and low dimensionality (liquid crystals), and an exposition of the underlying theories and/or experimental evidence. The new additions to this part are treatments of polymer crystallography and of reciprocal-space images of aperiodic crystals.

Part 5 contains introductory treatments of the theory of the interaction of radiation with matter, the so-called dynamical theory, as applied to X-ray, electron and neutron diffraction techniques. The chapter on the dynamical theory of neutron diffraction is new.

I am deeply grateful to the authors of the new contributions for making their expertise available to Volume B and for their

PREFACE

excellent collaboration. I also take special pleasure in thanking those authors of the first edition who revised and updated their contributions in view of recent developments. Last but not least, I wish to thank all the authors for their contributions and their patience, and am grateful to those authors who took my requests seriously. I hope that the updating and revision of future editions will be much easier and more expedient, mainly because of the new format of *International Tables*.

Four friends and greatly respected colleagues who contributed to the second edition of Volume B are no longer with us. These are Professors Arthur J. C. Wilson, Peter Goodman, Verner Schomaker and Boris K. Vainshtein. I asked Professors Michiyoshi Tanaka, John Cowley and Douglas Dorset if they were prepared to answer queries related to the contributions of the late Peter Goodman and Boris K. Vainshtein to Chapter 2.5. I am most grateful for their prompt agreement.

This editorial work was carried out at the School of Chemistry and the Computing Center of Tel Aviv University. The facilities they put at my disposal are gratefully acknowledged on my behalf and on behalf of the IUCr. I wish to thank many colleagues for interesting conversations and advice, and in particular Professor Theo Hahn with whom I discussed at length problems regarding Volume B and *International Tables* in general.

Given all these expert contributions, the publication of this volume would not have been possible without the expertise and devotion of the Technical Editors of the IUCr. My thanks go to Mrs Sue King, for her cooperation during the early stages of the work on the second edition of Volume B, while the material was being collected, and to Dr Nicola Ashcroft, for her collaboration during the final stages of the production of the volume, for her most careful and competent treatment of the proofs, and last but not least for her tactful and friendly attitude.

1.1. Reciprocal space in crystallography

BY U. SHMUELI

1.1.1. Introduction

The purpose of this chapter is to provide an introduction to several aspects of reciprocal space, which are of general importance in crystallography and which appear in the various chapters and sections to follow. We first summarize the basic definitions and briefly inspect some fundamental aspects of crystallography, while recalling that they can be usefully and simply discussed in terms of the concept of the reciprocal lattice. This introductory section is followed by a summary of the basic relationships between the direct and associated reciprocal lattices. We then introduce the elements of tensor-algebraic formulation of such dual relationships, with emphasis on those that are important in many applications of reciprocal space to crystallographic algorithms. We proceed with a section that demonstrates the role of mutually reciprocal bases in transformations of coordinates and conclude with a brief outline of some important analytical aspects of reciprocal space, most of which are further developed in other parts of this volume.

1.1.2. Reciprocal lattice in crystallography

The notion of mutually reciprocal triads of vectors dates back to the introduction of vector calculus by J. Willard Gibbs in the 1880s (*e.g.* Wilson, 1901). This concept appeared to be useful in the early interpretations of diffraction from single crystals (Ewald, 1913; Laue, 1914) and its first detailed exposition and the recognition of its importance in crystallography can be found in Ewald's (1921) article. The following free translation of Ewald's (1921) introduction, presented in a somewhat different notation, may serve the purpose of this section:

To the set of $\mathbf{a}_i$, there corresponds in the vector calculus a set of 'reciprocal vectors' $\mathbf{b}_i$, which are defined (by Gibbs) by the following properties:

$$\mathbf{a}_i \cdot \mathbf{b}_k = 0 \quad (\text{for } i \neq k) \quad (1.1.2.1)$$

and

$$\mathbf{a}_i \cdot \mathbf{b}_i = 1, \quad (1.1.2.2)$$

where i and k may each equal 1, 2 or 3. The first equation, (1.1.2.1), says that each vector $\mathbf{b}_k$ is perpendicular to two vectors $\mathbf{a}_i$, as follows from the vanishing scalar products. Equation (1.1.2.2) provides the norm of the vector $\mathbf{b}_i$: the length of this vector must be chosen such that the projection of $\mathbf{b}_i$ on the direction of $\mathbf{a}_i$ has the length $1/a_i$, where a_i is the magnitude of the vector $\mathbf{a}_i$. . .

The consequences of equations (1.1.2.1) and (1.1.2.2) were elaborated by Ewald (1921) and are very well documented in the subsequent literature, crystallographic as well as other.

As is well known, the reciprocal lattice occupies a rather prominent position in crystallography and there are nearly as many accounts of its importance as there are crystallographic texts. It is not intended to review its applications, in any detail, in the present section; this is done in the remaining chapters and sections of the present volume. It seems desirable, however, to mention by way of an introduction some fundamental geometrical, physical and mathematical aspects of crystallography, and try to give a unified demonstration of the usefulness of mutually reciprocal bases as an interpretive tool.

Consider the equation of a lattice plane in the direct lattice. It is shown in standard textbooks (*e.g.* Buerger, 1941) that this equation is given by

$$hx + ky + lz = n, \quad (1.1.2.3)$$

where h , k and l are relatively prime integers (*i.e.* not having a common factor other than +1 or -1), known as Miller indices of the lattice plane, x , y and z are the coordinates of any point lying in the plane and are expressed as fractions of the magnitudes of the basis vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ of the direct lattice, respectively, and n is an integer denoting the serial number of the lattice plane within the family of parallel and equidistant (hkl) planes, the interplanar spacing being denoted by d_{hkl} ; the value $n = 0$ corresponds to the (hkl) plane passing through the origin.

Let $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$ and $\mathbf{r}_L = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where u , v , w are any integers, denote the position vectors of the point xyz and a lattice point uvw lying in the plane (1.1.2.3), respectively, and assume that $\mathbf{r}$ and $\mathbf{r}_L$ are different vectors. If the plane normal is denoted by $\mathbf{N}$, where $\mathbf{N}$ is proportional to the vector product of two in-plane lattice vectors, the vector form of the equation of the lattice plane becomes

$$\mathbf{N} \cdot (\mathbf{r} - \mathbf{r}_L) = 0 \quad \text{or} \quad \mathbf{N} \cdot \mathbf{r} = \mathbf{N} \cdot \mathbf{r}_L. \quad (1.1.2.4)$$

For equations (1.1.2.3) and (1.1.2.4) to be identical, the plane normal $\mathbf{N}$ must satisfy the requirement that $\mathbf{N} \cdot \mathbf{r}_L = n$, where n is an (unrestricted) integer.

Let us now consider the basic diffraction relations (*e.g.* Lipson & Cochran, 1966). Suppose a parallel beam of monochromatic radiation, of wavelength λ , falls on a lattice of identical point scatterers. If it is assumed that the scattering is elastic, *i.e.* there is no change of the wavelength during this process, the wavevectors of the incident and scattered radiation have the same magnitude, which can conveniently be taken as $1/\lambda$. A consideration of path and phase differences between the waves outgoing from two point scatterers separated by the lattice vector $\mathbf{r}_L$ (defined as above) shows that the condition for their maximum constructive interference is given by

$$(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{r}_L = n, \quad (1.1.2.5)$$

where $\mathbf{s}_0$ and $\mathbf{s}$ are the wavevectors of the incident and scattered beams, respectively, and n is an arbitrary integer.

Since $\mathbf{r}_L = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, where u , v and w are unrestricted integers, equation (1.1.2.5) is equivalent to the equations of Laue:

$$\mathbf{h} \cdot \mathbf{a} = h, \quad \mathbf{h} \cdot \mathbf{b} = k, \quad \mathbf{h} \cdot \mathbf{c} = l, \quad (1.1.2.6)$$

where $\mathbf{h} = \mathbf{s} - \mathbf{s}_0$ is the diffraction vector, and h , k and l are integers corresponding to orders of diffraction from the three-dimensional lattice (Lipson & Cochran, 1966). The diffraction vector thus has to satisfy a condition that is analogous to that imposed on the normal to a lattice plane.

The next relevant aspect to be commented on is the Fourier expansion of a function having the periodicity of the crystal lattice. Such functions are *e.g.* the electron density, the density of nuclear matter and the electrostatic potential in the crystal, which are the operative definitions of crystal structure in X-ray, neutron and electron-diffraction methods of crystal structure determination. A Fourier expansion of such a periodic function may be thought of as a superposition of waves (*e.g.* Buerger, 1959), with wavevectors related to the interplanar spacings d_{hkl} , in the crystal lattice. Denoting the wavevector of a Fourier wave by $\mathbf{g}$ (a function of hkl), the phase of the Fourier wave at the point $\mathbf{r}$ in the crystal is given by $2\pi\mathbf{g} \cdot \mathbf{r}$, and the triple Fourier series corresponding to the expansion of the periodic function, say $G(\mathbf{r})$, can be written as

$$G(\mathbf{r}) = \sum_{\mathbf{g}} C(\mathbf{g}) \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}), \quad (1.1.2.7)$$

where $C(\mathbf{g})$ are the amplitudes of the Fourier waves, or Fourier

1.1. RECIPROCAL SPACE IN CRYSTALLOGRAPHY

coefficients, which are related to the experimental data. Numerous examples of such expansions appear throughout this volume.

The permissible wavevectors in the above expansion are restricted by the periodicity of the function $G(\mathbf{r})$. Since, by definition, $G(\mathbf{r}) = G(\mathbf{r} + \mathbf{r}_L)$, where $\mathbf{r}_L$ is a direct-lattice vector, the right-hand side of (1.1.2.7) must remain unchanged when $\mathbf{r}$ is replaced by $\mathbf{r} + \mathbf{r}_L$. This, however, can be true only if the scalar product $\mathbf{g} \cdot \mathbf{r}_L$ is an integer.

Each of the above three aspects of crystallography may lead, independently, to a useful introduction of the reciprocal vectors, and there are many examples of this in the literature. It is interesting, however, to consider the representation of the equation

$$\mathbf{v} \cdot \mathbf{r}_L = n, \quad (1.1.2.8)$$

which is common to all three, in its most convenient form. Obviously, the vector $\mathbf{v}$ which stands for the plane normal, the diffraction vector, and the wavevector in a Fourier expansion, may still be referred to any permissible basis and so may $\mathbf{r}_L$, by an appropriate transformation.

Let $\mathbf{v} = U\mathbf{A} + V\mathbf{B} + W\mathbf{C}$, where $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ are linearly independent vectors. Equation (1.1.2.8) can then be written as

$$(U\mathbf{A} + V\mathbf{B} + W\mathbf{C}) \cdot (u\mathbf{a} + v\mathbf{b} + w\mathbf{c}) = n, \quad (1.1.2.9)$$

or, in matrix notation,

$$(UVW) \begin{pmatrix} \mathbf{A} \\ \mathbf{B} \\ \mathbf{C} \end{pmatrix} \cdot (\mathbf{abc}) \begin{pmatrix} u \\ v \\ w \end{pmatrix} = n, \quad (1.1.2.10)$$

or

$$(UVW) \begin{pmatrix} \mathbf{A} \cdot \mathbf{a} & \mathbf{A} \cdot \mathbf{b} & \mathbf{A} \cdot \mathbf{c} \\ \mathbf{B} \cdot \mathbf{a} & \mathbf{B} \cdot \mathbf{b} & \mathbf{B} \cdot \mathbf{c} \\ \mathbf{C} \cdot \mathbf{a} & \mathbf{C} \cdot \mathbf{b} & \mathbf{C} \cdot \mathbf{c} \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix} = n. \quad (1.1.2.11)$$

The simplest representation of equation (1.1.2.8) results when the matrix of scalar products in (1.1.2.11) reduces to a unit matrix. This can be achieved (i) by choosing the basis vectors $\mathbf{ABC}$ to be orthonormal to the basis vectors $\mathbf{abc}$, while requiring that the components of $\mathbf{r}_L$ be integers, or (ii) by requiring that the bases $\mathbf{ABC}$ and $\mathbf{abc}$ coincide with the same orthonormal basis, *i.e.* expressing both $\mathbf{v}$ and $\mathbf{r}_L$, in (1.1.2.8), in the same Cartesian system. If we choose the first alternative, it is seen that:

(1) The components of the vector $\mathbf{v}$, and hence those of $\mathbf{N}$, $\mathbf{h}$ and $\mathbf{g}$, are of necessity integers, since u , v and w are already integral. The components of $\mathbf{v}$ include Miller indices; in the case of the lattice plane, they coincide with the orders of diffraction from a three-dimensional lattice of scatterers, and correspond to the summation indices in the triple Fourier series (1.1.2.7).

(2) The basis vectors $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ are reciprocal to $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, as can be seen by comparing the scalar products in (1.1.2.11) with those in (1.1.2.1) and (1.1.2.2). In fact, the bases $\mathbf{ABC}$ and $\mathbf{abc}$ are mutually reciprocal. Since there are no restrictions on the integers U , V and W , the vector $\mathbf{v}$ belongs to a lattice which, on account of its basis, is called the reciprocal lattice.

It follows that, at least in the present case, algebraic simplicity goes together with ease of interpretation, which certainly accounts for much of the importance of the reciprocal lattice in crystallography. The second alternative of reducing the matrix in (1.1.2.11) to a unit matrix, a transformation of (1.1.2.8) to a Cartesian system, leads to non-integral components of the vectors, which makes any interpretation of $\mathbf{v}$ or $\mathbf{r}_L$ much less transparent. However, transformations to Cartesian systems are often very useful in crystallographic computing and will be discussed below (see also Chapters 2.3 and 3.3 in this volume).

We shall, in what follows, abandon all the temporary notation used above and write the reciprocal-lattice vector as

$$\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (1.1.2.12)$$

or

$$\mathbf{h} = h_1\mathbf{a}^1 + h_2\mathbf{a}^2 + h_3\mathbf{a}^3 = \sum_{i=1}^3 h_i\mathbf{a}^i, \quad (1.1.2.13)$$

and denote the direct-lattice vectors by $\mathbf{r}_L = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, as above, or by

$$\mathbf{r}_L = u^1\mathbf{a}_1 + u^2\mathbf{a}_2 + u^3\mathbf{a}_3 = \sum_{i=1}^3 u^i\mathbf{a}_i. \quad (1.1.2.14)$$

The representations (1.1.2.13) and (1.1.2.14) are used in the tensor-algebraic formulation of the relationships between mutually reciprocal bases (see Section 1.1.4 below).

1.1.3. Fundamental relationships

We now present a brief derivation and a summary of the most important relationships between the direct and the reciprocal bases. The usual conventions of vector algebra are observed and the results are presented in the conventional crystallographic notation. Equations (1.1.2.1) and (1.1.2.2) now become

$$\mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{c}^* = \mathbf{c} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = 0 \quad (1.1.3.1)$$

and

$$\mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 1, \quad (1.1.3.2)$$

respectively, and the relationships are obtained as follows.

1.1.3.1. Basis vectors

It is seen from (1.1.3.1) that $\mathbf{a}^*$ must be proportional to the vector product of $\mathbf{b}$ and $\mathbf{c}$,

$$\mathbf{a}^* = K(\mathbf{b} \times \mathbf{c}),$$

and, since $\mathbf{a} \cdot \mathbf{a}^* = 1$, the proportionality constant K equals $1/[\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})]$. The mixed product $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$ can be interpreted as the positive volume of the unit cell in the direct lattice only if $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ form a *right-handed* set. If the above condition is fulfilled, we obtain

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}, \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V}, \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V} \quad (1.1.3.3)$$

and analogously

$$\mathbf{a} = \frac{\mathbf{b}^* \times \mathbf{c}^*}{V^*}, \quad \mathbf{b} = \frac{\mathbf{c}^* \times \mathbf{a}^*}{V^*}, \quad \mathbf{c} = \frac{\mathbf{a}^* \times \mathbf{b}^*}{V^*}, \quad (1.1.3.4)$$

where V and V^* are the volumes of the unit cells in the associated direct and reciprocal lattices, respectively. Use has been made of the fact that the mixed product, say $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$, remains unchanged under cyclic rearrangement of the vectors that appear in it.

1.1.3.2. Volumes

The reciprocal relationship of V and V^* follows readily. We have from equations (1.1.3.2), (1.1.3.3) and (1.1.3.4)

$$\mathbf{c} \cdot \mathbf{c}^* = \frac{(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{a}^* \times \mathbf{b}^*)}{VV^*} = 1.$$

If we make use of the vector identity

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$$(\mathbf{A} \times \mathbf{B}) \cdot (\mathbf{C} \times \mathbf{D}) = (\mathbf{A} \cdot \mathbf{C})(\mathbf{B} \cdot \mathbf{D}) - (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C}), \quad (1.1.3.5)$$

and equations (1.1.3.1) and (1.1.3.2), it is seen that $V^* = 1/V$.

1.1.3.3. Angular relationships

The relationships of the angles α, β, γ between the pairs of vectors $(\mathbf{b}, \mathbf{c})$, $(\mathbf{c}, \mathbf{a})$ and $(\mathbf{a}, \mathbf{b})$, respectively, and the angles $\alpha^*, \beta^*, \gamma^*$ between the corresponding pairs of reciprocal basis vectors, can be obtained by simple vector algebra. For example, we have from (1.1.3.3):

(i) $\mathbf{b}^* \cdot \mathbf{c}^* = b^* c^* \cos \alpha^*$, with

$$b^* = \frac{ca \sin \beta}{V} \quad \text{and} \quad c^* = \frac{ab \sin \gamma}{V}$$

and (ii)

$$\mathbf{b}^* \cdot \mathbf{c}^* = \frac{(\mathbf{c} \times \mathbf{a}) \cdot (\mathbf{a} \times \mathbf{b})}{V^2}.$$

If we make use of the identity (1.1.3.5), and compare the two expressions for $\mathbf{b}^* \cdot \mathbf{c}^*$, we readily obtain

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}. \quad (1.1.3.6)$$

Similarly,

$$\cos \beta^* = \frac{\cos \gamma \cos \alpha - \cos \beta}{\sin \gamma \sin \alpha} \quad (1.1.3.7)$$

and

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}. \quad (1.1.3.8)$$

The expressions for the cosines of the direct angles in terms of those of the reciprocal ones are analogous to (1.1.3.6)–(1.1.3.8). For example,

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}.$$

1.1.3.4. Matrices of metric tensors

Various computational and algebraic aspects of mutually reciprocal bases are most conveniently expressed in terms of the metric tensors of these bases. The tensors will be treated in some detail in the next section, and only the definitions of their matrices are given and interpreted below.

Consider the length of the vector $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$. This is given by

$$|\mathbf{r}| = [(x\mathbf{a} + y\mathbf{b} + z\mathbf{c}) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})]^{1/2} \quad (1.1.3.9)$$

and can be written in matrix form as

$$|\mathbf{r}| = [\mathbf{x}^T \mathbf{G} \mathbf{x}]^{1/2}, \quad (1.1.3.10)$$

where

$$\mathbf{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad \mathbf{x}^T = (xyz)$$

and

$$\mathbf{G} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix} \quad (1.1.3.11)$$

$$= \begin{pmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ba \cos \gamma & b^2 & bc \cos \alpha \\ ca \cos \beta & cb \cos \alpha & c^2 \end{pmatrix}. \quad (1.1.3.12)$$

This is the matrix of the metric tensor of the direct basis, or briefly the direct metric. The corresponding reciprocal metric is given by

$$\mathbf{G}^* = \begin{pmatrix} \mathbf{a}^* \cdot \mathbf{a}^* & \mathbf{a}^* \cdot \mathbf{b}^* & \mathbf{a}^* \cdot \mathbf{c}^* \\ \mathbf{b}^* \cdot \mathbf{a}^* & \mathbf{b}^* \cdot \mathbf{b}^* & \mathbf{b}^* \cdot \mathbf{c}^* \\ \mathbf{c}^* \cdot \mathbf{a}^* & \mathbf{c}^* \cdot \mathbf{b}^* & \mathbf{c}^* \cdot \mathbf{c}^* \end{pmatrix} \quad (1.1.3.13)$$

$$= \begin{pmatrix} a^{*2} & a^* b^* \cos \gamma^* & a^* c^* \cos \beta^* \\ b^* a^* \cos \gamma^* & b^{*2} & b^* c^* \cos \alpha^* \\ c^* a^* \cos \beta^* & c^* b^* \cos \alpha^* & c^{*2} \end{pmatrix}. \quad (1.1.3.14)$$

The matrices $\mathbf{G}$ and $\mathbf{G}^*$ are of fundamental importance in crystallographic computations and transformations of basis vectors and coordinates from direct to reciprocal space and *vice versa*. Examples of applications are presented in Part 3 of this volume and in the remaining sections of this chapter.

It can be shown (*e.g.* Buerger, 1941) that the determinants of $\mathbf{G}$ and $\mathbf{G}^*$ equal the squared volumes of the direct and reciprocal unit cells, respectively. Thus,

$$\det(\mathbf{G}) = [\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})]^2 = V^2 \quad (1.1.3.15)$$

and

$$\det(\mathbf{G}^*) = [\mathbf{a}^* \cdot (\mathbf{b}^* \times \mathbf{c}^*)]^2 = V^{*2}, \quad (1.1.3.16)$$

and a direct expansion of the determinants, from (1.1.3.12) and (1.1.3.14), leads to

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2} \quad (1.1.3.17)$$

and

$$V^* = a^* b^* c^* (1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*)^{1/2}. \quad (1.1.3.18)$$

The following algorithm has been found useful in computational applications of the above relationships to calculations in reciprocal space (*e.g.* data reduction) and in direct space (*e.g.* crystal geometry).

(1) Input the direct unit-cell parameters and construct the matrix of the metric tensor [*cf.* equation (1.1.3.12)].

(2) Compute the determinant of the matrix $\mathbf{G}$ and find the inverse matrix, $\mathbf{G}^{-1}$; this inverse matrix is just $\mathbf{G}^*$, the matrix of the metric tensor of the reciprocal basis (see also Section 1.1.4 below).

(3) Use the elements of $\mathbf{G}^*$, and equation (1.1.3.14), to obtain the parameters of the reciprocal unit cell.

The direct and reciprocal sets of unit-cell parameters, as well as the corresponding metric tensors, are now available for further calculations.

Explicit relations between direct- and reciprocal-lattice parameters, valid for the various crystal systems, are given in most textbooks on crystallography [see also Chapter 1.1 of Volume C (Koch, 1999)].

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1.1.4. Tensor-algebraic formulation

The present section summarizes the tensor-algebraic properties of mutually reciprocal sets of basis vectors, which are of importance in the various aspects of crystallography. This is not intended to be a systematic treatment of tensor algebra; for more thorough expositions of the subject the reader is referred to relevant crystallographic texts (*e.g.* Patterson, 1967; Sands, 1982), and other texts in the physical and mathematical literature that deal with tensor algebra and analysis.

Let us first recall that symbolic vector and matrix notations, in which basis vectors and coordinates do not appear explicitly, are often helpful in qualitative considerations. If, however, an expression has to be evaluated, the various quantities appearing in it must be presented in component form. One of the best ways to achieve a concise presentation of geometrical expressions in component form, while retaining much of their ‘transparent’ symbolic character, is their tensor-algebraic formulation.

1.1.4.1. Conventions

We shall adhere to the following conventions:

(i) Notation for direct and reciprocal basis vectors:

$$\mathbf{a} = \mathbf{a}_1, \mathbf{b} = \mathbf{a}_2, \mathbf{c} = \mathbf{a}_3$$

$$\mathbf{a}^* = \mathbf{a}^1, \mathbf{b}^* = \mathbf{a}^2, \mathbf{c}^* = \mathbf{a}^3.$$

Subscripted quantities are associated in tensor algebra with *covariant*, and superscripted with *contravariant* transformation properties. Thus the basis vectors of the direct lattice are represented as covariant quantities and those of the reciprocal lattice as contravariant ones.

(ii) Summation convention: if an index appears twice in an expression, once as subscript and once as superscript, a summation over this index is thereby implied and the summation sign is omitted. For example,

$$\sum_i \sum_j x^i T_{ij} x^j \text{ will be written } x^i T_{ij} x^j$$

since both i and j conform to the convention. Such repeating indices are often called *dummy* indices. The implied summation over repeating indices is also often used even when the indices are at the same level and the coordinate system is Cartesian; there is no distinction between contravariant and covariant quantities in Cartesian frames of reference (see Chapter 3.3).

(iii) Components (coordinates) of vectors referred to the covariant basis are written as contravariant quantities, and *vice versa*. For example,

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} = x^1\mathbf{a}_1 + x^2\mathbf{a}_2 + x^3\mathbf{a}_3 = x^i\mathbf{a}_i$$

$$\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = h_1\mathbf{a}^1 + h_2\mathbf{a}^2 + h_3\mathbf{a}^3 = h_i\mathbf{a}^i.$$

1.1.4.2. Transformations

A familiar concept but a fundamental one in tensor algebra is the transformation of coordinates. For example, suppose that an atomic position vector is referred to two unit-cell settings as follows:

$$\mathbf{r} = x^k \mathbf{a}_k \quad (1.1.4.1)$$

and

$$\mathbf{r} = x'^k \mathbf{a}'_k. \quad (1.1.4.2)$$

Let us multiply both sides of (1.1.4.1) and (1.1.4.2), on the right, by the vectors $\mathbf{a}^m$, $m = 1, 2$, or 3 , *i.e.* by the reciprocal vectors to the basis $\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3$. We obtain from (1.1.4.1)

$$x^k \mathbf{a}_k \cdot \mathbf{a}^m = x^k \delta_k^m = x^m,$$

where δ_k^m is the Kronecker symbol which equals 1 when $k = m$ and equals zero if $k \neq m$, and by comparison with (1.1.4.2) we have

$$x^m = x'^k T_k^m, \quad (1.1.4.3)$$

where $T_k^m = \mathbf{a}'_k \cdot \mathbf{a}^m$ is an element of the required transformation matrix. Of course, the same transformation could have been written as

$$x^m = T_k^m x'^k, \quad (1.1.4.4)$$

where $T_k^m = \mathbf{a}^m \cdot \mathbf{a}'_k$.

A *tensor* is a quantity that transforms as the product of coordinates, and the *rank* of a tensor is the number of transformations involved (Patterson, 1967; Sands, 1982). *E.g.* the product of two coordinates, as in the above example, transforms from the $\mathbf{a}'$ basis to the $\mathbf{a}$ basis as

$$x^m x^n = T_p^m T_q^n x'^p x'^q; \quad (1.1.4.5)$$

the same transformation law applies to the components of a contravariant tensor of rank two, the components of which are referred to the primed basis and are to be transformed to the unprimed one:

$$Q^{mn} = T_p^m T_q^n Q'^{pq}. \quad (1.1.4.6)$$

1.1.4.3. Scalar products

The expression for the scalar product of two vectors, say $\mathbf{u}$ and $\mathbf{v}$, depends on the bases to which the vectors are referred. If we admit only the covariant and contravariant bases defined above, we have four possible types of expression:

$$(I) \mathbf{u} = u^i \mathbf{a}_i, \mathbf{v} = v^j \mathbf{a}_j$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j (\mathbf{a}_i \cdot \mathbf{a}_j) \equiv u^i v^j g_{ij}, \quad (1.1.4.7)$$

$$(II) \mathbf{u} = u_i \mathbf{a}^i, \mathbf{v} = v_j \mathbf{a}^j$$

$$\mathbf{u} \cdot \mathbf{v} = u_i v_j (\mathbf{a}^i \cdot \mathbf{a}^j) \equiv u_i v_j g^{ij}, \quad (1.1.4.8)$$

$$(III) \mathbf{u} = u^i \mathbf{a}_i, \mathbf{v} = v_i \mathbf{a}^i$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v_j (\mathbf{a}_i \cdot \mathbf{a}^j) \equiv u^i v_j \delta_i^j = u^i v_i, \quad (1.1.4.9)$$

$$(IV) \mathbf{u} = u_i \mathbf{a}^i, \mathbf{v} = v^j \mathbf{a}_j$$

$$\mathbf{u} \cdot \mathbf{v} = u_i v^j (\mathbf{a}^i \cdot \mathbf{a}_j) \equiv u_i v^j \delta_j^i = u_i v^i. \quad (1.1.4.10)$$

(i) The sets of scalar products $g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$ (1.1.4.7) and $g^{ij} = \mathbf{a}^i \cdot \mathbf{a}^j$ (1.1.4.8) are known as the *metric* tensors of the covariant (direct) and contravariant (reciprocal) bases, respectively; the corresponding matrices are presented in conventional notation in equations (1.1.3.11) and (1.1.3.13). Numerous applications of these tensors to the computation of distances and angles in crystals are given in Chapter 3.1.

(ii) Equations (1.1.4.7) to (1.1.4.10) furnish the relationships between the covariant and contravariant *components* of the same vector. Thus, comparing (1.1.4.7) and (1.1.4.9), we have

$$v_i = v^j g_{ij}. \quad (1.1.4.11)$$

Similarly, using (1.1.4.8) and (1.1.4.10) we obtain the inverse relationship

$$v^j = v_i g^{ij}. \quad (1.1.4.12)$$

The corresponding relationships between covariant and contravariant *bases* can now be obtained if we refer a vector, say $\mathbf{v}$, to each of the bases

$$\mathbf{v} = v^i \mathbf{a}_i = v_k \mathbf{a}^k,$$

and make use of (1.1.4.11) and (1.1.4.12). Thus, *e.g.*,

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$$v^i \mathbf{a}_i = (v_k g^{ik}) \mathbf{a}_i = v_k \mathbf{a}^k.$$

Hence

$$\mathbf{a}^k = g^{ik} \mathbf{a}_i \quad (1.1.4.13)$$

and, similarly,

$$\mathbf{a}_k = g_{ik} \mathbf{a}^i. \quad (1.1.4.14)$$

(iii) The tensors g_{ij} and g^{ij} are symmetric, by definition.

(iv) It follows from (1.1.4.11) and (1.1.4.12) or (1.1.4.13) and (1.1.4.14) that the matrices of the direct and reciprocal metric tensors are mutually inverse, *i.e.*

$$\begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}^{-1} = \begin{pmatrix} g^{11} & g^{12} & g^{13} \\ g^{21} & g^{22} & g^{23} \\ g^{31} & g^{32} & g^{33} \end{pmatrix}, \quad (1.1.4.15)$$

and their determinants are mutually reciprocal.

1.1.4.4. Examples

There are numerous applications of tensor notation in crystallographic calculations, and many of them appear in the various chapters of this volume. We shall therefore present only a few examples.

(i) The (squared) magnitude of the diffraction vector $\mathbf{h} = h_i \mathbf{a}^i$ is given by

$$|\mathbf{h}|^2 = \frac{4 \sin^2 \theta}{\lambda^2} = h_i h_j g^{ij}. \quad (1.1.4.16)$$

This concise relationship is a starting point in a derivation of unit-cell parameters from experimental data.

(ii) The structure factor, including explicitly anisotropic displacement tensors, can be written in symbolic matrix notation as

$$F(\mathbf{h}) = \sum_{j=1}^N f_{(j)} \exp(-\mathbf{h}^T \boldsymbol{\beta}_{(j)} \mathbf{h}) \exp(2\pi i \mathbf{h}^T \mathbf{r}_{(j)}), \quad (1.1.4.17)$$

where $\boldsymbol{\beta}_{(j)}$ is the matrix of the anisotropic displacement tensor of the j th atom. In tensor notation, with the quantities referred to their natural bases, the structure factor can be written as

$$F(h_1 h_2 h_3) = \sum_{j=1}^N f_{(j)} \exp(-h_i h_k \beta_{(j)}^{ik}) \exp(2\pi i h_i x_{(j)}^i), \quad (1.1.4.18)$$

and similarly concise expressions can be written for the derivatives of the structure factor with respect to the positional and displacement parameters. The summation convention applies only to indices denoting components of vectors and tensors; the atom subscript j in (1.1.4.18) clearly does not qualify, and to indicate this it has been surrounded by parentheses.

(iii) Geometrical calculations, such as those described in the chapters of Part 3, may be carried out in any convenient basis but there are often some definite advantages to computations that are referred to the natural, non-Cartesian bases (see Chapter 3.1). Usually, the output positional parameters from structure refinement are available as contravariant components of the atomic position vectors. If we transform them by (1.1.4.11) to their covariant form, and store these covariant components of the atomic position vectors, the computation of scalar products using equations (1.1.4.9) or (1.1.4.10) is *almost as efficient as it would be if the coordinates were referred to a Cartesian system*. For example, the right-hand side of the vector identity (1.1.3.5), which is employed in the computation of dihedral angles, can be written as

$$(A_i C^i)(B_k D^k) - (A_i D^i)(B_k C^k).$$

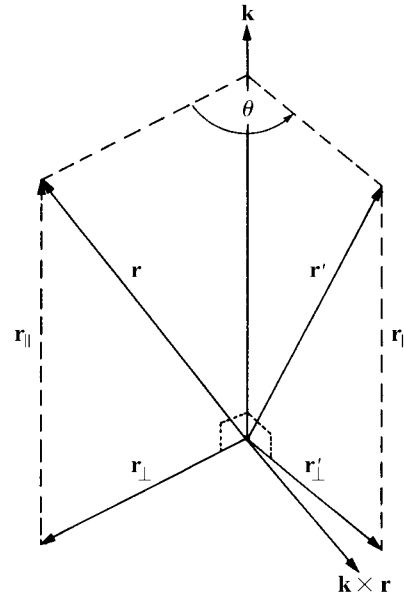


Fig. 1.1.4.1. Derivation of the general expression for the rotation operator. The figure illustrates schematically the decompositions and other simple geometrical considerations required for the derivation outlined in equations (1.1.4.22)–(1.1.4.28).

This is a typical application of reciprocal space to ordinary direct-space computations.

(iv) We wish to derive a tensor formulation of the vector product, along similar lines to those of Chapter 3.1. As with the scalar product, there are several such formulations and we choose that which has both vectors, say $\mathbf{u}$ and $\mathbf{v}$, and the resulting product, $\mathbf{u} \times \mathbf{v}$, referred to a covariant basis. We have

$$\begin{aligned} \mathbf{u} \times \mathbf{v} &= u^i \mathbf{a}_i \times v^j \mathbf{a}_j \\ &= u^i v^j (\mathbf{a}_i \times \mathbf{a}_j). \end{aligned} \quad (1.1.4.19)$$

If we make use of the relationships (1.1.3.3) between the direct and reciprocal basis vectors, it can be verified that

$$\mathbf{a}_i \times \mathbf{a}_j = V e_{kij} \mathbf{a}^k, \quad (1.1.4.20)$$

where V is the volume of the unit cell and the antisymmetric tensor e_{kij} equals +1, -1, or 0 according as kij is an even permutation of 123, an odd permutation of 123 or any two of the indices kij have the same value, respectively. We thus have

$$\begin{aligned} \mathbf{u} \times \mathbf{v} &= V e_{kij} u^i v^j \mathbf{a}^k \\ &= V g^{lk} e_{kij} u^i v^j \mathbf{a}_l, \end{aligned} \quad (1.1.4.21)$$

since by (1.1.4.13), $\mathbf{a}^k = g^{lk} \mathbf{a}_l$.

(v) *The rotation operator.* The general formulation of an expression for the rotation operator is of interest in crystal structure determination by Patterson techniques (see Chapter 2.3) and in molecular modelling (see Chapter 3.3), and another well known crystallographic application of this device is the derivation of the translation, libration and screw-motion tensors by the method of Schomaker & Trueblood (1968), discussed in Part 8 of Volume C (IT C, 1999) and in Chapter 1.2 of this volume. A digression on an elementary derivation of the above seems to be worthwhile.

Suppose we wish to rotate the vector $\mathbf{r}$, about an axis coinciding with the unit vector $\mathbf{k}$, through the angle θ and in the positive sense, *i.e.* an observer looking in the direction of $+\mathbf{k}$ will see $\mathbf{r}$ rotating in the clockwise sense. The vectors $\mathbf{r}$, $\mathbf{k}$ and the rotated (target) vector $\mathbf{r}'$ are referred to an origin on the axis of rotation (see Fig. 1.1.4.1). Our purpose is to express $\mathbf{r}'$ in terms of $\mathbf{r}$, $\mathbf{k}$ and θ by a general vector

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formula, and represent the components of the rotated vectors in coordinate systems that might be of interest.

Let us decompose the vector $\mathbf{r}$ and the (target) vector $\mathbf{r}'$ into their components which are parallel ($\parallel$) and perpendicular ($\perp$) to the axis of rotation:

$$\mathbf{r} = \mathbf{r}_{\parallel} + \mathbf{r}_{\perp} \quad (1.1.4.22)$$

and

$$\mathbf{r}' = \mathbf{r}'_{\parallel} + \mathbf{r}'_{\perp}. \quad (1.1.4.23)$$

It can be seen from Fig. 1.1.4.1 that the parallel components of $\mathbf{r}$ and $\mathbf{r}'$ are

$$\mathbf{r}_{\parallel} = \mathbf{r}'_{\parallel} = \mathbf{k}(\mathbf{k} \cdot \mathbf{r}) \quad (1.1.4.24)$$

and thus

$$\mathbf{r}_{\perp} = \mathbf{r} - \mathbf{k}(\mathbf{k} \cdot \mathbf{r}). \quad (1.1.4.25)$$

Only a suitable expression for $\mathbf{r}'_{\perp}$ is missing. We can find this by decomposing $\mathbf{r}'_{\perp}$ into its components (i) parallel to $\mathbf{r}_{\perp}$ and (ii) parallel to $\mathbf{k} \times \mathbf{r}_{\perp}$. We have, as in (1.1.4.24),

$$\mathbf{r}'_{\perp} = \frac{\mathbf{r}_{\perp}}{|\mathbf{r}_{\perp}|} \left(\frac{\mathbf{r}_{\perp}}{|\mathbf{r}_{\perp}|} \cdot \mathbf{r}'_{\perp} \right) + \frac{\mathbf{k} \times \mathbf{r}_{\perp}}{|\mathbf{k} \times \mathbf{r}_{\perp}|} \left(\frac{\mathbf{k} \times \mathbf{r}_{\perp}}{|\mathbf{k} \times \mathbf{r}_{\perp}|} \cdot \mathbf{r}'_{\perp} \right). \quad (1.1.4.26)$$

We observe, using Fig. 1.1.4.1, that

$$|\mathbf{r}'_{\perp}| = |\mathbf{r}_{\perp}| = |\mathbf{k} \times \mathbf{r}_{\perp}|$$

and

$$\mathbf{k} \times \mathbf{r}_{\perp} = \mathbf{k} \times \mathbf{r},$$

and, further,

$$\mathbf{r}'_{\perp} \cdot \mathbf{r}_{\perp} = |\mathbf{r}_{\perp}|^2 \cos \theta$$

and

$$\mathbf{r}'_{\perp} \cdot (\mathbf{k} \times \mathbf{r}_{\perp}) = \mathbf{k} \cdot (\mathbf{r}'_{\perp} \times \mathbf{r}_{\perp}) = |\mathbf{r}_{\perp}|^2 \sin \theta,$$

since the unit vector $\mathbf{k}$ is perpendicular to the plane containing the vectors $\mathbf{r}_{\perp}$ and $\mathbf{r}'_{\perp}$. Equation (1.1.4.26) now reduces to

$$\mathbf{r}'_{\perp} = \mathbf{r}_{\perp} \cos \theta + (\mathbf{k} \times \mathbf{r}) \sin \theta \quad (1.1.4.27)$$

and equations (1.1.4.23), (1.1.4.25) and (1.1.4.27) lead to the required result

$$\mathbf{r}' = \mathbf{k}(\mathbf{k} \cdot \mathbf{r})(1 - \cos \theta) + \mathbf{r} \cos \theta + (\mathbf{k} \times \mathbf{r}) \sin \theta. \quad (1.1.4.28)$$

The above general expression can be written as a linear transformation by referring the vectors to an appropriate basis or bases. We choose here $\mathbf{r} = x^j \mathbf{a}_j$, $\mathbf{r}' = x'^i \mathbf{a}_i$ and assume that the components of $\mathbf{k}$ are available in the direct and reciprocal bases.

If we make use of equations (1.1.4.9) and (1.1.4.21), (1.1.4.28) can be written as

$$x'^i = k^i(k_j x^j)(1 - \cos \theta) + \delta_j^i x^j \cos \theta + V g^{im} e_{mpj} k^p x^j \sin \theta, \quad (1.1.4.29)$$

or briefly

$$x'^i = R_j^i x^j, \quad (1.1.4.30)$$

where

$$R_j^i = k^i k_j (1 - \cos \theta) + \delta_j^i \cos \theta + V g^{im} e_{mpj} k^p \sin \theta \quad (1.1.4.31)$$

is a matrix element of the rotation operator $\mathbf{R}$ which carries the vector $\mathbf{r}$ into the vector $\mathbf{r}'$. Of course, the representation (1.1.4.31) of $\mathbf{R}$ depends on our choice of reference bases.

If all the vectors are referred to a Cartesian basis, that is three orthogonal unit vectors, the direct and reciprocal metric tensors reduce to a unit tensor, there is no difference between covariant and contravariant quantities, and equation (1.1.4.31) reduces to

$$R_{ij} = k_i k_j (1 - \cos \theta) + \delta_{ij} \cos \theta + e_{ipj} k_p \sin \theta, \quad (1.1.4.32)$$

where all the indices have been taken as subscripts, but the summation convention is still observed. The relative simplicity of (1.1.4.32), as compared to (1.1.4.31), often justifies the transformation of all the vector quantities to a Cartesian basis. This is certainly the case for any extensive calculation in which covariances of the structural parameters are not considered.

1.1.5. Transformations

1.1.5.1. Transformations of coordinates

It happens rather frequently that a vector referred to a given basis has to be re-expressed in terms of another basis, and it is then required to find the relationship between the components (coordinates) of the vector in the two bases. Such situations have already been indicated in the previous section. The purpose of the present section is to give a general method of finding such relationships (transformations), and discuss some simplifications brought about by the use of mutually reciprocal and Cartesian bases. We do not assume anything about the bases, in the general treatment, and hence the tensor formulation of Section 1.1.4 is not appropriate at this stage.

Let

$$\mathbf{r} = \sum_{j=1}^3 u_j(1) \mathbf{c}_j(1) \quad (1.1.5.1)$$

and

$$\mathbf{r} = \sum_{j=1}^3 u_j(2) \mathbf{c}_j(2) \quad (1.1.5.2)$$

be the *given* and *required* representations of the vector $\mathbf{r}$, respectively. Upon the formation of scalar products of equations (1.1.5.1) and (1.1.5.2) with the vectors of the second basis, and employing again the summation convention, we obtain

$$u_k(1) [\mathbf{c}_k(1) \cdot \mathbf{c}_l(2)] = u_k(2) [\mathbf{c}_k(2) \cdot \mathbf{c}_l(2)], \quad l = 1, 2, 3 \quad (1.1.5.3)$$

or

$$u_k(1) G_{kl}(12) = u_k(2) G_{kl}(22), \quad l = 1, 2, 3, \quad (1.1.5.4)$$

where $G_{kl}(12) = \mathbf{c}_k(1) \cdot \mathbf{c}_l(2)$ and $G_{kl}(22) = \mathbf{c}_k(2) \cdot \mathbf{c}_l(2)$. Similarly, if we choose the basis vectors $\mathbf{c}_l(1)$, $l = 1, 2, 3$, as the multipliers of (1.1.5.1) and (1.1.5.2), we obtain

$$u_k(1) G_{kl}(11) = u_k(2) G_{kl}(21), \quad l = 1, 2, 3, \quad (1.1.5.5)$$

where $G_{kl}(11) = \mathbf{c}_k(1) \cdot \mathbf{c}_l(1)$ and $G_{kl}(21) = \mathbf{c}_k(2) \cdot \mathbf{c}_l(1)$. Rewriting (1.1.5.4) and (1.1.5.5) in symbolic matrix notation, we have

$$\mathbf{u}^T(1) \mathbf{G}(12) = \mathbf{u}^T(2) \mathbf{G}(22), \quad (1.1.5.6)$$

leading to

$$\mathbf{u}^T(1) = \mathbf{u}^T(2) \{ \mathbf{G}(22) [\mathbf{G}(12)]^{-1} \}$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1) \{ \mathbf{G}(12) [\mathbf{G}(22)]^{-1} \}, \quad (1.1.5.7)$$

and

$$\mathbf{u}^T(1) \mathbf{G}(11) = \mathbf{u}^T(2) \mathbf{G}(21), \quad (1.1.5.8)$$

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leading to

$$\mathbf{u}^T(1) = \mathbf{u}^T(2)\{\mathbf{G}(21)[\mathbf{G}(11)]^{-1}\}$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1)\{\mathbf{G}(11)[\mathbf{G}(21)]^{-1}\}. \quad (1.1.5.9)$$

Equations (1.1.5.7) and (1.1.5.9) are symbolic general expressions for the transformation of the coordinates of $\mathbf{r}$ from one representation to the other.

In the general case, therefore, we require the matrices of scalar products of the basis vectors, $\mathbf{G}(12)$ and $\mathbf{G}(22)$ or $\mathbf{G}(11)$ and $\mathbf{G}(21)$ – depending on whether the basis $\mathbf{c}_k(2)$ or $\mathbf{c}_k(1)$, $k = 1, 2, 3$, was chosen to multiply scalarly equations (1.1.5.1) and (1.1.5.2). Note, however, the following simplifications.

(i) If the bases $\mathbf{c}_k(1)$ and $\mathbf{c}_k(2)$ are mutually reciprocal, each of the matrices of mixed scalar products, $\mathbf{G}(12)$ and $\mathbf{G}(21)$, reduces to a unit matrix. In this important special case, the transformation is effected by the matrices of the metric tensors of the bases in question. This can be readily seen from equations (1.1.5.7) and (1.1.5.9), which then reduce to the relationships between the covariant and contravariant components of the same vector [see equations (1.1.4.11) and (1.1.4.12) above].

(ii) If one of the bases, say $\mathbf{c}_k(2)$, is Cartesian, its metric tensor is by definition a unit tensor, and the transformations in (1.1.5.7) reduce to

$$\mathbf{u}^T(1) = \mathbf{u}^T(2)[\mathbf{G}(12)]^{-1}$$

and

$$\mathbf{u}^T(2) = \mathbf{u}^T(1)\mathbf{G}(12). \quad (1.1.5.10)$$

The transformation matrix is now the mixed matrix of the scalar products, whether or not the basis $\mathbf{c}_k(1)$, $k = 1, 2, 3$, is also Cartesian. If, however, both bases are Cartesian, the transformation can also be interpreted as a rigid rotation of the coordinate axes (see Chapter 3.3).

It should be noted that the above transformations do not involve any shift of the origin. Transformations involving such shifts, notably the symmetry transformations of the space group, are treated rather extensively in Volume A of *International Tables for Crystallography* (1995) [see e.g. Part 5 there (Arnold, 1983)].

1.1.5.2. Example

This example deals with the construction of a Cartesian system in a crystal with given basis vectors of its direct lattice. We shall also require that the Cartesian system bears a clear relationship to at least one direction in each of the direct and reciprocal lattices of the crystal; this may be useful in interpreting a physical property which has been measured along a given lattice vector or which is associated with a given lattice plane. For a better consistency of notation, the Cartesian components will be denoted as contravariant.

The appropriate version of equations (1.1.5.1) and (1.1.5.2) is now

$$\mathbf{r} = x^i \mathbf{a}_i \quad (1.1.5.11)$$

and

$$\mathbf{r} = X^k \mathbf{e}_k, \quad (1.1.5.12)$$

where the Cartesian basis vectors are: $\mathbf{e}_1 = \mathbf{r}_L/|\mathbf{r}_L|$, $\mathbf{e}_2 = \mathbf{r}^*/|\mathbf{r}^*|$ and $\mathbf{e}_3 = \mathbf{e}_1 \times \mathbf{e}_2$, and the vectors $\mathbf{r}_L$ and $\mathbf{r}^*$ are given by

$$\mathbf{r}_L = u^i \mathbf{a}_i \text{ and } \mathbf{r}^* = h_k \mathbf{a}^k,$$

where u^i and h_k , $i, k = 1, 2, 3$, are arbitrary integers. The vectors $\mathbf{r}_L$ and $\mathbf{r}^*$ must be mutually perpendicular, $\mathbf{r}_L \cdot \mathbf{r}^* = u^i h_i = 0$. The

$X^1(X)$ axis of the Cartesian system thus coincides with a direct-lattice vector, and the $X^2(Y)$ axis is parallel to a vector in the reciprocal lattice.

Since the basis in (1.1.5.12) is a Cartesian one, the required transformations are given by equations (1.1.5.10) as

$$x^i = X^k (T^{-1})_k^i \text{ and } X^i = x^k T_k^i, \quad (1.1.5.13)$$

where $T_k^i = \mathbf{a}_k \cdot \mathbf{e}_i$, $k, i = 1, 2, 3$, form the matrix of the scalar products. If we make use of the relationships between covariant and contravariant basis vectors, and the tensor formulation of the vector product, given in Section 1.1.4 above (see also Chapter 3.1), we obtain

$$\begin{aligned} T_k^1 &= \frac{1}{|\mathbf{r}_L|} g_{ki} u^i \\ T_k^2 &= \frac{1}{|\mathbf{r}^*|} h_k \\ T_k^3 &= \frac{V}{|\mathbf{r}_L||\mathbf{r}^*|} e_{kip} u^i g^{pl} h_l. \end{aligned} \quad (1.1.5.14)$$

Note that the other convenient choice, $\mathbf{e}_1 \propto \mathbf{r}^*$ and $\mathbf{e}_2 \propto \mathbf{r}_L$, interchanges the first two columns of the matrix $\mathbf{T}$ in (1.1.5.14) and leads to a change of the signs of the elements in the third column. This can be done by writing e_{kip} instead of e_{kpi} , while leaving the rest of T_k^3 unchanged.

1.1.6. Some analytical aspects of the reciprocal space

1.1.6.1. Continuous Fourier transform

Of great interest in crystallographic analyses are Fourier transforms and these are closely associated with the dual bases examined in this chapter. Thus, e.g., the inverse Fourier transform of the electron-density function of the crystal

$$F(\mathbf{h}) = \int_{\text{cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d^3 \mathbf{r}, \quad (1.1.6.1)$$

where $\rho(\mathbf{r})$ is the electron-density function at the point $\mathbf{r}$ and the integration extends over the volume of a unit cell, is the fundamental model of the contribution of the distribution of crystalline matter to the intensity of the scattered radiation. For the conventional Bragg scattering, the function given by (1.1.6.1), and known as the *structure factor*, may assume nonzero values *only* if $\mathbf{h}$ can be represented as a reciprocal-lattice vector. Chapter 1.2 is devoted to a discussion of the structure factor of the Bragg reflection, while Chapters 4.1, 4.2 and 4.3 discuss circumstances under which the scattering need not be confined to the points of the reciprocal lattice only, and may be represented by reciprocal-space vectors with non-integral components.

1.1.6.2. Discrete Fourier transform

The electron density $\rho(\mathbf{r})$ in (1.1.6.1) is one of the most common examples of a function which has the periodicity of the crystal. Thus, for an ideal (infinite) crystal the electron density $\rho(\mathbf{r})$ can be written as

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + u\mathbf{a} + v\mathbf{b} + w\mathbf{c}), \quad (1.1.6.2)$$

and, as such, it can be represented by a three-dimensional Fourier series of the form

$$\rho(\mathbf{r}) = \sum_{\mathbf{g}} C(\mathbf{g}) \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}), \quad (1.1.6.3)$$

where the periodicity requirement (1.1.6.2) enables one to represent all the $\mathbf{g}$ vectors in (1.1.6.3) as vectors in the reciprocal lattice (see also Section 1.1.2 above). If we insert the series (1.1.6.3) in the

1.1. RECIPROCAL SPACE IN CRYSTALLOGRAPHY

integrand of (1.1.6.1), interchange the order of summation and integration and make use of the fact that an integral of a periodic function taken over the entire period must vanish unless the integrand is a constant, equation (1.1.6.3) reduces to the conventional form

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (1.1.6.4)$$

where V is the volume of the unit cell in the direct lattice and the summation ranges over all the reciprocal lattice.

Fourier transforms, discrete as well as continuous, are among the most important mathematical tools of crystallography. The discussion of their mathematical principles, the modern algorithms for their computation and their numerous applications in crystallography form the subject matter of Chapter 1.3. Many more examples of applications of Fourier methods in crystallography are scattered throughout this volume and the crystallographic literature in general.

1.1.6.3. Bloch's theorem

It is in order to mention briefly the important role of reciprocal space and the reciprocal lattice in the field of the theory of solids. At the basis of these applications is the periodicity of the crystal structure and the effect it has on the dynamics (*cf.* Chapter 4.1) and electronic structure of the crystal. One of the earliest, and still most important, theorems of solid-state physics is due to Bloch (1928) and deals with the representation of the wavefunction of an electron which moves in a periodic potential. Bloch's theorem states that:

The eigenstates ψ of the one-electron Hamiltonian $\mathcal{H} = (-\hbar^2/2m)\nabla^2 + U(\mathbf{r})$, where $U(\mathbf{r})$ is the crystal potential and $U(\mathbf{r} + \mathbf{r}_L) = U(\mathbf{r})$ for all $\mathbf{r}_L$ in the Bravais lattice, can be chosen to have

the form of a plane wave times a function with the periodicity of the Bravais lattice.

Thus

$$\psi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u(\mathbf{r}), \quad (1.1.6.5)$$

where

$$u(\mathbf{r} + \mathbf{r}_L) = u(\mathbf{r}) \quad (1.1.6.6)$$

and $\mathbf{k}$ is the wavevector. The proof of Bloch's theorem can be found in most modern texts on solid-state physics (*e.g.* Ashcroft & Mermin, 1975). If we combine (1.1.6.5) with (1.1.6.6), an alternative form of the Bloch theorem results:

$$\psi(\mathbf{r} + \mathbf{r}_L) = \exp(i\mathbf{k} \cdot \mathbf{r}_L)\psi(\mathbf{r}). \quad (1.1.6.7)$$

In the important case where the wavefunction ψ is itself periodic, *i.e.*

$$\psi(\mathbf{r} + \mathbf{r}_L) = \psi(\mathbf{r}),$$

we must have $\exp(i\mathbf{k} \cdot \mathbf{r}_L) = 1$. Of course, this can be so only if the wavevector $\mathbf{k}$ equals 2π times a vector in the reciprocal lattice. It is also seen from equation (1.1.6.7) that the wavevector appearing in the phase factor can be reduced to a unit cell in the reciprocal lattice (the basis vectors of which contain the 2π factor), or to the equivalent polyhedron known as the *Brillouin zone* (*e.g.* Ziman, 1969). This periodicity in reciprocal space is of prime importance in the theory of solids. Some Brillouin zones are discussed in detail in Chapter 1.5.

Acknowledgements

I wish to thank Professor D. W. J. Cruickshank for bringing to my attention the contribution of M. von Laue (Laue, 1914), who was the first to introduce general reciprocal bases to crystallography.

1.2. The structure factor

BY P. COPPENS

1.2.1. Introduction

The *structure factor* is the central concept in structure analysis by diffraction methods. Its modulus is called the *structure amplitude*. The structure amplitude is a function of the indices of the set of scattering planes h , k and l , and is defined as the amplitude of scattering by the contents of the crystallographic unit cell, expressed in units of scattering. For X-ray scattering, that unit is the scattering by a single electron (2.82×10^{-15} m), while for neutron scattering by atomic nuclei, the unit of scattering length of 10^{-14} m is commonly used. The complex form of the structure factor means that the phase of the scattered wave is not simply related to that of the incident wave. However, the observable, which is the scattered intensity, must be real. It is proportional to the square of the scattering amplitude (see, *e.g.*, Lipson & Cochran, 1966).

The structure factor is directly related to the distribution of scattering matter in the unit cell which, in the X-ray case, is the electron distribution, time-averaged over the vibrational modes of the solid.

In this chapter we will discuss structure-factor expressions for X-ray and neutron scattering, and, in particular, the modelling that is required to obtain an analytical description in terms of the features of the electron distribution and the vibrational displacement parameters of individual atoms. We concentrate on the most basic developments; for further details the reader is referred to the cited literature.

1.2.2. General scattering expression for X-rays

The total scattering of X-rays contains both elastic and inelastic components. Within the first-order Born approximation (Born, 1926) it has been treated by several authors (*e.g.* Waller & Hartree, 1929; Feil, 1977) and is given by the expression

$$I_{\text{total}}(\mathbf{S}) = I_{\text{classical}} \sum_n \left| \int \psi_n^* \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \psi_0 \, d\mathbf{r} \right|^2, \quad (1.2.2.1)$$

where $I_{\text{classical}}$ is the classical Thomson scattering of an X-ray beam by a free electron, which is equal to $(e^2/mc^2)^2(1 + \cos^2 2\theta)/2$ for an unpolarized beam of unit intensity, ψ is the n -electron space-wavefunction expressed in the $3n$ coordinates of the electrons located at $\mathbf{r}_j$ and the integration is over the coordinates of all electrons. $\mathbf{S}$ is the scattering vector of length $2 \sin \theta / \lambda$.

The coherent elastic component of the scattering, in units of the scattering of a free electron, is given by

$$I_{\text{coherent, elastic}}(\mathbf{S}) = \left| \int \psi_0^* \sum_j \exp(2\pi i \mathbf{S} \cdot \mathbf{r}_j) \psi_0 \, d\mathbf{r} \right|^2. \quad (1.2.2.2)$$

If integration is performed over all coordinates but those of the j th electron, one obtains after summation over all electrons

$$I_{\text{coherent, elastic}}(\mathbf{S}) = \left| \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \right|^2, \quad (1.2.2.3)$$

where $\rho(\mathbf{r})$ is the electron distribution. The scattering amplitude $A(\mathbf{S})$ is then given by

$$A(\mathbf{S}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r} \quad (1.2.2.4a)$$

or

$$A(\mathbf{S}) = \hat{F}\{\rho(\mathbf{r})\}, \quad (1.2.2.4b)$$

where $\hat{F}$ is the Fourier transform operator.

1.2.3. Scattering by a crystal: definition of a structure factor

In a crystal of infinite size, $\rho(\mathbf{r})$ is a three-dimensional periodic function, as expressed by the convolution

$$\rho_{\text{crystal}}(\mathbf{r}) = \sum_n \sum_m \sum_p \rho_{\text{unit cell}}(\mathbf{r}) * \delta(\mathbf{r} - n\mathbf{a} - m\mathbf{b} - p\mathbf{c}), \quad (1.2.3.1)$$

where n , m and p are integers, and δ is the Dirac delta function.

Thus, according to the Fourier convolution theorem,

$$\begin{aligned} A(\mathbf{S}) &= \hat{F}\{\rho(\mathbf{r})\} \\ &= \sum_n \sum_m \sum_p \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} \hat{F}\{\delta(\mathbf{r} - n\mathbf{a} - m\mathbf{b} - p\mathbf{c})\}, \end{aligned} \quad (1.2.3.2)$$

which gives

$$A(\mathbf{S}) = \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} \sum_h \sum_k \sum_l \delta(\mathbf{S} - h\mathbf{a}^* - k\mathbf{b}^* - l\mathbf{c}^*). \quad (1.2.3.3)$$

Expression (1.2.3.3) is valid for a crystal with a very large number of unit cells, in which particle-size broadening is negligible. Furthermore, it does not account for multiple scattering of the beam within the crystal. Because of the appearance of the delta function, (1.2.3.3) implies that $\mathbf{S} = \mathbf{H}$ with $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$.

The first factor in (1.2.3.3), the scattering amplitude of one unit cell, is defined as the structure factor F :

$$F(\mathbf{H}) = \hat{F}\{\rho_{\text{unit cell}}(\mathbf{r})\} = \int_{\text{unit cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \, d\mathbf{r}. \quad (1.2.3.4)$$

1.2.4. The isolated-atom approximation in X-ray diffraction

To a reasonable approximation, the unit-cell density can be described as a superposition of isolated, spherical atoms located at $\mathbf{r}_j$.

$$\rho_{\text{unit cell}}(\mathbf{r}) = \sum_j \rho_{\text{atom},j}(\mathbf{r}) * \delta(\mathbf{r} - \mathbf{r}_j). \quad (1.2.4.1)$$

Substitution in (1.2.3.4) gives

$$F(\mathbf{H}) = \sum_j \hat{F}\{\rho_{\text{atom},j}\} \hat{F}\{\delta(\mathbf{r} - \mathbf{r}_j)\} = \sum_j f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \quad (1.2.4.2a)$$

or

$$\begin{aligned} F(h, k, l) &= \sum_j f_j \exp 2\pi i (hx_j + ky_j + lz_j) \\ &= \sum_j f_j \{ \cos 2\pi (hx_j + ky_j + lz_j) \\ &\quad + i \sin 2\pi (hx_j + ky_j + lz_j) \}. \end{aligned} \quad (1.2.4.2b)$$

$f_j(S)$, the spherical atomic scattering factor, or form factor, is the Fourier transform of the spherically averaged atomic density $\rho_j(r)$, in which the polar coordinate r is relative to the nuclear position. $f_j(S)$ can be written as (James, 1982)

1.2. THE STRUCTURE FACTOR

$$\begin{aligned}
 f_j(S) &= \int_{\text{atom}} \rho_j(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\mathbf{r} \\
 &= \int_{\varphi=0}^{\pi} \int_{\varphi=0}^{2\pi} \int_{r=0}^{\infty} \rho_j(r) \exp(2\pi i S r \cos \vartheta) r^2 \sin \vartheta dr d\vartheta d\varphi \\
 &= \int_0^r 4\pi r^2 \rho_j(r) \frac{\sin 2\pi S r}{2\pi S r} dr \equiv \int_0^r 4\pi r^2 \rho_j(r) j_0(2\pi S r) dr \\
 &\equiv \langle j_0 \rangle,
 \end{aligned} \tag{1.2.4.3}$$

where $j_0(2\pi S r)$ is the zero-order spherical Bessel function.

$\rho_j(r)$ represents either the static or the dynamic density of atom j . In the former case, the effect of thermal motion, treated in Section 1.2.9 and following, is not included in the expression.

When scattering is treated in the second-order Born approximation, additional terms occur which are in particular of importance for X-ray wavelengths with energies close to absorption edges of atoms, where the participation of free and bound excited states in the scattering process becomes very important, leading to *resonance scattering*. Inclusion of such contributions leads to two extra terms, which are both wavelength- and scattering-angle-dependent:

$$f_j(S, \lambda) = f_j^0(S) + f_j'(S, \lambda) + i f_j''(S, \lambda). \tag{1.2.4.4}$$

The treatment of resonance effects is beyond the scope of this chapter. We note however (a) that to a reasonable approximation the S -dependence of f_j' and f_j'' can be neglected, (b) that f_j' and f_j'' are not independent, but related through the Kramers–Kronig transformation, and (c) that in an anisotropic environment the atomic scattering factor becomes anisotropic, and accordingly is described as a tensor property. Detailed descriptions and appropriate references can be found in Materlick *et al.* (1994) and in Section 4.2.6 of *IT C* (1999).

The structure-factor expressions (1.2.4.2) can be simplified when the crystal class contains non-trivial symmetry elements. For example, when the origin of the unit cell coincides with a centre of symmetry ($x, y, z \rightarrow -x, -y, -z$) the sine term in (1.2.4.2b) cancels when the contributions from the symmetry-related atoms are added, leading to the expression

$$F(\mathbf{H}) = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j), \tag{1.2.4.2c}$$

where the summation is over the unique half of the unit cell only.

Further simplifications occur when other symmetry elements are present. They are treated in Chapter 1.4, which also contains a complete list of symmetry-specific structure-factor expressions valid in the spherical-atom isotropic-temperature-factor approximation.

1.2.5. Scattering of thermal neutrons

1.2.5.1. Nuclear scattering

The scattering of neutrons by atomic nuclei is described by the atomic scattering length b , related to the total cross section σ_{total} by the expression $\sigma_{\text{total}} = 4\pi b^2$. At present, there is no theory of nuclear forces which allows calculation of the scattering length, so that experimental values are to be used. Two types of nuclei can be distinguished (Squires, 1978). In the first type, the scattering is a resonance phenomenon and is associated with the formation of a compound nucleus (consisting of the original nucleus plus a neutron) with an energy close to that of an excited state. In the second type, the compound nucleus is not near an excited state and

the scattering length is essentially real and independent of the energy of the incoming neutron. In either case, b is independent of the Bragg angle θ , unlike the X-ray form factor, since the nuclear dimensions are very small relative to the wavelength of thermal neutrons.

The scattering length is not the same for different isotopes of an element. A random distribution of isotopes over the sites occupied by that element leads to an incoherent contribution, such that effectively $\sigma_{\text{total}} = \sigma_{\text{coherent}} + \sigma_{\text{incoherent}}$. Similarly for nuclei with non-zero spin, a spin incoherent scattering occurs as the spin states are, in general, randomly distributed over the sites of the nuclei.

For free or loosely bound nuclei, the scattering length is modified by $b_{\text{free}} = [M/(m + M)]b$, where M is the mass of the nucleus and m is the mass of the neutron. This effect is of consequence only for the lightest elements. It can, in particular, be of significance for hydrogen atoms. With this in mind, the structure-factor expression for elastic scattering can be written as

$$F(\mathbf{H}) = \sum_j b_{j, \text{coherent}} \exp 2\pi i(hx_j + ky_j + lz_j) \tag{1.2.4.2d}$$

by analogy to (1.2.4.2b).

1.2.5.2. Magnetic scattering

The interaction between the magnetic moments of the neutron and the unpaired electrons in solids leads to magnetic scattering. The total elastic scattering including both the nuclear and magnetic contributions is given by

$$|F(\mathbf{H})|_{\text{total}}^2 = |F_N(\mathbf{H}) + \mathbf{Q}(\mathbf{H}) \cdot \hat{\lambda}|^2, \tag{1.2.5.1a}$$

where the unit vector $\hat{\lambda}$ describes the polarization vector for the neutron spin, $F_N(\mathbf{H})$ is given by (1.2.4.2b) and $\mathbf{Q}$ is defined by

$$\mathbf{Q} = \frac{mc}{eh} \int \hat{\mathbf{H}} \times [\mathbf{M}(\mathbf{r}) \times \hat{\mathbf{H}}] \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}. \tag{1.2.5.2a}$$

$\mathbf{M}(\mathbf{r})$ is the vector field describing the electron-magnetization distribution and $\hat{\mathbf{H}}$ is a unit vector parallel to $\mathbf{H}$.

$\mathbf{Q}$ is thus proportional to the projection of $\mathbf{M}$ onto a direction orthogonal to $\mathbf{H}$ in the plane containing $\mathbf{M}$ and $\mathbf{H}$. The magnitude of this projection depends on $\sin \alpha$, where α is the angle between $\mathbf{Q}$ and $\mathbf{H}$, which prevents magnetic scattering from being a truly three-dimensional probe. If all moments $\mathbf{M}(\mathbf{r})$ are collinear, as may be achieved in paramagnetic materials by applying an external field, and for the maximum signal ($\mathbf{H}$ orthogonal to $\mathbf{M}$), (1.2.5.2a) becomes

$$\mathbf{Q} = \mathbf{M}(\mathbf{H}) = \frac{mc}{eh} \int \mathbf{M}(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r} \tag{1.2.5.2b}$$

and (1.2.5.1a) gives

$$|F|_{\text{total}}^2 = |F_N(\mathbf{H}) - M(\mathbf{H})|^2 \tag{1.2.5.1b}$$

and

$$|F|_{\text{total}}^2 = |F_N(\mathbf{H}) + M(\mathbf{H})|^2$$

for neutrons parallel and antiparallel to $\mathbf{M}(\mathbf{H})$, respectively.

1.2.6. Effect of bonding on the atomic electron density within the spherical-atom approximation: the kappa formalism

A first improvement beyond the isolated-atom formalism is to allow for changes in the radial dependence of the atomic electron distribution.

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table 1.2.7.1. Real spherical harmonic functions (x, y, z are direction cosines)

l	Symbol	C^*	Angular function, $c_{imp}^\dagger$	Normalization for wavefunctions, $M_{imp}^\ddagger$		Normalization for density functions, $L_{imp}^\S$	
				Expression	Numerical value	Expression	Numerical value
0	00	1	1	$(1/4\pi)^{1/2}$	0.28209	$1/4\pi$	0.07958
1	11+ 11- 10	1 1 1	$\begin{Bmatrix} x \\ y \\ z \end{Bmatrix}$	$(3/4\pi)^{1/2}$	0.48860	$1/\pi$	0.31831
2	20 21+ 21- 22+ 22-	1/2 3 3 6 6	$\begin{Bmatrix} 3z^2 - 1 \\ xz \\ yz \\ (x^2 - y^2)/2 \\ xy \end{Bmatrix}$	$(5/16\pi)^{1/2}$ $(15/4\pi)^{1/2}$	0.31539 1.09255	$\frac{3\sqrt{3}}{8\pi}$ 3/4	0.20675 0.75
3	30 31+ 31- 32+ 32- 33+ 33-	1/2 3/2 3/2 15 15 15 15	$\begin{Bmatrix} 5z^3 - 3z \\ x[5z^2 - 1] \\ y[5z^2 - 1] \\ (x^2 - y^2)z \\ 2xyz \\ x^3 - 3xy^2 \\ -y^3 + 3x^2y \end{Bmatrix}$	$(7/16\pi)^{1/2}$ $(21/32\pi)^{1/2}$ $(105/16\pi)^{1/2}$ $(35/32\pi)^{1/2}$	0.37318 0.45705 1.44531 0.59004	$\frac{10}{13\pi}$ $\left(\arctan\left(\frac{14}{5} - \frac{\pi}{4}\right)\right)^{-1}$ 1 4/3\pi	0.24485 0.32033 1 0.42441
4	40 41+ 41- 42+ 42- 43+ 43- 44+ 44-	1/8 5/2 5/2 15/2 15/2 105 105 105 105	$\begin{Bmatrix} 35z^4 - 30z^2 + 3 \\ x[7z^3 - 3z] \\ y[7z^3 - 3z] \\ (x^2 - y^2)[7z^2 - 1] \\ 2xy[7z^2 - 1] \\ (x^3 - 3xy^2)z \\ (-y^3 + 3x^2y)z \\ x^4 - 6x^2y^2 + y^4 \\ 4x^3y - 4xy^3 \end{Bmatrix}$	$(9/256\pi)^{1/2}$ $(45/32\pi)^{1/2}$ $(45/64\pi)^{1/2}$ $(315/32\pi)^{1/2}$ $(315/256\pi)^{1/2}$	0.10579 0.66905 0.47309 1.77013 0.62584	** $\frac{735}{512\sqrt{7} + 196}$ $\frac{105\sqrt{7}}{4(136 + 28\sqrt{7})}$ 5/4 15/32	0.06942 0.47400 0.33059 1.25 0.46875
5	50 51+ 51- 52+ 52- 53+ 53- 54+ 54- 55+ 55-	1/8 15/8 105/2 105/2 945 945	$\begin{Bmatrix} 63z^5 - 70z^3 - 15z \\ (21z^4 - 14z^2 + 1)x \\ (21z^4 - 14z^2 + 1)y \\ (3z^3 - z)(x^2 - y^2) \\ 2xy(3z^3 - z) \\ (9z^2 - 1)(x^3 - 3xy^2) \\ (9z^2 - 1)(3x^2y - y^3) \\ z(x^4 - 6x^2y^2 + y^4) \\ z(4x^3y - 4xy^3) \\ x^5 - 10x^3y^2 + 5xy^4 \\ 5x^4y - 10x^2y^3 + y^5 \end{Bmatrix}$	$(11/256\pi)^{1/2}$ $(165/256\pi)^{1/2}$ $(1155/64\pi)^{1/2}$ $(385/512\pi)^{1/2}$ $(3465/256\pi)^{1/2}$ $(693/512\pi)^{1/2}$	0.11695 0.45295 2.39677 0.48924 2.07566 0.65638	— — — — — —	0.07674 0.32298 1.68750 0.34515 1.50000 0.50930

Such changes may be due to electronegativity differences which lead to the transfer of electrons between the valence shells of different atoms. The electron transfer introduces a change in the screening of the nuclear charge by the electrons and therefore

affects the radial dependence of the atomic electron distribution (Coulson, 1961). A change in radial dependence of the density may also occur in a purely covalent bond, as, for example, in the H_2 molecule (Ruedenberg, 1962). It can be expressed as

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Table 1.2.7.1. *Real spherical harmonic functions* (x, y, z are direction cosines) (cont.)

l	Symbol	C^*	Angular function, $c_{lmp}^\dagger$	Normalization for wavefunctions, $M_{lmp}^\ddagger$		Normalization for density functions, $L_{lmp}^\S$	
				Expression	Numerical value	Expression	Numerical value
6	60	1/16	$231z^6 - 315z^4 + 105z^2 - 5$	$(13/1024\pi)^{1/2}$	0.06357	—	0.04171
	61+	21/8	$(33z^5 - 30z^3 + 5z)x$	$(273/256\pi)^{1/2}$	0.58262	—	0.41721
	61-		$(33z^5 - 30z^3 + 5z)y$				
	62+	105/8	$(33z^4 - 18z^2 + 1)(x^2 - y^2)$	$(1365/2048\pi)^{1/2}$	0.46060	—	0.32611
	62-		$2xy(33z^4 - 18z^2 + 1)$				
	63+	315/2	$(11z^3 - 3z)(x^3 - 3xy^2)$	$(1365/512\pi)^{1/2}$	0.92121	—	0.65132
	63-		$(11z^3 - 3z)(3x^2y - 3y^3)$				
7	64+	945/2	$(11z^2 - 1)(x^4 - 6x^2y^2 + y^4)$	$(819/1024\pi)^{1/2}$	0.50457	—	0.36104
	64-		$(11z^2 - 1)(4x^3y - 4xy^3)$				
	65+	10395	$z(x^5 - 10x^3y^2 + 5xy^4)$	$(9009/512\pi)^{1/2}$	2.36662	—	1.75000
	65-		$z(5x^4y - 10x^2y^3 + y^5)$				
	66+	10395	$x^6 - 15x^4y^2 + 15x^2y^4 - y^6$	$(3003/2048\pi)^{1/2}$	0.68318	—	0.54687
	66-		$6x^5y - 20x^3y^3 + 6xy^5$				
	70	1/16	$429z^7 - 693z^5 + 315z^3 - 35z$	$(15/1024\pi)^{1/2}$	0.06828	—	0.04480
7	71+	7/16	$(429z^6 - 495z^4 + 135z^2 - 5)x$	$(105/4096\pi)^{1/2}$	0.09033	—	0.06488
	71-		$(429z^6 - 495z^4 + 135z^2 - 5)y$				
	72+	63/8	$(143z^5 - 110z^3 + 15z)(x^2 - y^2)$	$(315/2048\pi)^{1/2}$	0.22127	—	0.15732
	72-		$2xy(143z^5 - 110z^3 + 15z)$				
	73+	315/8	$(143z^4 - 66z^2 + 3)(x^3 - 3xy^2)$	$(315/4096\pi)^{1/2}$	0.15646	—	0.11092
	73-		$(143z^4 - 66z^2 + 3)(3x^2y - y^3)$				
	74+	3465/2	$(13z^3 - 3z)(x^4 - 6x^2y^2 + y^4)$	$(3465/1024\pi)^{1/2}$	1.03783	—	0.74044
	74-		$(13z^3 - 3z)(4x^3y - 4xy^3)$				
	75+	10395/2	$(13z^3 - 1)(x^5 - 10x^3y^2 + 5xy^4)$	$(3465/4096\pi)^{1/2}$	0.51892	—	0.37723
	75-		$(13z^3 - 1)(5x^4y - 10x^2y^3 + y^5)$				
7	76+	135135	$z(x^6 - 15x^4y^2 + 15x^2y^4 - y^6)$	$(45045/2048\pi)^{1/2}$	2.6460	—	2.00000
	76-		$z(6x^5y + 20x^3y^3 - 6xy^5)$				
	77+	135135	$x^7 - 21x^5y^2 + 35x^3y^4 - 7xy^6$	$(6435/4096\pi)^{1/2}$	0.70716	—	0.58205
	77-		$7x^6y - 35x^4y^3 + 21x^2y^5 - y^7$				

* Common factor such that $C_{lm}c_{lmp} = P_l^m(\cos\theta)_{\sin m\varphi}^{\cos m\varphi}$.

† $x = \sin\theta \cos\varphi$, $y = \sin\theta \sin\varphi$, $z = \cos\theta$.

‡ As defined by $y_{lmp} = M_{lmp}c_{lmp}$ where c_{lmp} are Cartesian functions.

§ Paturle & Coppens (1988), as defined by $d_{lmp} = L_{lmp}c_{lmp}$ where c_{lmp} are Cartesian functions.

¶ $\ar = \arctan(2)$.

** $N_{\text{ang}} = \{(14A_-^5 - 14A_+^5 + 20A_+^3 - 20A_-^3 + 6A_- - 6A_+)2\pi\}^{-1}$ where $A_{\pm} = [(30 \pm \sqrt{480})/70]^{1/2}$.

$$\rho'_{\text{valence}}(r) = \kappa^3 \rho_{\text{valence}}(\kappa r) \quad (1.2.6.1)$$

The corresponding structure-factor expression is

$$F(\mathbf{H}) = \sum_j [P_{j, \text{core}} f_{j, \text{core}}(H) + P_{j, \text{valence}} f_{j, \text{valence}}(H/\kappa)] \times \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j), \quad (1.2.6.2)$$

(Coppens *et al.*, 1979), where ρ' is the modified density and κ is an expansion/contraction parameter, which is > 1 for valence-shell contraction and < 1 for expansion. The κ^3 factor results from the normalization requirement.

The valence density is usually defined as the outer electron shell from which charge transfer occurs. The inner or core electrons are much less affected by the change in occupancy of the outer shell and, in a reasonable approximation, retain their radial dependence.

where $P_{j, \text{core}}$ and $P_{j, \text{valence}}$ are the number of electrons (not necessarily integral) in the core and valence shell, respectively, and the atomic scattering factors $f_{j, \text{core}}$ and $f_{j, \text{valence}}$ are normalized to one electron. Here and in the following sections, the anomalous-scattering contributions are incorporated in the core scattering.

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1.2.7. Beyond the spherical-atom description: the atom-centred spherical harmonic expansion

1.2.7.1. Direct-space description of aspherical atoms

Even though the spherical-atom approximation is often adequate, atoms in a crystal are in a non-spherical environment; therefore, an accurate description of the atomic electron density requires non-spherical density functions. In general, such density functions can be written in terms of the three polar coordinates r , θ and φ . Under the assumption that the radial and angular parts can be separated, one obtains for the density function:

$$\Phi(r, \theta, \varphi) = R(r)\Theta(\theta, \varphi). \quad (1.2.7.1)$$

The angular functions Θ are based on the spherical harmonic functions Y_{lm} defined by

$$Y_{lm}(\theta, \varphi) = (-1)^m \left[\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^m(\cos \theta) \exp(im\varphi), \quad (1.2.7.2a)$$

with $-l \leq m \leq l$, where $P_l^m(\cos \theta)$ are the associated Legendre polynomials (see Arfken, 1970).

$$P_l^m(x) = (1-x^2)^{|m|/2} \frac{d^{|m|} P_l(x)}{dx^{|m|}},$$

$$P_l(x) = \frac{1}{l!2^l} \frac{d^l}{dx^l} [(x^2-1)^l].$$

The real spherical harmonic functions y_{lm} , $0 \leq m \leq l$, $p = +$ or $-$ are obtained as a linear combination of Y_{lm} :

$$y_{lm+}(\theta, \psi) = \left[\frac{(2l+1)(l-|m|)!}{2\pi(1+\delta_{m0})(l+|m|)!} \right]^{1/2} P_l^m(\cos \theta) \cos m\varphi$$

$$= N_{lm} P_l^m(\cos \theta) \cos m\varphi$$

$$= (-1)^m (Y_{lm} + Y_{l, -m}) \quad (1.2.7.2b)$$

and

$$y_{lm-}(\theta, \psi) = N_{lm} P_l^m(\cos \theta) \sin m\varphi$$

$$= (-1)^m (Y_{lm} - Y_{l, -m})/2i. \quad (1.2.7.2c)$$

The normalization constants N_{lm} are defined by the conditions

$$\int y_{lm}^2 d\Omega = 1, \quad (1.2.7.3a)$$

which are appropriate for normalization of wavefunctions. An alternative definition is used for charge-density basis functions:

$$\int |d_{lm}| d\Omega = 2 \text{ for } l > 0 \text{ and } \int |d_{lm}| d\Omega = 1 \text{ for } l = 0. \quad (1.2.7.3b)$$

The functions y_{lm} and d_{lm} differ only in the normalization constants. For the spherically symmetric function d_{00} , a population parameter equal to one corresponds to the function being populated by one electron. For the non-spherical functions with $l > 0$, a population parameter equal to one implies that one electron has shifted from the negative to the positive lobes of the function.

The functions y_{lm} and d_{lm} can be expressed in Cartesian coordinates, such that

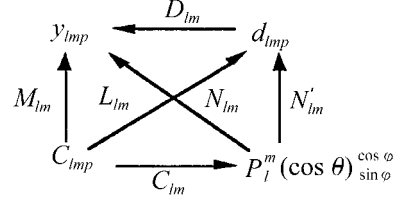
$$y_{lm} = M_{lm} c_{lm} \quad (1.2.7.4a)$$

and

$$d_{lm} = L_{lm} c_{lm}, \quad (1.2.7.4b)$$

where the c_{lm} are Cartesian functions. The relations between the various definitions of the real spherical harmonic functions are

summarized by



in which the direction of the arrows and the corresponding conversion factors X_{lm} define expressions of the type (1.2.7.4). The expressions for c_{lm} with $l \leq 4$ are listed in Table 1.2.7.1, together with the normalization factors M_{lm} and L_{lm} .

The spherical harmonic functions are mutually orthogonal and form a complete set, which, if taken to sufficiently high order, can be used to describe any arbitrary angular function.

The spherical harmonic functions are often referred to as multipoles since each represents the components of the charge distribution $\rho(\mathbf{r})$, which gives non-zero contribution to the integral $\Theta_{lm} = \int \rho(\mathbf{r}) c_{lm} r^l d\mathbf{r}$, where Θ_{lm} is an electrostatic multipole moment. Terms with increasing l are referred to as *monopolar* ($l = 0$), *dipolar* ($l = 1$), *quadrupolar* ($l = 2$), *octapolar* ($l = 3$), *hexadecapolar* ($l = 4$), *triacontadipolar* ($l = 5$) and *hexacontatetrapolar* ($l = 6$).

Site-symmetry restrictions for the real spherical harmonics as given by Kara & Kurki-Suonio (1981) are summarized in Table 1.2.7.2.

In cubic space groups, the spherical harmonic functions as defined by equations (1.2.7.2) are no longer linearly independent. The appropriate basis set for this symmetry consists of the 'Kubic Harmonics' of Von der Lage & Bethe (1947). Some low-order terms are listed in Table 1.2.7.3. Both wavefunction and density-function normalization factors are specified in Table 1.2.7.3.

A related basis set of angular functions has been proposed by Hirshfeld (1977). They are of the form $\cos^n \theta_k$, where θ_k is the angle with a specified set of $(n+1)(n+2)/2$ polar axes. The Hirshfeld functions are identical to a sum of spherical harmonics with $l = n, n-2, n-4, \dots (0, 1)$ for $n > 1$, as shown elsewhere (Hirshfeld, 1977).

The radial functions $R(r)$ can be selected in different manners. Several choices may be made, such as

$$R_l(r) = \frac{\zeta_l^{n_l+3}}{(n_l+2)!} r^{n_l} \exp(-\zeta_l r) \quad (\text{Slater type function}), \quad (1.2.7.5a)$$

where the coefficient n_l may be selected by examination of products of hydrogenic orbitals which give rise to a particular multipole (Hansen & Coppens, 1978). Values for the exponential coefficient ζ_l may be taken from energy-optimized coefficients for isolated atoms available in the literature (Clementi & Raimondi, 1963). A standard set has been proposed by Hehre *et al.* (1969). In the bonded atom, such values are affected by changes in nuclear screening due to migrations of charge, as described in part by equation (1.2.6.1).

Other alternatives are:

$$R_l(r) = \frac{\alpha^{n+1}}{n!} r^n \exp(-\alpha r^2) \quad (\text{Gaussian function}) \quad (1.2.7.5b)$$

or

$$R_l(r) = r^l L_n^{2l+2}(\gamma r) \exp\left(-\frac{\gamma r}{2}\right) \quad (\text{Laguerre function}), \quad (1.2.7.5c)$$

where L is a Laguerre polynomial of order n and degree $(2l+2)$.

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Table 1.2.7.2. *Index-picking rules of site-symmetric spherical harmonics (Kara & Kurki-Suonio, 1981)*

λ , μ and j are integers.

Symmetry	Choice of coordinate axes	Indices of allowed y_{lmp} , d_{lmp}
1	Any	All $(l, m, \pm)$
$\bar{1}$	Any	$(2\lambda, m, \pm)$
2	$2\parallel z$	$(l, 2\mu, \pm)$
m	$m \perp z$	$(l, l - 2j, \pm)$
$2/m$	$2\parallel z, m \perp z$	$(2\lambda, 2\mu, \pm)$
222	$2\parallel z, 2\parallel y$	$(2\lambda, 2\mu, +), (2\lambda + 1, 2\mu, -)$
$mm2$	$2\parallel z, m \perp y$	$(l, 2\mu, +)$
mmm	$m \perp z, m \perp y, m \perp x$	$(2\lambda, 2\mu, +)$
4	$4\parallel z$	$(l, 4\mu, \pm)$
$\bar{4}$	$\bar{4}\parallel z$	$(2\lambda, 4\mu, \pm), (2\lambda + 1, 4\mu + 2, \pm)$
$4/m$	$4\parallel z, m \perp z$	$(2\lambda, 4\mu, \pm)$
422	$4\parallel z, 2\parallel y$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu, -)$
$4mm$	$4\parallel z, m \perp y$	$(l, 4\mu, +)$
$\bar{4}2m$	$\bar{4}\parallel z, 2\parallel x$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu + 2, -)$
	$m \perp y$	$(2\lambda, 4\mu, +), (2\lambda + 1, 4\mu + 2, +)$
$4/mmm$	$4\parallel z, m \perp z, m \perp x$	$(2\lambda, 4\mu, +)$
3	$3\parallel z$	$(l, 3\mu, \pm)$
$\bar{3}$	$\bar{3}\parallel z$	$(2\lambda, 3\mu, \pm)$
32	$3\parallel z, 2\parallel y$	$(2\lambda, 3\mu, +), (2\lambda + 1, 3\mu, -)$
	$2\parallel x$	$(3\mu + 2j, 3\mu, +),$ $(3\mu + 2j + 1, 3\mu, -)$
$3m$	$3\parallel z, m \perp y$	$(l, 3\mu, +)$
	$m \perp x$	$(l, 6\mu, +), (l, 6\mu + 3, -)$
$\bar{3}m$	$\bar{3}\parallel z, m \perp y$	$(2\lambda, 3\mu, +)$
	$m \perp x$	$(2\lambda, 6\mu, +), (2\lambda, 6\mu + 3, -)$
6	$6\parallel z$	$(l, 6\mu, \pm)$
$\bar{6}$	$\bar{6}\parallel z$	$(2\lambda, 6\mu, \pm), (2\lambda + 1, 6\mu + 3, \pm)$
$6/m$	$6\parallel z, m \perp z$	$(2\lambda, 6\mu, \pm)$
622	$6\parallel z, 2\parallel y$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu, -)$
$6mm$	$6\parallel z, m\parallel y$	$(l, 6\mu, +)$
$\bar{6}m2$	$\bar{6}\parallel z, m \perp y$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu + 3, +)$
	$m \perp x$	$(2\lambda, 6\mu, +), (2\lambda + 1, 6\mu + 3, -)$
$6/mmm$	$6\parallel z, m \perp z, m \perp y$	$(2\lambda, 6\mu, +)$

In summary, in the multipole formalism the atomic density is described by

$$\rho_{\text{atomic}}(\mathbf{r}) = P_c \rho_{\text{core}} + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{l=0}^{l_{\text{max}}} \kappa^3 R_l(\kappa' r) \sum_{m=0}^l \sum_p P_{lmp} d_{lmp}(\mathbf{r}/r), \quad (1.2.7.6)$$

in which the leading terms are those of the kappa formalism [expressions (1.2.6.1), (1.2.6.2)]; the subscript p is either + or -.

The expansion in (1.2.7.6) is frequently truncated at the hexadecapolar ($l = 4$) level. For atoms at positions of high site symmetry the first allowed functions may occur at higher l values. For trigonally bonded atoms in organic molecules the $l = 3$ terms are often found to be the most significantly populated deformation functions.

1.2.7.2. Reciprocal-space description of aspherical atoms

The aspherical-atom form factor is obtained by substitution of (1.2.7.6) in expression (1.2.4.3a):

$$f_j(\mathbf{S}) = \int \rho_j(\mathbf{r}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\mathbf{r}. \quad (1.2.4.3a)$$

In order to evaluate the integral, the scattering operator $\exp(2\pi i \mathbf{S} \cdot \mathbf{r})$ must be written as an expansion of products of spherical harmonic functions. In terms of the complex spherical harmonic functions, the appropriate expression is (Weiss & Freeman, 1959; Cohen-Tannoudji *et al.*, 1977)

$$\exp(2\pi i \mathbf{S} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(2\pi S r) Y_{lm}(\theta, \varphi) Y_{lm}^*(\beta, \gamma). \quad (1.2.7.7a)$$

The Fourier transform of the product of a complex spherical harmonic function with normalization $\int |Y_{lm}|^2 d\Omega = 1$ and an arbitrary radial function $R_l(r)$ follows from the orthonormality properties of the spherical harmonic functions, and is given by

$$\int Y_{lm} R_l(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\tau = 4\pi i^l \int j_l(2\pi S r) R_l(r) r^2 dr Y_{lm}(\beta, \gamma), \quad (1.2.7.8a)$$

where j_l is the l th-order spherical Bessel function (Arfken, 1970), and θ and φ , β and γ are the angular coordinates of $\mathbf{r}$ and $\mathbf{S}$, respectively.

For the Fourier transform of the real spherical harmonic functions, the scattering operator is expressed in terms of the real spherical harmonics:

$$\exp(2\pi i \mathbf{S} \cdot \mathbf{r}) = \sum_{l=0}^{\infty} i^l j_l(2\pi S r) (2 - \delta_{m0}) (2l + 1) \sum_{m=0}^l \frac{(l - m)!}{(l + m)!} \times P_l^m(\cos \theta) P_l^m(\cos \beta) \cos[m(\phi - \gamma)], \quad (1.2.7.7b)$$

which leads to

$$\int y_{lmp}(\theta, \varphi) R_l(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\tau = 4\pi i^l \langle j_l \rangle y_{lmp}(\beta, \gamma). \quad (1.2.7.8b)$$

Since y_{lmp} occurs on both sides, the expression is independent of the normalization selected. Therefore, for the Fourier transform of the density functions d_{lmp}

$$\int d_{lmp}(\theta, \varphi) R_l(r) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\tau = 4\pi i^l \langle j_l \rangle d_{lmp}(\beta, \gamma). \quad (1.2.7.8c)$$

In (1.2.7.8b) and (1.2.7.8c), $\langle j_l \rangle$, the *Fourier-Bessel transform*, is the radial integral defined as

$$\langle j_l \rangle = \int j_l(2\pi S r) R_l(r) r^2 dr \quad (1.2.7.9)$$

of which $\langle j_0 \rangle$ in expression (1.2.4.3) is a special case. The functions $\langle j_l \rangle$ for Hartree-Fock valence shells of the atoms are tabulated in scattering-factor tables (IT IV, 1974). Expressions for the evaluation of $\langle j_l \rangle$ using the radial function (1.2.7.5a-c) have been given by Stewart (1980) and in closed form for (1.2.7.5a) by Avery & Watson (1977) and Su & Coppens (1990). The closed-form expressions are listed in Table 1.2.7.4.

Expressions (1.2.7.8) show that the Fourier transform of a direct-space spherical harmonic function is a reciprocal-space spherical harmonic function with the same l , m , or, in other words, the spherical harmonic functions are Fourier-transform invariant.

The scattering factors $f_{lmp}(\mathbf{S})$ of the aspherical density functions $R_l(r) d_{lmp}(\theta, \phi)$ in the multipole expansion (1.2.7.6) are thus given by

$$f_{lmp}(\mathbf{S}) = 4\pi i^l \langle j_l \rangle d_{lmp}(\beta, \gamma). \quad (1.2.7.8d)$$

The reciprocal-space spherical harmonic functions in this expression are identical to the functions given in Table 1.2.7.1, except for the replacement of the direction cosines x , y and z by the direction cosines of the scattering vector $\mathbf{S}$.

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Table 1.2.7.3. 'Kubic Harmonic' functions

(a) Coefficients in the expression $K_{lj} = \sum_{mp} k_{mpj}^l y_{lmp}$ with normalization $\int_0^\pi \int_0^{2\pi} |K_{lj}|^2 \sin \theta \, d\theta \, d\varphi = 1$ (Kara & Kurki-Suonio, 1981).

Even l		mp					
l	j	0+	2+	4+	6+	8+	10+
0	1	1					
4	1	$\frac{1}{2} \left(\frac{7}{3}\right)^{1/2}$ 0.76376		$\frac{1}{2} \left(\frac{5}{3}\right)^{1/2}$ 0.64550			
6	1	$\frac{1}{2} \left(\frac{1}{2}\right)^{1/2}$ 0.35355		$-\frac{1}{2} \left(\frac{7}{2}\right)^{1/2}$ -0.93541			
6	2		$\frac{1}{4} 11^{1/2}$ 0.82916		$-\frac{1}{4} 5^{1/2}$ -0.55902		
8	1	$\frac{1}{8} 33^{1/2}$ 0.71807		$\frac{1}{4} \left(\frac{7}{3}\right)^{1/2}$ 0.38188		$\frac{1}{8} \left(\frac{65}{3}\right)^{1/2}$ 0.58184	
10	1	$\frac{1}{8} \left(\frac{65}{6}\right)^{1/2}$ 0.41143		$-\frac{1}{4} \left(\frac{11}{2}\right)^{1/2}$ -0.58630		$-\frac{1}{8} \left(\frac{187}{6}\right)^{1/2}$ -0.69784	
10	2		$\frac{1}{8} \left(\frac{247}{6}\right)^{1/2}$ 0.80202		$\frac{1}{16} \left(\frac{19}{3}\right)^{1/2}$ 0.15729		$\frac{1}{16} 85^{1/2}$ 0.57622
l	j		2-	4-	6-	8-	
3	1		1				
7	1		$\frac{1}{2} \left(\frac{13}{6}\right)^{1/2}$ 0.73598		$\frac{1}{2} \left(\frac{11}{16}\right)^{1/2}$ 0.41458		
9	1		$\frac{1}{4} 3^{1/2}$ 0.43301		$-\frac{1}{4} 13^{1/2}$ -0.90139		
9	2		$\frac{1}{2} \left(\frac{17}{6}\right)^{1/2}$ 0.84163		$-\frac{1}{2} \left(\frac{7}{6}\right)^{1/2}$ -0.54006		

(b) Coefficients k_{mpj}^l and density normalization factors N_{lj} in the expression $K_{lj} = N_{lj} \sum_{mp} k_{mpj}^l u_{lmp}$ where $u_{lm\pm} = P_l^m(\cos \theta) \frac{\cos m\varphi}{\sin m\varphi}$ (Su & Coppens, 1994).

Even l		N_{lj}	mp				
l	j		0+	2+	4+	6+	8+
0	1	$1/4\pi = 0.079577$	1				
4	1	0.43454	1		+1/168		
6	1	0.25220	1		-1/360		
6	2	0.020833		1		-1/792	

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Table 1.2.7.3. 'Kubic Harmonic' functions (cont.)

Even l		N_{lj}	mp					
8	1	0.56292	1		1/5940		$\frac{1}{672} \times \frac{1}{5940}$	
10	1	0.36490	1		1/5460		$\frac{1}{4320} \times \frac{1}{5460}$	
10	2	0.0095165	1			1/43680		$-\frac{1}{456} \times \frac{1}{43680}$
l	j			2—	4—	6—	8—	
3	1	0.066667		1				
7	1	0.014612		1		1/1560		
9	1	0.0059569		1		1/2520		
9	2	0.00014800			1		$-1/4080$	

(c) Density-normalized Kubic harmonics as linear combinations of density-normalized spherical harmonic functions. Coefficients in the expression $K_{lj} = \sum_{mp} k_{mpj}'' d_{lmp}$. Density-type normalization is defined as $\int_0^\pi \int_0^{2\pi} |K_{lj}| \sin \theta \, d\theta \, d\varphi = 2 - \delta_{l0}$.

Even l		mp					
l	j	0+	2+	4+	6+	8+	10+
0	1	1					
4	1	0.78245		0.57939			
6	1	0.37790		-0.91682			
6	2		0.83848		-0.50000		
l	j	2—	4—	6—	8—		
3	1	1					
7	1	0.73145		0.63290			

(d) Index rules for cubic symmetries (Kurki-Suonio, 1977; Kara & Kurki-Suonio, 1981).

l	j	23 T	$m\bar{3}$ T_h	432 O	$43m$ T_d	$m\bar{3}m$ O_h
0	1	×	×	×	×	×
3	1	×			×	
4	1	×	×	×	×	×
6	1	×	×	×	×	×
6	2	×	×			
7	1	×			×	
8	1	×	×	×	×	×
9	1	×			×	
9	2	×		×		
10	1	×	×	×	×	×
10	2	×	×			

1.2.8. Fourier transform of orbital products

by (Stewart, 1969a)

If the wavefunction is written as a sum over normalized Slater determinants, each representing an antisymmetrized combination of occupied molecular orbitals χ_i expressed as linear combinations of atomic orbitals φ_ν , i.e. $\chi_i = \sum_\nu c_{i\nu} \varphi_\nu$, the electron density is given

$$\rho(\mathbf{r}) = \sum_i n_i \chi_i^2 = \sum_\mu \sum_\nu P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}), \quad (1.2.8.1)$$

with $n_i = 1$ or 2. The coefficients $P_{\mu\nu}$ are the populations of the

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orbital product density functions $\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})$ and are given by

$$P_{\mu\nu} = \sum_i n_i c_{i\mu} c_{i\nu}. \quad (1.2.8.2)$$

For a multi-Slater determinant wavefunction the electron density is expressed in terms of the occupied natural spin orbitals, leading again to (1.2.8.2) but with non-integer values for the coefficients n_i .

The summation (1.2.8.1) consists of one- and two-centre terms for which φ_μ and φ_ν are centred on the same or on different nuclei, respectively. The latter represent the overlap density, which is only significant if $\varphi_\mu(\mathbf{r})$ and $\varphi_\nu(\mathbf{r})$ have an appreciable value in the same region of space.

1.2.8.1. One-centre orbital products

If the atomic basis consists of hydrogenic type $s, p, d, f, \dots$ orbitals, the basis functions may be written as

$$\varphi(r, \theta, \varphi) = R_l(r) Y_{lm}(\theta, \varphi) \quad (1.2.8.3a)$$

or

$$\varphi(r, \theta, \varphi) = R_l(r) y_{lmp}(\theta, \varphi), \quad (1.2.8.3b)$$

which gives for corresponding values of the orbital products

$$\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r}) = R_l(r) R_{l'}(r) Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \quad (1.2.8.4a)$$

and

$$\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r}) = R_l(r) R_{l'}(r) y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi), \quad (1.2.8.4b)$$

respectively, where it has been assumed that the radial function depends only on l .

Because the spherical harmonic functions form a complete set, their products can be expressed as a linear combination of spherical harmonics. The coefficients in this expansion are the *Clebsch–Gordan coefficients* (Condon & Shortley, 1957), defined by

$$Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi) = \sum_L \sum_M C_{Ll'l'}^{Mmm'} Y_{LM}(\theta, \varphi) \quad (1.2.8.5a)$$

or the equivalent definition

$$C_{Ll'l'}^{Mmm'} = \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\varphi Y_{LM}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) Y_{l'm'}(\theta, \varphi). \quad (1.2.8.5b)$$

The $C_{Ll'l'}^{Mmm'}$ vanish, unless $L + l + l'$ is even, $|l - l'| < L < l + l'$ and $M = m + m'$.

The corresponding expression for y_{lmp} is

$$y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi) = \sum_L \sum_M C_{Ll'l'}^{Mmm'} y_{LMP}(\theta, \varphi), \quad (1.2.8.5c)$$

with $M = |m + m'|$ and $|m - m'|$ for $p = p'$, and $M = -|m + m'|$ and $-|m - m'|$ for $p = -p'$ and $P = p \times p'$.

Values of C and C' for $l \leq 2$ are given in Tables 1.2.8.1 and 1.2.8.2. They are valid for the functions Y_{lm} and y_{lmp} with normalization $\int |Y_{lm}|^2 d\Omega = 1$ and $\int y_{lmp}^2 d\Omega = 1$.

By using (1.2.8.5a) or (1.2.8.5c), the one-centre orbital products are expressed as a sum of spherical harmonic functions. It follows that the one-centre orbital product density basis set is formally equivalent to the multipole description, both in real and in reciprocal space. To obtain the relation between orbital products and the charge-density functions, the right-hand side of (1.2.8.5c) has to be multiplied by the ratio of the normalization constants, as the wavefunctions y_{lmp} and charge-density functions d_{lmp} are normalized in a different way as described by (1.2.7.3a) and (1.2.7.3b). Thus

$$y_{lmp}(\theta, \varphi) y_{l'm'p'}(\theta, \varphi) = \sum_L \sum_M R_{LMP} C_{Ll'l'}^{Mmm'} d_{LMP}(\theta, \varphi), \quad (1.2.8.6)$$

where $R_{LMP} = M_{LMP}$ (wavefunction)/ L_{LMP} (density function). The normalization constants M_{lmp} and L_{lmp} are given in Table 1.2.7.1, while the coefficients in the expressions (1.2.8.6) are listed in Table 1.2.8.3.

1.2.8.2. Two-centre orbital products

Fourier transform of the electron density as described by (1.2.8.1) requires explicit expressions for the two-centre orbital product scattering. Such expressions are described in the literature for both Gaussian (Stewart, 1969b) and Slater-type (Bentley & Stewart, 1973; Avery & Ørmen, 1979) atomic orbitals. The expressions can also be used for Hartree–Fock atomic functions, as expansions in terms of Gaussian- (Stewart, 1969b, 1970; Stewart & Hehre, 1970; Hehre *et al.*, 1970) and Slater-type (Clementi & Roetti, 1974) functions are available for many atoms.

1.2.9. The atomic temperature factor

Since the crystal is subject to vibrational oscillations, the observed elastic scattering intensity is an average over all normal modes of the crystal. Within the Born–Oppenheimer approximation, the theoretical electron density should be calculated for each set of nuclear coordinates. An average can be obtained by taking into account the statistical weight of each nuclear configuration, which may be expressed by the probability distribution function $P(\mathbf{u}_1, \dots, \mathbf{u}_N)$ for a set of displacement coordinates $\mathbf{u}_1, \dots, \mathbf{u}_N$.

In general, if $\rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N)$ is the electron density corresponding to the geometry defined by $\mathbf{u}_1, \dots, \mathbf{u}_N$, the time-averaged electron density is given by

$$\langle \rho(\mathbf{r}) \rangle = \int \rho(\mathbf{r}, \mathbf{u}_1, \dots, \mathbf{u}_N) P(\mathbf{u}_1, \dots, \mathbf{u}_N) d\mathbf{u}_1 \dots d\mathbf{u}_N. \quad (1.2.9.1)$$

When the crystal can be considered as consisting of perfectly following rigid entities, which may be molecules or atoms, expression (1.2.9.1) simplifies:

$$\langle \rho_{\text{rigid group}}(\mathbf{r}) \rangle = \int \rho_{\text{r.g., static}}(\mathbf{r} - \mathbf{u}) P(\mathbf{u}) d\mathbf{u} = \rho_{\text{r.g., static}} * P(\mathbf{u}). \quad (1.2.9.2)$$

In the approximation that the atomic electrons perfectly follow the nuclear motion, one obtains

$$\langle \rho_{\text{atom}}(\mathbf{r}) \rangle = \rho_{\text{atom, static}}(\mathbf{r}) * P(\mathbf{u}). \quad (1.2.9.3)$$

The Fourier transform of this convolution is the product of the Fourier transforms of the individual functions:

$$\langle f(\mathbf{H}) \rangle = f(\mathbf{H}) T(\mathbf{H}). \quad (1.2.9.4)$$

Thus $T(\mathbf{H})$, the atomic temperature factor, is the Fourier transform of the probability distribution $P(\mathbf{u})$.

1.2.10. The vibrational probability distribution and its Fourier transform in the harmonic approximation

For a harmonic oscillator, the probability distribution averaged over all populated energy levels is a Gaussian, centred at the equilibrium position. For the three-dimensional isotropic harmonic oscillator, the distribution is

$$P(u) = (2\pi \langle u^2 \rangle)^{-3/2} \exp\{-|u|^2/2\langle u^2 \rangle\}, \quad (1.2.10.1)$$

where $\langle u^2 \rangle$ is the mean-square displacement in any direction.

The corresponding trivariate normal distribution to be used for anisotropic harmonic motion is, in tensor notation,

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Table 1.2.7.4. Closed-form expressions for Fourier transform of Slater-type functions (Avery & Watson, 1977; Su & Coppens, 1990)

$$\langle j_k \rangle \equiv \int_0^\infty r^N \exp(-Zr) j_k(Kr) dr, K = 4\pi \sin \theta / \lambda.$$

k	N							
	1	2	3	4	5	6	7	8
0	$\frac{1}{K^2 + Z^2}$	$\frac{2Z}{(K^2 + Z^2)^2}$	$\frac{2(3Z^2 - K^2)}{(K^2 + Z^2)^3}$	$\frac{24Z(Z^2 - K^2)}{(K^2 + Z^2)^4}$	$\frac{24(5Z^2 - 10K^2Z^2 + K^4)}{(K^2 + Z^2)^5}$	$\frac{240Z(K^2 - 3Z^2)(3K^2 - Z^2)}{(K^2 + Z^2)^6}$	$\frac{720(7Z^6 - 35K^2Z^4 + 21K^4Z^2 - K^6)}{(K^2 + Z^2)^7}$	$\frac{40320(Z^7 - 7K^2Z^5 + 7K^4Z^3 - K^6Z)}{(K^2 + Z^2)^8}$
1		$\frac{2K}{(K^2 + Z^2)^2}$	$\frac{8KZ}{(K^2 + Z^2)^3}$	$\frac{8K(5Z^2 - K^2)}{(K^2 + Z^2)^4}$	$\frac{48KZ(5Z^2 - 3K^2)}{(K^2 + Z^2)^5}$	$\frac{48K(35Z^4 - 42K^2Z^2 + 3K^4)}{(K^2 + Z^2)^6}$	$\frac{1920KZ(7Z^4 - 14K^2Z^2 + 3K^4)}{(K^2 + Z^2)^7}$	$\frac{5760K(21Z^6 - 63K^2Z^4 + 27K^4Z^2 - K^6)}{(K^2 + Z^2)^8}$
2			$\frac{8K^2}{(K^2 + Z^2)^3}$	$\frac{48K^2Z}{(K^2 + Z^2)^4}$	$\frac{48K^2(7Z^2 - K^2)}{(K^2 + Z^2)^5}$	$\frac{384K^2Z(7Z^2 - 3K^2)}{(K^2 + Z^2)^6}$	$\frac{1152K^2(21Z^4 - 18K^2Z^2 + K^4)}{(K^2 + Z^2)^7}$	$\frac{11520K^2Z(21Z^4 - 30K^2Z^2 + 5K^4)}{(K^2 + Z^2)^8}$
3				$\frac{48K^3}{(K^2 + Z^2)^4}$	$\frac{384K^3Z}{(K^2 + Z^2)^5}$	$\frac{384K^3(9Z^2 - K^2)}{(K^2 + Z^2)^6}$	$\frac{11520K^3Z(3Z^2 - K^2)}{(K^2 + Z^2)^7}$	$\frac{11520K^3(33Z^4 - 22K^2Z^2 + K^4)}{(K^2 + Z^2)^8}$
4					$\frac{384K^4}{(K^2 + Z^2)^5}$	$\frac{3840K^4Z}{(K^2 + Z^2)^6}$	$\frac{3840K^4(11Z^2 - K^2)}{(K^2 + Z^2)^7}$	$\frac{46080K^4Z(11Z^2 - 3K^2)}{(K^2 + Z^2)^8}$
5						$\frac{3840K^5}{(K^2 + Z^2)^6}$	$\frac{46080K^5Z}{(K^2 + Z^2)^7}$	$\frac{40680K^5(13Z^2 - K^2)}{(K^2 + Z^2)^8}$
6							$\frac{46080K^6}{(K^2 + Z^2)^7}$	$\frac{645120K^6Z}{(K^2 + Z^2)^8}$
7								$\frac{645120K^7}{(K^2 + Z^2)^8}$

$$P(\mathbf{u}) = \frac{|\boldsymbol{\sigma}^{-1}|^{1/2}}{(2\pi)^{3/2}} \exp\left\{-\frac{1}{2} \boldsymbol{\sigma}_{jk}^{-1} (u^j u^k)\right\}. \quad (1.2.10.2a)$$

with

Here σ is the variance-covariance matrix, with covariant components, and $|\boldsymbol{\sigma}^{-1}|$ is the determinant of the inverse of σ . Summation over repeated indices has been assumed. The corresponding equation in matrix notation is

$$P(\mathbf{u}) = \frac{|\boldsymbol{\sigma}^{-1}|^{1/2}}{(2\pi)^{3/2}} \exp\left\{-\frac{1}{2} (\mathbf{u})^T \boldsymbol{\sigma}^{-1} (\mathbf{u})\right\}, \quad (1.2.10.2b)$$

where the superscript T indicates the transpose.

The characteristic function, or Fourier transform, of $P(\mathbf{u})$ is

$$T(\mathbf{H}) = \exp\{-2\pi^2 \sigma^{jk} h_j h_k\} \quad (1.2.10.3a)$$

or

$$T(\mathbf{H}) = \exp\{-2\pi^2 \mathbf{H}^T \boldsymbol{\sigma} \mathbf{H}\}. \quad (1.2.10.3b)$$

With the change of variable $b^{jk} = 2\pi^2 \sigma^{jk}$, (1.2.10.3a) becomes

$$T(\mathbf{H}) = \exp\{-b^{jk} h_j h_k\}.$$

1.2.11. Rigid-body analysis

The treatment of rigid-body motion of molecules or molecular fragments was developed by Cruickshank (1956) and expanded into a general theory by Schomaker & Trueblood (1968). The theory has been described by Johnson (1970b) and by Dunitz (1979). The latter reference forms the basis for the following treatment.

The most general motions of a rigid body consist of rotations about three axes, coupled with translations parallel to each of the axes. Such motions correspond to screw rotations. A libration around a vector $\boldsymbol{\lambda}$ ($\lambda_1, \lambda_2, \lambda_3$), with length corresponding to the magnitude of the rotation, results in a displacement $\delta \mathbf{r}$, such that

$$\delta \mathbf{r} = (\boldsymbol{\lambda} \times \mathbf{r}) = \mathbf{D} \mathbf{r} \quad (1.2.11.1)$$

$$\mathbf{D} = \begin{bmatrix} 0 & -\lambda_3 & \lambda_2 \\ \lambda_3 & 0 & -\lambda_1 \\ -\lambda_2 & \lambda_1 & 0 \end{bmatrix}, \quad (1.2.11.2)$$

or in tensor notation, assuming summation over repeated indices,

$$\delta r_i = D_{ij} r_j = -\varepsilon_{ijk} \lambda_k r_j \quad (1.2.11.3)$$

where the permutation operator ε_{ijk} equals +1 for i, j, k a cyclic permutation of the indices 1, 2, 3, or -1 for a non-cyclic permutation, and zero if two or more indices are equal. For $i = 1$, for example, only the ε_{123} and ε_{132} terms occur. Addition of a translational displacement gives

$$\delta r_i = D_{ij} r_j + t_i. \quad (1.2.11.4)$$

When a rigid body undergoes vibrations the displacements vary with time, so suitable averages must be taken to derive the mean-square displacements. If the librational and translational motions are independent, the cross products between the two terms in (1.2.11.4) average to zero and the elements of the mean-square displacement tensor of atom n , U_{ij}^n , are given by

$$\begin{aligned} U_{11}^n &= +L_{22}r_3^2 + L_{33}r_2^2 - 2L_{23}r_2r_3 + T_{11} \\ U_{22}^n &= +L_{33}r_1^2 + L_{11}r_3^2 - 2L_{13}r_1r_3 + T_{22} \\ U_{33}^n &= +L_{11}r_2^2 + L_{22}r_1^2 - 2L_{12}r_1r_2 + T_{33} \\ U_{12}^n &= -L_{33}r_1r_2 - L_{12}r_3^2 + L_{13}r_2r_3 + L_{23}r_1r_3 + T_{12} \\ U_{13}^n &= -L_{22}r_1r_3 + L_{12}r_2r_3 - L_{13}r_2^2 + L_{23}r_1r_2 + T_{13} \\ U_{23}^n &= -L_{11}r_2r_3 + L_{12}r_1r_3 - L_{13}r_1r_2 - L_{23}r_1^2 + T_{23}, \end{aligned} \quad (1.2.11.5)$$

where the coefficients $L_{ij} = \langle \lambda_i \lambda_j \rangle$ and $T_{ij} = \langle t_i t_j \rangle$ are the elements of the 3×3 libration tensor $\mathbf{L}$ and the 3×3 translation tensor $\mathbf{T}$,

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Table 1.2.8.1. *Products of complex spherical harmonics as defined by equation (1.2.7.2a)*

$Y_{00} Y_{00} = 0.28209479 Y_{00}$
$Y_{10} Y_{00} = 0.28209479 Y_{10}$
$Y_{10} Y_{10} = 0.25231325 Y_{20} + 0.28209479 Y_{00}$
$Y_{11} Y_{00} = 0.28209479 Y_{11}$
$Y_{11} Y_{10} = 0.21850969 Y_{21}$
$Y_{11} Y_{11} = 0.30901936 Y_{22}$
$Y_{11} Y_{1-1} = -0.12615663 Y_{20} + 0.28209479 Y_{00}$
$Y_{20} Y_{00} = 0.28209479 Y_{20}$
$Y_{20} Y_{10} = 0.24776669 Y_{30} + 0.25231325 Y_{10}$
$Y_{20} Y_{11} = 0.20230066 Y_{31} - 0.12615663 Y_{11}$
$Y_{20} Y_{20} = 0.24179554 Y_{40} + 0.18022375 Y_{20} + 0.28209479 Y_{00}$
$Y_{21} Y_{00} = 0.28209479 Y_{21}$
$Y_{21} Y_{10} = 0.23359668 Y_{31} + 0.21850969 Y_{11}$
$Y_{21} Y_{11} = 0.26116903 Y_{32}$
$Y_{21} Y_{1-1} = -0.14304817 Y_{30} + 0.21850969 Y_{10}$
$Y_{21} Y_{20} = 0.22072812 Y_{41} + 0.09011188 Y_{21}$
$Y_{21} Y_{21} = 0.25489487 Y_{42} + 0.22072812 Y_{22}$
$Y_{21} Y_{2-1} = -0.16119702 Y_{40} + 0.09011188 Y_{20} + 0.28209479 Y_{00}$
$Y_{22} Y_{00} = 0.28209479 Y_{22}$
$Y_{22} Y_{10} = 0.18467439 Y_{32}$
$Y_{22} Y_{11} = 0.31986543 Y_{33}$
$Y_{22} Y_{1-1} = -0.08258890 Y_{31} + 0.30901936 Y_{11}$
$Y_{22} Y_{20} = 0.15607835 Y_{42} - 0.18022375 Y_{22}$
$Y_{22} Y_{21} = 0.23841361 Y_{43}$
$Y_{22} Y_{2-1} = -0.09011188 Y_{41} + 0.22072812 Y_{21}$
$Y_{22} Y_{22} = 0.33716777 Y_{44}$
$Y_{22} Y_{2-2} = 0.04029926 Y_{40} - 0.18022375 Y_{20} + 0.28209479 Y_{00}$

Table 1.2.8.2. *Products of real spherical harmonics as defined by equations (1.2.7.2b) and (1.2.7.2c)*

$y_{00} y_{00} = 0.28209479 y_{00}$
$y_{10} y_{00} = 0.28209479 y_{10}$
$y_{10} y_{10} = 0.25231325 y_{20} + 0.28209479 y_{00}$
$y_{11\pm} y_{00} = 0.28209479 y_{11\pm}$
$y_{11\pm} y_{10} = 0.21850969 y_{21\pm}$
$y_{11\pm} y_{11\pm} = 0.21850969 y_{22\pm} - 0.12615663 y_{20} + 0.28209479 y_{00}$
$y_{11+} y_{11-} = 0.21850969 y_{22-}$
$y_{20} y_{00} = 0.28209479 y_{20}$
$y_{20} y_{10} = 0.24776669 y_{30} + 0.25231325 y_{10}$
$y_{20} y_{11\pm} = 0.20230066 y_{31\pm} - 0.12615663 y_{11\pm}$
$y_{20} y_{20} = 0.24179554 y_{40} + 0.18022375 y_{20} + 0.28209479 y_{00}$
$y_{21\pm} y_{00} = 0.28209479 y_{21\pm}$
$y_{21\pm} y_{10} = 0.23359668 y_{31\pm} + 0.21850969 y_{11\pm}$
$y_{21\pm} y_{11\pm} = \pm 0.18467439 y_{32\pm} - 0.14304817 y_{30} + 0.21850969 y_{10}$
$y_{21\pm} y_{11\mp} = 0.18467469 y_{32-}$
$y_{21\pm} y_{20} = 0.22072812 y_{41\pm} + 0.09011188 y_{21\pm}$
$y_{21\pm} y_{21\pm} = \pm 0.18022375 y_{42\pm} \pm 0.15607835 y_{22\pm}$
$y_{21+} y_{21-} = -0.16119702 y_{40} + 0.09011188 y_{20} + 0.28209479 y_{00}$
$y_{21+} y_{21-} = -0.18022375 y_{42-} + 0.15607835 y_{22-}$
$y_{22\pm} y_{00} = 0.28209479 y_{22\pm}$
$y_{22\pm} y_{10} = 0.18467439 y_{32\pm}$
$y_{22\pm} y_{11\pm} = \pm 0.22617901 y_{33\pm} - 0.05839917 y_{31\pm} + 0.21850969 y_{11\pm}$
$y_{22\pm} y_{11\mp} = 0.22617901 y_{33-} \pm 0.05839917 y_{31-} \mp 0.21850969 y_{11-}$
$y_{22\pm} y_{20} = 0.15607835 y_{42\pm} - 0.18022375 y_{22\pm}$
$y_{22\pm} y_{21\pm} = \pm 0.16858388 y_{43\pm} - 0.06371872 y_{41\pm} + 0.15607835 y_{21\pm}$
$y_{22\pm} y_{21\mp} = 0.16858388 y_{43-} \pm 0.06371872 y_{41-} \mp 0.15607835 y_{21-}$
$y_{22\pm} y_{22\pm} = \pm 0.23841361 y_{44\pm} + 0.04029926 y_{40} - 0.18022375 y_{20}$
$y_{22+} y_{22-} = 0.23841361 y_{44-}$

respectively. Since pairs of terms such as $\langle t_i t_j \rangle$ and $\langle t_j t_i \rangle$ correspond to averages over the same two scalar quantities, the **T** and **L** tensors are symmetrical.

If a rotation axis is correctly oriented, but incorrectly positioned, an additional translation component perpendicular to the rotation axes is introduced. The rotation angle and the parallel component of the translation are invariant to the position of the axis, but the perpendicular component is not. This implies that the **L** tensor is unaffected by any assumptions about the position of the libration axes, whereas the **T** tensor depends on the assumptions made concerning the location of the axes.

The quadratic correlation between librational and translational motions can be allowed for by including in (1.2.11.5) cross terms of the type $\langle D_{ik} t_j \rangle$, or, with (1.2.11.3),

$$U_{ij} = \langle D_{ik} D_{jl} \rangle r_k r_l + \langle D_{ik} t_j + D_{jl} t_i \rangle r_k + \langle t_i t_j \rangle \\ = A_{ijkl} r_k r_l + B_{ijk} r_k + \langle t_i t_j \rangle, \quad (1.2.11.6)$$

which leads to the explicit expressions such as

$$U_{11} = \langle \delta r_1 \rangle^2 = \langle \lambda_3^2 \rangle r_2^2 + \langle \lambda_2^2 \rangle r_3^2 - 2 \langle \lambda_2 \lambda_3 \rangle r_2 r_3 \\ - 2 \langle \lambda_3 t_1 \rangle r_2 - 2 \langle \lambda_2 t_1 \rangle r_3 + \langle t_1^2 \rangle, \\ U_{12} = \langle \delta r_1 \delta r_2 \rangle = - \langle \lambda_3^2 \rangle r_1 r_2 + \langle \lambda_1 \lambda_3 \rangle r_2 r_3 + \langle \lambda_2 \lambda_3 \rangle r_1 r_3 \\ - \langle \lambda_1 \lambda_2 \rangle r_3^2 + \langle \lambda_3 t_1 \rangle r_1 - \langle \lambda_1 t_1 \rangle r_3 \\ - \langle \lambda_3 t_2 \rangle + r_2 \langle \lambda_2 t_2 \rangle r_3 + \langle t_1 t_2 \rangle. \quad (1.2.11.7)$$

The products of the type $\langle \lambda_i t_j \rangle$ are the components of an additional tensor, **S**, which unlike the tensors **T** and **L** is

unsymmetrical, since $\langle \lambda_i t_j \rangle$ is different from $\langle \lambda_j t_i \rangle$. The terms involving elements of **S** may be grouped as

$$\langle \lambda_3 t_1 \rangle r_1 - \langle \lambda_3 t_2 \rangle r_2 + (\langle \lambda_2 t_2 \rangle - \langle \lambda_1 t_1 \rangle) r_3 \quad (1.2.11.8)$$

or

$$S_{31} r_1 - S_{32} r_2 + (S_{22} - S_{11}) r_3.$$

As the diagonal elements occur as differences in this expression, a constant may be added to each of the diagonal terms without changing the observational equations. In other words, the trace of **S** is indeterminate.

In terms of the **L**, **T** and **S** tensors, the observational equations are

$$U_{ij} = G_{ijkl} L_{kl} + H_{ijk} S_{kl} + T_{ij}. \quad (1.2.11.9)$$

The arrays G_{ijkl} and H_{ijk} involve the atomic coordinates $(x, y, z) = (r_1, r_2, r_3)$, and are listed in Table 1.2.11.1. Equations (1.2.11.9) for each of the atoms in the rigid body form the observational equations, from which the elements of **T**, **L** and **S** can be derived by a linear least-squares procedure. One of the diagonal elements of **S** must be fixed in advance or some other suitable constraint applied because of the indeterminacy of $\text{Tr}(\mathbf{S})$. It is common practice to set $\text{Tr}(\mathbf{S})$ equal to zero. There are thus eight elements of **S** to be determined, as well as the six each of **L** and **T**, for a total of 20 variables. A shift of origin leaves **L** invariant, but it intermixes **T** and **S**.

If the origin is located at a centre of symmetry, for each atom at **r** with vibration tensor **U**ⁿ there will be an equivalent atom at **-r** with

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Table 1.2.8.3. *Products of two real spherical harmonic functions y_{lmp} in terms of the density functions d_{lmp} defined by equation (1.2.7.3b)*

$y_{00} y_{00} = 1.0000d_{00}$
$y_{10} y_{00} = 0.43301d_{10}$
$y_{10} y_{10} = 0.38490d_{20} + 1.0d_{00}$
$y_{11\pm} y_{00} = 0.43302d_{11\pm}$
$y_{11\pm} y_{10} = 0.31831d_{21\pm}$
$y_{11\pm} y_{11\pm} = 0.31831d_{22+} - 0.19425d_{20} + 1.0d_{00}$
$y_{11+} y_{11-} = 0.31831d_{22-}$
$y_{20} y_{00} = 0.43033d_{20}$
$y_{20} y_{10} = 0.37762d_{30} + 0.38730d_{10}$
$y_{20} y_{11\pm} = 0.28864d_{31\pm} - 0.19365d_{11\pm}$
$y_{20} y_{20} = 0.36848d_{40} + 0.27493d_{20} + 1.0d_{00}$
$y_{21\pm} y_{00} = 0.41094d_{21\pm}$
$y_{21\pm} y_{10} = 0.33329d_{31\pm} + 0.33541d_{11\pm}$
$y_{21\pm} y_{11\pm} = \pm 0.26691d_{32+} - 0.21802d_{30} + 0.33541d_{10}$
$y_{21\pm} y_{11\mp} = -0.26691d_{32-}$
$y_{21\pm} y_{20} = 0.31155d_{41\pm} + 0.13127d_{21\pm}$
$y_{21\pm} y_{21\pm} = \pm 0.25791d_{42+} \pm 0.22736d_{22+} - 0.24565d_{40} + 0.13747d_{20} + 1.0d_{00}$
$y_{21+} y_{21-} = 0.25790d_{42-} + 0.22736d_{22-}$
$y_{22\pm} y_{00} = 0.41094d_{22\pm}$
$y_{22\pm} y_{10} = 0.26691d_{32\pm}$
$y_{22\pm} y_{11\pm} = \pm 0.31445d_{33+} - 0.083323d_{31+} + 0.33541d_{11+}$
$y_{22\pm} y_{11\mp} = 0.31445d_{33-} \pm 0.083323d_{31-} \mp 0.33541d_{11-}$
$y_{22\pm} y_{20} = 0.22335d_{42\pm} - 0.26254d_{22\pm}$
$y_{22\pm} y_{21\pm} = \pm 0.23873d_{43+} - 0.089938d_{41+} + 0.22736d_{21+}$
$y_{22\pm} y_{21\mp} = 0.23873d_{43-} \pm 0.089938d_{41-} \mp 0.22736d_{21-}$
$y_{22\pm} y_{22\pm} = \pm 0.31831d_{44+} + 0.061413d_{40} - 0.27493d_{20} + 1.0d_{00}$
$y_{22+} y_{22-} = 0.31831d_{44-}$

the same vibration tensor. When the observational equations for these two atoms are added, the terms involving elements of **S** disappear since they are linear in the components of **r**. The other terms, involving elements of the **T** and **L** tensors, are simply doubled, like the **Uⁿ** components.

The physical meaning of the **T** and **L** tensor elements is as follows. $T_{ij}l_i l_j$ is the mean-square amplitude of translational vibration in the direction of the unit vector **l** with components l_1, l_2, l_3 along the Cartesian axes and $L_{ij}l_i l_j$ is the mean-square amplitude of libration about an axis in this direction. The quantity $S_{ij}l_i l_j$ represents the mean correlation between libration about the axis **l** and translation parallel to this axis. This quantity, like $T_{ij}l_i l_j$, depends on the choice of origin, although the sum of the two quantities is independent of the origin.

The non-symmetrical tensor **S** can be written as the sum of a symmetric tensor with elements $S_{ij}^S = (S_{ij} + S_{ji})/2$ and a skew-symmetric tensor with elements $S_{ij}^A = (S_{ij} - S_{ji})/2$. Expressed in terms of principal axes, **S^S** consists of three principal screw correlations $\langle \lambda_i t_i \rangle$. Positive and negative screw correlations correspond to opposite senses of helicity. Since an arbitrary constant may be added to all three correlation terms, only the differences between them can be determined from the data.

The skew-symmetric part **S^A** is equivalent to a vector $(\boldsymbol{\lambda} \times \mathbf{t})/2$ with components $(\boldsymbol{\lambda} \times \mathbf{t})_i/2 = (\lambda_j t_k - \lambda_k t_j)/2$, involving correlations between a libration and a perpendicular translation. The components of **S^A** can be reduced to zero, and **S** made symmetric, by a change of origin. It can be shown that the origin shift that

Table 1.2.11.1. *The arrays G_{ijkl} and H_{ijkl} to be used in the observational equations $U_{ij} = G_{ijkl}L_{kl} + H_{ijkl}S_{kl} + T_{ij}$ [equation (1.2.11.9)]*

G_{ijkl}

ij	kl					
	11	22	33	23	31	12
11	0	z^2	y^2	$-2yz$	0	0
22	z^2	0	x^2	0	$-2xz$	0
33	y^2	x^2	0	0	0	$-2xy$
23	$-yz$	0	0	$-x^2$	xy	xz
31	0	$-xz$	0	xy	$-y^2$	yz
12	0	0	$-xy$	xz	yz	$-z^2$

H_{ijkl}

ij	kl								
	11	22	33	23	31	12	32	13	21
11	0	0	0	0	$-2y$	0	0	0	$2z$
22	0	0	0	0	0	$-2z$	$2x$	0	0
33	0	0	0	$-2x$	0	0	0	$2y$	0
23	0	$-x$	x	0	0	y	0	$-z$	0
31	y	0	$-y$	z	0	0	0	0	$-x$
12	$-z$	z	0	0	x	0	$-y$	0	0

symmetrizes **S** also minimizes the trace of **T**. In terms of the coordinate system based on the principal axes of **L**, the required origin shifts $\hat{\rho}_i$ are

$$\hat{\rho}_1 = \frac{\hat{S}_{23} - \hat{S}_{32}}{\hat{L}_{22} + \hat{L}_{33}} \quad \hat{\rho}_2 = \frac{\hat{S}_{31} - \hat{S}_{13}}{\hat{L}_{11} + \hat{L}_{33}} \quad \hat{\rho}_3 = \frac{\hat{S}_{12} - \hat{S}_{21}}{\hat{L}_{11} + \hat{L}_{22}}, \quad (1.2.11.10)$$

in which the carets indicate quantities referred to the principal axis system.

The description of the averaged motion can be simplified further by shifting to three generally non-intersecting libration axes, one each for each principal axis of **L**. Shifts of the **L₁** axis in the **L₂** and **L₃** directions by

$${}^1\hat{\rho}_2 = -\hat{S}_{13}/\hat{L}_{11} \quad \text{and} \quad {}^1\hat{\rho}_3 = \hat{S}_{12}/\hat{L}_{11}, \quad (1.2.11.11)$$

respectively, annihilate the S_{12} and S_{13} terms of the symmetrized **S** tensor and simultaneously effect a further reduction in $\text{Tr}(\mathbf{T})$ (the superscript denotes the axis that is shifted, the subscript the direction of the shift component). Analogous equations for displacements of the **L₂** and **L₃** axes are obtained by permutation of the indices. If all three axes are appropriately displaced, only the diagonal terms of **S** remain. Referred to the principal axes of **L**, they represent screw correlations along these axes and are independent of origin shifts.

The elements of the reduced **T** are

$${}^rT_{II} = \hat{T}_{II} - \sum_{K \neq I} (\hat{S}_{KI})^2 / \hat{L}_{KK}$$

$${}^rT_{IJ} = \hat{T}_{IJ} - \sum_K \hat{S}_{KI} \hat{S}_{KJ} / \hat{L}_{KK}, \quad J \neq I. \quad (1.2.11.12)$$

The resulting description of the average rigid-body motion is in terms of six independently distributed instantaneous motions – three screw librations about non-intersecting axes (with screw pitches given by $\hat{S}_{11}/\hat{L}_{11}$ etc.) and three translations. The parameter set consists of three libration and three translation amplitudes, six

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Table 1.2.12.1. *Some Hermite polynomials (Johnson & Levy, 1974; Zucker & Schulz, 1982)*

$H(\mathbf{u}) = 1$
$H_j(\mathbf{u}) = w_j$
$H_{jk}(\mathbf{u}) = w_j w_k - p_{jk}$
$H_{jkl}(\mathbf{u}) = w_j w_k w_l - (w_j p_{kl} + w_k p_{lj} + w_l p_{jk}) = w_j w_k w_l - 3w_j p_{kl}$
$H_{jklm}(\mathbf{u}) = w_j w_k w_l w_m - 6w_j w_k p_{lm} + 3p_{jk} p_{lm}$
$H_{jklmn}(\mathbf{u}) = w_j w_k w_l w_m w_n - 10w_j w_k w_n p_{lm} + 15w_j p_{jk} p_{lm}$
$H_{jklmnp}(\mathbf{u}) = w_j w_k w_l w_m w_n w_p - 15w_j w_k w_l p_{mp} + 45w_j p_{jk} p_{lm} p_{np} - 15p_{jk} p_{lm} p_{np}$
where $w_j \equiv p_{jk} u^k$ and p_{jk} are the elements of σ^{-1} , defined in expression (1.2.10.2). Indices between brackets indicate that the term is to be averaged over all permutations which produce distinct terms, keeping in mind that $p_{jk} = p_{kj}$ and $w_j w_k = w_k w_j$ as illustrated for H_{jkl} .

angles of orientation for the principal axes of $\mathbf{L}$ and $\mathbf{T}$, six coordinates of axis displacement, and three screw pitches, one of which has to be chosen arbitrarily, again for a total of 20 variables.

Since diagonal elements of $\mathbf{S}$ enter into the expression for rT_{II} , the indeterminacy of $\text{Tr}(\mathbf{S})$ introduces a corresponding indeterminacy in $r\mathbf{T}$. The constraint $\text{Tr}(\mathbf{S}) = 0$ is unaffected by the various rotations and translations of the coordinate systems used in the course of the analysis.

1.2.12. Treatment of anharmonicity

The probability distribution (1.2.10.2) is valid in the case of rectilinear harmonic motion. If the deviations from Gaussian shape are not too large, distributions may be used which are expansions with the Gaussian distribution as the leading term. Three such distributions are discussed in the following sections.

1.2.12.1. The Gram–Charlier expansion

The three-dimensional Gram–Charlier expansion, introduced into thermal-motion treatment by Johnson & Levy (1974), is an expansion of a function in terms of the zero and higher derivatives of a normal distribution (Kendall & Stuart, 1958). If D_j is the operator d/du^j ,

$$P(\mathbf{u}) = [1 - c^j D_j + \frac{1}{2!} c^{jk} D_j D_k - \frac{1}{3!} c^{jkl} D_j D_k D_l + \dots + (-1)^r \frac{c^{\alpha_1} \dots c^{\alpha_r}}{r!} D_{\alpha_1} D_{\alpha_2} \dots D_{\alpha_r}] P_0(\mathbf{u}), \quad (1.2.12.1)$$

where $P_0(\mathbf{u})$ is the harmonic distribution, $\alpha_1 = 1, 2$ or 3 , and the operator $D_{\alpha_1} \dots D_{\alpha_r}$ is the r th partial derivative $\partial^r / (\partial u^{\alpha_1} \dots \partial u^{\alpha_r})$. Summation is again implied over repeated indices.

The differential operators D may be eliminated by the use of three-dimensional Hermite polynomials $H_{\alpha_1 \dots \alpha_r}$ defined, by analogy with the one-dimensional Hermite polynomials, by the expression $D_{\alpha_1} \dots D_{\alpha_r} \exp(-\frac{1}{2} \sigma_{jk}^{-1} u^j u^k) = (-1)^r H_{\alpha_1 \dots \alpha_r}(\mathbf{u}) \exp(-\frac{1}{2} \sigma_{jk}^{-1} u^j u^k)$, (1.2.12.2)

which gives

$$P(\mathbf{u}) = \left[1 + \frac{1}{3!} c^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} c^{jklm} H_{jklm}(\mathbf{u}) + \frac{1}{5!} c^{jklmn} H_{jklmn}(\mathbf{u}) + \frac{1}{6!} c^{jklmnp} H_{jklmnp}(\mathbf{u}) + \dots \right] P_0(\mathbf{u}), \quad (1.2.12.3)$$

where the first and second terms have been omitted since they are equivalent to a shift of the mean and a modification of the harmonic term only. The permutations of $j, k, l \dots$ here, and in the following sections, include all combinations which produce different terms.

The coefficients c , defined by (1.2.12.1) and (1.2.12.2), are known as the *quasimoments* of the frequency function $P(\mathbf{u})$ (Kutznetsov *et al.*, 1960). They are related in a simple manner to the moments of the function (Kendall & Stuart, 1958) and are invariant to permutation of indices. There are 10, 15, 21 and 28 components of c for orders 3, 4, 5 and 6, respectively. The multivariate Hermite polynomials are functions of the elements of σ_{jk}^{-1} and of u^k , and are given in Table 1.2.12.1 for orders ≤ 6 (IT IV, 1974; Zucker & Schulz, 1982).

The Fourier transform of (1.2.12.3) is given by

$$T(\mathbf{H}) = \left[1 - \frac{4}{3} \pi^3 i c^{jkl} h_j h_k h_l + \frac{2}{3} \pi^4 c^{jklm} h_j h_k h_l h_m + \frac{4}{15} \pi^5 i c^{jklmn} h_j h_k h_l h_m h_n - \frac{4}{45} \pi^6 c^{jklmnp} h_j h_k h_l h_m h_n h_p + \dots \right] T_0(\mathbf{H}), \quad (1.2.12.4)$$

where $T_0(\mathbf{H})$ is the harmonic temperature factor. $T(\mathbf{H})$ is a power-series expansion about the harmonic temperature factor, with even and odd terms, respectively, real and imaginary.

1.2.12.2. The cumulant expansion

A second statistical expansion which has been used to describe the atomic probability distribution is that of Edgeworth (Kendall & Stuart, 1958; Johnson, 1969). It expresses the function $P(\mathbf{u})$ as

$$P(\mathbf{u}) = \exp \left(\kappa^j D_j + \frac{1}{2!} \kappa^{jk} D_j D_k - \frac{1}{3!} \kappa^{jkl} D_j D_k D_l + \frac{1}{4!} \kappa^{jklm} D_j D_k D_l D_m - \dots \right) P_0(\mathbf{u}). \quad (1.2.12.5a)$$

Like the moments μ of a distribution, the cumulants κ are descriptive constants. They are related to each other (in the one-dimensional case) by the identity

$$\exp \left\{ \kappa_1 t + \frac{\kappa_2 t^2}{2!} + \dots + \frac{\kappa_r t^r}{r!} + \dots \right\} = 1 + \mu_1 t + \frac{\mu_2 t^2}{2!} + \dots + \frac{\mu_r t^r}{r!}. \quad (1.2.12.5b)$$

When it is substituted for t , (1.2.12.5b) is the characteristic function, or Fourier transform of $P(t)$ (Kendall & Stuart, 1958).

The first two terms in the exponent of (1.2.12.5a) can be omitted if the expansion is around the equilibrium position and the harmonic term is properly described by $P_0(\mathbf{u})$.

The Fourier transform of (1.2.12.5a) is, by analogy with the left-hand part of (1.2.12.5b) (with t replaced by $2\pi i h$),

$$T(\mathbf{H}) = \exp \left[\frac{(2\pi i)^3}{3!} \kappa^{jkl} h_j h_k h_l + \frac{(2\pi i)^4}{4!} \kappa^{jklm} h_j h_k h_l h_m + \dots \right] T_0(\mathbf{H}) \\ = \exp \left[-\frac{4}{3} \pi^3 i \kappa^{jkl} h_j h_k h_l + \frac{2}{3} \pi^4 \kappa^{jklm} h_j h_k h_l h_m + \dots \right] T_0(\mathbf{H}), \quad (1.2.12.6)$$

where the first two terms have been omitted. Expression (1.2.12.6) is similar to (1.2.12.4) except that the entire series is in the exponent. Following Schwarzenbach (1986), (1.2.12.6) can be developed in a Taylor series, which gives

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$$T(\mathbf{H}) = \left\{ 1 + \frac{(2\pi i)^3}{3!} \kappa^{jkl} h_j h_k h_l + \frac{(2\pi i)^4}{4!} \kappa^{jklm} h_j h_k h_l h_m + \dots \right. \\ \left. + \frac{(2\pi i)^6}{6!} \left[\kappa^{jklmp} + \frac{6!}{2!(3!)^2} \kappa^{jkl} \kappa^{mnp} \right] h_j h_k h_l h_m h_n h_p \right. \\ \left. + \text{higher-order terms} \right\} T_0(\mathbf{H}). \quad (1.2.12.7)$$

This formulation, which is sometimes called the Edgeworth approximation (Zucker & Schulz, 1982), clearly shows the relation to the Gram–Charlier expansion (1.2.12.4), and corresponds to the probability distribution [analogous to (1.2.12.3)]

$$P(\mathbf{u}) = P_0(\mathbf{u}) \left\{ 1 + \frac{1}{3!} \kappa^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} \kappa^{jklm} H_{jklm}(\mathbf{u}) + \dots \right. \\ \left. + \frac{1}{6!} \left[\kappa^{jklmnp} + 10 \kappa^{jkl} \kappa^{mnp} \right] H_{jklmnp} \right. \\ \left. + \text{higher-order terms} \right\}. \quad (1.2.12.8)$$

The relation between the cumulants κ^{jkl} and the quasimoments c^{jkl} are apparent from comparison of (1.2.12.8) and (1.2.12.4):

$$\begin{aligned} c^{jkl} &= \kappa^{jkl} \\ c^{jklm} &= \kappa^{jklm} \\ c^{jklmn} &= \kappa^{jklmn} \\ c^{jklmnp} &= \kappa^{jklmnp} + 10 \kappa^{jkl} \kappa^{mnp}. \end{aligned} \quad (1.2.12.9)$$

The sixth- and higher-order cumulants and quasimoments differ. Thus the third-order cumulant κ^{jkl} contributes not only to the coefficient of H_{jkl} , but also to higher-order terms of the probability distribution function. This is also the case for cumulants of higher orders. It implies that for a finite truncation of (1.2.12.6), the probability distribution cannot be represented by a finite number of terms. This is a serious difficulty when a probability distribution is to be derived from an experimental temperature factor of the cumulant type.

1.2.12.3. The one-particle potential (OPP) model

When an atom is considered as an independent oscillator vibrating in a potential well $V(\mathbf{u})$, its distribution may be described by Boltzmann statistics.

$$P(\mathbf{u}) = N \exp\{-V(\mathbf{u})/kT\}, \quad (1.2.12.10)$$

with N , the normalization constant, defined by $\int P(\mathbf{u}) d\mathbf{u} = 1$. The classical expression (1.2.12.10) is valid in the high-temperature limit for which $kT \gg V(\mathbf{u})$.

Following Dawson (1967) and Willis (1969), the potential function may be expanded in terms of increasing order of products of the contravariant displacement coordinates:

$$V = V_0 + \alpha_j u^j + \beta_{jk} u^j u^k + \gamma_{jkl} u^j u^k u^l + \delta_{jklm} u^j u^k u^l u^m + \dots \quad (1.2.12.11)$$

The equilibrium condition gives $\alpha_j = 0$. Substitution into (1.2.12.10) leads to an expression which may be simplified by the assumption that the leading term is the harmonic component represented by β_{jk} :

$$P(\mathbf{u}) = N \exp\{-\beta'_{jk} u^j u^k\} \\ \times \{1 - \gamma'_{jkl} u^j u^k u^l - \delta'_{jklm} u^j u^k u^l u^m - \dots\}, \quad (1.2.12.12)$$

in which $\beta' = \beta/kT$ etc. and the normalization factor N depends on the level of truncation.

The probability distribution is related to the spherical harmonic expansion. The ten products of the displacement parameters $u^j u^k u^l$, for example, are linear combinations of the seven octapoles ($l = 3$) and three dipoles ($l = 1$) (Coppens, 1980). The thermal probability distribution and the aspherical atom description can be separated only because the latter is essentially confined to the valence shell, while the former applies to all electrons which follow the nuclear motion in the atomic scattering model.

The Fourier transform of the OPP distribution, in a general coordinate system, is (Johnson, 1970a; Scheringer, 1985a)

$$T(\mathbf{H}) = T_0(\mathbf{H}) \left[1 - \frac{4}{3} \pi^3 i \gamma'_{jkl} G^{jkl}(\mathbf{H}) + \frac{2}{3} \pi^4 \delta'_{jklm} G^{jklm}(\mathbf{H}) \right. \\ \left. + \frac{4}{15} \pi^5 i \varepsilon'_{jklmn} G^{jklmn}(\mathbf{H}) - \frac{4}{45} \pi^6 i \varphi'_{jklmnp} G^{jklmnp}(\mathbf{H}) \dots \right], \quad (1.2.12.13)$$

where T_0 is the harmonic temperature factor and G represents the Hermite polynomials in reciprocal space.

If the OPP temperature factor is expanded in the coordinate system which diagonalizes β_{jk} , simpler expressions are obtained in which the Hermite polynomials are replaced by products of the displacement coordinates u^j (Dawson *et al.*, 1967; Coppens, 1980; Tanaka & Marumo, 1983).

1.2.12.4. Relative merits of the three expansions

The relative merits of the Gram–Charlier and Edgeworth expansions have been discussed by Zucker & Schulz (1982), Kuhs (1983), and by Scheringer (1985b). In general, the Gram–Charlier expression is found to be preferable because it gives a better fit in the cases tested, and because its truncation is equivalent in real and reciprocal space. The latter is also true for the one-particle potential model, which is mathematically related to the Gram–Charlier expansion by the interchange of the real- and reciprocal-space expressions. The terms of the OPP model have a specific physical meaning. The model allows prediction of the temperature dependence of the temperature factor (Willis, 1969; Coppens, 1980), provided the potential function itself can be assumed to be temperature independent.

It has recently been shown that the Edgeworth expansion (1.2.12.5a) always has negative regions (Scheringer, 1985b). This implies that it is not a realistic description of a vibrating atom.

1.2.13. The generalized structure factor

In the generalized structure-factor formalism developed by Dawson (1975), the complex nature of both the atomic scattering factor and the generalized temperature factor are taken into account. We write for the atomic scattering factor:

$$f_j(\mathbf{H}) = f_{j,c}(\mathbf{H}) + i f_{j,a}(\mathbf{H}) + f'_j + i f''_j \quad (1.2.13.1a)$$

$$T_j(\mathbf{H}) = T_{j,c}(\mathbf{H}) + i T_{j,a}(\mathbf{H}) \quad (1.2.13.1b)$$

and

$$F(\mathbf{H}) = A(\mathbf{H}) + iB(\mathbf{H}), \quad (1.2.13.2)$$

where the subscripts c and a refer to the centrosymmetric and acentric components, respectively. Substitution in (1.2.4.2) gives for the real and imaginary components A and B of $F(\mathbf{H})$

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$$\begin{aligned}
 A(\mathbf{H}) = & \sum_j (f_{j,c} + f_j') [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c - \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a] \\
 & - (f_{j,a} + f_j'') [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a + \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c]
 \end{aligned}
 \tag{1.2.13.3a}$$

and

$$\begin{aligned}
 B(\mathbf{H}) = & \sum_j (f_{j,c} + f_j') [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a + \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c] \\
 & + (f_{j,a} + f_j'') [\cos(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_c - \sin(2\pi\mathbf{H} \cdot \mathbf{r}_j) T_a]
 \end{aligned}
 \tag{1.2.13.3b}$$

(McIntyre *et al.*, 1980; Dawson, 1967).

Expressions (1.2.13.3) illustrate the relation between valence-density anisotropy and anisotropy of thermal motion.

1.2.14. Conclusion

This chapter summarizes mathematical developments of the structure-factor formalism. The introduction of atomic asphericity

into the formalism and the treatment of thermal motion are interlinked. It is important that the complexities of the thermal probability distribution function can often be reduced by very low temperature experimentation. Results obtained with the multipole formalism for atomic asphericity can be used to derive physical properties and *d*-orbital populations of transition-metal atoms (*ITC*, 1999). In such applications, the deconvolution of the charge density and the thermal vibrations is essential. This deconvolution is dependent on the adequacy of the models summarized here.

Acknowledgements

The author would like to thank several of his colleagues who gave invaluable criticism of earlier versions of this manuscript. Corrections and additions were made following comments by P. J. Becker, D. Feil, N. K. Hansen, G. McIntyre, E. N. Maslen, S. Ohba, C. Scherlinger and D. Schwarzenbach. Z. Su contributed to the revised version of the manuscript. Support of this work by the US National Science Foundation (CHE8711736 and CHE9317770) is gratefully acknowledged.

1.3. Fourier transforms in crystallography: theory, algorithms and applications

BY G. BRICOGNE

1.3.1. General introduction

Since the publication of Volume II of *International Tables*, most aspects of the theory, computation and applications of Fourier transforms have undergone considerable development, often to the point of being hardly recognizable.

The mathematical analysis of the Fourier transformation has been extensively reformulated within the framework of distribution theory, following Schwartz's work in the early 1950s.

The computation of Fourier transforms has been revolutionized by the advent of digital computers and of the Cooley–Tukey algorithm, and progress has been made at an ever-accelerating pace in the design of new types of algorithms and in optimizing their interplay with machine architecture.

These advances have transformed both theory and practice in several fields which rely heavily on Fourier methods; much of electrical engineering, for instance, has become digital signal processing.

By contrast, crystallography has remained relatively unaffected by these developments. From the conceptual point of view, old-fashioned Fourier series are still adequate for the quantitative description of X-ray diffraction, as this rarely entails consideration of molecular transforms between reciprocal-lattice points. From the practical point of view, three-dimensional Fourier transforms have mostly been used as a tool for visualizing electron-density maps, so that only moderate urgency was given to trying to achieve ultimate efficiency in these relatively infrequent calculations.

Recent advances in phasing and refinement methods, however, have placed renewed emphasis on concepts and techniques long used in digital signal processing, e.g. flexible sampling, Shannon interpolation, linear filtering, and interchange between convolution and multiplication. These methods are iterative in nature, and thus generate a strong incentive to design new crystallographic Fourier transform algorithms making the fullest possible use of all available symmetry to save both storage and computation.

As a result, need has arisen for a modern and coherent account of Fourier transform methods in crystallography which would provide:

- (i) a simple and foolproof means of switching between the three different guises in which the Fourier transformation is encountered (Fourier transforms, Fourier series and discrete Fourier transforms), both formally and computationally;
- (ii) an up-to-date presentation of the most important algorithms for the efficient numerical calculation of discrete Fourier transforms;
- (iii) a systematic study of the incorporation of symmetry into the calculation of crystallographic discrete Fourier transforms;
- (iv) a survey of the main types of crystallographic computations based on the Fourier transformation.

The rapid pace of progress in these fields implies that such an account would be struck by quasi-immediate obsolescence if it were written solely for the purpose of compiling a catalogue of results and formulae 'customized' for crystallographic use. Instead, the emphasis has been placed on a mode of presentation in which most results and formulae are *derived* rather than listed. This does entail a substantial mathematical overhead, but has the advantage of preserving in its 'native' form the context within which these results are obtained. It is this context, rather than any particular set of results, which constitutes the most fertile source of new ideas and new applications, and as such can have any hope at all of remaining useful in the long run.

These conditions have led to the following choices:

- (i) the mathematical theory of the Fourier transformation has been cast in the language of Schwartz's theory of distributions

which has long been adopted in several applied fields, in particular electrical engineering, with considerable success; the extra work involved handsomely pays for itself by allowing the three different types of Fourier transformations to be treated together, and by making all properties of the Fourier transform consequences of a single property (the convolution theorem). This is particularly useful in all questions related to the sampling theorem;

- (ii) the various numerical algorithms have been presented as the consequences of basic algebraic phenomena involving Abelian groups, rings and finite fields; this degree of formalization greatly helps the subsequent incorporation of symmetry;

- (iii) the algebraic nature of space groups has been re-emphasized so as to build up a framework which can accommodate both the phenomena used to factor the discrete Fourier transform and those which underlie the existence (and lead to the classification) of space groups; this common ground is found in the notion of *module over a group ring* (i.e. integral representation theory), which is then applied to the formulation of a large number of algorithms, many of which are new;

- (iv) the survey of the main types of crystallographic computations has tried to highlight the roles played by various properties of the Fourier transformation, and the ways in which a better exploitation of these properties has been the driving force behind the discovery of more powerful methods.

In keeping with this philosophy, the theory is presented first, followed by the crystallographic applications. There are 'forward references' from mathematical results to the applications which later invoke them (thus giving 'real-life' examples rather than artificial ones), and 'backward references' as usual. In this way, the internal logic of the mathematical developments – the surest guide to future innovations – can be preserved, whereas the alternative solution of relegating these to appendices tends on the contrary to obscure that logic by subordinating it to that of the applications.

It is hoped that this attempt at an overall presentation of the main features of Fourier transforms and of their ubiquitous role in crystallography will be found useful by scientists both within and outside the field.

1.3.2. The mathematical theory of the Fourier transformation

1.3.2.1. Introduction

The Fourier transformation and the practical applications to which it gives rise occur in three different forms which, although they display a similar range of phenomena, normally require distinct formulations and different proof techniques:

- (i) *Fourier transforms*, in which both function and transform depend on continuous variables;
- (ii) *Fourier series*, which relate a periodic function to a discrete set of coefficients indexed by n -tuples of integers;
- (iii) *discrete Fourier transforms*, which relate finite-dimensional vectors by linear operations representable by matrices.

At the same time, the most useful property of the Fourier transformation – the exchange between multiplication and convolution – is mathematically the most elusive and the one which requires the greatest caution in order to avoid writing down meaningless expressions.

It is the unique merit of Schwartz's theory of distributions (Schwartz, 1966) that it affords complete control over all the troublesome phenomena which had previously forced mathematicians to settle for a piecemeal, fragmented theory of the Fourier transformation. By its ability to handle rigorously highly 'singular'

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objects (especially δ -functions, their derivatives, their tensor products, their products with smooth functions, their translates and lattices of these translates), distribution theory can deal with all the major properties of the Fourier transformation as particular instances of a single basic result (the exchange between multiplication and convolution), and can at the same time accommodate the three previously distinct types of Fourier theories within a unique framework. This brings great simplification to matters of central importance in crystallography, such as the relations between

- (a) periodization, and sampling or decimation;
- (b) Shannon interpolation, and masking by an indicator function;
- (c) section, and projection;
- (d) differentiation, and multiplication by a monomial;
- (e) translation, and phase shift.

All these properties become subsumed under the same theorem.

This striking synthesis comes at a slight price, which is the relative complexity of the notion of distribution. It is first necessary to establish the notion of topological vector space and to gain sufficient control (or, at least, understanding) over convergence behaviour in certain of these spaces. The key notion of *metrizability* cannot be circumvented, as it underlies most of the constructs and many of the proof techniques used in distribution theory. Most of Section 1.3.2.2 builds up to the fundamental result at the end of Section 1.3.2.2.6.2, which is basic to the definition of a distribution in Section 1.3.2.3.4 and to all subsequent developments.

The reader mostly interested in applications will probably want to reach this section by starting with his or her favourite topic in Section 1.3.4, and following the backward references to the relevant properties of the Fourier transformation, then to the proof of these properties, and finally to the definitions of the objects involved. Hopefully, he or she will then feel inclined to follow the forward references and thus explore the subject from the abstract to the practical. The books by Dieudonné (1969) and Lang (1965) are particularly recommended as general references for all aspects of analysis and algebra.

1.3.2.2. Preliminary notions and notation

Throughout this text, $\mathbb{R}$ will denote the set of real numbers, $\mathbb{Z}$ the set of rational (signed) integers and $\mathbb{N}$ the set of natural (unsigned) integers. The symbol $\mathbb{R}^n$ will denote the Cartesian product of n copies of $\mathbb{R}$:

$$\mathbb{R}^n = \mathbb{R} \times \dots \times \mathbb{R} \quad (n \text{ times}, n \geq 1),$$

so that an element $\mathbf{x}$ of $\mathbb{R}^n$ is an n -tuple of real numbers:

$$\mathbf{x} = (x_1, \dots, x_n).$$

Similar meanings will be attached to $\mathbb{Z}^n$ and $\mathbb{N}^n$.

The symbol $\mathbb{C}$ will denote the set of complex numbers. If $z \in \mathbb{C}$, its modulus will be denoted by $|z|$, its conjugate by $\bar{z}$ (not z^*), and its real and imaginary parts by $\Re(z)$ and $\Im(z)$:

$$\Re(z) = \frac{1}{2}(z + \bar{z}), \quad \Im(z) = \frac{1}{2i}(z - \bar{z}).$$

If X is a finite set, then $|X|$ will denote the number of its elements. If mapping f sends an element x of set X to the element $f(x)$ of set Y , the notation

$$f : x \mapsto f(x)$$

will be used; the plain arrow $\rightarrow$ will be reserved for denoting limits, as in

$$\lim_{p \rightarrow \infty} \left(1 + \frac{x}{p}\right)^p = e^x.$$

If X is any set and S is a subset of X , the *indicator function* χ_S of S is the real-valued function on X defined by

$$\begin{aligned} \chi_S(x) &= 1 & \text{if } x \in S \\ &= 0 & \text{if } x \notin S. \end{aligned}$$

1.3.2.2.1. Metric and topological notions in $\mathbb{R}^n$

The set $\mathbb{R}^n$ can be endowed with the structure of a vector space of dimension n over $\mathbb{R}$, and can be made into a Euclidean space by treating its standard basis as an orthonormal basis and defining the Euclidean norm:

$$\|\mathbf{x}\| = \left(\sum_{i=1}^n x_i^2\right)^{1/2}.$$

By misuse of notation, $\mathbf{x}$ will sometimes also designate the column vector of coordinates of $\mathbf{x} \in \mathbb{R}^n$; if these coordinates are referred to an orthonormal basis of $\mathbb{R}^n$, then

$$\|\mathbf{x}\| = (\mathbf{x}^T \mathbf{x})^{1/2},$$

where $\mathbf{x}^T$ denotes the transpose of $\mathbf{x}$.

The distance between two points $\mathbf{x}$ and $\mathbf{y}$ defined by $d(\mathbf{x}, \mathbf{y}) = \|\mathbf{x} - \mathbf{y}\|$ allows the topological structure of $\mathbb{R}$ to be transferred to $\mathbb{R}^n$, making it a *metric space*. The basic notions in a metric space are those of neighbourhoods, of open and closed sets, of limit, of continuity, and of convergence (see Section 1.3.2.2.6.1).

A subset S of $\mathbb{R}^n$ is *bounded* if $\sup \|\mathbf{x} - \mathbf{y}\| < \infty$ as $\mathbf{x}$ and $\mathbf{y}$ run through S ; it is *closed* if it contains the limits of all convergent sequences with elements in S . A subset K of $\mathbb{R}^n$ which is both bounded and closed has the property of being *compact*, i.e. that whenever K has been covered by a family of open sets, a finite subfamily can be found which suffices to cover K . Compactness is a very useful topological property for the purpose of proof, since it allows one to reduce the task of examining infinitely many local situations to that of examining only finitely many of them.

1.3.2.2.2. Functions over $\mathbb{R}^n$

Let φ be a complex-valued function over $\mathbb{R}^n$. The *support* of φ , denoted $\text{Supp } \varphi$, is the smallest closed subset of $\mathbb{R}^n$ outside which φ vanishes identically. If $\text{Supp } \varphi$ is compact, φ is said to have compact support.

If $\mathbf{t} \in \mathbb{R}^n$, the *translate* of φ by $\mathbf{t}$, denoted $\tau_{\mathbf{t}}\varphi$, is defined by

$$(\tau_{\mathbf{t}}\varphi)(\mathbf{x}) = \varphi(\mathbf{x} - \mathbf{t}).$$

Its support is the geometric translate of that of φ :

$$\text{Supp } \tau_{\mathbf{t}}\varphi = \{\mathbf{x} + \mathbf{t} | \mathbf{x} \in \text{Supp } \varphi\}.$$

If A is a non-singular linear transformation in $\mathbb{R}^n$, the *image* of φ by A , denoted $A^\# \varphi$, is defined by

$$(A^\# \varphi)(\mathbf{x}) = \varphi[A^{-1}(\mathbf{x})].$$

Its support is the geometric image of $\text{Supp } \varphi$ under A :

$$\text{Supp } A^\# \varphi = \{A(\mathbf{x}) | \mathbf{x} \in \text{Supp } \varphi\}.$$

If S is a non-singular affine transformation in $\mathbb{R}^n$ of the form

$$S(\mathbf{x}) = A(\mathbf{x}) + \mathbf{b}$$

with A linear, the image of φ by S is $S^\# \varphi = \tau_{\mathbf{b}}(A^\# \varphi)$, i.e.

$$(S^\# \varphi)(\mathbf{x}) = \varphi[A^{-1}(\mathbf{x} - \mathbf{b})].$$

Its support is the geometric image of $\text{Supp } \varphi$ under S :

$$\text{Supp } S^\# \varphi = \{S(\mathbf{x}) | \mathbf{x} \in \text{Supp } \varphi\}.$$

It may be helpful to visualize the process of forming the image of a function by a geometric operation as consisting of applying that operation to the *graph* of that function, which is equivalent to

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applying the *inverse* transformation to the coordinates $\mathbf{x}$. This use of the inverse later affords the ‘left-representation property’ [see Section 1.3.4.2.2.2(e)] when the geometric operations form a group, which is of fundamental importance in the treatment of crystallographic symmetry (Sections 1.3.4.2.2.4, 1.3.4.2.2.5).

1.3.2.2.3. Multi-index notation

When dealing with functions in n variables and their derivatives, considerable abbreviation of notation can be obtained through the use of multi-indices.

A *multi-index* $\mathbf{p} \in \mathbb{N}^n$ is an n -tuple of natural integers: $\mathbf{p} = (p_1, \dots, p_n)$. The *length* of $\mathbf{p}$ is defined as

$$|\mathbf{p}| = \sum_{i=1}^n p_i,$$

and the following abbreviations will be used:

- (i) $\mathbf{x}^{\mathbf{p}} = x_1^{p_1} \dots x_n^{p_n}$
- (ii) $D_{\mathbf{i}} f = \frac{\partial f}{\partial x_i} = \partial_i f$
- (iii) $D^{\mathbf{p}} f = D_1^{p_1} \dots D_n^{p_n} f = \frac{\partial^{|\mathbf{p}|} f}{\partial x_1^{p_1} \dots \partial x_n^{p_n}}$
- (iv) $\mathbf{q} \leq \mathbf{p}$ if and only if $q_i \leq p_i$ for all $i = 1, \dots, n$
- (v) $\mathbf{p} - \mathbf{q} = (p_1 - q_1, \dots, p_n - q_n)$
- (vi) $\mathbf{p}! = p_1! \times \dots \times p_n!$
- (vii) $\binom{\mathbf{p}}{\mathbf{q}} = \binom{p_1}{q_1} \times \dots \times \binom{p_n}{q_n}$.

Leibniz’s formula for the repeated differentiation of products then assumes the concise form

$$D^{\mathbf{p}}(fg) = \sum_{\mathbf{q} \leq \mathbf{p}} \binom{\mathbf{p}}{\mathbf{q}} D^{\mathbf{p}-\mathbf{q}} f D^{\mathbf{q}} g,$$

while the Taylor expansion of f to order m about $\mathbf{x} = \mathbf{a}$ reads

$$f(\mathbf{x}) = \sum_{|\mathbf{p}| \leq m} \frac{1}{\mathbf{p}!} [D^{\mathbf{p}} f(\mathbf{a})] (\mathbf{x} - \mathbf{a})^{\mathbf{p}} + o(\|\mathbf{x} - \mathbf{a}\|^m).$$

In certain sections the notation ∇f will be used for the gradient vector of f , and the notation $(\nabla \nabla^T) f$ for the Hessian matrix of its mixed second-order partial derivatives:

$$\nabla = \begin{pmatrix} \frac{\partial}{\partial x_1} \\ \vdots \\ \frac{\partial}{\partial x_n} \end{pmatrix}, \quad \nabla f = \begin{pmatrix} \frac{\partial f}{\partial x_1} \\ \vdots \\ \frac{\partial f}{\partial x_n} \end{pmatrix},$$

$$(\nabla \nabla^T) f = \begin{pmatrix} \frac{\partial^2 f}{\partial x_1^2} & \dots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \dots & \frac{\partial^2 f}{\partial x_n^2} \end{pmatrix}.$$

1.3.2.2.4. Integration, L^p spaces

The Riemann integral used in elementary calculus suffers from the drawback that vector spaces of Riemann-integrable functions over $\mathbb{R}^n$ are not *complete* for the topology of convergence in the

mean: a Cauchy sequence of integrable functions may converge to a non-integrable function.

To obtain the property of completeness, which is fundamental in functional analysis, it was necessary to extend the notion of integral. This was accomplished by Lebesgue [see Berberian (1962), Dieudonné (1970), or Chapter 1 of Dym & McKean (1972) and the references therein, or Chapter 9 of Sprecher (1970)], and entailed identifying functions which differed only on a subset of zero measure in $\mathbb{R}^n$ (such functions are said to be equal ‘almost everywhere’). The vector spaces $L^p(\mathbb{R}^n)$ consisting of function classes f modulo this identification for which

$$\|f\|_p = \left(\int_{\mathbb{R}^n} |f(\mathbf{x})|^p d^n \mathbf{x} \right)^{1/p} < \infty$$

are then complete for the topology induced by the norm $\|\cdot\|_p$: the limit of every Cauchy sequence of functions in L^p is itself a function in L^p (Riesz–Fischer theorem).

The space $L^1(\mathbb{R}^n)$ consists of those function classes f such that

$$\|f\|_1 = \int_{\mathbb{R}^n} |f(\mathbf{x})| d^n \mathbf{x} < \infty$$

which are called *summable* or *absolutely integrable*. The convolution product:

$$\begin{aligned} (f * g)(\mathbf{x}) &= \int_{\mathbb{R}^n} f(\mathbf{y}) g(\mathbf{x} - \mathbf{y}) d^n \mathbf{y} \\ &= \int_{\mathbb{R}^n} f(\mathbf{x} - \mathbf{y}) g(\mathbf{y}) d^n \mathbf{y} = (g * f)(\mathbf{x}) \end{aligned}$$

is well defined; combined with the vector space structure of L^1 , it makes L^1 into a (commutative) *convolution algebra*. However, this algebra has no unit element: there is no $f \in L^1$ such that $f * g = g$ for all $g \in L^1$; it has only approximate units, *i.e.* sequences (f_ν) such that $f_\nu * g$ tends to g in the L^1 topology as $\nu \rightarrow \infty$. This is one of the starting points of distribution theory.

The space $L^2(\mathbb{R}^n)$ of *square-integrable* functions can be endowed with a scalar product

$$(f, g) = \int_{\mathbb{R}^n} \overline{f(\mathbf{x})} g(\mathbf{x}) d^n \mathbf{x}$$

which makes it into a *Hilbert space*. The Cauchy–Schwarz inequality

$$|(f, g)| \leq [(f, f)(g, g)]^{1/2}$$

generalizes the fact that the absolute value of the cosine of an angle is less than or equal to 1.

The space $L^\infty(\mathbb{R}^n)$ is defined as the space of functions f such that

$$\|f\|_\infty = \lim_{p \rightarrow \infty} \|f\|_p = \lim_{p \rightarrow \infty} \left(\int_{\mathbb{R}^n} |f(\mathbf{x})|^p d^n \mathbf{x} \right)^{1/p} < \infty.$$

The quantity $\|f\|_\infty$ is called the ‘essential sup norm’ of f , as it is the smallest positive number which $|f(\mathbf{x})|$ exceeds only on a subset of zero measure in $\mathbb{R}^n$. A function $f \in L^\infty$ is called *essentially bounded*.

1.3.2.2.5. Tensor products. Fubini’s theorem

Let $f \in L^1(\mathbb{R}^m)$, $g \in L^1(\mathbb{R}^n)$. Then the function

$$f \otimes g : (\mathbf{x}, \mathbf{y}) \mapsto f(\mathbf{x})g(\mathbf{y})$$

is called the *tensor product* of f and g , and belongs to $L^1(\mathbb{R}^m \times \mathbb{R}^n)$. The finite linear combinations of functions of the form $f \otimes g$ span a subspace of $L^1(\mathbb{R}^m \times \mathbb{R}^n)$ called the tensor product of $L^1(\mathbb{R}^m)$ and $L^1(\mathbb{R}^n)$ and denoted $L^1(\mathbb{R}^m) \otimes L^1(\mathbb{R}^n)$.

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The integration of a general function over $\mathbb{R}^m \times \mathbb{R}^n$ may be accomplished in two steps according to *Fubini's theorem*. Given $F \in L^1(\mathbb{R}^m \times \mathbb{R}^n)$, the functions

$$F_1 : \mathbf{x} \mapsto \int_{\mathbb{R}^n} F(\mathbf{x}, \mathbf{y}) \, d^n \mathbf{y}$$

$$F_2 : \mathbf{y} \mapsto \int_{\mathbb{R}^m} F(\mathbf{x}, \mathbf{y}) \, d^m \mathbf{x}$$

exist for almost all $\mathbf{x} \in \mathbb{R}^m$ and almost all $\mathbf{y} \in \mathbb{R}^n$, respectively, are integrable, and

$$\int_{\mathbb{R}^m \times \mathbb{R}^n} F(\mathbf{x}, \mathbf{y}) \, d^m \mathbf{x} \, d^n \mathbf{y} = \int_{\mathbb{R}^m} F_1(\mathbf{x}) \, d^m \mathbf{x} = \int_{\mathbb{R}^n} F_2(\mathbf{y}) \, d^n \mathbf{y}.$$

Conversely, if any one of the integrals

$$(i) \quad \int_{\mathbb{R}^m \times \mathbb{R}^n} |F(\mathbf{x}, \mathbf{y})| \, d^m \mathbf{x} \, d^n \mathbf{y}$$

$$(ii) \quad \int_{\mathbb{R}^m} \left(\int_{\mathbb{R}^n} |F(\mathbf{x}, \mathbf{y})| \, d^n \mathbf{y} \right) \, d^m \mathbf{x}$$

$$(iii) \quad \int_{\mathbb{R}^n} \left(\int_{\mathbb{R}^m} |F(\mathbf{x}, \mathbf{y})| \, d^m \mathbf{x} \right) \, d^n \mathbf{y}$$

is finite, then so are the other two, and the identity above holds. It is then (and only then) permissible to change the order of integrations.

Fubini's theorem is of fundamental importance in the study of tensor products and convolutions of distributions.

1.3.2.2.6. Topology in function spaces

Geometric intuition, which often makes 'obvious' the topological properties of the real line and of ordinary space, cannot be relied upon in the study of function spaces: the latter are infinite-dimensional, and several inequivalent notions of convergence may exist. A careful analysis of topological concepts and of their interrelationship is thus a necessary prerequisite to the study of these spaces. The reader may consult Dieudonné (1969, 1970), Friedman (1970), Trèves (1967) and Yosida (1965) for detailed expositions.

1.3.2.2.6.1. General topology

Most topological notions are first encountered in the setting of *metric spaces*. A metric space E is a set equipped with a *distance function* d from $E \times E$ to the non-negative reals which satisfies:

- (i) $d(x, y) = d(y, x) \quad \forall x, y \in E$ (symmetry);
- (ii) $d(x, y) = 0$ iff $x = y$ (separation);
- (iii) $d(x, z) \leq d(x, y) + d(y, z) \quad \forall x, y, z \in E$ (triangular inequality).

By means of d , the following notions can be defined: open balls, neighbourhoods; open and closed sets, interior and closure; convergence of sequences, continuity of mappings; Cauchy sequences and completeness; compactness; connectedness. They suffice for the investigation of a great number of questions in analysis and geometry (see e.g. Dieudonné, 1969).

Many of these notions turn out to depend only on the properties of the collection $\mathcal{O}(E)$ of open subsets of E : two distance functions leading to the same $\mathcal{O}(E)$ lead to identical topological properties. An axiomatic reformulation of topological notions is thus possible: a *topology* in E is a collection $\mathcal{O}(E)$ of subsets of E which satisfy suitable axioms and are deemed open irrespective of the way they are obtained. From the practical standpoint, however, a topology which can be obtained from a distance function (called a *metrizable topology*) has the very useful property that *the notions of closure,*

limit and continuity may be defined by means of sequences. For non-metrizable topologies, these notions are much more difficult to handle, requiring the use of 'filters' instead of sequences.

In some spaces E , a topology may be most naturally defined by a family of *pseudo-distances* $(d_\alpha)_{\alpha \in A}$, where each d_α satisfies (i) and (iii) but not (ii). Such spaces are called *uniformizable*. If for every pair $(x, y) \in E \times E$ there exists $\alpha \in A$ such that $d_\alpha(x, y) \neq 0$, then the separation property can be recovered. If furthermore a *countable* subfamily of the d_α suffices to define the topology of E , the latter can be shown to be *metrizable*, so that limiting processes in E may be studied by means of sequences.

1.3.2.2.6.2. Topological vector spaces

The function spaces E of interest in Fourier analysis have an underlying vector space structure over the field $\mathbb{C}$ of complex numbers. A topology on E is said to be *compatible* with a vector space structure on E if vector addition [i.e. the map $(\mathbf{x}, \mathbf{y}) \mapsto \mathbf{x} + \mathbf{y}$] and scalar multiplication [i.e. the map $(\lambda, \mathbf{x}) \mapsto \lambda \mathbf{x}$] are both *continuous*; E is then called a *topological vector space*. Such a topology may be defined by specifying a 'fundamental system S of neighbourhoods of $\mathbf{0}$ ', which can then be translated by vector addition to construct neighbourhoods of other points $\mathbf{x} \neq \mathbf{0}$.

A *norm* ν on a vector space E is a non-negative real-valued function on $E \times E$ such that

- (i') $\nu(\lambda \mathbf{x}) = |\lambda| \nu(\mathbf{x})$ for all $\lambda \in \mathbb{C}$ and $\mathbf{x} \in E$;
- (ii') $\nu(\mathbf{x}) = 0$ if and only if $\mathbf{x} = \mathbf{0}$;
- (iii') $\nu(\mathbf{x} + \mathbf{y}) \leq \nu(\mathbf{x}) + \nu(\mathbf{y})$ for all $\mathbf{x}, \mathbf{y} \in E$.

Subsets of E defined by conditions of the form $\nu(\mathbf{x}) \leq r$ with $r > 0$ form a fundamental system of neighbourhoods of $\mathbf{0}$. The corresponding topology makes E a *normed space*. This topology is *metrizable*, since it is equivalent to that derived from the translation-invariant distance $d(\mathbf{x}, \mathbf{y}) = \nu(\mathbf{x} - \mathbf{y})$. Normed spaces which are *complete*, i.e. in which all Cauchy sequences converge, are called *Banach spaces*; they constitute the natural setting for the study of differential calculus.

A *semi-norm* σ on a vector space E is a positive real-valued function on $E \times E$ which satisfies (i') and (iii') but not (ii'). Given a set Σ of semi-norms on E such that any pair $(\mathbf{x}, \mathbf{y})$ in $E \times E$ is separated by at least one $\sigma \in \Sigma$, let B be the set of those subsets $\Gamma_{\sigma, r}$ of E defined by a condition of the form $\sigma(\mathbf{x}) \leq r$ with $\sigma \in \Sigma$ and $r > 0$; and let S be the set of finite intersections of elements of B . Then there exists a unique topology on E for which S is a fundamental system of neighbourhoods of $\mathbf{0}$. This topology is *uniformizable* since it is equivalent to that derived from the family of translation-invariant pseudo-distances $(\mathbf{x}, \mathbf{y}) \mapsto \sigma(\mathbf{x} - \mathbf{y})$. It is *metrizable* if and only if it can be constructed by the above procedure with Σ a *countable* set of semi-norms. If furthermore E is complete, E is called a *Fréchet space*.

If E is a topological vector space over $\mathbb{C}$, its *dual* E^* is the set of all linear mappings from E to $\mathbb{C}$ (which are also called *linear forms*, or *linear functionals*, over E). The subspace of E^* consisting of all linear forms which are *continuous* for the topology of E is called the *topological dual* of E and is denoted E' . If the topology on E is metrizable, then the continuity of a linear form $T \in E'$ at $f \in E$ can be ascertained by means of sequences, i.e. by checking that the sequence $[T(f_j)]$ of complex numbers converges to $T(f)$ in $\mathbb{C}$ whenever the sequence (f_j) converges to f in E .

1.3.2.3. Elements of the theory of distributions

1.3.2.3.1. Origins

At the end of the 19th century, Heaviside proposed under the name of 'operational calculus' a set of rules for solving a class of

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differential, partial differential and integral equations encountered in electrical engineering (today's 'signal processing'). These rules worked remarkably well but were devoid of mathematical justification (see Whittaker, 1928). In 1926, Dirac introduced his famous δ -function [see Dirac (1958), pp. 58–61], which was found to be related to Heaviside's constructs. Other singular objects, together with procedures to handle them, had already appeared in several branches of analysis [Cauchy's 'principal values'; Hadamard's 'finite parts' (Hadamard, 1932, 1952); Riesz's regularization methods for certain divergent integrals (Riesz, 1938, 1949)] as well as in the theories of Fourier series and integrals (see e.g. Bochner, 1932, 1959). Their very definition often verged on violating the rigorous rules governing limiting processes in analysis, so that subsequent recourse to limiting processes could lead to erroneous results; *ad hoc* precautions thus had to be observed to avoid mistakes in handling these objects.

In 1945–1950, Laurent Schwartz proposed his theory of distributions (see Schwartz, 1966), which provided a unified and definitive treatment of all these questions, with a striking combination of rigour and simplicity. Schwartz's treatment of Dirac's δ -function illustrates his approach in a most direct fashion. Dirac's original definition reads:

- (i) $\delta(\mathbf{x}) = 0$ for $\mathbf{x} \neq \mathbf{0}$,
- (ii) $\int_{\mathbb{R}^n} \delta(\mathbf{x}) d^n \mathbf{x} = 1$.

These two conditions are irreconcilable with Lebesgue's theory of integration: by (i), δ vanishes almost everywhere, so that its integral in (ii) must be 0, not 1.

A better definition consists in specifying that

- (iii) $\int_{\mathbb{R}^n} \delta(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x} = \varphi(\mathbf{0})$

for any function φ sufficiently well behaved near $\mathbf{x} = \mathbf{0}$. This is related to the problem of finding a unit for convolution (Section 1.3.2.2.4). As will now be seen, this definition is still unsatisfactory. Let the sequence (f_ν) in $L^1(\mathbb{R}^n)$ be an approximate convolution unit, e.g.

$$f_\nu(\mathbf{x}) = \left(\frac{\nu}{2\pi}\right)^{1/2} \exp(-\tfrac{1}{2}\nu^2 \|\mathbf{x}\|^2).$$

Then for any well behaved function φ the integrals

$$\int_{\mathbb{R}^n} f_\nu(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x}$$

exist, and the sequence of their numerical values tends to $\varphi(\mathbf{0})$. It is tempting to combine this with (iii) to conclude that δ is the limit of the sequence (f_ν) as $\nu \rightarrow \infty$. However,

$$\lim_{\nu \rightarrow \infty} f_\nu(\mathbf{x}) = 0 \quad \text{as } \nu \rightarrow \infty$$

almost everywhere in $\mathbb{R}^n$ and the crux of the problem is that

$$\begin{aligned} \varphi(\mathbf{0}) &= \lim_{\nu \rightarrow \infty} \int_{\mathbb{R}^n} f_\nu(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x} \\ &\neq \int_{\mathbb{R}^n} \left[\lim_{\nu \rightarrow \infty} f_\nu(\mathbf{x}) \right] \varphi(\mathbf{x}) d^n \mathbf{x} = 0 \end{aligned}$$

because the sequence (f_ν) does not satisfy the hypotheses of Lebesgue's dominated convergence theorem.

Schwartz's solution to this problem is deceptively simple: the regular behaviour one is trying to capture is an attribute not of the sequence of functions (f_ν) , but of the sequence of continuous linear functionals

$$T_\nu : \varphi \mapsto \int_{\mathbb{R}^n} f_\nu(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x}$$

which has as a limit the continuous functional

$$T : \varphi \mapsto \varphi(\mathbf{0}).$$

It is the latter functional which constitutes the proper definition of δ . The previous paradoxes arose because one insisted on writing down the simple linear operation T in terms of an integral.

The essence of Schwartz's theory of distributions is thus that, rather than try to define and handle 'generalized functions' *via* sequences such as (f_ν) [an approach adopted e.g. by Lighthill (1958) and Erdélyi (1962)], one should instead look at them as continuous linear functionals over spaces of well behaved functions.

There are many books on distribution theory and its applications. The reader may consult in particular Schwartz (1965, 1966), Gel'fand & Shilov (1964), Bremermann (1965), Trèves (1967), Challifour (1972), Friedlander (1982), and the relevant chapters of Hörmander (1963) and Yosida (1965). Schwartz (1965) is especially recommended as an introduction.

1.3.2.3.2. Rationale

The guiding principle which leads to requiring that the functions φ above (traditionally called 'test functions') should be well behaved is that correspondingly 'wilder' behaviour can then be accommodated in the limiting behaviour of the f_ν while still keeping the integrals $\int_{\mathbb{R}^n} f_\nu \varphi d^n \mathbf{x}$ under control. Thus

- (i) to minimize restrictions on the limiting behaviour of the f_ν at *infinity*, the φ 's will be chosen to have *compact support*;
- (ii) to minimize restrictions on the *local* behaviour of the f_ν , the φ 's will be chosen *infinitely differentiable*.

To ensure further the *continuity* of functionals such as T_ν with respect to the test function φ as the f_ν go increasingly wild, very strong control will have to be exercised in the way in which a sequence (φ_j) of test functions will be said to converge towards a limiting φ : conditions will have to be imposed not only on the values of the functions φ_j , but also on those of all their *derivatives*. Hence, defining a strong enough topology on the space of test functions φ is an *essential* prerequisite to the development of a satisfactory theory of distributions.

1.3.2.3.3. Test-function spaces

With this rationale in mind, the following function spaces will be defined for any open subset Ω of $\mathbb{R}^n$ (which may be the whole of $\mathbb{R}^n$):

- (a) $\mathcal{E}(\Omega)$ is the space of complex-valued functions over Ω which are indefinitely differentiable;
- (b) $\mathcal{D}(\Omega)$ is the subspace of $\mathcal{E}(\Omega)$ consisting of functions with (unspecified) compact support contained in $\mathbb{R}^n$;
- (c) $\mathcal{D}_K(\Omega)$ is the subspace of $\mathcal{D}(\Omega)$ consisting of functions whose (compact) support is contained within a fixed compact subset K of Ω .

When Ω is unambiguously defined by the context, we will simply write $\mathcal{E}$, $\mathcal{D}$, $\mathcal{D}_K$.

It sometimes suffices to require the existence of continuous derivatives only up to finite order m inclusive. The corresponding spaces are then denoted $\mathcal{E}^{(m)}$, $\mathcal{D}^{(m)}$, $\mathcal{D}_K^{(m)}$ with the convention that if $m = 0$, only continuity is required.

The *topologies* on these spaces constitute the most important ingredients of distribution theory, and will be outlined in some detail.

1.3.2.3.3.1. Topology on $\mathcal{E}(\Omega)$

It is defined by the family of semi-norms

$$\varphi \in \mathcal{E}(\Omega) \mapsto \sigma_{\mathbf{p}, K}(\varphi) = \sup_{\mathbf{x} \in K} |D^{\mathbf{p}} \varphi(\mathbf{x})|,$$

where $\mathbf{p}$ is a multi-index and K a compact subset of Ω . A

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fundamental system S of neighbourhoods of the origin in $\mathcal{E}(\Omega)$ is given by subsets of $\mathcal{E}(\Omega)$ of the form

$$V(m, \varepsilon, K) = \{\varphi \in \mathcal{E}(\Omega) \mid |\mathbf{p}| \leq m \Rightarrow \sigma_{\mathbf{p}, K}(\varphi) < \varepsilon\}$$

for all natural integers m , positive real ε , and compact subset K of Ω . Since a countable family of compact subsets K suffices to cover Ω , and since restricted values of ε of the form $\varepsilon = 1/N$ lead to the same topology, S is equivalent to a countable system of neighbourhoods and hence $\mathcal{E}(\Omega)$ is metrizable.

Convergence in $\mathcal{E}$ may thus be defined by means of sequences. A sequence (φ_ν) in $\mathcal{E}$ will be said to converge to 0 if for any given $V(m, \varepsilon, K)$ there exists ν_0 such that $\varphi_\nu \in V(m, \varepsilon, K)$ whenever $\nu > \nu_0$; in other words, if the φ_ν and all their derivatives $D^{\mathbf{p}}\varphi_\nu$ converge to 0 uniformly on any given compact K in Ω .

1.3.2.3.3.2. Topology on $\mathcal{Q}_K(\Omega)$

It is defined by the family of semi-norms

$$\varphi \in \mathcal{Q}_K(\Omega) \mapsto \sigma_{\mathbf{p}}(\varphi) = \sup_{\mathbf{x} \in K} |D^{\mathbf{p}}\varphi(\mathbf{x})|,$$

where K is now fixed. The fundamental system S of neighbourhoods of the origin in $\mathcal{Q}_K$ is given by sets of the form

$$V(m, \varepsilon) = \{\varphi \in \mathcal{Q}_K(\Omega) \mid |\mathbf{p}| \leq m \Rightarrow \sigma_{\mathbf{p}}(\varphi) < \varepsilon\}.$$

It is equivalent to the countable subsystem of the $V(m, 1/N)$, hence $\mathcal{Q}_K(\Omega)$ is metrizable.

Convergence in $\mathcal{Q}_K$ may thus be defined by means of sequences. A sequence (φ_ν) in $\mathcal{Q}_K$ will be said to converge to 0 if for any given $V(m, \varepsilon)$ there exists ν_0 such that $\varphi_\nu \in V(m, \varepsilon)$ whenever $\nu > \nu_0$; in other words, if the φ_ν and all their derivatives $D^{\mathbf{p}}\varphi_\nu$ converge to 0 uniformly in K .

1.3.2.3.3.3. Topology on $\mathcal{Q}(\Omega)$

It is defined by the fundamental system of neighbourhoods of the origin consisting of sets of the form

$$V((m), (\varepsilon)) = \left\{ \varphi \in \mathcal{Q}(\Omega) \mid |\mathbf{p}| \leq m_\nu \Rightarrow \sup_{\|\mathbf{x}\| \leq \nu} |D^{\mathbf{p}}\varphi(\mathbf{x})| < \varepsilon_\nu \text{ for all } \nu \right\},$$

where (m) is an increasing sequence (m_ν) of integers tending to $+\infty$ and (ε) is a decreasing sequence (ε_ν) of positive reals tending to 0, as $\nu \rightarrow \infty$.

This topology is *not metrizable*, because the sets of sequences (m) and (ε) are essentially uncountable. It can, however, be shown to be the *inductive limit* of the topology of the subspaces $\mathcal{Q}_K$, in the following sense: V is a neighbourhood of the origin in $\mathcal{Q}$ if and only if its intersection with $\mathcal{Q}_K$ is a neighbourhood of the origin in $\mathcal{Q}_K$ for any given compact K in Ω .

A sequence (φ_ν) in $\mathcal{Q}$ will thus be said to converge to 0 in $\mathcal{Q}$ if all the φ_ν belong to some $\mathcal{Q}_K$ (with K a compact subset of Ω independent of ν) and if (φ_ν) converges to 0 in $\mathcal{Q}_K$.

As a result, a complex-valued functional T on $\mathcal{Q}$ will be said to be continuous for the topology of $\mathcal{Q}$ if and only if, for any given compact K in Ω , its restriction to $\mathcal{Q}_K$ is continuous for the topology of $\mathcal{Q}_K$, i.e. maps convergent sequences in $\mathcal{Q}_K$ to convergent sequences in $\mathbb{C}$.

This property of $\mathcal{Q}$, i.e. having a non-metrizable topology which is the inductive limit of metrizable topologies in its subspaces $\mathcal{Q}_K$, conditions the whole structure of distribution theory and dictates that of many of its proofs.

1.3.2.3.3.4. Topologies on $\mathcal{E}^{(m)}$, $\mathcal{Q}_K^{(m)}$, $\mathcal{Q}^{(m)}$

These are defined similarly, but only involve conditions on derivatives up to order m .

1.3.2.3.4. Definition of distributions

A distribution T on Ω is a linear form over $\mathcal{Q}(\Omega)$, i.e. a map

$$T : \varphi \mapsto \langle T, \varphi \rangle$$

which associates linearly a complex number $\langle T, \varphi \rangle$ to any $\varphi \in \mathcal{Q}(\Omega)$, and which is *continuous* for the topology of that space. In the terminology of Section 1.3.2.2.6.2, T is an element of $\mathcal{Q}'(\Omega)$, the *topological dual* of $\mathcal{Q}(\Omega)$.

Continuity over $\mathcal{Q}$ is equivalent to continuity over $\mathcal{Q}_K$ for all compact K contained in Ω , and hence to the condition that for any sequence (φ_ν) in $\mathcal{Q}$ such that

- (i) $\text{Supp } \varphi_\nu$ is contained in some compact K independent of ν ,
- (ii) the sequences $(|D^{\mathbf{p}}\varphi_\nu|)$ converge uniformly to 0 on K for all multi-indices $\mathbf{p}$;

then the sequence of complex numbers $\langle T, \varphi_\nu \rangle$ converges to 0 in $\mathbb{C}$.

If the continuity of a distribution T requires (ii) for $|\mathbf{p}| \leq m$ only, T may be defined over $\mathcal{Q}^{(m)}$ and thus $T \in \mathcal{Q}'^{(m)}$; T is said to be a *distribution of finite order m* . In particular, for $m = 0$, $\mathcal{Q}^{(0)}$ is the space of continuous functions with compact support, and a distribution $T \in \mathcal{Q}'^{(0)}$ is a (Radon) *measure* as used in the theory of integration. Thus measures are particular cases of distributions.

Generally speaking, the *larger* a space of test functions, the *smaller* its topological dual:

$$m < n \Rightarrow \mathcal{Q}^{(m)} \supset \mathcal{Q}^{(n)} \Rightarrow \mathcal{Q}'^{(n)} \supset \mathcal{Q}'^{(m)}.$$

This clearly results from the observation that if the φ 's are allowed to be less regular, then less wildness can be accommodated in T if the continuity of the map $\varphi \mapsto \langle T, \varphi \rangle$ with respect to φ is to be preserved.

1.3.2.3.5. First examples of distributions

(i) The linear map $\varphi \mapsto \langle \delta, \varphi \rangle = \varphi(\mathbf{0})$ is a measure (i.e. a zeroth-order distribution) called Dirac's measure or (improperly) Dirac's ' δ -function'.

(ii) The linear map $\varphi \mapsto \langle \delta_{(\mathbf{a})}, \varphi \rangle = \varphi(\mathbf{a})$ is called Dirac's measure at point $\mathbf{a} \in \mathbb{R}^n$.

(iii) The linear map $\varphi \mapsto (-1)^{\mathbf{p}} D^{\mathbf{p}}\varphi(\mathbf{a})$ is a distribution of order $m = |\mathbf{p}| > 0$, and hence is not a measure.

(iv) The linear map $\varphi \mapsto \sum_{\nu > 0} \varphi^{(\nu)}(\nu)$ is a distribution of infinite order on $\mathbb{R}$: the order of differentiation is bounded for each φ (because φ has compact support) but is not as φ varies.

(v) If $(\mathbf{p}_\nu)$ is a sequence of multi-indices $\mathbf{p}_\nu = (p_{1\nu}, \dots, p_{n\nu})$ such that $|\mathbf{p}_\nu| \rightarrow \infty$ as $\nu \rightarrow \infty$, then the linear map $\varphi \mapsto \sum_{\nu > 0} (D^{\mathbf{p}_\nu}\varphi)(\mathbf{p}_\nu)$ is a distribution of infinite order on $\mathbb{R}^n$.

1.3.2.3.6. Distributions associated to locally integrable functions

Let f be a complex-valued function over Ω such that $\int_K |f(\mathbf{x})| d^n \mathbf{x}$ exists for any given compact K in Ω ; f is then called *locally integrable*.

The linear mapping from $\mathcal{Q}(\Omega)$ to $\mathbb{C}$ defined by

$$\varphi \mapsto \int_{\Omega} f(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x}$$

may then be shown to be continuous over $\mathcal{Q}(\Omega)$. It thus defines a *distribution* $T_f \in \mathcal{Q}'(\Omega)$:

$$\langle T_f, \varphi \rangle = \int_{\Omega} f(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x}.$$

As the continuity of T_f only requires that $\varphi \in \mathcal{Q}^{(0)}(\Omega)$, T_f is actually a Radon measure.

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It can be shown that two locally integrable functions f and g define the same distribution, i.e.

$$\langle T_f, \varphi \rangle = \langle T_g, \varphi \rangle \quad \text{for all } \varphi \in \mathcal{D},$$

if and only if they are equal almost everywhere. The classes of locally integrable functions modulo this equivalence form a vector space denoted $L^1_{\text{loc}}(\Omega)$; each element of $L^1_{\text{loc}}(\Omega)$ may therefore be identified with the distribution T_f defined by any one of its representatives f .

1.3.2.3.7. Support of a distribution

A distribution $T \in \mathcal{D}'(\Omega)$ is said to *vanish* on an open subset ω of Ω if it vanishes on all functions in $\mathcal{D}(\omega)$, i.e. if $\langle T, \varphi \rangle = 0$ whenever $\varphi \in \mathcal{D}(\omega)$.

The *support* of a distribution T , denoted $\text{Supp } T$, is then defined as the complement of the set-theoretic union of those open subsets ω on which T vanishes; or equivalently as the smallest closed subset of Ω outside which T vanishes.

When $T = T_f$ for $f \in L^1_{\text{loc}}(\Omega)$, then $\text{Supp } T = \text{Supp } f$, so that the two notions coincide. Clearly, if $\text{Supp } T$ and $\text{Supp } \varphi$ are disjoint subsets of Ω , then $\langle T, \varphi \rangle = 0$.

It can be shown that any distribution $T \in \mathcal{D}'$ with compact support may be extended from $\mathcal{D}$ to $\mathcal{E}$ while remaining continuous, so that $T \in \mathcal{E}'$; and that conversely, if $S \in \mathcal{E}'$, then its restriction T to $\mathcal{D}$ is a distribution with compact support. Thus, *the topological dual $\mathcal{E}'$ of $\mathcal{E}$ consists of those distributions in $\mathcal{D}'$ which have compact support*. This is intuitively clear since, if the condition of having compact support is fulfilled by T , it needs no longer be required of φ , which may then roam through $\mathcal{E}$ rather than $\mathcal{D}$.

1.3.2.3.8. Convergence of distributions

A sequence (T_j) of distributions will be said to converge in $\mathcal{D}'$ to a distribution T as $j \rightarrow \infty$ if, for any given $\varphi \in \mathcal{D}$, the sequence of complex numbers $(\langle T_j, \varphi \rangle)$ converges in $\mathbb{C}$ to the complex number $\langle T, \varphi \rangle$.

A series $\sum_{j=0}^{\infty} T_j$ of distributions will be said to converge in $\mathcal{D}'$ and to have distribution S as its sum if the sequence of partial sums $S_k = \sum_{j=0}^k T_j$ converges to S .

These definitions of convergence in $\mathcal{D}'$ assume that the limits T and S are known in advance, and are distributions. This raises the question of the *completeness* of $\mathcal{D}'$: if a sequence (T_j) in $\mathcal{D}'$ is such that the sequence $(\langle T_j, \varphi \rangle)$ has a limit in $\mathbb{C}$ for all $\varphi \in \mathcal{D}$, does the map

$$\varphi \mapsto \lim_{j \rightarrow \infty} \langle T_j, \varphi \rangle$$

define a distribution $T \in \mathcal{D}'$? In other words, does the limiting process preserve continuity with respect to φ ? It is a remarkable theorem that, because of the strong topology on $\mathcal{D}$, this is actually the case. An analogous statement holds for series. This notion of convergence does not coincide with any of the classical notions used for ordinary functions: for example, the sequence (φ_ν) with $\varphi_\nu(x) = \cos \nu x$ converges to 0 in $\mathcal{D}'(\mathbb{R})$, but fails to do so by any of the standard criteria.

An example of convergent sequences of distributions is provided by sequences which converge to δ . If (f_ν) is a sequence of locally summable functions on $\mathbb{R}^n$ such that

$$(i) \int_{\|\mathbf{x}\| < b} f_\nu(\mathbf{x}) d^n \mathbf{x} \rightarrow 1 \text{ as } \nu \rightarrow \infty \text{ for all } b > 0;$$

$$(ii) \int_{a \leq \|\mathbf{x}\| \leq 1/a} f_\nu(\mathbf{x}) d^n \mathbf{x} \rightarrow 0 \text{ as } \nu \rightarrow \infty \text{ for all } 0 < a < 1;$$

(iii) there exists $d > 0$ and $M > 0$ such that $\int_{\|\mathbf{x}\| < d} f_\nu(\mathbf{x}) d^n \mathbf{x} < M$ for all ν ;
then the sequence (T_{f_ν}) of distributions converges to δ in $\mathcal{D}'(\mathbb{R}^n)$.

1.3.2.3.9. Operations on distributions

As a general rule, the definitions are chosen so that the operations coincide with those on functions whenever a distribution is associated to a function.

Most definitions consist in transferring to a distribution T an operation which is well defined on $\varphi \in \mathcal{D}$ by ‘transposing’ it in the duality product $\langle T, \varphi \rangle$; this procedure will map T to a new distribution provided the original operation maps $\mathcal{D}$ continuously into itself.

1.3.2.3.9.1. Differentiation

(a) Definition and elementary properties

If T is a distribution on $\mathbb{R}^n$, its partial derivative $\partial_i T$ with respect to x_i is defined by

$$\langle \partial_i T, \varphi \rangle = -\langle T, \partial_i \varphi \rangle$$

for all $\varphi \in \mathcal{D}$. This does define a distribution, because the partial differentiations $\varphi \mapsto \partial_i \varphi$ are continuous for the topology of $\mathcal{D}$.

Suppose that $T = T_f$ with f a locally integrable function such that $\partial_i f$ exists and is almost everywhere continuous. Then integration by parts along the x_i axis gives

$$\begin{aligned} \int_{\mathbb{R}^n} \partial_i f(x_1, \dots, x_i, \dots, x_n) \varphi(x_1, \dots, x_i, \dots, x_n) dx_i \\ = (f\varphi)(x_1, \dots, +\infty, \dots, x_n) - (f\varphi)(x_1, \dots, -\infty, \dots, x_n) \\ - \int_{\mathbb{R}^n} f(x_1, \dots, x_i, \dots, x_n) \partial_i \varphi(x_1, \dots, x_i, \dots, x_n) dx_i; \end{aligned}$$

the integrated term vanishes, since φ has compact support, showing that $\partial_i T_f = T_{\partial_i f}$.

The test functions $\varphi \in \mathcal{D}$ are infinitely differentiable. Therefore, transpositions like that used to define $\partial_i T$ may be repeated, so that *any distribution is infinitely differentiable*. For instance,

$$\langle \partial_{ij}^2 T, \varphi \rangle = -\langle \partial_j T, \partial_i \varphi \rangle = \langle T, \partial_{ij}^2 \varphi \rangle,$$

$$\langle D^{\mathbf{p}} T, \varphi \rangle = (-1)^{|\mathbf{p}|} \langle T, D^{\mathbf{p}} \varphi \rangle,$$

$$\langle \Delta T, \varphi \rangle = \langle T, \Delta \varphi \rangle,$$

where Δ is the Laplacian operator. The derivatives of Dirac’s δ distribution are

$$\langle D^{\mathbf{p}} \delta, \varphi \rangle = (-1)^{|\mathbf{p}|} \langle \delta, D^{\mathbf{p}} \varphi \rangle = (-1)^{|\mathbf{p}|} D^{\mathbf{p}} \varphi(\mathbf{0}).$$

It is remarkable that *differentiation is a continuous operation* for the topology on $\mathcal{D}'$: if a sequence (T_j) of distributions converges to distribution T , then the sequence $(D^{\mathbf{p}} T_j)$ of derivatives converges to $D^{\mathbf{p}} T$ for any multi-index $\mathbf{p}$, since as $j \rightarrow \infty$

$$\langle D^{\mathbf{p}} T_j, \varphi \rangle = (-1)^{|\mathbf{p}|} \langle T_j, D^{\mathbf{p}} \varphi \rangle \rightarrow (-1)^{|\mathbf{p}|} \langle T, D^{\mathbf{p}} \varphi \rangle = \langle D^{\mathbf{p}} T, \varphi \rangle.$$

An analogous statement holds for series: any convergent series of distributions may be differentiated termwise to all orders. This illustrates how ‘robust’ the constructs of distribution theory are in comparison with those of ordinary function theory, where similar statements are notoriously untrue.

(b) Differentiation under the duality bracket

Limiting processes and differentiation may also be carried out under the duality bracket $\langle, \rangle$ as under the integral sign with ordinary functions. Let the function $\varphi = \varphi(\mathbf{x}, \lambda)$ depend on a parameter $\lambda \in \Lambda$ and a vector $\mathbf{x} \in \mathbb{R}^n$ in such a way that all functions

$$\varphi_\lambda : \mathbf{x} \mapsto \varphi(\mathbf{x}, \lambda)$$

be in $\mathcal{D}(\mathbb{R}^n)$ for all $\lambda \in \Lambda$. Let $T \in \mathcal{D}'(\mathbb{R}^n)$ be a distribution, let

$$I(\lambda) = \langle T, \varphi_\lambda \rangle$$

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and let $\lambda_0 \in \Lambda$ be given parameter value. Suppose that, as λ runs through a small enough neighbourhood of λ_0 ,

- (i) all the φ_λ have their supports in a fixed compact subset K of $\mathbb{R}^n$;
- (ii) all the derivatives $D^p \varphi_\lambda$ have a partial derivative with respect to λ which is continuous with respect to $\mathbf{x}$ and λ .

Under these hypotheses, $I(\lambda)$ is differentiable (in the usual sense) with respect to λ near λ_0 , and its derivative may be obtained by ‘differentiation under the $\langle, \rangle$ sign’:

$$\frac{dI}{d\lambda} = \langle T, \partial_\lambda \varphi_\lambda \rangle.$$

(c) Effect of discontinuities

When a function f or its derivatives are no longer continuous, the derivatives $D^p T_f$ of the associated distribution T_f may no longer coincide with the distributions associated to the functions $D^p f$.

In dimension 1, the simplest example is Heaviside’s unit step function Y [$Y(x) = 0$ for $x < 0$, $Y(x) = 1$ for $x \geq 0$]:

$$\langle (T_Y)', \varphi \rangle = -\langle (T_Y), \varphi' \rangle = -\int_0^{+\infty} \varphi'(x) dx = \varphi(0) = \langle \delta, \varphi \rangle.$$

Hence $(T_Y)' = \delta$, a result long used ‘heuristically’ by electrical engineers [see also Dirac (1958)].

Let f be infinitely differentiable for $x < 0$ and $x > 0$ but have discontinuous derivatives $f^{(m)}$ at $x = 0$ [$f^{(0)}$ being f itself] with jumps $\sigma_m = f^{(m)}(0+) - f^{(m)}(0-)$. Consider the functions:

$$\begin{aligned} g_0 &= f - \sigma_0 Y \\ g_1 &= g'_0 - \sigma_1 Y \\ &\text{-----} \\ g_k &= g'_{k-1} - \sigma_k Y. \end{aligned}$$

The g_k are continuous, their derivatives g'_k are continuous almost everywhere [which implies that $(T_{g_k})' = T_{g'_k}$ and $g'_k = f^{(k+1)}$ almost everywhere]. This yields immediately:

$$\begin{aligned} (T_f)' &= T_{f'} + \sigma_0 \delta \\ (T_f)'' &= T_{f''} + \sigma_0 \delta' + \sigma_1 \delta \\ &\text{-----} \\ (T_f)^{(m)} &= T_{f^{(m)}} + \sigma_0 \delta^{(m-1)} + \dots + \sigma_{m-1} \delta. \\ &\text{-----} \end{aligned}$$

Thus the ‘distributional derivatives’ $(T_f)^{(m)}$ differ from the usual functional derivatives $T_{f^{(m)}}$ by singular terms associated with discontinuities.

In dimension n , let f be infinitely differentiable everywhere except on a smooth hypersurface S , across which its partial derivatives show discontinuities. Let σ_0 and σ_ν denote the discontinuities of f and its normal derivative $\partial_\nu \varphi$ across S (both σ_0 and σ_ν are functions of position on S), and let $\delta_{(S)}$ and $\partial_\nu \delta_{(S)}$ be defined by

$$\begin{aligned} \langle \delta_{(S)}, \varphi \rangle &= \int_S d^{n-1} S \\ \langle \partial_\nu \delta_{(S)}, \varphi \rangle &= -\int_S \partial_\nu \varphi d^{n-1} S. \end{aligned}$$

Integration by parts shows that

$$\partial_i T_f = T_{\partial_i f} + \sigma_0 \cos \theta_i \delta_{(S)},$$

where θ_i is the angle between the x_i axis and the normal to S along which the jump σ_0 occurs, and that the Laplacian of T_f is given by

$$\Delta(T_f) = T_{\Delta f} + \sigma_\nu \delta_{(S)} + \partial_\nu [\sigma_0 \delta_{(S)}].$$

The latter result is a statement of Green’s theorem in terms of distributions. It will be used in Section 1.3.4.4.3.5 to calculate the Fourier transform of the indicator function of a molecular envelope.

1.3.2.3.9.2. Integration of distributions in dimension 1

The reverse operation from differentiation, namely calculating the ‘indefinite integral’ of a distribution S , consists in finding a distribution T such that $T' = S$.

For all $\chi \in \mathcal{D}$ such that $\chi = \psi'$ with $\psi \in \mathcal{D}$, we must have

$$\langle T, \chi \rangle = -\langle S, \psi \rangle.$$

This condition defines T in a ‘hyperplane’ $\mathcal{H}$ of $\mathcal{D}$, whose equation

$$\langle 1, \chi \rangle \equiv \langle 1, \psi' \rangle = 0$$

reflects the fact that ψ has compact support.

To specify T in the whole of $\mathcal{D}$, it suffices to specify the value of $\langle T, \varphi_0 \rangle$ where $\varphi_0 \in \mathcal{D}$ is such that $\langle 1, \varphi_0 \rangle = 1$: then any $\varphi \in \mathcal{D}$ may be written uniquely as

$$\varphi = \lambda \varphi_0 + \psi'$$

with

$$\lambda = \langle 1, \varphi \rangle, \quad \chi = \varphi - \lambda \varphi_0, \quad \psi(x) = \int_0^x \chi(t) dt,$$

and T is defined by

$$\langle T, \varphi \rangle = \lambda \langle T, \varphi_0 \rangle - \langle S, \psi \rangle.$$

The freedom in the choice of φ_0 means that T is defined up to an additive constant.

1.3.2.3.9.3. Multiplication of distributions by functions

The product αT of a distribution T on $\mathbb{R}^n$ by a function α over $\mathbb{R}^n$ will be defined by transposition:

$$\langle \alpha T, \varphi \rangle = \langle T, \alpha \varphi \rangle \quad \text{for all } \varphi \in \mathcal{D}.$$

In order that αT be a distribution, the mapping $\varphi \mapsto \alpha \varphi$ must send $\mathcal{D}(\mathbb{R}^n)$ continuously into itself; hence *the multipliers α must be infinitely differentiable*. The product of two general distributions cannot be defined. The need for a careful treatment of multipliers of distributions will become clear when it is later shown (Section 1.3.2.5.8) that the Fourier transformation turns convolutions into multiplications and *vice versa*.

If T is a distribution of order m , then α needs only have continuous derivatives up to order m . For instance, δ is a distribution of order zero, and $\alpha \delta = \alpha(\mathbf{0}) \delta$ is a distribution provided α is continuous; this relation is of fundamental importance in the theory of sampling and of the properties of the Fourier transformation related to sampling (Sections 1.3.2.6.4, 1.3.2.6.6). More generally, $D^p \delta$ is a distribution of order $|\mathbf{p}|$, and the following formula holds for all $\alpha \in \mathcal{D}^{(m)}$ with $m = |\mathbf{p}|$:

$$\alpha(D^p \delta) = \sum_{\mathbf{q} \leq \mathbf{p}} (-1)^{|\mathbf{p}-\mathbf{q}|} \binom{\mathbf{p}}{\mathbf{q}} (D^{\mathbf{p}-\mathbf{q}} \alpha)(\mathbf{0}) D^{\mathbf{q}} \delta.$$

The derivative of a product is easily shown to be

$$\partial_i(\alpha T) = (\partial_i \alpha) T + \alpha(\partial_i T)$$

and generally for any multi-index $\mathbf{p}$

$$D^p(\alpha T) = \sum_{\mathbf{q} \leq \mathbf{p}} \binom{\mathbf{p}}{\mathbf{q}} (D^{\mathbf{p}-\mathbf{q}} \alpha)(\mathbf{0}) D^{\mathbf{q}} T.$$

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1.3.2.3.9.4. Division of distributions by functions

Given a distribution S on $\mathbb{R}^n$ and an infinitely differentiable multiplier function α , the division problem consists in finding a distribution T such that $\alpha T = S$.

If α never vanishes, $T = S/\alpha$ is the unique answer. If $n = 1$, and if α has only isolated zeros of finite order, it can be reduced to a collection of cases where the multiplier is x^m , for which the general solution can be shown to be of the form

$$T = U + \sum_{i=0}^{m-1} c_i \delta^{(i)},$$

where U is a particular solution of the division problem $x^m U = S$ and the c_i are arbitrary constants.

In dimension $n > 1$, the problem is much more difficult, but is of fundamental importance in the theory of linear partial differential equations, since the Fourier transformation turns the problem of solving these into a division problem for distributions [see Hörmander (1963)].

1.3.2.3.9.5. Transformation of coordinates

Let σ be a smooth non-singular change of variables in $\mathbb{R}^n$, i.e. an infinitely differentiable mapping from an open subset Ω of $\mathbb{R}^n$ to Ω' in $\mathbb{R}^n$, whose Jacobian

$$J(\sigma) = \det \left[\frac{\partial \sigma(\mathbf{x})}{\partial \mathbf{x}} \right]$$

vanishes nowhere in Ω . By the implicit function theorem, the inverse mapping σ^{-1} from Ω' to Ω is well defined.

If f is a locally summable function on Ω , then the function $\sigma^\# f$ defined by

$$(\sigma^\# f)(\mathbf{x}) = f[\sigma^{-1}(\mathbf{x})]$$

is a locally summable function on Ω' , and for any $\varphi \in \mathcal{D}(\Omega')$ we may write:

$$\begin{aligned} \int_{\Omega'} (\sigma^\# f)(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x} &= \int_{\Omega'} f[\sigma^{-1}(\mathbf{x})] \varphi(\mathbf{x}) d^n \mathbf{x} \\ &= \int_{\Omega'} f(\mathbf{y}) \varphi[\sigma(\mathbf{y})] |J(\sigma)| d^n \mathbf{y} \quad \text{by } \mathbf{x} = \sigma(\mathbf{y}). \end{aligned}$$

In terms of the associated distributions

$$\langle T_{\sigma^\# f}, \varphi \rangle = \langle T_f, |J(\sigma)| (\sigma^{-1})^\# \varphi \rangle.$$

This operation can be extended to an arbitrary distribution T by defining its *image* $\sigma^\# T$ under coordinate transformation σ through

$$\langle \sigma^\# T, \varphi \rangle = \langle T, |J(\sigma)| (\sigma^{-1})^\# \varphi \rangle,$$

which is well defined provided that σ is *proper*, i.e. that $\sigma^{-1}(K)$ is compact whenever K is compact.

For instance, if $\sigma: \mathbf{x} \mapsto \mathbf{x} + \mathbf{a}$ is a *translation* by a vector $\mathbf{a}$ in $\mathbb{R}^n$, then $|J(\sigma)| = 1$; $\sigma^\#$ is denoted by $\tau_{\mathbf{a}}$, and the translate $\tau_{\mathbf{a}} T$ of a distribution T is defined by

$$\langle \tau_{\mathbf{a}} T, \varphi \rangle = \langle T, \tau_{-\mathbf{a}} \varphi \rangle.$$

Let $A: \mathbf{x} \mapsto \mathbf{A}\mathbf{x}$ be a linear transformation defined by a non-singular matrix $\mathbf{A}$. Then $J(A) = \det \mathbf{A}$, and

$$\langle A^\# T, \varphi \rangle = |\det \mathbf{A}| \langle T, (A^{-1})^\# \varphi \rangle.$$

This formula will be shown later (Sections 1.3.2.6.5, 1.3.4.2.1.1) to be the basis for the definition of the reciprocal lattice.

In particular, if $\mathbf{A} = -\mathbf{I}$, where $\mathbf{I}$ is the identity matrix, A is an inversion through a centre of symmetry at the origin, and denoting $A^\# \varphi$ by $\check{\varphi}$ we have:

$$\langle \check{T}, \varphi \rangle = \langle T, \check{\varphi} \rangle.$$

T is called an even distribution if $\check{T} = T$, an odd distribution if $\check{T} = -T$.

If $\mathbf{A} = \lambda \mathbf{I}$ with $\lambda > 0$, A is called a *dilation* and

$$\langle A^\# T, \varphi \rangle = \lambda^n \langle T, (A^{-1})^\# \varphi \rangle.$$

Writing symbolically δ as $\delta(\mathbf{x})$ and $A^\# \delta$ as $\delta(\mathbf{x}/\lambda)$, we have:

$$\delta(\mathbf{x}/\lambda) = \lambda^n \delta(\mathbf{x}).$$

If $n = 1$ and f is a function with isolated simple zeros x_j , then in the same symbolic notation

$$\delta[f(x)] = \sum_j \frac{1}{|f'(x_j)|} \delta(x_j),$$

where each $\lambda_j = 1/|f'(x_j)|$ is analogous to a ‘Lorentz factor’ at zero x_j .

1.3.2.3.9.6. Tensor product of distributions

The purpose of this construction is to extend Fubini’s theorem to distributions. Following Section 1.3.2.2.5, we may define the tensor product $L_{\text{loc}}^1(\mathbb{R}^m) \otimes L_{\text{loc}}^1(\mathbb{R}^n)$ as the vector space of finite linear combinations of functions of the form

$$f \otimes g: (\mathbf{x}, \mathbf{y}) \mapsto f(\mathbf{x})g(\mathbf{y}),$$

where $\mathbf{x} \in \mathbb{R}^m, \mathbf{y} \in \mathbb{R}^n, f \in L_{\text{loc}}^1(\mathbb{R}^m)$ and $g \in L_{\text{loc}}^1(\mathbb{R}^n)$.

Let $S_{\mathbf{x}}$ and $T_{\mathbf{y}}$ denote the distributions associated to f and g , respectively, the subscripts $\mathbf{x}$ and $\mathbf{y}$ acting as mnemonics for $\mathbb{R}^m$ and $\mathbb{R}^n$. It follows from Fubini’s theorem (Section 1.3.2.2.5) that $f \otimes g \in L_{\text{loc}}^1(\mathbb{R}^m \times \mathbb{R}^n)$, and hence defines a distribution over $\mathbb{R}^m \times \mathbb{R}^n$; the rearrangement of integral signs gives

$$\langle S_{\mathbf{x}} \otimes T_{\mathbf{y}}, \varphi_{\mathbf{x}, \mathbf{y}} \rangle = \langle S_{\mathbf{x}}, \langle T_{\mathbf{y}}, \varphi_{\mathbf{x}, \mathbf{y}} \rangle \rangle = \langle T_{\mathbf{y}}, \langle S_{\mathbf{x}}, \varphi_{\mathbf{x}, \mathbf{y}} \rangle \rangle$$

for all $\varphi_{\mathbf{x}, \mathbf{y}} \in \mathcal{D}(\mathbb{R}^m \times \mathbb{R}^n)$. In particular, if $\varphi(\mathbf{x}, \mathbf{y}) = u(\mathbf{x})v(\mathbf{y})$ with $u \in \mathcal{D}(\mathbb{R}^m), v \in \mathcal{D}(\mathbb{R}^n)$, then

$$\langle S \otimes T, u \otimes v \rangle = \langle S, u \rangle \langle T, v \rangle.$$

This construction can be extended to general distributions $S \in \mathcal{D}'(\mathbb{R}^m)$ and $T \in \mathcal{D}'(\mathbb{R}^n)$. Given any test function $\varphi \in \mathcal{D}(\mathbb{R}^m \times \mathbb{R}^n)$, let $\varphi_{\mathbf{x}}$ denote the map $\mathbf{y} \mapsto \varphi(\mathbf{x}, \mathbf{y})$; let $\varphi_{\mathbf{y}}$ denote the map $\mathbf{x} \mapsto \varphi(\mathbf{x}, \mathbf{y})$; and define the two functions $\theta(\mathbf{x}) = \langle T, \varphi_{\mathbf{x}} \rangle$ and $\omega(\mathbf{y}) = \langle S, \varphi_{\mathbf{y}} \rangle$. Then, by the lemma on differentiation under the $\langle, \rangle$ sign of Section 1.3.2.3.9.1, $\theta \in \mathcal{D}(\mathbb{R}^m), \omega \in \mathcal{D}(\mathbb{R}^n)$, and there exists a unique distribution $S \otimes T$ such that

$$\langle S \otimes T, \varphi \rangle = \langle S, \theta \rangle = \langle T, \omega \rangle.$$

$S \otimes T$ is called the *tensor product* of S and T .

With the mnemonic introduced above, this definition reads identically to that given above for distributions associated to locally integrable functions:

$$\langle S_{\mathbf{x}} \otimes T_{\mathbf{y}}, \varphi_{\mathbf{x}, \mathbf{y}} \rangle = \langle S_{\mathbf{x}}, \langle T_{\mathbf{y}}, \varphi_{\mathbf{x}, \mathbf{y}} \rangle \rangle = \langle T_{\mathbf{y}}, \langle S_{\mathbf{x}}, \varphi_{\mathbf{x}, \mathbf{y}} \rangle \rangle.$$

The tensor product of distributions is associative:

$$(R \otimes S) \otimes T = R \otimes (S \otimes T).$$

Derivatives may be calculated by

$$D_{\mathbf{x}}^p D_{\mathbf{y}}^q (S_{\mathbf{x}} \otimes T_{\mathbf{y}}) = (D_{\mathbf{x}}^p S_{\mathbf{x}}) \otimes (D_{\mathbf{y}}^q T_{\mathbf{y}}).$$

The support of a tensor product is the Cartesian product of the supports of the two factors.

1.3.2.3.9.7. Convolution of distributions

The convolution $f * g$ of two functions f and g on $\mathbb{R}^n$ is defined by

$$(f * g)(\mathbf{x}) = \int_{\mathbb{R}^n} f(\mathbf{y}) g(\mathbf{x} - \mathbf{y}) d^n \mathbf{y} = \int_{\mathbb{R}^n} f(\mathbf{x} - \mathbf{y}) g(\mathbf{y}) d^n \mathbf{y}$$

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whenever the integral exists. This is the case when f and g are both in $L^1(\mathbb{R}^n)$; then $f * g$ is also in $L^1(\mathbb{R}^n)$. Let S, T and W denote the distributions associated to f, g and $f * g$, respectively: a change of variable immediately shows that for any $\varphi \in \mathcal{D}(\mathbb{R}^n)$,

$$\langle W, \varphi \rangle = \int_{\mathbb{R}^n \times \mathbb{R}^n} f(\mathbf{x})g(\mathbf{y})\varphi(\mathbf{x} + \mathbf{y}) \, d^n \mathbf{x} \, d^n \mathbf{y}.$$

Introducing the map σ from $\mathbb{R}^n \times \mathbb{R}^n$ to $\mathbb{R}^n$ defined by $\sigma(\mathbf{x}, \mathbf{y}) = \mathbf{x} + \mathbf{y}$, the latter expression may be written:

$$\langle S_{\mathbf{x}} \otimes T_{\mathbf{y}}, \varphi \circ \sigma \rangle$$

(where $\circ$ denotes the composition of mappings) or by a slight abuse of notation:

$$\langle W, \varphi \rangle = \langle S_{\mathbf{x}} \otimes T_{\mathbf{y}}, \varphi(\mathbf{x} + \mathbf{y}) \rangle.$$

A difficulty arises in extending this definition to general distributions S and T because the mapping σ is not proper: if K is compact in $\mathbb{R}^n$, then $\sigma^{-1}(K)$ is a cylinder with base K and generator the ‘second bisector’ $\mathbf{x} + \mathbf{y} = \mathbf{0}$ in $\mathbb{R}^n \times \mathbb{R}^n$. However, $\langle S \otimes T, \varphi \circ \sigma \rangle$ is defined whenever the intersection between $\text{Supp } (S \otimes T) = (\text{Supp } S) \times (\text{Supp } T)$ and $\sigma^{-1}(\text{Supp } \varphi)$ is compact.

We may therefore define the *convolution* $S * T$ of two distributions S and T on $\mathbb{R}^n$ by

$$\langle S * T, \varphi \rangle = \langle S \otimes T, \varphi \circ \sigma \rangle = \langle S_{\mathbf{x}} \otimes T_{\mathbf{y}}, \varphi(\mathbf{x} + \mathbf{y}) \rangle$$

whenever the following *support condition* is fulfilled:

‘the set $\{(\mathbf{x}, \mathbf{y}) | \mathbf{x} \in A, \mathbf{y} \in B, \mathbf{x} + \mathbf{y} \in K\}$ is compact in $\mathbb{R}^n \times \mathbb{R}^n$ for all K compact in $\mathbb{R}^n$ ’.

The latter condition is met, in particular, if S or T has compact support. The support of $S * T$ is easily seen to be contained in the closure of the vector sum

$$A + B = \{\mathbf{x} + \mathbf{y} | \mathbf{x} \in A, \mathbf{y} \in B\}.$$

Convolution by a fixed distribution S is a *continuous* operation for the topology on $\mathcal{D}'$: it maps convergent sequences (T_j) to convergent sequences $(S * T_j)$. Convolution is commutative: $S * T = T * S$.

The convolution of p distributions $T_1, \dots, T_p$ with supports $A_1, \dots, A_p$ can be defined by

$$\langle T_1 * \dots * T_p, \varphi \rangle = \langle (T_1)_{\mathbf{x}_1} \otimes \dots \otimes (T_p)_{\mathbf{x}_p}, \varphi(\mathbf{x}_1 + \dots + \mathbf{x}_p) \rangle$$

whenever the following generalized support condition:

‘the set $\{(\mathbf{x}_1, \dots, \mathbf{x}_p) | \mathbf{x}_1 \in A_1, \dots, \mathbf{x}_p \in A_p, \mathbf{x}_1 + \dots + \mathbf{x}_p \in K\}$ is compact in $(\mathbb{R}^n)^p$ for all K compact in $\mathbb{R}^n$ ’

is satisfied. It is then associative. Interesting examples of associativity failure, which can be traced back to violations of the support condition, may be found in Bracewell (1986, pp. 436–437).

It follows from previous definitions that, for all distributions $T \in \mathcal{D}'$, the following identities hold:

- (i) $\delta * T = T$: δ is the unit convolution;
- (ii) $\delta_{\mathbf{a}} * T = \tau_{\mathbf{a}} T$: translation is a convolution with the corresponding translate of δ ;
- (iii) $(D^p \delta) * T = D^p T$: differentiation is a convolution with the corresponding derivative of δ ;
- (iv) translates or derivatives of a convolution may be obtained by translating or differentiating any one of the factors: convolution ‘commutes’ with translation and differentiation, a property used in Section 1.3.4.4.7.7 to speed up least-squares model refinement for macromolecules.

The latter property is frequently used for the purpose of *regularization*: if T is a distribution, α an infinitely differentiable function, and at least one of the two has compact support, then $T * \alpha$ is an infinitely differentiable ordinary function. Since sequences

(α_ν) of such functions α can be constructed which have compact support and converge to δ , it follows that any distribution T can be obtained as the limit of infinitely differentiable functions $T * \alpha_\nu$. In topological jargon: $\mathcal{D}(\mathbb{R}^n)$ is ‘everywhere dense’ in $\mathcal{D}'(\mathbb{R}^n)$. A standard function in $\mathcal{D}$ which is often used for such proofs is defined as follows: put

$$\begin{aligned} \theta(x) &= \frac{1}{A} \exp\left(-\frac{1}{1-x^2}\right) & \text{for } |x| \leq 1, \\ &= 0 & \text{for } |x| \geq 1, \end{aligned}$$

with

$$A = \int_{-1}^{+1} \exp\left(-\frac{1}{1-x^2}\right) dx$$

(so that θ is in $\mathcal{D}$ and is normalized), and put

$$\begin{aligned} \theta_\varepsilon(x) &= \frac{1}{\varepsilon} \theta\left(\frac{x}{\varepsilon}\right) & \text{in dimension 1,} \\ \theta_\varepsilon(\mathbf{x}) &= \prod_{j=1}^n \theta_\varepsilon(x_j) & \text{in dimension } n. \end{aligned}$$

Another related result, also proved by convolution, is the *structure theorem*: the restriction of a distribution $T \in \mathcal{D}'(\mathbb{R}^n)$ to a bounded open set Ω in $\mathbb{R}^n$ is a derivative of finite order of a continuous function.

Properties (i) to (iv) are the basis of the symbolic or operational calculus (see Carslaw & Jaeger, 1948; Van der Pol & Bremmer, 1955; Churchill, 1958; Erdélyi, 1962; Moore, 1971) for solving integro-differential equations with constant coefficients by turning them into convolution equations, then using factorization methods for convolution algebras (Schwartz, 1965).

1.3.2.4. Fourier transforms of functions

1.3.2.4.1. Introduction

Given a complex-valued function f on $\mathbb{R}^n$ subject to suitable regularity conditions, its Fourier transform $\mathcal{F}[f]$ and Fourier cotransform $\bar{\mathcal{F}}[f]$ are defined as follows:

$$\begin{aligned} \mathcal{F}[f](\xi) &= \int_{\mathbb{R}^n} f(\mathbf{x}) \exp(-2\pi i \xi \cdot \mathbf{x}) \, d^n \mathbf{x} \\ \bar{\mathcal{F}}[f](\xi) &= \int_{\mathbb{R}^n} f(\mathbf{x}) \exp(+2\pi i \xi \cdot \mathbf{x}) \, d^n \mathbf{x}, \end{aligned}$$

where $\xi \cdot \mathbf{x} = \sum_{i=1}^n \xi_i x_i$ is the ordinary scalar product. The terminology and sign conventions given above are the standard ones in mathematics; those used in crystallography are slightly different (see Section 1.3.4.2.1.1). These transforms enjoy a number of remarkable properties, whose natural settings entail different regularity assumptions on f : for instance, properties relating to convolution are best treated in $L^1(\mathbb{R}^n)$, while Parseval’s theorem requires the Hilbert space structure of $L^2(\mathbb{R}^n)$. After a brief review of these classical properties, the Fourier transformation will be examined in a space $\mathcal{S}'(\mathbb{R}^n)$ particularly well suited to accommodating the full range of its properties, which will later serve as a space of test functions to extend the Fourier transformation to distributions.

There exists an abundant literature on the ‘Fourier integral’. The books by Carslaw (1930), Wiener (1933), Titchmarsh (1948), Katznelson (1968), Sneddon (1951, 1972), and Dym & McKean (1972) are particularly recommended.

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1.3.2.4.2. Fourier transforms in L^1

1.3.2.4.2.1. Linearity

Both transformations $\mathcal{F}$ and $\tilde{\mathcal{F}}$ are obviously linear maps from L^1 to L^∞ when these spaces are viewed as vector spaces over the field $\mathbb{C}$ of complex numbers.

1.3.2.4.2.2. Effect of affine coordinate transformations

$\mathcal{F}$ and $\tilde{\mathcal{F}}$ turn translations into phase shifts:

$$\begin{aligned}\mathcal{F}[\tau_{\mathbf{a}}f](\xi) &= \exp(-2\pi i \xi \cdot \mathbf{a}) \mathcal{F}[f](\xi) \\ \tilde{\mathcal{F}}[\tau_{\mathbf{a}}f](\xi) &= \exp(+2\pi i \xi \cdot \mathbf{a}) \tilde{\mathcal{F}}[f](\xi).\end{aligned}$$

Under a general linear change of variable $\mathbf{x} \mapsto \mathbf{A}\mathbf{x}$ with non-singular matrix $\mathbf{A}$, the transform of $A^\#f$ is

$$\begin{aligned}\mathcal{F}[A^\#f](\xi) &= \int_{\mathbb{R}^n} f(\mathbf{A}^{-1}\mathbf{x}) \exp(-2\pi i \xi \cdot \mathbf{x}) d^n \mathbf{x} \\ &= \int_{\mathbb{R}^n} f(\mathbf{y}) \exp(-2\pi i (\mathbf{A}^T \xi) \cdot \mathbf{y}) |\det \mathbf{A}| d^n \mathbf{y} \\ &\quad \text{by } \mathbf{x} = \mathbf{A}\mathbf{y} \\ &= |\det \mathbf{A}| \mathcal{F}[f](\mathbf{A}^T \xi)\end{aligned}$$

i.e.

$$\mathcal{F}[A^\#f] = |\det \mathbf{A}| [(\mathbf{A}^{-1})^T]^\# \mathcal{F}[f]$$

and similarly for $\tilde{\mathcal{F}}$. The matrix $(\mathbf{A}^{-1})^T$ is called the *contragredient* of matrix $\mathbf{A}$.

Under an affine change of coordinates $\mathbf{x} \mapsto S(\mathbf{x}) = \mathbf{A}\mathbf{x} + \mathbf{b}$ with non-singular matrix $\mathbf{A}$, the transform of $S^\#f$ is given by

$$\begin{aligned}\mathcal{F}[S^\#f](\xi) &= \mathcal{F}[\tau_{\mathbf{b}}(A^\#f)](\xi) \\ &= \exp(-2\pi i \xi \cdot \mathbf{b}) \mathcal{F}[A^\#f](\xi) \\ &= \exp(-2\pi i \xi \cdot \mathbf{b}) |\det \mathbf{A}| \mathcal{F}[f](\mathbf{A}^T \xi)\end{aligned}$$

with a similar result for $\tilde{\mathcal{F}}$, replacing $-i$ by $+i$.

1.3.2.4.2.3. Conjugate symmetry

The kernels of the Fourier transformations $\mathcal{F}$ and $\tilde{\mathcal{F}}$ satisfy the following identities:

$$\exp(\pm 2\pi i \xi \cdot \mathbf{x}) = \exp[\pm 2\pi i \xi \cdot (-\mathbf{x})] = \exp[\pm 2\pi i (-\xi) \cdot \mathbf{x}].$$

As a result the transformations $\mathcal{F}$ and $\tilde{\mathcal{F}}$ themselves have the following ‘conjugate symmetry’ properties [where the notation $\check{f}(\mathbf{x}) = f(-\mathbf{x})$ of Section 1.3.2.2.2 will be used]:

$$\begin{aligned}\mathcal{F}[f](\xi) &= \overline{\mathcal{F}[\check{f}](-\xi)} = \overline{\mathcal{F}[\check{f}]}(\xi) \\ \tilde{\mathcal{F}}[f](\xi) &= \tilde{\mathcal{F}}[\check{f}](\xi).\end{aligned}$$

Therefore,

(i) f real $\Leftrightarrow f = \check{f} \Leftrightarrow \mathcal{F}[f] = \overline{\mathcal{F}[\check{f}]} \Leftrightarrow \mathcal{F}[f](\xi) = \overline{\mathcal{F}[f]}(-\xi)$: $\mathcal{F}[f]$ is said to possess *Hermitian symmetry*;

(ii) f centrosymmetric $\Leftrightarrow f = \check{f} \Leftrightarrow \mathcal{F}[f] = \overline{\mathcal{F}[\check{f}]}$;

(iii) f real centrosymmetric $\Leftrightarrow f = \check{f} = \overline{\check{f}} \Leftrightarrow \mathcal{F}[f] = \overline{\mathcal{F}[f]} = \overline{\mathcal{F}[\check{f}]} \Leftrightarrow \mathcal{F}[f]$ real centrosymmetric.

Conjugate symmetry is the basis of Friedel’s law (Section 1.3.4.2.1.4) in crystallography.

1.3.2.4.2.4. Tensor product property

Another elementary property of $\mathcal{F}$ is its naturality with respect to tensor products. Let $u \in L^1(\mathbb{R}^m)$ and $v \in L^1(\mathbb{R}^n)$, and let $\mathcal{F}_{\mathbf{x}}, \mathcal{F}_{\mathbf{y}}, \mathcal{F}_{\mathbf{x}, \mathbf{y}}$ denote the Fourier transformations in $L^1(\mathbb{R}^m), L^1(\mathbb{R}^n)$ and $L^1(\mathbb{R}^m \times \mathbb{R}^n)$, respectively. Then

$$\mathcal{F}_{\mathbf{x}, \mathbf{y}}[u \otimes v] = \mathcal{F}_{\mathbf{x}}[u] \otimes \mathcal{F}_{\mathbf{y}}[v].$$

Furthermore, if $f \in L^1(\mathbb{R}^m \times \mathbb{R}^n)$, then $\mathcal{F}_{\mathbf{y}}[f] \in L^1(\mathbb{R}^n)$ as a function of $\mathbf{x}$ and $\mathcal{F}_{\mathbf{x}}[f] \in L^1(\mathbb{R}^m)$ as a function of $\mathbf{y}$, and

$$\mathcal{F}_{\mathbf{x}, \mathbf{y}}[f] = \mathcal{F}_{\mathbf{x}}[\mathcal{F}_{\mathbf{y}}[f]] = \mathcal{F}_{\mathbf{y}}[\mathcal{F}_{\mathbf{x}}[f]].$$

This is easily proved by using Fubini’s theorem and the fact that $(\xi, \eta) \cdot (\mathbf{x}, \mathbf{y}) = \xi \cdot \mathbf{x} + \eta \cdot \mathbf{y}$, where $\mathbf{x}, \xi \in \mathbb{R}^m, \mathbf{y}, \eta \in \mathbb{R}^n$. This property may be written:

$$\mathcal{F}_{\mathbf{x}, \mathbf{y}} = \mathcal{F}_{\mathbf{x}} \otimes \mathcal{F}_{\mathbf{y}}.$$

1.3.2.4.2.5. Convolution property

If f and g are summable, their convolution $f * g$ exists and is summable, and

$$\mathcal{F}[f * g](\xi) = \int_{\mathbb{R}^n} \left[\int_{\mathbb{R}^n} f(\mathbf{y}) g(\mathbf{x} - \mathbf{y}) d^n \mathbf{y} \right] \exp(-2\pi i \xi \cdot \mathbf{x}) d^n \mathbf{x}.$$

With $\mathbf{x} = \mathbf{y} + \mathbf{z}$, so that

$$\exp(-2\pi i \xi \cdot \mathbf{x}) = \exp(-2\pi i \xi \cdot \mathbf{y}) \exp(-2\pi i \xi \cdot \mathbf{z}),$$

and with Fubini’s theorem, rearrangement of the double integral gives:

$$\mathcal{F}[f * g] = \mathcal{F}[f] \times \mathcal{F}[g]$$

and similarly

$$\tilde{\mathcal{F}}[f * g] = \tilde{\mathcal{F}}[f] \times \tilde{\mathcal{F}}[g].$$

Thus the Fourier transform and cotransform turn convolution into multiplication.

1.3.2.4.2.6. Reciprocity property

In general, $\mathcal{F}[f]$ and $\tilde{\mathcal{F}}[f]$ are not summable, and hence cannot be further transformed; however, as they are essentially bounded, their products with the Gaussians $G_t(\xi) = \exp(-2\pi^2 \|\xi\|^2 t)$ are summable for all $t > 0$, and it can be shown that

$$f = \lim_{t \rightarrow 0} \mathcal{F}[G_t \mathcal{F}[f]] = \lim_{t \rightarrow 0} \mathcal{F}[G_t \tilde{\mathcal{F}}[f]],$$

where the limit is taken in the topology of the L^1 norm $\|\cdot\|_1$. Thus $\mathcal{F}$ and $\tilde{\mathcal{F}}$ are (in a sense) mutually inverse, which justifies the common practice of calling $\tilde{\mathcal{F}}$ the ‘inverse Fourier transformation’.

1.3.2.4.2.7. Riemann–Lebesgue lemma

If $f \in L^1(\mathbb{R}^n)$, i.e. is summable, then $\mathcal{F}[f]$ and $\tilde{\mathcal{F}}[f]$ exist and are continuous and essentially bounded:

$$\|\mathcal{F}[f]\|_\infty = \|\tilde{\mathcal{F}}[f]\|_\infty \leq \|f\|_1.$$

In fact one has the much stronger property, whose statement constitutes the *Riemann–Lebesgue lemma*, that $\mathcal{F}[f](\xi)$ and $\tilde{\mathcal{F}}[f](\xi)$ both tend to zero as $\|\xi\| \rightarrow \infty$.

1.3.2.4.2.8. Differentiation

Let us now suppose that $n = 1$ and that $f \in L^1(\mathbb{R})$ is differentiable with $f' \in L^1(\mathbb{R})$. Integration by parts yields

$$\begin{aligned}\mathcal{F}[f'](\xi) &= \int_{-\infty}^{+\infty} f'(x) \exp(-2\pi i \xi \cdot x) dx \\ &= [f(x) \exp(-2\pi i \xi \cdot x)]_{-\infty}^{+\infty} \\ &\quad + 2\pi i \xi \int_{-\infty}^{+\infty} f(x) \exp(-2\pi i \xi \cdot x) dx.\end{aligned}$$

Since f' is summable, f has a limit when $x \rightarrow \pm\infty$, and this limit must be 0 since f is summable. Therefore

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$$\mathcal{F}[f'](\xi) = (2\pi i \xi) \mathcal{F}[f](\xi)$$

with the bound

$$\|2\pi i \xi \mathcal{F}[f]\|_\infty \leq \|f'\|_1$$

so that $|\mathcal{F}[f](\xi)|$ decreases faster than $1/|\xi| \rightarrow \infty$.

This result can be easily extended to several dimensions and to any multi-index $\mathbf{m}$: if f is summable and has continuous summable partial derivatives up to order $|\mathbf{m}|$, then

$$\mathcal{F}[D^{\mathbf{m}}f](\xi) = (2\pi i \xi)^{\mathbf{m}} \mathcal{F}[f](\xi)$$

and

$$\|(2\pi i \xi)^{\mathbf{m}} \mathcal{F}[f]\|_\infty \leq \|D^{\mathbf{m}}f\|_1.$$

Similar results hold for $\tilde{\mathcal{F}}$, with $2\pi i \xi$ replaced by $-2\pi i \xi$. Thus, the more differentiable f is, with summable derivatives, the faster $\mathcal{F}[f]$ and $\tilde{\mathcal{F}}[f]$ decrease at infinity.

The property of turning differentiation into multiplication by a monomial has many important applications in crystallography, for instance differential syntheses (Sections 1.3.4.2.1.9, 1.3.4.4.7.2, 1.3.4.4.7.5) and moment-generating functions [Section 1.3.4.5.2.1(c)].

1.3.2.4.2.9. Decrease at infinity

Conversely, assume that f is summable on $\mathbb{R}^n$ and that f decreases fast enough at infinity for $\mathbf{x}^{\mathbf{m}}f$ also to be summable, for some multi-index $\mathbf{m}$. Then the integral defining $\mathcal{F}[f]$ may be subjected to the differential operator $D^{\mathbf{m}}$, still yielding a convergent integral: therefore $D^{\mathbf{m}}\mathcal{F}[f]$ exists, and

$$D^{\mathbf{m}}(\mathcal{F}[f])(\xi) = \mathcal{F}[(-2\pi i \mathbf{x})^{\mathbf{m}}f](\xi)$$

with the bound

$$\|D^{\mathbf{m}}(\mathcal{F}[f])\|_\infty = \|(2\pi \mathbf{x})^{\mathbf{m}}f\|_1.$$

Similar results hold for $\tilde{\mathcal{F}}$, with $-2\pi i \mathbf{x}$ replaced by $2\pi i \mathbf{x}$. Thus, the faster f decreases at infinity, the more $\mathcal{F}[f]$ and $\tilde{\mathcal{F}}[f]$ are differentiable, with bounded derivatives. This property is the converse of that described in Section 1.3.2.4.2.8, and their combination is fundamental in the definition of the function space $\mathcal{S}$ in Section 1.3.2.4.4.1, of tempered distributions in Section 1.3.2.5, and in the extension of the Fourier transformation to them.

1.3.2.4.2.10. The Paley–Wiener theorem

An extreme case of the last instance occurs when f has *compact support*: then $\mathcal{F}[f]$ and $\tilde{\mathcal{F}}[f]$ are so regular that they may be analytically continued from $\mathbb{R}^n$ to $\mathbb{C}^n$ where they are *entire functions*, i.e. have no singularities at finite distance (Paley & Wiener, 1934). This is easily seen for $\mathcal{F}[f]$: giving vector $\xi \in \mathbb{R}^n$ a vector $\eta \in \mathbb{R}^n$ of imaginary parts leads to

$$\begin{aligned} \mathcal{F}[f](\xi + i\eta) &= \int_{\mathbb{R}^n} f(\mathbf{x}) \exp[-2\pi i(\xi + i\eta) \cdot \mathbf{x}] d^n \mathbf{x} \\ &= \mathcal{F}[\exp(2\pi \eta \cdot \mathbf{x})f](\xi), \end{aligned}$$

where the latter transform always exists since $\exp(2\pi \eta \cdot \mathbf{x})f$ is summable with respect to $\mathbf{x}$ for all values of η . This analytic continuation forms the basis of the saddlepoint method in probability theory [Section 1.3.4.5.2.1(f)] and leads to the use of maximum-entropy distributions in the statistical theory of direct phase determination [Section 1.3.4.5.2.2(e)].

By Liouville's theorem, an entire function in $\mathbb{C}^n$ cannot vanish identically on the complement of a compact subset of $\mathbb{R}^n$ without vanishing everywhere: therefore $\mathcal{F}[f]$ cannot have compact support if f has, and hence $\mathcal{Q}(\mathbb{R}^n)$ is *not stable by Fourier transformation*.

1.3.2.4.3. Fourier transforms in L^2

Let f belong to $L^2(\mathbb{R}^n)$, i.e. be such that

$$\|f\|_2 = \left(\int_{\mathbb{R}^n} |f(\mathbf{x})|^2 d^n \mathbf{x} \right)^{1/2} < \infty.$$

1.3.2.4.3.1. Invariance of L^2

$\mathcal{F}[f]$ and $\tilde{\mathcal{F}}[f]$ exist and are functions in L^2 , i.e. $\mathcal{F}L^2 = L^2$, $\tilde{\mathcal{F}}L^2 = L^2$.

1.3.2.4.3.2. Reciprocity

$\mathcal{F}[\mathcal{F}[f]] = f$ and $\tilde{\mathcal{F}}[\tilde{\mathcal{F}}[f]] = f$, equality being taken as ‘almost everywhere’ equality. This again leads to calling $\tilde{\mathcal{F}}$ the ‘inverse Fourier transformation’ rather than the Fourier cotransformation.

1.3.2.4.3.3. Isometry

$\mathcal{F}$ and $\tilde{\mathcal{F}}$ preserve the L^2 norm:

$$\|\mathcal{F}[f]\|_2 = \|\tilde{\mathcal{F}}[f]\|_2 = \|f\|_2 \text{ (Parseval's/Plancherel's theorem).}$$

This property, which may be written in terms of the inner product $(\cdot)$ in $L^2(\mathbb{R}^n)$ as

$$(\mathcal{F}[f], \mathcal{F}[g]) = (\tilde{\mathcal{F}}[f], \tilde{\mathcal{F}}[g]) = (f, g),$$

implies that $\mathcal{F}$ and $\tilde{\mathcal{F}}$ are *unitary* transformations of $L^2(\mathbb{R}^n)$ into itself, i.e. infinite-dimensional ‘rotations’.

1.3.2.4.3.4. Eigenspace decomposition of L^2

Some light can be shed on the geometric structure of these rotations by the following simple considerations. Note that

$$\begin{aligned} \mathcal{F}^2[f](\mathbf{x}) &= \int_{\mathbb{R}^n} \mathcal{F}[f](\xi) \exp(-2\pi i \mathbf{x} \cdot \xi) d^n \xi \\ &= \tilde{\mathcal{F}}[\mathcal{F}[f]](-\mathbf{x}) = f(-\mathbf{x}) \end{aligned}$$

so that $\mathcal{F}^4$ (and similarly $\tilde{\mathcal{F}}^4$) is the identity map. Any eigenvalue of $\mathcal{F}$ or $\tilde{\mathcal{F}}$ is therefore a fourth root of unity, i.e. ± 1 or $\pm i$, and $L^2(\mathbb{R}^n)$ splits into an orthogonal direct sum

$$\mathbf{H}_0 \otimes \mathbf{H}_1 \otimes \mathbf{H}_2 \otimes \mathbf{H}_3,$$

where $\mathcal{F}$ (respectively $\tilde{\mathcal{F}}$) acts in each subspace $\mathbf{H}_k$ ($k = 0, 1, 2, 3$) by multiplication by $(-i)^k$. Orthonormal bases for these subspaces can be constructed from Hermite functions (cf. Section 1.3.2.4.4.2). This method was used by Wiener (1933, pp. 51–71).

1.3.2.4.3.5. The convolution theorem and the isometry property

In L^2 , the convolution theorem (when applicable) and the Parseval/Plancherel theorem are not independent. Suppose that $f, g, f \times g$ and $f * g$ are all in L^2 (without questioning whether these properties are independent). Then $f * g$ may be written in terms of the inner product in L^2 as follows:

$$(f * g)(\mathbf{x}) = \int_{\mathbb{R}^n} f(\mathbf{x} - \mathbf{y})g(\mathbf{y}) d^n \mathbf{y} = \int_{\mathbb{R}^n} \overline{\tilde{f}(\mathbf{y} - \mathbf{x})}g(\mathbf{y}) d^n \mathbf{y},$$

i.e.

$$(f * g)(\mathbf{x}) = (\tau_{\mathbf{x}} \tilde{f}, g).$$

Invoking the isometry property, we may rewrite the right-hand side as

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$$\begin{aligned}
 (\mathcal{F}[\tau_{\mathbf{x}} \check{f}], \mathcal{F}[g]) &= (\exp(-2\pi i \mathbf{x} \cdot \boldsymbol{\xi}) \overline{\mathcal{F}[f]}_{\boldsymbol{\xi}}, \mathcal{F}[g]_{\boldsymbol{\xi}}) \\
 &= \int_{\mathbb{R}^n} (\mathcal{F}[f] \times \mathcal{F}[g])(\mathbf{x}) \\
 &\quad \times \exp(+2\pi i \mathbf{x} \cdot \boldsymbol{\xi}) d^n \boldsymbol{\xi} \\
 &= \mathcal{F}[\mathcal{F}[f] \times \mathcal{F}[g]],
 \end{aligned}$$

so that the initial identity yields the convolution theorem.

To obtain the converse implication, note that

$$\begin{aligned}
 (f, g) &= \int_{\mathbb{R}^n} \overline{f(\mathbf{y})} g(\mathbf{y}) d^n \mathbf{y} = (\check{f} * g)(\mathbf{0}) \\
 &= \mathcal{F}[\mathcal{F}[\check{f}] \times \mathcal{F}[g]](\mathbf{0}) \\
 &= \int_{\mathbb{R}^n} \overline{\mathcal{F}[f](\boldsymbol{\xi})} \mathcal{F}[g](\boldsymbol{\xi}) d^n \boldsymbol{\xi} = (\mathcal{F}[f], \mathcal{F}[g]),
 \end{aligned}$$

where conjugate symmetry (Section 1.3.2.4.2.2) has been used.

These relations have an important application in the calculation by Fourier transform methods of the derivatives used in the refinement of macromolecular structures (Section 1.3.4.4.7).

1.3.2.4.4. Fourier transforms in $\mathcal{S}$

1.3.2.4.4.1. Definition and properties of $\mathcal{S}$

The duality established in Sections 1.3.2.4.2.8 and 1.3.2.4.2.9 between the local differentiability of a function and the rate of decrease at infinity of its Fourier transform prompts one to consider the space $\mathcal{S}(\mathbb{R}^n)$ of functions f on $\mathbb{R}^n$ which are infinitely differentiable and all of whose derivatives are rapidly decreasing, so that for all multi-indices $\mathbf{k}$ and $\mathbf{p}$

$$(\mathbf{x}^{\mathbf{k}} D^{\mathbf{p}} f)(\mathbf{x}) \rightarrow 0 \quad \text{as } \|\mathbf{x}\| \rightarrow \infty.$$

The product of $f \in \mathcal{S}$ by any polynomial over $\mathbb{R}^n$ is still in $\mathcal{S}$ ($\mathcal{S}$ is an algebra over the ring of polynomials). Furthermore, $\mathcal{S}$ is invariant under translations and differentiation.

If $f \in \mathcal{S}$, then its transforms $\mathcal{F}[f]$ and $\mathcal{F}[f]$ are

- (i) infinitely differentiable because f is rapidly decreasing;
- (ii) rapidly decreasing because f is infinitely differentiable;

hence $\mathcal{F}[f]$ and $\mathcal{F}[f]$ are in $\mathcal{S}$: $\mathcal{S}$ is invariant under $\mathcal{F}$ and $\mathcal{F}$.

Since $L^1 \supset \mathcal{S}$ and $L^2 \supset \mathcal{S}$, all properties of $\mathcal{F}$ and $\mathcal{F}$ already encountered above are enjoyed by functions of $\mathcal{S}$, with all restrictions on differentiability and/or integrability lifted. For instance, given two functions f and g in $\mathcal{S}$, then both fg and $f * g$ are in $\mathcal{S}$ (which was not the case with L^1 nor with L^2) so that the reciprocity theorem inherited from L^2

$$\mathcal{F}[\mathcal{F}[f]] = f \quad \text{and} \quad \mathcal{F}[\mathcal{F}[f]] = f$$

allows one to state the reverse of the convolution theorem first established in L^1 :

$$\begin{aligned}
 \mathcal{F}[fg] &= \mathcal{F}[f] * \mathcal{F}[g] \\
 \mathcal{F}[fg] &= \mathcal{F}[f] * \mathcal{F}[g].
 \end{aligned}$$

1.3.2.4.4.2. Gaussian functions and Hermite functions

Gaussian functions are particularly important elements of $\mathcal{S}$. In dimension 1, a well known contour integration (Schwartz, 1965, p. 184) yields

$$\mathcal{F}[\exp(-\pi x^2)](\xi) = \mathcal{F}[\exp(-\pi x^2)](\xi) = \exp(-\pi \xi^2),$$

which shows that the ‘standard Gaussian’ $\exp(-\pi x^2)$ is invariant under $\mathcal{F}$ and $\mathcal{F}$. By a tensor product construction, it follows that the same is true of the standard Gaussian

$$G(\mathbf{x}) = \exp(-\pi \|\mathbf{x}\|^2)$$

in dimension n :

$$\mathcal{F}[G](\boldsymbol{\xi}) = \mathcal{F}[G](\boldsymbol{\xi}) = G(\boldsymbol{\xi}).$$

In other words, G is an eigenfunction of $\mathcal{F}$ and $\mathcal{F}$ for eigenvalue 1 (Section 1.3.2.4.3.4).

A complete system of eigenfunctions may be constructed as follows. In dimension 1, consider the family of functions

$$H_m = \frac{D^m G^2}{G} \quad (m \geq 0),$$

where D denotes the differentiation operator. The first two members of the family

$$H_0 = G, \quad H_1 = 2DG,$$

are such that $\mathcal{F}[H_0] = H_0$, as shown above, and

$$DG(x) = -2\pi x G(x) = i(2\pi i x) G(x) = i \mathcal{F}[DG](x),$$

hence

$$\mathcal{F}[H_1] = (-i)H_1.$$

We may thus take as an induction hypothesis that

$$\mathcal{F}[H_m] = (-i)^m H_m.$$

The identity

$$D\left(\frac{D^m G^2}{G}\right) = \frac{D^{m+1} G^2}{G} - \frac{DG D^m G^2}{G}$$

may be written

$$H_{m+1}(x) = (DH_m)(x) - 2\pi x H_m(x),$$

and the two differentiation theorems give:

$$\mathcal{F}[DH_m](\xi) = (2\pi i \xi) \mathcal{F}[H_m](\xi)$$

$$\mathcal{F}[-2\pi x H_m](\xi) = -iD(\mathcal{F}[H_m])(\xi).$$

Combination of this with the induction hypothesis yields

$$\begin{aligned}
 \mathcal{F}[H_{m+1}](\xi) &= (-i)^{m+1} [(DH_m)(\xi) - 2\pi \xi H_m(\xi)] \\
 &= (-i)^{m+1} H_{m+1}(\xi),
 \end{aligned}$$

thus proving that H_m is an eigenfunction of $\mathcal{F}$ for eigenvalue $(-i)^m$ for all $m \geq 0$. The same proof holds for $\mathcal{F}$, with eigenvalue i^m . If these eigenfunctions are normalized as

$$\mathcal{H}_m(x) = \frac{(-1)^m 2^{1/4}}{\sqrt{m! 2^m \pi^{1/2}}} H_m(x),$$

then it can be shown that the collection of *Hermite functions* $\{\mathcal{H}_m(x)\}_{m \geq 0}$ constitutes an orthonormal basis of $L^2(\mathbb{R})$ such that $\mathcal{H}_m$ is an eigenfunction of $\mathcal{F}$ (respectively $\mathcal{F}$) for eigenvalue $(-i)^m$ (respectively i^m).

In dimension n , the same construction can be extended by tensor product to yield the multivariate Hermite functions

$$\mathcal{H}_{\mathbf{m}}(\mathbf{x}) = \mathcal{H}_{m_1}(x_1) \times \mathcal{H}_{m_2}(x_2) \times \dots \times \mathcal{H}_{m_n}(x_n)$$

(where $\mathbf{m} \geq \mathbf{0}$ is a multi-index). These constitute an orthonormal basis of $L^2(\mathbb{R}^n)$, with $\mathcal{H}_{\mathbf{m}}$ an eigenfunction of $\mathcal{F}$ (respectively $\mathcal{F}$) for eigenvalue $(-i)^{|\mathbf{m}|}$ (respectively $i^{|\mathbf{m}|}$). Thus the subspaces $\mathbf{H}_k$ of Section 1.3.2.4.3.4 are spanned by those $\mathcal{H}_{\mathbf{m}}$ with $|\mathbf{m}| \equiv k \pmod{4}$ ($k = 0, 1, 2, 3$).

General multivariate Gaussians are usually encountered in the non-standard form

$$G_{\mathbf{A}}(\mathbf{x}) = \exp(-\frac{1}{2} \mathbf{x}^T \cdot \mathbf{A} \mathbf{x}),$$

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where $\mathbf{A}$ is a symmetric positive-definite matrix. Diagonalizing $\mathbf{A}$ as $\mathbf{E}\mathbf{A}\mathbf{E}^T$ with $\mathbf{E}\mathbf{E}^T$ the identity matrix, and putting $\mathbf{A}^{1/2} = \mathbf{E}\mathbf{A}^{1/2}\mathbf{E}^T$, we may write

$$G_{\mathbf{A}}(\mathbf{x}) = G\left[\left(\frac{\mathbf{A}}{2\pi}\right)^{1/2} \mathbf{x}\right]$$

i.e.

$$G_{\mathbf{A}} = [(2\pi\mathbf{A}^{-1})^{1/2}]^{\#} G;$$

hence (by Section 1.3.2.4.2.3)

$$\mathcal{F}[G_{\mathbf{A}}] = |\det(2\pi\mathbf{A}^{-1})|^{1/2} \left[\left(\frac{\mathbf{A}}{2\pi}\right)^{1/2}\right]^{\#} G,$$

i.e.

$$\mathcal{F}[G_{\mathbf{A}}](\xi) = |\det(2\pi\mathbf{A}^{-1})|^{1/2} G[(2\pi\mathbf{A}^{-1})^{1/2}\xi],$$

i.e. finally

$$\mathcal{F}[G_{\mathbf{A}}] = |\det(2\pi\mathbf{A}^{-1})|^{1/2} G_{4\pi^2\mathbf{A}^{-1}}.$$

This result is widely used in crystallography, *e.g.* to calculate form factors for anisotropic atoms (Section 1.3.4.2.2.6) and to obtain transforms of derivatives of Gaussian atomic densities (Section 1.3.4.4.7.10).

1.3.2.4.4.3. Heisenberg's inequality, Hardy's theorem

The result just obtained, which also holds for $\tilde{\mathcal{F}}$, shows that the 'peakier' $G_{\mathbf{A}}$, the 'broader' $\mathcal{F}[G_{\mathbf{A}}]$. This is a general property of the Fourier transformation, expressed in dimension 1 by the *Heisenberg inequality* (Weyl, 1931):

$$\begin{aligned} & \left(\int x^2 |f(x)|^2 dx \right) \left(\int \xi^2 |\mathcal{F}[f](\xi)|^2 d\xi \right) \\ & \geq \frac{1}{16\pi^2} \left(\int |f(x)|^2 dx \right)^2, \end{aligned}$$

where, by a beautiful theorem of Hardy (1933), equality can only be attained for f Gaussian. Hardy's theorem is even stronger: if both f and $\mathcal{F}[f]$ behave at infinity as constant multiples of G , then each of them is *everywhere* a constant multiple of G ; if both f and $\mathcal{F}[f]$ behave at infinity as constant multiples of $G \times$ monomial, then each of them is a finite linear combination of Hermite functions. Hardy's theorem is invoked in Section 1.3.4.4.5 to derive the optimal procedure for spreading atoms on a sampling grid in order to obtain the most accurate structure factors.

The search for optimal compromises between the confinement of f to a compact domain in x -space and of $\mathcal{F}[f]$ to a compact domain in ξ -space leads to consideration of prolate spheroidal wavefunctions (Pollack & Slepian, 1961; Landau & Pollack, 1961, 1962).

1.3.2.4.4.4. Symmetry property

A final formal property of the Fourier transform, best established in $\mathcal{S}$, is its *symmetry*: if f and g are in $\mathcal{S}$, then by Fubini's theorem

$$\begin{aligned} \langle \mathcal{F}[f], g \rangle &= \int_{\mathbb{R}^n} \left(\int_{\mathbb{R}^n} f(\mathbf{x}) \exp(-2\pi i \xi \cdot \mathbf{x}) d^n \mathbf{x} \right) g(\xi) d^n \xi \\ &= \int_{\mathbb{R}^n} f(\mathbf{x}) \left(\int_{\mathbb{R}^n} g(\xi) \exp(-2\pi i \xi \cdot \mathbf{x}) d^n \xi \right) d^n \mathbf{x} \\ &= \langle f, \mathcal{F}[g] \rangle. \end{aligned}$$

This possibility of 'transposing' $\mathcal{F}$ (and $\tilde{\mathcal{F}}$) from the left to the right of the duality bracket will be used in Section 1.3.2.5.4 to extend the Fourier transformation to distributions.

1.3.2.4.5. Various writings of Fourier transforms

Other ways of writing Fourier transforms in $\mathbb{R}^n$ exist besides the one used here. All have the form

$$\mathcal{F}_{h,\omega}[f](\xi) = \frac{1}{h^n} \int_{\mathbb{R}^n} f(\mathbf{x}) \exp(-i\omega \xi \cdot \mathbf{x}) d^n \mathbf{x},$$

where h is real positive and ω real non-zero, with the reciprocity formula written:

$$f(\mathbf{x}) = \frac{1}{k^n} \int_{\mathbb{R}^n} \mathcal{F}_{h,\omega}[f](\xi) \exp(+i\omega \xi \cdot \mathbf{x}) d^n \mathbf{x}$$

with k real positive. The consistency condition between h, k and ω is

$$hk = \frac{2\pi}{|\omega|}.$$

The usual choices are:

- (i) $\omega = \pm 2\pi, h = k = 1$ (as here);
- (ii) $\omega = \pm 1, h = 1, k = 2\pi$ (in probability theory and in solid-state physics);
- (iii) $\omega = \pm 1, h = k = \sqrt{2\pi}$ (in much of classical analysis).

It should be noted that conventions (ii) and (iii) introduce numerical factors of 2π in convolution and Parseval formulae, while (ii) breaks the symmetry between $\mathcal{F}$ and $\tilde{\mathcal{F}}$.

1.3.2.4.6. Tables of Fourier transforms

The books by Campbell & Foster (1948), Erdélyi (1954), and Magnus *et al.* (1966) contain extensive tables listing pairs of functions and their Fourier transforms. Bracewell (1986) lists those pairs particularly relevant to electrical engineering applications.

1.3.2.5. Fourier transforms of tempered distributions

1.3.2.5.1. Introduction

It was found in Section 1.3.2.4.2 that the usual space of test functions $\mathcal{D}$ is not invariant under $\mathcal{F}$ and $\tilde{\mathcal{F}}$. By contrast, the space $\mathcal{S}$ of infinitely differentiable rapidly decreasing functions is invariant under $\mathcal{F}$ and $\tilde{\mathcal{F}}$, and furthermore transposition formulae such as

$$\langle \mathcal{F}[f], g \rangle = \langle f, \mathcal{F}[g] \rangle$$

hold for all $f, g \in \mathcal{S}$. It is precisely this type of transposition which was used successfully in Sections 1.3.2.3.9.1 and 1.3.2.3.9.3 to define the derivatives of distributions and their products with smooth functions.

This suggests using $\mathcal{S}$ instead of $\mathcal{D}$ as a space of test functions φ , and defining the Fourier transform $\mathcal{F}[T]$ of a distribution T by

$$\langle \mathcal{F}[T], \varphi \rangle = \langle T, \mathcal{F}[\varphi] \rangle$$

whenever T is capable of being extended from $\mathcal{D}$ to $\mathcal{S}$ while remaining continuous. It is this latter proviso which will be subsumed under the adjective 'tempered'. As was the case with the construction of $\mathcal{S}'$, it is the definition of a sufficiently strong topology (*i.e.* notion of convergence) in $\mathcal{S}$ which will play a key role in transferring to the elements of its topological dual $\mathcal{S}'$ (called tempered distributions) all the properties of the Fourier transformation.

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Besides the general references to distribution theory mentioned in Section 1.3.2.3.1 the reader may consult the books by Zemanian (1965, 1968). Lavoine (1963) contains tables of Fourier transforms of distributions.

1.3.2.5.2. $\mathcal{S}$ as a test-function space

A notion of convergence has to be introduced in $\mathcal{S}(\mathbb{R}^n)$ in order to be able to define and test the continuity of linear functionals on it.

A sequence (φ_j) of functions in $\mathcal{S}$ will be said to converge to 0 if, for any given multi-indices $\mathbf{k}$ and $\mathbf{p}$, the sequence $(\mathbf{x}^{\mathbf{k}} D^{\mathbf{p}} \varphi_j)$ tends to 0 uniformly on $\mathbb{R}^n$.

It can be shown that $\mathcal{D}(\mathbb{R}^n)$ is dense in $\mathcal{S}(\mathbb{R}^n)$. Translation is continuous for this topology. For any linear differential operator $P(D) = \sum_{\mathbf{p}} a_{\mathbf{p}} D^{\mathbf{p}}$ and any polynomial $Q(\mathbf{x})$ over $\mathbb{R}^n$, $(\varphi_j) \rightarrow 0$ implies $[Q(\mathbf{x}) \times P(D)\varphi_j] \rightarrow 0$ in the topology of $\mathcal{S}$. Therefore, differentiation and multiplication by polynomials are continuous for the topology on $\mathcal{S}$.

The Fourier transformations $\mathcal{F}$ and $\tilde{\mathcal{F}}$ are also continuous for the topology of $\mathcal{S}$. Indeed, let (φ_j) converge to 0 for the topology on $\mathcal{S}$. Then, by Section 1.3.2.4.2,

$$\|(2\pi\xi)^{\mathbf{m}} D^{\mathbf{p}} (\mathcal{F}[\varphi_j])\|_{\infty} \leq \|D^{\mathbf{m}} [(2\pi\mathbf{x})^{\mathbf{p}} \varphi_j]\|_1.$$

The right-hand side tends to 0 as $j \rightarrow \infty$ by definition of convergence in $\mathcal{S}$, hence $\|\xi\|^{\mathbf{m}} D^{\mathbf{p}} (\mathcal{F}[\varphi_j]) \rightarrow 0$ uniformly, so that $(\mathcal{F}[\varphi_j]) \rightarrow 0$ in $\mathcal{S}$ as $j \rightarrow \infty$. The same proof applies to $\tilde{\mathcal{F}}$.

1.3.2.5.3. Definition and examples of tempered distributions

A distribution $T \in \mathcal{D}'(\mathbb{R}^n)$ is said to be *tempered* if it can be extended into a continuous linear functional on $\mathcal{S}$.

If $\mathcal{S}'(\mathbb{R}^n)$ is the topological dual of $\mathcal{S}(\mathbb{R}^n)$, and if $S \in \mathcal{S}'(\mathbb{R}^n)$, then its restriction to $\mathcal{D}$ is a tempered distribution; conversely, if $T \in \mathcal{D}'$ is tempered, then its extension to $\mathcal{S}$ is unique (because $\mathcal{D}$ is dense in $\mathcal{S}$), hence it defines an element S of $\mathcal{S}'$. We may therefore identify $\mathcal{S}'$ and the space of tempered distributions.

A distribution with compact support is tempered, i.e. $\mathcal{S}' \supset \mathcal{E}'$. By transposition of the corresponding properties of $\mathcal{S}$, it is readily established that the derivative, translate or product by a polynomial of a tempered distribution is still a tempered distribution.

These inclusion relations may be summarized as follows: since $\mathcal{S}$ contains $\mathcal{D}$ but is contained in $\mathcal{E}$, the reverse inclusions hold for the topological duals, and hence $\mathcal{S}'$ contains $\mathcal{E}'$ but is contained in $\mathcal{D}'$.

A locally summable function f on $\mathbb{R}^n$ will be said to be of *polynomial growth* if $|f(\mathbf{x})|$ can be majorized by a polynomial in $\|\mathbf{x}\|$ as $\|\mathbf{x}\| \rightarrow \infty$. It is easily shown that such a function f defines a tempered distribution T_f via

$$\langle T_f, \varphi \rangle = \int_{\mathbb{R}^n} f(\mathbf{x}) \varphi(\mathbf{x}) d^n \mathbf{x}.$$

In particular, polynomials over $\mathbb{R}^n$ define tempered distributions, and so do functions in $\mathcal{S}$. The latter remark, together with the transposition identity (Section 1.3.2.4.4), invites the extension of $\mathcal{F}$ and $\tilde{\mathcal{F}}$ from $\mathcal{S}$ to $\mathcal{S}'$.

1.3.2.5.4. Fourier transforms of tempered distributions

The Fourier transform $\mathcal{F}[T]$ and cotransform $\tilde{\mathcal{F}}[T]$ of a tempered distribution T are defined by

$$\begin{aligned} \langle \mathcal{F}[T], \varphi \rangle &= \langle T, \mathcal{F}[\varphi] \rangle \\ \langle \tilde{\mathcal{F}}[T], \varphi \rangle &= \langle T, \tilde{\mathcal{F}}[\varphi] \rangle \end{aligned}$$

for all test functions $\varphi \in \mathcal{S}$. Both $\mathcal{F}[T]$ and $\tilde{\mathcal{F}}[T]$ are themselves tempered distributions, since the maps $\varphi \mapsto \mathcal{F}[\varphi]$ and $\varphi \mapsto \tilde{\mathcal{F}}[\varphi]$

are both linear and continuous for the topology of $\mathcal{S}$. In the same way that $\mathbf{x}$ and ξ have been used consistently as arguments for φ and $\mathcal{F}[\varphi]$, respectively, the notation $T_{\mathbf{x}}$ and $\mathcal{F}[T]_{\xi}$ will be used to indicate which variables are involved.

When T is a distribution with compact support, its Fourier transform may be written

$$\mathcal{F}[T]_{\xi} = \langle T_{\mathbf{x}}, \exp(-2\pi i \xi \cdot \mathbf{x}) \rangle$$

since the function $\mathbf{x} \mapsto \exp(-2\pi i \xi \cdot \mathbf{x})$ is in $\mathcal{E}$ while $T_{\mathbf{x}} \in \mathcal{E}'$. It can be shown, as in Section 1.3.2.4.2, to be analytically continuable into an entire function over $\mathbb{C}^n$.

1.3.2.5.5. Transposition of basic properties

The duality between differentiation and multiplication by a monomial extends from $\mathcal{S}$ to $\mathcal{S}'$ by transposition:

$$\begin{aligned} \mathcal{F}[D_{\mathbf{x}}^{\mathbf{p}} T]_{\xi} &= (2\pi i \xi)^{\mathbf{p}} \mathcal{F}[T]_{\xi} \\ D_{\xi}^{\mathbf{p}} (\mathcal{F}[T]_{\xi}) &= \mathcal{F}[(-2\pi i \mathbf{x})^{\mathbf{p}} T]_{\xi}. \end{aligned}$$

Analogous formulae hold for $\tilde{\mathcal{F}}$, with i replaced by $-i$.

The formulae expressing the duality between translation and phase shift, e.g.

$$\begin{aligned} \mathcal{F}[\tau_{\mathbf{a}} T]_{\xi} &= \exp(-2\pi i \mathbf{a} \cdot \xi) \mathcal{F}[T]_{\xi} \\ \tau_{\alpha} (\mathcal{F}[T]_{\xi}) &= \mathcal{F}[\exp(2\pi i \alpha \cdot \mathbf{x}) T]_{\xi}; \end{aligned}$$

between a linear change of variable and its contragredient, e.g.

$$\mathcal{F}[A^{\#} T] = |\det \mathbf{A}| [(A^{-1})^T]^{\#} \mathcal{F}[T];$$

are obtained similarly by transposition from the corresponding identities in $\mathcal{S}$. They give a transposition formula for an affine change of variables $\mathbf{x} \mapsto S(\mathbf{x}) = \mathbf{A}\mathbf{x} + \mathbf{b}$ with non-singular matrix $\mathbf{A}$:

$$\begin{aligned} \mathcal{F}[S^{\#} T] &= \exp(-2\pi i \xi \cdot \mathbf{b}) \mathcal{F}[A^{\#} T] \\ &= \exp(-2\pi i \xi \cdot \mathbf{b}) |\det \mathbf{A}| [(A^{-1})^T]^{\#} \mathcal{F}[T], \end{aligned}$$

with a similar result for $\tilde{\mathcal{F}}$, replacing $-i$ by $+i$.

Conjugate symmetry is obtained similarly:

$$\mathcal{F}[\bar{T}] = \overline{\mathcal{F}[T]}, \quad \tilde{\mathcal{F}}[\bar{T}] = \overline{\tilde{\mathcal{F}}[T]},$$

with the same identities for $\tilde{\mathcal{F}}$.

The tensor product property also transposes to tempered distributions: if $U \in \mathcal{S}'(\mathbb{R}^m)$, $V \in \mathcal{S}'(\mathbb{R}^n)$,

$$\begin{aligned} \mathcal{F}[U_{\mathbf{x}} \otimes V_{\mathbf{y}}] &= \mathcal{F}[U]_{\xi} \otimes \mathcal{F}[V]_{\eta} \\ \tilde{\mathcal{F}}[U_{\mathbf{x}} \otimes V_{\mathbf{y}}] &= \tilde{\mathcal{F}}[U]_{\xi} \otimes \tilde{\mathcal{F}}[V]_{\eta}. \end{aligned}$$

1.3.2.5.6. Transforms of δ -functions

Since δ has compact support,

$$\mathcal{F}[\delta_{\mathbf{x}}]_{\xi} = \langle \delta_{\mathbf{x}}, \exp(-2\pi i \xi \cdot \mathbf{x}) \rangle = 1_{\xi}, \quad \text{i.e. } \mathcal{F}[\delta] = 1.$$

It is instructive to show that conversely $\mathcal{F}[1] = \delta$ without invoking the reciprocity theorem. Since $\partial_j 1 = 0$ for all $j = 1, \dots, n$, it follows from Section 1.3.2.3.9.4 that $\mathcal{F}[1] = c\delta$; the constant c can be determined by using the invariance of the standard Gaussian G established in Section 1.3.2.4.3:

$$\langle \mathcal{F}[1]_{\mathbf{x}}, G_{\mathbf{x}} \rangle = \langle 1_{\xi}, G_{\xi} \rangle = 1;$$

hence $c = 1$. Thus, $\mathcal{F}[1] = \delta$.

The basic properties above then read (using multi-indices to denote differentiation):

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$$\begin{aligned}\mathcal{F}[\delta_{\mathbf{x}}^{(\mathbf{m})}]_{\xi} &= (2\pi i \xi)^{\mathbf{m}}, & \mathcal{F}[\mathbf{x}^{\mathbf{m}}]_{\xi} &= (-2\pi i)^{-|\mathbf{m}|} \delta_{\xi}^{(\mathbf{m})}; \\ \mathcal{F}[\delta_{\mathbf{a}}]_{\xi} &= \exp(-2\pi i \mathbf{a} \cdot \xi), & \mathcal{F}[\exp(2\pi i \mathbf{a} \cdot \mathbf{x})]_{\xi} &= \delta_{\mathbf{a}},\end{aligned}$$

with analogous relations for $\tilde{\mathcal{F}}$, i becoming $-i$. Thus derivatives of δ are mapped to monomials (and *vice versa*), while translates of δ are mapped to ‘phase factors’ (and *vice versa*).

1.3.2.5.7. Reciprocity theorem

The previous results now allow a self-contained and rigorous proof of the reciprocity theorem between $\mathcal{F}$ and $\tilde{\mathcal{F}}$ to be given, whereas in traditional settings (*i.e.* in L^1 and L^2) the implicit handling of δ through a limiting process is always the sticking point.

Reciprocity is first established in $\mathcal{S}$ as follows:

$$\begin{aligned}\tilde{\mathcal{F}}[\mathcal{F}[\varphi]](\mathbf{x}) &= \int_{\mathbb{R}^n} \mathcal{F}[\varphi](\xi) \exp(2\pi i \xi \cdot \mathbf{x}) d^n \xi \\ &= \int_{\mathbb{R}^n} \mathcal{F}[\tau_{-\mathbf{x}}\varphi](\xi) d^n \xi \\ &= \langle 1, \mathcal{F}[\tau_{-\mathbf{x}}\varphi] \rangle \\ &= \langle \mathcal{F}[1], \tau_{-\mathbf{x}}\varphi \rangle \\ &= \langle \tau_{\mathbf{x}}\delta, \varphi \rangle \\ &= \varphi(\mathbf{x})\end{aligned}$$

and similarly

$$\mathcal{F}[\tilde{\mathcal{F}}[\varphi]](\mathbf{x}) = \varphi(\mathbf{x}).$$

The reciprocity theorem is then proved in $\mathcal{S}'$ by transposition:

$$\tilde{\mathcal{F}}[\mathcal{F}[T]] = \mathcal{F}[\tilde{\mathcal{F}}[T]] = T \quad \text{for all } T \in \mathcal{S}'.$$

Thus the Fourier cotransformation $\tilde{\mathcal{F}}$ in $\mathcal{S}'$ may legitimately be called the ‘inverse Fourier transformation’.

The method of Section 1.3.2.4.3 may then be used to show that $\tilde{\mathcal{F}}$ and $\mathcal{F}$ both have period 4 in $\mathcal{S}'$.

1.3.2.5.8. Multiplication and convolution

Multiplier functions $\alpha(\mathbf{x})$ for tempered distributions must be infinitely differentiable, as for ordinary distributions; furthermore, they must grow sufficiently slowly as $\|\mathbf{x}\| \rightarrow \infty$ to ensure that $\alpha\varphi \in \mathcal{S}$ for all $\varphi \in \mathcal{S}$ and that the map $\varphi \mapsto \alpha\varphi$ is continuous for the topology of $\mathcal{S}$. This leads to choosing for multipliers the subspace $\mathcal{O}_M$ consisting of functions $\alpha \in \mathcal{E}$ of *polynomial growth*. It can be shown that if f is in $\mathcal{O}_M$, then the associated distribution T_f is in $\mathcal{S}'$ (*i.e.* is a tempered distribution); and that conversely if T is in $\mathcal{S}'$, $\mu * T$ is in $\mathcal{O}_M$ for all $\mu \in \mathcal{Q}$.

Corresponding restrictions must be imposed to define the space $\mathcal{O}'_C$ of those distributions T whose convolution $S * T$ with a tempered distribution S is still a tempered distribution: T must be such that, for all $\varphi \in \mathcal{S}$, $\theta(\mathbf{x}) = \langle T_{\mathbf{y}}, \varphi(\mathbf{x} + \mathbf{y}) \rangle$ is in $\mathcal{S}$; and such that the map $\varphi \mapsto \theta$ be continuous for the topology of $\mathcal{S}$. This implies that S is ‘rapidly decreasing’. It can be shown that if f is in $\mathcal{S}$, then the associated distribution T_f is in $\mathcal{O}'_C$; and that conversely if T is in $\mathcal{O}'_C$, $\mu * T$ is in $\mathcal{S}$ for all $\mu \in \mathcal{Q}$.

The two spaces $\mathcal{O}_M$ and $\mathcal{O}'_C$ are mapped into each other by the Fourier transformation

$$\begin{aligned}\mathcal{F}(\mathcal{O}_M) &= \tilde{\mathcal{F}}(\mathcal{O}_M) = \mathcal{O}'_C \\ \mathcal{F}(\mathcal{O}'_C) &= \tilde{\mathcal{F}}(\mathcal{O}'_C) = \mathcal{O}_M\end{aligned}$$

and the convolution theorem takes the form

$$\begin{aligned}\mathcal{F}[\alpha S] &= \mathcal{F}[\alpha] * \mathcal{F}[S] & S \in \mathcal{S}', \alpha \in \mathcal{O}_M, \mathcal{F}[\alpha] \in \mathcal{O}'_C; \\ \mathcal{F}[S * T] &= \mathcal{F}[S] \times \mathcal{F}[T] & S \in \mathcal{S}', T \in \mathcal{O}'_C, \mathcal{F}[T] \in \mathcal{O}_M.\end{aligned}$$

The same identities hold for $\tilde{\mathcal{F}}$. Taken together with the reciprocity theorem, these show that $\mathcal{F}$ and $\tilde{\mathcal{F}}$ establish mutually inverse isomorphisms between $\mathcal{O}_M$ and $\mathcal{O}'_C$, and exchange multiplication for convolution in $\mathcal{S}'$.

It may be noticed that most of the basic properties of $\mathcal{F}$ and $\tilde{\mathcal{F}}$ may be deduced from this theorem and from the properties of δ . Differentiation operators $D^{\mathbf{m}}$ and translation operators $\tau_{\mathbf{a}}$ are convolutions with $D^{\mathbf{m}}\delta$ and $\tau_{\mathbf{a}}\delta$; they are turned, respectively, into multiplication by monomials $(\pm 2\pi i \xi)^{\mathbf{m}}$ (the transforms of $D^{\mathbf{m}}\delta$) or by phase factors $\exp(\pm 2\pi i \xi \cdot \mathbf{a})$ (the transforms of $\tau_{\mathbf{a}}\delta$).

Another consequence of the convolution theorem is the duality established by the Fourier transformation between sections and projections of a function and its transform. For instance, in $\mathbb{R}^3$, the *projection* of $f(x, y, z)$ on the x, y plane along the z axis may be written

$$(\delta_x \otimes \delta_y \otimes 1_z) * f;$$

its Fourier transform is then

$$(1_{\xi} \otimes 1_{\eta} \otimes \delta_{\zeta}) \times \mathcal{F}[f],$$

which is the *section* of $\mathcal{F}[f]$ by the plane $\zeta = 0$, orthogonal to the z axis used for projection. There are numerous applications of this property in crystallography (Section 1.3.4.2.1.8) and in fibre diffraction (Section 1.3.4.5.1.3).

1.3.2.5.9. L^2 aspects, Sobolev spaces

The special properties of $\mathcal{F}$ in the space of square-integrable functions $L^2(\mathbb{R}^n)$, such as Parseval’s identity, can be accommodated within distribution theory: if $u \in L^2(\mathbb{R}^n)$, then T_u is a tempered distribution in $\mathcal{S}'$ (the map $u \mapsto T_u$ being continuous) and it can be shown that $S = \mathcal{F}[T_u]$ is of the form S_v , where $u = \mathcal{F}[u]$ is the Fourier transform of u in $L^2(\mathbb{R}^n)$. By Plancherel’s theorem, $\|u\|_2 = \|v\|_2$.

This embedding of L^2 into $\mathcal{S}'$ can be used to derive the convolution theorem for L^2 . If u and v are in $L^2(\mathbb{R}^n)$, then $u * v$ can be shown to be a bounded continuous function; thus $u * v$ is not in L^2 , but it is in $\mathcal{S}'$, so that its Fourier transform is a distribution, and

$$\mathcal{F}[u * v] = \mathcal{F}[u] \times \mathcal{F}[v].$$

Spaces of tempered distributions related to $L^2(\mathbb{R}^n)$ can be defined as follows. For any real s , define the Sobolev space $H_s(\mathbb{R}^n)$ to consist of all tempered distributions $S \in \mathcal{S}'(\mathbb{R}^n)$ such that

$$(1 + |\xi|^2)^{s/2} \mathcal{F}[S]_{\xi} \in L^2(\mathbb{R}^n).$$

These spaces play a fundamental role in the theory of partial differential equations, and in the mathematical theory of tomographic reconstruction – a subject not unrelated to the crystallographic phase problem (Natterer, 1986).

1.3.2.6. Periodic distributions and Fourier series

1.3.2.6.1. Terminology

Let $\mathbb{Z}^n$ be the subset of $\mathbb{R}^n$ consisting of those points with (signed) integer coordinates; it is an n -dimensional *lattice*, *i.e.* a free Abelian group on n generators. A particularly simple set of n generators is given by the standard basis of $\mathbb{R}^n$, and hence $\mathbb{Z}^n$ will be called the *standard lattice* in $\mathbb{R}^n$. Any other ‘non-standard’ n -dimensional lattice Λ in $\mathbb{R}^n$ is the image of this standard lattice by a general linear transformation.

If we identify any two points in $\mathbb{R}^n$ whose coordinates are congruent modulo $\mathbb{Z}^n$, *i.e.* differ by a vector in $\mathbb{Z}^n$, we obtain the *standard n -torus* $\mathbb{R}^n / \mathbb{Z}^n$. The latter may be viewed as $(\mathbb{R} / \mathbb{Z})^n$, *i.e.* as the Cartesian product of n circles. The same identification may be carried out modulo a non-standard lattice Λ , yielding a *non-*

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standard n -torus $\mathbb{R}^n/\Lambda$. The correspondence to crystallographic terminology is that ‘standard’ coordinates over the standard 3-torus $\mathbb{R}^3/\mathbb{Z}^3$ are called ‘fractional’ coordinates over the unit cell; while Cartesian coordinates, *e.g.* in ångströms, constitute a set of non-standard coordinates.

Finally, we will denote by I the unit cube $[0, 1]^n$ and by C_ε the subset

$$C_\varepsilon = \{\mathbf{x} \in \mathbb{R}^n \mid |x_j| < \varepsilon \text{ for all } j = 1, \dots, n\}.$$

1.3.2.6.2. $\mathbb{Z}^n$ -periodic distributions in $\mathbb{R}^n$

A distribution $T \in \mathcal{D}'(\mathbb{R}^n)$ is called *periodic with period lattice* $\mathbb{Z}^n$ (or $\mathbb{Z}^n$ -periodic) if $\tau_{\mathbf{m}}T = T$ for all $\mathbf{m} \in \mathbb{Z}^n$ (in crystallography the period lattice is the *direct* lattice).

Given a distribution with compact support $T^0 \in \mathcal{E}'(\mathbb{R}^n)$, then $T = \sum_{\mathbf{m} \in \mathbb{Z}^n} \tau_{\mathbf{m}}T^0$ is a $\mathbb{Z}^n$ -periodic distribution. Note that we may write $T = r * T^0$, where $r = \sum_{\mathbf{m} \in \mathbb{Z}^n} \delta_{(\mathbf{m})}$ consists of Dirac δ 's at all nodes of the period lattice $\mathbb{Z}^n$.

Conversely, any $\mathbb{Z}^n$ -periodic distribution T may be written as $r * T^0$ for some $T^0 \in \mathcal{E}'$. To retrieve such a ‘motif’ T^0 from T , a function ψ will be constructed in such a way that $\psi \in \mathcal{D}$ (hence has compact support) and $r * \psi = 1$; then $T^0 = \psi T$. Indicator functions (Section 1.3.2.2) such as χ_1 or $\chi_{C_{1/2}}$ cannot be used directly, since they are discontinuous; but regularized versions of them may be constructed by convolution (see Section 1.3.2.3.9.7) as $\psi_0 = \chi_{C_\varepsilon} * \theta_\eta$, with ε and η such that $\psi_0(\mathbf{x}) = 1$ on $C_{1/2}$ and $\psi_0(\mathbf{x}) = 0$ outside $C_{3/4}$. Then the function

$$\psi = \frac{\psi_0}{\sum_{\mathbf{m} \in \mathbb{Z}^n} \tau_{\mathbf{m}}\psi_0}$$

has the desired property. The sum in the denominator contains at most 2^n non-zero terms at any given point $\mathbf{x}$ and acts as a smoothly varying ‘multiplicity correction’.

1.3.2.6.3. Identification with distributions over $\mathbb{R}^n/\mathbb{Z}^n$

Throughout this section, ‘periodic’ will mean ‘ $\mathbb{Z}^n$ -periodic’.

Let $s \in \mathbb{R}$, and let $[s]$ denote the largest integer $\leq s$. For $\mathbf{x} = (x_1, \dots, x_n) \in \mathbb{R}^n$, let $\tilde{\mathbf{x}}$ be the unique vector $(\tilde{x}_1, \dots, \tilde{x}_n)$ with $\tilde{x}_j = x_j - [x_j]$. If $\mathbf{x}, \mathbf{y} \in \mathbb{R}^n$, then $\tilde{\mathbf{x}} = \tilde{\mathbf{y}}$ if and only if $\mathbf{x} - \mathbf{y} \in \mathbb{Z}^n$. The image of the map $\mathbf{x} \mapsto \tilde{\mathbf{x}}$ is thus $\mathbb{R}^n$ modulo $\mathbb{Z}^n$, or $\mathbb{R}^n/\mathbb{Z}^n$.

If f is a periodic function over $\mathbb{R}^n$, then $\tilde{\mathbf{x}} = \tilde{\mathbf{y}}$ implies $f(\mathbf{x}) = f(\mathbf{y})$; we may thus define a function $\tilde{f}$ over $\mathbb{R}^n/\mathbb{Z}^n$ by putting $\tilde{f}(\tilde{\mathbf{x}}) = f(\mathbf{x})$ for any $\mathbf{x} \in \mathbb{R}^n$ such that $\mathbf{x} - \tilde{\mathbf{x}} \in \mathbb{Z}^n$. Conversely, if $\tilde{f}$ is a function over $\mathbb{R}^n/\mathbb{Z}^n$, then we may define a function f over $\mathbb{R}^n$ by putting $f(\mathbf{x}) = \tilde{f}(\tilde{\mathbf{x}})$, and f will be periodic. Periodic functions over $\mathbb{R}^n$ may thus be identified with functions over $\mathbb{R}^n/\mathbb{Z}^n$, and this identification preserves the notions of convergence, local summability and differentiability.

Given $\varphi^0 \in \mathcal{D}(\mathbb{R}^n)$, we may define

$$\varphi(\mathbf{x}) = \sum_{\mathbf{m} \in \mathbb{Z}^n} (\tau_{\mathbf{m}}\varphi^0)(\mathbf{x})$$

since the sum only contains finitely many non-zero terms; φ is periodic, and $\tilde{\varphi} \in \mathcal{D}(\mathbb{R}^n/\mathbb{Z}^n)$. Conversely, if $\tilde{\varphi} \in \mathcal{D}(\mathbb{R}^n/\mathbb{Z}^n)$ we may define $\varphi \in \mathcal{E}(\mathbb{R}^n)$ periodic by $\varphi(\mathbf{x}) = \tilde{\varphi}(\tilde{\mathbf{x}})$, and $\varphi^0 \in \mathcal{D}(\mathbb{R}^n)$ by putting $\varphi^0 = \psi\varphi$ with ψ constructed as above.

By transposition, a distribution $\tilde{T} \in \mathcal{D}'(\mathbb{R}^n/\mathbb{Z}^n)$ defines a unique periodic distribution $T \in \mathcal{D}'(\mathbb{R}^n)$ by $\langle T, \varphi^0 \rangle = \langle \tilde{T}, \tilde{\varphi} \rangle$; conversely, $T \in \mathcal{D}'(\mathbb{R}^n)$ periodic defines uniquely $\tilde{T} \in \mathcal{D}'(\mathbb{R}^n/\mathbb{Z}^n)$ by $\langle \tilde{T}, \tilde{\varphi} \rangle = \langle T, \varphi^0 \rangle$.

We may therefore identify $\mathbb{Z}^n$ -periodic distributions over $\mathbb{R}^n$ with distributions over $\mathbb{R}^n/\mathbb{Z}^n$. We will, however, use mostly the former

presentation, as it is more closely related to the crystallographer’s perception of periodicity (see Section 1.3.4.1).

1.3.2.6.4. Fourier transforms of periodic distributions

The content of this section is perhaps the central result in the relation between Fourier theory and crystallography (Section 1.3.4.2.1.1).

Let $T = r * T^0$ with r defined as in Section 1.3.2.6.2. Then $r \in \mathcal{D}'$, $T^0 \in \mathcal{E}'$ hence $T^0 \in \mathcal{O}'_C$, so that $T \in \mathcal{D}'$: $\mathbb{Z}^n$ -periodic distributions are tempered, hence have a Fourier transform. The convolution theorem (Section 1.3.2.5.8) is applicable, giving:

$$\mathcal{F}[T] = \mathcal{F}[r] \times \mathcal{F}[T^0]$$

and similarly for $\tilde{\mathcal{F}}$.

Since $\mathcal{F}[\delta_{(\mathbf{m})}](\xi) = \exp(-2\pi i \xi \cdot \mathbf{m})$, formally

$$\mathcal{F}[r]_\xi = \sum_{\mathbf{m} \in \mathbb{Z}^n} \exp(-2\pi i \xi \cdot \mathbf{m}) = Q,$$

say.

It is readily shown that Q is tempered and periodic, so that $Q = \sum_{\mu \in \mathbb{Z}^n} \tau_\mu(\psi Q)$, while the periodicity of r implies that

$$[\exp(-2\pi i \xi_j) - 1]\psi Q = 0, \quad j = 1, \dots, n.$$

Since the first factors have single isolated zeros at $\xi_j = 0$ in $C_{3/4}$, $\psi Q = c\delta$ (see Section 1.3.2.3.9.4) and hence by periodicity $Q = cr$; convoluting with χ_{C_1} shows that $c = 1$. Thus we have the fundamental result:

$$\boxed{\mathcal{F}[r] = r}$$

so that

$$\mathcal{F}[T] = r \times \mathcal{F}[T^0];$$

i.e., according to Section 1.3.2.3.9.3,

$$\mathcal{F}[T]_\xi = \sum_{\mu \in \mathbb{Z}^n} \mathcal{F}[T^0](\mu) \times \delta_{(\mu)}.$$

The right-hand side is a *weighted* lattice distribution, whose nodes $\mu \in \mathbb{Z}^n$ are weighted by the *sample values* $\mathcal{F}[T^0](\mu)$ of the transform of the motif T^0 at those nodes. Since $T^0 \in \mathcal{E}'$, the latter values may be written

$$\mathcal{F}[T^0](\mu) = \langle T^0_x, \exp(-2\pi i \mu \cdot \mathbf{x}) \rangle.$$

By the structure theorem for distributions with compact support (Section 1.3.2.3.9.7), T^0 is a derivative of finite order of a continuous function; therefore, from Section 1.3.2.4.2.8 and Section 1.3.2.5.8, $\mathcal{F}[T^0](\mu)$ grows at most polynomially as $\|\mu\| \rightarrow \infty$ (see also Section 1.3.2.6.10.3 about this property). Conversely, let $W = \sum_{\mu \in \mathbb{Z}^n} w_\mu \delta_{(\mu)}$ be a weighted lattice distribution such that the weights w_μ grow at most polynomially as $\|\mu\| \rightarrow \infty$. Then W is a tempered distribution, whose Fourier cotransform $T_x = \sum_{\mu \in \mathbb{Z}^n} w_\mu \exp(+2\pi i \mu \cdot \mathbf{x})$ is periodic. If T is now written as $r * T^0$ for some $T^0 \in \mathcal{E}'$, then by the reciprocity theorem

$$w_\mu = \mathcal{F}[T^0](\mu) = \langle T^0_x, \exp(-2\pi i \mu \cdot \mathbf{x}) \rangle.$$

Although the choice of T^0 is not unique, and need not yield back the same motif as may have been used to build T initially, different choices of T^0 will lead to the same coefficients w_μ because of the periodicity of $\exp(-2\pi i \mu \cdot \mathbf{x})$.

The Fourier transformation thus establishes a duality between periodic distributions and weighted lattice distributions. The pair of relations

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$$\begin{aligned} \text{(i)} \quad w_{\boldsymbol{\mu}} &= \langle T_{\mathbf{x}}^0, \exp(-2\pi i \boldsymbol{\mu} \cdot \mathbf{x}) \rangle \\ \text{(ii)} \quad T_{\mathbf{x}} &= \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} w_{\boldsymbol{\mu}} \exp(+2\pi i \boldsymbol{\mu} \cdot \mathbf{x}) \end{aligned}$$

are referred to as the *Fourier analysis* and the *Fourier synthesis* of T , respectively (there is a discrepancy between this terminology and the crystallographic one, see Section 1.3.4.2.1.1). In other words, any periodic distribution $T \in \mathcal{S}'$ may be represented by a Fourier series (ii), whose coefficients are calculated by (i). The convergence of (ii) towards T in $\mathcal{S}'$ will be investigated later (Section 1.3.2.6.10).

1.3.2.6.5. The case of non-standard period lattices

Let Λ denote the non-standard lattice consisting of all vectors of the form $\sum_{j=1}^n m_j \mathbf{a}_j$, where the m_j are rational integers and $\mathbf{a}_1, \dots, \mathbf{a}_n$ are n linearly independent vectors in $\mathbb{R}^n$. Let R be the corresponding lattice distribution: $R = \sum_{\mathbf{x} \in \Lambda} \delta(\mathbf{x})$.

Let $\mathbf{A}$ be the non-singular $n \times n$ matrix whose successive columns are the coordinates of vectors $\mathbf{a}_1, \dots, \mathbf{a}_n$ in the standard basis of $\mathbb{R}^n$; $\mathbf{A}$ will be called the *period matrix* of Λ , and the mapping $\mathbf{x} \mapsto \mathbf{A}\mathbf{x}$ will be denoted by A . According to Section 1.3.2.3.9.5 we have

$$\langle R, \varphi \rangle = \sum_{\mathbf{m} \in \mathbb{Z}^n} \varphi(\mathbf{A}\mathbf{m}) = \langle r, (\mathbf{A}^{-1})^{\#} \varphi \rangle = |\det \mathbf{A}|^{-1} \langle A^{\#} r, \varphi \rangle$$

for any $\varphi \in \mathcal{S}$, and hence $R = |\det \mathbf{A}|^{-1} A^{\#} r$. By Fourier transformation, according to Section 1.3.2.5.5,

$$\mathcal{F}[R] = |\det \mathbf{A}|^{-1} \mathcal{F}[A^{\#} r] = [(\mathbf{A}^{-1})^T]^{\#} \mathcal{F}[r] = [(\mathbf{A}^{-1})^T]^{\#} r,$$

which we write:

$$\mathcal{F}[R] = |\det \mathbf{A}|^{-1} R^*$$

with

$$R^* = |\det \mathbf{A}| [(\mathbf{A}^{-1})^T]^{\#} r.$$

R^* is a lattice distribution:

$$R^* = \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} \delta_{[(\mathbf{A}^{-1})^T \boldsymbol{\mu}]} = \sum_{\boldsymbol{\xi} \in \Lambda^*} \delta(\boldsymbol{\xi})$$

associated with the *reciprocal lattice* Λ^* whose basis vectors $\mathbf{a}_1^*, \dots, \mathbf{a}_n^*$ are the columns of $(\mathbf{A}^{-1})^T$. Since the latter matrix is equal to the adjoint matrix (i.e. the matrix of co-factors) of $\mathbf{A}$ divided by $\det \mathbf{A}$, the components of the reciprocal basis vectors can be written down explicitly (see Section 1.3.4.2.1.1 for the crystallographic case $n = 3$).

A distribution T will be called Λ -periodic if $\tau_{\boldsymbol{\xi}} T = T$ for all $\boldsymbol{\xi} \in \Lambda$; as previously, T may be written $R * T^0$ for some motif distribution T^0 with compact support. By Fourier transformation,

$$\begin{aligned} \mathcal{F}[T] &= |\det \mathbf{A}|^{-1} R^* \cdot \mathcal{F}[T^0] \\ &= |\det \mathbf{A}|^{-1} \sum_{\boldsymbol{\xi} \in \Lambda^*} \mathcal{F}[T^0](\boldsymbol{\xi}) \delta(\boldsymbol{\xi}) \\ &= |\det \mathbf{A}|^{-1} \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} \mathcal{F}[T^0][(\mathbf{A}^{-1})^T \boldsymbol{\mu}] \delta_{[(\mathbf{A}^{-1})^T \boldsymbol{\mu}]} \end{aligned}$$

so that $\mathcal{F}[T]$ is a weighted reciprocal-lattice distribution, the weight attached to node $\boldsymbol{\xi} \in \Lambda^*$ being $|\det \mathbf{A}|^{-1}$ times the value $\mathcal{F}[T^0](\boldsymbol{\xi})$ of the Fourier transform of the motif T^0 .

This result may be further simplified if T and its motif T^0 are referred to the standard period lattice $\mathbb{Z}^n$ by defining t and t^0 so that $T = A^{\#} t$, $T^0 = A^{\#} t^0$, $t = r * t^0$. Then

$$\mathcal{F}[T^0](\boldsymbol{\xi}) = |\det \mathbf{A}| \mathcal{F}[t^0](\mathbf{A}^T \boldsymbol{\xi}),$$

hence

$$\mathcal{F}[T^0][(\mathbf{A}^{-1})^T \boldsymbol{\mu}] = |\det \mathbf{A}| \mathcal{F}[t^0](\boldsymbol{\mu}),$$

so that

$$\mathcal{F}[T] = \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} \mathcal{F}[t^0](\boldsymbol{\mu}) \delta_{[(\mathbf{A}^{-1})^T \boldsymbol{\mu}]}$$

in non-standard coordinates, while

$$\mathcal{F}[t] = \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} \mathcal{F}[t^0](\boldsymbol{\mu}) \delta(\boldsymbol{\mu})$$

in standard coordinates.

The reciprocity theorem may then be written:

$$\text{(iii)} \quad W_{\boldsymbol{\xi}} = |\det \mathbf{A}|^{-1} \langle T_{\mathbf{x}}^0, \exp(-2\pi i \boldsymbol{\xi} \cdot \mathbf{x}) \rangle, \quad \boldsymbol{\xi} \in \Lambda^*$$

$$\text{(iv)} \quad T_{\mathbf{x}} = \sum_{\boldsymbol{\xi} \in \Lambda^*} W_{\boldsymbol{\xi}} \exp(+2\pi i \boldsymbol{\xi} \cdot \mathbf{x})$$

in non-standard coordinates, or equivalently:

$$\text{(v)} \quad w_{\boldsymbol{\mu}} = \langle t_{\mathbf{x}}^0, \exp(-2\pi i \boldsymbol{\mu} \cdot \mathbf{x}) \rangle, \quad \boldsymbol{\mu} \in \mathbb{Z}^n$$

$$\text{(vi)} \quad t_{\mathbf{x}} = \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} w_{\boldsymbol{\mu}} \exp(+2\pi i \boldsymbol{\mu} \cdot \mathbf{x})$$

in standard coordinates. It gives an n -dimensional Fourier series representation for any periodic distribution over $\mathbb{R}^n$. The convergence of such series in $\mathcal{S}'(\mathbb{R}^n)$ will be examined in Section 1.3.2.6.10.

1.3.2.6.6. Duality between periodization and sampling

Let T^0 be a distribution with compact support (the ‘motif’). Its Fourier transform $\mathcal{F}[T^0]$ is analytic (Section 1.3.2.5.4) and may thus be used as a multiplier.

We may rephrase the preceding results as follows:

(i) if T^0 is ‘periodized by R ’ to give $R * T^0$, then $\mathcal{F}[T^0]$ is ‘sampled by R^* ’ to give $|\det \mathbf{A}|^{-1} R^* \cdot \mathcal{F}[T^0]$;

(ii) if $\mathcal{F}[T^0]$ is ‘sampled by R^* ’ to give $R^* \cdot \mathcal{F}[T^0]$, then T^0 is ‘periodized by R ’ to give $|\det \mathbf{A}| R * T^0$.

Thus the Fourier transformation establishes a duality between the periodization of a distribution by a period lattice Λ and the sampling of its transform at the nodes of lattice Λ^* reciprocal to Λ . This is a particular instance of the convolution theorem of Section 1.3.2.5.8.

At this point it is traditional to break the symmetry between $\mathcal{F}$ and $\tilde{\mathcal{F}}$ which distribution theory has enabled us to preserve even in the presence of periodicity, and to perform two distinct identifications:

(i) a Λ -periodic distribution T will be handled as a distribution $\tilde{T}$ on $\mathbb{R}^n/\Lambda$, was done in Section 1.3.2.6.3;

(ii) a weighted lattice distribution $W = \sum_{\boldsymbol{\mu} \in \mathbb{Z}^n} W_{\boldsymbol{\mu}} \delta_{[(\mathbf{A}^{-1})^T \boldsymbol{\mu}]}$ will be identified with the collection $\{W_{\boldsymbol{\mu}} | \boldsymbol{\mu} \in \mathbb{Z}^n\}$ of its n -tuply indexed coefficients.

1.3.2.6.7. The Poisson summation formula

Let $\varphi \in \mathcal{S}$, so that $\mathcal{F}[\varphi] \in \mathcal{S}$. Let R be the lattice distribution associated to lattice Λ , with period matrix $\mathbf{A}$, and let R^* be associated to the reciprocal lattice Λ^* . Then we may write:

$$\begin{aligned} \langle R, \varphi \rangle &= \langle R, \tilde{\mathcal{F}}[\mathcal{F}[\varphi]] \rangle \\ &= \langle \tilde{\mathcal{F}}[R], \mathcal{F}[\varphi] \rangle \\ &= |\det \mathbf{A}|^{-1} \langle R^*, \mathcal{F}[\varphi] \rangle \end{aligned}$$

i.e.

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$$\sum_{\mathbf{x} \in \Lambda} \varphi(\mathbf{x}) = |\det \mathbf{A}|^{-1} \sum_{\xi \in \Lambda^*} \mathcal{F}[\varphi](\xi).$$

This identity, which also holds for $\tilde{\mathcal{F}}$, is called the *Poisson summation formula*. Its usefulness follows from the fact that the speed of decrease at infinity of φ and $\mathcal{F}[\varphi]$ are inversely related (Section 1.3.2.4.4.3), so that if one of the series (say, the left-hand side) is slowly convergent, the other (say, the right-hand side) will be rapidly convergent. This procedure has been used by Ewald (1921) [see also Bertaut (1952), Born & Huang (1954)] to evaluate lattice sums (Madelung constants) involved in the calculation of the internal electrostatic energy of crystals (see Chapter 3.4 in this volume on convergence acceleration techniques for crystallographic lattice sums).

When φ is a multivariate Gaussian

$$\varphi(\mathbf{x}) = G_{\mathbf{B}}(\mathbf{x}) = \exp(-\frac{1}{2}\mathbf{x}^T \mathbf{B} \mathbf{x}),$$

then

$$\mathcal{F}[\varphi](\xi) = |\det(2\pi\mathbf{B}^{-1})|^{1/2} G_{\mathbf{B}^{-1}}(\xi),$$

and Poisson's summation formula for a lattice with period matrix $\mathbf{A}$ reads:

$$\begin{aligned} \sum_{\mathbf{m} \in \mathbb{Z}^n} G_{\mathbf{B}}(\mathbf{A}\mathbf{m}) &= |\det \mathbf{A}|^{-1} |\det(2\pi\mathbf{B}^{-1})|^{1/2} \\ &\times \sum_{\mu \in \mathbb{Z}^n} G_{4\pi^2 \mathbf{B}^{-1}}[(\mathbf{A}^{-1})^T \mu] \end{aligned}$$

or equivalently

$$\sum_{\mathbf{m} \in \mathbb{Z}^n} G_{\mathbf{C}}(\mathbf{m}) = |\det(2\pi\mathbf{C}^{-1})|^{1/2} \sum_{\mu \in \mathbb{Z}^n} G_{4\pi^2 \mathbf{C}^{-1}}(\mu)$$

with $\mathbf{C} = \mathbf{A}^T \mathbf{B} \mathbf{A}$.

1.3.2.6.8. Convolution of Fourier series

Let $S = R * S^0$ and $T = R * T^0$ be two Λ -periodic distributions, the motifs S^0 and T^0 having compact support. The convolution $S * T$ does not exist, because S and T do not satisfy the support condition (Section 1.3.2.3.9.7). However, the three distributions R , S^0 and T^0 do satisfy the generalized support condition, so that their convolution is defined; then, by associativity and commutativity:

$$R * S^0 * T^0 = S * T^0 = S^0 * T.$$

By Fourier transformation and by the convolution theorem:

$$\begin{aligned} R^* \times \mathcal{F}[S^0 * T^0] &= (R^* \times \mathcal{F}[S^0]) \times \mathcal{F}[T^0] \\ &= \mathcal{F}[T^0] \times (R^* \times \mathcal{F}[S^0]). \end{aligned}$$

Let $\{U_{\xi}\}_{\xi \in \Lambda^*}$, $\{V_{\xi}\}_{\xi \in \Lambda^*}$ and $\{W_{\xi}\}_{\xi \in \Lambda^*}$ be the sets of Fourier coefficients associated to S , T and $S * T^0 (= S^0 * T)$, respectively. Identifying the coefficients of δ_{ξ} for $\xi \in \Lambda^*$ yields the forward version of the convolution theorem for Fourier series:

$$W_{\xi} = |\det \mathbf{A}| U_{\xi} V_{\xi}.$$

The backward version of the theorem requires that T be infinitely differentiable. The distribution $S \times T$ is then well defined and its Fourier coefficients $\{Q_{\xi}\}_{\xi \in \Lambda^*}$ are given by

$$Q_{\xi} = \sum_{\eta \in \Lambda^*} U_{\eta} V_{\xi - \eta}.$$

1.3.2.6.9. Toeplitz forms, Szegö's theorem

Toeplitz forms were first investigated by Toeplitz (1907, 1910, 1911a). They occur in connection with the 'trigonometric moment problem' (Shohat & Tamarkin, 1943; Akhiezer, 1965) and

probability theory (Grenander, 1952) and play an important role in several direct approaches to the crystallographic phase problem [see Sections 1.3.4.2.1.10, 1.3.4.5.2.2(e)]. Many aspects of their theory and applications are presented in the book by Grenander & Szegö (1958).

1.3.2.6.9.1. Toeplitz forms

Let $f \in L^1(\mathbb{R}/\mathbb{Z})$ be real-valued, so that its Fourier coefficients satisfy the relations $c_{-m}(f) = \overline{c_m(f)}$. The Hermitian form in $n+1$ complex variables

$$T_n[f](\mathbf{u}) = \sum_{\mu=0}^n \sum_{\nu=0}^n \overline{u_{\mu}} c_{\mu-\nu} u_{\nu}$$

is called the n th *Toeplitz form* associated to f . It is a straightforward consequence of the convolution theorem and of Parseval's identity that $T_n[f]$ may be written:

$$T_n[f](\mathbf{u}) = \int_0^1 \left| \sum_{\nu=0}^n u_{\nu} \exp(2\pi i \nu x) \right|^2 f(x) dx.$$

1.3.2.6.9.2. The Toeplitz–Carathéodory–Herglotz theorem

It was shown independently by Toeplitz (1911b), Carathéodory (1911) and Herglotz (1911) that a function $f \in L^1$ is almost everywhere non-negative if and only if the Toeplitz forms $T_n[f]$ associated to f are positive semidefinite for all values of n .

This is equivalent to the infinite system of determinantal inequalities

$$D_n = \det \begin{pmatrix} c_0 & c_{-1} & \cdot & \cdot & c_{-n} \\ c_1 & c_0 & c_{-1} & \cdot & \cdot \\ \cdot & c_1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & c_{-1} \\ c_n & \cdot & \cdot & c_1 & c_0 \end{pmatrix} \geq 0 \quad \text{for all } n.$$

The D_n are called *Toeplitz determinants*. Their application to the crystallographic phase problem is described in Section 1.3.4.2.1.10.

1.3.2.6.9.3. Asymptotic distribution of eigenvalues of Toeplitz forms

The eigenvalues of the Hermitian form $T_n[f]$ are defined as the $n+1$ real roots of the characteristic equation $\det \{T_n[f - \lambda]\} = 0$. They will be denoted by

$$\lambda_1^{(n)}, \lambda_2^{(n)}, \dots, \lambda_{n+1}^{(n)}.$$

It is easily shown that if $m \leq f(x) \leq M$ for all x , then $m \leq \lambda_{\nu}^{(n)} \leq M$ for all n and all $\nu = 1, \dots, n+1$. As $n \rightarrow \infty$ these bounds, and the distribution of the $\lambda^{(n)}$ within these bounds, can be made more precise by introducing two new notions.

(i) *Essential bounds*: define $\text{ess inf } f$ as the largest m such that $f(x) \geq m$ except for values of x forming a set of measure 0; and define $\text{ess sup } f$ similarly.

(ii) *Equal distribution*. For each n , consider two sets of $n+1$ real numbers:

$$a_1^{(n)}, a_2^{(n)}, \dots, a_{n+1}^{(n)}, \quad \text{and} \quad b_1^{(n)}, b_2^{(n)}, \dots, b_{n+1}^{(n)}.$$

Assume that for each ν and each n , $|a_{\nu}^{(n)}| < K$ and $|b_{\nu}^{(n)}| < K$ with K independent of ν and n . The sets $\{a_{\nu}^{(n)}\}$ and $\{b_{\nu}^{(n)}\}$ are said to be equally distributed in $[-K, +K]$ if, for any function F over $[-K, +K]$,

$$\lim_{n \rightarrow \infty} \frac{1}{n+1} \sum_{\nu=1}^{n+1} [F(a_{\nu}^{(n)}) - F(b_{\nu}^{(n)})] = 0.$$

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We may now state an important theorem of Szegő (1915, 1920). Let $f \in L^1$, and put $m = \text{ess inf } f$, $M = \text{ess sup } f$. If m and M are finite, then for any continuous function $F(\lambda)$ defined in the interval $[m, M]$ we have

$$\lim_{n \rightarrow \infty} \frac{1}{n+1} \sum_{\nu=1}^{n+1} F(\lambda_\nu^{(n)}) = \int_0^1 F[f(x)] \, dx.$$

In other words, the eigenvalues $\lambda_\nu^{(n)}$ of the T_n and the values $f[\nu/(n+2)]$ of f on a regular subdivision of $]0, 1[$ are equally distributed.

Further investigations into the spectra of Toeplitz matrices may be found in papers by Hartman & Wintner (1950, 1954), Kac *et al.* (1953), Widom (1965), and in the notes by Hirschman & Hughes (1977).

1.3.2.6.9.4. Consequences of Szegő's theorem

(i) If the λ 's are ordered in ascending order, then

$$\lim_{n \rightarrow \infty} \lambda_1^{(n)} = m = \text{ess inf } f, \quad \lim_{n \rightarrow \infty} \lambda_{n+1}^{(n)} = M = \text{ess sup } f.$$

Thus, when $f \geq 0$, the condition number $\lambda_{n+1}^{(n)}/\lambda_1^{(n)}$ of $T_n[f]$ tends towards the 'essential dynamic range' M/m of f .

(ii) Let $F(\lambda) = \lambda^s$ where s is a positive integer. Then

$$\lim_{n \rightarrow \infty} \frac{1}{n+1} \sum_{\nu=1}^{n+1} [\lambda_\nu^{(n)}]^s = \int_0^1 [f(x)]^s \, dx.$$

(iii) Let $m > 0$, so that $\lambda_\nu^{(n)} > 0$, and let $D_n(f) = \det T_n(f)$. Then

$$D_n(f) = \prod_{\nu=1}^{n+1} \lambda_\nu^{(n)},$$

hence

$$\log D_n(f) = \sum_{\nu=1}^{n+1} \log \lambda_\nu^{(n)}.$$

Putting $F(\lambda) = \log \lambda$, it follows that

$$\lim_{n \rightarrow \infty} [D_n(f)]^{1/(n+1)} = \exp \left\{ \int_0^1 \log f(x) \, dx \right\}.$$

Further terms in this limit were obtained by Szegő (1952) and interpreted in probabilistic terms by Kac (1954).

1.3.2.6.10. Convergence of Fourier series

The investigation of the convergence of Fourier series and of more general trigonometric series has been the subject of intense study for over 150 years [see *e.g.* Zygmund (1976)]. It has been a constant source of new mathematical ideas and theories, being directly responsible for the birth of such fields as set theory, topology and functional analysis.

This section will briefly survey those aspects of the classical results in dimension 1 which are relevant to the practical use of Fourier series in crystallography. The books by Zygmund (1959), Tolstov (1962) and Katznelson (1968) are standard references in the field, and Dym & McKean (1972) is recommended as a stimulant.

1.3.2.6.10.1. Classical L^1 theory

The space $L^1(\mathbb{R}/\mathbb{Z})$ consists of (equivalence classes of) complex-valued functions f on the circle which are summable, *i.e.* for which

$$\|f\|_1 \equiv \int_0^1 |f(x)| \, dx < +\infty.$$

It is a convolution algebra: If f and g are in L^1 , then $f * g$ is in L^1 . The m th Fourier coefficient $c_m(f)$ of f ,

$$c_m(f) = \int_0^1 f(x) \exp(-2\pi i m x) \, dx$$

is bounded: $|c_m(f)| \leq \|f\|_1$, and by the Riemann–Lebesgue lemma $c_m(f) \rightarrow 0$ as $m \rightarrow \infty$. By the convolution theorem, $c_m(f * g) = c_m(f)c_m(g)$.

The p th partial sum $S_p(f)$ of the Fourier series of f ,

$$S_p(f)(x) = \sum_{|m| \leq p} c_m(f) \exp(2\pi i m x),$$

may be written, by virtue of the convolution theorem, as $S_p(f) = D_p * f$, where

$$D_p(x) = \sum_{|m| \leq p} \exp(2\pi i m x) = \frac{\sin[(2p+1)\pi x]}{\sin \pi x}$$

is the *Dirichlet kernel*. Because D_p comprises numerous slowly decaying oscillations, both positive and negative, $S_p(f)$ may not converge towards f in a strong sense as $p \rightarrow \infty$. Indeed, spectacular pathologies are known to exist where the partial sums, examined pointwise, diverge everywhere (Zygmund, 1959, Chapter VIII). When f is piecewise continuous, but presents isolated jumps, convergence near these jumps is marred by the *Gibbs phenomenon*: $S_p(f)$ always 'overshoots the mark' by about 9%, the area under the spurious peak tending to 0 as $p \rightarrow \infty$ but not its height [see Larmor (1934) for the history of this phenomenon].

By contrast, the *arithmetic mean* of the partial sums, also called the p th Cesàro sum,

$$C_p(f) = \frac{1}{p+1} [S_0(f) + \dots + S_p(f)],$$

converges to f in the sense of the L^1 norm: $\|C_p(f) - f\|_1 \rightarrow 0$ as $p \rightarrow \infty$. If furthermore f is *continuous*, then the convergence is *uniform*, *i.e.* the error is bounded everywhere by a quantity which goes to 0 as $p \rightarrow \infty$. It may be shown that

$$C_p(f) = F_p * f,$$

where

$$\begin{aligned} F_p(x) &= \sum_{|m| \leq p} \left(1 - \frac{|m|}{p+1}\right) \exp(2\pi i m x) \\ &= \frac{1}{p+1} \left[\frac{\sin(p+1)\pi x}{\sin \pi x} \right]^2 \end{aligned}$$

is the *Fejér kernel*. F_p has over D_p the advantage of being everywhere positive, so that the Cesàro sums $C_p(f)$ of a positive function f are always positive.

The de la Vallée Poussin kernel

$$V_p(x) = 2F_{2p+1}(x) - F_p(x)$$

has a trapezoidal distribution of coefficients and is such that $c_m(V_p) = 1$ if $|m| \leq p+1$; therefore $V_p * f$ is a trigonometric polynomial with the same Fourier coefficients as f over that range of values of m .

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The Poisson kernel

$$P_r(x) = 1 + 2 \sum_{m=1}^{\infty} r^m \cos 2\pi m x$$

$$= \frac{1 - r^2}{1 - 2r \cos 2\pi m x + r^2}$$

with $0 \leq r < 1$ gives rise to an Abel summation procedure [Tolstov (1962, p. 162); Whittaker & Watson (1927, p. 57)] since

$$(P_r * f)(x) = \sum_{m \in \mathbb{Z}} c_m(f) r^{|m|} \exp(2\pi i m x).$$

Compared with the other kernels, P_r has the disadvantage of not being a trigonometric polynomial; however, P_r is the real part of the Cauchy kernel (Cartan, 1961; Ahlfors, 1966):

$$P_r(x) = \Re \left[\frac{1 + r \exp(2\pi i x)}{1 - r \exp(2\pi i x)} \right]$$

and hence provides a link between trigonometric series and analytic functions of a complex variable.

Other methods of summation involve forming a moving average of f by convolution with other sequences of functions $\alpha_p(\mathbf{x})$ besides D_p of F_p which ‘tend towards δ ’ as $p \rightarrow \infty$. The convolution is performed by multiplying the Fourier coefficients of f by those of α_p , so that one forms the quantities

$$S'_p(f)(x) = \sum_{|m| \leq p} c_m(\alpha_p) c_m(f) \exp(2\pi i m x).$$

For instance the ‘sigma factors’ of Lanczos (Lanczos, 1966, p. 65), defined by

$$\sigma_m = \frac{\sin[m\pi/p]}{m\pi/p},$$

lead to a summation procedure whose behaviour is intermediate between those using the Dirichlet and the Fejér kernels; it corresponds to forming a moving average of f by convolution with

$$\alpha_p = P\chi_{[-1/(2p), 1/(2p)]} * D_p,$$

which is itself the convolution of a ‘rectangular pulse’ of width $1/p$ and of the Dirichlet kernel of order p .

A review of the summation problem in crystallography is given in Section 1.3.4.2.1.3.

1.3.2.6.10.2. Classical L^2 theory

The space $L^2(\mathbb{R}/\mathbb{Z})$ of (equivalence classes of) square-integrable complex-valued functions f on the circle is contained in $L^1(\mathbb{R}/\mathbb{Z})$, since by the Cauchy–Schwarz inequality

$$\|f\|_1^2 = \left(\int_0^1 |f(x)| \times 1 \, dx \right)^2$$

$$\leq \left(\int_0^1 |f(x)|^2 \, dx \right) \left(\int_0^1 1^2 \, dx \right) = \|f\|_2^2 \leq \infty.$$

Thus all the results derived for L^1 hold for L^2 , a great simplification over the situation in $\mathbb{R}$ or $\mathbb{R}^n$ where neither L^1 nor L^2 was contained in the other.

However, more can be proved in L^2 , because L^2 is a Hilbert space (Section 1.3.2.2.4) for the inner product

$$(f, g) = \int_0^1 \overline{f(x)} g(x) \, dx,$$

and because the family of functions $\{\exp(2\pi i m x)\}_{m \in \mathbb{Z}}$ constitutes an orthonormal Hilbert basis for L^2 .

The sequence of Fourier coefficients $c_m(f)$ of $f \in L^2$ belongs to the space $\ell^2(\mathbb{Z})$ of square-summable sequences:

$$\sum_{m \in \mathbb{Z}} |c_m(f)|^2 < \infty.$$

Conversely, every element $c = (c_m)$ of ℓ^2 is the sequence of Fourier coefficients of a unique function in L^2 . The inner product

$$(c, d) = \sum_{m \in \mathbb{Z}} \overline{c_m} d_m$$

makes ℓ^2 into a Hilbert space, and the map from L^2 to ℓ^2 established by the Fourier transformation is an isometry (Parseval/Plancherel):

$$\|f\|_{L^2} = \|c(f)\|_{\ell^2}$$

or equivalently:

$$(f, g) = (c(f), c(g)).$$

This is a useful property in applications, since (f, g) may be calculated either from f and g themselves, or from their Fourier coefficients $c(f)$ and $c(g)$ (see Section 1.3.4.4.6) for crystallographic applications).

By virtue of the orthogonality of the basis $\{\exp(2\pi i m x)\}_{m \in \mathbb{Z}}$, the partial sum $S_p(f)$ is the best mean-square fit to f in the linear subspace of L^2 spanned by $\{\exp(2\pi i m x)\}_{|m| \leq p}$, and hence (Bessel’s inequality)

$$\sum_{|m| \leq p} |c_m(f)|^2 = \|f\|_2^2 - \sum_{|M| \geq p} |c_M(f)|^2 \leq \|f\|_2^2.$$

1.3.2.6.10.3. The viewpoint of distribution theory

The use of distributions enlarges considerably the range of behaviour which can be accommodated in a Fourier series, even in the case of general dimension n where classical theories meet with even more difficulties than in dimension 1.

Let $\{w_m\}_{m \in \mathbb{Z}}$ be a sequence of complex numbers with $|w_m|$ growing at most polynomially as $|m| \rightarrow \infty$, say $|w_m| \leq C|m|^K$. Then the sequence $\{w_m/(2\pi i m)^{K+2}\}_{m \in \mathbb{Z}}$ is in ℓ^2 and even defines a continuous function $f \in L^2(\mathbb{R}/\mathbb{Z})$ and an associated tempered distribution $T_f \in \mathcal{D}'(\mathbb{R}/\mathbb{Z})$. Differentiation of T_f ($K+2$) times then yields a tempered distribution whose Fourier transform leads to the original sequence of coefficients. Conversely, by the structure theorem for distributions with compact support (Section 1.3.2.3.9.7), the motif T^0 of a $\mathbb{Z}$ -periodic distribution is a derivative of finite order of a continuous function; hence its Fourier coefficients will grow at most polynomially with $|m|$ as $|m| \rightarrow \infty$.

Thus distribution theory allows the manipulation of Fourier series whose coefficients exhibit polynomial growth as their order goes to infinity, while those derived from functions had to tend to 0 by virtue of the Riemann–Lebesgue lemma. The distribution-theoretic approach to Fourier series holds even in the case of general dimension n , where classical theories meet with even more difficulties (see Ash, 1976) than in dimension 1.

1.3.2.7. The discrete Fourier transformation

1.3.2.7.1. Shannon’s sampling theorem and interpolation formula

Let $\varphi \in \mathcal{E}(\mathbb{R}^n)$ be such that $\Phi = \mathcal{F}[\varphi]$ has compact support K . Let φ be sampled at the nodes of a lattice Λ^* , yielding the lattice distribution $R^* \times \varphi$. The Fourier transform of this sampled version of φ is

$$\mathcal{F}[R^* \times \varphi] = |\det \mathbf{A}| (R * \Phi),$$

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which is essentially Φ periodized by period lattice $\Lambda = (\Lambda^*)^*$, with period matrix $\mathbf{A}$.

Let us assume that Λ is such that the translates of K by different period vectors of Λ are disjoint. Then we may recover Φ from $R * \Phi$ by masking the contents of a ‘unit cell’ $\mathcal{V}$ of Λ (i.e. a fundamental domain for the action of Λ in $\mathbb{R}^n$) whose boundary does not meet K . If $\chi_{\mathcal{V}}$ is the indicator function of $\mathcal{V}$, then

$$\Phi = \chi_{\mathcal{V}} \times (R * \Phi).$$

Transforming both sides by $\tilde{\mathcal{F}}$ yields

$$\varphi = \tilde{\mathcal{F}} \left[\chi_{\mathcal{V}} \times \frac{1}{|\det \mathbf{A}|} \tilde{\mathcal{F}}[R^* \times \varphi] \right],$$

i.e.

$$\varphi = \left(\frac{1}{V} \tilde{\mathcal{F}}[\chi_{\mathcal{V}}] \right) * (R^* \times \varphi)$$

since $|\det \mathbf{A}|$ is the volume V of $\mathcal{V}$.

This interpolation formula is traditionally credited to Shannon (1949), although it was discovered much earlier by Whittaker (1915). It shows that φ may be recovered from its sample values on Λ^* (i.e. from $R^* \times \varphi$) provided Λ^* is sufficiently fine that no overlap (or ‘aliasing’) occurs in the periodization of Φ by the dual lattice Λ . The interpolation kernel is the transform of the normalized indicator function of a unit cell of Λ containing the support K of Φ .

If K is contained in a sphere of radius $1/\Delta$ and if Λ and Λ^* are rectangular, the length of each basis vector of Λ must be greater than $2/\Delta$, and thus the sampling interval must be smaller than $\Delta/2$. This requirement constitutes the Shannon sampling criterion.

1.3.2.7.2. Duality between subdivision and decimation of period lattices

1.3.2.7.2.1. Geometric description of sublattices

Let $\Lambda_{\mathbf{A}}$ be a period lattice in $\mathbb{R}^n$ with matrix $\mathbf{A}$, and let $\Lambda_{\mathbf{A}}^*$ be the lattice reciprocal to $\Lambda_{\mathbf{A}}$, with period matrix $(\mathbf{A}^{-1})^T$. Let $\Lambda_{\mathbf{B}}, \mathbf{B}, \Lambda_{\mathbf{B}}^*$ be defined similarly, and let us suppose that $\Lambda_{\mathbf{A}}$ is a sublattice of $\Lambda_{\mathbf{B}}$, i.e. that $\Lambda_{\mathbf{B}} \supset \Lambda_{\mathbf{A}}$ as a set.

The relation between $\Lambda_{\mathbf{A}}$ and $\Lambda_{\mathbf{B}}$ may be described in two different fashions: (i) multiplicatively, and (ii) additively.

(i) We may write $\mathbf{A} = \mathbf{B}\mathbf{N}$ for some non-singular matrix $\mathbf{N}$ with integer entries. $\mathbf{N}$ may be viewed as the period matrix of the coarser lattice $\Lambda_{\mathbf{A}}$ with respect to the period basis of the finer lattice $\Lambda_{\mathbf{B}}$. It will be more convenient to write $\mathbf{A} = \mathbf{D}\mathbf{B}$, where $\mathbf{D} = \mathbf{B}\mathbf{N}\mathbf{B}^{-1}$ is a rational matrix (with integer determinant since $\det \mathbf{D} = \det \mathbf{N}$) in terms of which the two lattices are related by

$$\Lambda_{\mathbf{A}} = \mathbf{D}\Lambda_{\mathbf{B}}.$$

(ii) Call two vectors in $\Lambda_{\mathbf{B}}$ congruent modulo $\Lambda_{\mathbf{A}}$ if their difference lies in $\Lambda_{\mathbf{A}}$. Denote the set of congruence classes (or ‘cosets’) by $\Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$, and the number of these classes by $[\Lambda_{\mathbf{B}} : \Lambda_{\mathbf{A}}]$. The ‘coset decomposition’

$$\Lambda_{\mathbf{B}} = \bigcup_{\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}} (\ell + \Lambda_{\mathbf{A}})$$

represents $\Lambda_{\mathbf{B}}$ as the disjoint union of $[\Lambda_{\mathbf{B}} : \Lambda_{\mathbf{A}}]$ translates of $\Lambda_{\mathbf{A}}$. $\Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$ is a finite lattice with $[\Lambda_{\mathbf{B}} : \Lambda_{\mathbf{A}}]$ elements, called the residual lattice of $\Lambda_{\mathbf{B}}$ modulo $\Lambda_{\mathbf{A}}$.

The two descriptions are connected by the relation $[\Lambda_{\mathbf{B}} : \Lambda_{\mathbf{A}}] = \det \mathbf{D} = \det \mathbf{N}$, which follows from a volume calculation. We may also combine (i) and (ii) into

$$(iii) \quad \Lambda_{\mathbf{B}} = \bigcup_{\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}} (\ell + \mathbf{D}\Lambda_{\mathbf{B}})$$

which may be viewed as the n -dimensional equivalent of the Euclidean algorithm for integer division: ℓ is the ‘remainder’ of the division by $\Lambda_{\mathbf{A}}$ of a vector in $\Lambda_{\mathbf{B}}$, the quotient being the matrix $\mathbf{D}$.

1.3.2.7.2.2. Sublattice relations for reciprocal lattices

Let us now consider the two reciprocal lattices $\Lambda_{\mathbf{A}}^*$ and $\Lambda_{\mathbf{B}}^*$. Their period matrices $(\mathbf{A}^{-1})^T$ and $(\mathbf{B}^{-1})^T$ are related by: $(\mathbf{B}^{-1})^T = (\mathbf{A}^{-1})^T \mathbf{N}^T$, where $\mathbf{N}^T$ is an integer matrix; or equivalently by $(\mathbf{B}^{-1})^T = \mathbf{D}^T (\mathbf{A}^{-1})^T$. This shows that the roles are reversed in that $\Lambda_{\mathbf{B}}^*$ is a sublattice of $\Lambda_{\mathbf{A}}^*$, which we may write:

$$(i)^* \quad \Lambda_{\mathbf{B}}^* = \mathbf{D}^T \Lambda_{\mathbf{A}}^*$$

$$(ii)^* \quad \Lambda_{\mathbf{A}}^* = \bigcup_{\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*} (\ell^* + \Lambda_{\mathbf{B}}^*).$$

The residual lattice $\Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$ is finite, with $[\Lambda_{\mathbf{A}}^* : \Lambda_{\mathbf{B}}^*] = \det \mathbf{D} = \det \mathbf{N} = [\Lambda_{\mathbf{B}} : \Lambda_{\mathbf{A}}]$, and we may again combine (i)^{*} and (ii)^{*} into

$$(iii)^* \quad \Lambda_{\mathbf{A}}^* = \bigcup_{\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*} (\ell^* + \mathbf{D}^T \Lambda_{\mathbf{A}}^*).$$

1.3.2.7.2.3. Relation between lattice distributions

The above relations between lattices may be rewritten in terms of the corresponding lattice distributions as follows:

$$(i) \quad R_{\mathbf{A}} = \frac{1}{|\det \mathbf{D}|} \mathbf{D}^{\#} R_{\mathbf{B}}^*$$

$$(ii) \quad R_{\mathbf{B}} = T_{\mathbf{B}/\mathbf{A}} * R_{\mathbf{A}}$$

$$(i)^* \quad R_{\mathbf{B}}^* = \frac{1}{|\det \mathbf{D}|} (\mathbf{D}^T)^{\#} R_{\mathbf{A}}^*$$

$$(ii)^* \quad R_{\mathbf{A}}^* = T_{\mathbf{A}/\mathbf{B}}^* * R_{\mathbf{B}}^*$$

where

$$T_{\mathbf{B}/\mathbf{A}} = \sum_{\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}} \delta_{(\ell)}$$

and

$$T_{\mathbf{A}/\mathbf{B}}^* = \sum_{\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*} \delta_{(\ell^*)}$$

are (finite) residual-lattice distributions. We may incorporate the factor $1/|\det \mathbf{D}|$ in (i) and (i)^{*} into these distributions and define

$$S_{\mathbf{B}/\mathbf{A}} = \frac{1}{|\det \mathbf{D}|} T_{\mathbf{B}/\mathbf{A}}, \quad S_{\mathbf{A}/\mathbf{B}}^* = \frac{1}{|\det \mathbf{D}|} T_{\mathbf{A}/\mathbf{B}}^*.$$

Since $|\det \mathbf{D}| = [\Lambda_{\mathbf{B}} : \Lambda_{\mathbf{A}}] = [\Lambda_{\mathbf{A}}^* : \Lambda_{\mathbf{B}}^*]$, convolution with $S_{\mathbf{B}/\mathbf{A}}$ and $S_{\mathbf{A}/\mathbf{B}}^*$ has the effect of averaging the translates of a distribution under the elements (or ‘cosets’) of the residual lattices $\Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$ and $\Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$, respectively. This process will be called ‘coset averaging’. Eliminating $R_{\mathbf{A}}$ and $R_{\mathbf{B}}$ between (i) and (ii), and $R_{\mathbf{A}}^*$ and $R_{\mathbf{B}}^*$ between (i)^{*} and (ii)^{*}, we may write:

$$(i') \quad R_{\mathbf{A}} = \mathbf{D}^{\#} (S_{\mathbf{B}/\mathbf{A}} * R_{\mathbf{A}})$$

$$(ii') \quad R_{\mathbf{B}} = S_{\mathbf{B}/\mathbf{A}} * (\mathbf{D}^{\#} R_{\mathbf{B}})$$

$$(i')^* \quad R_{\mathbf{B}}^* = (\mathbf{D}^T)^{\#} (S_{\mathbf{A}/\mathbf{B}}^* * R_{\mathbf{B}}^*)$$

$$(ii')^* \quad R_{\mathbf{A}}^* = S_{\mathbf{A}/\mathbf{B}}^* * [(\mathbf{D}^T)^{\#} R_{\mathbf{A}}^*].$$

These identities show that period subdivision by convolution with

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$S_{\mathbf{B}/\mathbf{A}}$ (respectively $S_{\mathbf{A}/\mathbf{B}}^*$) on the one hand, and *period decimation* by ‘dilation’ by $\mathbf{D}^\#$ on the other hand, are mutually inverse operations on $R_{\mathbf{A}}$ and $R_{\mathbf{B}}$ (respectively $R_{\mathbf{A}}^*$ and $R_{\mathbf{B}}^*$).

1.3.2.7.2.4. Relation between Fourier transforms

Finally, let us consider the relations between the *Fourier transforms* of these lattice distributions. Recalling the basic relation of Section 1.3.2.6.5,

$$\begin{aligned}\mathcal{F}[R_{\mathbf{A}}] &= \frac{1}{|\det \mathbf{A}|} R_{\mathbf{A}}^* \\ &= \frac{1}{|\det \mathbf{D}\mathbf{B}|} T_{\mathbf{A}/\mathbf{B}}^* * R_{\mathbf{B}}^* && \text{by (ii)*} \\ &= \left(\frac{1}{|\det \mathbf{D}|} T_{\mathbf{A}/\mathbf{B}}^* \right) * \left(\frac{1}{|\det \mathbf{B}|} R_{\mathbf{B}}^* \right)\end{aligned}$$

i.e.

$$(iv) \quad \mathcal{F}[R_{\mathbf{A}}] = S_{\mathbf{A}/\mathbf{B}}^* * \mathcal{F}[R_{\mathbf{B}}]$$

and similarly:

$$(v) \quad \mathcal{F}[R_{\mathbf{B}}] = S_{\mathbf{B}/\mathbf{A}} * \mathcal{F}[R_{\mathbf{A}}^*].$$

Thus $R_{\mathbf{A}}$ (respectively $R_{\mathbf{B}}^*$), a *decimated* version of $R_{\mathbf{B}}$ (respectively $R_{\mathbf{A}}^*$), is transformed by $\mathcal{F}$ into a *subdivided* version of $\mathcal{F}[R_{\mathbf{B}}]$ (respectively $\mathcal{F}[R_{\mathbf{A}}^*]$).

The converse is also true:

$$\begin{aligned}\mathcal{F}[R_{\mathbf{B}}] &= \frac{1}{|\det \mathbf{B}|} R_{\mathbf{B}}^* \\ &= \frac{1}{|\det \mathbf{B}|} \frac{1}{|\det \mathbf{D}|} (\mathbf{D}^T)^\# R_{\mathbf{A}}^* && \text{by (i)*} \\ &= (\mathbf{D}^T)^\# \left(\frac{1}{|\det \mathbf{A}|} R_{\mathbf{A}}^* \right)\end{aligned}$$

i.e.

$$(iv') \quad \mathcal{F}[R_{\mathbf{B}}] = (\mathbf{D}^T)^\# \mathcal{F}[R_{\mathbf{A}}]$$

and similarly

$$(v') \quad \mathcal{F}[R_{\mathbf{A}}^*] = \mathbf{D}^\# \mathcal{F}[R_{\mathbf{B}}].$$

Thus $R_{\mathbf{B}}$ (respectively $R_{\mathbf{A}}^*$), a *subdivided* version of $R_{\mathbf{A}}$ (respectively $R_{\mathbf{B}}^*$) is transformed by $\mathcal{F}$ into a *decimated* version of $\mathcal{F}[R_{\mathbf{A}}]$ (respectively $\mathcal{F}[R_{\mathbf{B}}^*]$). Therefore, the *Fourier transform exchanges subdivision and decimation of period lattices for lattice distributions*.

Further insight into this phenomenon is provided by applying $\tilde{\mathcal{F}}$ to both sides of (iv) and (v) and invoking the convolution theorem:

$$(iv'') \quad R_{\mathbf{A}} = \tilde{\mathcal{F}}[S_{\mathbf{A}/\mathbf{B}}^*] \times R_{\mathbf{B}}$$

$$(v'') \quad R_{\mathbf{B}}^* = \tilde{\mathcal{F}}[S_{\mathbf{B}/\mathbf{A}}] \times R_{\mathbf{A}}^*.$$

These identities show that multiplication by the transform of the period-subdividing distribution $S_{\mathbf{A}/\mathbf{B}}^*$ (respectively $S_{\mathbf{B}/\mathbf{A}}$) has the effect of decimating $R_{\mathbf{B}}$ to $R_{\mathbf{A}}$ (respectively $R_{\mathbf{A}}^*$ to $R_{\mathbf{B}}^*$). They clearly imply that, if $\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$ and $\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$, then

$$\begin{aligned}\tilde{\mathcal{F}}[S_{\mathbf{A}/\mathbf{B}}^*](\ell) &= 1 \text{ if } \ell = \mathbf{0} && \text{(i.e. if } \ell \text{ belongs} \\ &&& \text{to the class of } \Lambda_{\mathbf{A}}), \\ &= 0 \text{ if } \ell \neq \mathbf{0}; \\ \tilde{\mathcal{F}}[S_{\mathbf{B}/\mathbf{A}}](\ell^*) &= 1 \text{ if } \ell^* = \mathbf{0} && \text{(i.e. if } \ell^* \text{ belongs} \\ &&& \text{to the class of } \Lambda_{\mathbf{B}}^*), \\ &= 0 \text{ if } \ell^* \neq \mathbf{0}.\end{aligned}$$

Therefore, the duality between subdivision and decimation may be viewed as another aspect of that between convolution and multiplication.

There is clearly a strong analogy between the sampling/periodization duality of Section 1.3.2.6.6 and the decimation/subdivision duality, which is viewed most naturally in terms of subgroup relationships: both sampling and decimation involve restricting a function to a *discrete additive subgroup* of the domain over which it is initially given.

1.3.2.7.2.5. Sublattice relations in terms of periodic distributions

The usual presentation of this duality is not in terms of lattice distributions, but of periodic distributions obtained by convolving them with a motif.

Given $T^0 \in \mathcal{E}'(\mathbb{R}^n)$, let us form $R_{\mathbf{A}} * T^0$, then *decimate* its transform $(1/|\det \mathbf{A}|)R_{\mathbf{A}}^* \times \tilde{\mathcal{F}}[T^0]$ by keeping only its values at the points of the coarser lattice $\Lambda_{\mathbf{B}}^* = \mathbf{D}^T \Lambda_{\mathbf{A}}^*$; as a result, $R_{\mathbf{A}}^*$ is replaced by $(1/|\det \mathbf{D}|)R_{\mathbf{B}}^*$, and the reverse transform then yields

$$\frac{1}{|\det \mathbf{D}|} R_{\mathbf{B}} * T^0 = S_{\mathbf{B}/\mathbf{A}} * (R_{\mathbf{A}} * T^0) \quad \text{by (ii),}$$

which is the *coset-averaged* version of the original $R_{\mathbf{A}} * T^0$. The converse situation is analogous to that of Shannon's sampling theorem. Let a function $\varphi \in \mathcal{E}(\mathbb{R}^n)$ whose transform $\Phi = \tilde{\mathcal{F}}[\varphi]$ has compact support be sampled as $R_{\mathbf{B}} \times \varphi$ at the nodes of $\Lambda_{\mathbf{B}}$. Then

$$\mathcal{F}[R_{\mathbf{B}} \times \varphi] = \frac{1}{|\det \mathbf{B}|} (R_{\mathbf{B}}^* * \Phi)$$

is periodic with period lattice $\Lambda_{\mathbf{B}}^*$. If the sampling lattice $\Lambda_{\mathbf{B}}$ is decimated to $\Lambda_{\mathbf{A}} = \mathbf{D}\Lambda_{\mathbf{B}}$, the inverse transform becomes

$$\begin{aligned}\mathcal{F}[R_{\mathbf{A}} \times \varphi] &= \frac{1}{|\det \mathbf{D}|} (R_{\mathbf{A}}^* * \Phi) \\ &= S_{\mathbf{A}/\mathbf{B}}^* * (R_{\mathbf{B}}^* * \Phi) && \text{by (ii)*,}\end{aligned}$$

hence becomes periodized more finely by averaging over the cosets of $\Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$. With this finer periodization, the various copies of $\text{Supp } \Phi$ may start to overlap (a phenomenon called ‘aliasing’), indicating that decimation has produced too coarse a sampling of φ .

1.3.2.7.3. Discretization of the Fourier transformation

Let $\varphi^0 \in \mathcal{E}(\mathbb{R}^n)$ be such that $\Phi^0 = \tilde{\mathcal{F}}[\varphi^0]$ has compact support (φ^0 is said to be *band-limited*). Then $\varphi = R_{\mathbf{A}} * \varphi^0$ is $\Lambda_{\mathbf{A}}$ -periodic, and $\Phi = \tilde{\mathcal{F}}[\varphi] = (1/|\det \mathbf{A}|)R_{\mathbf{A}}^* \times \Phi^0$ is such that only a finite number of points $\lambda_{\mathbf{A}}^*$ of $\Lambda_{\mathbf{A}}^*$ have a non-zero Fourier coefficient $\Phi^0(\lambda_{\mathbf{A}}^*)$ attached to them. We may therefore find a *decimation* $\Lambda_{\mathbf{B}}^* = \mathbf{D}^T \Lambda_{\mathbf{A}}^*$ of $\Lambda_{\mathbf{A}}^*$ such that the distinct translates of $\text{Supp } \Phi^0$ by vectors of $\Lambda_{\mathbf{B}}^*$ do not intersect.

The distribution Φ can be uniquely recovered from $R_{\mathbf{B}}^* * \Phi$ by the procedure of Section 1.3.2.7.1, and we may write:

$$\begin{aligned}R_{\mathbf{B}}^* * \Phi &= \frac{1}{|\det \mathbf{A}|} R_{\mathbf{B}}^* * (R_{\mathbf{A}}^* \times \Phi^0) \\ &= \frac{1}{|\det \mathbf{A}|} R_{\mathbf{A}}^* \times (R_{\mathbf{B}}^* * \Phi^0) \\ &= \frac{1}{|\det \mathbf{A}|} R_{\mathbf{B}}^* * [T_{\mathbf{A}/\mathbf{B}}^* \times (R_{\mathbf{B}}^* * \Phi^0)];\end{aligned}$$

these rearrangements being legitimate because Φ^0 and $T_{\mathbf{A}/\mathbf{B}}^*$ have compact supports which are intersection-free under the action of $\Lambda_{\mathbf{B}}^*$. By virtue of its $\Lambda_{\mathbf{B}}^*$ -periodicity, this distribution is entirely characterized by its ‘motif’ Φ with respect to $\Lambda_{\mathbf{B}}^*$.

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$$\tilde{\Phi} = \frac{1}{|\det \mathbf{A}|} T_{\mathbf{A}/\mathbf{B}}^* \times (R_{\mathbf{B}}^* * \Phi^0).$$

Similarly, φ may be uniquely recovered by Shannon interpolation from the distribution sampling its values at the nodes of $\Lambda_{\mathbf{B}} = \mathbf{D}^{-1} \Lambda_{\mathbf{A}}$ ($\Lambda_{\mathbf{B}}$ is a *subdivision* of $\Lambda_{\mathbf{B}}$). By virtue of its $\Lambda_{\mathbf{A}}$ -periodicity, this distribution is completely characterized by its motif:

$$\tilde{\varphi} = T_{\mathbf{B}/\mathbf{A}} \times \varphi = T_{\mathbf{B}/\mathbf{A}} \times (R_{\mathbf{A}}^* * \varphi^0).$$

Let $\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$ and $\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$, and define the two sets of coefficients

$$\begin{aligned} (1) \quad \tilde{\varphi}(\ell) &= \varphi(\ell + \lambda_{\mathbf{A}}) && \text{for any } \lambda_{\mathbf{A}} \in \Lambda_{\mathbf{A}} \\ &&& \text{(all choices of } \lambda_{\mathbf{A}} \text{ give the same } \tilde{\varphi}), \\ (2) \quad \tilde{\Phi}(\ell^*) &= \Phi^0(\ell^* + \lambda_{\mathbf{B}}^*) && \text{for the unique } \lambda_{\mathbf{B}}^* \text{ (if it exists)} \\ &&& \text{such that } \ell^* + \lambda_{\mathbf{B}}^* \in \text{Supp } \Phi^0, \\ &= 0 && \text{if no such } \lambda_{\mathbf{B}}^* \text{ exists.} \end{aligned}$$

Define the two distributions

$$\omega = \sum_{\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}} \tilde{\varphi}(\ell) \delta_{(\ell)}$$

and

$$\Omega = \sum_{\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*} \tilde{\Phi}(\ell^*) \delta_{(\ell^*)}.$$

The relation between ω and Ω has two equivalent forms:

$$\begin{aligned} (i) \quad R_{\mathbf{A}} * \omega &= \mathcal{F}[R_{\mathbf{B}}^* * \Omega] \\ (ii) \quad \tilde{\mathcal{F}}[R_{\mathbf{A}} * \omega] &= R_{\mathbf{B}}^* * \Omega. \end{aligned}$$

By (i), $R_{\mathbf{A}} * \omega = |\det \mathbf{B}| R_{\mathbf{B}} \times \mathcal{F}[\Omega]$. Both sides are weighted lattice distributions concentrated at the nodes of $\Lambda_{\mathbf{B}}$, and equating the weights at $\lambda_{\mathbf{B}} = \ell + \lambda_{\mathbf{A}}$ gives

$$\tilde{\varphi}(\ell) = \frac{1}{|\det \mathbf{D}|} \sum_{\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*} \tilde{\Phi}(\ell^*) \exp[-2\pi i \ell^* \cdot (\ell + \lambda_{\mathbf{A}})].$$

Since $\ell^* \in \Lambda_{\mathbf{A}}^*$, $\ell^* \cdot \lambda_{\mathbf{A}}$ is an integer, hence

$$\tilde{\varphi}(\ell) = \frac{1}{|\det \mathbf{D}|} \sum_{\ell^* \in \Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*} \tilde{\Phi}(\ell^*) \exp(-2\pi i \ell^* \cdot \ell).$$

By (ii), we have

$$\frac{1}{|\det \mathbf{A}|} R_{\mathbf{B}}^* * [T_{\mathbf{A}/\mathbf{B}}^* \times (R_{\mathbf{B}}^* * \Phi^0)] = \frac{1}{|\det \mathbf{A}|} \tilde{\mathcal{F}}[R_{\mathbf{A}} * \omega].$$

Both sides are weighted lattice distributions concentrated at the nodes of $\Lambda_{\mathbf{B}}^*$, and equating the weights at $\lambda_{\mathbf{A}}^* = \ell^* + \lambda_{\mathbf{B}}^*$ gives

$$\tilde{\Phi}(\ell^*) = \sum_{\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}} \tilde{\varphi}(\ell) \exp[+2\pi i \ell \cdot (\ell^* + \lambda_{\mathbf{B}}^*)].$$

Since $\ell \in \Lambda_{\mathbf{B}}$, $\ell \cdot \lambda_{\mathbf{B}}^*$ is an integer, hence

$$\tilde{\Phi}(\ell^*) = \sum_{\ell \in \Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}} \tilde{\varphi}(\ell) \exp(+2\pi i \ell \cdot \ell^*).$$

Now the decimation/subdivision relations between $\Lambda_{\mathbf{A}}$ and $\Lambda_{\mathbf{B}}$ may be written:

$$\mathbf{A} = \mathbf{D}\mathbf{B} = \mathbf{B}\mathbf{N},$$

so that

$$\begin{aligned} \ell &= \mathbf{B}\mathbf{k} && \text{for } \mathbf{k} \in \mathbb{Z}^n \\ \ell^* &= (\mathbf{A}^{-1})^T \mathbf{k}^* && \text{for } \mathbf{k}^* \in \mathbb{Z}^n \end{aligned}$$

with $(\mathbf{A}^{-1})^T = (\mathbf{B}^{-1})^T (\mathbf{N}^{-1})^T$, hence finally

$$\ell^* \cdot \ell = \ell \cdot \ell^* = \mathbf{k}^* \cdot (\mathbf{N}^{-1} \mathbf{k}).$$

Denoting $\tilde{\varphi}(\mathbf{B}\mathbf{k})$ by $\psi(\mathbf{k})$ and $\tilde{\Phi}[(\mathbf{A}^{-1})^T \mathbf{k}^*]$ by $\Psi(\mathbf{k}^*)$, the relation between ω and Ω may be written in the equivalent form

$$\begin{aligned} (i) \quad \psi(\mathbf{k}) &= \frac{1}{|\det \mathbf{N}|} \sum_{\mathbf{k}^* \in \mathbb{Z}^n/\mathbf{N}^T \mathbb{Z}^n} \Psi(\mathbf{k}^*) \exp[-2\pi i \mathbf{k}^* \cdot (\mathbf{N}^{-1} \mathbf{k})] \\ (ii) \quad \Psi(\mathbf{k}^*) &= \sum_{\mathbf{k} \in \mathbb{Z}^n/\mathbf{N} \mathbb{Z}^n} \psi(\mathbf{k}) \exp[+2\pi i \mathbf{k}^* \cdot (\mathbf{N}^{-1} \mathbf{k})], \end{aligned}$$

where the summations are now over *finite* residual lattices in standard form.

Equations (i) and (ii) describe two mutually inverse linear transformations $\mathcal{F}(\mathbf{N})$ and $\tilde{\mathcal{F}}(\mathbf{N})$ between two vector spaces $W_{\mathbf{N}}$ and $W_{\mathbf{N}}^*$ of dimension $|\det \mathbf{N}|$. $\mathcal{F}(\mathbf{N})$ [respectively $\tilde{\mathcal{F}}(\mathbf{N})$] is the *discrete* Fourier (respectively inverse Fourier) transform associated to matrix $\mathbf{N}$.

The vector spaces $W_{\mathbf{N}}$ and $W_{\mathbf{N}}^*$ may be viewed from two different standpoints:

(1) as vector spaces of *weighted residual-lattice distributions*, of the form $\alpha(\mathbf{x}) T_{\mathbf{B}/\mathbf{A}}$ and $\beta(\mathbf{x}) T_{\mathbf{A}/\mathbf{B}}^*$; the canonical basis of $W_{\mathbf{N}}$ (respectively $W_{\mathbf{N}}^*$) then consists of the $\delta_{(\mathbf{k})}$ for $\mathbf{k} \in \mathbb{Z}^n/\mathbf{N} \mathbb{Z}^n$ [respectively $\delta_{(\mathbf{k}^*)}$ for $\mathbf{k}^* \in \mathbb{Z}^n/\mathbf{N}^T \mathbb{Z}^n$];

(2) as vector spaces of *weight vectors* for the $|\det \mathbf{N}|$ δ -functions involved in the expression for $T_{\mathbf{B}/\mathbf{A}}$ (respectively $T_{\mathbf{A}/\mathbf{B}}^*$); the canonical basis of $W_{\mathbf{N}}$ (respectively $W_{\mathbf{N}}^*$) consists of weight vectors $\mathbf{u}_{\mathbf{k}}$ (respectively $\mathbf{v}_{\mathbf{k}^*}$) giving weight 1 to element $\mathbf{k}$ (respectively $\mathbf{k}^*$) and 0 to the others.

These two spaces are said to be ‘isomorphic’ (a relation denoted $\cong$), the isomorphism being given by the one-to-one correspondence:

$$\begin{aligned} \omega = \sum_{\mathbf{k}} \psi(\mathbf{k}) \delta_{(\mathbf{k})} &\leftrightarrow \psi = \sum_{\mathbf{k}} \psi(\mathbf{k}) \mathbf{u}_{\mathbf{k}} \\ \Omega = \sum_{\mathbf{k}^*} \Psi(\mathbf{k}^*) \delta_{(\mathbf{k}^*)} &\leftrightarrow \Psi = \sum_{\mathbf{k}^*} \Psi(\mathbf{k}^*) \mathbf{v}_{\mathbf{k}^*}. \end{aligned}$$

The second viewpoint will be adopted, as it involves only linear algebra. However, it is most helpful to keep the first one in mind and to think of the data or results of a discrete Fourier transform as representing (through their sets of unique weights) two periodic lattice distributions related by the full, distribution-theoretic Fourier transform.

We therefore view $W_{\mathbf{N}}$ (respectively $W_{\mathbf{N}}^*$) as the vector space of complex-valued functions over the finite residual lattice $\Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$ (respectively $\Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$) and write:

$$\begin{aligned} W_{\mathbf{N}} &\cong L(\Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}) \cong L(\mathbb{Z}^n/\mathbf{N} \mathbb{Z}^n) \\ W_{\mathbf{N}}^* &\cong L(\Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*) \cong L(\mathbb{Z}^n/\mathbf{N}^T \mathbb{Z}^n) \end{aligned}$$

since a vector such as ψ is in fact the function $\mathbf{k} \mapsto \psi(\mathbf{k})$.

The two spaces $W_{\mathbf{N}}$ and $W_{\mathbf{N}}^*$ may be equipped with the following Hermitian inner products:

$$\begin{aligned} (\varphi, \psi)_W &= \sum_{\mathbf{k}} \overline{\varphi(\mathbf{k})} \psi(\mathbf{k}) \\ (\Phi, \Psi)_{W^*} &= \sum_{\mathbf{k}^*} \overline{\Phi(\mathbf{k}^*)} \Psi(\mathbf{k}^*), \end{aligned}$$

which makes each of them into a *Hilbert space*. The canonical bases $\{\mathbf{u}_{\mathbf{k}} | \mathbf{k} \in \mathbb{Z}^n/\mathbf{N} \mathbb{Z}^n\}$ and $\{\mathbf{v}_{\mathbf{k}^*} | \mathbf{k}^* \in \mathbb{Z}^n/\mathbf{N}^T \mathbb{Z}^n\}$ and $W_{\mathbf{N}}$ and $W_{\mathbf{N}}^*$ are *orthonormal* for their respective product.

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1.3.2.7.4. Matrix representation of the discrete Fourier transform (DFT)

By virtue of definitions (i) and (ii),

$$\begin{aligned}\mathcal{F}(\mathbf{N})\mathbf{v}_{k^*} &= \frac{1}{|\det \mathbf{N}|} \sum_k \exp[-2\pi i k^* \cdot (\mathbf{N}^{-1}k)] \mathbf{u}_k \\ \tilde{\mathcal{F}}(\mathbf{N})\mathbf{u}_k &= \sum_{k^*} \exp[+2\pi i k^* \cdot (\mathbf{N}^{-1}k)] \mathbf{v}_{k^*}\end{aligned}$$

so that $\mathcal{F}(\mathbf{N})$ and $\tilde{\mathcal{F}}(\mathbf{N})$ may be represented, in the canonical bases of $W_{\mathbf{N}}$ and $W_{\mathbf{N}}^*$, by the following matrices:

$$\begin{aligned}[\mathcal{F}(\mathbf{N})]_{kk^*} &= \frac{1}{|\det \mathbf{N}|} \exp[-2\pi i k^* \cdot (\mathbf{N}^{-1}k)] \\ [\tilde{\mathcal{F}}(\mathbf{N})]_{k^*k} &= \exp[+2\pi i k^* \cdot (\mathbf{N}^{-1}k)].\end{aligned}$$

When $\mathbf{N}$ is symmetric, $\mathbb{Z}^n/\mathbf{N}\mathbb{Z}^n$ and $\mathbb{Z}^n/\mathbf{N}^T\mathbb{Z}^n$ may be identified in a natural manner, and the above matrices are symmetric.

When $\mathbf{N}$ is diagonal, say $\mathbf{N} = \text{diag}(\nu_1, \nu_2, \dots, \nu_n)$, then the tensor product structure of the full multidimensional Fourier transform (Section 1.3.2.4.2.4)

$$\mathcal{F}_{\mathbf{x}} = \mathcal{F}_{x_1} \otimes \mathcal{F}_{x_2} \otimes \dots \otimes \mathcal{F}_{x_n}$$

gives rise to a tensor product structure for the DFT matrices. The tensor product of matrices is defined as follows:

$$\mathbf{A} \otimes \mathbf{B} = \begin{pmatrix} a_{11}\mathbf{B} & \dots & a_{1n}\mathbf{B} \\ \vdots & & \vdots \\ a_{n1}\mathbf{B} & \dots & a_{nn}\mathbf{B} \end{pmatrix}.$$

Let the index vectors k and k^* be ordered in the same way as the elements in a Fortran array, e.g. for k with k_1 increasing fastest, k_2 next fastest, $\dots$, k_n slowest; then

$$\mathcal{F}(\mathbf{N}) = \mathcal{F}(\nu_1) \otimes \mathcal{F}(\nu_2) \otimes \dots \otimes \mathcal{F}(\nu_n),$$

where

$$[\mathcal{F}(\nu_j)]_{k_j, k_j^*} = \frac{1}{\nu_j} \exp\left(-2\pi i \frac{k_j^* k_j}{\nu_j}\right),$$

and

$$\tilde{\mathcal{F}}(\mathbf{N}) = \tilde{\mathcal{F}}(\nu_1) \otimes \tilde{\mathcal{F}}(\nu_2) \otimes \dots \otimes \tilde{\mathcal{F}}(\nu_n),$$

where

$$[\tilde{\mathcal{F}}(\nu_j)]_{k_j^*, k_j} = \exp\left(+2\pi i \frac{k_j^* k_j}{\nu_j}\right).$$

1.3.2.7.5. Properties of the discrete Fourier transform

The DFT inherits most of the properties of the Fourier transforms, but with certain numerical factors ('Jacobians') due to the transition from continuous to discrete measure.

(1) *Linearity* is obvious.

(2) *Shift property.* If $(\tau_a \psi)(k) = \psi(k - a)$ and $(\tau_a^* \Psi)(k^*) = \Psi(k^* - a^*)$, where subtraction takes place by modular vector arithmetic in $\mathbb{Z}^n/\mathbf{N}\mathbb{Z}^n$ and $\mathbb{Z}^n/\mathbf{N}^T\mathbb{Z}^n$, respectively, then the following identities hold:

$$\begin{aligned}\tilde{\mathcal{F}}(\mathbf{N})[\tau_a \psi](k^*) &= \exp[+2\pi i k^* \cdot (\mathbf{N}^{-1}a)] \tilde{\mathcal{F}}(\mathbf{N})[\psi](k^*) \\ \mathcal{F}(\mathbf{N})[\tau_a^* \Psi](k) &= \exp[-2\pi i k \cdot (\mathbf{N}^{-1}a^*)] \mathcal{F}(\mathbf{N})[\Psi](k).\end{aligned}$$

(3) *Differentiation identities.* Let vectors ψ and Ψ be constructed from $\varphi^0 \in \mathcal{E}(\mathbb{R}^n)$ as in Section 1.3.2.7.3, hence be related by the DFT. If $D^{\mathbf{p}}\psi$ designates the vector of sample values of $D_{\mathbf{x}}^{\mathbf{p}}\varphi^0$ at the points of $\Lambda_{\mathbf{B}}/\Lambda_{\mathbf{A}}$, and $D^{\mathbf{p}}\Psi$ the vector of values of $D_{\xi}^{\mathbf{p}}\Phi^0$ at points of

$\Lambda_{\mathbf{A}}^*/\Lambda_{\mathbf{B}}^*$, then for all multi-indices $\mathbf{p} = (p_1, p_2, \dots, p_n)$

$$\begin{aligned}(D^{\mathbf{p}}\psi)(k) &= \tilde{\mathcal{F}}(\mathbf{N})[(+2\pi i k^*)^{\mathbf{p}}\Psi](k) \\ (D^{\mathbf{p}}\Psi)(k^*) &= \mathcal{F}(\mathbf{N})[(-2\pi i k)^{\mathbf{p}}\psi](k^*)\end{aligned}$$

or equivalently

$$\begin{aligned}\tilde{\mathcal{F}}(\mathbf{N})[D^{\mathbf{p}}\psi](k^*) &= (+2\pi i k^*)^{\mathbf{p}}\Psi(k^*) \\ \mathcal{F}(\mathbf{N})[D^{\mathbf{p}}\Psi](k) &= (-2\pi i k)^{\mathbf{p}}\psi(k).\end{aligned}$$

(4) *Convolution property.* Let $\varphi \in W_{\mathbf{N}}$ and $\Phi \in W_{\mathbf{N}}^*$ (respectively ψ and Ψ) be related by the DFT, and define

$$\begin{aligned}(\varphi * \psi)(k) &= \sum_{k' \in \mathbb{Z}^n/\mathbf{N}\mathbb{Z}^n} \varphi(k') \psi(k - k') \\ (\Phi * \Psi)(k^*) &= \sum_{k'^* \in \mathbb{Z}^n/\mathbf{N}^T\mathbb{Z}^n} \Phi(k'^*) \Psi(k^* - k'^*).\end{aligned}$$

Then

$$\begin{aligned}\tilde{\mathcal{F}}(\mathbf{N})[\Phi * \Psi](k) &= |\det \mathbf{N}| \varphi(k) \psi(k) \\ \mathcal{F}(\mathbf{N})[\varphi * \psi](k^*) &= \Phi(k^*) \Psi(k^*)\end{aligned}$$

and

$$\begin{aligned}\tilde{\mathcal{F}}(\mathbf{N})[\varphi \times \psi](k^*) &= \frac{1}{|\det \mathbf{N}|} (\Phi * \Psi)(k^*) \\ \mathcal{F}(\mathbf{N})[\Phi \times \Psi](k) &= (\varphi * \psi)(k).\end{aligned}$$

Since addition on $\mathbb{Z}^n/\mathbf{N}\mathbb{Z}^n$ and $\mathbb{Z}^n/\mathbf{N}^T\mathbb{Z}^n$ is modular, this type of convolution is called *cyclic convolution*.

(5) *Parseval/Plancherel property.* If $\varphi, \psi, \Phi, \Psi$ are as above, then

$$\begin{aligned}(\mathcal{F}(\mathbf{N})[\Phi], \mathcal{F}(\mathbf{N})[\Psi])_W &= \frac{1}{|\det \mathbf{N}|} (\Phi, \Psi)_{W^*} \\ (\tilde{\mathcal{F}}(\mathbf{N})[\varphi], \tilde{\mathcal{F}}(\mathbf{N})[\psi])_W &= \frac{1}{|\det \mathbf{N}|} (\varphi, \psi)_W.\end{aligned}$$

(6) *Period 4.* When $\mathbf{N}$ is symmetric, so that the ranges of indices k and k^* can be identified, it makes sense to speak of powers of $\mathcal{F}(\mathbf{N})$ and $\tilde{\mathcal{F}}(\mathbf{N})$. Then the 'standardized' matrices $(1/|\det \mathbf{N}|^{1/2})\mathcal{F}(\mathbf{N})$ and $(1/|\det \mathbf{N}|^{1/2})\tilde{\mathcal{F}}(\mathbf{N})$ are *unitary* matrices whose fourth power is the identity matrix (Section 1.3.2.4.3.4); their eigenvalues are therefore ± 1 and $\pm i$.

1.3.3. Numerical computation of the discrete Fourier transform

1.3.3.1. Introduction

The Fourier transformation's most remarkable property is undoubtedly that of turning convolution into multiplication. As distribution theory has shown, other valuable properties – such as the shift property, the conversion of differentiation into multiplication by monomials, and the duality between periodicity and sampling – are special instances of the convolution theorem.

This property is exploited in many areas of applied mathematics and engineering (Campbell & Foster, 1948; Sneddon, 1951; Champeney, 1973; Bracewell, 1986). For example, the passing of a signal through a linear filter, which results in its being convolved with the response of the filter to a δ -function 'impulse', may be modelled as a multiplication of the signal's transform by the transform of the impulse response (also called transfer function). Similarly, the solution of systems of partial differential equations may be turned by Fourier transformation into a division problem for distributions. In both cases, the formulations obtained after Fourier transformation are considerably simpler than the initial ones, and lend themselves to constructive solution techniques.

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Whenever the functions to which the Fourier transform is applied are band-limited, or can be well approximated by band-limited functions, the discrete Fourier transform (DFT) provides a means of constructing explicit numerical solutions to the problems at hand. A great variety of investigations in physics, engineering and applied mathematics thus lead to DFT calculations, to such a degree that, at the time of writing, about 50% of all supercomputer CPU time is alleged to be spent calculating DFTs.

The straightforward use of the defining formulae for the DFT leads to calculations of size N^2 for N sample points, which become unfeasible for any but the smallest problems. Much ingenuity has therefore been exerted on the design and implementation of faster algorithms for calculating the DFT (McClellan & Rader, 1979; Nussbaumer, 1981; Blahut, 1985; Brigham, 1988). The most famous is that of Cooley & Tukey (1965) which heralded the age of digital signal processing. However, it had been preceded by the prime factor algorithm of Good (1958, 1960), which has lately been the basis of many new developments. Recent historical research (Goldstine, 1977, pp. 249–253; Heideman *et al.*, 1984) has shown that Gauss essentially knew the Cooley–Tukey algorithm as early as 1805 (before Fourier's 1807 work on harmonic analysis!); while it has long been clear that Dirichlet knew of the basis of the prime factor algorithm and used it extensively in his theory of multiplicative characters [see *e.g.* Chapter I of Ayoub (1963), and Chapters 6 and 8 of Apostol (1976)]. Thus the computation of the DFT, far from being a purely technical and rather narrow piece of specialized numerical analysis, turns out to have very rich connections with such central areas of pure mathematics as number theory (algebraic and analytic), the representation theory of certain Lie groups and coding theory – to list only a few. The interested reader may consult Auslander & Tolimieri (1979); Auslander, Feig & Winograd (1982, 1984); Auslander & Tolimieri (1985); Tolimieri (1985).

One-dimensional algorithms are examined first. The Sande mixed-radix version of the Cooley–Tukey algorithm only calls upon the additive structure of congruence classes of integers. The prime factor algorithm of Good begins to exploit some of their multiplicative structure, and the use of relatively prime factors leads to a stronger factorization than that of Sande. Fuller use of the multiplicative structure, *via* the group of units, leads to the Rader algorithm; and the factorization of short convolutions then yields the Winograd algorithms.

Multidimensional algorithms are at first built as tensor products of one-dimensional elements. The problem of factoring the DFT in several dimensions simultaneously is then examined. The section ends with a survey of attempts at formalizing the interplay between algorithm structure and computer architecture for the purpose of automating the design of optimal DFT code.

It was originally intended to incorporate into this section a survey of all the basic notions and results of abstract algebra which are called upon in the course of these developments, but time limitations have made this impossible. This material, however, is adequately covered by the first chapter of Tolimieri *et al.* (1989) in a form tailored for the same purposes. Similarly, the inclusion of numerous detailed examples of the algorithms described here has had to be postponed to a later edition, but an abundant supply of such examples may be found in the signal processing literature, for instance in the books by McClellan & Rader (1979), Blahut (1985), and Tolimieri *et al.* (1989).

1.3.3.2. One-dimensional algorithms

Throughout this section we will denote by $e(t)$ the expression $\exp(2\pi it)$, $t \in \mathbb{R}$. The mapping $t \mapsto e(t)$ has the following properties:

$$\begin{aligned} e(t_1 + t_2) &= e(t_1)e(t_2) \\ e(-t) &= \overline{e(t)} = [e(t)]^{-1} \\ e(t) &= 1 \Leftrightarrow t \in \mathbb{Z}. \end{aligned}$$

Thus e defines an isomorphism between the additive group $\mathbb{R}/\mathbb{Z}$ (the reals modulo the integers) and the multiplicative group of complex numbers of modulus 1. It follows that the mapping $\ell \mapsto e(\ell/N)$, where $\ell \in \mathbb{Z}$ and N is a positive integer, defines an isomorphism between the one-dimensional residual lattice $\mathbb{Z}/N\mathbb{Z}$ and the multiplicative group of N th roots of unity.

The DFT on N points then relates vectors $\mathbf{X}$ and $\mathbf{X}^*$ in W and W^* through the linear transformations:

$$\begin{aligned} F(N) : \quad X(k) &= \frac{1}{N} \sum_{k^* \in \mathbb{Z}/N\mathbb{Z}} X^*(k^*) e(-k^*k/N) \\ \bar{F}(N) : \quad X^*(k^*) &= \sum_{k \in \mathbb{Z}/N\mathbb{Z}} X(k) e(k^*k/N). \end{aligned}$$

1.3.3.2.1. The Cooley–Tukey algorithm

The presentation of Gentleman & Sande (1966) will be followed first [see also Cochran *et al.* (1967)]. It will then be reinterpreted in geometric terms which will prepare the way for the treatment of multidimensional transforms in Section 1.3.3.3.

Suppose that the number of sample points N is composite, say $N = N_1 N_2$. We may write k to the base N_1 and k^* to the base N_2 as follows:

$$\begin{aligned} k &= k_1 + N_1 k_2 & k_1 &\in \mathbb{Z}/N_1\mathbb{Z}, & k_2 &\in \mathbb{Z}/N_2\mathbb{Z} \\ k^* &= k_1^* + k_1^* N_2 & k_1^* &\in \mathbb{Z}/N_1\mathbb{Z}, & k_2^* &\in \mathbb{Z}/N_2\mathbb{Z}. \end{aligned}$$

The defining relation for $\bar{F}(N)$ may then be written:

$$\begin{aligned} X^*(k_2^* + k_1^* N_2) &= \sum_{k_1 \in \mathbb{Z}/N_1\mathbb{Z}} \sum_{k_2 \in \mathbb{Z}/N_2\mathbb{Z}} X(k_1 + N_1 k_2) \\ &\quad \times e \left[\frac{(k_2^* + k_1^* N_2)(k_1 + N_1 k_2)}{N_1 N_2} \right]. \end{aligned}$$

The argument of $e[\cdot]$ may be expanded as

$$\frac{k_2^* k_1}{N} + \frac{k_1^* k_1}{N_1} + \frac{k_2^* k_2}{N_2} + k_1^* k_2,$$

and the last summand, being an integer, may be dropped:

$$\begin{aligned} X^*(k_2^* + k_1^* N_2) &= \sum_{k_1} \left\{ e \left(\frac{k_2^* k_1}{N} \right) \left[\sum_{k_2} X(k_1 + N_1 k_2) e \left(\frac{k_2^* k_2}{N_2} \right) \right] \right\} \\ &\quad \times e \left(\frac{k_1^* k_1}{N_1} \right). \end{aligned}$$

This computation may be decomposed into five stages, as follows:

- (i) form the N_1 vectors $\mathbf{Y}_{k_1}$ of length N_2 by the prescription

$$Y_{k_1}(k_2) = X(k_1 + N_1 k_2), \quad k_1 \in \mathbb{Z}/N_1\mathbb{Z}, \quad k_2 \in \mathbb{Z}/N_2\mathbb{Z};$$

- (ii) calculate the N_1 transforms $\mathbf{Y}_{k_1}^*$ on N_2 points:

$$\mathbf{Y}_{k_1}^* = \bar{F}(N_2)[\mathbf{Y}_{k_1}], \quad k_1 \in \mathbb{Z}/N_1\mathbb{Z};$$

- (iii) form the N_2 vectors $\mathbf{Z}_{k_2^*}$ of length N_1 by the prescription

$$\mathbf{Z}_{k_2^*}(k_1) = e \left(\frac{k_2^* k_1}{N} \right) Y_{k_1}^*(k_2^*), \quad k_1 \in \mathbb{Z}/N_1\mathbb{Z}, \quad k_2^* \in \mathbb{Z}/N_2\mathbb{Z};$$

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(iv) calculate the N_2 transforms $\mathbf{Z}_{k_2}^*$ on N_1 points:

$$\mathbf{Z}_{k_2}^* = \bar{F}(N_1)[\mathbf{Z}_{k_2}^*], \quad k_2 \in \mathbb{Z}/N_2\mathbb{Z};$$

(v) collect $X^*(k_2^* + k_1^*N_2)$ as $Z_{k_1}^*(k_1^*)$.

If the intermediate transforms in stages (ii) and (iv) are performed *in place*, i.e. with the results overwriting the data, then at stage (v) the result $X^*(k_2^* + k_1^*N_2)$ will be found at address $k_1^* + N_1k_2^*$. This phenomenon is called *scrambling* by ‘digit reversal’, and stage (v) is accordingly known as *unscrambling*.

The initial N -point transform $\bar{F}(N)$ has thus been performed as N_1 transforms $\bar{F}(N_2)$ on N_2 points, followed by N_2 transforms $\bar{F}(N_1)$ on N_1 points, thereby reducing the arithmetic cost from $(N_1N_2)^2$ to $N_1N_2(N_1 + N_2)$. The phase shifts applied at stage (iii) are traditionally called ‘twiddle factors’, and the transposition between k_1 and k_2^* can be performed by the fast recursive technique of Eklundh (1972). Clearly, this procedure can be applied recursively if N_1 and N_2 are themselves composite, leading to an overall arithmetic cost of order $N \log N$ if N has no large prime factors.

The Cooley–Tukey factorization may also be derived from a geometric rather than arithmetic argument. The decomposition $k = k_1 + N_1k_2$ is associated to a geometric partition of the residual lattice $\mathbb{Z}/N\mathbb{Z}$ into N_1 copies of $\mathbb{Z}/N_2\mathbb{Z}$, each translated by $k_1 \in \mathbb{Z}/N_1\mathbb{Z}$ and ‘blown up’ by a factor N_1 . This partition in turn induces a (direct sum) decomposition of $\mathbf{X}$ as

$$\mathbf{X} = \sum_{k_1} \mathbf{X}_{k_1},$$

where

$$\begin{aligned} X_{k_1}(k) &= X(k) \quad \text{if } k \equiv k_1 \pmod{N_1}, \\ &= 0 \quad \text{otherwise.} \end{aligned}$$

According to (i), $\mathbf{X}_{k_1}$ is related to $\mathbf{Y}_{k_1}$ by *decimation by N_1 and offset by k_1* . By Section 1.3.2.7.2, $\bar{F}(N)[\mathbf{X}_{k_1}]$ is related to $\bar{F}(N_2)[\mathbf{Y}_{k_1}]$ by *periodization by N_2 and phase shift by $e(k^*k_1/N)$* , so that

$$X^*(k^*) = \sum_{k_1} e\left(\frac{k^*k_1}{N}\right) Y_{k_1}^*(k_2^*),$$

the periodization by N_2 being reflected by the fact that $Y_{k_1}^*$ does not depend on k_1^* . Writing $k^* = k_2^* + k_1^*N_2$ and expanding k^*k_1 shows that the phase shift contains both the twiddle factor $e(k_2^*k_1/N)$ and the kernel $e(k_1^*k_1/N_1)$ of $\bar{F}(N_1)$. The Cooley–Tukey algorithm is thus naturally associated to the coset decomposition of a lattice modulo a sublattice (Section 1.3.2.7.2).

It is readily seen that essentially the same factorization can be obtained for $F(N)$, up to the complex conjugation of the twiddle factors. The normalizing constant $1/N$ arises from the normalizing constants $1/N_1$ and $1/N_2$ in $F(N_1)$ and $F(N_2)$, respectively.

Factors of 2 are particularly simple to deal with and give rise to a characteristic computational structure called a ‘butterfly loop’. If $N = 2M$, then two options exist:

(a) using $N_1 = 2$ and $N_2 = M$ leads to collecting the even-numbered coordinates of $\mathbf{X}$ into $\mathbf{Y}_0$ and the odd-numbered coordinates into $\mathbf{Y}_1$

$$\begin{aligned} Y_0(k_2) &= X(2k_2), & k_2 &= 0, \dots, M-1, \\ Y_1(k_2) &= X(2k_2+1), & k_2 &= 0, \dots, M-1, \end{aligned}$$

and writing:

$$\begin{aligned} X^*(k_2^*) &= Y_0^*(k_2^*) + e(k_2^*/N) Y_1^*(k_2^*), \\ k_2^* &= 0, \dots, M-1; \\ X^*(k_2^* + M) &= Y_0^*(k_2^*) - e(k_2^*/N) Y_1^*(k_2^*), \\ k_2^* &= 0, \dots, M-1. \end{aligned}$$

This is the original version of Cooley & Tukey, and the process of formation of $\mathbf{Y}_0$ and $\mathbf{Y}_1$ is referred to as ‘decimation in time’ (i.e. decimation along the *data* index $\mathbf{k}$).

(b) using $N_1 = M$ and $N_2 = 2$ leads to forming

$$\begin{aligned} Z_0(k_1) &= X(k_1) + X(k_1 + M), & k_1 &= 0, \dots, M-1, \\ Z_1(k_1) &= [X(k_1) - X(k_1 + M)]e\left(\frac{k_1}{N}\right), & k_1 &= 0, \dots, M-1, \end{aligned}$$

then obtaining separately the even-numbered and odd-numbered components of $\mathbf{X}^*$ by transforming $\mathbf{Z}_0$ and $\mathbf{Z}_1$:

$$\begin{aligned} X^*(2k_1^*) &= Z_0^*(k_1^*), & k_1^* &= 0, \dots, M-1; \\ X^*(2k_1^* + 1) &= Z_1^*(k_1^*), & k_1^* &= 0, \dots, M-1. \end{aligned}$$

This version is due to Sande (Gentleman & Sande, 1966), and the process of separately obtaining even-numbered and odd-numbered results has led to its being referred to as ‘decimation in frequency’ (i.e. decimation along the *result* index k^*).

By repeated factoring of the number N of sample points, the calculation of $F(N)$ and $\bar{F}(N)$ can be reduced to a succession of stages, the smallest of which operate on single prime factors of N . The reader is referred to Gentleman & Sande (1966) for a particularly lucid analysis of the programming considerations which help implement this factorization efficiently; see also Singleton (1969). Powers of two are often grouped together into factors of 4 or 8, which are advantageous in that they require fewer complex multiplications than the repeated use of factors of 2. In this approach, large prime factors P are detrimental, since they require a full P^2 -size computation according to the defining formula.

1.3.3.2.2. The Good (or prime factor) algorithm

1.3.3.2.2.1. Ring structure on $\mathbb{Z}/N\mathbb{Z}$

The set $\mathbb{Z}/N\mathbb{Z}$ of congruence classes of integers modulo an integer N [see e.g. Apostol (1976), Chapter 5] inherits from $\mathbb{Z}$ not only the additive structure used in deriving the Cooley–Tukey factorization, but also a *multiplicative* structure in which the product of two congruence classes mod N is uniquely defined as the class of the ordinary product (in $\mathbb{Z}$) of representatives of each class. The multiplication can be distributed over addition in the usual way, endowing $\mathbb{Z}/N\mathbb{Z}$ with the structure of a *commutative ring*.

If N is composite, the ring $\mathbb{Z}/N\mathbb{Z}$ has *zero divisors*. For example, let $N = N_1N_2$, let $n_1 \equiv N_1 \pmod{N}$, and let $n_2 \equiv N_2 \pmod{N}$: then $n_1n_2 \equiv 0 \pmod{N}$. In the general case, a product of non-zero elements will be zero whenever these elements collect together all the factors of N . These circumstances give rise to a fundamental theorem in the theory of commutative rings, the *Chinese Remainder Theorem* (CRT), which will now be stated and proved [see Apostol (1976), Chapter 5; Schroeder (1986), Chapter 16].

1.3.3.2.2.2. The Chinese remainder theorem

Let $N = N_1N_2 \dots N_d$ be factored into a product of pairwise coprime integers, so that $\text{g.c.d.}(N_i, N_j) = 1$ for $i \neq j$. Then the system of congruence equations

$$\ell \equiv \ell_j \pmod{N_j}, \quad j = 1, \dots, d,$$

has a unique solution $\ell \pmod{N}$. In other words, each $\ell \in \mathbb{Z}/N\mathbb{Z}$ is

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associated in a one-to-one fashion to the d -tuple $(\ell_1, \ell_2, \dots, \ell_d)$ of its residue classes in $\mathbb{Z}/N_1\mathbb{Z}, \mathbb{Z}/N_2\mathbb{Z}, \dots, \mathbb{Z}/N_d\mathbb{Z}$.

The proof of the CRT goes as follows. Let

$$Q_j = \frac{N}{N_j} = \prod_{i \neq j} N_i.$$

Since g.c.d. $(N_j, Q_j) = 1$ there exist integers n_j and q_j such that

$$n_j N_j + q_j Q_j = 1, \quad j = 1, \dots, d,$$

then the integer

$$\ell = \sum_{i=1}^d \ell_i q_i Q_i \mod N$$

is the solution. Indeed,

$$\ell \equiv \ell_j q_j Q_j \mod N_j$$

because all terms with $i \neq j$ contain N_j as a factor; and

$$q_j Q_j \equiv 1 \mod N_j$$

by the defining relation for q_j .

It may be noted that

$$\begin{aligned} (q_i Q_i)(q_j Q_j) &\equiv 0 \mod N \text{ for } i \neq j, \\ (q_j Q_j)^2 &\equiv q_j Q_j \mod N, \quad j = 1, \dots, d, \end{aligned}$$

so that the $q_j Q_j$ are mutually orthogonal *idempotents* in the ring $\mathbb{Z}/N\mathbb{Z}$, with properties formally similar to those of mutually orthogonal *projectors onto subspaces* in linear algebra. The analogy is exact, since by virtue of the CRT the ring $\mathbb{Z}/N\mathbb{Z}$ may be considered as the direct product

$$\mathbb{Z}/N_1\mathbb{Z} \times \mathbb{Z}/N_2\mathbb{Z} \times \dots \times \mathbb{Z}/N_d\mathbb{Z}$$

via the two mutually inverse mappings:

- (i) $\ell \mapsto (\ell_1, \ell_2, \dots, \ell_d)$ by $\ell \equiv \ell_j \mod N_j$ for each j ;
- (ii) $(\ell_1, \ell_2, \dots, \ell_d) \mapsto \ell$ by $\ell = \sum_{i=1}^d \ell_i q_i Q_i \mod N$.

The mapping defined by (ii) is sometimes called the ‘CRT reconstruction’ of ℓ from the ℓ_j .

These two mappings have the property of sending sums to sums and products to products, i.e.:

- (i) $\ell + \ell' \mapsto (\ell_1 + \ell'_1, \ell_2 + \ell'_2, \dots, \ell_d + \ell'_d)$
 $\ell \ell' \mapsto (\ell_1 \ell'_1, \ell_2 \ell'_2, \dots, \ell_d \ell'_d)$
- (ii) $(\ell_1 + \ell'_1, \ell_2 + \ell'_2, \dots, \ell_d + \ell'_d) \mapsto \ell + \ell'$
 $(\ell_1 \ell'_1, \ell_2 \ell'_2, \dots, \ell_d \ell'_d) \mapsto \ell \ell'$

(the last proof requires using the properties of the idempotents $q_j Q_j$). This may be described formally by stating that the CRT establishes a *ring isomorphism*:

$$\mathbb{Z}/N\mathbb{Z} \cong (\mathbb{Z}/N_1\mathbb{Z}) \times \dots \times (\mathbb{Z}/N_d\mathbb{Z}).$$

1.3.3.2.3. The prime factor algorithm

The CRT will now be used to factor the N -point DFT into a tensor product of d transforms, the j th of length N_j .

Let the indices k and k^* be subjected to the following mappings:

- (i) $k \mapsto (k_1, k_2, \dots, k_d), k_j \in \mathbb{Z}/N_j\mathbb{Z}$, by $k_j \equiv k \mod N_j$ for each j , with reconstruction formula

$$k = \sum_{i=1}^d k_i q_i Q_i \mod N;$$

- (ii) $k^* \mapsto (k_1^*, k_2^*, \dots, k_d^*), k_j^* \in \mathbb{Z}/N_j\mathbb{Z}$, by $k_j^* \equiv q_j k^* \mod N_j$ for each j , with reconstruction formula

$$k^* = \sum_{i=1}^d k_i^* Q_i \mod N.$$

Then

$$\begin{aligned} k^* k &= \left(\sum_{i=1}^d k_i^* Q_i \right) \left(\sum_{j=1}^d k_j q_j Q_j \right) \mod N \\ &= \sum_{i,j=1}^d k_i^* k_j q_j Q_i Q_j \mod N. \end{aligned}$$

Cross terms with $i \neq j$ vanish since they contain all the factors of N , hence

$$\begin{aligned} k^* k &= \sum_{j=1}^d q_j Q_j^2 k_j^* k_j \mod N \\ &= \sum_{j=1}^d (1 - n_j N_j) Q_j k_j^* k_j \mod N. \end{aligned}$$

Dividing by N , which may be written as $N_j Q_j$ for each j , yields

$$\begin{aligned} \frac{k^* k}{N} &= \sum_{j=1}^d (1 - n_j N_j) \frac{Q_j}{N_j Q_j} k_j^* k_j \mod 1 \\ &= \sum_{j=1}^d \left(\frac{1}{N_j} - n_j \right) k_j^* k_j \mod 1, \end{aligned}$$

and hence

$$\frac{k^* k}{N} \equiv \sum_{j=1}^d \frac{k_j^* k_j}{N_j} \mod 1.$$

Therefore, by the multiplicative property of $e(\cdot)$,

$$e\left(\frac{k^* k}{N}\right) \equiv \bigotimes_{j=1}^d e\left(\frac{k_j^* k_j}{N_j}\right).$$

Let $\mathbf{X} \in L(\mathbb{Z}/N\mathbb{Z})$ be described by a one-dimensional array $X(k)$ indexed by k . The index mapping (i) turns $\mathbf{X}$ into an element of $L(\mathbb{Z}/N_1\mathbb{Z} \times \dots \times \mathbb{Z}/N_d\mathbb{Z})$ described by a d -dimensional array $X(k_1, \dots, k_d)$; the latter may be transformed by $\bar{F}(N_1) \otimes \dots \otimes \bar{F}(N_d)$ into a new array $X^*(k_1^*, k_2^*, \dots, k_d^*)$. Finally, the one-dimensional array of results $X^*(k^*)$ will be obtained by reconstructing k^* according to (ii).

The prime factor algorithm, like the Cooley–Tukey algorithm, reindexes a 1D transform to turn it into d separate transforms, but the use of coprime factors and CRT index mapping leads to the further gain that *no twiddle factors* need to be applied between the successive transforms (see Good, 1971). This makes up for the cost of the added complexity of the CRT index mapping.

The natural factorization of N for the prime factor algorithm is thus its factorization into prime powers: $\bar{F}(N)$ is then the tensor product of separate transforms (one for each prime power factor $N_j = p_j^{v_j}$) whose results can be reassembled without twiddle factors. The separate factors p_j within each N_j must then be dealt with by another algorithm (e.g. Cooley–Tukey, which does require twiddle factors). Thus, the DFT on a prime number of points remains undecomposable.

1.3.3.2.3. The Rader algorithm

The previous two algorithms essentially reduce the calculation of the DFT on N points for N composite to the calculation of smaller DFTs on prime numbers of points, the latter remaining irreducible. However, Rader (1968) showed that the p -point DFT for p an odd

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prime can itself be factored by invoking some extra arithmetic structure present in $\mathbb{Z}/p\mathbb{Z}$.

1.3.3.2.3.1. N an odd prime

The ring $\mathbb{Z}/p\mathbb{Z} = \{0, 1, 2, \dots, p-1\}$ has the property that its $p-1$ non-zero elements, called *units*, form a *multiplicative group* $U(p)$. In particular, all units $r \in U(p)$ have a unique multiplicative inverse in $\mathbb{Z}/p\mathbb{Z}$, i.e. a unit $s \in U(p)$ such that $rs \equiv 1 \pmod{p}$. This endows $\mathbb{Z}/p\mathbb{Z}$ with the structure of a *finite field*.

Furthermore, $U(p)$ is a *cyclic group*, i.e. consists of the successive powers $g^m \pmod{p}$ of a generator g called a *primitive root mod p* (such a g may not be unique, but it always exists). For instance, for $p = 7$, $U(7) = \{1, 2, 3, 4, 5, 6\}$ is generated by $g = 3$, whose successive powers mod 7 are:

$$g^0 = 1, \quad g^1 = 3, \quad g^2 = 2, \quad g^3 = 6, \quad g^4 = 4, \quad g^5 = 5$$

[see Apostol (1976), Chapter 10].

The basis of Rader's algorithm is to bring to light a hidden regularity in the matrix $F(p)$ by permuting the basis vectors $\mathbf{u}_k$ and $\mathbf{v}_{k^*}$ of $L(\mathbb{Z}/p\mathbb{Z})$ as follows:

$$\begin{aligned} \mathbf{u}'_0 &= \mathbf{u}_0 \\ \mathbf{u}'_m &= \mathbf{u}_k \quad \text{with } k = g^m, \quad m = 1, \dots, p-1; \\ \mathbf{v}'_0 &= \mathbf{v}_0 \\ \mathbf{v}'_{m^*} &= \mathbf{v}_{k^*} \quad \text{with } k^* = g^{m^*}, \quad m^* = 1, \dots, p-1; \end{aligned}$$

where g is a primitive root mod p .

With respect to these new bases, the matrix representing $\bar{F}(p)$ will have the following elements:

$$\begin{aligned} \text{element } (0, 0) &= 1 \\ \text{element } (0, m+1) &= 1 \quad \text{for all } m = 0, \dots, p-2, \\ \text{element } (m^*+1, 0) &= 1 \quad \text{for all } m^* = 0, \dots, p-2, \\ \text{element } (m^*+1, m+1) &= e\left(\frac{k^*k}{p}\right) \\ &= e(g^{(m^*+m)/p}) \\ &\quad \text{for all } m^* = 0, \dots, p-2. \end{aligned}$$

Thus the 'core' $\bar{C}(p)$ of matrix $\bar{F}(p)$, of size $(p-1) \times (p-1)$, formed by the elements with two non-zero indices, has a so-called *skew-circulant* structure because element (m^*, m) depends only on $m^* + m$. Simplification may now occur because multiplication by $\bar{C}(p)$ is closely related to a *cyclic convolution*. Introducing the notation $C(m) = e(g^{m/p})$ we may write the relation $\mathbf{Y}^* = \bar{F}(p)\mathbf{Y}$ in the permuted bases as

$$\begin{aligned} Y^*(0) &= \sum_k Y(k) \\ Y^*(m^*+1) &= Y(0) + \sum_{m=0}^{p-2} C(m^*+m)Y(m+1) \\ &= Y(0) + \sum_{m=0}^{p-2} C(m^*-m)Z(m) \\ &= Y(0) + (\mathbf{C} * \mathbf{Z})(m^*), \quad m^* = 0, \dots, p-2, \end{aligned}$$

where $\mathbf{Z}$ is defined by $Z(m) = Y(p-m-2)$, $m = 0, \dots, p-2$.

Thus $\mathbf{Y}^*$ may be obtained by cyclic convolution of $\mathbf{C}$ and $\mathbf{Z}$, which may for instance be calculated by

$$\mathbf{C} * \mathbf{Z} = F(p-1)[\bar{F}(p-1)[\mathbf{C}] \times \bar{F}(p-1)[\mathbf{Z}]],$$

where $\times$ denotes the component-wise multiplication of vectors. Since p is odd, $p-1$ is always divisible by 2 and may even be

highly composite. In that case, factoring $\bar{F}(p-1)$ by means of the Cooley–Tukey or Good methods leads to an algorithm of complexity $p \log p$ rather than p^2 for $\bar{F}(p)$. An added bonus is that, because $g^{(p-1)/2} = -1$, the elements of $\bar{F}(p-1)[\mathbf{C}]$ can be shown to be either purely real or purely imaginary, which halves the number of real multiplications involved.

1.3.3.2.3.2. N a power of an odd prime

This idea was extended by Winograd (1976, 1978) to the treatment of prime powers $N = p^\nu$, using the cyclic structure of the multiplicative group of units $U(p^\nu)$. The latter consists of all those elements of $\mathbb{Z}/p^\nu\mathbb{Z}$ which are not divisible by p , and thus has $q_\nu = p^{\nu-1}(p-1)$ elements. It is cyclic, and there exist primitive roots g modulo p^ν such that

$$U(p^\nu) = \{1, g, g^2, g^3, \dots, g^{q_\nu-1}\}.$$

The $p^{\nu-1}$ elements divisible by p , which are divisors of zero, have to be treated separately just as 0 had to be treated separately for $N = p$.

When $k^* \notin U(p^\nu)$, then $k^* = pk_1^*$ with $k_1^* \in \mathbb{Z}/p^{\nu-1}\mathbb{Z}$. The results $X^*(pk_1^*)$ are p -decimated, hence can be obtained via the $p^{\nu-1}$ -point DFT of the $p^{\nu-1}$ -periodized data $\mathbf{Y}$:

$$X^*(pk_1^*) = \bar{F}(p^{\nu-1})[\mathbf{Y}](k_1^*)$$

with

$$Y(k_1) = \sum_{k_2 \in \mathbb{Z}/p\mathbb{Z}} X(k_1 + p^{\nu-1}k_2).$$

When $k^* \in U(p^\nu)$, then we may write

$$X^*(k^*) = X_0^*(k^*) + X_1^*(k^*),$$

where $\mathbf{X}_0^*$ contains the contributions from $k \notin U(p^\nu)$ and $\mathbf{X}_1^*$ those from $k \in U(p^\nu)$. By a converse of the previous calculation, $\mathbf{X}_0^*$ arises from p -decimated data $\mathbf{Z}$, hence is the $p^{\nu-1}$ -periodization of the $p^{\nu-1}$ -point DFT of these data:

$$X_0^*(p^{\nu-1}k_1^* + k_2^*) = \bar{F}(p^{\nu-1})[\mathbf{Z}](k_2^*)$$

with

$$Z(k_2) = X(pk_2), \quad k_2 \in \mathbb{Z}/p^{\nu-1}\mathbb{Z}$$

(the $p^{\nu-1}$ -periodicity follows implicitly from the fact that the transform on the right-hand side is independent of $k_1^* \in \mathbb{Z}/p\mathbb{Z}$).

Finally, the contribution X_1^* from all $k \in U(p^\nu)$ may be calculated by reindexing by the powers of a primitive root g modulo p^ν , i.e. by writing

$$X_1^*(g^{m^*}) = \sum_{m=0}^{q_\nu-1} X(g^m) e(g^{(m^*+m)/p^\nu})$$

then carrying out the multiplication by the skew-circulant matrix core as a convolution.

Thus the DFT of size p^ν may be reduced to two DFTs of size $p^{\nu-1}$ (dealing, respectively, with p -decimated results and p -decimated data) and a convolution of size $q_\nu = p^{\nu-1}(p-1)$. The latter may be 'diagonalized' into a multiplication by purely real or purely imaginary numbers (because $g^{(q_\nu/2)} = -1$) by two DFTs, whose factoring in turn leads to DFTs of size $p^{\nu-1}$ and $p-1$. This method, applied recursively, allows the complete decomposition of the DFT on p^ν points into arbitrarily small DFTs.

1.3.3.2.3.3. N a power of 2

When $N = 2^\nu$, the same method can be applied, except for a slight modification in the calculation of $\mathbf{X}_1^*$. There is no primitive root modulo 2^ν for $\nu > 2$: the group $U(2^\nu)$ is the direct product of *two* cyclic groups, the first (of order 2) generated by -1 , the second (of order $N/4$) generated by 3 or 5. One then uses a representation

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$$k = (-1)^{m_1} 5^{m_2}$$

$$k^* = (-1)^{m_1^*} 5^{m_2^*}$$

and the reindexed core matrix gives rise to a two-dimensional convolution. The latter may be carried out by means of two 2D DFTs on $2 \times (N/4)$ points.

1.3.3.2.4. The Winograd algorithms

The cyclic convolutions generated by Rader's multiplicative reindexing may be evaluated more economically than through DFTs if they are re-examined within a new algebraic setting, namely the theory of congruence classes of polynomials [see, for instance, Blahut (1985), Chapter 2; Schroeder (1986), Chapter 24].

The set, denoted $\mathbb{K}[X]$, of polynomials in one variable with coefficients in a given field $\mathbb{K}$ has many of the formal properties of the set $\mathbb{Z}$ of rational integers: it is a *ring* with no zero divisors and has a *Euclidean algorithm* on which a theory of divisibility can be built.

Given a polynomial $P(z)$, then for every $W(z)$ there exist unique polynomials $Q(z)$ and $R(z)$ such that

$$W(z) = P(z)Q(z) + R(z)$$

and

$$\text{degree}(R) < \text{degree}(P).$$

$R(z)$ is called the *residue* of $H(z)$ modulo $P(z)$. Two polynomials $H_1(z)$ and $H_2(z)$ having the same residue modulo $P(z)$ are said to be *congruent* modulo $P(z)$, which is denoted by

$$H_1(z) \equiv H_2(z) \pmod{P(z)}.$$

If $H(z) \equiv 0 \pmod{P(z)}$, $H(z)$ is said to be *divisible* by $P(z)$. If $H(z)$ only has divisors of degree zero in $\mathbb{K}[X]$, it is said to be *irreducible over $\mathbb{K}$* (this notion depends on $\mathbb{K}$). Irreducible polynomials play in $\mathbb{K}[X]$ a role analogous to that of prime numbers in $\mathbb{Z}$, and any polynomial over $\mathbb{K}$ has an essentially unique factorization as a product of irreducible polynomials.

There exists a *Chinese remainder theorem* (CRT) for polynomials. Let $P(z) = P_1(z) \dots P_d(z)$ be factored into a product of pairwise coprime polynomials [i.e. $P_i(z)$ and $P_j(z)$ have no common factor for $i \neq j$]. Then the system of congruence equations

$$H(z) \equiv H_j(z) \pmod{P_j(z)}, \quad j = 1, \dots, d,$$

has a unique solution $H(z)$ modulo $P(z)$. This solution may be constructed by a procedure similar to that used for integers. Let

$$Q_j(z) = P(z)/P_j(z) = \prod_{i \neq j} P_i(z).$$

Then P_j and Q_j are coprime, and the Euclidean algorithm may be used to obtain polynomials $p_j(z)$ and $q_j(z)$ such that

$$p_j(z)P_j(z) + q_j(z)Q_j(z) = 1.$$

With $S_i(z) = q_i(z)Q_i(z)$, the polynomial

$$H(z) = \sum_{i=1}^d S_i(z)H_i(z) \pmod{P(z)}$$

is easily shown to be the desired solution.

As with integers, it can be shown that the 1:1 correspondence between $H(z)$ and $H_j(z)$ sends sums to sums and products to products, i.e. establishes a *ring isomorphism*:

$$\mathbb{K}[X] \pmod{P} \cong (\mathbb{K}[X] \pmod{P_1}) \times \dots \times (\mathbb{K}[X] \pmod{P_d}).$$

These results will now be applied to the efficient calculation of cyclic convolutions. Let $\mathbf{U} = (u_0, u_1, \dots, u_{N-1})$ and $\mathbf{V} = (v_0, v_1, \dots, v_{N-1})$ be two vectors of length N , and let $\mathbf{W} =$

$(w_0, w_1, \dots, w_{N-1})$ be obtained by cyclic convolution of $\mathbf{U}$ and $\mathbf{V}$:

$$w_n = \sum_{m=0}^{N-1} u_m v_{n-m}, \quad n = 0, \dots, N-1.$$

The very simple but crucial result is that this cyclic convolution may be carried out by *polynomial multiplication modulo $(z^N - 1)$* : if

$$\begin{aligned} U(z) &= \sum_{l=0}^{N-1} u_l z^l \\ V(z) &= \sum_{m=0}^{N-1} v_m z^m \\ W(z) &= \sum_{n=0}^{N-1} w_n z^n \end{aligned}$$

then the above relation is equivalent to

$$W(z) \equiv U(z)V(z) \pmod{(z^N - 1)}.$$

Now the polynomial $z^N - 1$ can be *factored* over the field of rational numbers into irreducible factors called *cyclotomic polynomials*: if d is the number of divisors of N , including 1 and N , then

$$z^N - 1 = \prod_{i=1}^d P_i(z),$$

where the cyclotomics $P_i(z)$ are well known (Nussbaumer, 1981; Schroeder, 1986, Chapter 22). We may now invoke the CRT, and exploit the ring isomorphism it establishes to simplify the calculation of $W(z)$ from $U(z)$ and $V(z)$ as follows:

(i) compute the d residual polynomials

$$U_i(z) \equiv U(z) \pmod{P_i(z)}, \quad i = 1, \dots, d,$$

$$V_i(z) \equiv V(z) \pmod{P_i(z)}, \quad i = 1, \dots, d;$$

(ii) compute the d polynomial products

$$W_i(z) \equiv U_i(z)V_i(z) \pmod{P_i(z)}, \quad i = 1, \dots, d;$$

(iii) use the CRT reconstruction formula just proved to recover $W(z)$ from the $W_i(z)$:

$$W(z) \equiv \sum_{i=1}^d S_i(z)W_i(z) \pmod{(z^N - 1)}.$$

When N is not too large, i.e. for 'short cyclic convolutions', the $P_i(z)$ are very simple, with coefficients 0 or ± 1 , so that (i) only involves a small number of additions. Furthermore, special techniques have been developed to multiply general polynomials modulo cyclotomic polynomials, thus helping keep the number of multiplications in (ii) and (iii) to a minimum. As a result, cyclic convolutions can be calculated rapidly when N is sufficiently composite.

It will be recalled that Rader's multiplicative indexing often gives rise to cyclic convolutions of length $p - 1$ for p an odd prime. Since $p - 1$ is highly composite for all $p \leq 50$ other than 23 and 47, these cyclic convolutions can be performed more efficiently by the above procedure than by DFT.

These combined algorithms are due to Winograd (1977, 1978, 1980), and are known collectively as 'Winograd small FFT algorithms'. Winograd also showed that they can be thought of as bringing the DFT matrix $\mathbf{F}$ to the following 'normal form':

$$\mathbf{F} = \mathbf{CBA},$$

where

$\mathbf{A}$ is an integer matrix with entries 0, ± 1 , defining the 'pre-additions',

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$\mathbf{B}$ is a diagonal matrix of multiplications,

$\mathbf{C}$ is a matrix with entries $0, \pm 1, \pm i$, defining the ‘post-additions’.

The elements on the diagonal of $\mathbf{B}$ can be shown to be either real or pure imaginary, by the same argument as in Section 1.3.3.2.3.1. Matrices $\mathbf{A}$ and $\mathbf{C}$ may be rectangular rather than square, so that intermediate results may require extra storage space.

1.3.3.3. Multidimensional algorithms

From an algorithmic point of view, the distinction between one-dimensional (1D) and multidimensional DFTs is somewhat blurred by the fact that some factoring techniques turn a 1D transform into a multidimensional one. The distinction made here, however, is a practical one and is based on the dimensionality of the indexing sets for data and results. This section will therefore be concerned with the problem of factoring the DFT when the *indexing sets* for the input data and output results are multidimensional.

1.3.3.3.1. The method of successive one-dimensional transforms

The DFT was defined in Section 1.3.2.7.4 in an n -dimensional setting and it was shown that when the decimation matrix $\mathbf{N}$ is diagonal, say $\mathbf{N} = \text{diag}(N^{(1)}, N^{(2)}, \dots, N^{(n)})$, then $\bar{F}(\mathbf{N})$ has a tensor product structure:

$$\bar{F}(\mathbf{N}) = \bar{F}(N^{(1)}) \otimes \bar{F}(N^{(2)}) \otimes \dots \otimes \bar{F}(N^{(n)}).$$

This may be rewritten as follows:

$$\begin{aligned} \bar{F}(\mathbf{N}) &= [\bar{F}(N^{(1)}) \otimes I_{N^{(2)}} \otimes \dots \otimes I_{N^{(n)}}] \\ &\quad \times [I_{N^{(1)}} \otimes \bar{F}(N^{(2)}) \otimes \dots \otimes I_{N^{(n)}}] \\ &\quad \times \dots \\ &\quad \times [I_{N^{(1)}} \otimes I_{N^{(2)}} \otimes \dots \otimes \bar{F}(N^{(n)})], \end{aligned}$$

where the I 's are identity matrices and $\times$ denotes ordinary matrix multiplication. The matrix within each bracket represents a one-dimensional DFT along one of the n dimensions, the other dimensions being left untransformed. As these matrices commute, the order in which the successive 1D DFTs are performed is immaterial.

This is the most straightforward method for building an n -dimensional algorithm from existing 1D algorithms. It is known in crystallography under the name of ‘Beavers–Lipson factorization’ (Section 1.3.4.3.1), and in signal processing as the ‘row–column method’.

1.3.3.3.2. Multidimensional factorization

Substantial reductions in the arithmetic cost, as well as gains in flexibility, can be obtained if the factoring of the DFT is carried out in several dimensions simultaneously. The presentation given here is a generalization of that of Mersereau & Speake (1981), using the abstract setting established independently by Auslander, Tolimieri & Winograd (1982).

Let us return to the general n -dimensional setting of Section 1.3.2.7.4, where the DFT was defined for an arbitrary decimation matrix $\mathbf{N}$ by the formulae (where $|\mathbf{N}|$ denotes $|\det \mathbf{N}|$):

$$\begin{aligned} F(\mathbf{N}) : \quad X(\mathbf{k}) &= \frac{1}{|\mathbf{N}|} \sum_{\mathbf{k}^*} X^*(\mathbf{k}^*) e[-\mathbf{k}^* \cdot (\mathbf{N}^{-1}\mathbf{k})] \\ \bar{F}(\mathbf{N}) : \quad X^*(\mathbf{k}^*) &= \sum_{\mathbf{k}} X(\mathbf{k}) e[\mathbf{k}^* \cdot (\mathbf{N}^{-1}\mathbf{k})] \end{aligned}$$

with

$$\mathbf{k} \in \mathbb{Z}^n / \mathbf{N}\mathbb{Z}^n, \quad \mathbf{k}^* \in \mathbb{Z}^n / \mathbf{N}^T \mathbb{Z}^n.$$

1.3.3.3.2.1. Multidimensional Cooley–Tukey factorization

Let us now assume that this decimation can be factored into d successive decimations, *i.e.* that

$$\mathbf{N} = \mathbf{N}_1 \mathbf{N}_2 \dots \mathbf{N}_{d-1} \mathbf{N}_d$$

and hence

$$\mathbf{N}^T = \mathbf{N}_d^T \mathbf{N}_{d-1}^T \dots \mathbf{N}_2^T \mathbf{N}_1^T.$$

Then the coset decomposition formulae corresponding to these successive decimations (Section 1.3.2.7.1) can be combined as follows:

$$\begin{aligned} \mathbb{Z}^n &= \bigcup_{\mathbf{k}_1} (\mathbf{k}_1 + \mathbf{N}_1 \mathbb{Z}^n) \\ &= \bigcup_{\mathbf{k}_1} \left\{ \mathbf{k}_1 + \mathbf{N}_1 \left[\bigcup_{\mathbf{k}_2} (\mathbf{k}_2 + \mathbf{N}_2 \mathbb{Z}^n) \right] \right\} \\ &= \dots \\ &= \bigcup_{\mathbf{k}_1} \dots \bigcup_{\mathbf{k}_d} (\mathbf{k}_1 + \mathbf{N}_1 \mathbf{k}_2 + \dots + \mathbf{N}_1 \mathbf{N}_2 \times \dots \times \mathbf{N}_{d-1} \mathbf{k}_d + \mathbf{N} \mathbb{Z}^n) \end{aligned}$$

with $\mathbf{k}_j \in \mathbb{Z}^n / \mathbf{N}_j \mathbb{Z}^n$. Therefore, any $\mathbf{k} \in \mathbb{Z} / \mathbf{N} \mathbb{Z}^n$ may be written uniquely as

$$\mathbf{k} = \mathbf{k}_1 + \mathbf{N}_1 \mathbf{k}_2 + \dots + \mathbf{N}_1 \mathbf{N}_2 \times \dots \times \mathbf{N}_{d-1} \mathbf{k}_d.$$

Similarly:

$$\begin{aligned} \mathbb{Z}^n &= \bigcup_{\mathbf{k}_d^*} (\mathbf{k}_d^* + \mathbf{N}_d^T \mathbb{Z}^n) \\ &= \dots \\ &= \bigcup_{\mathbf{k}_d^*} \dots \bigcup_{\mathbf{k}_1^*} (\mathbf{k}_d^* + \mathbf{N}_d^T \mathbf{k}_{d-1}^* + \dots + \mathbf{N}_d^T \times \dots \times \mathbf{N}_2^T \mathbf{k}_1^* \\ &\quad + \mathbf{N}^T \mathbb{Z}^n) \end{aligned}$$

so that any $\mathbf{k}^* \in \mathbb{Z}^n / \mathbf{N}^T \mathbb{Z}^n$ may be written uniquely as

$$\mathbf{k}^* = \mathbf{k}_d^* + \mathbf{N}_d^T \mathbf{k}_{d-1}^* + \dots + \mathbf{N}_d^T \times \dots \times \mathbf{N}_2^T \mathbf{k}_1^*$$

with $\mathbf{k}_j^* \in \mathbb{Z}^n / \mathbf{N}_j^T \mathbb{Z}^n$. These decompositions are the vector analogues of the multi-radix number representation systems used in the Cooley–Tukey factorization.

We may then write the definition of $\bar{F}(\mathbf{N})$ with $d = 2$ factors as

$$\begin{aligned} X^*(\mathbf{k}_2^* + \mathbf{N}_2^T \mathbf{k}_1^*) &= \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} X(\mathbf{k}_1 + \mathbf{N}_1 \mathbf{k}_2) \\ &\quad \times e[(\mathbf{k}_2^{*T} + \mathbf{k}_1^{*T} \mathbf{N}_2) \mathbf{N}_2^{-1} \mathbf{N}_1^{-1} (\mathbf{k}_1 + \mathbf{N}_1 \mathbf{k}_2)]. \end{aligned}$$

The argument of $e(-)$ may be expanded as

$$\mathbf{k}_2^* \cdot (\mathbf{N}_1^{-1} \mathbf{k}_1) + \mathbf{k}_1^* \cdot (\mathbf{N}_1^{-1} \mathbf{k}_1) + \mathbf{k}_2^* \cdot (\mathbf{N}_2^{-1} \mathbf{k}_2) + \mathbf{k}_1^* \cdot \mathbf{k}_2.$$

The first summand may be recognized as a twiddle factor, the second and third as the kernels of $\bar{F}(\mathbf{N}_1)$ and $\bar{F}(\mathbf{N}_2)$, respectively, while the fourth is an integer which may be dropped. We are thus led to a ‘vector-radix’ version of the Cooley–Tukey algorithm, in which the successive decimations may be introduced in all n dimensions simultaneously by general integer matrices. The computation may be decomposed into five stages analogous to those of the one-dimensional algorithm of Section 1.3.3.2.1:

(i) form the $|\mathbf{N}_1|$ vectors $\mathbf{Y}_{\mathbf{k}_1}$ of shape $\mathbf{N}_2$ by

$$\mathbf{Y}_{\mathbf{k}_1}(\mathbf{k}_2) = X(\mathbf{k}_1 + \mathbf{N}_1 \mathbf{k}_2), \quad \mathbf{k}_1 \in \mathbb{Z}^n / \mathbf{N}_1 \mathbb{Z}^n, \quad \mathbf{k}_2 \in \mathbb{Z}^n / \mathbf{N}_2 \mathbb{Z}^n;$$

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(ii) calculate the $|\mathbf{N}_1|$ transforms $\mathbf{Y}_{\mathbf{k}_1}^*$ on $|\mathbf{N}_2|$ points:

$$Y_{\mathbf{k}_1}^*(\mathbf{k}_2^*) = \sum_{\mathbf{k}_2} e[\mathbf{k}_2^* \cdot (\mathbf{N}_2^{-1} \mathbf{k}_2)] Y_{\mathbf{k}_1}(\mathbf{k}_2), \quad \mathbf{k}_1 \in \mathbb{Z}^n / \mathbf{N}_1 \mathbb{Z}^n;$$

(iii) form the $|\mathbf{N}_2|$ vectors $\mathbf{Z}_{\mathbf{k}_2^*}$ of shape $\mathbf{N}_1$ by

$$\begin{aligned} Z_{\mathbf{k}_2^*}(\mathbf{k}_1) &= e[\mathbf{k}_2^* \cdot (\mathbf{N}_1^{-1} \mathbf{k}_1)] Y_{\mathbf{k}_1}^*(\mathbf{k}_2^*), \quad \mathbf{k}_1 \in \mathbb{Z}^n / \mathbf{N}_1 \mathbb{Z}^n, \\ \mathbf{k}_2^* &\in \mathbb{Z}^n / \mathbf{N}_2^T \mathbb{Z}^n; \end{aligned}$$

(iv) calculate the $|\mathbf{N}_2|$ transforms $\mathbf{Z}_{\mathbf{k}_2^*}$ on $|\mathbf{N}_1|$ points:

$$Z_{\mathbf{k}_2^*}^*(\mathbf{k}_1^*) = \sum_{\mathbf{k}_1} e[\mathbf{k}_1^* \cdot (\mathbf{N}_1^{-1} \mathbf{k}_1)] Z_{\mathbf{k}_2^*}(\mathbf{k}_1), \quad \mathbf{k}_2^* \in \mathbb{Z}^n / \mathbf{N}_2^T \mathbb{Z}^n;$$

(v) collect $X^*(\mathbf{k}_2^* + \mathbf{N}_2^T \mathbf{k}_1^*)$ as $Z_{\mathbf{k}_2^*}^*(\mathbf{k}_1^*)$.

The initial $|\mathbf{N}|$ -point transform $\bar{F}(\mathbf{N})$ can thus be performed as $|\mathbf{N}_1|$ transforms $\bar{F}(\mathbf{N}_2)$ on $|\mathbf{N}_2|$ points, followed by $|\mathbf{N}_2|$ transforms $\bar{F}(\mathbf{N}_1)$ on $|\mathbf{N}_1|$ points. This process can be applied successively to all d factors. The same decomposition applies to $F(\mathbf{N})$, up to the complex conjugation of twiddle factors, the normalization factor $1/|\mathbf{N}|$ being obtained as the product of the factors $1/|\mathbf{N}_j|$ in the successive partial transforms $F(\mathbf{N}_j)$.

The geometric interpretation of this factorization in terms of partial transforms on translates of sublattices applies in full to this n -dimensional setting; in particular, the twiddle factors are seen to be related to the residual translations which place the sublattices in register within the big lattice. If the intermediate transforms are performed *in place*, then the quantity

$$X^*(\mathbf{k}_d^* + \mathbf{N}_d^T \mathbf{k}_{d-1}^* + \dots + \mathbf{N}_d^T \mathbf{N}_{d-1}^T \times \dots \times \mathbf{N}_2^T \mathbf{k}_1^*)$$

will eventually be found at location

$$\mathbf{k}_1^* + \mathbf{N}_1 \mathbf{k}_2^* + \dots + \mathbf{N}_1 \mathbf{N}_2 \times \dots \times \mathbf{N}_{d-1} \mathbf{k}_d^*,$$

so that the final results will have to be *unscrambled* by a process which may be called ‘coset reversal’, the vector equivalent of digit reversal.

Factoring by 2 in all n dimensions simultaneously, *i.e.* taking $\mathbf{N} = 2\mathbf{M}$, leads to ‘ n -dimensional butterflies’. Decimation in time corresponds to the choice $\mathbf{N}_1 = 2\mathbf{I}$, $\mathbf{N}_2 = \mathbf{M}$, so that $\mathbf{k}_1 \in \mathbb{Z}^n / 2\mathbb{Z}^n$ is an n -dimensional parity class; the calculation then proceeds by

$$\begin{aligned} Y_{\mathbf{k}_1}(\mathbf{k}_2) &= X(\mathbf{k}_1 + 2\mathbf{k}_2), \quad \mathbf{k}_1 \in \mathbb{Z}^n / 2\mathbb{Z}^n, \quad \mathbf{k}_2 \in \mathbb{Z}^n / \mathbf{M} \mathbb{Z}^n, \\ Y_{\mathbf{k}_1}^* &= \bar{F}(\mathbf{M})[\mathbf{Y}_{\mathbf{k}_1}], \quad \mathbf{k}_1 \in \mathbb{Z}^n / 2\mathbb{Z}^n; \\ X^*(\mathbf{k}_2^* + \mathbf{M}^T \mathbf{k}_1^*) &= \sum_{\mathbf{k}_1 \in \mathbb{Z}^n / 2\mathbb{Z}^n} (-1)^{\mathbf{k}_1^* \cdot \mathbf{k}_1} \\ &\quad \times e[\mathbf{k}_2^* \cdot (\mathbf{N}_1^{-1} \mathbf{k}_1)] Y_{\mathbf{k}_1}^*(\mathbf{k}_2^*). \end{aligned}$$

Decimation in frequency corresponds to the choice $\mathbf{N}_1 = \mathbf{M}$, $\mathbf{N}_2 = 2\mathbf{I}$, so that $\mathbf{k}_2 \in \mathbb{Z}^n / 2\mathbb{Z}^n$ labels ‘octant’ blocks of shape $\mathbf{M}$; the calculation then proceeds through the following steps:

$$\begin{aligned} Z_{\mathbf{k}_2^*}(\mathbf{k}_1) &= \left[\sum_{\mathbf{k}_2 \in \mathbb{Z}^n / 2\mathbb{Z}^n} (-1)^{\mathbf{k}_2^* \cdot \mathbf{k}_2} X(\mathbf{k}_1 + \mathbf{M} \mathbf{k}_2) \right] \\ &\quad \times e[\mathbf{k}_2^* \cdot (\mathbf{N}_1^{-1} \mathbf{k}_1)], \\ Z_{\mathbf{k}_2^*}^* &= \bar{F}(\mathbf{M})[\mathbf{Z}_{\mathbf{k}_2^*}], \\ X^*(\mathbf{k}_2^* + 2\mathbf{k}_1^*) &= Z_{\mathbf{k}_2^*}^*(\mathbf{k}_1^*), \end{aligned}$$

i.e. the 2^n parity classes of results, corresponding to the different $\mathbf{k}_2^* \in \mathbb{Z}^n / 2\mathbb{Z}^n$, are obtained separately. When the dimension n is 2 and the decimating matrix is diagonal, this analysis reduces to the ‘vector radix FFT’ algorithms proposed by Rivard (1977) and Harris *et al.* (1977). These lead to substantial reductions in the number M of multiplications compared to the row-column method:

M is reduced to $3M/4$ by simultaneous 2×2 factoring, and to $15M/32$ by simultaneous 4×4 factoring.

The use of a non-diagonal decimating matrix may bring savings in computing time if the spectrum of the band-limited function under study is of such a shape as to pack more compactly in a non-rectangular than in a rectangular lattice (Mersereau, 1979). If, for instance, the support K of the spectrum Φ is contained in a sphere, then a decimation matrix producing a close packing of these spheres will yield an aliasing-free DFT algorithm with fewer sample points than the standard algorithm using a rectangular lattice.

1.3.3.3.2.2. Multidimensional prime factor algorithm

Suppose that the decimation matrix $\mathbf{N}$ is diagonal

$$\mathbf{N} = \text{diag}(N^{(1)}, N^{(2)}, \dots, N^{(n)})$$

and let each diagonal element be written in terms of its prime factors:

$$N^{(i)} = \prod_{j=1}^m p_j^{\nu(i,j)},$$

where m is the total number of distinct prime factors present in the $N^{(i)}$.

The CRT may be used to turn each 1D transform along dimension i ($i = 1, \dots, n$) into a multidimensional transform with a separate ‘pseudo-dimension’ for each distinct prime factor of $N^{(i)}$; the number μ_i of these pseudo-dimensions is equal to the cardinality of the set:

$$\{j \in \{1, \dots, m\} | \nu(i,j) > 0 \text{ for some } i\}.$$

The full n -dimensional transform thus becomes μ -dimensional, with $\mu = \sum_{i=1}^n \mu_i$.

We may now permute the μ pseudo-dimensions so as to bring into contiguous position those corresponding to the same prime factor p_j ; the m resulting groups of pseudo-dimensions are said to define ‘ p -primary’ blocks. The initial transform is now written as a tensor product of m p -primary transforms, where transform j is on

$$p_j^{\nu(1,j)} \times p_j^{\nu(2,j)} \times \dots \times p_j^{\nu(n,j)}$$

points [by convention, dimension i is not transformed if $\nu(i,j) = 0$]. These p -primary transforms may be computed, for instance, by multidimensional Cooley–Tukey factorization (Section 1.3.3.3.1), which is faster than the straightforward row-column method. The final results may then be obtained by reversing all the permutations used.

The extra gain with respect to the multidimensional Cooley–Tukey method is that *there are no twiddle factors between p -primary pieces corresponding to different primes p* .

The case where $\mathbf{N}$ is not diagonal has been examined by Guessoum & Mersereau (1986).

1.3.3.3.2.3. Nesting of Winograd small FFTs

Suppose that the CRT has been used as above to map an n -dimensional DFT to a μ -dimensional DFT. For each $\kappa = 1, \dots, \mu$ [κ runs over those pairs (i, j) such that $\nu(i, j) > 0$], the Rader/Winograd procedure may be applied to put the matrix of the κ th 1D DFT in the CBA normal form of a Winograd small FFT. The full DFT matrix may then be written, up to permutation of data and results, as

$$\bigotimes_{\kappa=1}^{\mu} (\mathbf{C}_{\kappa} \mathbf{B}_{\kappa} \mathbf{A}_{\kappa}).$$

A well known property of the tensor product of matrices allows this to be rewritten as

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$$\left(\bigotimes_{\gamma=1}^{\mu} \mathbf{C}_{\gamma} \right) \times \left(\bigotimes_{\beta=1}^{\mu} \mathbf{B}_{\beta} \right) \times \left(\bigotimes_{\alpha=1}^{\mu} \mathbf{A}_{\alpha} \right)$$

and thus to form a matrix in which the *combined* pre-addition, multiplication and post-addition matrices have been *precomputed*. This procedure, called *nesting*, can be shown to afford a reduction of the arithmetic operation count compared to the row-column method (Morris, 1978).

Clearly, the nesting rearrangement need not be applied to all μ dimensions, but can be restricted to any desired subset of them.

1.3.3.3.2.4. The Nussbaumer–Quandalle algorithm

Nussbaumer's approach views the DFT as the evaluation of certain polynomials constructed from the data (as in Section 1.3.3.2.4). For instance, putting $\omega = e(1/N)$, the 1D N -point DFT

$$X^*(k^*) = \sum_{k=0}^{N-1} X(k) \omega^{k^* k}$$

may be written

$$X^*(k^*) = Q(\omega^{k^*}),$$

where the polynomial Q is defined by

$$Q(z) = \sum_{k=0}^{N-1} X(k) z^k.$$

Let us consider (Nussbaumer & Quandalle, 1979) a 2D transform of size $N \times N$:

$$X^*(k_1^*, k_2^*) = \sum_{k_1=0}^{N-1} \sum_{k_2=0}^{N-1} X(k_1, k_2) \omega^{k_1^* k_1 + k_2^* k_2}.$$

By introduction of the polynomials

$$\begin{aligned} Q_{k_2}(z) &= \sum_{k_1} X(k_1, k_2) z^{k_1} \\ R_{k_2^*}(z) &= \sum_{k_2} \omega^{k_2^* k_2} Q_{k_2}(z), \end{aligned}$$

this may be rewritten:

$$X^*(k_1^*, k_2^*) = R_{k_2^*}(\omega^{k_1^*}) = \sum_{k_2} \omega^{k_2^* k_2} Q_{k_2}(\omega^{k_1^*}).$$

Let us now suppose that k_1^* is coprime to N . Then k_1^* has a unique inverse modulo N (denoted by $1/k_1^*$), so that multiplication by k_1^* simply permutes the elements of $\mathbb{Z}/N\mathbb{Z}$ and hence

$$\sum_{k_2=0}^{N-1} f(k_2) = \sum_{k_2=0}^{N-1} f(k_1^* k_2)$$

for any function f over $\mathbb{Z}/N\mathbb{Z}$. We may thus write:

$$\begin{aligned} X^*(k_1^*, k_2^*) &= \sum_{k_2} \omega^{k_1^* k_2^* k_2} Q_{k_1^* k_2}(\omega^{k_1^*}) \\ &= S_{k_1^* k_2}(\omega^{k_1^*}) \end{aligned}$$

where

$$S_{k^*}(z) = \sum_{k_2} z^{k^* k_2} Q_{k_2}(z).$$

Since only the value of polynomial $S_{k^*}(z)$ at $z = \omega^{k_1^*}$ is involved in the result, the computation of S_{k^*} may be carried out modulo the unique cyclotomic polynomial $P(z)$ such that $P(\omega^{k_1^*}) = 0$. Thus, if we define:

$$T_{k^*}(z) = \sum_{k_2} z^{k^* k_2} Q_{k_2}(z) \bmod P(z)$$

we may write:

$$X^*(k_1^*, k_2^*) = T_{k_1^* k_2^*}(\omega^{k_1^*})$$

or equivalently

$$X^*\left(k_1^*, \frac{k_2^*}{k_1^*}\right) = T_{k_2^*}(\omega^{k_1^*}).$$

For N an odd prime p , all non-zero values of k_1^* are coprime with p so that the $p \times p$ -point DFT may be calculated as follows:

(1) form the polynomials

$$T_{k_2^*}(z) = \sum_{k_1} \sum_{k_2} X(k_1, k_2) z^{k_1 + k_2^* k_2} \bmod P(z)$$

for $k_2^* = 0, \dots, p-1$;

(2) evaluate $T_{k_2^*}(\omega^{k_1^*})$ for $k_1^* = 0, \dots, p-1$;

(3) put $X^*(k_1^*, k_2^*/k_1^*) = T_{k_2^*}(\omega^{k_1^*})$;

(4) calculate the terms for $k_1^* = 0$ separately by

$$X^*(0, k_2^*) = \sum_{k_1} \left[\sum_{k_2} X(k_1, k_2) \right] \omega^{k_2^* k_2}.$$

Step (1) is a set of p 'polynomial transforms' involving no multiplications; step (2) consists of p DFTs on p points each since if

$$T_{k_2^*}(z) = \sum_{k_1} Y_{k_2^*}(k_1) z^{k_1}$$

then

$$T_{k_2^*}(\omega^{k_1^*}) = \sum_{k_1} Y_{k_2^*}(k_1) \omega^{k_1^* k_1} = Y_{k_2^*}^*(k_1^*);$$

step (3) is a permutation; and step (4) is a p -point DFT. Thus the 2D DFT on $p \times p$ points, which takes $2p$ p -point DFTs by the row-column method, involves only $(p+1)$ p -point DFTs; the other DFTs have been replaced by polynomial transforms involving only additions.

This procedure can be extended to n dimensions, and reduces the number of 1D p -point DFTs from np^{n-1} for the row-column method to $(p^n - 1)/(p - 1)$, at the cost of introducing extra additions in the polynomial transforms.

A similar algorithm has been formulated by Auslander *et al.* (1983) in terms of Galois theory.

1.3.3.3.3. Global algorithm design

1.3.3.3.3.1. From local pieces to global algorithms

The mathematical analysis of the structure of DFT computations has brought to light a broad variety of possibilities for reducing or reshaping their arithmetic complexity. All of them are 'analytic' in that they break down large transforms into a succession of smaller ones.

These results may now be considered from the converse 'synthetic' viewpoint as providing a list of procedures for assembling them:

(i) the building blocks are one-dimensional p -point algorithms for p a small prime;

(ii) the low-level connectors are the multiplicative reindexing methods of Rader and Winograd, or the polynomial transform reindexing method of Nussbaumer and Quandalle, which allow the construction of efficient algorithms for larger primes p , for prime powers p^ν , and for p -primary pieces of shape $p^\nu \times \dots \times p^\nu$;

(iii) the high-level connectors are the additive reindexing scheme of Cooley–Tukey, the Chinese remainder theorem reindexing, and the tensor product construction;

(iv) nesting may be viewed as the 'glue' which seals all elements.

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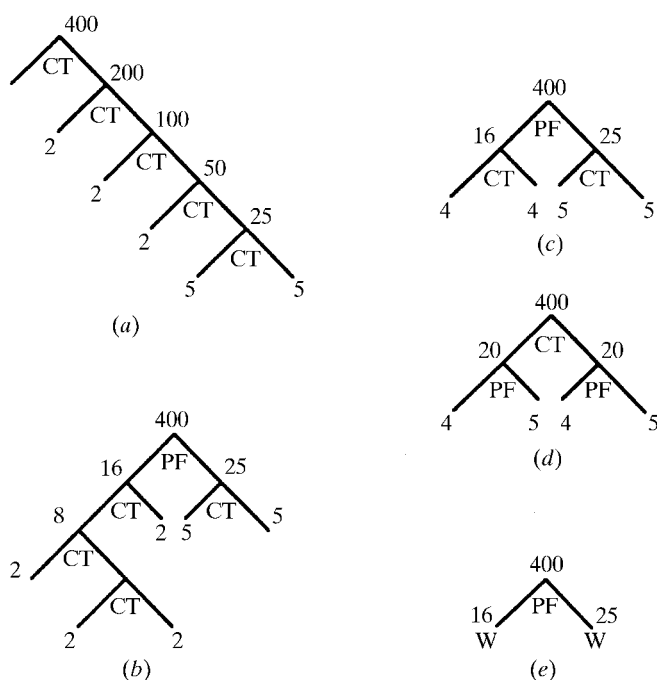


Fig. 1.3.3.1. A few global algorithms for computing a 400-point DFT. CT: Cooley–Tukey factorization. PF: prime factor (or Good) factorization. W: Winograd algorithm.

The simplest DFT may then be carried out into a global algorithm in many different ways. The diagrams in Fig. 1.3.3.1 illustrate a few of the options available to compute a 400-point DFT. They may differ greatly in their arithmetic operation counts.

1.3.3.3.2. Computer architecture considerations

To obtain a truly useful measure of the computational complexity of a DFT algorithm, its arithmetic operation count must be tempered by computer architecture considerations. Three main types of trade-offs must be borne in mind:

- (i) reductions in floating-point (f.p.) arithmetic count are obtained by reindexing, hence at the cost of an increase in integer arithmetic on addresses, although some shortcuts may be found (Uhrich, 1969; Burrus & Eschenbacher, 1981);
- (ii) reduction in the f.p. multiplication count usually leads to a large increase in the f.p. addition count (Morris, 1978);
- (iii) nesting can increase execution speed, but causes a loss of modularity and hence complicates program development (Silverman, 1977; Kolba & Parks, 1977).

Many of the mathematical developments above took place in the context of single-processor serial computers, where f.p. addition is substantially cheaper than f.p. multiplication but where integer address arithmetic has to compete with f.p. arithmetic for processor cycles. As a result, the alternatives to the Cooley–Tukey algorithm hardly ever led to particularly favourable trade-offs, thus creating the impression that there was little to gain by switching to more exotic algorithms.

The advent of new machine architectures with vector and/or parallel processing features has greatly altered this picture (Pease, 1968; Korn & Lambiotte, 1979; Fornberg, 1981; Swartzrauber, 1984):

- (i) *pipelining* equalizes the cost of f.p. addition and f.p. multiplication, and the ideal ‘blend’ of the two types of operations depends solely on the number of adder and multiplier units available in each machine;
- (ii) integer address arithmetic is delegated to specialized arithmetic and logical units (ALUs) operating concurrently with

the f.p. units, so that complex reindexing schemes may be used without loss of overall efficiency.

Another major consideration is that of data flow [see *e.g.* Nawab & McClellan (1979)]. Serial machines only have few registers and few paths connecting them, and allow little or no overlap between computation and data movement. New architectures, on the other hand, comprise banks of vector registers (or ‘cache memory’) besides the usual internal registers, and dedicated ALUs can service data transfers between several of them simultaneously and concurrently with computation.

In this new context, the devices described in Sections 1.3.3.2 and 1.3.3.3 for altering the balance between the various types of arithmetic operations, and reshaping the data flow during the computation, are invaluable. The field of machine-dependent DFT algorithm design is thriving on them [see *e.g.* Temperton (1983*a,b,c*, 1985); Agarwal & Cooley (1986, 1987)].

1.3.3.3.3. The Johnson–Burrus family of algorithms

In order to explore systematically all possible algorithms for carrying out a given DFT computation, and to pick the one best suited to a given machine, attempts have been made to develop:

- (i) a high-level notation of describing all the ingredients of a DFT computation, including data permutation and data flow;
- (ii) a formal calculus capable of operating on these descriptions so as to represent all possible reorganizations of the computation;
- (iii) an automatic procedure for evaluating the performance of a given algorithm on a specific architecture.

Task (i) can be accomplished by systematic use of a tensor product notation to represent the various stages into which the DFT can be factored (reindexing, small transforms on subsets of indices, twiddle factors, digit-reversal permutations).

Task (ii) may for instance use the Winograd **CBA** normal form for each small transform, then apply the rules governing the rearrangement of tensor product $\otimes$ and ordinary product $\times$ operations on matrices. The matching of these rearrangements to the architecture of a vector and/or parallel computer can be formalized algebraically [see *e.g.* Chapter 2 of Tolimieri *et al.* (1989)].

Task (iii) is a complex search which requires techniques such as dynamic programming (Bellman, 1958).

Johnson & Burrus (1983) have proposed and tested such a scheme to identify the optimal trade-offs between prime factor nesting and Winograd nesting of small Winograd transforms. In step (ii), they further decomposed the pre-addition matrix **A** and post-addition matrix **C** into several factors, so that the number of design options available becomes very large: the N -point DFT when N has four factors can be calculated in over 10^{12} distinct ways.

This large family of nested algorithms contains the prime factor algorithm and the Winograd algorithms as particular cases, but usually achieves greater efficiency than either by reducing the f.p. multiplication count while keeping the number of f.p. additions small.

There is little doubt that this systematic approach will be extended so as to incorporate all available methods of restructuring the DFT.

1.3.4. Crystallographic applications of Fourier transforms

1.3.4.1. Introduction

The central role of the Fourier transformation in X-ray crystallography is a consequence of the kinematic approximation used in the description of the scattering of X-rays by a distribution of electrons (Bragg, 1915; Duane, 1925; Havighurst, 1925*a,b*; Zachariasen, 1945; James, 1948*a*, Chapters 1 and 2; Lipson & Cochran, 1953, Chapter 1; Bragg, 1975).

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Let $\rho(\mathbf{X})$ be the density of electrons in a sample of matter contained in a finite region V which is being illuminated by a parallel monochromatic X-ray beam with wavevector $\mathbf{K}_0$. Then the far-field amplitude scattered in a direction corresponding to wavevector $\mathbf{K} = \mathbf{K}_0 + \mathbf{H}$ is proportional to

$$\begin{aligned} F(\mathbf{H}) &= \int_V \rho(\mathbf{X}) \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) d^3 \mathbf{X} \\ &= \tilde{\mathcal{F}}[\rho](\mathbf{H}) \\ &= \langle \rho_{\mathbf{x}}, \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \rangle. \end{aligned}$$

In certain model calculations, the ‘sample’ may contain not only volume charges, but also point, line and surface charges. These singularities may be accommodated by letting ρ be a distribution, and writing

$$F(\mathbf{H}) = \tilde{\mathcal{F}}[\rho](\mathbf{H}) = \langle \rho_{\mathbf{x}}, \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \rangle.$$

F is still a well behaved function (analytic, by Section 1.3.2.4.2.10) because ρ has been assumed to have compact support.

If the sample is assumed to be an infinite crystal, so that ρ is now a *periodic* distribution, the customary limiting process by which it is shown that F becomes a discrete series of peaks at reciprocal-lattice points (see *e.g.* von Laue, 1936; Ewald, 1940; James, 1948a p. 9; Lipson & Taylor, 1958, pp. 14–27; Ewald, 1962, pp. 82–101; Warren, 1969, pp. 27–30) is already subsumed under the treatment of Section 1.3.2.6.

1.3.4.2. Crystallographic Fourier transform theory

1.3.4.2.1. Crystal periodicity

1.3.4.2.1.1. Period lattice, reciprocal lattice and structure factors

Let ρ be the distribution of electrons in a crystal. Then, by definition of a crystal, ρ is Λ -periodic for some period lattice Λ (Section 1.3.2.6.5) so that there exists a motif distribution ρ^0 with compact support such that

$$\rho = R * \rho^0,$$

where $R = \sum_{\mathbf{x} \in \Lambda} \delta(\mathbf{x})$. The lattice Λ is usually taken to be the finest for which the above representation holds.

Let Λ have a basis $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ over the integers, these basis vectors being expressed in terms of a standard orthonormal basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ as

$$\mathbf{a}_k = \sum_{j=1}^3 a_{jk} \mathbf{e}_j.$$

Then the matrix

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

is the period matrix of Λ (Section 1.3.2.6.5) with respect to the unit lattice with basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$, and the volume V of the unit cell is given by $V = |\det \mathbf{A}|$.

By Fourier transformation

$$\tilde{\mathcal{F}}[\rho] = R^* \times \tilde{\mathcal{F}}[\rho^0],$$

where $R^* = \sum_{\mathbf{H} \in \Lambda^*} \delta(\mathbf{H})$ is the lattice distribution associated to the reciprocal lattice Λ^* . The basis vectors $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ have coordinates in $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ given by the columns of $(\mathbf{A}^{-1})^T$, whose expression in terms of the cofactors of $\mathbf{A}$ (see Section 1.3.2.6.5) gives the familiar formulae involving the cross product of vectors for $n = 3$. The $\mathbf{H}$ -distribution F of scattered amplitudes may be written

$$F = \tilde{\mathcal{F}}[\rho]_{\mathbf{H}} = \sum_{\mathbf{H} \in \Lambda^*} \tilde{\mathcal{F}}[\rho^0](\mathbf{H}) \delta(\mathbf{H}) = \sum_{\mathbf{H} \in \Lambda^*} F_{\mathbf{H}} \delta(\mathbf{H})$$

and is thus a weighted reciprocal-lattice distribution, the weight $F_{\mathbf{H}}$ attached to each node $\mathbf{H} \in \Lambda^*$ being the value at $\mathbf{H}$ of the transform $\tilde{\mathcal{F}}[\rho^0]$ of the motif ρ^0 . Taken in conjunction with the assumption that the scattering is elastic, *i.e.* that $\mathbf{H}$ only changes the direction but not the magnitude of the incident wavevector $\mathbf{K}_0$, this result yields the usual forms (Laue or Bragg) of the diffraction conditions: $\mathbf{H} \in \Lambda^*$, and simultaneously $\mathbf{H}$ lies on the Ewald sphere.

By the reciprocity theorem, ρ^0 can be recovered if F is known for all $\mathbf{H} \in \Lambda^*$ as follows [Section 1.3.2.6.5, *e.g.* (iv)]:

$$\rho_{\mathbf{x}} = \frac{1}{V} \sum_{\mathbf{H} \in \Lambda^*} F_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{X}).$$

These relations may be rewritten in terms of standard, or ‘fractional crystallographic’, coordinates by putting

$$\mathbf{X} = \mathbf{A} \mathbf{x}, \quad \mathbf{H} = (\mathbf{A}^{-1})^T \mathbf{h},$$

so that a unit cell of the crystal corresponds to $\mathbf{x} \in \mathbb{R}^3 / \mathbb{Z}^3$, and that $\mathbf{h} \in \mathbb{Z}^3$. Defining ρ and ρ^0 by

$$\rho = \frac{1}{V} A^{\#} \rho, \quad \rho^0 = \frac{1}{V} A^{\#} \rho^0$$

so that

$$\rho(\mathbf{X}) d^3 \mathbf{X} = \rho(\mathbf{x}) d^3 \mathbf{x}, \quad \rho^0(\mathbf{X}) d^3 \mathbf{X} = \rho^0(\mathbf{x}) d^3 \mathbf{x},$$

we have

$$\begin{aligned} \tilde{\mathcal{F}}[\rho]_{\mathbf{h}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \delta(\mathbf{h}), \\ F(\mathbf{h}) &= \langle \rho_{\mathbf{x}}^0, \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) \rangle \\ &= \int_{\mathbb{R}^3 / \mathbb{Z}^3} \rho^0(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) d^3 \mathbf{x} \quad \text{if } \rho^0 \in L_{\text{loc}}^1(\mathbb{R}^3 / \mathbb{Z}^3), \\ \rho_{\mathbf{x}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}). \end{aligned}$$

These formulae are valid for an arbitrary motif distribution ρ^0 , provided the convergence of the Fourier series for ρ is considered from the viewpoint of distribution theory (Section 1.3.2.6.10.3).

The experienced crystallographer may notice the absence of the familiar factor $1/V$ from the expression for ρ just given. This is because we use the (mathematically) natural unit for ρ , the *electron per unit cell*, which matches the dimensionless nature of the crystallographic coordinates $\mathbf{x}$ and of the associated volume element $d^3 \mathbf{x}$. The traditional factor $1/V$ was the result of the somewhat inconsistent use of $\mathbf{x}$ as an argument but of $d^3 \mathbf{X}$ as a volume element to obtain ρ in electrons per unit volume (*e.g.* $\text{\AA}^{-3}$). A fortunate consequence of the present convention is that nuisance factors of V or $1/V$, which used to abound in convolution or scalar product formulae, are now absent.

It should be noted at this point that the crystallographic terminology regarding $\tilde{\mathcal{F}}$ and $\tilde{\mathcal{F}}$ differs from the standard mathematical terminology introduced in Section 1.3.2.4.1 and applied to periodic distributions in Section 1.3.2.6.4: F is the *inverse* Fourier transform of ρ rather than its Fourier transform, and the calculation of ρ is called a Fourier *synthesis* in crystallography even though it is mathematically a Fourier analysis. The origin of this discrepancy may be traced to the fact that the mathematical theory of the Fourier transformation originated with the study of *temporal* periodicity, while crystallography deals with *spatial* periodicity; since the expression for the phase factor of a plane wave is $\exp[2\pi i(\nu t - \mathbf{K} \cdot \mathbf{X})]$, the difference in sign between the

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contributions from time *versus* spatial displacements makes this conflict unavoidable.

1.3.4.2.1.2. Structure factors in terms of form factors

In many cases, ρ^0 is a sum of translates of atomic electron-density distributions. Assume there are n distinct chemical types of atoms, with N_j identical isotropic atoms of type j described by an electron distribution ρ_j about their centre of mass. According to quantum mechanics each ρ_j is a smooth rapidly decreasing function of $\mathbf{x}$, i.e. $\rho_j \in \mathcal{S}$, hence $\rho^0 \in \mathcal{S}$ and (ignoring the effect of thermal agitation)

$$\rho^0(\mathbf{x}) = \sum_{j=1}^n \left[\sum_{k_j=1}^{N_j} \rho_j(\mathbf{x} - \mathbf{x}_{k_j}) \right],$$

which may be written (Section 1.3.2.5.8)

$$\rho^0 = \sum_{j=1}^n \left[\rho_j * \left(\sum_{k_j=1}^{N_j} \delta(\mathbf{x}_{k_j}) \right) \right].$$

By Fourier transformation:

$$F(\mathbf{h}) = \sum_{j=1}^n \left\{ \tilde{\mathcal{F}}[\rho_j](\mathbf{h}) \times \left[\sum_{k_j=1}^{N_j} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_{k_j}) \right] \right\}.$$

Defining the form factor f_j of atom j as a function of $\mathbf{h}$ to be

$$f_j(\mathbf{h}) = \tilde{\mathcal{F}}[\rho_j](\mathbf{h})$$

we have

$$F(\mathbf{h}) = \sum_{j=1}^n f_j(\mathbf{h}) \times \left[\sum_{k_j=1}^{N_j} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_{k_j}) \right].$$

If $\mathbf{X} = \mathbf{A}\mathbf{x}$ and $\mathbf{H} = (\mathbf{A}^{-1})^T \mathbf{h}$ are the real- and reciprocal-space coordinates in Å and Å⁻¹, and if $\rho_j(\|\mathbf{X}\|)$ is the spherically symmetric electron-density function for atom type j , then

$$f_j(\mathbf{H}) = \int_0^\infty 4\pi \|\mathbf{X}\|^2 \rho_j(\|\mathbf{X}\|) \frac{\sin(2\pi \|\mathbf{H}\| \|\mathbf{X}\|)}{2\pi \|\mathbf{H}\| \|\mathbf{X}\|} d\|\mathbf{X}\|.$$

More complex expansions are used for electron-density studies (see Chapter 1.2 in this volume). Anisotropic Gaussian atoms may be dealt with through the formulae given in Section 1.3.2.4.4.2.

1.3.4.2.1.3. Fourier series for the electron density and its summation

The convergence of the Fourier series for ρ

$$\rho(\mathbf{x}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

is usually examined from the classical point of view (Section 1.3.2.6.10). The summation of multiple Fourier series meets with considerable difficulties, because there is no natural order in $\mathbb{Z}^n$ to play the role of the natural order in $\mathbb{Z}$ (Ash, 1976). In crystallography, however, the structure factors $F(\mathbf{h})$ are often obtained within spheres $\|\mathbf{H}\| \leq \Delta^{-1}$ for increasing resolution (decreasing Δ). Therefore, successive estimates of ρ are most naturally calculated as the corresponding partial sums (Section 1.3.2.6.10.1):

$$S_\Delta(\rho)(\mathbf{x}) = \sum_{\|(\mathbf{A}^{-1})^T \mathbf{h}\| \leq \Delta^{-1}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}).$$

This may be written

$$S_\Delta(\rho)(\mathbf{x}) = (D_\Delta * \rho)(\mathbf{x}),$$

where D_Δ is the ‘spherical Dirichlet kernel’

$$D_\Delta(\mathbf{x}) = \sum_{\|(\mathbf{A}^{-1})^T \mathbf{h}\| \leq \Delta^{-1}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}).$$

D_Δ exhibits numerous negative ripples around its central peak. Thus the ‘series termination errors’ incurred by using $S_\Delta(\rho)$ instead of ρ consist of negative ripples around each atom, and may lead to a Gibbs-like phenomenon (Section 1.3.2.6.10.1) near a molecular boundary.

As in one dimension, Cesàro sums (arithmetic means of partial sums) have better convergence properties, as they lead to a convolution by a ‘spherical Fejér kernel’ which is everywhere positive. Thus Cesàro summation will always produce positive approximations to a positive electron density. Other positive summation kernels were investigated by Pepinsky (1952) and by Waser & Schomaker (1953).

1.3.4.2.1.4. Friedel’s law, anomalous scatterers

If the wavelength λ of the incident X-rays is far from any absorption edge of the atoms in the crystal, there is a constant phase shift in the scattering, and the electron density may be considered to be *real-valued*. Then

$$\begin{aligned} F(\mathbf{h}) &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) d^3\mathbf{x} \\ &= \overline{\int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \exp[2\pi i (-\mathbf{h}) \cdot \mathbf{x}] d^3\mathbf{x}} \\ &= \overline{F(-\mathbf{h})} \text{ since } \overline{\rho(\mathbf{x})} = \rho(\mathbf{x}). \end{aligned}$$

Thus if

$$F(\mathbf{h}) = |F(\mathbf{h})| \exp(i\varphi(\mathbf{h})),$$

then

$$|F(-\mathbf{h})| = |F(\mathbf{h})| \quad \text{and} \quad \varphi(-\mathbf{h}) = -\varphi(\mathbf{h}).$$

This is Friedel’s law (Friedel, 1913). The set $\{F_{\mathbf{h}}\}$ of Fourier coefficients is said to have *Hermitian symmetry*.

If λ is close to some absorption edge(s), the proximity to resonance induces an extra phase shift, whose effect may be represented by letting $\rho(\mathbf{x})$ take on *complex values*. Let

$$\rho(\mathbf{x}) = \rho^R(\mathbf{x}) + i\rho^I(\mathbf{x})$$

and correspondingly, by termwise Fourier transformation

$$F(\mathbf{h}) = F^R(\mathbf{h}) + iF^I(\mathbf{h}).$$

Since $\rho^R(\mathbf{x})$ and $\rho^I(\mathbf{x})$ are both real, $F^R(\mathbf{h})$ and $F^I(\mathbf{h})$ are both Hermitian symmetric, hence

$$F(-\mathbf{h}) = \overline{F^R(\mathbf{h})} + i\overline{F^I(\mathbf{h})},$$

while

$$\overline{F(\mathbf{h})} = \overline{F^R(\mathbf{h})} - i\overline{F^I(\mathbf{h})}.$$

Thus $F(-\mathbf{h}) \neq \overline{F(\mathbf{h})}$, so that Friedel’s law is violated. The components $F^R(\mathbf{h})$ and $F^I(\mathbf{h})$, which do obey Friedel’s law, may be expressed as:

$$F^R(\mathbf{h}) = \frac{1}{2}[F(\mathbf{h}) + \overline{F(-\mathbf{h})}],$$

$$F^I(\mathbf{h}) = \frac{1}{2i}[F(\mathbf{h}) - \overline{F(-\mathbf{h})}].$$

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1.3.4.2.1.5. *Parseval's identity and other L^2 theorems*
By Section 1.3.2.4.3.3 and Section 1.3.2.6.10.2,

$$\sum_{\mathbf{h} \in \mathbb{Z}^3} |F(\mathbf{h})|^2 = \int_{\mathbb{R}^3/\mathbb{Z}^3} |\rho(\mathbf{x})|^2 d^3\mathbf{x} = V \int_{\mathbb{R}^3/\Lambda} |\rho(\mathbf{X})|^2 d^3\mathbf{X}.$$

Usually $\rho(\mathbf{x})$ is real and positive, hence $|\rho(\mathbf{x})| = \rho(\mathbf{x})$, but the identity remains valid even when $\rho(\mathbf{x})$ is made complex-valued by the presence of anomalous scatterers.

If $\{G_{\mathbf{h}}\}$ is the collection of structure factors belonging to another electron density $\sigma = A^{\#}\sigma$ with the same period lattice as ρ , then

$$\begin{aligned} \sum_{\mathbf{h} \in \mathbb{Z}^3} \overline{F(\mathbf{h})} G(\mathbf{h}) &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \overline{\rho(\mathbf{x})} \sigma(\mathbf{x}) d^3\mathbf{x} \\ &= V \int_{\mathbb{R}^3/\Lambda} \rho(\mathbf{X}) \sigma(\mathbf{X}) d^3\mathbf{X}. \end{aligned}$$

Thus, norms and inner products may be evaluated either from structure factors or from 'maps'.

1.3.4.2.1.6. *Convolution, correlation and Patterson function*

Let $\rho = r * \rho^0$ and $\sigma = r * \sigma^0$ be two electron densities referred to crystallographic coordinates, with structure factors $\{F_{\mathbf{h}}\}_{\mathbf{h} \in \mathbb{Z}^3}$ and $\{G_{\mathbf{h}}\}_{\mathbf{h} \in \mathbb{Z}^3}$, so that

$$\begin{aligned} \rho_{\mathbf{x}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \\ \sigma_{\mathbf{x}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} G(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}). \end{aligned}$$

The distribution $\omega = r * (\rho^0 * \sigma^0)$ is well defined, since the generalized support condition (Section 1.3.2.3.9.7) is satisfied. The forward version of the convolution theorem implies that if

$$\omega_{\mathbf{x}} = \sum_{\mathbf{h} \in \mathbb{Z}^3} W(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}),$$

then

$$W(\mathbf{h}) = F(\mathbf{h})G(\mathbf{h}).$$

If either ρ^0 or σ^0 is infinitely differentiable, then the distribution $\psi = \rho \times \sigma$ exists, and if we analyse it as

$$\psi_{\mathbf{x}} = \sum_{\mathbf{h} \in \mathbb{Z}^3} Y(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}),$$

then the backward version of the convolution theorem reads:

$$Y(\mathbf{h}) = \sum_{\mathbf{k} \in \mathbb{Z}^3} F(\mathbf{h})G(\mathbf{h} - \mathbf{k}).$$

The *cross correlation* $\kappa[\rho, \sigma]$ between ρ and σ is the $\mathbb{Z}^3$ -periodic distribution defined by:

$$\kappa = \check{\rho}^0 * \sigma.$$

If ρ^0 and σ^0 are locally integrable,

$$\begin{aligned} \kappa[\rho, \sigma](\mathbf{t}) &= \int_{\mathbb{R}^3} \rho^0(\mathbf{x}) \sigma(\mathbf{x} + \mathbf{t}) d^3\mathbf{x} \\ &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \sigma(\mathbf{x} + \mathbf{t}) d^3\mathbf{x}. \end{aligned}$$

Let

$$\kappa(\mathbf{t}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} K(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}).$$

The combined use of the shift property and of the forward convolution theorem then gives immediately:

$$K(\mathbf{h}) = \overline{F(\mathbf{h})} G(\mathbf{h});$$

hence the Fourier series representation of $\kappa[\rho, \sigma]$:

$$\kappa[\rho, \sigma](\mathbf{t}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} \overline{F(\mathbf{h})} G(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}).$$

Clearly, $\kappa[\rho, \sigma] = (\kappa[\sigma, \rho])^*$, as shown by the fact that permuting F and G changes $K(\mathbf{h})$ into its complex conjugate.

The *auto-correlation* of ρ is defined as $\kappa[\rho, \rho]$ and is called the *Patterson function* of ρ . If ρ consists of point atoms, *i.e.*

$$\rho^0 = \sum_{j=1}^N Z_j \delta_{(\mathbf{x}_j)},$$

then

$$\kappa[\rho, \rho] = r * \left[\sum_{j=1}^N \sum_{k=1}^N Z_j Z_k \delta_{(\mathbf{x}_j - \mathbf{x}_k)} \right]$$

contains information about interatomic vectors. It has the Fourier series representation

$$\kappa[\rho, \rho](\mathbf{t}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} |F(\mathbf{h})|^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}),$$

and is therefore calculable from the diffraction intensities alone. It was first proposed by Patterson (1934, 1935*a,b*) as an extension to crystals of the radially averaged correlation function used by Warren & Gingrich (1934) in the study of powders.

1.3.4.2.1.7. *Sampling theorems, continuous transforms, interpolation*

Shannon's sampling and interpolation theorem (Section 1.3.2.7.1) takes two different forms, according to whether the property of finite bandwidth is assumed in real space or in reciprocal space.

(1) The most usual setting is in reciprocal space (see Sayre, 1952*c*). Only a finite number of diffraction intensities can be recorded and phased, and for physical reasons the cutoff criterion is the resolution $\Delta = 1/\|\mathbf{H}\|_{\max}$. Electron-density maps are thus calculated as partial sums (Section 1.3.4.2.1.3), which may be written in Cartesian coordinates as

$$S_{\Delta}(\rho)(\mathbf{X}) = \sum_{\mathbf{H} \in \Lambda^*, \|\mathbf{H}\| \leq \Delta^{-1}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{X}).$$

$S_{\Delta}(\rho)$ is band-limited, the support of its spectrum being contained in the solid sphere Σ_{Δ} defined by $\|\mathbf{H}\| \leq \Delta^{-1}$. Let χ_{Δ} be the indicator function of Σ_{Δ} . The transform of the normalized version of χ_{Δ} is (see below, Section 1.3.4.4.3.5)

$$\begin{aligned} I_{\Delta}(\mathbf{X}) &= \frac{3\Delta^3}{4\pi} \mathcal{F}[\chi_{\Delta}](\mathbf{X}) \\ &= \frac{3}{u^3} (\sin u - u \cos u) \quad \text{where } u = 2\pi \frac{\|\mathbf{X}\|}{\Delta}. \end{aligned}$$

By Shannon's theorem, it suffices to calculate $S_{\Delta}(\rho)$ on an integral subdivision Γ of the period lattice Λ such that the sampling criterion is satisfied (*i.e.* that the translates of Σ_{Δ} by vectors of Γ^* do not overlap). Values of $S_{\Delta}(\rho)$ may then be calculated at an arbitrary point $\mathbf{X}$ by the interpolation formula:

$$S_{\Delta}(\rho)(\mathbf{X}) = \sum_{\mathbf{Y} \in \Gamma} I_{\Delta}(\mathbf{X} - \mathbf{Y}) S_{\Delta}(\rho)(\mathbf{Y}).$$

(2) The reverse situation occurs whenever the support of the motif ρ^0 does not fill the whole unit cell, *i.e.* whenever there exists a region M (the 'molecular envelope'), strictly smaller than the unit cell, such that the translates of M by vectors of r do not overlap and that

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$$\chi_M \times \rho^0 = \rho^0.$$

It then follows that $\rho = r * (\chi_M \times \rho)$. Defining the ‘interference function’ G as the normalized indicator function of M according to

$$G(\boldsymbol{\eta}) = \frac{1}{\text{vol}(M)} \tilde{\mathcal{F}}[\chi_M](\boldsymbol{\eta})$$

we may invoke Shannon’s theorem to calculate the value $\tilde{\mathcal{F}}[\rho^0](\boldsymbol{\xi})$ at an arbitrary point $\boldsymbol{\xi}$ of reciprocal space from its sample values $F(\mathbf{h}) = \tilde{\mathcal{F}}[\rho^0](\mathbf{h})$ at points of the reciprocal lattice as

$$\tilde{\mathcal{F}}[\rho^0](\boldsymbol{\xi}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} \mathbf{G}(\boldsymbol{\xi} - \mathbf{h}) F(\mathbf{h}).$$

This aspect of Shannon’s theorem constitutes the mathematical basis of phasing methods based on geometric redundancies created by solvent regions and/or noncrystallographic symmetries (Bricogne, 1974). The connection between Shannon’s theorem and the phase problem was first noticed by Sayre (1952b). He pointed out that the Patterson function of ρ , written as $\kappa[\rho, \rho] = r * (\rho^0 * \rho^0)$, may be viewed as consisting of a motif $\kappa^0 = \rho^0 * \rho^0$ (containing all the internal interatomic vectors) which is periodized by convolution with r . As the translates of κ^0 by vectors of $\mathbb{Z}^3$ do overlap, the sample values of the intensities $|F(\mathbf{h})|^2$ at nodes of the reciprocal lattice do not provide enough data to interpolate intensities $|F(\boldsymbol{\xi})|^2$ at arbitrary points of reciprocal space. Thus the loss of phase is intimately related to the impossibility of intensity interpolation, implying in return that any indication of intensity values attached to non-integral points of the reciprocal lattice is a potential source of phase information.

1.3.4.2.1.8. Sections and projections

It was shown at the end of Section 1.3.2.5.8 that the convolution theorem establishes, under appropriate assumptions, a duality between sectioning a smooth function (viewed as a multiplication by a δ -function in the sectioning coordinate) and projecting its transform (viewed as a convolution with the function $\mathbf{1}$ everywhere equal to 1 as a function of the projection coordinate). This duality follows from the fact that $\mathcal{F}$ and $\tilde{\mathcal{F}}$ map $\mathbf{1}_{x_i}$ to δ_{x_i} and δ_{x_i} to $\mathbf{1}_{x_i}$ (Section 1.3.2.5.6), and from the tensor product property (Section 1.3.2.5.5).

In the case of periodic distributions, projection and section must be performed with respect to directions or subspaces which are integral with respect to the period lattice if the result is to be periodic; furthermore, projections must be performed only on the contents of *one* repeating unit along the direction of projection, or else the result would diverge. The same relations then hold between principal central sections and projections of the electron density and the dual principal central projections and sections of the weighted reciprocal lattice, *e.g.*

$$\rho(x_1, 0, 0) \leftrightarrow \sum_{h_1, h_2} F(h_1, h_2, h_3),$$

$$\rho(x_1, x_2, 0) \leftrightarrow \sum_{h_3} F(h_1, h_2, h_3),$$

$$\rho_{1,2}(x_3) = \int_{\mathbb{R}^2/\mathbb{Z}^2} \rho(x_1, x_2, x_3) dx_1 dx_2 \leftrightarrow F(0, 0, h_3),$$

$$\rho_1(x_2, x_3) = \int_{\mathbb{R}/\mathbb{Z}} \rho(x_1, x_2, x_3) dx_1 \leftrightarrow F(0, h_2, h_3)$$

etc.

When the sections are principal but not central, it suffices to use the shift property of Section 1.3.2.5.5. When the sections or projections are not principal, they can be made principal by changing to new primitive bases B and B^* for Λ and Λ^* , respectively, the transition matrices $\mathbf{P}$ and $\mathbf{P}^*$ to these new bases

being related by $\mathbf{P}^* = (\mathbf{P}^{-1})^T$ in order to preserve duality. This change of basis must be such that one of these matrices (say, $\mathbf{P}$) should have a given integer vector $\mathbf{u}$ as its first column, $\mathbf{u}$ being related to the line or plane defining the section or projection of interest.

The problem of constructing a matrix $\mathbf{P}$ given $\mathbf{u}$ received an erroneous solution in Volume II of *International Tables* (Patterson, 1959), which was subsequently corrected in 1962. Unfortunately, the solution proposed there is complicated and does not suggest a general approach to the problem. It therefore seems worthwhile to record here an effective procedure which solves this problem in any dimension n (Watson, 1970).

Let

$$\mathbf{u} = \begin{pmatrix} u_1 \\ \vdots \\ u_n \end{pmatrix}$$

be a primitive integral vector, *i.e.* g.c.d. $(u_1, \dots, u_n) = 1$. Then an $n \times n$ integral matrix $\mathbf{P}$ with $\det \mathbf{P} = 1$ having $\mathbf{u}$ as its first column can be constructed by induction as follows. For $n = 1$ the result is trivial. For $n = 2$ it can be solved by means of the Euclidean algorithm, which yields z_1, z_2 such that $u_1 z_2 - u_2 z_1 = 1$, so that we

may take $\mathbf{P} = \begin{pmatrix} u_1 & z_1 \\ u_2 & z_2 \end{pmatrix}$. Note that, if $\mathbf{z} = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}$ is a solution,

then $\mathbf{z} + m\mathbf{u}$ is another solution for any $m \in \mathbb{Z}$. For $n \geq 3$, write

$$\mathbf{u} = \begin{pmatrix} u_1 \\ d\mathbf{z} \end{pmatrix} \text{ with } d = \text{g.c.d.}(u_2, \dots, u_n) \text{ so that both } \mathbf{z} = \begin{pmatrix} z_2 \\ \vdots \\ z_n \end{pmatrix}$$

and $\begin{pmatrix} u_1 \\ d \end{pmatrix}$ are primitive. By the inductive hypothesis there is an integral 2×2 matrix $\mathbf{V}$ with $\begin{pmatrix} u_1 \\ d \end{pmatrix}$ as its first column, and an

integral $(n-1) \times (n-1)$ matrix $\mathbf{Z}$ with $\mathbf{z}$ as its first column, with $\det \mathbf{V} = 1$ and $\det \mathbf{Z} = 1$.

Now put

$$\mathbf{P} = \begin{pmatrix} 1 & \\ & \mathbf{Z} \end{pmatrix} \begin{pmatrix} \mathbf{V} \\ & \mathbf{I}_{n-2} \end{pmatrix},$$

i.e.

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & z_2 & * & \dots & * \\ 0 & z_3 & * & \dots & * \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & z_n & * & \dots & * \end{pmatrix} \begin{pmatrix} u_1 & * & 0 & \dots & 0 \\ d & * & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 1 \end{pmatrix}.$$

The first column of $\mathbf{P}$ is

$$\begin{pmatrix} u_1 \\ dz_2 \\ \vdots \\ dz_n \end{pmatrix} = \mathbf{u},$$

and its determinant is 1, QED.

The incremental step from dimension $n-1$ to dimension n is the construction of 2×2 matrix $\mathbf{V}$, for which there exist infinitely many solutions labelled by an integer m_{n-1} . Therefore, the collection of matrices $\mathbf{P}$ which solve the problem is labelled by $n-1$ arbitrary integers $(m_1, m_2, \dots, m_{n-1})$. This freedom can be used to adjust the shape of the basis B .

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Once $\mathbf{P}$ has been chosen, the calculation of general sections and projections is transformed into that of *principal* sections and projections by the changes of coordinates:

$$\mathbf{x} = \mathbf{P}\mathbf{x}', \quad \mathbf{h} = \mathbf{P}^*\mathbf{h}',$$

and an appeal to the tensor product property.

Booth (1945a) made use of the convolution theorem to form the Fourier coefficients of 'bounded projections', which provided a compromise between 2D and 3D Fourier syntheses. If it is desired to compute the projection on the (x, y) plane of the electron density lying between the planes $z = z_1$ and $z = z_2$, which may be written as

$$[\rho \times (\mathbf{1}_x \otimes \mathbf{1}_y \otimes \chi_{[z_1, z_2]})] * (\delta_x \otimes \delta_y \otimes \mathbf{1}_z).$$

The transform is then

$$[F * (\delta_h \otimes \delta_k \otimes \tilde{\mathcal{F}}[\chi_{[z_1, z_2]}])] \times (\mathbf{1}_h \otimes \mathbf{1}_k \otimes \delta_l),$$

giving for coefficient (h, k) :

$$\sum_{l \in \mathbb{Z}} F(h, k, l) \exp\{2\pi i l [(z_1 + z_2)/2]\} \times \frac{\sin \pi l (z_1 - z_2)}{\pi l}.$$

1.3.4.2.1.9. Differential syntheses

Another particular instance of the convolution theorem is the duality between differentiation and multiplication by a monomial (Sections 1.3.2.4.2.8, 1.3.2.5.8).

In the present context, this result may be written

$$\begin{aligned} \tilde{\mathcal{F}} \left[\frac{\partial^{m_1+m_2+m_3} \rho}{\partial X_1^{m_1} \partial X_2^{m_2} \partial X_3^{m_3}} \right] (\mathbf{H}) \\ = (-2\pi i)^{m_1+m_2+m_3} H_1^{m_1} H_2^{m_2} H_3^{m_3} F(\mathbf{A}^T \mathbf{H}) \end{aligned}$$

in Cartesian coordinates, and

$$\tilde{\mathcal{F}} \left[\frac{\partial^{m_1+m_2+m_3} \rho}{\partial x_1^{m_1} \partial x_2^{m_2} \partial x_3^{m_3}} \right] (\mathbf{h}) = (-2\pi i)^{m_1+m_2+m_3} h_1^{m_1} h_2^{m_2} h_3^{m_3} F(\mathbf{h})$$

in crystallographic coordinates.

A particular case of the first formula is

$$-4\pi^2 \sum_{\mathbf{H} \in \Lambda^*} \|\mathbf{H}\|^2 F(\mathbf{A}^T \mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{X}) = \Delta \rho(\mathbf{X}),$$

where

$$\Delta \rho = \sum_{j=1}^3 \frac{\partial^2 \rho}{\partial X_j^2}$$

is the Laplacian of ρ .

The second formula has been used with $|\mathbf{m}| = 1$ or 2 to compute 'differential syntheses' and refine the location of maxima (or other stationary points) in electron-density maps. Indeed, the values at $\mathbf{x}$ of the gradient vector $\nabla \rho$ and Hessian matrix $(\nabla \nabla^T) \rho$ are readily obtained as

$$\begin{aligned} (\nabla \rho)(\mathbf{x}) &= \sum_{\mathbf{h} \in \mathbb{Z}^3} (-2\pi i \mathbf{h}) F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \\ [(\nabla \nabla^T) \rho](\mathbf{x}) &= \sum_{\mathbf{h} \in \mathbb{Z}^3} (-4\pi^2 \mathbf{h} \mathbf{h}^T) F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \end{aligned}$$

and a step of Newton iteration towards the nearest stationary point of ρ will proceed by

$$\mathbf{x} \mapsto \mathbf{x} - \{[(\nabla \nabla^T) \rho](\mathbf{x})\}^{-1} (\nabla \rho)(\mathbf{x}).$$

The modern use of Fourier transforms to speed up the computation of derivatives for model refinement will be described in Section 1.3.4.4.7.

The converse property is also useful: it relates the derivatives of the continuous transform $\tilde{\mathcal{F}}[\rho^0]$ to the moments of ρ^0 :

$$\frac{\partial^{m_1+m_2+m_3} \tilde{\mathcal{F}}[\rho^0]}{\partial X_1^{m_1} \partial X_2^{m_2} \partial X_3^{m_3}} (\mathbf{H}) = \tilde{\mathcal{F}}[(2\pi i)^{m_1+m_2+m_3} X_1^{m_1} X_2^{m_2} X_3^{m_3} \rho_x^0](\mathbf{H}).$$

For $|\mathbf{m}| = 2$ and $\mathbf{H} = \mathbf{0}$, this identity gives the well known relation between the Hessian matrix of the transform $\tilde{\mathcal{F}}[\rho^0]$ at the origin of reciprocal space and the inertia tensor of the motif ρ^0 . This is a particular case of the moment-generating properties of $\tilde{\mathcal{F}}$, which will be further developed in Section 1.3.4.5.2.

1.3.4.2.1.10. Toeplitz forms, determinantal inequalities and Szegő's theorem

The classical results presented in Section 1.3.2.6.9 can be readily generalized to the case of triple Fourier series; no new concept is needed, only an obvious extension of the notation.

Let ρ be real-valued, so that Friedel's law holds and $F(-\mathbf{h}) = F(\mathbf{h})$. Let $\mathbf{H}$ be a finite set of indices comprising the origin: $\mathbf{H} = \{\mathbf{h}_0 = \mathbf{0}, \mathbf{h}_1, \dots, \mathbf{h}_n\}$. Then the Hermitian form in $n + 1$ complex variables

$$T_{\mathbf{H}}[\rho](\mathbf{u}) = \sum_{j, k=0}^n F(\mathbf{h}_j - \mathbf{h}_k) \bar{u}_j u_k$$

is called the Toeplitz form of order $\mathbf{H}$ associated to ρ . By the convolution theorem and Parseval's identity,

$$T_{\mathbf{H}}[\rho](\mathbf{u}) = \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \left| \sum_{j=0}^n u_j \exp(2\pi i \mathbf{h}_j \cdot \mathbf{x}) \right|^2 d^3 \mathbf{x}.$$

If ρ is almost everywhere non-negative, then for all $\mathbf{H}$ the forms $T_{\mathbf{H}}[\rho]$ are positive semi-definite and therefore all Toeplitz determinants $D_{\mathbf{H}}[\rho]$ are non-negative, where

$$D_{\mathbf{H}}[\rho] = \det \{ [F(\mathbf{h}_j - \mathbf{h}_k)] \}.$$

The Toeplitz–Carathéodory–Herglotz theorem given in Section 1.3.2.6.9.2 states that the converse is true: if $D_{\mathbf{H}}[\rho] \geq 0$ for all $\mathbf{H}$, then ρ is almost everywhere non-negative. This result is known in the crystallographic literature through the papers of Karle & Hauptman (1950), MacGillavry (1950), and Goedkoop (1950), following previous work by Harker & Kasper (1948) and Gillis (1948a,b).

Szegő's study of the asymptotic distribution of the eigenvalues of Toeplitz forms as their order tends to infinity remains valid. Some precautions are needed, however, to define the notion of a sequence $(\mathbf{H}_k)$ of finite subsets of indices tending to infinity: it suffices that the $\mathbf{H}_k$ should consist essentially of the reciprocal-lattice points $\mathbf{h}$ contained within a domain of the form $k\Omega$ (k -fold dilation of Ω) where Ω is a convex domain in $\mathbb{R}^3$ containing the origin (Widom, 1960). Under these circumstances, the eigenvalues $\lambda_{\nu}^{(n)}$ of the Toeplitz forms $T_{\mathbf{H}_k}[\rho]$ become equidistributed with the sample values $\rho_{\nu}^{(n)}$ of ρ on a grid satisfying the Shannon sampling criterion for the data in $\mathbf{H}_k$ (cf. Section 1.3.2.6.9.3).

A particular consequence of this equidistribution is that the geometric means of the $\lambda_{\nu}^{(n)}$ and of the $\rho_{\nu}^{(n)}$ are equal, and hence as in Section 1.3.2.6.9.4

$$\lim_{k \rightarrow \infty} \{D_{\mathbf{H}_k}[\rho]\}^{1/|\mathbf{H}_k|} = \exp \left\{ \int_{\mathbb{R}^3/\mathbb{Z}^3} \log \rho(\mathbf{x}) d^3 \mathbf{x} \right\},$$

where $|\mathbf{H}_k|$ denotes the number of reflections in $\mathbf{H}_k$. Complementary terms giving a better comparison of the two sides were obtained by Widom (1960, 1975) and Linnik (1975).

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This formula played an important role in the solution of the 2D Ising model by Onsager (1944) (see Montroll *et al.*, 1963). It is also encountered in phasing methods involving the ‘Burg entropy’ (Britten & Collins, 1982; Narayan & Nityananda, 1982; Bricogne, 1982, 1984, 1988).

1.3.4.2.2. Crystal symmetry

1.3.4.2.2.1. Crystallographic groups

The description of a crystal given so far has dealt only with its invariance under the action of the (discrete Abelian) group of translations by vectors of its period lattice Λ .

Let the crystal now be embedded in Euclidean 3-space, so that it may be acted upon by the group $M(3)$ of rigid (*i.e.* distance-preserving) motions of that space. The group $M(3)$ contains a normal subgroup $T(3)$ of translations, and the quotient group $M(3)/T(3)$ may be identified with the 3-dimensional orthogonal group $O(3)$. The period lattice Λ of a crystal is a discrete uniform subgroup of $T(3)$.

The possible invariance properties of a crystal under the action of $M(3)$ are captured by the following definition: a *crystallographic group* is a subgroup Γ of $M(3)$ if

- (i) $\Gamma \cap T(3) = \Lambda$, a period lattice and a normal subgroup of Γ ;
- (ii) the factor group $G = \Gamma/\Lambda$ is finite.

The two properties are not independent: by a theorem of Bieberbach (1911), they follow from the assumption that Λ is a discrete subgroup of $M(3)$ which operates without accumulation point and with a compact fundamental domain (see Auslander, 1965). These two assumptions imply that G acts on Λ through an integral representation, and this observation leads to a complete enumeration of all distinct Γ 's. The mathematical theory of these groups is still an active research topic (see, for instance, Farkas, 1981), and has applications to Riemannian geometry (Wolf, 1967).

This classification of crystallographic groups is described elsewhere in these *Tables* (Wondratschek, 1995), but it will be surveyed briefly in Section 1.3.4.2.2.3 for the purpose of establishing further terminology and notation, after recalling basic notions and results concerning groups and group actions in Section 1.3.4.2.2.2.

1.3.4.2.2.2. Groups and group actions

The books by Hall (1959) and Scott (1964) are recommended as reference works on group theory.

(a) Left and right actions

Let G be a group with identity element e , and let X be a set. An *action* of G on X is a mapping from $G \times X$ to X with the property that, if gx denotes the image of (g, x) , then

- (i) $(g_1 g_2)x = g_1(g_2 x)$ for all $g_1, g_2 \in G$ and all $x \in X$,
- (ii) $ex = x$ for all $x \in X$.

An element g of G thus induces a mapping T_g of X into itself defined by $T_g(x) = gx$, with the ‘representation property’:

- (iii) $T_{g_1 g_2} = T_{g_1} T_{g_2}$ for all $g_1, g_2 \in G$.

Since G is a group, every g has an inverse g^{-1} ; hence every mapping T_g has an inverse $T_{g^{-1}}$, so that each T_g is a permutation of X .

Strictly speaking, what has just been defined is a *left* action. A *right* action of G on X is defined similarly as a mapping $(g, x) \mapsto xg$ such that

- (i') $x(g_1 g_2) = (xg_1)g_2$ for all $g_1, g_2 \in G$ and all $x \in X$,
- (ii') $xe = x$ for all $x \in X$.

The mapping T'_g defined by $T'_g(x) = xg$ then has the ‘right-representation’ property:

- (iii') $T'_{g_1 g_2} = T'_{g_2} T'_{g_1}$ for all $g_1, g_2 \in G$.

The essential difference between left and right actions is of course not whether the elements of G are written on the left or right of those of X : it lies in the difference between (iii) and (iii'). In a left action the product $g_1 g_2$ in G operates on $x \in X$ by g_2 operating first, then g_1 operating on the result; in a right action, g_1 operates first, then g_2 . This distinction will be of importance in Sections 1.3.4.2.2.4 and 1.3.4.2.2.5. In the sequel, we will use left actions unless otherwise stated.

(b) Orbits and isotropy subgroups

Let x be a fixed element of X . Two fundamental entities are associated to x :

- (1) the subset of G consisting of all g such that $gx = x$ is a subgroup of G , called the *isotropy subgroup* of x and denoted G_x ;
- (2) the subset of X consisting of all elements gx with g running through G is called the *orbit* of x under G and is denoted Gx .

Through these definitions, the action of G on X can be related to the internal structure of G , as follows. Let G/G_x denote the collection of distinct left cosets of G_x in G , *i.e.* of distinct subsets of G of the form gG_x . Let $|G|$, $|G_x|$, $|Gx|$ and $|G/G_x|$ denote the numbers of elements in the corresponding sets. The number $|G/G_x|$ of distinct cosets of G_x in G is also denoted $[G : G_x]$ and is called the *index* of G_x in G ; by Lagrange's theorem

$$[G : G_x] = |G/G_x| = \frac{|G|}{|G_x|}.$$

Now if g_1 and g_2 are in the same coset of G_x , then $g_2 = g_1 g'$ with $g' \in G_x$, and hence $g_1 x = g_2 x$; the converse is obviously true. Therefore, the mapping from cosets to orbit elements

$$gG_x \mapsto gx$$

establishes a one-to-one correspondence between the distinct left cosets of G_x in G and the elements of the orbit of x under G . It follows that the number of distinct elements in the orbit of x is equal to the index of G_x in G :

$$|Gx| = [G : G_x] = \frac{|G|}{|G_x|},$$

and that the elements of the orbit of x may be listed without repetition in the form

$$Gx = \{\gamma x | \gamma \in G/G_x\}.$$

Similar definitions may be given for a right action of G on X . The set of distinct right cosets $G_x g$ in G , denoted $G_x \backslash G$, is then in one-to-one correspondence with the distinct elements in the orbit xG of x .

(c) Fundamental domain and orbit decomposition

The group properties of G imply that two orbits under G are either disjoint or equal. The set X may thus be written as the *disjoint* union

$$X = \bigcup_{i \in I} Gx_i,$$

where the x_i are elements of distinct orbits and I is an indexing set labelling them. The subset $D = \{x_i\}_{i \in I}$ is said to constitute a *fundamental domain* (mathematical terminology) or an *asymmetric unit* (crystallographic terminology) for the action of G on X : it contains one representative x_i of each distinct orbit. Clearly, other fundamental domains may be obtained by choosing different representatives for these orbits.

If X is finite and if f is an arbitrary complex-valued function over X , the ‘integral’ of f over X may be written as a sum of integrals over the distinct orbits, yielding the *orbit decomposition formula*:

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$$\begin{aligned}\sum_{x \in X} f(x) &= \sum_{i \in I} \left(\sum_{y_i \in Gx_i} f(y_i) \right) = \sum_{i \in I} \left(\sum_{\gamma_i \in G/G_{x_i}} f(\gamma_i x_i) \right) \\ &= \sum_{i \in I} \frac{1}{|G_{x_i}|} \left(\sum_{g_i \in G} f(g_i x_i) \right).\end{aligned}$$

In particular, taking $f(x) = 1$ for all x and denoting by $|X|$ the number of elements of X :

$$|X| = \sum_{i \in I} |Gx_i| = \sum_{i \in I} |G/G_{x_i}| = \sum_{i \in I} \frac{|G|}{|G_{x_i}|}.$$

(d) *Conjugation, normal subgroups, semi-direct products*

A group G acts on itself by *conjugation*, i.e. by associating to $g \in G$ the mapping C_g defined by

$$C_g(h) = ghg^{-1}.$$

Indeed, $C_g(hk) = C_g(h)C_g(k)$ and $[C_g(h)]^{-1} = C_{g^{-1}}(h)$. In particular, C_g operates on the set of subgroups of G , two subgroups H and K being called conjugate if $H = C_g(K)$ for some $g \in G$; for example, it is easily checked that $G_{gx} = C_g(G_x)$. The orbits under this action are the *conjugacy classes* of subgroups of G , and the isotropy subgroup of H under this action is called the *normalizer* of H in G .

If $\{H\}$ is a one-element orbit, H is called a *self-conjugate* or *normal* subgroup of G ; the cosets of H in G then form a group G/H called the *factor group* of G by H .

Let G and H be two groups, and suppose that G acts on H by *automorphisms* of H , i.e. in such a way that

$$\begin{aligned}g(h_1 h_2) &= g(h_1)g(h_2) \\ g(e_H) &= e_H \quad (\text{where } e_H \text{ is the identity element of } H). \\ g(h^{-1}) &= (g(h))^{-1}\end{aligned}$$

Then the symbols $[g, h]$ with $g \in G, h \in H$ form a group K under the product rule:

$$[g_1, h_1][g_2, h_2] = [g_1 g_2, h_1 g_1(h_2)]$$

{associativity checks; $[e_G, e_H]$ is the identity; $[g, h]$ has inverse $[g^{-1}, g^{-1}(h^{-1})]$. The group K is called the *semi-direct product* of H by G , denoted $K = H \rtimes G$.

The elements $[g, e_H]$ form a subgroup of K isomorphic to G , the elements $[e_G, h]$ form a normal subgroup of K isomorphic to H , and the action of G on H may be represented as an action by conjugation in the sense that

$$C_{[g, e_H]}([e_G, h]) = [e_G, g(h)].$$

A familiar example of semi-direct product is provided by the group of Euclidean motions $M(3)$ (Section 1.3.4.2.2.1). An element S of $M(3)$ may be written $S = [R, t]$ with $R \in O(3)$, the orthogonal group, and $t \in T(3)$, the translation group, and the product law

$$[R_1, t_1][R_2, t_2] = [R_1 R_2, t_1 + R_1(t_2)]$$

shows that $M(3) = T(3) \rtimes O(3)$ with $O(3)$ acting on $T(3)$ by rotating the translation vectors.

(e) *Associated actions in function spaces*

For every left action T_g of G in X , there is an associated left action $T_g^\#$ of G on the space $L(X)$ of complex-valued functions over X , defined by ‘change of variable’ (Section 1.3.2.3.9.5):

$$[T_g^\# f](x) = f((T_g)^{-1}x) = f(g^{-1}x).$$

Indeed for any g_1, g_2 in G ,

$$\begin{aligned}[T_{g_1}^\# [T_{g_2}^\# f]](x) &= [T_{g_2}^\# f]((T_{g_1})^{-1}x) = f[T_{g_2}^{-1} T_{g_1}^{-1}x] \\ &= f((T_{g_1} T_{g_2})^{-1}x);\end{aligned}$$

since $T_{g_1} T_{g_2} = T_{g_1 g_2}$, it follows that

$$T_{g_1}^\# T_{g_2}^\# = T_{g_1 g_2}^\#.$$

It is clear that the change of variable must involve the action of g^{-1} (not g) if $T^\#$ is to define a *left* action; using g instead would yield a *right* action.

The linear representation operators $T_g^\#$ on $L(X)$ provide the most natural instrument for stating and exploiting symmetry properties which a function may possess with respect to the action of G . Thus a function $f \in L(X)$ will be called *G-invariant* if $f(gx) = f(x)$ for all $g \in G$ and all $x \in X$. The value $f(x)$ then depends on x only through its orbit Gx , and f is uniquely defined once it is specified on a fundamental domain $D = \{x_i\}_{i \in I}$; its integral over X is then a weighted sum of its values in D :

$$\sum_{x \in X} f(x) = \sum_{i \in I} [G : G_{x_i}] f(x_i).$$

The G -invariance of f may be written:

$$T_g^\# f = f \quad \text{for all } g \in G.$$

Thus f is invariant under each $T_g^\#$, which obviously implies that f is invariant under the linear operator in $L(X)$

$$A_G = \frac{1}{|G|} \sum_{g \in G} T_g^\#,$$

which averages an arbitrary function by the action of G . Conversely, if $A_G f = f$, then

$$T_{g_0}^\# f = T_{g_0}^\# (A_G f) = (T_{g_0}^\# A_G) f = A_G f = f \quad \text{for all } g_0 \in G,$$

so that the two statements of the G -invariance of f are equivalent. The identity

$$T_{g_0}^\# A_G = A_G \quad \text{for all } g_0 \in G$$

is easily proved by observing that the map $g \mapsto g_0 g$ (g_0 being any element of G) is a one-to-one map from G into itself, so that

$$\sum_{g \in G} T_g^\# = \sum_{g \in G} T_{g_0 g}^\#$$

as these sums differ only by the order of the terms. The same identity implies that A_G is a *projector*:

$$(A_G)^2 = A_G,$$

and hence that its eigenvalues are either 0 or 1. In summary, we may say that the invariance of f under G is equivalent to f being an eigenfunction of the associated projector A_G for eigenvalue 1.

(f) *Orbit exchange*

One final result about group actions which will be used repeatedly later is concerned with the case when X has the structure of a Cartesian product:

$$X = X_1 \times X_2 \times \dots \times X_n$$

and when G acts *diagonally* on X , i.e. acts on each X_j separately:

$$gx = g(x_1, x_2, \dots, x_n) = (gx_1, gx_2, \dots, gx_n).$$

Then complete sets (but not usually minimal sets) of representatives

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of the distinct orbits for the action of G in X may be obtained in the form

$$D_k = X_1 \times \dots \times X_{k-1} \times \{x_{i_k}^{(k)}\}_{i_k \in I_k} \times X_{k+1} \times \dots \times X_n$$

for each $k = 1, 2, \dots, n$, i.e. by taking a fundamental domain in X_k and all the elements in X_j with $j \neq k$. The action of G on each D_k does indeed generate the whole of X : given an arbitrary element $y = (y_1, y_2, \dots, y_n)$ of X , there is an index $i_k \in I_k$ such that $y_k \in Gx_{i_k}^{(k)}$ and a coset of $G_{x_{i_k}^{(k)}}$ in G such that $y_k = \gamma x_{i_k}^{(k)}$ for any representative γ of that coset; then

$$y = \gamma(\gamma^{-1}y_1, \dots, \gamma^{-1}y_{k-1}, x_{i_k}^{(k)}, \gamma^{-1}y_{k+1}, \dots, \gamma^{-1}y_n)$$

which is of the form $y = \gamma d_k$ with $d_k \in D_k$.

The various D_k are related in a simple manner by ‘transposition’ or ‘orbit exchange’ (the latter name is due to J. W. Cooley). For instance, D_j may be obtained from D_k ($j \neq k$) as follows: for each $y_j \in X_j$ there exists $g(y_j) \in G$ and $i_j(y_j) \in I_j$ such that $y_j = g(y_j)x_{i_j(y_j)}^{(j)}$; therefore

$$D_j = \bigcup_{y_j \in X_j} [g(y_j)]^{-1} D_k,$$

since the fundamental domain of X_k is thus expanded to the whole of X_k , while X_j is reduced to its fundamental domain. In other words: orbits are simultaneously collapsed in the j th factor and expanded in the k th.

When G operates without fixed points in each X_k (i.e. $G_{x_k} = \{e\}$ for all $x_k \in X_k$), then each D_k is a fundamental domain for the action of G in X . The existence of fixed points in some or all of the X_k complicates the situation in that for each k and each $x_k \in X_k$ such that $G_{x_k} \neq \{e\}$ the action of G/G_{x_k} on the other factors must be examined. Shenefelt (1988) has made a systematic study of orbit exchange for space group $P622$ and its subgroups.

Orbit exchange will be encountered, in a great diversity of forms, as the basic mechanism by which intermediate results may be rearranged between the successive stages of the computation of crystallographic Fourier transforms (Section 1.3.4.3).

1.3.4.2.2.3. Classification of crystallographic groups

Let Γ be a crystallographic group, Λ the normal subgroup of its lattice translations, and G the finite factor group Γ/Λ . Then G acts on Λ by conjugation [Section 1.3.4.2.2(d)] and this action, being a mapping of a lattice into itself, is representable by matrices with integer entries.

The classification of crystallographic groups proceeds from this observation in the following three steps:

Step 1: find all possible finite abstract groups G which can be represented by 3×3 integer matrices.

Step 2: for each such G find all its inequivalent representations by 3×3 integer matrices, equivalence being defined by a change of primitive lattice basis (i.e. conjugation by a 3×3 integer matrix with determinant ± 1).

Step 3: for each G and each equivalence class of integral representations of G , find all inequivalent extensions of the action of G from Λ to $T(3)$, equivalence being defined by an affine coordinate change [i.e. conjugation by an element of $A(3)$].

Step 1 leads to the following groups, listed in association with the crystal system to which they later give rise:

$\mathbb{Z}/2\mathbb{Z}$	monoclinic
$\mathbb{Z}/2\mathbb{Z} \oplus \mathbb{Z}/2\mathbb{Z}$	orthorhombic
$\mathbb{Z}/3\mathbb{Z}, (\mathbb{Z}/3\mathbb{Z}) \rtimes \{\alpha\}$	trigonal
$\mathbb{Z}/4\mathbb{Z}, (\mathbb{Z}/4\mathbb{Z}) \rtimes \{\alpha\}$	tetragonal
$\mathbb{Z}/6\mathbb{Z}, (\mathbb{Z}/6\mathbb{Z}) \rtimes \{\alpha\}$	hexagonal
$(\mathbb{Z}/2\mathbb{Z} \oplus \mathbb{Z}/2\mathbb{Z}) \rtimes \{S_3\}$	cubic

and the extension of these groups by a centre of inversion. In this list $\rtimes$ denotes a semi-direct product [Section 1.3.4.2.2(d)], α denotes the automorphism $g \mapsto g^{-1}$, and S_3 (the group of permutations on three letters) operates by permuting the copies of $\mathbb{Z}/2\mathbb{Z}$ (using the subgroup A_3 of cyclic permutations gives the tetrahedral subsystem).

Step 2 leads to a list of 73 equivalence classes called *arithmetic classes* of representations $g \mapsto \mathbf{R}_g$, where $\mathbf{R}_g$ is a 3×3 integer matrix, with $\mathbf{R}_{g_1 g_2} = \mathbf{R}_{g_1} \mathbf{R}_{g_2}$ and $\mathbf{R}_e = \mathbf{I}_3$. This enumeration is more familiar if equivalence is relaxed so as to allow conjugation by rational 3×3 matrices with determinant ± 1 : this leads to the 32 crystal classes. The difference between an arithmetic class and its rational class resides in the choice of a lattice mode ($P, A/B/C, I, F$ or R). Arithmetic classes always refer to a primitive lattice, but may use inequivalent integral representations for a given geometric symmetry element; while crystallographers prefer to change over to a non-primitive lattice, if necessary, in order to preserve the same integral representation for a given geometric symmetry element. The matrices $\mathbf{P}$ and $\mathbf{Q} = \mathbf{P}^{-1}$ describing the changes of basis between primitive and centred lattices are listed in Table 5.1 and illustrated in Figs. 5.3 to 5.9, pp. 76–79, of Volume A of *International Tables* (Arnold, 1995).

Step 3 gives rise to a system of congruences for the systems of non-primitive translations $\{\mathbf{t}_g\}_{g \in G}$ which may be associated to the matrices $\{\mathbf{R}_g\}_{g \in G}$ of a given arithmetic class, namely:

$$\mathbf{t}_{g_1 g_2} \equiv \mathbf{R}_{g_1} \mathbf{t}_{g_2} + \mathbf{t}_{g_1} \pmod{\Lambda},$$

first derived by Frobenius (1911). If equivalence under the action of $A(3)$ is taken into account, 219 classes are found. If equivalence is defined with respect to the action of the subgroup $A^+(3)$ of $A(3)$ consisting only of transformations with determinant $+1$, then 230 classes called *space-group types* are obtained. In particular, associating to each of the 73 arithmetic classes a trivial set of non-primitive translations ($\mathbf{t}_g = \mathbf{0}$ for all $g \in G$) yields the 73 symmorphic space groups. This third step may also be treated as an abstract problem concerning group extensions, using cohomological methods [Ascher & Janner (1965); see Janssen (1973) for a summary]; the connection with Frobenius’s approach, as generalized by Zassenhaus (1948), is examined in Ascher & Janner (1968).

The finiteness of the number of space-group types in dimension 3 was shown by Bieberbach (1912) to be the case in arbitrary dimension. The reader interested in N -dimensional space-group theory for $N > 3$ may consult Brown (1969), Brown *et al.* (1978), Schwarzenberger (1980), and Engel (1986). The standard reference for integral representation theory is Curtis & Reiner (1962).

All three-dimensional space groups G have the property of being *solvable*, i.e. that there exists a chain of subgroups

$$G = G_r > G_{r-1} > \dots > G_1 > G_0 = \{e\},$$

where each G_{i-1} is a normal subgroup of G_i and the factor group G_i/G_{i-1} is a *cyclic* group of some order m_i ($1 \leq i \leq r$). This property may be established by inspection, or deduced from a famous theorem of Burnside [see Burnside (1911), pp. 322–323] according to which any group G such that $|G| = p^\alpha q^\beta$, with p and q distinct primes, is solvable; in the case at hand, $p = 2$ and $q = 3$.

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The whole classification of 3D space groups can be performed swiftly by a judicious use of the solvability property (L. Auslander, personal communication).

Solvability facilitates the indexing of elements of G in terms of generators and relations (Coxeter & Moser, 1972; Magnus *et al.*, 1976) for the purpose of calculation. By definition of solvability, elements $g_1, g_2, \dots, g_r$ may be chosen in such a way that the cyclic factor group G_i/G_{i-1} is generated by the coset $g_i G_{i-1}$. The set $\{g_1, g_2, \dots, g_r\}$ is then a system of generators for G such that the defining relations [see Brown *et al.* (1978), pp. 26–27] have the particularly simple form

$$\begin{aligned} g_1^{m_1} &= e, \\ g_i^{m_i} &= g_{i-1}^{a(i,i-1)} g_{i-2}^{a(i,i-2)} \dots g_1^{a(i,1)} \quad \text{for } 2 \leq i \leq r, \\ g_i^{-1} g_j^{-1} g_i g_j &= g_{j-1}^{b(i,j,j-1)} g_{j-2}^{b(i,j,j-2)} \dots g_1^{b(i,j,1)} \quad \text{for } 1 \leq i < j \leq r, \end{aligned}$$

with $0 \leq a(i, h) < m_h$ and $0 \leq b(i, j, h) < m_h$. Each element g of G may then be obtained uniquely as an ‘ordered word’:

$$g = g_r^{k_r} g_{r-1}^{k_{r-1}} \dots g_1^{k_1},$$

with $0 \leq k_i < m_i$ for all $i = 1, \dots, r$, using the algorithm of Jürgensen (1970). Such generating sets and defining relations are tabulated in Brown *et al.* (1978, pp. 61–76). An alternative list is given in Janssen (1973, Table 4.3, pp. 121–123, and Appendix D, pp. 262–271).

1.3.4.2.2.4. Crystallographic group action in real space

The action of a crystallographic group Γ may be written in terms of standard coordinates in $\mathbb{R}^3/\mathbb{Z}^3$ as

$$(g, \mathbf{x}) \mapsto S_g(\mathbf{x}) = \mathbf{R}_g \mathbf{x} + \mathbf{t}_g \pmod{\Lambda}, \quad g \in G,$$

with

$$S_{g_1 g_2} = S_{g_1} S_{g_2}.$$

An important characteristic of the representation $\theta : g \mapsto S_g$ is its *reducibility*, i.e. whether or not it has invariant subspaces other than $\{\mathbf{0}\}$ and the whole of $\mathbb{R}^3/\mathbb{Z}^3$. For triclinic, monoclinic and orthorhombic space groups, θ is reducible to a direct sum of three one-dimensional representations:

$$\mathbf{R}_g = \begin{pmatrix} \mathbf{R}_g^{(1)} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{R}_g^{(2)} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{R}_g^{(3)} \end{pmatrix};$$

for trigonal, tetragonal and hexagonal groups, it is reducible to a direct sum of two representations, of dimension 2 and 1, respectively; while for tetrahedral and cubic groups, it is irreducible.

By Schur’s lemma (see *e.g.* Ledermann, 1987), any matrix which commutes with all the matrices $\mathbf{R}_g$ for $g \in G$ must be a scalar multiple of the identity in each invariant subspace.

In the reducible cases, the reductions involve changes of basis which will be *rational*, not integral, for those arithmetic classes corresponding to non-primitive lattices. Thus the simplification of having maximally reduced representation has as its counterpart the use of non-primitive lattices.

The notions of orbit, isotropy subgroup and fundamental domain (or asymmetric unit) for the action of G on $\mathbb{R}^3/\mathbb{Z}^3$ are inherited directly from the general setting of Section 1.3.4.2.2.2. Points $\mathbf{x}$ for which $G_{\mathbf{x}} \neq \{e\}$ are called *special positions*, and the various types of isotropy subgroups which may be encountered in crystallographic groups have been labelled by means of Wyckoff symbols. The representation operators $S_g^\#$ in $L(\mathbb{R}^3/\mathbb{Z}^3)$ have the form:

$$[S_g^\# f](\mathbf{x}) = f[S_g^{-1}(\mathbf{x})] = f[\mathbf{R}_g^{-1}(\mathbf{x} - \mathbf{t}_g)].$$

The operators $R_g^\#$ associated to the purely rotational part of each transformation S_g will also be used. Note the relation: $S_g^\# = \tau_{\mathbf{t}_g} R_g^\#$.

Let a crystal structure be described by the list of the atoms in its unit cell, indexed by $k \in K$. Let the electron-density distribution about the centre of mass of atom k be described by ρ_k with respect to the standard coordinates $\mathbf{x}$. Then the motif ρ^0 may be written as a sum of translates:

$$\rho^0 = \sum_{k \in K} \tau_{\mathbf{x}_k} \rho_k$$

and the crystal electron density is $\rho = r^* \rho^0$.

Suppose that ρ is invariant under Γ . If $\mathbf{x}_{k_1}$ and $\mathbf{x}_{k_2}$ are in the same orbit, say $\mathbf{x}_{k_2} = S_g(\mathbf{x}_{k_1})$, then

$$\tau_{\mathbf{x}_{k_2}} \rho_{k_2} = S_g^\#(\tau_{\mathbf{x}_{k_1}} \rho_{k_1}).$$

Therefore if $\mathbf{x}_k$ is a special position and thus $G_{\mathbf{x}_k} \neq \{e\}$, then

$$S_g^\#(\tau_{\mathbf{x}_k} \rho_k) = \tau_{\mathbf{x}_k} \rho_k \quad \text{for all } g \in G_{\mathbf{x}_k}.$$

This identity implies that

$$\mathbf{R}_g \mathbf{x}_k + \mathbf{t}_g \equiv \mathbf{x}_k \pmod{\Lambda}$$

(the special position condition), and that

$$\rho_k = R_g^\# \rho_k,$$

i.e. that ρ_k must be invariant by the pure rotational part of $G_{\mathbf{x}_k}$. Trueblood (1956) investigated the consequences of this invariance on the thermal vibration tensor of an atom in a special position (see Section 1.3.4.2.2.6 below).

Let J be a subset of K such that $\{\mathbf{x}_j\}_{j \in J}$ contains exactly one atom from each orbit. An orbit decomposition yields an expression for ρ^0 in terms of symmetry-unique atoms:

$$\rho^0 = \sum_{j \in J} \left(\sum_{\gamma_j \in G/G_{\mathbf{x}_j}} S_{\gamma_j}^\#(\tau_{\mathbf{x}_j} \rho_j) \right)$$

or equivalently

$$\rho^0(\mathbf{x}) = \sum_{j \in J} \left\{ \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \rho_j [\mathbf{R}_{\gamma_j}^{-1}(\mathbf{x} - \mathbf{t}_{\gamma_j}) - \mathbf{x}_j] \right\}.$$

If the atoms are assumed to be Gaussian, write

$$\begin{aligned} \rho_j(\mathbf{X}) &= \frac{Z_j}{|\det \pi \mathbf{U}_j|^{1/2}} \\ &\times \exp\left(-\frac{1}{2} \mathbf{X}^T \mathbf{U}_j^{-1} \mathbf{X}\right) \text{ in Cartesian } \text{\AA} \text{ coordinates,} \end{aligned}$$

where Z_j is the total number of electrons, and where the matrix $\mathbf{U}_j$ combines the Gaussian spread of the electrons in atom j at rest with the covariance matrix of the random positional fluctuations of atom j caused by thermal agitation.

In crystallographic coordinates:

$$\begin{aligned} \rho_j(\mathbf{x}) &= \frac{Z_j}{|\det \pi \mathbf{Q}_j|^{1/2}} \\ &\times \exp\left(-\frac{1}{2} \mathbf{x}^T \mathbf{Q}_j^{-1} \mathbf{x}\right) \text{ with } \mathbf{Q}_j = \mathbf{A}^{-1} \mathbf{U}_j (\mathbf{A}^{-1})^T. \end{aligned}$$

If atom k is in a special position $\mathbf{x}_k$, then the matrix $\mathbf{Q}_k$ must satisfy the identity

$$\mathbf{R}_g \mathbf{Q}_k \mathbf{R}_g^{-1} = \mathbf{Q}_k$$

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for all g in the isotropy subgroup of $\mathbf{x}_k$. This condition may also be written in Cartesian coordinates as

$$\mathbf{T}_g \mathbf{U}_k \mathbf{T}_g^{-1} = \mathbf{U}_k,$$

where

$$\mathbf{T}_g = \mathbf{A} \mathbf{R}_g \mathbf{A}^{-1}.$$

This is a condensed form of the symmetry properties derived by Trueblood (1956).

1.3.4.2.2.5. Crystallographic group action in reciprocal space

An elementary discussion of this topic may be found in Chapter 1.4 of this volume.

Having established that the symmetry of a crystal may be most conveniently stated and handled *via* the left representation $g \mapsto S_g^\#$ of G given by its action on electron-density distributions, it is natural to transpose this action by the identity of Section 1.3.2.5.5:

$$\begin{aligned} \tilde{\mathcal{F}}[S_g^\# T]_\xi &= \tilde{\mathcal{F}}[\tau_{\mathbf{t}_g}(R_g^\# T)]_\xi \\ &= \exp(2\pi i \xi \cdot \mathbf{t}_g) [(\mathbf{R}_g^{-1})^T]^\# \tilde{\mathcal{F}}[T]_\xi \end{aligned}$$

for any tempered distribution T , i.e.

$$\tilde{\mathcal{F}}[S_g^\# T](\xi) = \exp(2\pi i \xi \cdot \mathbf{t}_g) \tilde{\mathcal{F}}[T](\mathbf{R}_g^T \xi)$$

whenever the transforms are functions.

Putting $T = \rho$, a $\mathbb{Z}^3$ -periodic distribution, this relation defines a left action S_g^* of G on $L(\mathbb{Z}^3)$ given by

$$(S_g^* F)(\mathbf{h}) = \exp(2\pi i \xi \cdot \mathbf{t}_g) F(\mathbf{R}_g^T \mathbf{h})$$

which is conjugate to the action $S_g^\#$ in the sense that

$$\tilde{\mathcal{F}}[S_g^\# \rho] = S_g^* \tilde{\mathcal{F}}[\rho], \quad \text{i.e. } S_g^* = \tilde{\mathcal{F}} S_g^\# \tilde{\mathcal{F}}.$$

The identity $S_g^\# \rho = \rho$ expressing the G -invariance of ρ is then equivalent to the identity $S_g^* F = F$ between its structure factors, i.e. (Waser, 1955a)

$$F(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_g) F(\mathbf{R}_g^T \mathbf{h}).$$

If G is made to act on $\mathbb{Z}^3$ via

$$\theta^*: (g, \mathbf{h}) \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h},$$

the usual notions of orbit, isotropy subgroup (denoted $G_{\mathbf{h}}$) and fundamental domain may be attached to this action. The above relation then shows that the spectrum $\{F(\mathbf{h})\}_{\mathbf{h} \in \mathbb{Z}^3}$ is entirely known if it is specified on a fundamental domain D^* containing one reciprocal-lattice point from each orbit of this action.

A reflection $\mathbf{h}$ is called *special* if $G_{\mathbf{h}} \neq \{e\}$. Then for any $g \in G_{\mathbf{h}}$ we have $\mathbf{R}_g^T \mathbf{h} = \mathbf{h}$, and hence

$$F(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_g) F(\mathbf{h}),$$

implying that $F(\mathbf{h}) = 0$ unless $\mathbf{h} \cdot \mathbf{t}_g \equiv 0 \pmod{1}$. Special reflections $\mathbf{h}$ for which $\mathbf{h} \cdot \mathbf{t}_g \not\equiv 0 \pmod{1}$ for some $g \in G_{\mathbf{h}}$ are thus *systematically absent*. This phenomenon is an instance of the duality between periodization and decimation of Section 1.3.2.7.2: if $\mathbf{t}_g \neq \mathbf{0}$, the projection of ρ on the direction of $\mathbf{h}$ has period $(\mathbf{t}_g \cdot \mathbf{h})/(\mathbf{h} \cdot \mathbf{h}) < 1$, hence its transform (which is the portion of F supported by the central line through $\mathbf{h}$) will be decimated, giving rise to the above condition.

A reflection $\mathbf{h}$ is called *centric* if $G_{\mathbf{h}} = G(-\mathbf{h})$, i.e. if the orbit of $\mathbf{h}$ contains $-\mathbf{h}$. Then $\mathbf{R}_\gamma^T \mathbf{h} = -\mathbf{h}$ for some coset γ in $G/G_{\mathbf{h}}$, so that the following relation must hold:

$$|F(\mathbf{h})| \exp(i\varphi_{\mathbf{h}}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_\gamma) |F(-\mathbf{h})| \exp(i\varphi_{-\mathbf{h}}).$$

In the absence of dispersion, Friedel's law gives rise to the *phase restriction*:

$$\varphi_{\mathbf{h}} \equiv \pi \mathbf{h} \cdot \mathbf{t}_\gamma \pmod{\pi}.$$

The value of the restricted phase is independent of the choice of coset representative γ . Indeed, if γ' is another choice, then $\gamma' = g\gamma$ with $g \in G_{\mathbf{h}}$ and by the Frobenius congruences $\mathbf{t}_{\gamma'} = \mathbf{R}_g \mathbf{t}_\gamma + \mathbf{t}_g$, so that

$$\mathbf{h} \cdot \mathbf{t}_{\gamma'} \equiv (\mathbf{R}_g^T \mathbf{h}) \cdot \mathbf{t}_\gamma + \mathbf{h} \cdot \mathbf{t}_g \pmod{1}.$$

Since $g \in G_{\mathbf{h}}$, $\mathbf{R}_g^T \mathbf{h} = \mathbf{h}$ and $\mathbf{h} \cdot \mathbf{t}_g \equiv 0 \pmod{1}$ if $\mathbf{h}$ is not a systematic absence: thus

$$\pi \mathbf{h} \cdot \mathbf{t}_{\gamma'} \equiv \pi \mathbf{h} \cdot \mathbf{t}_\gamma \pmod{\pi}.$$

The treatment of centred lattices may be viewed as another instance of the duality between periodization and decimation (Section 1.3.2.7.2): the periodization of the electron density by the non-primitive lattice translations has as its counterpart in reciprocal space the decimation of the transform by the 'reflection conditions' describing the allowed reflections, the decimation and periodization matrices being each other's contragredient.

The reader may consult the papers by Bienenstock & Ewald (1962) and Wells (1965) for earlier approaches to this material.

1.3.4.2.2.6. Structure-factor calculation

Structure factors may be calculated from a list of symmetry-unique atoms by Fourier transformation of the orbit decomposition formula for the motif ρ^0 given in Section 1.3.4.2.2.4:

$$\begin{aligned} F(\mathbf{h}) &= \tilde{\mathcal{F}}[\rho^0](\mathbf{h}) \\ &= \tilde{\mathcal{F}} \left[\sum_{j \in J} \left(\sum_{\gamma_j \in G/G_{\mathbf{x}_j}} S_{\gamma_j}^\#(\tau_{\mathbf{x}_j} \rho_j) \right) \right](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \tilde{\mathcal{F}}[\tau_{\mathbf{x}_j} \mathbf{R}_{\gamma_j}^\# \tau_{\mathbf{x}_j} \rho_j](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_{\gamma_j}) \\ &\quad \times [(\mathbf{R}_{\gamma_j}^{-1})^T]^\# [\exp(2\pi i \xi \cdot \mathbf{x}_j) \tilde{\mathcal{F}}[\rho_j]_\xi](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_{\gamma_j}) \\ &\quad \times \exp[2\pi i (\mathbf{R}_{\gamma_j}^T \mathbf{h}) \cdot \mathbf{x}_j] \tilde{\mathcal{F}}[\rho_j](\mathbf{R}_{\gamma_j}^T \mathbf{h}); \end{aligned}$$

i.e. finally:

$$F(\mathbf{h}) = \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\} \tilde{\mathcal{F}}[\rho_j](\mathbf{R}_{\gamma_j}^T \mathbf{h}).$$

In the case of Gaussian atoms, the atomic transforms are

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp[-\frac{1}{2} \mathbf{h}^T (4\pi^2 \mathbf{Q}_j) \mathbf{h}]$$

or equivalently

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{H}) = Z_j \exp[-\frac{1}{2} \mathbf{H}^T (4\pi^2 \mathbf{U}_j) \mathbf{H}].$$

Two common forms of equivalent temperature factors (incorporating both atomic form and thermal motion) are

(i) isotropic B :

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp(-\frac{1}{4} B_j \mathbf{H}^T \mathbf{H}),$$

so that $\mathbf{U}_j = (B_j/8\pi^2) \mathbf{I}$, or $\mathbf{Q}_j = (B_j/8\pi^2) \mathbf{A}^{-1} (\mathbf{A}^{-1})^T$;

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(ii) anisotropic β 's:

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp(-\mathbf{h}^T \boldsymbol{\beta}_j \mathbf{h}),$$

so that $\boldsymbol{\beta}_j = 2\pi^2 \mathbf{Q}_j = 2\pi^2 \mathbf{A}^{-1} \mathbf{U}_j (\mathbf{A}^{-1})^T$, or $\mathbf{U}_j = (1/2\pi^2) \mathbf{A} \boldsymbol{\beta}_j \mathbf{A}^T$.

In the first case, $\tilde{\mathcal{F}}[\rho_j](\mathbf{R}_{\gamma_j}^T \mathbf{h})$ does not depend on γ_j , and therefore:

$$F(\mathbf{h}) = \sum_{j \in J} Z_j \exp\{-\frac{1}{4} \boldsymbol{\beta}_j \mathbf{h}^T [\mathbf{A}^{-1} (\mathbf{A}^{-1})^T] \mathbf{h}\} \\ \times \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\}.$$

In the second case, however, no such simplification can occur:

$$F(\mathbf{h}) = \sum_{j \in J} Z_j \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp[-\mathbf{h}^T (\mathbf{R}_{\gamma_j} \boldsymbol{\beta}_j \mathbf{R}_{\gamma_j}^T) \mathbf{h}] \\ \times \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\}.$$

These formulae, or special cases of them, were derived by Rollett & Davies (1955), Waser (1955b), and Trueblood (1956).

The computation of structure factors by applying the discrete Fourier transform to a set of electron-density values calculated on a grid will be examined in Section 1.3.4.4.5.

1.3.4.2.2.7. Electron-density calculations

A formula for the Fourier synthesis of electron-density maps from symmetry-unique structure factors is readily obtained by orbit decomposition:

$$\rho(\mathbf{x}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}) \\ = \sum_{l \in L} \left[\sum_{\gamma_l \in G/G_{\mathbf{h}_l}} F(\mathbf{R}_{\gamma_l}^T \mathbf{h}_l) \exp[-2\pi i (\mathbf{R}_{\gamma_l}^T \mathbf{h}_l) \cdot \mathbf{x}] \right] \\ = \sum_{l \in L} F(\mathbf{h}_l) \left[\sum_{\gamma_l \in G/G_{\mathbf{h}_l}} \exp\{-2\pi i \mathbf{h}_l \cdot [S_{\gamma_l}(\mathbf{x})]\} \right],$$

where L is a subset of $\mathbb{Z}^3$ such that $\{\mathbf{h}_l\}_{l \in L}$ contains exactly one point of each orbit for the action $\theta^* : (g, \mathbf{h}) \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h}$ of G on $\mathbb{Z}^3$. The physical electron density per cubic ångström is then

$$\rho(\mathbf{X}) = \frac{1}{V} \rho(\mathbf{A}\mathbf{x})$$

with V in $\text{\AA}^3$.

In the absence of anomalous scatterers in the crystal and of a centre of inversion $-\mathbf{I}$ in Γ , the spectrum $\{F(\mathbf{h})\}_{\mathbf{h} \in \mathbb{Z}^3}$ has an extra symmetry, namely the Hermitian symmetry expressing Friedel's law (Section 1.3.4.2.1.4). The action of a centre of inversion may be added to that of Γ to obtain further simplification in the above formula: under this extra action, an orbit $G\mathbf{h}_l$ with $\mathbf{h}_l \neq \mathbf{0}$ is either mapped into itself or into the disjoint orbit $G(-\mathbf{h}_l)$; the terms corresponding to $+\mathbf{h}_l$ and $-\mathbf{h}_l$ may then be grouped *within* the common orbit in the first case, and *between* the two orbits in the second case.

Case 1: $G(-\mathbf{h}_l) = G\mathbf{h}_l$, $\mathbf{h}_l$ is *centric*. The cosets in $G/G_{\mathbf{h}_l}$ may be partitioned into two disjoint classes by picking one coset in each of the two-coset orbits of the action of $-\mathbf{I}$. Let $(G/G_{\mathbf{h}_l})^+$ denote one such class: then the *reduced orbit*

$$\{\mathbf{R}_{\gamma_l}^T \mathbf{h}_l | \gamma_l \in (G/G_{\mathbf{h}_l})^+\}$$

contains exactly once the Friedel-unique half of the full orbit $G\mathbf{h}_l$, and thus

$$|(G/G_{\mathbf{h}_l})^+| = \frac{1}{2} |G/G_{\mathbf{h}_l}|.$$

Grouping the summands for $+\mathbf{h}_l$ and $-\mathbf{h}_l$ yields a real-valued summand

$$2F(\mathbf{h}_l) \sum_{\gamma_l \in (G/G_{\mathbf{h}_l})^+} \cos[2\pi \mathbf{h}_l \cdot [S_{\gamma_l}(\mathbf{x})] - \varphi_{\mathbf{h}_l}].$$

Case 2: $G(-\mathbf{h}_l) \neq G\mathbf{h}_l$, $\mathbf{h}_l$ is *acentric*. The two orbits are then disjoint, and the summands corresponding to $+\mathbf{h}_l$ and $-\mathbf{h}_l$ may be grouped together into a single real-valued summand

$$2F(\mathbf{h}_l) \sum_{\gamma_l \in G/G_{\mathbf{h}_l}} \cos[2\pi \mathbf{h}_l \cdot [S_{\gamma_l}(\mathbf{x})] - \varphi_{\mathbf{h}_l}].$$

In order to reindex the collection of all summands of ρ , put

$$L = L_c \cup L_a,$$

where L_c labels the Friedel-unique centric reflections in L and L_a the acentric ones, and let L_a^+ stand for a subset of L_a containing a unique element of each pair $\{+\mathbf{h}_l, -\mathbf{h}_l\}$ for $l \in L_a$. Then

$$\rho(\mathbf{x}) = F(\mathbf{0}) \\ + \sum_{c \in L_c} \left[2F(\mathbf{h}_c) \sum_{\gamma_c \in (G/G_{\mathbf{h}_c})^+} \cos[2\pi \mathbf{h}_c \cdot [S_{\gamma_c}(\mathbf{x})] - \varphi_{\mathbf{h}_c}] \right] \\ + \sum_{a \in L_a^+} \left[2F(\mathbf{h}_a) \sum_{\gamma_a \in G/G_{\mathbf{h}_a}} \cos[2\pi \mathbf{h}_a \cdot [S_{\gamma_a}(\mathbf{x})] - \varphi_{\mathbf{h}_a}] \right].$$

1.3.4.2.2.8. Parseval's theorem with crystallographic symmetry

The general statement of Parseval's theorem given in Section 1.3.4.2.1.5 may be rewritten in terms of symmetry-unique structure factors and electron densities by means of orbit decomposition.

In reciprocal space,

$$\sum_{\mathbf{h} \in \mathbb{Z}^3} \overline{F_1(\mathbf{h})} F_2(\mathbf{h}) = \sum_{l \in L} \sum_{\gamma_l \in G/G_{\mathbf{h}_l}} \overline{F_1(\mathbf{R}_{\gamma_l}^T \mathbf{h}_l)} F_2(\mathbf{R}_{\gamma_l}^T \mathbf{h}_l);$$

for each l , the summands corresponding to the various γ_l are equal, so that the left-hand side is equal to

$$F_1(\mathbf{0}) F_2(\mathbf{0}) \\ + \sum_{c \in L_c} 2|(G/G_{\mathbf{h}_c})^+| |F_1(\mathbf{h}_c)| |F_2(\mathbf{h}_c)| \cos[\varphi_1(\mathbf{h}_c) - \varphi_2(\mathbf{h}_c)] \\ + \sum_{a \in L_a^+} 2|G/G_{\mathbf{h}_a}| |F_1(\mathbf{h}_a)| |F_2(\mathbf{h}_a)| \cos[\varphi_1(\mathbf{h}_a) - \varphi_2(\mathbf{h}_a)].$$

In real space, the triple integral may be rewritten as

$$\int_{\mathbb{R}^3/\mathbb{Z}^3} \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) d^3 \mathbf{x} = |G| \int_D \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) d^3 \mathbf{x}$$

(where D is the asymmetric unit) if ρ_1 and ρ_2 are smooth densities, since the set of special positions has measure zero. If, however, the integral is approximated as a sum over a G -invariant grid defined by decimation matrix $\mathbf{N}$, special positions on this grid must be taken into account:

$$\frac{1}{|\mathbf{N}|} \sum_{\mathbf{k} \in \mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3} \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) \\ = \frac{1}{|\mathbf{N}|} \sum_{\mathbf{x} \in D} [G : G_{\mathbf{x}}] \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) \\ = \frac{|G|}{|\mathbf{N}|} \sum_{\mathbf{x} \in D} \frac{1}{|G_{\mathbf{x}}|} \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}),$$

where the discrete asymmetric unit D contains exactly one point in each orbit of G in $\mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3$.

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1.3.4.2.2.9. Convolution theorems with crystallographic symmetry

The standard convolution theorems derived in the absence of symmetry are readily seen to follow from simple properties of functions $e^\pm(\mathbf{h}, \mathbf{x}) = \exp(\pm 2\pi i \mathbf{h} \cdot \mathbf{x})$ (denoted simply e in formulae which are valid for both signs), namely:

- (i) $e(\mathbf{h}, \mathbf{x}) \times e(\mathbf{k}, \mathbf{x}) = e(\mathbf{h} + \mathbf{k}, \mathbf{x})$,
- (ii) $e(\mathbf{h}, \mathbf{x}) \times e(\mathbf{h}, \mathbf{y}) = e(\mathbf{h}, \mathbf{x} + \mathbf{y})$.

These relations imply that the families of functions

$$\{\mathbf{x} \mapsto e(\mathbf{h}, \mathbf{x})\}_{\mathbf{h} \in \mathbb{Z}^3} \quad \text{in real space}$$

and

$$\{\mathbf{h} \mapsto e(\mathbf{h}, \mathbf{x})\}_{\mathbf{x} \in \mathbb{R}^3/\mathbb{Z}^3} \quad \text{in reciprocal space}$$

both generate an *algebra* of functions, *i.e.* a vector space endowed with an internal multiplication, since (i) and (ii) show how to ‘linearize products’.

Friedel’s law (when applicable) on the one hand, and the Fourier relation between intensities and the Patterson function on the other hand, both follow from the property

$$(iii) \quad \overline{e(\mathbf{h}, \mathbf{x})} = e(-\mathbf{h}, \mathbf{x}) = e(\mathbf{h}, -\mathbf{x}).$$

When crystallographic symmetry is present, the convolution theorems remain valid in their original form if written out in terms of ‘expanded’ data, but acquire a different form when rewritten in terms of symmetry-unique data only. This rewriting is made possible by the extra relation (Section 1.3.4.2.2.5)

$$(iv) \quad S_{g^{-1}}^\# e(\mathbf{h}, \mathbf{x}) \equiv e[\mathbf{h}, S_g(\mathbf{x})] = e(\mathbf{h}, \mathbf{t}_g) e(\mathbf{R}_g^T \mathbf{h}, \mathbf{x})$$

or equivalently

$$(iv') \quad S_g^\# e(\mathbf{h}, \mathbf{x}) \equiv e[\mathbf{h}, S_g^{-1}(\mathbf{x})] \\ = e[(-\mathbf{R}_g^{-1})^T \mathbf{h}, \mathbf{t}_g] e[(\mathbf{R}_g^{-1})^T \mathbf{h}, \mathbf{x}].$$

The kernels of symmetrized Fourier transforms are not the functions e but rather the symmetrized sums

$$\Xi^\pm(\mathbf{h}, \mathbf{x}) = \sum_{g \in G} e^\pm[\mathbf{h}, S_g(\mathbf{x})] = \sum_{g \in G} e^\pm[\mathbf{h}, S_g^{-1}(\mathbf{x})]$$

for which the linearization formulae are readily obtained using (i), (ii) and (iv) as

- (i)_G $\Xi^\pm(\mathbf{h}, \mathbf{x}) \Xi^\pm(\mathbf{k}, \mathbf{x}) = \sum_{g \in G} e^\pm(\mathbf{k}, \mathbf{t}_g) \Xi^\pm(\mathbf{h} + \mathbf{R}_g^T \mathbf{k}, \mathbf{x})$,
- (ii)_G $\Xi^\pm(\mathbf{h}, \mathbf{x}) \Xi^\pm(\mathbf{h}, \mathbf{y}) = \sum_{g \in G} \Xi^\pm[\mathbf{h}, \mathbf{x} + S_g(\mathbf{y})]$,

where the choice of sign in $\pm$ must be the same throughout each formula.

Formulae (i)_G defining the ‘structure-factor algebra’ associated to G were derived by Bertaut (1955c, 1956b,c, 1959a,b) and Bertaut & Waser (1957) in another context.

The forward convolution theorem (in discrete form) then follows. Let

$$F_1(\mathbf{h}) = \sum_{\mathbf{y} \in D} \frac{1}{|G_{\mathbf{y}}|} \rho_1(\mathbf{y}) \Xi^+(\mathbf{h}, \mathbf{y}), \\ F_2(\mathbf{h}) = \sum_{\mathbf{z} \in D} \frac{1}{|G_{\mathbf{z}}|} \rho_2(\mathbf{z}) \Xi^+(\mathbf{h}, \mathbf{z}),$$

then

$$F_1(\mathbf{h}) F_2(\mathbf{h}) = \sum_{\mathbf{x} \in D} \frac{1}{|G_{\mathbf{x}}|} \sigma(\mathbf{x}) \Xi^+(\mathbf{h}, \mathbf{x})$$

with

$$\sigma(\mathbf{x}) = \frac{1}{|N|} \sum_{\mathbf{z} \in D} \sum_{g \in G} \frac{|G_{\mathbf{x}}|}{|G_{\mathbf{x}-S_g(\mathbf{z})}| \times |G_{\mathbf{z}}|} \rho_1[\mathbf{x} - S_g(\mathbf{z})] \rho_2(\mathbf{z}).$$

The backward convolution theorem is derived similarly. Let

$$\rho_1(\mathbf{x}) = \sum_{\mathbf{k} \in D^*} \frac{1}{|G_{\mathbf{k}}|} F_1(\mathbf{k}) \Xi^-(\mathbf{k}, \mathbf{x}), \\ \rho_2(\mathbf{x}) = \sum_{\mathbf{l} \in D^*} \frac{1}{|G_{\mathbf{l}}|} F_2(\mathbf{l}) \Xi^-(\mathbf{l}, \mathbf{x}),$$

then

$$\rho_1(\mathbf{x}) \rho_2(\mathbf{x}) = \sum_{\mathbf{h} \in D^*} \frac{1}{|G_{\mathbf{h}}|} F(\mathbf{h}) \Xi^-(\mathbf{h}, \mathbf{x})$$

with

$$F(\mathbf{h}) = \sum_{\mathbf{l} \in D^*} \sum_{g \in G} \frac{|G_{\mathbf{h}}|}{|G_{\mathbf{h}-\mathbf{R}_g^T(\mathbf{l})}| \times |G_{\mathbf{l}}|} e^-(\mathbf{l}, \mathbf{t}_g) F_1(\mathbf{h} - \mathbf{R}_g^T \mathbf{l}) F_2(\mathbf{l}).$$

Both formulae are simply orbit decompositions of their symmetry-free counterparts.

1.3.4.2.2.10. Correlation and Patterson functions

Consider two model electron densities ρ_1 and ρ_2 with the same period lattice $\mathbb{Z}^3$ and the same space group G . Write their motifs in terms of atomic electron densities (Section 1.3.4.2.2.4) as

$$\rho_1^0 = \sum_{j_1 \in J_1} \left(\sum_{\gamma_{j_1} \in G/G_{\mathbf{x}_{j_1}^{(1)}}} S_{\gamma_{j_1}}^\# (\tau_{\mathbf{x}_{j_1}^{(1)}} \rho_{j_1}^{(1)}) \right), \\ \rho_2^0 = \sum_{j_2 \in J_2} \left(\sum_{\gamma_{j_2} \in G/G_{\mathbf{x}_{j_2}^{(2)}}} S_{\gamma_{j_2}}^\# (\tau_{\mathbf{x}_{j_2}^{(2)}} \rho_{j_2}^{(2)}) \right),$$

where J_1 and J_2 label the symmetry-unique atoms placed at positions $\{\mathbf{x}_{j_1}^{(1)}\}_{j_1 \in J_1}$ and $\{\mathbf{x}_{j_2}^{(2)}\}_{j_2 \in J_2}$, respectively.

To calculate the correlation between ρ_1 and ρ_2 we need the following preliminary formulae, which are easily established: if $S(\mathbf{x}) = \mathbf{R}\mathbf{x} + \mathbf{t}$ and f is an arbitrary function on $\mathbb{R}^3$, then

$$(R^\# f)^\vee = R^\# \check{f}, \quad (\tau_{\mathbf{x}} f)^\vee = \tau_{-\mathbf{x}} \check{f}, \quad R^\#(\tau_{\mathbf{x}} f) = \tau_{\mathbf{R}\mathbf{x}} f,$$

hence

$$S^\#(\tau_{\mathbf{x}} f) = \tau_{S(\mathbf{x})} R^\# f \quad \text{and} \quad [S^\#(\tau_{\mathbf{x}} f)]^\vee = \tau_{-S(\mathbf{x})} R^\# \check{f};$$

and

$$S_1^\# f_1 * S_2^\# f_2 = S_1^\# [f_1 * (S_1^{-1} S_2)^\# f_2] = S_2^\# [(S_2^{-1} S_1)^\# f_1 * f_2].$$

The cross correlation $\rho_1^0 * \rho_2^0$ between motifs is therefore

$$\check{\rho}_1^0 * \rho_2^0 = \sum_{j_1} \sum_{j_2} \sum_{\gamma_{j_1}} \sum_{\gamma_{j_2}} [S_{\gamma_{j_1}}^\# (\tau_{\mathbf{x}_{j_1}^{(1)}} \rho_{j_1}^{(1)})]^\vee * [S_{\gamma_{j_2}}^\# (\tau_{\mathbf{x}_{j_2}^{(2)}} \rho_{j_2}^{(2)})] \\ = \sum_{j_1} \sum_{j_2} \sum_{\gamma_{j_1}} \sum_{\gamma_{j_2}} \tau_{S_{\gamma_{j_2}}(\mathbf{x}_{j_2}^{(2)}) - S_{\gamma_{j_1}}(\mathbf{x}_{j_1}^{(1)})} [(R_{\gamma_{j_1}}^\# \rho_{j_1}^{(1)}) * (R_{\gamma_{j_2}}^\# \rho_{j_2}^{(2)})]$$

which contains a peak of shape $(R_{\gamma_{j_1}}^\# \rho_{j_1}^{(1)}) * (R_{\gamma_{j_2}}^\# \rho_{j_2}^{(2)})$ at the interatomic vector $S_{\gamma_{j_2}}(\mathbf{x}_{j_2}^{(2)}) - S_{\gamma_{j_1}}(\mathbf{x}_{j_1}^{(1)})$ for each $j_1 \in J_1, j_2 \in J_2, \gamma_{j_1} \in G/G_{\mathbf{x}_{j_1}^{(1)}}, \gamma_{j_2} \in G/G_{\mathbf{x}_{j_2}^{(2)}}$.

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The cross-correlation $r * \tilde{\rho}_1^0 * \tilde{\rho}_2^0$ between the original electron densities is then obtained by further periodizing by $\mathbb{Z}^3$.

Note that these expressions are valid for any choice of 'atomic' density functions $\rho_{j_1}^{(1)}$ and $\rho_{j_2}^{(2)}$, which may be taken as molecular fragments if desired (see Section 1.3.4.4.8).

If G contains elements g such that $\mathbf{R}_g$ has an eigenspace E_1 with eigenvalue 1 and an invariant complementary subspace E_2 , while $\mathbf{t}_g$ has a non-zero component $\mathbf{t}_g^{(1)}$ in E_1 , then the Patterson function $r * \tilde{\rho}^0 * \tilde{\rho}^0$ will contain *Harker peaks* (Harker, 1936) of the form

$$S_g(\mathbf{x}) - \mathbf{x} = \mathbf{t}_g^{(1)} \oplus (S_g^{(2)}(\mathbf{x}) - \mathbf{x})$$

[where $S_g^{(s)}$ represent the action of g in E_2] in the translate of E_1 by $\mathbf{t}_g^{(1)}$.

1.3.4.3. Crystallographic discrete Fourier transform algorithms

1.3.4.3.1. Historical introduction

In 1929, W. L. Bragg demonstrated the practical usefulness of the Fourier transform relation between electron density and structure factors by determining the structure of diopside from three principal projections calculated numerically by 2D Fourier summation (Bragg, 1929). It was immediately realized that the systematic use of this powerful method, and of its extension to three dimensions, would entail considerable amounts of numerical computation which had to be organized efficiently. As no other branch of applied science had yet needed this type of computation, crystallographers had to invent their own techniques.

The first step was taken by Beevers & Lipson (1934) who pointed out that a 2D summation could be factored into successive 1D summations. This is essentially the tensor product property of the Fourier transform (Sections 1.3.2.4.2.4, 1.3.3.3.1), although its aspect is rendered somewhat complicated by the use of sines and cosines instead of complex exponentials. Computation is economized to the extent that the cost of an $N \times N$ transform grows with N as $2N^3$ rather than N^4 . Generalization to 3D is immediate, reducing computation size from N^6 to $3N^4$ for an $N \times N \times N$ transform. The complication introduced by using expressions in terms of sines and cosines is turned to advantage when symmetry is present, as certain families of terms are systematically absent or are simply related to each other; multiplicity corrections must, however, be introduced. The necessary information was tabulated for each space group by Lonsdale (1936), and was later incorporated into Volume I of *International Tables*.

The second step was taken by Beevers & Lipson (1936) and Lipson & Beevers (1936) in the form of the invention of the 'Beevers-Lipson strips', a practical device which was to assist a whole generation of crystallographers in the numerical computation of crystallographic Fourier sums. The strips comprise a set of 'cosine strips' tabulating the functions

$$A \cos\left(\frac{2\pi hm}{60}\right) \quad (A = 1, 2, \dots, 99; h = 1, 2, \dots, 99)$$

and a set of 'sine strips' tabulating the functions

$$B \sin\left(\frac{2\pi hm}{60}\right) \quad (B = 1, 2, \dots, 99; h = 1, 2, \dots, 99)$$

for the 16 arguments $m = 0, 1, \dots, 15$. Function values are rounded to the nearest integer, and those for other arguments m may be obtained by using the symmetry properties of the sine and cosine functions. A Fourier summation of the form

$$Y(m) = \sum_{j=1}^n \left[A_j \cos\left(\frac{2\pi h_j m}{60}\right) + B_j \sin\left(\frac{2\pi h_j m}{60}\right) \right]$$

is then performed by selecting the n cosine strips labelled (A_j, h_j) and the n sine strips labelled (B_j, h_j) , placing them in register, and adding the tabulated values columnwise. The number 60 was chosen as the l.c.m. of 12 (itself the l.c.m. of the orders of all possible non-primitive translations) and of 10 (for decimal convenience). The limited accuracy imposed by the two-digit tabulation was later improved by Robertson's sorting board (Robertson, 1936a,b) or by the use of separate strips for each decimal digit of the amplitude (Booth, 1948b), which allowed three-digit tabulation while keeping the set of strips within manageable size. Cochran (1948a) found that, for most structures under study at the time, the numerical inaccuracies of the method were less than the level of error in the experimental data. The sampling rate was subsequently increased from 60 to 120 (Beevers, 1952) to cope with larger unit cells.

Further gains in speed and accuracy were sought through the construction of special-purpose mechanical, electro-mechanical, electronic or optical devices. Two striking examples are the mechanical computer RUFUS built by Robertson (1954, 1955, 1961) on the principle of previous strip methods (see also Robertson, 1932) and the electronic analogue computer X-RAC built by Pepinsky, capable of real-time calculation and display of 2D and 3D Fourier syntheses (Pepinsky, 1947; Pepinsky & Sayre, 1948; Pepinsky *et al.*, 1961; see also Suryan, 1957). The optical methods of Lipson & Taylor (1951, 1958) also deserve mention. Many other ingenious devices were invented, whose descriptions may be found in Booth (1948b), Niggli (1961), and Lipson & Cochran (1968).

Later, commercial punched-card machines were programmed to carry out Fourier summations or structure-factor calculations (Shaffer *et al.*, 1946a,b; Cox *et al.*, 1947, 1949; Cox & Jeffrey, 1949; Donohue & Schomaker, 1949; Grems & Kasper, 1949; Hodgson *et al.*, 1949; Greenhalgh & Jeffrey, 1950; Kitz & Marchington, 1953).

The modern era of digital electronic computation of Fourier series was initiated by the work of Bennett & Kendrew (1952), Mayer & Trueblood (1953), Ahmed & Cruickshank (1953b), Sparks *et al.* (1956) and Fowweather (1955). Their Fourier-synthesis programs used Beevers-Lipson factorization, the program by Sparks *et al.* being the first 3D Fourier program useable for all space groups (although these were treated as $P1$ or $P\bar{1}$ by data expansion). Ahmed & Barnes (1958) then proposed a general programming technique to allow full use of symmetry elements (orthorhombic or lower) in the 3D Beevers-Lipson factorization process, including multiplicity corrections. Their method was later adopted by Shoemaker & Sly (1961), and by crystallographic program writers at large.

The discovery of the FFT algorithm by Cooley & Tukey in 1965, which instantly transformed electrical engineering and several other disciplines, paradoxically failed to have an immediate impact on crystallographic computing. A plausible explanation is that the calculation of large 3D Fourier maps was a relatively infrequent task which was not thought to constitute a bottleneck, as crystallographers had learned to settle most structural questions by means of cheaper 2D sections or projections. It is significant in this respect that the first use of the FFT in crystallography by Barrett & Zwick (1971) should have occurred as part of an iterative scheme for improving protein phases by density modification in real space, which required a much greater number of Fourier transformations than any previous method. Independently, Bondot (1971) had attracted attention to the merits of the FFT algorithm.

The FFT program used by Barrett & Zwick had been written for signal-processing applications. It was restricted to sampling rates of the form 2^n , and was not designed to take advantage of crystallographic symmetry at any stage of the calculation; Bantz & Zwick (1974) later improved this situation somewhat.

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It was the work of Ten Eyck (1973) and Immirzi (1973, 1976) which led to the general adoption of the FFT in crystallographic computing. Immirzi treated all space groups as $P1$ by data expansion. Ten Eyck based his program on a versatile multi-radix FFT routine (Gentleman & Sande, 1966) coupled with a flexible indexing scheme for dealing efficiently with multidimensional transforms. He also addressed the problems of incorporating symmetry elements of order 2 into the factorization of 1D transforms, and of transposing intermediate results by other symmetry elements. He was thus able to show that in a large number of space groups (including the 74 space groups having orthorhombic or lower symmetry) it is possible to calculate only the unique results from the unique data within the logic of the FFT algorithm. Ten Eyck wrote and circulated a package of programs for computing Fourier maps and re-analysing them into structure factors in some simple space groups ($P1$, $P1$, $P2$, $P2/m$, $P2_1$, $P222$, $P2_12_12_1$, $Pmmm$). This package was later augmented by a handful of new space-group-specific programs contributed by other crystallographers ($P2_12_12_1$, $I222$, $P3_12_1$, $P4_12_12_1$). The writing of such programs is an undertaking of substantial complexity, which has deterred all but the bravest: the usual practice is now to expand data for a high-symmetry space group to the largest subgroup for which a specific FFT program exists in the package, rather than attempt to write a new program. Attempts have been made to introduce more modern approaches to the calculation of crystallographic Fourier transforms (Auslander, Feig & Winograd, 1982; Auslander & Shenefelt, 1987; Auslander *et al.*, 1988) but have not gone beyond the stage of preliminary studies.

The task of fully exploiting the FFT algorithm in crystallographic computations is therefore still unfinished, and it is the purpose of this section to provide a systematic treatment such as that (say) of Ahmed & Barnes (1958) for the Beevers–Lipson algorithm.

Ten Eyck's approach, based on the reducibility of certain space groups, is extended by the derivation of a universal transposition formula for intermediate results. It is then shown that space groups which are not completely reducible may nevertheless be treated by three-dimensional Cooley–Tukey factorization in such a way that their symmetry may be fully exploited, whatever the shape of their asymmetric unit. Finally, new factorization methods with built-in symmetries are presented. The unifying concept throughout this presentation is that of 'group action' on indexing sets, and of 'orbit exchange' when this action has a composite structure; it affords new ways of rationalizing the use of symmetry, or of improving computational speed, or both.

1.3.4.3.2. Defining relations and symmetry considerations

A finite set of reflections $\{F_{\mathbf{h}}\}_{\mathbf{h} \in L}$ can be periodized without aliasing by the translations of a suitable sublattice $\mathbf{N}^T \Lambda^*$ of the reciprocal lattice Λ^* ; the converse operation in real space is the sampling of ρ at points $\mathbf{X}$ of a grid of the form $\mathbf{N}^{-1}\Lambda$ (Section 1.3.2.7.3). In standard coordinates, $\{F_{\mathbf{h}}\}_{\mathbf{h} \in L}$ is periodized by $\mathbf{N}^T \mathbb{Z}^3$, and ρ is sampled at points $\mathbf{x} \in \mathbf{N}^{-1}\mathbb{Z}^3$.

In the absence of symmetry, the unique data are
 – the $F_{\mathbf{h}}$ indexed by $\mathbf{h} \in \mathbb{Z}^3/\mathbf{N}^T \mathbb{Z}^3$ in reciprocal space;
 – the $\rho_{\mathbf{x}}$ indexed by $\mathbf{x} \in (\mathbf{N}^{-1}\mathbb{Z}^3)/\mathbb{Z}^3$; or equivalently the $\rho_{\mathbf{m}}$ indexed by $\mathbf{m} \in \mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3$, where $\mathbf{x} = \mathbf{N}^{-1}\mathbf{m}$.

They are connected by the ordinary DFT relations:

$$F_{\mathbf{h}} = \frac{1}{|\det \mathbf{N}|} \sum_{\mathbf{x} \in (\mathbf{N}^{-1}\mathbb{Z}^3)/\mathbb{Z}^3} \rho_{\mathbf{x}} \exp(2\pi i \mathbf{h} \cdot \mathbf{x})$$

or

$$F_{\mathbf{h}} = \frac{1}{|\det \mathbf{N}|} \sum_{\mathbf{m} \in \mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3} \rho_{\mathbf{m}} \exp[2\pi i \mathbf{h} \cdot (\mathbf{N}^{-1}\mathbf{m})]$$

and

$$\rho_{\mathbf{x}} = \sum_{\mathbf{h} \in \mathbb{Z}^3/\mathbf{N}^T \mathbb{Z}^3} F_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

or

$$\rho_{\mathbf{m}} = \sum_{\mathbf{h} \in \mathbb{Z}^3/\mathbf{N}^T \mathbb{Z}^3} F_{\mathbf{h}} \exp[-2\pi i \mathbf{h} \cdot (\mathbf{N}^{-1}\mathbf{m})].$$

In the presence of symmetry, the unique data are
 – $\{\rho_{\mathbf{x}}\}_{\mathbf{x} \in D}$ or $\{\rho_{\mathbf{m}}\}_{\mathbf{m} \in D}$ in real space (by abuse of notation, D will denote an asymmetric unit for $\mathbf{x}$ or for $\mathbf{m}$ indifferently);
 – $\{F_{\mathbf{h}}\}_{\mathbf{h} \in D^*}$ in reciprocal space.

The previous summations may then be subjected to orbital decomposition, to yield the following 'crystallographic DFT' (CDFT) defining relations:

$$\begin{aligned} F_{\mathbf{h}} &= \frac{1}{|\det \mathbf{N}|} \sum_{\mathbf{x} \in D} \rho_{\mathbf{x}} \left[\sum_{\gamma \in G/G_{\mathbf{x}}} \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma}(\mathbf{x})]\} \right] \\ &= \frac{1}{|\det \mathbf{N}|} \sum_{\mathbf{x} \in D} \rho_{\mathbf{x}} \left[\frac{1}{|G_{\mathbf{x}}|} \sum_{g \in G} \exp\{2\pi i \mathbf{h} \cdot [S_g(\mathbf{x})]\} \right], \\ \rho_{\mathbf{x}} &= \sum_{\mathbf{h} \in D^*} F_{\mathbf{h}} \left[\sum_{\gamma \in G/G_{\mathbf{x}}} \exp\{-2\pi i \mathbf{h} \cdot [S_{\gamma}(\mathbf{x})]\} \right] \\ &= \sum_{\mathbf{h} \in D^*} F_{\mathbf{h}} \left[\frac{1}{|G_{\mathbf{x}}|} \sum_{g \in G} \exp\{-2\pi i \mathbf{h} \cdot [S_g(\mathbf{x})]\} \right], \end{aligned}$$

with the obvious alternatives in terms of $\rho_{\mathbf{m}}$, $\mathbf{m} = \mathbf{N}\mathbf{x}$. Our problem is to evaluate the CDFT for a given space group as efficiently as possible, in spite of the fact that the group action has spoilt the simple tensor-product structure of the ordinary three-dimensional DFT (Section 1.3.3.3.1).

Two procedures are available to carry out the 3D summations involved as a succession of smaller summations:

(1) *decomposition* into successive transforms of *fewer dimensions* but on the *same number of points* along these dimensions. This possibility depends on the reducibility of the space group, as defined in Section 1.3.4.2.2.4, and simply invokes the tensor product property of the DFT;

(2) *factorization* of the transform into transforms of the *same number of dimensions* as the original one, but on *fewer points* along each dimension. This possibility depends on the arithmetic factorability of the decimation matrix $\mathbf{N}$, as described in Section 1.3.3.3.2.

Clearly, a symmetry expansion to the largest fully reducible subgroup of the space group will give maximal decomposability, but will require computing more than the unique results from more than the unique data. Economy will follow from factoring the transforms in the subspaces within which the space group acts irreducibly.

For irreducible subspaces of dimension 1, the group action is readily incorporated into the factorization of the transform, as first shown by Ten Eyck (1973).

For irreducible subspaces of dimension 2 or 3, the ease of incorporation of symmetry into the factorization depends on the type of factorization method used. The multidimensional Cooley–Tukey method (Section 1.3.3.3.1) is rather complicated; the multidimensional Good method (Section 1.3.3.3.2.2) is somewhat simpler; and the Rader/Winograd factorization admits a generalization, based on the arithmetic of certain rings of *algebraic*

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integers, which accommodates 2D crystallographic symmetries in a most powerful and pleasing fashion.

At each stage of the calculation, it is necessary to keep track of the definition of the asymmetric unit and of the symmetry properties of the numbers being manipulated. This requirement applies not only to the initial data and to the final results, where these are familiar; but also to all the intermediate quantities produced by partial transforms (on subsets of factors, or subsets of dimensions, or both), where they are less familiar. Here, the general formalism of transposition (or ‘orbit exchange’) described in Section 1.3.4.2.2 plays a central role.

1.3.4.3.3. Interaction between symmetry and decomposition

Suppose that the space-group action is reducible, *i.e.* that for each $g \in G$

$$\mathbf{R}_g = \begin{pmatrix} \mathbf{R}'_g & \mathbf{0} \\ \mathbf{0} & \mathbf{R}''_g \end{pmatrix}, \quad \mathbf{t}_g = \begin{pmatrix} \mathbf{t}'_g \\ \mathbf{t}''_g \end{pmatrix};$$

by Schur’s lemma, the decimation matrix must then be of the form

$$\mathbf{N} = \begin{pmatrix} \mathbf{N}' & \mathbf{0} \\ \mathbf{0} & \mathbf{N}'' \end{pmatrix} \text{ if it is to commute with all the } \mathbf{R}_g.$$

Putting $\mathbf{x} = \begin{pmatrix} \mathbf{x}' \\ \mathbf{x}'' \end{pmatrix}$ and $\mathbf{h} = \begin{pmatrix} \mathbf{h}' \\ \mathbf{h}'' \end{pmatrix}$, we may define

$$\begin{aligned} S'_g(\mathbf{x}') &= \mathbf{R}'_g \mathbf{x}' + \mathbf{t}'_g, \\ S''_g(\mathbf{x}'') &= \mathbf{R}''_g \mathbf{x}'' + \mathbf{t}''_g, \end{aligned}$$

and write $S_g = S'_g \oplus S''_g$ (direct sum) as a shorthand for $S_g(\mathbf{x}) = \begin{pmatrix} S'_g(\mathbf{x}') \\ S''_g(\mathbf{x}'') \end{pmatrix}$.

We may also define the representation operators $S_g^{\#}$ and S_g^{**} acting on functions of $\mathbf{x}'$ and $\mathbf{x}''$, respectively (as in Section 1.3.4.2.2.4), and the operators S_g^* and $S_g^{\#}$ acting on functions of $\mathbf{h}'$ and $\mathbf{h}''$, respectively (as in Section 1.3.4.2.2.5). Then we may write

$$S_g^{\#} = (S'_g)^{\#} \oplus (S''_g)^{\#}$$

and

$$S_g^* = (S'_g)^* \oplus (S''_g)^*$$

in the sense that g acts on $f(\mathbf{x}) \equiv f(\mathbf{x}', \mathbf{x}'')$ by

$$(S_g^{\#} f)(\mathbf{x}', \mathbf{x}'') = f[(S'_g)^{-1}(\mathbf{x}'), (S''_g)^{-1}(\mathbf{x}'')]$$

and on $\Phi(\mathbf{h}) \equiv \Phi(\mathbf{h}', \mathbf{h}'')$ by

$$\begin{aligned} (S_g^* \Phi)(\mathbf{h}', \mathbf{h}'') &= \exp(2\pi i \mathbf{h}' \cdot \mathbf{t}'_g) \exp(2\pi i \mathbf{h}'' \cdot \mathbf{t}''_g) \\ &\quad \times \Phi[\mathbf{R}_g^T \mathbf{h}', \mathbf{R}_g^T \mathbf{h}'']. \end{aligned}$$

Thus equipped we may now derive concisely a general identity describing the symmetry properties of intermediate quantities of the form

$$\begin{aligned} T(\mathbf{x}', \mathbf{h}'') &= \sum_{\mathbf{h}'} F(\mathbf{h}', \mathbf{h}'') \exp(-2\pi i \mathbf{h}' \cdot \mathbf{x}') \\ &= \frac{1}{|\det \mathbf{N}'|} \sum_{\mathbf{x}''} \rho(\mathbf{x}', \mathbf{x}'') \exp(+2\pi i \mathbf{h}'' \cdot \mathbf{x}''), \end{aligned}$$

which arise through partial transformation of F on $\mathbf{h}'$ or of ρ on $\mathbf{x}''$. The action of $g \in G$ on these quantities will be

- (i) through $(S'_g)^{\#}$ on the function $\mathbf{x}' \mapsto T(\mathbf{x}', \mathbf{h}'')$,
- (ii) through $(S''_g)^*$ on the function $\mathbf{h}'' \mapsto T(\mathbf{x}', \mathbf{h}'')$,

and hence the symmetry properties of T are expressed by the identity

$$T = [(S'_g)^{\#} \oplus (S''_g)^*] T.$$

Applying this relation not to T but to $[(S'_{g^{-1}})^{\#} \oplus (S''_e)^*] T$ gives

$$[(S'_{g^{-1}})^{\#} \oplus (S''_e)^*] T = [(S'_e)^{\#} \oplus (S''_g)^*] T,$$

i.e.

$$T(S'_g(\mathbf{x}'), \mathbf{h}'') = \exp(2\pi i \mathbf{h}'' \cdot \mathbf{t}''_g) T(\mathbf{x}', \mathbf{R}_g^T \mathbf{h}'').$$

If the unique $F(\mathbf{h}) \equiv F(\mathbf{h}', \mathbf{h}'')$ were initially indexed by

$$(\text{all } \mathbf{h}') \times (\text{unique } \mathbf{h}'')$$

(see Section 1.3.4.2.2.2), this formula allows the reindexing of the intermediate results $T(\mathbf{x}', \mathbf{h}'')$ from the initial form

$$(\text{all } \mathbf{x}') \times (\text{unique } \mathbf{h}'')$$

to the final form

$$(\text{unique } \mathbf{x}') \times (\text{all } \mathbf{h}''),$$

on which the second transform (on $\mathbf{h}''$) may now be performed, giving the final results $\rho(\mathbf{x}', \mathbf{x}'')$ indexed by

$$(\text{unique } \mathbf{x}') \times (\text{all } \mathbf{x}''),$$

which is an asymmetric unit. An analogous interpretation holds if one is going from ρ to F .

The above formula solves the general problem of transposing from one invariant subspace to another, and is the main device for decomposing the CDFT. Particular instances of this formula were derived and used by Ten Eyck (1973); it is useful for orthorhombic groups, and for dihedral groups containing screw axes n_m with g.c.d. $(m, n) = 1$. For comparison with later uses of orbit exchange, it should be noted that the type of intermediate results just dealt with is obtained after transforming on *all* factors in *one* summand.

A central piece of information for driving such a decomposition is the definition of the full asymmetric unit in terms of the asymmetric units in the invariant subspaces. As indicated at the end of Section 1.3.4.2.2.2, this is straightforward when G acts without fixed points, but becomes more involved if fixed points do exist. To this day, no systematic ‘calculus of asymmetric units’ exists which can automatically generate a complete description of the asymmetric unit of an arbitrary space group in a form suitable for directing the orbit exchange process, although Shenefelt (1988) has outlined a procedure for dealing with space group $P622$ and its subgroups. The asymmetric unit definitions given in Volume A of *International Tables* are incomplete in this respect, in that they do not specify the possible residual symmetries which may exist on the boundaries of the domains.

1.3.4.3.4. Interaction between symmetry and factorization

Methods for factoring the DFT in the absence of symmetry were examined in Sections 1.3.3.2 and 1.3.3.3. They are based on the observation that the finite sets which index both data and results are endowed with certain algebraic structures (*e.g.* are Abelian groups, or rings), and that subsets of indices may be found which are not merely subsets but *substructures* (*e.g.* subgroups or subrings). Summation over these substructures leads to partial transforms, and the way in which substructures fit into the global structure indicates how to reassemble the partial results into the final results. As a rule, the richer the algebraic structure which is identified in the indexing set, the more powerful the factoring method.

1. GENERAL RELATIONSHIPS AND TECHNIQUES

The ability of a given factoring method to accommodate crystallographic symmetry will thus be determined by the extent to which the crystallographic group action respects (or fails to respect) the partitioning of the index set into the substructures pertaining to that method. This remark justifies trying to gain an overall view of the algebraic structures involved, and of the possibilities of a crystallographic group acting ‘naturally’ on them.

The index sets $\{\mathbf{m} | \mathbf{m} \in \mathbb{Z}^3 / \mathbf{N}\mathbb{Z}^3\}$ and $\{\mathbf{h} | \mathbf{h} \in \mathbb{Z}^3 / \mathbf{N}^T \mathbb{Z}^3\}$ are finite Abelian groups under component-wise addition. If an iterated addition is viewed as an action of an integer scalar $n \in \mathbb{Z}$ via

$$\begin{aligned} n\mathbf{h} &= \mathbf{h} + \mathbf{h} + \dots + \mathbf{h} & (n \text{ times}) & \quad \text{for } n > 0, \\ &= \mathbf{0} & & \quad \text{for } n = 0, \\ &= -(\mathbf{h} + \mathbf{h} + \dots + \mathbf{h}) & (|n| \text{ times}) & \quad \text{for } n < 0, \end{aligned}$$

then an Abelian group becomes a *module* over the ring $\mathbb{Z}$ (or, for short, a $\mathbb{Z}$ -module), a module being analogous to a vector space but with scalars drawn from a ring rather than a field. The left actions of a crystallographic group G by

$$g : \mathbf{m} \mapsto \mathbf{R}_g \mathbf{m} + \mathbf{N} \mathbf{t}_g \pmod{\mathbf{N}\mathbb{Z}^3}$$

and by

$$g : \mathbf{h} \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h} \pmod{\mathbf{N}^T \mathbb{Z}^3}$$

can be combined with this $\mathbb{Z}$ action as follows:

$$\begin{aligned} \sum_{g \in G} n_g g : \mathbf{m} &\mapsto \sum_{g \in G} n_g (\mathbf{R}_g \mathbf{m} + \mathbf{N} \mathbf{t}_g) \pmod{\mathbf{N}\mathbb{Z}^3}, \\ \sum_{g \in G} n_g g : \mathbf{h} &\mapsto \sum_{g \in G} n_g [(\mathbf{R}_g^{-1})^T \mathbf{h}] \pmod{\mathbf{N}^T \mathbb{Z}^3}. \end{aligned}$$

This provides a left action, on the indexing sets, of the set

$$\mathbb{Z}G = \left\{ \sum_{g \in G} n_g g \mid n_g \in \mathbb{Z} \text{ for each } g \in G \right\}$$

of symbolic linear combinations of elements of G with integral coefficients. If addition and multiplication are defined in $\mathbb{Z}G$ by

$$\left(\sum_{g_1 \in G} a_{g_1} g_1 \right) + \left(\sum_{g_2 \in G} b_{g_2} g_2 \right) = \sum_{g \in G} (a_g + b_g) g$$

and

$$\left(\sum_{g_1 \in G} a_{g_1} g_1 \right) \times \left(\sum_{g_2 \in G} b_{g_2} g_2 \right) = \sum_{g \in G} c_g g,$$

with

$$c_g = \sum_{g' \in G} a_{g'} b_{(g')^{-1}g},$$

then $\mathbb{Z}G$ is a *ring*, and the action defined above makes the indexing sets into $\mathbb{Z}G$ -modules. The ring $\mathbb{Z}G$ is called the *integral group ring* of G (Curtis & Reiner, 1962, p. 44).

From the algebraic standpoint, therefore, the interaction between symmetry and factorization can be expected to be favourable whenever the indexing sets of partial transforms are $\mathbb{Z}G$ -submodules of the main $\mathbb{Z}G$ -modules.

1.3.4.3.4.1. Multidimensional Cooley–Tukey factorization

Suppose, as in Section 1.3.3.3.2.1, that the decimation matrix $\mathbf{N}$ may be factored as $\mathbf{N}_1 \mathbf{N}_2$. Then any grid point index $\mathbf{m} \in \mathbb{Z}^3 / \mathbf{N}\mathbb{Z}^3$ in real space may be written

$$\mathbf{m} = \mathbf{m}_1 + \mathbf{N}_1 \mathbf{m}_2$$

with $\mathbf{m}_1 \in \mathbb{Z}^3 / \mathbf{N}_1 \mathbb{Z}^3$ and $\mathbf{m}_2 \in \mathbb{Z}^3 / \mathbf{N}_2 \mathbb{Z}^3$ determined by

$$\begin{aligned} \mathbf{m}_1 &= \mathbf{m} \pmod{\mathbf{N}_1 \mathbb{Z}^3}, \\ \mathbf{m}_2 &= \mathbf{N}_1^{-1} (\mathbf{m} - \mathbf{m}_1) \pmod{\mathbf{N}_2 \mathbb{Z}^3}. \end{aligned}$$

These relations establish a one-to-one correspondence $\mathbf{m} \leftrightarrow (\mathbf{m}_1, \mathbf{m}_2)$ between $I = \mathbb{Z}^3 / \mathbf{N}\mathbb{Z}^3$ and the Cartesian product $I_1 \times I_2$ of $I_1 = \mathbb{Z}^3 / \mathbf{N}_1 \mathbb{Z}^3$ and $I_2 = \mathbb{Z}^3 / \mathbf{N}_2 \mathbb{Z}^3$, and hence $I \cong I_1 \times I_2$ as a set. However $I \not\cong I_1 \times I_2$ as an Abelian group, since in general $\mathbf{m} + \mathbf{m}' \not\leftrightarrow (\mathbf{m}_1 + \mathbf{m}'_1, \mathbf{m}_2 + \mathbf{m}'_2)$ because there can be a ‘carry’ from the addition of the first components into the second components; therefore, $I \not\cong I_1 \times I_2$ as a $\mathbb{Z}G$ -module, which shows that the incorporation of symmetry into the Cooley–Tukey algorithm is not a trivial matter.

Let $g \in G$ act on I through

$$g : \mathbf{m} \mapsto S_g(\mathbf{m}) = \mathbf{R}_g \mathbf{m} + \mathbf{N} \mathbf{t}_g \pmod{\mathbf{N}\mathbb{Z}^3}$$

and suppose that $\mathbf{N}$ ‘integerizes’ all the non-primitive translations $\mathbf{t}_g$ so that we may write

$$\mathbf{N} \mathbf{t}_g = \mathbf{t}_g^{(1)} + \mathbf{N}_1 \mathbf{t}_g^{(2)},$$

with $\mathbf{t}_g^{(1)} \in I_1$ and $\mathbf{t}_g^{(2)} \in I_2$ determined as above. Suppose further that $\mathbf{N}_1, \mathbf{N}_1$ and $\mathbf{N}_2$ commute with $\mathbf{R}_g$ for all $g \in G$, i.e. (by Schur’s lemma, Section 1.3.4.2.2.4) that these matrices are integer multiples of the identity in each G -invariant subspace. The action of g on $\mathbf{m} = \mathbf{N} \mathbf{x} \pmod{\mathbf{N}\mathbb{Z}^3}$ leads to

$$\begin{aligned} S_g(\mathbf{m}) &= \mathbf{N} [\mathbf{R}_g (\mathbf{N}^{-1} \mathbf{m}) + \mathbf{t}_g] \pmod{\mathbf{N}\mathbb{Z}^3} \\ &= \mathbf{N} \mathbf{R}_g \mathbf{N}^{-1} (\mathbf{m}_1 + \mathbf{N}_1 \mathbf{m}_2) + \mathbf{t}_g^{(1)} + \mathbf{N}_1 \mathbf{t}_g^{(2)} \pmod{\mathbf{N}\mathbb{Z}^3} \\ &= \mathbf{R}_g \mathbf{m}_1 + \mathbf{t}_g^{(1)} + \mathbf{N}_1 (\mathbf{R}_g \mathbf{m}_2 + \mathbf{t}_g^{(2)}) \pmod{\mathbf{N}\mathbb{Z}^3}, \end{aligned}$$

which we may decompose as

$$S_g(\mathbf{m}) = [S_g(\mathbf{m})]_1 + \mathbf{N}_1 [S_g(\mathbf{m})]_2$$

with

$$[S_g(\mathbf{m})]_1 \equiv S_g(\mathbf{m}) \pmod{\mathbf{N}_1 \mathbb{Z}^3}$$

and

$$[S_g(\mathbf{m})]_2 \equiv \mathbf{N}_1^{-1} \{S_g(\mathbf{m}) - [S_g(\mathbf{m})]_1\} \pmod{\mathbf{N}_2 \mathbb{Z}^3}.$$

Introducing the notation

$$\begin{aligned} S_g^{(1)}(\mathbf{m}_1) &= \mathbf{R}_g \mathbf{m}_1 + \mathbf{t}_g^{(1)} \pmod{\mathbf{N}_1 \mathbb{Z}^3}, \\ S_g^{(2)}(\mathbf{m}_2) &= \mathbf{R}_g \mathbf{m}_2 + \mathbf{t}_g^{(2)} \pmod{\mathbf{N}_2 \mathbb{Z}^3}, \end{aligned}$$

the two components of $S_g(\mathbf{m})$ may be written

$$\begin{aligned} [S_g(\mathbf{m})]_1 &= S_g^{(1)}(\mathbf{m}_1), \\ [S_g(\mathbf{m})]_2 &= S_g^{(2)}(\mathbf{m}_2) + \boldsymbol{\mu}_2(g, \mathbf{m}_1) \pmod{\mathbf{N}_2 \mathbb{Z}^3}, \end{aligned}$$

with

$$\boldsymbol{\mu}_2(g, \mathbf{m}_1) = \mathbf{N}_1^{-1} \{(\mathbf{R}_g \mathbf{m}_1 + \mathbf{t}_g^{(1)}) - [S_g(\mathbf{m}_1)]_1\} \pmod{\mathbf{N}_2 \mathbb{Z}^3}.$$

The term $\boldsymbol{\mu}_2$ is the geometric equivalent of a *carry* or *borrow*: it arises because $\mathbf{R}_g \mathbf{m}_1 + \mathbf{t}_g^{(1)}$, calculated as a vector in $\mathbb{Z}^3 / \mathbf{N}\mathbb{Z}^3$, may be outside the unit cell $\mathbf{N}_1[0, 1]^3$, and may need to be brought back into it by a ‘large’ translation with a non-zero component in the $\mathbf{m}_2$ space; equivalently, the action of g may need to be applied around different permissible origins for different values of $\mathbf{m}_1$, so as to map the unit cell into itself without any recourse to lattice translations. [Readers familiar with the cohomology of groups (see e.g. Hall, 1959; MacLane, 1963) will recognize $\boldsymbol{\mu}_2$ as the cocycle of the extension of $\mathbb{Z}G$ -modules described by the exact sequence $0 \rightarrow I_2 \rightarrow I \rightarrow I_1 \rightarrow 0$.]

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Thus G acts on I in a rather complicated fashion: although $g \mapsto S_g^{(1)}$ does define a left action in I_1 alone, no action can be defined in I_2 alone because μ_2 depends on $\mathbf{m}_1$. However, because S_g , $S_g^{(1)}$ and $S_g^{(2)}$ are left actions, it follows that μ_2 satisfies the identity

$$\mu_2(gg', \mathbf{m}_1) = S_g^{(2)}[\mu_2(g', \mathbf{m}_1)] + \mu_2[g, S_g^{(1)}(\mathbf{m}_1)] \mod \mathbf{N}_2\mathbb{Z}^3$$

for all g, g' in G and all $\mathbf{m}_1$ in I_1 . In particular, $\mu_2(\mathbf{e}, \mathbf{m}_1) = \mathbf{0}$ for all $\mathbf{m}_1$, and

$$\mu_2(g^{-1}, \mathbf{m}_1) = -S_{g^{-1}}^{(2)}\{\mu_2[g, S_{g^{-1}}^{(1)}(\mathbf{m}_1)]\} \mod \mathbf{N}_2\mathbb{Z}^3.$$

This action will now be used to achieve optimal use of symmetry in the multidimensional Cooley–Tukey algorithm of Section 1.3.3.2.1. Let us form an array Y according to

$$Y(\mathbf{m}_1, \mathbf{m}_2) = \rho(\mathbf{m}_1 + \mathbf{N}_1\mathbf{m}_2)$$

for all $\mathbf{m}_2 \in I_2$ but only for the *unique* $\mathbf{m}_1$ under the action $S_g^{(1)}$ of G in I_1 . Except in special cases which will be examined later, these vectors contain essentially an asymmetric unit of electron-density data, up to some redundancies on boundaries. We may then compute the partial transform on $\mathbf{m}_2$:

$$Y^*(\mathbf{m}_1, \mathbf{h}_2) = \frac{1}{|\det \mathbf{N}_2|} \sum_{\mathbf{m}_2 \in I_2} Y(\mathbf{m}_1, \mathbf{m}_2) e[\mathbf{h}_2 \cdot (\mathbf{N}_2^{-1}\mathbf{m}_2)].$$

Using the symmetry of ρ in the form $\rho = S_g^\# \rho$ yields by the procedure of Section 1.3.3.2 the transposition formula

$$Y^*(S_g^{(1)}(\mathbf{m}_1), \mathbf{h}_2) = e\{\mathbf{h}_2 \cdot [\mathbf{N}_2^{-1}(\mathbf{t}_g^{(2)} + \mu_2(g, \mathbf{m}_1))]\} \times Y^*(\mathbf{m}_1, [\mathbf{R}_g^{(2)}]^T \mathbf{h}_2).$$

By means of this identity we can transpose intermediate results Y^* initially indexed by

$$(\text{unique } \mathbf{m}_1) \times (\text{all } \mathbf{h}_2),$$

so as to have them indexed by

$$(\text{all } \mathbf{m}_1) \times (\text{unique } \mathbf{h}_2).$$

We may then apply twiddle factors to get

$$Z(\mathbf{m}_1, \mathbf{h}_2) = e[\mathbf{h}_2 \cdot (\mathbf{N}^{-1}\mathbf{m}_1)] Y^*(\mathbf{m}_1, \mathbf{h}_2)$$

and carry out the second transform

$$Z^*(\mathbf{h}_1, \mathbf{h}_2) = \frac{1}{|\det \mathbf{N}_1|} \sum_{\mathbf{m}_1 \in I_1} Z(\mathbf{m}_1, \mathbf{h}_2) e[\mathbf{h}_1 \cdot (\mathbf{N}_1^{-1}\mathbf{m}_1)].$$

The final results are indexed by

$$(\text{all } \mathbf{h}_1) \times (\text{unique } \mathbf{h}_2),$$

which yield essentially an asymmetric unit of structure factors after unscrambling by:

$$F(\mathbf{h}_2 + \mathbf{N}_2^T \mathbf{h}_1) = Z^*(\mathbf{h}_1, \mathbf{h}_2).$$

The transposition formula above applies to intermediate results when going backwards from F to ρ , provided these results are considered *after* the twiddle-factor stage. A transposition formula applicable *before* that stage can be obtained by characterizing the action of G on $\mathbf{h}$ (including the effects of periodization by $\mathbf{N}^T\mathbb{Z}^3$) in a manner similar to that used for $\mathbf{m}$.

Let

$$\mathbf{h} = \mathbf{h}_2 + \mathbf{N}_2^T \mathbf{h}_1,$$

with

$$\begin{aligned} \mathbf{h}_2 &= \mathbf{h} \mod \mathbf{N}_2^T \mathbb{Z}^3, \\ \mathbf{h}_1 &= (\mathbf{N}_2^{-1})^T (\mathbf{h} - \mathbf{h}_2) \mod \mathbf{N}_1^T \mathbb{Z}^3. \end{aligned}$$

We may then write

$$\mathbf{R}_g^T \mathbf{h} = [\mathbf{R}_g^T \mathbf{h}]_2 + \mathbf{N}_2^T [\mathbf{R}_g^T \mathbf{h}]_1,$$

with

$$\begin{aligned} [\mathbf{R}_g^T \mathbf{h}]_2 &= [\mathbf{R}_g^{(2)}]^T \mathbf{h}_2 \mod \mathbf{N}_2^T \mathbb{Z}^3, \\ [\mathbf{R}_g^T \mathbf{h}]_1 &= [\mathbf{R}_g^{(1)}]^T \mathbf{h}_1 + \boldsymbol{\eta}_1(g, \mathbf{h}_2) \mod \mathbf{N}_1^T \mathbb{Z}^3. \end{aligned}$$

Here $[\mathbf{R}_g^{(2)}]^T$, $[\mathbf{R}_g^{(1)}]^T$ and $\boldsymbol{\eta}_1$ are defined by

$$\begin{aligned} [\mathbf{R}_g^{(2)}]^T \mathbf{h}_2 &= \mathbf{R}_g^T \mathbf{h} \mod \mathbf{N}_2^T \mathbb{Z}^3, \\ [\mathbf{R}_g^{(1)}]^T \mathbf{h}_1 &= \mathbf{R}_g^T \mathbf{h} \mod \mathbf{N}_1^T \mathbb{Z}^3 \end{aligned}$$

and

$$\boldsymbol{\eta}_1(g, \mathbf{h}_2) = (\mathbf{N}_2^{-1})^T (\mathbf{R}_g^T \mathbf{h}_2 - [\mathbf{R}_g^{(2)}]^T \mathbf{h}_2) \mod \mathbf{N}_1^T \mathbb{Z}^3.$$

Let us then form an array Z^* according to

$$Z^*(\mathbf{h}'_1, \mathbf{h}'_2) = F(\mathbf{h}'_2 + \mathbf{N}_2^T \mathbf{h}'_1)$$

for all $\mathbf{h}'_1$ but only for the *unique* $\mathbf{h}'_2$ under the action of G in $\mathbb{Z}^3/\mathbf{N}_2^T \mathbb{Z}^3$, and transform on $\mathbf{h}'_1$ to obtain

$$Z(\mathbf{m}_1, \mathbf{h}_2) = \sum_{\mathbf{h}'_1 \in \mathbb{Z}^3/\mathbf{N}_1^T \mathbb{Z}^3} Z^*(\mathbf{h}'_1, \mathbf{h}'_2) e[-\mathbf{h}'_1 \cdot (\mathbf{N}_1^{-1}\mathbf{m}_1)].$$

Putting $\mathbf{h}' = \mathbf{R}_g^T \mathbf{h}$ and using the symmetry of F in the form

$$F(\mathbf{h}') = F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}_g),$$

where

$$\begin{aligned} \mathbf{h} \cdot \mathbf{t}_g &= (\mathbf{h}_2^T + \mathbf{h}_1^T \mathbf{N}_2) (\mathbf{N}_2^{-1} \mathbf{N}_1^{-1}) (\mathbf{t}_g^{(1)} + \mathbf{N}_1 \mathbf{t}_g^{(2)}) \\ &\equiv \mathbf{h}_2 \cdot \mathbf{t}_g + \mathbf{h}_2 \cdot (\mathbf{N}_1^{-1} \mathbf{t}_g^{(1)}) \mod 1 \end{aligned}$$

yields by a straightforward rearrangement

$$\begin{aligned} Z(\mathbf{m}_1, [\mathbf{R}_g^{(2)}]^T \mathbf{h}_2) &= e[-\{\mathbf{h}_2 \cdot \mathbf{t}_g + \boldsymbol{\eta}_1(g, \mathbf{h}_2) \cdot (\mathbf{N}_1^{-1}\mathbf{m}_1)\}] \\ &\times Z\{S_g^{(1)}(\mathbf{m}_1), \mathbf{h}_2\}. \end{aligned}$$

This formula allows the transposition of intermediate results Z from an indexing by

$$(\text{all } \mathbf{m}_1) \times (\text{unique } \mathbf{h}_2)$$

to an indexing by

$$(\text{unique } \mathbf{m}_1) \times (\text{all } \mathbf{h}_2).$$

We may then apply the twiddle factors to obtain

$$Y^*(\mathbf{m}_1, \mathbf{h}_2) = e[-\mathbf{h}_2 \cdot (\mathbf{N}^{-1}\mathbf{m}_1)] Z(\mathbf{m}_1, \mathbf{h}_2)$$

and carry out the second transform on $\mathbf{h}_2$

$$Y(\mathbf{m}_1, \mathbf{m}_2) = \sum_{\mathbf{h}_2 \in \mathbb{Z}^3/\mathbf{N}_2^T \mathbb{Z}^3} Y^*(\mathbf{m}_1, \mathbf{h}_2) e[-\mathbf{h}_2 \cdot (\mathbf{N}_2^{-1}\mathbf{m}_2)].$$

The results, indexed by

$$(\text{unique } \mathbf{m}_1) \times (\text{all } \mathbf{m}_2)$$

yield essentially an asymmetric unit of electron densities by the rearrangement

$$\rho(\mathbf{m}_1 + \mathbf{N}_1\mathbf{m}_2) = Y(\mathbf{m}_1, \mathbf{m}_2).$$

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The equivalence of the two transposition formulae up to the intervening twiddle factors is readily established, using the relation

$$\mathbf{h}_2 \cdot [\mathbf{N}_2^{-1} \boldsymbol{\mu}_2(g, \mathbf{m}_1)] = \boldsymbol{\eta}_1(g, \mathbf{h}_2) \cdot (\mathbf{N}_1^{-1} \mathbf{m}_1) \bmod 1$$

which is itself a straightforward consequence of the identity

$$\mathbf{h} \cdot [\mathbf{N}^{-1} S_g(\mathbf{m})] = \mathbf{h} \cdot \mathbf{t}_g + (\mathbf{R}_g^T \mathbf{h}) \cdot (\mathbf{N}^{-1} \mathbf{m}).$$

To complete the characterization of the effect of symmetry on the Cooley–Tukey factorization, and of the economy of computation it allows, it remains to consider the possibility that some values of $\mathbf{m}_1$ may be invariant under some transformations $g \in G$ under the action $\mathbf{m}_1 \mapsto S_g^{(1)}(\mathbf{m}_1)$.

Suppose that $\mathbf{m}_1$ has a non-trivial isotropy subgroup $G_{\mathbf{m}_1}$, and let $g \in G_{\mathbf{m}_1}$. Then each subarray $Y_{\mathbf{m}_1}$ defined by

$$Y_{\mathbf{m}_1}(\mathbf{m}_2) = Y(\mathbf{m}_1, \mathbf{m}_2) = \rho(\mathbf{m}_1 + \mathbf{N}_1 \mathbf{m}_2)$$

satisfies the identity

$$\begin{aligned} Y_{\mathbf{m}_1}(\mathbf{m}_2) &= Y_{S_g^{(1)}(\mathbf{m}_1)}[S_g^{(2)}(\mathbf{m}_2) + \boldsymbol{\mu}_2(g, \mathbf{m}_1)] \\ &= Y_{\mathbf{m}_1}[S_g^{(2)}(\mathbf{m}_2) + \boldsymbol{\mu}_2(g, \mathbf{m}_1)] \end{aligned}$$

so that the data for the transform on $\mathbf{m}_2$ have residual symmetry properties. In this case the identity satisfied by $\boldsymbol{\mu}_2$ simplifies to

$$\boldsymbol{\mu}_2(gg', \mathbf{m}_1) = S_g^{(2)}[\boldsymbol{\mu}_2(g', \mathbf{m}_1)] + \boldsymbol{\mu}_2(g, \mathbf{m}_1) \bmod \mathbf{N}_2 \mathbb{Z}^3,$$

which shows that the mapping $g \mapsto \boldsymbol{\mu}_2(g, \mathbf{m}_1)$ satisfies the Frobenius congruences (Section 1.3.4.2.2.3). Thus the internal symmetry of subarray $Y_{\mathbf{m}_1}$ with respect to the action of G on $\mathbf{m}_2$ is given by $G_{\mathbf{m}_1}$ acting on $\mathbb{Z}^3/\mathbf{N}_2 \mathbb{Z}^3$ via

$$\mathbf{m}_2 \mapsto S_g^{(2)}(\mathbf{m}_2) + \boldsymbol{\mu}_2(g, \mathbf{m}_1) \bmod \mathbf{N}_2 \mathbb{Z}^3.$$

The transform on $\mathbf{m}_2$ needs only be performed for one out of $[G : G_{\mathbf{m}_1}]$ distinct arrays $Y_{\mathbf{m}_1}$ (results for the others being obtainable by the transposition formula), and this transform is $G_{\mathbf{m}_1}$ -symmetric. In other words, the following cases occur:

- (i) $G_{\mathbf{m}_1} = \{e\}$ maximum saving in computation (by $|G|$);
 $\mathbf{m}_2$ -transform has no symmetry.
- (ii) $G_{\mathbf{m}_1} = G' < G$ saving in computation by a factor of $[G : G']$;
 $\mathbf{m}_2$ -transform is G' -symmetric.
- (iii) $G_{\mathbf{m}_1} = G$ no saving in computation;
 $\mathbf{m}_2$ -transform is G -symmetric.

The symmetry properties of the $\mathbf{m}_2$ -transform may themselves be exploited in a similar way if $\mathbf{N}_2$ can be factored as a product of smaller decimation matrices; otherwise, an appropriate symmetrized DFT routine may be provided, using for instance the idea of ‘multiplexing/demultiplexing’ (Section 1.3.4.3.5). We thus have a recursive *descent procedure*, in which the deeper stages of the recursion deal with transforms on *fewer points*, or of *lower symmetry* (usually both).

The same analysis applies to the $\mathbf{h}_1$ -transforms on the subarrays $Z_{\mathbf{h}_2}^*$, and leads to a similar descent procedure.

In conclusion, crystallographic symmetry can be fully exploited to reduce the amount of computation to the minimum required to obtain the unique results from the unique data. No such analysis was so far available in cases where the asymmetric units in real and reciprocal space are not parallelepipeds. An example of this procedure will be given in Section 1.3.4.3.6.5.

1.3.4.3.4.2. Multidimensional Good factorization

This procedure was described in Section 1.3.3.3.2.2. The main difference with the Cooley–Tukey factorization is that if $\mathbf{N} = \mathbf{N}_1 \mathbf{N}_2 \dots \mathbf{N}_{d-1} \mathbf{N}_d$, where the different factors are pairwise coprime, then the Chinese remainder theorem reindexing makes $\mathbb{Z}^3/\mathbf{N} \mathbb{Z}^3$ isomorphic to a direct sum.

$$\mathbb{Z}^3/\mathbf{N} \mathbb{Z}^3 \cong (\mathbb{Z}^3/\mathbf{N}_1 \mathbb{Z}^3) \oplus \dots \oplus (\mathbb{Z}^3/\mathbf{N}_d \mathbb{Z}^3),$$

where each p -primary piece is endowed with an induced $\mathbb{Z}G$ -module structure by letting G operate in the usual way but with the corresponding modular arithmetic. The situation is thus more favourable than with the Cooley–Tukey method, since there is no interference between the factors (no ‘carry’). In the terminology of Section 1.3.4.2.2.2, G acts *diagonally* on this direct sum, and results of a partial transform may be transposed by orbit exchange as in Section 1.3.4.3.4.1 but without the extra terms $\boldsymbol{\mu}$ or $\boldsymbol{\eta}$. The analysis of the symmetry properties of partial transforms also carries over, again without the extra terms. Further simplification occurs for all p -primary pieces with p other than 2 or 3, since all non-primitive translations (including those associated to lattice centring) disappear modulo p .

Thus the cost of the CRT reindexing is compensated by the computational savings due to the absence of twiddle factors and of other phase shifts associated with non-primitive translations and with geometric ‘carries’.

Within each p -primary piece, however, higher powers of p may need to be split up by a Cooley–Tukey factorization, or carried out directly by a suitably adapted Winograd algorithm.

1.3.4.3.4.3. Crystallographic extension of the Rader/Winograd factorization

As was the case in the absence of symmetry, the two previous classes of algorithms can only factor the global transform into partial transforms on prime numbers of points, but cannot break the latter down any further. Rader’s idea of using the action of the group of units $U(p)$ to obtain further factorization of a p -primary transform has been used in ‘scalar’ form by Auslander & Shenefelt (1987), Shenefelt (1988), and Auslander *et al.* (1988). It will be shown here that it can be adapted to the crystallographic case so as to take advantage also of the possible existence of n -fold cyclic symmetry elements ($n = 3, 4, 6$) in a two-dimensional transform (Bricogne & Tolimieri, 1990). This adaptation entails the use of certain rings of *algebraic* integers rather than ordinary integers, whose connection with the handling of cyclic symmetry will now be examined.

Let G be the group associated with a threefold axis of symmetry: $G = \{e, g, g^2\}$ with $g^3 = e$. In a standard trigonal basis, G has matrix representation

$$\mathbf{R}_e = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{I}, \quad \mathbf{R}_g = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}, \quad \mathbf{R}_{g^2} = \begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$$

in real space,

$$\mathbf{R}_e^* = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{I}, \quad \mathbf{R}_g^* = \begin{pmatrix} -1 & -1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{R}_{g^2}^* = \begin{pmatrix} 0 & 1 \\ -1 & -1 \end{pmatrix}$$

in reciprocal space. Note that

$$\mathbf{R}_g^* = [\mathbf{R}_{g^2}^{-1}]^T = \mathbf{R}_g^T,$$

and that

$$\mathbf{R}_g^T = \mathbf{J}^{-1} \mathbf{R}_g \mathbf{J}, \quad \text{where } \mathbf{J} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

so that $\mathbf{R}_g$ and $\mathbf{R}_g^T$ are conjugate in the group of 2×2 unimodular

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integer matrices. The group ring $\mathbb{Z}G$ is commutative, and has the structure of the polynomial ring $\mathbb{Z}[X]$ with the single relation $X^2 + X + 1 = 0$ corresponding to the minimal polynomial of $\mathbf{R}_g$. In the terminology of Section 1.3.3.2.4, the ring structure of $\mathbb{Z}G$ is obtained from that of $\mathbb{Z}[X]$ by carrying out polynomial addition and multiplication modulo $X^2 + X + 1$, then replacing X by any generator of G . This type of construction forms the very basis of algebraic number theory [see Artin (1944, Section IIc) for an illustration of this viewpoint], and $\mathbb{Z}G$ as just defined is isomorphic to the ring $\mathbb{Z}[\omega]$ of algebraic integers of the form $a + b\omega$ [$a, b \in \mathbb{Z}, \omega = \exp(2\pi i/3)$] under the identification $X \leftrightarrow \omega$. Addition in this ring is defined component-wise, while multiplication is defined by

$$(a_1 + b_1\omega) \times (a_2 + b_2\omega) = (a_1a_2 - b_1b_2) + [(a_1 - b_1)b_2 + b_1a_2]\omega.$$

In the case of a fourfold axis, $G = \{e, g, g^2, g^3\}$ with $g^4 = e$, and

$$\mathbf{R}_g = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = \mathbf{R}_g^*, \quad \text{with again } \mathbf{R}_g^T = \mathbf{J}^{-1}\mathbf{R}_g\mathbf{J}.$$

$\mathbb{Z}G$ is obtained from $\mathbb{Z}[X]$ by carrying out polynomial arithmetic modulo $X^2 + 1$. This identifies $\mathbb{Z}G$ with the ring $\mathbb{Z}[i]$ of Gaussian integers of the form $a + bi$, in which addition takes place component-wise while multiplication is defined by

$$(a_1 + b_1i) \times (a_2 + b_2i) = (a_1a_2 - b_1b_2) + (a_1b_2 + b_1a_2)i.$$

In the case of a sixfold axis, $G = \{e, g, g^2, g^3, g^4, g^5\}$ with $g^6 = e$, and

$$\mathbf{R}_g = \begin{pmatrix} 1 & -1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{R}_g^* = \begin{pmatrix} 0 & -1 \\ 1 & 1 \end{pmatrix}, \quad \mathbf{R}_g^T = \mathbf{J}^{-1}\mathbf{R}_g\mathbf{J}.$$

$\mathbb{Z}G$ is isomorphic to $\mathbb{Z}[\omega]$ under the mapping $g \leftrightarrow 1 + \omega$ since $(1 + \omega)^6 = 1$.

Thus in all cases $\mathbb{Z}G \cong \mathbb{Z}[X]/P(X)$ where $P(X)$ is an irreducible quadratic polynomial with integer coefficients.

The actions of G on lattices in real and reciprocal space (Sections 1.3.4.2.2.4, 1.3.4.2.2.5) extend naturally to actions of $\mathbb{Z}G$ on $\mathbb{Z}^2$ in which an element $z = a + bg$ of $\mathbb{Z}G$ acts via

$$\mathbf{m} = \begin{pmatrix} m_1 \\ m_2 \end{pmatrix} \mapsto z\mathbf{m} = (a\mathbf{I} + b\mathbf{R}_g)\begin{pmatrix} m_1 \\ m_2 \end{pmatrix}$$

in real space, and via

$$\mathbf{h} = \begin{pmatrix} h_1 \\ h_2 \end{pmatrix} \mapsto z\mathbf{h} = (a\mathbf{I} + b\mathbf{R}_g^T)\begin{pmatrix} h_1 \\ h_2 \end{pmatrix}$$

in reciprocal space. These two actions are related by conjugation, since

$$(a\mathbf{I} + b\mathbf{R}_g^T) = \mathbf{J}^{-1}(a\mathbf{I} + b\mathbf{R}_g)\mathbf{J}$$

and the following identity (which is fundamental in the sequel) holds:

$$(z\mathbf{h}) \cdot \mathbf{m} = \mathbf{h} \cdot (z\mathbf{m}) \quad \text{for all } \mathbf{m}, \mathbf{h} \in \mathbb{Z}^2.$$

Let us now consider the calculation of a $p \times p$ two-dimensional DFT with n -fold cyclic symmetry ($n = 3, 4, 6$) for an odd prime $p \geq 5$. Denote $\mathbb{Z}/p\mathbb{Z}$ by $\mathbb{Z}_p$. Both the data and the results of the DFT are indexed by $\mathbb{Z}_p \times \mathbb{Z}_p$; hence the action of $\mathbb{Z}G$ on these indices is in fact an action of $\mathbb{Z}_pG$, the latter being obtained from $\mathbb{Z}G$ by carrying out all integer arithmetic in $\mathbb{Z}G$ modulo p . The algebraic structure of $\mathbb{Z}_pG$ combines the symmetry-carrying ring structure of $\mathbb{Z}G$ with the finite field structure of $\mathbb{Z}_p$ used in Section 1.3.3.2.3.1, and holds the key to a symmetry-adapted factorization of the DFT at hand.

The structure of $\mathbb{Z}_pG$ depends on whether $P(X)$ remains irreducible when considered as a polynomial over $\mathbb{Z}_p$. Thus two cases arise:

- (1) $P(X)$ remains irreducible mod p , i.e. there is no n th root of unity in $\mathbb{Z}_p$;
- (2) $P(X)$ factors as $(X - u)(X - v)$, i.e. there are n th roots of unity in $\mathbb{Z}_p$.

These two cases require different developments.

Case 1. $\mathbb{Z}_pG$ is a finite field with p^2 elements. There is essentially (i.e. up to isomorphism) only one such field, denoted $GF(p^2)$, and its group of units is a cyclic group with $p^2 - 1$ elements. If γ is a generator of this group of units, the input data $\rho_{\mathbf{m}}$ with $\mathbf{m} \neq \mathbf{0}$ may be reordered as

$$\mathbf{m}_0, \gamma\mathbf{m}_0, \gamma^2\mathbf{m}_0, \gamma^3\mathbf{m}_0, \dots, \gamma^{p^2-2}\mathbf{m}_0$$

by the *real-space action* of γ ; while the results $F_{\mathbf{h}}$ with $\mathbf{h} \neq \mathbf{0}$ may be reordered as

$$\mathbf{h}_0, \gamma\mathbf{h}_0, \gamma^2\mathbf{h}_0, \gamma^3\mathbf{h}_0, \dots, \gamma^{p^2-2}\mathbf{h}_0$$

by the *reciprocal-space action* of γ , where $\mathbf{m}_0$ and $\mathbf{h}_0$ are arbitrary non-zero indices.

The core $\mathbf{C}_{p \times p}$ of the DFT matrix, defined by

$$\mathbf{F}_{p \times p} = \begin{pmatrix} 1 & 1 & \dots & 1 \\ 1 & & & \\ \vdots & & \mathbf{C}_{p \times p} & \\ 1 & & & \end{pmatrix},$$

will then have a skew-circulant structure (Section 1.3.3.2.3.1) since

$$(\mathbf{C}_{p \times p})_{jk} = e \left[\frac{(\gamma^j \mathbf{h}_0) \cdot (\gamma^k \mathbf{m}_0)}{p} \right] = e \left[\frac{\mathbf{h}_0 \cdot (\gamma^{j+k} \mathbf{m}_0)}{p} \right]$$

depends only on $j + k$. Multiplication by $\mathbf{C}_{p \times p}$ may then be turned into a cyclic convolution of length $p^2 - 1$, which may be factored by two DFTs (Section 1.3.3.2.3.1) or by Winograd's techniques (Section 1.3.3.2.4). The latter factorization is always favourable, as it is easily shown that $p^2 - 1$ is divisible by 24 for any odd prime $p \geq 5$. This procedure is applicable even if no symmetry is present in the data.

Assume now that cyclic symmetry of order $n = 3, 4$ or 6 is present. Since n divides 24 hence divides $p^2 - 1$, the generator g of this symmetry is representable as $\gamma^{(p^2-1)/n}$ for a suitable generator γ of the group of units. The reordered data will then be $(p^2 - 1)/n$ -periodic rather than simply $(p^2 - 1)$ -periodic; hence the reindexed results will be n -decimated (Section 1.3.2.7.2), and the $(p^2 - 1)/n$ non-zero results can be calculated by applying the DFT to the $(p^2 - 1)/n$ unique input data. In this way, the n -fold symmetry can be used in full to calculate the core contributions from the unique data to the unique results by a DFT of length $(p^2 - 1)/n$.

It is a simple matter to incorporate non-primitive translations into this scheme. For example, when going from structure factors to electron densities, reordered data items separated by $(p^2 - 1)/n$ are not equal but differ by a phase shift proportional to their index mod p , whose effect is simply to shift the origin of the n -decimated transformed sequence. The same economy of computation can therefore be achieved as in the purely cyclic case.

Dihedral symmetry elements, which map g to g^{-1} (Section 1.3.4.2.2.3), induce extra one-dimensional symmetries of order 2 in the reordered data which can also be fully exploited to reduce computation.

Case 2. If $p \geq 5$, it can be shown that the two roots u and v are always distinct. Then, by the Chinese remainder theorem (CRT) for polynomials (Section 1.3.3.2.4) we have a ring isomorphism

$$\mathbb{Z}_p[X]/P(X) \cong \{\mathbb{Z}_p[X]/(X - u)\} \times \{\mathbb{Z}_p[X]/(X - v)\}$$

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defined by sending a polynomial $Q(X)$ from the left-hand-side ring to its two residue classes modulo $X - u$ and $X - v$, respectively. Since the latter are simply the constants $Q(u)$ and $Q(v)$, the CRT reindexing has the particularly simple form

$$a + bX \mapsto (a + bu, a + bv) = (\alpha, \beta)$$

or equivalently

$$\begin{pmatrix} a \\ b \end{pmatrix} \mapsto \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \mathbf{M} \begin{pmatrix} a \\ b \end{pmatrix} \bmod p, \quad \text{with } \mathbf{M} = \begin{pmatrix} 1 & u \\ 1 & v \end{pmatrix}.$$

The CRT reconstruction formula similarly simplifies to

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \mapsto \begin{pmatrix} a \\ b \end{pmatrix} = \mathbf{M}^{-1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \bmod p, \\ \text{with } \mathbf{M}^{-1} = \frac{1}{v - u} \begin{pmatrix} v & -u \\ -1 & 1 \end{pmatrix}.$$

The use of the CRT therefore amounts to the *simultaneous diagonalization* (by $\mathbf{M}$) of all the matrices representing the elements of $\mathbb{Z}_p G$ in the basis $(1, X)$.

A first consequence of this diagonalization is that the internal structure of $\mathbb{Z}_p G$ becomes clearly visible. Indeed, $\mathbb{Z}_p G$ is mapped isomorphically to a direct product of two copies of $\mathbb{Z}_p$, in which arithmetic is carried out *component-wise* between eigenvalues α and β . Thus if

$$z = a + bX \xleftrightarrow{\text{CRT}} (\alpha, \beta), \\ z' = a' + b'X \xleftrightarrow{\text{CRT}} (\alpha', \beta'),$$

then

$$z + z' \xleftrightarrow{\text{CRT}} (\alpha + \alpha', \beta + \beta'), \\ zz' \xleftrightarrow{\text{CRT}} (\alpha\alpha', \beta\beta').$$

Taking in particular

$$z \xleftrightarrow{\text{CRT}} (\alpha, 0) \neq (0, 0), \\ z' \xleftrightarrow{\text{CRT}} (0, \beta) \neq (0, 0),$$

we have $zz' = 0$, so that $\mathbb{Z}_p G$ contains zero divisors; therefore $\mathbb{Z}_p G$ is not a field. On the other hand, if $z \xleftrightarrow{\text{CRT}} (\alpha, \beta)$ with $\alpha \neq 0$ and $\beta \neq 0$, then α and β belong to the group of units $U(p)$ (Section 1.3.3.2.3.1) and hence have inverses α^{-1} and β^{-1} ; it follows that z is a unit in $\mathbb{Z}_p G$, with inverse $z^{-1} \xleftrightarrow{\text{CRT}} (\alpha^{-1}, \beta^{-1})$. Therefore, $\mathbb{Z}_p G$ consists of four distinct pieces:

$$\begin{aligned} & 0 \xleftrightarrow{\text{CRT}} \{(0, 0)\}, \\ & D_1 \xleftrightarrow{\text{CRT}} \{(\alpha, 0) | \alpha \in U(p)\} \cong U(p), \\ & D_2 \xleftrightarrow{\text{CRT}} \{(0, \beta) | \beta \in U(p)\} \cong U(p), \\ & U \xleftrightarrow{\text{CRT}} \{(\alpha, \beta) | \alpha \in U(p), \beta \in U(p)\} \cong U(p) \times U(p). \end{aligned}$$

A second consequence of this diagonalization is that the actions of $\mathbb{Z}_p G$ on indices $\mathbf{m}$ and $\mathbf{h}$ can themselves be brought to diagonal form by basis changes:

$$\begin{aligned} \mathbf{m} & \mapsto (a\mathbf{I} + b\mathbf{R}_g)\mathbf{m} \\ \text{becomes } \boldsymbol{\mu} & \mapsto \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \boldsymbol{\mu} \quad \text{with } \boldsymbol{\mu} = \mathbf{M}\mathbf{m}, \\ \mathbf{h} & \mapsto (a\mathbf{I} + b\mathbf{R}_g^T)\mathbf{h} \\ \text{becomes } \boldsymbol{\eta} & \mapsto \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \boldsymbol{\eta} \quad \text{with } \boldsymbol{\eta} = \mathbf{M}\mathbf{J}\mathbf{h}. \end{aligned}$$

Thus the sets of indices $\boldsymbol{\mu}$ and $\boldsymbol{\eta}$ can be split into four pieces as $\mathbb{Z}_p G$ itself, according as these indices have none, one or two of their coordinates in $U(p)$. These pieces will be labelled by the same symbols – 0, D_1 , D_2 and U – as those of $\mathbb{Z}_p G$.

The scalar product $\mathbf{h} \cdot \mathbf{m}$ may be written in terms of $\boldsymbol{\eta}$ and $\boldsymbol{\mu}$ as

$$\mathbf{h} \cdot \mathbf{m} = [\boldsymbol{\eta} \cdot ((\mathbf{M}^{-1})^T \mathbf{J} \mathbf{M}^{-1}) \boldsymbol{\mu}],$$

and an elementary calculation shows that the matrix $= (\mathbf{M}^{-1})^T \mathbf{J} \mathbf{M}^{-1}$ is *diagonal* by virtue of the relation

$$uv = \text{constant term in } P(X) = 1.$$

Therefore, $\mathbf{h} \cdot \mathbf{m} = 0$ if $\mathbf{h} \in D_1$ and $\boldsymbol{\mu} \in D_2$ or *vice versa*.

We are now in a position to rearrange the DFT matrix $\mathbf{F}_{p \times p}$. Clearly, the structure of $\mathbf{F}_{p \times p}$ is more complex than in case 1, as there are three types of ‘core’ matrices:

- type 1: $D \times D$ (with $D = D_1$ or D_2);
- type 2: $D \times U$ or $U \times D$;
- type 3: $U \times U$.

(Submatrices of type $D_1 \times D_2$ and $D_2 \times D_1$ have all their elements equal to 1 by the previous remark.)

Let γ be a generator of $U(p)$. We may reorder the elements in D_1 , D_2 and U – and hence the data and results indexed by these elements – according to powers of γ . This requires one exponent in each of D_1 and D_2 , and two exponents in U . For instance, in the $\mathbf{h}$ -index space:

$$\begin{aligned} D_1 &= \left\{ \begin{pmatrix} \gamma & 0 \\ 0 & 0 \end{pmatrix}^j \begin{pmatrix} \eta_1 \\ 0 \end{pmatrix} \middle| j = 1, \dots, p-1 \right\} \\ D_2 &= \left\{ \begin{pmatrix} 0 & 0 \\ 0 & \gamma \end{pmatrix}^j \begin{pmatrix} 0 \\ \eta_2 \end{pmatrix} \middle| j = 1, \dots, p-1 \right\} \\ U &= \left\{ \begin{pmatrix} \gamma & 0 \\ 0 & 1 \end{pmatrix}^{j_1} \begin{pmatrix} 1 & 0 \\ 0 & \gamma \end{pmatrix}^{j_2} \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} \middle| j_1 = 1, \dots, p-1; \right. \\ & \quad \left. j_2 = 1, \dots, p-1 \right\} \end{aligned}$$

and similarly for the $\boldsymbol{\mu}$ index.

Since the diagonal matrix $\boldsymbol{\Delta}$ commutes with all the matrices representing the action of γ , this rearrangement will induce skew-circulant structures in all the core matrices. The corresponding cyclic convolutions may be carried out by Rader’s method, *i.e.* by diagonalizing them by means of two $(p-1)$ -point one-dimensional DFTs in the $D \times D$ pieces and of two $(p-1) \times (p-1)$ -point two-dimensional DFTs in the $U \times U$ piece (the $U \times D$ and $D \times U$ pieces involve extra section and projection operations).

In the absence of symmetry, no computational saving is achieved, since the same reordering could have been applied to the initial $\mathbb{Z}_p \times \mathbb{Z}_p$ indexing, without the CRT reindexing.

In the presence of n -fold cyclic symmetry, however, the rearranged $\mathbf{F}_{p \times p}$ lends itself to an n -fold reduction in size. The basic fact is that whenever case 2 occurs, $p-1$ is divisible by n (*i.e.* $p-1$ is divisible by 6 when $n=3$ or 6, and by 4 when $n=4$), say

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$p - 1 = nq$. If g is a generator of the cyclic symmetry, the generator γ of $U(p)$ may be chosen in such a way that $g = \gamma^q$. The action of g is then to increment the j index in D_1 and D_2 by q , and the (j_1, j_2) index in U by (q, q) . Since the data items whose indices are related in this way have identical values, the DFTs used to diagonalize the Rader cyclic convolutions will operate on *periodized data*, hence yield *decimated results*; and the non-zero results will be obtained from the unique data by DFTs n times smaller than their counterparts in the absence of symmetry.

A more thorough analysis is needed to obtain a Winograd factorization into the normal from CBA in the presence of symmetry (see Bricogne & Tolimieri, 1990).

Non-primitive translations and dihedral symmetry may also be accommodated within this framework, as in case 1.

This reindexing by means of algebraic integers yields larger orbits, hence more efficient algorithms, than that of Auslander *et al.* (1988) which only uses ordinary integers acting by scalar dilation.

1.3.4.3.5. Treatment of conjugate and parity-related symmetry properties

Most crystallographic Fourier syntheses are real-valued and originate from Hermitian-symmetric collections of Fourier coefficients. Hermitian symmetry is closely related to the action of a centre of inversion in reciprocal space, and thus interacts strongly with all other genuinely crystallographic symmetry elements of order 2. All these symmetry properties are best treated by factoring by 2 and reducing the computation of the initial transform to that of a collection of smaller transforms with less symmetry or none at all.

1.3.4.3.5.1. Hermitian-symmetric or real-valued transforms

The computation of a DFT with Hermitian-symmetric or real-valued data can be carried out at a cost of half that of an ordinary transform, essentially by ‘multiplexing’ pairs of special partial transforms into general complex transforms, and then ‘demultiplexing’ the results on the basis of their symmetry properties. The treatment given below is for general dimension n ; a subset of cases for $n = 1$ was treated by Ten Eyck (1973).

(a) Underlying group action

Hermitian symmetry is not a geometric symmetry, but it is defined in terms of the action in reciprocal space of point group $G = \bar{1}$, i.e. $G = \{e, -e\}$, where e acts as $\mathbf{I}$ (the $n \times n$ identity matrix) and $-e$ acts as $-\mathbf{I}$.

This group action on $\mathbb{Z}^n / N\mathbb{Z}^n$ with $N = N_1 N_2$ will now be characterized by the calculation of the cocycle η_1 (Section 1.3.4.3.4.1) under the assumption that N_1 and N_2 are both *diagonal*. For this purpose it is convenient to associate to any integer vector

$$\mathbf{v} = \begin{pmatrix} v_1 \\ \vdots \\ v_n \end{pmatrix} \text{ in } \mathbb{Z}^n \text{ the vector } \boldsymbol{\zeta}(\mathbf{v}) \text{ whose } j\text{th component is}$$

$$\begin{cases} 0 & \text{if } v_j = 0 \\ 1 & \text{if } v_j \neq 0. \end{cases}$$

Let $\mathbf{m} = \mathbf{m}_1 + N_1 \mathbf{m}_2$, and hence $\mathbf{h} = \mathbf{h}_2 + N_2 \mathbf{h}_1$. Then

$$\begin{aligned} -\mathbf{h}_2 \bmod N\mathbb{Z}^n &= N\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2, \\ -\mathbf{h}_2 \bmod N_2\mathbb{Z}^n &= N_2\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2, \end{aligned}$$

hence

$$\begin{aligned} \eta_1(-e, \mathbf{h}_2) &= N_2^{-1} \{ [N\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2] - [N_2\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2] \} \bmod N_1\mathbb{Z}^n \\ &= -\boldsymbol{\zeta}(\mathbf{h}_2) \bmod N_1\mathbb{Z}^n. \end{aligned}$$

Therefore $-e$ acts by

$$(\mathbf{h}_2, \mathbf{h}_1) \mapsto [N_2\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2, N_1\boldsymbol{\zeta}(\mathbf{h}_1) - \mathbf{h}_1 - \boldsymbol{\zeta}(\mathbf{h}_2)].$$

Hermitian symmetry is traditionally dealt with by factoring by 2, i.e. by assuming $N = 2M$. If $N_2 = 2I$, then each $\mathbf{h}_2$ is invariant under G , so that each partial vector $\mathbf{Z}_{\mathbf{h}_2}^*$ (Section 1.3.4.3.4.1) inherits the symmetry internally, with a ‘modulation’ by $\eta_1(g, \mathbf{h}_2)$. The ‘multiplexing–demultiplexing’ technique provides an efficient treatment of this singular case.

(b) Calculation of structure factors

The computation may be summarized as follows:

$$\rho \xrightarrow{\text{dec}(N_1)} \mathbf{Y} \xrightarrow{\bar{F}(N_2)} \mathbf{Y}^* \xrightarrow{\text{TW}} \mathbf{Z} \xrightarrow{\bar{F}(N_1)} \mathbf{Z}^* \xrightarrow{\text{rev}(N_2)} \mathbf{F}$$

where $\text{dec}(N_1)$ is the initial decimation given by $\mathbf{Y}_{\mathbf{m}_1}(\mathbf{m}_2) = \rho(\mathbf{m}_1 + N_1 \mathbf{m}_2)$, TW is the transposition and twiddle-factor stage, and $\text{rev}(N_2)$ is the final unscrambling by coset reversal given by $F(\mathbf{h}_2 + N_2 \mathbf{h}_1) = \mathbf{Z}_{\mathbf{h}_2}^*(\mathbf{h}_1)$.

(i) Decimation in time ($N_1 = 2I, N_2 = M$)

The decimated vectors $\mathbf{Y}_{\mathbf{m}_1}$ are real and hence have Hermitian transforms $\mathbf{Y}_{\mathbf{m}_1}^*$. The 2^n values of $\mathbf{m}_1$ may be grouped into 2^{n-1} pairs $(\mathbf{m}_1', \mathbf{m}_1'')$ and the vectors corresponding to each pair may be multiplexed into a general complex vector

$$\mathbf{Y} = \mathbf{Y}_{\mathbf{m}_1'} + i\mathbf{Y}_{\mathbf{m}_1''}.$$

The transform $\mathbf{Y}^* = \bar{F}(\mathbf{M})[\mathbf{Y}]$ can then be resolved into the separate transforms $\mathbf{Y}_{\mathbf{m}_1'}^*$ and $\mathbf{Y}_{\mathbf{m}_1''}^*$ by using the Hermitian symmetry of the latter, which yields the demultiplexing formulae

$$\begin{aligned} Y_{\mathbf{m}_1'}^*(\mathbf{h}_2) + iY_{\mathbf{m}_1''}^*(\mathbf{h}_2) &= Y^*(\mathbf{h}_2) \\ \overline{Y_{\mathbf{m}_1'}^*(\mathbf{h}_2)} + i\overline{Y_{\mathbf{m}_1''}^*(\mathbf{h}_2)} &= Y^*[\mathbf{M}\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2]. \end{aligned}$$

The number of partial transforms $\bar{F}(\mathbf{M})$ is thus reduced from 2^n to 2^{n-1} . Once this separation has been achieved, the remaining steps need only be carried out for a unique half of the values of $\mathbf{h}_2$.

(ii) Decimation in frequency ($N_1 = M, N_2 = 2I$)

Since $\mathbf{h}_2 \in \mathbb{Z}^n / 2\mathbb{Z}^n$ we have $-\mathbf{h}_2 = \mathbf{h}_2$ and $\boldsymbol{\zeta}(\mathbf{h}_2) = \mathbf{h}_2 \bmod 2\mathbb{Z}^n$. The vectors of decimated and scrambled results $\mathbf{Z}_{\mathbf{h}_2}^*$ then obey the symmetry relations

$$\mathbf{Z}_{\mathbf{h}_2}^*(\mathbf{h}_1 - \mathbf{h}_2) = \overline{\mathbf{Z}_{\mathbf{h}_2}^*[\mathbf{M}\boldsymbol{\zeta}(\mathbf{h}_1) - \mathbf{h}_1]}$$

which can be used to halve the number of $\bar{F}(\mathbf{M})$ necessary to compute them, as follows.

Having formed the vectors $\mathbf{Z}_{\mathbf{h}_2}$ given by

$$\mathbf{Z}_{\mathbf{h}_2}(\mathbf{m}_1) = \left[\sum_{\mathbf{m}_2 \in \mathbb{Z}^n / 2\mathbb{Z}^n} \frac{(-1)^{\mathbf{h}_2 \cdot \mathbf{m}_2}}{2^n} \rho(\mathbf{m}_1 + \mathbf{M}\mathbf{m}_2) \right] e[\mathbf{h}_2 \cdot (N^{-1}\mathbf{m}_1)],$$

we may group the 2^n values of $\mathbf{h}_2$ into 2^{n-1} pairs $(\mathbf{h}_2', \mathbf{h}_2'')$ and for each pair form the multiplexed vector:

$$\mathbf{Z} = \mathbf{Z}_{\mathbf{h}_2'} + i\mathbf{Z}_{\mathbf{h}_2''}.$$

After calculating the 2^{n-1} transforms $\mathbf{Z}^* = \bar{F}(\mathbf{M})[\mathbf{Z}]$, the 2^n individual transforms $\mathbf{Z}_{\mathbf{h}_2'}^*$ and $\mathbf{Z}_{\mathbf{h}_2''}^*$ can be separated by using for each pair the demultiplexing formulae

$$\begin{aligned} Z_{\mathbf{h}_2'}^*(\mathbf{h}_1) + iZ_{\mathbf{h}_2''}^*(\mathbf{h}_1) &= Z^*(\mathbf{h}_1) \\ Z_{\mathbf{h}_2'}^*(\mathbf{h}_1 - \mathbf{h}_2') + iZ_{\mathbf{h}_2''}^*(\mathbf{h}_1 - \mathbf{h}_2'') &= \overline{Z^*[\mathbf{M}\boldsymbol{\zeta}(\mathbf{h}_1) - \mathbf{h}_1]} \end{aligned}$$

which can be solved recursively. If all pairs are chosen so that they differ only in the j th coordinate $(\mathbf{h}_2)_j$, the recursion is along $(\mathbf{h}_1)_j$ and can be initiated by introducing the (real) values of $Z_{\mathbf{h}_2'}^*$ and $Z_{\mathbf{h}_2''}^*$ at $(\mathbf{h}_1)_j = 0$ and $(\mathbf{h}_1)_j = M_j$, accumulated e.g. while forming $\mathbf{Z}$ for that pair. Only points with $(\mathbf{h}_1)_j$ going from 0 to $\frac{1}{2}M_j$ need be resolved,

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and they contain the unique half of the Hermitian-symmetric transform $\mathbf{F}$.

(c) Calculation of electron densities

The computation may be summarized as follows:

$$\mathbf{F} \xrightarrow{\text{scr}(\mathbf{N}_2)} \mathbf{Z}^* \xrightarrow{F(\mathbf{N}_1)} \mathbf{Z} \xrightarrow{\text{TW}} \mathbf{Y}^* \xrightarrow{F(\mathbf{N}_2)} \mathbf{Y} \xrightarrow{\text{nat}(\mathbf{N}_1)} \rho$$

where $\text{scr}(\mathbf{N}_2)$ is the decimation with coset reversal given by $\mathbf{Z}_{\mathbf{h}_2}^*(\mathbf{h}_1) = F(\mathbf{h}_2 + \mathbf{N}_2\mathbf{h}_1)$, TW is the transposition and twiddle-factor stage, and $\text{nat}(\mathbf{N}_1)$ is the recovery in natural order given by $\rho(\mathbf{m}_1 + \mathbf{N}_1\mathbf{m}_2) = Y_{\mathbf{m}_1}(\mathbf{m}_2)$.

(i) Decimation in time ($\mathbf{N}_1 = \mathbf{M}, \mathbf{N}_2 = 2\mathbf{I}$)

The last transformation $F(2\mathbf{I})$ has a real-valued matrix, and the final result ρ is real-valued. It follows that the vectors $\mathbf{Y}_{\mathbf{m}_1}^*$ of intermediate results after the twiddle-factor stage are real-valued, hence lend themselves to multiplexing along the real and imaginary components of half as many general complex vectors.

Let the 2^n initial vectors $\mathbf{Z}_{\mathbf{h}_2}^*$ be multiplexed into 2^{n-1} vectors

$$\mathbf{Z}^* = \mathbf{Z}_{\mathbf{h}_2'}^* + i\mathbf{Z}_{\mathbf{h}_2''}^*$$

[one for each pair $(\mathbf{h}_2', \mathbf{h}_2'')$], each of which yields by $F(\mathbf{M})$ a vector

$$\mathbf{Z} = \mathbf{Z}_{\mathbf{h}_2'} + i\mathbf{Z}_{\mathbf{h}_2''}.$$

The real-valuedness of the $\mathbf{Y}_{\mathbf{m}_1}^*$ may be used to recover the separate result vectors for $\mathbf{h}_2'$ and $\mathbf{h}_2''$. For this purpose, introduce the abbreviated notation

$$\begin{aligned} e[-\mathbf{h}_2' \cdot (\mathbf{N}^{-1}\mathbf{m}_1)] &= (c' + is')(\mathbf{m}_1) \\ e[-\mathbf{h}_2'' \cdot (\mathbf{N}^{-1}\mathbf{m}_1)] &= (c'' + is'')(\mathbf{m}_1) \\ R_{\mathbf{h}_2}(\mathbf{m}_1) &= Y_{\mathbf{m}_1}^*(\mathbf{h}_2) \\ \mathbf{R}' &= \mathbf{R}_{\mathbf{h}_2'}, \quad \mathbf{R}'' = \mathbf{R}_{\mathbf{h}_2''}. \end{aligned}$$

Then we may write

$$\begin{aligned} \mathbf{Z} &= (c' + is')\mathbf{R}' + i(c'' + is'')\mathbf{R}'' \\ &= (c'\mathbf{R}' + s''\mathbf{R}'') + i(-s'\mathbf{R}' + c''\mathbf{R}'') \end{aligned}$$

or, equivalently, for each $\mathbf{m}_1$,

$$\begin{pmatrix} \text{Re } \mathbf{Z} \\ \text{Im } \mathbf{Z} \end{pmatrix} = \begin{pmatrix} c' & s'' \\ -s' & c'' \end{pmatrix} \begin{pmatrix} \mathbf{R}' \\ \mathbf{R}'' \end{pmatrix}.$$

Therefore $\mathbf{R}'$ and $\mathbf{R}''$ may be retrieved from $\mathbf{Z}$ by the ‘demultiplexing’ formula:

$$\begin{pmatrix} \mathbf{R}' \\ \mathbf{R}'' \end{pmatrix} = \frac{1}{c'c'' + s's''} \begin{pmatrix} c'' & -s'' \\ s' & c' \end{pmatrix} \begin{pmatrix} \text{Re } \mathbf{Z} \\ \text{Im } \mathbf{Z} \end{pmatrix}$$

which is valid at all points $\mathbf{m}_1$ where $c'c'' + s's'' \neq 0$, i.e. where

$$\cos[2\pi(\mathbf{h}_2' - \mathbf{h}_2'') \cdot (\mathbf{N}^{-1}\mathbf{m}_1)] \neq 0.$$

Demultiplexing fails when

$$(\mathbf{h}_2' - \mathbf{h}_2'') \cdot (\mathbf{N}^{-1}\mathbf{m}_1) = \frac{1}{2} \bmod 1.$$

If the pairs $(\mathbf{h}_2', \mathbf{h}_2'')$ are chosen so that their members differ only in one coordinate (the j th, say), then the exceptional points are at $(\mathbf{m}_1)_j = \frac{1}{2}M_j$ and the missing transform values are easily obtained e.g. by accumulation while forming $\mathbf{Z}^*$.

The final stage of the calculation is then

$$\rho(\mathbf{m}_1 + \mathbf{M}\mathbf{m}_2) = \sum_{\mathbf{h}_2 \in \mathbf{Z}^n/2\mathbf{Z}^n} (-1)^{\mathbf{h}_2 \cdot \mathbf{m}_2} R_{\mathbf{h}_2}(\mathbf{m}_1).$$

(ii) Decimation in frequency ($\mathbf{N}_1 = 2\mathbf{I}, \mathbf{N}_2 = \mathbf{M}$)

The last transformation $F(\mathbf{M})$ gives the real-valued results ρ , therefore the vectors $\mathbf{Y}_{\mathbf{m}_1}^*$ after the twiddle-factor stage each have Hermitian symmetry.

A first consequence is that the intermediate vectors $\mathbf{Z}_{\mathbf{h}_2}$ need only be computed for the unique half of the values of $\mathbf{h}_2$, the other half being related by the Hermitian symmetry of $\mathbf{Y}_{\mathbf{m}_1}^*$.

A second consequence is that the 2^n vectors $\mathbf{Y}_{\mathbf{m}_1}^*$ may be condensed into 2^{n-1} general complex vectors

$$\mathbf{Y}^* = \mathbf{Y}_{\mathbf{m}_1'}^* + i\mathbf{Y}_{\mathbf{m}_1''}^*$$

[one for each pair $(\mathbf{m}_1', \mathbf{m}_1'')$] to which a general complex $F(\mathbf{M})$ may be applied to yield

$$\mathbf{Y} = \mathbf{Y}_{\mathbf{m}_1'} + i\mathbf{Y}_{\mathbf{m}_1''}$$

with $\mathbf{Y}_{\mathbf{m}_1'}$ and $\mathbf{Y}_{\mathbf{m}_1''}$ real-valued. The final results can therefore be retrieved by the particularly simple demultiplexing formulae:

$$\begin{aligned} \rho(\mathbf{m}_1' + 2\mathbf{m}_2) &= \text{Re } Y(\mathbf{m}_2), \\ \rho(\mathbf{m}_1'' + 2\mathbf{m}_2) &= \text{Im } Y(\mathbf{m}_2). \end{aligned}$$

1.3.4.3.5.2. Hermitian-antisymmetric or pure imaginary transforms

A vector $\mathbf{X} = \{X(\mathbf{k}) | \mathbf{k} \in \mathbb{Z}^n / \mathbf{N}\mathbb{Z}^n\}$ is said to be Hermitian-antisymmetric if

$$X(\mathbf{k}) = -\overline{X(-\mathbf{k})} \text{ for all } \mathbf{k}.$$

Its transform $\mathbf{X}^*$ then satisfies

$$X^*(\mathbf{k}^*) = -\overline{X^*(-\mathbf{k}^*)} \text{ for all } \mathbf{k}^*,$$

i.e. is purely imaginary.

If $\mathbf{X}$ is Hermitian-antisymmetric, then $\mathbf{F} = \pm i\mathbf{X}$ is Hermitian-symmetric, with $\rho = \pm i\mathbf{X}^*$ real-valued. The treatment of Section 1.3.4.3.5.1 may therefore be adapted, with trivial factors of i or -1 , or used as such in conjunction with changes of variable by multiplication by $\pm i$.

1.3.4.3.5.3. Complex symmetric and antisymmetric transforms

The matrix $-\mathbf{I}$ is its own contragredient, and hence (Section 1.3.2.4.2.2) the transform of a symmetric (respectively antisymmetric) function is symmetric (respectively antisymmetric). In this case the group $G = \{e, -e\}$ acts in both real and reciprocal space as $\{\mathbf{I}, -\mathbf{I}\}$. If $\mathbf{N} = \mathbf{N}_1\mathbf{N}_2$ with both factors diagonal, then $-e$ acts by

$$\begin{aligned} (\mathbf{m}_1, \mathbf{m}_2) &\mapsto [\mathbf{N}_1\boldsymbol{\zeta}(\mathbf{m}_1) - \mathbf{m}_1, \mathbf{N}_2\boldsymbol{\zeta}(\mathbf{m}_2) - \mathbf{m}_2 - \boldsymbol{\zeta}(\mathbf{m}_1)], \\ (\mathbf{h}_2, \mathbf{h}_1) &\mapsto [\mathbf{N}_2\boldsymbol{\zeta}(\mathbf{h}_2) - \mathbf{h}_2, \mathbf{N}_1\boldsymbol{\zeta}(\mathbf{h}_1) - \mathbf{h}_1 - \boldsymbol{\zeta}(\mathbf{h}_2)], \end{aligned}$$

i.e.

$$\begin{aligned} \boldsymbol{\mu}_2(-e, \mathbf{m}_1) &= -\boldsymbol{\zeta}(\mathbf{m}_1) \bmod \mathbf{N}_2\mathbb{Z}^n, \\ \boldsymbol{\eta}_1(-e, \mathbf{h}_2) &= -\boldsymbol{\zeta}(\mathbf{h}_2) \bmod \mathbf{N}_1\mathbb{Z}^n. \end{aligned}$$

The symmetry or antisymmetry properties of $\mathbf{X}$ may be written

$$X(-\mathbf{m}) = -\varepsilon X(\mathbf{m}) \text{ for all } \mathbf{m},$$

with $\varepsilon = +1$ for symmetry and $\varepsilon = -1$ for antisymmetry.

The computation will be summarized as

$$\mathbf{X} \xrightarrow{\text{dec}(\mathbf{N}_1)} \mathbf{Y} \xrightarrow{\bar{F}(\mathbf{N}_2)} \mathbf{Y}^* \xrightarrow{\text{TW}} \mathbf{Z} \xrightarrow{\bar{F}(\mathbf{N}_1)} \mathbf{Z}^* \xrightarrow{\text{rev}(\mathbf{N}_2)} \mathbf{X}^*$$

with the same indexing as that used for structure-factor calculation. In both cases it will be shown that a transform $F(\mathbf{N})$ with $\mathbf{N} = 2\mathbf{M}$ and $\mathbf{M}$ diagonal can be computed using only 2^{n-1} partial transforms $F(\mathbf{M})$ instead of 2^n .

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(i) *Decimation in time* ($\mathbf{N}_1 = 2\mathbf{I}, \mathbf{N}_2 = \mathbf{M}$)

Since $\mathbf{m}_1 \in \mathbb{Z}^n/2\mathbb{Z}^n$ we have $-\mathbf{m}_1 = \mathbf{m}_1$ and $\zeta(\mathbf{m}_1) = \mathbf{m}_1 \bmod 2\mathbb{Z}^n$, so that the symmetry relations for each parity class of data $\mathbf{Y}_{\mathbf{m}_1}$ read

$$Y_{\mathbf{m}_1}[\mathbf{M}\zeta(\mathbf{m}_2) - \mathbf{m}_2 - \mathbf{m}_1] = \varepsilon Y_{\mathbf{m}_1}(\mathbf{m}_2)$$

or equivalently

$$\tau_{\mathbf{m}_1} \mathbf{Y}_{\mathbf{m}_1} = \varepsilon \check{\mathbf{Y}}_{\mathbf{m}_1}.$$

Transforming by $F(\mathbf{M})$, this relation becomes

$$e[-\mathbf{h}_2 \cdot (\mathbf{M}^{-1}\mathbf{m}_1)] \mathbf{Y}_{\mathbf{m}_1}^* = \varepsilon \mathbf{Y}_{\mathbf{m}_1}^*.$$

Each parity class thus obeys a different symmetry relation, so that we may multiplex them in pairs by forming for each pair $(\mathbf{m}'_1, \mathbf{m}''_1)$ the vector

$$\mathbf{Y} = \mathbf{Y}_{\mathbf{m}'_1} + \mathbf{Y}_{\mathbf{m}''_1}.$$

Putting

$$e[-\mathbf{h}_2 \cdot (\mathbf{M}^{-1}\mathbf{m}'_1)] = (c' + is')(\mathbf{h}_2)$$

$$e[-\mathbf{h}_2 \cdot (\mathbf{M}^{-1}\mathbf{m}''_1)] = (c'' + is'')(\mathbf{h}_2)$$

we then have the demultiplexing relations for each $\mathbf{h}_2$:

$$\begin{aligned} Y_{\mathbf{m}'_1}^*(\mathbf{h}_2) + Y_{\mathbf{m}''_1}^*(\mathbf{h}_2) &= Y^*(\mathbf{h}_2) \\ (c' + is')(\mathbf{h}_2) Y_{\mathbf{m}'_1}^*(\mathbf{h}_2) + (c'' + is'')(\mathbf{h}_2) Y_{\mathbf{m}''_1}^*(\mathbf{h}_2) \\ &= \varepsilon Y^*[\mathbf{M}\zeta(\mathbf{h}_2) - \mathbf{h}_2] \end{aligned}$$

which can be solved recursively. Transform values at the exceptional points $\mathbf{h}_2$ where demultiplexing fails (*i.e.* where $c' + is' = c'' + is''$) can be accumulated while forming $\mathbf{Y}$.

Only the unique half of the values of $\mathbf{h}_2$ need to be considered at the demultiplexing stage and at the subsequent TW and $F(2\mathbf{I})$ stages.

(ii) *Decimation in frequency* ($\mathbf{N}_1 = \mathbf{M}, \mathbf{N}_2 = 2\mathbf{I}$)

The vectors of final results $\mathbf{Z}_{\mathbf{h}_2}^*$ for each parity class $\mathbf{h}_2$ obey the symmetry relations

$$\tau_{\mathbf{h}_2} \mathbf{Z}_{\mathbf{h}_2}^* = \varepsilon \check{\mathbf{Z}}_{\mathbf{h}_2}^*,$$

which are different for each $\mathbf{h}_2$. The vectors $\mathbf{Z}_{\mathbf{h}_2}$ of intermediate results after the twiddle-factor stage may then be multiplexed in pairs as

$$\mathbf{Z} = \mathbf{Z}_{\mathbf{h}'_2} + \mathbf{Z}_{\mathbf{h}''_2}.$$

After transforming by $F(\mathbf{M})$, the results $\mathbf{Z}^*$ may be demultiplexed by using the relations

$$\begin{aligned} Z_{\mathbf{h}'_2}^*(\mathbf{h}_1) + Z_{\mathbf{h}''_2}^*(\mathbf{h}_1) &= Z^*(\mathbf{h}_1) \\ Z_{\mathbf{h}'_2}^*(\mathbf{h}_1 - \mathbf{h}'_2) + Z_{\mathbf{h}''_2}^*(\mathbf{h}_1 - \mathbf{h}''_2) &= \varepsilon Z^*[\mathbf{M}\zeta(\mathbf{h}_1) - \mathbf{h}_1] \end{aligned}$$

which can be solved recursively as in Section 1.3.4.3.5.1(b)(ii).

1.3.4.3.5.4. Real symmetric transforms

Conjugate symmetric (Section 1.3.2.4.2.3) implies that if the data $\mathbf{X}$ are real and symmetric [*i.e.* $X(\mathbf{k}) = \bar{X}(\mathbf{k})$ and $X(-\mathbf{k}) = X(\mathbf{k})$], then so are the results $\mathbf{X}^*$. Thus if ρ contains a centre of symmetry, $\mathbf{F}$ is real symmetric. There is no distinction (other than notation) between structure-factor and electron-density calculation; the algorithms will be described in terms of the former. It will be shown that if $\mathbf{N} = 2\mathbf{M}$, a real symmetric transform can be computed with only 2^{n-2} partial transforms $F(\mathbf{M})$ instead of 2^n .

(i) *Decimation in time* ($\mathbf{N}_1 = 2\mathbf{I}, \mathbf{N}_2 = \mathbf{M}$)

Since $\mathbf{m}_1 \in \mathbb{Z}^n/2\mathbb{Z}^n$ we have $-\mathbf{m}_1 = \mathbf{m}_1$ and $\zeta(\mathbf{m}_1) = \mathbf{m}_1 \bmod 2\mathbb{Z}^n$. The decimated vectors $\mathbf{Y}_{\mathbf{m}_1}$ are not only real, but

have an internal symmetry expressed by

$$\mathbf{Y}_{\mathbf{m}_1}[\mathbf{M}\zeta(\mathbf{m}_2) - \mathbf{m}_2 - \mathbf{m}_1] = \varepsilon \mathbf{Y}_{\mathbf{m}_1}(\mathbf{m}_2).$$

This symmetry, however, is different for each $\mathbf{m}_1$ so that we may multiplex two such vectors $\mathbf{Y}_{\mathbf{m}'_1}$ and $\mathbf{Y}_{\mathbf{m}''_1}$ into a general *real* vector

$$\mathbf{Y} = \mathbf{Y}_{\mathbf{m}'_1} + \mathbf{Y}_{\mathbf{m}''_1},$$

for each of the 2^{n-1} pairs $(\mathbf{m}'_1, \mathbf{m}''_1)$. The 2^{n-1} Hermitian-symmetric transform vectors

$$\mathbf{Y}^* = \mathbf{Y}_{\mathbf{m}'_1}^* + \mathbf{Y}_{\mathbf{m}''_1}^*$$

can then be evaluated by the methods of Section 1.3.4.3.5.1(b) at the cost of only 2^{n-2} general complex $F(\mathbf{M})$.

The demultiplexing relations by which the separate vectors $\mathbf{Y}_{\mathbf{m}'_1}^*$ and $\mathbf{Y}_{\mathbf{m}''_1}^*$ may be recovered are most simply obtained by observing that the vectors $\mathbf{Z}$ after the twiddle-factor stage are real-valued since $F(2\mathbf{I})$ has a real matrix. Thus, as in Section 1.3.4.3.5.1(c)(i),

$$\mathbf{Y}_{\mathbf{m}'_1}^* = (c' - is')\mathbf{R}'$$

$$\mathbf{Y}_{\mathbf{m}''_1}^* = (c'' - is'')\mathbf{R}'',$$

where $\mathbf{R}'$ and $\mathbf{R}''$ are real vectors and where the multipliers $(c' - is')$ and $(c'' - is'')$ are the inverse twiddle factors. Therefore,

$$\begin{aligned} \mathbf{Y}^* &= (c' - is')\mathbf{R}' + (c'' - is'')\mathbf{R}'' \\ &= (c'\mathbf{R}' + c''\mathbf{R}'') - i(s'\mathbf{R}' + s''\mathbf{R}'') \end{aligned}$$

and hence the demultiplexing relation for each $\mathbf{h}_2$:

$$\begin{pmatrix} \mathbf{R}' \\ \mathbf{R}'' \end{pmatrix} = \frac{1}{c's'' - s'c''} \begin{pmatrix} s'' & -c'' \\ -s' & c' \end{pmatrix} \begin{pmatrix} \text{Re } \mathbf{Y}^* \\ -\text{Im } \mathbf{Y}^* \end{pmatrix}.$$

The values of $\mathbf{R}'_{\mathbf{h}_2}$ and $\mathbf{R}''_{\mathbf{h}_2}$ at those points $\mathbf{h}_2$ where $c's'' - s'c'' = 0$ can be evaluated directly while forming $\mathbf{Y}$. This demultiplexing and the final stage of the calculation, namely

$$F(\mathbf{h}_2 + \mathbf{M}\mathbf{h}_1) = \frac{1}{2^n} \sum_{\mathbf{m}_1 \in \mathbb{Z}^n/2\mathbb{Z}^n} (-1)^{\mathbf{h}_1 \cdot \mathbf{m}_1} R_{\mathbf{m}_1}(\mathbf{h}_2)$$

need only be carried out for the unique half of the range of $\mathbf{h}_2$.

(ii) *Decimation in frequency* ($\mathbf{N}_1 = \mathbf{M}, \mathbf{N}_2 = 2\mathbf{I}$)

Similarly, the vectors $\mathbf{Z}_{\mathbf{h}_2}^*$ of decimated and scrambled results are real and obey internal symmetries

$$\tau_{\mathbf{h}_2} \mathbf{Z}_{\mathbf{h}_2}^* = \varepsilon \check{\mathbf{Z}}_{\mathbf{h}_2}^*$$

which are different for each $\mathbf{h}_2$. For each of the 2^{n-1} pairs $(\mathbf{h}'_2, \mathbf{h}''_2)$ the multiplexed vector

$$\mathbf{Z} = \mathbf{Z}_{\mathbf{h}'_2} + \mathbf{Z}_{\mathbf{h}''_2}$$

is a Hermitian-symmetric vector without internal symmetry, and the 2^{n-1} real vectors

$$\mathbf{Z}^* = \mathbf{Z}_{\mathbf{h}'_2}^* + \mathbf{Z}_{\mathbf{h}''_2}^*$$

may be evaluated at the cost of only 2^{n-2} general complex $F(\mathbf{M})$ by the methods of Section 1.3.4.3.5.1(c). The individual transforms $\mathbf{Z}_{\mathbf{h}'_2}$ and $\mathbf{Z}_{\mathbf{h}''_2}$ may then be retrieved *via* the demultiplexing relations

$$\begin{aligned} Z_{\mathbf{h}'_2}^*(\mathbf{h}_1) + Z_{\mathbf{h}''_2}^*(\mathbf{h}_1) &= Z^*(\mathbf{h}_1) \\ Z_{\mathbf{h}'_2}^*(\mathbf{h}_1 - \mathbf{h}'_2) + Z_{\mathbf{h}''_2}^*(\mathbf{h}_1 - \mathbf{h}''_2) &= Z^*[\mathbf{M}\zeta(\mathbf{h}_1) - \mathbf{h}_1] \end{aligned}$$

which can be solved recursively as described in Section 1.3.4.3.5.1(b)(ii). This yields the unique half of the real symmetric results $\mathbf{F}$.

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1.3.4.3.5.5. Real antisymmetric transforms

If $\mathbf{X}$ is real antisymmetric, then its transform $\mathbf{X}^*$ is purely imaginary and antisymmetric. The double-multiplexing techniques used for real symmetric transforms may therefore be adapted with only minor changes involving signs and factors of i .

1.3.4.3.5.6. Generalized multiplexing

So far the multiplexing technique has been applied to pairs of vectors with similar types of parity-related and/or conjugate symmetry properties, in particular the same value of ε .

It can be generalized so as to accommodate mixtures of vectors with different symmetry characteristics. For example if $\mathbf{X}_1$ is Hermitian-symmetric and $\mathbf{X}_2$ is Hermitian-antisymmetric, so that $\mathbf{X}_1^*$ is real-valued while $\mathbf{X}_2^*$ has purely imaginary values, the multiplexing process should obviously form $\mathbf{X} = \mathbf{X}_1 + \mathbf{X}_2$ (instead of $\mathbf{X} = \mathbf{X}_1 + i\mathbf{X}_2$ if both had the same type of symmetry), and demultiplexing consists in separating

$$\begin{aligned}\mathbf{X}_1^* &= \mathcal{Re} \mathbf{X}^* \\ \mathbf{X}_2^* &= i\mathcal{Im} \mathbf{X}^*.\end{aligned}$$

The general multiplexing formula for pairs of vectors may therefore be written

$$\mathbf{X} = \mathbf{X}_1 + \omega \mathbf{X}_2,$$

where ω is a phase factor (*e.g.* 1 or i) chosen in such a way that all non-exceptional components of $\mathbf{X}_1$ and $\mathbf{X}_2$ (or $\mathbf{X}_1^*$ and $\mathbf{X}_2^*$) be embedded in the complex plane $\mathbb{C}$ along linearly independent directions, thus making multiplexing possible.

It is possible to develop a more general form of multiplexing/demultiplexing for more than two vectors, which can be used to deal with symmetry elements of order 3, 4 or 6. It is based on the theory of group characters (Ledermann, 1987).

1.3.4.3.6. Global crystallographic algorithms

All the necessary ingredients are now available for calculating the CDFT for any given space group.

1.3.4.3.6.1. Triclinic groups

Space group $P1$ is dealt with by the methods of Section 1.3.4.3.5.1 and $\bar{P}1$ by those of Section 1.3.4.3.5.4.

1.3.4.3.6.2. Monoclinic groups

A general monoclinic transformation is of the form

$$S_g : \mathbf{x} \mapsto \mathbf{R}_g \mathbf{x} + \mathbf{t}_g$$

with $\mathbf{R}_g$ a diagonal matrix whose entries are $+1$ or -1 , and $\mathbf{t}_g$ a vector whose entries are 0 or $\frac{1}{2}$. We may thus decompose both real and reciprocal space into a direct sum of a subspace $\mathbb{Z}^{n_+}$ where $\mathbf{R}_g$ acts as the identity, and a subspace $\mathbb{Z}^{n_-}$ where $\mathbf{R}_g$ acts as minus the identity, with $n_+ + n_- = n = 3$. All usual entities may be correspondingly written as direct sums, for instance:

$$\begin{aligned}\mathbf{R}_g &= \mathbf{R}_g^+ \oplus \mathbf{R}_g^-, & \mathbf{N} &= \mathbf{N}^+ \oplus \mathbf{N}^-, & \mathbf{M} &= \mathbf{M}^+ \oplus \mathbf{M}^-, \\ \mathbf{t}_g &= \mathbf{t}_g^+ \oplus \mathbf{t}_g^-, & \mathbf{t}_g^{(1)} &= \mathbf{t}_g^{(1)+} \oplus \mathbf{t}_g^{(1)-}, & \mathbf{t}_g^{(2)} &= \mathbf{t}_g^{(2)+} \oplus \mathbf{t}_g^{(2)-}, \\ \mathbf{m} &= \mathbf{m}^+ \oplus \mathbf{m}^-, & \mathbf{m}_1 &= \mathbf{m}_1^+ \oplus \mathbf{m}_1^-, & \mathbf{m}_2 &= \mathbf{m}_2^+ \oplus \mathbf{m}_2^-, \\ \mathbf{h} &= \mathbf{h}^+ \oplus \mathbf{h}^-, & \mathbf{h}_1 &= \mathbf{h}_1^+ \oplus \mathbf{h}_1^-, & \mathbf{h}_2 &= \mathbf{h}_2^+ \oplus \mathbf{h}_2^-. \end{aligned}$$

We will use factoring by 2, with decimation in frequency when computing structure factors, and decimation in time when computing electron densities; this corresponds to $\mathbf{N} = \mathbf{N}_1 \mathbf{N}_2$ with $\mathbf{N}_1 = \mathbf{M}$, $\mathbf{N}_2 = 2\mathbf{I}$. The non-primitive translation vector $\mathbf{Nt}_g$ then belongs to $\mathbf{M}\mathbb{Z}^n$, and thus

$$\mathbf{t}_g^{(1)} = \mathbf{0} \bmod \mathbf{M}\mathbb{Z}^n, \quad \mathbf{t}_g^{(2)} \in \mathbb{Z}^n / 2\mathbb{Z}^n.$$

The symmetry relations obeyed by ρ and F are as follows: for electron densities

$$\rho(\mathbf{m}^+, \mathbf{m}^-) = \rho(\mathbf{m}^+ + \mathbf{N}^+ \mathbf{t}_g^+, -\mathbf{m}^- - \mathbf{N}^- \mathbf{t}_g^-)$$

or, after factoring by 2,

$$\begin{aligned}\rho(\mathbf{m}_1^+, \mathbf{m}_2^+, \mathbf{m}_1^-, \mathbf{m}_2^-) \\ = \rho(\mathbf{m}_1^+, \mathbf{m}_2^+ + \mathbf{t}_g^{(2)+}, \mathbf{M}^- \boldsymbol{\zeta}(\mathbf{m}_1^-) - \mathbf{m}_1^- - \mathbf{m}_2^-, \mathbf{m}_2^- + \mathbf{t}_g^{(2)-});\end{aligned}$$

while for structure factors

$$F(\mathbf{h}^+, \mathbf{h}^-) = \exp[2\pi i(\mathbf{h}^+ \cdot \mathbf{t}_g^+ + \mathbf{h}^- \cdot \mathbf{t}_g^-)] F(\mathbf{h}^+, -\mathbf{h}^-)$$

with its Friedel counterpart

$$F(\mathbf{h}^+, \mathbf{h}^-) = \exp[2\pi i(\mathbf{h}^+ \cdot \mathbf{t}_g^+ + \mathbf{h}^- \cdot \mathbf{t}_g^-)] \overline{F(-\mathbf{h}^+, \mathbf{h}^-)}$$

or, after factoring by 2,

$$\begin{aligned}F(\mathbf{h}_1^+, \mathbf{h}_2^+, \mathbf{h}_1^-, \mathbf{h}_2^-) &= (-1)^{\mathbf{h}_2^+ \cdot \mathbf{t}_g^{(2)+} + \mathbf{h}_2^- \cdot \mathbf{t}_g^{(2)-}} \\ &\times F(\mathbf{h}_1^+, \mathbf{h}_2^+, \mathbf{M}^- \boldsymbol{\zeta}(\mathbf{h}_1^-) - \mathbf{h}_1^- - \mathbf{h}_2^-, \mathbf{h}_2^-)\end{aligned}$$

with Friedel counterpart

$$\begin{aligned}F(\mathbf{h}_1^+, \mathbf{h}_2^+, \mathbf{h}_1^-, \mathbf{h}_2^-) \\ = (-1)^{\mathbf{h}_2^+ \cdot \mathbf{t}_g^{(2)+} + \mathbf{h}_2^- \cdot \mathbf{t}_g^{(2)-}} \overline{F[\mathbf{M}^+ \boldsymbol{\zeta}(\mathbf{h}_1^+) - \mathbf{h}_1^+ - \mathbf{h}_2^+, \mathbf{h}_2^+, \mathbf{h}_1^-, \mathbf{h}_2^-]}.\end{aligned}$$

When calculating electron densities, two methods may be used.

(i) Transform on $\mathbf{h}^-$ first.

The partial vectors defined by $X_{\mathbf{h}^+, \mathbf{h}_2^-} = F(\mathbf{h}^+, \mathbf{h}_1^-, \mathbf{h}_2^-)$ obey symmetry relations of the form

$$X(\mathbf{h}_1^- - \mathbf{h}_2^-) = \varepsilon X[\mathbf{M}^- \boldsymbol{\zeta}(\mathbf{h}_1^-) - \mathbf{h}_1^-]$$

with $\varepsilon = \pm 1$ independent of $\mathbf{h}_1^-$. This is the same relation as for the same parity class of data for a (complex or real) symmetric ($\varepsilon = +1$) or antisymmetric ($\varepsilon = -1$) transform. The same techniques can be used to decrease the number of $F(\mathbf{M}^-)$ by multiplexing pairs of such vectors and demultiplexing their transforms. Partial vectors with different values of ε may be mixed in this way (Section 1.3.4.3.5.6).

Once $F(\mathbf{N}^-)$ is completed, its results have Hermitian symmetry with respect to $\mathbf{h}^+$, and the methods of Section 1.3.4.3.5.1 may be used to obtain the unique electron densities.

(ii) Transform on $\mathbf{h}^+$ first.

The partial vectors defined by $X_{\mathbf{h}^-, \mathbf{h}_2^+} = F(\mathbf{h}_1^+, \mathbf{h}_2^+, \mathbf{h}^-)$ obey symmetry relations of the form

$$X(\mathbf{h}_1^+ - \mathbf{h}_2^+) = \varepsilon X[\mathbf{M}^+ \boldsymbol{\zeta}(\mathbf{h}_1^+) - \mathbf{h}_1^+]$$

with $\varepsilon = \pm 1$ independent of $\mathbf{h}_1^+$. This is the same relation as for the same parity class of data for a Hermitian symmetric ($\varepsilon = +1$) or antisymmetric ($\varepsilon = -1$) transform. The same techniques may be used to decrease the number of $F(\mathbf{M}^+)$. This generalizes the procedure described by Ten Eyck (1973) for treating dyad axes, *i.e.* for the case $n_+ = 1$, $\mathbf{t}_g^{(2)-} = \mathbf{0}$, and $\mathbf{t}_g^{(2)+} = \mathbf{0}$ (simple dyad) or $\mathbf{t}_g^{(2)+} \neq \mathbf{0}$ (screw dyad).

Once $F(\mathbf{N}^+)$ is completed, its results have Hermitian symmetry properties with respect to $\mathbf{h}^-$ which can be used to obtain the unique electron densities.

Structure factors may be computed by applying the reverse procedures in the reverse order.

1.3.4.3.6.3. Orthorhombic groups

Almost all orthorhombic space groups are generated by two monoclinic transformations g_1 and g_2 of the type described in Section 1.3.4.3.6.2, with the addition of a centre of inversion $-e$ for centrosymmetric groups. The only exceptions are *Fdd2* and *Fddd*

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which contain diamond glides, in which some non-primitive translations are 'square roots' not of primitive lattice translations, but of centring translations. The generic case will be examined first.

To calculate electron densities, the unique octant of data may first be transformed on $\mathbf{h}^+$ (respectively $\mathbf{h}^-$) as in Section 1.3.4.3.6.2 using the symmetry pertaining to generator g_1 . These intermediate results may then be expanded by generator g_2 by the formula of Section 1.3.4.3.3 prior to the final transform on $\mathbf{h}^-$ (respectively $\mathbf{h}^+$). To calculate structure factors, the reverse operations are applied in the reverse order.

The two exceptional groups $Fdd2$ and $Fddd$ only require a small modification. The F -centring causes the systematic absence of parity classes with mixed parities, leaving only (000) and (111). For the former, the phase factors $\exp[2\pi i(\mathbf{h}^+ \cdot \mathbf{t}_g^+ + \mathbf{h}^- \cdot \mathbf{t}_g^-)]$ in the symmetry relations of Section 1.3.4.3.6.2 become powers of (-1) so that one is back to the generic case. For the latter, these phase factors are odd powers of i which it is a simple matter to incorporate into a modified multiplexing/demultiplexing procedure.

1.3.4.3.6.4. Trigonal, tetragonal and hexagonal groups

All the symmetries in this class of groups can be handled by the generalized Rader/Winograd algorithms of Section 1.3.4.3.4.3, but no implementation of these is yet available.

In groups containing axes of the form n_m with g.c.d. $(m, n) = 1$ (i.e. $3_1, 3_2, 4_1, 4_3, 6_1, 6_5$) along the c direction, the following procedure may be used (Ten Eyck, 1973):

(i) to calculate electron densities, the unique structure factors indexed by

$$[\text{unique } (h, k)] \times (\text{all } l)$$

are transformed on l ; the results are rearranged by the transposition formula of Section 1.3.4.3.3 so as to be indexed by

$$[\text{all } (h, k)] \times \left[\text{unique } \left(\frac{1}{n} \right) \text{th of } z \right]$$

and are finally transformed on (h, k) to produce an asymmetric unit. For a dihedral group, the extra twofold axis may be used in the transposition to produce a unique $(1/2n)$ th of z .

(ii) to calculate structure factors, the unique densities in $(1/n)$ th of z [or $(1/2n)$ th for a dihedral group] are first transformed on x and y , then transposed by the formula of Section 1.3.4.3.3 to reindex the intermediate results by

$$[\text{unique } (h, k)] \times (\text{all } z);$$

the last transform on z is then carried out.

1.3.4.3.6.5. Cubic groups

These are usually treated as their orthorhombic or tetragonal subgroups, as the body-diagonal threefold axis cannot be handled by ordinary methods of decomposition.

The three-dimensional factorization technique of Section 1.3.4.3.4.1 allows a complete treatment of cubic symmetry. Factoring by 2 along all three dimensions gives four types (i.e. orbits) of parity classes:

(000)	with residual threefold symmetry,
(100), (010), (001)	related by threefold axis,
(110), (101), (011)	related by threefold axis,
(111)	with residual threefold symmetry.

Orbit exchange using the threefold axis thus allows one to reduce the number of partial transforms from 8 to 4 (one per orbit). Factoring by 3 leads to a reduction from 27 to 11 (in this case, further reduction to 9 can be gained by multiplexing the three

diagonal classes with residual threefold symmetry into a single class; see Section 1.3.4.3.5.6). More generally, factoring by q leads to a reduction from q^3 to $\frac{1}{3}(q^3 - q) - q$. Each of the remaining transforms then has a symmetry induced from the orthorhombic or tetragonal subgroup, which can be treated as above.

No implementation of this procedure is yet available.

1.3.4.3.6.6. Treatment of centred lattices

Lattice centring is an instance of the duality between periodization and decimation: the extra translational periodicity of ρ induces a decimation of $\mathbf{F} = \{F_{\mathbf{h}}\}$ described by the 'reflection conditions' on $\mathbf{h}$. As was pointed out in Section 1.3.4.2.2.3, non-primitive lattices are introduced in order to retain the same matrix representation for a given geometric symmetry operation in all the arithmetic classes in which it occurs. From the computational point of view, therefore, the main advantage in using centred lattices is that it *maximizes decomposability* (Section 1.3.4.2.2.4); reindexing to a primitive lattice would for instance often destroy the diagonal character of the matrix representing a dyad.

In the usual procedure involving three successive one-dimensional transforms, the loss of efficiency caused by the duplication of densities or the systematic vanishing of certain classes of structure factors may be avoided by using a multiplexing/demultiplexing technique (Ten Eyck, 1973):

(i) for base-centred or body-centred lattices, two successive planes of structure factors may be overlaid into a single plane; after transformation, the results belonging to each plane may be separated by parity considerations;

(ii) for face-centred lattices the same method applies, using four successive planes (the third and fourth with an origin translation);

(iii) for rhombohedral lattices in hexagonal coordinates, three successive planes may be overlaid, and the results may be separated by linear combinations involving cube roots of unity.

The three-dimensional factorization technique of Section 1.3.4.3.4.1 is particularly well suited to the treatment of centred lattices: if the decimation matrix of $\mathbf{N}$ contains as a factor $\mathbf{N}_1$ a matrix which 'integerizes' all the non-primitive lattice vectors, then centring is reflected by the systematic vanishing of certain classes of vectors of decimated data or results, which can simply be omitted from the calculation. An alternative possibly is to reindex on a primitive lattice and use different representative matrices for the symmetry operations: the loss of decomposability is of little consequence in this three-dimensional scheme, although it substantially complicates the definition of the cocycles μ_2 and η_1 .

1.3.4.3.6.7. Programming considerations

The preceding sections have been devoted to showing how the raw computational efficiency of a crystallographic Fourier transform *algorithm* can be maximized. This section will briefly discuss another characteristic (besides speed) which a crystallographic Fourier transform *program* may be required to possess if it is to be useful in various applications: a convenient and versatile mode of presentation of input data or output results.

The standard crystallographic FFT programs (Ten Eyck, 1973, 1985) are rather rigid in this respect, and use rather rudimentary data structures (lists of structure-factor values, and two-dimensional arrays containing successive sections of electron-density maps). It is frequently the case that considerable reformatting of these data or results must be carried out before they can be used in other computations; for instance, maps have to be converted from 2D sections to 3D 'bricks' before they can be inspected on a computer graphics display.

The explicitly three-dimensional approach to the factorization of the DFT and the use of symmetry offers the possibility of richer and more versatile data structures. For instance, the use of 'decimation in frequency' in real space and of 'decimation in time' in reciprocal

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space leads to data structures in which real-space coordinates are handled by blocks (thus preserving, at least locally, the three-dimensional topological connectivity of the maps) while reciprocal-space indices are handled by parity classes or their generalizations for factors other than 2 (thus making the treatment of centred lattices extremely easy). This global three-dimensional indexing also makes it possible to carry symmetry and multiplicity characteristics for each subvector of intermediate results for the purpose of automating the use of the orbit exchange mechanism.

Brünger (1989) has described the use of a similar three-dimensional factoring technique in the context of structure-factor calculations for the refinement of macromolecular structures.

1.3.4.4. Basic crystallographic computations

1.3.4.4.1. Introduction

Fourier transform (FT) calculations play an indispensable role in crystallography, because the Fourier transformation is inherent in the diffraction phenomenon itself.

Besides this obligatory use, the FT has numerous other applications, motivated more often by its mathematical properties than by direct physical reasoning (although the latter can be supplied after the fact). Typically, many crystallographic computations turn out to be convolutions in disguise, which can be speeded up by orders of magnitude through a judicious use of the FT. Several recent advances in crystallographic computation have been based on this kind of observation.

1.3.4.4.2. Fourier synthesis of electron-density maps

Bragg (1929) was the first to use this type of calculation to assist structure determination. Progress in computing techniques since that time was reviewed in Section 1.3.4.3.1.

The usefulness of the maps thus obtained can be adversely affected by three main factors:

- (i) limited resolution;
- (ii) errors in the data;
- (iii) computational errors.

Limited resolution causes 'series-termination errors' first investigated by Bragg & West (1930), who used an optical analogy with the numerical aperture of a microscope. James (1948*b*) gave a quantitative description of this phenomenon as a convolution with the 'spherical Dirichlet kernel' (Section 1.3.4.2.1.3), which reflects the truncation of the Fourier spectrum by multiplication with the indicator function of the limiting resolution sphere. Bragg & West (1930) suggested that the resulting ripples might be diminished by applying an artificial temperature factor to the data, which performs a further convolution with a Gaussian point-spread function. When the electron-density map is to be used for model refinement, van Reijen (1942) suggested using Fourier coefficients calculated from the model when no observation is available, as a means of combating series-termination effects.

Errors in the data introduce errors in the electron-density maps, with the same mean-square value by virtue of Parseval's theorem. Special positions accrue larger errors (Cruickshank & Rollett, 1953; Cruickshank, 1965*a*). To minimize the mean-square electron-density error due to large phase uncertainties, Blow & Crick (1959) introduced the 'best Fourier' which uses centroid Fourier coefficients; the associated error level in the electron-density map was evaluated by Blow & Crick (1959) and Dickerson *et al.* (1961*a,b*).

Computational errors used to be a serious concern when Beevers-Lipson strips were used, and Cochran (1948*a*) carried out a critical evaluation of the accuracy limitations imposed by strip methods. Nowadays, the FFT algorithm implemented on digital computers with a word size of at least 32 bits gives results accurate

to six decimal places or better in most applications (see Gentleman & Sande, 1966).

1.3.4.4.3. Fourier analysis of modified electron-density maps

Various approaches to the phase problem are based on certain modifications of the electron-density map, followed by Fourier analysis of the modified map and extraction of phase information from the resulting Fourier coefficients.

1.3.4.4.3.1. Squaring

Sayre (1952*a*) derived his 'squaring method equation' for structures consisting of equal, resolved and spherically symmetric atoms by observing that squaring such an electron density is equivalent merely to sharpening each atom into its square. Thus

$$F_{\mathbf{h}} = \theta_{\mathbf{h}} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h}-\mathbf{k}},$$

where $\theta_{\mathbf{h}} = f(\mathbf{h})/f^{\text{sq}}(\mathbf{h})$ is the ratio between the form factor $f(\mathbf{h})$ common to all the atoms and the form factor $f^{\text{sq}}(\mathbf{h})$ for the squared version of that atom.

Most of the central results of direct methods, such as the tangent formula, are an immediate consequence of Sayre's equation. Phase refinement for a macromolecule by enforcement of the squaring method equation was demonstrated by Sayre (1972, 1974).

1.3.4.4.3.2. Other non-linear operations

A category of phase improvement procedures known as 'density modification' is based on the pointwise application of various quadratic or cubic 'filters' to electron-density maps after removal of negative regions (Hoppe & Gassmann, 1968; Hoppe *et al.*, 1970; Barrett & Zwick, 1971; Gassmann & Zechmeister, 1972; Collins, 1975; Collins *et al.*, 1976; Gassmann, 1976). These operations are claimed to be equivalent to reciprocal-space phase-refinement techniques such as those based on the tangent formula. Indeed the replacement of

$$\rho(\mathbf{x}) = \sum_{\mathbf{h}} F_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

by $P[\rho(\mathbf{x})]$, where P is a polynomial

$$P(\rho) = a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \dots$$

yields

$$P[\rho(\mathbf{x})] = a_0 + \sum_{\mathbf{h}} \left[a_1 F_{\mathbf{h}} + a_2 \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h}-\mathbf{k}} + a_3 \sum_{\mathbf{k}} \sum_{\mathbf{l}} F_{\mathbf{k}} F_{\mathbf{l}} F_{\mathbf{h}-\mathbf{k}-\mathbf{l}} + \dots \right] \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

and hence gives rise to the convolution-like families of terms encountered in direct methods. This equivalence, however, has been shown to be rather superficial (Bricogne, 1982) because the 'uncertainty principle' embodied in Heisenberg's inequality (Section 1.3.2.4.4.3) imposes severe limitations on the effectiveness of any procedure which operates *pointwise* in *both* real and reciprocal space.

In applying such methods, sampling considerations must be given close attention. If the spectrum of ρ extends to resolution Δ and if the pointwise non-linear filter involves a polynomial P of degree n , then $P(\rho)$ should be sampled at intervals of at most $\Delta/2n$ to accommodate the full bandwidth of its spectrum.

1.3.4.4.3.3. Solvent flattening

Crystals of proteins and nucleic acids contain large amounts of mother liquor, often in excess of 50% of the unit-cell volume,

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occupying connected channels. The well ordered electron density $\rho_M(\mathbf{x})$ corresponding to the macromolecule thus occupies only a periodic subregion $\mathcal{U}$ of the crystal. Thus

$$\rho_M = \chi_{\mathcal{U}} \times \rho_M,$$

implying the convolution identity between structure factors (Main & Woolfson, 1963):

$$F_M(\mathbf{h}) = \sum_{\mathbf{k}} \tilde{\mathcal{F}} \left[\frac{1}{\mathcal{U}} \chi_{\mathcal{U}} \right] (\mathbf{h} - \mathbf{k}) F_M(\mathbf{k})$$

which is a form of the Shannon interpolation formula (Sections 1.3.2.7.1, 1.3.4.2.1.7; Bricogne, 1974; Colman, 1974).

It is often possible to obtain an approximate ‘molecular envelope’ $\mathcal{U}$ from a poor electron-density map ρ , either interactively by computer graphics (Bricogne, 1976) or automatically by calculating a moving average of the electron density within a small sphere S . The latter procedure can be implemented in real space (Wang, 1985). However, as it is a convolution of ρ with χ_S , it can be speeded up considerably (Leslie, 1987) by computing the moving average ρ_{mav} as

$$\rho_{\text{mav}}(\mathbf{x}) = \tilde{\mathcal{F}}[\tilde{\mathcal{F}}[\rho] \times \tilde{\mathcal{F}}[\chi_S]](\mathbf{x}).$$

This remark is identical in substance to Booth’s method of computation of ‘bounded projections’ (Booth, 1945a) described in Section 1.3.4.2.1.8, except that the summation is kept three-dimensional.

The iterative use of the estimated envelope $\mathcal{U}$ for the purpose of phase improvement (Wang, 1985) is a submethod of the previously developed method of molecular averaging, which is described below. Sampling rules for the Fourier analysis of envelope-truncated maps will be given there.

1.3.4.4.3.4. Molecular averaging by noncrystallographic symmetries

Macromolecules and macromolecular assemblies frequently crystallize with several identical subunits in the asymmetric metric unit, or in several crystal forms containing the same molecule in different arrangements. Rossmann & Blow (1963) recognized that intensity data collected from such structures are redundant (Sayre, 1952b) and that their redundancy could be a source of phase information.

The phase constraints implied by the consistency of geometrically redundant intensities were first derived by Rossmann & Blow (1963), and were generalized by Main & Rossmann (1966). Crowther (1967, 1969) reformulated them as linear eigenvalue equations between structure factors, for which he proposed an iterative matrix solution method. Although useful in practice (Jack, 1973), this reciprocal-space approach required computations of size $\propto N^2$ for N reflections, so that N could not exceed a few thousands.

The theory was then reformulated in real space (Bricogne, 1974), showing that the most costly step in Crowther’s procedure could be carried out much more economically by averaging the electron densities of all crystallographically independent subunits, then rebuilding the crystal(s) from this averaged subunit, flattening the density in the solvent region(s) by resetting it to its average value. This operation is a *projection* [by virtue of Section 1.3.4.2.2.2(d)]. The overall complexity was thus reduced from N^2 to $N \log N$. The design and implementation of a general-purpose program package for averaging, reconstructing and solvent-flattening electron-density maps (Bricogne, 1976) led rapidly to the first high-resolution determinations of virus structures (Bloomer *et al.*, 1978; Harrison *et al.*, 1978), with $N \sim 200\,000$.

The considerable gain in speed is a consequence of the fact that the masking operations used to retrieve the various copies of the common subunit are carried out by simple *pointwise multiplication*

by an indicator function χ_U in real space, whereas they involve a *convolution* with $\tilde{\mathcal{F}}[\chi_U]$ in reciprocal space.

The averaging by noncrystallographic symmetries of an electron-density map calculated by FFT – hence sampled on a grid which is an integral subdivision of the period lattice – necessarily entails the interpolation of densities at non-integral points of that grid. The effect of interpolation on the structure factors recalculated from an averaged map was examined by Bricogne (1976). This study showed that, if linear interpolation is used, the initial map should be calculated on a fine grid, of size $\Delta/5$ or $\Delta/6$ at resolution Δ (instead of the previously used value of $\Delta/3$). The analysis about to be given applies to all interpolation schemes which consist in a *convolution* of the sampled density with a fixed *interpolation kernel function* K .

Let ρ be a $\mathbb{Z}^3$ -periodic function. Let K be the interpolation kernel in ‘normalized’ form, *i.e.* such that $\int_{\mathbb{R}^3} K(\mathbf{x}) d^3\mathbf{x} = 1$ and scaled so as to interpolate between sample values given on a unit grid $\mathbb{Z}^3$; in the case of linear interpolation, K is the ‘trilinear wedge’

$$K(\mathbf{x}) = W(x)W(y)W(z),$$

where

$$W(t) = 1 - |t| \quad \text{if } |t| \leq 1, \\ = 0 \quad \text{if } |t| \geq 1.$$

Let ρ be sampled on a grid $\mathcal{G}_1 = \mathbf{N}_1^{-1}\mathbb{Z}^3$, and let $I_{\mathbf{N}_1}\rho$ denote the function interpolated from this sampled version of ρ . Then:

$$I_{\mathbf{N}_1}\rho = \left[\rho \times \sum_{\mathbf{m} \in \mathbb{Z}^3} \delta_{(\mathbf{N}_1^{-1}\mathbf{m})} \right] * [(\mathbf{N}_1^{-1})^\# K],$$

where $[(\mathbf{N}_1^{-1})^\# K](\mathbf{x}) = K(\mathbf{N}_1\mathbf{x})$, so that

$$\begin{aligned} \tilde{\mathcal{F}}[I_{\mathbf{N}_1}\rho] &= \left[\tilde{\mathcal{F}}[\rho] * |\det \mathbf{N}_1| \sum_{\mathbf{k}_1 \in \mathbb{Z}^3} \delta_{(\mathbf{N}_1^T \mathbf{k}_1)} \right] \\ &\quad \times \left[\frac{1}{|\det \mathbf{N}_1|} (\mathbf{N}_1^T)^\# \tilde{\mathcal{F}}[K] \right] \\ &= \left[\sum_{\mathbf{k}_1 \in \mathbb{Z}^3} \tau_{\mathbf{N}_1^T \mathbf{k}_1} \tilde{\mathcal{F}}[\rho] \right] \times (\mathbf{N}_1^T)^\# \tilde{\mathcal{F}}[K]. \end{aligned}$$

The transform of $I_{\mathbf{N}_1}\rho$ thus consists of

(i) a ‘main band’ corresponding to $\mathbf{k}_1 = \mathbf{0}$, which consists of the true transform $\tilde{\mathcal{F}}[\rho](\boldsymbol{\xi})$ attenuated by multiplication by the central region of $\tilde{\mathcal{F}}[K][(\mathbf{N}_1^{-1})^T \boldsymbol{\xi}]$; in the case of linear interpolation, for example,

$$\tilde{\mathcal{F}}[K](\xi, \eta, \zeta) = \left(\frac{\sin \pi \xi}{\pi \xi} \right)^2 \left(\frac{\sin \pi \eta}{\pi \eta} \right)^2 \left(\frac{\sin \pi \zeta}{\pi \zeta} \right)^2;$$

(ii) a series of ‘ghost bands’ corresponding to $\mathbf{k}_1 \neq \mathbf{0}$, which consist of translates of $\tilde{\mathcal{F}}[\rho]$ multiplied by the tail regions of $(\mathbf{N}_1^T)^\# \tilde{\mathcal{F}}[K]$.

Thus $I_{\mathbf{N}_1}\rho$ is not band-limited even if ρ is. Supposing, however, that ρ is band-limited and that grid $\mathcal{G}_1$ satisfies the Shannon sampling criterion, we see that there will be no overlap between the different bands: $\tilde{\mathcal{F}}[\rho]$ may therefore be recovered from the main band by compensating its attenuation, which is approximately a temperature-factor correction.

For numerical work, however, $I_{\mathbf{N}_1}\rho$ must be resampled onto another grid $\mathcal{G}_2$, which causes its transform to become periodized into

$$|\det \mathbf{N}_2| \sum_{\mathbf{k}_2 \in \mathbb{Z}^3} \tau_{\mathbf{N}_2^T \mathbf{k}_2} \left\{ \left[\sum_{\mathbf{k}_1 \in \mathbb{Z}^3} \tau_{\mathbf{N}_1^T \mathbf{k}_1} \tilde{\mathcal{F}}[\rho] \right] (\mathbf{N}_1^T)^\# \tilde{\mathcal{F}}[K] \right\}.$$

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This now causes the main band $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{0}$ to become contaminated by the ghost bands ($\mathbf{k}_1 \neq \mathbf{0}$) of the translates ($\mathbf{k}_2 \neq \mathbf{0}$) of $I_{N_1 \rho}$.

Aliasing errors may be minimized by increasing the sampling rate in grid $\mathcal{G}_1$ well beyond the Shannon minimum, which rapidly reduces the r.m.s. content of the ghost bands.

The sampling rate in grid $\mathcal{G}_2$ needs only exceed the Shannon minimum to the extent required to accommodate the increase in bandwidth due to convolution with $\tilde{\mathcal{F}}[\chi_U]$, which is the reciprocal-space counterpart of envelope truncation (or solvent flattening) in real space.

1.3.4.4.3.5. Molecular-envelope transforms via Green's theorem

Green's theorem stated in terms of distributions (Section 1.3.2.3.9.1) is particularly well suited to the calculation of the Fourier transforms $\tilde{\mathcal{F}}[\chi_U]$ of indicator functions. Let f be the indicator function χ_U and let S be the boundary of U (assumed to be a smooth surface). The jump σ_0 in the value of f across S along the outer normal vector is $\sigma_0 = -1$, the jump σ_ν in the normal derivative of f across S is $\sigma_\nu = 0$, and the Laplacian of f as a function is (almost everywhere) 0 so that $T_{\Delta f} = 0$. Green's theorem then reads:

$$\begin{aligned}\Delta(T_f) &= T_{\Delta f} + \sigma_\nu \delta_{(S)} + \partial_\nu[\sigma_0 \delta_{(S)}] \\ &= -\partial_\nu[\delta_{(S)}].\end{aligned}$$

The function $e_{\mathbf{H}}(\mathbf{X}) = \exp(2\pi i \mathbf{H} \cdot \mathbf{X})$ satisfies the identity $\Delta e_{\mathbf{H}} = -4\pi^2 \|\mathbf{H}\|^2 e_{\mathbf{H}}$. Therefore, in Cartesian coordinates:

$$\begin{aligned}\bar{F}[\chi_U](\mathbf{H}) &= \langle T_{\chi_U}, e_{\mathbf{H}} \rangle \\ &= -\frac{1}{4\pi^2 \|\mathbf{H}\|^2} \langle T_{\chi_U}, \Delta e_{\mathbf{H}} \rangle \\ &= -\frac{1}{4\pi^2 \|\mathbf{H}\|^2} \langle \Delta(T_{\chi_U}), e_{\mathbf{H}} \rangle \quad [\text{Section 1.3.2.3.9.1(a)}] \\ &= -\frac{1}{4\pi^2 \|\mathbf{H}\|^2} \langle -\partial_\nu[\delta_{(S)}], e_{\mathbf{H}} \rangle \\ &= -\frac{1}{4\pi^2 \|\mathbf{H}\|^2} \int_S \partial_\nu e_{\mathbf{H}} \, d^2S \quad [\text{Section 1.3.2.3.9.1(c)}] \\ &= -\frac{1}{4\pi^2 \|\mathbf{H}\|^2} \int_S 2\pi i \mathbf{H} \cdot \mathbf{n} \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \, d^2S,\end{aligned}$$

i.e.

$$\tilde{\mathcal{F}}[\chi_U](\mathbf{H}) = \frac{1}{2\pi i \|\mathbf{H}\|^2} \int_S \mathbf{H} \cdot \mathbf{n} \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \, d^2S,$$

where $\mathbf{n}$ is the outer normal to S . This formula was used by von Laue (1936) for a different purpose, namely to calculate the transforms of crystal shapes (see also Ewald, 1940). If the surface S is given by a triangulation, the surface integral becomes a sum over all faces, since $\mathbf{n}$ is constant on each face. If U is a solid sphere with radius R , an integration by parts gives immediately:

$$\begin{aligned}\frac{1}{\text{vol}(U)} \tilde{\mathcal{F}}[\chi_U](\mathbf{H}) &= \frac{3}{X^3} [\sin X - X \cos X] \\ &\text{with } X = 2\pi \|\mathbf{H}\| R.\end{aligned}$$

1.3.4.4.4. Structure factors from model atomic parameters

An atomic model of a crystal structure consists of a list of symmetry-unique atoms described by their positions, their thermal

agitation and their chemical identity (which can be used as a pointer to form-factor tables). Form factors are usually parameterized as sums of Gaussians, and thermal agitation by a Gaussian temperature factor or tensor. The formulae given in Section 1.3.4.2.2.6 for Gaussian atoms are therefore adequate for most purposes. High-resolution electron-density studies use more involved parameterizations.

Early calculations were carried out by means of Bragg–Lipson charts (Bragg & Lipson, 1936) which gave a graphical representation of the symmetrized trigonometric sums Ξ of Section 1.3.4.2.2.9. The approximation of form factors by Gaussians goes back to the work of Vand *et al.* (1957) and Forsyth & Wells (1959). Agarwal (1978) gave simplified expansions suitable for medium-resolution modelling of macromolecular structures.

This method of calculating structure factors is expensive because *each* atom sends contributions of essentially equal magnitude to *all* structure factors in a resolution shell. The calculation is therefore of size $\propto N \mathcal{N}$ for N atoms and $\mathcal{N}$ reflections. Since N and $\mathcal{N}$ are roughly proportional at a given resolution, this method is very costly for large structures.

Two distinct programming strategies are available (Rollett, 1965) according to whether the fast loop is on all atoms for each reflection, or on all reflections for each atom. The former method was favoured in the early times when computers were unreliable. The latter was shown by Burnett & Nordman (1974) to be more amenable to efficient programming, as no multiplication is required in calculating the arguments of the sine/cosine terms: these can be accumulated by integer addition, and used as subscripts in referencing a trigonometric function table.

1.3.4.4.5. Structure factors via model electron-density maps

Robertson (1936*b*) recognized the similarity between the calculation of structure factors by Fourier summation and the calculation of Fourier syntheses, the main difference being of course that atomic coordinates do not usually lie exactly on a grid obtained by integer subdivision of the crystal lattice. He proposed to address this difficulty by the use of his sorting board, which could extend the scale of subdivision and thus avoid phase errors. In this way the calculation of structure factors became amenable to Beevers–Lipson strip methods, with considerable gain of speed.

Later, Beevers & Lipson (1952) proposed that trigonometric functions attached to atomic positions falling between the grid points on which Beevers–Lipson strips were based should be obtained by linear interpolation from the values found on the strips for the closest grid points. This amounts (Section 1.3.4.4.3.4) to using atoms in the shape of a trilinear wedge, whose form factor was indicated in Section 1.3.4.4.3.4 and gives rise to aliasing effects (see below) not considered by Beevers & Lipson.

The correct formulation of this idea came with the work of Sayre (1951), who showed that structure factors could be calculated by Fourier analysis of a sampled electron-density map previously generated on a subdivision $\mathbf{N}^{-1}\Lambda$ of the crystal lattice Λ . When generating such a map, care must be taken to distribute onto the sample grid not only the electron densities of all the atoms in the asymmetric motif, but also those of their images under space-group symmetries and lattice translations. Considerable savings in computation occur, especially for large structures, because atoms are *localized*: each atom sends contributions to only a few grid points in real space, rather than to all reciprocal-lattice points. The generation of the sampled electron-density map is still of complexity $\propto N \mathcal{N}$ for N atoms and $\mathcal{N}$ reflections, but the proportionality constant is smaller than that in Section 1.3.4.4.4 by orders of magnitude; the extra cost of Fourier analysis, proportional to $\mathcal{N} \log \mathcal{N}$, is negligible.

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The idea of approximating a Fourier transform by a discrete transform on sampled values had already been used by Whittaker (1948), who tested it on the first three odd Hermite functions and did not consider the problem of aliasing errors. By contrast, Sayre gave a lucid analysis of the sampling problems associated to this technique. If the periodic sampled map is written in the form of a weighted lattice distribution (as in Section 1.3.2.7.3) as

$$\rho^s = \sum_{\mathbf{m} \in \mathbb{Z}^3} \rho(\mathbf{N}^{-1}\mathbf{m}) \delta_{(\mathbf{N}^{-1}\mathbf{m})},$$

then its discrete Fourier transform yields

$$F^s(\mathbf{h}) = \sum_{\boldsymbol{\eta} \in \mathbb{Z}^3} F(\mathbf{h} + \mathbf{N}^T \boldsymbol{\eta})$$

so that each correct value $F(\mathbf{h})$ is corrupted by its aliases $F(\mathbf{h} + \mathbf{N}^T \boldsymbol{\eta})$ for $\boldsymbol{\eta} \neq \mathbf{0}$.

To cure this aliasing problem, Sayre used ‘hypothetical atoms’ with form factors equal to those of standard atoms within the resolution range of interest, but set to zero outside that range. This amounts to using atomic densities with built-in series-termination errors, which has the detrimental effect of introducing slowly decaying ripples around the atom which require incrementing sample densities at many more grid points per atom.

Sayre considered another cure in the form of an artificial temperature factor B (Bragg & West, 1930) applied to all atoms. This spreads each atom on more grid points in real space but speeds up the decay of its transform in reciprocal space, thus allowing the use of a coarser sampling grid in real space. He discounted it as spoiling the agreement with observed data, but Ten Eyck (1977) pointed out that this agreement could be restored by applying the negative of the artificial temperature factor to the results. This idea cannot be carried to extremes: if B is chosen too large, the atoms will be so spread out in real space as each to occupy a sizeable fraction of the unit cell and the advantage of atom localization will be lost; furthermore, the form factors will fall off so rapidly that round-off error amplification will occur when the results are sharpened back. Clearly, there exists an optimal combination of B and sampling rate yielding the most economical computation for a given accuracy at a given resolution, and a formula will now be given to calculate it.

Let us make the simplifying assumption that all atoms are roughly equal and that their common form factor can be represented by an equivalent temperature factor B_{eq} . Let $\Delta = 1/d_{\text{max}}^*$ be the resolution to which structure factors are wanted. The Shannon sampling interval is $\Delta/2 = 1/2d_{\text{max}}^*$. Let σ be the oversampling rate, so that the actual sampling interval in the map is $\Delta/2\sigma = 1/2\sigma d_{\text{max}}^*$; then consecutive copies of the transform are separated by a distance $2\sigma d_{\text{max}}^*$ in reciprocal space. Let the artificial temperature factor B_{extra} be added, and let

$$B = B_{\text{eq}} + B_{\text{extra}}.$$

The worst aliasing occurs at the outer resolution limit d_{max}^* , where the ‘signal’ due to an atom is proportional to

$$\exp[(-B/4)(d_{\text{max}}^*)^2],$$

while the ‘noise’ due to the closest alias is proportional to

$$\exp\{(-B/4)[(2\sigma - 1)d_{\text{max}}^*]^2\}.$$

Thus the signal-to-noise ratio, or quality factor, Q is

$$\exp[B\sigma(\sigma - 1)(d_{\text{max}}^*)^2].$$

If a certain value of Q is desired (e.g. $Q = 100$ for 1% accuracy), then the equation

$$B = \frac{\log Q}{\sigma(\sigma - 1)(d_{\text{max}}^*)^2}$$

defines B in terms of σ , d_{max}^* and Q .

The overall cost of the structure-factor calculation from N atoms is then

(i) $C_1 \times B^{2/3} \times N$ for density generation,

(ii) $C_2 \times (2\sigma d_{\text{max}}^*)^3 \times \log[(2\sigma d_{\text{max}}^*)^3]$ for Fourier analysis,

where C_1 and C_2 are constant depending on the speed of the computer used. This overall cost may be minimized with respect to σ for given d_{max}^* and Q , determining the optimal B (and hence B_{extra}) in passing by the above relation.

Sayre (1951) did observe that applying an artificial temperature factor in real space would not create series-termination ripples: the resulting atoms would have a smaller effective radius than his hypothetical atoms, so that step (i) would be faster. This optimality of Gaussian smearing is ultimately a consequence of Hardy’s theorem (Section 1.3.2.4.4.3).

1.3.4.4.6. Derivatives for variational phasing techniques

Some methods of phase determination rely on maximizing a certain global criterion $S[\rho]$ involving the electron density, of the form $\int_{\mathbb{R}^3/\mathbb{Z}^3} K[\rho(\mathbf{x})] d^3\mathbf{x}$, under constraint of agreement with the observed structure-factor amplitudes, typically measured by a χ^2 residual C . Several recently proposed methods use for $S[\rho]$ various measures of entropy defined by taking $K(\rho) = -\rho \log(\rho/\mu)$ or $K(\rho) = \log \rho$ (Bricogne, 1982; Britten & Collins, 1982; Narayan & Nityananda, 1982; Bryan *et al.*, 1983; Wilkins *et al.*, 1983; Bricogne, 1984; Navaza, 1985; Livesey & Skilling, 1985). Sayre’s use of the squaring method to improve protein phases (Sayre, 1974) also belongs to this category, and is amenable to the same computational strategies (Sayre, 1980).

These methods differ from the density-modification procedures of Section 1.3.4.4.3.2 in that they seek an optimal solution by moving electron densities (or structure factors) *jointly* rather than pointwise, i.e. by moving along suitably chosen *search directions* $v_i(\mathbf{x})$ [or $V_i(\mathbf{h})$].

For computational purposes, these search directions may be handled either as column vectors of sample values $\{v_i(\mathbf{N}^{-1}\mathbf{m})\}_{\mathbf{m} \in \mathbb{Z}^3/\mathbb{N}\mathbb{Z}^3}$ on a grid in real space, or as column vectors of Fourier coefficients $\{V_i(\mathbf{h})\}_{\mathbf{h} \in \mathbb{Z}^3/\mathbb{N}^T\mathbb{Z}^3}$ in reciprocal space. These column vectors are the coordinates of the same vector $\mathbf{V}_i$ in an abstract vector space $\mathcal{V} \cong L(\mathbb{Z}^3/\mathbb{N}\mathbb{Z}^3)$ of dimension $\mathcal{N} = |\det \mathbf{N}|$ over $\mathbb{R}$, but referred to two different bases which are related by the DFT and its inverse (Section 1.3.2.7.3).

The problem of finding the optimum of S for a given value of C amounts to achieving collinearity between the gradients ∇S and ∇C of S and of C in $\mathcal{V}$, the scalar ratio between them being a Lagrange multiplier. In order to move towards such a solution from a trial position, the dependence of ∇S and ∇C on position in $\mathcal{V}$ must be represented. This involves the $\mathcal{N} \times \mathcal{N}$ Hessian matrices $\mathbf{H}(S)$ and $\mathbf{H}(C)$, whose size precludes their use in the whole of $\mathcal{V}$. Restricting the search to a smaller *search subspace* of dimension n spanned by $\{\mathbf{V}_i\}_{i=1, \dots, n}$ we may build local quadratic models of S and C (Bryan & Skilling, 1980; Burch *et al.*, 1983) with respect to n coordinates $\mathbf{X}$ in that subspace:

$$\begin{aligned} S(\mathbf{X}) &= S(\mathbf{X}_0) + \mathbf{S}_0^T(\mathbf{X} - \mathbf{X}_0) \\ &\quad + \frac{1}{2}(\mathbf{X} - \mathbf{X}_0)^T \mathbf{H}_0(S)(\mathbf{X} - \mathbf{X}_0) \\ C(\mathbf{X}) &= C(\mathbf{X}_0) + \mathbf{C}_0^T(\mathbf{X} - \mathbf{X}_0) \\ &\quad + \frac{1}{2}(\mathbf{X} - \mathbf{X}_0)^T \mathbf{H}_0(C)(\mathbf{X} - \mathbf{X}_0). \end{aligned}$$

The coefficients of these linear models are given by scalar products:

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$$\begin{aligned}[\mathbf{S}_0]_i &= (\mathbf{V}_i, \nabla S) \\ [\mathbf{C}_0]_i &= (\mathbf{V}_i, \nabla C) \\ [\mathbf{H}_0(S)]_{ij} &= [\mathbf{V}_i, \mathbf{H}(S) \mathbf{V}_j] \\ [\mathbf{H}_0(C)]_{ij} &= [\mathbf{V}_i, \mathbf{H}(C) \mathbf{V}_j]\end{aligned}$$

which, by virtue of Parseval's theorem, may be evaluated either in real space or in reciprocal space (Bricogne, 1984). In doing so, special positions and reflections must be taken into account, as in Section 1.3.4.2.2.8. Scalar products involving S are best evaluated by real-space grid summation, because $\mathbf{H}(S)$ is *diagonal* in this representation; those involving C are best calculated by reciprocal-space summation, because $\mathbf{H}(C)$ is at worst 2×2 *block-diagonal* in this representation. Using these Hessian matrices in the wrong space would lead to prohibitively expensive convolutions instead of scalar (or at worst 2×2 matrix) multiplications.

1.3.4.4.7. Derivatives for model refinement

Since the origins of X-ray crystal structure analysis, the calculation of crystallographic Fourier series has been closely associated with the process of refinement. Fourier coefficients *with phases* were obtained for all or part of the measured reflections in the basis of some trial model for all or part of the structure, and Fourier syntheses were then used to complete and improve this initial model. This approach is clearly described in the classic paper by Bragg & West (1929), and was put into practice in the determination of the structures of topaz (Alston & West, 1929) and diopside (Warren & Bragg, 1929). Later, more systematic methods of arriving at a trial model were provided by the Patterson synthesis (Patterson, 1934, 1935*a,b*; Harker, 1936) and by isomorphous replacement (Robertson, 1935, 1936*c*). The role of Fourier syntheses, however, remained essentially unchanged [see Robertson (1937) for a review] until more systematic methods of structure refinement were introduced in the 1940s. A particularly good account of the processes of structure completion and refinement may be found in Chapters 15 and 16 of Stout & Jensen (1968).

It is beyond the scope of this section to review the vast topic of refinement methods: rather, it will give an account of those aspects of their development which have sought improved power by exploiting properties of the Fourier transformation. It is of more than historical interest that some recent advances in the crystallographic refinement of macromolecular structures had been anticipated by Cochran and Cruickshank in the early 1950s.

1.3.4.4.7.1. The method of least squares

Hughes (1941) was the first to use the already well established multivariate least-squares method (Whittaker & Robinson, 1944) to refine initial estimates of the parameters describing a model structure. The method gained general acceptance through the programming efforts of Friedlander *et al.* (1955), Sparks *et al.* (1956), Busing & Levy (1961), and others.

The Fourier relations between ρ and F (Section 1.3.4.2.2.6) are used to derive the 'observational equations' connecting the structure parameters $\{u_p\}_{p=1, \dots, n}$ to the observations $\{|F_{\mathbf{h}}|^{\text{obs}}, (\sigma_{\mathbf{h}}^2)^{\text{obs}}\}_{\mathbf{h} \in \mathcal{H}}$ comprising the amplitudes and their experimental variances for a set $\mathcal{H}$ of unique reflections.

The normal equations giving the corrections $\delta \mathbf{u}$ to the parameters are then

$$(\mathbf{A}^T \mathbf{W} \mathbf{A}) \delta \mathbf{u} = -\mathbf{A}^T \mathbf{W} \Delta,$$

where

$$\begin{aligned}A_{hp} &= \frac{\partial |F_{\mathbf{h}}^{\text{calc}}|}{\partial u_p} \\ \Delta_{\mathbf{h}} &= |F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}} \\ \mathbf{W} &= \text{diag} (W_{\mathbf{h}}) \quad \text{with} \quad W_{\mathbf{h}} = \frac{1}{(\sigma_{\mathbf{h}}^2)^{\text{obs}}}.\end{aligned}$$

To calculate the elements of $\mathbf{A}$, write:

$$F = |F| \exp(i\varphi) = \alpha + i\beta;$$

hence

$$\begin{aligned}\frac{\partial |F|}{\partial u} &= \frac{\partial \alpha}{\partial u} \cos \varphi + \frac{\partial \beta}{\partial u} \sin \varphi \\ &= \Re \left[\frac{\partial F}{\partial u} \overline{\exp(i\varphi)} \right] = \Re \left[\frac{\partial F}{\partial u} \exp(i\varphi) \right].\end{aligned}$$

In the simple case of atoms with real-valued form factors and isotropic thermal agitation in space group $P1$,

$$F_{\mathbf{h}}^{\text{calc}} = \sum_{j \in J} g_j(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_j),$$

where

$$g_j(\mathbf{h}) = Z_j f_j(\mathbf{h}) \exp[-\frac{1}{4} B_j (d_{\mathbf{h}}^*)^2],$$

Z_j being a fractional occupancy.

Positional derivatives with respect to $\mathbf{x}_j$ are given by

$$\begin{aligned}\frac{\partial F_{\mathbf{h}}^{\text{calc}}}{\partial \mathbf{x}_j} &= (2\pi i \mathbf{h}) g_j(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_j) \\ \frac{\partial |F_{\mathbf{h}}^{\text{calc}}|}{\partial \mathbf{x}_j} &= \Re [(-2\pi i \mathbf{h}) g_j(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) \exp(i\varphi_{\mathbf{h}}^{\text{calc}})]\end{aligned}$$

so that the corresponding 3×1 subvector of the right-hand side of the normal equations reads:

$$\begin{aligned}- \sum_{\mathbf{h} \in \mathcal{H}} W_{\mathbf{h}} \frac{\partial |F_{\mathbf{h}}^{\text{calc}}|}{\partial \mathbf{x}_j} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}}) \\ = -\Re \left[\sum_{\mathbf{h} \in \mathcal{H}} g_j(\mathbf{h}) (-2\pi i \mathbf{h}) W_{\mathbf{h}} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}}) \right. \\ \left. \times \exp(i\varphi_{\mathbf{h}}^{\text{calc}}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) \right].\end{aligned}$$

The setting up and solution of the normal equations lends itself well to computer programming and has the advantage of providing a thorough analysis of the accuracy of its results (Cruickshank, 1965*b*, 1970; Rollett, 1970). It is, however, an expensive task, of complexity $\propto n \times |\mathcal{H}|^2$, which is unaffordable for macromolecules.

1.3.4.4.7.2. Booth's differential Fourier syntheses

It was the use of Fourier syntheses in the completion of trial structures which provided the incentive to find methods for computing 2D and 3D syntheses efficiently, and led to the Beevers-Lipson strips. The limited accuracy of the latter caused the estimated positions of atoms (identified as peaks in the maps) to be somewhat in error. Methods were therefore sought to improve the accuracy with which the coordinates of the electron-density maxima could be determined. The naive method of peak-shape analysis from densities recalculated on a $3 \times 3 \times 3$ grid using high-accuracy trigonometric tables entailed 27 summations per atom.

Booth (1946*a*) suggested examining the rapidly varying derivatives of the electron density rather than its slowly varying values. If

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$$\rho(\mathbf{x}) = \sum_{\mathbf{h}} F_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

then the gradient vector $\nabla_{\mathbf{x}}\rho$ of ρ at $\mathbf{x}^0$

$$(\nabla_{\mathbf{x}}\rho)(\mathbf{x}^0) = \sum_{\mathbf{h}} F_{\mathbf{h}}(-2\pi i \mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}^0)$$

can be calculated by means of three Fourier summations from the 3×1 vector of Fourier coefficients

$$(-2\pi i \mathbf{h}) F_{\mathbf{h}}.$$

Similarly, the Hessian matrix of ρ at $\mathbf{x}^0$

$$[(\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T)\rho](\mathbf{x}^0) = \sum_{\mathbf{h}} F_{\mathbf{h}}(-4\pi^2 \mathbf{h}\mathbf{h}^T) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}^0)$$

can be calculated by six Fourier summations from the unique elements of the symmetric matrix of Fourier coefficients:

$$-4\pi^2 \begin{pmatrix} h^2 & hk & hl \\ hk & k^2 & kl \\ hl & kl & l^2 \end{pmatrix} F_{\mathbf{h}}.$$

The scalar maps giving the components of the gradient and Hessian matrix of ρ will be called differential syntheses of 1st order and 2nd order respectively. If $\mathbf{x}^0$ is approximately but not exactly a maximum of ρ , then the Newton–Raphson estimate of the true maximum $\mathbf{x}^*$ is given by:

$$\mathbf{x}^* = \mathbf{x}^0 - [(\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T)\rho](\mathbf{x}^0)^{-1} [\nabla_{\mathbf{x}}\rho(\mathbf{x}^0)].$$

This calculation requires only nine accurate Fourier summations (instead of 27), and this number is further reduced to four if the peak is assumed to be spherically symmetrical.

The resulting positions are affected by series-termination errors in the differential syntheses. Booth (1945c, 1946c) proposed a ‘back-shift correction’ to eliminate them, and extended this treatment to the acentric case (Booth, 1946b). He cautioned against the use of an artificial temperature factor to fight series-termination errors (Brill *et al.*, 1939), as this could be shown to introduce coordinate errors by causing overlap between atoms (Booth, 1946c, 1947a,b).

Cruickshank was able to derive estimates for the standard uncertainties of the atomic coordinates obtained in this way (Cox & Cruickshank, 1948; Cruickshank, 1949a,b) and to show that they agreed with those provided by the least-squares method.

The calculation of differential Fourier syntheses was incorporated into the crystallographic programs of Ahmed & Cruickshank (1953b) and of Sparks *et al.* (1956).

1.3.4.4.7.3. Booth’s method of steepest descents

Having defined the now universally adopted R factors (Booth, 1945b) as criteria of agreement between observed and calculated amplitudes or intensities, Booth proposed that R should be minimized with respect to the set of atomic coordinates $\{\mathbf{x}_j\}_{j \in J}$ by descending along the gradient of R in parameter space (Booth, 1947c,d). This ‘steepest descents’ procedure was compared with Patterson methods by Cochran (1948d).

When calculating the necessary derivatives, Booth (1948a, 1949) used the formulae given above in connection with least squares. This method was implemented by Qurashi (1949) and by Vand (1948, 1951) with parameter-rescaling modifications which made it very close to the least-squares method (Cruickshank, 1950; Qurashi & Vand, 1953; Qurashi, 1953).

1.3.4.4.7.4. Cochran’s Fourier method

Cochran (1948b,c, 1951a) undertook to exploit an algebraic similarity between the right-hand side of the normal equations in the least-squares method on the one hand, and the expression for the

coefficients used in Booth’s differential syntheses on the other hand (see also Booth, 1948a). In doing so he initiated a remarkable sequence of formal and computational developments which are still actively pursued today.

Let $\rho_C(\mathbf{x})$ be the electron-density map corresponding to the current atomic model, with structure factors $|F_{\mathbf{h}}^{\text{calc}}| \exp(i\varphi_{\mathbf{h}}^{\text{calc}})$; and let $\rho_O(\mathbf{x})$ be the map calculated from observed moduli and calculated phases, *i.e.* with coefficients $\{|F_{\mathbf{h}}|^{\text{obs}} \exp(i\varphi_{\mathbf{h}}^{\text{calc}})\}_{\mathbf{h} \in \mathcal{H}}$. If there are enough data for ρ_C to have a resolved peak at each model atomic position $\mathbf{x}_j$, then

$$(\nabla_{\mathbf{x}}\rho_C)(\mathbf{x}_j) = \mathbf{0} \quad \text{for each } j \in J;$$

while if the calculated phases $\varphi_{\mathbf{h}}^{\text{calc}}$ are good enough, ρ_O will also have peaks at each $\mathbf{x}_j$:

$$(\nabla_{\mathbf{x}}\rho_O)(\mathbf{x}_j) = \mathbf{0} \quad \text{for each } j \in J.$$

It follows that

$$\begin{aligned} [\nabla_{\mathbf{x}}(\rho_C - \rho_O)](\mathbf{x}_j) &= \sum_{\mathbf{h}} (-2\pi i \mathbf{h}) [(|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}}) \exp(i\varphi_{\mathbf{h}}^{\text{calc}})] \\ &\quad \times \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) \\ &= \mathbf{0} \quad \text{for each } j \in J, \end{aligned}$$

where the summation is over all reflections in $\mathcal{H}$ or related to $\mathcal{H}$ by space-group and Friedel symmetry (overlooking multiplicity factors!). This relation is less sensitive to series-termination errors than either of the previous two, since the spectrum of ρ_O could have been extrapolated beyond the data in $\mathcal{H}$ by using that of ρ_C [as in van Reijen (1942)] without changing its right-hand side.

Cochran then used the identity

$$\frac{\partial F_{\mathbf{h}}^{\text{calc}}}{\partial \mathbf{x}_j} = (2\pi i \mathbf{h}) g_j(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_j)$$

in the form

$$(-2\pi i \mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) = \frac{1}{g_j(\mathbf{h})} \frac{\partial F_{\mathbf{h}}^{\text{calc}}}{\partial \mathbf{x}_j}$$

to rewrite the previous relation as

$$\begin{aligned} &[\nabla_{\mathbf{x}}(\rho_C - \rho_O)](\mathbf{x}_j) \\ &= \sum_{\mathbf{h}} \frac{1}{g_j(\mathbf{h})} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}}) \mathcal{R}e \left[\frac{\partial F_{\mathbf{h}}^{\text{calc}}}{\partial \mathbf{x}_j} \exp(i\varphi_{\mathbf{h}}^{\text{calc}}) \right] \\ &= \sum_{\mathbf{h}} \frac{1}{g_j(\mathbf{h})} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}}) \frac{\partial |F_{\mathbf{h}}^{\text{calc}}|}{\partial \mathbf{x}_j} \\ &= \mathbf{0} \quad \text{for each } j \in J \end{aligned}$$

(the operation $\mathcal{R}e$ [] on the first line being neutral because of Friedel symmetry). This is equivalent to the vanishing of the 3×1 subvector of the right-hand side of the normal equations associated to a least-squares refinement in which the weights would be

$$W_{\mathbf{h}} = \frac{1}{g_j(\mathbf{h})}.$$

Cochran concluded that, for equal-atom structures with $g_j(\mathbf{h}) = g(\mathbf{h})$ for all j , the positions $\mathbf{x}_j$ obtained by Booth’s method applied to the difference map $\rho_O - \rho_C$ are such that they minimize the residual

$$\frac{1}{2} \sum_{\mathbf{h}} \frac{1}{g(\mathbf{h})} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}})^2$$

with respect to the atomic positions. If it is desired to minimize the residual of the ordinary least-squares method, then the differential

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synthesis method should be applied to the *weighted* difference map

$$\sum_{\mathbf{h}} \frac{W_{\mathbf{h}}}{g(\mathbf{h})} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}^{\text{obs}}|) \exp(i\varphi_{\mathbf{h}}^{\text{calc}}).$$

He went on to show (Cochran, 1951*b*) that the refinement of temperature factors could also be carried out by inspecting appropriate derivatives of the weighted difference map.

This Fourier method was used by Freer *et al.* (1976) in conjunction with a stereochemical regularization procedure to refine protein structures.

1.3.4.4.7.5. Cruickshank's modified Fourier method

Cruickshank consolidated and extended Cochran's derivations in a series of classic papers (Cruickshank, 1949*b*, 1950, 1952, 1956). He was able to show that all the coefficients involved in the right-hand side and normal matrix of the least-squares method could be calculated by means of suitable differential Fourier syntheses *even when the atoms overlap*. This remarkable achievement lay essentially dormant until its independent rediscovery by Agarwal in 1978 (Section 1.3.4.4.7.6).

To ensure rigorous equivalence between the summations over $\mathbf{h} \in \mathcal{H}$ (in the expressions of least-squares right-hand side and normal matrix elements) and genuine Fourier summations, multiplicity-corrected weights were introduced by:

$$w_{\mathbf{h}} = \frac{1}{|G_{\mathbf{h}}|} W_{\mathbf{h}} \quad \text{if } \mathbf{h} \in G\mathbf{h} \quad \text{with } \mathbf{h} \in \mathcal{H},$$

$$w_{\mathbf{h}} = 0 \quad \text{otherwise,}$$

where $G\mathbf{h}$ denotes the orbit of $\mathbf{h}$ and $G_{\mathbf{h}}$ its isotropy subgroup (Section 1.3.4.2.2.5). Similarly, derivatives with respect to parameters of symmetry-unique atoms were expressed, *via* the chain rule, as sums over the orbits of these atoms.

Let $p = 1, \dots, n$ be the label of a parameter u_p belonging to atoms with label j . Then Cruickshank showed that the p th element of the right-hand side of the normal equations can be obtained as $D_{p,j}(\mathbf{x}_j)$, where $D_{p,j}$ is a differential synthesis of the form

$$D_{p,j}(\mathbf{x}) = \sum_{\mathbf{h}} P_p(\mathbf{h}) g_j(\mathbf{h}) w_{\mathbf{h}} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}^{\text{obs}}|) \times \exp(i\varphi_{\mathbf{h}}^{\text{calc}}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

with $P_p(\mathbf{h})$ a polynomial in (h, k, l) depending on the type of parameter p . The correspondence between parameter type and the associated polynomial extends Booth's original range of differential syntheses, and is recapitulated in the following table.

Parameter type	$P(h, k, l)$
x coordinate	$-2\pi i h$
y coordinate	$-2\pi i k$
z coordinate	$-2\pi i l$
B isotropic	$-\frac{1}{4}(d_{\mathbf{h}}^*)^2$
B^{11} anisotropic	$-h^2$
B^{12} anisotropic	$-hk$
B^{13} anisotropic	$-hl$
B^{22} anisotropic	$-k^2$
B^{23} anisotropic	$-kl$
B^{33} anisotropic	$-l^2$

Unlike Cochran's original heuristic argument, this result does not depend on the atoms being resolved.

Cruickshank (1952) also considered the elements of the normal matrix, of the form

$$\sum_{\mathbf{h}} w_{\mathbf{h}} \frac{\partial |F_{\mathbf{h}}^{\text{calc}}|}{\partial u_p} \frac{\partial |F_{\mathbf{h}}^{\text{calc}}|}{\partial u_q}$$

associated with positional parameters. The 3×3 block for parameters $\mathbf{x}_j$ and $\mathbf{x}_k$ may be written

$$\sum_{\mathbf{h}} w_{\mathbf{h}} (\mathbf{h}\mathbf{h}^T) \Re [(-2\pi i) g_j(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) \exp(i\varphi_{\mathbf{h}}^{\text{calc}})] \times \Re [(-2\pi i) g_k(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_k) \exp(i\varphi_{\mathbf{h}}^{\text{calc}})]$$

which, using the identity

$$\Re(z_1) \Re(z_2) = \frac{1}{2} [\Re(z_1 z_2) + \Re(z_1 \bar{z}_2)],$$

becomes

$$2\pi^2 \sum_{\mathbf{h}} w_{\mathbf{h}} (\mathbf{h}\mathbf{h}^T) g_j(\mathbf{h}) g_k(\mathbf{h}) \times \{ \exp[-2\pi i \mathbf{h} \cdot (\mathbf{x}_j - \mathbf{x}_k)] - \exp(2i\varphi_{\mathbf{h}}^{\text{calc}}) \exp[-2\pi i \mathbf{h} \cdot (\mathbf{x}_j + \mathbf{x}_k)] \}$$

(Friedel's symmetry makes $\Re$ redundant on the last line). Cruickshank argued that the first term would give a good approximation to the diagonal blocks of the normal matrix and to those off-diagonal blocks for which $\mathbf{x}_j$ and $\mathbf{x}_k$ are close. On this basis he was able to justify the '*n*-shift rule' of Shoemaker *et al.* (1950). Cruickshank gave this derivation in a general space group, but using a very terse notation which somewhat obscures it. Using the symmetrized trigonometric structure-factor kernel Ξ^- of Section 1.3.4.2.2.9 and its multiplication formula, the above expression is seen to involve the values of a Fourier synthesis at points of the form $\mathbf{x}_j \pm S_g(\mathbf{x}_k)$.

Cruickshank (1956) showed that this analysis could also be applied to the refinement of temperature factors.

These two results made it possible to obtain all coefficients involved in the normal equations by looking up the values of certain differential Fourier syntheses at $\mathbf{x}_j$ or at $\mathbf{x}_j \pm S_g(\mathbf{x}_k)$. At the time this did not confer any superiority over the standard form of the least-squares procedure, because the accurate computation of Fourier syntheses was an expensive operation. The modified Fourier method was used by Truter (1954) and by Ahmed & Cruickshank (1953*a*), and was incorporated into the program system described by Cruickshank *et al.* (1961). A more recent comparison with the least-squares method was made by Dietrich (1972).

There persisted, however, some confusion about the nature of the relationship between Fourier and least-squares methods, caused by the extra factors $g_j(\mathbf{h})$ which make it necessary to compute a differential synthesis for each type of atom. This led Cruickshank to conclude that 'in spite of their remarkable similarities the least-squares and modified-Fourier methods are fundamentally distinct'.

1.3.4.4.7.6. Agarwal's FFT implementation of the Fourier method

Agarwal (1978) rederived and completed Cruickshank's results at a time when the availability of the FFT algorithm made the Fourier method of calculating the coefficients of the normal equations much more economical than the standard method, especially for macromolecules.

As obtained by Cruickshank, the modified Fourier method required a full 3D Fourier synthesis

– for each type of parameter, since this determines [*via* the polynomial $P_p(\mathbf{h})$] the type of differential synthesis to be computed;

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– for each type of atom $j \in J$, since the coefficients of the differential synthesis must be multiplied by $g_j(\mathbf{h})$.

Agarwal disposed of the latter dependence by pointing out that the multiplication involved is equivalent to a real-space *convolution* between the differential synthesis and $\sigma_j(\mathbf{x})$, the standard electron density ρ_j for atom type j (Section 1.3.4.2.1.2) smeared by the isotropic thermal agitation of that atom. Since σ_j is *localized*, this convolution involves only a small number of grid points. The requirement of a distinct differential synthesis for each parameter type, however, continued to hold, and created some difficulties at the FFT level because the symmetries of differential syntheses are more complex than ordinary space-group symmetries. Jack & Levitt (1978) sought to avoid the calculation of difference syntheses by using instead finite differences calculated from ordinary Fourier or difference Fourier maps.

In spite of its complication, this return to the Fourier implementation of the least-squares method led to spectacular increases in speed (Isaacs & Agarwal, 1978; Agarwal, 1980; Baker & Dodson, 1980) and quickly gained general acceptance (Dodson, 1981; Isaacs, 1982a,b, 1984).

1.3.4.4.7.7. Lifchitz's reformulation

Lifchitz [see Agarwal *et al.* (1981), Agarwal (1981)] proposed that the idea of treating certain multipliers in Cruickshank's modified differential Fourier syntheses by means of a convolution in real space should be applied not only to $g_j(\mathbf{h})$, but also to the polynomials $P_p(\mathbf{h})$ which determine the type of differential synthesis being calculated. This leads to convoluting $\partial\sigma_j/\partial u_p$ with the *same* ordinary weighted difference Fourier synthesis, rather than σ_j with the differential synthesis of type p . In this way, a *single* Fourier synthesis, with *ordinary* (scalar) symmetry properties, needs be computed; the parameter type and atom type both intervene through the function $\partial\sigma_j/\partial u_p$ with which it is convoluted. This approach has been used as the basis of an efficient general-purpose least-squares refinement program for macromolecular structures (Tronrud *et al.*, 1987).

This rearrangement amounts to using the fact (Section 1.3.2.3.9.7) that convolution commutes with differentiation. Let

$$D(\mathbf{x}) = \sum_{\mathbf{h}} w_{\mathbf{h}} (|F_{\mathbf{h}}^{\text{calc}}| - |F_{\mathbf{h}}|^{\text{obs}}) \exp(i\varphi_{\mathbf{h}}^{\text{calc}}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

be the inverse-variance weighted difference map, and let us assume that parameter u_p belongs to atom j . Then the Agarwal form for the p th component of the right-hand side of the normal equations is

$$\left(\frac{\partial D}{\partial u_p} * \sigma_j \right) (x_j),$$

while the Lifchitz form is

$$\left(D * \frac{\partial \sigma_j}{\partial u_p} \right) (x_j).$$

1.3.4.4.7.8. A simplified derivation

A very simple derivation of the previous results will now be given, which suggests the possibility of many generalizations.

The weighted difference map $D(\mathbf{x})$ has coefficients $D_{\mathbf{h}}$ which are the gradients of the global residual with respect to each $F_{\mathbf{h}}^{\text{calc}}$:

$$D_{\mathbf{h}} = \frac{\partial R}{\partial A_{\mathbf{h}}^{\text{calc}}} + i \frac{\partial R}{\partial B_{\mathbf{h}}^{\text{calc}}}.$$

By the chain rule, a variation of each $F_{\mathbf{h}}^{\text{calc}}$ by $\delta F_{\mathbf{h}}^{\text{calc}}$ will result in a variation of R by δR with

$$\delta R = \sum_{\mathbf{h}} \left[\frac{\partial R}{\partial A_{\mathbf{h}}^{\text{calc}}} \delta A_{\mathbf{h}}^{\text{calc}} + \frac{\partial R}{\partial B_{\mathbf{h}}^{\text{calc}}} \delta B_{\mathbf{h}}^{\text{calc}} \right] = \mathcal{R}e \sum_{\mathbf{h}} [\overline{D_{\mathbf{h}}} \delta F_{\mathbf{h}}^{\text{calc}}].$$

The $\mathcal{R}e$ operation is superfluous because of Friedel symmetry, so that δR may be simply written in terms of the Hermitian scalar product in $\ell^2(\mathbb{Z}^3)$:

$$\delta R = (\mathbf{D}, \delta \mathbf{F}^{\text{calc}}).$$

If ρ^{calc} is the transform of $\delta \mathbf{F}^{\text{calc}}$, we have also by Parseval's theorem

$$\delta R = (D, \delta \rho^{\text{calc}}).$$

We may therefore write

$$D(\mathbf{x}) = \frac{\partial R}{\partial \rho^{\text{calc}}(\mathbf{x})},$$

which states that $D(\mathbf{x})$ is the functional derivative of R with respect to ρ^{calc} .

The right-hand side of the normal equations has $\partial R/\partial u_p$ for its p th element, and this may be written

$$\frac{\partial R}{\partial u_p} = \int_{\mathbb{R}^3/\mathbb{Z}^3} \frac{\partial R}{\partial \rho^{\text{calc}}(\mathbf{x})} \frac{\partial \rho^{\text{calc}}(\mathbf{x})}{\partial u_p} d^2\mathbf{x} = \left(D, \frac{\partial \rho^{\text{calc}}}{\partial u_p} \right).$$

If u_p belongs to atom j , then

$$\frac{\partial \rho^{\text{calc}}}{\partial u_p} = \frac{\partial(\tau_{\mathbf{x}_j} \sigma_j)}{\partial u_p} = \tau_{\mathbf{x}_j} \left(\frac{\partial \sigma_j}{\partial u_p} \right);$$

hence

$$\frac{\partial R}{\partial u_p} = \left(D, \tau_{\mathbf{x}_j} \left(\frac{\partial \sigma_j}{\partial u_p} \right) \right).$$

By the identity of Section 1.3.2.4.3.5, this is identical to Lifchitz's expression $(D * \partial\sigma_j/\partial u_p)(\mathbf{x}_j)$. The present derivation in terms of scalar products [see Brunger (1989) for another presentation of it] is conceptually simpler, since it invokes only the chain rule [other uses of which have been reviewed by Lunin (1985)] and Parseval's theorem; economy of computation is obviously related to the good localization of $\partial \rho^{\text{calc}}/\partial u_p$ compared to $\partial F^{\text{calc}}/\partial u_p$. Convolutions, whose meaning is less clear, are no longer involved; they were a legacy of having first gone over to reciprocal space *via* differential syntheses in the 1940s.

Cast in this form, the calculation of derivatives by FFT methods appears as a particular instance of the procedure described in connection with variational techniques (Section 1.3.4.4.6) to calculate the coefficients of local quadratic models in a search subspace; this is far from surprising since varying the electron density through a variation of the parameters of an atomic model is a particular case of the 'free' variations considered by the variational approach. The latter procedure would accommodate in a very natural fashion the joint consideration of an energetic (Jack & Levitt, 1978; Brunger *et al.*, 1987; Brunger, 1988; Brunger *et al.*, 1989; Kuriyan *et al.*, 1989) or stereochemical (Konnert, 1976; Sussman *et al.*, 1977; Konnert & Hendrickson, 1980; Hendrickson & Konnert, 1980; Tronrud *et al.*, 1987) restraint function (which would play the role of S) and of the crystallographic residual (which would be C). It would even have over the latter the superiority of affording a genuine *second-order* approximation, albeit only in a subspace, hence the ability of detecting negative curvature and the resulting bifurcation behaviour (Bricogne, 1984). Current methods are unable to do this because they use only *first-order* models, and this is known to degrade severely the overall efficiency of the refinement process.

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1.3.4.4.7.9. Discussion of macromolecular refinement techniques

The impossibility of carrying out a full-matrix least-squares refinement of a macromolecular crystal structure, caused by excessive computational cost and by the paucity of observations, led Diamond (1971) to propose a real-space refinement method in which stereochemical knowledge was used to keep the number of free parameters to a minimum. Refinement took place by a least-squares fit between the ‘observed’ electron-density map and a model density consisting of Gaussian atoms. This procedure, coupled to iterative recalculation of the phases, led to the first highly refined protein structures obtained without using full-matrix least squares (Huber *et al.*, 1974; Bode & Schwager, 1975; Deisenhofer & Steigemann, 1975; Takano, 1977*a,b*).

Real-space refinement takes advantage of the localization of atoms (each parameter interacts only with the density near the atom to which it belongs) and gives the most immediate description of stereochemical constraints. A disadvantage is that fitting the ‘observed’ electron density amounts to treating the phases of the structure factors as observed quantities, and to ignoring the experimental error estimates on their moduli. The method is also much more vulnerable to series-termination errors and accidentally missing data than the least-squares method. These objections led to the progressive disuse of Diamond’s method, and to a switch towards reciprocal-space least squares following Agarwal’s work.

The connection established above between the Cruickshank–Agarwal modified Fourier method and the simple use of the chain rule affords a partial refutation to both the premises of Diamond’s method and to the objections made against it:

(i) it shows that refinement *can* be performed through localized computations in real space *without* having to treat the phases as observed quantities;

(ii) at the same time, it shows that measurement errors on the moduli *can* be fully utilized in real space, *via* the Fourier synthesis of the functional derivative $\partial R / \partial \rho^{\text{calc}}(\mathbf{x})$ or by means of the coefficients of a quadratic model of R in a search subspace.

1.3.4.4.7.10. Sampling considerations

The calculation of the inner products $(D, \partial \rho^{\text{calc}} / \partial u_p)$ from a sampled gradient map D requires even more caution than that of structure factors *via* electron-density maps described in Section 1.3.4.4.5, because the functions $\partial \sigma_j / \partial u_p$ have transforms which extend even further in reciprocal space than the σ_j themselves. Analytically, if the σ_j are Gaussians, the $\partial \sigma_j / \partial u_p$ are finite sums of multivariate Hermite functions (Section 1.3.2.4.4.2) and hence the same is true of their transforms. The difference map D must therefore be finely sampled and the relation between error and sampling rate may be investigated as in Section 1.3.4.4.5. An examination of the sampling rates commonly used (*e.g.* one third of the resolution) shows that they are insufficient. Tronrud *et al.* (1987) propose to relax this requirement by applying an artificial temperature factor to σ_j (*cf.* Section 1.3.4.4.5) and the negative of that temperature factor to D , a procedure of questionable validity because the latter ‘sharpening’ operation is ill defined [the function $\exp(-\|\mathbf{x}\|^2)$ does not define a tempered distribution, so the associativity properties of convolution may be lost]. A more robust procedure would be to compute the scalar product by means of a more sophisticated numerical quadrature formula than a mere grid sum.

1.3.4.4.8. Miscellaneous correlation functions

Certain correlation functions can be useful to detect the presence of multiple copies of the same molecule (known or unknown) in the asymmetric unit of a crystal of unknown structure.

Suppose that a crystal contains one or several copies of a molecule $\mathcal{M}$ in its asymmetric unit. If $\mu(\mathbf{x})$ is the electron density of that molecule in some reference position and orientation, then

$$\rho^0 = \sum_{j \in J} \left[\sum_{g \in G} S_g^{\#} (T_j^{\#} \mu) \right],$$

where $T_j : \mathbf{x} \mapsto \mathbf{C}_j \mathbf{x} + \mathbf{d}_j$ describes the placement of the j th copy of the molecule with respect to the reference copy. It is assumed that each such copy is in a general position, so that there is no isotropy subgroup.

The methods of Section 1.3.4.2.2.9 (with ρ_j replaced by $C_j^{\#} \mu$, and $\mathbf{x}_j$ by $\mathbf{d}_j$) lead to the following expression for the auto-correlation of ρ^0 :

$$\check{\rho}^0 * \rho^0 = \sum_{j_1} \sum_{j_2} \sum_{g_1} \sum_{g_2} \tau_{S_{g_2}(\mathbf{d}_{j_2}) - S_{g_1}(\mathbf{d}_{j_1})} \times [(R_{g_1}^{\#} C_{j_1}^{\#} \check{\mu}) * (R_{g_2}^{\#} C_{j_2}^{\#} \mu)].$$

If μ is unknown, consider the subfamily σ of terms with $j_1 = j_2 = j$ and $g_1 = g_2 = g$:

$$\sigma = \sum_j \sum_g R_g^{\#} C_j^{\#} (\check{\mu} * \mu).$$

The scalar product $(\sigma, R^{\#} \sigma)$ in which R is a variable rotation will have a peak whenever

$$R = (R_{g_1} C_{j_1})^{-1} (R_{g_2} C_{j_2})$$

since two copies of the ‘self-Patterson’ $\check{\mu} * \mu$ of the molecule will be brought into coincidence. If the interference from terms in the Patterson $\pi = r * \check{\rho}^0 * \rho^0$ other than those present in σ is not too serious, the ‘self-rotation function’ $(\pi, R^{\#} \pi)$ (Rossmann & Blow, 1962; Crowther, 1972) will show the same peaks, from which the rotations $\{C_j\}_{j \in J}$ may be determined, either individually or jointly if for instance they form a group.

If μ is known, then its self-Patterson $\check{\mu} * \mu$ may be calculated, and the C_j may be found by examining the ‘cross-rotation function’ $[\pi, R^{\#} (\check{\mu} * \mu)]$ which will have peaks at $R = R_g C_j, g \in G, j \in J$. Once the C_j are known, then the various copies $C_j^{\#} \mu$ of $\mathcal{M}$ may be Fourier-analysed into structure factors:

$$M_j(\mathbf{h}) = \mathcal{F}[C_j^{\#} \mu](\mathbf{h}).$$

The cross terms with $j_1 \neq j_2, g_1 \neq g_2$ in $\check{\rho}^0 * \rho^0$ then contain ‘motifs’

$$(R_{g_1}^{\#} C_{j_1}^{\#} \check{\mu}) * (R_{g_2}^{\#} C_{j_2}^{\#} \mu),$$

with Fourier coefficients

$$\overline{M_{j_1}(\mathbf{R}_{g_1}^T \mathbf{h})} \times M_{j_2}(\mathbf{R}_{g_2}^T \mathbf{h}),$$

translated by $S_{g_2}(\mathbf{d}_{j_2}) - S_{g_1}(\mathbf{d}_{j_1})$. Therefore the ‘translation functions’ (Crowther & Blow, 1967)

$$\mathcal{T}_{j_1 g_1, j_2 g_2}(\mathbf{s}) = \sum_{\mathbf{h}} |F_{\mathbf{h}}|^2 \overline{M_{j_1}(\mathbf{R}_{g_1}^T \mathbf{h})} \times M_{j_2}(\mathbf{R}_{g_2}^T \mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{s})$$

will have peaks at $\mathbf{s} = S_{g_2}(\mathbf{d}_{j_2}) - S_{g_1}(\mathbf{d}_{j_1})$ corresponding to the detection of these motifs.

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1.3.4.5. Related applications

1.3.4.5.1. Helical diffraction

The theory of diffraction by helical structures (Cochran *et al.*, 1952; Klug *et al.*, 1958) has played an important part in the study of polypeptides, of nucleic acids and of tobacco mosaic virus.

1.3.4.5.1.1. Circular harmonic expansions in polar coordinates

Let $f = f(x, y)$ be a reasonably regular function in two-dimensional real space. Going over to polar coordinates

$$x = r \cos \varphi \quad y = r \sin \varphi$$

and writing, by slight misuse of notation, $f(r, \varphi)$ for $f(r \cos \varphi, r \sin \varphi)$ we may use the periodicity of f with respect to φ to expand it as a Fourier series (Byerly, 1893):

$$f(r, \varphi) = \sum_{n \in \mathbb{Z}} f_n(r) \exp(in\varphi)$$

with

$$f_n(r) = \frac{1}{2\pi} \int_0^{2\pi} f(r, \varphi) \exp(-in\varphi) d\varphi.$$

Similarly, in reciprocal space, if $F = F(\xi, \eta)$ and if

$$\xi = R \cos \psi \quad \eta = R \sin \psi$$

then

$$F(R, \psi) = \sum_{n \in \mathbb{Z}} i^n F_n(R) \exp(in\psi)$$

with

$$F_n(R) = \frac{1}{2\pi i^n} \int_0^{2\pi} F(R, \psi) \exp(-in\psi) d\psi,$$

where the phase factor i^n has been introduced for convenience in the forthcoming step.

1.3.4.5.1.2. The Fourier transform in polar coordinates

The Fourier transform relation between f and F may then be written in terms of f_n 's and F_n 's. Observing that $\xi x + \eta y = Rr \cos(\varphi - \psi)$, and that (Watson, 1944)

$$\int_0^{2\pi} \exp(iX \cos \theta + in\theta) d\theta = 2\pi i^n J_n(X),$$

we obtain:

$$\begin{aligned} F(R, \psi) &= \int_0^\infty \int_0^{2\pi} \left[\sum_{n \in \mathbb{Z}} f_n(r) \exp(in\varphi) \right] \\ &\quad \times \exp[2\pi i R r \cos(\varphi - \psi)] r dr d\varphi \\ &= \sum_{n \in \mathbb{Z}} i^n \left[\int_0^\infty f_n(r) J_n(2\pi R r) 2\pi r dr \right] \exp(in\psi); \end{aligned}$$

hence, by the uniqueness of the Fourier expansion of F :

$$F_n(R) = \int_0^\infty f_n(r) J_n(2\pi R r) 2\pi r dr.$$

The inverse Fourier relationship leads to

$$f_n(r) = \int_0^\infty F_n(R) J_n(2\pi R r) 2\pi R dR.$$

The integral transform involved in the previous two equations is

called the *Hankel transform* (see *e.g.* Titchmarsh, 1922; Sneddon, 1972) of order n .

1.3.4.5.1.3. The transform of an axially periodic fibre

Let ρ be the electron-density distribution in a fibre, which is assumed to have translational periodicity with period 1 along z , and to have compact support with respect to the (x, y) coordinates. Thus ρ may be written

$$\rho = \left[\delta_x \otimes \delta_y \otimes \left(\sum_{k \in \mathbb{Z}} \delta_{(k)} \right) \right]_z * \rho^0,$$

where $\rho^0 = \rho^0(x, y, z)$ is the motif.

By the tensor product property, the inverse Fourier transform $F = \mathcal{F}_{xyz}[\rho]$ may be written

$$F = \left[1_\xi \otimes 1_\eta \otimes \left(\sum_{l \in \mathbb{Z}} \delta_{(l)} \right) \right]_\zeta \times \tilde{\mathcal{F}}[\rho^0]$$

and hence consists of 'layers' labelled by l :

$$F = \sum_{l \in \mathbb{Z}} F(\xi, \eta, l) (\delta_{(l)})_\zeta$$

with

$$F(\xi, \eta, l) = \int_0^1 \tilde{\mathcal{F}}_{xy}[\rho^0](\xi, \eta, z) \exp(2\pi i l z) dz.$$

Changing to polar coordinates in the (x, y) and (ξ, η) planes decomposes the calculation of F from ρ into the following steps:

$$g_{nl}(r) = \frac{1}{2\pi} \int_0^{2\pi} \int_0^1 \rho(r, \varphi, z) \exp[i(-n\varphi + 2\pi l z)] d\varphi dz$$

$$G_{nl}(R) = \int_0^\infty g_{nl}(r) J_n(2\pi R r) 2\pi r dr$$

$$F(R, \psi, l) = \sum_{n \in \mathbb{Z}} i^n G_{nl}(R) \exp(in\psi)$$

and the calculation of ρ from F into:

$$G_{nl}(R) = \frac{1}{2\pi i^n} \int_0^{2\pi} F(R, \psi, l) \exp(-in\psi) d\psi$$

$$g_{nl}(r) = \int_0^\infty G_{nl}(R) J_n(2\pi R r) 2\pi R dR$$

$$\rho(r, \varphi, z) = \sum_{n \in \mathbb{Z}} \sum_{l \in \mathbb{Z}} g_{nl}(r) \exp[i(n\varphi - 2\pi l z)].$$

These formulae are seen to involve a 2D Fourier series with respect to the two periodic coordinates φ and z , and Hankel transforms along the radial coordinates. The two periodicities in φ and z are independent, so that all combinations of indices (n, l) occur in the Fourier summations.

1.3.4.5.1.4. Helical symmetry and associated selection rules

Helical symmetry involves a 'clutching' between the two (hitherto independent) periodicities in φ (period 2π) and z (period 1) which causes a subdivision of the period lattice and hence a decimation (governed by 'selection rules') of the Fourier coefficients.

Let $\mathbf{i}$ and $\mathbf{j}$ be the basis vectors along $\varphi/2\pi$ and z . The integer lattice with basis $(\mathbf{i}, \mathbf{j})$ is a period lattice for the (φ, z) dependence of the electron density ρ of an axially periodic fibre considered in Section 1.3.4.5.1.3:

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$$\rho(r, \varphi + 2\pi k_1, z + k_2) = \rho(r, \varphi, z).$$

Suppose the fibre now has *helical* symmetry, with u copies of the same molecule in t turns, where $\text{g.c.d.}(u, t) = 1$. Using the Euclidean algorithm, write $u = \lambda t + \mu$ with λ and μ positive integers and $\mu < t$. The period lattice for the (φ, z) dependence of ρ may be defined in terms of the new basis vectors:

I, joining subunit 0 to subunit l in the same turn;

J, joining subunit 0 to subunit λ after wrapping around.

In terms of the original basis

$$\mathbf{I} = \frac{t}{u} \mathbf{i} + \frac{1}{u} \mathbf{j}, \quad \mathbf{J} = \frac{-\mu}{u} \mathbf{i} + \frac{\lambda}{u} \mathbf{j}.$$

If α and β are coordinates along **I** and **J**, respectively,

$$\begin{pmatrix} \varphi/2\pi \\ z \end{pmatrix} = \frac{1}{u} \begin{pmatrix} t & -\mu \\ 1 & \lambda \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

or equivalently

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \lambda & \mu \\ -1 & t \end{pmatrix} \begin{pmatrix} \varphi/2\pi \\ z \end{pmatrix}.$$

By Fourier transformation,

$$\begin{aligned} \left(\frac{\varphi}{2\pi}, z\right) &\Leftrightarrow (-n, l) \\ (\alpha, \beta) &\Leftrightarrow (m, p) \end{aligned}$$

with the transformations between indices given by the contragredients of those between coordinates, *i.e.*

$$\begin{pmatrix} n \\ l \end{pmatrix} = \begin{pmatrix} -\lambda & 1 \\ -\mu & t \end{pmatrix} \begin{pmatrix} m \\ p \end{pmatrix}$$

and

$$\begin{pmatrix} m \\ p \end{pmatrix} = \frac{1}{u} \begin{pmatrix} -t & 1 \\ \mu & \lambda \end{pmatrix} \begin{pmatrix} n \\ l \end{pmatrix}.$$

It follows that

$$l = tn + um,$$

or alternatively that

$$\mu n = up - \lambda l,$$

which are two equivalent expressions of the *selection rules* describing the decimation of the transform. These rules imply that only certain orders n contribute to a given layer l .

The 2D Fourier analysis may now be performed by analysing a *single* subunit referred to coordinates α and β to obtain

$$h_{m,p}(r) = \int_0^1 \int_0^1 \rho(r, \alpha, \beta) \exp[2\pi i(m\alpha + p\beta)] d\alpha d\beta$$

and then reindexing to get only the allowed g_{nl} 's by

$$g_{nl}(r) = uh_{-\lambda m+p, \mu m+tp}(r).$$

This is u times faster than analysing u subunits with respect to the (φ, z) coordinates.

1.3.4.5.2. Application to probability theory and direct methods

The Fourier transformation plays a central role in the branch of probability theory concerned with the limiting behaviour of sums of large numbers of independent and identically distributed random variables or random vectors. This privileged role is a consequence of the convolution theorem and of the 'moment-generating'

properties which follow from the exchange between differentiation and multiplication by monomials. When the limit theorems are applied to the calculation of joint probability distributions of structure factors, which are themselves closely related to the Fourier transformation, a remarkable phenomenon occurs, which leads to the saddlepoint approximation and to the maximum-entropy method.

1.3.4.5.2.1. Analytical methods of probability theory

The material in this section is not intended as an introduction to probability theory [for which the reader is referred to Cramér (1946), Petrov (1975) or Bhattacharya & Rao (1976)], but only as an illustration of the role played by the Fourier transformation in certain specific areas which are used in formulating and implementing direct methods of phase determination.

(a) Convolution of probability densities

The addition of independent random variables or vectors leads to the convolution of their probability distributions: if $\mathbf{X}_1$ and $\mathbf{X}_2$ are two n -dimensional random vectors independently distributed with probability densities P_1 and P_2 , respectively, then their sum $\mathbf{X} = \mathbf{X}_1 + \mathbf{X}_2$ has probability density $\mathcal{P}$ given by

$$\begin{aligned} \mathcal{P}(\mathbf{X}) &= \int_{\mathbf{R}^n} P_1(\mathbf{X}_1) P_2(\mathbf{X} - \mathbf{X}_1) d^n \mathbf{X}_1 \\ &= \int_{\mathbf{R}^n} P_1(\mathbf{X} - \mathbf{X}_2) P_2(\mathbf{X}_2) d^n \mathbf{X}_2 \end{aligned}$$

i.e.

$$\mathcal{P} = P_1 * P_2.$$

This result can be extended to the case where P_1 and P_2 are singular measures (distributions of order zero, Section 1.3.2.3.4) and do not have a density with respect to the Lebesgue measure in $\mathbb{R}^n$.

(b) Characteristic functions

This convolution can be turned into a simple multiplication by considering the Fourier transforms (called the *characteristic functions*) of P_1 , P_2 and $\mathcal{P}$, defined with a slightly different normalization in that there is no factor of 2π in the exponent (see Section 1.3.2.4.5), *e.g.*

$$C(\mathbf{t}) = \int_{\mathbf{R}^n} P(\mathbf{X}) \exp(i\mathbf{t} \cdot \mathbf{X}) d^n \mathbf{X}.$$

Then by the convolution theorem

$$\mathcal{C}(\mathbf{t}) = C_1(\mathbf{t}) \times C_2(\mathbf{t}),$$

so that $\mathcal{P}(\mathbf{X})$ may be evaluated by Fourier inversion of its characteristic function as

$$\mathcal{P}(\mathbf{X}) = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} C_1(\mathbf{t}) C_2(\mathbf{t}) \exp(-i\mathbf{t} \cdot \mathbf{X}) d^n \mathbf{t}$$

(see Section 1.3.2.4.5 for the normalization factors).

It follows from the differentiation theorem that the partial derivatives of the characteristic function $C(\mathbf{t})$ at $\mathbf{t} = \mathbf{0}$ are related to the moments of a distribution P by the identities

$$\begin{aligned} \mu_{r_1 r_2 \dots r_n} &\equiv \int_D P(\mathbf{X}) X_1^{r_1} X_2^{r_2} \dots X_n^{r_n} d^n \mathbf{X} \\ &= i^{-(r_1 + \dots + r_n)} \frac{\partial^{r_1 + \dots + r_n} C}{\partial t_1^{r_1} \dots \partial t_n^{r_n}} \Big|_{\mathbf{t}=\mathbf{0}} \end{aligned}$$

for any n -tuple of non-negative integers $(r_1, r_2, \dots, r_n)$.

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(c) Moment-generating functions

The above relation can be freed from powers of i by defining (at least formally) the *moment-generating function*:

$$M(\mathbf{t}) = \int_{\mathbb{R}^n} P(\mathbf{X}) \exp(\mathbf{t} \cdot \mathbf{X}) d^n \mathbf{X}$$

which is related to $C(\mathbf{t})$ by $C(\mathbf{t}) = M(i\mathbf{t})$ so that the inversion formula reads

$$\mathcal{P}(\mathbf{X}) = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} M_1(i\mathbf{t}) M_2(i\mathbf{t}) \exp(-i\mathbf{t} \cdot \mathbf{X}) d^n \mathbf{t}.$$

The moment-generating function is well defined, in particular, for any probability distribution with compact support, in which case it may be continued analytically from a function over $\mathbb{R}^n$ into an entire function of n complex variables by virtue of the Paley–Wiener theorem (Section 1.3.2.4.2.10). Its moment-generating properties are summed up in the following relations:

$$\mu_{r_1 r_2 \dots r_n} = \left. \frac{\partial^{r_1 + \dots + r_n} M}{\partial t_1^{r_1} \dots \partial t_n^{r_n}} \right|_{\mathbf{t}=\mathbf{0}}.$$

(d) Cumulant-generating functions

The multiplication of moment-generating functions may be further simplified into the addition of their logarithms:

$$\log \mathcal{M} = \log M_1 + \log M_2,$$

or equivalently of the coefficients of their Taylor series at $\mathbf{t} = \mathbf{0}$, viz:

$$\kappa_{r_1 r_2 \dots r_n} = \left. \frac{\partial^{r_1 + \dots + r_n} (\log M)}{\partial t_1^{r_1} \dots \partial t_n^{r_n}} \right|_{\mathbf{t}=\mathbf{0}}.$$

These coefficients are called *cumulants*, since they add when the independent random vectors to which they belong are added, and $\log M$ is called the *cumulant-generating function*. The inversion formula for $\mathcal{P}$ then reads

$$\mathcal{P}(\mathbf{X}) = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \exp[\log M_1(i\mathbf{t}) + \log M_2(i\mathbf{t}) - i\mathbf{t} \cdot \mathbf{X}] d^n \mathbf{t}.$$

(e) Asymptotic expansions and limit theorems

Consider an n -dimensional random vector $\mathbf{X}$ of the form

$$\mathbf{X} = \mathbf{X}_1 + \mathbf{X}_2 + \dots + \mathbf{X}_N,$$

where the N summands are independent n -dimensional random vectors identically distributed with probability density P . Then the distribution $\mathcal{P}$ of $\mathbf{X}$ may be written in closed form as a Fourier transform:

$$\begin{aligned} \mathcal{P}(\mathbf{X}) &= \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} M^N(i\mathbf{t}) \exp(-i\mathbf{t} \cdot \mathbf{X}) d^n \mathbf{t} \\ &= \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \exp[N \log M(i\mathbf{t}) - i\mathbf{t} \cdot \mathbf{X}] d^n \mathbf{t}, \end{aligned}$$

where

$$M(\mathbf{t}) = \int_{\mathbb{R}^n} P(\mathbf{Y}) \exp(\mathbf{t} \cdot \mathbf{Y}) d^n \mathbf{Y}$$

is the moment-generating function common to all the summands.

This an exact expression for $\mathcal{P}$, which may be exploited analytically or numerically in certain favourable cases. Supposing for instance that P has compact support, then its characteristic function $M(i\mathbf{t})$ can be sampled finely enough to accommodate the bandwidth of the support of $\mathcal{P} = P^{*N}$ (this sampling rate clearly depends on n) so that the above expression for $\mathcal{P}$ can be used for its

numerical evaluation as the *discrete* Fourier transform of $M^N(i\mathbf{t})$. This exact method is practical only for small values of the dimension n .

In all other cases some form of approximation must be used in the Fourier inversion of $M^N(i\mathbf{t})$. For this purpose it is customary (Cramér, 1946) to expand the cumulant-generating function around $\mathbf{t} = \mathbf{0}$ with respect to the carrying variables $\mathbf{t}$:

$$\log[M^N(i\mathbf{t})] = \sum_{\mathbf{r} \in \mathbb{N}^n} \frac{N \kappa_{\mathbf{r}}}{\mathbf{r}!} (i\mathbf{t})^{\mathbf{r}},$$

where $\mathbf{r} = (r_1, r_2, \dots, r_n)$ is a multi-index (Section 1.3.2.2.3). The first-order terms may be eliminated by recentring $\mathcal{P}$ around its vector of first-order cumulants

$$\langle \mathbf{X} \rangle = \sum_{j=1}^N \langle \mathbf{X}_j \rangle,$$

where $\langle \cdot \rangle$ denotes the mathematical expectation of a random vector. The second-order terms may be grouped separately from the terms of third or higher order to give

$$\begin{aligned} M^N(i\mathbf{t}) &= \exp(-\frac{1}{2} N \mathbf{t}^T \mathbf{Q} \mathbf{t}) \\ &\times \exp \left\{ \sum_{|\mathbf{r}| \geq 3} \frac{N \kappa_{\mathbf{r}}}{\mathbf{r}!} (i\mathbf{t})^{\mathbf{r}} \right\}, \end{aligned}$$

where $\mathbf{Q} = \nabla \nabla^T (\log M)$ is the covariance matrix of the multivariate distribution P . Expanding the exponential gives rise to a series of terms of the form

$$\exp(-\frac{1}{2} N \mathbf{t}^T \mathbf{Q} \mathbf{t}) \times \text{monomial in } t_1, t_2, \dots, t_n,$$

each of which may now be subjected to a Fourier transformation to yield a Hermite function of $\mathbf{t}$ (Section 1.3.2.4.4.2) with coefficients involving the cumulants κ of P . Taking the transformed terms in natural order gives an asymptotic expansion of P for large N called the *Gram–Charlier series* of $\mathcal{P}$, while grouping the terms according to increasing powers of $1/\sqrt{N}$ gives another asymptotic expansion called the *Edgeworth series* of $\mathcal{P}$. Both expansions comprise a leading Gaussian term which embodies the *central-limit theorem*:

$$\mathcal{P}(\mathbf{E}) = \frac{1}{\sqrt{\det(2\pi\mathbf{Q})}} \exp(-\frac{1}{2} \mathbf{E}^T \mathbf{Q}^{-1} \mathbf{E}), \quad \text{where } \mathbf{E} = \frac{\mathbf{X} - \langle \mathbf{X} \rangle}{\sqrt{N}}.$$

(f) The saddlepoint approximation

A limitation of the Edgeworth series is that it gives an accurate estimate of $\mathcal{P}(\mathbf{X})$ only in the vicinity of $\mathbf{X} = \langle \mathbf{X} \rangle$, i.e. for small values of $\mathbf{E}$. These convergence difficulties are easily understood: one is substituting a *local* approximation to $\log M$ (viz a Taylor-series expansion valid near $\mathbf{t} = \mathbf{0}$) into an integral, whereas integration is a *global* process which consults values of $\log M$ far from $\mathbf{t} = \mathbf{0}$.

It is possible, however, to let the point $\mathbf{t}$ where $\log M$ is expanded as a Taylor series depend on the particular value $\mathbf{X}^*$ of $\mathbf{X}$ for which an accurate evaluation of $\mathcal{P}(\mathbf{X})$ is desired. This is the essence of the *saddlepoint method* (Fowler, 1936; Khinchin 1949; Daniels, 1954; de Bruijn, 1970; Bleistein & Handelsman, 1986), which uses an analytical continuation of $M(\mathbf{t})$ from a function over $\mathbb{R}^n$ to a function over $\mathbb{C}^n$ (see Section 1.3.2.4.2.10). Putting then $\mathbf{t} = \mathbf{s} - i\tau$, the $\mathbb{C}^n$ version of Cauchy's theorem (Hörmander, 1973) gives rise to the identity

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$$\mathcal{P}(\mathbf{X}^*) = \frac{\exp(-\boldsymbol{\tau} \cdot \mathbf{X}^*)}{(2\pi)^n} \times \int_{\mathbb{R}^n} \exp \left\{ N \left[\log M(\boldsymbol{\tau} + i\mathbf{s}) - i\mathbf{s} \cdot \frac{\mathbf{X}^*}{N} \right] \right\} d^n \mathbf{s}$$

for any $\boldsymbol{\tau} \in \mathbb{R}^n$. By a convexity argument involving the positive-definiteness of covariance matrix $\mathbf{Q}$, there is a unique value of $\boldsymbol{\tau}$ such that

$$\nabla(\log M)|_{\mathbf{t}=\mathbf{0}-i\boldsymbol{\tau}} = \frac{\mathbf{X}^*}{N}.$$

At the *saddlepoint* $\mathbf{t}^* = \mathbf{0} - i\boldsymbol{\tau}$, the modulus of the integrand above is a maximum and its phase is stationary with respect to the integration variable $\mathbf{s}$: as N tends to infinity, all contributions to the integral cancel because of rapid oscillation, except those coming from the immediate vicinity of $\mathbf{t}^*$ where there is no oscillation. A Taylor expansion of $\log M^N$ to second order with respect to $\mathbf{s}$ at $\mathbf{t}^*$ then gives

$$\log M^N(\boldsymbol{\tau} + i\mathbf{s}) \approx \log M^N(\boldsymbol{\tau}) + i\mathbf{s} \cdot \mathbf{X}^* - \frac{N}{2} [\mathbf{s}^T \mathbf{Q} \mathbf{s}]$$

and hence

$$\mathcal{P}(\mathbf{X}^*) \approx \exp[\log M^N(\boldsymbol{\tau}) - \boldsymbol{\tau} \cdot \mathbf{X}^*] \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \exp(-\frac{1}{2} \mathbf{s}^T \mathbf{Q} \mathbf{s}) d^n \mathbf{s}.$$

The last integral is elementary and gives the ‘saddlepoint approximation’:

$$\mathcal{P}^{\text{SP}}(\mathbf{X}^*) = \frac{\exp(\mathbf{S})}{\sqrt{\det(2\pi \mathbf{Q})}},$$

where

$$\mathbf{S} = \log M^N(\boldsymbol{\tau}) - \boldsymbol{\tau} \cdot \mathbf{X}^*$$

and where

$$\mathbf{Q} = \nabla \nabla^T (\log M^N) = N \mathbf{Q}.$$

This approximation scheme amounts to using the ‘conjugate distribution’ (Khinchin, 1949)

$$P_{\boldsymbol{\tau}}(\mathbf{X}_j) = P(\mathbf{X}_j) \frac{\exp(\boldsymbol{\tau} \cdot \mathbf{X}_j)}{M(\boldsymbol{\tau})}$$

instead of the original distribution $P(\mathbf{X}_j) = P_0(\mathbf{X}_j)$ for the common distribution of all N random vectors $\mathbf{X}_j$. The exponential modulation results from the analytic continuation of the characteristic (or moment-generating) function into $\mathbb{C}^n$, as in Section 1.3.2.4.2.10. The saddlepoint approximation $\mathcal{P}^{\text{SP}}$ is only the leading term of an asymptotic expansion (called the *saddlepoint expansion*) for $\mathcal{P}$, which is actually the Edgeworth expansion associated with $P_{\boldsymbol{\tau}}^*$.

1.3.4.5.2.2. The statistical theory of phase determination

The methods of probability theory just surveyed were applied to various problems formally similar to the crystallographic phase problem [e.g. the ‘problem of the random walk’ of Pearson (1905)] by Rayleigh (1880, 1899, 1905, 1918, 1919) and Kluyver (1906). They became the basis of the statistical theory of communication with the classic papers of Rice (1944, 1945).

The Gram–Charlier and Edgeworth series were introduced into crystallography by Bertaut (1955*a,b,c*, 1956*a*) and by Klug (1958), respectively, who showed them to constitute the mathematical basis of numerous formulae derived by Hauptman & Karle (1953). The saddlepoint approximation was introduced by Bricogne (1984) and was shown to be related to variational methods involving the

maximization of certain entropy criteria. This connection exhibits most of the properties of the Fourier transform at play simultaneously, and will now be described as a final illustration.

(a) Definitions and conventions

Let H be a set of unique non-origin reflections $\mathbf{h}$ for a crystal with lattice Λ and space group G . Let H contain n_a acentric and n_c centric reflections. Structure-factor values attached to all reflections in H will comprise $n = 2n_a + n_c$ real numbers. For $\mathbf{h}$ acentric, $\alpha_{\mathbf{h}}$ and $\beta_{\mathbf{h}}$ will be the real and imaginary parts of the complex structure factor; for $\mathbf{h}$ centric, $\gamma_{\mathbf{h}}$ will be the real coordinate of the (possibly complex) structure factor measured along a real axis rotated by one of the two angles $\theta_{\mathbf{h}}$, π apart, to which the phase is restricted modulo 2π (Section 1.3.4.2.2.5). These n real coordinates will be arranged as a column vector containing the acentric then the centric data, i.e. in the order

$$\alpha_1, \beta_1, \alpha_2, \beta_2, \dots, \alpha_{n_a}, \beta_{n_a}, \gamma_1, \gamma_2, \dots, \gamma_{n_c}.$$

(b) Vectors of trigonometric structure-factor expressions

Let $\boldsymbol{\xi}(\mathbf{x})$ denote the vector of trigonometric structure-factor expressions associated with $\mathbf{x} \in D$, where D denotes the asymmetric unit. These are defined as follows:

$$\begin{aligned} \alpha_{\mathbf{h}}(\mathbf{x}) + i\beta_{\mathbf{h}}(\mathbf{x}) &= \Xi(\mathbf{h}, \mathbf{x}) \quad \text{for } \mathbf{h} \text{ acentric} \\ \gamma_{\mathbf{h}}(\mathbf{x}) &= \exp(-i\theta_{\mathbf{h}}) \Xi(\mathbf{h}, \mathbf{x}) \quad \text{for } \mathbf{h} \text{ centric,} \end{aligned}$$

where

$$\Xi(\mathbf{h}, \mathbf{x}) = \frac{1}{|G_{\mathbf{x}}|} \sum_{g \in G} \exp\{2\pi i \mathbf{h} \cdot [S_g(\mathbf{x})]\}.$$

According to the convention above, the coordinates of $\boldsymbol{\xi}(\mathbf{x})$ in $\mathbb{R}^n$ will be arranged in a column vector as follows:

$$\begin{aligned} \xi_{2r-1}(\mathbf{x}) &= \alpha_{\mathbf{h}_r}(\mathbf{x}) \quad \text{for } r = 1, \dots, n_a, \\ \xi_{2r}(\mathbf{x}) &= \beta_{\mathbf{h}_r}(\mathbf{x}) \quad \text{for } r = 1, \dots, n_a, \\ \xi_{n_a+r}(\mathbf{x}) &= \gamma_{\mathbf{h}_r}(\mathbf{x}) \quad \text{for } r = n_a + 1, \dots, n_a + n_c. \end{aligned}$$

(c) Distributions of random atoms and moment-generating functions

Let position $\mathbf{x}$ in D now become a random vector with probability density $m(\mathbf{x})$. Then $\boldsymbol{\xi}(\mathbf{x})$ becomes itself a random vector in $\mathbb{R}^n$, whose distribution $p(\boldsymbol{\xi})$ is the image of distribution $m(\mathbf{x})$ through the mapping $\mathbf{x} \rightarrow \boldsymbol{\xi}(\mathbf{x})$ just defined. The locus of $\boldsymbol{\xi}(\mathbf{x})$ in $\mathbb{R}^n$ is a compact algebraic manifold $\mathcal{V}$ (the multidimensional analogue of a Lissajous curve), so that p is a singular measure (a distribution of order 0, Section 1.3.2.3.4, concentrated on that manifold) with compact support. The average with respect to p of any function Ω over $\mathbb{R}^n$ which is infinitely differentiable in a neighbourhood of $\mathcal{V}$ may be calculated as an average with respect to m over D by the ‘induction formula’:

$$\langle p, \Omega \rangle = \int_D m(\mathbf{x}) \Omega[\boldsymbol{\xi}(\mathbf{x})] d^3 \mathbf{x}.$$

In particular, one can calculate the moment-generating function M for distribution p as

$$M(\mathbf{t}) \equiv \langle p_{\boldsymbol{\xi}}, \exp(\mathbf{t} \cdot \boldsymbol{\xi}) \rangle = \int_D m(\mathbf{x}) \exp[\mathbf{t} \cdot \boldsymbol{\xi}(\mathbf{x})] d^3 \mathbf{x}$$

and hence calculate the moments μ (respectively cumulants κ) of p by differentiation of M (respectively $\log M$) at $\mathbf{t} = \mathbf{0}$:

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$$\begin{aligned}\mu_{r_1 r_2 \dots r_n} &\equiv \int_D m(\mathbf{x}) \xi_1^{r_1}(\mathbf{x}) \xi_2^{r_2}(\mathbf{x}) \dots \xi_n^{r_n}(\mathbf{x}) d^3 \mathbf{x} \\ &= \frac{\partial^{r_1 + \dots + r_n} (M)}{\partial t_1^{r_1} \dots \partial t_n^{r_n}} \\ \kappa_{r_1 r_2 \dots r_n} &= \frac{\partial^{r_1 + \dots + r_n} (\log M)}{\partial t_1^{r_1} \dots \partial t_n^{r_n}}.\end{aligned}$$

The structure-factor algebra for group G (Section 1.3.4.2.2.9) then allows one to express products of ξ 's as linear combinations of other ξ 's, and hence to express all moments and cumulants of distribution $p(\xi)$ as linear combinations of real and imaginary parts of Fourier coefficients of the prior distribution of atoms $m(\mathbf{x})$. This plays a key role in the use of non-uniform distributions of atoms.

(d) The joint probability distribution of structure factors

In the random-atom model of an equal-atom structure, N atoms are placed randomly, independently of each other, in the asymmetric unit D of the crystal with probability density $m(\mathbf{x})$. For point atoms of unit weight, the vector $\mathbf{F}$ of structure-factor values for reflections $\mathbf{h} \in H$ may be written

$$\mathbf{F} = \sum_{l=1}^N \xi^{[l]},$$

where the N copies $\xi^{[l]}$ of random vector ξ are independent and have the same distribution $p(\xi)$.

The joint probability distribution $\mathcal{P}(\mathbf{F})$ is then [Section 1.3.4.5.2.1(e)]

$$\mathcal{P}(\mathbf{X}) = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \exp[N \log M(it) - it \cdot \mathbf{X}] d^n t.$$

For low dimensionality n it is possible to carry out the Fourier transformation numerically after discretization, provided $M(it)$ is sampled sufficiently finely that no aliasing results from taking its N th power (Barakat, 1974). This exact approach can also accommodate heterogeneity, and has been used first in the field of intensity statistics (Shmueli *et al.*, 1984, 1985; Shmueli & Weiss, 1987, 1988), then in the study of the Σ_1 and Σ_2 relations in triclinic space groups (Shmueli & Weiss, 1985, 1986). Some of these applications are described in Chapter 2.1 of this volume. This method could be extended to the construction of any joint probability distribution (j.p.d.) in any space group by using the generic expression for the moment-generating function (m.g.f.) derived by Bricogne (1984). It is, however, limited to small values of n by the necessity to carry out n -dimensional FFTs on large arrays of sample values.

The asymptotic expansions of Gram–Charlier and Edgeworth have good convergence properties only if $F_{\mathbf{h}}$ lies in the vicinity of $\langle F_{\mathbf{h}} \rangle = N \mathcal{F}[m](\mathbf{h})$ for all $\mathbf{h} \in H$. Previous work on the j.p.d. of structure factors has used for $m(\mathbf{x})$ a uniform distribution, so that $\langle \mathbf{F} \rangle = \mathbf{0}$; as a result, the corresponding expansions are accurate only if all moduli $|F_{\mathbf{h}}|$ are small, in which case the j.p.d. contains little phase information.

The saddlepoint method [Section 1.3.4.5.2.1(f)] constitutes the method of choice for evaluating the joint probability $\mathcal{P}(\mathbf{F}^*)$ of structure factors when some of the moduli in $\mathbf{F}^*$ are large. As shown previously, this approximation amounts to using the ‘conjugate distribution’

$$p_{\tau}(\xi) = p(\xi) \frac{\exp(\tau \cdot \xi)}{M(\tau)}$$

instead of the original distribution $p(\xi) = p_0(\xi)$ for the distribution of random vector ξ . This conjugate distribution p_{τ} is induced from

the modified distribution of atoms

$$q_{\tau}(\mathbf{x}) = m(\mathbf{x}) \frac{\exp[\tau \cdot \xi(\mathbf{x})]}{M(\tau)}, \quad (\text{SP1})$$

where, by the induction formula, $M(\tau)$ may be written as

$$M(\tau) = \int_D m(\mathbf{x}) \exp[\tau \cdot \xi(\mathbf{x})] d^3 \mathbf{x} \quad (\text{SP2})$$

and where τ is the unique solution of the saddlepoint equation:

$$\nabla_{\tau}(\log M^N) = \mathbf{F}^*. \quad (\text{SP3})$$

The desired approximation is then

$$\mathcal{P}^{\text{SP}}(\mathbf{F}^*) = \frac{\exp(\mathbf{S})}{\sqrt{\det(2\pi \mathcal{Q})}},$$

where

$$\mathbf{S} = \log M^N(\tau) - \tau \cdot \mathbf{F}^*$$

and where

$$\mathcal{Q} = \nabla \nabla^T (\log M^N) = \mathbf{N} \mathbf{Q}.$$

Finally, the elements of the Hessian matrix $\mathbf{Q} = \nabla \nabla^T (\log M)$ are just the trigonometric second-order cumulants of distribution p , and hence can be calculated *via* structure-factor algebra from the Fourier coefficients of $q_{\tau}(\mathbf{x})$. All the quantities involved in the expression for $\mathcal{P}^{\text{SP}}(\mathbf{F}^*)$ are therefore effectively computable from the initial data $m(\mathbf{x})$ and $\mathbf{F}^*$.

(e) Maximum-entropy distributions of atoms

One of the main results in Bricogne (1984) is that the modified distribution $q_{\tau}(\mathbf{x})$ in (SP1) is the unique distribution which has maximum entropy $\mathcal{J}_m(q)$ relative to $m(\mathbf{x})$, where

$$\mathcal{J}_m(q) = - \int_D q(\mathbf{x}) \log \left[\frac{q(\mathbf{x})}{m(\mathbf{x})} \right] d^3 \mathbf{x},$$

under the constraint that $\mathbf{F}^*$ be the centroid vector of the corresponding conjugate distribution $\mathcal{P}_{\tau}(\mathbf{F})$. The traditional notation of maximum-entropy (ME) theory (Jaynes, 1957, 1968, 1983) is in this case (Bricogne, 1984)

$$q^{\text{ME}}(\mathbf{x}) = m(\mathbf{x}) \frac{\exp[\lambda \cdot \xi(\mathbf{x})]}{Z(\lambda)} \quad (\text{ME1})$$

$$Z(\lambda) = \int_D m(\mathbf{x}) \exp[\lambda \cdot \xi(\mathbf{x})] d^3 \mathbf{x} \quad (\text{ME2})$$

$$\nabla_{\lambda}(\log Z^N) = \mathbf{F}^* \quad (\text{ME3})$$

so that Z is identical to the m.g.f. M , and the coordinates τ of the saddlepoint are the Lagrange multipliers λ for the constraints $\mathbf{F}^*$.

Jaynes's ME theory also gives an estimate for $\mathcal{P}(\mathbf{F}^*)$:

$$\mathcal{P}^{\text{ME}}(\mathbf{F}^*) \approx \exp(\mathcal{J}),$$

where

$$\mathcal{J} = \log Z^N - \lambda \cdot \mathbf{F}^* = N \mathcal{J}_m(\mathbf{q}^{\text{ME}})$$

is the total entropy and is the counterpart to $\mathbf{S}$ under the equivalence just established.

$\mathcal{P}^{\text{ME}}$ is identical to $\mathcal{P}^{\text{SP}}$, but lacks the denominator. The latter, which is the normalization factor of a multivariate Gaussian with covariance matrix $\mathcal{Q}$, may easily be seen to arise through Szegő's theorem (Sections 1.3.2.6.9.4, 1.3.4.2.1.10) from the extra logarithmic term in Stirling's formula

$$\log(q!) \approx q \log q - q + \frac{1}{2} \log(2\pi q)$$

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(see, for instance, Reif, 1965) beyond the first two terms which serve to define entropy, since

$$\frac{1}{n} \log \det (2\pi \mathbf{Q}) \approx \int_{\mathbb{R}^3/\mathbb{Z}^3} \log 2\pi q^{\text{ME}}(\mathbf{x}) d^3\mathbf{x}.$$

The relative effect of this extra normalization factor depends on the ratio

$$\frac{n}{N} = \frac{\text{dimension of } \mathbf{F} \text{ over } \mathbb{R}}{\text{number of atoms}}.$$

The above relation between entropy maximization and the saddlepoint approximation is the basis of a Bayesian statistical approach to the phase problem (Bricogne, 1988) where the assumptions under which joint distributions of structure factors are sought incorporate many new ingredients (such as molecular boundaries, isomorphous substitutions, known fragments, noncrystallographic symmetries, multiple crystal forms) besides trial phase choices for basis reflections. The ME criterion intervenes in the construction of $q^{\text{ME}}(\mathbf{x})$ under these assumptions, and the distribution $q^{\text{ME}}(\mathbf{x})$ is a very useful computational intermediate in obtaining the approximate joint probability $\mathcal{P}^{\text{SP}}(\mathbf{F}^*)$ and the associated conditional distributions and likelihood functions.

(f) Role of the Fourier transformation

The formal developments presented above make use of the following properties of the Fourier transformation:

- (i) the convolution theorem, which turns the convolution of probability distributions into the multiplication of their characteristic functions;
- (ii) the differentiation property, which confers moment-generating properties to characteristic functions;
- (iii) the reciprocity theorem, which allows the retrieval of a probability distribution from its characteristic or moment-generating function;
- (iv) the Paley–Wiener theorem, which allows the analytic continuation of characteristic functions associated to probability

distributions with compact support, and thus gives rise to conjugate families of distributions;

(v) Bertaut’s structure-factor algebra (a discrete symmetrized version of the convolution theorem), which allows the calculation of all necessary moments and cumulants when the dimension n is small;

(vi) Szegő’s theorem, which provides an asymptotic approximation of the normalization factor when n is large.

This multi-faceted application seems an appropriate point at which to end this description of the Fourier transformation and of its use in crystallography.

Acknowledgements

Many aspects of the theory of discrete Fourier transform algorithms and of its extension to incorporate crystallographic symmetry have been the focus of a long-standing collaborative effort between Professor Louis Auslander, Professor Richard Tolimieri, their co-workers and the writer. I am most grateful to them for many years of mathematical stimulation and enjoyment, for introducing me to the ‘big picture’ of the discrete Fourier transform which they have elaborated over the past decade, and for letting me describe here some of their unpublished work. In particular, the crystallographic extensions of the Rader/Winograd algorithms presented in Section 1.3.4.3.4.3 were obtained by Richard Tolimieri, in a collaboration partially supported by NIH grant GM 32362 (to the writer).

I am indebted to the Editor for many useful and constructive suggestions of possible improvements to the text, only a few of which I have been able to implement. I hope to incorporate many more of them in the future. I also wish to thank Dr D. Sayre for many useful comments on an early draft of the manuscript.

This contribution was written during the tenure of a Visiting Fellowship at Trinity College, Cambridge, with partial financial support from Trinity College and the MRC Laboratory of Molecular Biology. I am most grateful to both institutions for providing ideal working conditions.

1.4. Symmetry in reciprocal space

BY U. SHMUELI

WITH APPENDIX 1.4.2 BY U. SHMUELI, S. R. HALL AND R. W. GROSSE-KUNSTLEVE

1.4.1. Introduction

Crystallographic symmetry, as reflected in functions on reciprocal space, can be considered from two complementary points of view.

(1) One can assume the existence of a certain permissible symmetry of the density function of crystalline (scattering) matter, a function which due to its three-dimensional periodicity can be expanded in a triple Fourier series (e.g. Bragg, 1966), and inquire about the effects of this symmetry on the Fourier coefficients – the structure factors. Since there exists a one-to-one correspondence between the triplets of summation indices in the Fourier expansion and vectors in the reciprocal lattice (Ewald, 1921), the above approach leads to consequences of the symmetry of the density function which are relevant to the representation of its Fourier image in reciprocal space. The symmetry properties of these Fourier coefficients, which are closely related to the crystallographic experiment, can then be readily established.

This traditional approach, the essentials of which are the basis of Sections 4.5–4.7 of Volume I (IT I, 1952), and which was further developed in the works of Buerger (1949, 1960), Waser (1955), Bertaut (1964) and Wells (1965), is one of the cornerstones of crystallographic practice and will be followed in the present chapter, as far as the basic principles are concerned.

(2) The alternative approach, proposed by Bienenstock & Ewald (1962), also presumes a periodic density function in crystal space and its Fourier expansion associated with the reciprocal. However, the argument starts from the Fourier coefficients, taken as a discrete set of complex functions, and linear transformations are sought which leave the magnitudes of these functions unchanged; the variables on which these transformations operate are h, k, l and φ – the Fourier summation indices (i.e., components of a reciprocal-lattice vector) and the phase of the Fourier coefficient, respectively. These transformations, or the groups they constitute, are then interpreted in terms of the symmetry of the density function in direct space. This direct analysis of symmetry in reciprocal space will also be discussed.

We start the next section with a brief discussion of the point-group symmetries of associated direct and reciprocal lattices. The weighted reciprocal lattice is then briefly introduced and the relation between the values of the weight function at symmetry-related points of the weighted reciprocal lattice is discussed in terms of the Fourier expansion of a periodic function in crystal space. The remaining part of Section 1.4.2 is devoted to the formulation of the Fourier series and its coefficients (values of the weight function) in terms of space-group-specific symmetry factors, an extensive tabulation of which is presented in Appendix 1.4.3. This is a revised version of the structure-factor tables given in Sections 4.5–4.7 of Volume I (IT I, 1952). Appendix 1.4.4 contains a reciprocal-space representation of the 230 crystallographic space groups and some explanatory material related to these space-group tables is given in Section 1.4.4; the latter are interpreted in terms of the two viewpoints discussed above. The tabular material given in this chapter is compatible with the direct-space symmetry tables given in Volume A (IT A, 1983) with regard to the space-group settings and choices of the origin.

Most of the tabular material, the new symmetry-factor tables in Appendix 1.4.3 and the space-group tables in Appendix 1.4.4 have been generated by computer with the aid of a combination of numeric and symbolic programming techniques. The algorithm underlying this procedure is briefly summarized in Appendix 1.4.1. Appendix 1.4.2 deals with computer-adapted space-group symbols,

including the set of symbols that were used in the preparation of the present tables.

1.4.2. Effects of symmetry on the Fourier image of the crystal

1.4.2.1. Point-group symmetry of the reciprocal lattice

Regarding the reciprocal lattice as a collection of points generated from a given direct lattice, it is fairly easy to see that each of the two associated lattices must have the same point-group symmetry. The set of all the rotations that bring the direct lattice into self-coincidence can be thought of as interchanging equivalent families of lattice planes in all the permissible manners. A family of lattice planes in the direct lattice is characterized by a common normal and a certain interplanar distance, and these two characteristics uniquely define the direction and magnitude, respectively, of a vector in the reciprocal lattice, as well as the lattice line associated with this vector and passing through the origin. It follows that any symmetry operation on the direct lattice must also bring the reciprocal lattice into self-coincidence, i.e. it must also be a symmetry operation on the reciprocal lattice. The roles of direct and reciprocal lattices in the above argument can of course be interchanged without affecting the conclusion.

The above elementary considerations recall that for any point group (not necessarily the full point group of a lattice), the operations which leave the lattice unchanged must also leave unchanged its associated reciprocal. This equivalence of point-group symmetries of the associated direct and reciprocal lattices is fundamental to crystallographic symmetry in reciprocal space, in both points of view mentioned in Section 1.4.1.

With regard to the effect of any given point-group operation on each of the two associated lattices, we recall that:

(i) If $\mathbf{P}$ is a point-group rotation operator acting on the direct lattice (e.g. by rotation through the angle α about a given axis), the effect of this rotation on the associated reciprocal lattice is that of applying the inverse rotation operator, $\mathbf{P}^{-1}$ (i.e. rotation through $-\alpha$ about a direction parallel to the direct axis); this is readily found from the requirement that the scalar product $\mathbf{h}^T \mathbf{r}_L$, where $\mathbf{h}$ and $\mathbf{r}_L$ are vectors in the reciprocal and direct lattices, respectively, remains invariant under the application of a point-group operation to the crystal.

(ii) If our matrix representation of the rotation operator is such that the point-group operation is applied to the direct-lattice (column) vector by *premultiplying* it with the matrix $\mathbf{P}$, the corresponding operation on the reciprocal lattice is applied by *postmultiplying* the (row) vector $\mathbf{h}^T$ with the point-group rotation matrix. We can thus write, e.g., $\mathbf{h}^T \mathbf{r}_L = (\mathbf{h}^T \mathbf{P}^{-1})(\mathbf{P} \mathbf{r}_L) = [(\mathbf{P}^{-1})^T \mathbf{h}]^T (\mathbf{P} \mathbf{r}_L)$. Note, however, that the orthogonality relationship: $\mathbf{P}^{-1} = \mathbf{P}^T$ is not satisfied if $\mathbf{P}$ is referred to some oblique crystal systems, higher than the orthorhombic.

Detailed descriptions of the 32 crystallographic point groups are presented in the crystallographic and other literature; their complete tabulation is given in Chapter 10 of Volume A (IT A, 1983).

1.4.2.2. Relationship between structure factors at symmetry-related points of the reciprocal lattice

Of main interest in the context of the present chapter are symmetry relationships that concern the values of a function defined at the points of the reciprocal lattice. Such functions, of crystal-

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lographic interest, are Fourier-transform representations of direct-space functions that have the periodicity of the crystal, the structure factor as a Fourier transform of the electron-density function being a representative example (see *e.g.* Lipson & Taylor, 1958). The value of such a function, attached to a reciprocal-lattice point, is called the weight of this point and the set of all such weighted points is often termed the weighted reciprocal lattice. This section deals with a fundamental relationship between functions (weights) associated with reciprocal-lattice points, which are related by point-group symmetry, the weights here considered being the structure factors of Bragg reflections (*cf.* Chapter 1.2).

The electron density, an example of a three-dimensional periodic function with the periodicity of the crystal, can be represented by the Fourier series

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{r}), \quad (1.4.2.1)$$

where $\mathbf{h}$ is a reciprocal-lattice vector, V is the volume of the (direct) unit cell, $F(\mathbf{h})$ is the structure factor at the point $\mathbf{h}$ and $\mathbf{r}$ is a position vector of a point in direct space, at which the density is given. The summation in (1.4.2.1) extends over all the reciprocal lattice.

Let $\mathbf{r}' = \mathbf{P}\mathbf{r} + \mathbf{t}$ be a space-group operation on the crystal, where $\mathbf{P}$ and $\mathbf{t}$ are its rotation and translation parts, respectively, and $\mathbf{P}$ must therefore be a point-group operator. We then have, by definition, $\rho(\mathbf{r}) = \rho(\mathbf{P}\mathbf{r} + \mathbf{t})$ and the Fourier representation of the electron density, at the equivalent position $\mathbf{P}\mathbf{r} + \mathbf{t}$, is given by

$$\begin{aligned} \rho(\mathbf{P}\mathbf{r} + \mathbf{t}) &= \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp[-2\pi i \mathbf{h}^T (\mathbf{P}\mathbf{r} + \mathbf{t})] \\ &= \frac{1}{V} \sum_{\mathbf{h}} [F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t})] \\ &\quad \times \exp[-2\pi i (\mathbf{P}^T \mathbf{h})^T \mathbf{r}], \end{aligned} \quad (1.4.2.2)$$

noting that $\mathbf{h}^T \mathbf{P} = (\mathbf{P}^T \mathbf{h})^T$. Since $\mathbf{P}$ is a point-group operator, the vectors $\mathbf{P}^T \mathbf{h}$ in (1.4.2.2) must range over all the reciprocal lattice and a comparison of the functional forms of the equivalent expansions (1.4.2.1) and (1.4.2.2) shows that the coefficients of the exponentials $\exp[-2\pi i (\mathbf{P}^T \mathbf{h})^T \mathbf{r}]$ in (1.4.2.2) must be the structure factors at the points $\mathbf{P}^T \mathbf{h}$ in the reciprocal lattice. Thus

$$F(\mathbf{P}^T \mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t}), \quad (1.4.2.3)$$

wherefrom it follows that the magnitudes of the structure factors at $\mathbf{h}$ and $\mathbf{P}^T \mathbf{h}$ are the same:

$$|F(\mathbf{P}^T \mathbf{h})| = |F(\mathbf{h})|, \quad (1.4.2.4)$$

and their phases are related by

$$\varphi(\mathbf{P}^T \mathbf{h}) = \varphi(\mathbf{h}) - 2\pi \mathbf{h}^T \mathbf{t}. \quad (1.4.2.5)$$

The relationship (1.4.2.3) between structure factors of symmetry-related reflections was first derived by Waser (1955), starting from a representation of the structure factor as a Fourier transform of the electron-density function.

It follows that an application of a point-group transformation to the (weighted) reciprocal lattice leaves the moduli of the structure factors unchanged. The distribution of diffracted intensities obeys, in fact, the same point-group symmetry as that of the crystal. If, however, anomalous dispersion is negligibly small, and the point group of the crystal is noncentrosymmetric, the apparent symmetry of the diffraction pattern will also contain a false centre of symmetry and, of course, all the additional elements generated by the inclusion of this centre. Under these circumstances, the diffraction pattern from a single crystal may belong to one of the eleven centrosymmetric point groups, known as Laue groups (*IT* I, 1952).

According to equation (1.4.2.5), the phases of the structure factors of symmetry-related reflections differ, in the general case, by a phase shift that depends on the translation part of the space-group operation involved. Only when the space group is symmorphic, *i.e.* it contains no translations other than those of the Bravais lattice, will the distribution of the phases obey the point-group symmetry of the crystal. These phase shifts are considered in detail in Section 1.4.4 where their tabulation is presented and the alternative interpretation (Bienenstock & Ewald, 1962) of symmetry in reciprocal space, mentioned in Section 1.4.1, is given.

Equation (1.4.2.3) can be usefully applied to a classification of all the general systematic absences or – as defined in the space-group tables in the main editions of *IT* (1935, 1952, 1983, 1987, 1992) – general conditions for possible reflections. These systematic absences are associated with special positions in the reciprocal lattice – special with respect to the point-group operations $\mathbf{P}$ appearing in the relevant relationships. If, in a given relationship, we have $\mathbf{P}^T \mathbf{h} = \mathbf{h}$, equation (1.4.2.3) reduces to

$$F(\mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t}). \quad (1.4.2.6)$$

Of course, $F(\mathbf{h})$ may then be nonzero only if $\cos(2\pi \mathbf{h}^T \mathbf{t})$ equals unity, or the scalar product $\mathbf{h}^T \mathbf{t}$ is an integer. This well known result leads to a ready determination of lattice absences, as well as those produced by screw-axis and glide-plane translations, and is routinely employed in crystallographic computing. An exhaustive classification of the general conditions for possible reflections is given in the space-group tables (*IT*, 1952, 1983). It should be noted that since the axes of rotation and planes of reflection in the reciprocal lattice are parallel to the corresponding elements in the direct lattice (Buerger, 1960), the component of $\mathbf{t}$ that depends on the location of the corresponding space-group symmetry element in direct space does not contribute to the scalar product $\mathbf{h}^T \mathbf{t}$ in (1.4.2.6), and it is only the intrinsic part of the translation $\mathbf{t}$ (*IT* A, 1983) that usually matters.

It may, however, be of interest to note that some screw axes in direct space cannot give rise to any systematic absences. For example, the general Wyckoff position No. (10) in the space group $Pa\bar{3}$ (No. 205) (*IT* A, 1983) has the coordinates $\bar{y}$, $\frac{1}{2} + z$, $\frac{1}{2} - x$, and corresponds to the space-group operation

$$(\mathbf{P}, \mathbf{t}) = (\mathbf{P}, \mathbf{t}_i + \mathbf{t}_l) = \left[\begin{pmatrix} 0 & \bar{1} & 0 \\ 0 & 0 & 1 \\ \bar{1} & 0 & 0 \end{pmatrix}, \begin{pmatrix} -\frac{1}{3} \\ \frac{1}{3} \\ \frac{1}{3} \end{pmatrix} + \begin{pmatrix} \frac{1}{6} \\ \frac{1}{6} \\ \frac{1}{6} \end{pmatrix} \right], \quad (1.4.2.7)$$

where $\mathbf{t}_i$ and $\mathbf{t}_l$ are the intrinsic and location-dependent components of the translation part $\mathbf{t}$, and are parallel and perpendicular, respectively, to the threefold axis of rotation represented by the matrix $\mathbf{P}$ in (1.4.2.7) (*IT* A, 1983; Shmueli, 1984). This is clearly a threefold screw axis, parallel to $[\bar{1}\bar{1}1]$. The reciprocal-lattice vectors which remain unchanged, when postmultiplied by $\mathbf{P}$ (or premultiplied by its transpose), have the form: $\mathbf{h}^T = (h\bar{h}\bar{h})$; this is the special position for the present example. We see that (i) $\mathbf{h}^T \mathbf{t}_l = 0$, as expected, and (ii) $\mathbf{h}^T \mathbf{t}_i = -h$. Since the scalar product $\mathbf{h}^T \mathbf{t}$ is an integer, there are no values of index h for which the structure factor $F(h\bar{h}\bar{h})$ must be absent.

Other approaches to systematically absent reflections include a direct inspection of the structure-factor equation (Lipson & Cochran, 1966), which is of considerable didactical value, and the utilization of transformation properties of direct and reciprocal base vectors and lattice-point coordinates (Buerger, 1942).

Finally, the relationship between the phases of symmetry-related reflections, given by (1.4.2.5), is of fundamental as well as practical importance in the theories and techniques of crystal structure

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determination which operate in reciprocal space (Part 2 of this volume).

1.4.2.3. Symmetry factors for space-group-specific Fourier summations

The weighted reciprocal lattice, with weights taken as the structure factors, is synonymous with the discrete space of the coefficients of a Fourier expansion of the electron density, or the Fourier space (F space) of the latter. Accordingly, the asymmetric unit of the Fourier space can be defined as the subset of structure factors within which the relationship (1.4.2.3) does not hold – except at special positions in the reciprocal lattice. If the point group of the crystal is of order g , this is also the order of the corresponding factor-group representation of the space group (*IT* A, 1983) and there exist g relationships of the form of (1.4.2.3):

$$F(\mathbf{P}_s^T \mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}^T \mathbf{t}_s). \quad (1.4.2.8)$$

We can thus decompose the summation in (1.4.2.1) into g sums, each extending over an asymmetric unit of the F space. It must be kept in mind, however, that some classes of reciprocal-lattice vectors may be common to more than one asymmetric unit, and thus each reciprocal-lattice point will be assigned an occupancy factor, denoted by $q(\mathbf{h})$, such that $q(\mathbf{h}) = 1$ for a general position and $q(\mathbf{h}) = 1/m(\mathbf{h})$ for a special one, where $m(\mathbf{h})$ is the multiplicity – or the order of the point group that leaves $\mathbf{h}$ unchanged. Equation (1.4.2.1) can now be rewritten as

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{s=1}^g \sum_{\mathbf{h}_a} q(\mathbf{h}_a) F(\mathbf{P}_s^T \mathbf{h}_a) \exp[-2\pi i (\mathbf{P}_s^T \mathbf{h}_a)^T \mathbf{r}], \quad (1.4.2.9)$$

where the inner summation in (1.4.2.9) extends over the reference asymmetric unit of the Fourier space, which is associated with the identity operation of the space group. Substituting from (1.4.2.8) for $F(\mathbf{P}_s^T \mathbf{h}_a)$, and interchanging the order of the summations in (1.4.2.9), we obtain

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}_a} q(\mathbf{h}_a) F(\mathbf{h}_a) \sum_{s=1}^g \exp[-2\pi i \mathbf{h}_a^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)] \quad (1.4.2.10)$$

$$= \frac{1}{V} \sum_{\mathbf{h}_a} q(\mathbf{h}_a) F(\mathbf{h}_a) [A(\mathbf{h}_a) - iB(\mathbf{h}_a)], \quad (1.4.2.11)$$

where

$$A(\mathbf{h}) = \sum_{s=1}^g \cos[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)] \quad (1.4.2.12)$$

and

$$B(\mathbf{h}) = \sum_{s=1}^g \sin[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)]. \quad (1.4.2.13)$$

The symmetry factors A and B are well known as geometric or trigonometric structure factors and a considerable part of Volume I of *IT* (1952) is dedicated to their tabulation. Their formal association with the structure factor – following from direct-space arguments – is closely related to that shown in equation (1.4.2.11) (see Section 1.4.2.4). Simplified trigonometric expressions for A and B are given in Tables A1.4.3.1–A1.4.3.7 in Appendix 1.4.3 for all the two- and three-dimensional crystallographic space groups, and for all the parities of hkl for which A and B assume different functional forms. These expressions are there given for general reflections and can also be used for special ones, provided the occupancy factors $q(\mathbf{h})$ have been properly accounted for.

Equation (1.4.2.11) is quite general and can, of course, be applied to noncentrosymmetric Fourier summations, without neglect of dispersion. Further simplifications are obtained in the centrosym-

metric case, when the space-group origin is chosen at a centre of symmetry, and in the noncentrosymmetric case, when dispersion is neglected. In each of the latter two cases the summation over $\mathbf{h}_a$ is restricted to reciprocal-lattice vectors that are not related by real or apparent inversion (denoted by $\mathbf{h}_a > 0$), and we obtain

$$\rho(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{h}_a > 0} q(\mathbf{h}_a) F(\mathbf{h}_a) A(\mathbf{h}_a) \quad (1.4.2.14)$$

and

$$\rho(\mathbf{r}) = \frac{2}{V} \sum_{\mathbf{h}_a > 0} q(\mathbf{h}_a) |F(\mathbf{h}_a)| [A(\mathbf{h}_a) \cos \varphi(\mathbf{h}_a) + B(\mathbf{h}_a) \sin \varphi(\mathbf{h}_a)] \quad (1.4.2.15)$$

for the dispersionless centrosymmetric and noncentrosymmetric cases, respectively.

1.4.2.4. Symmetry factors for space-group-specific structure-factor formulae

The explicit dependence of structure-factor summations on the space-group symmetry of the crystal can also be expressed in terms of symmetry factors, in an analogous manner to that described for the electron density in the previous section. It must be pointed out that while the above treatment only presumes that the electron density can be represented by a three-dimensional Fourier series, the present one is restricted by the assumption that the atoms are isotropic with regard to their motion and shape (*cf.* Chapter 1.2).

Under the above assumptions, *i.e.* for isotropically vibrating spherical atoms, the structure factor can be written as

$$F(\mathbf{h}) = \sum_{j=1}^N f_j \exp(2\pi i \mathbf{h}^T \mathbf{r}_j), \quad (1.4.2.16)$$

where $\mathbf{h}^T = (hkl)$ is the diffraction vector, N is the number of atoms in the unit cell, f_j is the atomic scattering factor including its temperature factor and depending on the magnitude of $\mathbf{h}$ only, and $\mathbf{r}_j$ is the position vector of the j th atom referred to the origin of the unit cell.

If the crystal belongs to a point group of order m_p and the multiplicity of its Bravais lattice is m_L , there are $g' = m_p \times m_L$ general equivalent positions in the unit cell of the space group (*IT* A, 1983). We can thus rewrite (1.4.2.16), grouping the contributions of the symmetry-related atoms, as

$$F(\mathbf{h}) = \sum_j f_j \sum_{s=1}^{g'} \exp[2\pi i \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)], \quad (1.4.2.17)$$

where $\mathbf{P}_s$ and $\mathbf{t}_s$ are the rotation and translation parts of the s th space-group operation respectively. The inner summation in (1.4.2.17) contains the dependence of the structure factor of reflection $\mathbf{h}$ on the space-group symmetry of the crystal and is known as the (complex) geometric or trigonometric structure factor.

Equation (1.4.2.17) can be rewritten as

$$F(\mathbf{h}) = \sum_j f_j [A_j(\mathbf{h}) + iB_j(\mathbf{h})], \quad (1.4.2.18)$$

where

$$A_j(\mathbf{h}) = \sum_{s=1}^{g'} \cos[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r}_j + \mathbf{t}_s)] \quad (1.4.2.19)$$

and

$$B_j(\mathbf{h}) = \sum_{s=1}^{g'} \sin[2\pi \mathbf{h}^T (\mathbf{P}_s \mathbf{r}_j + \mathbf{t}_s)] \quad (1.4.2.20)$$

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are the real and imaginary parts of the trigonometric structure factor. Equations (1.4.2.19) and (1.4.2.20) are *mathematically* identical to equations (1.4.2.11) and (1.4.2.12), respectively, apart from the numerical coefficients which appear in the expressions for A and B , for space groups with centred lattices: while only the order of the point group need be considered in connection with the Fourier expansion of the electron density (see above), the multiplicity of the Bravais lattice must of course appear in (1.4.2.19) and (1.4.2.20).

Analogous functional forms are arrived at by considerations of symmetry in direct and reciprocal spaces. These quantities are therefore convenient representations of crystallographic symmetry in its interaction with the diffraction experiment and have been indispensable in all of the early crystallographic computing related to structure determination. Their applications to modern crystallographic computing have been largely superseded by fast Fourier techniques, in reciprocal space, and by direct use of matrix and vector representations of space-group operators, in direct space, especially in cases of low space-group symmetry. It should be noted, however, that the degree of simplification of the trigonometric structure factors generally increases with increasing symmetry (see, *e.g.*, Section 1.4.3), and the gain of computing efficiency becomes significant when problems involving high symmetries are treated with this 'old-fashioned' tool. Analytic expressions for the trigonometric structure factors are of course indispensable in studies in which the knowledge of the functional form of the structure factor is required [*e.g.* in theories of structure-factor statistics and direct methods of phase determination (see Chapters 2.1 and 2.2)].

Equations (1.4.2.19) and (1.4.2.20) are simple but their expansion and simplification for all the space groups and relevant hkl subsets can be an extremely tedious undertaking when carried out in the conventional manner. As shown below, this process has been automated by a suitable combination of symbolic and numeric high-level programming procedures.

1.4.3. Structure-factor tables

1.4.3.1. Some general remarks

This section is a revised version of the structure-factor tables contained in Sections 4.5 through 4.7 of Volume I (*ITI*, 1952). As in the previous edition, it is intended to present a comprehensive list of explicit expressions for the real and the imaginary parts of the trigonometric structure factor, for all the 17 plane groups and the 230 space groups, and for the hkl subsets for which the trigonometric structure factor assumes different functional forms. The tables given here are also confined to the case of general Wyckoff positions (*ITI*, 1952). However, the expressions are presented in a much more concise symbolic form and are amenable to computation just like the explicit trigonometric expressions in Volume I (*ITI*, 1952). The present tabulation is based on equations (1.4.2.19) and (1.4.2.20), *i.e.* the numerical coefficients in A and B which appear in Tables A1.4.3.1–A1.4.3.7 in Appendix 1.4.3 are appropriate to space-group-specific structure-factor formulae. The functional form of A and B is, however, the same when applied to Fourier summations (see Section 1.4.2.3).

1.4.3.2. Preparation of the structure-factor tables

The lists of the coordinates of the general equivalent positions, presented in *IT A* (1983), as well as in earlier editions of the *Tables*, are sufficient for the expansion of the summations in (1.4.2.19) and (1.4.2.20) and the simplification of the resulting expressions can be performed using straightforward algebra and trigonometry (see, *e.g.*, *ITI*, 1952). As mentioned above, the preparation of the present structure-factor tables has been automated and its stages can be summarized as follows:

- (i) Generation of the coordinates of the general positions, starting from a computer-adapted space-group symbol (Shmueli, 1984).
- (ii) Formation of the scalar products, appearing in (1.4.2.19) and (1.4.2.20), and their separation into components depending on the rotation and translation parts of the space-group operations:

$$\mathbf{h}^T(\mathbf{P}_s, \mathbf{t}_s)\mathbf{r} = \mathbf{h}^T\mathbf{P}_s\mathbf{r} + \mathbf{h}^T\mathbf{t}_s \quad (1.4.3.1)$$

for the space groups which are not associated with a unique axis; the left-hand side of (1.4.3.1) is separated into contributions of the relevant plane group and unique axis for the remaining space groups.

- (iii) Analysis of the translation-dependent parts of the scalar products and automatic determination of all the parities of hkl for which A and B must be computed and simplified.

- (iv) Expansion of equations (1.4.2.19) and (1.4.2.20) and their reduction to trigonometric expressions comparable to those given in the structure-factor tables in Volume I of *IT* (1952).

- (v) Representation of the results in terms of a small number of building blocks, of which the expressions were found to be composed. These representations are described in Section 1.4.3.3.

All the stages outlined above were carried out with suitably designed computer programs, written in numerically and symbolically oriented languages. A brief summary of the underlying algorithms is presented in Appendix 1.4.1. The computer-adapted space-group symbols used in these computations are described in Section A1.4.2.2 and presented in Table A1.4.2.1.

1.4.3.3. Symbolic representation of A and B

We shall first discuss the symbols for the space groups that are not associated with a unique axis. These comprise the triclinic, orthorhombic and cubic space groups. The symbols are also used for the seven rhombohedral space groups which are referred to rhombohedral axes (*ITI*, 1952; *IT A*, 1983).

The abbreviation of triple products of trigonometric functions such as, *e.g.*, denoting $\cos(2\pi hx) \sin(2\pi ky) \cos(2\pi lz)$ by csc , is well known (*ITI*, 1952), and can be conveniently used in representing A and B for triclinic and orthorhombic space groups. However, the simplified expressions for A and B in space groups of higher symmetry also possess a high degree of regularity, as is apparent from an examination of the structure-factor tables in Volume I (*ITI*, 1952), and as confirmed by the preparation of the present tables. An example, illustrating this for the cubic system, is given below.

The trigonometric structure factor for the space group $Pm\bar{3}$ (No. 200) is given by

$$A = 8[\cos(2\pi hx) \cos(2\pi ky) \cos(2\pi lz) + \cos(2\pi hy) \cos(2\pi kz) \cos(2\pi lx) + \cos(2\pi hz) \cos(2\pi kx) \cos(2\pi ly)], \quad (1.4.3.2)$$

and the sum of the above nine-function block and the following one:

$$8[\cos(2\pi hx) \cos(2\pi kz) \cos(2\pi ly) + \cos(2\pi hz) \cos(2\pi ky) \cos(2\pi lx) + \cos(2\pi hy) \cos(2\pi kx) \cos(2\pi lz)] \quad (1.4.3.3)$$

is the trigonometric structure factor for the space group $Pm\bar{3}m$ (No. 221, *ITI*, 1952, *IT A*, 1983). It is obvious that the only difference between the nine-function blocks in (1.4.3.2) and (1.4.3.3) is that the permutation of the coordinates xyz is *cyclic* or *even* in (1.4.3.2), while it is *non-cyclic* or *odd* in (1.4.3.3).

It was observed during the generation of the present tables that the expressions for A and B for all the cubic space groups, and all the relevant hkl subsets, can be represented in terms of such 'even' and 'odd' nine-function blocks. Moreover, it was found that the order of the trigonometric functions in each such block remains the same in

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each of its three terms (triple products). This is not surprising since each of the above space groups contains threefold axes of rotation along [111] and related directions, and such permutations of xyz for fixed hkl (or *vice versa*) are expected. It was therefore possible to introduce two permutation operators and represent A and B in terms of the following two basic blocks:

$$\begin{aligned} \text{Epqr} = & p(2\pi hx)q(2\pi ky)r(2\pi lz) + p(2\pi hy)q(2\pi kz)r(2\pi lx) \\ & + p(2\pi hz)q(2\pi kx)r(2\pi ly) \end{aligned} \quad (1.4.3.4)$$

and

$$\begin{aligned} \text{Opqr} = & p(2\pi hx)q(2\pi kz)r(2\pi ly) + p(2\pi hz)q(2\pi ky)r(2\pi lx) \\ & + p(2\pi hy)q(2\pi kx)r(2\pi lz), \end{aligned} \quad (1.4.3.5)$$

where each of p , q and r can be a sine or a cosine, and appears at the same position in each of the three terms of a block. The capital prefixes E and O were chosen to represent even and odd permutations of the coordinates xyz , respectively.

For example, the trigonometric structure factor for the space group $Pa\bar{3}$ (No. 205, *IT* I, 1952, *IT* A, 1983) can now be tabulated as follows:

A	B	$h+k$	$k+l$	$h+l$
8Eccc	0	even	even	even
– 8Ecsc	0	even	odd	odd
– 8Escs	0	odd	even	odd
– 8Essc	0	odd	odd	even

(*cf.* Table A1.4.3.7), where the sines and cosines are abbreviated by s and c , respectively. It is interesting to note that the only maximal non-isomorphic subgroup of $Pa\bar{3}$, not containing a threefold axis, is the orthorhombic $Pbca$ (see *IT* A, 1983, p. 621), and this group-subgroup relationship is reflected in the functional forms of the trigonometric structure factors; the representation of A and B for $Pbca$ is in fact analogous to that of $Pa\bar{3}$, including the parities of hkl and the corresponding forms of the triple products, except that the prefix E – associated with the threefold rotation – is absent from $Pbca$. The expression for A for the space group $Pm\bar{3}m$ [the sum of (1.4.3.2) and (1.4.3.3)] now simply reads: $A = 8(\text{Eccc} + \text{Occc})$.

As pointed out above, the permutation operators also apply to rhombohedral space groups that are referred to rhombohedral axes (Table A1.4.3.6), and the corresponding expressions for $R\bar{3}$ and $R\bar{3}$ bear the same relationship to those for $P\bar{1}$ and $P\bar{1}$ (Table A1.4.3.2), respectively, as that shown above for the related $Pa\bar{3}$ and $Pbca$.

When in any given standard space-group setting one of the coordinate axes is parallel to a unique axis, the point-group rotation matrices can be partitioned into 2×2 and 1×1 diagonal blocks, the former corresponding to an operation of the plane group resulting from the projection of the space group down the unique axis. If, for example, the unique axis is parallel to c , we can decompose the scalar product in (1.4.2.19) and (1.4.2.20) as follows:

$$\begin{aligned} \mathbf{h}^T(\mathbf{P}_s \mathbf{r} + \mathbf{t}_s) = & (h \ k) \left[\begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \end{pmatrix} \right] \\ & + l(P_{33}z + t_3), \end{aligned} \quad (1.4.3.6)$$

where the first scalar product on the right-hand side of (1.4.3.6) contains the contribution of a plane group and the second product is the contribution of the unique axis itself. The above decomposition often leads to a convenient factorization of A and B , and is applicable to monoclinic, tetragonal and hexagonal families, the latter including rhombohedral space groups that are referred to hexagonal axes.

The symbols used in Tables A1.4.3.3, A1.4.3.5 and A1.4.3.6 are based on such decompositions. In those few cases where explicit

expressions must be given we make use of the convention of replacing $\cos(2\pi u)$ by $c(u)$ and $\sin(2\pi u)$ by $s(u)$. For example, $\cos[2\pi(hy + kx)]$ etc. is given as $c(hy + kx)$ etc. The symbols are defined below.

Monoclinic space groups (Table A1.4.3.3)

The following symbols are used in this system:

$$\begin{aligned} c(hl) &= \cos[2\pi(hx + lz)], & c(hk) &= \cos[2\pi(hx + ky)] \\ s(hl) &= \sin[2\pi(hx + lz)], & s(hk) &= \sin[2\pi(hx + ky)] \end{aligned} \quad (1.4.3.7)$$

so that any expression for A or B in the monoclinic system has the form $Kp(hl)q(ky)$ or $Kp(hk)q(lz)$ for the second or first setting, respectively, where p and q can each be a sine or a cosine and K is a numerical constant.

Tetragonal space groups (Table A1.4.3.5)

The most frequently occurring expressions in the summations for A and B in this system are of the form

$$P(pq) = p(2\pi hx)q(2\pi ky) + p(2\pi kx)q(2\pi hy) \quad (1.4.3.8)$$

and

$$M(pq) = p(2\pi hx)q(2\pi ky) - p(2\pi kx)q(2\pi hy), \quad (1.4.3.9)$$

where p and q can each be a sine or a cosine. These are typical contributions related to square plane groups.

Trigonal and hexagonal space groups (Table A1.4.3.6)

The contributions of plane hexagonal space groups to the first term in (1.4.3.6) are

$$\begin{aligned} p_1 &= hx + ky, & p_2 &= kx + iy, & p_3 &= ix + hy, \\ q_1 &= kx + hy, & q_2 &= hx + iy, & q_3 &= ix + ky, \end{aligned} \quad (1.4.3.10)$$

where $i = -h - k$ (*IT* I, 1952). The symbols which represent the frequently occurring expressions in this family, and given in terms of (1.4.3.10), are

$$\begin{aligned} C(hki) &= \cos(2\pi p_1) + \cos(2\pi p_2) + \cos(2\pi p_3) \\ C(khi) &= \cos(2\pi q_1) + \cos(2\pi q_2) + \cos(2\pi q_3) \\ S(hki) &= \sin(2\pi p_1) + \sin(2\pi p_2) + \sin(2\pi p_3) \\ S(khi) &= \sin(2\pi q_1) + \sin(2\pi q_2) + \sin(2\pi q_3) \end{aligned} \quad (1.4.3.11)$$

and these quite often appear as the following sums and differences:

$$\begin{aligned} \text{PH(cc)} &= C(hki) + C(khi), & \text{PH(ss)} &= S(hki) + S(khi) \\ \text{MH(cc)} &= C(hki) - C(khi), & \text{MH(ss)} &= S(hki) - S(khi). \end{aligned} \quad (1.4.3.12)$$

The symbols defined in this section are briefly redefined in the appropriate tables, which also contain the conditions for vanishing symbols.

1.4.3.4. Arrangement of the tables

The expressions for A and B are usually presented in terms of the short symbols defined above for all the representations of the plane groups and space groups given in Volume A (*IT* A, 1983), and are fully consistent with the unit-cell choices and space-group origins employed in that volume. The tables are arranged by crystal families and the expressions appear in the order of the appearance of the corresponding plane and space groups in the space-group tables in *IT* A (1983).

The main items in a table entry, not necessarily in the following order, are: (i) the conventional space-group number, (ii) the short Hermann–Mauguin space-group symbol, (iii) brief remarks on the choice of the space-group origin and setting, where appropriate, (iv) the real (A) and imaginary (B) parts of the trigonometric structure factor, and (v) the parity of the hkl subset to which the expressions

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for A and B pertain. Full space-group symbols are given in the monoclinic system only, since they are indispensable for the recognition of the settings and glide planes appearing in the various representations of monoclinic space groups given in *IT A* (1983).

1.4.4. Symmetry in reciprocal space: space-group tables

1.4.4.1. Introduction

The purpose of this section, and the accompanying table, is to provide a representation of the 230 three-dimensional crystallographic space groups in terms of two fundamental quantities that characterize a weighted reciprocal lattice: (i) coordinates of point-symmetry-related points in the reciprocal lattice, and (ii) phase shifts of the weight functions that are associated with the translation parts of the various space-group operations. Table A1.4.4.1 in Appendix 1.4.4 collects the above information for all the space-group settings which are listed in *IT A* (1983) for the same choice of the space-group origins and following the same numbering scheme used in that volume. Table A1.4.4.1 was generated by computer using the space-group algorithm described by Shmueli (1984) and the space-group symbols given in Table A1.4.2.1 in Appendix 1.4.2. It is shown in a later part of this section that Table A1.4.4.1 can also be regarded as a table of symmetry groups in Fourier space, in the Bienenstock–Ewald (1962) sense which was mentioned in Section 1.4.1. The section is concluded with a brief description of the correspondence between Bravais-lattice types in direct and reciprocal spaces.

1.4.4.2. Arrangement of the space-group tables

Table A1.4.4.1 is subdivided into point-group sections and space-group subsections, as outlined below.

(i) *The point-group heading.* This heading contains a short Hermann–Mauguin symbol of a point group, the crystal system and the symbol of the Laue group with which the point group is associated. Each point-group heading is followed by the set of space groups which are isomorphic to the point group indicated, the set being enclosed within a box.

(ii) *The space-group heading.* This heading contains, for each space group listed in Volume A (*IT A*, 1983), the short Hermann–Mauguin symbol of the space group, its conventional space-group number and (in parentheses) the serial number of its representation in Volume A; this is also the serial number of the explicit space-group symbol in Table A1.4.2.1 from which the entry was derived. Additional items are full space-group symbols, given only for the monoclinic space groups in their settings that are given in Volume A (*IT*, 1983), and self-explanatory comments as required.

(iii) *The table entry.* In the context of the analysis in Section 1.4.2.2, the format of a table entry is: $\mathbf{h}^T \mathbf{P}_n : -\mathbf{h}^T \mathbf{t}_n$, where $(\mathbf{P}_n, \mathbf{t}_n)$ is the n th space-group operator, and the phase shift $\mathbf{h}^T \mathbf{t}_n$ is expressed in units of 2π [see equations (1.4.2.3) and (1.4.2.5)]. More explicitly, the general format of a table entry is

$$(n) h_n k_n l_n : -p_n q_n r_n / m. \quad (1.4.4.1)$$

In (1.4.4.1), n is the serial number of the space-group operation to which this entry pertains and is the same as the number of the general Wyckoff position generated by this operation and given in *IT A* (1983) for the space group appearing in the space-group heading. The first part of an entry, $h_n k_n l_n$, contains the coordinates of the reciprocal-lattice vector that was generated from the reference vector (hkl) by the rotation part of the n th space-group operation. These rotation parts of the table entries, for a given space group, thus constitute the set of reciprocal-lattice points that are generated by the corresponding point group (*not Laue group*). The second part of an entry is an abbreviation of the phase shift which is associated with the n th operation and thus

$$-p_n q_n r_n / m \text{ denotes } -2\pi(hp_n + kq_n + lr_n)/m, \quad (1.4.4.2)$$

where the fractions p_n/m , q_n/m and r_n/m are the components of the translation part $\mathbf{t}_n$ of the n th space-group operation. The phase-shift part of an entry is given only if $(p_n q_n r_n)$ is *not* a vector in the direct lattice, since such a vector would give rise to a trivial phase shift (an integer multiple of 2π).

1.4.4.3. Effect of direct-space transformations

The phase shifts given in Table A1.4.4.1 depend on the translation parts of the space-group operations and these translations are determined, all or in part, by the choice of the space-group origin. It is a fairly easy matter to find the phase shifts that correspond to a given shift of the space-group origin in direct space, directly from Table A1.4.4.1. Moreover, it is also possible to modify the table entries so that a more general transformation, including a change of crystal axes as well as a shift of the space-group origin, can be directly accounted for. We employ here the frequently used concise notation due to Seitz (1935) (see also *IT A*, 1983).

Let the direct-space transformation be given by

$$\mathbf{r}_{\text{new}} = \mathbf{T} \mathbf{r}_{\text{old}} + \mathbf{v}, \quad (1.4.4.3)$$

where $\mathbf{T}$ is a non-singular 3×3 matrix describing the change of the coordinate system and $\mathbf{v}$ is an origin-shift vector. The components of $\mathbf{T}$ and $\mathbf{v}$ are referred to the old system, and $\mathbf{r}_{\text{new}}$ ($\mathbf{r}_{\text{old}}$) is the position vector of a point in the crystal, referred to the new (old) system, respectively. If we denote a space-group operation referred to the new and old systems by $(\mathbf{P}_{\text{new}}, \mathbf{t}_{\text{new}})$ and $(\mathbf{P}_{\text{old}}, \mathbf{t}_{\text{old}})$, respectively, we have

$$(\mathbf{P}_{\text{new}}, \mathbf{t}_{\text{new}}) = (\mathbf{T}, \mathbf{v})(\mathbf{P}_{\text{old}}, \mathbf{t}_{\text{old}})(\mathbf{T}, \mathbf{v})^{-1} \quad (1.4.4.4)$$

$$= (\mathbf{T} \mathbf{P}_{\text{old}} \mathbf{T}^{-1}, \mathbf{v} - \mathbf{T} \mathbf{P}_{\text{old}} \mathbf{T}^{-1} \mathbf{v} + \mathbf{T} \mathbf{t}_{\text{old}}). \quad (1.4.4.5)$$

It follows from (1.4.4.2) and (1.4.4.5) that if the old entry of Table A1.4.4.1 is given by

$$(n) \mathbf{h}^T \mathbf{P} : -\mathbf{h}^T \mathbf{t},$$

the transformed entry becomes

$$(n) \mathbf{h}^T \mathbf{T} \mathbf{P} \mathbf{T}^{-1} : \mathbf{h}^T \mathbf{T} \mathbf{P} \mathbf{T}^{-1} \mathbf{v} - \mathbf{h}^T \mathbf{v} - \mathbf{h}^T \mathbf{T} \mathbf{t}, \quad (1.4.4.6)$$

and in the important special cases of a pure change of setting ($\mathbf{v} = 0$) or a pure shift of the space-group origin ($\mathbf{T}$ is the unit matrix $\mathbf{I}$), (1.4.4.6) reduces to

$$(n) \mathbf{h}^T \mathbf{T} \mathbf{P} \mathbf{T}^{-1} : -\mathbf{h}^T \mathbf{T} \mathbf{t} \quad (1.4.4.7)$$

or

$$(n) \mathbf{h}^T \mathbf{P} : \mathbf{h}^T \mathbf{P} \mathbf{v} - \mathbf{h}^T \mathbf{v} - \mathbf{h}^T \mathbf{t}, \quad (1.4.4.8)$$

respectively. The rotation matrices $\mathbf{P}$ are readily obtained by visual or programmed inspection of the old entries: if, for example, $\mathbf{h}^T \mathbf{P}$ is $kh\bar{l}$, we must have $P_{21} = 1$, $P_{12} = 1$ and $P_{33} = 1$, the remaining P_{ij} 's being equal to zero. Similarly, if $\mathbf{h}^T \mathbf{P}$ is kil , where $i = -h - k$, we have

$$(kil) = (k, -h - k, l) = (hkl) \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The rotation matrices can also be obtained by reference to Chapter 7 and Tables 11.2 and 11.3 in Volume A (*IT A*, 1983).

As an example, consider the phase shifts corresponding to the operation No. (16) of the space group $P4/nmm$ (No. 129) in its two origins given in Volume A (*IT A*, 1983). For an Origin 2-to-Origin 1 transformation we find there $\mathbf{v} = (\frac{1}{4}, -\frac{1}{4}, 0)$ and the old Origin 2

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entry in Table A1.4.4.1 is (16) khl ($\mathbf{t}$ is zero). The appropriate entry for the Origin 1 description of this operation should therefore be $\mathbf{h}^T \mathbf{P} \mathbf{v} - \mathbf{h}^T \mathbf{v} = k/4 - h/4 - h/4 + k/4 = -h/2 + k/2$, as given by (1.4.4.8), or $-(h+k)/2$ if a trivial shift of 2π is subtracted. The (new) Origin 1 entry thus becomes: (16) khl : $-110/2$, as listed in Table A1.4.4.1.

1.4.4.4. Symmetry in Fourier space

As shown below, Table A1.4.4.1 can also be regarded as a collection of the general equivalent positions of the symmetry groups of Fourier space, in the sense of the treatment by Bienenstock & Ewald (1962). This interpretation of the table is, however, restricted to the underlying periodic function being real and positive (see the latter reference). The symmetry formalism can be treated with the aid of the original 4×4 matrix notation, but it appears that a concise Seitz-type notation suits better the present introductory interpretation.

The symmetry dependence of the fundamental relationship (1.4.2.5)

$$\varphi(\mathbf{h}^T \mathbf{P}_n) = \varphi(\mathbf{h}) - 2\pi \mathbf{h}^T \mathbf{t}_n$$

is given by a table entry of the form: $(n) \mathbf{h}^T \mathbf{P} : -\mathbf{h}^T \mathbf{t}$, where the phase shift is given in units of 2π , and the structure-dependent phase $\varphi(\mathbf{h})$ is omitted. Defining a combination law analogous to Seitz's product of two operators of affine transformation:

$$[\mathbf{a}^T : b](\mathbf{R}, \mathbf{r}) = [\mathbf{a}^T \mathbf{R} : \mathbf{a}^T \mathbf{r} + b], \quad (1.4.4.9)$$

where $\mathbf{R}$ is a 3×3 matrix, $\mathbf{a}^T$ is a row vector, $\mathbf{r}$ is a column vector and b is a scalar, we can write the general form of a table entry as

$$[\mathbf{h}^T : \delta](\mathbf{P}, -\mathbf{t}) = [\mathbf{h}^T \mathbf{P} : -\mathbf{h}^T \mathbf{t} + \delta], \quad (1.4.4.10)$$

where δ is a constant phase shift which we take as zero. The positions $[\mathbf{h}^T : 0]$ and $[\mathbf{h}^T \mathbf{P} : -\mathbf{h}^T \mathbf{t}]$ are now related by the operation $(\mathbf{P}, -\mathbf{t})$ via the combination law (1.4.4.9), which is a shorthand transcription of the 4×4 matrix notation of Bienenstock & Ewald (1962), with the appropriate sign of $\mathbf{t}$.

Let us evaluate the result of a successive application of two such operators, say $(\mathbf{P}, -\mathbf{t})$ and $(\mathbf{Q}, -\mathbf{v})$ to the reference position $[\mathbf{h}^T : 0]$ in Fourier space:

$$\begin{aligned} [\mathbf{h}^T : 0](\mathbf{P}, -\mathbf{t})(\mathbf{Q}, -\mathbf{v}) &= [\mathbf{h}^T : 0](\mathbf{PQ}, -\mathbf{Pv} - \mathbf{t}) \\ &= [\mathbf{h}^T \mathbf{PQ} : -\mathbf{h}^T \mathbf{Pv} - \mathbf{h}^T \mathbf{t}], \end{aligned} \quad (1.4.4.11)$$

and perform an inverse operation:

$$\begin{aligned} [\mathbf{h}^T \mathbf{P} : -\mathbf{h}^T \mathbf{t}](\mathbf{P}, -\mathbf{t})^{-1} &= [\mathbf{h}^T \mathbf{P} : -\mathbf{h}^T \mathbf{t}](\mathbf{P}^{-1}, \mathbf{P}^{-1} \mathbf{t}) \\ &= [\mathbf{h}^T \mathbf{P} \mathbf{P}^{-1} : \mathbf{h}^T \mathbf{P} \mathbf{P}^{-1} \mathbf{t} - \mathbf{h}^T \mathbf{t}] \\ &= [\mathbf{h}^T : 0]. \end{aligned} \quad (1.4.4.12)$$

These equations confirm the validity of the shorthand notation (1.4.4.9) and illustrate the group nature of the operators $(\mathbf{P}, -\mathbf{t})$ in the present context.

Following Bienenstock & Ewald, the operators $(\mathbf{P}, -\mathbf{t})$ are symmetry operators that act on the positions $[\mathbf{h}^T : 0]$ in Fourier space, provided they satisfy the following requirements: (i) the application of such an operator leaves the magnitude of the (generally) complex Fourier coefficient unchanged, and (ii) after g successive applications of an operator, where g is the order of its rotation part, the phase remains unchanged up to a shift by an integer multiple of 2π (a trivial phase shift, corresponding to a translation by a lattice vector in direct space).

If our function is the electron density in the crystal, the first requirement is obviously satisfied since $|F(\mathbf{h})| = |F(\mathbf{h}^T \mathbf{P})|$, where

F is the structure factor [cf. equation (1.4.2.4)]. In order to make use of the second requirement in deriving permissible symmetry operators on Fourier space, all the relevant transformations, *i.e.* those which have rotation operators of the orders 1, 2, 3, 4 and 6, must be individually examined. A comprehensive example, covering most of the tetragonal system, can be found in Bienenstock & Ewald (1962).

It is of interest to illustrate the above process for a simple particular instance. Consider an operation, the rotation part of which involves a mirror plane, and assume that it is associated with the monoclinic system, in the second setting (unique axis b). We denote the operator by $(\mathbf{m}, -\mathbf{u})$, where $\mathbf{u}^T = (uvw)$, and the permissible values of u, v and w are to be determined. The operation is of order 2, and according to requirement (ii) above we have to evaluate

$$\begin{aligned} [\mathbf{h}^T : 0](\mathbf{m}, -\mathbf{u})^2 &= [\mathbf{h}^T : 0](\mathbf{I}, -\mathbf{mu} - \mathbf{u}) \\ &= [\mathbf{h}^T : -\mathbf{h}^T (\mathbf{m} + \mathbf{I}) \mathbf{u}] \\ &= [hkl : -2(hu + lw)], \end{aligned} \quad (1.4.4.13)$$

where

$$\mathbf{m} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

is the matrix representing the operation of reflection and $\mathbf{I}$ is the unit matrix. For $(\mathbf{m}, -\mathbf{u})$ to be an admissible symmetry operator, the phase-shift part of (1.4.4.13), *i.e.* $-2(hu + lw)$, must be an integer (multiple of 2π). The smallest non-negative values of u and w which satisfy this are the pairs: $u = w = 0$, $u = \frac{1}{2}$ and $w = 0$, $u = 0$ and $w = \frac{1}{2}$, and $u = w = \frac{1}{2}$. We have thus obtained four symmetry operators in Fourier space, which are identical (except for the sign of their translational parts) to those of the direct-space monoclinic mirror and glide-plane operations. The fact that the component v cancels out simply means that an arbitrary component of the phase shift can be added along the b^* axis; this is concurrent with arbitrary direct-space translations that appear in the characterization of individual types of space-group operations [see *e.g.* Koch & Fischer (1983)].

Each of the 230 space groups, which leaves invariant a (real and non-negative) function with the periodicity of the crystal, thus has its counterpart which determines the symmetry of the Fourier expansion coefficients of this function, with equivalent positions given in Table A1.4.4.1.

1.4.4.5. Relationships between direct and reciprocal Bravais lattices

Centred Bravais lattices in crystal space give rise to systematic absences of certain classes of reflections (IT I, 1952; IT A, 1983) and the corresponding points in the reciprocal lattice have accordingly zero weights. These absences are periodic in reciprocal space and their 'removal' from the reciprocal lattice results in a lattice which – like the direct one – must belong to one of the fourteen Bravais lattice types. This must be so since the point group of a crystal leaves its lattice – and also the associated reciprocal lattice – unchanged. The magnitudes of the structure factors (the weight functions) are also invariant under the operation of this point group.

The correspondence between the types of centring in direct and reciprocal lattices is given in Table 1.4.4.1.

Notes:

(i) The vectors $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$, appearing in the definition of the multiple unit cell in the reciprocal lattice, define this lattice *prior to*

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Table 1.4.4.1. Correspondence between types of centring in direct and reciprocal lattices

Direct lattice		Reciprocal lattice		
Lattice type(s)	Centring translations	Lattice type(s)	Restriction on hkl	Multiple unit cell
P, R		P, R		$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$
A	$0, \frac{1}{2}, \frac{1}{2}$	A	$k + l = 2n$	$\mathbf{a}^*, 2\mathbf{b}^*, 2\mathbf{c}^*$
B	$\frac{1}{2}, 0, \frac{1}{2}$	B	$h + l = 2n$	$2\mathbf{a}^*, \mathbf{b}^*, 2\mathbf{c}^*$
C	$\frac{1}{2}, \frac{1}{2}, 0$	C	$h + k = 2n$	$2\mathbf{a}^*, 2\mathbf{b}^*, \mathbf{c}^*$
I	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	F	$h + k + l = 2n$	$2\mathbf{a}^*, 2\mathbf{b}^*, 2\mathbf{c}^*$
F	$0, \frac{1}{2}, \frac{1}{2}$ $\frac{1}{2}, 0, \frac{1}{2}$ $\frac{1}{2}, \frac{1}{2}, 0$	I	$k + l = 2n$ $h + l = 2n$ $h + k = 2n$	$2\mathbf{a}^*, 2\mathbf{b}^*, 2\mathbf{c}^*$
R_{hex}	$\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$	R_{hex}	$-h + k + l = 3n$	$3\mathbf{a}^*, 3\mathbf{b}^*, 3\mathbf{c}^*$

the removal of lattice points with zero weights (absences). All the restrictions on hkl pertain to indexing on $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$.

(ii) The centring type of the reciprocal lattice refers to the multiple unit cell given in the table.

(iii) The centring type denoted by R_{hex} is a representation of the rhombohedral lattice R by a triple hexagonal unit cell, in the obverse setting (IT I, 1952), i.e. according to the transformation

$$\begin{aligned}\mathbf{a} &= \mathbf{a}_R - \mathbf{b}_R \\ \mathbf{b} &= \mathbf{b}_R - \mathbf{c}_R \\ \mathbf{c} &= \mathbf{a}_R + \mathbf{b}_R + \mathbf{c}_R,\end{aligned}\tag{1.4.4.14}$$

where $\mathbf{a}_R$, $\mathbf{b}_R$ and $\mathbf{c}_R$ pertain to a primitive unit cell in the rhombohedral lattice R .

The corresponding multiple reciprocal cell, with centring denoted by R_{hex} , contains nine lattice points with coordinates 000, 021, 012, 101, 202, 110, 220, 211 and 122 – indexed on the usual reciprocal to the triple hexagonal unit cell defined by (1.4.4.14). Detailed derivations of these correspondences are given by Buerger (1942), and an elementary proof of the reciprocity of I and F lattices can be found, e.g., in pamphlet No. 4 of the Commission on Crystallographic Teaching (Authier, 1981). Intuitive proofs follow directly from the restrictions on hkl , given in Table 1.4.4.1.

Appendix 1.4.1.

Comments on the preparation and usage of the tables

(U. SHMUELI)

The straightforward but rather extensive calculations and text processing related to Tables A1.4.3.1 through A1.4.3.7 and Table A1.4.4.1 in Appendices 1.4.3 and 1.4.4, respectively, were performed with the aid of a combination of FORTRAN and REDUCE (Hearn, 1973) programs, designed so as to enable the author to produce the table entries directly from a space-group symbol and with a minimum amount of intermediate manual intervention. The first stage of the calculation, the generation of a space group (coordinates of the equivalent positions), was accomplished with the program *SPGRGEN*, the algorithm of

which was described in some detail elsewhere (Shmueli, 1984). A complete list of computer-adapted space-group symbols, processed by *SPGRGEN* and not given in the latter reference, is presented in Table A1.4.2.1 of Appendix 1.4.2.

The generation of the space group is followed by a construction of symbolic expressions for the scalar products $\mathbf{h}^T(\mathbf{Pr} + \mathbf{t})$; e.g. for position No. (13) in the space group $P4_132$ (No. 213, IT I, 1952, IT A, 1983), this scalar product is given by $h(\frac{3}{4} + y) + k(\frac{1}{4} + x) + l(\frac{1}{4} - z)$. The construction of the various table entries consists of expanding the sines and cosines of these scalar products, performing the required summations, and simplifying the result where possible. The construction of the scalar products in a FORTRAN program is fairly easy and the extremely tedious trigonometric calculations required by equations (1.4.2.19) and (1.4.2.20) can be readily performed with the aid of one of several available computer-algebraic languages (for a review, see *Computers in the New Laboratory – a Nature Survey*, 1981); the REDUCE language was employed for the above purpose.

Since the REDUCE programs required for the summations in (1.4.2.19) and (1.4.2.20) for the various space groups were seen to have much in common, it was decided to construct a FORTRAN interface which would process the space-group input and prepare automatically REDUCE programs for the algebraic work. The least straightforward problem encountered during this work was the need to ‘convince’ the interface to generate hkl parity assignments which are appropriate to the space-group information input. This was solved for all the crystal families except the hexagonal by setting up a ‘basis’ of the form: $h/2, k/2, l/2, (k + l)/2, \dots, (h + k + l)/4$ and representing the translation parts of the scalar products, $\mathbf{h}^T\mathbf{t}$, as sums of such ‘basis functions’. A subsequent construction of an automatic parity routine proved to be easy and the interface could thus produce any number of REDUCE programs for the summations in (1.4.2.19) and (1.4.2.20) using a list of space-group symbols as the sole input. These included trigonal and hexagonal space groups with translation components of $\frac{1}{2}$. This approach seemed to be too awkward for some space groups containing threefold and sixfold screw axes, and these were treated individually.

There is little to say about the REDUCE programs, except that the output they generate is at the same level of trigonometric complexity as the expressions for A and B appearing in Volume I (IT I, 1952). This could have been improved by making use of the pattern-matching capabilities that are incorporated in REDUCE, but

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it was found more convenient to construct a FORTRAN interpreter which would detect in the REDUCE output the basic building blocks of the trigonometric structure factors (see Section 1.4.3.3) and perform the required transformations.

Tables A1.4.3.1–A1.4.3.7 were thus constructed with the aid of a chain composed of (i) a space-group generating routine, (ii) a FORTRAN interface, which processes the space-group input and ‘writes’ a complete REDUCE program, (iii) execution of the REDUCE program and (iv) a FORTRAN interpreter of the REDUCE output in terms of the abbreviated symbols to be used in the tables. The computation was at a ‘one-group-at-a-time’ basis and the automation of its repetition was performed by means of procedural constructs at the operating-system level. The construction of Table A1.4.4.1 involved only the preliminary stage of the processing of the space-group information by the FORTRAN interface. All the computations were carried out on a Cyber 170-855 at the Tel Aviv University Computation Center.

It is of some importance to comment on the recommended usage of the tables included in this chapter in automatic computations. If, for example, we wish to compute the expression: $A = -8(\text{Escs} + \text{Ossc})$, use can be made of the facility provided by most versions of FORTRAN of transferring subprogram names as parameters of a FUNCTION. We thus need only two FUNCTIONS for any calculation of A and B for a cubic space group, one FUNCTION for the block of even permutations of x , y and z :

```
FUNCTION E(P, Q, R)
EXTERNAL SIN, COS
COMMON/TSF/TPH, TPK, TPL, X, Y, Z
E = P(TPH * X) * Q(TPK * Y) * R(TPL * Z)
1 + P(TPH * Z) * Q(TPK * X) * R(TPL * Y)
2 + P(TPH * Y) * Q(TPK * Z) * R(TPL * X)
RETURN
END
```

where TPH, TPK and TPL denote $2\pi h$, $2\pi k$ and $2\pi l$, respectively, and a similar FUNCTION, say O(P,Q,R), for the block of odd permutations of x , y and z . The calling statement in the calling (sub)program can thus be:

$$A = -8 * (E(\text{SIN}, \text{COS}, \text{SIN}) + O(\text{SIN}, \text{SIN}, \text{COS})).$$

A small number of such FUNCTIONS suffices for all the space-group-specific computations that involve trigonometric structure factors.

Appendix 1.4.2.

Space-group symbols for numeric and symbolic computations

A1.4.2.1. Introduction (U. SHMUELI, S. R. HALL AND R. W. GROSSE-KUNSTLEVE)

This appendix lists two sets of computer-adapted space-group symbols which are implemented in existing crystallographic software and can be employed in the automated generation of space-group representations. The computer generation of space-group symmetry information is of well known importance in many

crystallographic calculations, numeric as well as symbolic. A prerequisite for a computer program that generates this information is a set of computer-adapted space-group symbols which are based on the generating elements of the space group to be derived. The sets of symbols to be presented are:

(i) *Explicit symbols*. These symbols are based on the classification of crystallographic point groups and space groups by Zachariasen (1945). These symbols are termed *explicit* because they contain in an explicit manner the rotation and translation parts of the space-group generators of the space group to be derived and used. These computer-adapted explicit symbols were proposed by Shmueli (1984), who also describes in detail their implementation in the program *SPGRGEN*. This program was used for the automatic preparation of the structure-factor tables for the 17 plane groups and 230 space groups, listed in Appendix 1.4.3, and the 230 space groups in reciprocal space, listed in Appendix 1.4.4. The explicit symbols presented in this appendix are adapted to the 306 representations of the 230 space groups as presented in *IT A* (1983) with regard to the standard settings and choice of space-group origins.

The symmetry-generating algorithm underlying the explicit symbols, and their definition, are given in Section A1.4.2.2 of this appendix and the explicit symbols are listed in Table A1.4.2.1.

(ii) *Hall symbols*. These symbols are based on the implied-origin notation of Hall (1981*a,b*), who also describes in detail the algorithm implemented in the program *SGNAME* (Hall, 1981*a*). In the first edition of *IT B* (1993), the term ‘concise space-group symbols’ was used for this notation. In recent years, however, the term ‘Hall symbols’ has come into use in symmetry papers (Altermatt & Brown, 1987; Grosse-Kunstleve, 1999), software applications (Hovmöller, 1992; Grosse-Kunstleve, 1995; Larine *et al.*, 1995; Dowty, 1997) and data-handling approaches (Bourne *et al.*, 1998). This term has therefore been adopted for the second edition.

The main difference in the definition of the Hall symbols between this edition and the first edition of *IT B* is the generalization of the origin-shift vector to a full change-of-basis matrix. The examples have been expanded to show how this matrix is applied. The notation has also been made more consistent, and a typographical error in a default axis direction has been corrected.* The lattice centring symbol ‘H’ has been added to Table A1.4.2.2. In addition, Hall symbols are now provided for 530 settings to include all settings from Table 4.3.1 of *IT A* (1983). Namely, all non-standard symbols for the monoclinic and orthorhombic space groups are included.

Some of the space-group symbols listed in Table A1.4.2.7 differ from those listed in Table B.6 (p. 119) of the first edition of *IT B*. This is because the symmetry of many space groups can be represented by more than one subset of ‘generator’ elements and these lead to different Hall symbols. The symbols listed in this edition have been selected after first sorting the symmetry elements into a strictly prescribed order based on the shape of their Seitz matrices, whereas those in Table B.6 were selected from symmetry elements in the order of *IT I* (1965). Software for selecting the Hall symbols listed in Table A1.4.2.7 is freely available (Hall, 1997). These symbols and their equivalents in the first edition of *IT B* will generate identical symmetry elements, but the former may be used as a reference table in a strict mapping procedure between different symmetry representations (Hall *et al.*, 2000).

The Hall symbols are defined in Section A1.4.2.3 of this appendix and are listed in Table A1.4.2.7.

* The correct default axis direction $\mathbf{a} - \mathbf{b}$ of an N preceded by 3 or 6 replaces $\mathbf{a} + \mathbf{b}$ on p. 117, right-hand column, line 4, in the first edition of *IT B*.

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A1.4.2.2. Explicit symbols (U. SHMUELI)

As shown elsewhere (Shmueli, 1984), the set of representative operators of a crystallographic space group [*i.e.* the set that is listed for each space group in the symmetry tables of *IT A* (1983) and automatically regenerated for the purpose of compiling the symmetry tables in the present chapter] may have one of the following forms:

$$\begin{aligned} &\{(\mathbf{Q}, \mathbf{u})\}, \\ &\{(\mathbf{Q}, \mathbf{u})\} \times \{(\mathbf{R}, \mathbf{v})\}, \quad \text{or} \\ &\{(\mathbf{P}, \mathbf{t})\} \times [\{(\mathbf{Q}, \mathbf{u})\} \times \{(\mathbf{R}, \mathbf{v})\}], \end{aligned} \quad (\text{A1.4.2.1})$$

where $\mathbf{P}$, $\mathbf{Q}$ and $\mathbf{R}$ are point-group operators, and $\mathbf{t}$, $\mathbf{u}$ and $\mathbf{v}$ are zero vectors or translations not belonging to the lattice-translations subgroup. Each of the forms in (A1.4.2.1), enclosed in braces, is evaluated as, *e.g.*,

$$\{(\mathbf{P}, \mathbf{t})\} = \{(\mathbf{I}, \mathbf{0}), (\mathbf{P}, \mathbf{t}), (\mathbf{P}, \mathbf{t})^2, \dots, (\mathbf{P}, \mathbf{t})^{g-1}\}, \quad (\text{A1.4.2.2})$$

where $\mathbf{I}$ is a unit operator and g is the order of the rotation operator $\mathbf{P}$ (*i.e.* $\mathbf{P}^g = \mathbf{I}$). The representative operations of the space group are evaluated by expanding the generators into cyclic groups, as in (A1.4.2.2), and forming, as needed, ordered products of the expanded groups as indicated in (A1.4.2.1) and explained in detail in the original article (Shmueli, 1984). The rotation and translation parts of the generators $(\mathbf{P}, \mathbf{t})$, $(\mathbf{Q}, \mathbf{u})$ and $(\mathbf{R}, \mathbf{v})$ presented here were adapted to the settings and choices of origin used in the main symmetry tables of *IT A* (1983).

The general structure of a three-generator symbol, corresponding to the last line of (A1.4.2.1), as represented in Table A1.4.2.1, is

$$\text{LSC}\$r_1\text{Pt}_1\text{t}_2\text{t}_3\$r_2\text{Qu}_1\text{u}_2\text{u}_3\$r_3\text{Rv}_1\text{v}_2\text{v}_3, \quad (\text{A1.4.2.3})$$

where

L – lattice type; can be P, A, B, C, I, F, or R. The symbol R is used only for the seven rhombohedral space groups in their representations in rhombohedral and hexagonal axes [obverse setting (*IT I*, 1952)].

S – crystal system; can be A (triclinic), M (monoclinic), O (orthorhombic), T (tetragonal), R (trigonal), H (hexagonal) or C (cubic).

C – status of centrosymmetry; can be C or N according as the space group is centrosymmetric or noncentrosymmetric, respectively.

\$ – this character is followed by six characters that define a generator of the space group.

r_i – indicator of the type of rotation that follows: r_i is P or I according as the rotation part of the i th generator is proper or improper, respectively.

P, Q, R – two-character symbols of matrix representations of the point-group rotation operators $\mathbf{P}$, $\mathbf{Q}$ and $\mathbf{R}$, respectively (see below).

$t_1t_2t_3, u_1u_2u_3, v_1v_2v_3$ – components of the translation parts of the generators, given in units of $\frac{1}{12}$; *e.g.* the translation part $(0 \frac{1}{2} \frac{3}{4})$ is given in Table A1.4.2.1 as 069. An exception: $(0 \ 0 \ \frac{5}{6})$ is denoted by 005 and not by 0010.

The two-character symbols for the matrices of rotation, which appear in the explicit space-group symbols in Table A1.4.2.1, are defined as follows:

$$\begin{aligned} 1A &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & 2A &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} & 2B &= \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \\ 2C &= \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} & 2D &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} & 2E &= \begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \\ 2F &= \begin{pmatrix} 1 & \bar{1} & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} & 2G &= \begin{pmatrix} 1 & 0 & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} & 3Q &= \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \\ 3C &= \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} & 4C &= \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & 6C &= \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \end{aligned}$$

where only matrices of proper rotation are given (and required), since the corresponding matrices of improper rotation are created by the program for appropriate value of the r_i indicator. The first character of a symbol is the order of the axis of rotation and the second character specifies its orientation: in terms of direct-space lattice vectors, we have

$$\begin{aligned} A &= [100], B = [010], C = [001], D = [110], \\ E &= [1\bar{1}0], F = [100], G = [210] \text{ and } Q = [111] \end{aligned}$$

for the standard orientations of the axes of rotation. Note that the axes 2F, 2G, 3C and 6C appear in trigonal and hexagonal space groups.

In the above scheme a space group is determined by one, two or at most three generators [see (A1.4.2.1)]. It should be pointed out that a convenient way of achieving a representation of the space group in any setting and relative to any origin is to start from the standard generators in Table A1.4.2.1 and let the computer program perform the appropriate transformation of the generators only, as in equations (1.4.4.4) and (1.4.4.5). The subsequent expansion of the transformed generators and the formation of the required products [see (A1.4.2.1) and (A1.4.2.2)] leads to the new representation of the space group.

In order to illustrate an explicit space-group symbol consider, for example, the symbol for the space group $Ia\bar{3}d$, as given in Table A1.4.2.1:

$$\text{ICC}\$I3Q000\$P4C393\$P2D933.$$

The first three characters tell us that the Bravais lattice of this space group is of type I, that the space group is centrosymmetric and that it belongs to the cubic system. We then see that the generators are (i) an improper threefold axis along $[111]$ ($I3Q$) with a zero translation part, (ii) a proper fourfold axis along $[001]$ ($P4C$) with translation part $(1/4, 3/4, 1/4)$ and (iii) a proper twofold axis along $[110]$ ($P2D$) with translation part $(3/4, 1/4, 1/4)$.

If we make use of the above-outlined interpretation of the explicit symbol (A1.4.2.3), the space-group symmetry transformations in direct space, corresponding to these three generators of the space group $Ia\bar{3}d$, become

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Table A1.4.2.1. *Explicit symbols*

No.	Short Hermann–Mauguin symbol	Comments	Explicit symbols	No.	Short Hermann–Mauguin symbol	Comments	Explicit symbols
1	$P1$		PAN\$P1A000	15	$C2/c$	$C12/c1$	CMC\$I1A000\$P2B006
2	$P\bar{1}$		PAC\$I1A000	15	$C2/c$	$A12/n1$	AMC\$I1A000\$P2B606
3	$P2$	$P121$	PMN\$P2B000	15	$C2/c$	$I12/a1$	IMC\$I1A000\$P2B600
3	$P2$	$P112$	PMN\$P2C000	15	$C2/c$	$A112/a$	AMC\$I1A000\$P2C600
4	$P2_1$	$P12_11$	PMN\$P2B060	15	$C2/c$	$B112/n$	BMC\$I1A000\$P2C660
4	$P2_1$	$P112_1$	PMN\$P2C006	15	$C2/c$	$I112/b$	IMC\$I1A000\$P2C060
5	$C2$	$C121$	CMN\$P2B000	16	$P222$		PON\$P2C000\$P2A000
5	$C2$	$A121$	AMN\$P2B000	17	$P222_1$		PON\$P2C006\$P2A000
5	$C2$	$I121$	IMN\$P2B000	18	$P2_12_12$		PON\$P2C000\$P2A660
5	$C2$	$A112$	AMN\$P2C000	19	$P2_12_12_1$		PON\$P2C606\$P2A660
5	$C2$	$B112$	BMN\$P2C000	20	$C222_1$		CON\$P2C006\$P2A000
5	$C2$	$I112$	IMN\$P2C000	21	$C222$		CON\$P2C000\$P2A000
6	Pm	$P1m1$	PMN\$I2B000	22	$F222$		FON\$P2C000\$P2A000
6	Pm	$P11m$	PMN\$I2C000	23	$I222$		ION\$P2C000\$P2A000
7	Pc	$P1c1$	PMN\$I2B006	24	$I2_12_12_1$		ION\$P2C606\$P2A660
7	Pc	$P1n1$	PMN\$I2B606	25	$Pmm2$		PON\$P2C000\$I2A000
7	Pc	$P1a1$	PMN\$I2B600	26	$Pmc2_1$		PON\$P2C006\$I2A000
7	Pc	$P11a$	PMN\$I2C600	27	$Pcc2$		PON\$P2C000\$I2A006
7	Pc	$P11n$	PMN\$I2C660	28	$Pma2$		PON\$P2C000\$I2A600
7	Pc	$P11b$	PMN\$I2C060	29	$Pca2_1$		PON\$P2C006\$I2A606
8	Cm	$C1m1$	CMN\$I2B000	30	$Pnc2$		PON\$P2C000\$I2A066
8	Cm	$A1m1$	AMN\$I2B000	31	$Pmn2_1$		PON\$P2C606\$I2A000
8	Cm	$I1m1$	IMN\$I2B000	32	$Pba2$		PON\$P2C000\$I2A660
8	Cm	$A11m$	AMN\$I2C000	33	$Pna2_1$		PON\$P2C006\$I2A666
8	Cm	$B11m$	BMN\$I2C000	34	$Pnn2$		PON\$P2C000\$I2A666
8	Cm	$I11m$	IMN\$I2C000	35	$Cmm2$		CON\$P2C000\$I2A000
9	Cc	$C1c1$	CMN\$I2B006	36	$Cmc2_1$		CON\$P2C006\$I2A000
9	Cc	$A1n1$	AMN\$I2B606	37	$Ccc2$		CON\$P2C000\$I2A006
9	Cc	$I1a1$	IMN\$I2B600	38	$Amm2$		AON\$P2C000\$I2A000
9	Cc	$A11a$	AMN\$I2C600	39	$Abm2$		AON\$P2C000\$I2A060
9	Cc	$B11n$	BMN\$I2C660	40	$Ama2$		AON\$P2C000\$I2A600
9	Cc	$I11b$	IMN\$I2C060	41	$Aba2$		AON\$P2C000\$I2A660
10	$P2/m$	$P12/m1$	PMC\$I1A000\$P2B000	42	$Fmm2$		FON\$P2C000\$I2A000
10	$P2/m$	$P112/m$	PMC\$I1A000\$P2C000	43	$Fdd2$		FON\$P2C000\$I2A333
11	$P2_1/m$	$P12_1/m1$	PMC\$I1A000\$P2B060	44	$Imm2$		ION\$P2C000\$I2A000
11	$P2_1/m$	$P112_1/m$	PMC\$I1A000\$P2C006	45	$Iba2$		ION\$P2C000\$I2A660
12	$C2/m$	$C12/m1$	CMC\$I1A000\$P2B000	46	$Ima2$		ION\$P2C000\$I2A600
12	$C2/m$	$A12/m1$	AMC\$I1A000\$P2B000	47	$Pmmm$		POC\$I1A000\$P2C000\$P2A000
12	$C2/m$	$I12/m1$	IMC\$I1A000\$P2B000	48	$Pnnn$	Origin 1	POC\$I1A666\$P2C000\$P2A000
12	$C2/m$	$A112/m$	AMC\$I1A000\$P2C000	48	$Pnnn$	Origin 2	POC\$I1A000\$P2C660\$P2A066
12	$C2/m$	$B112/m$	BMC\$I1A000\$P2C000	49	$Pccm$		POC\$I1A000\$P2C000\$P2A006
12	$C2/m$	$I112/m$	IMC\$I1A000\$P2C000	50	$Pban$	Origin 1	POC\$I1A660\$P2C000\$P2A000
13	$P2/c$	$P12/c1$	PMC\$I1A000\$P2B006	50	$Pban$	Origin 2	POC\$I1A000\$P2C660\$P2A060
13	$P2/c$	$P12/n1$	PMC\$I1A000\$P2B606	51	$Pmma$		POC\$I1A000\$P2C600\$P2A600
13	$P2/c$	$P12/a1$	PMC\$I1A000\$P2B600	52	$Pnna$		POC\$I1A000\$P2C600\$P2A066
13	$P2/c$	$P112/a$	PMC\$I1A000\$P2C600	53	$Pmna$		POC\$I1A000\$P2C606\$P2A000
13	$P2/c$	$P112/n$	PMC\$I1A000\$P2C660	54	$Pcca$		POC\$I1A000\$P2C600\$P2A606
13	$P2/c$	$P112/b$	PMC\$I1A000\$P2C060	55	$Pbam$		POC\$I1A000\$P2C000\$P2A660
14	$P2_1/c$	$P12_1/c1$	PMC\$I1A000\$P2B066	56	$Pccn$		POC\$I1A000\$P2C660\$P2A606
14	$P2_1/c$	$P12_1/n1$	PMC\$I1A000\$P2B666	57	$Pbcm$		POC\$I1A000\$P2C006\$P2A060
14	$P2_1/c$	$P12_1/a1$	PMC\$I1A000\$P2B660	58	$Pnnm$		POC\$I1A000\$P2C000\$P2A666
14	$P2_1/c$	$P112_1/a$	PMC\$I1A000\$P2C606	59	$Pmmn$	Origin 1	POC\$I1A660\$P2C000\$P2A660
14	$P2_1/c$	$P112_1/n$	PMC\$I1A000\$P2C666	59	$Pmmn$	Origin 2	POC\$I1A000\$P2C660\$P2A600
14	$P2_1/c$	$P112_1/b$	PMC\$I1A000\$P2C066	60	$Pbcn$		POC\$I1A000\$P2C666\$P2A660

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.2.1. *Explicit symbols (cont.)*

No.	Short Hermann–Mauguin symbol	Comments	Explicit symbols	No.	Short Hermann–Mauguin symbol	Comments	Explicit symbols
61	<i>Pbca</i>		POC\$I1A000\$P2C606\$P2A660	110	<i>I4₁cd</i>		ITN\$P4C063\$I2A660
62	<i>Pnma</i>		POC\$I1A000\$P2C606\$P2A666	111	<i>P4₂m</i>		PTN\$I4C000\$P2A000
63	<i>Cmcm</i>		COC\$I1A000\$P2C006\$P2A000	112	<i>P4₂c</i>		PTN\$I4C000\$P2A006
64	<i>Cmca</i>		COC\$I1A000\$P2C066\$P2A000	113	<i>P4₂₁m</i>		PTN\$I4C000\$P2A660
65	<i>Cmmm</i>		COC\$I1A000\$P2C000\$P2A000	114	<i>P4₂₁c</i>		PTN\$I4C000\$P2A666
66	<i>Cccm</i>		COC\$I1A000\$P2C000\$P2A006	115	<i>P4₂m2</i>		PTN\$I4C000\$P2D000
67	<i>Cmma</i>		COC\$I1A000\$P2C060\$P2A000	116	<i>P4₂c2</i>		PTN\$I4C000\$P2D006
68	<i>Ccca</i>	Origin 1	COC\$I1A066\$P2C660\$P2A660	117	<i>P4₂b2</i>		PTN\$I4C000\$P2D660
68	<i>Ccca</i>	Origin 2	COC\$I1A000\$P2C600\$P2A606	118	<i>P4₂n2</i>		PTN\$I4C000\$P2D666
69	<i>Fmmm</i>		FOC\$I1A000\$P2C000\$P2A000	119	<i>I4₂m2</i>		ITN\$I4C000\$P2D000
70	<i>Fddd</i>	Origin 1	FOC\$I1A333\$P2C000\$P2A000	120	<i>I4₂c2</i>		ITN\$I4C000\$P2D006
70	<i>Fddd</i>	Origin 2	FOC\$I1A000\$P2C990\$P2A099	121	<i>I4₂d</i>		ITN\$I4C000\$P2A000
71	<i>Immm</i>		IOC\$I1A000\$P2C000\$P2A000	122	<i>I4₂d</i>		ITN\$I4C000\$P2A609
72	<i>Ibam</i>		IOC\$I1A000\$P2C000\$P2A660	123	<i>P4₂/mmm</i>		PTC\$I1A000\$P4C000\$P2A000
73	<i>Ibca</i>		IOC\$I1A000\$P2C606\$P2A660	124	<i>P4₂/mcc</i>		PTC\$I1A000\$P4C000\$P2A006
74	<i>Imma</i>		IOC\$I1A000\$P2C060\$P2A000	125	<i>P4₂/nbm</i>	Origin 1	PTC\$I1A660\$P4C000\$P2A000
75	<i>P4</i>		PTN\$P4C000	125	<i>P4₂/nbm</i>	Origin 2	PTC\$I1A000\$P4C600\$P2A060
76	<i>P4₁</i>		PTN\$P4C003	126	<i>P4₂/nnc</i>	Origin 1	PTC\$I1A666\$P4C000\$P2A000
77	<i>P4₂</i>		PTN\$P4C006	126	<i>P4₂/nnc</i>	Origin 2	PTC\$I1A000\$P4C600\$P2A066
78	<i>P4₃</i>		PTN\$P4C009	127	<i>P4₂/mbm</i>		PTC\$I1A000\$P4C000\$P2A660
79	<i>I4</i>		ITN\$P4C000	128	<i>P4₂/mnc</i>		PTC\$I1A000\$P4C000\$P2A666
80	<i>I4₁</i>		ITN\$P4C063	129	<i>P4₂/nmm</i>	Origin 1	PTC\$I1A660\$P4C660\$P2A660
81	<i>P4₂</i>		PTN\$I4C000	129	<i>P4₂/nmm</i>	Origin 2	PTC\$I1A000\$P4C600\$P2A600
82	<i>I4₂</i>		ITN\$I4C000	130	<i>P4₂/ncc</i>	Origin 1	PTC\$I1A660\$P4C660\$P2A666
83	<i>P4₂/m</i>		PTC\$I1A000\$P4C000	130	<i>P4₂/ncc</i>	Origin 2	PTC\$I1A000\$P4C600\$P2A606
84	<i>P4₂/m</i>		PTC\$I1A000\$P4C006	131	<i>P4₂/mnc</i>		PTC\$I1A000\$P4C006\$P2A000
85	<i>P4₂/n</i>	Origin 1	PTC\$I1A660\$P4C660	132	<i>P4₂/mcm</i>		PTC\$I1A000\$P4C006\$P2A006
85	<i>P4₂/n</i>	Origin 2	PTC\$I1A000\$P4C600	133	<i>P4₂/nbc</i>	Origin 1	PTC\$I1A666\$P4C666\$P2A006
86	<i>P4₂/n</i>	Origin 1	PTC\$I1A666\$P4C666	133	<i>P4₂/nbc</i>	Origin 2	PTC\$I1A000\$P4C606\$P2A060
86	<i>P4₂/n</i>	Origin 2	PTC\$I1A000\$P4C066	134	<i>P4₂/nmm</i>	Origin 1	PTC\$I1A666\$P4C666\$P2A000
87	<i>I4₂/m</i>		ITC\$I1A000\$P4C000	134	<i>P4₂/nmm</i>	Origin 2	PTC\$I1A000\$P4C606\$P2A066
88	<i>I4₁/a</i>	Origin 1	ITC\$I1A063\$P4C063	135	<i>P4₂/mbc</i>		PTC\$I1A000\$P4C006\$P2A660
88	<i>I4₁/a</i>	Origin 2	ITC\$I1A000\$P4C933	136	<i>P4₂/mnm</i>		PTC\$I1A000\$P4C666\$P2A666
89	<i>P4₂2</i>		PTN\$P4C000\$P2A000	137	<i>P4₂/nmc</i>	Origin 1	PTC\$I1A666\$P4C666\$P2A666
90	<i>P4₂2</i>		PTN\$P4C660\$P2A660	137	<i>P4₂/nmc</i>	Origin 2	PTC\$I1A000\$P4C606\$P2A600
91	<i>P4₁22</i>		PTN\$P4C003\$P2A006	138	<i>P4₂/ncm</i>	Origin 1	PTC\$I1A666\$P4C666\$P2A660
92	<i>P4₁2₁2</i>		PTN\$P4C663\$P2A669	138	<i>P4₂/ncm</i>	Origin 2	PTC\$I1A000\$P4C606\$P2A606
93	<i>P4₂22</i>		PTN\$P4C006\$P2A000	139	<i>I4₂/mmm</i>		ITC\$I1A000\$P4C000\$P2A000
94	<i>P4₂2₁2</i>		PTN\$P4C666\$P2A666	140	<i>I4₂/mcm</i>		ITC\$I1A000\$P4C000\$P2A006
95	<i>P4₃22</i>		PTN\$P4C009\$P2A006	141	<i>I4₁/amd</i>	Origin 1	ITC\$I1A063\$P4C063\$P2A063
96	<i>P4₃2₁2</i>		PTN\$P4C669\$P2A663	141	<i>I4₁/amd</i>	Origin 2	ITC\$I1A000\$P4C393\$P2A000
97	<i>I4₂22</i>		ITN\$P4C000\$P2A000	142	<i>I4₁/acd</i>	Origin 1	ITC\$I1A063\$P4C063\$P2A069
98	<i>I4₁22</i>		ITN\$P4C063\$P2A063	142	<i>I4₁/acd</i>	Origin 2	ITC\$I1A000\$P4C393\$P2A006
99	<i>P4₂mm</i>		PTN\$P4C000\$I2A000	143	<i>P3</i>		PRN\$P3C000
100	<i>P4₂bm</i>		PTN\$P4C000\$I2A660	144	<i>P3₁</i>		PRN\$P3C004
101	<i>P4₂cm</i>		PTN\$P4C006\$I2A006	145	<i>P3₂</i>		PRN\$P3C008
102	<i>P4₂nm</i>		PTN\$P4C666\$I2A666	146	<i>R3</i>	Hexagonal axes	RRN\$P3C000
103	<i>P4₂cc</i>		PTN\$P4C000\$I2A006	146	<i>R3</i>	Rhombohedral axes	PRN\$P3Q000
104	<i>P4₂nc</i>		PTN\$P4C000\$I2A666	147	<i>P3₂</i>		PRC\$I3C000
105	<i>P4₂mc</i>		PTN\$P4C006\$I2A000	148	<i>R3₂</i>	Hexagonal axes	RRC\$I3C000
106	<i>P4₂bc</i>		PTN\$P4C006\$I2A660	148	<i>R3₂</i>	Rhombohedral axes	PRC\$I3Q000
107	<i>I4₂mm</i>		ITN\$P4C000\$I2A000	149	<i>P312</i>		PRN\$P3C000\$P2G000
108	<i>I4₂cm</i>		ITN\$P4C000\$I2A006	150	<i>P321</i>		PRN\$P3C000\$P2F000
109	<i>I4₂md</i>		ITN\$P4C063\$I2A666	151	<i>P3112</i>		PRN\$P3C004\$P2G000

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.2.1. *Explicit symbols (cont.)*

	Short Hermann– Mauguin symbol				Short Hermann– Mauguin symbol			
No.		Comments	Explicit symbols	No.		Comments	Explicit symbols	
152	$P3_121$	Hexagonal axes Rhombohedral axes	PRN\$P3C004\$P2F008	192	$P6/mcc$	Origin 1 Origin 2	PHC\$I1A000\$P6C000\$P2F006	
153	$P3_212$		PRN\$P3C008\$P2G000	193	$P6_3/mcm$		PHC\$I1A000\$P6C006\$P2F006	
154	$P3_221$		PRN\$P3C008\$P2F004	194	$P6_3/mmc$		PHC\$I1A000\$P6C006\$P2F000	
155	$R32$		RRN\$P3C000\$P2F000	195	$P23$		PCN\$P3Q000\$P2C000\$P2A000	
155	$R32$		PRN\$P3Q000\$P2E000	196	$F23$		FCN\$P3Q000\$P2C000\$P2A000	
156	$P3m1$		PRN\$P3C000\$I2F000	197	$I23$		ICN\$P3Q000\$P2C000\$P2A000	
157	$P31m$		PRN\$P3C000\$I2G000	198	$P2_13$		PCN\$P3Q000\$P2C606\$P2A660	
158	$P3c1$		PRN\$P3C000\$I2F006	199	$I2_13$		ICN\$P3Q000\$P2C606\$P2A660	
159	$P31c$		PRN\$P3C000\$I2G006	200	$Pm\bar{3}$		PCC\$I3Q000\$P2C000\$P2A000	
160	$R3m$		Hexagonal axes	RRN\$P3C000\$I2F000	201		$Pn\bar{3}$	PCC\$I3Q666\$P2C000\$P2A000
160	$R3m$	Rhombohedral axes	PRN\$P3Q000\$I2E000	201	$Pn\bar{3}$	Origin 2	PCC\$I3Q000\$P2C660\$P2A066	
161	$R3c$	Hexagonal axes	RRN\$P3C000\$I2F006	202	$Fm\bar{3}$	Origin 1 Origin 2	FCC\$I3Q000\$P2C000\$P2A000	
161	$R3c$	Rhombohedral axes	PRN\$P3Q000\$I2E666	203	$Fd\bar{3}$		FCC\$I3Q333\$P2C000\$P2A000	
162	$P\bar{3}1m$	Hexagonal axes Rhombohedral axes	PRC\$I3C000\$P2G000	203	$Fd\bar{3}$	Origin 1 Origin 2	FCC\$I3Q000\$P2C330\$P2A033	
163	$P\bar{3}1c$		PRC\$I3C000\$P2G006	204	$Im\bar{3}$		ICC\$I3Q000\$P2C000\$P2A000	
164	$P\bar{3}m1$		PRC\$I3C000\$P2F000	205	$Pa\bar{3}$	PCC\$I3Q000\$P2C606\$P2A660		
165	$P\bar{3}c1$		PRC\$I3C000\$P2F006	206	$Ia\bar{3}$	ICC\$I3Q000\$P2C606\$P2A660		
166	$R\bar{3}m$		Hexagonal axes	RRC\$I3C000\$P2F000	207	$P432$	PCN\$P3Q000\$P4C000\$P2D000	
166	$R\bar{3}m$	Rhombohedral axes	PRC\$I3Q000\$P2E000	208	$P4_232$	PCN\$P3Q000\$P4C666\$P2D666		
167	$R\bar{3}c$	Hexagonal axes	RRC\$I3C000\$P2F006	209	$F432$	FCN\$P3Q000\$P4C000\$P2D000		
167	$R\bar{3}c$	Rhombohedral axes	PRC\$I3Q000\$P2E666	210	$F4_132$	FCN\$P3Q000\$P4C993\$P2D939		
168	$P6$	Hexagonal axes Rhombohedral axes	PHN\$P6C000	211	$I432$	ICN\$P3Q000\$P4C000\$P2D000		
169	$P6_1$		PHN\$P6C002	212	$P4_332$	PCN\$P3Q000\$P4C939\$P2D399		
170	$P6_5$		PHN\$P6C005	213	$P4_132$	PCN\$P3Q000\$P4C393\$P2D933		
171	$P6_2$		PHN\$P6C004	214	$I4_132$	ICN\$P3Q000\$P4C393\$P2D933		
172	$P6_4$		PHN\$P6C008	215	$P\bar{4}3m$	PCN\$P3Q000\$I4C000\$I2D000		
173	$P6_3$		PHN\$P6C006	216	$F\bar{4}3m$	FCN\$P3Q000\$I4C000\$I2D000		
174	$P\bar{6}$		PHN\$I6C000	217	$I\bar{4}3m$	ICN\$P3Q000\$I4C000\$I2D000		
175	$P6/m$		PHC\$I1A000\$P6C000	218	$P\bar{4}3n$	PCN\$P3Q000\$I4C666\$I2D666		
176	$P6_3/m$		PHC\$I1A000\$P6C006	219	$F\bar{4}3c$	FCN\$P3Q000\$I4C666\$I2D666		
177	$P622$		PHN\$P6C000\$P2F000	220	$I\bar{4}3d$	ICN\$P3Q000\$I4C939\$I2D399		
178	$P6_122$		PHN\$P6C002\$P2F000	221	$Pm\bar{3}m$	PCC\$I3Q000\$P4C000\$P2D000		
179	$P6_522$	PHN\$P6C005\$P2F000	222	$Pn\bar{3}n$	Origin 1	PCC\$I3Q666\$P4C000\$P2D000		
180	$P6_222$	PHN\$P6C004\$P2F000	222	$Pn\bar{3}n$	Origin 2	PCC\$I3Q000\$P4C600\$P2D006		
181	$P6_422$	PHN\$P6C008\$P2F000	223	$Pm\bar{3}n$	Origin 1 Origin 2	PCC\$I3Q000\$P4C666\$P2D666		
182	$P6_322$	PHN\$P6C006\$P2F000	224	$Pn\bar{3}m$		PCC\$I3Q666\$P4C666\$P2D666		
183	$P6mm$	Hexagonal axes Rhombohedral axes	PHN\$P6C000\$I2F000	224	$Pn\bar{3}m$	Origin 1 Origin 2	PCC\$I3Q000\$P4C066\$P2D660	
184	$P6cc$		PHN\$P6C000\$I2F006	225	$Fm\bar{3}m$		FCC\$I3Q000\$P4C000\$P2D000	
185	$P6_3cm$		PHN\$P6C006\$I2F006	226	$Fm\bar{3}c$	Origin 1 Origin 2	FCC\$I3Q000\$P4C666\$P2D666	
186	$P6_3mc$		PHN\$P6C006\$I2F000	227	$Fd\bar{3}m$		FCC\$I3Q333\$P4C993\$P2D939	
187	$P\bar{6}m2$		PHN\$I6C000\$P2G000	227	$Fd\bar{3}m$		FCC\$I3Q000\$P4C693\$P2D936	
188	$P\bar{6}c2$		PHN\$I6C006\$P2G000	228	$Fd\bar{3}c$		Origin 1	FCC\$I3Q999\$P4C993\$P2D939
189	$P\bar{6}2m$		PHN\$I6C000\$P2F000	228	$Fd\bar{3}c$		Origin 2	FCC\$I3Q000\$P4C093\$P2D930
190	$P\bar{6}2c$		PHN\$I6C006\$P2F000	229	$Im\bar{3}m$		ICC\$I3Q000\$P4C000\$P2D000	
191	$P6/mmm$		PHC\$I1A000\$P6C000\$P2F000	230	$Ia\bar{3}d$		ICC\$I3Q000\$P4C393\$P2D933	

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.2.2. *Lattice symbol L*

The lattice symbol *L* implies Seitz matrices for the lattice translations. For noncentrosymmetric lattices the rotation parts of the Seitz matrices are for *I* (see Table A1.4.2.4). For centrosymmetric lattices the rotation parts are *I* and *−I*. The translation parts in the fourth columns of the Seitz matrices are listed in the last column of the table. The total number of matrices implied by each symbol is given by *nS*.

Noncentrosymmetric		Centrosymmetric		Implied lattice translation(s)
Symbol	<i>nS</i>	Symbol	<i>nS</i>	
P	1	−P	2	0, 0, 0
A	2	−A	4	0, 0, 0 0, $\frac{1}{2}$, $\frac{1}{2}$
B	2	−B	4	0, 0, 0 $\frac{1}{2}$, 0, $\frac{1}{2}$
C	2	−C	4	0, 0, 0 $\frac{1}{2}$, $\frac{1}{2}$, 0
I	2	−I	4	0, 0, 0 $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$
R	3	−R	6	0, 0, 0 $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3}$ $\frac{1}{3}$, $\frac{2}{3}$, $\frac{2}{3}$
H	3	−H	6	0, 0, 0 $\frac{2}{3}$, $\frac{1}{3}$, 0 $\frac{1}{3}$, $\frac{2}{3}$, 0
F	4	−F	8	0, 0, 0 0, $\frac{1}{2}$, $\frac{1}{2}$ $\frac{1}{2}$, 0, $\frac{1}{2}$ $\frac{1}{2}$, $\frac{1}{2}$, 0

$$\begin{aligned} \left[\begin{pmatrix} 0 & 0 & \bar{1} \\ \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \right] &= \begin{pmatrix} \bar{z} \\ \bar{x} \\ \bar{y} \end{pmatrix}, \\ \left[\begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} \frac{1}{4} \\ \frac{3}{4} \\ \frac{1}{4} \end{pmatrix} \right] &= \begin{pmatrix} \frac{1}{4} - y \\ \frac{3}{4} + x \\ \frac{1}{4} + z \end{pmatrix}, \\ \left[\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} \frac{3}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{pmatrix} \right] &= \begin{pmatrix} \frac{3}{4} + y \\ \frac{1}{4} + x \\ \frac{1}{4} - z \end{pmatrix}. \end{aligned}$$

The corresponding symmetry transformations in reciprocal space, in the notation of Section 1.4.4, are

$$\left[(hkl) \begin{pmatrix} 0 & 0 & \bar{1} \\ \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \end{pmatrix} : -(hkl) \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \right] = [\bar{k}\bar{l}h : 0];$$

similarly, $[k\bar{h}l : -131/4]$ and $[kh\bar{l} : -311/4]$ are obtained from the second and third generator of $Ia\bar{3}d$, respectively.

The first column of Table A1.4.2.1 lists the conventional space-group number. The second column shows the conventional short Hermann–Mauguin or international space-group symbol, and the third column, *Comments*, shows the full international space-group symbol *only* for the different settings of the monoclinic space groups that are given in the main space-group tables of *IT A* (1983). Other comments pertain to the choice of the space-group origin – where there are alternatives – and to axial systems. The fourth column shows the explicit space-group symbols described above for each of the settings considered in *IT A* (1983).

A1.4.2.3. Hall symbols (S. R. HALL AND R. W. GROSSE-KUNSTLEVE)

The explicit-origin space-group notation proposed by Hall (1981a) is based on a subset of the symmetry operations, in the form of Seitz matrices, sufficient to uniquely define a space group. The concise unambiguous nature of this notation makes it well suited to handling symmetry in computing and database applications.

Table A1.4.2.7 lists space-group notation in several formats. The first column of Table A1.4.2.7 lists the space-group numbers with axis codes appended to identify the non-standard settings. The second column lists the Hermann–Mauguin symbols in computer-entry format with appended codes to identify the origin and cell choice when there are alternatives. The general forms of the Hall notation are listed in the fourth column and the computer-entry representations of these symbols are listed in the third column. The computer-entry format is the general notation expressed as case-insensitive ASCII characters with the overline (bar) symbol replaced by a minus sign.

The Hall notation has the general form:

$$\mathbf{L}[\mathbf{N}_T^A]_1 \dots [\mathbf{N}_T^A]_p \mathbf{V}. \quad (\text{A1.4.2.4})$$

L is the symbol specifying the lattice translational symmetry (see Table A1.4.2.2). The integral translations are implicitly included in the set of generators. If **L** has a leading minus sign, it also specifies an inversion centre at the origin. $[\mathbf{N}_T^A]_n$ specifies the 4×4 Seitz matrix **S**_n of a symmetry element in the minimum set which defines the space-group symmetry (see Tables A1.4.2.3 to A1.4.2.6), and **p** is the number of elements in the set. **V** is a change-of-basis operator needed for less common descriptions of the space-group symmetry.

Table A1.4.2.3. *Translation symbol T*

The symbol *T* specifies the translation elements of a Seitz matrix. Alphabetical symbols (given in the first column) specify translations along a fixed direction. Numerical symbols (given in the third column) specify translations as a fraction of the rotation order $|N|$ and in the direction of the implied or explicitly defined axis.

Translation symbol	Translation vector	Subscript symbol	Fractional translation
<i>a</i>	$\frac{1}{2}, 0, 0$	<i>l</i> in 3_1	$\frac{1}{3}$
<i>b</i>	$0, \frac{1}{2}, 0$	<i>2</i> in 3_2	$\frac{2}{3}$
<i>c</i>	$0, 0, \frac{1}{2}$	<i>l</i> in 4_1	$\frac{1}{4}$
<i>n</i>	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	<i>3</i> in 4_3	$\frac{3}{4}$
<i>u</i>	$\frac{1}{4}, 0, 0$	<i>l</i> in 6_1	$\frac{1}{6}$
<i>v</i>	$0, \frac{1}{4}, 0$	<i>2</i> in 6_2	$\frac{1}{3}$
<i>w</i>	$0, 0, \frac{1}{4}$	<i>4</i> in 6_4	$\frac{2}{3}$
<i>d</i>	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	<i>5</i> in 6_5	$\frac{5}{6}$

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Table A1.4.2.4. *Rotation matrices for principal axes*

The 3×3 matrices for *proper* rotations along the three principal unit-cell directions are given below. The matrices for *improper* rotations (-1 , -2 , -3 , -4 and -6) are identical except that the signs of the elements are reversed.

Axis	Symbol A	Rotation order				
		1	2	3	4	6
a	<i>x</i>	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & 1 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \bar{1} \\ 0 & 1 & 0 \end{pmatrix}$
b	<i>y</i>	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 1 \end{pmatrix}$
c	<i>z</i>	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

The matrix symbol $\mathbf{N}_T^A$ is composed of three parts: **N** is the symbol denoting the $|\mathbf{N}|$ -fold order of the rotation matrix (see Tables A1.4.2.4, A1.4.2.5 and A1.4.2.6), **T** is a subscript symbol denoting the *translation* vector (see Table A1.4.2.3) and **A** is a superscript symbol denoting the *axis* of rotation.

The computer-entry format of the Hall notation contains the rotation-order symbol **N** as positive integers 1, 2, 3, 4, or 6 for proper rotations and as negative integers -1 , -2 , -3 , -4 or -6 for improper rotations. The **T** translation symbols 1, 2, 3, 4, 5, 6, *a*, *b*, *c*, *n*, *u*, *v*, *w*, *d* are described in Table A1.4.2.3. These translations apply additively [*e.g.* *ad* signifies a $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ translation]. The **A** axis symbols *x*, *y*, *z* denote rotations about the axes **a**, **b** and **c**, respectively (see Table A1.4.2.4). The axis symbols '' and ' signal rotations about the body-diagonal vectors **a + b** (or alternatively **b + c** or **c + a**) and **a - b** (or alternatively **b - c** or **c - a**) (see Table

A1.4.2.5). The axis symbol * always refers to a threefold rotation along **a + b + c** (see Table A1.4.2.6).

The change-of-basis operator **V** has the general form (v_x, v_y, v_z) . The vectors v_x , v_y and v_z are specified by

$$\begin{aligned} v_x &= r_{1,1}X + r_{1,2}Y + r_{1,3}Z + \mathbf{t}_1 \\ v_y &= r_{2,1}X + r_{2,2}Y + r_{2,3}Z + \mathbf{t}_2, \\ v_z &= r_{3,1}X + r_{3,2}Y + r_{3,3}Z + \mathbf{t}_3 \end{aligned}$$

where $r_{i,j}$ and $\mathbf{t}_i$ are fractions or real numbers. Terms in which $r_{i,j}$ or $\mathbf{t}_i$ are zero need not be specified. The 4×4 change-of-basis matrix operator **V** is defined as

$$\mathbf{V} = \begin{pmatrix} r_{1,1} & r_{1,2} & r_{1,3} & \mathbf{t}_1 \\ r_{2,1} & r_{2,2} & r_{2,3} & \mathbf{t}_2 \\ r_{3,1} & r_{3,2} & r_{3,3} & \mathbf{t}_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Table A1.4.2.5. *Rotation matrices for face-diagonal axes*

The symbols for face-diagonal twofold rotations are $2'$ and $2''$. The face-diagonal axis direction is determined by the axis of the preceding rotation $\mathbf{N}^x$, $\mathbf{N}^y$ or $\mathbf{N}^z$. Note that the single prime ' is the default and may be omitted.

Preceding rotation	Rotation	Axis	Matrix
$\mathbf{N}^x$	$2'$	b - c	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \end{pmatrix}$
	$2''$	b + c	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$
$\mathbf{N}^y$	$2'$	a - c	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$
	$2''$	a + c	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & \bar{1} & 0 \\ 1 & 0 & 0 \end{pmatrix}$
$\mathbf{N}^z$	$2'$	a - b	$\begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$
	$2''$	a + b	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$

The transformed symmetry operations are derived from the specified Seitz matrices $\mathbf{S}_n$ as

$$\mathbf{S}'_n = \mathbf{V} \cdot \mathbf{S}_n \cdot \mathbf{V}^{-1}$$

and from the integral translations $\mathbf{t}(1, 0, 0)$, $\mathbf{t}(0, 1, 0)$ and $\mathbf{t}(0, 0, 1)$ as

$$(\mathbf{t}'_n, \mathbf{1})^T = \mathbf{V} \cdot (\mathbf{t}_n, \mathbf{1})^T.$$

A shorthand form of **V** may be used when the change-of-basis operator only translates the origin of the basis system. In this form v_x , v_y and v_z are specified simply as shifts in twelfths, implying the matrix operator

Table A1.4.2.6. *Rotation matrix for the body-diagonal axis*

The symbol for the threefold rotation in the **a + b + c** direction is 3^* . Note that for cubic space groups the body-diagonal axis is implied and the asterisk * may be omitted.

Axis	Rotation	Matrix
a + b + c	3^*	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$

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$$\mathbf{V} = \begin{pmatrix} 1 & 0 & 0 & v_x/12 \\ 0 & 1 & 0 & v_y/12 \\ 0 & 0 & 1 & v_z/12 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

In the shorthand form of $\mathbf{V}$, the commas separating the vectors may be omitted.

A1.4.2.3.1. Default axes

For most symbols the rotation axes applicable to each $\mathbf{N}$ are implied and an explicit axis symbol $\mathbf{A}$ is not needed. The rules for default axis directions are:

- (i) the *first* rotation or roto-inversion has an axis direction of $\mathbf{c}$;
- (ii) the *second* rotation (if $|\mathbf{N}|$ is 2) has an axis direction of $\mathbf{a}$ if preceded by an $|\mathbf{N}|$ of 2 or 4, $\mathbf{a}-\mathbf{b}$ if preceded by an $|\mathbf{N}|$ of 3 or 6;
- (iii) the *third* rotation (if $|\mathbf{N}|$ is 3) has an axis direction of $\mathbf{a} + \mathbf{b} + \mathbf{c}$.

A1.4.2.3.2. Example matrices

The following examples show how the notation expands to Seitz matrices.

The notation $\bar{2}_c^x$ represents an improper twofold rotation along $\mathbf{a}$ and a $\mathbf{c}/2$ translation:

$$-2xc = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The notation 3^* represents a threefold rotation along $\mathbf{a} + \mathbf{b} + \mathbf{c}$:

$$3^* = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The notation 4_{vw} represents a fourfold rotation along $\mathbf{c}$ (implied) and translation of $\mathbf{b}/4$ and $\mathbf{c}/4$:

$$4vw = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & \frac{1}{4} \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The notation $6_1 2 (0 0 -1)$ represents a 6_1 screw along $\mathbf{c}$, a twofold rotation along $\mathbf{a} - \mathbf{b}$ and an origin shift of $-\mathbf{c}/12$. Note that the 6_1 matrix is unchanged by the shifted origin whereas the 2 matrix is changed by $-\mathbf{c}/6$.

$$6_1 2 (0 0 -1)$$

$$= \begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{6} \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & \frac{5}{6} \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The change-of-basis vector $(0 0 -1)$ could also be entered as $(x, y, z - 1/12)$.

The *reverse setting of the R-centred lattice* (hexagonal axes) is specified using a change-of-basis transformation applied to the standard *obverse setting* (see Table A1.4.2.2). The obverse Seitz matrices are

$$R 3 = \begin{pmatrix} 1 & 0 & 0 & \frac{1}{3} \\ 0 & 1 & 0 & \frac{2}{3} \\ 0 & 0 & 1 & \frac{2}{3} \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & \frac{2}{3} \\ 0 & 1 & 0 & \frac{1}{3} \\ 0 & 0 & 1 & \frac{1}{3} \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The reverse-setting Seitz matrices are

$$R 3 (-x, -y, z) = \begin{pmatrix} 1 & 0 & 0 & \frac{1}{3} \\ 0 & 1 & 0 & \frac{2}{3} \\ 0 & 0 & 1 & \frac{1}{3} \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & \frac{2}{3} \\ 0 & 1 & 0 & \frac{1}{3} \\ 0 & 0 & 1 & \frac{2}{3} \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

The conventional primitive hexagonal lattice may be transformed to a *C-centred orthohexagonal setting* using the change-of-basis operator

$$P 6 (x - 1/2y, 1/2y, z) = \begin{pmatrix} \frac{1}{2} & -\frac{3}{2} & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

In this case the lattice translation for the *C* centring is obtained by transforming the integral translation $\mathbf{t}(0, 1, 0)$:

$$\mathbf{V} \cdot (0 \ 1 \ 0 \ 1)^T = \begin{pmatrix} 1 & -\frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & 0 & 1 \end{pmatrix}^T.$$

The standard setting of an *I*-centred tetragonal space group may be transformed to a primitive setting using the change-of-basis operator

$$I 4 (y + z, x + z, x + y) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Note that in the primitive setting, the fourfold axis is along $\mathbf{a} + \mathbf{b}$.

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Table A1.4.2.7. *Hall symbols*

The first column, n:c, lists the space-group numbers and axis codes separated by a colon. The second column lists the Hermann–Mauguin symbols in computer-entry format. The third column lists the Hall symbols in computer-entry format and the fourth column lists the Hall symbols as described in Tables A1.4.2.2–A1.4.2.6.

n:c	H–M entry	Hall entry	Hall symbol	n:c	H–M entry	Hall entry	Hall symbol
1	P 1	p 1	P 1	9:-a2	B n 1 1	b -2xab	$B \bar{2}^x_{ab}$
2	P -1	-p 1	$\bar{P} 1$	9:-a3	I b 1 1	i -2xb	$I \bar{2}^x_b$
3:b	P 1 2 1	p 2y	P 2 ^y	10:b	P 1 2/m 1	-p 2y	$\bar{P} 2^y$
3:c	P 1 1 2	p 2	P 2	10:c	P 1 1 2/m	-p 2	$\bar{P} 2$
3:a	P 2 1 1	p 2x	P 2 ^x	10:a	P 2/m 1 1	-p 2x	$\bar{P} 2^x$
4:b	P 1 21 1	p 2yb	P 2 ^y _b	11:b	P 1 21/m 1	-p 2yb	$\bar{P} 2^y_b$
4:c	P 1 1 21	p 2c	P 2 _c	11:c	P 1 1 21/m	-p 2c	$\bar{P} 2_c$
4:a	P 21 1 1	p 2xa	P 2 ^x _a	11:a	P 21/m 1 1	-p 2xa	$\bar{P} 2^x_a$
5:b1	C 1 2 1	c 2y	C 2 ^y	12:b1	C 1 2/m 1	-c 2y	$\bar{C} 2^y$
5:b2	A 1 2 1	a 2y	A 2 ^y	12:b2	A 1 2/m 1	-a 2y	$\bar{A} 2^y$
5:b3	I 1 2 1	i 2y	I 2 ^y	12:b3	I 1 2/m 1	-i 2y	$\bar{I} 2^y$
5:c1	A 1 1 2	a 2	A 2	12:c1	A 1 1 2/m	-a 2	$\bar{A} 2$
5:c2	B 1 1 2	b 2	B 2	12:c2	B 1 1 2/m	-b 2	$\bar{B} 2$
5:c3	I 1 1 2	i 2	I 2	12:c3	I 1 1 2/m	-i 2	$\bar{I} 2$
5:a1	B 2 1 1	b 2x	B 2 ^x	12:a1	B 2/m 1 1	-b 2x	$\bar{B} 2^x$
5:a2	C 2 1 1	c 2x	C 2 ^x	12:a2	C 2/m 1 1	-c 2x	$\bar{C} 2^x$
5:a3	I 2 1 1	i 2x	I 2 ^x	12:a3	I 2/m 1 1	-i 2x	$\bar{I} 2^x$
6:b	P 1 m 1	p -2y	P $\bar{2}^y$	13:b1	P 1 2/c 1	-p 2yc	$\bar{P} 2^y_c$
6:c	P 1 1 m	p -2	P $\bar{2}$	13:b2	P 1 2/n 1	-p 2yac	$\bar{P} 2^y_{ac}$
6:a	P m 1 1	p -2x	P $\bar{2}^x$	13:b3	P 1 2/a 1	-p 2ya	$\bar{P} 2^y_a$
7:b1	P 1 c 1	p -2yc	P $\bar{2}^y_c$	13:c1	P 1 1 2/a	-p 2a	$\bar{P} 2_a$
7:b2	P 1 n 1	p -2yac	P $\bar{2}^y_{ac}$	13:c2	P 1 1 2/n	-p 2ab	$\bar{P} 2_{ab}$
7:b3	P 1 a 1	p -2ya	P $\bar{2}^y_a$	13:c3	P 1 1 2/b	-p 2b	$\bar{P} 2_b$
7:c1	P 1 1 a	p -2a	P $\bar{2}_a$	13:a1	P 2/b 1 1	-p 2xb	$\bar{P} 2^x_b$
7:c2	P 1 1 n	p -2ab	P $\bar{2}_{ab}$	13:a2	P 2/n 1 1	-p 2xbc	$\bar{P} 2^x_{bc}$
7:c3	P 1 1 b	p -2b	P $\bar{2}_b$	13:a3	P 2/c 1 1	-p 2xc	$\bar{P} 2^x_c$
7:a1	P b 1 1	p -2xb	P $\bar{2}^x_b$	14:b1	P 1 21/c 1	-p 2ybc	$\bar{P} 2^y_{bc}$
7:a2	P n 1 1	p -2xbc	P $\bar{2}^x_{bc}$	14:b2	P 1 21/n 1	-p 2yn	$\bar{P} 2^y_n$
7:a3	P c 1 1	p -2xc	P $\bar{2}^x_c$	14:b3	P 1 21/a 1	-p 2yab	$\bar{P} 2^y_{ab}$
8:b1	C 1 m 1	c -2y	C $\bar{2}^y$	14:c1	P 1 1 21/a	-p 2ac	$\bar{P} 2_{ac}$
8:b2	A 1 m 1	a -2y	A $\bar{2}^y$	14:c2	P 1 1 21/n	-p 2n	$\bar{P} 2_n$
8:b3	I 1 m 1	i -2y	I $\bar{2}^y$	14:c3	P 1 1 21/b	-p 2bc	$\bar{P} 2_{bc}$
8:c1	A 1 1 m	a -2	A $\bar{2}$	14:a1	P 21/b 1 1	-p 2xab	$\bar{P} 2^x_{ab}$
8:c2	B 1 1 m	b -2	B $\bar{2}$	14:a2	P 21/n 1 1	-p 2xn	$\bar{P} 2^x_n$
8:c3	I 1 1 m	i -2	I $\bar{2}$	14:a3	P 21/c 1 1	-p 2xac	$\bar{P} 2^x_{ac}$
8:a1	B m 1 1	b -2x	B $\bar{2}^x$	15:b1	C 1 2/c 1	-c 2yc	$\bar{C} 2^y_c$
8:a2	C m 1 1	c -2x	C $\bar{2}^x$	15:b2	A 1 2/n 1	-a 2yab	$\bar{A} 2^y_{ab}$
8:a3	I m 1 1	i -2x	I $\bar{2}^x$	15:b3	I 1 2/a 1	-i 2ya	$\bar{I} 2^y_a$
9:b1	C 1 c 1	c -2yc	C $\bar{2}^y_c$	15:-b1	A 1 2/a 1	-a 2ya	$\bar{A} 2^y_a$
9:b2	A 1 n 1	a -2yab	A $\bar{2}^y_{ab}$	15:-b2	C 1 2/n 1	-c 2yac	$\bar{C} 2^y_{ac}$
9:b3	I 1 a 1	i -2ya	I $\bar{2}^y_a$	15:-b3	I 1 2/c 1	-i 2yc	$\bar{I} 2^y_c$
9:-b1	A 1 a 1	a -2ya	A $\bar{2}^y_a$	15:c1	A 1 1 2/a	-a 2a	$\bar{A} 2_a$
9:-b2	C 1 n 1	c -2yac	C $\bar{2}^y_{ac}$	15:c2	B 1 1 2/n	-b 2ab	$\bar{B} 2_{ab}$
9:-b3	I 1 c 1	i -2yc	I $\bar{2}^y_c$	15:c3	I 1 1 2/b	-i 2b	$\bar{I} 2_b$
9:c1	A 1 1 a	a -2a	A $\bar{2}_a$	15:-c1	B 1 1 2/b	-b 2b	$\bar{B} 2_b$
9:c2	B 1 1 n	b -2ab	B $\bar{2}_{ab}$	15:-c2	A 1 1 2/n	-a 2ab	$\bar{A} 2_{ab}$
9:c3	I 1 1 b	i -2b	I $\bar{2}_b$	15:-c3	I 1 1 2/a	-i 2a	$\bar{I} 2_a$
9:-c1	B 1 1 b	b -2b	B $\bar{2}_b$	15:a1	B 2/b 1 1	-b 2xb	$\bar{B} 2^x_b$
9:-c2	A 1 1 n	a -2ab	A $\bar{2}_{ab}$	15:a2	C 2/n 1 1	-c 2xac	$\bar{C} 2^x_{ac}$
9:-c3	I 1 1 a	i -2a	I $\bar{2}_a$	15:a3	I 2/c 1 1	-i 2xc	$\bar{I} 2^x_c$
9:a1	B b 1 1	b -2xb	B $\bar{2}^x_b$	15:-a1	C 2/c 1 1	-c 2xc	$\bar{C} 2^x_c$
9:a2	C n 1 1	c -2xac	C $\bar{2}^x_{ac}$	15:-a2	B 2/n 1 1	-b 2xab	$\bar{B} 2^x_{ab}$
9:a3	I c 1 1	i -2xc	I $\bar{2}^x_c$	15:-a3	I 2/b 1 1	-i 2xb	$\bar{I} 2^x_b$
9:-a1	C c 1 1	c -2xc	C $\bar{2}^x_c$	16	P 2 2 2	p 2 2	P 2 2

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Table A1.4.2.7. *Hall symbols (cont.)*

n:c	H-M entry	Hall entry	Hall symbol	n:c	H-M entry	Hall entry	Hall symbol
17	P 2 2 21	p 2c 2	P 2 _c 2	33:ba-c	P b n 21	p 2c -2ab	P 2 _c 2 _{ab}
17:cab	P 21 2 2	p 2a 2a	P 2 _a 2 _a	33:cab	P 21 n b	p -2bc 2a	P 2 _{bc} 2 _a
17:bca	P 2 21 2	p 2 2b	P 2 2 _b	33:-cba	P 21 c n	p -2n 2a	P 2 _n 2 _a
18	P 21 21 2	p 2 2ab	P 2 2 _{ab}	33:bca	P c 21 n	p -2n -2ac	P 2 _n 2 _{ac}
18:cab	P 2 21 21	p 2bc 2	P 2 _{bc} 2	33:a-cb	P n 21 a	p -2ac -2n	P 2 _{ac} 2 _n
18:bca	P 21 2 21	p 2ac 2ac	P 2 _{ac} 2 _{ac}	34	P n n 2	p 2 -2n	P 2 2 _n
19	P 21 21 21	p 2ac 2ab	P 2 _{ac} 2 _{ab}	34:cab	P 2 n n	p -2n 2	P 2 _n 2
20	C 2 2 21	c 2c 2	C 2 _c 2	34:bca	P n 2 n	p -2n -2n	P 2 _n 2 _n
20:cab	A 21 2 2	a 2a 2a	A 2 _a 2 _a	35	C m m 2	c 2 -2	C 2 2
20:bca	B 2 21 2	b 2 2b	B 2 2 _b	35:cab	A 2 m m	a -2 2	A 2 2
21	C 2 2 2	c 2 2	C 2 2	35:bca	B m 2 m	b -2 -2	B 2 2
21:cab	A 2 2 2	a 2 2	A 2 2	36	C m c 21	c 2c -2	C 2 _c 2
21:bca	B 2 2 2	b 2 2	B 2 2	36:ba-c	C c m 21	c 2c -2c	C 2 _c 2 _c
22	F 2 2 2	f 2 2	F 2 2	36:cab	A 21 m a	a -2a 2a	A 2 _a 2 _a
23	I 2 2 2	i 2 2	I 2 2	36:-cba	A 21 a m	a -2 2a	A 2 2 _a
24	I 21 21 21	i 2b 2c	I 2 _b 2 _c	36:bca	B b 21 m	b -2 -2b	B 2 2 _b
25	P m m 2	p 2 -2	P 2 2	36:a-cb	B m 21 b	b -2b -2	B 2 _b 2
25:cab	P 2 m m	p -2 2	P 2 2	37	C c c 2	c 2 -2c	C 2 2 _c
25:bca	P m 2 m	p -2 -2	P 2 2	37:cab	A 2 a a	a -2a 2	A 2 _a 2
26	P m c 21	p 2c -2	P 2 _c 2	37:bca	B b 2 b	b -2b -2b	B 2 _b 2 _b
26:ba-c	P c m 21	p 2c -2c	P 2 _c 2 _c	38	A m m 2	a 2 -2	A 2 2
26:cab	P 21 m a	p -2a 2a	P 2 _a 2 _a	38:ba-c	B m m 2	b 2 -2	B 2 2
26:-cba	P 21 a m	p -2 2a	P 2 2 _a	38:cab	B 2 m m	b -2 2	B 2 2
26:bca	P b 21 m	p -2 -2b	P 2 2 _b	38:-cba	C 2 m m	c -2 2	C 2 2
26:a-cb	P m 21 b	p -2b -2	P 2 _b 2	38:bca	C m 2 m	c -2 -2	C 2 2
27	P c c 2	p 2 -2c	P 2 2 _c	38:a-cb	A m 2 m	a -2 -2	A 2 2
27:cab	P 2 a a	p -2a 2	P 2 _a 2	39	A b m 2	a 2 -2b	A 2 2 _b
27:bca	P b 2 b	p -2b -2b	P 2 _b 2 _b	39:ba-c	B m a 2	b 2 -2a	B 2 2 _a
28	P m a 2	p 2 -2a	P 2 2 _a	39:cab	B 2 c m	b -2a 2	B 2 _a 2
28:ba-c	P b m 2	p 2 -2b	P 2 2 _b	39:-cba	C 2 m b	c -2a 2	C 2 _a 2
28:cab	P 2 m b	p -2b 2	P 2 _b 2	39:bca	C m 2 a	c -2a -2a	C 2 _a 2 _a
28:-cba	P 2 c m	p -2c 2	P 2 _c 2	39:a-cb	A c 2 m	a -2b -2b	A 2 _b 2 _b
28:bca	P c 2 m	p -2c -2c	P 2 _c 2 _c	40	A m a 2	a 2 -2a	A 2 2 _a
28:a-cb	P m 2 a	p -2a -2a	P 2 _a 2 _a	40:ba-c	B b m 2	b 2 -2b	B 2 2 _b
29	P c a 21	p 2c -2ac	P 2 _c 2 _{ac}	40:cab	B 2 m b	b -2b 2	B 2 _b 2
29:ba-c	P b c 21	p 2c -2b	P 2 _c 2 _b	40:-cba	C 2 c m	c -2c 2	C 2 _c 2
29:cab	P 21 a b	p -2b 2a	P 2 _b 2 _a	40:bca	C c 2 m	c -2c -2c	C 2 _c 2 _c
29:-cba	P 21 c a	p -2ac 2a	P 2 _{ac} 2 _a	40:a-cb	A m 2 a	a -2a -2a	A 2 _a 2 _a
29:bca	P c 21 b	p -2bc -2c	P 2 _{bc} 2 _c	41	A b a 2	a 2 -2ab	A 2 2 _{ab}
29:a-cb	P b 21 a	p -2a -2ab	P 2 _a 2 _{ab}	41:ba-c	B b a 2	b 2 -2ab	B 2 2 _{ab}
30	P n c 2	p 2 -2bc	P 2 2 _{bc}	41:cab	B 2 c b	b -2ab 2	B 2 _{ab} 2
30:ba-c	P c n 2	p 2 -2ac	P 2 2 _{ac}	41:-cba	C 2 c b	c -2ac 2	C 2 _{ac} 2
30:cab	P 2 n a	p -2ac 2	P 2 _{ac} 2	41:bca	C c 2 a	c -2ac -2ac	C 2 _{ac} 2 _{ac}
30:-cba	P 2 a n	p -2ab 2	P 2 _{ab} 2	41:a-cb	A c 2 a	a -2ab -2ab	A 2 _{ab} 2 _{ab}
30:bca	P b 2 n	p -2ab -2ab	P 2 _{ab} 2 _{ab}	42	F m m 2	f 2 -2	F 2 2
30:a-cb	P n 2 b	p -2bc -2bc	P 2 _{bc} 2 _{bc}	42:cab	F 2 m m	f -2 2	F 2 2
31	P m n 21	p 2ac -2	P 2 _{ac} 2	42:bca	F m 2 m	f -2 -2	F 2 2
31:ba-c	P n m 21	p 2bc -2bc	P 2 _{bc} 2 _{bc}	43	F d d 2	f 2 -2d	F 2 2 _d
31:cab	P 21 m n	p -2ab 2ab	P 2 _{ab} 2 _{ab}	43:cab	F 2 d d	f -2d 2	F 2 _d 2
31:-cba	P 21 n m	p -2 2ac	P 2 2 _{ac}	43:bca	F d 2 d	f -2d -2d	F 2 _d 2 _d
31:bca	P n 21 m	p -2 -2bc	P 2 2 _{bc}	44	I m m 2	i 2 -2	I 2 2
31:a-cb	P m 21 n	p -2ab -2	P 2 _{ab} 2	44:cab	I 2 m m	i -2 2	I 2 2
32	P b a 2	p 2 -2ab	P 2 2 _{ab}	44:bca	I m 2 m	i -2 -2	I 2 2
32:cab	P 2 c b	p -2bc 2	P 2 _{bc} 2	45	I b a 2	i 2 -2c	I 2 2 _c
32:bca	P c 2 a	p -2ac -2ac	P 2 _{ac} 2 _{ac}	45:cab	I 2 c b	i -2a 2	I 2 _a 2
33	P n a 21	p 2c -2n	P 2 _c 2 _n	45:bca	I c 2 a	i -2b -2b	I 2 _b 2 _b

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.2.7. *Hall symbols (cont.)*

n:c	H-M entry	Hall entry	Hall symbol	n:c	H-M entry	Hall entry	Hall symbol
46	I m a 2	i 2 -2a	I 2 $\bar{2}_a$	58:bca	P n m n	-p 2n 2n	$\bar{P} 2_n 2_n$
46:ba-c	I b m 2	i 2 -2b	I 2 $\bar{2}_b$	59:1	P m m n:1	p 2 2ab -1ab	P 2 $2_{ab} \bar{1}_{ab}$
46:cab	I 2 m b	i -2b 2	I $\bar{2}_b 2$	59:2	P m m n:2	-p 2ab 2a	$\bar{P} 2_{ab} 2_a$
46:-cba	I 2 c m	i -2c 2	I $\bar{2}_c 2$	59:1cab	P n m m:1	p 2bc 2 -1bc	P $2_{bc} 2 \bar{1}_{bc}$
46:bca	I c 2 m	i -2c -2c	I $\bar{2}_c \bar{2}_c$	59:2cab	P n m m:2	-p 2c 2bc	$\bar{P} 2_c 2_{bc}$
46:a-cb	I m 2 a	i -2a -2a	I $\bar{2}_a \bar{2}_a$	59:1bca	P m n m:1	p 2ac 2ac -1ac	P $2_{ac} 2_{ac} \bar{1}_{ac}$
47	P m m m	-p 2 2	$\bar{P} 2 2$	59:2bca	P m n m:2	-p 2c 2a	$\bar{P} 2_c 2_a$
48:1	P n n n:1	p 2 2 -1n	P 2 2 $\bar{1}_n$	60	P b c n	-p 2n 2ab	$\bar{P} 2_n 2_{ab}$
48:2	P n n n:2	-p 2ab 2bc	$\bar{P} 2_{ab} 2_{bc}$	60:ba-c	P c a n	-p 2n 2c	$\bar{P} 2_n 2_c$
49	P c c m	-p 2 2c	$\bar{P} 2 2_c$	60:cab	P n c a	-p 2a 2n	$\bar{P} 2_a 2_n$
49:cab	P m a a	-p 2a 2	$\bar{P} 2_a 2$	60:-cba	P n a b	-p 2bc 2n	$\bar{P} 2_{bc} 2_n$
49:bca	P b m b	-p 2b 2b	$\bar{P} 2_b 2_b$	60:bca	P b n a	-p 2ac 2b	$\bar{P} 2_{ac} 2_b$
50:1	P b a n:1	p 2 2 -1ab	P 2 2 $\bar{1}_{ab}$	60:a-cb	P c n b	-p 2b 2ac	$\bar{P} 2_b 2_{ac}$
50:2	P b a n:2	-p 2ab 2b	$\bar{P} 2_{ab} 2_b$	61	P b c a	-p 2ac 2ab	$\bar{P} 2_{ac} 2_{ab}$
50:1cab	P n c b:1	p 2 2 -1bc	P 2 2 $\bar{1}_{bc}$	61:ba-c	P c a b	-p 2bc 2ac	$\bar{P} 2_{bc} 2_{ac}$
50:2cab	P n c b:2	-p 2b 2bc	$\bar{P} 2_b 2_{bc}$	62	P n m a	-p 2ac 2n	$\bar{P} 2_{ac} 2_n$
50:1bca	P c n a:1	p 2 2 -1ac	P 2 2 $\bar{1}_{ac}$	62:ba-c	P m n b	-p 2bc 2a	$\bar{P} 2_{bc} 2_a$
50:2bca	P c n a:2	-p 2a 2c	$\bar{P} 2_a 2_c$	62:cab	P b n m	-p 2c 2ab	$\bar{P} 2_c 2_{ab}$
51	P m m a	-p 2a 2a	$\bar{P} 2_a 2_a$	62:-cba	P c m n	-p 2n 2ac	$\bar{P} 2_n 2_{ac}$
51:ba-c	P m m b	-p 2b 2	$\bar{P} 2_b 2$	62:bca	P m c n	-p 2n 2a	$\bar{P} 2_n 2_a$
51:cab	P b m m	-p 2 2b	$\bar{P} 2 2_b$	62:a-cb	P n a m	-p 2c 2n	$\bar{P} 2_c 2_n$
51:-cba	P c m m	-p 2c 2c	$\bar{P} 2_c 2_c$	63	C m c m	-c 2c 2	$\bar{C} 2_c 2$
51:bca	P m c m	-p 2c 2	$\bar{P} 2_c 2$	63:ba-c	C c m m	-c 2c 2c	$\bar{C} 2_c 2_c$
51:a-cb	P m a m	-p 2 2a	$\bar{P} 2 2_a$	63:cab	A m m a	-a 2a 2a	$\bar{A} 2_a 2_a$
52	P n n a	-p 2a 2bc	$\bar{P} 2_a 2_{bc}$	63:-cba	A m a m	-a 2 2a	$\bar{A} 2 2_a$
52:ba-c	P n n b	-p 2b 2n	$\bar{P} 2_b 2_n$	63:bca	B b m m	-b 2 2b	$\bar{B} 2 2_b$
52:cab	P b n n	-p 2n 2b	$\bar{P} 2_n 2_b$	63:a-cb	B m m b	-b 2b 2	$\bar{B} 2_b 2$
52:-cba	P c n n	-p 2ab 2c	$\bar{P} 2_{ab} 2_c$	64	C m c a	-c 2ac 2	$\bar{C} 2_{ac} 2$
52:bca	P n c n	-p 2ab 2n	$\bar{P} 2_{ab} 2_n$	64:ba-c	C c m b	-c 2ac 2ac	$\bar{C} 2_{ac} 2_{ac}$
52:a-cb	P n a n	-p 2n 2bc	$\bar{P} 2_n 2_{bc}$	64:cab	A b m a	-a 2ab 2ab	$\bar{A} 2_{ab} 2_{ab}$
53	P m n a	-p 2ac 2	$\bar{P} 2_{ac} 2$	64:-cba	A c a m	-a 2 2ab	$\bar{A} 2 2_{ab}$
53:ba-c	P n m b	-p 2bc 2bc	$\bar{P} 2_{bc} 2_{bc}$	64:bca	B b c m	-b 2 2ab	$\bar{B} 2 2_{ab}$
53:cab	P b m n	-p 2ab 2ab	$\bar{P} 2_{ab} 2_{ab}$	64:a-cb	B m a b	-b 2ab 2	$\bar{B} 2_{ab} 2$
53:-cba	P c n m	-p 2 2ac	$\bar{P} 2 2_{ac}$	65	C m m m	-c 2 2	$\bar{C} 2 2$
53:bca	P n c m	-p 2 2bc	$\bar{P} 2 2_{bc}$	65:cab	A m m m	-a 2 2	$\bar{A} 2 2$
53:a-cb	P m a n	-p 2ab 2	$\bar{P} 2_{ab} 2$	65:bca	B m m m	-b 2 2	$\bar{B} 2 2$
54	P c c a	-p 2a 2ac	$\bar{P} 2_a 2_{ac}$	66	C c c m	-c 2 2c	$\bar{C} 2 2_c$
54:ba-c	P c c b	-p 2b 2c	$\bar{P} 2_b 2_c$	66:cab	A m a a	-a 2a 2	$\bar{A} 2_a 2$
54:cab	P b a a	-p 2a 2b	$\bar{P} 2_a 2_b$	66:bca	B b m b	-b 2b 2b	$\bar{B} 2_b 2_b$
54:-cba	P c a a	-p 2ac 2c	$\bar{P} 2_{ac} 2_c$	67	C m m a	-c 2a 2	$\bar{C} 2_a 2$
54:bca	P b c b	-p 2bc 2b	$\bar{P} 2_{bc} 2_b$	67:ba-c	C m m b	-c 2a 2a	$\bar{C} 2_a 2_a$
54:a-cb	P b a b	-p 2b 2ab	$\bar{P} 2_b 2_{ab}$	67:cab	A b m m	-a 2b 2b	$\bar{A} 2_b 2_b$
55	P b a m	-p 2 2ab	$\bar{P} 2 2_{ab}$	67:-cba	A c m m	-a 2 2b	$\bar{A} 2 2_b$
55:cab	P m c b	-p 2bc 2	$\bar{P} 2_{bc} 2$	67:bca	B m c m	-b 2 2a	$\bar{B} 2 2_a$
55:bca	P c m a	-p 2ac 2ac	$\bar{P} 2_{ac} 2_{ac}$	67:a-cb	B m a m	-b 2a 2	$\bar{B} 2_a 2$
56	P c c n	-p 2ab 2ac	$\bar{P} 2_{ab} 2_{ac}$	68:1	C c c a:1	c 2 2 -1ac	C 2 2 $\bar{1}_{ac}$
56:cab	P n a a	-p 2ac 2bc	$\bar{P} 2_{ac} 2_{bc}$	68:2	C c c a:2	-c 2a 2ac	$\bar{C} 2_a 2_{ac}$
56:bca	P b n b	-p 2bc 2ab	$\bar{P} 2_{bc} 2_{ab}$	68:1ba-c	C c c b:1	c 2 2 -1ac	C 2 2 $\bar{1}_{ac}$
57	P b c m	-p 2c 2b	$\bar{P} 2_c 2_b$	68:2ba-c	C c c b:2	-c 2a 2c	$\bar{C} 2_a 2_c$
57:ba-c	P c a m	-p 2c 2ac	$\bar{P} 2_c 2_{ac}$	68:1cab	A b a a:1	a 2 2 -1ab	A 2 2 $\bar{1}_{ab}$
57:cab	P m c a	-p 2ac 2a	$\bar{P} 2_{ac} 2_a$	68:2cab	A b a a:2	-a 2a 2b	$\bar{A} 2_a 2_b$
57:-cba	P m a b	-p 2b 2a	$\bar{P} 2_b 2_a$	68:1-cba	A c a a:1	a 2 2 -1ab	A 2 2 $\bar{1}_{ab}$
57:bca	P b m a	-p 2a 2ab	$\bar{P} 2_a 2_{ab}$	68:2-cba	A c a a:2	-a 2ab 2b	$\bar{A} 2_{ab} 2_b$
57:a-cb	P c m b	-p 2bc 2c	$\bar{P} 2_{bc} 2_c$	68:1bca	B b c b:1	b 2 2 -1ab	B 2 2 $\bar{1}_{ab}$
58	P n n m	-p 2 2n	$\bar{P} 2 2_n$	68:2bca	B b c b:2	-b 2ab 2b	$\bar{B} 2_{ab} 2_b$
58:cab	P m n n	-p 2n 2	$\bar{P} 2_n 2$	68:1a-cb	B b a b:1	b 2 2 -1ab	B 2 2 $\bar{1}_{ab}$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.2.7. Hall symbols (cont.)

n:c	H-M entry	Hall entry	Hall symbol	n:c	H-M entry	Hall entry	Hall symbol
68:2a-cb	B b a b:2	-b 2b 2ab	$\bar{B} 2_b 2_{ab}$	112	P -4 2 c	p -4 2c	$P \bar{4} 2_c$
69	F m m m	-f 2 2	$\bar{F} 2 2$	113	P -4 21 m	p -4 2ab	$P \bar{4} 2_{ab}$
70:1	F d d d:1	f 2 2 -1d	$F 2 2 \bar{1}_d$	114	P -4 21 c	p -4 2n	$P \bar{4} 2_n$
70:2	F d d d:2	-f 2uv 2vw	$\bar{F} 2_{uv} 2_{vw}$	115	P -4 m 2	p -4 -2	$P \bar{4} \bar{2}$
71	I m m m	-i 2 2	$\bar{I} 2 2$	116	P -4 c 2	p -4 -2c	$P \bar{4} \bar{2}_c$
72	I b a m	-i 2 2c	$\bar{I} 2 2_c$	117	P -4 b 2	p -4 -2ab	$P \bar{4} \bar{2}_{ab}$
72:cab	I m c b	-i 2a 2	$\bar{I} 2_a 2$	118	P -4 n 2	p -4 -2n	$P \bar{4} \bar{2}_n$
72:bca	I c m a	-i 2b 2b	$\bar{I} 2_b 2_b$	119	I -4 m 2	i -4 -2	$I \bar{4} \bar{2}$
73	I b c a	-i 2b 2c	$\bar{I} 2_b 2_c$	120	I -4 c 2	i -4 -2c	$I \bar{4} \bar{2}_c$
73:ba-c	I c a b	-i 2a 2b	$\bar{I} 2_a 2_b$	121	I -4 2 m	i -4 2	$I \bar{4} 2$
74	I m m a	-i 2b 2	$\bar{I} 2_b 2$	122	I -4 2 d	i -4 2bw	$I \bar{4} 2_{bw}$
74:ba-c	I m m b	-i 2a 2a	$\bar{I} 2_a 2_a$	123	P 4/m m m	-p 4 2	$\bar{P} 4 2$
74:cab	I b m m	-i 2c 2c	$\bar{I} 2_c 2_c$	124	P 4/m c c	-p 4 2c	$\bar{P} 4 2_c$
74:-cba	I c m m	-i 2 2b	$\bar{I} 2 2_b$	125:1	P 4/n b m:1	p 4 2 -1ab	$P 4 2 \bar{1}_{ab}$
74:bca	I m c m	-i 2 2a	$\bar{I} 2 2_a$	125:2	P 4/n b m:2	-p 4a 2b	$\bar{P} 4_a 2_b$
74:a-cb	I m a m	-i 2c 2	$\bar{I} 2_c 2$	126:1	P 4/n n c:1	p 4 2 -1n	$P 4 2 \bar{1}_n$
75	P 4	p 4	P 4	126:2	P 4/n n c:2	-p 4a 2bc	$\bar{P} 4_a 2_{bc}$
76	P 41	p 4w	P 4 _w	127	P 4/m b m	-p 4 2ab	$\bar{P} 4 2_{ab}$
77	P 42	p 4c	P 4 _c	128	P 4/m n c	-p 4 2n	$\bar{P} 4 2_n$
78	P 43	p 4cw	P 4 _{cw}	129:1	P 4/n m m:1	p 4ab 2ab -1ab	$P 4_{ab} 2_{ab} \bar{1}_{ab}$
79	I 4	i 4	I 4	129:2	P 4/n m m:2	-p 4a 2a	$\bar{P} 4_a 2_a$
80	I 41	i 4bw	I 4 _{bw}	130:1	P 4/n c c:1	p 4ab 2n -1ab	$P 4_{ab} 2_n \bar{1}_{ab}$
81	P -4	p -4	$P \bar{4}$	130:2	P 4/n c c:2	-p 4a 2ac	$\bar{P} 4_a 2_{ac}$
82	I -4	i -4	$I \bar{4}$	131	P 42/m m c	-p 4c 2	$\bar{P} 4_c 2$
83	P 4/m	-p 4	$\bar{P} 4$	132	P 42/m c m	-p 4c 2c	$\bar{P} 4_c 2_c$
84	P 42/m	-p 4c	$\bar{P} 4_c$	133:1	P 42/n b c:1	p 4n 2c -1n	$P 4_n 2_c \bar{1}_n$
85:1	P 4/n:1	p 4ab -1ab	$P 4_{ab} \bar{1}_{ab}$	133:2	P 42/n b c:2	-p 4ac 2b	$\bar{P} 4_{ac} 2_b$
85:2	P 4/n:2	-p 4a	$\bar{P} 4_a$	134:1	P 42/n n m:1	p 4n 2 -1n	$P 4_n 2 \bar{1}_n$
86:1	P 42/n:1	p 4n -1n	$P 4_n \bar{1}_n$	134:2	P 42/n n m:2	-p 4ac 2bc	$\bar{P} 4_{ac} 2_{bc}$
86:2	P 42/n:2	-p 4bc	$\bar{P} 4_{bc}$	135	P 42/m b c	-p 4c 2ab	$\bar{P} 4_c 2_{ab}$
87	I 4/m	-i 4	$\bar{I} 4$	136	P 42/m n m	-p 4n 2n	$\bar{P} 4_n 2_n$
88:1	I 41/a:1	i 4bw -1bw	$I 4_{bw} \bar{1}_{bw}$	137:1	P 42/n m c:1	p 4n 2n -1n	$P 4_n 2_n \bar{1}_n$
88:2	I 41/a:2	-i 4ad	$\bar{I} 4_{ad}$	137:2	P 42/n m c:2	-p 4ac 2a	$\bar{P} 4_{ac} 2_a$
89	P 4 2 2	p 4 2	P 4 2	138:1	P 42/n c m:1	p 4n 2ab -1n	$P 4_n 2_{ab} \bar{1}_n$
90	P 4 21 2	p 4ab 2ab	$P 4_{ab} 2_{ab}$	138:2	P 42/n c m:2	-p 4ac 2ac	$\bar{P} 4_{ac} 2_{ac}$
91	P 41 2 2	p 4w 2c	$P 4_w 2_c$	139	I 4/m m m	-i 4 2	$\bar{I} 4 2$
92	P 41 21 2	p 4abw 2nw	$P 4_{abw} 2_{nw}$	140	I 4/m c m	-i 4 2c	$\bar{I} 4 2_c$
93	P 42 2 2	p 4c 2	$P 4_c 2$	141:1	I 41/a m d:1	i 4bw 2bw -1bw	$I 4_{bw} 2_{bw} \bar{1}_{bw}$
94	P 42 21 2	p 4n 2n	$P 4_n 2_n$	141:2	I 41/a m d:2	-i 4bd 2	$\bar{I} 4_{bd} 2$
95	P 43 2 2	p 4cw 2c	$P 4_{cw} 2_c$	142:1	I 41/a c d:1	i 4bw 2aw -1bw	$I 4_{bw} 2_{aw} \bar{1}_{bw}$
96	P 43 21 2	p 4nw 2abw	$P 4_{nw} 2_{abw}$	142:2	I 41/a c d:2	-i 4bd 2c	$\bar{I} 4_{bd} 2_c$
97	I 4 2 2	i 4 2	$I 4 2$	143	P 3	p 3	P 3
98	I 41 2 2	i 4bw 2bw	$I 4_{bw} 2_{bw}$	144	P 31	p 31	P 3 ₁
99	P 4 m m	p 4 -2	$P 4 \bar{2}$	145	P 32	p 32	P 3 ₂
100	P 4 b m	p 4 -2ab	$P 4 \bar{2}_{ab}$	146:h	R 3:h	r 3	R 3
101	P 42 c m	p 4c -2c	$P 4_c \bar{2}_c$	146:r	R 3:r	p 3*	P 3*
102	P 42 n m	p 4n -2n	$P 4_n \bar{2}_n$	147	P -3	-p 3	$\bar{P} 3$
103	P 4 c c	p 4 -2c	$P 4 \bar{2}_c$	148:h	R -3:h	-r 3	$\bar{R} 3$
104	P 4 n c	p 4 -2n	$P 4 \bar{2}_n$	148:r	R -3:r	-p 3*	$\bar{P} 3^*$
105	P 42 m c	p 4c -2	$P 4_c \bar{2}$	149	P 3 1 2	p 3 2	P 3 2
106	P 42 b c	p 4c -2ab	$P 4_c \bar{2}_{ab}$	150	P 3 2 1	p 3 2"	P 3 2"
107	I 4 m m	i 4 -2	$I 4 \bar{2}$	151	P 31 1 2	p 31 2 (0 0 4)	P 3 ₁ 2 (0 0 4)
108	I 4 c m	i 4 -2c	$I 4 \bar{2}_c$	152	P 31 2 1	p 31 2"	P 3 ₁ 2"
109	I 41 m d	i 4bw -2	$I 4_{bw} \bar{2}$	153	P 32 1 2	p 32 2 (0 0 2)	P 3 ₂ 2 (0 0 2)
110	I 41 c d	i 4bw -2c	$I 4_{bw} \bar{2}_c$	154	P 32 2 1	p 32 2"	P 3 ₂ 2"
111	P -4 2 m	p -4 2	$P \bar{4} 2$	155:h	R 3 2:h	r 3 2"	R 3 2"

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.2.7. *Hall symbols (cont.)*

n:c	H-M entry	Hall entry	Hall symbol	n:c	H-M entry	Hall entry	Hall symbol
155:r	R 3 2:r	p 3* 2	P 3* 2	194	P 63/m m c	-p 6c 2c	$\bar{P} 6_c 2_c$
156	P 3 m 1	p 3 -2"	P 3 $\bar{2}''$	195	P 2 3	p 2 2 3	P 2 2 3
157	P 3 1 m	p 3 -2	P 3 $\bar{2}$	196	F 2 3	f 2 2 3	F 2 2 3
158	P 3 c 1	p 3 -2"c	P 3 $\bar{2}_c''$	197	I 2 3	i 2 2 3	I 2 2 3
159	P 3 1 c	p 3 -2c	P 3 $\bar{2}_c$	198	P 21 3	p 2ac 2ab 3	P $2_{ac} 2_{ab} 3$
160:h	R 3 m:h	r 3 -2"	R 3 $\bar{2}''$	199	I 21 3	i 2b 2c 3	I $2_b 2_c 3$
160:r	R 3 m:r	p 3* -2	P 3* $\bar{2}$	200	P m -3	-p 2 2 3	$\bar{P} 2 2 3$
161:h	R 3 c:h	r 3 -2"c	R 3 $\bar{2}_c''$	201:1	P n -3:1	p 2 2 3 -1n	P 2 2 3 $\bar{1}_n$
161:r	R 3 c:r	p 3* -2n	P 3* $\bar{2}_n$	201:2	P n -3:2	-p 2ab 2bc 3	$\bar{P} 2_{ab} 2_{bc} 3$
162	P -3 1 m	-p 3 2	$\bar{P} 3 2$	202	F m -3	-f 2 2 3	$\bar{F} 2 2 3$
163	P -3 1 c	-p 3 2c	$\bar{P} 3 2_c$	203:1	F d -3:1	f 2 2 3 -1d	F 2 2 3 $\bar{1}_d$
164	P -3 m 1	-p 3 2"	$\bar{P} 3 2''$	203:2	F d -3:2	-f 2uv 2vw 3	$\bar{F} 2_{uv} 2_{vw} 3$
165	P -3 c 1	-p 3 2"c	$\bar{P} 3 2_c''$	204	I m -3	-i 2 2 3	$\bar{I} 2 2 3$
166:h	R -3 m:h	-r 3 2"	$\bar{R} 3 2''$	205	P a -3	-p 2ac 2ab 3	$\bar{P} 2_{ac} 2_{ab} 3$
166:r	R -3 m:r	-p 3* 2	$\bar{P} 3^* 2$	206	I a -3	-i 2b 2c 3	$\bar{I} 2_b 2_c 3$
167:h	R -3 c:h	-r 3 2"c	$\bar{R} 3 2_c''$	207	P 4 3 2	p 4 2 3	P 4 2 3
167:r	R -3 c:r	-p 3* 2n	$\bar{P} 3^* 2_n$	208	P 42 3 2	p 4n 2 3	P $4_n 2 3$
168	P 6	p 6	P 6	209	F 4 3 2	f 4 2 3	F 4 2 3
169	P 61	p 61	P 6 ₁	210	F 41 3 2	f 4d 2 3	F $4_d 2 3$
170	P 65	p 65	P 6 ₅	211	I 4 3 2	i 4 2 3	I 4 2 3
171	P 62	p 62	P 6 ₂	212	P 43 3 2	p 4acd 2ab 3	P $4_{acd} 2_{ab} 3$
172	P 64	p 64	P 6 ₄	213	P 41 3 2	p 4bd 2ab 3	P $4_{bd} 2_{ab} 3$
173	P 63	p 6c	P 6 _c	214	I 41 3 2	i 4bd 2c 3	I $4_{bd} 2_c 3$
174	P -6	p -6	P $\bar{6}$	215	P -4 3 m	p -4 2 3	P $\bar{4} 2 3$
175	P 6/m	-p 6	$\bar{P} 6$	216	F -4 3 m	f -4 2 3	F $\bar{4} 2 3$
176	P 63/m	-p 6c	$\bar{P} 6_c$	217	I -4 3 m	i -4 2 3	I $\bar{4} 2 3$
177	P 6 2 2	p 6 2	P 6 2	218	P -4 3 n	p -4n 2 3	P $\bar{4}_n 2 3$
178	P 61 2 2	p 61 2 (0 0 5)	P 6 ₁ 2 (0 0 5)	219	F -4 3 c	f -4a 2 3	F $\bar{4}_a 2 3$
179	P 65 2 2	p 65 2 (0 0 1)	P 6 ₅ 2 (0 0 1)	220	I -4 3 d	i -4bd 2c 3	I $\bar{4}_{bd} 2_c 3$
180	P 62 2 2	p 62 2 (0 0 4)	P 6 ₂ 2 (0 0 4)	221	P m -3 m	-p 4 2 3	$\bar{P} 4 2 3$
181	P 64 2 2	p 64 2 (0 0 2)	P 6 ₄ 2 (0 0 2)	222:1	P n -3 n:1	p 4 2 3 -1n	P 4 2 3 $\bar{1}_n$
182	P 63 2 2	p 6c 2c	P 6 _c 2 _c	222:2	P n -3 n:2	-p 4a 2bc 3	$\bar{P} 4_a 2_{bc} 3$
183	P 6 m m	p 6 -2	P 6 $\bar{2}$	223	P m -3 n	-p 4n 2 3	$\bar{P} 4_n 2 3$
184	P 6 c c	p 6 -2c	P 6 $\bar{2}_c$	224:1	P n -3 m:1	p 4n 2 3 -1n	P $4_n 2 3 \bar{1}_n$
185	P 63 c m	p 6c -2	P 6 _c $\bar{2}$	224:2	P n -3 m:2	-p 4bc 2bc 3	$\bar{P} 4_{bc} 2_{bc} 3$
186	P 63 m c	p 6c -2c	P 6 _c $\bar{2}_c$	225	F m -3 m	-f 4 2 3	$\bar{F} 4 2 3$
187	P -6 m 2	p -6 2	P $\bar{6} 2$	226	F m -3 c	-f 4a 2 3	$\bar{F} 4_a 2 3$
188	P -6 c 2	p -6c 2	P $\bar{6}_c 2$	227:1	F d -3 m:1	f 4d 2 3 -1d	F $4_d 2 3 \bar{1}_d$
189	P -6 2 m	p -6 -2	P $\bar{6} \bar{2}$	227:2	F d -3 m:2	-f 4vw 2vw 3	$\bar{F} 4_{vw} 2_{vw} 3$
190	P -6 2 c	p -6c -2c	P $\bar{6}_c \bar{2}_c$	228:1	F d -3 c:1	f 4d 2 3 -1ad	F $4_d 2 3 \bar{1}_{ad}$
191	P 6/m m m	-p 6 2	$\bar{P} 6 2$	228:2	F d -3 c:2	-f 4ud 2vw 3	$\bar{F} 4_{ud} 2_{vw} 3$
192	P 6/m c c	-p 6 2c	$\bar{P} 6 2_c$	229	I m -3 m	-i 4 2 3	$\bar{I} 4 2 3$
193	P 63/m c m	-p 6c 2	$\bar{P} 6_c 2$	230	I a -3 d	-i 4bd 2c 3	$\bar{I} 4_{bd} 2_c 3$

The codes appended to the space-group numbers listed in the first column identify the relationship between the symmetry elements and the crystal cell. Where no code is given the first choice listed below applies.

Monoclinic. Code = <unique axis><cell choice>: unique axis choices [cf. *IT A* (1983) Table 4.3.1] b, -b, c, -c, a, -a; cell choices [cf. *IT A* (1983) Table 4.3.1] 1, 2, 3.

Orthorhombic. Code = <origin choice><setting>: origin choices 1, 2; setting choices [cf. *IT A* (1983) Table 4.3.1] abc, ba-c, cab, -cba, bca, a-cb.

Tetragonal, cubic. Code = <origin choice>: origin choices 1, 2.

Trigonal. Code = <cell choice>: cell choices h (hexagonal), r (rhombohedral).

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Appendix 1.4.3.

Structure-factor tables

Table A1.4.3.1. *Plane groups*

The symbols appearing in this table are explained in Section 1.4.3 and in Tables A1.4.3.3 (monoclinic), A1.4.3.5 (tetragonal) and A1.4.3.6 (trigonal and hexagonal).

System	No.	Symbol	Parity	A	B
Oblique	1	$p1$		$c(hk)$	$s(hk)$
	2	$p2$		$2c(hk)$	0
Rectangular	3	pm		$2c(hx)c(ky)$	$2c(hx)s(ky)$
	4	pg	$k = 2n$	$2c(hx)c(ky)$	$2c(hx)s(ky)$
			$k = 2n + 1$	$-2s(hx)s(ky)$	$2s(hx)c(ky)$
	5	cm		$4c(hx)c(ky)$	$4c(hx)s(ky)$
	6	$p2mm$		$4c(hx)c(ky)$	0
	7	$p2mg$	$h = 2n$	$4c(hx)c(ky)$	0
			$h = 2n + 1$	$-4s(hx)s(ky)$	0
	8	$p2gg$	$h + k = 2n$	$4c(hx)c(ky)$	0
Square			$h + k = 2n + 1$	$-4s(hx)s(ky)$	0
	9	$c2mm$		$8c(hx)c(ky)$	0
	10	$p4$		$2[P(cc) - M(ss)]$	0
	11	$p4mm$		$4P(cc)$	0
	12	$p4gm$	$h + k = 2n$	$4P(cc)$	0
Hexagonal			$h + k = 2n + 1$	$-4M(ss)$	0
	13	$p3$		$C(hki)$	$S(hki)$
	14	$p3m1$		$PH(cc)$	$MH(ss)$
	15	$p31m$		$PH(cc)$	$PH(ss)$
	16	$p6$		$2C(hki)$	0
	17	$p6mm$		$2PH(cc)$	0

Table A1.4.3.2. *Triclinic space groups*

For the definition of the triple products ccc , csc etc., see Table A1.4.3.4.

$P1$ [No. 1]

hkl	A	B
All	$\cos 2\pi(hx + ky + lz) = ccc - css - scs - ssc$	$\sin 2\pi(hx + ky + lz) = scc + csc + ccs - sss$

$P\bar{1}$ [No. 2]

hkl	A	B
All	$2(ccc - css - scs - ssc)$	0

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.3. *Monoclinic space groups*

Each expression for A or B in the monoclinic system and for the space-group settings chosen in *IT A* is represented in terms of one of the following symbols:

$$\begin{aligned} c(hl)c(ky) &= \cos[2\pi(hx + lz)] \cos(2\pi ky), & c(hk)c(lz) &= \cos[2\pi(hx + ky)] \cos(2\pi lz), \\ c(hl)s(ky) &= \cos[2\pi(hx + lz)] \sin(2\pi ky), & c(hk)s(lz) &= \cos[2\pi(hx + ky)] \sin(2\pi lz), \\ s(hl)c(ky) &= \sin[2\pi(hx + lz)] \cos(2\pi ky), & s(hk)c(lz) &= \sin[2\pi(hx + ky)] \cos(2\pi lz), \\ s(hl)s(ky) &= \sin[2\pi(hx + lz)] \sin(2\pi ky), & s(hk)s(lz) &= \sin[2\pi(hx + ky)] \sin(2\pi lz), \end{aligned} \quad (\text{A1.4.3.1})$$

where the left-hand column of expressions corresponds to space-group representations in the second setting, with b taken as the unique axis, and the right-hand column corresponds to representations in the first setting, with c taken as the unique axis.

The lattice types in this table are P , A , B , C and I , and are all explicit in the full space-group symbol only (see below). Note that $s(hl)$, $s(hk)$, $s(ky)$ and $s(lz)$ are zero for $h = l = 0$, $h = k = 0$, $k = 0$ and $l = 0$, respectively.

No.	Group symbol		Parity	A	B	Unique axis
	Short	Full				
3	$P2$	$P121$		$2c(hl)c(ky)$	$2c(hl)s(ky)$	b
3	$P2$	$P112$		$2c(hk)c(lz)$	$2c(hk)s(lz)$	c
4	$P2_1$	$P12_11$	$k = 2n$	$2c(hl)c(ky)$	$2c(hl)s(ky)$	b
			$k = 2n + 1$	$-2s(hl)s(ky)$	$2s(hl)c(ky)$	
4	$P2_1$	$P112_1$	$l = 2n$	$2c(hk)c(lz)$	$2c(hk)s(lz)$	c
			$l = 2n + 1$	$-2s(hk)s(lz)$	$2s(hk)c(lz)$	
5	$C2$	$C121$		$4c(hl)c(ky)$	$4c(hl)s(ky)$	b
5	$C2$	$A121$		$4c(hl)c(ky)$	$4c(hl)s(ky)$	b
5	$C2$	$I121$		$4c(hl)c(ky)$	$4c(hl)s(ky)$	b
5	$C2$	$A112$		$4c(hk)c(lz)$	$4c(hk)s(lz)$	c
5	$C2$	$B112$		$4c(hk)c(lz)$	$4c(hk)s(lz)$	c
5	$C2$	$I112$		$4c(hk)c(lz)$	$4c(hk)s(lz)$	c
6	Pm	$P1m1$		$2c(hl)c(ky)$	$2s(hl)c(ky)$	b
6	Pm	$P11m$		$2c(hk)c(lz)$	$2s(hk)c(lz)$	c
7	Pc	$P1c1$	$l = 2n$	$2c(hl)c(ky)$	$2s(hl)c(ky)$	b
			$l = 2n + 1$	$-2s(hl)s(ky)$	$2c(hl)s(ky)$	
7	Pc	$P1n1$	$h + l = 2n$	$2c(hl)c(ky)$	$2s(hl)c(ky)$	b
			$h + l = 2n + 1$	$-2s(hl)s(ky)$	$2c(hl)s(ky)$	
7	Pc	$P1a1$	$h = 2n$	$2c(hl)c(ky)$	$2s(hl)c(ky)$	b
			$h = 2n + 1$	$-2s(hl)s(ky)$	$2c(hl)s(ky)$	
7	Pc	$P11a$	$h = 2n$	$2c(hk)c(lz)$	$2s(hk)c(lz)$	c
			$h = 2n + 1$	$-2s(hk)s(lz)$	$2c(hk)s(lz)$	
7	Pc	$P11n$	$h + k = 2n$	$2c(hk)c(lz)$	$2s(hk)c(lz)$	c
			$h + k = 2n + 1$	$-2s(hk)s(lz)$	$2c(hk)s(lz)$	
7	Pc	$P11b$	$k = 2n$	$2c(hk)c(lz)$	$2s(hk)c(lz)$	c
			$k = 2n + 1$	$-2s(hk)s(lz)$	$2c(hk)s(lz)$	
8	Cm	$C1m1$		$4c(hl)c(ky)$	$4s(hl)c(ky)$	b
8	Cm	$A1m1$		$4c(hl)c(ky)$	$4s(hl)c(ky)$	b
8	Cm	$I1m1$		$4c(hl)c(ky)$	$4s(hl)c(ky)$	b
8	Cm	$A11m$		$4c(hk)c(lz)$	$4s(hk)c(lz)$	c
8	Cm	$B11m$		$4c(hk)c(lz)$	$4s(hk)c(lz)$	c
8	Cm	$I11m$		$4c(hk)c(lz)$	$4s(hk)c(lz)$	c
9	Cc	$C1c1$	$l = 2n$	$4c(hl)c(ky)$	$4s(hl)c(ky)$	b
			$l = 2n + 1$	$-4s(hl)s(ky)$	$4c(hl)s(ky)$	
9	Cc	$A1n1$	$h + l = 2n$	$4c(hl)c(ky)$	$4s(hl)c(ky)$	b
			$h + l = 2n + 1$	$-4s(hl)s(ky)$	$4c(hl)s(ky)$	
9	Cc	$I1a1$	$h = 2n$	$4c(hl)c(ky)$	$4s(hl)c(ky)$	b
			$h = 2n + 1$	$-4s(hl)s(ky)$	$4c(hl)s(ky)$	
9	Cc	$A11a$	$h = 2n$	$4c(hk)c(lz)$	$4s(hk)c(lz)$	c
			$h = 2n + 1$	$-4s(hk)s(lz)$	$4c(hk)s(lz)$	
9	Cc	$B11n$	$h + k = 2n$	$4c(hk)c(lz)$	$4s(hk)c(lz)$	c
			$h + k = 2n + 1$	$-4s(hk)s(lz)$	$4c(hk)s(lz)$	
9	Cc	$I11b$	$k = 2n$	$4c(hk)c(lz)$	$4s(hk)c(lz)$	c
			$k = 2n + 1$	$-4s(hk)s(lz)$	$4c(hk)s(lz)$	
10	$P2/m$	$P12/m1$		$4c(hl)c(ky)$	0	b

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Table A1.4.3.3. *Monoclinic space groups (cont.)*

No.	Group symbol		Parity	A	B	Unique axis
	Short	Full				
10	$P2/m$	$P112/m$		$4c(hk)c(lz)$	0	c
11	$P2_1/m$	$P12_1/m1$	$k = 2n$	$4c(hl)c(ky)$	0	b
			$k = 2n + 1$	$-4s(hl)s(ky)$	0	
11	$P2_1/m$	$P112_1/m$	$l = 2n$	$4c(hk)c(lz)$	0	c
			$l = 2n + 1$	$-4s(hk)s(lz)$	0	
12	$C2/m$	$C12/m1$		$8c(hl)c(ky)$	0	b
12	$C2/m$	$A12/m1$		$8c(hl)c(ky)$	0	b
12	$C2/m$	$I12/m1$		$8c(hl)c(ky)$	0	b
12	$C2/m$	$A112/m$		$8c(hk)c(lz)$	0	c
12	$C2/m$	$B112/m$		$8c(hk)c(lz)$	0	c
12	$C2/m$	$I112/m$		$8c(hk)c(lz)$	0	c
13	$P2/c$	$P12/c1$	$l = 2n$	$4c(hl)c(ky)$	0	b
			$l = 2n + 1$	$-4s(hl)s(ky)$	0	
13	$P2/c$	$P12/n1$	$h + l = 2n$	$4c(hl)c(ky)$	0	b
			$h + l = 2n + 1$	$-4s(hl)s(ky)$	0	
13	$P2/c$	$P12/a1$	$h = 2n$	$4c(hl)c(ky)$	0	b
			$h = 2n + 1$	$-4s(hl)s(ky)$	0	
13	$P2/c$	$P112/a$	$h = 2n$	$4c(hk)c(lz)$	0	c
			$h = 2n + 1$	$-4s(hk)s(lz)$	0	
13	$P2/c$	$P112/n$	$h + k = 2n$	$4c(hk)c(lz)$	0	c
			$h + k = 2n + 1$	$-4s(hk)s(lz)$	0	
13	$P2/c$	$P112/b$	$k = 2n$	$4c(hk)c(lz)$	0	c
			$k = 2n + 1$	$-4s(hk)s(lz)$	0	
14	$P2_1/c$	$P12_1/c1$	$k + l = 2n$	$4c(hl)c(ky)$	0	b
			$k + l = 2n + 1$	$-4s(hl)s(ky)$	0	
14	$P2_1/c$	$P12_1/n1$	$h + k + l = 2n$	$4c(hl)c(ky)$	0	b
			$h + k + l = 2n + 1$	$-4s(hl)s(ky)$	0	
14	$P2_1/c$	$P12_1/a1$	$h + k = 2n$	$4c(hl)c(ky)$	0	b
			$h + k = 2n + 1$	$-4s(hl)s(ky)$	0	
14	$P2_1/c$	$P112_1/a$	$h + l = 2n$	$4c(hk)c(lz)$	0	c
			$h + l = 2n + 1$	$-4s(hk)s(lz)$	0	
14	$P2_1/c$	$P112_1/n$	$h + k + l = 2n$	$4c(hk)c(lz)$	0	c
			$h + k + l = 2n + 1$	$-4s(hk)s(lz)$	0	
14	$P2_1/c$	$P112_1/b$	$k + l = 2n$	$4c(hk)c(lz)$	0	c
			$k + l = 2n + 1$	$-4s(hk)s(lz)$	0	
15	$C2/c$	$C12/c1$	$l = 2n$	$8c(hl)c(ky)$	0	b
			$l = 2n + 1$	$-8s(hl)s(ky)$	0	
15	$C2/c$	$A12/n1$	$h + l = 2n$	$8c(hl)c(ky)$	0	b
			$h + l = 2n + 1$	$-8s(hl)s(ky)$	0	
15	$C2/c$	$I12/a1$	$h = 2n$	$8c(hl)c(ky)$	0	b
			$h = 2n + 1$	$-8s(hl)s(ky)$	0	
15	$C2/c$	$A112/a$	$h = 2n$	$8c(hk)c(lz)$	0	c
			$h = 2n + 1$	$-8s(hk)s(lz)$	0	
15	$C2/c$	$B112/n$	$h + k = 2n$	$8c(hk)c(lz)$	0	c
			$h + k = 2n + 1$	$-8s(hk)s(lz)$	0	
15	$C2/c$	$I112/b$	$k = 2n$	$8c(hk)c(lz)$	0	c
			$k = 2n + 1$	$-8s(hk)s(lz)$	0	

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Table A1.4.3.4. *Orthorhombic space groups*

The expressions for A and B for the orthorhombic space groups in their standard settings [as in *IT A* (1983)] contain one, two or four terms of the form

$$pqr = p(2\pi hx)q(2\pi ky)r(2\pi lz) \quad (\text{A1.4.3.2})$$

preceded by a signed numerical constant, where p , q and r can each be either a sine or a cosine function, and the arguments of the functions in any product of the form (A1.4.3.2) are ordered as in (A1.4.3.2). These products are given in this table as ccc , ccs , csc , scc , ssc , scs , css and/or sss , where c and s are abbreviations for 'sin' and 'cos', respectively.

Note that pqr vanishes if at least one of p , q and r is a sine, and the corresponding index h , k or l is zero.

No.	Symbol	Origin	Parity	A	B
16	$P222$			4ccc	−4sss
17	$P222_1$		$l = 2n$	4ccc	−4sss
			$l = 2n + 1$	−4css	4scc
18	$P2_12_12$		$h + k = 2n$	4ccc	−4sss
			$h + k = 2n + 1$	−4ssc	4ccs
19	$P2_12_12_1$		$h + k = 2n; k + l = 2n$	4ccc	−4sss
			$h + k = 2n; k + l = 2n + 1$	−4css	4scc
			$h + k = 2n + 1; k + l = 2n$	−4scs	4csc
			$h + k = 2n + 1; k + l = 2n + 1$	−4ssc	4ccs
20	$C222_1$		$l = 2n$	8ccc	−8sss
			$l = 2n + 1$	−8css	8scc
21	$C222$			8ccc	−8sss
22	$F222$			16ccc	−16sss
23	$I222$			8ccc	−8sss
24	$I2_12_12_1$		h, k, l all even	8ccc	−8sss
			$h = 2n; k, l = 2n + 1$	−8scs	8csc
			$k = 2n; l, h = 2n + 1$	−8ssc	8ccs
			$l = 2n; h, k = 2n + 1$	−8css	8scc
25	$Pmm2$			4ccc	4ccs
26	$Pmc2_1$		$l = 2n$	4ccc	4ccs
			$l = 2n + 1$	−4css	4csc
27	$Pcc2$		$l = 2n$	4ccc	4ccs
			$l = 2n + 1$	−4ssc	−4sss
28	$Pma2$		$h = 2n$	4ccc	4ccs
			$h = 2n + 1$	−4ssc	−4sss
29	$Pca2_1$		$h = 2n; l = 2n$	4ccc	4ccs
			$h = 2n; l = 2n + 1$	−4scs	4scc
			$h = 2n + 1; l = 2n$	−4ssc	−4sss
			$h = 2n + 1; l = 2n + 1$	−4css	4csc
30	$Pnc2$		$k + l = 2n$	4ccc	4ccs
			$k + l = 2n + 1$	−4ssc	4sss
31	$Pmn2_1$		$h + l = 2n$	4ccc	4ccs
			$h + l = 2n + 1$	−4css	4csc
32	$Pba2$		$h + k = 2n$	4ccc	4ccs
			$h + k = 2n + 1$	−4ssc	−4sss
33	$Pna2_1$		$h + k = 2n; l = 2n$	4ccc	4ccs
			$h + k = 2n; l = 2n + 1$	−4scs	4scc
			$h + k = 2n + 1; l = 2n$	−4ssc	−4sss
			$h + k = 2n + 1; l = 2n + 1$	−4css	4csc
34	$Pnn2$		$h + k + l = 2n$	4ccc	4ccs
			$h + k + l = 2n + 1$	−4ssc	−4sss
35	$Cmm2$			8ccc	8ccs
36	$Cmc2_1$		$l = 2n$	8ccc	8ccs
			$l = 2n + 1$	−8css	8csc
37	$Ccc2$		$l = 2n$	8ccc	8ccs
			$l = 2n + 1$	−8ssc	−8sss
38	$Amm2$			8ccc	8ccs
39	$Abm2$		$k = 2n$	8ccc	8ccs
			$k = 2n + 1$	−8ssc	−8sss
40	$Ama2$		$h = 2n$	8ccc	8ccs

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.3.4. *Orthorhombic space groups (cont.)*

No.	Symbol	Origin	Parity	A	B
41	<i>Aba2</i>		$h = 2n + 1$	$-8ssc$	$-8sss$
			$h + k = 2n$	$8ccc$	$8ccs$
			$h + k = 2n + 1$	$-8ssc$	$-8sss$
42	<i>Fmm2</i>			$16ccc$	$16ccs$
43	<i>Fdd2</i>		$h + k + l = 4n$	$16ccc$	$16ccs$
			$h + k + l = 4n + 1$	$8(ccc - ssc - ccs - sss)$	$8(ccs - sss + ccc + ssc)$
			$h + k + l = 4n + 2$	$-16ssc$	$-16sss$
			$h + k + l = 4n + 3$	$8(ccc - ssc + ccs + sss)$	$8(ccs - sss - ccc - ssc)$
44	<i>Imm2</i>			$8ccc$	$8ccs$
45	<i>Iba2</i>		$l = 2n$	$8ccc$	$8ccs$
			$l = 2n + 1$	$-8ssc$	$-8sss$
46	<i>Iam2</i>		$h = 2n$	$8ccc$	$8ccs$
			$h = 2n + 1$	$-8ssc$	$-8sss$
47	<i>Pmmm</i>			$8ccc$	0
48	<i>Pnnn</i>	(1)	$h + k + l = 2n$	$8ccc$	0
			$h + k + l = 2n + 1$	0	$-8sss$
48	<i>Pnnn</i>	(2)	$h + k = 2n; k + l = 2n$	$8ccc$	0
			$h + k = 2n; k + l = 2n + 1$	$-8ssc$	0
			$h + k = 2n + 1; k + l = 2n$	$-8css$	0
			$h + k = 2n + 1; k + l = 2n + 1$	$-8scs$	0
49	<i>Pccm</i>		$l = 2n$	$8ccc$	0
			$l = 2n + 1$	$-8ssc$	0
50	<i>Pban</i>	(1)	$h + k = 2n$	$8ccc$	0
			$h + k = 2n + 1$	0	$-8sss$
50	<i>Pban</i>	(2)	$h = 2n; k = 2n$	$8ccc$	0
			$h = 2n; k = 2n + 1$	$-8scs$	0
			$h = 2n + 1; k = 2n$	$-8css$	0
			$h = 2n + 1; k = 2n + 1$	$-8ssc$	0
51	<i>Pmma</i>		$h = 2n$	$8ccc$	0
			$h = 2n + 1$	$-8scs$	0
52	<i>Pnna</i>		$h = 2n; k + l = 2n$	$8ccc$	0
			$h = 2n; k + l = 2n + 1$	$-8ssc$	0
			$h = 2n + 1; k + l = 2n$	$-8css$	0
			$h = 2n + 1; k + l = 2n + 1$	$-8scs$	0
53	<i>Pmna</i>		$h + l = 2n$	$8ccc$	0
			$h + l = 2n + 1$	$-8css$	0
54	<i>Pcca</i>		$h = 2n; l = 2n$	$8ccc$	0
			$h = 2n; l = 2n + 1$	$-8ssc$	0
			$h = 2n + 1; l = 2n$	$-8scs$	0
			$h = 2n + 1; l = 2n + 1$	$-8css$	0
55	<i>Pbam</i>		$h + k = 2n$	$8ccc$	0
			$h + k = 2n + 1$	$-8ssc$	0
56	<i>Pccn</i>		$h + k = 2n; h + l = 2n$	$8ccc$	0
			$h + k = 2n; h + l = 2n + 1$	$-8ssc$	0
			$h + k = 2n + 1; h + l = 2n$	$-8css$	0
			$h + k = 2n + 1; h + l = 2n + 1$	$-8scs$	0
57	<i>Pbcm</i>		$k = 2n; l = 2n$	$8ccc$	0
			$k = 2n; l = 2n + 1$	$-8css$	0
			$k = 2n + 1; l = 2n$	$-8ssc$	0
			$k = 2n + 1; l = 2n + 1$	$-8scs$	0
58	<i>Pnnm</i>		$h + k + l = 2n$	$8ccc$	0
			$h + k + l = 2n + 1$	$-8ssc$	0
59	<i>Pmnm</i>	(1)	$h + k = 2n$	$8ccc$	0
			$h + k = 2n + 1$	0	$8ccs$
59	<i>Pmnm</i>	(2)	$h = 2n; k = 2n$	$8ccc$	0
			$h = 2n; k = 2n + 1$	$-8css$	0

1.4. SYMMETRY IN RECIPROCAL SPACE
Table A1.4.3.4. *Orthorhombic space groups (cont.)*

No.	Symbol	Origin	Parity	A	B
60	<i>Pbcn</i>		$h = 2n + 1; k = 2n$	$-8scs$	0
			$h = 2n + 1; k = 2n + 1$	$-8ssc$	0
			$h + k = 2n; l = 2n$	$8ccc$	0
			$h + k = 2n; l = 2n + 1$	$-8css$	0
			$h + k = 2n + 1; l = 2n$	$-8scs$	0
61	<i>Pbca</i>		$h + k = 2n + 1; l = 2n + 1$	$-8ssc$	0
			$h + k = 2n; k + l = 2n$	$8ccc$	0
			$h + k = 2n; k + l = 2n + 1$	$-8css$	0
			$h + k = 2n + 1; k + l = 2n$	$-8scs$	0
			$h + k = 2n + 1; k + l = 2n + 1$	$-8ssc$	0
62	<i>Pnma</i>		$h + l = 2n; k = 2n$	$8ccc$	0
			$h + l = 2n; k = 2n + 1$	$-8ssc$	0
			$h + l = 2n + 1; k = 2n$	$-8scs$	0
			$h + l = 2n + 1; k = 2n + 1$	$-8css$	0
63	<i>Cmcm</i>		$l = 2n$	$16ccc$	0
			$l = 2n + 1$	$-16css$	0
64	<i>Cmca</i>		$k + l = 2n$	$16ccc$	0
			$k + l = 2n + 1$	$-16css$	0
65	<i>Cmmm</i>			$16ccc$	0
66	<i>Cccm</i>		$l = 2n$	$16ccc$	0
			$l = 2n + 1$	$-16ssc$	0
67	<i>Cmma</i>		$h = 2n$	$16ccc$	0
			$h = 2n + 1$	$-16css$	0
68	<i>Ccca</i>	(1)	$h + l = 2n$	$16ccc$	0
			$h + l = 2n + 1$	0	$-16sss$
68	<i>Ccca</i>	(2)	$k = 2n; l = 2n$	$16ccc$	0
			$k = 2n; l = 2n + 1$	$-16ssc$	0
			$k = 2n + 1; l = 2n$	$-16scs$	0
			$k = 2n + 1; l = 2n + 1$	$-16css$	0
				$32ccc$	0
69	<i>Fmmm</i>			$32ccc$	0
70	<i>Fddd</i>	(1)	$h + k + l = 4n$	$16(ccc - sss)$	A
			$h + k + l = 4n + 1$	0	$-32sss$
70	<i>Fddd</i>	(2)	$h + k + l = 4n + 2$	$16(ccc + sss)$	$-A$
			$h + k + l = 4n + 3$		
			$h + k = 4n; k + l = 4n; l + h = 4n$	$32ccc$	0
			$h + k = 4n; k + l = 4n + 2;$ $l + h = 4n + 2$	$-32ssc$	0
			$h + k = 4n + 2; k + l = 4n;$ $l + h = 4n + 2$	$-32css$	0
			$h + k = 4n + 2; k + l = 4n + 2;$ $l + h = 4n$	$-32scs$	0
			$h + k = 4n + 2; k + l = 4n + 2;$ $l + h = 4n + 2$	$-16(ccc + ssc + scs + css)$	0
			$h + k = 4n + 2; k + l = 4n; l + h = 4n$	$16(ccc + ssc - scs - css)$	0
			$h + k = 4n; k + l = 4n + 2; l + h = 4n$	$16(ccc - ssc - scs + css)$	0
			$h + k = 4n; k + l = 4n; l + h = 4n + 2$	$16(ccc - ssc + scs - css)$	0
				$16ccc$	0
			$l = 2n$	$16ccc$	0
			$l = 2n + 1$	$-16ssc$	0
			$h = 2n; k = 2n$	$16ccc$	0
			$h = 2n; k = 2n + 1$	$-16scs$	0
73	<i>Ibca</i>		$h = 2n + 1; k = 2n$	$-16ssc$	0
			$h = 2n + 1; k = 2n + 1$	$-16css$	0
			$k = 2n$	$16ccc$	0
74	<i>Imma</i>		$k = 2n + 1$	$-16css$	0

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.3.5. *Tetragonal space groups*

The symbols appearing in this table are based on the factorization of the scalar product appearing in equations (1.4.2.19) and (1.4.2.20) into its plane-group and unique-axis components. The symbols are

$$\begin{aligned} P(pq) &= p(2\pi hx)q(2\pi ky) + p(2\pi hy)q(2\pi kx) \\ M(pq) &= p(2\pi hx)q(2\pi ky) - p(2\pi hy)q(2\pi kx), \end{aligned} \quad (\text{A1.4.3.3})$$

where p and q can each be a sine or a cosine.

Explicit trigonometric functions given in the table follow the convention

$$c(u) = \cos(2\pi u) \quad s(u) = \sin(2\pi u).$$

Conditions for vanishing symbols:

$$P(ss) = M(ss) = 0 \quad \text{if } h = 0 \quad \text{or } k = 0,$$

$$P(sc) = M(sc) = 0 \quad \text{if } h = 0,$$

$$P(cs) = M(cs) = 0 \quad \text{if } k = 0,$$

$$M(cc) = M(ss) = 0 \quad \text{if } h = k \quad \text{or } h = -k,$$

and any explicit sine function vanishes if all the indices (h and k , or l) appearing in its argument are zero.

$P4$ [No. 75]

hkl	A	B
All	$2[P(cc) - M(ss)]c(lz)$	$2[P(cc) - M(ss)]s(lz)$

$P4_1$ [No. 76] (enantiomorphous to $P4_3$ [No. 78])

l	A	B
$4n$	$2[P(cc) - M(ss)]c(lz)$	$2[P(cc) - M(ss)]s(lz)$
$4n + 1$	$-2[s(hx + ky)s(lz) - s(hy - kx)c(lz)]$	$2[s(hx + ky)c(lz) + s(hy - kx)s(lz)]$
$4n + 2$	$2[M(cc) - P(ss)]c(lz)$	$2[M(cc) - P(ss)]s(lz)$
$4n + 3$	$-2[s(hx + ky)s(lz) + s(hy - kx)c(lz)]$	$2[s(hx + ky)c(lz) - s(hy - kx)s(lz)]$

$P4_2$ [No. 77]

l	A	B
$2n$	$2[P(cc) - M(ss)]c(lz)$	$2[P(cc) - M(ss)]s(lz)$
$2n + 1$	$2[M(cc) - P(ss)]c(lz)$	$2[M(cc) - P(ss)]s(lz)$

$P4_3$ [No. 78] (enantiomorphous to $P4_1$ [No. 76])

l	A	B
$4n$	$2[P(cc) - M(ss)]c(lz)$	$2[P(cc) - M(ss)]s(lz)$
$4n + 1$	$-2[s(hx + ky)s(lz) + s(hy - kx)c(lz)]$	$2[s(hx + ky)c(lz) - s(hy - kx)s(lz)]$
$4n + 2$	$2[M(cc) - P(ss)]c(lz)$	$2[M(cc) - P(ss)]s(lz)$
$4n + 3$	$-2[s(hx + ky)s(lz) - s(hy - kx)c(lz)]$	$2[s(hx + ky)c(lz) + s(hy - kx)s(lz)]$

$I4$ [No. 79]

hkl	A	B
All	$4[P(cc) - M(ss)]c(lz)$	$4[P(cc) - M(ss)]s(lz)$

$I4_1$ [No. 80]

$2h + l$	A	B
$4n$	$4[P(cc) - M(ss)]c(lz)$	$4[P(cc) - M(ss)]s(lz)$
$4n + 1$	$4[c(hx + ky)c(lz) + c(hy - kx)s(lz)]$	$4[c(hx + ky)s(lz) - c(hy - kx)c(lz)]$
$4n + 2$	$4[M(cc) - P(ss)]c(lz)$	$4[M(cc) - P(ss)]s(lz)$
$4n + 3$	$4[c(hx + ky)c(lz) - c(hy - kx)s(lz)]$	$4[c(hx + ky)s(lz) + c(hy - kx)c(lz)]$

1.4. SYMMETRY IN RECIPROCAL SPACE
Table A1.4.3.5. *Tetragonal space groups (cont.)*

$P\bar{4}$ [No. 81]

hkl	A	B
All	$2[P(cc) - M(ss)]c(lz)$	$2[M(cc) - P(ss)]s(lz)$

$I\bar{4}$ [No. 82]

hkl	A	B
All	$4[P(cc) - M(ss)]c(lz)$	$4[M(cc) - P(ss)]s(lz)$

$P4/m$ [No. 83]

hkl	A	B
All	$4[P(cc) - M(ss)]c(lz)$	0

$P4_2/m$ [No. 84] ($B = 0$ for all h, k, l)

l	A
$2n$	$4[P(cc) - M(ss)]c(lz)$
$2n + 1$	$4[M(cc) - P(ss)]c(lz)$

$P4/n$ [No. 85, Origin 1]

$h + k$	A	B
$2n$	$4[P(cc) - M(ss)]c(lz)$	0
$2n + 1$	0	$4[M(cc) - P(ss)]s(lz)$

$P4/n$ [No. 85, Origin 2] ($B = 0$ for all h, k, l)

h	k	A
$2n$	$2n$	$4[P(cc) - M(ss)]c(lz)$
$2n$	$2n + 1$	$-4[P(cs) + M(sc)]s(lz)$
$2n + 1$	$2n$	$-4[M(cs) + P(sc)]s(lz)$
$2n + 1$	$2n + 1$	$4[M(cc) - P(ss)]c(lz)$

$P4_2/n$ [No. 86, Origin 1]

$h + k + l$	A	B
$2n$	$4[P(cc) - M(ss)]c(lz)$	0
$2n + 1$	0	$4[M(cc) - P(ss)]s(lz)$

$P4_2/n$ [No. 86, Origin 2] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	$4[P(cc) - M(ss)]c(lz)$
$2n$	$2n + 1$	$2n + 1$	$4[M(cc) - P(ss)]c(lz)$
$2n + 1$	$2n + 1$	$2n$	$-4[M(cs) + P(sc)]s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-4[P(cs) + M(sc)]s(lz)$

$I4/m$ [No. 87]

hkl	A	B
All	$8[P(cc) - M(ss)]c(lz)$	0

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Table A1.4.3.5. *Tetragonal space groups (cont.)*

$I4_1/a$ [No. 88, Origin 1]

$2k + l$	A	B
$4n$	$8[P(cc) - M(ss)]c(lz)$	0
$4n + 1$	$4[P(cc) - M(ss)]c(lz) + [M(cc) - P(ss)]s(lz)$	A
$4n + 2$	0	$8[M(cc) - P(ss)]s(lz)$
$4n + 3$	$4[P(cc) - M(ss)]c(lz) - [M(cc) - P(ss)]s(lz)$	$-A$

$I4_1/a$ [No. 88, Origin 2] ($B = 0$ for all h, k, l)

h	k	$h + k + l$	A
$2n$	$2n$	$4n$	$8[P(cc) - M(ss)]c(lz)$
$2n$	$2n + 1$	$4n$	$-8[s(hx + ky)s(lz) - c(hy - kx)c(lz)]$
$2n + 1$	$2n$	$4n$	$8[c(hx + ky)c(lz) - s(hy - kx)s(lz)]$
$2n + 1$	$2n + 1$	$4n$	$-8[M(cs) + P(sc)]s(lz)$
$2n$	$2n$	$4n + 2$	$8[M(cc) - P(ss)]c(lz)$
$2n$	$2n + 1$	$4n + 2$	$-8[s(hx + ky)s(lz) + c(hy - kx)c(lz)]$
$2n + 1$	$2n$	$4n + 2$	$8[c(hx + ky)c(lz) + s(hy - kx)s(lz)]$
$2n + 1$	$2n + 1$	$4n + 2$	$-8[P(cs) + M(sc)]s(lz)$

$P422$ [No. 89]

hkl	A	B
All	$4P(cc)c(lz)$	$-4M(ss)s(lz)$

$P4_12$ [No. 90]

$h + k$	A	B
$2n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$2n + 1$	$-4P(ss)c(lz)$	$4M(cc)s(lz)$

$P4_122$ [No. 91] (enantiomorphous to $P4_322$ [No. 95])

l	A	B
$4n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$4n + 1$	$-4[s(hx)c(ky)s(lz) - c(kx)s(hy)c(lz)]$	$4[c(hx)s(ky)c(lz) - s(kx)c(hy)s(lz)]$
$4n + 2$	$4M(cc)c(lz)$	$-4P(ss)s(lz)$
$4n + 3$	$-4[s(hx)c(ky)s(lz) + c(kx)s(hy)c(lz)]$	$4[c(hx)s(ky)c(lz) + s(kx)c(hy)s(lz)]$

$P4_12_12$ [No. 92] (enantiomorphous to $P4_32_12$ [No. 96])

$2h + 2k + l$	A	B
$4n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$4n + 1$	$2\{[P(sc) - P(cs)]c(lz) - [M(cs) - M(sc)]s(lz)\}$	$2\{[P(sc) + P(cs)]c(lz) + [M(cs) - M(sc)]s(lz)\}$
$4n + 2$	$-4P(ss)c(lz)$	$4M(cc)s(lz)$
$4n + 3$	$-2\{[P(sc) - P(cs)]c(lz) + [M(cs) + M(sc)]s(lz)\}$	$2\{[P(sc) + P(cs)]c(lz) - [M(cs) - M(sc)]s(lz)\}$

$P4_222$ [No. 93]

l	A	B
$2n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$2n + 1$	$4M(cc)c(lz)$	$-4P(ss)s(lz)$

1.4. SYMMETRY IN RECIPROCAL SPACE
Table A1.4.3.5. *Tetragonal space groups (cont.)*

$P4_22_12$ [No. 94]

$h + k + l$	A	B
$2n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$2n + 1$	$-4P(ss)c(lz)$	$4M(cc)s(lz)$

$P4_322$ [No. 95] (enantiomorphous to $P4_122$ [No. 91])

l	A	B
$4n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$4n + 1$	$-4[s(hx)c(ky)s(lz) + c(kx)s(hy)c(lz)]$	$4[c(hx)s(ky)c(lz) + s(kx)c(hy)c(lz)]$
$4n + 2$	$4M(cc)c(lz)$	$-4P(ss)s(lz)$
$4n + 3$	$-4[s(hx)c(ky)s(lz) - c(kx)s(hy)c(lz)]$	$4[c(hx)s(ky)c(lz) - s(kx)c(hy)c(lz)]$

$P4_32_12$ [No. 96] (enantiomorphous to $P4_12_12$ [No. 92])

$2h + 2k + l$	A	B
$4n$	$4P(cc)c(lz)$	$-4M(ss)s(lz)$
$4n + 1$	$-2\{[P(sc) - P(cs)]c(lz) + [M(cs) + M(sc)]s(lz)\}$	$2\{[P(sc) + P(cs)]c(lz) - [M(cs) - M(sc)]s(lz)\}$
$4n + 2$	$-4P(ss)c(lz)$	$4M(cc)s(lz)$
$4n + 3$	$2\{[P(sc) - P(cs)]c(lz) - [M(cs) + M(sc)]s(lz)\}$	$2\{[P(sc) + P(cs)]c(lz) + [M(cs) - M(sc)]s(lz)\}$

$I422$ [No. 97]

hkl	A	B
All	$8P(cc)c(lz)$	$-8M(ss)s(lz)$

$I4_122$ [No. 98]

$2k + l$	A	B
$4n$	$8P(cc)c(lz)$	$-8M(ss)s(lz)$
$4n + 1$	$4\{[P(cc) - P(ss)]c(lz) + [M(cc) + M(ss)]s(lz)\}$	$4\{[P(cc) + P(ss)]c(lz) + [M(cc) - M(ss)]s(lz)\}$
$4n + 2$	$-8P(ss)c(lz)$	$8M(cc)s(lz)$
$4n + 3$	$4\{[P(cc) - P(ss)]c(lz) - [M(cc) + M(ss)]s(lz)\}$	$-4\{[P(cc) + P(ss)]c(lz) - [M(cc) - M(ss)]s(lz)\}$

$P4mm$ [No. 99]

hkl	A	B
All	$4P(cc)c(lz)$	$4P(cc)s(lz)$

$P4bm$ [No. 100]

$h + k$	A	B
$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$-4M(ss)s(lz)$

$P4_2cm$ [No. 101]

l	A	B
$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$-4P(ss)c(lz)$	$-4P(ss)s(lz)$

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Table A1.4.3.5. *Tetragonal space groups (cont.)*

$P4_2nm$ [No. 102]

$h + k + l$	A	B
$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$-4P(ss)c(lz)$	$-4P(ss)s(lz)$

$P4cc$ [No. 103]

l	A	B
$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$-4M(ss)s(lz)$

$P4nc$ [No. 104]

$h + k + l$	A	B
$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$-4M(ss)s(lz)$

$P4_2mc$ [No. 105]

l	A	B
$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$4M(cc)c(lz)$	$4M(cc)s(lz)$

$P4_2bc$ [No. 106]

$h + k$	l	A	B
$2n$	$2n$	$4P(cc)c(lz)$	$4P(cc)s(lz)$
$2n + 1$	$2n$	$-4M(ss)c(lz)$	$-4M(ss)s(lz)$
$2n$	$2n + 1$	$4M(cc)c(lz)$	$4M(cc)s(lz)$
$2n + 1$	$2n + 1$	$-4P(ss)c(lz)$	$-4P(ss)s(lz)$

$I4mm$ [No. 107]

hkl	A	B
All	$8P(cc)c(lz)$	$8P(cc)s(lz)$

$I4cm$ [No. 108]

l	A	B
$2n$	$8P(cc)c(lz)$	$8P(cc)s(lz)$
$2n + 1$	$-8M(ss)c(lz)$	$-8M(ss)s(lz)$

$I4_1md$ [No. 109]

$2k + l$	A	B
$4n$	$8P(cc)c(lz)$	$8P(cc)s(lz)$
$4n + 1$	$8[c(hx)c(ky)c(lz) - c(kx)c(hy)s(lz)]$	$8[c(hx)c(ky)s(lz) + c(kx)c(hy)c(lz)]$
$4n + 2$	$8M(cc)c(lz)$	$8M(cc)s(lz)$
$4n + 3$	$8[c(hx)c(ky)c(lz) + c(kx)c(hy)s(lz)]$	$8[c(hx)c(ky)s(lz) - c(kx)c(hy)c(lz)]$

1.4. SYMMETRY IN RECIPROCAL SPACE
Table A1.4.3.5. *Tetragonal space groups (cont.)*

$I4_1cd$ [No. 110]

$2k + l$	A	B
$4n$	$8P(cc)c(lz)$	$8P(cc)s(lz)$
$4n + 1$	$-8[s(hx)s(ky)c(lz) + s(kx)s(hy)s(lz)]$	$-8[s(hx)s(ky)s(lz) - s(kx)s(hy)c(lz)]$
$4n + 2$	$8M(cc)c(lz)$	$8M(cc)s(lz)$
$4n + 3$	$-8[s(hx)s(ky)c(lz) - s(kx)s(hy)s(lz)]$	$-8[s(hx)s(ky)s(lz) + s(kx)s(hy)c(lz)]$

$P\bar{4}2m$ [No. 111]

hkl	A	B
All	$4P(cc)c(lz)$	$-4P(ss)s(lz)$

$P\bar{4}2c$ [No. 112]

l	A	B
$2n$	$4P(cc)c(lz)$	$-4P(ss)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$4M(cc)s(lz)$

$P\bar{4}2_1m$ [No. 113]

$h + k$	A	B
$2n$	$4P(cc)c(lz)$	$-4P(ss)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$4M(cc)s(lz)$

$P\bar{4}2_1c$ [No. 114]

$h + k + l$	A	B
$2n$	$4P(cc)c(lz)$	$-4P(ss)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$4M(cc)s(lz)$

$P\bar{4}m2$ [No. 115]

hkl	A	B
All	$4P(cc)c(lz)$	$4M(cc)s(lz)$

$P\bar{4}c2$ [No. 116]

l	A	B
$2n$	$4P(cc)c(lz)$	$4M(cc)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$-4P(ss)s(lz)$

$P\bar{4}b2$ [No. 117]

$h + k$	A	B
$2n$	$4P(cc)c(lz)$	$4M(cc)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$-4P(ss)s(lz)$

$P\bar{4}n2$ [No. 118]

$h + k + l$	A	B
$2n$	$4P(cc)c(lz)$	$4M(cc)s(lz)$
$2n + 1$	$-4M(ss)c(lz)$	$-4P(ss)s(lz)$

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Table A1.4.3.5. *Tetragonal space groups (cont.)*

$\bar{I}4m2$ [No. 119]

hkl	A	B
All	$8P(cc)c(lz)$	$8M(cc)s(lz)$

$\bar{I}4c2$ [No. 120]

l	A	B
$2n$	$8P(cc)c(lz)$	$8M(cc)s(lz)$
$2n + 1$	$-8M(ss)c(lz)$	$-8P(ss)s(lz)$

$\bar{I}42m$ [No. 121]

hkl	A	B
All	$8P(cc)c(lz)$	$-8P(ss)s(lz)$

$\bar{I}42d$ [No. 122]

$2h + l$	A	B
$4n$	$8P(cc)c(lz)$	$-8P(ss)s(lz)$
$4n + 1$	$4\{[P(cc) - M(ss)]c(lz) - [M(cc) + P(ss)]s(lz)\}$	$-4\{[P(cc) + M(ss)]c(lz) - [M(cc) - P(ss)]s(lz)\}$
$4n + 2$	$-8M(ss)c(lz)$	$8M(cc)s(lz)$
$4n + 3$	$4\{[P(cc) - M(ss)]c(lz) + [M(cc) + P(ss)]s(lz)\}$	$4\{[P(cc) + M(ss)]c(lz) + [M(cc) - P(ss)]s(lz)\}$

$P4/mmm$ [No. 123]

hkl	A	B
All	$8P(cc)c(lz)$	0

$P4/mcc$ [No. 124] ($B = 0$ for all h, k, l)

l	A
$2n$	$8P(cc)c(lz)$
$2n + 1$	$-8M(ss)c(lz)$

$P4/nbm$ [No. 125, Origin 1]

$h + k$	A	B
$2n$	$8P(cc)c(lz)$	0
$2n + 1$	0	$-8M(ss)s(lz)$

$P4/nbm$ [No. 125, Origin 2] ($B = 0$ for all h, k, l)

h	k	A
$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n + 1$	$-8M(sc)s(lz)$
$2n + 1$	$2n$	$-8M(cs)s(lz)$
$2n + 1$	$2n + 1$	$-8P(ss)c(lz)$

1.4. SYMMETRY IN RECIPROCAL SPACE
Table A1.4.3.5. *Tetragonal space groups (cont.)*

$P4/nnc$ [No. 126, Origin 1]

$h + k + l$	A	B
$2n$	$8P(cc)c(lz)$	0
$2n + 1$	0	$-8M(ss)s(lz)$

$P4/nnc$ [No. 126, Origin 2] ($B = 0$ for all h, k, l)

h	k	l	A
$2n$	$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n$	$2n + 1$	$-8M(ss)c(lz)$
$2n$	$2n + 1$	$2n$	$-8M(sc)s(lz)$
$2n$	$2n + 1$	$2n + 1$	$-8P(cs)s(lz)$
$2n + 1$	$2n$	$2n$	$-8M(cs)s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-8P(sc)s(lz)$
$2n + 1$	$2n + 1$	$2n$	$-8P(ss)c(lz)$
$2n + 1$	$2n + 1$	$2n + 1$	$8M(cc)c(lz)$

$P4/mbm$ [No. 127] ($B = 0$ for all h, k, l)

$h + k$	A
$2n$	$8P(cc)c(lz)$
$2n + 1$	$-8M(ss)c(lz)$

$P4/mnc$ [No. 128] ($B = 0$ for all h, k, l)

$h + k + l$	A
$2n$	$8P(cc)c(lz)$
$2n + 1$	$-8M(ss)c(lz)$

$P4/nmm$ [No. 129, Origin 1]

$h + k$	A	B
$2n$	$8P(cc)c(lz)$	0
$2n + 1$	0	$8M(cc)s(lz)$

$P4/nmm$ [No. 129, Origin 2] ($B = 0$ for all h, k, l)

h	k	A
$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n + 1$	$-8P(cs)s(lz)$
$2n + 1$	$2n$	$-8P(sc)s(lz)$
$2n + 1$	$2n + 1$	$-8P(ss)c(lz)$

$P4/ncc$ [No. 130, Origin 1]

$h + k$	l	A	B
$2n$	$2n$	$8P(cc)c(lz)$	0
$2n$	$2n + 1$	$-8M(ss)c(lz)$	0
$2n + 1$	$2n$	0	$8M(cc)s(lz)$
$2n + 1$	$2n + 1$	0	$-8P(ss)s(lz)$

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Table A1.4.3.5. *Tetragonal space groups (cont.)*

$P4/ncc$ [No. 130, Origin 2] ($B = 0$ for all h, k, l)

h	k	l	A
$2n$	$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n$	$2n + 1$	$-8M(ss)c(lz)$
$2n$	$2n + 1$	$2n$	$-8P(cs)s(lz)$
$2n$	$2n + 1$	$2n + 1$	$-8M(sc)s(lz)$
$2n + 1$	$2n$	$2n$	$-8P(sc)s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-8M(cs)s(lz)$
$2n + 1$	$2n + 1$	$2n$	$-8P(ss)c(lz)$
$2n + 1$	$2n + 1$	$2n + 1$	$8M(cc)c(lz)$

$P4_2/mmc$ [No. 131] ($B = 0$ for all h, k, l)

l	A
$2n$	$8P(cc)c(lz)$
$2n + 1$	$8M(cc)c(lz)$

$P4_2/mcm$ [No. 132] ($B = 0$ for all h, k, l)

l	A
$2n$	$8P(cc)c(lz)$
$2n + 1$	$-8P(ss)c(lz)$

$P4_2/nbc$ [No. 133, Origin 1]

$h + k + l$	l	A	B
$2n$	$2n$	$8P(cc)c(lz)$	0
$2n$	$2n + 1$	$-8M(ss)c(lz)$	0
$2n + 1$	$2n$	0	$-8P(ss)s(lz)$
$2n + 1$	$2n + 1$	0	$8M(cc)s(lz)$

$P4_2/nbc$ [No. 133, Origin 2] ($B = 0$ for all h, k, l)

h	k	l	A
$2n$	$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n$	$2n + 1$	$8M(cc)c(lz)$
$2n$	$2n + 1$	$2n$	$-8M(sc)s(lz)$
$2n$	$2n + 1$	$2n + 1$	$-8P(sc)s(lz)$
$2n + 1$	$2n$	$2n$	$-8M(cs)s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-8P(cs)s(lz)$
$2n + 1$	$2n + 1$	$2n$	$-8P(ss)c(lz)$
$2n + 1$	$2n + 1$	$2n + 1$	$-8M(ss)c(lz)$

$P4_2/nmm$ [No. 134, Origin 1]

$h + k + l$	A	B
$2n$	$8P(cc)c(lz)$	0
$2n + 1$	0	$-8P(ss)s(lz)$

$P4_2/nmm$ [No. 134, Origin 2] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n + 1$	$2n + 1$	$-8P(ss)c(lz)$
$2n + 1$	$2n + 1$	$2n$	$-8M(sc)s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-8M(cs)s(lz)$

1.4. SYMMETRY IN RECIPROCAL SPACE
Table A1.4.3.5. *Tetragonal space groups (cont.)*

$P4_2/mbc$ [No. 135] ($B = 0$ for all h, k, l)

$h + k$	l	A
$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n + 1$	$8M(cc)c(lz)$
$2n + 1$	$2n$	$-8M(ss)c(lz)$
$2n + 1$	$2n + 1$	$-8P(ss)c(lz)$

$P4_2/mmm$ [No. 136] ($B = 0$ for all h, k, l)

$h + k + l$	A
$2n$	$8P(cc)c(lz)$
$2n + 1$	$-8P(ss)c(lz)$

$P4_2/nmc$ [No. 137, Origin 1]

$h + k + l$	A	B
$2n$	$8P(cc)c(lz)$	0
$2n + 1$	0	$8M(cc)s(lz)$

$P4_2/nmc$ [No. 137, Origin 2] ($B = 0$ for all h, k, l)

h	k	l	A
$2n$	$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n$	$2n + 1$	$8M(cc)c(lz)$
$2n$	$2n + 1$	$2n$	$-8P(cs)s(lz)$
$2n$	$2n + 1$	$2n + 1$	$-8M(cs)s(lz)$
$2n + 1$	$2n$	$2n$	$-8P(sc)s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-8M(sc)s(lz)$
$2n + 1$	$2n + 1$	$2n$	$-8P(ss)c(lz)$
$2n + 1$	$2n + 1$	$2n + 1$	$-8M(ss)c(lz)$

$P4_2/ncm$ [No. 138, Origin 1]

$h + k$	l	A	B
$2n$	$2n$	$8P(cc)c(lz)$	0
$2n + 1$	$2n + 1$	$-8M(ss)c(lz)$	0
$2n + 1$	$2n$	0	$8M(cc)s(lz)$
$2n$	$2n + 1$	0	$-8P(ss)s(lz)$

$P4_2/ncm$ [No. 138, Origin 2] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	$8P(cc)c(lz)$
$2n$	$2n + 1$	$2n + 1$	$-8P(ss)c(lz)$
$2n + 1$	$2n + 1$	$2n$	$-8P(cs)s(lz)$
$2n + 1$	$2n$	$2n + 1$	$-8P(sc)s(lz)$

$I4/mmm$ [No. 139]

hkl	A	B
All	$16P(cc)c(lz)$	0

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Table A1.4.3.5. *Tetragonal space groups (cont.)*

$I4/mcm$ [No. 140] ($B = 0$ for all h, k, l)

l	A
$2n$	$16P(cc)c(lz)$
$2n + 1$	$-16M(ss)c(lz)$

$I4_1/amd$ [No. 141, Origin 1]

$2h + l$	A	B
$4n$	$16P(cc)c(lz)$	0
$4n + 1$	$8[P(cc)c(lz) - M(cc)s(lz)]$	$-A$
$4n + 2$	0	$16M(cc)s(lz)$
$4n + 3$	$8[P(cc)c(lz) + M(cc)s(lz)]$	A

$I4_1/amd$ [No. 141, Origin 2] ($B = 0$ for all h, k, l)

h	k	$h + k + l$	A
$2n$	$2n$	$4n$	$16P(cc)c(lz)$
$2n$	$2n + 1$	$4n$	$-16[c(hx)s(ky)s(lz) + c(kx)c(hy)c(lz)]$
$2n + 1$	$2n$	$4n$	$16[c(hx)c(ky)c(lz) + c(kx)s(hy)s(lz)]$
$2n + 1$	$2n + 1$	$4n$	$-16[c(hx)s(ky)s(lz) + c(kx)s(hy)s(lz)]$
$2n$	$2n$	$4n + 2$	$16M(cc)c(lz)$
$2n$	$2n + 1$	$4n + 2$	$-16[c(hx)s(ky)s(lz) - c(kx)c(hy)c(lz)]$
$2n + 1$	$2n$	$4n + 2$	$16[c(hx)c(ky)c(lz) - c(kx)s(hy)s(lz)]$
$2n + 1$	$2n + 1$	$4n + 2$	$-16[c(hx)s(ky)s(lz) - c(kx)s(hy)s(lz)]$

$I4_1/acd$ [No. 142, Origin 1]

$2h + l$	A	B
$4n$	$16P(cc)c(lz)$	0
$4n + 1$	$-8[M(ss)c(lz) - P(ss)s(lz)]$	$-A$
$4n + 2$	0	$16M(cc)s(lz)$
$4n + 3$	$-8[M(ss)c(lz) + P(ss)s(lz)]$	A

$I4_1/acd$ [No. 142, Origin 2] ($B = 0$ for all h, k, l)

h	k	$h + k + l$	A
$2n$	$2n$	$4n$	$16P(cc)c(lz)$
$2n$	$2n + 1$	$4n$	$-16[s(hx)c(ky)s(lz) + s(kx)s(hy)c(lz)]$
$2n + 1$	$2n$	$4n$	$-16[s(hx)s(ky)c(lz) + s(kx)c(hy)s(lz)]$
$2n + 1$	$2n + 1$	$4n$	$-16[c(hx)s(ky)s(lz) + c(kx)s(hy)s(lz)]$
$2n$	$2n$	$4n + 2$	$16M(cc)c(lz)$
$2n$	$2n + 1$	$4n + 2$	$-16[s(hx)c(ky)s(lz) - s(kx)s(hy)c(lz)]$
$2n + 1$	$2n$	$4n + 2$	$-16[s(hx)s(ky)c(lz) - s(kx)c(hy)s(lz)]$
$2n + 1$	$2n + 1$	$4n + 2$	$-16[c(hx)s(ky)s(lz) - c(kx)s(hy)s(lz)]$

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.6. *Trigonal and hexagonal space groups*

The table lists the expressions for A and B for the space groups belonging to the hexagonal family. For the space groups that are referred to hexagonal axes the expressions are given in terms of symbols related to the decomposition of the scalar products into their plane-group and unique-axis components [cf. equations (1.4.3.10)–(1.4.3.12)]. The symbols for the seven rhombohedral space groups in their rhombohedral-axes representation are the same as those used for the cubic space groups [cf. equations (1.4.3.4) and (1.4.3.5), and the notes at the start of Table A1.4.3.7]. Factors of the forms $\cos(2\pi x)$ and $\sin(2\pi x)$ are abbreviated by $c(x)$ and $s(x)$, respectively. All the symbols used in this table are repeated below. Most expressions are given in terms of

$$\begin{aligned} C(hki) &= c(p_1) + c(p_2) + c(p_3), \\ C(khi) &= c(q_1) + c(q_2) + c(q_3) \text{ and} \\ S(hki) &= s(p_1) + s(p_2) + s(p_3), \\ S(khi) &= s(q_1) + s(q_2) + s(q_3), \end{aligned} \quad (\text{A1.4.3.4})$$

where

$$\begin{aligned} p_1 &= hx + ky, \quad p_2 = kx + iy, \quad p_3 = ix + hy, \\ q_1 &= kx + hy, \quad q_2 = hx + iy, \quad q_3 = ix + ky, \end{aligned} \quad (\text{A1.4.3.5})$$

and the abbreviations

$$\begin{aligned} \text{PH(cc)} &= C(hki) + C(khi), \\ \text{PH(ss)} &= S(hki) + S(khi), \\ \text{MH(cc)} &= C(hki) - C(khi) \text{ and} \\ \text{MH(ss)} &= S(hki) - S(khi). \end{aligned} \quad (\text{A1.4.3.6})$$

In addition, the following abbreviations are employed for some space groups:

$$u_1 = lz, \quad u_2 = lz + \frac{1}{3} \text{ and } u_3 = lz - \frac{1}{3}.$$

Conditions for vanishing symbols:

$$\begin{aligned} S(hki) &= S(khi) = 0 \text{ if } h = k = 0, \\ \text{PH(ss)} &= 0 \text{ if } h = -k \text{ (or } k = -i \text{ or } i = -h), \\ \text{MH(cc)} &= 0 \text{ if } |h| = |k| \text{ (or } |k| = |i| \text{ or } |i| = |h|) \end{aligned}$$

and any explicit sine function vanishes if all the indices (h and k , or l) appearing in its argument are zero.

$P3$ [No. 143]

hkl	A	B
All	$C(hki)c(lz) - S(hki)s(lz)$	$C(hki)s(lz) + S(hki)c(lz)$

$P3_1$ [No. 144] (enantiomorphous to $P3_2$ [No. 145])

l	A	B
$3n$	as for $P3$ [No. 143]	
$3n + 1$	$c(p_1 + u_1) + c(p_2 + u_2) + c(p_3 + u_3)$	$s(p_1 + u_1) + s(p_2 + u_2) + s(p_3 + u_3)$
$3n + 2$	$c(p_1 + u_1) + c(p_2 + u_3) + c(p_3 + u_2)$	$s(p_1 + u_1) + s(p_2 + u_3) + s(p_3 + u_2)$

$P3_2$ [No. 145] (enantiomorphous to $P3_1$ [No. 144])

l	A, B
$3n$	as for $P3$ [No. 143]
$3n + 1$	as for $l = 3n + 2$ in $P3_1$ [No. 144]
$3n + 2$	as for $l = 3n + 1$ in $P3_1$ [No. 144]

$R3$ [No. 146] (rhombohedral axes)

hkl	A	B
All	$c(hx + ky + lz) + c(kx + ly + hz) + c(lx + hy + kz)$	$s(hx + ky + lz) + s(kx + ly + hz) + s(lx + hy + kz)$

$R3$ [No. 146] (hexagonal axes)

hkl	A	B
All	$3[C(hki)c(lz) - S(hki)s(lz)]$	$3[C(hki)s(lz) + S(hki)c(lz)]$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.3.6. *Trigonal and hexagonal space groups (cont.)*

$P\bar{3}$ [No. 147]

hkl	A	B
All	$2[C(hki)c(lz) - S(hki)s(lz)]$	0

$R\bar{3}$ [No. 148] (rhombohedral axes)

hkl	A	B
All	$2[c(hx + ky + lz) + c(kx + ly + hz) + c(lx + hy + kz)]$	0

$R\bar{3}$ [No. 148] (hexagonal axes)

hkl	A	B
All	$6[C(hki)c(lz) - S(hki)s(lz)]$	0

$P312$ [No. 149]

hkl	A	B
All	$PH(cc)c(lz) - PH(ss)s(lz)$	$MH(cc)s(lz) + MH(ss)c(lz)$

$P321$ [No. 150]

hkl	A	B
All	$PH(cc)c(lz) - MH(ss)s(lz)$	$PH(ss)c(lz) + MH(cc)s(lz)$

$P3_112$ [No. 151] (enantiomorphous to $P3_212$ [No. 153])

l	A	B
$3n$	as for $P312$ [No. 149]	
$3n + 1$	$c(p_1 + u_1) + c(p_2 + u_2) + c(p_3 + u_3) + c(q_1 + u_2) + c(q_2 + u_3) + c(q_3 + u_1)$	$s(p_1 + u_1) + s(p_2 + u_2) + s(p_3 + u_3) - s(q_1 + u_2) - s(q_2 + u_3) - s(q_3 + u_1)$
$3n + 2$	$c(p_1 + u_1) + c(p_2 + u_3) + c(p_3 + u_2) + c(q_1 + u_3) + c(q_2 + u_2) + c(q_3 + u_1)$	$s(p_1 + u_1) + s(p_2 + u_3) + s(p_3 + u_2) - s(q_1 + u_3) - s(q_2 + u_2) - s(q_3 + u_1)$

$P3_212$ [No. 152] (enantiomorphous to $P3_121$ [No. 154])

l	A	B
$3n$	as for $P321$ [No. 150]	
$3n + 1$	$c(p_1 + u_1) + c(p_2 + u_2) + c(p_3 + u_3) + c(q_1 - u_1) + c(q_2 - u_2) + c(q_3 - u_3)$	$s(p_1 + u_1) + s(p_2 + u_2) + s(p_3 + u_3) + s(q_1 - u_1) + s(q_2 - u_2) + s(q_3 - u_3)$
$3n + 2$	$c(p_1 + u_1) + c(p_2 + u_3) + c(p_3 + u_2) + c(q_1 - u_1) + c(q_2 - u_3) + c(q_3 - u_2)$	$s(p_1 + u_1) + s(p_2 + u_3) + s(p_3 + u_2) + s(q_1 - u_1) + s(q_2 - u_3) + s(q_3 - u_2)$

$P3_212$ [No. 153] (enantiomorphous to $P3_112$ [No. 151])

l	A, B
$3n$	as for $P312$ [No. 149]
$3n + 1$	as for $l = 3n + 2$ in $P3_112$ [No. 151]
$3n + 2$	as for $l = 3n + 1$ in $P3_112$ [No. 151]

$P3_221$ [No. 154] (enantiomorphous to $P3_121$ [No. 152])

l	A, B
$3n$	as for $P321$ [No. 150]
$3n + 1$	as for $l = 3n + 2$ in $P3_212$ [No. 152]
$3n + 2$	as for $l = 3n + 1$ in $P3_212$ [No. 152]

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.6. *Trigonal and hexagonal space groups (cont.)*

*R*32 [No. 155] (rhombohedral axes)

<i>hkl</i>	<i>A</i>	<i>B</i>
All	$E_{ccc} - E_{css} - E_{scs} - E_{ssc} + O_{ccc} - O_{css} - O_{scs} - O_{ssc}$	$E_{sc} + E_{cs} + E_{cc} - E_{ss} - O_{sc} - O_{cs} - O_{cc} + O_{ss}$

*R*32 [No. 155] (hexagonal axes)

<i>hkl</i>	<i>A</i>	<i>B</i>
All	$3[PH(cc)c(lz) - MH(ss)s(lz)]$	$3[PH(ss)c(lz) + MH(cc)s(lz)]$

*P*3*m*1 [No. 156]

<i>hkl</i>	<i>A</i>	<i>B</i>
All	$PH(cc)c(lz) - MH(ss)s(lz)$	$PH(cc)s(lz) + MH(ss)c(lz)$

*P*31*m* [No. 157]

<i>hkl</i>	<i>A</i>	<i>B</i>
All	$PH(cc)c(lz) - PH(ss)s(lz)$	$PH(cc)s(lz) + PH(ss)c(lz)$

*P*3*c*1 [No. 158]

<i>l</i>	<i>A</i>	<i>B</i>
<i>2n</i>	$PH(cc)c(lz) - MH(ss)s(lz)$	$PH(cc)s(lz) + MH(ss)c(lz)$
<i>2n + 1</i>	$MH(cc)c(lz) - PH(ss)s(lz)$	$PH(ss)c(lz) + MH(cc)s(lz)$

*P*31*c* [No. 159]

<i>l</i>	<i>A</i>	<i>B</i>
<i>2n</i>	$PH(cc)c(lz) - PH(ss)s(lz)$	$PH(cc)s(lz) + PH(ss)c(lz)$
<i>2n + 1</i>	$MH(cc)c(lz) - MH(ss)s(lz)$	$MH(cc)s(lz) + MH(ss)c(lz)$

*R*3*m* [No. 160] (rhombohedral axes)

<i>hkl</i>	<i>A</i>	<i>B</i>
All	$E_{ccc} - E_{css} - E_{scs} - E_{ssc} + O_{ccc} - O_{css} - O_{scs} - O_{ssc}$	$E_{sc} + E_{cs} + E_{cc} - E_{ss} + O_{sc} + O_{cs} + O_{cc} - O_{ss}$

*R*3*m* [No. 160] (hexagonal axes)

<i>hkl</i>	<i>A</i>	<i>B</i>
All	$3[PH(cc)c(lz) - MH(ss)s(lz)]$	$3[PH(cc)s(lz) + MH(ss)c(lz)]$

*R*3*c* [No. 161] (rhombohedral axes)

<i>h + k + l</i>	<i>A</i>	<i>B</i>
<i>2n</i>	$E_{ccc} - E_{css} - E_{scs} - E_{ssc} + O_{ccc} - O_{css} - O_{scs} - O_{ssc}$	$E_{sc} + E_{cs} + E_{cc} - E_{ss} + O_{sc} + O_{cs} + O_{cc} - O_{ss}$
<i>2n + 1</i>	$E_{ccc} - E_{css} - E_{scs} - E_{ssc} - O_{ccc} + O_{css} + O_{scs} + O_{ssc}$	$E_{sc} + E_{cs} + E_{cc} - E_{ss} - O_{sc} - O_{cs} - O_{cc} + O_{ss}$

*R*3*c* [No. 161] (hexagonal axes)

<i>l</i>	<i>A</i>	<i>B</i>
<i>2n</i>	$3[PH(cc)c(lz) - MH(ss)s(lz)]$	$3[PH(cc)s(lz) + MH(ss)c(lz)]$
<i>2n + 1</i>	$3[MH(cc)c(lz) - PH(ss)s(lz)]$	$3[PH(ss)c(lz) + MH(cc)s(lz)]$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.3.6. *Trigonal and hexagonal space groups (cont.)*

$P\bar{3}1m$ [No. 162] ($B = 0$ for all h, k, l)

A
$2[\text{PH}(\text{cc})\text{c}(l_z) - \text{PH}(\text{ss})\text{s}(l_z)]$

$P\bar{3}1c$ [No. 163] ($B = 0$ for all h, k, l)

l	A
$2n$	$2[\text{PH}(\text{cc})\text{c}(l_z) - \text{PH}(\text{ss})\text{s}(l_z)]$
$2n + 1$	$2[\text{MH}(\text{cc})\text{c}(l_z) - \text{MH}(\text{ss})\text{s}(l_z)]$

$P\bar{3}m1$ [No. 164] ($B = 0$ for all h, k, l)

A
$2[\text{PH}(\text{cc})\text{c}(l_z) - \text{MH}(\text{ss})\text{s}(l_z)]$

$P\bar{3}c1$ [No. 165] ($B = 0$ for all h, k, l)

l	A
$2n$	$2[\text{PH}(\text{cc})\text{c}(l_z) - \text{MH}(\text{ss})\text{s}(l_z)]$
$2n + 1$	$2[\text{MH}(\text{cc})\text{c}(l_z) - \text{PH}(\text{ss})\text{s}(l_z)]$

$R\bar{3}m$ [No. 166] (rhombohedral axes, $B = 0$ for all h, k, l)

A
$2(\text{Eccc} - \text{Ecsc} - \text{Escs} - \text{Essc} + \text{Occc} - \text{Ocsc} - \text{Oscs} - \text{Ossc})$

$R\bar{3}m$ [No. 166] (hexagonal axes, $B = 0$ for all h, k, l)

A
$6[\text{PH}(\text{cc})\text{c}(l_z) - \text{MH}(\text{ss})\text{s}(l_z)]$

$R\bar{3}c$ [No. 167] (rhombohedral axes, $B = 0$ for all h, k, l)

$h + k + l$	A
$2n$	$2(\text{Eccc} - \text{Ecsc} - \text{Escs} - \text{Essc} + \text{Occc} - \text{Ocsc} - \text{Oscs} - \text{Ossc})$
$2n + 1$	$2(\text{Eccc} - \text{Ecsc} - \text{Escs} - \text{Essc} - \text{Occc} + \text{Ocsc} + \text{Oscs} + \text{Ossc})$

$R\bar{3}c$ [No. 167] (hexagonal axes, $B = 0$ for all h, k, l)

l	A
$2n$	$6[\text{PH}(\text{cc})\text{c}(l_z) - \text{MH}(\text{ss})\text{s}(l_z)]$
$2n + 1$	$6[\text{MH}(\text{cc})\text{c}(l_z) - \text{PH}(\text{ss})\text{s}(l_z)]$

$P6$ [No. 168]

hkl	A	B
All	$2C(hk)l_z$	$2C(hk)l_z$

$P6_1$ [No. 169] (enantiomorphous to $P6_5$ [No. 170])

l	A	B
$6n$	as for $P6$ [No.168]	
$6n + 1$	$-2[s(p_1)s(u_1) + s(p_2)s(u_2) + s(p_3)s(u_3)]$	$2[s(p_1)c(u_1) + s(p_2)c(u_2) + s(p_3)c(u_3)]$
$6n + 2$	$2[c(p_1)c(u_1) + c(p_2)c(u_2) + c(p_3)c(u_3)]$	$2[c(p_1)s(u_1) + c(p_2)s(u_2) + c(p_3)s(u_3)]$
$6n + 3$	$-2S(hk)l_z$	$2S(hk)l_z$
$6n + 4$	$2[c(p_1)c(u_1) + c(p_2)c(u_2) + c(p_3)c(u_3)]$	$2[c(p_1)s(u_1) + c(p_2)s(u_2) + c(p_3)s(u_3)]$
$6n + 5$	$-2[s(p_1)s(u_1) + s(p_2)s(u_2) + s(p_3)s(u_3)]$	$2[s(p_1)c(u_1) + s(p_2)c(u_2) + s(p_3)c(u_3)]$

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.6. *Trigonal and hexagonal space groups (cont.)*

$P6_5$ [No. 170] (enantiomorphous to $P6_1$ [No. 169])

l	A, B
$6n$	as for $P6$ [No. 168]
$6n + 1$	as for $l = 6n + 5$ in $P6_1$ [No. 169]
$6n + 2$	as for $l = 6n + 4$ in $P6_1$ [No. 169]
$6n + 3$	as for $l = 6n + 3$ in $P6_1$ [No. 169]
$6n + 4$	as for $l = 6n + 2$ in $P6_1$ [No. 169]
$6n + 5$	as for $l = 6n + 1$ in $P6_1$ [No. 169]

$P6_2$ [No. 171] (enantiomorphous to $P6_4$ [No. 172])

l	A, B
$3n$	as for $P6$ [No. 168]
$3n + 1$	as for $l = 6n + 2$ in $P6_1$ [No. 169]
$3n + 2$	as for $l = 6n + 4$ in $P6_1$ [No. 169]

$P6_4$ [No. 172] (enantiomorphous to $P6_2$ [No. 171])

l	A, B
$3n$	as for $P6$ [No. 168]
$3n + 1$	as for $l = 6n + 4$ in $P6_1$ [No. 169]
$3n + 2$	as for $l = 6n + 2$ in $P6_1$ [No. 169]

$P6_3$ [No. 173]

l	A, B
$2n$	as for $P6$ [No. 168]
$2n + 1$	as for $l = 6n + 3$ in $P6_1$ [No. 169]

$P\bar{6}$ [No. 174]

hkl	A	B
All	$2C(hk\bar{i})c(lz)$	$2S(hk\bar{i})c(lz)$

$P6/m$ [No. 175]

hkl	A	B
All	$4C(hk\bar{i})c(lz)$	0

$P6_3/m$ [No. 176]

l	A	B
$2n$	$4C(hk\bar{i})c(lz)$	0
$2n + 1$	$-4S(hk\bar{i})s(lz)$	0

$P622$ [No. 177]

hkl	A	B
All	$2PH(cc)c(lz)$	$2MH(cc)s(lz)$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.3.6. *Trigonal and hexagonal space groups (cont.)*

$P6_122$ [No. 178] (enantiomorphous to $P6_522$ [No. 179])

l	A	B
$6n$	as for $P622$ [No. 177]	
$6n + 1$	$-2[s(p_1)s(u_1) + s(p_2)s(u_2) + s(p_3)s(u_3) - s(q_1)s(u_3) - s(q_2)s(u_1) - s(q_3)s(u_2)]$	$2[s(p_1)c(u_1) + s(p_2)c(u_2) + s(p_3)c(u_3) + s(q_1)c(u_3) + s(q_2)c(u_1) + s(q_3)c(u_2)]$
$6n + 2$	$2[c(p_1)c(u_1) + c(p_2)c(u_3) + c(p_3)c(u_2) + c(q_1)c(u_2) + c(q_2)c(u_1) + c(q_3)c(u_3)]$	$2[c(p_1)s(u_1) + c(p_2)s(u_3) + c(p_3)s(u_2) - c(q_1)s(u_2) - c(q_2)s(u_1) - c(q_3)s(u_3)]$
$6n + 3$	$-2MH(ss)s(lz)$	$2PH(ss)c(lz)$
$6n + 4$	$2[c(p_1)c(u_1) + c(p_2)c(u_2) + c(p_3)c(u_3) + c(q_1)c(u_3) + c(q_2)c(u_1) + c(q_3)c(u_2)]$	$2[c(p_1)s(u_1) + c(p_2)s(u_2) + c(p_3)s(u_3) - c(q_1)s(u_3) - c(q_2)s(u_1) - c(q_3)s(u_2)]$
$6n + 5$	$-2[s(p_1)s(u_1) + s(p_2)s(u_3) + s(p_3)s(u_2) - s(q_1)s(u_2) - s(q_2)s(u_1) - s(q_3)s(u_3)]$	$2[s(p_1)c(u_1) + s(p_2)c(u_3) + s(p_3)c(u_2) + s(q_1)c(u_2) + s(q_2)c(u_1) + s(q_3)c(u_3)]$

$P6_522$ [No. 179] (enantiomorphous to $P6_122$ [No. 178])

l	A, B
$6n$	as for $P622$ [No. 177]
$6n + 1$	as for $l = 6n + 5$ in $P6_122$ [No. 178]
$6n + 2$	as for $l = 6n + 4$ in $P6_122$ [No. 178]
$6n + 3$	as for $l = 6n + 3$ in $P6_122$ [No. 178]
$6n + 4$	as for $l = 6n + 2$ in $P6_122$ [No. 178]
$6n + 5$	as for $l = 6n + 1$ in $P6_122$ [No. 178]

$P6_222$ [No. 180] (enantiomorphous to $P6_422$ [No. 181])

l	A, B
n	as for $P622$ [No. 177]
$3n + 1$	as for $l = 6n + 2$ in $P6_122$ [No. 178]
$3n + 2$	as for $l = 6n + 4$ in $P6_122$ [No. 178]

$P6_422$ [No. 181] (enantiomorphous to $P6_222$ [No. 180])

l	A, B
$3n$	as for $P622$ [No. 177]
$3n + 1$	as for $l = 6n + 4$ in $P6_122$ [No. 178]
$3n + 2$	as for $l = 6n + 2$ in $P6_122$ [No. 178]

$P6_322$ [No. 182]

l	A, B
$2n$	as for $P622$ [No. 177]
$2n + 1$	as for $l = 6n + 3$ in $P6_122$ [No. 178]

$P6mm$ [No. 183]

hkl	A	B
All	$2PH(cc)c(lz)$	$2PH(cc)s(lz)$

$P6cc$ [No. 184]

l	A	B
$2n$	$2PH(cc)c(lz)$	$2PH(cc)s(lz)$
$2n + 1$	$2MH(cc)c(lz)$	$2MH(cc)s(lz)$

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.6. *Trigonal and hexagonal space groups (cont.)*

$P6_3cm$ [No. 185]

l	A	B
$2n$	$2PH(cc)c(lz)$	$2PH(cc)s(lz)$
$2n + 1$	$-2PH(ss)s(lz)$	$2PH(ss)c(lz)$

$P6_3mc$ [No. 186]

l	A	B
$2n$	$2PH(cc)c(lz)$	$2PH(cc)s(lz)$
$2n + 1$	$-2MH(ss)s(lz)$	$2MH(ss)c(lz)$

$P\bar{6}m2$ [No. 187]

hkl	A	B
All	$2PH(cc)c(lz)$	$2MH(ss)c(lz)$

$P\bar{6}c2$ [No. 188]

l	A	B
$2n$	$2PH(cc)c(lz)$	$2MH(ss)c(lz)$
$2n + 1$	$-2PH(ss)s(lz)$	$2MH(cc)s(lz)$

$P\bar{6}2m$ [No. 189]

hkl	A	B
All	$2PH(cc)c(lz)$	$2PH(ss)c(lz)$

$P\bar{6}2c$ [No. 190]

l	A	B
$2n$	$2PH(cc)c(lz)$	$2PH(ss)c(lz)$
$2n + 1$	$-2MH(ss)s(lz)$	$2MH(cc)s(lz)$

$P6/mmm$ [No. 191]

hkl	A	B
All	$4PH(cc)c(lz)$	0

$P6/mcc$ [No. 192] ($B = 0$ for all h, k, l)

l	A
$2n$	$4PH(cc)c(lz)$
$2n + 1$	$4MH(cc)c(lz)$

$P6_3/mcm$ [No. 193] ($B = 0$ for all h, k, l)

l	A
$2n$	$4PH(cc)c(lz)$
$2n + 1$	$-4PH(ss)s(lz)$

$P6_3/mmc$ [No. 194] ($B = 0$ for all h, k, l)

l	A
$2n$	$4PH(cc)c(lz)$
$2n + 1$	$-4MH(ss)s(lz)$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.3.7. *Cubic space groups*

The symbols appearing in this table are related to the pqr representation used with the orthorhombic space groups as follows: Each of the symbols defined below is a sum of three pqr terms, where the order of hkl is fixed in each of the three terms and that of xyz is permuted.

This table and parts of Table A1.4.3.6 (rhombohedral space groups referred to rhombohedral axes) are given in terms of the following two symbols:

$$Epqr = p(hx)q(ky)r(lz) + p(hy)q(kz)r(lx) + p(hz)q(kx)r(ly) \quad (A1.4.3.7)$$

and

$$Opqr = p(hx)q(kz)r(ly) + p(hz)q(ky)r(lx) + p(hy)q(kx)r(lz), \quad (A1.4.3.8)$$

where p , q and r can each be a sine or a cosine, and the factor 2π has been absorbed in the abbreviations (see text). As in Tables A1.4.3.1–A1.4.3.6, cosine and sine are abbreviated by c and s , respectively. The permutation of the coordinates is even in $Epqr$ and odd in $Opqr$.

Conditions for vanishing symbols:

$Epqr = Opqr = 0$ if at least one of p , q , r is a sine and the index h , k or l in its argument is zero,

$$Eccc - Occc = 0 \text{ if } |h| = |k| \text{ (or } |k| = |l| \text{ or } |l| = |h|),$$

$$Esss - Osss = 0 \text{ if } |h| = |k| \text{ (or } |k| = |l| \text{ or } |l| = |h|),$$

$$Ecsc - Ocsc = Escs - Oesc = 0 \text{ if } |k| = |l|,$$

$$Escs - Oesc = Ecsc - Oesc = 0 \text{ if } |l| = |h| \text{ and}$$

$$Essc - Ossc = Eccs - Occs = 0 \text{ if } |h| = |k|.$$

$P23$ [No. 195]

hkl	A	B
All	$4Eccc$	$-4Esss$

$F23$ [No. 196]

hkl	A	B
All	$16Eccc$	$-16Esss$

$I23$ [No. 197]

hkl	A	B
All	$8Eccc$	$-8Esss$

$P2_13$ [No. 198]

$h+k$	$k+l$	$h+l$	A	B
$2n$	$2n$	$2n$	$4Eccc$	$-4Esss$
$2n$	$2n+1$	$2n+1$	$-4Ecsc$	$4Escs$
$2n+1$	$2n$	$2n+1$	$-4Escs$	$4Ecsc$
$2n+1$	$2n+1$	$2n$	$-4Essc$	$4Eccs$

$I2_13$ [No. 199]

$h+k$	$k+l$	$h+l$	A	B
$2n$	$2n$	$2n$	$8Eccc$	$-8Esss$
$2n+1$	$2n$	$2n+1$	$-8Escs$	$8Ecsc$
$2n+1$	$2n+1$	$2n$	$-8Essc$	$8Eccs$
$2n$	$2n+1$	$2n+1$	$-8Ecsc$	$8Escs$

$Pm\bar{3}$ [No. 200]

hkl	A	B
All	$8Eccc$	0

$Pn\bar{3}$ (Origin 1) [No. 201]

$h+k+l$	A	B
$2n$	$8Eccc$	0
$2n+1$	0	$-8Esss$

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.7. *Cubic space groups (cont.)*

$Pn\bar{3}$ (Origin 2) [No. 201] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	8Eccc
$2n$	$2n + 1$	$2n + 1$	−8Essc
$2n + 1$	$2n$	$2n + 1$	−8Ecsc
$2n + 1$	$2n + 1$	$2n$	−8Escs

$Fm\bar{3}$ [No. 202]

hkl	A	B
All	32Eccc	0

$Fd\bar{3}$ (Origin 1) [No. 203]

$h + k + l$	A	B
$4n$	32Eccc	0
$4n + 1$	16(Eccc − Ecsc)	A
$4n + 2$	0	−32Esss
$4n + 3$	16(Eccc + Ecsc)	− A

$Fd\bar{3}$ (Origin 2) [No. 203] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$4n$	$4n$	$4n$	32Eccc
$4n$	$4n + 2$	$4n + 2$	−32Essc
$4n + 2$	$4n$	$4n + 2$	−32Ecsc
$4n + 2$	$4n + 2$	$4n$	−32Escs
$4n + 2$	$4n + 2$	$4n + 2$	−16(Eccc + Ecsc + Escs + Ecsc)
$4n + 2$	$4n$	$4n$	16(Eccc − Ecsc − Escs + Ecsc)
$4n$	$4n + 2$	$4n$	16(Eccc + Ecsc − Escs − Ecsc)
$4n$	$4n$	$4n + 2$	16(Eccc − Ecsc + Escs − Ecsc)

$Im\bar{3}$ [No. 204]

hkl	A	B
All	16Eccc	0

$Pa\bar{3}$ [No. 205] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	8Eccc
$2n$	$2n + 1$	$2n + 1$	−8Ecsc
$2n + 1$	$2n$	$2n + 1$	−8Escs
$2n + 1$	$2n + 1$	$2n$	−8Essc

$Ia\bar{3}$ [No. 206] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	16Eccc
$2n$	$2n + 1$	$2n + 1$	−16Ecsc
$2n + 1$	$2n$	$2n + 1$	−16Escs
$2n + 1$	$2n + 1$	$2n$	−16Essc

$P432$ [No. 207]

hkl	A	B
All	4(Eccc + Ocsc)	−4(Essc − Osss)

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Table A1.4.3.7. *Cubic space groups (cont.)*

$P4_232$ [No. 208]

$h + k + l$	A	B
$2n$	$4(\text{Eccc} + \text{Occc})$	$-4(\text{Esss} - \text{Osss})$
$2n + 1$	$4(\text{Eccc} - \text{Occc})$	$-4(\text{Esss} + \text{Osss})$

$F432$ [No. 209]

hkl	A	B
All	$16(\text{Eccc} + \text{Occc})$	$-16(\text{Esss} - \text{Osss})$

$F4_132$ [No. 210]

$h + k + l$	A	B
$4n$	$16(\text{Eccc} + \text{Occc})$	$-16(\text{Esss} - \text{Osss})$
$4n + 1$	$16(\text{Eccc} - \text{Osss})$	$-16(\text{Esss} - \text{Occc})$
$4n + 2$	$16(\text{Eccc} - \text{Occc})$	$-16(\text{Esss} + \text{Osss})$
$4n + 3$	$16(\text{Eccc} + \text{Osss})$	$-16(\text{Esss} + \text{Occc})$

$I432$ [No. 211]

hkl	A	B
All	$8(\text{Eccc} + \text{Occc})$	$-8(\text{Esss} - \text{Osss})$

$P4_332$ [No. 212] (enantiomorphous to $P4_132$ [No. 213])

$h + k$	$k + l$	$h + l$	$h + k + l$	A	B
$2n$	$2n$	$2n$	$4n$	$4(\text{Eccc} + \text{Occc})$	$-4(\text{Esss} - \text{Osss})$
$2n$	$2n + 1$	$2n + 1$	$4n$	$-4(\text{Ecsc} + \text{Oscs})$	$4(\text{Eccc} - \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n$	$-4(\text{Ecsc} + \text{Ossc})$	$4(\text{Ecsc} - \text{Occc})$
$2n + 1$	$2n + 1$	$2n$	$4n$	$-4(\text{Eccc} + \text{Ossc})$	$4(\text{Eccc} - \text{Ossc})$
$2n$	$2n$	$2n$	$4n + 1$	$4(\text{Eccc} - \text{Osss})$	$-4(\text{Esss} - \text{Occc})$
$2n$	$2n + 1$	$2n + 1$	$4n + 1$	$-4(\text{Ecsc} - \text{Occc})$	$4(\text{Eccc} - \text{Oscs})$
$2n + 1$	$2n$	$2n + 1$	$4n + 1$	$-4(\text{Ecsc} - \text{Occc})$	$4(\text{Ecsc} - \text{Ossc})$
$2n + 1$	$2n + 1$	$2n$	$4n + 1$	$-4(\text{Eccc} - \text{Ossc})$	$4(\text{Eccc} - \text{Ossc})$
$2n$	$2n$	$2n$	$4n + 2$	$4(\text{Eccc} - \text{Occc})$	$-4(\text{Esss} + \text{Osss})$
$2n$	$2n + 1$	$2n + 1$	$4n + 2$	$-4(\text{Ecsc} - \text{Oscs})$	$4(\text{Eccc} + \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n + 2$	$-4(\text{Ecsc} - \text{Ossc})$	$4(\text{Ecsc} + \text{Occc})$
$2n + 1$	$2n + 1$	$2n$	$4n + 2$	$-4(\text{Eccc} + \text{Ossc})$	$4(\text{Eccc} + \text{Ossc})$
$2n$	$2n$	$2n$	$4n + 3$	$4(\text{Eccc} + \text{Osss})$	$-4(\text{Esss} + \text{Occc})$
$2n$	$2n + 1$	$2n + 1$	$4n + 3$	$-4(\text{Ecsc} + \text{Oscs})$	$4(\text{Eccc} + \text{Oscs})$
$2n + 1$	$2n$	$2n + 1$	$4n + 3$	$-4(\text{Ecsc} + \text{Occc})$	$4(\text{Ecsc} + \text{Ossc})$
$2n + 1$	$2n + 1$	$2n$	$4n + 3$	$-4(\text{Eccc} + \text{Ossc})$	$4(\text{Eccc} + \text{Ossc})$

$P4_132$ [No. 213] (enantiomorphous to $P4_332$ [No. 212])

h	k	l	$h + k + l$	A	B
$2n$	$2n$	$2n$	$4n$	$4(\text{Eccc} + \text{Occc})$	$-4(\text{Esss} - \text{Osss})$
$2n$	$2n + 1$	$2n + 1$	$4n$	$-4(\text{Ecsc} + \text{Ossc})$	$4(\text{Eccc} - \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n$	$-4(\text{Eccc} + \text{Ossc})$	$4(\text{Eccc} - \text{Ossc})$
$2n + 1$	$2n + 1$	$2n$	$4n$	$-4(\text{Ecsc} + \text{Oscs})$	$4(\text{Eccc} - \text{Oscs})$
$2n + 1$	$2n + 1$	$2n + 1$	$4n + 1$	$4(\text{Eccc} + \text{Osss})$	$-4(\text{Esss} + \text{Occc})$
$2n$	$2n$	$2n + 1$	$4n + 1$	$-4(\text{Ecsc} + \text{Occc})$	$4(\text{Eccc} + \text{Oscs})$
$2n + 1$	$2n$	$2n$	$4n + 1$	$-4(\text{Ecsc} + \text{Occc})$	$4(\text{Ecsc} + \text{Ossc})$
$2n$	$2n + 1$	$2n$	$4n + 1$	$-4(\text{Eccc} + \text{Ossc})$	$4(\text{Eccc} + \text{Ossc})$
$2n$	$2n$	$2n$	$4n + 2$	$4(\text{Eccc} - \text{Occc})$	$-4(\text{Esss} + \text{Osss})$
$2n$	$2n + 1$	$2n + 1$	$4n + 2$	$-4(\text{Ecsc} - \text{Ossc})$	$4(\text{Eccc} + \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n + 2$	$-4(\text{Eccc} - \text{Ossc})$	$4(\text{Eccc} + \text{Ossc})$

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.7. *Cubic space groups (cont.)*

h	k	l	$h + k + l$	A	B
$2n + 1$	$2n + 1$	$2n$	$4n + 2$	$-4(\text{Ecsc} - \text{Oscs})$	$4(\text{Escc} + \text{Oesc})$
$2n + 1$	$2n + 1$	$2n + 1$	$4n + 3$	$4(\text{Eccc} - \text{Osss})$	$-4(\text{Escc} - \text{Occc})$
$2n$	$2n$	$2n + 1$	$4n + 3$	$-4(\text{Ecsc} - \text{Oesc})$	$4(\text{Escc} - \text{Oscs})$
$2n + 1$	$2n$	$2n$	$4n + 3$	$-4(\text{Escc} - \text{Occc})$	$4(\text{Ecsc} - \text{Ossc})$
$2n$	$2n + 1$	$2n$	$4n + 3$	$-4(\text{Escc} - \text{Oscs})$	$4(\text{Eccc} - \text{Oess})$

$I4_132$ [No. 214]

h	k	l	$h + k + l$	A	B
$2n$	$2n$	$2n$	$4n$	$8(\text{Eccc} + \text{Occc})$	$-8(\text{Escc} - \text{Ossc})$
$2n$	$2n + 1$	$2n + 1$	$4n$	$-8(\text{Ecsc} + \text{Ossc})$	$8(\text{Ecsc} - \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n$	$-8(\text{Escc} + \text{Occc})$	$8(\text{Eccc} - \text{Oscs})$
$2n + 1$	$2n + 1$	$2n$	$4n$	$-8(\text{Ecsc} + \text{Oscs})$	$8(\text{Escc} - \text{Oesc})$
$2n$	$2n$	$2n$	$4n + 2$	$8(\text{Eccc} - \text{Occc})$	$-8(\text{Escc} + \text{Ossc})$
$2n$	$2n + 1$	$2n + 1$	$4n + 2$	$-8(\text{Ecsc} - \text{Ossc})$	$8(\text{Ecsc} + \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n + 2$	$-8(\text{Escc} - \text{Occc})$	$8(\text{Eccc} + \text{Oscs})$
$2n + 1$	$2n + 1$	$2n$	$4n + 2$	$-8(\text{Ecsc} - \text{Oscs})$	$8(\text{Escc} + \text{Oesc})$

$P\bar{4}3m$ [No. 215]

hkl	A	B
All	$4(\text{Eccc} + \text{Occc})$	$-4(\text{Escc} + \text{Ossc})$

$F\bar{4}3m$ [No. 216]

hkl	A	B
All	$16(\text{Eccc} + \text{Occc})$	$-16(\text{Escc} + \text{Ossc})$

$I\bar{4}3m$ [No. 217]

hkl	A	B
All	$8(\text{Eccc} + \text{Occc})$	$-8(\text{Escc} + \text{Ossc})$

$P\bar{4}3n$ [No. 218]

$h + k + l$	A	B
$2n$	$4(\text{Eccc} + \text{Occc})$	$-4(\text{Escc} + \text{Ossc})$
$2n + 1$	$4(\text{Eccc} - \text{Occc})$	$-4(\text{Escc} - \text{Ossc})$

$F\bar{4}3c$ [No. 219]

$h + k + l$	A	B
$2n$	$16(\text{Eccc} + \text{Occc})$	$-16(\text{Escc} + \text{Ossc})$
$2n + 1$	$16(\text{Eccc} - \text{Occc})$	$-16(\text{Escc} - \text{Ossc})$

$I\bar{4}3d$ [No. 220]

h	k	l	$h + k + l$	A	B
$2n$	$2n$	$2n$	$4n$	$8(\text{Eccc} + \text{Occc})$	$-8(\text{Escc} + \text{Ossc})$
$2n$	$2n + 1$	$2n + 1$	$4n$	$-8(\text{Ecsc} + \text{Ossc})$	$8(\text{Ecsc} + \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n$	$-8(\text{Escc} + \text{Occc})$	$8(\text{Eccc} + \text{Oscs})$
$2n + 1$	$2n + 1$	$2n$	$4n$	$-8(\text{Ecsc} + \text{Oscs})$	$8(\text{Escc} + \text{Oesc})$
$2n$	$2n$	$2n$	$4n + 2$	$8(\text{Eccc} - \text{Occc})$	$-8(\text{Escc} - \text{Ossc})$
$2n$	$2n + 1$	$2n + 1$	$4n + 2$	$-8(\text{Ecsc} - \text{Ossc})$	$8(\text{Ecsc} - \text{Occc})$
$2n + 1$	$2n$	$2n + 1$	$4n + 2$	$-8(\text{Escc} - \text{Occc})$	$8(\text{Eccc} - \text{Oscs})$
$2n + 1$	$2n + 1$	$2n$	$4n + 2$	$-8(\text{Ecsc} - \text{Oscs})$	$8(\text{Escc} - \text{Oesc})$

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Table A1.4.3.7. *Cubic space groups (cont.)*

$Pm\bar{3}m$ [No. 221]

hkl	A	B
All	$8(\text{Eccc} + \text{Occc})$	0

$Pn\bar{3}n$ (Origin 1) [No. 222]

$h + k + l$	A	B
$2n$	$8(\text{Eccc} + \text{Occc})$	0
$2n + 1$	0	$-8(\text{Esss} - \text{Osss})$

$Pn\bar{3}n$ (Origin 2) [No. 222] ($B = 0$ for all h, k, l)

h	k	l	A
$2n$	$2n$	$2n$	$8(\text{Eccc} + \text{Occc})$
$2n$	$2n + 1$	$2n + 1$	$-8(\text{Ecsc} + \text{Ocsc})$
$2n + 1$	$2n$	$2n + 1$	$-8(\text{Escs} + \text{Oscs})$
$2n + 1$	$2n + 1$	$2n$	$-8(\text{Essc} + \text{Ossc})$
$2n + 1$	$2n + 1$	$2n + 1$	$8(\text{Eccc} - \text{Occc})$
$2n + 1$	$2n$	$2n$	$-8(\text{Ecsc} - \text{Ocsc})$
$2n$	$2n + 1$	$2n$	$-8(\text{Escs} - \text{Oscs})$
$2n$	$2n$	$2n + 1$	$-8(\text{Essc} - \text{Ossc})$

$Pm\bar{3}n$ [No. 223] ($B = 0$ for all h, k, l)

$h + k + l$	A
$2n$	$8(\text{Eccc} + \text{Occc})$
$2n + 1$	$8(\text{Eccc} - \text{Occc})$

$Pn\bar{3}m$ (Origin 1) [No. 224]

$h + k + l$	A	B
$2n$	$8(\text{Eccc} + \text{Occc})$	0
$2n + 1$	0	$-8(\text{Esss} + \text{Osss})$

$Pn\bar{3}m$ (Origin 2) [No. 224] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$2n$	$2n$	$2n$	$8(\text{Eccc} + \text{Occc})$
$2n$	$2n + 1$	$2n + 1$	$-8(\text{Essc} + \text{Ossc})$
$2n + 1$	$2n$	$2n + 1$	$-8(\text{Ecsc} + \text{Ocsc})$
$2n + 1$	$2n + 1$	$2n$	$-8(\text{Escs} + \text{Oscs})$

$Fm\bar{3}m$ [No. 225]

hkl	A	B
All	$32(\text{Eccc} + \text{Occc})$	0

$Fm\bar{3}c$ [No. 226] ($B = 0$ for all h, k, l)

$h + k + l$	A
$2n$	$32(\text{Eccc} + \text{Occc})$
$2n + 1$	$32(\text{Eccc} - \text{Occc})$

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.3.7. *Cubic space groups (cont.)*

$Fd\bar{3}m$ (Origin 1) [No. 227]

$h + k + l$	A	B
$4n$	$32(\text{Eccc} + \text{Occc})$	0
$4n + 1$	$16(\text{Eccc} - \text{Esss} + \text{Occc} - \text{Osss})$	A
$4n + 2$	0	$-32(\text{Esss} + \text{Osss})$
$4n + 3$	$16(\text{Eccc} + \text{Esss} + \text{Occc} + \text{Osss})$	$-A$

$Fd\bar{3}m$ (Origin 2) [No. 227] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$4n$	$4n$	$4n$	$32(\text{Eccc} + \text{Occc})$
$4n$	$4n + 2$	$4n + 2$	$-32(\text{Essc} + \text{Ossc})$
$4n + 2$	$4n$	$4n + 2$	$-32(\text{Ecsc} + \text{Ocsc})$
$4n + 2$	$4n + 2$	$4n$	$-32(\text{Escs} + \text{Oscs})$
$4n + 2$	$4n + 2$	$4n + 2$	$-16(\text{Eccc} + \text{Esss} + \text{Escs} + \text{Essc} + \text{Occc} + \text{Ocsc} + \text{Oscs} + \text{Ossc})$
$4n + 2$	$4n$	$4n$	$16(\text{Eccc} - \text{Esss} - \text{Escs} + \text{Essc} + \text{Occc} - \text{Ocsc} - \text{Oscs} + \text{Ossc})$
$4n$	$4n + 2$	$4n$	$16(\text{Eccc} + \text{Esss} - \text{Escs} - \text{Essc} + \text{Occc} + \text{Ocsc} - \text{Oscs} - \text{Ossc})$
$4n$	$4n$	$4n + 2$	$16(\text{Eccc} - \text{Esss} + \text{Escs} - \text{Essc} + \text{Occc} - \text{Ocsc} + \text{Oscs} - \text{Ossc})$

$Fd\bar{3}c$ (Origin 1) [No. 228]

$h + k + l$	A	B
$4n$	$32(\text{Eccc} + \text{Occc})$	0
$4n + 1$	$16(\text{Eccc} + \text{Esss} - \text{Occc} - \text{Osss})$	$-A$
$4n + 2$	0	$-32(\text{Esss} + \text{Osss})$
$4n + 3$	$16(\text{Eccc} - \text{Esss} - \text{Occc} + \text{Osss})$	A

$Fd\bar{3}c$ (Origin 2) [No. 228] ($B = 0$ for all h, k, l)

$h + k$	$k + l$	$h + l$	A
$4n$	$4n$	$4n$	$32(\text{Eccc} + \text{Occc})$
$4n$	$4n + 2$	$4n + 2$	$-32(\text{Essc} + \text{Ossc})$
$4n + 2$	$4n$	$4n + 2$	$-32(\text{Ecsc} + \text{Ocsc})$
$4n + 2$	$4n + 2$	$4n$	$-32(\text{Escs} + \text{Oscs})$
$4n + 2$	$4n + 2$	$4n + 2$	$-16(\text{Eccc} + \text{Esss} + \text{Escs} + \text{Essc} - \text{Occc} - \text{Ocsc} - \text{Oscs} - \text{Ossc})$
$4n + 2$	$4n$	$4n$	$16(\text{Eccc} - \text{Esss} - \text{Escs} + \text{Essc} - \text{Occc} + \text{Ocsc} + \text{Oscs} - \text{Ossc})$
$4n$	$4n + 2$	$4n$	$16(\text{Eccc} + \text{Esss} - \text{Escs} - \text{Essc} - \text{Occc} - \text{Ocsc} + \text{Oscs} + \text{Ossc})$
$4n$	$4n$	$4n + 2$	$16(\text{Eccc} - \text{Esss} + \text{Escs} - \text{Essc} - \text{Occc} + \text{Ocsc} - \text{Oscs} + \text{Ossc})$

$Im\bar{3}m$ [No. 229]

hkl	A	B
All	$16(\text{Eccc} + \text{Occc})$	0

$Ia\bar{3}d$ [No. 230] ($B = 0$ for all h, k, l)

h	k	l	$h + k + l$	A
$2n$	$2n$	$2n$	$4n$	$16(\text{Eccc} + \text{Occc})$
$2n$	$2n + 1$	$2n + 1$	$4n$	$-16(\text{Escs} + \text{Ossc})$
$2n + 1$	$2n$	$2n + 1$	$4n$	$-16(\text{Essc} + \text{Ocsc})$
$2n + 1$	$2n + 1$	$2n$	$4n$	$-16(\text{Escs} + \text{Oscs})$
$2n$	$2n$	$2n$	$4n + 2$	$16(\text{Eccc} - \text{Occc})$
$2n$	$2n + 1$	$2n + 1$	$4n + 2$	$-16(\text{Escs} - \text{Ossc})$
$2n + 1$	$2n$	$2n + 1$	$4n + 2$	$-16(\text{Essc} - \text{Ocsc})$
$2n + 1$	$2n + 1$	$2n$	$4n + 2$	$-16(\text{Escs} - \text{Oscs})$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Appendix 1.4.4.

Crystallographic space groups in reciprocal space

Table A1.4.4.1. *Crystallographic space groups in reciprocal space*

The table entries are described in detail in Section 1.4.4.1. The general format of an entry is

$$(n) \mathbf{h}^T \mathbf{P}_n : -\mathbf{h}^T \mathbf{t}_n$$

or

$$(n) \mathbf{h}^T \mathbf{P}_n : ,$$

according as the phase-shift part of the entry is nonzero or zero modulo 2π , respectively.

Notes:

(1) For centrosymmetric space groups with the centre located at the unit-cell origin only those entries are given which correspond to symmetry operations not related by inversion. If the origin in such space groups is chosen elsewhere, all the entries corresponding to the operations of the point group are presented.

(2) For trigonal and hexagonal space groups referred to hexagonal axes the Miller–Bravais indices hkl are employed, and for the rhombohedral space groups referred to rhombohedral axes the indices are denoted by hkl (cf. *IT* I, 1952).

Point group: 1 Triclinic Laue group: $\bar{1}$
$P1$ No. 1 (1) (1) hkl :

Point group: $\bar{1}$ Triclinic Laue group: $\bar{1}$
$P\bar{1}$ No. 2 (2) (1) hkl :

Point group: 2 Monoclinic Laue group: 2/m
$P2$ $P121$ Unique axis b No. 3 (3) (1) hkl : (2) $\bar{h}k\bar{l}$:
$P2$ $P112$ Unique axis c No. 3 (4) (1) hkl : (2) $\bar{h}k\bar{l}$:
$P2_1$ $P12_11$ Unique axis b No. 4 (5) (1) hkl : (2) $\bar{h}k\bar{l}$: $-010/2$
$P2_1$ $P112_1$ Unique axis c No. 4 (6) (1) hkl : (2) $\bar{h}k\bar{l}$: $-001/2$
$C2$ $C121$ Unique axis b No. 5 (7) (1) hkl : (2) $\bar{h}k\bar{l}$:
$C2$ $A121$ Unique axis b No. 5 (8) (1) hkl : (2) $\bar{h}k\bar{l}$:
$C2$ $I121$ Unique axis b No. 5 (9) (1) hkl : (2) $\bar{h}k\bar{l}$:
$C2$ $A112$ Unique axis c No. 5 (10) (1) hkl : (2) $\bar{h}k\bar{l}$:
$C2$ $B112$ Unique axis c No. 5 (11) (1) hkl : (2) $\bar{h}k\bar{l}$:
$C2$ $I112$ Unique axis c No. 5 (12) (1) hkl : (2) $\bar{h}k\bar{l}$:

Point group: m Monoclinic Laue group: 2/m
Pm $P1m1$ Unique axis b No. 6 (13) (1) hkl : (2) $\bar{h}k\bar{l}$:
Pm $P11m$ Unique axis c No. 6 (14) (1) hkl : (2) $\bar{h}k\bar{l}$:
Pc $P1c1$ Unique axis b No. 7 (15) (1) hkl : (2) $\bar{h}k\bar{l}$: $-001/2$
Pc $P1n1$ Unique axis b No. 7 (16) (1) hkl : (2) $\bar{h}k\bar{l}$: $-101/2$
Pc $P1a1$ Unique axis b No. 7 (17) (1) hkl : (2) $\bar{h}k\bar{l}$: $-100/2$
Pc $P11a$ Unique axis c No. 7 (18) (1) hkl : (2) $\bar{h}k\bar{l}$: $-100/2$
Pc $P11n$ Unique axis c No. 7 (19) (1) hkl : (2) $\bar{h}k\bar{l}$: $-110/2$
Pc $P11b$ Unique axis c No. 7 (20) (1) hkl : (2) $\bar{h}k\bar{l}$: $-010/2$
Cm $C1m1$ Unique axis b No. 8 (21) (1) hkl : (2) $\bar{h}k\bar{l}$:
Cm $A1m1$ Unique axis b No. 8 (22) (1) hkl : (2) $\bar{h}k\bar{l}$:
Cm $I1m1$ Unique axis b No. 8 (23) (1) hkl : (2) $\bar{h}k\bar{l}$:
Cm $A11m$ Unique axis c No. 8 (24) (1) hkl : (2) $\bar{h}k\bar{l}$:
Cm $B11m$ Unique axis c No. 8 (25) (1) hkl : (2) $\bar{h}k\bar{l}$:
Cm $I11m$ Unique axis c No. 8 (26) (1) hkl : (2) $\bar{h}k\bar{l}$:

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

Cc	$C1c1$	Unique axis b	No. 9 (27)
(1) hkl :	(2) $h\bar{k}l$:	$-001/2$	
Cc	$A1n1$	Unique axis b	No. 9 (28)
(1) hkl :	(2) $h\bar{k}l$:	$-101/2$	
Cc	$I1a1$	Unique axis b	No. 9 (29)
(1) hkl :	(2) $h\bar{k}l$:	$-100/2$	
Cc	$A11a$	Unique axis c	No. 9 (30)
(1) hkl :	(2) $h\bar{k}l$:	$-100/2$	
Cc	$B11n$	Unique axis c	No. 9 (31)
(1) hkl :	(2) $h\bar{k}l$:	$-110/2$	
Cc	$I11b$	Unique axis c	No. 9 (32)
(1) hkl :	(2) $h\bar{k}l$:	$-010/2$	

Point group: $2/m$ Monoclinic Laue group: $2/m$			
$P2/m$	$P12/m1$	Unique axis b	No. 10 (33)
(1) hkl :	(2) $h\bar{k}l$:		
$P2/m$	$P112/m$	Unique axis c	No. 10 (34)
(1) hkl :	(2) $h\bar{k}l$:		
$P2_1/m$	$P12_1/m1$	Unique axis b	No. 11 (35)
(1) hkl :	(2) $h\bar{k}l$:	$-010/2$	
$P2_1/m$	$P112_1/m$	Unique axis c	No. 11 (36)
(1) hkl :	(2) $h\bar{k}l$:	$-001/2$	
$C2/m$	$C12/m1$	Unique axis b	No. 12 (37)
(1) hkl :	(2) $h\bar{k}l$:		
$C2/m$	$A12/m1$	Unique axis b	No. 12 (38)
(1) hkl :	(2) $h\bar{k}l$:		
$C2/m$	$I12/m1$	Unique axis b	No. 12 (39)
(1) hkl :	(2) $h\bar{k}l$:		
$C2/m$	$A112/m$	Unique axis c	No. 12 (40)
(1) hkl :	(2) $h\bar{k}l$:		
$C2/m$	$B112/m$	Unique axis c	No. 12 (41)
(1) hkl :	(2) $h\bar{k}l$:		
$C2/m$	$I112/m$	Unique axis c	No. 12 (42)
(1) hkl :	(2) $h\bar{k}l$:		
$P2/c$	$P12/c1$	Unique axis b	No. 13 (43)
(1) hkl :	(2) $h\bar{k}l$:	$-001/2$	
$P2/c$	$P12/n1$	Unique axis b	No. 13 (44)
(1) hkl :	(2) $h\bar{k}l$:	$-101/2$	
$P2/c$	$P12/a1$	Unique axis b	No. 13 (45)
(1) hkl :	(2) $h\bar{k}l$:	$-100/2$	

$P2/c$	$P112/a$	Unique axis c	No. 13 (46)
(1) hkl :	(2) $h\bar{k}l$:	$-100/2$	
$P2/c$	$P112/n$	Unique axis c	No. 13 (47)
(1) hkl :	(2) $h\bar{k}l$:	$-110/2$	
$P2/c$	$P112/b$	Unique axis c	No. 13 (48)
(1) hkl :	(2) $h\bar{k}l$:	$-010/2$	
$P2_1/c$	$P12_1/c1$	Unique axis b	No. 14 (49)
(1) hkl :	(2) $h\bar{k}l$:	$-011/2$	
$P2_1/c$	$P12_1/n1$	Unique axis b	No. 14 (50)
(1) hkl :	(2) $h\bar{k}l$:	$-111/2$	
$P2_1/c$	$P12_1/a1$	Unique axis b	No. 14 (51)
(1) hkl :	(2) $h\bar{k}l$:	$-110/2$	
$P2_1/c$	$P112_1/a$	Unique axis c	No. 14 (52)
(1) hkl :	(2) $h\bar{k}l$:	$-101/2$	
$P2_1/c$	$P112_1/n$	Unique axis c	No. 14 (53)
(1) hkl :	(2) $h\bar{k}l$:	$-111/2$	
$P2_1/c$	$P112_1/b$	Unique axis c	No. 14 (54)
(1) hkl :	(2) $h\bar{k}l$:	$-011/2$	
$C2/c$	$C12/c1$	Unique axis b	No. 15 (55)
(1) hkl :	(2) $h\bar{k}l$:	$-001/2$	
$C2/c$	$A12/n1$	Unique axis b	No. 15 (56)
(1) hkl :	(2) $h\bar{k}l$:	$-101/2$	
$C2/c$	$I12/a1$	Unique axis b	No. 15 (57)
(1) hkl :	(2) $h\bar{k}l$:	$-100/2$	
$C2/c$	$A112/a$	Unique axis c	No. 15 (58)
(1) hkl :	(2) $h\bar{k}l$:	$-100/2$	
$C2/c$	$B112/n$	Unique axis c	No. 15 (59)
(1) hkl :	(2) $h\bar{k}l$:	$-110/2$	
$C2/c$	$I112/b$	Unique axis c	No. 15 (60)
(1) hkl :	(2) $h\bar{k}l$:	$-010/2$	

Point group: 222 Orthorhombic Laue group: mmm			
$P222$	No. 16 (61)		
(1) hkl :	(2) $h\bar{k}l$:	(3) $h\bar{k}l$:	(4) $h\bar{k}l$:
$P222_1$	No. 17 (62)		
(1) hkl :	(2) $h\bar{k}l$:	(3) $h\bar{k}l$:	(4) $h\bar{k}l$:
	$-001/2$	$-001/2$	
$P2_12_12$	No. 18 (63)		
(1) hkl :	(2) $h\bar{k}l$:	(3) $h\bar{k}l$:	(4) $h\bar{k}l$:
		$-110/2$	$-110/2$

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

$P2_12_12_1$ No. 19 (64)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}\bar{l}$: -110/2
$C222_1$ No. 20 (65)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}\bar{l}$:
$C222$ No. 21 (66)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$F222$ No. 22 (67)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$I222$ No. 23 (68)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$I2_12_12_1$ No. 24 (69)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}\bar{l}$: -110/2

Point group: $mm2$	Orthorhombic	Laue group: mmm	
$Pmm2$ No. 25 (70)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$Pmc2_1$ No. 26 (71)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}\bar{l}$:
$Pcc2$ No. 27 (72)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}\bar{l}$: -001/2
$Pma2$ No. 28 (73)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -100/2	(4) $h\bar{k}\bar{l}$: -100/2
$Pca2_1$ No. 29 (74)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -100/2	(4) $h\bar{k}\bar{l}$: -101/2
$Pnc2$ No. 30 (75)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}\bar{l}$: -011/2
$Pmn2_1$ No. 31 (76)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -101/2	(4) $h\bar{k}\bar{l}$:
$Pba2$ No. 32 (77)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}\bar{l}$: -110/2
$Pna2_1$ No. 33 (78)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}\bar{l}$: -111/2
$Pnn2$ No. 34 (79)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -111/2	(4) $h\bar{k}\bar{l}$: -111/2
$Cmm2$ No. 35 (80)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$Cmc2_1$ No. 36 (81)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}\bar{l}$:

$Ccc2$ No. 37 (82)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}\bar{l}$: -001/2
$Amm2$ No. 38 (83)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$Abm2$ No. 39 (84)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -010/2	(4) $h\bar{k}\bar{l}$: -010/2
$Ama2$ No. 40 (85)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -100/2	(4) $h\bar{k}\bar{l}$: -100/2
$Aba2$ No. 41 (86)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}\bar{l}$: -110/2
$Fmm2$ No. 42 (87)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$Fdd2$ No. 43 (88)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -313/4	(4) $h\bar{k}\bar{l}$: -133/4
$Imm2$ No. 44 (89)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$Iba2$ No. 45 (90)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}\bar{l}$: -110/2
$Ima2$ No. 46 (91)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -100/2	(4) $h\bar{k}\bar{l}$: -100/2

Point group: mmm	Orthorhombic	Laue group: mmm	
$Pmmm$ No. 47 (92)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
$Pnnn$ Origin 1 No. 48 (93)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) $\bar{h}\bar{k}l$: -111/2	(6) $h\bar{k}\bar{l}$: -111/2	(7) $\bar{h}k\bar{l}$: -111/2	(8) $h\bar{k}\bar{l}$: -111/2
$Pnnn$ Origin 2 No. 48 (94)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $\bar{h}k\bar{l}$: -101/2	(4) $h\bar{k}\bar{l}$: -011/2
$Pccm$ No. 49 (95)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}\bar{l}$: -001/2
$Pban$ Origin 1 No. 50 (96)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) $\bar{h}\bar{k}l$: -110/2	(6) $h\bar{k}\bar{l}$: -110/2	(7) $\bar{h}k\bar{l}$: -110/2	(8) $h\bar{k}\bar{l}$: -110/2
$Pban$ Origin 2 No. 50 (97)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $\bar{h}k\bar{l}$: -100/2	(4) $h\bar{k}\bar{l}$: -010/2
$Pmma$ No. 51 (98)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -100/2	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$: -100/2
$Pnna$ No. 52 (99)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -100/2	(3) $\bar{h}k\bar{l}$: -111/2	(4) $h\bar{k}\bar{l}$: -011/2

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

<i>Pmna</i> No. 53 (100)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -101/2	(4) $h\bar{k}l$:
<i>Pcca</i> No. 54 (101)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -100/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}l$: -101/2
<i>Pbam</i> No. 55 (102)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}l$: -110/2
<i>Pccn</i> No. 56 (103)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}l$: -101/2
<i>Pbcm</i> No. 57 (104)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}l$: -010/2
<i>Pnnm</i> No. 58 (105)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -111/2	(4) $h\bar{k}l$: -111/2
<i>Pmmn</i> Origin 1 No. 59 (106)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}l$: -110/2
	(5) $\bar{h}k\bar{l}$: -110/2	(6) $h\bar{k}l$: -110/2	(7) $\bar{h}k\bar{l}$:	(8) $\bar{h}k\bar{l}$:
<i>Pmmn</i> Origin 2 No. 59 (107)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $\bar{h}k\bar{l}$: -010/2	(4) $h\bar{k}l$: -100/2
<i>Pbcn</i> No. 60 (108)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -111/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}l$: -110/2
<i>Pbca</i> No. 61 (109)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}l$: -110/2
<i>Pnma</i> No. 62 (110)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -010/2	(4) $h\bar{k}l$: -111/2
<i>Cmcm</i> No. 63 (111)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}l$:
<i>Cmca</i> No. 64 (112)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -011/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}l$:
<i>Cmmm</i> No. 65 (113)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}l$:
<i>Cccm</i> No. 66 (114)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}l$: -001/2
<i>Cmma</i> No. 67 (115)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -010/2	(3) $\bar{h}k\bar{l}$: -010/2	(4) $h\bar{k}l$:
<i>Ccca</i> Origin 1 No. 68 (116)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}l$: -110/2
	(5) $\bar{h}k\bar{l}$: -011/2	(6) $h\bar{k}l$: -101/2	(7) $\bar{h}k\bar{l}$: -011/2	(8) $\bar{h}k\bar{l}$: -101/2
<i>Ccca</i> Origin 2 No. 68 (117)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -100/2	(3) $\bar{h}k\bar{l}$: -001/2	(4) $h\bar{k}l$: -101/2

<i>Fmmm</i> No. 69 (118)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}l$:
<i>Fddd</i> Origin 1 No. 70 (119)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}l$:
	(5) $\bar{h}k\bar{l}$: -111/4	(6) $h\bar{k}l$: -111/4	(7) $\bar{h}k\bar{l}$: -111/4	(8) $\bar{h}k\bar{l}$: -111/4
<i>Fddd</i> Origin 2 No. 70 (120)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -330/4	(3) $\bar{h}k\bar{l}$: -303/4	(4) $h\bar{k}l$: -033/4
<i>Immm</i> No. 71 (121)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}l$:
<i>Ibam</i> No. 72 (122)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -110/2	(4) $h\bar{k}l$: -110/2
<i>Ibca</i> No. 73 (123)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}k\bar{l}$: -011/2	(4) $h\bar{k}l$: -110/2
<i>Imma</i> No. 74 (124)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -010/2	(3) $\bar{h}k\bar{l}$: -010/2	(4) $h\bar{k}l$:

Point group: 4 Tetragonal Laue group: 4/m				
<i>P4</i> No. 75 (125)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $\bar{h}k\bar{l}$:
<i>P4₁</i> No. 76 (126)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -001/4	(4) $\bar{h}k\bar{l}$: -003/4
<i>P4₂</i> No. 77 (127)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$: -001/2	(4) $\bar{h}k\bar{l}$: -001/2
<i>P4₃</i> No. 78 (128)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $\bar{h}k\bar{l}$: -003/4	(4) $\bar{h}k\bar{l}$: -001/4
<i>I4</i> No. 79 (129)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $\bar{h}k\bar{l}$:
<i>I4₁</i> No. 80 (130)	(1) hkl :	(2) $\bar{h}\bar{k}l$: -111/2	(3) $\bar{h}k\bar{l}$: -021/4	(4) $\bar{h}k\bar{l}$: -203/4

Point group: $\bar{4}$ Tetragonal Laue group: 4/m				
<i>P$\bar{4}$</i> No. 81 (131)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $\bar{h}k\bar{l}$:
<i>I$\bar{4}$</i> No. 82 (132)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $\bar{h}k\bar{l}$:

Point group: 4/m Tetragonal Laue group: 4/m				
<i>P4/m</i> No. 83 (133)	(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $\bar{h}k\bar{l}$:

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

$P4_2/m$ No. 84 (134)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
$P4/n$ Origin 1 No. 85 (135)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -110/2	(4) $\bar{k}hl$: -110/2
(5) $\bar{h}\bar{k}l$: -110/2	(6) $hk\bar{l}$: -110/2	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4/n$ Origin 2 No. 85 (136)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $k\bar{h}l$: -100/2	(4) $\bar{k}hl$: -010/2
$P4_2/n$ Origin 1 No. 86 (137)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -111/2	(6) $hk\bar{l}$: -111/2	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4_2/n$ Origin 2 No. 86 (138)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $k\bar{h}l$: -011/2	(4) $\bar{k}hl$: -101/2
$I4/m$ No. 87 (139)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
$I4_1/a$ Origin 1 No. 88 (140)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -111/2	(3) $k\bar{h}l$: -021/4	(4) $\bar{k}hl$: -203/4
(5) $\bar{h}\bar{k}l$: -021/4	(6) $hk\bar{l}$: -203/4	(7) $\bar{k}h\bar{l}$:	(8) khl : -111/2
$I4_1/a$ Origin 2 No. 88 (141)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $k\bar{h}l$: -311/4	(4) $\bar{k}hl$: -333/4

Point group: 422 Tetragonal Laue group: 4/mmm			
$P422$ No. 89 (142)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$:	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P42_12$ No. 90 (143)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -110/2	(4) $\bar{k}hl$: -110/2
(5) $\bar{h}\bar{k}l$: -110/2	(6) $hk\bar{l}$: -110/2	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4_122$ No. 91 (144)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $k\bar{h}l$: -001/4	(4) $\bar{k}hl$: -003/4
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$: -001/2	(7) $\bar{k}h\bar{l}$: -003/4	(8) khl : -001/4
$P4_12_12$ No. 92 (145)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $k\bar{h}l$: -221/4	(4) $\bar{k}hl$: -223/4
(5) $\bar{h}\bar{k}l$: -221/4	(6) $hk\bar{l}$: -223/4	(7) $\bar{k}h\bar{l}$:	(8) khl : -001/2
$P4_222$ No. 93 (146)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$:	(7) $\bar{k}h\bar{l}$: -001/2	(8) khl : -001/2
$P4_22_12$ No. 94 (147)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -111/2	(6) $hk\bar{l}$: -111/2	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4_322$ No. 95 (148)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $k\bar{h}l$: -003/4	(4) $\bar{k}hl$: -001/4
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$: -001/2	(7) $\bar{k}h\bar{l}$: -001/4	(8) khl : -003/4

$P4_32_12$ No. 96 (149)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -001/2	(3) $k\bar{h}l$: -223/4	(4) $\bar{k}hl$: -221/4
(5) $\bar{h}\bar{k}l$: -223/4	(6) $hk\bar{l}$: -221/4	(7) $\bar{k}h\bar{l}$:	(8) khl : -001/2
$I422$ No. 97 (150)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$:	(7) $\bar{k}h\bar{l}$:	(8) khl :
$I4_122$ No. 98 (151)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -111/2	(3) $k\bar{h}l$: -021/4	(4) $\bar{k}hl$: -203/4
(5) $\bar{h}\bar{k}l$: -203/4	(6) $hk\bar{l}$: -021/4	(7) $\bar{k}h\bar{l}$: -111/2	(8) khl :

Point group: 4mm Tetragonal Laue group: 4/mmm			
$P4mm$ No. 99 (152)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$:	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4bm$ No. 100 (153)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$: -110/2	(6) $hk\bar{l}$: -110/2	(7) $\bar{k}h\bar{l}$: -110/2	(8) khl : -110/2
$P4_2cm$ No. 101 (154)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$: -001/2	(6) $hk\bar{l}$: -001/2	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4_2nm$ No. 102 (155)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -111/2	(6) $hk\bar{l}$: -111/2	(7) $\bar{k}h\bar{l}$:	(8) khl :
$P4cc$ No. 103 (156)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$: -001/2	(6) $hk\bar{l}$: -001/2	(7) $\bar{k}h\bar{l}$: -001/2	(8) khl : -001/2
$P4nc$ No. 104 (157)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$: -111/2	(6) $hk\bar{l}$: -111/2	(7) $\bar{k}h\bar{l}$: -111/2	(8) khl : -111/2
$P4_2mc$ No. 105 (158)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$:	(7) $\bar{k}h\bar{l}$: -001/2	(8) khl : -001/2
$P4_2bc$ No. 106 (159)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$: -110/2	(6) $hk\bar{l}$: -110/2	(7) $\bar{k}h\bar{l}$: -111/2	(8) khl : -111/2
$I4mm$ No. 107 (160)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$:	(6) $hk\bar{l}$:	(7) $\bar{k}h\bar{l}$:	(8) khl :
$I4cm$ No. 108 (161)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$: -001/2	(6) $hk\bar{l}$: -001/2	(7) $\bar{k}h\bar{l}$: -001/2	(8) khl : -001/2

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.4.1. Crystallographic space groups in reciprocal space (cont.)

$I4_1md$ No. 109 (162)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -111/2	(3) $k\bar{h}l$: -021/4	(4) $\bar{k}hl$: -203/4
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$: -111/2	(7) $\bar{k}hl$: -203/4	(8) khl : -021/4
$I4_1cd$ No. 110 (163)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -111/2	(3) $k\bar{h}l$: -021/4	(4) $\bar{k}hl$: -203/4
(5) $\bar{h}k\bar{l}$: -001/2	(6) $\bar{h}kl$: -110/2	(7) $\bar{k}hl$: -201/4	(8) khl : -023/4

Point group: $\bar{4}2m$ Tetragonal Laue group: $4/mmm$			
$P\bar{4}2m$ No. 111 (164)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $\bar{k}hl$:	(8) khl :
$P\bar{4}2c$ No. 112 (165)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -001/2	(6) $\bar{h}kl$: -001/2	(7) $\bar{k}hl$: -001/2	(8) khl : -001/2
$P\bar{4}2_1m$ No. 113 (166)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -110/2	(6) $\bar{h}kl$: -110/2	(7) $\bar{k}hl$: -110/2	(8) khl : -110/2
$P\bar{4}2_1c$ No. 114 (167)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -111/2	(6) $\bar{h}kl$: -111/2	(7) $\bar{k}hl$: -111/2	(8) khl : -111/2
$P\bar{4}m2$ No. 115 (168)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $kh\bar{l}$:	(8) $\bar{k}hl$:
$P\bar{4}c2$ No. 116 (169)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -001/2	(6) $\bar{h}kl$: -001/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}hl$: -001/2
$P\bar{4}b2$ No. 117 (170)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -110/2	(6) $\bar{h}kl$: -110/2	(7) $kh\bar{l}$: -110/2	(8) $\bar{k}hl$: -110/2
$P\bar{4}n2$ No. 118 (171)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -111/2	(6) $\bar{h}kl$: -111/2	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}hl$: -111/2
$\bar{I}4m2$ No. 119 (172)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $kh\bar{l}$:	(8) $\bar{k}hl$:
$\bar{I}4c2$ No. 120 (173)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -001/2	(6) $\bar{h}kl$: -001/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}hl$: -001/2
$\bar{I}42m$ No. 121 (174)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $\bar{k}hl$:	(8) khl :
$\bar{I}42d$ No. 122 (175)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -203/4	(6) $\bar{h}kl$: -203/4	(7) $\bar{k}hl$: -021/4	(8) khl : -021/4

Point group: $4/mmm$ Tetragonal Laue group: $4/mmm$			
$P4/mmm$ No. 123 (176)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $kh\bar{l}$:	(8) $\bar{k}hl$:
$P4/mcc$ No. 124 (177)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -001/2	(6) $\bar{h}kl$: -001/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}hl$: -001/2
$P4/nbm$ Origin 1 No. 125 (178)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $kh\bar{l}$:	(8) $\bar{k}hl$:
(9) $\bar{h}k\bar{l}$: -110/2	(10) hkl : -110/2	(11) $\bar{k}hl$: -110/2	(12) khl : -110/2
(13) $\bar{h}k\bar{l}$: -110/2	(14) $\bar{h}kl$: -110/2	(15) $\bar{k}hl$: -110/2	(16) khl : -110/2
$P4/nbm$ Origin 2 No. 125 (179)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $k\bar{h}l$: -100/2	(4) $\bar{k}hl$: -010/2
(5) $\bar{h}k\bar{l}$: -100/2	(6) $\bar{h}kl$: -010/2	(7) $kh\bar{l}$:	(8) $\bar{k}hl$: -110/2
$P4/nnc$ Origin 1 No. 126 (180)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$:	(6) $\bar{h}kl$:	(7) $kh\bar{l}$:	(8) $\bar{k}hl$:
(9) $\bar{h}k\bar{l}$: -111/2	(10) hkl : -111/2	(11) $\bar{k}hl$: -111/2	(12) khl : -111/2
(13) $\bar{h}k\bar{l}$: -111/2	(14) $\bar{h}kl$: -111/2	(15) $\bar{k}hl$: -111/2	(16) khl : -111/2
$P4/nnc$ Origin 2 No. 126 (181)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $k\bar{h}l$: -100/2	(4) $\bar{k}hl$: -010/2
(5) $\bar{h}k\bar{l}$: -101/2	(6) $\bar{h}kl$: -011/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}hl$: -111/2
$P4/mbm$ No. 127 (182)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -110/2	(6) $\bar{h}kl$: -110/2	(7) $kh\bar{l}$: -110/2	(8) $\bar{k}hl$: -110/2
$P4/mnc$ No. 128 (183)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}k\bar{l}$: -111/2	(6) $\bar{h}kl$: -111/2	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}hl$: -111/2
$P4/nmm$ Origin 1 No. 129 (184)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -110/2	(4) $\bar{k}hl$: -110/2
(5) $\bar{h}k\bar{l}$: -110/2	(6) $\bar{h}kl$: -110/2	(7) $kh\bar{l}$:	(8) $\bar{k}hl$:
(9) $\bar{h}k\bar{l}$: -110/2	(10) hkl : -110/2	(11) $\bar{k}hl$:	(12) khl :
(13) $\bar{h}k\bar{l}$:	(14) $\bar{h}kl$:	(15) $\bar{k}hl$: -110/2	(16) khl : -110/2
$P4/nmm$ Origin 2 No. 129 (185)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $k\bar{h}l$: -100/2	(4) $\bar{k}hl$: -010/2
(5) $\bar{h}k\bar{l}$: -010/2	(6) $\bar{h}kl$: -100/2	(7) $kh\bar{l}$: -110/2	(8) $\bar{k}hl$:
$P4/ncc$ Origin 1 No. 130 (186)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $k\bar{h}l$: -110/2	(4) $\bar{k}hl$: -110/2
(5) $\bar{h}k\bar{l}$: -111/2	(6) $\bar{h}kl$: -111/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}hl$: -001/2
(9) $\bar{h}k\bar{l}$: -110/2	(10) hkl : -110/2	(11) $\bar{k}hl$:	(12) khl :
(13) $\bar{h}k\bar{l}$: -001/2	(14) $\bar{h}kl$: -001/2	(15) $\bar{k}hl$: -111/2	(16) khl : -111/2
$P4/ncc$ Origin 2 No. 130 (187)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $k\bar{h}l$: -100/2	(4) $\bar{k}hl$: -010/2
(5) $\bar{h}k\bar{l}$: -011/2	(6) $\bar{h}kl$: -101/2	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}hl$: -001/2

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table A1.4.4.1. Crystallographic space groups in reciprocal space (cont.)

$P4_2/mmc$ No. 131 (188)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$:	(6) $h\bar{k}l$:	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}\bar{h}l$: -001/2
$P4_2/mcm$ No. 132 (189)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$: -001/2	(6) $h\bar{k}l$: -001/2	(7) $kh\bar{l}$:	(8) $\bar{k}\bar{h}l$:
$P4_2/nbc$ Origin 1 No. 133 (190)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -001/2	(6) $h\bar{k}l$: -001/2	(7) $kh\bar{l}$: -110/2	(8) $\bar{k}\bar{h}l$: -110/2
(9) $\bar{h}\bar{k}l$: -111/2	(10) $h\bar{k}l$: -111/2	(11) $\bar{k}h\bar{l}$:	(12) $k\bar{h}l$:
(13) $\bar{h}\bar{k}l$: -110/2	(14) $\bar{h}kl$: -110/2	(15) $\bar{k}h\bar{l}$: -001/2	(16) $kh\bar{l}$: -001/2
$P4_2/nbc$ Origin 2 No. 133 (191)			
(1) hkl :	(2) $\bar{h}kl$: -110/2	(3) $k\bar{h}l$: -101/2	(4) $\bar{k}hl$: -011/2
(5) $\bar{h}\bar{k}l$: -100/2	(6) $h\bar{k}l$: -010/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}\bar{h}l$: -111/2
$P4_2/nmm$ Origin 1 No. 134 (192)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$:	(6) $h\bar{k}l$:	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}\bar{h}l$: -111/2
(9) $\bar{h}\bar{k}l$: -111/2	(10) $h\bar{k}l$: -111/2	(11) $\bar{k}h\bar{l}$:	(12) $k\bar{h}l$:
(13) $\bar{h}\bar{k}l$: -111/2	(14) $\bar{h}kl$: -111/2	(15) $\bar{k}h\bar{l}$:	(16) $kh\bar{l}$:
$P4_2/nmm$ Origin 2 No. 134 (193)			
(1) hkl :	(2) $\bar{h}kl$: -110/2	(3) $k\bar{h}l$: -101/2	(4) $\bar{k}hl$: -011/2
(5) $\bar{h}\bar{k}l$: -101/2	(6) $h\bar{k}l$: -011/2	(7) $kh\bar{l}$:	(8) $\bar{k}\bar{h}l$: -110/2
$P4_2/mbc$ No. 135 (194)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -001/2	(4) $\bar{k}hl$: -001/2
(5) $\bar{h}\bar{k}l$: -110/2	(6) $h\bar{k}l$: -110/2	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}\bar{h}l$: -111/2
$P4_2/nmm$ No. 136 (195)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -111/2	(6) $h\bar{k}l$: -111/2	(7) $kh\bar{l}$:	(8) $\bar{k}\bar{h}l$:
$P4_2/nmc$ Origin 1 No. 137 (196)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -111/2	(6) $h\bar{k}l$: -111/2	(7) $kh\bar{l}$:	(8) $\bar{k}\bar{h}l$:
(9) $\bar{h}\bar{k}l$: -111/2	(10) $h\bar{k}l$: -111/2	(11) $\bar{k}h\bar{l}$:	(12) $k\bar{h}l$:
(13) $\bar{h}\bar{k}l$:	(14) $\bar{h}kl$:	(15) $\bar{k}h\bar{l}$: -111/2	(16) $kh\bar{l}$: -111/2
$P4_2/nmc$ Origin 2 No. 137 (197)			
(1) hkl :	(2) $\bar{h}kl$: -110/2	(3) $k\bar{h}l$: -101/2	(4) $\bar{k}hl$: -011/2
(5) $\bar{h}\bar{k}l$: -010/2	(6) $h\bar{k}l$: -100/2	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}\bar{h}l$: -001/2
$P4_2/nmc$ Origin 1 No. 138 (198)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$: -111/2	(4) $\bar{k}hl$: -111/2
(5) $\bar{h}\bar{k}l$: -110/2	(6) $h\bar{k}l$: -110/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}\bar{h}l$: -001/2
(9) $\bar{h}\bar{k}l$: -111/2	(10) $h\bar{k}l$: -111/2	(11) $\bar{k}h\bar{l}$:	(12) $k\bar{h}l$:
(13) $\bar{h}\bar{k}l$: -001/2	(14) $\bar{h}kl$: -001/2	(15) $\bar{k}h\bar{l}$: -110/2	(16) $kh\bar{l}$: -110/2
$P4_2/nmc$ Origin 2 No. 138 (199)			
(1) hkl :	(2) $\bar{h}kl$: -110/2	(3) $k\bar{h}l$: -101/2	(4) $\bar{k}hl$: -011/2
(5) $\bar{h}\bar{k}l$: -011/2	(6) $h\bar{k}l$: -101/2	(7) $kh\bar{l}$: -110/2	(8) $\bar{k}\bar{h}l$:
$I4/mmm$ No. 139 (200)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$:	(6) $h\bar{k}l$:	(7) $kh\bar{l}$:	(8) $\bar{k}\bar{h}l$:
$I4/mcm$ No. 140 (201)			
(1) hkl :	(2) $\bar{h}kl$:	(3) $k\bar{h}l$:	(4) $\bar{k}hl$:
(5) $\bar{h}\bar{k}l$: -001/2	(6) $h\bar{k}l$: -001/2	(7) $kh\bar{l}$: -001/2	(8) $\bar{k}\bar{h}l$: -001/2

$I4_1/amd$ Origin 1 No. 141 (202)			
(1) hkl :	(2) $\bar{h}kl$: -111/2	(3) $k\bar{h}l$: -021/4	(4) $\bar{k}hl$: -203/4
(5) $\bar{h}\bar{k}l$: -203/4	(6) $h\bar{k}l$: -021/4	(7) $kh\bar{l}$: -111/2	(8) $\bar{k}\bar{h}l$:
(9) $\bar{h}\bar{k}l$: -021/4	(10) $h\bar{k}l$: -203/4	(11) $\bar{k}h\bar{l}$:	(12) $k\bar{h}l$: -111/2
(13) $\bar{h}\bar{k}l$: -111/2	(14) $\bar{h}kl$:	(15) $\bar{k}h\bar{l}$: -203/4	(16) $kh\bar{l}$: -021/4
$I4_1/amd$ Origin 2 No. 141 (203)			
(1) hkl :	(2) $\bar{h}kl$: -101/2	(3) $k\bar{h}l$: -131/4	(4) $\bar{k}hl$: -113/4
(5) $\bar{h}\bar{k}l$: -101/2	(6) $h\bar{k}l$:	(7) $kh\bar{l}$: -131/4	(8) $\bar{k}\bar{h}l$: -113/4
$I4_1/acd$ Origin 1 No. 142 (204)			
(1) hkl :	(2) $\bar{h}kl$: -111/2	(3) $k\bar{h}l$: -021/4	(4) $\bar{k}hl$: -203/4
(5) $\bar{h}\bar{k}l$: -201/4	(6) $h\bar{k}l$: -023/4	(7) $kh\bar{l}$: -110/2	(8) $\bar{k}\bar{h}l$: -001/2
(9) $\bar{h}\bar{k}l$: -021/4	(10) $h\bar{k}l$: -203/4	(11) $\bar{k}h\bar{l}$:	(12) $k\bar{h}l$: -111/2
(13) $\bar{h}\bar{k}l$: -110/2	(14) $\bar{h}kl$: -001/2	(15) $\bar{k}h\bar{l}$: -201/4	(16) $kh\bar{l}$: -023/4
$I4_1/acd$ Origin 2 No. 142 (205)			
(1) hkl :	(2) $\bar{h}kl$: -101/2	(3) $k\bar{h}l$: -131/4	(4) $\bar{k}hl$: -113/4
(5) $\bar{h}\bar{k}l$: -100/2	(6) $h\bar{k}l$: -001/2	(7) $kh\bar{l}$: -133/4	(8) $\bar{k}\bar{h}l$: -111/4

Point group: 3 Trigonal Laue group: $\bar{3}$		
$P3$ No. 143 (206)		
(1) hkl :	(2) kil :	(3) ihl :
$P3_1$ No. 144 (207)		
(1) hkl :	(2) kil : -001/3	(3) ihl : -002/3
$P3_2$ No. 145 (208)		
(1) hkl :	(2) kil : -002/3	(3) ihl : -001/3
$R3$ (hexagonal axes) No. 146 (209)		
(1) hkl :	(2) kil :	(3) ihl :
$R3$ (rhombohedral axes) No. 146 (210)		
(1) hkl :	(2) klh :	(3) lkh :

Point group: $\bar{3}$ Trigonal Laue group: $\bar{3}$		
$P\bar{3}$ No. 147 (211)		
(1) hkl :	(2) kil :	(3) ihl :
$R\bar{3}$ (hexagonal axes) No. 148 (212)		
(1) hkl :	(2) kil :	(3) ihl :
$R\bar{3}$ (rhombohedral axes) No. 148 (213)		
(1) hkl :	(2) klh :	(3) lkh :

Point group: 32 Trigonal Laue group: $\bar{3}m$		
$P312$ No. 149 (214)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}\bar{h}l$:	(5) $\bar{h}\bar{i}l$:	(6) $\bar{i}\bar{k}l$:
$P321$ No. 150 (215)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $kh\bar{l}$:	(5) $h\bar{i}l$:	(6) $\bar{i}\bar{k}l$:

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

$P3_112$ No. 151 (216)		
(1) hkl :	(2) kil : $-001/3$	(3) ihl : $-002/3$
(4) $\bar{k}hl$: $-002/3$	(5) $\bar{h}il$: $-001/3$	(6) $\bar{i}kl$:
$P3_121$ No. 152 (217)		
(1) hkl :	(2) kil : $-001/3$	(3) ihl : $-002/3$
(4) $\bar{k}hl$:	(5) $\bar{h}il$: $-002/3$	(6) $\bar{i}kl$: $-001/3$
$P3_212$ No. 153 (218)		
(1) hkl :	(2) kil : $-002/3$	(3) ihl : $-001/3$
(4) $\bar{k}hl$: $-001/3$	(5) $\bar{h}il$: $-002/3$	(6) $\bar{i}kl$:
$P3_221$ No. 154 (219)		
(1) hkl :	(2) kil : $-002/3$	(3) ihl : $-001/3$
(4) $\bar{k}hl$:	(5) $\bar{h}il$: $-001/3$	(6) $\bar{i}kl$: $-002/3$
$R32$ (hexagonal axes) No. 155 (220)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$:	(5) $\bar{h}il$:	(6) $\bar{i}kl$:
$R32$ (rhombohedral axes) No. 155 (221)		
(1) hkl :	(2) klh :	(3) lkh :
(4) $\bar{k}hl$:	(5) $\bar{h}lk$:	(6) $\bar{l}kh$:

Point group: $3m$ Trigonal Laue group: $\bar{3}m$		
$P3m1$ No. 156 (222)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$:	(5) $\bar{h}il$:	(6) $\bar{i}kl$:
$P31m$ No. 157 (223)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $kh\bar{l}$:	(5) $h\bar{i}l$:	(6) $ik\bar{l}$:
$P3c1$ No. 158 (224)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$: $-001/2$	(5) $\bar{h}il$: $-001/2$	(6) $\bar{i}kl$: $-001/2$
$P31c$ No. 159 (225)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $kh\bar{l}$: $-001/2$	(5) $h\bar{i}l$: $-001/2$	(6) $ik\bar{l}$: $-001/2$
$R3m$ (hexagonal axes) No. 160 (226)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$:	(5) $\bar{h}il$:	(6) $\bar{i}kl$:
$R3m$ (rhombohedral axes) No. 160 (227)		
(1) hkl :	(2) klh :	(3) lkh :
(4) $kh\bar{l}$:	(5) $h\bar{l}k$:	(6) $lk\bar{h}$:
$R3c$ (hexagonal axes) No. 161 (228)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$: $-001/2$	(5) $\bar{h}il$: $-001/2$	(6) $\bar{i}kl$: $-001/2$
$R3c$ (rhombohedral axes) No. 161 (229)		
(1) hkl :	(2) klh :	(3) lkh :
(4) $kh\bar{l}$: $-111/2$	(5) $h\bar{l}k$: $-111/2$	(6) $lk\bar{h}$: $-111/2$

Point group: $\bar{3}m$ Trigonal Laue group: $\bar{3}m$		
$P\bar{3}1m$ No. 162 (230)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$:	(5) $\bar{h}il$:	(6) $\bar{i}kl$:
$P\bar{3}1c$ No. 163 (231)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$: $-001/2$	(5) $\bar{h}il$: $-001/2$	(6) $\bar{i}kl$: $-001/2$
$P\bar{3}m1$ No. 164 (232)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $kh\bar{l}$:	(5) $h\bar{i}l$:	(6) $ik\bar{l}$:
$P\bar{3}c1$ No. 165 (233)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$: $-001/2$	(5) $\bar{h}il$: $-001/2$	(6) $\bar{i}kl$: $-001/2$
$R\bar{3}m$ (hexagonal axes) No. 166 (234)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$:	(5) $\bar{h}il$:	(6) $\bar{i}kl$:
$R\bar{3}m$ (rhombohedral axes) No. 166 (235)		
(1) hkl :	(2) klh :	(3) lkh :
(4) $\bar{k}hl$:	(5) $\bar{h}lk$:	(6) $\bar{l}kh$:
$R\bar{3}c$ (hexagonal axes) No. 167 (236)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{k}hl$: $-001/2$	(5) $\bar{h}il$: $-001/2$	(6) $\bar{i}kl$: $-001/2$
$R\bar{3}c$ (rhombohedral axes) No. 168 (237)		
(1) hkl :	(2) klh :	(3) lkh :
(4) $\bar{k}hl$: $-111/2$	(5) $\bar{h}lk$: $-111/2$	(6) $\bar{l}kh$: $-111/2$

Point group: 6 Hexagonal Laue group: $6/m$		
$P6$ No. 168 (238)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}kl$:	(5) $\bar{k}il$:	(6) $\bar{i}hl$:
$P6_1$ No. 169 (239)		
(1) hkl :	(2) kil : $-001/3$	(3) ihl : $-002/3$
(4) $\bar{h}kl$: $-001/2$	(5) $\bar{k}il$: $-005/6$	(6) $\bar{i}hl$: $-001/6$
$P6_5$ No. 170 (240)		
(1) hkl :	(2) kil : $-002/3$	(3) ihl : $-001/3$
(4) $\bar{h}kl$: $-001/2$	(5) $\bar{k}il$: $-001/6$	(6) $\bar{i}hl$: $-005/6$
$P6_2$ No. 171 (241)		
(1) hkl :	(2) kil : $-002/3$	(3) ihl : $-001/3$
(4) $\bar{h}kl$:	(5) $\bar{k}il$: $-002/3$	(6) $\bar{i}hl$: $-001/3$
$P6_4$ No. 172 (242)		
(1) hkl :	(2) kil : $-001/3$	(3) ihl : $-002/3$
(4) $\bar{h}kl$:	(5) $\bar{k}il$: $-001/3$	(6) $\bar{i}hl$: $-002/3$

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Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

$P6_3$ No. 173 (243)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-001/2$	(6) $i\bar{h}l$: $-001/2$

Point group: $\bar{6}$	Hexagonal	Laue group: $6/m$
$P\bar{6}$ No. 174 (244)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $h\bar{k}l$:	(5) $\bar{k}il$:	(6) $i\bar{h}l$:

Point group: $6/m$	Hexagonal	Laue group: $6/m$
$P6/m$ No. 175 (245)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$:	(6) $i\bar{h}l$:
$P6_3/m$ No. 176 (246)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-001/2$	(6) $i\bar{h}l$: $-001/2$

Point group: 622	Hexagonal	Laue group: $6/mmm$
$P622$ No. 177 (247)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$:	(6) $i\bar{h}l$:
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $\bar{k}h\bar{l}$:	(11) $\bar{h}il$:	(12) $\bar{i}kl$:
$P6_122$ No. 178 (248)		
(1) hkl :	(2) kil : $-001/3$	(3) ihl : $-002/3$
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-005/6$	(6) $i\bar{h}l$: $-001/6$
(7) $kh\bar{l}$: $-001/3$	(8) $h\bar{i}l$:	(9) $i\bar{k}l$: $-002/3$
(10) $\bar{k}h\bar{l}$: $-005/6$	(11) $\bar{h}il$: $-001/2$	(12) $\bar{i}kl$: $-001/6$
$P6_522$ No. 179 (249)		
(1) hkl :	(2) kil : $-002/3$	(3) ihl : $-001/3$
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-001/6$	(6) $i\bar{h}l$: $-005/6$
(7) $kh\bar{l}$: $-002/3$	(8) $h\bar{i}l$:	(9) $i\bar{k}l$: $-001/3$
(10) $\bar{k}h\bar{l}$: $-001/6$	(11) $\bar{h}il$: $-001/2$	(12) $\bar{i}kl$: $-005/6$
$P6_222$ No. 180 (250)		
(1) hkl :	(2) kil : $-002/3$	(3) ihl : $-001/3$
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$: $-002/3$	(6) $i\bar{h}l$: $-001/3$
(7) $kh\bar{l}$: $-002/3$	(8) $h\bar{i}l$:	(9) $i\bar{k}l$: $-001/3$
(10) $\bar{k}h\bar{l}$: $-002/3$	(11) $\bar{h}il$:	(12) $\bar{i}kl$: $-001/3$
$P6_422$ No. 181 (251)		
(1) hkl :	(2) kil : $-001/3$	(3) ihl : $-002/3$
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$: $-001/3$	(6) $i\bar{h}l$: $-002/3$
(7) $kh\bar{l}$: $-001/3$	(8) $h\bar{i}l$:	(9) $i\bar{k}l$: $-002/3$
(10) $\bar{k}h\bar{l}$: $-001/3$	(11) $\bar{h}il$:	(12) $\bar{i}kl$: $-002/3$
$P6_322$ No. 182 (252)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-001/2$	(6) $i\bar{h}l$: $-001/2$
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $\bar{k}h\bar{l}$: $-001/2$	(11) $\bar{h}il$: $-001/2$	(12) $\bar{i}kl$: $-001/2$

Point group: $6mm$	Hexagonal	Laue group: $6/mmm$
$P6mm$ No. 183 (253)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$:	(6) $i\bar{h}l$:
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $kh\bar{l}$:	(11) $h\bar{i}l$:	(12) $i\bar{k}l$:
$P6cc$ No. 184 (254)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$:	(6) $i\bar{h}l$:
(7) $kh\bar{l}$: $-001/2$	(8) $h\bar{i}l$: $-001/2$	(9) $i\bar{k}l$: $-001/2$
(10) $kh\bar{l}$: $-001/2$	(11) $h\bar{i}l$: $-001/2$	(12) $i\bar{k}l$: $-001/2$
$P6_3cm$ No. 185 (255)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-001/2$	(6) $i\bar{h}l$: $-001/2$
(7) $kh\bar{l}$: $-001/2$	(8) $h\bar{i}l$: $-001/2$	(9) $i\bar{k}l$: $-001/2$
(10) $kh\bar{l}$:	(11) $h\bar{i}l$:	(12) $i\bar{k}l$:
$P6_3mc$ No. 186 (256)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$: $-001/2$	(5) $\bar{k}il$: $-001/2$	(6) $i\bar{h}l$: $-001/2$
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $kh\bar{l}$: $-001/2$	(11) $h\bar{i}l$: $-001/2$	(12) $i\bar{k}l$: $-001/2$

Point group: $\bar{6}m2$	Hexagonal	Laue group: $6/mmm$
$P\bar{6}m2$ No. 187 (257)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $h\bar{k}l$:	(5) $k\bar{i}l$:	(6) $i\bar{h}l$:
(7) $\bar{k}h\bar{l}$:	(8) $\bar{h}il$:	(9) $\bar{i}kl$:
(10) $\bar{k}h\bar{l}$:	(11) $\bar{h}il$:	(12) $\bar{i}kl$:
$P\bar{6}c2$ No. 188 (258)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $h\bar{k}l$: $-001/2$	(5) $k\bar{i}l$: $-001/2$	(6) $i\bar{h}l$: $-001/2$
(7) $\bar{k}h\bar{l}$: $-001/2$	(8) $\bar{h}il$: $-001/2$	(9) $\bar{i}kl$: $-001/2$
(10) $\bar{k}h\bar{l}$:	(11) $\bar{h}il$:	(12) $\bar{i}kl$:
$P\bar{6}2m$ No. 189 (259)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $h\bar{k}l$:	(5) $k\bar{i}l$:	(6) $i\bar{h}l$:
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $kh\bar{l}$:	(11) $h\bar{i}l$:	(12) $i\bar{k}l$:
$P\bar{6}2c$ No. 190 (260)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $h\bar{k}l$: $-001/2$	(5) $k\bar{i}l$: $-001/2$	(6) $i\bar{h}l$: $-001/2$
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $kh\bar{l}$: $-001/2$	(11) $h\bar{i}l$: $-001/2$	(12) $i\bar{k}l$: $-001/2$

Point group: $6/mmm$	Hexagonal	Laue group: $6/mmm$
$P6/mmm$ No. 191 (261)		
(1) hkl :	(2) kil :	(3) ihl :
(4) $\bar{h}\bar{k}l$:	(5) $\bar{k}il$:	(6) $i\bar{h}l$:
(7) $kh\bar{l}$:	(8) $h\bar{i}l$:	(9) $i\bar{k}l$:
(10) $\bar{k}h\bar{l}$:	(11) $\bar{h}il$:	(12) $\bar{i}kl$:

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

Point group: $m\bar{3}$ Cubic Laue group: $m\bar{3}$			
$Pm\bar{3}$ No. 200 (270)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}h$:
(9) lhk :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}\bar{k}$:
$Pn\bar{3}$ Origin 1 No. 201 (271)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}h$:
(9) lhk :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}\bar{k}$:
(13) $\bar{h}\bar{k}l$: -111/2	(14) $h\bar{k}\bar{l}$: -111/2	(15) $\bar{h}k\bar{l}$: -111/2	(16) $\bar{h}\bar{k}l$: -111/2
(17) $\bar{k}\bar{l}h$: -111/2	(18) $k\bar{l}h$: -111/2	(19) $\bar{k}l\bar{h}$: -111/2	(20) $\bar{k}\bar{l}h$: -111/2
(21) $\bar{l}\bar{h}k$: -111/2	(22) $l\bar{h}\bar{k}$: -111/2	(23) $\bar{l}h\bar{k}$: -111/2	(24) $\bar{l}h\bar{k}$: -111/2

Point group: 432	Cubic	Laue group: $m\bar{3}m$	
<i>P</i> 432 No. 207 (279)			
(1) <i>hkl</i> :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) <i>klh</i> :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}h$:
(9) <i>lhk</i> :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}k$:
(13) <i>kh\bar{l}</i> :	(14) $k\bar{h}\bar{l}$:	(15) khl :	(16) $k\bar{h}l$:
(17) $\bar{h}l\bar{k}$:	(18) $\bar{h}lk$:	(19) $\bar{h}l\bar{k}$:	(20) $hl\bar{k}$:
(21) $\bar{l}kh$:	(22) $\bar{l}k\bar{h}$:	(23) $lk\bar{h}$:	(24) lkh :
<i>P</i> 4 ₂ 32 No. 208 (280)			
(1) <i>hkl</i> :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) <i>klh</i> :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}h$:
(9) <i>lhk</i> :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}k$:
(13) $kh\bar{l}:-111/2$	(14) $k\bar{h}\bar{l}:-111/2$	(15) $\bar{k}h\bar{l}:-111/2$	(16) $\bar{k}\bar{h}l:-111/2$
(17) $\bar{h}l\bar{k}:-111/2$	(18) $\bar{h}lk:-111/2$	(19) $\bar{h}l\bar{k}:-111/2$	(20) $hl\bar{k}:-111/2$
(21) $\bar{l}kh:-111/2$	(22) $\bar{l}k\bar{h}:-111/2$	(23) $lk\bar{h}:-111/2$	(24) $lkh:-111/2$
<i>F</i> 432 No. 209 (281)			
(1) <i>hkl</i> :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) <i>klh</i> :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}h$:
(9) <i>lhk</i> :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}k$:
(13) $kh\bar{l}$:	(14) $k\bar{h}\bar{l}$:	(15) $\bar{k}hl$:	(16) $\bar{k}\bar{h}l$:

Table A1.4.4.1. *Crystallographic space groups in reciprocal space (cont.)*

Point group: $\bar{4}3m$	Cubic	Laue group: $m\bar{3}m$
$P\bar{4}3m$ No. 215 (287)		
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:
(4) $h\bar{k}l$:	(5) $k\bar{l}h$:	(6) $\bar{k}l\bar{h}$:
(7) lkh :	(8) $\bar{l}h\bar{k}$:	(9) $l\bar{h}k$:
(10) $kh\bar{l}$:	(11) $\bar{k}h\bar{l}$:	(12) $\bar{h}k\bar{l}$:
(13) hkl :	(14) $\bar{h}\bar{k}l$:	(15) $\bar{h}k\bar{l}$:
(16) $h\bar{k}l$:	(17) $k\bar{l}h$:	(18) $\bar{k}l\bar{h}$:
(19) lkh :	(20) $\bar{l}h\bar{k}$:	(21) $l\bar{h}k$:
(22) $kh\bar{l}$:	(23) $\bar{k}h\bar{l}$:	(24) $\bar{h}k\bar{l}$:
$F\bar{4}3m$ No. 216 (288)		
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:
(4) $h\bar{k}l$:	(5) $k\bar{l}h$:	(6) $\bar{k}l\bar{h}$:
(7) lkh :	(8) $\bar{l}h\bar{k}$:	(9) $l\bar{h}k$:
(10) $kh\bar{l}$:	(11) $\bar{k}h\bar{l}$:	(12) $\bar{h}k\bar{l}$:
(13) hkl :	(14) $\bar{h}\bar{k}l$:	(15) $\bar{h}k\bar{l}$:
(16) $h\bar{k}l$:	(17) $k\bar{l}h$:	(18) $\bar{k}l\bar{h}$:
(19) lkh :	(20) $\bar{l}h\bar{k}$:	(21) $l\bar{h}k$:
(22) $kh\bar{l}$:	(23) $\bar{k}h\bar{l}$:	(24) $\bar{h}k\bar{l}$:

Point group: $m\bar{3}m$ Cubic		Laue group: $m\bar{3}m$	
$Pm\bar{3}m$ No. 221 (293)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}\bar{h}$:
(9) lkh :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}\bar{k}$:
(13) $kh\bar{l}$:	(14) $\bar{k}h\bar{l}$:	(15) $\bar{k}hl$:	(16) $k\bar{h}\bar{l}$:
(17) $h\bar{l}k$:	(18) $\bar{h}\bar{l}k$:	(19) $\bar{h}lk$:	(20) $h\bar{l}k$:
(21) $l\bar{k}h$:	(22) $\bar{l}\bar{k}h$:	(23) $\bar{l}k\bar{h}$:	(24) $l\bar{k}h$:
$Pn\bar{3}n$ Origin 1 No. 222 (294)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}k\bar{l}$:	(4) $h\bar{k}\bar{l}$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}l\bar{h}$:	(8) $k\bar{l}\bar{h}$:
(9) lkh :	(10) $\bar{l}\bar{h}k$:	(11) $\bar{l}h\bar{k}$:	(12) $l\bar{h}\bar{k}$:
(13) $kh\bar{l}$:	(14) $\bar{k}h\bar{l}$:	(15) $\bar{k}hl$:	(16) $k\bar{h}\bar{l}$:
(17) $h\bar{l}k$:	(18) $\bar{h}\bar{l}k$:	(19) $\bar{h}lk$:	(20) $h\bar{l}k$:
(21) $l\bar{k}h$:	(22) $\bar{l}\bar{k}h$:	(23) $\bar{l}k\bar{h}$:	(24) $l\bar{k}h$:
(25) $h\bar{k}l$: −111/2	(26) $h\bar{k}l$: −111/2	(27) $h\bar{k}l$: −111/2	(28) $h\bar{k}l$: −111/2
(29) $\bar{k}l\bar{h}$: −111/2	(30) $\bar{k}l\bar{h}$: −111/2	(31) $\bar{k}l\bar{h}$: −111/2	(32) $\bar{k}l\bar{h}$: −111/2
(33) $\bar{l}h\bar{k}$: −111/2	(34) $\bar{l}h\bar{k}$: −111/2	(35) $\bar{l}h\bar{k}$: −111/2	(36) $\bar{l}h\bar{k}$: −111/2
(37) $\bar{k}h\bar{l}$: −111/2	(38) $\bar{k}h\bar{l}$: −111/2	(39) $\bar{k}h\bar{l}$: −111/2	(40) $\bar{k}h\bar{l}$: −111/2
(41) $\bar{h}\bar{l}k$: −111/2	(42) $\bar{h}\bar{l}k$: −111/2	(43) $\bar{h}\bar{l}k$: −111/2	(44) $\bar{h}\bar{l}k$: −111/2
(45) $\bar{l}\bar{k}h$: −111/2	(46) $\bar{l}\bar{k}h$: −111/2	(47) $\bar{l}\bar{k}h$: −111/2	(48) $\bar{l}\bar{k}h$: −111/2
$Pn\bar{3}n$ Origin 2 No. 222 (295)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: −110/2	(3) $\bar{h}k\bar{l}$: −101/2	(4) $h\bar{k}\bar{l}$: −011/2
(5) klh :	(6) $\bar{k}\bar{l}h$: −011/2	(7) $\bar{k}l\bar{h}$: −110/2	(8) $k\bar{l}\bar{h}$: −101/2
(9) lkh :	(10) $\bar{l}\bar{h}k$: −101/2	(11) $\bar{l}h\bar{k}$: −011/2	(12) $l\bar{h}\bar{k}$: −110/2
(13) $kh\bar{l}$: −001/2	(14) $\bar{k}h\bar{l}$: −111/2	(15) $\bar{k}hl$: −010/2	(16) $k\bar{h}\bar{l}$: −100/2

1.4. SYMMETRY IN RECIPROCAL SPACE

Table A1.4.4.1. Crystallographic space groups in reciprocal space (cont.)

(17) $\bar{h}\bar{k}l$: -001/2	(18) $\bar{h}\bar{k}l$: -100/2	(19) $\bar{h}\bar{k}l$: -111/2	(20) $\bar{h}\bar{k}l$: -010/2
(21) $\bar{l}kh$: -001/2	(22) $\bar{l}kh$: -010/2	(23) $\bar{l}kh$: -100/2	(24) $\bar{l}kh$: -111/2
<i>Pm</i>$\bar{3}n$ No. 223 (296)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}\bar{k}l$:	(4) $\bar{h}\bar{k}l$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}\bar{l}h$:	(8) $\bar{k}\bar{l}h$:
(9) lkh :	(10) $\bar{l}kh$:	(11) $\bar{l}kh$:	(12) $\bar{l}kh$:
(13) $kh\bar{l}$: -111/2	(14) $\bar{k}\bar{h}\bar{l}$: -111/2	(15) $\bar{k}\bar{h}\bar{l}$: -111/2	(16) $\bar{k}\bar{h}\bar{l}$: -111/2
(17) $\bar{h}\bar{k}l$: -111/2	(18) $\bar{h}\bar{k}l$: -111/2	(19) $\bar{h}\bar{k}l$: -111/2	(20) $\bar{h}\bar{k}l$: -111/2
(21) $\bar{l}kh$: -111/2	(22) $\bar{l}kh$: -111/2	(23) $\bar{l}kh$: -111/2	(24) $\bar{l}kh$: -111/2
<i>Pn</i>$\bar{3}m$ Origin 1 No. 224 (297)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}\bar{k}l$:	(4) $\bar{h}\bar{k}l$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}\bar{l}h$:	(8) $\bar{k}\bar{l}h$:
(9) lkh :	(10) $\bar{l}kh$:	(11) $\bar{l}kh$:	(12) $\bar{l}kh$:
(13) $kh\bar{l}$: -111/2	(14) $\bar{k}\bar{h}\bar{l}$: -111/2	(15) $\bar{k}\bar{h}\bar{l}$: -111/2	(16) $\bar{k}\bar{h}\bar{l}$: -111/2
(17) $\bar{h}\bar{k}l$: -111/2	(18) $\bar{h}\bar{k}l$: -111/2	(19) $\bar{h}\bar{k}l$: -111/2	(20) $\bar{h}\bar{k}l$: -111/2
(21) $\bar{l}kh$: -111/2	(22) $\bar{l}kh$: -111/2	(23) $\bar{l}kh$: -111/2	(24) $\bar{l}kh$: -111/2
(25) $\bar{h}\bar{k}l$: -111/2	(26) $\bar{h}\bar{k}l$: -111/2	(27) $\bar{h}\bar{k}l$: -111/2	(28) $\bar{h}\bar{k}l$: -111/2
(29) $\bar{k}\bar{l}h$: -111/2	(30) $\bar{k}\bar{l}h$: -111/2	(31) $\bar{k}\bar{l}h$: -111/2	(32) $\bar{k}\bar{l}h$: -111/2
(33) $\bar{l}kh$: -111/2	(34) $\bar{l}kh$: -111/2	(35) $\bar{l}kh$: -111/2	(36) $\bar{l}kh$: -111/2
(37) $\bar{k}\bar{h}\bar{l}$:	(38) $\bar{k}hl$:	(39) $\bar{k}\bar{h}\bar{l}$:	(40) $\bar{k}\bar{h}\bar{l}$:
(41) $\bar{h}\bar{k}l$:	(42) $\bar{h}\bar{k}l$:	(43) $h\bar{k}l$:	(44) $\bar{h}\bar{k}l$:
(45) $\bar{l}kh$:	(46) $\bar{l}kh$:	(47) $\bar{l}kh$:	(48) lkh :
<i>Pn</i>$\bar{3}m$ Origin 2 No. 224 (298)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -110/2	(3) $\bar{h}\bar{k}l$: -101/2	(4) $\bar{h}\bar{k}l$: -011/2
(5) klh :	(6) $\bar{k}\bar{l}h$: -011/2	(7) $\bar{k}\bar{l}h$: -110/2	(8) $\bar{k}\bar{l}h$: -101/2
(9) lkh :	(10) $\bar{l}kh$: -101/2	(11) $\bar{l}kh$: -011/2	(12) $\bar{l}kh$: -110/2
(13) $kh\bar{l}$: -110/2	(14) $\bar{k}\bar{h}\bar{l}$:	(15) $\bar{k}\bar{h}\bar{l}$: -101/2	(16) $\bar{k}\bar{h}\bar{l}$: -011/2
(17) $\bar{h}\bar{k}l$: -110/2	(18) $\bar{h}\bar{k}l$: -011/2	(19) $\bar{h}\bar{k}l$:	(20) $\bar{h}\bar{k}l$: -101/2
(21) $\bar{l}kh$: -110/2	(22) $\bar{l}kh$: -101/2	(23) $\bar{l}kh$: -011/2	(24) $\bar{l}kh$:
<i>Fm</i>$\bar{3}m$ No. 225 (299)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}\bar{k}l$:	(4) $\bar{h}\bar{k}l$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}\bar{l}h$:	(8) $\bar{k}\bar{l}h$:
(9) lkh :	(10) $\bar{l}kh$:	(11) $\bar{l}kh$:	(12) $\bar{l}kh$:
(13) $kh\bar{l}$:	(14) $\bar{k}\bar{h}\bar{l}$:	(15) $\bar{k}\bar{h}\bar{l}$:	(16) $\bar{k}\bar{h}\bar{l}$:
(17) $\bar{h}\bar{k}l$:	(18) $\bar{h}\bar{k}l$:	(19) $\bar{h}\bar{k}l$:	(20) $\bar{h}\bar{k}l$:
(21) $\bar{l}kh$:	(22) $\bar{l}kh$:	(23) $\bar{l}kh$:	(24) $\bar{l}kh$:
<i>Fm</i>$\bar{3}c$ No. 226 (300)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}\bar{k}l$:	(4) $\bar{h}\bar{k}l$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}\bar{l}h$:	(8) $\bar{k}\bar{l}h$:
(9) lkh :	(10) $\bar{l}kh$:	(11) $\bar{l}kh$:	(12) $\bar{l}kh$:
(13) $kh\bar{l}$: -111/2	(14) $\bar{k}\bar{h}\bar{l}$: -111/2	(15) $\bar{k}\bar{h}\bar{l}$: -111/2	(16) $\bar{k}\bar{h}\bar{l}$: -111/2
(17) $\bar{h}\bar{k}l$: -111/2	(18) $\bar{h}\bar{k}l$: -111/2	(19) $\bar{h}\bar{k}l$: -111/2	(20) $\bar{h}\bar{k}l$: -111/2
(21) $\bar{l}kh$: -111/2	(22) $\bar{l}kh$: -111/2	(23) $\bar{l}kh$: -111/2	(24) $\bar{l}kh$: -111/2
<i>Fd</i>$\bar{3}m$ Origin 1 No. 227 (301)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -011/2	(3) $\bar{h}\bar{k}l$: -110/2	(4) $\bar{h}\bar{k}l$: -101/2
(5) klh :	(6) $\bar{k}\bar{l}h$: -101/2	(7) $\bar{k}\bar{l}h$: -011/2	(8) $\bar{k}\bar{l}h$: -110/2
(9) lkh :	(10) $\bar{l}kh$: -110/2	(11) $\bar{l}kh$: -101/2	(12) $\bar{l}kh$: -011/2
(13) $kh\bar{l}$: -313/4	(14) $\bar{k}\bar{h}\bar{l}$: -111/4	(15) $\bar{k}\bar{h}\bar{l}$: -133/4	(16) $\bar{k}\bar{h}\bar{l}$: -331/4
(17) $\bar{h}\bar{k}l$: -313/4	(18) $\bar{h}\bar{k}l$: -331/4	(19) $\bar{h}\bar{k}l$: -111/4	(20) $\bar{h}\bar{k}l$: -133/4
(21) $\bar{l}kh$: -313/4	(22) $\bar{l}kh$: -331/4	(23) $\bar{l}kh$: -111/4	(24) $\bar{l}kh$: -133/4
<i>Fd</i>$\bar{3}m$ Origin 2 No. 227 (302)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -312/4	(3) $\bar{h}\bar{k}l$: -123/4	(4) $\bar{h}\bar{k}l$: -231/4
(5) klh :	(6) $\bar{k}\bar{l}h$: -231/4	(7) $\bar{k}\bar{l}h$: -312/4	(8) $\bar{k}\bar{l}h$: -123/4
(9) lkh :	(10) $\bar{l}kh$: -123/4	(11) $\bar{l}kh$: -231/4	(12) $\bar{l}kh$: -312/4
(13) $kh\bar{l}$: -312/4	(14) $\bar{k}\bar{h}\bar{l}$:	(15) $\bar{k}\bar{h}\bar{l}$: -123/4	(16) $\bar{k}\bar{h}\bar{l}$: -231/4
(17) $\bar{h}\bar{k}l$: -312/4	(18) $\bar{h}\bar{k}l$: -231/4	(19) $\bar{h}\bar{k}l$:	(20) $\bar{h}\bar{k}l$: -123/4
(21) $\bar{l}kh$: -312/4	(22) $\bar{l}kh$: -123/4	(23) $\bar{l}kh$: -231/4	(24) $\bar{l}kh$:
<i>Fd</i>$\bar{3}c$ Origin 1 No. 228 (303)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -011/2	(3) $\bar{h}\bar{k}l$: -110/2	(4) $\bar{h}\bar{k}l$: -101/2
(5) klh :	(6) $\bar{k}\bar{l}h$: -101/2	(7) $\bar{k}\bar{l}h$: -011/2	(8) $\bar{k}\bar{l}h$: -110/2
(9) lkh :	(10) $\bar{l}kh$: -110/2	(11) $\bar{l}kh$: -101/2	(12) $\bar{l}kh$: -011/2
(13) $kh\bar{l}$: -313/4	(14) $\bar{k}\bar{h}\bar{l}$: -111/4	(15) $\bar{k}\bar{h}\bar{l}$: -133/4	(16) $\bar{k}\bar{h}\bar{l}$: -331/4
(17) $\bar{h}\bar{k}l$: -313/4	(18) $\bar{h}\bar{k}l$: -331/4	(19) $\bar{h}\bar{k}l$: -111/4	(20) $\bar{h}\bar{k}l$: -133/4
(21) $\bar{l}kh$: -313/4	(22) $\bar{l}kh$: -133/4	(23) $\bar{l}kh$: -313/4	(24) $\bar{l}kh$: -111/4
(25) $\bar{h}\bar{k}l$: -333/4	(26) $\bar{h}\bar{k}l$: -311/4	(27) $\bar{h}\bar{k}l$: -113/4	(28) $\bar{h}\bar{k}l$: -131/4
(29) $\bar{k}\bar{l}h$: -333/4	(30) $\bar{k}\bar{l}h$: -131/4	(31) $\bar{k}\bar{l}h$: -311/4	(32) $\bar{k}\bar{l}h$: -113/4
(33) $\bar{l}kh$: -333/4	(34) $\bar{l}kh$: -113/4	(35) $\bar{l}kh$: -131/4	(36) $\bar{l}kh$: -311/4
(37) $\bar{k}\bar{h}\bar{l}$: -010/2	(38) $\bar{k}hl$: -111/2	(39) $\bar{k}\bar{h}\bar{l}$: -100/2	(40) $\bar{k}\bar{h}\bar{l}$: -001/2
(41) $\bar{h}\bar{k}l$: -010/2	(42) $\bar{h}\bar{k}l$: -001/2	(43) $h\bar{k}l$: -111/2	(44) $\bar{h}\bar{k}l$: -100/2
(45) $\bar{l}kh$: -010/2	(46) $\bar{l}kh$: -100/2	(47) $\bar{l}kh$: -001/2	(48) lkh : -111/2
<i>Fd</i>$\bar{3}c$ Origin 2 No. 228 (304)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -132/4	(3) $\bar{h}\bar{k}l$: -321/4	(4) $\bar{h}\bar{k}l$: -213/4
(5) klh :	(6) $\bar{k}\bar{l}h$: -213/4	(7) $\bar{k}\bar{l}h$: -132/4	(8) $\bar{k}\bar{l}h$: -321/4
(9) lkh :	(10) $\bar{l}kh$: -321/4	(11) $\bar{l}kh$: -213/4	(12) $\bar{l}kh$: -132/4
(13) $kh\bar{l}$: -310/4	(14) $\bar{k}\bar{h}\bar{l}$: -111/2	(15) $\bar{k}\bar{h}\bar{l}$: -103/4	(16) $\bar{k}\bar{h}\bar{l}$: -031/4
(17) $\bar{h}\bar{k}l$: -310/4	(18) $\bar{h}\bar{k}l$: -031/4	(19) $\bar{h}\bar{k}l$: -111/2	(20) $\bar{h}\bar{k}l$: -103/4
(21) $\bar{l}kh$: -310/4	(22) $\bar{l}kh$: -103/4	(23) $\bar{l}kh$: -031/4	(24) $\bar{l}kh$: -111/2
<i>Im</i>$\bar{3}m$ No. 229 (305)			
(1) hkl :	(2) $\bar{h}\bar{k}l$:	(3) $\bar{h}\bar{k}l$:	(4) $\bar{h}\bar{k}l$:
(5) klh :	(6) $\bar{k}\bar{l}h$:	(7) $\bar{k}\bar{l}h$:	(8) $\bar{k}\bar{l}h$:
(9) lkh :	(10) $\bar{l}kh$:	(11) $\bar{l}kh$:	(12) $\bar{l}kh$:
(13) $kh\bar{l}$:	(14) $\bar{k}\bar{h}\bar{l}$:	(15) $\bar{k}\bar{h}\bar{l}$:	(16) $\bar{k}\bar{h}\bar{l}$:
(17) $\bar{h}\bar{k}l$:	(18) $\bar{h}\bar{k}l$:	(19) $\bar{h}\bar{k}l$:	(20) $\bar{h}\bar{k}l$:
(21) $\bar{l}kh$:	(22) $\bar{l}kh$:	(23) $\bar{l}kh$:	(24) $\bar{l}kh$:
<i>Ia</i>$\bar{3}d$ No. 230 (306)			
(1) hkl :	(2) $\bar{h}\bar{k}l$: -101/2	(3) $\bar{h}\bar{k}l$: -011/2	(4) $\bar{h}\bar{k}l$: -110/2
(5) klh :	(6) $\bar{k}\bar{l}h$: -110/2	(7) $\bar{k}\bar{l}h$: -101/2	(8) $\bar{k}\bar{l}h$: -011/2
(9) lkh :	(10) $\bar{l}kh$: -011/2	(11) $\bar{l}kh$: -110/2	(12) $\bar{l}kh$: -101/2
(13) $kh\bar{l}$: -311/4	(14) $\bar{k}\bar{h}\bar{l}$: -333/4	(15) $\bar{k}\bar{h}\bar{l}$: -113/4	(16) $\bar{k}\bar{h}\bar{l}$: -131/4
(17) $\bar{h}\bar{k}l$: -311/4	(18) $\bar{h}\bar{k}l$: -131/4	(19) $\bar{h}\bar{k}l$: -333/4	(20) $\bar{h}\bar{k}l$: -113/4
(21) $\bar{l}kh$: -311/4	(22) $\bar{l}kh$: -113/4	(23) $\bar{l}kh$: -131/4	(24) $\bar{l}kh$: -333/4

1.5. Crystallographic viewpoints in the classification of space-group representations

BY M. I. AROYO AND H. WONDRATSCHEK

1.5.1. List of symbols

$\mathcal{G}; \mathcal{S}$	Group, especially space group; site-symmetry group
G	Element of group $\mathcal{G}$
$\mathcal{G}_0$	Symmorphic space group
$\mathcal{P}$ or $\bar{\mathcal{G}}$	Point group of space group $\mathcal{G}$
$\mathcal{T}$	Translation subgroup of space group $\mathcal{G}$
$R, S; W$	Matrix; matrix part of a symmetry operation
w	Column part of a symmetry operation
X	Point of point space
$x, y, z; x_i$	Coordinates of a point or coefficients of a vector
x	Column of point coordinates or of vector coefficients
L	Vector lattice of the space group $\mathcal{G}$
a, b, c or $(a_k)^T$	Basis vectors or row of basis vectors of the lattice L of $\mathcal{G}$
t	Vector of the lattice L of $\mathcal{G}$
L^*	Reciprocal lattice of the space group $\mathcal{G}$
a^*, b^*, c^* or (a_k^*)	Basis vectors or column of basis vectors of the reciprocal lattice L^*
K	Vector of the reciprocal lattice L^*
k	Vector of reciprocal space
$\mathcal{G}^*$	Reciprocal-space group
$\bar{\mathcal{G}}^k$	Little co-group of k
$\mathcal{L}^k$	Little group of k
$\Gamma(\mathcal{G})$	(Matrix) representation of $\mathcal{G}$

1.5.2. Introduction

This new chapter on representations widens the scope of the general topics of reciprocal space treated in this volume.

Space-group representations play a growing role in physical applications of crystal symmetry. They are treated in a number of papers and books but comparison of the terms and the listed data is difficult. The main reason for this is the lack of standards in the classification and nomenclature of representations. As a result, the reader is confronted with different numbers of types and barely comparable notations used by the different authors, see *e.g.* Stokes & Hatch (1988), Table 7.

The k vectors, which can be described as vectors in reciprocal space, play a decisive role in the description and classification of space-group representations. Their symmetry properties are determined by the so-called *reciprocal-space group* $\mathcal{G}^*$ which is always isomorphic to a symmorphic space group $\mathcal{G}_0$. The different symmetry types of k vectors correspond to the different kinds of point orbits in the symmorphic space groups $\mathcal{G}_0$. The classification of point orbits into Wyckoff positions in *International Tables for Crystallography* Volume A (*IT A*) (1995) can be used directly to classify the irreducible representations of a space group, abbreviated *irreps*; the Wyckoff positions of the symmorphic space groups $\mathcal{G}_0$ form a basis for a *natural* classification of the irreps. This was first discovered by Wintgen (1941). Similar results have been obtained independently by Raghavacharyulu (1961), who introduced the term reciprocal-space group. In this chapter a classification of irreps is provided which is based on Wintgen's idea.

Although this idea is now more than 50 years old, it has been utilized only rarely and has not yet found proper recognition in the literature and in the existing tables of space-group irreps. Slater (1962) described the correspondence between the special k vectors

of the Brillouin zone and the Wyckoff positions of space group $Pm\bar{3}m$. Similarly, Jan (1972) compared Wyckoff positions with points of the Brillouin zone when describing the symmetry $Pm\bar{3}$ of the Fermi surface for the pyrite structure. However, the widespread tables of Miller & Love (1967), Zak *et al.* (1969), Bradley & Cracknell (1972) (abbreviated as BC), Cracknell *et al.* (1979) (abbreviated as CDML), and Kovalev (1986) have not made use of this kind of classification and its possibilities, and the existing tables are unnecessarily complicated, *cf.* Boyle (1986).

In addition, historical reasons have obscured the classification of irreps and impeded their application. The first considerations of irreps dealt only with space groups of translation lattices (Bouckaert *et al.*, 1936). Later, other space groups were taken into consideration as well. Instead of treating these (lower) symmetries as such, their irreps were derived and classified by starting from the irreps of lattice space groups and proceeding to those of lower symmetry. This procedure has two consequences:

(1) those k vectors that are special in a lattice space group are also correspondingly listed in the low-symmetry space group even if they have lost their special properties due to the symmetry reduction;

(2) during the symmetry reduction unnecessary new types of k vectors and symbols for them are introduced.

The use of the reciprocal-space group $\mathcal{G}^*$ avoids both these detours.

In this chapter we consider in more detail the reciprocal-space-group approach and show that widely used crystallographic conventions can be adopted for the classification of space-group representations. Some basic concepts are developed in Section 1.5.3. Possible conventions are discussed in Section 1.5.4. The consequences and advantages of this approach are demonstrated and discussed using examples in Section 1.5.5.

1.5.3. Basic concepts

The aim of this section is to give a brief overview of some of the basic concepts related to groups and their representations. Its content should be of some help to readers who wish to refresh their knowledge of space groups and representations, and to familiarize themselves with the kind of description in this chapter. However, it can not serve as an introductory text for these subjects. The interested reader is referred to books dealing with space-group theory, representations of space groups and their applications in solid-state physics: see Bradley & Cracknell (1972) or the forthcoming Chapter 1.2 of *IT D (Physical properties of crystals)* by Janssen (2001).

1.5.3.1. Representations of finite groups

Group theory is the proper tool for studying symmetry in science. The elements of the crystallographic groups are rigid motions (isometries) with regard to performing one after another. The set of all isometries that map an object onto itself always fulfils the group postulates and is called the symmetry or the symmetry group of that object; the isometry itself is called a symmetry operation. Symmetry groups of crystals are dealt with in this chapter. In addition, groups of matrices with regard to matrix multiplication (matrix groups) are considered frequently. Such groups will sometimes be called realizations or representations of abstract groups.

Many applications of group theory to physical problems are closely related to representation theory, *cf.* Rosen (1981) and

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references therein. In this section, matrix representations Γ of finite groups $\mathcal{G}$ are considered. The concepts of *homomorphism* and *matrix groups* are of essential importance.

A group $\mathcal{B}$ is a homomorphic image of a group $\mathcal{A}$ if there exists a mapping of the elements A_i of $\mathcal{A}$ onto the elements B_k of $\mathcal{B}$ that preserves the multiplication relation (in general several elements of $\mathcal{A}$ are mapped onto one element of $\mathcal{B}$): if $A_i \rightarrow B_i$ and $A_k \rightarrow B_k$, then $A_i A_k \rightarrow B_i B_k$ holds for all elements of $\mathcal{A}$ and $\mathcal{B}$ (the image of the product is equal to the product of the images). In the special case of a one-to-one mapping, the homomorphism is called an *isomorphism*.

A matrix group is a group whose elements are non-singular square matrices. The law of combination is matrix multiplication and the group inverse is the inverse matrix. In the following we will be concerned with some basic properties of finite matrix groups relevant to representations.

Let $\mathcal{M}_1$ and $\mathcal{M}_2$ be two matrix groups whose matrices are of the same dimension. They are said to be equivalent if there exists a (non-singular) matrix S such that $\mathcal{M}_2 = S^{-1} \mathcal{M}_1 S$ holds. Equivalence implies isomorphism but the inverse is not true: two matrix groups may be isomorphic without being equivalent. According to the theorem of Schur-Auerbach, every finite matrix group is equivalent to a unitary matrix group (by a unitary matrix group we understand a matrix group consisting entirely of unitary matrices).

A matrix group $\mathcal{M}$ is *reducible* if it is equivalent to a matrix group in which every matrix M is of the form

$$R = \begin{pmatrix} D_1 & X \\ O & D_2 \end{pmatrix},$$

see e.g. Lomont (1959), p. 47. The group $\mathcal{M}$ is *completely reducible* if it is equivalent to a matrix group in which for all matrices R the submatrices X are O matrices (consisting of zeros only). According to the theorem of Maschke, a finite matrix group is completely reducible if it is reducible. A matrix group is *irreducible* if it is not reducible.

A (matrix) representation $\Gamma(\mathcal{G})$ of a group $\mathcal{G}$ is a homomorphic mapping of $\mathcal{G}$ onto a matrix group $\mathcal{M}(\mathcal{G})$. In a representation Γ every element $G \in \mathcal{G}$ is associated with a matrix $M(G)$. The dimension of the matrices is called the dimension of the representation.

The above-mentioned theorems on finite matrix groups can be applied directly to representations: we can restrict the considerations to unitary representations only. Further, since every finite matrix group is either completely reducible into irreducible constituents or irreducible, it follows that the infinite set of all matrix representations of a group is known in principle once the irreducible representations are known. Naturally, the question of how to construct all nonequivalent irreducible representations of a finite group and how to classify them arises.

Linear representations are especially important for applications. In this chapter only linear representations of space groups will be considered. Realizations and representations are homomorphic images of abstract groups, but not all of them are linear. In particular, the action of space groups on point space is a nonlinear realization of the abstract space groups because isometries and thus symmetry operations W of space groups $\mathcal{G}$ are nonlinear operations. The same holds for their description by matrix-column pairs (W, w) ,† by the general position, or by augmented (4×4) matrices, see *IT A*, Part 8. Therefore, the isomorphic matrix representation of a space group, mostly used by crystallographers and listed in the space-group tables of *IT A* as the general position, is not linear.

1.5.3.2. Space groups

In crystallography one deals with real crystals. In many cases the treatment of the crystal is much simpler, but nevertheless describes the crystal and its properties very well, if the real crystal is replaced by an ‘ideal crystal’. The real crystal is then considered to be a finite piece of an undisturbed, periodic, and thus infinitely extended arrangement of particles or their centres: ideal crystals are periodic objects in three-dimensional point space E^3 , also called direct space. Periodicity means that there are translations among the symmetry operations of ideal crystals. The symmetry group of an ideal crystal is called its space group $\mathcal{G}$.

Space groups $\mathcal{G}$ are of special interest for our problem because:

- (1) their irreps are the subject of the classification to be discussed;
- (2) this classification makes use of the isomorphism of certain groups to the so-called symmorphic space groups $\mathcal{G}_0$.

Therefore, space groups are introduced here in a slightly more detailed manner than the other concepts. In doing this we follow the definitions and symbolism of *IT A*, Part 8.

To each space group $\mathcal{G}$ belongs an infinite set $\mathcal{T}$ of translations, the *translation lattice* of $\mathcal{G}$. The lattice $\mathcal{T}$ forms an infinite Abelian invariant subgroup of $\mathcal{G}$. For each translation its translation vector is defined. The set of all translation vectors is called the *vector lattice* $\mathbf{L}$ of $\mathcal{G}$. Because of the finite size of the atoms constituting the real crystal, the lengths of the translation vectors of the ideal crystal cannot be arbitrarily small; rather there is a lower limit $\delta > 0$ for their length in the range of a few Å.

When referred to a coordinate system $(O, \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, consisting of an origin O and a basis $\mathbf{a}_k$, the elements W , i.e. the symmetry operations of the space group $\mathcal{G}$, are described by matrix-column pairs (W, w) with matrix part W and column part w . The translations of $\mathcal{G}$ are represented by pairs (I, t_i) , where I is the (3×3) unit matrix and t_i is the column of coefficients of the translation vector $\mathbf{t}_i \in \mathbf{L}$. The basis can always be chosen such that all columns $\mathbf{t}_i$ and no other columns of translations consist of integers. Such a basis $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ is called a *primitive basis*. For each vector lattice $\mathbf{L}$ there exists an infinite number of primitive bases.

The space group $\mathcal{G}$ can be decomposed into left cosets relative to $\mathcal{T}$:

$$\mathcal{G} = \mathcal{T} \cup (W_2, w_2)\mathcal{T} \cup \dots \cup (W_i, w_i)\mathcal{T} \cup \dots \cup (W_n, w_n)\mathcal{T}. \quad (1.5.3.1)$$

The coset representatives form the finite set $V = \{(W_v, w_v)\}, v = 1, \dots, n$, with $(W_1, w_1) = (I, o)$, where o is the column consisting of zeros only. The factor group $\mathcal{G}/\mathcal{T}$ is isomorphic to the *point group* $\mathcal{P}$ of $\mathcal{G}$ (called $\bar{\mathcal{G}}$ in books on representation theory) describing the symmetry of the external shape of the macroscopic crystal and being represented by the matrices $W_1, W_2, \dots, W_n$. If V can be chosen such that all $w_v = o$, then $\mathcal{G}$ is called a *symmorphic space group* $\mathcal{G}_0$. A symmorphic space group can be recognized easily from its conventional Hermann–Mauguin symbol which does not contain any screw or glide component. In terms of group theory, a symmorphic space group is the semidirect product of $\mathcal{T}$ and $\mathcal{P}$, cf. *BC*, p. 44. In symmorphic space groups $\mathcal{G}_0$ (and in no others) there are site-symmetry groups which are isomorphic to the point group $\mathcal{P}$ of $\mathcal{G}_0$.

Space groups can be classified into 219 (*affine*) *space-group types* either by isomorphism or by affine equivalence; the 230 *crystallographic* space-group types are obtained by restricting the transformations available for affine equivalence to those with positive determinant, cf. *IT A*, Section 8.2.1. Many important properties of space groups are shared by all space groups of a type. In such a case one speaks of *properties of the type*. For example, if a space group is symmorphic, then all space groups of its type are

† In physics often written as the Seitz symbol $(W|w)$.

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symmorphic, so that one normally speaks of a symmorphic space-group type.

With the concept of symmorphic space groups one can also define the arithmetic crystal classes: Let $\mathcal{G}_0$ be a symmorphic space group referred to a primitive basis and $V = \{(\mathbf{W}_v, \mathbf{w}_v)\}$ its set of coset representatives with $\mathbf{w}_v = \mathbf{o}$ for all columns. To $\mathcal{G}_0$ all those space groups $\mathcal{G}$ can be assigned for which a primitive basis can be found such that the matrix parts $\mathbf{W}_v$ of their sets V are the same as those of $\mathcal{G}_0$, only the columns $\mathbf{w}_v$ may differ. In this way, to a type of symmorphic space groups $\mathcal{G}_0$, other types of space groups are assigned, *i.e.* the space-group types are classified according to the symmorphic space-group types. These classes are called *arithmetic crystal classes* of space groups or of space-group types.

There are 73 arithmetic crystal classes corresponding to the 73 types of symmorphic space groups; between 1 and 16 space-group types belong to an arithmetic crystal class. A matrix-algebraic definition of arithmetic crystal classes and a proposal for their nomenclature can be found in *IT A*, Section 8.2.2; see also Section 8.3.4 and Table 8.2.

1.5.3.3. Representations of the translation group $\mathcal{T}$ and the reciprocal lattice

For representation theory we follow the terminology of BC and CDML.

Let $\mathcal{G}$ be referred to a primitive basis. For the following, the infinite set of translations, based on discrete cyclic groups of infinite order, will be replaced by a (very large) finite set in the usual way. One assumes the Born–von Karman boundary conditions

$$(\mathbf{I}, \mathbf{t}_{bi})^{N_i} = (\mathbf{I}, N_i) = (\mathbf{I}, \mathbf{o}) \quad (1.5.3.2)$$

to hold, where $\mathbf{t}_{bi} = (1, 0, 0)$, $(0, 1, 0)$ or $(0, 0, 1)$ and N_i is a large integer for $i = 1, 2$ or 3 , respectively. Then for any lattice translation $(\mathbf{I}, \mathbf{t})$,

$$(\mathbf{I}, N\mathbf{t}) = (\mathbf{I}, \mathbf{o}) \quad (1.5.3.3)$$

holds, where $N\mathbf{t}$ is the column (N_1t_1, N_2t_2, N_3t_3) . If the (infinitely many) translations mapped in this way onto $(\mathbf{I}, \mathbf{o})$ form a normal subgroup $\mathcal{T}_1$ of $\mathcal{G}$, then the mapping described by (1.5.3.3) is a homomorphism. There exists a factor group $\mathcal{G}' = \mathcal{G}/\mathcal{T}_1$ of $\mathcal{G}$ relative to $\mathcal{T}_1$ with translation subgroup $\mathcal{T}' = \mathcal{T}/\mathcal{T}_1$ which is finite and is sometimes called the *finite space group*.

Only the irreducible representations (irreps) of these finite space groups will be considered. The definitions of space-group type, symmorphic space group *etc.* can be transferred to these groups. Because $\mathcal{T}$ is Abelian, $\mathcal{T}'$ is also Abelian. Replacing the space group $\mathcal{G}$ by $\mathcal{G}'$ means that the especially well developed theory of representations of finite groups can be applied, *cf.* Lomont (1959), Jansen & Boon (1967). For convenience, the prime ' will be omitted and the symbol $\mathcal{G}$ will be used instead of $\mathcal{G}'$; $\mathcal{T}'$ will be denoted by $\mathcal{T}$ in the following.

Because $\mathcal{T}$ (formerly $\mathcal{T}'$) is Abelian, its irreps $\Gamma(\mathcal{T})$ are one-dimensional and consist of (complex) roots of unity. Owing to equations (1.5.3.2) and (1.5.3.3), the irreps $\Gamma^{q_1q_2q_3}[(\mathbf{I}, \mathbf{t})]$ of $\mathcal{T}$ have the form

$$\Gamma^{q_1q_2q_3}[(\mathbf{I}, \mathbf{t})] = \exp \left[-2\pi i \left(q_1 \frac{t_1}{N_1} + q_2 \frac{t_2}{N_2} + q_3 \frac{t_3}{N_3} \right) \right], \quad (1.5.3.4)$$

where $\mathbf{t}$ is the column (t_1, t_2, t_3) , $q_j = 0, 1, 2, \dots, N_j - 1$, $j = 1, 2, 3$, and t_k and q_j are integers.

Given a primitive basis $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ of $\mathbf{L}$, mathematicians and crystallographers define the *basis of the dual or reciprocal lattice* $\mathbf{L}^*$ by

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}, \quad (1.5.3.5)$$

where $\mathbf{a} \cdot \mathbf{a}^*$ is the scalar product between the vectors and δ_{ij} is the unit matrix (see *e.g.* Chapter 1.1, Section 1.1.3). Texts on the physics of solids redefine the basis $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ of the *reciprocal lattice* $\mathbf{L}^*$, lengthening each of the basis vectors $\mathbf{a}_j^*$ by the factor 2π . Therefore, in the physicist's convention the relation between the bases of direct and reciprocal lattice reads (*cf.* BC, p. 86):

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}. \quad (1.5.3.6)$$

In the present chapter only the physicist's basis of the reciprocal lattice is employed, and hence the use of $\mathbf{a}_j^*$ should not lead to misunderstandings. The set of all vectors $\mathbf{K}_i^\dagger$

$$\mathbf{K} = k_1\mathbf{a}_1^* + k_2\mathbf{a}_2^* + k_3\mathbf{a}_3^*, \quad (1.5.3.7)$$

k_i integer, is called the lattice reciprocal to $\mathbf{L}$ or the *reciprocal lattice* $\mathbf{L}^*$.[‡]

If one adopts the notation of *IT A*, Part 5, the basis of direct space is denoted by a row $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)^T$, where $()^T$ means transposed. For reciprocal space, the basis is described by a column $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$.

To each lattice generated from a basis $(\mathbf{a}_i)^T$ a reciprocal lattice is generated from the basis $(\mathbf{a}_i^*)$. Both lattices, $\mathbf{L}$ and $\mathbf{L}^*$, can be compared most easily by referring the direct lattice $\mathbf{L}$ to its *conventional* basis $(\mathbf{a}_i)^T$ as defined in Chapters 2.1 and 9.1 of *IT A*. In this case, the lattice $\mathbf{L}$ may be primitive or centred. If $(\mathbf{a}_i)^T$ forms a primitive basis of $\mathbf{L}$, *i.e.* if $\mathbf{L}$ is primitive, then the basis $(\mathbf{a}_i^*)$ forms a primitive basis of $\mathbf{L}^*$. If $\mathbf{L}$ is centred, *i.e.* $(\mathbf{a}_i)^T$ is not a primitive basis of $\mathbf{L}$, then there exists a centring matrix $\mathbf{P}$, $0 < \det(\mathbf{P}) < 1$, by which three linearly independent vectors of $\mathbf{L}$ with rational coefficients are generated from those with integer coefficients, *cf.* *IT A*, Table 5.1.

Moreover, $\mathbf{P}$ can be chosen such that the set of vectors

$$(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3)^T = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)^T \mathbf{P} \quad (1.5.3.8)$$

forms a primitive basis of $\mathbf{L}$. Then the basis vectors $(\mathbf{p}_1^*, \mathbf{p}_2^*, \mathbf{p}_3^*)$ of the lattice reciprocal to the lattice generated by $(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3)^T$ are determined by

$$(\mathbf{p}_1^*, \mathbf{p}_2^*, \mathbf{p}_3^*) = \mathbf{P}^{-1}(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*) \quad (1.5.3.9)$$

and form a primitive basis of $\mathbf{L}^*$.

Because $\det(\mathbf{P}^{-1}) > 1$, not all vectors $\mathbf{K}$ of the form (1.5.3.7) belong to $\mathbf{L}^*$. If k_1, k_2, k_3 are the (integer) coefficients of these vectors $\mathbf{K}$ referred to $(\mathbf{a}_i^*)$ and $k_{p1}\mathbf{p}_1^* + k_{p2}\mathbf{p}_2^* + k_{p3}\mathbf{p}_3^*$ are the vectors of $\mathbf{L}^*$, then $\mathbf{K} = (k_j)^T(\mathbf{a}_j^*) = (k_j)^T \mathbf{P}(\mathbf{p}_j^*) = (k_{pi})^T(\mathbf{p}_i^*)$ is a vector of $\mathbf{L}^*$ if and only if the coefficients

$$(k_{p1}, k_{p2}, k_{p3})^T = (k_1, k_2, k_3)^T \mathbf{P} \quad (1.5.3.10)$$

are integers. In other words, $(k_1, k_2, k_3)^T$ has to fulfil the equation

$$(k_1, k_2, k_3)^T = (k_{p1}, k_{p2}, k_{p3})^T \mathbf{P}^{-1}. \quad (1.5.3.11)$$

As is well known, the Bravais type of the reciprocal lattice $\mathbf{L}^*$ is not necessarily the same as that of its direct lattice $\mathbf{L}$. If $\mathbf{W}$ is the matrix of a (point-) symmetry operation of the direct lattice, referred to its basis $(\mathbf{a}_i)^T$, then $\mathbf{W}^{-1}$ is the matrix of the same symmetry operation of the reciprocal lattice but referred to the dual basis $(\mathbf{a}_i^*)$. This does not affect the symmetry because in a (symmetry) group the inverse of each element in the group also belongs to the group. Therefore, the (point) symmetries of a lattice

[†] In crystallography vectors are designated by small bold-faced letters. With $\mathbf{K}$ we make an exception in order to follow the tradition of physics. A crystallographic alternative would be $\mathbf{k}^*$.

[‡] The lattice $\mathbf{L}$ is often called the *direct lattice*. These names are historically introduced and cannot be changed, although equations (1.5.3.5) and (1.5.3.6) show that essentially neither of the lattices is preferred: they form a pair of *mutually reciprocal* lattices.

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and its reciprocal lattice are always the same. However, there may be differences in the matrix descriptions due to the different orientations of $\mathbf{L}$ and $\mathbf{L}^*$ relative to the symmetry elements of $\bar{\mathcal{G}}$ and due to the reference to the different bases $(\mathbf{a}_i)^T$ and $(\mathbf{a}_i^*)$. For example, if $\mathbf{L}$ has the point symmetry (Hermann–Mauguin symbol) $\bar{3}m1$, then the symbol for the point symmetry of $\mathbf{L}^*$ is $\bar{3}1m$ and vice versa.

1.5.3.4. Irreducible representations of space groups and the reciprocal-space group

Let $(\mathbf{a}_i)^T$ be a conventional basis of the lattice $\mathbf{L}$ of the space group $\mathcal{G}$. From (1.5.3.6), $k_i = q_i/N_i$ and $\mathbf{k} = \sum_{k=1}^3 k_i \mathbf{a}_i^*$, equation (1.5.3.4) can be written

$$\Gamma^{q_1 q_2 q_3}[(\mathbf{I}, \mathbf{t})] = \Gamma^{\mathbf{k}}[(\mathbf{I}, \mathbf{t})] = \exp[-i\mathbf{k} \cdot \mathbf{t}]. \quad (1.5.3.12)$$

Equation (1.5.3.12) has the same form if a primitive basis $(\mathbf{p}_i)^T$ of $\mathbf{L}$ has been chosen. In this case, the vector $\mathbf{k}$ is given by $\mathbf{k} = \sum_{i=1}^3 k_{pi} \mathbf{p}_i^*$.

Let a primitive basis $(\mathbf{p}_i)^T$ be chosen for the lattice $\mathbf{L}$. The set of all vectors $\mathbf{k}$ (known as wavevectors) forms a discontinuous array. Consider two wavevectors $\mathbf{k}$ and $\mathbf{k}' = \mathbf{k} + \mathbf{K}$, where $\mathbf{K}$ is a vector of the reciprocal lattice $\mathbf{L}^*$. Obviously, $\mathbf{k}$ and $\mathbf{k}'$ describe the same irrep of $\mathcal{T}$. Therefore, to determine all irreps of $\mathcal{T}$ it is necessary to consider only the wavevectors of a small region of the reciprocal space, where the translation of this region by all vectors of $\mathbf{L}^*$ fills the reciprocal space without gap or overlap. Such a region is called a *fundamental region* of $\mathbf{L}^*$. (The nomenclature in literature is not quite uniform. We follow here widely adopted definitions.)

The fundamental region of $\mathbf{L}^*$ is not uniquely determined. Two types of fundamental regions are of interest in this chapter:

(1) The *first Brillouin zone* is that range of $\mathbf{k}$ space around $\mathbf{o}$ for which $|\mathbf{k}| \leq |\mathbf{K} - \mathbf{k}|$ holds for any vector $\mathbf{K} \in \mathbf{L}^*$ (Wigner–Seitz cell or *domain of influence* in $\mathbf{k}$ space). The Brillouin zone is used in books and articles on irreps of space groups.

(2) The *crystallographic unit cell in reciprocal space*, for short *unit cell*, is the set of all $\mathbf{k}$ vectors with $0 \leq k_i < 1$. It corresponds to the unit cell used in crystallography for the description of crystal structures in direct space.

Let $\mathbf{k}$ be some vector according to (1.5.3.12) and $\mathbf{W}$ be the matrices of $\bar{\mathcal{G}}$. The following definitions are useful:

Definition. The set of all vectors $\mathbf{k}'$ fulfilling the condition

$$\mathbf{k}' = \mathbf{k}\mathbf{W} + \mathbf{K}, \quad \mathbf{W} \in \bar{\mathcal{G}}, \quad \mathbf{K} \in \mathbf{L}^* \quad (1.5.3.13)$$

is called the *orbit* of $\mathbf{k}$.

Definition. The set of all matrices $\mathbf{W} \in \bar{\mathcal{G}}$ for which

$$\mathbf{k} = \mathbf{k}\mathbf{W} + \mathbf{K}, \quad \mathbf{K} \in \mathbf{L}^* \quad (1.5.3.14)$$

forms a group which is called the *little co-group* $\bar{\mathcal{G}}^{\mathbf{k}}$ of $\mathbf{k}$. The vector $\mathbf{k}$ is called *general* if $\bar{\mathcal{G}}^{\mathbf{k}} = \{\mathbf{I}\}$; otherwise $\bar{\mathcal{G}}^{\mathbf{k}} > \{\mathbf{I}\}$ and $\mathbf{k}$ is called *special*.

The little co-group $\bar{\mathcal{G}}^{\mathbf{k}}$ is a subgroup of the point group $\bar{\mathcal{G}}$. Consider the coset decomposition of $\bar{\mathcal{G}}$ relative to $\bar{\mathcal{G}}^{\mathbf{k}}$.

Definition. If $\{\mathbf{W}_m\}$ is a set of coset representatives of $\bar{\mathcal{G}}$ relative to $\bar{\mathcal{G}}^{\mathbf{k}}$, then the set $\{\mathbf{k}\mathbf{W}_m\}$ is called the *star* of $\mathbf{k}$ and the vectors $\mathbf{k}\mathbf{W}_m$ are called the *arms* of the star.

The number of arms of the star of $\mathbf{k}$ is equal to the order $|\bar{\mathcal{G}}|$ of the point group $\bar{\mathcal{G}}$ divided by the order $|\bar{\mathcal{G}}^{\mathbf{k}}|$ of the symmetry group $\bar{\mathcal{G}}^{\mathbf{k}}$ of $\mathbf{k}$. If $\mathbf{k}$ is general, then there are $|\bar{\mathcal{G}}|$ vectors from the orbit of $\mathbf{k}$ in each fundamental region and $|\bar{\mathcal{G}}|$ arms of the star. If $\mathbf{k}$ is special with

little co-group $\bar{\mathcal{G}}^{\mathbf{k}}$, then the number of arms of the star of $\mathbf{k}$ and the number of $\mathbf{k}$ vectors in the fundamental region from the orbit of $\mathbf{k}$ is $|\bar{\mathcal{G}}|/|\bar{\mathcal{G}}^{\mathbf{k}}|$.

Definition. The group of all elements $(\mathbf{W}, \mathbf{w}) \in \mathcal{G}$ for which $\mathbf{W} \in \bar{\mathcal{G}}^{\mathbf{k}}$ is called the *little group* $\mathcal{L}^{\mathbf{k}}$ of $\mathbf{k}$.

Equation (1.5.3.14) for $\mathbf{k}$ resembles the equation

$$\mathbf{x} = \mathbf{W}\mathbf{x} + \mathbf{t}, \quad \mathbf{t} \in \mathbf{L} \quad (1.5.3.15)$$

by which the fixed points of the symmetry operation $(\mathbf{W}, \mathbf{t})$ of a symmorphic space group $\mathcal{G}_0$ are determined. Indeed, the orbits of $\mathbf{k}$ defined by (1.5.3.13) correspond to the point orbits of $\mathcal{G}_0$, the little co-group $\bar{\mathcal{G}}^{\mathbf{k}}$ of $\mathbf{k}$ corresponds to the site-symmetry group of that point $\mathbf{X}$ whose coordinates (x_i) have the same values as the vector coefficients $(k_i)^T$ of $\mathbf{k}$, and the star of $\mathbf{k}$ corresponds to a set of representatives of $\mathbf{X}$ in $\mathcal{G}_0$. (The analogue of the little group $\mathcal{L}^{\mathbf{k}}$ is rarely considered in crystallography.)

All symmetry operations of $\mathcal{G}_0$ may be obtained as combinations of an operation that leaves the origin fixed with a translation of $\mathbf{L}$, i.e. are of the kind $(\mathbf{W}, \mathbf{t}) = (\mathbf{I}, \mathbf{t})(\mathbf{W}, \mathbf{o})$. We now define the analogous group for the $\mathbf{k}$ vectors. Whereas $\mathcal{G}_0$ is a realization of the corresponding abstract group in direct (point) space, the group to be defined will be a realization of it in reciprocal (vector) space.

Definition. The group $\mathcal{G}^*$ which is the semidirect product of the point group $\bar{\mathcal{G}}$ and the translation group of the reciprocal lattice $\mathbf{L}^*$ of $\mathcal{G}$ is called the *reciprocal-space group* of $\mathcal{G}$.

The elements of $\mathcal{G}^*$ are the operations $(\mathbf{W}, \mathbf{K}) = (\mathbf{I}, \mathbf{K})(\mathbf{W}, \mathbf{o})$ with $\mathbf{W} \in \bar{\mathcal{G}}$ and $\mathbf{K} \in \mathbf{L}^*$. In order to emphasize that $\mathcal{G}^*$ is a group acting on reciprocal space and not the inverse of a space group (whatever that may mean) we insert a hyphen ‘-’ between ‘reciprocal’ and ‘space’.

From the definition of $\mathcal{G}^*$ it follows that space groups of the same type define the same type of reciprocal-space group $\mathcal{G}^*$. Moreover, as $\mathcal{G}^*$ does not depend on the column parts of the space-group operations, all space groups of the same arithmetic crystal class determine the same type of $\mathcal{G}^*$; for arithmetic crystal class see Section 1.5.3.2. Following Wintgen (1941), the types of reciprocal-space groups $\mathcal{G}^*$ are listed for the arithmetic crystal classes of space groups, i.e. for all space groups $\mathcal{G}$, in Appendix 1.5.1.

1.5.4. Conventions in the classification of space-group irreps

Because of the isomorphism between the reciprocal-space groups $\mathcal{G}^*$ and the symmorphic space groups $\mathcal{G}_0$ one can introduce crystallographic conventions in the classification of space-group irreps. These conventions will be compared with those which have mainly been used up to now. Illustrative examples to the following more theoretical considerations are discussed in Section 1.5.5.1.

1.5.4.1. Fundamental regions

Different types of regions of reciprocal space may be chosen as fundamental regions, see Section 1.5.3.4. The most frequently used type is the first Brillouin zone, which is the Wigner–Seitz cell (or Voronoi region, Dirichlet domain, domain of influence; cf. IT A, Chapter 9.1) of the reciprocal lattice. It has the property that with each $\mathbf{k}$ vector also its star belongs to the Brillouin zone. Such a choice has three advantages:

(1) the Brillouin zone is always primitive and it manifests the point symmetry of the reciprocal lattice $\mathbf{L}^*$ of $\mathcal{G}$;

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(2) only $\mathbf{k}$ vectors of the boundary of the Brillouin zone may have little-group representations which are obtained from projective representations of the little co-group $\bar{G}^{\mathbf{k}}$, see e.g. BC, p. 156;

(3) for physical reasons, the Brillouin zone may be the most convenient fundamental region.

Of these advantages only the third may be essential. For the classification of irreps the minimal domains, see Section 1.5.4.2, are much more important than the fundamental regions. The minimal domain does not display the point-group symmetry anyway and the distinguished $\mathbf{k}$ vectors always belong to its boundary however the minimal domain may be chosen.

The serious disadvantage of the Brillouin zone is its often complicated shape which, moreover, depends on the lattice parameters of $\mathbf{L}^*$. The body that represents the Brillouin zone belongs to one of the five Fedorov polyhedra (more or less distorted versions of the cubic forms cube, rhombdodecahedron or cuboctahedron, of the hexagonal prism, or of the tetragonal elongated rhombdodecahedron). A more detailed description is that by the 24 *symmetrische Sorten* (Delaunay sorts) of Delaunay (1933), Figs. 11 and 12. According to this classification, the Brillouin zone may display three types of polyhedra of cubic, one type of hexagonal, two of rhombohedral, three of tetragonal, six of orthorhombic, six of monoclinic, and three types of triclinic symmetry.

For low symmetries the shape of the Brillouin zone is so variable that BC, p. 90 ff. chose a primitive unit cell of $\mathbf{L}^*$ for the fundamental regions of triclinic and monoclinic crystals. This cell also reflects the point symmetry of $\mathbf{L}^*$, it has six faces only, and although its shape varies with the lattice constants all cells are affinely equivalent. For space groups of higher symmetry, BC and most other authors prefer the Brillouin zone.

Considering $\mathbf{L}^*$ as a lattice, one can refer it to its conventional crystallographic lattice basis. Referred to this basis, the *unit cell* of $\mathbf{L}^*$ is always an alternative to the Brillouin zone. With the exception of the hexagonal lattice, the unit cell of $\mathbf{L}^*$ reflects the point symmetry, it has only six faces and its shape is always affinely equivalent for varying lattice constants. For a space group $\mathcal{G}$ with a primitive lattice, the above-defined conventional unit cell of $\mathbf{L}^*$ is also primitive. If $\mathcal{G}$ has a centred lattice, then $\mathbf{L}^*$ also belongs to a type of centred lattice and the *conventional* cell of $\mathbf{L}^*$ [not to be confused with the cell spanned by the basis $(\mathbf{a}_j^*)$ dual to the basis $(\mathbf{a}_j)^T$] is larger than necessary. However, this is not disturbing because in this context the fundamental region is an auxiliary construction only for the definition of the minimal domain; see Section 1.5.4.2.

1.5.4.2. Minimal domains

One can show that all irreps of $\mathcal{G}$ can be built up from the irreps $\Gamma^{\mathbf{k}}$ of $\mathcal{T}$. Moreover, to find all irreps of $\mathcal{G}$ it is only necessary to consider one $\mathbf{k}$ vector from each orbit of $\mathbf{k}$, cf. CDML, p. 31.

Definition. A simply connected part of the fundamental region which contains *exactly one* $\mathbf{k}$ vector of each orbit of $\mathbf{k}$ is called a *minimal domain* Φ .

The choice of the minimal domain is by no means unique. One of the difficulties in comparing the published data on irreps of space groups is due to the different representation domains found in the literature.

The number of $\mathbf{k}$ vectors of each general $\mathbf{k}$ orbit in a fundamental region is always equal to the order of the point group $\bar{G}$ of $\mathcal{G}$; see Section 1.5.3.4. Therefore, the volume of the minimal domain Φ in reciprocal space is $1/|\bar{G}|$ of the volume of the fundamental region. Now we can restrict the search for all irreps of $\mathcal{G}$ to the $\mathbf{k}$ vectors within a minimal domain Φ .

In general, in representation theory of space groups the Brillouin zone is taken as the fundamental region and Φ is called a *representation domain*.† Again, the volume of a representation domain in reciprocal space is $1/|\bar{G}|$ of the volume of the Brillouin zone. In addition, as the Brillouin zone contains for each $\mathbf{k}$ vector all $\mathbf{k}$ vectors of the star of $\mathbf{k}$, by application of all symmetry operations $\mathbf{W} \in \bar{G}$ to Φ one obtains the Brillouin zone; cf. BC, p. 147. As the Brillouin zone may change its geometrical type depending on the lattice constants, the type of the representation domain may also vary with varying lattice constants; see examples (3) and (4) in Section 1.5.5.1.

The simplest crystal structures are the lattice-like structures that are built up of translationally equivalent points (centres of particles) only. For such a structure the point group $\bar{G}$ of the space group $\mathcal{G}$ is equal to the point group Q of its lattice $\mathbf{L}$. Such point groups are called *holohedral*, the space group $\mathcal{G}$ is called *holosymmetric*. There are seven holohedral point groups of three dimensions: $1, 2/m, mmm, 4/mmm, \bar{3}m, 6/mmm$ and $m\bar{3}m$. For the non-holosymmetric space groups $\mathcal{G}$, $\bar{G} < Q$ holds.

In books on representation theory of space groups, holosymmetric space groups play a distinguished role. Their representation domains are called *basic domains* Ω . For holosymmetric space groups $\Omega = \Phi$ holds. If $\mathcal{G}$ is non-holosymmetric, i.e. $\bar{G} < Q$ holds, Ω is defined by Q and is smaller than the representation domain Φ by a factor which is equal to the index of $\bar{G}$ in Q . In the literature these basic domains are considered to be of primary importance. In Miller & Love (1967) only the irreps for the $\mathbf{k}$ vectors of the basic domains Ω are listed. Section 5.5 of BC and Davies & Cracknell (1976) state that such a listing is not sufficient for the non-holosymmetric space groups because $\Omega < \Phi$. Section 5.5 of BC shows how to overcome this deficiency; Chapter 4 of CDML introduces new types of $\mathbf{k}$ vectors for the parts of Φ not belonging to Ω .

The crystallographic analogue of the representation domain in direct space is the *asymmetric unit*, cf. IT A. According to its definition it is a simply connected smallest part of space from which by application of all symmetry operations of the space group the whole space is exactly filled. For each space-group type the asymmetric units of IT A belong to the same topological type independent of the lattice constants. They are chosen as ‘simple’ bodies by inspection rather than by applying clearly stated rules. Among the asymmetric units of the 73 symmorphic space-group types $\mathcal{G}_0$ there are 31 parallelepipeds, 27 prisms (13 trigonal, 6 tetragonal and 8 pentagonal) for the non-cubic, and 15 pyramids (11 trigonal and 4 tetragonal) for the cubic $\mathcal{G}_0$.

The asymmetric units of IT A – transferred to the groups $\mathcal{G}^*$ of reciprocal space – are alternatives for the representation domains of the literature. They are formulated as closed bodies. Therefore, for inner points $\mathbf{k}$, the asymmetric units of IT A fulfil the condition that each star of $\mathbf{k}$ is represented exactly once. For the surface, however, these conditions either have to be worked out or one gives up the condition of uniqueness and replaces *exactly* by *at least* in the definition of the minimal domain (see preceding footnote). The examples of Section 1.5.5.1 show that the conditions for the boundary of the asymmetric unit and its special points, lines and

† From definition 3.7.1 on p. 147 of BC, it does not follow that a representation domain contains *exactly one* $\mathbf{k}$ vector from each star. The condition ‘The intersection of the representation domain with its symmetrically equivalent domains is empty’ is missing. Lines 14 to 11 from the bottom of p. 149, however, state that such a property of the representation domain is intended. The representation domains of CDML, Figs. 3.15–3.29 contain *at least one* $\mathbf{k}$ vector of each star (Vol. 1, pp. 31, 57 and 65). On pp. 66, 67 a procedure is described for eliminating those $\mathbf{k}$ vectors from the representation domain which occur more than once. In the definition of Altmann (1977), p. 204, the representation domain contains *exactly one* arm (prong) per star.

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Table 1.5.4.1. Conventional coefficients $(k_i)^T$ of $\mathbf{k}$ expressed by the adjusted coefficients (k_{ai}) of *IT A* for the different Bravais types of lattices in direct space

Lattice types	k_1	k_2	k_3
aP, mP, oP, tP, cP, rP	k_{a1}	k_{a2}	k_{a3}
mA, oA	k_{a1}	$2k_{a2}$	$2k_{a3}$
mC, oC	$2k_{a1}$	$2k_{a2}$	k_{a3}
oF, cF, oI, cI	$2k_{a1}$	$2k_{a2}$	$2k_{a3}$
tI	$k_{a1} + k_{a2}$	$-k_{a1} + k_{a2}$	$2k_{a3}$
hP	$k_{a1} - k_{a2}$	k_{a2}	k_{a3}
hR (hexagonal)	$2k_{a1} - k_{a2}$	$-k_{a1} + 2k_{a2}$	$3k_{a3}$

Table 1.5.4.2. Primitive coefficients $(k_{pi})^T$ of $\mathbf{k}$ from CDML expressed by the adjusted coefficients (k_{ai}) of *IT A* for the different Bravais types of lattices in direct space

Lattice types	k_{p1}	k_{p2}	k_{p3}
aP, mP, oP, tP, cP, rP	k_{a1}	k_{a2}	k_{a3}
mA, oA	k_{a1}	$k_{a2} - k_{a3}$	$k_{a2} + k_{a3}$
mC, oC	$k_{a1} - k_{a2}$	$k_{a1} + k_{a2}$	k_{a3}
oF, cF	$k_{a2} + k_{a3}$	$k_{a1} + k_{a3}$	$k_{a1} + k_{a2}$
oI, cI	$-k_{a1} + k_{a2} + k_{a3}$	$k_{a1} - k_{a2} + k_{a3}$	$k_{a1} + k_{a2} - k_{a3}$
tI	$-k_{a1} + k_{a3}$	$k_{a1} + k_{a3}$	$k_{a2} - k_{a3}$
hP	$k_{a1} - k_{a2}$	k_{a2}	k_{a3}
hR (hexagonal)	$k_{a1} + k_{a3}$	$-k_{a1} + k_{a2} + k_{a3}$	$-k_{a2} + k_{a3}$

planes are in many cases much easier to formulate than those for the representation domain.

The $\mathbf{k}$ -vector coefficients. For each $\mathbf{k}$ vector one can derive a set of irreps of the space group $\mathcal{G}$. Different $\mathbf{k}$ vectors of a $\mathbf{k}$ orbit give rise to equivalent irreps. Thus, for the calculation of the irreps of the space groups it is essential to identify the orbits of $\mathbf{k}$ vectors in reciprocal space. This means finding the sets of all $\mathbf{k}$ vectors that are related by the operations of the reciprocal-space group $\mathcal{G}^*$ according to equation (1.5.3.13). The classification of these $\mathbf{k}$ orbits can be done in analogy to that of the point orbits of the symmorphic space groups, as is apparent from the comparison of equations (1.5.3.14) and (1.5.3.15).

The classes of point orbits in direct space under a space group $\mathcal{G}$ are well known and are listed in the space-group tables of *IT A*. They are labelled by *Wyckoff letters*. The stabilizer $S_{\mathcal{G}}(X)$ of a point X is called the *site-symmetry group* of X , and a *Wyckoff position* consists of all orbits for which the site-symmetry groups are conjugate subgroups of $\mathcal{G}$. Let $\mathcal{G}$ be a symmorphic space group $\mathcal{G}_0$. Owing to the isomorphism between the reciprocal-space groups $\mathcal{G}^*$ and the symmorphic space groups $\mathcal{G}_0$, the complete list of the types of special $\mathbf{k}$ vectors of $\mathcal{G}^*$ is provided by the Wyckoff positions of $\mathcal{G}_0$. The groups $S_{\mathcal{G}_0}(X)$ and $\mathcal{G}^k$ correspond to each other and the multiplicity of the Wyckoff position (divided by the number of centring vectors per unit cell for centred lattices) equals the number of arms of the star of $\mathbf{k}$. Let the vectors $\mathbf{t}$ of $\mathbf{L}$ be referred to the conventional basis $(\mathbf{a}_i)^T$ of the space-group tables of *IT A*, as defined in Chapters 2.1 and 9.1 of *IT A*. Then, for the construction of the irreducible representations Γ^k of $\mathcal{T}$ the coefficients of the $\mathbf{k}$ vectors must be referred to the basis $(\mathbf{a}_j^*)$ of reciprocal space dual to $(\mathbf{a}_i)^T$ in direct space. These $\mathbf{k}$ -vector coefficients may be different from the conventional coordinates of $\mathcal{G}_0$ listed in the Wyckoff positions of *IT A*.

Example. Let $\mathcal{G}$ be a space group with an *I*-centred cubic lattice $\mathbf{L}$, conventional basis $(\mathbf{a}_i)^T$. Then $\mathbf{L}^*$ is an *F*-centred lattice. If referred to the conventional basis $(\mathbf{a}_j^*)$ with $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}$, the $\mathbf{k}$ vectors with coefficients 1 0 0, 0 1 0 and 0 0 1 do not belong to $\mathbf{L}^*$ due to the ‘extinction laws’ well known in X-ray crystallography. However, in the standard basis of $\mathcal{G}_0$, isomorphic to $\mathcal{G}^*$, the vectors 1 0 0, 0 1 0 and 0 0 1 point to the vertices of the face-centred cube and thus correspond to 2 0 0, 0 2 0 and 0 0 2 referred to the conventional basis $(\mathbf{a}_j^*)$.

In the following, three bases and, therefore, three kinds of coefficients of $\mathbf{k}$ will be distinguished:

(1) Coefficients referred to the conventional basis $(\mathbf{a}_j^*)$ in reciprocal space, dual to the conventional basis $(\mathbf{a}_i)^T$ in direct space. The corresponding $\mathbf{k}$ -vector coefficients, $(k_j)^T$, will be called *conventional coefficients*.

(2) Coefficients of $\mathbf{k}$ referred to a primitive basis $(\mathbf{a}_{pi}^*)$ in reciprocal space (which is dual to a primitive basis in direct space).

The corresponding coefficients will be called *primitive coefficients* $(k_{pi})^T$. For a centred lattice the coefficients $(k_{pi})^T$ are different from the conventional coefficients $(k_i)^T$. In most of the physics literature related to space-group representations these primitive coefficients are used, e.g. by CDML.

(3) The coefficients of $\mathbf{k}$ referred to the conventional basis of $\mathcal{G}_0$. These coefficients will be called *adjusted coefficients* $(k_{ai})^T$.

The relations between conventional and adjusted coefficients are listed for the different Bravais types of reciprocal lattices in Table 1.5.4.1, and those between adjusted and primitive coordinates in Table 1.5.4.2. If adjusted coefficients are used, then *IT A* is as suitable for dealing with irreps as it is for handling space-group symmetry.

1.5.4.3. Wintgen positions

In order to avoid confusion, in the following the analogues to the Wyckoff positions of $\mathcal{G}_0$ will be called *Wintgen positions* of $\mathcal{G}^*$; the *coordinates* of the Wyckoff position are replaced by the $\mathbf{k}$ -vector coefficients of the Wintgen position, the *Wyckoff letter* will be called the *Wintgen letter*, and the symbols for the *site symmetries* of $\mathcal{G}_0$ are to be read as the symbols for the *little co-groups* $\mathcal{G}^k$ of the $\mathbf{k}$ vectors in $\mathcal{G}^*$. The *multiplicity* of a Wyckoff position is retained in the Wintgen symbol in order to facilitate the use of *IT A* for the description of symmetry in $\mathbf{k}$ space. However, it is equal to the *multiplicity of the star of $\mathbf{k}$* only in the case of primitive lattices $\mathbf{L}^*$.

In analogy to a Wyckoff position, a Wintgen position is a set of orbits of $\mathbf{k}$ vectors. Each orbit as well as each star of $\mathbf{k}$ can be represented by any one of its $\mathbf{k}$ vectors. The zero, one, two or three parameters in the $\mathbf{k}$ -vector coefficients define points, lines, planes or the full parameter space. The different stars of a Wintgen position are obtained by changing the parameters.

Remark. Because reciprocal space is a vector space, there is no origin choice and the Wintgen letters are unique (in contrast to the Wyckoff letters, which may depend on the origin choice). Therefore, the introduction of *Wintgen sets* in analogy to the *Wyckoff sets* of *IT A*, Section 8.3.2 is not necessary.

It may be advantageous to describe the different stars belonging to a Wintgen position in a *uniform* way. For this purpose one can define:

Definition. Two $\mathbf{k}$ vectors of a Wintgen position are *uni-arm* if one can be obtained from the other by parameter variation. The *description of the stars* of a Wintgen position is *uni-arm* if the $\mathbf{k}$ vectors representing these stars are uni-arm.

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Table 1.5.5.1. The **k**-vector types for the space groups $Im\bar{3}m$ and $Ia\bar{3}d$

Comparison of the **k**-vector labels and parameters of CDML with the Wyckoff positions of *IT A* for $Fm\bar{3}m$, (O_h^5), isomorphic to the reciprocal-space group $\mathcal{G}^*$ of $m\bar{3}mI$. The parameter ranges in the last column are chosen such that each star of **k** is represented exactly once. The sign $\sim$ means symmetrically equivalent. The coordinates x, y, z of *IT A* are related to the **k**-vector coefficients of CDML by $x = 1/2(k_2 + k_3)$, $y = 1/2(k_1 + k_3)$, $z = 1/2(k_1 + k_2)$.

k -vector label, CDML	Wyckoff position, <i>IT A</i>	Parameters (see Fig. 1.5.5.1b), <i>IT A</i>
Γ 0, 0, 0	4 <i>a m</i> $\bar{3}m$	0, 0, 0
H $\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}$	4 <i>b m</i> $\bar{3}m$	$\frac{1}{2}, 0, 0$
P $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	8 <i>c 4</i> $\bar{3}m$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$
N 0, 0, $\frac{1}{2}$	24 <i>d m.mm</i>	$\frac{1}{4}, \frac{1}{4}, 0$
Δ $\alpha, -\alpha, \alpha$	24 <i>e 4m.m</i>	$x, 0, 0: 0 < x < \frac{1}{2}$
Λ α, α, α F $\frac{1}{2} - \alpha, -\frac{1}{2} + 3\alpha, \frac{1}{2} - \alpha$ $\sim F_1$ (Fig. 1.5.5.1b) $\sim F_2$ (Fig. 1.5.5.1b) $\Lambda \cup F_1 \sim \Gamma H_2 \setminus P$	32 <i>f .3m</i> 32 <i>f .3m</i> 32 <i>f .3m</i> 32 <i>f .3m</i> 32 <i>f .3m</i>	$x, x, x: 0 < x < \frac{1}{4}$ $\frac{1}{2} - x, x, x: 0 < x < \frac{1}{4}$ $x, x, x: \frac{1}{4} < x < \frac{1}{2}$ $x, x, \frac{1}{2} - x: 0 < x < \frac{1}{4}$ $x, x, x: 0 < x < \frac{1}{2}$ with $x \neq \frac{1}{4}$
D $\alpha, \alpha, \frac{1}{2} - \alpha$	48 <i>g 2.mm</i>	$\frac{1}{4}, \frac{1}{4}, z: 0 < z < \frac{1}{4}$
Σ 0, 0, α	48 <i>h m.m2</i>	$x, x, 0: 0 < x < \frac{1}{4}$
G $\frac{1}{2} - \alpha, -\frac{1}{2} + \alpha, \frac{1}{2}$	48 <i>i m.m2</i>	$\frac{1}{2} - x, x, 0: 0 < x < \frac{1}{4}$
A $\alpha, -\alpha, \beta$	96 <i>j m..</i>	$x, y, 0: 0 < y < x < \frac{1}{2} - y$
B $\alpha + \beta, -\alpha + \beta, \frac{1}{2} - \beta$ $\sim PH_1N_1$ (Fig. 1.5.5.1b) C α, α, β J α, β, α $\sim \Gamma PH_1$ (Fig. 1.5.5.1b) $C \cup B \cup J \sim \Gamma NN_1H_1$	96 <i>k ..m</i> 96 <i>k ..m</i> 96 <i>k ..m</i> 96 <i>k ..m</i> 96 <i>k ..m</i> 96 <i>k ..m</i>	$\frac{1}{4} + x, \frac{1}{4} - x, z: 0 < z < \frac{1}{4} - x < \frac{1}{4}$ $x, x, z: 0 < x < \frac{1}{2} - x < z < \frac{1}{2}$ $x, x, z: 0 < z < x < \frac{1}{4}$ $x, y, y: 0 < y < x < \frac{1}{2} - y$ $x, x, z: 0 < x < z < \frac{1}{2} - x$ $x, x, z: 0 < x < \frac{1}{4}, 0 < z < \frac{1}{2}$ with $z \neq x$, $z \neq \frac{1}{2} - x$.
GP α, β, γ	192 <i>l 1</i>	$x, y, z: 0 < z < y < x < \frac{1}{2} - y$

For non-holosymmetric space groups the representation domain Φ is a multiple of the basic domain Ω . CDML introduced new letters for stars of **k** vectors in those parts of Φ which do not belong to Ω . If one can make a new **k** vector uni-arm to some **k** vector of the basic domain Ω by an appropriate choice of Φ and Ω , one can extend the parameter range of this **k** vector of Ω to Φ instead of introducing new letters. It turns out that indeed most of these new letters are unnecessary. This restricts the introduction of new types of **k** vectors to the few cases where it is indispensable. Extension of the parameter range for **k** means that the corresponding representations can also be obtained by parameter variation. Such representations can be considered to belong to the same type. In this way a large number of superfluous **k**-vector names, which pretend a greater variety of types of irreps than really exists, can be avoided (Boyle, 1986). For examples see Section 1.5.5.1.

1.5.5. Examples and conclusions

1.5.5.1. Examples

In this section, four examples are considered in each of which the *crystallographic* classification scheme for the irreps is compared with the *traditional* one:†

† Corresponding tables and figures for all space groups are available at http://www.cryst.ehu.es/cryst/get_kvec.html.

(1) **k**-vector types of the arithmetic crystal class $m\bar{3}mI$ (space groups $Im\bar{3}m$ and $Ia\bar{3}d$), reciprocal-space group isomorphic to $Fm\bar{3}m$; $\Phi = \Omega$; see Table 1.5.5.1 and Fig. 1.5.5.1;

(2) **k**-vector types of the arithmetic crystal class $m\bar{3}I$ ($Im\bar{3}$ and $Ia\bar{3}$), reciprocal-space group isomorphic to $Fm\bar{3}$, $\Phi > \Omega$; see Table 1.5.5.2 and Fig. 1.5.5.2;

(3) **k**-vector types of the arithmetic crystal class $4/mmmI$ ($I4/mmm$, $I4/mcm$, $I4_1/amd$ and $I4_1/acd$), reciprocal-space group isomorphic to $I4/mmm$. Here $\Phi = \Omega$ changes for different ratios of the lattice constants a and c ; see Table 1.5.5.3 and Fig. 1.5.5.3;

(4) **k**-vector types of the arithmetic crystal class $mm2F$ ($Fmm2$ and $Fdd2$), reciprocal-space group isomorphic to $Imm2$. Here $\Phi > \Omega$ changes for different ratios of the lattice constants a, b and c ; see Table 1.5.5.4 and Fig. 1.5.5.4.

The asymmetric units of *IT A* are displayed in Figs. 1.5.5.1 to 1.5.5.4 by dashed lines. In Tables 1.5.5.1 to 1.5.5.4, the **k**-vector types of CDML are compared with the Wintgen (Wyckoff) positions of *IT A*. The parameter ranges are chosen such that each star of **k** is represented exactly once. Sets of symmetry points, lines or planes of CDML which belong to the same Wintgen position are separated by horizontal lines in Tables 1.5.5.1 to 1.5.5.3. The uni-arm description is listed in the last entry of each Wintgen position in Tables 1.5.5.1 and 1.5.5.2. In Table 1.5.5.4, so many **k**-vector types of CDML belong to each Wintgen position that the latter are used as headings under which the CDML types are listed.

1.5. CLASSIFICATION OF SPACE-GROUP REPRESENTATIONS

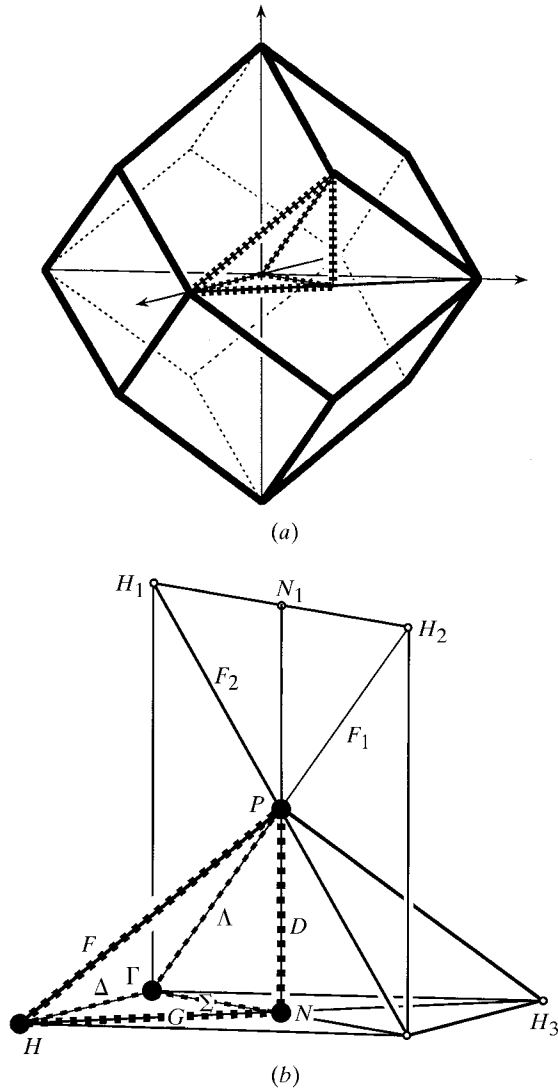


Fig. 1.5.5.1. Symmorphic space group $Fm\bar{3}m$ (isomorphic to the reciprocal space group $\mathcal{G}^*$ of $m\bar{3}ml$). (a) The asymmetric unit (thick dashed edges) imbedded in the Brillouin zone, which is a cubic rhombododecahedron. (b) The asymmetric unit ΓHNP , IT A, p. 678. The representation domain ΓNH_3P of CDML is obtained by reflecting ΓHNP through the plane of ΓNP . Coordinates of the points: $\Gamma = 0, 0, 0$; $N = \frac{1}{4}, \frac{1}{4}, 0 \sim N_1 = \frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; $H = \frac{1}{2}, 0, 0 \sim H_1 = 0, 0, \frac{1}{2} \sim H_2 = \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \sim H_3 = 0, \frac{1}{2}, 0$; $P = \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; the sign $\sim$ means symmetrically equivalent. Lines: $\Lambda = \Gamma P = x, x, x$; $F = HP = \frac{1}{2} - x, x, x \sim F_1 = PH_2 = x, x, x \sim F_2 = PH_1 = x, x, \frac{1}{2} - x$; $\Delta = \Gamma H = x, 0, 0$; $\Sigma = \Gamma N = x, x, 0$; $D = NP = \frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; $G = NH = x, \frac{1}{2} - x, 0$. Planes: $A = \Gamma HN = x, y, 0$; $B = HNP = x, \frac{1}{2} - x, z \sim PN_1H_1 = x, x, z$; $C = \Gamma NP = x, x, z$; $J = \Gamma HP = x, y, y \sim \Gamma PH_1 = x, x, z$. Large black circles: corners of the asymmetric unit (special points); small open circles: other special points; dashed lines: edges of the asymmetric unit (special lines). For the parameter ranges see Table 1.5.5.1.

1.5.5.2. Results

(1) The higher the symmetry of the point group $\bar{\mathcal{G}}$ of $\mathcal{G}$, the more one is restricted in the choice of the boundaries of the minimal domain. This is because a symmetry element (rotation or rotoinversion axis, plane of reflection, centre of inversion) cannot occur in the interior of the minimal domain but only on its boundary. However, even for holosymmetric space groups of highest symmetry, the description by Brillouin zone and representation domain is not as concise as possible, cf. CDML.

Examples:

(a) In $m\bar{3}ml$ and $m\bar{3}I$ there are the Λ and F lines of $\mathbf{k}$ vectors $\mathbf{k}_1(\alpha, \alpha, \alpha)$ and $\mathbf{k}_2(\frac{1}{2} - \alpha, -\frac{1}{2} + 3\alpha, \frac{1}{2} - \alpha)$ in CDML, see Tables 1.5.5.1 and 1.5.5.2, Figs. 1.5.5.1 and 1.5.5.2. Do they belong to the same Wintgen position, i.e. do their irreps belong to the same type? There is a twofold rotation $2x, \frac{1}{4}, \frac{1}{4}$ which maps $\mathbf{k}_2$ onto $\mathbf{k}'_2 = (\frac{1}{2} - \alpha, \frac{1}{2} - \alpha, \frac{1}{2} - \alpha \in F_1)$ (the rotation 2 is described in the primitive basis of CDML by $k'_1 = k_3$, $k'_2 = -k_1 - k_2 - k_3 + 1$, $k'_3 = k_1$). The $\mathbf{k}$ vectors $\mathbf{k}_1$ and $\mathbf{k}'_2$ are uni-arm and form the line $\Gamma H_2 \setminus P = \Lambda \cup F_1 \sim \Lambda \cup F$ which protrudes from the body of the asymmetric unit like a flagpole. This proves that $\mathbf{k}_1$ and $\mathbf{k}_2$ belong to the same Wintgen position, which is $32f \cdot 3m x, x, x$.

Owing to the shape of the asymmetric unit of $IT A$ (which is similar here to that of the representation domain in CDML), the line x, x, x is kinked into the parts Λ and F . One may choose even between F_1 (uni-arm to Λ) or F_2 (completing the plane $C = \Gamma NP$). The latter transformation is performed by applying the symmetry operation $3^- x, x, x$ for $F \rightarrow F_2$.

Remark. The uni-arm description unmasks those $\mathbf{k}$ vectors (e.g. those of line F) which lie on the boundary of the Brillouin zone but belong to a Wintgen position which also contains inner $\mathbf{k}$ vectors (line Λ). Such $\mathbf{k}$ vectors cannot give rise to little-group representations obtained from projective representations of the little co-group $\bar{\mathcal{G}}^{\mathbf{k}}$.

(b) In Table 1.5.5.1 for $m\bar{3}ml$, see also Fig. 1.5.5.1, the $\mathbf{k}$ -vector planes $B = HNP$, $C = \Gamma NP$ and $J = \Gamma HP$ of CDML belong to the same Wintgen position $96k \cdot m$. In the asymmetric unit of $IT A$ (as in the representation domain of CDML) the plane x, x, z is kinked into parts belonging to different arms of the star of $\mathbf{k}$. Transforming, e.g., B and J to the plane of C by $2 \frac{1}{4}, y, \frac{1}{4} (B \rightarrow PN_1H_1)$ and $3^- x, x, x (J \rightarrow \Gamma PH_1)$, one obtains a complete plane (ΓNN_1H_1 for C, B and J) as a uni-arm description of the Wintgen position $96k \cdot m$. This plane protrudes from the body of the asymmetric unit like a wing.

Remark. One should avoid the term *equivalent* for the relation between Λ and F or between B, C and J as it is used by Stokes *et al.* (1993). BC, p. 95 give the definition: 'Two $\mathbf{k}$ vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are equivalent if $\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{K}$, where $\mathbf{K} \in \mathbf{L}^*$ '. One can also express this by saying: 'Two $\mathbf{k}$ vectors are equivalent if they differ by a vector $\mathbf{K}$ of the (reciprocal) lattice.' We prefer to extend this equivalence by saying: 'Two $\mathbf{k}$ vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are equivalent if and only if they belong to the same orbit of $\mathbf{k}$ ', i.e. if there is a matrix part W and a vector $\mathbf{K} \in \mathbf{L}^*$ belonging to $\mathcal{G}^*$ such that $\mathbf{k}_2 = W\mathbf{k}_1 + \mathbf{K}$, see equation (1.5.3.13). Alternatively, this can be expressed as: 'Two $\mathbf{k}$ vectors are equivalent if and only if they belong to the same or to translationally equivalent stars of $\mathbf{k}$.' The $\mathbf{k}$ vectors of Λ and F or of B, C and J are not even equivalent under this broader definition, see Davies & Dirl (1987). If the representatives of the $\mathbf{k}$ -vector stars are chosen uni-arm, as in the examples, their non-equivalence is evident.

(2) In general two trends can be observed:

(a) The lower the symmetry of the crystal system, the more irreps of CDML, recognized by different letters, belong to the same Wintgen position. This trend is due to the splitting of lines and planes into pieces because of the more and more complicated shape of the Brillouin zone. Faces and lines on the surface of the Brillouin zone may appear or disappear depending on the lattice parameters, causing different descriptions of Wintgen positions. This does not happen in unit cells or their asymmetric units; see Sections 1.5.4.1 and 1.5.4.2.

Examples:

(i) The boundary conditions (parameter ranges) for the special lines and planes of the asymmetric unit and for general $\mathbf{k}$ vectors of

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table 1.5.5.2. The **k**-vector types for the space groups $Im\bar{3}$ and $Ia\bar{3}$

Comparison of the **k**-vector labels and parameters of CDML with the Wyckoff positions of $IT A$ for $Fm\bar{3}$ (T_h^3), isomorphic to the reciprocal-space group $\mathcal{G}^*$ of $m\bar{3}I$. The parameter ranges in $Fm\bar{3}$ are obtained by extending those of $Fm\bar{3}m$ such that each star of **k** is represented exactly once. The **k**-vector types of $(Fm\bar{3}m)^*$, see Table 1.5.5.1, are also listed. The sign $\sim$ means symmetrically equivalent. Lines in parentheses are not special lines but belong to special planes. As in Table 1.5.5.1, the coordinates x, y, z of $IT A$ are related to the **k**-vector coefficients of CDML by $x = 1/2(k_2 + k_3)$, $y = 1/2(k_1 + k_3)$, $z = 1/2(k_1 + k_2)$.

k-vector label, CDML		Wyckoff position, $IT A$	Parameters (see Fig. 1.5.5.2b), $IT A$
$(Fm\bar{3}m)^*$	$(Fm\bar{3})^*$	$Fm\bar{3}$	
Γ	Γ	$4 a m\bar{3}$.	0, 0, 0
H	H	$4 b m\bar{3}$.	$\frac{1}{2}, 0, 0$
P	P	$8 c 23$.	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$
N	N	$24 d 2/m..$	$\frac{1}{4}, \frac{1}{4}, 0$
Δ	Δ	$24 e mm2..$	$x, 0, 0: 0 < x < \frac{1}{2}$
Λ	Λ	$32 f .3$.	$x, x, x: 0 < x < \frac{1}{4}$
F	F	$32 f .3$.	$\frac{1}{2} - x, x, x: 0 < x < \frac{1}{4}$
$\sim F_1$	$\sim F_1$	$32 f .3$.	$x, x, x: \frac{1}{4} < x < \frac{1}{2}$
$\Lambda \cup F_1 \sim \Gamma H_2 \setminus P$	$\Lambda \cup F_1 \sim \Gamma H_2 \setminus P$	$32 f .3$.	$x, x, x: 0 < x < \frac{1}{2}$ with $x \neq \frac{1}{4}$
D	D	$48 g 2..$	$\frac{1}{4}, \frac{1}{4}, z: 0 < z < \frac{1}{4}$
Σ	Σ	$48 h m..$	$x, y, 0: 0 < x = y < \frac{1}{4}$
G	G	$48 h m..$	$x, y, 0: 0 < y = \frac{1}{2} - x < \frac{1}{4}$
A	A	$48 h m..$	$x, y, 0: 0 < y < x < \frac{1}{2} - y$
	$AA - \alpha, \alpha, \beta$	$48 h m..$	$x, y, 0: 0 < \frac{1}{2} - x < y < x$
	$A \cup AA \cup \Sigma \cup G$	$48 h m..$	$x, y, 0: 0 < y < x < \frac{1}{2} \cup$ $\cup 0 < y = x < \frac{1}{4}$
C	$\subset GP$	$96 i 1$	$x, y, z: 0 < z < x = y < \frac{1}{4}$
B	$\subset GP$	$96 i 1$	$x, y, z: 0 < z < y = \frac{1}{2} - x < \frac{1}{4}$
J	$\subset GP$	$96 i 1$	$x, y, z: 0 < z = y < x < \frac{1}{2} - y$
GP	$\subset GP$	$96 i 1$	$x, y, z: 0 < z < y < x < \frac{1}{2} - y$
	$\subset GP$	$96 i 1$	$x, y, z: 0 < z < \frac{1}{2} - x < y < x$
	GP	$96 i 1$	$x, y, z: 0 < z \leq y \leq x \leq \frac{1}{2} - y \cup$ $\cup x, y, z: 0 < z < \frac{1}{2} - x < y < x$

the reciprocal-space group $(F4/mmm)^*$ (setting $I4/mmm$) are listed in Table 1.5.5.3. The main condition of the representation domain is that of the boundary plane $x, y, z = \{1 + (c/a)^2[1 - 2(x + y)]\}/4$, which for $c/a < 1$ forms the triangle Z_0Z_1P (Figs. 1.5.5.3a,b) but for $c/a > 1$ forms the pentagon S_1RPGS (Figs. 1.5.5.3c,d). The inner points of these boundary planes are points of the general position GP with the exception of the line $Q = x, \frac{1}{2} - x, \frac{1}{4}$, which is a twofold rotation axis. The boundary conditions for the representation domain depend on c/a ; they are much more complicated than those for the asymmetric unit (for this the boundary condition is simply $x, y, \frac{1}{4}$).

(ii) In the reciprocal-space group $(Im\bar{3})^*$, see Figs. 1.5.5.4(a) to (c), the lines Λ and Q belong to Wintgen position $2 a mm2$; G and H belong to $2 b mm2$; Δ and R, Σ and U, A and C , and B and D belong to the general position GP . The decisive boundary plane is $x/a^2 + y/b^2 + z/c^2 = d^2/4$, where $d^2 = 1/a^2 + 1/b^2 + 1/c^2$, or $xa^{*2} + yb^{*2} + zc^{*2} = d^{*2}/4$, where $d^{*2} = a^{*2} + b^{*2} + c^{*2}$. There is no relation of the lattice constants for which all the above-mentioned lines are realized on the surface of the representation domain simultaneously, either two or three of them do not appear and the length of the others depends on the boundary plane; see Table 1.5.5.4 and Figs. 1.5.5.4(a) to (c). Again, the boundary conditions for the asymmetric unit are independent of the lattice parameters, all lines mentioned above are present and their parameters run from 0 to $\frac{1}{2}$.

(b) The more symmetry a space group has lost compared to its holosymmetric space group, the more letters of irreps are introduced, cf. CDML. In most cases these additional labels can be easily avoided by *extension of the parameter range* in the **k**-vector space of the holosymmetric group.

Example. Extension of the plane $A = \Gamma NH$, Wintgen position $96 j m..$ of $(Fm\bar{3}m)^*$, to $A \cup AA = \Gamma_1 NH$ in the reciprocal-space group $(Fm\bar{3})^*$ of the arithmetic crystal class $m\bar{3}I$, cf. Tables 1.5.5.1 and 1.5.5.2 and Fig. 1.5.5.2. Both planes, A and AA , belong to Wintgen position $48 h m..$ of $(Fm\bar{3})^*$.

In addition, in the transition from a holosymmetric space group $\mathcal{H}$ to a non-holosymmetric space group $\mathcal{G}$, the order of the little co-group $\bar{\mathcal{H}}^k$ of a special **k** vector of $\mathcal{H}^*$ may be reduced in $\bar{\mathcal{G}}^k$. Such a **k** vector may then be incorporated into a more general Wintgen position of $\bar{\mathcal{G}}^k$ and described by an extension of the parameter range.

Example. Plane $\Gamma H\Gamma_1 = x, y, 0$: In $(Fm\bar{3}m)^*$, see Fig. 1.5.5.1, all points (Γ, H, N) and lines (Δ, Σ, G) of the boundary of the asymmetric unit are special. In $(Fm\bar{3})^*$, see Fig. 1.5.5.2, the lines Δ and $H\Gamma_1 \sim \Delta$ ($\sim$ means equivalent) are special but Σ, G and $N\Gamma_1 \sim N\Gamma = \Sigma$ belong to the plane $(A \cup AA)$. The free parameter range on the line $\Gamma\Gamma_1$ is $\frac{1}{2}$ of the full parameter range of $\Gamma\Gamma_1$, see Section 1.5.5.3. Therefore, the parameter ranges of $(A \cup AA \cup G \cup \Sigma)$ in $x, y, 0$ can be taken as: $0 < y < x < \frac{1}{2}$ for $A \cup AA \cup G$ and (for Σ) $0 < y = x < \frac{1}{4}$.

1.5. CLASSIFICATION OF SPACE-GROUP REPRESENTATIONS

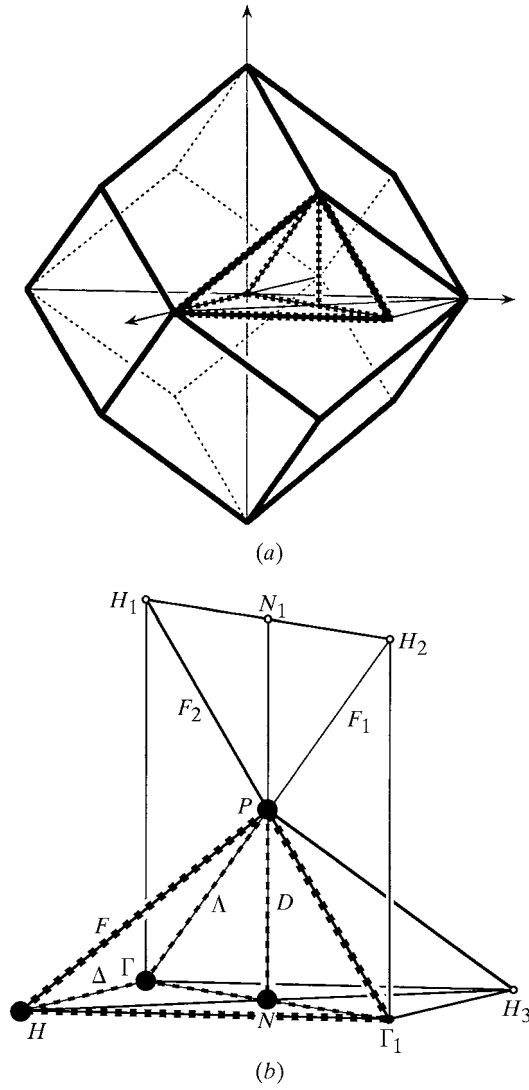


Fig. 1.5.5.2. Symmorphic space group $F\bar{3}m$ (isomorphic to the reciprocal space group $\mathcal{G}^*$ of $m\bar{3}l$). (a) The asymmetric unit (thick dashed edges) half imbedded in and half protruding from the Brillouin zone, which is a cubic rhombododecahedron (as in Fig. 1.5.5.1). (b) The asymmetric unit $\Gamma HT_1 P$, IT A, p. 610. The representation domain of CDML is $\Gamma HH_3 P$. Both bodies have ΓHNP in common; $HT_1 NP$ is mapped onto $\Gamma NH_3 P$ by a twofold rotation around NP . The representation domain as the asymmetric unit would be the better choice because it is congruent to the asymmetric unit of IT A and is fully imbedded in the Brillouin zone. Coordinates of the points: $\Gamma = 0, 0, 0 \sim \Gamma_1 = \frac{1}{2}, \frac{1}{2}, 0$; $P = \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $H = \frac{1}{2}, 0, 0 \sim H_1 = 0, 0, \frac{1}{2} \sim H_2 = \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \sim H_3 = 0, \frac{1}{2}, 0$; $N = \frac{1}{4}, \frac{1}{4}, 0 \sim N_1 = \frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; the sign $\sim$ means symmetrically equivalent. Lines: $\Lambda = \Gamma P = x, x, x \sim P\Gamma_1 = x, x, \frac{1}{2} - x$; $F = HP = \frac{1}{2} - x, x, x \sim F_1 = PH_2 = x, x, x \sim F_2 = PH_1 = x, x, \frac{1}{2} - x$; $\Delta = \Gamma H = x, 0, 0 \sim HT_1 = \frac{1}{2}, y, 0$; $D = PN = \frac{1}{4}, \frac{1}{4}, z$. ($G = NH = x, \frac{1}{2} - x, 0$ and $\Sigma = \Gamma N = x, x, 0 \sim N\Gamma_1 = x, x, 0$ are not special lines.) Planes: $A = \Gamma HN = x, y, 0$; $AA = \Gamma_1 NH = x, y, 0$; $B = HNP = x, \frac{1}{2} - x, z \sim PN_1 H_1 = x, x, z$; $C = \Gamma NP = x, x, z$; $J = \Gamma HP = x, y, y \sim \Gamma PH_1 = x, x, z$. (The boundary planes B, C and J are parts of the general position GP .) Large black circles: special points of the asymmetric unit; small black circle: special point $\Gamma_1 \sim \Gamma$; small open circles: other special points; dashed lines: edges and special line D of the asymmetric unit. The edge $\Gamma\Gamma_1$ is not a special line but is part of the boundary plane $A \cup AA$. For the parameter ranges see Table 1.5.5.2.

Is it easy to recognize those letters of CDML which belong to the same Wintgen position? In $(I4/mmm)^*$, the lines Λ and V (V exists for $c/a < 1$ only) are parallel, as are Σ and F , but the lines Y and U are not (F and U exist for $c/a > 1$ only). The planes $C = x, y, 0$ and $D = x, y, \frac{1}{2}$ (D for $c/a > 1$ only) are parallel but the planes $A = 0, y, z$ and $E = x, \frac{1}{2}, z$ are not. Nevertheless, each of these pairs belongs to one Wintgen position, i.e. describes one type of $\mathbf{k}$ vector.

1.5.5.3. Parameter ranges

For the uni-arm description of a Wintgen position it is easy to check whether the parameter ranges for the general or special constituents of the representation domain or asymmetric unit have been stated correctly. For this purpose one may define the *field* of $\mathbf{k}$ as the parameter space (point, line, plane or space) of a Wintgen position. For the check, one determines that part of the field of $\mathbf{k}$ which is inside the unit cell. The order of the little co-group $\bar{\mathcal{G}}^k$ ($\bar{\mathcal{G}}^k$ represents those operations which leave the field of $\mathbf{k}$ fixed pointwise) is divided by the order of the stabilizer [which is the set of all symmetry operations (*modulo* integer translations) that leave the field *invariant as a whole*]. The result gives the independent fraction of the above-determined volume of the unit cell or the area of the plane or length of the line.

If the description is not uni-arm, the uni-arm parameter range will be split into the parameter ranges of the different arms. The parameter ranges of the different arms are not necessarily equal; see the second of the following examples.

Examples:

(1) Line $\Lambda \cup F_1$: In $(Fm\bar{3}m)^*$ the line x, x, x has stabilizer $\bar{3}m$ and little co-group $\bar{\mathcal{G}}^k = 3m$. Therefore, the divisor is 2 and x runs from 0 to $\frac{1}{2}$ in $0 < x < 1$.

(2) Plane $B \cup C \cup J$: In $(Fm\bar{3}m)^*$, the stabilizer of x, x, z is generated by $m.mm$ and the centring translation $t(\frac{1}{2}, \frac{1}{2}, 0)$ modulo integer translations ($\text{mod } \mathbf{T}_{\text{int}}$). They generate a group of order 16; $\bar{\mathcal{G}}^k$ is m of order 2. The fraction of the plane is $\frac{2}{16} = \frac{1}{8}$ of the area $2^{1/2}a^2$, as expressed by the parameter ranges $0 < x < \frac{1}{4}$, $0 < z < \frac{1}{2}$. There are six arms of the star of x, x, z : x, x, z ; $\bar{x}, x, z$; $x, y, \bar{x}$; x, y, y ; $x, \bar{y}, y$. Three of them are represented in the boundary of the representation domain: $B = HNP$, $C = \Gamma NP$ and $J = \Gamma HP$; see Fig. 1.5.5.1. The areas of their parameter ranges are $\frac{1}{32}$, $\frac{1}{32}$ and $\frac{1}{16}$, respectively; the sum is $\frac{1}{8}$.

The same result holds for $(Fm\bar{3})^*$: the stabilizer is generated by $2/m..$ and $t(\frac{1}{2}, \frac{1}{2}, 0) \text{ mod } \mathbf{T}_{\text{int}}$ and is of order 8, $|\bar{\mathcal{G}}^k| = |\{1\}| = 1$, the quotient is again $\frac{1}{8}$, the parameter range is the same as for $(Fm\bar{3}m)^*$. The planes $HT_1 P$ and $NT_1 P$ are equivalent to $J = \Gamma HP$ and $C = \Gamma NP$, and do not contribute to the parameter ranges.

(3) Plane $x, y, 0$: In $(Fm\bar{3}m)^*$ the stabilizer of plane A is generated by $4/mmm$ and $t(\frac{1}{2}, \frac{1}{2}, 0)$, order 32, $\bar{\mathcal{G}}^k$ (site-symmetry group) $m..$, order 2. Consequently, ΓHN is $\frac{1}{16}$ of the unit square a^2 : $0 < y < x < \frac{1}{2} - y$. In $(Fm\bar{3})^*$, the stabilizer of $A \cup AA$ is $mmm.$ plus $t(\frac{1}{2}, \frac{1}{2}, 0)$, order 16, with the same group $\bar{\mathcal{G}}^k$. Therefore, ΓHT_1 is $\frac{1}{8}$ of the unit square a^2 in $(Fm\bar{3})^*$: $0 < y < x < \frac{1}{2}$.

(4) Line $x, x, 0$: In $(Fm\bar{3}m)^*$ the stabilizer is generated by $m.mm$ and $t(\frac{1}{2}, \frac{1}{2}, 0) \text{ mod } \mathbf{T}_{\text{int}}$, order 16, $\bar{\mathcal{G}}^k$ is $m.2m$ of order 4. The divisor is 4 and thus $0 < x < \frac{1}{4}$. In $(Fm\bar{3})^*$ the stabilizer is generated by $2/m..$ and $t(\frac{1}{2}, \frac{1}{2}, 0) \text{ mod } \mathbf{T}_{\text{int}}$, order 8, and $\bar{\mathcal{G}}^k = m..$, order 2; the divisor is 4 again and $0 < x < \frac{1}{4}$ is restricted to the same range.†

Data for the independent parameter ranges are essential to make sure that exactly one $\mathbf{k}$ vector per orbit is represented in the representation domain Φ or in the asymmetric unit. Such data are

† Boyle & Kennedy (1988) propose general rules for the parameter ranges of $\mathbf{k}$ -vector coefficients referred to a primitive basis. The ranges listed in Tables 1.5.5.1 to 1.5.5.4 possibly do not follow these rules.

1. GENERAL RELATIONSHIPS AND TECHNIQUES

Table 1.5.5.3. The **k**-vector types for the space groups $I4/mmm$, $I4/mcm$, $I4_1/amd$ and $I4_1/acd$

Comparison of the **k**-vector labels and parameters of CDML with the Wyckoff positions of $IT A$ for $I4/mmm$ (D_{4h}^{17}), isomorphic to the reciprocal-space group $\mathcal{G}^*$ of $4/mmm$. For the asymmetric unit, see Fig. 1.5.5.3. Two ratios of the lattice constants are distinguished for the representation domains of CDML: $a > c$ and $a < c$, see Figs. 1.5.5.3(a, b) and (c, d). The sign $\sim$ means symmetrically equivalent. The parameter ranges for the planes and the general position GP refer to the asymmetric unit. The coordinates x, y, z of $IT A$ are related to the **k**-vector coefficients of CDML by $x = 1/2(-k_1 + k_2)$, $y = 1/2(k_1 + k_2 + 2k_3)$, $z = 1/2(k_1 + k_2)$.

k-vector labels, CDML		Wyckoff position, $IT A$	Parameters (see Fig. 1.5.5.3), $IT A$	
$a > c$	$a < c$		$a > c$	$a < c^\dagger$
$\Gamma 0, 0, 0$	$\Gamma 0, 0, 0$	$2 a 4/mmm$	$0, 0, 0$	
$M -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$M \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$	$2 b 4/mmm$	$\frac{1}{2}, \frac{1}{2}, 0$	$0, 0, \frac{1}{2}$
$X 0, 0, \frac{1}{2}$	$X 0, 0, \frac{1}{2}$	$4 c mmm.$	$0, \frac{1}{2}, 0$	
$P \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$P \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$4 d \bar{4}m2$	$0, \frac{1}{2}, \frac{1}{4}$	
$N 0, \frac{1}{2}, 0$	$N 0, \frac{1}{2}, 0$	$8 f ..2/m$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	
$\Lambda \alpha, \alpha, -\alpha$ $V -\frac{1}{2} + \alpha, \frac{1}{2} + \alpha, \frac{1}{2} - \alpha$	$\Lambda \alpha, \alpha, -\alpha$ —	$4 e 4mm$ $4 e 4mm$	$0, 0, z: 0 < z \leq z_0^\ddagger$ $\frac{1}{2}, \frac{1}{2}, z: 0 < z < z_1 = \frac{1}{2} - z_0$	$0 < z < \frac{1}{2}$ —
$W \alpha, \alpha, \frac{1}{2} - \alpha$	$W \alpha, \alpha, \frac{1}{2} - \alpha$	$8 g 2mm.$	$0, \frac{1}{2}, z: 0 < z < \frac{1}{4}$	
$\Sigma -\alpha, \alpha, \alpha$ —	$\Sigma -\alpha, \alpha, \alpha$ $F \frac{1}{2} - \alpha, \frac{1}{2} + \alpha, -\frac{1}{2} + \alpha$	$8 h m.2m$ $8 h m.2m$	$x, x, 0: 0 < x < \frac{1}{2}$ —	$0 < x \leq s_1$ $x, x, \frac{1}{2}: 0 < x < s = \frac{1}{2} - s_1$
$\Delta 0, 0, \alpha$	$\Delta 0, 0, \alpha$	$8 i m2m.$	$0, y, 0: 0 < y < \frac{1}{2}$	
$Y -\alpha, \alpha, \frac{1}{2}$ —	$Y -\alpha, \alpha, \frac{1}{2}$ $U \frac{1}{2}, \frac{1}{2}, -\frac{1}{2} + \alpha$	$8 j m2m.$ $8 j m2m.$	$x, \frac{1}{2}, 0: 0 < x < \frac{1}{2}$ —	$0 < x \leq r$ $0, y, \frac{1}{2}: 0 < y < g = \frac{1}{2} - r$
$Q \frac{1}{4} - \alpha, \frac{1}{4} + \alpha, \frac{1}{4} - \alpha$	$Q \frac{1}{4} - \alpha, \frac{1}{4} + \alpha, \frac{1}{4} - \alpha$	$16 k ..2$	$x, \frac{1}{2} - x, \frac{1}{4}: 0 < x < \frac{1}{4}$	
$C -\alpha, \alpha, \beta$ —	$C -\alpha, \alpha, \beta$ $D \frac{1}{2} - \alpha, \frac{1}{2} + \alpha, -\frac{1}{2} + \beta$	$16 l m..$ $16 l m..$	$x, y, 0: 0 < x < y < \frac{1}{2}\S$ —	— $x, y, \frac{1}{2}$
$B \alpha, \beta, -\alpha$	$B \alpha, \beta, -\alpha$	$16 m ..m$	$x, x, z: 0 < x < \frac{1}{2}, 0 < z < \frac{1}{4} \cup 0 < x < \frac{1}{4}, z = \frac{1}{4}$	
$A \alpha, \alpha, \beta$ $E \alpha - \beta, \alpha + \beta, \frac{1}{2} - \alpha$	$A \alpha, \alpha, \beta$ $E \alpha - \beta, \alpha + \beta, \frac{1}{2} - \alpha$	$16 n .m.$ $16 n .m.$	$0, y, z: 0 < y < \frac{1}{2}, 0 < z < \frac{1}{2}\P$ $x, \frac{1}{2}, z: \text{transferred to } A = 0, y, z$	
$GP \alpha, \beta, \gamma$	$GP \alpha, \beta, \gamma$	$32 o 1$	$x, y, z: 0 < x < y < \frac{1}{2}, 0 < z < \frac{1}{4} \cup 0 < x < y < \frac{1}{2} - x, z = \frac{1}{4}$	

† If the parameter range is different from that for $a > c$.

‡ z_0 is a coordinate of point Z_0 etc., see Figs. 1.5.5.3(b), (d).

§ For $a < c$, the parameter range includes the equivalent of $D = MSG$.

¶ The parameter range includes A and the equivalent of E .

much more difficult to calculate for the representation domains and cannot be found in the cited tables of irreps.

In the way just described the *inner* parameter range can be fixed. In addition, the *boundaries* of the parameter range must be determined:

(5) Line x, x, x : In $(Fm\bar{3}m)^*$ and $(Fm\bar{3})^*$ the points $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) are special points; the parameter ranges are open: $0 < x < \frac{1}{4}, \frac{1}{4} < x < \frac{1}{2}$.

(6) Plane x, x, z : In $(Fm\bar{3}m)^*$ all corners Γ, N, N_1, H_1 and all edges are either special points or special lines. Therefore, the parameter ranges are open: $x, x, z: 0 < x < \frac{1}{4}, 0 < z < \frac{1}{2}$, where the lines $x, x, x: 0 \leq x \leq \frac{1}{4}$ and $x, x, \frac{1}{2} - x: 0 \leq x \leq \frac{1}{4}$ are special lines and thus excepted.

(7) Plane $x, y, 0$: In both $(Fm\bar{3}m)^*$ and $(Fm\bar{3})^*$, $0 < x$ and $0 < y$ holds. The **k** vectors of line $x, x, 0$ have little co-groups of higher order and belong to another Wintgen position in the representation domain (or asymmetric unit) of $(Fm\bar{3}m)^*$. Therefore, $x, y, 0$ is open at its boundary $x, x, 0$ in the range $0 < x < \frac{1}{4}$. In the asymmetric unit

of $(Fm\bar{3})^*$ the line $x, x, 0: 0 < x < \frac{1}{4}$ belongs to the plane, in this range the boundary of plane A is closed. The other range $x, x, 0: \frac{1}{4} < x < \frac{1}{2}$ is equivalent to the range $0 < x < \frac{1}{4}$ and thus does not belong to the asymmetric unit; here the boundary of AA is open.

1.5.5.4. Conclusions

As has been shown, $IT A$ can serve as a basis for the classification of irreps of space groups by using the concept of reciprocal-space groups:

(a) The asymmetric units of $IT A$ are minimal domains of **k** space which are in many cases simpler than the representation domains of the Brillouin zones. However, the asymmetric units of $IT A$ are not designed particularly for this use, cf. Section 1.5.4.2. Therefore, it should be checked whether they are the optimal choice for this purpose. Otherwise, other asymmetric units could easily be introduced.

1.5. CLASSIFICATION OF SPACE-GROUP REPRESENTATIONS

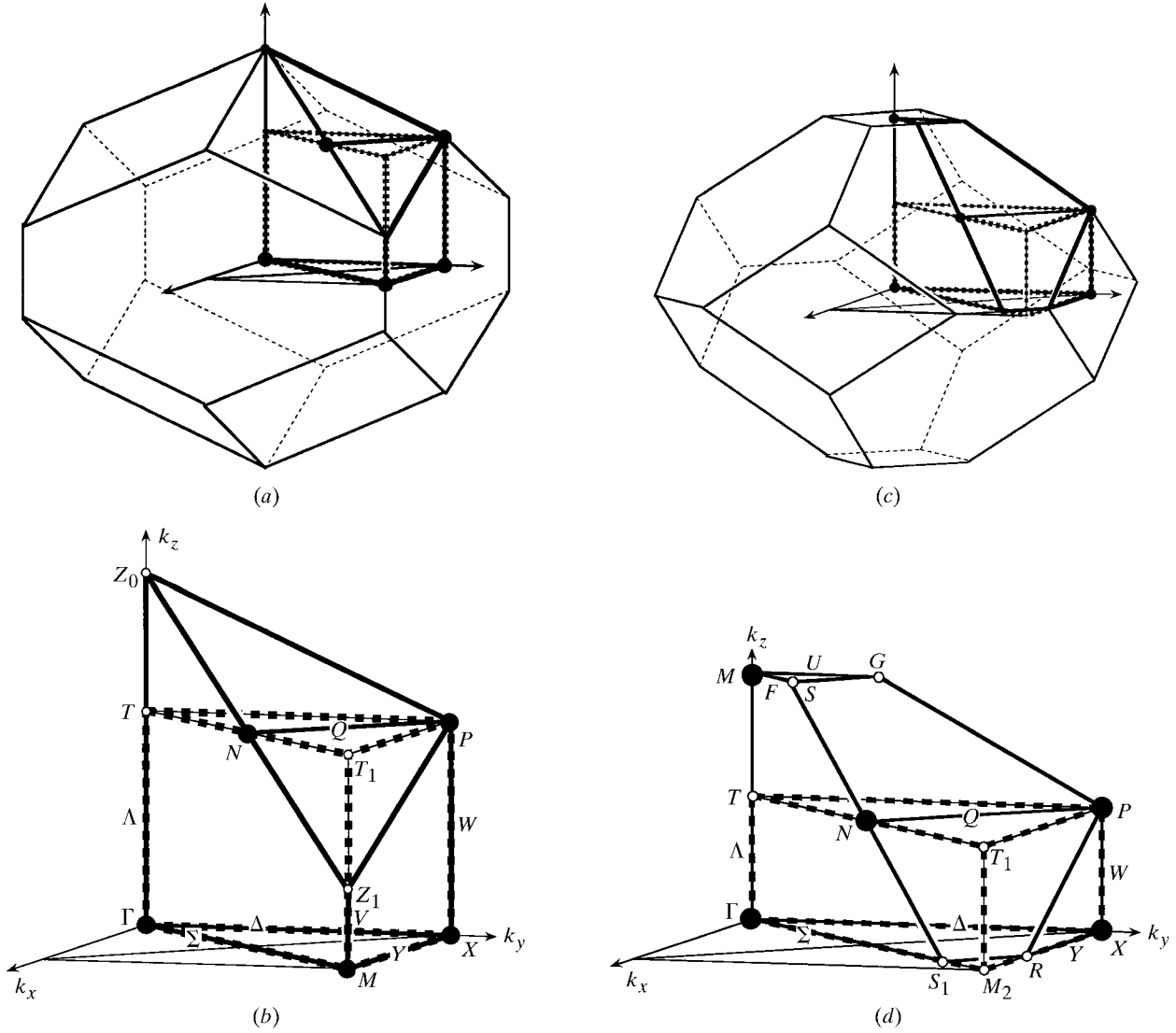


Fig. 1.5.5.3. (a), (b). Symmorphic space group $I4/mmm$ (isomorphic to the reciprocal-space group $\mathcal{G}^*$ of $4/mmmI$). Diagrams for $a > c$, i.e. $c^* > a^*$. In the figures $a = 1.25c$, i.e. $c^* = 1.25a^*$. (a) Representation domain (thick lines) and asymmetric unit (thick dashed lines, partly protruding) imbedded in the Brillouin zone, which is a tetragonal elongated rhombododecahedron. (b) Representation domain ΓMXZ_1PZ_0 and asymmetric unit $\Gamma MXTT_1P$ of $I4/mmm$, IT A, p. 468. The part $\Gamma MXTNZ_1P$ is common to both bodies; the part $TNPZ_0$ is equivalent to the part NZ_1PT_1 by a twofold rotation around the axis $Q = NP$. Coordinates of the points: $\Gamma = 0, 0, 0$; $X = 0, \frac{1}{2}, 0$; $M = \frac{1}{2}, \frac{1}{2}, 0$; $P = 0, \frac{1}{2}, \frac{1}{4}$; $N = \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $T = 0, 0, \frac{1}{4} \sim T_1 = \frac{1}{2}, \frac{1}{2}, \frac{1}{4}$; $Z_0 = 0, 0, z_0 \sim Z_1 = \frac{1}{2}, \frac{1}{2}, z_1$ with $z_0 = [1 + (c/a)^2]/4$; $z_1 = \frac{1}{2} - z_0$; the sign $\sim$ means symmetrically equivalent. Lines: $\Lambda = \Gamma Z_0 = 0, 0, z$; $V = Z_1M = \frac{1}{2}, \frac{1}{2}, z$; $W = XP = 0, \frac{1}{2}, z$; $\Sigma = \Gamma M = x, x, 0$; $\Delta = \Gamma X = 0, y, 0$; $Y = XM = x, \frac{1}{2}, 0$; $Q = PN = x, \frac{1}{2} - x, \frac{1}{4}$. The lines Z_0Z_1 , Z_1P and PZ_0 have no special symmetry but belong to special planes. Planes: $C = \Gamma MX = x, y, 0$; $B = \Gamma Z_0Z_1M = x, x, z$; $A = \Gamma XPZ_0 = 0, y, z$; $E = MXPZ_1 = x, \frac{1}{2}, z$. The plane Z_0Z_1P belongs to the general position GP . Large black circles: special points belonging to the representation domain; small open circles: $T \sim T_1$ and $Z_0 \sim Z_1$ belonging to special lines; thick lines: edges of the representation domain and special line $Q = NP$; dashed lines: edges of the asymmetric unit. For the parameter ranges see Table 1.5.5.3.

(c), (d). Symmorphic space group $I4/mmm$ (isomorphic to the reciprocal-space group $\mathcal{G}^*$ of $4/mmmI$). Diagrams for $c > a$, i.e. $a^* > c^*$. In the figures $c = 1.25a$, i.e. $a^* = 1.25c^*$. (c) Representation domain (thick lines) and asymmetric unit (dashed lines, partly protruding) imbedded in the Brillouin zone, which is a tetragonal cuboctahedron. (d) Representation domain $\Gamma S_1RXPMSG$ and asymmetric unit ΓM_2XTT_1P of $I4/mmm$, IT A, p. 468. The part ΓS_1RXTNP is common to both bodies; the part $TNPMSG$ is equivalent to the part $T_1NPM_2S_1R$ by a twofold rotation around the axis $Q = NP$. Coordinates of the points: $\Gamma = 0, 0, 0$; $X = 0, \frac{1}{2}, 0$; $N = \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $M = 0, 0, \frac{1}{2} \sim M_2 = \frac{1}{2}, \frac{1}{2}, 0$; $T = 0, 0, \frac{1}{4} \sim T_1 = \frac{1}{2}, \frac{1}{2}, \frac{1}{4}$; $P = 0, \frac{1}{2}, \frac{1}{4}$; $S = s, s, \frac{1}{2} \sim S_1 = s_1, s_1, 0$ with $s = [1 - (a/c)^2]/4$; $s_1 = \frac{1}{2} - s$; $R = r, \frac{1}{2}, 0 \sim G = 0, g, \frac{1}{2}$ with $r = (a/c)^2/2$; $g = \frac{1}{2} - r$; the sign $\sim$ means symmetrically equivalent. Lines: $\Lambda = \Gamma M = 0, 0, z$; $W = XP = 0, \frac{1}{2}, z$; $\Sigma = \Gamma S_1 = x, x, 0$; $F = MS = x, x, \frac{1}{2}$; $\Delta = \Gamma X = 0, y, 0$; $Y = XR = x, \frac{1}{2}, 0$; $U = MG = 0, y, \frac{1}{2}$; $Q = PN = x, \frac{1}{2} - x, \frac{1}{4}$. The lines $GS \sim S_1R$, $SN \sim NS_1$ and $GP \sim PR$ have no special symmetry but belong to special planes. Planes: $C = \Gamma S_1RX = x, y, 0$; $D = MSG = x, y, \frac{1}{2}$; $B = \Gamma S_1SM = x, x, z$; $A = \Gamma XPGM = 0, y, z$; $E = RXP = x, \frac{1}{2}, z$. The plane S_1RPGS belongs to the general position GP . Large black circles: special points belonging to the representation domain; small open circles: $M_2 \sim M$; the points $T \sim T_1$, $S \sim S_1$ and $G \sim R$ belong to special lines; thick lines: edges of the representation domain and special line $Q = NP$; dashed lines: edges of the asymmetric unit. For the parameter ranges see Table 1.5.5.3.

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Table 1.5.5.4. The **k**-vector types for the space groups *Fmm2* and *Fdd2*

Comparison of the **k**-vector labels and parameters of CDML with the Wyckoff positions of *IT A* for *Imm2* (C_{2h}^{20}), isomorphic to the reciprocal-space group $\mathcal{G}^*$ of *mm2F*. For the asymmetric unit see Fig. 1.5.5.4. Four ratios of the lattice constants are distinguished in CDML, Fig. 3.6 for the representation domains: (a) $a^{*2} < b^{*2} + c^{*2}$, $b^{*2} < c^{*2} + a^{*2}$ and $c^{*2} < a^{*2} + b^{*2}$ (see Fig. 1.5.5.4a); (b) $c^{*2} > a^{*2} + b^{*2}$ (see Fig. 1.5.5.4b); (c) $b^{*2} > c^{*2} + a^{*2}$ [not displayed because essentially the same as (d)]; (d) $a^{*2} > b^{*2} + c^{*2}$ (see Fig. 1.5.5.4c). The vertices of the Brillouin zones of Fig. 3.6(a)–(d) with a variable coordinate are not designated in CDML. In Figs. 1.5.5.4 (a), (b) and (c) they are denoted as follows: the end point of the line Λ is Λ_0 , of line Δ is Δ_0 , of line Σ is Σ_0 , of line A is A_0 etc. The variable coordinate of the end point is λ_0 , δ_0 , σ_0 , a_0 etc., respectively. The line A_0B_0 is called *ab* etc. The plane (111) is called φ . It has the equation in the $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ basis $\varphi: a^{*2}x + b^{*2}y + c^{*2}z = d^{*2}/4$ with $d^{*2} = a^{*2} + b^{*2} + c^{*2}$. From this equation one calculates the variable coordinates of the vertices of the Brillouin zone: Λ_0 0,0, λ_0 with $\lambda_0 = d^{*2}/4c^{*2}$; Q_0 $\frac{1}{2}, \frac{1}{2}, q_0$ with $q_0 = \frac{1}{2} - \lambda_0$; Δ_0 0, δ_0 ,0 with $\delta_0 = d^{*2}/4b^{*2}$; R_0 $\frac{1}{2}, r_0, \frac{1}{2}$ with $r_0 = \frac{1}{2} - \delta_0$; Σ_0 $\sigma_0, 0, 0$ with $\sigma_0 = d^{*2}/4a^{*2}$; U_0 $u_0, \frac{1}{2}, \frac{1}{2}$ with $u_0 = \frac{1}{2} - \sigma_0$; A_0 $a_0, 0, \frac{1}{2}$ with $a_0 = \frac{1}{4} + (b^{*2} - c^{*2})/4a^{*2}$; C_0 $c_0, \frac{1}{2}, 0$ with $c_0 = \frac{1}{2} - a_0$; B_0 $0, b_0, \frac{1}{2}$ with $b_0 = \frac{1}{4} + (a^{*2} - c^{*2})/4b^{*2}$; D_0 $\frac{1}{2}, d_0, 0$ with $d_0 = \frac{1}{2} - b_0$; G_0 $\frac{1}{2}, 0, g_0$ with $g_0 = \frac{1}{4} + (b^{*2} - a^{*2})/4c^{*2}$; H_0 $0, \frac{1}{2}, h_0$ with $h_0 = \frac{1}{2} - g_0$. The coordinates x, y, z of *IT A* are related to the **k**-vector coefficients of CDML by $x = 1/2(-k_1 + k_2 + k_3)$, $y = 1/2(k_1 - k_2 + k_3)$, $z = 1/2(k_1 + k_2 - k_3)$. If necessary, a lattice vector has been added or a twofold screw rotation around the axis $\frac{1}{4}, \frac{1}{4}, z$ has been performed in order to shift the range of coordinates to $0 \leq x, y, z \leq \frac{1}{2}$. For example, $-\alpha, -\alpha, 0 \sim 0, 0, -z'$ with $0 < z' < \lambda_0$ is replaced by $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z' = \frac{1}{2}, \frac{1}{2}, z$ with $\frac{1}{2} - \lambda_0 < z < \frac{1}{2}$. (The sign $\sim$ means symmetrically equivalent.)

Wyckoff position: 2 *a* *mm2*. Parameter range in asymmetric unit: 0, 0, z and $\frac{1}{2}, \frac{1}{2}, z$: $0 \leq z < \frac{1}{2}$ (or 0, 0, z : $0 \leq z < 1$).

k-vector label, CDML	Type of Brillouin zone as in:					
	Fig. 1.5.5.4(a)		Fig. 1.5.5.4(b)		Fig. 1.5.5.4(c)	
	CDML	IT A	CDML	IT A	CDML	IT A
Γ	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0	0, 0, 0
Z	$\frac{1}{2}, \frac{1}{2}, 0$	0, 0, $\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 1$	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, 0$	0, 0, $\frac{1}{2}$
Λ	$\alpha, \alpha, 0$	0, 0, z : $0 < z < \frac{1}{2}$	$\alpha, \alpha, 0$	0, 0, z : $0 < z \leq \lambda_0$	$\alpha, \alpha, 0$	0, 0, z : $0 < z < \frac{1}{2}$
LE	$-\alpha, -\alpha, 0$	$\frac{1}{2}, \frac{1}{2}, z$: $0 < z < \frac{1}{2}$	$-\alpha, -\alpha, 0$	$\frac{1}{2}, \frac{1}{2}, z$: $\frac{1}{2} - \lambda_0 < z < \frac{1}{2}$	$-\alpha, -\alpha, 0$	$\frac{1}{2}, \frac{1}{2}, z$: $0 < z < \frac{1}{2}$
Q			$\frac{1}{2} + \alpha, \frac{1}{2} + \alpha, 1$	$\frac{1}{2}, \frac{1}{2}, z$: $0 < z \leq q_0$		
QA			$\frac{1}{2} - \alpha, \frac{1}{2} - \alpha, 1$	0, 0, z : $\frac{1}{2} - q_0 < z < \frac{1}{2}$		

Wyckoff position: 2 *b* *mm2*. Parameter range in asymmetric unit: $\frac{1}{2}, 0, z$ and $0, \frac{1}{2}, z$: $0 \leq z < \frac{1}{2}$ (or uni-arm $\frac{1}{2}, 0, z$: $0 \leq z < 1$).

k-vector label, CDML	Type of Brillouin zone as in:					
	Fig. 1.5.5.4(a)		Fig. 1.5.5.4(b)		Fig. 1.5.5.4(c)	
	CDML	IT A	CDML	IT A	CDML	IT A
T	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, 0$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, 0$	$1, \frac{1}{2}, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{2}$
Y	$\frac{1}{2}, 0, \frac{1}{2}$	0, $\frac{1}{2}, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	0, $\frac{1}{2}, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	0, $\frac{1}{2}, 0$
G	$\alpha, \frac{1}{2} + \alpha, \frac{1}{2}$	$\frac{1}{2}, 0, z$: $0 < z \leq g_0$	$\alpha, \frac{1}{2} + \alpha, \frac{1}{2}$	$\frac{1}{2}, 0, z$: $0 < z \leq g_0$		
GA	$-\alpha, \frac{1}{2} - \alpha, \frac{1}{2}$	0, $\frac{1}{2}, z$: $\frac{1}{2} - g_0 < z < \frac{1}{2}$	$-\alpha, \frac{1}{2} - \alpha, \frac{1}{2}$	0, $\frac{1}{2}, z$: $\frac{1}{2} - g_0 < z < \frac{1}{2}$		
H	$\frac{1}{2} + \alpha, \alpha, \frac{1}{2}$	0, $\frac{1}{2}, z$: $0 < z \leq h_0$	$\frac{1}{2} + \alpha, \alpha, \frac{1}{2}$	0, $\frac{1}{2}, z$: $0 < z \leq h_0$	$\frac{1}{2} + \alpha, \alpha, \frac{1}{2}$	0, $\frac{1}{2}, z$: $0 < z < \frac{1}{2}$
HA	$\frac{1}{2} - \alpha, -\alpha, \frac{1}{2}$	$\frac{1}{2}, 0, z$: $\frac{1}{2} - h_0 < z < \frac{1}{2}$	$\frac{1}{2} - \alpha, -\alpha, \frac{1}{2}$	$\frac{1}{2}, 0, z$: $\frac{1}{2} - h_0 < z < \frac{1}{2}$	$\frac{1}{2} - \alpha, -\alpha, \frac{1}{2}$	$\frac{1}{2}, 0, z$: $0 < z < \frac{1}{2}$

(b) All **k**-vector stars giving rise to the same type of irreps belong to the same Wintgen position. In the tables they are collected in one box and are designated by the same Wintgen letter.

(c) The Wyckoff positions of *IT A*, interpreted as Wintgen positions, provide a complete list of the special **k** vectors in the Brillouin zone; the site symmetry of *IT A* is the little co-group $\bar{\mathcal{G}}^{\mathbf{k}}$ of **k**; the multiplicity per primitive unit cell is the number of arms of the star of **k**.

(d) The Wintgen positions with 0, 1, 2 or 3 variable parameters correspond to special **k**-vector points, **k**-vector lines, **k**-vector planes or to the set of all general **k** vectors, respectively.

(e) The complete set of types of irreps is obtained by considering the irreps of one **k** vector per Wintgen position in the uni-arm description or one star of **k** per Wintgen position otherwise. A complete set of inequivalent irreps of $\mathcal{G}$ is obtained from these irreps by varying the parameters within the asymmetric unit or the representation domain of $\mathcal{G}^*$.

(f) For listing each irrep exactly once, the calculation of the parameter range of **k** is often much simpler in the asymmetric unit of the unit cell than in the representation domain of the Brillouin zone.

(g) The consideration of the basic domain Ω in relation to the representation domain Φ is unnecessary. It may even be misleading, because special **k**-vector subspaces of Ω frequently belong to more general types of **k** vectors in Φ . Space groups $\mathcal{G}$ with non-holohedral point groups can be referred to their reciprocal-space groups $\mathcal{G}^*$ directly without reference to the types of irreps of the corresponding holosymmetric space group. If Ω is used, and if the representation domain Φ is larger than Ω , then in most cases the irreps of Φ can be obtained from those of Ω by extending the parameter ranges of **k**.

(h) The classification by Wintgen letters facilitates the derivation of the correlation tables for the irreps of a group–subgroup chain. The necessary splitting rules for Wyckoff (and thus Wintgen) positions are well known.

In principle, both approaches are equivalent: the *traditional* one by Brillouin zone, basic domain and representation domain, and the *crystallographic* one by unit cell and asymmetric unit of *IT A*. Moreover, it is not difficult to relate one approach to the other, see the figures and Tables 1.5.5.1 to 1.5.5.4. The conclusions show that the *crystallographic* approach for the description of irreps of space groups has several advantages as compared to the *traditional*

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Table 1.5.5.4. The **k**-vector types for the space groups *Fmm2* and *Fdd2* (cont.)

Wyckoff position: 4 *c* .*m*. Parameter range in asymmetric unit: $x, 0, z$ and $x, \frac{1}{2}, z$: $0 < x < \frac{1}{2}$; $0 \leq z < \frac{1}{2}$ (or $x, 0, z$: $0 < x < \frac{1}{2}$; $0 \leq z < 1$).

k-vector label, CDML	Type of Brillouin zone as in:					
	Fig. 1.5.5.4(a)		Fig. 1.5.5.4(b)		Fig. 1.5.5.4(c)	
	CDML	IT A	CDML	IT A	CDML	IT A
Σ	$0, \alpha, \alpha$	$x, 0, 0: 0 < x < \frac{1}{2}$	$0, \alpha, \alpha$	$x, 0, 0: 0 < x < \frac{1}{2}$	$0, \alpha, \alpha$	$x, 0, 0: 0 < x \leq \sigma_0$
<i>U</i>					$1, \frac{1}{2} + \alpha, \frac{1}{2} + \alpha$	$x, 0, 0: \frac{1}{2} - u_0 < x < \frac{1}{2}$
<i>A</i>	$\frac{1}{2}, \frac{1}{2} + \alpha, \alpha$	$x, 0, \frac{1}{2}: 0 < x \leq a_0$			$\frac{1}{2}, \frac{1}{2} + \alpha, \alpha$	$x, 0, \frac{1}{2}: 0 < x \leq a_0$
<i>C</i>	$\frac{1}{2}, \alpha, \frac{1}{2} + \alpha$	$x, 0, \frac{1}{2}: \frac{1}{2} - c_0 < x < \frac{1}{2}$	$\frac{1}{2}, \alpha, \frac{1}{2} + \alpha$	$x, 0, \frac{1}{2}: 0 < x < \frac{1}{2}$	$\frac{1}{2}, \alpha, \frac{1}{2} + \alpha$	$x, 0, \frac{1}{2}: \frac{1}{2} - c_0 < x < \frac{1}{2}$
<i>J</i>	$\alpha, \alpha + \beta, \beta$	$x, 0, z: 0 < x < \frac{1}{2}; 0 < z < \frac{1}{2}, ga^\dagger$	$\alpha, \alpha + \beta, \beta$	$x, 0, z: 0 < x < \frac{1}{2}; 0 < z \leq \lambda g$	$\alpha, \alpha + \beta, \beta$	$x, 0, z: 0 < z < \frac{1}{2}; 0 < x \leq \sigma a$
<i>JA</i>	$-\alpha, -\alpha + \beta, \beta$	$x, \frac{1}{2}, z: 0 < x < \frac{1}{2}; 0, ch < z < \frac{1}{2}$	$-\alpha, -\alpha + \beta, \beta$	$x, \frac{1}{2}, z: 0 < x < \frac{1}{2}; qh < z < \frac{1}{2}$	$-\alpha, -\alpha + \beta, \beta$	$x, \frac{1}{2}, z: 0 < z < \frac{1}{2}; cu < x < \frac{1}{2}$
<i>K</i>	$\frac{1}{2} + \alpha, \alpha + \beta, \frac{1}{2} + \beta$	$x, \frac{1}{2}, z: 0 < x < c_0; 0 < z \leq ch$	$\frac{1}{2} + \alpha, \alpha + \beta, \frac{1}{2} + \beta$	$x, \frac{1}{2}, z: 0 < x < \frac{1}{2}; 0 < z \leq qh$	$\frac{1}{2} + \alpha, \alpha + \beta, \frac{1}{2} + \beta$	$x, \frac{1}{2}, z: 0 < z < \frac{1}{2}; 0 < x \leq cu$
<i>KA</i>	$\frac{1}{2} - \alpha, -\alpha + \beta, \frac{1}{2} + \beta$	$x, 0, z: a_0 = \frac{1}{2} - c_0 < x < \frac{1}{2}; ga \leq z < \frac{1}{2}$	$\frac{1}{2} - \alpha, -\alpha + \beta, \frac{1}{2} + \beta$	$x, 0, z: 0 < x < \frac{1}{2}; g\lambda < z < \frac{1}{2}$	$\frac{1}{2} - \alpha, -\alpha + \beta, \frac{1}{2} + \beta$	$x, 0, z: 0 < z < \frac{1}{2}; a\sigma < x < \frac{1}{2}$

$\dagger 0 < z < \frac{1}{2}$, *ga* means $0 < z < \text{minimum}(\frac{1}{2} \text{ and } ga)$ where *ga* is the line G_0A_0 .

Wyckoff position: 4 *d* *m*... Parameter range in asymmetric unit: $0, y, z$ and $\frac{1}{2}, y, z$: $0 < y < \frac{1}{2}$; $0 \leq z < \frac{1}{2}$ (or uni-arm $0, y, z$: $0 < y < \frac{1}{2}$; $0 \leq z < 1$).

k-vector label, CDML	Type of Brillouin zone as in:					
	Fig. 1.5.5.4(a)		Fig. 1.5.5.4(b)		Fig. 1.5.5.4(c)	
	CDML	IT A	CDML	IT A	CDML	IT A
Δ	$\alpha, 0, \alpha$	$0, y, 0: 0 < y < \frac{1}{2}$	$\alpha, 0, \alpha$	$0, y, 0: 0 < y < \frac{1}{2}$	$\alpha, 0, \alpha$	$0, y, 0: 0 < y < \frac{1}{2}$
<i>B</i>	$\frac{1}{2} + \alpha, \frac{1}{2}, \alpha$	$0, y, \frac{1}{2}: 0 < y \leq b_0$			$\frac{1}{2} + \alpha, \frac{1}{2}, \alpha$	$0, y, \frac{1}{2}: 0 < y < \frac{1}{2}$
<i>D</i>	$\alpha, \frac{1}{2}, \frac{1}{2} + \alpha$	$0, y, \frac{1}{2}: b_0 = \frac{1}{2} - d_0 < y < \frac{1}{2}$	$\alpha, \frac{1}{2}, \frac{1}{2} + \alpha$	$\frac{1}{2}, y, 0: 0 < y < \frac{1}{2}$		
<i>E</i>	$\alpha + \beta, \alpha, \beta$	$0, y, z: 0 < y < \frac{1}{2}; 0 < z < \frac{1}{2}, hb$	$\alpha + \beta, \alpha, \beta$	$0, y, z: 0 < y < \frac{1}{2}; 0 < z \leq h\lambda$	$\alpha + \beta, \alpha, \beta$	$0, y, z: 0 < y, z < \frac{1}{2}$
<i>EA</i>	$-\alpha + \beta, -\alpha, \beta$	$\frac{1}{2}, y, z: 0 < y < \frac{1}{2}; gd, 0 < z < \frac{1}{2}$	$-\alpha + \beta, -\alpha, \beta$	$\frac{1}{2}, y, z: 0 < y < \frac{1}{2}; qg < z < \frac{1}{2}$	$-\alpha + \beta, -\alpha, \beta$	$\frac{1}{2}, y, z: 0 < y, z < \frac{1}{2}$
<i>F</i>	$\alpha + \beta, \frac{1}{2} + \alpha, \frac{1}{2} + \beta$	$\frac{1}{2}, y, z: 0 < y < d_0; 0 < z \leq dg$	$\alpha + \beta, \frac{1}{2} + \alpha, \frac{1}{2} + \beta$	$\frac{1}{2}, y, z: 0 < y < \frac{1}{2}; 0 < z \leq qg$		
<i>FA</i>	$-\alpha + \beta, \frac{1}{2} - \alpha, \frac{1}{2} + \beta$	$0, y, z: b_0 = \frac{1}{2} - d_0 < y < \frac{1}{2}; hb \leq z < \frac{1}{2}$	$-\alpha + \beta, \frac{1}{2} - \alpha, \frac{1}{2} + \beta$	$0, y, z: 0 < y < \frac{1}{2}; h\lambda < z < \frac{1}{2}$		

Wyckoff position: (general position) 8 *e* 1 *x, y, z*. Parameter range in asymmetric unit: $0 < x, y < \frac{1}{2}$; $0 \leq z < \frac{1}{2}$.

k-vector label, CDML	Type of Brillouin zone as in:					
	Fig. 1.5.5.4(a)		Fig. 1.5.5.4(b)		Fig. 1.5.5.4(c)	
	CDML	IT A	CDML	IT A	CDML	IT A
<i>GP</i>	α, β, γ	x, y, z	α, β, γ	x, y, z	α, β, γ	x, y, z

approach. Owing to these advantages, CDML have already accepted the crystallographic approach for triclinic and monoclinic space groups. However, the advantages are not restricted to such low symmetries. In particular, the simple boundary conditions and shapes of the asymmetric units result in simple equations for the boundaries and shapes of volume elements, and facilitate numerical calculations, integrations *etc.* If there are special reasons to prefer **k** vectors inside or on the boundary of the Brillouin zone to those

outside, then the advantages and disadvantages of both approaches have to be compared again in order to find the optimal method for the solution of the problem.

The crystallographic approach may be realized in three different ways:

(1) In the *uni-arm description* one lists each **k**-vector star exactly once by indicating the parameter field of the representing **k** vector. Advantages are the transparency of the presentation and the

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relatively small effort required to derive the list. A disadvantage may be that there are protruding flagpoles or wings. Points of these lines or planes are no longer neighbours of inner points (an inner point has a full three-dimensional sphere of neighbours which belong to the asymmetric unit).

(2) In the *compact description* one lists each $\mathbf{k}$ vector exactly once such that each point of the asymmetric unit is either an inner point itself or has inner points as neighbours. Such a description may not be uni-arm for some Wintgen positions, and the determination of the parameter ranges may become less straightforward. Under this approach, all points fulfil the conditions for the asymmetric units of *IT A*, which are always closed. The boundary conditions of *IT A* have to be modified: in reality the boundary is not closed everywhere; there are frequently open parts (see Section 1.5.5.3).

(3) In the *non-unique description* one gives up the condition that each $\mathbf{k}$ vector is listed exactly once. The uni-arm and the compact descriptions are combined but the equivalence relations ($\sim$) are stated explicitly for those $\mathbf{k}$ vectors which occur in more than one entry. Such tables are most informative and not too complicated for practical applications.

Acknowledgements

The authors wish to thank the editor of this volume, Uri Shmueli, for his patient support, for his encouragement and for his valuable help. They are grateful to the Chairman of the Commission on *International Tables*, Theo Hahn, for his interest and advice. The material in this chapter was first published as an article of the same title in *Z. Kristallogr.* (1995), **210**, 243–254. We are indebted to R. Oldenbourg Verlag, Munich, Germany, for allowing us to reprint parts of this article.

Appendix 1.5.1.

Reciprocal-space groups $\mathcal{G}^*$

This table is based on Table 1 of Wintgen (1941).

In order to obtain the Hermann–Mauguin symbol of $\mathcal{G}^*$ from that of $\mathcal{G}$, one replaces any screw rotations by rotations and any glide reflections by reflections. The result is the symmorphic space group $\mathcal{G}_0$ assigned to $\mathcal{G}$. For most space groups $\mathcal{G}$, the reciprocal-space group $\mathcal{G}^*$ is isomorphic to $\mathcal{G}_0$, *i.e.* $\mathcal{G}^*$ and $\mathcal{G}$ belong to the same arithmetic crystal class. In the following cases the arithmetic crystal classes of $\mathcal{G}$ and $\mathcal{G}^*$ are different, *i.e.* $\mathcal{G}^*$ can not be obtained in this simple way:

(1) If the lattice symbol of $\mathcal{G}$ is F or I , it has to be replaced by I or F . The tetragonal space groups form an exception to this rule; for these the symbol I persists.

(2) The other exceptions are listed in the following table (for the symbols of the arithmetic crystal classes see *IT A*, Section 8.2.2):

Arithmetic crystal class of $\mathcal{G}$	Reciprocal-space group $\mathcal{G}^*$
$\bar{4}m2I$	$I\bar{4}2m$
$\bar{4}2mI$	$I\bar{4}m2$
$321P$	$P312$
$312P$	$P321$
$3m1P$	$P31m$
$31mP$	$P3m1$
$\bar{3}1mP$	$P\bar{3}m1$
$\bar{3}m1P$	$P\bar{3}1m$
$\bar{6}m2P$	$P\bar{6}2m$
$\bar{6}2mP$	$P\bar{6}m2$

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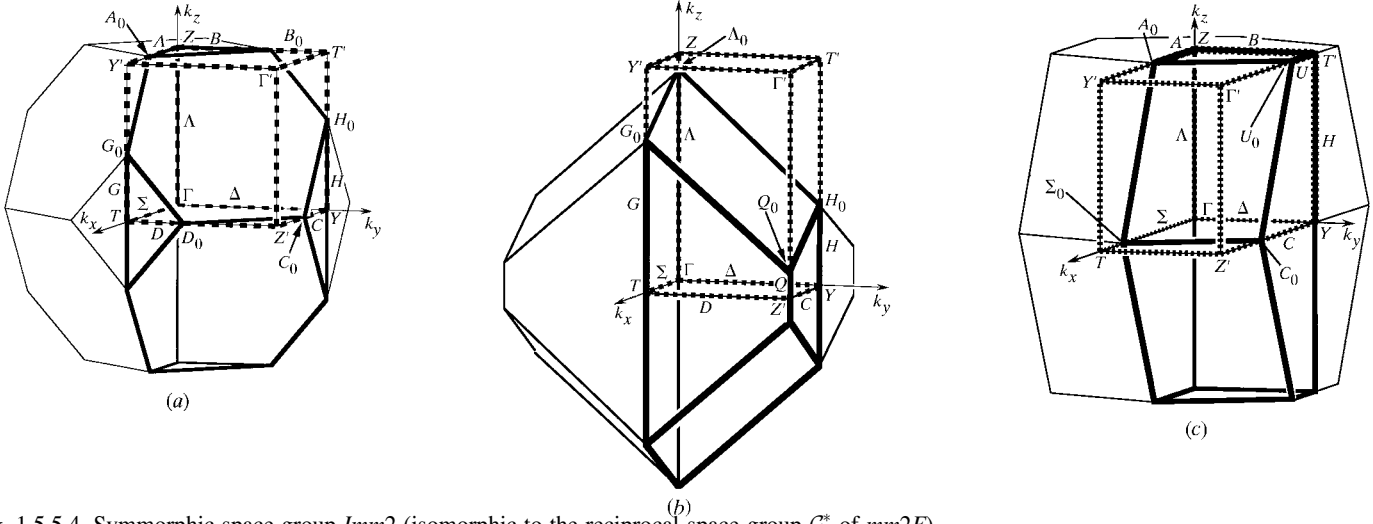


Fig. 1.5.5.4. Symmorphic space group $Imm2$ (isomorphic to the reciprocal-space group $\mathcal{G}^*$ of $mm2F$).

(a) Brillouin zone (thin lines), representation domain (thick lines) and asymmetric unit (dashed lines, partly protruding) imbedded in the Brillouin zone, which is an orthorhombic cuboctahedron. The diagram is drawn for $a^{*2} = 9, b^{*2} = 8, c^{*2} = 7$, i.e. $a^{*2} + b^{*2} > c^{*2}$. The endpoint of line A is A_0 etc., the free coordinate of A_0 is a_0 etc. Asymmetric unit $\Gamma TZ'YZY'\Gamma T'$ of $Imm2$, IT A, p. 246. The part $\Gamma TD_0C_0YG_0H_0ZA_0B_0$ is common to both bodies; the part $A_0Y'\Gamma T'B_0G_0H_0D_0Z'C_0$ is equivalent to the part of the representation domain with negative z values through a twofold screw rotation 2_1 around the axis $\frac{1}{4}, \frac{1}{4}, z$. Coordinates of the points: $\Gamma = 0, 0, 0 \sim \Gamma' = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $Y = 0, \frac{1}{2}, 0 \sim Y' = \frac{1}{2}, 0, \frac{1}{2}$; $Z = 0, 0, \frac{1}{2} \sim Z' = \frac{1}{2}, \frac{1}{2}, 0$; $T = \frac{1}{2}, 0, 0 \sim T' = 0, \frac{1}{2}, \frac{1}{2}$; $C_0 = c_0, \frac{1}{2}, 0 \sim A_0 = a_0, 0, \frac{1}{2}$; $D_0 = \frac{1}{2}, d_0, 0 \sim B_0 = 0, b_0, \frac{1}{2}$; $G_0 = \frac{1}{2}, 0, g_0 \sim H_0 = 0, \frac{1}{2}, h_0$. The coordinates of the points are $c_0 = 1/4[1 - (b^{*2} - c^{*2})/a^{*2}]$; $a_0 = 1/2 - c_0$; $d_0 = 1/4[1 - (a^{*2} - c^{*2})/b^{*2}]$; $b_0 = 1/2 - d_0$; $g_0 = 1/4[1 - (a^{*2} - b^{*2})/c^{*2}]$; $h_0 = 1/2 - g_0$. The sign $\sim$ means symmetrically equivalent. There are no special points. The points Γ, T, Y, Z, G_0 and H_0 belong to special lines; A_0, B_0, C_0 and D_0 belong to special planes. The points with negative z coordinates are equivalent to those already listed. Lines: $\Lambda = \Gamma Z = 0, 0, z$; $G = TG_0 = \frac{1}{2}, 0, z$; $H = YH_0 = 0, \frac{1}{2}, z$. The lines $\Sigma = \Gamma T = x, 0, 0$; $C = YC_0 = x, \frac{1}{2}, 0$; $A = ZA_0 = x, 0, \frac{1}{2}$; $\Delta = \Gamma Y = 0, y, 0$; $B = ZB_0 = 0, y, \frac{1}{2}$; $D = TD_0 = \frac{1}{2}, y, 0$; A_0G_0, G_0D_0, C_0H_0 and H_0B_0 have no special symmetry but belong to special planes, the lines D_0C_0 and B_0A_0 belong to the general position GP . The lines $\Gamma Z, TG_0, YH_0, D_0G_0, C_0H_0, G_0A_0, H_0B_0, ZA_0, ZB_0$ and A_0B_0 of the representation domain to the points Z, G_0, H_0, A_0 and B_0 with negative z coordinates are equivalent to lines of the asymmetric unit not belonging to the representation domain. Planes: $E = \Gamma YH_0B_0Z = 0, y, z$; $F = TD_0G_0 = \frac{1}{2}, y, z$; $J = \Gamma ZA_0G_0T = x, 0, z$; $K = YH_0C_0 = x, \frac{1}{2}, z$. The planes $x, y, 0$; $x, y, \frac{1}{2}$; and $D_0C_0H_0B_0A_0G_0$ belong to the general position GP , as do the negative counterparts of the latter two. The planes $\Gamma Z\bar{A}_0\bar{G}_0T, \Gamma Z\bar{B}_0\bar{H}_0Y, Y\bar{H}_0\bar{C}_0$ and $TD_0\bar{G}_0$ of the representation domain to the points Z, A_0, B_0, G_0 and H_0 with negative z coordinates are equivalent to planes of the asymmetric unit not belonging to the representation domain. For the parameter ranges see Table 1.5.5.4.

(b) Brillouin zone (thin lines), representation domain (thick lines) and asymmetric unit (dashed lines, partly protruding) imbedded in the Brillouin zone, which is an orthorhombic elongated rhombdodecahedron. The diagram is drawn for $a^{*2} = 4, b^{*2} = 9, c^{*2} = 16$, i.e. $a^{*2} + b^{*2} < c^{*2}$. The endpoint of line G is G_0 etc., the free coordinate of G_0 is g_0 etc. Asymmetric unit $\Gamma TZ'YZY'\Gamma T'$ of $Imm2$, IT A, p. 246. The part $\Gamma TZ'YQ_0H_0\Lambda_0G_0$ is common to both bodies; the part $ZY'\Gamma T'\Lambda_0G_0Q_0H_0$ is equivalent to the part of the representation domain with negative z values through a twofold screw rotation 2_1 around the axis $\frac{1}{4}, \frac{1}{4}, z$. Coordinates of the points: $\Gamma = 0, 0, 0 \sim \Gamma' = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $Y = 0, \frac{1}{2}, 0 \sim Y' = \frac{1}{2}, 0, \frac{1}{2}$; $Z = 0, 0, \frac{1}{2} \sim Z' = \frac{1}{2}, \frac{1}{2}, 0$; $T = \frac{1}{2}, 0, 0 \sim T' = 0, \frac{1}{2}, \frac{1}{2}$; $\Lambda_0 = 0, 0, \lambda_0 \sim Q_0 = \frac{1}{2}, \frac{1}{2}, q_0$; $G_0 = \frac{1}{2}, 0, g_0 \sim H_0 = 0, \frac{1}{2}, h_0$. The coordinates of the points are $\lambda_0 = 1/4[1 + (a^{*2} + b^{*2})/c^{*2}]$; $q_0 = 1/2 - \lambda_0$; $g_0 = 1/4[1 + (b^{*2} - a^{*2})/c^{*2}]$; $h_0 = 1/2 - g_0$. The sign $\sim$ means symmetrically equivalent. There are no special points. The points $\Gamma, T, Y, Z', \Lambda_0, Q_0, G_0$ and H_0 belong to special lines. The points with negative z coordinates are equivalent to those already listed. Lines: $\Lambda = \Gamma\Lambda_0 = 0, 0, z$; $Q = Z'Q_0 = \frac{1}{2}, \frac{1}{2}, z$; $G = TG_0 = \frac{1}{2}, 0, z$; $H = YH_0 = 0, \frac{1}{2}, z$. The lines $\Sigma = \Gamma T = x, 0, 0$; $C = YZ' = x, \frac{1}{2}, 0$; $\Delta = \Gamma Y = 0, y, 0$; $D = TZ' = \frac{1}{2}, y, 0$; $Q_0G_0, G_0\Lambda_0, \Lambda_0H_0$ and H_0Q_0 have no special symmetry but belong to special planes. The lines $\Gamma\bar{\Lambda}_0, Z'\bar{Q}_0, T\bar{G}_0$ and $Y\bar{H}_0$ of the representation domain to the points $\bar{\Lambda}, \bar{Q}_0, \bar{G}_0$ and $\bar{H}_0$ with negative z coordinates are equivalent to lines of the asymmetric unit not belonging to the representation domain. Planes: $E = \Gamma YH_0\Lambda_0 = 0, y, z$; $F = TZ'Q_0G_0 = \frac{1}{2}, y, z$; $J = \Gamma\Lambda_0G_0T = x, 0, z$; $K = YH_0Q_0Z' = x, \frac{1}{2}, z$. The planes $x, y, 0$ and $\Lambda_0G_0Q_0H_0$ belong to the general position GP , as does the negative counterpart of $\Lambda_0G_0Q_0H_0$. The planes $\Gamma\bar{\Lambda}_0\bar{G}_0T, \Gamma\bar{\Lambda}_0\bar{H}_0Y, Y\bar{H}_0\bar{Q}_0Z'$ and $T\bar{G}_0\bar{Q}_0Z'$ of the representation domain to the points $\bar{\Lambda}, \bar{Q}_0, \bar{G}_0$ and $\bar{H}_0$ with negative z coordinates are equivalent to planes of the asymmetric unit not belonging to the representation domain. For the parameter ranges see Table 1.5.5.4.

(c) Brillouin zone (thin lines), representation domain (thick lines) and asymmetric unit (dashed lines, partly protruding) imbedded in the Brillouin zone, which is an orthorhombic elongated rhombdodecahedron. The diagram is drawn for $a^{*2} = 49, b^{*2} = 9, c^{*2} = 16$, i.e. $a^{*2} > b^{*2} + c^{*2}$. The endpoint of line A is A_0 etc., the free coordinate of A_0 is a_0 etc. Asymmetric unit $\Gamma TZ'YZY'\Gamma T'$ of $Imm2$, IT A, p. 246. The part $\Gamma\Sigma_0C_0YZA_0U_0T'$ is common to both bodies; the part $\Sigma_0TZ'C_0A_0Y'\Gamma T'U_0$ is equivalent to the part of the representation domain with negative z values through a twofold screw rotation 2_1 around the axis $\frac{1}{4}, \frac{1}{4}, z$. Coordinates of the points: $\Gamma = 0, 0, 0 \sim \Gamma' = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $Y = 0, \frac{1}{2}, 0 \sim Y' = \frac{1}{2}, 0, \frac{1}{2}$; $Z = 0, 0, \frac{1}{2} \sim Z' = \frac{1}{2}, \frac{1}{2}, 0$; $T = \frac{1}{2}, 0, 0 \sim T' = 0, \frac{1}{2}, \frac{1}{2}$; $\Sigma_0 = \sigma_0, 0, 0 \sim U_0 = u_0, \frac{1}{2}, \frac{1}{2}$; $A_0 = a_0, 0, \frac{1}{2} \sim C_0 = c_0, \frac{1}{2}, 0$. The coordinates of the points are $\sigma_0 = 1/4[1 + (b^{*2} + c^{*2})/a^{*2}]$; $u_0 = 1/2 - \sigma_0$; $a_0 = 1/4[1 + (b^{*2} - c^{*2})/a^{*2}]$; $c_0 = 1/2 - a_0$. The sign $\sim$ means symmetrically equivalent. There are no special points. The points Γ, Z, Y and T' belong to special lines, Σ_0, U_0, A_0 and C_0 belong to special planes. The points with negative z coordinates are equivalent to those already listed. Lines: $\Lambda = \Gamma Z = 0, 0, z$; $H = YT' = 0, \frac{1}{2}, z$. The lines $\Sigma = \Gamma\Sigma_0 = x, 0, 0$; $U = T'U_0 = x, \frac{1}{2}, \frac{1}{2}$; $A = ZA_0 = x, 0, \frac{1}{2}$; $C = YC_0 = x, \frac{1}{2}, 0$; $\Delta = \Gamma Y = 0, y, 0$; $B = ZT' = 0, y, \frac{1}{2}$; $U_0A_0, A_0\Sigma_0, \Sigma_0C_0$ and C_0U_0 have no special symmetry but belong to special planes. The lines $\Gamma\bar{Z}$ and $Y\bar{T}'$ of the representation domain to the points $\bar{Z}$ and $\bar{T}'$ with negative z coordinates are equivalent to lines of the asymmetric unit not belonging to the representation domain. Planes: $E = \Gamma YT'Z = 0, y, z$; $J = \Gamma\Sigma_0A_0Z = x, 0, z$; $K = YC_0U_0T' = x, \frac{1}{2}, z$. The planes $x, y, 0$; $x, y, \frac{1}{2}$; and $\Sigma_0C_0U_0A_0$ belong to the general position GP , as does the negative counterpart of $\Sigma_0C_0U_0A_0$. The planes $\Gamma\bar{Z}\bar{T}'\bar{Y}, \Gamma\Sigma_0\bar{A}_0\bar{Z}$ and $Y\bar{T}'\bar{U}_0\bar{C}_0$ of the representation domain to the points $\bar{Z}, \bar{T}', A_0$ and U_0 with negative z coordinates are equivalent to planes of the asymmetric unit not belonging to the representation domain. For the parameter ranges see Table 1.5.5.4.

The fourth possible type of Brillouin zone with $b^{*2} > a^{*2} + c^{*2}$ is similar to that displayed in (c). It can be obtained from this by exchanging a^* and b^* and changing the letters for the points, lines and planes correspondingly.

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2.1. Statistical properties of the weighted reciprocal lattice

BY U. SHMUELI AND A. J. C. WILSON

2.1.1. Introduction

The structure factor of the hkl reflection is given by

$$F(hkl) = \sum_{j=1}^N f_j \exp[2\pi i(hx_j + ky_j + lz_j)], \quad (2.1.1.1)$$

where f_j is the atomic scattering factor [complex if there is appreciable dispersion; see Chapter 1.2 and *IT C* (1999, Section 4.2.6)], x_j, y_j, z_j are the fractional coordinates of the j th atom and N is the number of atoms in the unit cell. The present chapter is concerned with the statistical properties of the structure factor F and the intensity $I = FF^*$, such as their average values, variances, higher moments and their probability density distributions.

Equation (2.1.1.1) expresses F as a function of two conceptually different sets of variables: hkl taking on integral values in reciprocal space and xyz in general having non-integral values in direct space, although the special positions tabulated for each space group in *IT A* (1983) may include the integers 0 and 1. In special positions, the non-integers often include rational fractions, but in general positions they are in principle irrational. Although hkl and xyz appear to be symmetrical variables in (2.1.1.1), these limitations on their values mean that one can consider two different sets of statistical properties. In the first we seek, for example, the average intensity of the hkl reflection (indices fixed) as the positional parameters of the N atoms are distributed with equal probability over the continuous range 0–1. In the second, we seek, for example, the average intensity of the observable reflections (or of a subgroup of them having about the same value of $\sin \theta$) with the values of xyz held constant at the values they have, or are postulated to have, in a crystal structure. Other examples are obtained by substituting the words ‘probability density’ for ‘average intensity’. For brevity, we may call the statistics resulting from the first process *fixed-index* (continuously variable parameters being understood), and those resulting from the second process *fixed-parameter* (integral indices being understood). Theory based on the first process is (comparatively) easy; theory based on the second hardly exists, although there is a good deal of theory concerning the conditions under which the two processes will lead to the same result (Hauptman & Karle, 1953; Giacovazzo, 1977, 1980). Mathematically, of course, the condition is that the phase angle

$$\vartheta = 2\pi(hx + ky + lz) \quad (2.1.1.2)$$

should be distributed with uniform probability over the range 0– 2π , whichever set of variables is regarded as fixed, but it is not clear when this distribution can be expected in practice for fixed-parameter averaging. The usual conclusion is that the uniform distribution will be realized if there are enough atoms, if the atomic coordinates do not approximate to rational fractions, if there are enough reflections and if stereochemical effects are negligible (Shmueli *et al.*, 1984).

Obviously, the second process (fixed parameters, varying integral indices) corresponds to the observable reality, and various approximations to it have been attempted, in preference to assuming its equivalence with the first. For example, a third (approximate) method of averaging has been used (Wilson, 1949, 1981): xyz are held fixed and hkl are treated as continuous variables.

2.1.2. The average intensity of general reflections

2.1.2.1. Mathematical background

The process may be illustrated by evaluating, or attempting to evaluate, the average intensity of reflection by the three processes.

The intensity of reflection is given by multiplying equation (2.1.1.1) by its complex conjugate:

$$I = FF^* \quad (2.1.2.1)$$

$$= \sum_{j,k} f_j f_k^* \exp\{2\pi i[h(x_j - x_k) + \dots]\} \quad (2.1.2.2)$$

$$= \Sigma + \sum_{j \neq k} f_j f_k^* \exp\{2\pi i[h(x_j - x_k) + \dots]\}, \quad (2.1.2.3)$$

where

$$\Sigma = \sum_j f_j f_j^* \quad (2.1.2.4)$$

is the sum of the squares of the moduli of the atomic scattering factors. Wilson (1942) argued, without detailed calculation, that the average value of the exponential term would be zero and hence that

$$\langle I \rangle = \Sigma. \quad (2.1.2.5)$$

Averaging equation (2.1.2.3) for hkl fixed, xyz ranging uniformly over the unit cell – the first process described above – gives this result identically, without complication or approximation. Ordinarily the second process cannot be carried out. We can, however, postulate a special case in which it is possible. We take a homoatomic structure and before averaging we correct the f 's for temperature effects and the fall-off with $\sin \theta$, so that ff^* is the same for all the atoms and is independent of hkl . If the range of hkl over which the expression for I has to be averaged is taken as a parallelepiped in reciprocal space with h ranging from $-H$ to $+H$, k from $-K$ to $+K$, l from $-L$ to $+L$, equation (2.1.2.2) can be factorized into the product of the sums of three geometrical progressions. Algebraic manipulation then easily leads to

$$\begin{aligned} \langle I \rangle = ff^* \sum_j \sum_k & \frac{\sin \pi N_H (x_j - x_k)}{N_H \sin \pi (x_j - x_k)} \\ & \times \frac{\sin \pi N_K (y_j - y_k)}{N_K \sin \pi (y_j - y_k)} \frac{\sin \pi N_L (z_j - z_k)}{N_L \sin \pi (z_j - z_k)}, \end{aligned} \quad (2.1.2.6)$$

where $N_H = 2H + 1$, $N_K = 2K + 1$ and $N_L = 2L + 1$. The terms with $j = k$ give Σ , but the remaining terms are not zero. Because of the periodic nature of the trigonometric terms, the effective coordinate differences are never greater than 0.5 and in a structure of any complexity there will be many much less than 0.5. For $HKL = 000$, in fact, $\langle I \rangle$ becomes the square of the modulus of the sum of the atomic scattering factors,

$$\langle I \rangle = \Phi \Phi^*, \quad (2.1.2.7)$$

where

$$\Phi = \sum_{j=1}^N f_j, \quad (2.1.2.8)$$

and not the sum of the squares of their moduli; for larger HKL , $\langle I \rangle$ rapidly decreases to Σ and then oscillates about that value. Wilson (1949, especially Section 2.1.1) suggested that the regions of averaging should be chosen so that at least one index of every reflection is ≥ 2 if $\langle I \rangle$ is to be identified with Σ , and this has proven to be a useful rule-of-thumb.

The third process of averaging replaces the sum over integral values of the indices by an integration over continuous values, the appropriate values of the limits in this example being $-(H + 1/2)$ to $+(H + 1/2)$. The effect is to replace the sines in the

2.1. STATISTICAL PROPERTIES OF THE WEIGHTED RECIPROCAL LATTICE

denominators, but not in the numerators, of equation (2.1.2.6) by their arguments, and this is equivalent to the approximation $\sin x \simeq x$ in the denominators only. This is a good approximation for atoms close together in the structure and thus giving the largest terms in the sums in equation (2.1.2.6), and gives the correct sign and order of magnitude even for x having its maximum value of $\pi/2$.

2.1.2.2. Physical background

The preceding section has used mathematical arguments. From a physical point of view, the radiation diffracted by atoms that are resolved will interfere destructively, so that the resulting intensity will be the sum of the intensities diffracted by individual atoms, whereas that from completely unresolved atoms will interfere constructively, so that *amplitudes* rather than intensities add. In intermediate cases there will be partial constructive interference. Resolution in accordance with the Rayleigh (1879) criterion requires that $s = (2 \sin \theta)/\lambda$ should be greater than half the reciprocal of the minimum interatomic distance in the crystal (Wilson, 1979); full resolution requires a substantial multiple of this. This criterion is essentially equivalent to that proposed from the study of a special case of the second process in the preceding section.

2.1.2.3. An approximation for organic compounds

In organic compounds there are very many interatomic distances of about 1.5 or 1.4 Å. Adoption of the preceding criterion would mean that the inner portion of the region of reciprocal space accessible by the use of copper $K\alpha$ radiation is not within the sphere of intensity statistics based on fixed-index (first process) averaging. No substantial results are available for fixed-parameter (second process) averaging, and very few from the approximation to it (third process).

To the extent to which the third process is acceptable, an approximation to the variation of $\langle I \rangle$ with $\sin \theta$ is obtainable. The exponent in equation (2.1.2.2) can be written as

$$2\pi i s r_{jk} \cos \psi, \quad (2.1.2.9)$$

where s is the radial distance in reciprocal space, r_{jk} is the distance from the j th to the k th atom and ψ is the angle between the vectors s and r . Averaging over a sphere of radius s , with ψ treated as the co-latitude, gives

$$\langle I \rangle = \sum_j \sum_k f_j f_k \frac{\sin 2\pi s r_{jk}}{2\pi s r_{jk}}. \quad (2.1.2.10)$$

This is the familiar Debye expression. It has the correct limits for s zero and s large, and is in accord with the argument from resolution.

2.1.2.4. Effect of centring

In the preceding discussion there has been a tacit assumption that the lattice is primitive. A centred crystal can always be referred to a primitive lattice and if this is done no change is required. If the centred lattice is retained, many reflections are identically zero and the intensity of the non-zero reflections is enhanced by a factor of two (I and C lattices) or four (F lattice), so that the average intensity of all the reflections, zero and non-zero taken together, is unchanged.

Other symmetry elements affect only zones and rows of reflections, and so do not affect the general average when the total number of reflections is large. Their effect on zones and rows is discussed in Section 2.1.3.

Table 2.1.3.1. *Intensity-distribution effects of symmetry elements causing systematic absences*

Abbreviations and orientation of axes: A = acentric distribution, C = centric distribution, Z = systematically zero, S = distribution parameter, $\langle I \rangle$ = average intensity. Axes are parallel to c , planes are perpendicular to c .

Element	Reflections	Distribution	S/Σ	$\langle I \rangle/\Sigma$
2_1	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(Z + A)/2$	1	2
$3_1, 3_2$	hkl	A	1	1
	$hk0$	A	1	1
	$00l$	$(2Z + A)/3$	1	3
$4_1, 4_3$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(3Z + A)/4$	1	4
4_2	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(Z + A)/2$	2	4
$6_1, 6_5$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(5Z + A)/6$	1	6
$6_2, 6_4$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(2Z + A)/3$	2	6
6_3	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(Z + A)/2$	3	6
a	hkl	A	1	1
	$hk0$	$(Z + A)/2$	1	2
	$00l$	C	1	1
	$0k0$	A	2	2
C, I	All	$(Z + A)/2$	1	2
F	All	$(3Z + A)/2$	1	4

2.1.3. The average intensity of zones and rows

2.1.3.1. Symmetry elements producing systematic absences

Symmetry elements can be divided into two types: those that cause systematic absences and those that do not. Those producing systematic absences (glide planes and screw axes) produce at the same time groups of reflections (confined to zones and rows in reciprocal space, respectively) with an average intensity an integral* multiple of the general average. The effects for single symmetry elements of this type are given in Table 2.1.3.1 for the general reflections hkl and separately for any zones and rows that are affected. The 'average multipliers' are given in the column headed $\langle I \rangle/\Sigma$; 'distribution' and 'distribution parameters' are treated in Section 2.1.5. As for the centring, the fraction of reflections missing and the integer multiplying the average are related in such a way that the overall intensity is unchanged. The

* The multiple is given as an exact integer for fixed-index averaging, an approximate integer for fixed-parameter averaging. Statements should be understood to refer to fixed-index averaging unless the contrary is explicitly stated.

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Table 2.1.3.2. *Intensity-distribution effects of symmetry elements not causing systematic absences*

Abbreviations and orientation of axes: *A* = acentric distribution, *C* = centric distribution, *S* = distribution parameter, $\langle I \rangle$ = average intensity. Axes are parallel to *c*, planes are perpendicular to *c*.

Element	Reflections	Distribution	$S/\Sigma = \langle I \rangle/\Sigma$
1	All	<i>A</i>	1
$\bar{1}$	All	<i>C</i>	1
2	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>C</i>	1
	<i>00l</i>	<i>A</i>	2
$\bar{2} = m$	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>A</i>	2
	<i>00l</i>	<i>C</i>	1
3	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>A</i>	1
	<i>00l</i>	<i>A</i>	3
$\bar{3}$	<i>hkl</i>	<i>C</i>	1
	<i>hk0</i>	<i>C</i>	1
	<i>00l</i>	<i>C</i>	3
4	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>C</i>	1
	<i>00l</i>	<i>A</i>	4
$\bar{4}$	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>C</i>	1
	<i>00l</i>	<i>C</i>	2
6	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>C</i>	1
	<i>00l</i>	<i>A</i>	6
$\bar{6} = 3/m$	<i>hkl</i>	<i>A</i>	1
	<i>hk0</i>	<i>A</i>	2
	<i>00l</i>	<i>C</i>	3

mechanism for compensation for the reflections with enhanced intensity is obvious.

2.1.3.2. *Symmetry elements not producing systematic absences*

Certain symmetry elements not producing absences (mirror planes and rotation axes) cause equivalent atoms to coincide in a plane or a line projection and hence produce a zone or row in reciprocal space for which the average intensity is an integral multiple of the general average (Wilson, 1950); the effects of single such symmetry elements are given in Table 2.1.3.2. There is, however, no obvious mechanism for compensation for this enhancement. When reflections are few this may be an important matter in assigning an approximate absolute scale by comparing observed and calculated intensities. Wilson (1964), Nigam (1972) and Nigam & Wilson (1980), noting that in such cases the finite size of atoms results in forbidden ranges of positional parameters, have shown that there is a diminution of the intensity of layers (rows) in the immediate neighbourhood of the enhanced zones (rows), just sufficient to compensate for the enhancement. In forming general averages, therefore, reflections from enhanced zones or rows should be included at their full intensity, not divided by the multiplier; the

matter is discussed in more detail by Wilson (1987a). It should be noted, however, that organic structures containing molecules related by rotation axes are rare, and such structures related by mirror planes are even rarer (Wilson, 1993).

2.1.3.3. *More than one symmetry element*

Further alterations of the intensities occur if two or more such symmetry elements are present in the space group. The effects were treated in detail by Rogers (1950), who used them to construct a table for the determination of space groups by supplementing the usual knowledge of Laue group with statistical information. Only two pairs of space groups, the orthorhombic *I*222 and *I*2₁2₁2₁, and their cubic supergroups *I*23 and *I*2₁3₁, remained unresolved. Examination of this table shows that what statistical information does is to resolve the Laue group into point groups; the further resolution into space groups is equivalent to the use of Table 3.2 in *IT A* (1983). The statistical consequences of each point group, as given by Rogers, are reproduced in Table 2.1.3.3.

2.1.4. Probability density distributions – mathematical preliminaries

For the purpose of this chapter, ‘ideal’ probability distributions or probability density functions are the asymptotic forms obtained by the use of the central-limit theorem when the number of atoms in the unit cell, *N*, is sufficiently large. In order to derive them it is necessary to outline the properties of characteristic functions and to state alternative conditions for the validity of the central-limit theorem; the distributions themselves are derived in Section 2.1.5.

2.1.4.1. *Characteristic functions*

The average value of $\exp(itx)$ is very important in probability theory; it is called the characteristic function of the distribution $f(x)$ and is denoted by $C_x(t)$ or, when no confusion can arise, by $C(t)$. It exists for all legitimate distributions, whether discrete or continuous. In the continuous case it is given by

$$C(t) = \int_{-\infty}^{\infty} \exp(itx)f(x) dx, \quad (2.1.4.1)$$

and is thus the Fourier transform of $f(x)$. In many cases it can be obtained from known integrals. For example, for the Cauchy distribution,

$$C(t) = \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(itx)}{a^2 + x^2} dx \quad (2.1.4.2)$$

$$= \exp(-a|t|), \quad (2.1.4.3)$$

and for the normal distribution,

$$C(t) = (2\pi\sigma^2)^{-1/2} \int_{-\infty}^{\infty} \exp\left(\frac{-(x-m)^2}{2\sigma^2}\right) \exp(itx) dx \quad (2.1.4.4)$$

$$= \exp\left(imt - \frac{\sigma^2 t^2}{2}\right). \quad (2.1.4.5)$$

Since the characteristic function is the Fourier transform of the distribution function, the converse is true, and if the characteristic function is known the probability distribution function can be obtained by the use of Fourier inversion theorem,

$$f(x) = (1/2\pi) \int_{-\infty}^{\infty} \exp(-itx)C(t) dt. \quad (2.1.4.6)$$

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Table 2.1.3.3. *Average multiples for the 32 point groups (modified from Rogers, 1950).*

The multiple gives S/Σ for the row and zone corresponding to the principal axis of the point-group symbol; those for the secondary and tertiary axes are given when the symbol contains such axes.

Point group	Principal		Secondary		Tertiary	
	Row	Zone	Row	Zone	Row	Zone
1	1	1				
$\bar{1}$	1	1				
2	2	1				
m	1	2				
$2/m$	2	2				
222	2	1	2	1	2	1
$mm2$	2	2	2	2	4	1
mmm	4	2	4	2	4	2
4	4	1				
$\bar{4}$	2	1				
$4/m$	4	2				
422	4	1*	2	1	2	1
$4mm$	8	1	2	2	2	2
$\bar{4}2m$	4	1	2	1	2	2
$4/mmm$	8	2	4	2	4	2
3	3	1				
$\bar{3}$	3	1				
321	3	1	2	1	1	1
$3m1$	6	1	1	2	2	
$31m$	6	1	2	2	2	1
6	6	1				
$\bar{6}$	3	2				
$6/m$	6	2				
622	6	1	2	1	2	1
$6mm$	12	1	2	2	2	2
$\bar{6}m2$	6	2	2	2	4	1
$6/mmm$	12	2	4	2	4	2
231	2	1	3	1	1	1
$m\bar{3}1$	4	2	3	1	1	1
432	4	1	3	1	2	1
$\bar{4}3m$	4	1	6	1	2	2
$m\bar{3}m$	8	2	6	2	4	2

Note. The pairs of point groups, 1 and $\bar{1}$ and 3 and $\bar{3}$, not distinguished by average multiples, may be distinguished by their centric and acentric probability density functions.

* The entry for the principal zone for the point group 422 was given incorrectly as 2 in the first edition of this volume.

An alternative approach to the derivation of the distribution from a known characteristic function will be discussed below.

The most important property of characteristic functions in crystallography is the following: if x and y are independent random variables with characteristic functions $C_x(t)$ and $C_y(t)$, the characteristic function of their sum

$$z = x + y \quad (2.1.4.7)$$

is the product

$$C_z(t) = C_x(t)C_y(t). \quad (2.1.4.8)$$

Obviously this can be extended to any number of independent random variables.

When the moments exist, the characteristic function can be expanded in a power series in which the k th term is $m_k(it)^k/k!$. If the power series

$$\exp(itx) = 1 + itx + \frac{(it)^2x^2}{2!} + \frac{(it)^3x^3}{3!} + \dots \quad (2.1.4.9)$$

is substituted in equation (2.1.4.1), one obtains

$$C(t) = 1 + itm'_1 + \frac{(it)^2m'_2}{2!} + \frac{(it)^3m'_3}{3!} + \dots \quad (2.1.4.10)$$

The moments are written with primes in order to indicate that equation (2.1.4.10) is valid for moments about an arbitrary origin as well as for moments about the mean. If the random variable is transformed by a change of origin and scale, say

$$y = \frac{x - a}{b}, \quad (2.1.4.11)$$

the characteristic function for y becomes

$$C_y(t) = b \exp(-iat/b)C_x(t). \quad (2.1.4.12)$$

2.1.4.2. The cumulant-generating function

A function that is often more useful than the characteristic function is its logarithm, the cumulant-generating function:

$$K(t) = \log C(t) = k_1 + \frac{k_2(it)^2}{2!} + \frac{k_3(it)^3}{3!} + \dots, \quad (2.1.4.13)$$

where the k 's are called the *cumulants* and may be regarded as being defined by the equation. They can be evaluated in terms of the moments by combining the series (2.1.4.10) for $C(t)$ with the ordinary series for the logarithm and equating the coefficients of t^r . In most cases the process as described is tedious, but it can be shortened by use of a general method [Stuart & Ord (1994), Section 3.14, pp. 87–88; Exercise 3.19, p. 119]. Obviously, the cumulants exist only if the moments exist. The first few relations are

$$\begin{aligned} k_0 &= 0 \\ k_1 &= m'_1 \\ k_2 &= m_2 = m'_2 - (m'_1)^2 \\ k_3 &= m_3 = m'_3 - 3m'_2m'_1 + 2(m'_1)^2 \\ k_4 &= m_4 - 3(m_2)^2 \\ &= m'_4 - m'_3m'_1 - 3(m'_2)^2 + 12m'_2(m'_1)^2 - 6(m'_1)^4. \end{aligned} \quad (2.1.4.14)$$

Such expressions and their converses up to k_{10} are given by Stuart & Ord (1994, pp. 88–91). Since all the cumulants except k_1 can be expressed in terms of the central moments only (*i.e.*, those unprimed), only k_1 is changed by a change of the origin. Because of this property, they are sometimes called the semi-invariants (or seminvariants) of the distribution. Since addition of random variables is equivalent to the multiplication of their characteristic functions [equation (2.1.4.8)] and multiplication of functions is equivalent to the addition of their logarithms, each cumulant of the distribution of the sum of a number of random variables is equal to the sum of the cumulants of the distribution functions of the individual variables – hence the name cumulants. Although the cumulants (except k_1) are independent of a change of origin, they are not independent of a change of scale. As for the moments, a

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change of scale simply multiplies them by a power of the scale factor; if $y = x/b$

$$(k_y)_r = (k_x)_r / b^r. \quad (2.1.4.15)$$

The cumulants of the normal distribution are particularly simple. From equation (2.1.4.5), the cumulant-generating function of a normal distribution is

$$K(t) = imt - \sigma^2 t^2 / 2 \quad (2.1.4.16)$$

$$k_1 = m \quad (2.1.4.17)$$

$$k_2 = \sigma^2, \quad (2.1.4.18)$$

all cumulants with $r > 2$ are identically zero.

2.1.4.3. The central-limit theorem

A simple form of this important theorem can be stated as follows:

If $x_1, x_2, \dots, x_n$ are independent and identically distributed random variables, each of them having the same mean m and variance σ^2 , then the sum

$$S_n = \sum_{j=1}^n x_j \quad (2.1.4.19)$$

tends to be normally distributed – independently of the distribution(s) of the individual random variables – with mean nm and variance $n\sigma^2$, provided n is sufficiently large.

In order to prove this theorem, let us define a standardized random variable corresponding to the sum S_n , i.e., such that its mean is zero and its variance is unity:

$$\hat{S}_n = \frac{S_n - nm}{\sigma\sqrt{n}} = \frac{\sum_{j=1}^n (x_j - m)}{\sigma\sqrt{n}} \equiv \sum_{j=1}^n \frac{W_j}{\sqrt{n}}, \quad (2.1.4.20)$$

where $W_j = (x_j - m)/\sigma$ is a standardized single random variable. The characteristic function of $\hat{S}_n$ is therefore given by

$$C_n(\hat{S}_n, t) = \langle \exp(it\hat{S}_n) \rangle = \left\langle \exp \left[it \sum_{j=1}^n \frac{W_j}{\sqrt{n}} \right] \right\rangle \quad (2.1.4.21)$$

$$= \prod_{j=1}^n \left\langle \exp \left[it \frac{W_j}{\sqrt{n}} \right] \right\rangle \quad (2.1.4.22)$$

$$= \left\{ \left\langle \exp \left[it \frac{W_1}{\sqrt{n}} \right] \right\rangle \right\}^n, \quad (2.1.4.23)$$

where the brackets $\langle \rangle$ denote the operation of averaging with respect to the appropriate probability density function (p.d.f.) [cf. equation (2.1.4.1)]. Equation (2.1.4.22) follows from equation (2.1.4.21) by the assumption of independence, while the assumption of identically distributed variables leads to the identity of the characteristic functions of the individual variables – as seen in equation (2.1.4.23).

On the assumption that moments of all the orders exist – a most plausible assumption in situations usually encountered in structure-factor statistics – we can now expand the characteristic function of a single variable in a power series [cf. equation (2.1.4.10)]:

$$\begin{aligned} \left\langle \exp \left[it \frac{W_1}{\sqrt{n}} \right] \right\rangle &= \left\langle \sum_{r=0}^{\infty} \frac{(it)^r}{r!} \frac{W_1^r}{n^{r/2}} \right\rangle \\ &= \sum_{r=0}^{\infty} \frac{(it)^r}{r!} \frac{\langle W_1^r \rangle}{n^{r/2}} \\ &\equiv 1 - \frac{t^2}{2n} + \frac{\zeta(t, n)}{n}, \end{aligned} \quad (2.1.4.24)$$

since $\langle W_1 \rangle = 0$, $\langle W_1^2 \rangle = 1$, and the quantity denoted by $\zeta(t, n)$ in (2.1.4.24) is given by

$$\zeta(t, n) = \sum_{r=3}^{\infty} \frac{(it)^r}{r!} \frac{\langle W_1^r \rangle}{n^{(r/2)-1}}. \quad (2.1.4.25)$$

The characteristic function of $\hat{S}_n$ is therefore

$$\langle \exp(it\hat{S}_n) \rangle = \left[1 - \frac{t^2}{2n} + \frac{\zeta(t, n)}{n} \right]^n. \quad (2.1.4.26)$$

Now, as is seen from (2.1.4.25), for every fixed t the quantity $\zeta(t, n)$ tends to zero as n tends to infinity. The cumulant-generating function of the standardized sum then becomes

$$\log C_n(\hat{S}_n, t) = n \log \left[1 - \frac{1}{n} \left(\frac{t^2}{2} - \zeta(t, n) \right) \right] \quad (2.1.4.27)$$

and the logarithm on the right-hand side of equation (2.1.4.27) has the form $\log(1 - z)$ with $|z| \rightarrow 0$ as $n \rightarrow \infty$. We may therefore use the expansion

$$\log(1 - z) = - \left(z + \frac{z^2}{2} + \frac{z^3}{3} + \dots \right),$$

which is valid for $|z| < 1$. We then obtain

$$\begin{aligned} \log C_n(\hat{S}_n, t) &= -n \left[\frac{1}{n} \left(\frac{t^2}{2} - \zeta(t, n) \right) + \frac{1}{2n^2} \left(\frac{t^2}{2} - \zeta(t, n) \right)^2 \right. \\ &\quad \left. + \frac{1}{3n^3} \left(\frac{t^2}{2} - \zeta(t, n) \right)^3 + \dots \right] \\ &= -\frac{t^2}{2} + \zeta(t, n) - \frac{1}{2n} \left(\frac{t^2}{2} - \zeta(t, n) \right)^2 \\ &\quad - \frac{1}{3n^2} \left(\frac{t^2}{2} - \zeta(t, n) \right)^3 - \dots \end{aligned}$$

and finally, for every fixed t ,

$$\lim_{n \rightarrow \infty} \log C_n(\hat{S}_n, t) = -\frac{t^2}{2}. \quad (2.1.4.28)$$

Since the logarithm is a continuous function of t , it follows directly that

$$\lim_{n \rightarrow \infty} C_n(\hat{S}_n, t) = \exp \left(-\frac{t^2}{2} \right). \quad (2.1.4.29)$$

The right-hand side of (2.1.4.29) is just the characteristic function of a standardized normal p.d.f., i.e., a normal p.d.f. with zero mean and unit variance [cf. equation (2.1.4.5)]. The asymptotic expression for the p.d.f. of the standardized sum is therefore obtained as

$$p(\hat{S}) = \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{\hat{S}^2}{2} \right),$$

which proves the above version of the central-limit theorem.

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Surprisingly, this theorem has a very wide applicability and values of n as low as 30 are often large enough for the theorem to be useful. Situations in which the normal p.d.f. must be modified or replaced by an altogether different one are dealt with in Sections 2.1.7 and 2.1.8 of this chapter.

2.1.4.4. Conditions of validity

The above outline of a proof of the central-limit theorem depended on the existence of moments of all orders. The components of structure factors always possess finite moments of all orders, but the existence of moments beyond the second is not necessary for the validity of the theorem and it can be proved under much less stringent conditions. In fact, if all the random variables in equation (2.1.4.19) have the *same* distribution – as in a homoatomic structure – the only requirement is that the second moments of the distributions should exist [the Lindeberg–Lévy theorem (*e.g.* Cramér, 1951)]. If the distributions are not the same – as in a heteroatomic structure – some further condition is necessary to ensure that no individual random variable dominates the sum. The Liapounoff proof requires the existence of third absolute moments, but this is regarded as aesthetically displeasing; a theorem that ultimately involves only means and variances should require only means and variances in the proof. The Lindeberg–Cramér conditions meet this aesthetic criterion. Roughly, the conditions are that S^2 , the variance of the sum, should tend to infinity and σ_j^2/S^2 , where σ_j^2 is the variance of the j th random variable, should tend to zero for all j as n tends to infinity. The precise formulation is quoted by Kendall & Stuart (1977, p. 207).

2.1.4.5. Non-independent variables

The central-limit theorem, under certain conditions, remains valid even when the variables summed in equation (2.1.4.19) are not independent. The conditions have been investigated by Bernstein (1922, 1927); roughly they amount to requiring that the variables should not be too closely correlated. The theorem applies, in particular, when each x_r is related to a finite number, $f(n)$, of its neighbours, when the x 's are said to be $f(n)$ dependent. The $f(n)$ dependence seems plausible for crystallographic applications, since the positions of atoms close together in a structure are closely correlated by interatomic forces, whereas those far apart will show little correlation if there is any flexibility in the asymmetric unit when unconstrained. Harker's (1953) idea of 'globs' seems equivalent to $f(n)$ dependence. Long-range stereochemical effects, as in pseudo-graphitic aromatic hydrocarbons, would presumably produce long-range correlations and make $f(n)$ dependence less plausible. If Bernstein's conditions are satisfied, the central-limit theorem would apply, but the actual value of $\langle x^2 \rangle - \langle x \rangle^2$ would have to be used for the variance, instead of the sum of the variances of the random variables in (2.1.4.19). Because of the correlations the two values are no longer equal.

French & Wilson (1978) seem to have been the first to appeal explicitly to the central-limit theorem extended to non-independent variables, but many previous workers [for typical references, see Wilson (1981)] tacitly made the replacement – in the X-ray case substituting the local mean intensity for the sum of the squares of the atomic scattering factors.

2.1.5. Ideal probability density distributions

In applications of the central-limit theorem, and its extensions, to intensity statistics the x_j 's of equation (2.1.4.19) have the form (atomic scattering factor of the j th atom) times (a trigonometric expression characteristic of the space group and Wyckoff position; also known as the trigonometric structure factor). These trigono-

metric expressions for all the space groups, and general Wyckoff positions, are given in Tables A1.4.3.1 through A1.4.3.7, and their first few even moments (fixed-index averaging) are given in Table 2.1.7.1. One cannot, of course, conclude that the magnitudes of the structure factor always have a normal distribution – even if the structure is homoatomic; one must look at each problem and see what components of the structure factor can be put in the form (2.1.4.19), deduce the m and σ^2 to be used for each, and combine the components to obtain the asymptotic (large N , not large x) expression for the problem in question. Ordinarily the components are the real and the imaginary parts of the structure factor; the structure factor is purely real only if the structure is centrosymmetric, the space-group origin is chosen at a crystallographic centre and the atoms are non-dispersive.

2.1.5.1. Ideal acentric distributions

The ideal acentric distributions are obtained by applying the central-limit theorem to the real and the imaginary parts of the structure factor, as given by equation (2.1.1.1). Consider first a crystal with no rotational symmetry (space group $P1$). The real part, A , of the structure factor is then given by

$$A = \sum_{j=1}^N f_j \cos \vartheta_j, \quad (2.1.5.1)$$

where N is the number of atoms in the unit cell and ϑ_j is the phase angle of the j th atom. The central-limit theorem then states that A tends to be normally distributed about its mean value with variance equal to its mean-square deviation from its mean. Under the assumption that the phase angles ϑ_j are uniformly distributed on the 0 – 2π range, the mean value of each cosine is zero, so that its variance is

$$\sigma^2 = \sum_{j=1}^N f_j^2 \langle \cos^2 \vartheta_j \rangle. \quad (2.1.5.2)$$

Under the same assumption, the mean value of each $\cos^2 \vartheta$ is one-half, so that the variance becomes

$$\sigma^2 = (1/2) \sum_{j=1}^N f_j^2 = (1/2) \Sigma, \quad (2.1.5.3)$$

where Σ is the sum of the squares of the atomic scattering factors [*cf.* equation (2.1.2.4)]. The asymptotic form of the distribution of A is therefore given by

$$p(A) \, dA = (\pi\Sigma)^{-1/2} \exp(-A^2/\Sigma) \, dA. \quad (2.1.5.4)$$

A similar calculation, with sines instead of cosines, gives an analogous distribution for the imaginary part B , so that the joint probability of the real and imaginary parts of F is

$$p(A, B) \, dA \, dB = (\pi\Sigma)^{-1} \exp[-(A^2 + B^2)/\Sigma] \, dA \, dB. \quad (2.1.5.5)$$

Ordinarily, however, we are more interested in the distribution of the magnitude, $|F|$, of the structure factor than in the distribution of A and B . Using polar coordinates in equation (2.1.5.5) [$A = |F| \cos \phi$, $B = |F| \sin \phi$] and integrating over the angle ϕ gives

$$p(|F|) \, d|F| = (2|F|/\Sigma) \exp(-|F|^2/\Sigma) \, d|F|. \quad (2.1.5.6)$$

It is usually convenient, in structure-factor and intensity statistics, to express the results in terms of the normalized structure factor E and its magnitude $|E|$. If $|F|$ has been put on an absolute scale (see Section 2.2.4.3), we have

$$E = \frac{F}{\sqrt{\Sigma}} \quad \text{and} \quad |E| = \frac{|F|}{\sqrt{\Sigma}}, \quad (2.1.5.7)$$

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so that

$$p(|E|) d|E| = 2|E| \exp(-|E|^2) d|E| \quad (2.1.5.8)$$

is the normalized-structure-factor version of (2.1.5.6).

Distributions resulting from noncentrosymmetric crystals are known as *acentric* distributions; those arising from centrosymmetric crystals are known as *centric*. These adjectives are used to describe *distributions*, not crystal symmetry.

2.1.5.2. Ideal centric distributions

When a non-dispersive crystal is centrosymmetric, and the space-group origin is chosen at a crystallographic centre of symmetry, the imaginary part B of its structure amplitude is zero. In the simplest case, space group $P\bar{1}$, the contribution of the j th atom plus its centrosymmetric counterpart is $2f_j \cos \vartheta_j$. The calculation of $p(A)$ goes through as before, with allowance for the fact that there are $N/2$ pairs instead of N independent atoms, giving

$$p(A) dA = (2\pi\Sigma)^{-1/2} \exp[-A^2/(2\Sigma)] dA \quad (2.1.5.9)$$

or equivalently

$$p(|F|) d|F| = [2/(\pi\Sigma)]^{1/2} \exp[-|F|^2/(2\Sigma)] d|F| \quad (2.1.5.10)$$

or

$$p(|E|) d|E| = (2/\pi)^{1/2} \exp(-|E|^2/2) d|E|. \quad (2.1.5.11)$$

2.1.5.3. Effect of other symmetry elements on the ideal acentric and centric distributions

Additional crystallographic symmetry elements do not produce any essential alterations in the ideal centric or acentric distribution; their main effect is to replace the parameter Σ by a 'distribution parameter', called S by Wilson (1950) and Rogers (1950), in certain groups of reflections. In addition, in noncentrosymmetric space groups, the distribution of certain groups of reflections becomes centric, though the general reflections remain acentric. The changes are summarized in Tables 2.1.3.1 and 2.1.3.2. The values of S are integers for lattice centring, glide planes and those screw axes that produce absences, and approximate integers for rotation axes and mirror planes; the modulations of the average intensity in reciprocal space outlined in Section 2.1.3.2 apply.

It should be noted that if intensities are normalized to the average of the group to which they belong, rather than to the general average, the distributions given in equations (2.1.5.8) and (2.1.5.11) are not affected.

2.1.5.4. Other ideal distributions

The distributions just derived are asymptotic, as they are limiting values for large N . They are the only ideal distributions, in this sense, when there is only strict crystallographic symmetry and no dispersion. However, other ideal (asymptotic) distributions arise when there is noncrystallographic symmetry, or if there is dispersion. The *subcentric* distribution,

$$p(|E|) d|E| = \frac{2|E|}{(1-k^2)^{1/2}} \exp[-|E|^2/(1-k^2)] \times I_0\left(\frac{k|E|^2}{1-k^2}\right) d|E|, \quad (2.1.5.12)$$

where $I_0(x)$ is a modified Bessel function of the first kind and k is the ratio of the scattering from the centrosymmetric part to the total scattering, arises when a noncentrosymmetric crystal contains centrosymmetric parts or when dispersion introduces effective

noncentrosymmetry into the scattering from a centrosymmetric crystal (Srinivasan & Parthasarathy, 1976, ch. III; Wilson, 1980a,b; Shmueli & Wilson, 1983). The *bicentric* distribution

$$p(|E|) d|E| = \pi^{-3/2} \exp(-|E|^2/8) K_0(|E|^2/8) d|E| \quad (2.1.5.13)$$

arises, for example, when the 'asymmetric unit in a centrosymmetric crystal is a centrosymmetric molecule' (Lipson & Woolfson, 1952); $K_0(x)$ is a modified Bessel function of the second kind. There are higher hypercentric, hyperparallel and sesquicentric analogues (Wilson, 1952; Rogers & Wilson, 1953; Wilson, 1956). The ideal subcentric and bicentric distributions are expressed in terms of known functions, but the higher hypercentric and the sesquicentric distributions have so far been studied only through their moments and integral representations. Certain hypersymmetric distributions can be expressed in terms of Meijer's G functions (Wilson, 1987b).

2.1.5.5. Relation to distributions of I

When only the intrinsic probability distributions are being considered, it does not greatly matter whether the variable chosen is the intensity of reflection (I), or its positive square root, the modulus of the structure factor ($|F|$), since both are necessarily real and non-negative. In an obvious notation, the relation between the intensity distribution and the structure-factor distribution is

$$p_I(I) = (1/2)I^{-1/2}p_{|F|}(I^{1/2}) \quad (2.1.5.14)$$

or

$$p_{|F|}(|F|) = 2|F|p_I(|F|^2). \quad (2.1.5.15)$$

Statistical fluctuations in counting rates, however, introduce a small but finite probability of negative observed intensities (Wilson, 1978a, 1980a) and thus of imaginary structure factors. This practical complication is treated in *IT C* (1999, Parts 7 and 8).

Both the ideal centric and acentric distributions are simple members of the family of gamma distributions, defined by

$$\gamma_n(x) dx = [\Gamma(n)]^{-1} x^{n-1} \exp(-x) dx, \quad (2.1.5.16)$$

where n is a parameter, not necessarily integral, and $\Gamma(n)$ is the gamma function. Thus the ideal acentric intensity distribution is

$$p(I) dI = \exp(-I/\Sigma) d(I/\Sigma) \quad (2.1.5.17)$$

$$= \gamma_1(I/\Sigma) d(I/\Sigma) \quad (2.1.5.18)$$

and the ideal centric intensity distribution is

$$p(I) dI = (2\Sigma/\pi)^{1/2} \exp[-I/(2\Sigma)] d[I/(2\Sigma)] \quad (2.1.5.19)$$

$$= \gamma_{1/2}[I/(2\Sigma)] d[I/(2\Sigma)]. \quad (2.1.5.20)$$

The properties of gamma distributions and of the related beta distributions, summarized in Table 2.1.5.1, are used in Section 2.1.6 to derive the probability density functions of sums and of ratios of intensities drawn from one of the ideal distributions.

2.1.5.6. Cumulative distribution functions

The integral of the probability density function $f(x)$ from the lower end of its range up to an arbitrary value x is called the cumulative probability distribution, or simply the distribution function, $F(x)$, of x . It can always be written

$$F(x) = \int_{-\infty}^x f(u) du; \quad (2.1.5.21)$$

if the lower end of its range is not actually $-\infty$ one takes $f(x)$ as identically zero between $-\infty$ and the lower end of its range. For the distribution of A [equation (2.1.5.4) or (2.1.5.9)] the lower limit is in

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Table 2.1.5.1. *Some properties of gamma and beta distributions*

If $x_1, x_2, \dots, x_n$ are independent gamma-distributed variables with parameters $p_1, p_2, \dots, p_n$, their sum is a gamma-distributed variable with $p = p_1 + p_2 + \dots + p_n$.

If x and y are independent gamma-distributed variables with parameters p and q , then the ratio $u = x/y$ has the distribution $\beta_2(u; p, q)$.

With the same notation, the ratio $v = x/(x + y)$ has the distribution $\beta_1(v; p, q)$.

Differences and products of gamma-distributed variables do not lead to simple results. For proofs, details and references see Kendall & Stuart (1977).

Name of the distribution, its functional form, mean and variance
Gamma distribution with parameter p: $\gamma_p(x) = [\Gamma(x)]^{-1} x^{p-1} \exp(-x); \quad p \leq x \leq \infty, \quad p > 0$ mean: $\langle x \rangle = p$; variance: $\langle (x - \langle x \rangle)^2 \rangle = p$.
Beta distribution of first kind with parameters p and q: $\beta_1(x; p, q) = \frac{\Gamma(p+q)}{\Gamma(p)\Gamma(q)} x^{p-1} (1-x)^{q-1}; \quad 0 \leq x \leq \infty, \quad p, q > 0$ mean: $\langle x \rangle = p/(p+q)$; variance: $\langle (x - \langle x \rangle)^2 \rangle = pq/[(p+q)^2(p+q+1)]$.
Beta distribution of second kind with parameters p and q: $\beta_2(x; p, q) = \frac{\Gamma(p+q)}{\Gamma(p)\Gamma(q)} x^{p-1} (1+x)^{-p-q}; \quad 0 \leq x \leq \infty, \quad p, q > 0$ mean: $\langle x \rangle = p/(q-1)$; variance: $\langle (x - \langle x \rangle)^2 \rangle = p(p+q-1)/[(q-1)(q-2)]$.

fact $-\infty$; for the distribution of $|F|$, $|E|$, I and I/Σ the lower end of the range is zero. In such cases, equation (2.1.5.21) becomes

$$F(x) = \int_0^x f(x) dx. \quad (2.1.5.22)$$

In crystallographic applications the cumulative distribution is usually denoted by $N(x)$, rather than by the capital letter corresponding to the probability density function designation. The cumulative forms of the ideal acentric and centric distributions (Howells *et al.*, 1950) have found many applications. For the acentric distribution of $|E|$ [equation (2.1.5.8)] the integration is readily carried out:

$$N(|E|) = 2 \int_0^{|E|} y \exp(-y^2) dy = 1 - \exp(-|E|^2). \quad (2.1.5.23)$$

The integral for the centric distribution of $|E|$ [equation (2.1.5.11)] cannot be expressed in terms of elementary functions, but the integral required has so many important applications in statistics that it has been given a special name and symbol, the error function $\text{erf}(x)$, defined by

$$\text{erf}(x) = (2/\pi^{1/2}) \int_0^x \exp(-t^2) dt. \quad (2.1.5.24)$$

For the centric distribution, then

$$N(|E|) = (2/\pi)^{1/2} \int_0^{|E|} y \exp(-y^2/2) dy \quad (2.1.5.25)$$

$$= \text{erf}(|E|/2^{1/2}). \quad (2.1.5.26)$$

The error function is extensively tabulated [see *e.g.* Abramowitz & Stegun (1972), pp. 310–311, and a closely related function on pp. 966–973].

2.1.6. Distributions of sums, averages and ratios

2.1.6.1. Distributions of sums and averages

In Section 2.1.2.1, it was shown that the average intensity of a sufficient number of reflections is Σ [equation (2.1.2.4)]. When the number of reflections is not ‘sufficient’, their mean value will show statistical fluctuations about Σ ; such statistical fluctuations are in addition to any systematic variation resulting from non-independence of atomic positions, as discussed in Sections 2.1.2.1–2.1.2.3. We thus need to consider the probability density functions of sums like

$$J_n = \sum_{i=1}^n G_i, \quad (2.1.6.1)$$

and averages like

$$Y = J_n/n, \quad (2.1.6.2)$$

where G_i is the intensity of the i th reflection. The probability density distributions are easily obtained from a property of gamma distributions: If $x_1, x_2, \dots, x_n$ are independent gamma-distributed variables with parameters $p_1, p_2, \dots, p_n$, their sum is a gamma-distributed variable with parameter p equal to the sum of the parameters. The sum of n intensities drawn from an acentric distribution thus has the distribution

$$p(J_n) dJ_n = \gamma_n(J_n/\Sigma) d(J_n/\Sigma); \quad (2.1.6.3)$$

the parameters of the variables added are all equal to unity, so that their sum is p . Similarly, the sum of n intensities drawn from a centric distribution has the distribution

$$p(J_n) dJ_n = \gamma_{n/2}[J_n/(2\Sigma)] d[J_n/(2\Sigma)]; \quad (2.1.6.4)$$

each parameter has the value of one-half. The corresponding distributions of the averages of n intensities are then

$$p(Y) dY = \gamma_n(nY/\Sigma) d(nY/\Sigma) \quad (2.1.6.5)$$

for the acentric case, and

$$p(Y) dY = \gamma_{n/2}[nY/(2\Sigma)] d[nY/(2\Sigma)] \quad (2.1.6.6)$$

for the centric. In both cases the expected value of Y is Σ and the variances are Σ^2/n and $2\Sigma^2/n$, respectively, just as would be expected.

2.1.6.2. Distribution of ratios

Ratios like

$$S_{n,m} = J_n/K_m, \quad (2.1.6.7)$$

where J_n is given by equation (2.1.6.1),

$$K_m = \sum_{j=1}^m H_j, \quad (2.1.6.8)$$

and the H_j 's are the intensities of a set of reflections (which may or may not overlap with those included in J_n), are used in correlating intensities measured under different conditions. They arise in

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correlating reflections on different layer lines from the same or different specimens, in correlating the same reflections from different crystals, in normalizing intensities to the local average or to Σ , and in certain systematic trial-and-error methods of structure determination (see Rabinovich & Shakked, 1984, and references therein). There are three main cases:

(i) G_i and H_i refer to the *same* reflection; for example, they might be the observed and calculated quantities for the hkl reflection measured under different conditions or for different crystals of the same substance; or

(ii) G_i and H_i are *unrelated*; for example, the observed and calculated values for the hkl reflection for a completely wrong trial structure, of values for entirely different reflections, as in reducing photographic measurements on different layer lines to the same scale; or

(iii) the G_i 's are a subset of the H_i 's, so that $G_i = H_i$ for $i < n$ and $m > n$.

Aside from the scale factor, in case (i) G_i and H_i will differ chiefly through relatively small statistical fluctuations and uncorrected systematic errors, whereas in case (ii) the differences will be relatively large because of the inherent differences in the intensities. Here we are concerned only with cases (ii) and (iii); the practical problems of case (i) are postponed to IT C (1999).

There is little in the crystallographic literature concerning the probability distribution of sums like (2.1.6.1) or ratios like (2.1.6.7); certain results are reviewed by Srinivasan & Parthasarathy (1976, ch. 5), but with a bias toward partially related structures that makes it difficult to apply them to the immediate problem.

In case (ii) (G_i and H_i independent), acentric distribution, Table 2.1.5.1 gives the distribution of the ratio

$$u = nY/(mZ) \quad (2.1.6.9)$$

$$p(u) du = \beta_2[nY/(mZ); n, m] d[nY/(mZ)], \quad (2.1.6.10)$$

where β_2 is a beta distribution of the second kind, Y is given by equation (2.1.6.2) and Z by

$$Z = K_m/m, \quad (2.1.6.11)$$

where n is the number of intensities included in the numerator and m is the number in the denominator. The expected value of Y/Z is then

$$\langle Y/Z \rangle = \frac{m}{m-1} = 1 + \frac{1}{m} + \dots \quad (2.1.6.12)$$

with variance

$$\sigma^2 = \frac{(n+m-1)m^2}{(m-1)^2(m-2)n}. \quad (2.1.6.13)$$

One sees that Y/Z is a biased estimate of the scaling factor between two sets of intensities and the bias, of the order of m^{-1} , depends only on the number of intensities averaged in the denominator. This may seem odd at first sight, but it becomes plausible when one remembers that the mean of a quantity is an unbiased estimator of itself, but the reciprocal of a mean is not an unbiased estimator of the mean of a reciprocal. The mean exists only if $m > 1$ and the variance only for $m > 2$.

In the centric case, the expression for the distribution of the ratio of the two means Y and Z becomes

$$p(u) du = \beta_2[nY/(mZ); n/2, m/2] d[nY/(mZ)] \quad (2.1.6.14)$$

with the expected value of Y/Z equal to

$$\langle Y/Z \rangle = \frac{m}{m-2} = 1 + \frac{2}{m} + \dots \quad (2.1.6.15)$$

and with its variance equal to

$$\sigma^2 = \frac{2(n+m-2)m^2}{(m-2)^2(m-4)n}. \quad (2.1.6.16)$$

For the same number of reflections, the bias in $\langle Y/Z \rangle$ and the variance for the centric distribution are considerably larger than for the acentric. For both distributions the variance of the scaling factor approaches zero when n and m become large. The variances are large for m small, in fact 'infinite' if the number of terms averaged in the denominator is sufficiently small. These biases are readily removed by multiplying Y/Z by $(m-1)/m$ or $(m-2)/m$. Many methods of estimating scaling factors – perhaps most – also introduce bias (Wilson, 1975; Lomer & Wilson, 1975; Wilson, 1976, 1978c) that is not so easily removed. Wilson (1986a) has given reasons for supposing that the bias of the ratio (2.1.6.7) approximates to

$$1 + \frac{\sigma^2(I)}{m\langle I \rangle^2}, \quad (2.1.6.17)$$

whatever the intensity distribution. Equations (2.1.6.12) and (2.1.6.15) are consistent with this.

2.1.6.3. Intensities scaled to the local average

When the G_i 's are a subset of the H_i 's, the beta distributions of the second kind are replaced by beta distributions of the first kind, with means and variances readily found from Table 2.1.5.1. The distribution of such a ratio is chiefly of interest when Y relates to a single reflection and Z relates to a group of m intensities including Y . This corresponds to normalizing intensities to the local average. Its distribution is

$$p(I/\langle I \rangle) d(I/\langle I \rangle) = \beta_1(I/n\langle I \rangle; 1, n-1) d(I/n\langle I \rangle) \quad (2.1.6.18)$$

in the acentric case, with an expected value of $I/\langle I \rangle$ of unity; there is no bias, as is obvious *a priori*. The variance of $I/\langle I \rangle$ is

$$\sigma^2 = \frac{n-1}{n+1}, \quad (2.1.6.19)$$

which is less than the variance of the intensities normalized to an 'infinite' population by a fraction of the order of $2/n$. Unlike the variance of the scaling factor, the variance of the normalized intensity approaches unity as n becomes large. For intensities having a centric distribution, the distribution normalized to the local average is given by

$$p(I/\langle I \rangle) d(I/\langle I \rangle) = \beta_1[I/n\langle I \rangle; 1/2, (n-1)/2] d(I/n\langle I \rangle), \quad (2.1.6.20)$$

with an expected value of $I/\langle I \rangle$ of unity and with variance

$$\sigma^2 = \frac{2(n-1)}{n+2}, \quad (2.1.6.21)$$

less than that for an 'infinite' population by a fraction of about $3/n$.

Similar considerations apply to intensities normalized to Σ in the usual way, since they are equal to those normalized to $\langle I \rangle$ multiplied by $\langle I \rangle/\Sigma$.

2.1.6.4. The use of normal approximations

Since J_n and K_m [equations (2.1.6.1) and (2.1.6.8)] are sums of identically distributed variables conforming to the conditions of the central-limit theorem, it is tempting to approximate their distributions by normal distributions with the correct mean and variance. This would be reasonably satisfactory for the distributions of J_n and K_m themselves for quite small values of n and m , but unsatisfactory for the distribution of their ratio for any values of n and m , even large. The ratio of two variables with normal distributions is

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notorious for its rather indeterminate mean and 'infinite' variance, resulting from the 'tail' of the denominator distributions extending through zero to negative values. The leading terms of the ratio distribution are given by Kendall & Stuart (1977, p. 288).

2.1.7. Non-ideal distributions: the correction-factor approach

2.1.7.1. Introduction

The probability density functions (p.d.f.'s) of the magnitude of the structure factor, presented in Section 2.1.5, are based on the central-limit theorem discussed above. In particular, the centric and acentric p.d.f.'s given by equations (2.1.5.11) and (2.1.5.8), respectively, are expected to account for the statistical properties of diffraction patterns obtained from crystals consisting of nearly equal atoms, which obey the fundamental assumptions of uniformity and independence of the atomic contributions and are not affected by noncrystallographic symmetry and dispersion. It is also assumed there that the number of atoms in the asymmetric unit is large. Distributions of structure-factor magnitudes which are based on the central-limit theorem, and thus obey the above assumptions, have been termed 'ideal', and the subjects of the following sections are those distributions for which some of the above assumptions/restrictions are not fulfilled; the latter distributions will be called 'non-ideal'.

We recall that the assumption of uniformity consists of the requirement that the fractional part of the scalar product $hx + ky + lz$ be uniformly distributed over the $[0, 1]$ interval, which holds well if x, y, z are rationally independent (Hauptman & Karle, 1953), and permits one to regard the atomic contribution to the structure factor as a random variable. This is of course a necessary requirement for any statistical treatment. If, however, the atomic composition of the asymmetric unit is widely heterogeneous, the structure factor is then a sum of unequally distributed random variables and the Lindeberg-Lévy version of the central-limit theorem (cf. Section 2.1.4.4) cannot be expected to apply. Other versions of this theorem might still predict a normal p.d.f. of the sum, but at the expense of a correspondingly large number of terms/atoms. It is well known that atomic heterogeneity gives rise to severe deviations from ideal behaviour (e.g. Howells *et al.*, 1950) and one of the aims of crystallographic statistics has been the introduction of a correct dependence on the atomic composition into the non-ideal p.d.f.'s [for a review of the early work on non-ideal distributions see Srinivasan & Parthasarathy (1976)]. A somewhat less well known fact is that the dependence of the p.d.f.'s of $|E|$ on space-group symmetry becomes more conspicuous as the composition becomes more heterogeneous (e.g. Shmueli, 1979; Shmueli & Wilson, 1981). Hence both the composition and the symmetry dependence of the intensity statistics are of interest. Other problems, which likewise give rise to non-ideal p.d.f.'s, are the presence of heavy atoms in (variable) special positions, heterogeneous structures with complete or partial noncrystallographic symmetry, and the presence of outstandingly heavy dispersive scatterers.

The need for theoretical representations of non-ideal p.d.f.'s is exemplified in Fig. 2.1.7.1(a), which shows the ideal centric and acentric p.d.f.'s together with a frequency histogram of $|E|$ values, recalculated for a centrosymmetric structure containing a platinum atom in the asymmetric unit of $P\bar{1}$ (Faggiani *et al.*, 1980). Clearly, the deviation from the Gaussian p.d.f., predicted by the central-limit theorem, is here very large and a comparison with the possible ideal distributions can (in this case) lead to wrong conclusions.

Two general approaches have so far been employed in derivations of non-ideal p.d.f.'s which account for the above-mentioned problems: the correction-factor approach, to be dealt

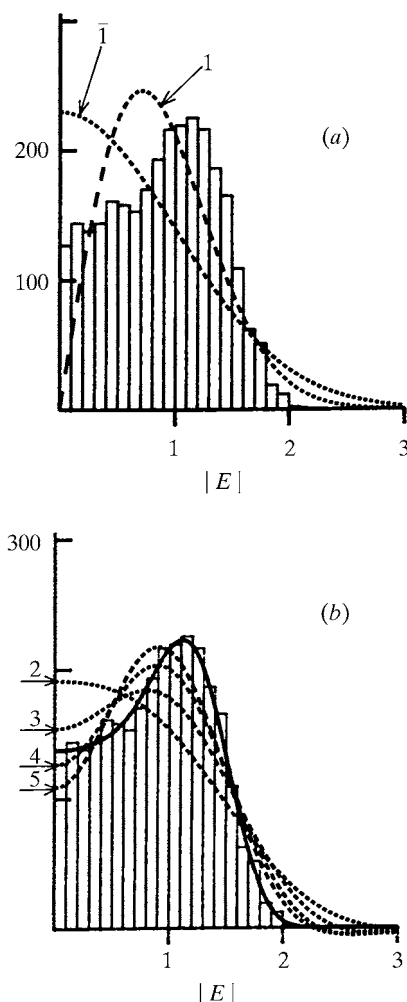


Fig. 2.1.7.1. Atomic heterogeneity and intensity statistics. The histogram appearing in (a) and (b) was constructed from $|E|$ values which were recalculated from atomic parameters published for the centrosymmetric structure of $C_6H_{18}Cl_2N_4O_4Pt$ (Faggiani *et al.*, 1980). The space group of the crystal is $P\bar{1}$, $Z = 2$, i.e. all the atoms are located in general positions. (a) A comparison of the recalculated distribution of $|E|$ with the ideal centric [equation (2.1.5.11)] and acentric [equation (2.1.5.8)] p.d.f.'s, denoted by $\bar{1}$ and 1 , respectively. (b) The same recalculated histogram along with the centric correction-factor p.d.f. [equation (2.1.7.5)], truncated after two, three, four and five terms (dashed lines), and with that accurately computed for the correct space-group Fourier p.d.f. [equations (2.1.8.5) and (2.1.8.22)] (solid line).

with in the following sections, and the more recently introduced Fourier method, to which Section 2.1.8 is dedicated. In what follows, we introduce briefly the mathematical background of the correction-factor approach, apply this formalism to centric and acentric non-ideal p.d.f.'s, and present the numerical values of the moments of the trigonometric structure factor which permit an approximate evaluation of such p.d.f.'s for all the three-dimensional space groups.

2.1.7.2. Mathematical background

Suppose that $p(x)$ is a p.d.f. which accurately describes the experimental distribution of the random variable x , where x is related to a sum of random variables and can be assumed to obey (to some approximation) an ideal p.d.f., say $p^{(0)}(x)$, based on the central-limit theorem. In the correction-factor approach we seek to represent $p(x)$ as

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$$p(x) = p^{(0)}(x) \sum_k d_k f_k(x), \quad (2.1.7.1)$$

where d_k are coefficients which depend on the cause of the deviation of $p(x)$ from the central-limit theorem approximation and $f_k(x)$ are suitably chosen functions of x . A choice of the set $\{f_k\}$ is deemed suitable, if only from a practical point of view, if it allows the convenient introduction of the cause of the above deviation of $p(x)$ into the expansion coefficients d_k . This requirement is satisfied – also from a theoretical point of view – by taking $f_k(x)$ as a set of polynomials which are orthogonal with respect to the ideal p.d.f., taken as their weight function (e.g. Cramér, 1951). That is, the functions $f_k(x)$ so chosen have to obey the relationship

$$\int_a^b f_k(x) f_m(x) p^{(0)}(x) dx = \delta_{km} = \begin{cases} 1, & \text{if } 2k = m \\ 0, & \text{if } 2k \neq m \end{cases}, \quad (2.1.7.2)$$

where $[a, b]$ is the range of existence of all the functions involved. It can be readily shown that the coefficients d_k are given by

$$d_k = \int_a^b f_k(x) p(x) dx = \langle f_k(x) \rangle = \sum_{n=0}^k c_n^{(k)} \langle x^n \rangle, \quad (2.1.7.3)$$

where the brackets $\langle \rangle$ in equation (2.1.7.3) denote averaging with respect to the *unknown* p.d.f. $p(x)$ and $c_n^{(k)}$ is the coefficient of the n th power of x in the polynomial $f_k(x)$. The coefficients d_k are thus directly related to the moments of the non-ideal distribution and the coefficients of the powers of x in the orthogonal polynomials. The latter coefficients can be obtained by the Gram–Schmidt procedure (e.g. Spiegel, 1974), or by direct use of the Szegő determinants (e.g. Cramér, 1951), for any weight function that has finite moments. However, the feasibility of the present approach depends on our ability to obtain the moments $\langle x^n \rangle$ *without* the knowledge of the non-ideal p.d.f., $p(x)$.

2.1.7.3. Application to centric and acentric distributions

We shall summarize here the non-ideal centric and acentric distributions of the magnitude of the normalized structure factor E (e.g. Shmueli & Wilson, 1981; Shmueli, 1982). We assume that (i) all the atoms are located in general positions and have rationally independent coordinates, (ii) all the scatterers are dispersionless, and (iii) there is no noncrystallographic symmetry. Arbitrary atomic composition and space-group symmetry are admitted. The appropriate weight functions and the corresponding orthogonal polynomials are

$p^{(0)}(E)$	$f_k(x)$	Non-ideal distribution
$(2/\pi)^{1/2} \exp(- E ^2/2)$	$He_{2k}(E)/[(2k)!]^{1/2}$	Centric
$2 E \exp(- E ^2)$	$L_k(E ^2)$	Acentric

(2.1.7.4)

where He_k and L_k are Hermite and Laguerre polynomials, respectively, as defined, for example, by Abramowitz & Stegun (1972). Equations (2.1.7.2), (2.1.7.3) and (2.1.7.4) suffice for the general formulation of the above non-ideal p.d.f.'s of $|E|$. Their full derivation entails (i) the expression of a sufficient number of moments of $|E|$ in terms of absolute moments of the trigonometric structure factor (e.g. Shmueli & Wilson, 1981; Shmueli, 1982) and (ii) calculation of the latter moments for the various symmetries (Wilson, 1978b; Shmueli & Kaldor, 1981, 1983). The notation below is similar to that employed by Shmueli (1982).

These non-ideal p.d.f.'s of $|E|$, for which the first five expansion terms are available, are given by

$$p_c(|E|) = p_c^{(0)}(|E|) \left[1 + \sum_{k=2}^{\infty} \frac{A_{2k}}{(2k)!} He_{2k}(|E|) \right] \quad (2.1.7.5)$$

and

$$p_a(|E|) = p_a^{(0)}(|E|) \left[1 + \sum_{k=2}^{\infty} \frac{(-1)^k B_{2k}}{k!} L_k(|E|^2) \right] \quad (2.1.7.6)$$

for centrosymmetric and noncentrosymmetric space groups, respectively, where $p_c^{(0)}(|E|)$ and $p_a^{(0)}(|E|)$ are the ideal centric and acentric p.d.f.'s [see (2.1.7.4)] and the unified form of the coefficients A_{2k} and B_{2k} , for $k = 2, 3, 4$ and 5 , is

$$\begin{aligned} A_4 \quad \text{or} \quad B_4 &= a_4 Q_4 \\ A_6 \quad \text{or} \quad B_6 &= a_6 Q_6 \\ A_8 \quad \text{or} \quad B_8 &= a_8 Q_8 + U(a_4^2 Q_4^2 - \gamma_4^2) \\ A_{10} \quad \text{or} \quad B_{10} &= a_{10} Q_{10} + V(a_4 a_6 Q_4 Q_6 - \gamma_4 \gamma_6 Q_{10}) \\ &\quad + W \gamma_4^2 Q_{10} \end{aligned} \quad (2.1.7.7)$$

(Shmueli, 1982), where $U = 35$ or 18 , $V = 210$ or 100 and $W = 3150$ or 900 according as A_{2k} or B_{2k} is required, respectively, and the other quantities in equation (2.1.7.7) are given below. The *composition-dependent* terms in equations (2.1.7.7) are

$$Q_{2k} = \frac{\sum_{j=1}^m f_j^{2k}}{(\sum_{n=1}^m f_n^2)^k}, \quad (2.1.7.8)$$

where m is the number of atoms in the asymmetric unit, f_j , $j = 1, \dots, m$ are their scattering factors, and the *symmetry* dependence is expressed by the coefficients a_{2k} in equation (2.1.7.7), as follows:

$$a_{2k} = (-1)^{k-1} (k-1)! \alpha_{k0} + \sum_{p=2}^k (-1)^{k-p} (k-p)! \alpha_{kp} \gamma_{2p}, \quad (2.1.7.9)$$

where

$$\alpha_{kp} = \binom{k}{p} \frac{(2k-1)!!}{(2p-1)!!} \quad \text{or} \quad \binom{k}{p} \frac{k!}{p!} \quad (2.1.7.10)$$

according as the space group is centrosymmetric or noncentrosymmetric, respectively, and γ_{2p} in equation (2.1.7.9) is given by

$$\gamma_{2p} = \frac{\langle |T|^{2p} \rangle}{\langle |T|^2 \rangle^p}, \quad (2.1.7.11)$$

where $\langle |T|^k \rangle$ is the k th absolute moment of the trigonometric structure factor

$$T(\mathbf{h}) = \sum_{s=1}^g \exp[2\pi i \mathbf{h}^T (\mathbf{P}_s \mathbf{r} + \mathbf{t}_s)] \equiv \xi(\mathbf{h}) + i\eta(\mathbf{h}). \quad (2.1.7.12)$$

In equation (2.1.7.12), g is the number of general equivalent positions listed in *ITA* (1983) for the space group in question, times the multiplicity of the Bravais lattice, $(\mathbf{P}_s, \mathbf{t}_s)$ is the s th space-group operator and $\mathbf{r}$ is an atomic position vector.

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Table 2.1.7.1. *Some even absolute moments of the trigonometric structure factor*

The symbols p , q , r and s denote the second, fourth, sixth and eighth absolute moments of the trigonometric structure factor T [equation (2.1.7.12)], respectively, and the columns of the table contain (for some conciseness) p , q , r/p and s/p^2 . The numbers in parentheses, appearing beside some space-group entries, refer to hkl subsets which are defined in the note at the end of the table. These subset references are identical with those given by Shmueli & Kaldor (1981, 1983). The symbols q , r and s are also equivalent to $\gamma_4 P^2$, $\gamma_6 P^3$ and $\gamma_8 P^4$, respectively, where γ_{2n} are the normalized absolute moments given by equation (2.1.7.11).

Space groups(s)	p	q	r/p	s/p^2
Point group: 1 $P1$	1	1	1	1
Point group: $\bar{1}$ $P\bar{1}$	2	6	10	17
Point groups: 2, m All P All C	2 4	6 48	10 160	17 560
Point group: $2/m$ All P All C	4 8	36 288	100 1600	$306\frac{1}{4}$ 9800
Point group: 222 All P All C and I $F222$	4 8 16	28 224 1792	64 1024 16384	$169\frac{3}{4}$ 5432 173824
Point group: $mm2$ All P All A , C and I $Fmm2$ $Fdd2$ (1) $Fdd2$ (2)	4 8 16 16 16	36 288 2304 2304 1280	100 1600 25600 25600 7168	$306\frac{1}{4}$ 9800 313600 313600 43264
Point group: mmm All P All C and I $Fmmm$ $Fddd$ (1) $Fddd$ (2)	8 16 32 32 32	216 1728 13824 13824 7680	1000 16000 256000 256000 71680	$5359\frac{3}{8}$ 171500 5488000 5488000 757120
Point group: 4 $P4$, $P4_2$ $P4_1^*$ (3) $P4_1^*$ (4) $I4$ $I4_1$ (5) $I4_1$ (6)	4 4 4 8 8 8	36 36 20 288 288 160	100 100 28 1600 1600 448	$306\frac{1}{4}$ $306\frac{1}{4}$ $42\frac{1}{4}$ 9800 9800 1352
Point group: $\bar{4}$ $P\bar{4}$ $I\bar{4}$	4 8	28 224	64 1024	$169\frac{3}{4}$ 5432
Point group: $4/m$ All P $I4/m$ $I4_1/a$ (7) $I4_1/a$ (8)	8 16 16 16	216 1728 1728 960	1000 16000 16000 4480	$5359\frac{3}{8}$ 171500 171500 23660
Point group: 422 $P422$, $P4_212$, $P4_222$, $P4_2212$ $P122$, $P4_1212^*$ (3) $P4_122$, $P4_1212^*$ (4) $I422$ $I4_122$ (7) $I4_122$ (8)	8 8 8 16 16 16	136 136 104 1088 1088 832	424 424 208 6784 6784 3328	$1682\frac{1}{8}$ $1682\frac{1}{8}$ $470\frac{1}{8}$ 53828 53828 15044

Space groups(s)	p	q	r/p	s/p^2
Point group: $4mm$ All P $I4mm$, $I4cm$ $I4_1md$, $I4_1cd$ (7) $I4_1md$, $I4_1cd$ (8)	8 16 16 16	168 1344 1344 832	640 10240 10240 3328	$2970\frac{5}{5}$ 95060 95060 15188
Point groups: $\bar{4}2m$, $4m2$ All P $I\bar{4}m2$, $I\bar{4}2m$, $I\bar{4}c2$ $I\bar{4}2d$ (5) $I\bar{4}2d$ (6)	8 16 16 16	136 1088 1088 832	424 6784 6784 3328	$1682\frac{1}{8}$ 53828 53828 15044
Point group: $4/mmm$ All P $I4/mmm$, $I4/mcm$ $I4_1/amd$, $I4_1/acd$ (5) $I4_1/amd$, $I4_1/acd$ (6)	16 32 32 32	1008 8064 8064 4992	6400 102400 102400 33280	$51985\frac{15}{16}$ 1663550 1663550 265790
Point group: 3 All P and R	3	15	31	71
Point group: $\bar{3}$ All P and R	6	90	310	1242
Point group: 32 All P and R	6	66	166	508
Point group: $3m$ $P3m1$, $P31m$, $R3m$ $P3c1$, $P31c$, (3); $R3c$ (1) $P3c1$, $P31c$, (4); $R3c$ (2)	6 6 6 6	66 66 66 66	178 178 154 154	604 604 412 412
Point group: $\bar{3}m$ $P\bar{3}1m$, $P\bar{3}m1$, $R\bar{3}m$ $P\bar{3}1c$, $P\bar{3}c1$ (3); $R\bar{3}c$ (1) $P\bar{3}1c$, $P\bar{3}c1$ (4); $R\bar{3}c$ (2)	12 12 12 12	396 396 396 396	1780 1780 1540 1540	$10578\frac{3}{4}$ $10578\frac{3}{4}$ $7218\frac{3}{4}$ $7218\frac{3}{4}$
Point group: 6 $P6$ $P6_1^*$ (9) $P6_1^*$ (10) $P6_1^*$ (11) $P6_1^*$ (12) $P6_2^*$ (13) $P6_2^*$ (14) $P6_3$ (3) $P6_3$ (4)	6 6 6 6 6 6 6 6 6	90 90 54 54 90 90 54 90 90	340 340 91 97 280 340 97 340 280	1522 1522 161 193 962 1522 193 1522 962
Point group: $\bar{6}$ $P\bar{6}$	6	90	310	1242
Point group: $6/m$ $P6/m$ $P6_3/m$ (3)	12 12 12	540 540 540	3400 3400 3400	$26643\frac{3}{4}$ $26643\frac{3}{4}$ $26643\frac{3}{4}$

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Table 2.1.7.1. *Some even absolute moments of the trigonometric structure factor (cont.)*

Space groups(s)	p	q	r/p	s/p^2
$P6_3/m$ (4)	12	540	2800	$16843\frac{3}{4}$
Point group: 622				
$P622$	12	324	1150	$5506\frac{1}{4}$
$P6_122^*$ (9)	12	324	1150	$5506\frac{1}{4}$
$P6_122^*$ (10)	12	252	577	$1537\frac{3}{4}$
$P6_122^*$ (11)	12	252	583	$1601\frac{3}{4}$
$P6_122^*$ (12)	12	324	1090	$4746\frac{1}{4}$
$P6_222^*$ (13)	12	324	1150	$5506\frac{1}{4}$
$P6_222^*$ (14)	12	252	583	$1601\frac{3}{4}$
$P6_322$ (3)	12	324	1150	$5506\frac{1}{4}$
$P6_322$ (4)	12	324	1090	$4746\frac{1}{4}$
Point group: 6mm				
$P6mm$	12	396	1930	$12818\frac{3}{4}$
$P6cc$ (3)	12	396	1930	$12818\frac{3}{4}$
$P6cc$ (4)	12	396	1450	$6098\frac{3}{4}$
$P6_3cm, P6_3mc$ (3)	12	396	1930	$12818\frac{3}{4}$
$P6_3cm, P6_3mc$ (4)	12	396	1630	$8338\frac{3}{4}$
Point groups: 6m2, 62m				
$P6m2, P62m$	12	396	1780	$10578\frac{3}{4}$
$P6c2, P62c$ (3)	12	396	1780	$10578\frac{3}{4}$
$P6c2, P62c$ (4)	12	396	1540	$7218\frac{3}{4}$
Point group: 6/mmm				
$P6/mmm$	24	2376	19300	$224328\frac{1}{8}$
$P6/mcc$ (3)	24	2376	19300	$224328\frac{1}{8}$
$P6/mcc$ (4)	24	2376	14500	$106728\frac{1}{8}$
$P6/mcm, P6/mmc$ (3)	24	2376	19300	$224328\frac{1}{8}$
$P6/mcm, P6/mmc$ (4)	24	2376	16300	$145928\frac{1}{8}$
Point group: 23				
$P23, P2_13$	12	276	760	$2695\frac{1}{4}$
$I23, I2_13$	24	2208	12160	86248
$F23$	48	17664	194560	2759936
Point group: m3				
$Pm\bar{3}, Pn\bar{3}, Pa\bar{3}$	24	1800	9400	$67703\frac{1}{8}$
$Im\bar{3}, Ia\bar{3}$	48	14400	150400	2166500
$Fm\bar{3}$	96	115200	2406400	69328000
$Fd\bar{3}$ (1)	96	115200	2406400	69328000
$Fd\bar{3}$ (2)	96	96768	1484800	28183680

Space groups(s)	p	q	r/p	s/p^2
Point group: 432				
$P432, P4_232$	24	1272	4648	$25216\frac{7}{8}$
$P4_132^*$ (15)	24	1272	4648	$25216\frac{7}{8}$
$P4_132^*$ (16)	24	1176	3568	$13916\frac{7}{8}$
$P4_132^*$ (17)	24	1080	2776	$8664\frac{7}{8}$
$P4_132^*$ (18)	24	984	2272	$6580\frac{7}{8}$
$I432$	48	10176	74368	806940
$I4_132$ (15)	48	10176	74368	806940
$I4_132$ (17)	48	8640	44416	277276
$F432$	96	81408	1189888	25822080
$F4_132$ (15)	96	81408	1189888	25822080
$F4_132$ (18)	96	62976	581632	6738816
Point group: 43m				
$P\bar{4}3m$	24	1272	5128	$32896\frac{7}{8}$
$P\bar{4}3n$ (1)	24	1272	5128	$32896\frac{7}{8}$
$P\bar{4}3n$ (2)	24	1272	4168	$17536\frac{7}{8}$
$I\bar{4}3m$	48	10176	82048	1052700
$I\bar{4}3d$ (15); (20)	48	10176	82048	1052700
$I\bar{4}3d$ (15); (21)	48	10176	66688	561180
$I\bar{4}3d$ (17)	48	8640	44416	277276
$F\bar{4}3m$	96	81408	1312768	33686400
$F\bar{4}3c$ (15)	96	81408	1312768	33686400
$F\bar{4}3c$ (18)	96	81408	1067008	17957760
Point group: m3m				
$Pm\bar{3}m, Pn\bar{3}m$	48	8784	72160	$972717\frac{13}{16}$
$Pn\bar{3}n, Pm\bar{3}n$ (1)	48	8784	72160	$972717\frac{13}{16}$
$Pn\bar{3}n, Pm\bar{3}n$ (2)	48	8784	56800	$488877\frac{13}{16}$
$Im\bar{3}m$	96	70272	1154560	31126970
$Ia\bar{3}d$ (15); (20)	96	70272	1154560	31126970
$Ia\bar{3}d$ (15); (21)	96	51840	432640	4497850
$Ia\bar{3}d$ (17)	96	70272	908800	15644090
$Fm\bar{3}m$	192	562176	18472960	996063040
$Fm\bar{3}c$ (1)	192	562176	18472960	996063040
$Fm\bar{3}c$ (2)	192	562176	14540800	500610880
$Fd\bar{3}m$ (1)	192	562176	18472960	996063040
$Fd\bar{3}m$ (2)	192	414720	7782400	205432640
$Fd\bar{3}c$ (1)	192	562176	18472960	996063040
$Fd\bar{3}c$ (2)	192	414720	6799360	136619840

Note. hkl subsets: (1) $h+k+l=2n$; (2) $h+k+l=2n+1$; (3) $l=2n$; (4) $l=2n+1$; (5) $2h+l=2n$; (6) $2h+l=2n+1$; (7) $2k+l=2n$; (8) $2k+l=2n+1$; (9) $l=6n$; (10) $l=6n+1, 6n+5$; (11) $l=6n+2, 6n+4$; (12) $l=6n+3$; (13) $l=3n$; (14) $l=3n+1, 3n+2$; (15) hkl all even; (16) only one index odd; (17) only one index even; (18) hkl all odd; (19) two indices odd; (20) $h+k+l=4n$; (21) $h+k+l=4n+2$.

* And the enantiomorphous space group.

The cumulative distribution functions, obtained by integrating equations (2.1.7.5) and (2.1.7.6), are given by

$$N_c(|E|) = \operatorname{erf}\left(\frac{|E|}{\sqrt{2}}\right) - \frac{2}{\sqrt{\pi}} \exp\left(-\frac{|E|^2}{2}\right) \times \left[\sum_{k=2}^{\infty} \frac{A_{2k}}{(2k)!} He_{2k-1}(|E|) \right] \quad (2.1.7.13)$$

and

$$N_a(|E|) = 1 - \exp(-|E|^2) + \exp(-|E|^2) \times \left\{ \sum_{k=2}^{\infty} \frac{(-1)^k B_{2k}}{k!} [L_{k-1}(|E|^2) - L_k(|E|^2)] \right\} \quad (2.1.7.14)$$

for centrosymmetric and noncentrosymmetric space groups, respectively, where the coefficients are defined in equations (2.1.7.7)–(2.1.7.12). Note that the first term on the right-hand side

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Table 2.1.7.2. *Closed expressions for γ_{2k} [equation (2.1.7.11)] for space groups of low symmetry*

The normalized moments γ_{2k} are expressed in terms of M_k , where

$$M_k = \frac{(2k)!}{2^k (k!)^2} = \frac{(2k-1)!!}{k!},$$

and l' , which takes on the values 1, 2 or 4 according as the Bravais lattice is of type P , one of the types A , B , C or I , or type F , respectively. The expressions for γ_{2k} are identical for all the space groups based on a given point group, except $Fdd2$ and $Fddd$. The expressions are valid for general reflections and under the restrictions given in the text.

Point group(s)	Expression for γ_{2k}
1	1
$\bar{1}, 2, m$	$l'^{k-1} M_k$
$2/m, mm2$	$l'^{k-1} M_k^2$
mmm	$l'^{k-1} M_k^3$
222	$\frac{l'^{k-1}}{2^k (k!)^2} \sum_{p=0}^k (M_p M_{k-p})^3 [p!(k-p)!]^2$

of equation (2.1.7.13) and the first two terms on the right-hand side of equation (2.1.7.14) are just the cumulative distributions derived from the ideal centric and acentric p.d.f.'s in Section 2.1.5.6.

The moments $\langle |T|^{2k} \rangle$ were compiled for all the space groups by Wilson (1978*b*) for $k = 1$ and 2, and by Shmueli & Kaldor (1981, 1983) for $k = 1, 2, 3$ and 4. These results are presented in Table 2.1.7.1. Closed expressions for the normalized moments γ_{2p} were obtained by Shmueli (1982) for the triclinic, monoclinic and orthorhombic space groups except $Fdd2$ and $Fddd$ (see Table 2.1.7.2). The composition-dependent terms, Q_{2k} , are most conveniently computed as weighted averages over the ranges of $(\sin \theta)/\lambda$ which were used in the construction of the Wilson plot for the computation of the $|E|$ values.

2.1.7.4. Fourier versus Hermite approximations

As noted in Section 2.1.8.7 below, the Fourier representation of the probability distribution of $|F|$ is usually much better than the particular orthogonal-function representation discussed in Section 2.1.7.3. Many, perhaps most, non-ideal centric distributions look like slight distortions of the ideal (Gaussian) distribution and have no resemblance to a cosine function. The empirical observation thus seems paradoxical. The probable explanation has been pointed out by Wilson (1986*b*). A truncated Fourier series is a best approximation, in the least-squares sense, to the function represented. The particular orthogonal-function approach used in equation (2.1.7.5), on the other hand, is not a least-squares approximation to $p_c(|E|)$, but is a least-squares approximation to

$$p_c(|E|) \exp(|E|^2/4). \quad (2.1.7.15)$$

The usual expansions (often known as Gram–Charlier or Edgeworth) thus give great weight to fitting the distribution of the (comparatively few) strong reflections, at the expense of a poor fit for the (much more numerous) weak-to-medium ones. Presumably, a similar situation exists for the representation of acentric distributions, but this has not been investigated in detail. Since the centric distributions $p_c(|E|)$ often look nearly Gaussian, one is led to ask if there is an expansion in orthogonal functions that (i) has the leading term $p_c(|E|)$ and (ii) is a least-squares (as well as an

orthogonal-function)* fit to $p_c(|E|)$. One does exist, based on the orthogonal functions

$$f_k = n(x) He_k(2^{1/2}x), \quad (2.1.7.16)$$

where $n(x)$ is the Gaussian distribution (Myller-Lebedeff, 1907). Unfortunately, no reasonably simple relationship between the coefficients d_k and readily evaluated properties of $p_c(|E|)$ has been found, and the Myller-Lebedeff expansion has not, as yet, been applied in crystallography. Although Stuart & Ord (1994, p. 112) dismiss it in a three-line footnote, it does have important applications in astronomy (van der Marel & Franx, 1993; Gerhard, 1993).

2.1.8. Non-ideal distributions: the Fourier method

The starting point of the method described in the previous section is the central-limit theorem approximation, and the method consists of finding correction factors which result in better approximations to the actual p.d.f. Conceptually, this is equivalent to improving the approximation of the characteristic function [cf. equation (2.1.4.10)] over that which led to the central-limit theorem result.

The method to be described in this section does not depend on any initial approximation and will be shown to utilize the dependence of the exact value of the characteristic function on the space-group symmetry, atomic composition and other factors. This approach has its origin in a simple but ingenious observation by Barakat (1974), who noted that if a random variable has lower and upper bounds then the corresponding p.d.f. can be non-zero only within these bounds and can therefore be expanded in an ordinary Fourier series and set to zero (identically) outside the bounded interval. Barakat's (1974) work dealt with intensity statistics of laser speckle, where sinusoidal waves are involved, as in the present problem. This method was applied by Weiss & Kiefer (1983) to testing the accuracy of a steepest-descent approximation to the exact solution of the problem of random walk, and its first application to crystallographic intensity statistics soon followed (Shmueli *et al.*, 1984). Crystallographic (*e.g.* Shmueli & Weiss, 1987; Rabinovich *et al.*, 1991*a,b*) and noncrystallographic (Shmueli *et al.*, 1985; Shmueli & Weiss, 1985*a*; Shmueli, Weiss & Wilson, 1989; Shmueli *et al.*, 1990) symmetry was found to be tractable by this approach, as well as joint conditional p.d.f.'s of several structure factors (Shmueli & Weiss, 1985*b*, 1986; Shmueli, Rabinovich & Weiss, 1989). The Fourier method is illustrated below by deriving the exact counterparts of equations (2.1.7.5) and (2.1.7.6) and specifying them for some simple symmetries. We shall then indicate a method of treating higher symmetries and present results which will suffice for evaluation of Fourier p.d.f.'s of $|E|$ for a wide range of space groups.

2.1.8.1. General representations of p.d.f.'s of $|E|$ by Fourier series

We assume, as before, that (i) the atomic phase factors $\vartheta_j = 2\pi \mathbf{h}^T \mathbf{r}_j$ [cf. equation (2.1.1.2)] are uniformly distributed on $(0-2\pi)$ and (ii) the atomic contributions to the structure factor are independent. For a centrosymmetric space group, with the origin chosen at a centre of symmetry, the random variable is the (real) normalized structure factor E and its bounds are $-E_M$ and E_M , where

* The condition for this desirable property seems to be that the weight function in equation (2.1.7.2) should be unity.

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$$E_M = \sum_{j=1}^N n_j, \text{ with } n_j = \frac{f_j}{\left(\sum_{k=1}^N f_k^2\right)^{1/2}}. \quad (2.1.8.1)$$

Here, E_M is the maximum possible value of E and f_j is the conventional scattering factor of the j th atom, including its temperature factor. The p.d.f., $p(E)$, can be non-zero in the range $(-E_M, E_M)$ only and can thus be expanded in the Fourier series

$$p(E) = (\alpha/2) \sum_{k=-\infty}^{\infty} C_k \exp(-\pi i k \alpha E), \quad (2.1.8.2)$$

where $\alpha = 1/E_M$. Only the real part of $p(E)$ is relevant. The Fourier coefficients can be obtained in the conventional manner by integrating over the range $(-E_M, E_M)$,

$$C_k = \int_{-E_M}^{E_M} p(E) \exp(\pi i k \alpha E) dE. \quad (2.1.8.3)$$

Since, however, $p(E) = 0$ for $E < -E_M$ and $E > E_M$, it is possible and convenient to replace the limits of integration in equation (2.1.8.3) by infinity. Thus

$$C_k = \int_{-\infty}^{\infty} p(E) \exp(\pi i k \alpha E) dE = \langle \exp(\pi i k \alpha E) \rangle. \quad (2.1.8.4)$$

Equation (2.1.8.4) shows that C_k is a Fourier transform of the p.d.f. $p(E)$ and, as such, it is the value of the corresponding characteristic function at the point $t_k = \pi \alpha k$ [i.e., $C_k = C(\pi \alpha k)$], where the characteristic function $C(t)$ is defined by equation (2.1.4.1). It is also seen that C_k is the expected value of the exponential $\exp(\pi i k \alpha E)$. It follows that the feasibility of the present approach depends on one's ability to evaluate the characteristic function in closed form *without* the knowledge of the p.d.f.; this is analogous to the problem of evaluating absolute moments of the structure factor for the correction-factor approach, discussed in Section 2.1.7. Fortunately, in crystallographic applications these calculations are feasible, provided individual isotropic motion is assumed. The formal expression for the p.d.f. of $|E|$, for any centrosymmetric space group, is therefore

$$p(|E|) = \alpha \left[1 + 2 \sum_{k=1}^{\infty} C_k \cos(\pi k \alpha |E|) \right], \quad (2.1.8.5)$$

where use is made of the assumption that $p(E) = p(-E)$, and the Fourier coefficients are evaluated from equation (2.1.8.4).

The p.d.f. of $|E|$ for a noncentrosymmetric space group is obtained by first deriving the joint p.d.f. of the real and imaginary parts of E and then integrating out its phase. The general expression for E is

$$E = A + iB = |E| \cos \varphi + i|E| \sin \varphi, \quad (2.1.8.6)$$

where φ is the phase of E . The required joint p.d.f. is

$$p(A, B) = (\alpha^2/4) \sum_m \sum_n C_{mn} \exp[-\pi i \alpha (mA + nB)], \quad (2.1.8.7)$$

and introducing polar coordinates $m = r \sin \Delta$ and $n = r \cos \Delta$, where $r = \sqrt{m^2 + n^2}$ and $\Delta = \tan^{-1}(m/n)$, we have

$$p(|E|, \varphi) = (\alpha^2/4) |E| \sum_m \sum_n C_{mn} \exp[-\pi i \alpha |E| \times \sqrt{m^2 + n^2} \sin(\varphi + \Delta)]. \quad (2.1.8.8)$$

Integrating out the phase φ , we obtain

$$p(|E|) = (\pi \alpha^2 |E|/2) \sum_m \sum_n C_{mn} J_0(\pi \alpha |E| \sqrt{m^2 + n^2}), \quad (2.1.8.9)$$

where $J_0(x)$ is the Bessel function of the first kind (e.g. Abramowitz & Stegun, 1972). This is a general form of the p.d.f. of $|E|$ for a noncentrosymmetric space group. The Fourier coefficients are obtained, similarly to the above, as

$$C_{mn} = \langle \exp[\pi i \alpha (mA + nB)] \rangle \quad (2.1.8.10)$$

and the average in equation (2.1.8.10), just as that in equation (2.1.8.4), is evaluated in terms of integrals over the appropriate trigonometric structure factors. In terms of the characteristic function for a joint p.d.f. of A and B , the Fourier coefficient in equation (2.1.8.10) is given by $C_{mn} = C(\pi \alpha m, \pi \alpha n)$.

We shall denote the characteristic function by $C(t_1)$ if it corresponds to a Fourier coefficient of a Fourier series for a centrosymmetric space group and by $C(t_1, t_2)$ or by $C(t, \Delta)$, where $t = (t_1^2 + t_2^2)^{1/2}$ and $\Delta = \tan^{-1}(t_1/t_2)$, if it corresponds to a Fourier series for a noncentrosymmetric space group.

2.1.8.2. Fourier-Bessel series

Equations (2.1.8.5) and (2.1.8.9) are the exact counterparts of equations (2.1.7.5) and (2.1.7.6), respectively. The computational effort required to evaluate equation (2.1.8.9) is somewhat greater than that for (2.1.8.5), because a double Fourier series has to be summed. The p.d.f. for *any* noncentrosymmetric space group can be expressed by a double Fourier series, but this can be simplified if the characteristic function depends on $t = (t_1^2 + t_2^2)^{1/2}$ alone, rather than on t_1 and t_2 separately. In such cases the p.d.f. of $|E|$ for a noncentrosymmetric space group can be expanded in a *single* Fourier-Bessel series (Barakat, 1974; Weiss & Kiefer, 1983; Shmueli *et al.*, 1984). The general form of this expansion is

$$p(|E|) = 2\alpha^2 |E| \sum_{u=1}^{\infty} D_u J_0(\alpha \lambda_u |E|), \quad (2.1.8.11)$$

where

$$D_u = \frac{C(\alpha \lambda_u)}{J_1^2(\lambda_u)} \quad (2.1.8.12)$$

and

$$C(\alpha \lambda_u) = \prod_{j=1}^{N/g} C_{ju}, \quad (2.1.8.13)$$

where $J_1(x)$ is the Bessel function of the first kind, and λ_u is the u th root of the equation $J_0(x) = 0$; the atomic contribution C_{ju} to equation (2.1.8.13) is computed as

$$C_{ju} = C(\alpha n_j \lambda_u). \quad (2.1.8.14)$$

The roots λ_u are tabulated in the literature (e.g. Abramowitz & Stegun, 1972), but can be most conveniently computed as follows. The first five roots are given by

$$\lambda_1 = 2.404825577$$

$$\lambda_2 = 5.5200781103$$

$$\lambda_3 = 8.6537279129$$

$$\lambda_4 = 11.7915344390$$

$$\lambda_5 = 14.9309177085$$

and the higher ones can be obtained from McMahon's approximation (cf. Abramowitz & Stegun, 1972)

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$$\lambda_u = \beta + \frac{1}{8\beta} - \frac{124}{3(8\beta)^3} + \frac{120928}{15(8\lambda)^5} - \frac{401743168}{105(8\lambda)^7} + \dots, \quad (2.1.8.15)$$

where $\beta = (u - \frac{1}{4})\pi$. For $u > 5$ the values given by equation (2.1.8.15) have a relative error less than 10^{-11} so that no refinement of roots of higher orders is needed (Shmueli *et al.*, 1984). Numerical computations of single Fourier–Bessel series are of course faster than those of the double Fourier series, but both representations converge fairly rapidly.

2.1.8.3. Simple examples

Consider the Fourier coefficient of the p.d.f. of $|E|$ for the centrosymmetric space group $P\bar{1}$. The normalized structure factor is given by

$$E = 2 \sum_{j=1}^{N/2} n_j \cos \vartheta_j, \quad \text{with} \quad \vartheta_j = 2\pi \mathbf{h}^T \cdot \mathbf{r}_j, \quad (2.1.8.16)$$

and the Fourier coefficient is

$$C_k = \langle \exp(\pi i k \alpha E) \rangle \quad (2.1.8.17)$$

$$= \left\langle \exp \left[2\pi i k \alpha \sum_{j=1}^{N/2} n_j \cos \vartheta_j \right] \right\rangle \quad (2.1.8.18)$$

$$= \left\langle \prod_{j=1}^{N/2} \exp(2\pi i k \alpha n_j \cos \vartheta_j) \right\rangle \quad (2.1.8.19)$$

$$= \prod_{j=1}^{N/2} \langle \exp(2\pi i k \alpha n_j \cos \vartheta_j) \rangle \quad (2.1.8.20)$$

$$= \prod_{j=1}^{N/2} \left\{ (1/2\pi) \int_{-\pi}^{\pi} \exp(2\pi i k \alpha n_j \cos \vartheta) d\vartheta \right\} \quad (2.1.8.21)$$

$$= \prod_{j=1}^{N/2} J_0(2\pi k \alpha n_j). \quad (2.1.8.22)$$

Equation (2.1.8.20) is obtained from equation (2.1.8.19) if we make use of the assumption of independence, the assumption of uniformity allows us to rewrite equation (2.1.8.20) as (2.1.8.21), and the expression in the braces in the latter equation is just a definition of the Bessel function $J_0(2\pi k \alpha n_j)$ (e.g. Abramowitz & Stegun, 1972).

Let us now consider the Fourier coefficient of the p.d.f. of $|E|$ for the noncentrosymmetric space group $P1$. We have

$$A = \sum_{j=1}^N n_j \cos \vartheta_j \quad \text{and} \quad B = \sum_{j=1}^N n_j \sin \vartheta_j. \quad (2.1.8.23)$$

These expressions for A and B are substituted in equation (2.1.8.10), resulting in

$$C_{mn} = \left\langle \prod_{j=1}^N \exp[\pi i \alpha n_j (m \cos \vartheta_j + n \sin \vartheta_j)] \right\rangle \quad (2.1.8.24)$$

$$= \left\langle \prod_{j=1}^N \exp[\pi i \alpha n_j \sqrt{m^2 + n^2} \sin(\vartheta_j + \Delta)] \right\rangle \quad (2.1.8.25)$$

$$= \prod_{j=1}^N J_0(\pi \alpha n_j \sqrt{m^2 + n^2}). \quad (2.1.8.26)$$

Equation (2.1.8.24) leads to (2.1.8.25) by introducing polar coordinates analogous to those leading to equation (2.1.8.8), and equation (2.1.8.26) is then obtained by making use of the assumptions of independence and uniformity in an analogous manner to that detailed in equations (2.1.8.12)–(2.1.8.22) above.

The right-hand side of equation (2.1.8.26) is to be used as a Fourier coefficient of the double Fourier series given by (2.1.8.9). Since, however, this coefficient depends on $(m^2 + n^2)^{1/2}$ alone rather than on m and n separately, the p.d.f. of $|E|$ for $P1$ can also be represented by a Fourier–Bessel series [cf. equation (2.1.8.11)] with coefficient

$$D_u = \frac{1}{J_1^2(\lambda_u)} \prod_{j=1}^N J_0(\alpha n_j \lambda_u), \quad (2.1.8.27)$$

where λ_u is the u th root of the equation $J_0(x) = 0$.

2.1.8.4. A more complicated example

We now illustrate the methodology of deriving characteristic functions for space groups of higher symmetries, following the method of Rabinovich *et al.* (1991a,b). The derivation is performed for the space group $P\bar{6}$ [No. 174]. According to Table A1.4.3.6, the real and imaginary parts of the normalized structure factor are given by

$$\begin{aligned} A &= 2 \sum_{j=1}^{N/6} n_j [C(hki)c(lz)]_j \\ &= 2 \sum_{j=1}^{N/6} n_j \cos \tau_j \sum_{k=1}^3 \cos \alpha_{jk} \end{aligned} \quad (2.1.8.28)$$

and

$$\begin{aligned} B &= 2 \sum_{j=1}^{N/6} n_j [S(hki)c(lz)]_j \\ &= 2 \sum_{j=1}^{N/6} n_j \cos \tau_j \sum_{k=1}^3 \sin \alpha_{jk}, \end{aligned} \quad (2.1.8.29)$$

where

$$\begin{aligned} \alpha_{j1} &= 2\pi(hx_j + ky_j), \\ \alpha_{j2} &= 2\pi(kx_j + iy_j), \\ \alpha_{j3} &= 2\pi(ix_j + hy_j), \\ \tau_j &= 2\pi lz_j. \end{aligned}$$

Note that $\alpha_{j1} + \alpha_{j2} + \alpha_{j3} = 0$, i.e., one of these contributions depends on the other two; this is a recurring problem in calculations pertaining to trigonal and hexagonal systems. For brevity, we write directly the general form of the characteristic function from which the functional form of the Fourier coefficient can be readily obtained. The characteristic function is given by

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$$C(t_1, t_2) = \langle \exp[i(t_1 A + t_2 B)] \rangle \quad (2.1.8.30)$$

$$= \prod_{j=1}^{N/6} \left\langle \exp \left[2in_j \cos \tau_j \sum_{k=1}^3 (t_1 \cos \alpha_{jk} + t_2 \sin \alpha_{jk}) \right] \right\rangle \quad (2.1.8.31)$$

$$= \prod_{j=1}^{N/6} \left\langle \exp \left[2in_j t \cos \tau_j \sum_{k=1}^3 (\sin \Delta \cos \alpha_{jk} + \cos \Delta \sin \alpha_{jk}) \right] \right\rangle \quad (2.1.8.32)$$

$$= \prod_{j=1}^{N/6} \left\langle \exp \left[2in_j t \cos \tau_j \sum_{k=1}^3 \sin(\alpha_{jk} + \Delta) \right] \right\rangle, \quad (2.1.8.33)$$

where $\Delta = \tan^{-1}(t_1/t_2)$, $t = (t_1^2 + t_2^2)^{1/2}$ and the assumption of independence was used. If we further employ the assumption of uniformity, while remembering that the angular variables α_{jk} are not independent, the characteristic function can be written as

$$C(t_1, t_2) = \prod_{j=1}^{N/6} \left\{ (1/2\pi) \int_{-\pi}^{\pi} d\tau \left([1/(2\pi)^2] \right. \right. \\ \times \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} d\alpha_1 d\alpha_2 d\alpha_3 \delta_{2\pi}(\alpha_1 + \alpha_2 + \alpha_3) \\ \times \left. \left. \exp \left[2in_j t \cos \tau \sum_{k=1}^3 \sin(\alpha_k + \Delta) \right] \right) \right\}, \quad (2.1.8.34)$$

where

$$\delta_{2\pi}(\alpha) = \frac{1}{2\pi} \sum_{k=-\infty}^{\infty} \exp(-ik\alpha) \quad (2.1.8.35)$$

is the Fourier representation of the periodic delta function. Equation (2.1.8.34) then becomes

$$C(t_1, t_2) = \prod_{j=1}^{N/6} \left\{ (1/2\pi) \int_{-\pi}^{\pi} d\tau \sum_{k=-\infty}^{\infty} \left[(1/2\pi) \right. \right. \\ \times \left. \left. \int_{-\pi}^{\pi} \exp(-ik\alpha + 2in_j t \cos \tau \sin(\alpha + \Delta)) d\alpha \right]^3 \right\}. \quad (2.1.8.36)$$

If we change the variable α to $\alpha' - \Delta$, $\sin(\alpha + \Delta)$ becomes $\sin \alpha'$ and $-ik\alpha = -ik\alpha' + ik\Delta$. Hence

$$C(t_1, t_2) = \prod_{j=1}^{N/6} \left\{ (1/2\pi) \int_{-\pi}^{\pi} d\tau \sum_{k=-\infty}^{\infty} \exp(3ik\Delta) J_k^3(2n_j t \cos \tau) \right\}. \quad (2.1.8.37)$$

The imaginary part of the summation, involving Bessel functions of odd orders, vanishes upon integration and the latter is restricted to the positive quadrant in τ . Thus, upon replacing cosines by sines (this is permissible at this stage) the atomic contribution to the characteristic function becomes

$$C_j(t, \Delta) = (2/\pi) \int_0^{\pi/2} \left[J_0^3(2n_j t \sin \tau) \right. \\ \left. + 2 \sum_{k=1}^{\infty} \cos(6k\Delta) J_k^3(2n_j t \sin \tau) \right] d\tau \quad (2.1.8.38)$$

and a double Fourier series must be used for the p.d.f.

2.1.8.5. Atomic characteristic functions

Expressions for the atomic contributions to the characteristic functions were obtained by Rabinovich *et al.* (1991a) for a wide range of space groups, by methods similar to those described above. These expressions are collected in Table 2.1.8.1 in terms of symbols which are defined below. The following abbreviations are used in the subsequent definitions of the symbols:

$$s_{\pm} = 2an_j \sin(\tau \pm \rho), \\ c_{\pm} = 2an_j \cos(\tau \pm \rho) \quad \text{and} \\ \sigma_{\pm} = 2an_j \sin(\tau \pm 2\pi/3 + \rho),$$

and the symbols appearing in Table 2.1.8.1 are given below:

$$^{(a)}L_j(a, \rho) = \langle J_0(s_+) J_0(s_-) \rangle_{\tau} \\ = \sum_{k=-\infty}^{\infty} \cos(4k\rho) J_k^4 \\ = J_0^4(an_j) + 2 \sum_{k=1}^{\infty} \cos(4k\rho) J_k^4(an_j),$$

$$^{(b)}Q_j^{(1)}(a, \rho) = \langle J_0^2(s_+) J_0^2(s_-) \rangle_{\tau},$$

$$^{(c)}Q_j^{(2)}(a, \rho) = \langle J_0(s_+) J_0(s_-) J_0(c_+) J_0(c_-) \rangle_{\tau},$$

$$^{(d)}T_j(a, \rho) = \sum_{k=-\infty}^{\infty} \exp(6ik\rho) J_k^6(an_j) \\ = J_0^6(an_j) + 2 \sum_{k=1}^{\infty} \cos(6k\rho) J_k^6(an_j),$$

$$^{(e)}H_j^{(1)}(a, \mu) = \left\langle \mathcal{R} \left[S_j^{(1)}(\tau; a, \mu, 0) \right] \right\rangle_{\tau},$$

$$^{(f)}H_j^{(2)}(a, \mu) = \left\langle \mathcal{R} \left[S_j^{(2)}(\tau; a, \mu, 0) \right] \right\rangle_{\tau},$$

$$^{(g)}\tilde{H}_j^{(1)}(a, \mu_1, \mu_2, \rho) = \left\langle \mathcal{R} \left[S_j^{(1)}(\tau; a, \mu_1, \rho) \right. \right. \\ \left. \left. \times S_j^{(1)}(\tau; a, \mu_2, -\rho) \right] \right\rangle_{\tau},$$

$$^{(h)}\tilde{H}_j^{(2)}(a, \mu_1, \mu_2, \rho) = \left\langle \mathcal{R} \left[S_j^{(2)}(\tau; a, \mu_1, \rho) \right. \right. \\ \left. \left. \times S_j^{(2)}(\tau; a, \mu_2, -\rho) \right] \right\rangle_{\tau},$$

where

$$S_j^{(1)}(\tau; a, \mu, \rho) = \sum_{k=-\infty}^{\infty} e^{3ik\mu} J_k^3(s_+)$$

and

$$S_j^{(2)}(\tau; a, \mu, \rho) = \sum_{k=-\infty}^{\infty} e^{3ik\mu} J_k(s_+) J_k(\sigma_+) J_k(\sigma_-).$$

The averages appearing in the above summary are, in general, computed as

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Table 2.1.8.1. *Atomic contributions to characteristic functions for $p(|E|)$*

The table lists symbolic expressions for the atomic contributions to exact characteristic functions (abbreviated as c.f.) for $p(|E|)$, to be computed as single Fourier series (centric), double Fourier series (acentric) and single Fourier–Bessel series (acentric), as defined in Sections 2.1.8.1 and 2.1.8.2. The symbolic expressions are defined in Section 2.1.8.5. The table is arranged by point groups, space groups and parities of the reflection indices analogously to the table of moments, Table 2.1.7.1, and covers all the space groups and statistically different parities of hkl up to and including space group $Fd\bar{3}$. The expressions are valid for atoms in general positions, for general reflections and presume the absence of noncrystallographic symmetry and of dispersive scatterers.

Space group(s)	g	Atomic c.f.	Remarks	Space group(s)	g	Atomic c.f.	Remarks
Point group: 1 $P1$	1	$J_0(m_j)$		$I4mm, I4cm$	16	$Q_j^{(1)}(2t, 0)$	
Point group: $\bar{1}$ $P\bar{1}$	2	$J_0(2t_1 n_j)$		$I4_1md, I4_1cd$	16	$Q_j^{(1)}(2t, 0)$	$2k + l = 2n$
					16	$Q_j^{(1)}(2t, \pi/4)$	$2k + l = 2n + 1$
Point groups: 2, m All P	2	$J_0^2(m_j)$		Point groups: $\bar{4}2m, \bar{4}m2$			
All C	4	$J_0^2(2m_j)$		All P	8	$Q_j^{(1)}(t, \Delta)$	
Point group: $2/m$ All P	4	$J_0^2(2t_1 n_j)$		$\bar{I}42m, \bar{I}4m2, \bar{I}4c2$	16	$Q_j^{(1)}(2t, \Delta)$	$2h + l = 2n$
All C	8	$J_0^2(4t_1 n_j)$		$\bar{I}42d$	16	$Q_j^{(1)}(2t, \Delta)$	$2h + l = 2n + 1$
					16	$Q_j^{(2)}(2t, \Delta)$	
Point group: 222 All P	4	$L_j(t, \Delta)^{(a)}$		Point group: $4/mmm$			
All C and I	8	$L_j(2t, \Delta)$		All P	16	$Q_j^{(1)}(2t_1, 0)$	
$F222$	16	$L_j(4t, \Delta)$		$I4/mmm, I4/mcm$	32	$Q_j^{(1)}(4t_1, 0)$	$l = 2n$
Point group: $mm2$ All P	4	$L_j(t, 0)$		$I4_1/amd, I4_1/acd$	32	$Q_j^{(1)}(4t_1, 0)$	$l = 2n + 1$
All C and I	8	$L_j(2t, 0)$			32	$Q_j^{(1)}(4t_1, \pi/4)$	
$Fmm2$	16	$L_j(4t, 0)$	$h + k + l = 2n$	Point group: 3 All P and R	3	$J_0^3(m_j)$	
$Fdd2$	16	$L_j(4t, 0)$	$h + k + l = 2n + 1$	Point group: $\bar{3}$ All P and R	6	$J_0^3(2t_1 n_j)$	
	16	$L_j(4t, \pi/4)$		Point group: 32 All P and R	6	$T_j(t, \Delta)^{(d)}$	
Point group: mmm All P	8	$L_j(2t_1, 0)$		Point group: $3m$ $P3m1, P31m, R3m$	6	$T_j(t, \pi/2)$	$l = 2n (P),$
All C and I	16	$L_j(4t_1, 0)$		$P3c1, P31c, R3c$	6	$T_j(t, \pi/2)$	$h + k + l = 2n (R)$
$Fmmm$	32	$L_j(8t_1, 0)$	$h + k + l = 2n$		6	$T_j(t, 0)$	$l = 2n + 1 (P),$
$Fddd$	32	$L_j(8t_1, 0)$	$h + k + l = 2n + 1$				$h + k + l = 2n + 1 (R)$
	32	$L_j(8t_1, \pi/4)$		Point group: $\bar{3}m$ $P\bar{3}m1, P\bar{3}1m, R\bar{3}m$	12	$T_j(2t_1, \pi/2)$	$l = 2n (P),$
Point group: 4 $P4, P4_2$	4	$L_j(t, 0)$	$l = 2n$	$P\bar{3}c1, P\bar{3}1c, R\bar{3}c$	12	$T_j(2t_1, \pi/2)$	$h + k + l = 2n (R)$
$P4_1^*$	4	$L_j(t, 0)$	$l = 2n + 1$		12	$T_j(2t_1, 0)$	$l = 2n + 1 (P),$
$I4$	8	$L_j(t, \pi/4)$					$h + k + l = 2n + 1 (R)$
$I4_1$	8	$L_j(2t, 0)$	$2h + l = 2n$	Point group: 6 $P6$	6	$H_j^{(1)}(t, \pi/2)^{(e)}$	
	8	$L_j(2t, \pi/4)$	$2h + l = 2n + 1$	$P6_1^*$	6	$H_j^{(1)}(t, \pi/2)$	$l = 6n$
Point group: $\bar{4}$ $P\bar{4}$	4	$L_j(t, \Delta)$			6	$H_j^{(2)}(t, 0)^{(f)}$	$l = 6n + 1, 6n + 5$
$\bar{I}4$	8	$L_j(2t, \Delta)$			6	$H_j^{(2)}(t, \pi/2)$	$l = 6n + 2, 6n + 4$
Point group: $4/m$ All P	8	$L_j(2t_1, 0)$			6	$H_j^{(1)}(t, 0)$	$l = 6n + 3$
$I4/m$	16	$L_j(4t_1, 0)$		$P6_2^*$	6	$H_j^{(1)}(t, \pi/2)$	$l = 3n$
$I4_1/a$	16	$L_j(4t_1, 0)$	$l = 2n$		6	$H_j^{(2)}(t, \pi/2)$	$l = 3n \pm 1$
	16	$L_j(4t_1, \pi/4)$	$l = 2n + 1$	$P6_3$	6	$H_j^{(1)}(t, \pi/2)$	$l = 2n$
Point group: 422 $P422, P4_212, P4_222,$ $P4_22_12$	8	$Q_j^{(1)}(t, \Delta)^{(b)}$			6	$H_j^{(1)}(t, 0)$	$l = 2n + 1$
$P4_122, P4_12_12^*$	8	$Q_j^{(1)}(t, \Delta)$	$l = 2n$	Point group: $\bar{6}$ $P\bar{6}$	6	$H_j^{(1)}(t, \Delta)$	
	8	$Q_j^{(2)}(t, \Delta)^{(c)}$	$l = 2n + 1$	Point group: $6/m$ $P6/m$	12	$H_j^{(1)}(2t_1, \pi/2)$	$l = 2n$
$I422$	16	$Q_j^{(1)}(2t, \Delta)$	$2k + l = 2n$	$P6_3/m$	12	$H_j^{(1)}(2t_1, \pi/2)$	$l = 2n + 1$
$I4_122$	16	$Q_j^{(1)}(2t, \Delta)$	$2k + l = 2n + 1$		12	$H_j^{(1)}(2t_1, 0)$	
	16	$Q_j^{(2)}(2t, \Delta)$		Point group: 622 $P622$	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)^{(g)}$	
Point group: $4mm$ All P	8	$Q_j^{(1)}(t, 0)$					

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Table 2.1.8.1. Atomic contributions to characteristic functions for $p(|E|)$ (cont.)

Space group(s)	g	Atomic c.f.	Remarks
$P6_122^*$	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)$	$l = 6n$
	12	$\tilde{H}_j^{(2)}(t, 0, 0, \Delta)^{(h)}$	$l = 6n + 1, 6n + 5$
	12	$\tilde{H}_j^{(2)}(t, \pi/2, \pi/2, \Delta)$	$l = 6n + 2, 6n + 4$
	12	$\tilde{H}_j^{(1)}(t, 0, 0, \Delta)$	$l = 6n + 3$
$P6_222^*$	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)$	$l = 3n$
	12	$\tilde{H}_j^{(2)}(t, \pi/2, \pi/2, \Delta)$	$l = 3n \pm 1$
$P6_322$	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, \Delta)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, 0, 0, \Delta)$	$l = 2n + 1$
Point group: $6mm$			
$P6mm$	12	$\tilde{H}_j^{(1)}(t, \pi/2, \pi/2, 0)$	
$P6cc$	12	$\tilde{H}_j^{(1)}(t, \pi/2, \pi/2, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, \pi/2, -\pi/2, 0)$	$l = 2n + 1$
$P6_3cm, P6_3mc$	12	$\tilde{H}_j^{(1)}(t, \pi/2, \pi/2, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(t, 0, 0, 0)$	$l = 2n + 1$
Point groups: $\bar{6}2m, \bar{6}m2$			
$P\bar{6}2m, P\bar{6}m2$	12	$\tilde{H}_j^{(1)}(t, \Delta, \Delta, 0)$	
$P\bar{6}2c, P\bar{6}c2$	12	$\tilde{H}_j^{(1)}(t, \Delta, \Delta, 0)$	$l = 2n$

* And the enantiomorphous space group.

Space group(s)	g	Atomic c.f.	Remarks
	12	$\tilde{H}_j^{(1)}(t, \Delta + \pi/2, -\Delta - \pi/2, 0)$	$l = 2n + 1$
Point group: $6/mmm$			
$P6/mmm$	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, \pi/2, 0)$	
$P6/mcc$	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, \pi/2, 0)$	$l = 2n$
	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, -\pi/2, 0)$	$l = 2n + 1$
$P6_3/mcm, P6_3/mmc$	24	$\tilde{H}_j^{(1)}(2t_1, \pi/2, \pi/2, 0)$	$l = 2n$
	24	$\tilde{H}_j^{(1)}(2t_1, 0, 0, 0)$	$l = 2n + 1$
Point group: 23			
$P23, P2_13$	12	$L_j^3(t, \Delta)$	
$I23, I2_13$	24	$L_j^3(2t, \Delta)$	
$F23$	48	$L_j^3(4t, \Delta)$	
Point group: $m\bar{3}$			
$Pm\bar{3}, Pn\bar{3}, Pa\bar{3}$	24	$L_j^3(2t_1, 0)$	
$Im\bar{3}, Ia\bar{3}$	48	$L_j^3(4t_1, 0)$	
$Fm\bar{3}$	96	$L_j^3(8t_1, 0)$	
$Fd\bar{3}$	96	$L_j^3(8t_1, 0)$	$h + k + l = 2n$
	96	$L_j^3(8t_1, \pi/4)$	$h + k + l = 2n + 1$

$$\langle f(\tau) \rangle = (2/\pi) \int_0^{\pi/2} f(\tau) d\tau, \quad (2.1.8.39)$$

except $H_j^{(2)}$ and $\tilde{H}_j^{(2)}$ which are computed as

$$\langle f(\tau) \rangle = (3/\pi) \int_0^{\pi/3} f(\tau) d\tau, \quad (2.1.8.40)$$

where $f(\tau)$ is any of the atomic characteristic functions indicated above. The superscripts preceding the symbols in the above summary are appended to the corresponding symbols in Table 2.1.8.1 on their first occurrence.

2.1.8.6. Other non-ideal Fourier p.d.f.'s

As pointed out above, the representation of the p.d.f.'s by Fourier series is also applicable to effects of noncrystallographic symmetry. Thus, Shmueli *et al.* (1985) obtained the following Fourier coefficient for the bicentric distribution in the space group $P\bar{1}$

$$C_k = (2/\pi) \int_0^{\pi/2} \left[\prod_{j=1}^{N/4} J_0(4\pi k \alpha n_j \cos \vartheta) \right] d\vartheta \quad (2.1.8.41)$$

to be used with equation (2.1.8.5). Furthermore, if we use the important property of the characteristic function as outlined in Section 2.1.4.1, it is easy to write down the Fourier coefficient for a $P\bar{1}$ asymmetric unit containing a centrosymmetric fragment centred at a noncrystallographic centre and a number of atoms not related by symmetry. This Fourier for the above partially bicentric arrangement is a product of expressions (2.1.8.17) and (2.1.8.41), with the appropriate number of atoms in each factor (Shmueli & Weiss, 1985a). While the purely bicentric p.d.f. obtained by using (2.1.8.41) with (2.1.8.5) is significantly different from the ideal bicentric p.d.f. given by equation (2.1.5.13) only when the atomic

composition is sufficiently heterogeneous, the above partially bicentric p.d.f. appears to be a useful development even for an equal-atom structure.

The problem of the coexistence of several noncrystallographic centres of symmetry within the asymmetric unit of $P\bar{1}$, and its effect on the p.d.f. of $|E|$, was examined by Shmueli, Weiss & Wilson (1989) by the Fourier method. The latter study indicates that the strongest effect is produced by the presence of a single noncrystallographic centre.

Another kind of noncrystallographic symmetry is that arising from the presence of centrosymmetric fragments in a noncentrosymmetric structure – the subcentric arrangement already discussed in Section 2.1.5.4. A Fourier-series representation of a non-ideal p.d.f. corresponding to this case was developed by Shmueli, Rabinovich & Weiss (1989), and was also applied to the mathematically equivalent effects of dispersion and presence of heavy scatterers in centrosymmetric special positions in a noncentrosymmetric space group.

A variety of other non-ideal p.d.f.'s occur when heavy atoms are present in special positions (Shmueli & Weiss, 1988). Without going into the details of this development, it can be noted that if the atoms are distributed among k types of Wyckoff positions, the characteristic function corresponding to the p.d.f. of $|E|$ is a product of the k characteristic functions, each of which is related to one of these special positions; the same property of the characteristic function as that in Section 2.1.4.1 is here utilized.

2.1.8.7. Comparison of the correction-factor and Fourier approaches

The need for theoretical non-ideal distributions was exemplified by Fig. 2.1.7.1(a), referred to above, and the performance of the two approaches described above, for this particular example, is shown in

2.1. STATISTICAL PROPERTIES OF THE WEIGHTED RECIPROCAL LATTICE

Fig. 2.1.7.1(b). Briefly, the Fourier p.d.f. shows an excellent agreement with the histogram of recalculated $|E|$ values, while the agreement attained by the Hermite correction factor is much less satisfactory, even for the (longest available to us) five-term expansion. It must be pointed out that (i) the inadequacy of 'short' correction factors, in the example shown, is due to the large deviation from the ideal behaviour and (ii) the number of terms used there in the Fourier summation is twenty, whereafter the summation is terminated. Obviously, the computation of twenty (or more) Fourier coefficients is easier than that of five terms in the correction factor. The convergence of the Fourier series is very satisfactory. It appears that the (analytically) exact Fourier approach is the preferred one in cases of large or intermediate deviations, while the correction-factor approach may cope well with small ones. As far as the availability of symmetry-dependent centric and acentric p.d.f.'s is concerned, correction factors are available for all the space groups (see Table 2.1.7.1), while Fourier coefficients of

p.d.f.'s are available for the first 206 space groups (see Table 2.1.8.1). It should be pointed out that p.d.f.'s based on the correction-factor method cope very well with cubic symmetries higher than $Fd\bar{3}$, even if the asymmetric unit of the space group is strongly heterogeneous (Rabinovich *et al.*, 1991b).

Both approaches described in this section are related to the characteristic function of the required p.d.f. The correction-factor p.d.f.'s (2.1.7.5) and (2.1.7.6) can be obtained by expanding the logarithm of the appropriate characteristic function in a series of cumulants [*e.g.* equation (2.1.4.13); see also Shmueli & Wilson (1982)], truncating the series and performing its term-by-term Fourier inversion. The Fourier p.d.f., on the other hand, is computed by forming a Fourier series whose coefficients are *exact* analytical forms of the characteristic function at points related to the summation indices [*e.g.* equations (2.1.8.5), (2.1.8.9) and (2.1.8.11), and Table 2.1.8.1] and truncating the series when the terms become small enough.

2.2. Direct methods

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2.2.1. List of symbols and abbreviations

f_j	atomic scattering factor of j th atom
Z_j	atomic number of j th atom
N	number of atoms in the unit cell
m	order of the point group
$[\sigma_r]_p, [\sigma_r]_q, [\sigma_r]_N, \dots = \sum_{j=1}^p Z_j^r, \sum_{j=1}^q Z_j^r, \sum_{j=1}^N Z_j^r, \dots$	

$[\sigma_r]_N$ is always abbreviated to σ_r when N is the number of atoms in the cell

$$\sum_p, \sum_q, \sum_N, \dots = \sum_{j=1}^p f_j^2, \sum_{j=1}^q f_j^2, \sum_{j=1}^N f_j^2, \dots$$

s.f.	structure factor
n.s.f.	normalized structure factor
cs.	centrosymmetric
ncs.	noncentrosymmetric
s.i.	structure invariant
s.s.	structure seminvariant
$\mathbf{C} = (\mathbf{R}, \mathbf{T})$	symmetry operator; $\mathbf{R}$ is the rotational part, $\mathbf{T}$ the translational part
$\varphi_{\mathbf{h}}$	phase of the structure factor $F_{\mathbf{h}} = F_{\mathbf{h}} \exp(i\varphi_{\mathbf{h}})$

2.2.2. Introduction

Direct methods are today the most widely used tool for solving small crystal structures. They work well both for equal-atom molecules and when a few heavy atoms exist in the structure. In recent years the theoretical background of direct methods has been improved to take into account a large variety of prior information (the form of the molecule, its orientation, a partial structure, the presence of pseudosymmetry or of a superstructure, the availability of isomorphous data or of data affected by anomalous-dispersion effects, ...). Owing to this progress and to the increasing availability of powerful computers, a number of effective, highly automated packages for the practical solution of the phase problem are today available to the scientific community.

The *ab initio* crystal structure solution of macromolecules seems not to exceed the potential of direct methods. Many efforts will certainly be devoted to this task in the near future: a report of the first achievements is given in Section 2.2.10.

This chapter describes both the traditional direct methods tools and the most recent and revolutionary techniques suitable for macromolecules.

The theoretical background and tables useful for origin specification are given in Section 2.2.3; in Section 2.2.4 the procedures for normalizing structure factors are summarized. Phase-determining formulae (inequalities, probabilistic formulae for triplet, quartet and quintet invariants, and for one- and two-phase s.s.'s, determinantal formulae) are given in Section 2.2.5. In Section 2.2.6 the connection between direct methods and related techniques in real space is discussed. Practical procedures for solving crystal structures are described in Sections 2.2.7 and 2.2.8, and references to the most extensively used packages are given in Section 2.2.9. The techniques suitable for the *ab initio* crystal structure solution of macromolecules are described in Section 2.2.10.2. The integration of direct methods with isomorphous-replacement and anomalous-dispersion techniques is briefly described in Sections 2.2.10.3 and 2.2.10.4.

The reader will find full coverage of the most important aspects of direct methods in the recent books by Giacovazzo (1998) and Woolfson & Fan (1995).

2.2.3. Origin specification

(a) Once the origin has been chosen, the symmetry operators $\mathbf{C}_s \equiv (\mathbf{R}_s, \mathbf{T}_s)$ and, through them, the algebraic form of the s.f. remain fixed.

A shift of the origin through a vector with coordinates $\mathbf{X}_0$ transforms $\varphi_{\mathbf{h}}$ into

$$\varphi'_{\mathbf{h}} = \varphi_{\mathbf{h}} - 2\pi \mathbf{h} \cdot \mathbf{X}_0 \quad (2.2.3.1)$$

and the symmetry operators $\mathbf{C}_s$ into $\mathbf{C}'_s = (\mathbf{R}'_s, \mathbf{T}'_s)$, where

$$\mathbf{R}'_s = \mathbf{R}_s; \mathbf{T}'_s = \mathbf{T}_s + (\mathbf{R}_s - \mathbf{I})\mathbf{X}_0 \quad s = 1, 2, \dots, m. \quad (2.2.3.2)$$

(b) *Allowed or permissible origins* (Hauptman & Karle, 1953, 1959) for a given algebraic form of the s.f. are all those points in direct space which, when taken as origin, maintain the same symmetry operators $\mathbf{C}_s$. The allowed origins will therefore correspond to those points having the same symmetry environment in the sense that they are related to the symmetry elements in the same way. For instance, if $\mathbf{T}_s = 0$ for $s = 1, \dots, 8$, then the allowed origins in $Pmmm$ are the eight inversion centres.

To each functional form of the s.f. a set of permissible origins will correspond.

(c) A translation between permissible origins will be called a *permissible* or *allowed translation*. Trivial allowed translations correspond to the lattice periods or to their multiples. A change of origin by an allowed translation does not change the algebraic form of the s.f. Thus, according to (2.2.3.2), all origins allowed by a fixed functional form of the s.f. will be connected by translational vectors $\mathbf{X}_p$ such that

$$(\mathbf{R}_s - \mathbf{I})\mathbf{X}_p = \mathbf{V}, \quad s = 1, 2, \dots, m, \quad (2.2.3.3)$$

where $\mathbf{V}$ is a vector with zero or integer components.

In centred space groups, an origin translation corresponding to a centring vector $\mathbf{B}_v$ does not change the functional form of the s.f. Therefore all vectors $\mathbf{B}_v$ represent permissible translations. $\mathbf{X}_p$ will then be an allowed translation (Giacovazzo, 1974) not only when, as imposed by (2.2.3.3), the difference $\mathbf{T}'_s - \mathbf{T}_s$ is equal to one or more lattice units, but also when, for any s , the condition

$$(\mathbf{R}_s - \mathbf{I})\mathbf{X}_p = \mathbf{V} + \alpha \mathbf{B}_v, \quad s = 1, 2, \dots, m; \quad \alpha = 0, 1 \quad (2.2.3.4)$$

is satisfied.

We will call any set of cs. or ncs. space groups having the same allowed origin translations a Hauptman–Karle group (H–K group). The 94 ncs. primitive space groups, the 62 primitive cs. groups, the 44 ncs. centred space groups and the 30 cs. centred space groups can be collected into 13, 4, 14 and 5 H–K groups, respectively (Hauptman & Karle, 1953, 1956; Karle & Hauptman, 1961; Lessinger & Wondratschek, 1975). In Tables 2.2.3.1–2.2.3.4 the H–K groups are given together with the allowed origin translations.

(d) Let us consider a product of structure factors

$$\begin{aligned} F_{\mathbf{h}_1}^{A_1} \times F_{\mathbf{h}_2}^{A_2} \times \dots \times F_{\mathbf{h}_n}^{A_n} &= \prod_{j=1}^n F_{\mathbf{h}_j}^{A_j} \\ &= \exp \left(i \sum_{j=1}^n A_j \varphi_{\mathbf{h}_j} \right) \prod_{j=1}^n |F_{\mathbf{h}_j}|^{A_j}, \end{aligned} \quad (2.2.3.5)$$

A_j being integer numbers.

The factor $\sum_{j=1}^n A_j \varphi_{\mathbf{h}_j}$ is the phase of the product (2.2.3.5). A *structure invariant* (s.i.) is a product (2.2.3.5) such that

2.2. DIRECT METHODS

Table 2.2.3.1. Allowed origin translations, seminvariant moduli and phases for centrosymmetric primitive space groups

	H-K group					
	$(h, k, l)\underline{P}(2, 2, 2)$		$(h + k, l)\underline{P}(2, 2)$		$(l)\underline{P}(2)$	$(h + k + l)\underline{P}(2)$
Space group	$P\bar{1}$	$Pmna$	$P\frac{4}{m}$	$P\frac{4}{n}mm$	$P\bar{3}$	$R\bar{3}$
	$P\frac{2}{m}$	$Pcca$	$P\frac{4_2}{m}$	$P\frac{4}{n}cc$	$P\bar{3}1m$	$R\bar{3}m$
	$P\frac{2_1}{m}$	$Pbam$	$P\frac{4}{n}$	$P\frac{4_2}{m}mc$	$P\bar{3}1c$	$R\bar{3}c$
	$P\frac{2}{c}$	$Pccn$	$P\frac{4_2}{n}$	$P\frac{4_2}{m}cm$	$P\bar{3}m1$	$Pm\bar{3}$
	$P\frac{2_1}{c}$	$Pbcm$	$P\frac{4}{m}mm$	$P\frac{4_2}{n}bc$	$P\bar{3}c1$	$Pn\bar{3}$
	$Pmmm$	$Pnnm$	$P\frac{4}{m}cc$	$P\frac{4_2}{n}nm$	$P\frac{6}{m}$	$Pa\bar{3}$
	$Pnnn$	$Pmmn$	$P\frac{4}{n}bm$	$P\frac{4_2}{m}bc$	$P\frac{6_3}{m}$	$Pm\bar{3}m$
	$Pccm$	$Pbcn$	$P\frac{4}{n}nc$	$P\frac{4_2}{m}nm$	$P\frac{6}{m}mm$	$Pn\bar{3}n$
	$Pban$	$Pbca$	$P\frac{4}{m}bm$	$P\frac{4_2}{n}mc$	$P\frac{6}{m}cc$	$Pm\bar{3}n$
	$Pmma$	$Pnma$	$P\frac{4}{m}nc$	$P\frac{4_2}{n}cm$	$P\frac{6_3}{m}cm$	$Pn\bar{3}m$
	$Pnna$				$P\frac{6_3}{m}mc$	
Allowed origin translations	$(0, 0, 0);$ $(\frac{1}{2}, 0, 0);$ $(0, \frac{1}{2}, 0);$ $(0, 0, \frac{1}{2});$	$(0, \frac{1}{2}, \frac{1}{2});$ $(\frac{1}{2}, 0, \frac{1}{2});$ $(\frac{1}{2}, \frac{1}{2}, 0);$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2});$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$		$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
Vector $\mathbf{h}_s$ seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, k, l)		$(h + k, l)$		(l)	$(h + k + l)$
Seminvariant modulus ω_s	$(2, 2, 2)$		$(2, 2)$		(2)	(2)
Seminvariant phases	φ_{eee}		$\varphi_{eee}; \varphi_{ooo}$		$\varphi_{eee}; \varphi_{eoe}$ $\varphi_{oeo}; \varphi_{ooo}$	$\varphi_{eee}; \varphi_{ooo}$ $\varphi_{eoo}; \varphi_{eoo}$
Number of sem independent phases to be specified	3		2		1	1

$$\sum_{j=1}^n A_j \mathbf{h}_j = 0. \quad (2.2.3.6)$$

$$\sum_{j=1}^n A_j (\mathbf{h}_j \cdot \mathbf{X}_p) = r, \quad p = 1, 2, \dots \quad (2.2.3.8)$$

Since $|F_{\mathbf{h}_j}|$ are usually known from experiment, it is often said that s.i.'s are combinations of phases

$$\sum_{j=1}^n A_j \varphi_{\mathbf{h}_j}, \quad (2.2.3.7)$$

for which (2.2.3.6) holds.

$F_0, F_{\mathbf{h}}F_{-\mathbf{h}}, F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}}}, F_{\mathbf{h}}F_{\mathbf{k}}F_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}}}, F_{\mathbf{h}}F_{\mathbf{k}}F_{\mathbf{l}}F_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{p}}}$ are examples of s.i.'s for $n = 1, 2, 3, 4, 5$.

The value of any s.i. does not change with an arbitrary shift of the space-group origin and thus it will depend on the crystal structure only.

(e) A *structure seminvariant* (s.s.) is a product of structure factors [or a combination of phases (2.2.3.7)] whose value is unchanged when the origin is moved by an allowed translation.

Let $\mathbf{X}_p$'s be the permissible origin translations of the space group. Then the product (2.2.3.5) [or the sum (2.2.3.7)] is an s.s., if, in accordance with (2.2.3.1),

where r is a positive integer, null or a negative integer.

Conditions (2.2.3.8) can be written in the following more useful form (Hauptman & Karle, 1953):

$$\sum_{j=1}^n A_j \mathbf{h}_{s_j} \equiv 0 \pmod{\omega_s}, \quad (2.2.3.9)$$

where $\mathbf{h}_{s_j}$ is the vector seminvariantly associated with the vector $\mathbf{h}_j$ and ω_s is the seminvariant modulus. In Tables 2.2.3.1–2.2.3.4, the reflection $\mathbf{h}_s$ seminvariantly associated with $\mathbf{h} = (h, k, l)$, the seminvariant modulus ω_s and seminvariant phases are given for every H-K group.

The symbol of any group (cf. Giacovazzo, 1974) has the structure $\mathbf{h}_s L \omega_s$, where L stands for the lattice symbol. This symbol is underlined if the space group is cs.

By definition, if the class of permissible origin has been chosen, that is to say, if the algebraic form of the symmetry operators has been fixed, then the value of an s.s. does not depend on the origin but on the crystal structure only.

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.2.3.2. Allowed origin translations, seminvariant moduli and phases for noncentrosymmetric primitive space groups

	H-K group					
	$(h, k, l)P(0, 0, 0)$	$(h, k, l)P(2, 0, 2)$	$(h, k, l)P(0, 2, 0)$	$(h, k, l)P(2, 2, 2)$	$(h, k, l)P(2, 2, 0)$	$(h + k, l)P(2, 0)$
Space group	$P1$	$P2$ $P2_1$	Pm Pc	$P222$ $P222_1$ $P2_12_12$ $P2_12_12_1$	$Pmm2$ $Pmc2_1$ $Pcc2$ $Pma2$ $Pca2_1$ $Pnc2$ $Pmn2_1$ $Pba2$ $Pna2_1$ $Pnn2$	$P4$ $P4_1$ $P4_2$ $P4_3$ $P4mm$ $P4bm$ $P4_2cm$ $P4_2nm$ $P4cc$ $P4nc$ $P4_2mc$ $P4_2bc$
Allowed origin translations	(x, y, z)	$(0, y, 0)$ $(0, y, \frac{1}{2})$ $(\frac{1}{2}, y, 0)$ $(\frac{1}{2}, y, \frac{1}{2})$	$(x, 0, z)$ $(x, \frac{1}{2}, z)$	$(0, 0, 0)$ $(\frac{1}{2}, 0, 0)$ $(0, \frac{1}{2}, 0)$ $(0, 0, \frac{1}{2})$ $(0, \frac{1}{2}, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, z)$ $(0, \frac{1}{2}, z)$ $(\frac{1}{2}, 0, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$	$(0, 0, z)$ $(\frac{1}{2}, \frac{1}{2}, z)$
Vector $\mathbf{h}_s$ seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, k, l)	(h, k, l)	(h, k, l)	(h, k, l)	(h, k, l)	$(h + k, l)$
Seminvariant modulus ω_s	$(0, 0, 0)$	$(2, 0, 2)$	$(0, 2, 0)$	$(2, 2, 2)$	$(2, 2, 0)$	$(2, 0)$
Seminvariant phases	φ_{000}	φ_{e0e}	φ_{0e0}	φ_{eee}	φ_{ee0}	φ_{ee0} φ_{o00}
Allowed variations for the semindependent phases	$\ \infty\ $	$\ \infty\ , \ 2\ $ if $k = 0$	$\ \infty\ , \ 2\ $ if $h = l = 0$	$\ 2\ $	$\ \infty\ , \ 2\ $ if $l = 0$	$\ \infty\ , \ 2\ $ if $l = 0$
Number of semindependent phases to be specified	3	3	3	3	3	2

(f) Suppose that we have chosen the symmetry operators $\mathbf{C}_s$ and thus fixed the functional form of the s.f.'s and the set of allowed origins. In order to describe the structure in direct space a unique reference origin must be fixed. Thus the phase-determining process must also require a unique permissible origin congruent to the values assigned to the phases. More specifically, at the beginning of the structure-determining process by direct methods we shall assign as many phases as necessary to define a unique origin among those allowed (and, as we shall see, possibly to fix the enantiomorph). From the theory developed so far it is obvious that arbitrary phases can be assigned to one or more s.f.'s if there is at least one allowed origin which, fixed as the origin of the unit cell, will give those phase values to the chosen reflections. The concept of *linear dependence* will help us to fix the origin.

(g) n phases $\varphi_{\mathbf{h}_j}$ are *linearly semindependent* (Hauptman & Karle, 1956) when the n vectors $\mathbf{h}_{s_j}$ seminvariantly associated with the $\mathbf{h}_j$ are linearly dependent modulo ω_s , ω_s being the seminvariant modulus of the space group. In other words, when

$$\sum_{j=1}^n A_j \mathbf{h}_{s_j} \equiv 0 \pmod{\omega_s}, \quad A_q \not\equiv 0 \pmod{\omega_s} \quad (2.2.3.10)$$

is satisfied. The second condition means that at least one A_q exists that is not congruent to zero modulo each of the components of ω_s . If (2.2.3.10) is not satisfied for any n -set of integers A_j , the phases $\varphi_{\mathbf{h}_j}$ are *linearly semindependent*. If (2.2.3.10) is valid for $n = 1$ and $A = 1$, then $\mathbf{h}_1$ is said to be linearly semindependent and $\varphi_{\mathbf{h}_1}$ is an s.s. It may be concluded that a seminvariant phase is linearly semindependent, and, *vice versa*, that a phase linearly semindependent is an s.s. In Tables 2.2.3.1–2.2.3.4 the allowed variations (which are those due to the allowed origin translations) for the semindependent phases are given for every H-K group. If $\varphi_{\mathbf{h}_1}$ is linearly semindependent its value can be fixed arbitrarily because at least one origin compatible with the given value exists. Once $\varphi_{\mathbf{h}_1}$ is assigned, the necessary condition to be able to fix a second phase $\varphi_{\mathbf{h}_2}$ is that it should be linearly semindependent of $\varphi_{\mathbf{h}_1}$.

2.2. DIRECT METHODS

Table 2.2.3.2. (*cont.*)

H–K group						
$(h+k, l)P(2, 2)$	$(h-k, l)P(3, 0)$	$(2h+4k+3l)P(6)$	$(l)P(0)$	$(l)P(2)$	$(h+k+l)P(0)$	$(h+k+l)P(2)$
$P\bar{4}$ $P422$ $P4_212$ $P4_122$ $P4_12_12$ $P4_222$ $P4_22_12$ $P4_322$ $P4_32_12$ $P\bar{4}2m$ $P\bar{4}2c$ $P\bar{4}2_1m$ $P\bar{4}2_1c$ $P\bar{4}m2$ $P\bar{4}c2$ $P\bar{4}b2$ $P\bar{4}n2$	$P3$ $P3_1$ $P3_2$ $P3m1$ $P3c1$	$P312$ $P3_112$ $P3_212$ $P6$ $P\bar{6}m2$ $P\bar{6}c2$	$P31m$ $P31c$ $P6$ $P6_1$ $P6_5$ $P6_4$ $P6_3$ $P6_2$ $P6mm$ $P6cc$ $P6_3cm$ $P6_3mc$	$P321$ $P3_121$ $P3_221$ $P622$ $P6_122$ $P6_522$ $P6_222$ $P6_422$ $P6_322$ $P\bar{6}2m$ $P\bar{6}2c$	$R3$ $R3m$ $R3c$	$R32$ $P23$ $P2_13$ $P432$ $P4_232$ $P4_332$ $P4_132$ $P\bar{4}3m$ $P\bar{4}3n$
$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, z)$ $(\frac{1}{3}, \frac{2}{3}, z)$ $(\frac{2}{3}, \frac{1}{3}, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{3}, \frac{2}{3}, 0)$ $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ $(\frac{2}{3}, \frac{1}{3}, 0)$ $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$	$(0, 0, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	(x, x, x)	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
$(h+k, l)$	$(h-k, l)$	$(2h+4k+3l)$	(l)	(l)	$(h+k+l)$	$(h+k+l)$
$(2, 2)$	$(3, 0)$	(6)	(0)	(2)	(0)	(2)
φ_{eee} φ_{ooo}	φ_{hkl} if $h-k=0$ $(\text{mod } 3)$	φ_{hkl} if $2h+4k+3l=0$ $(\text{mod } 6)$	φ_{hk0}	φ_{hke}	$\varphi_{h, k, \bar{h}+\bar{k}}$	$\varphi_{eee}; \varphi_{ooe}$ $\varphi_{ooo}; \varphi_{ooo}$
$\ 2\ $	$\ \infty\ , \ 3\ $ if $l=0$	$\ 2\ $ if $h \equiv k \pmod{3}$ $\ 3\ $ if $l \equiv 0 \pmod{2}$	$\ \infty\ $	$\ 2\ $	$\ \infty\ $	$\ 2\ $
2	2	1	1	1	1	1

Similarly, the necessary condition to be able arbitrarily to assign a third phase φ_{h_3} is that it should be linearly semindependent from φ_{h_1} and φ_{h_2} .

In general, the number of linearly semindependent phases is equal to the dimension of the seminvariant vector ω_s (see Tables 2.2.3.1–2.2.3.4). The reader will easily verify in $(h, k, l)P(2, 2, 2)$ that the three phases $\varphi_{ooo}, \varphi_{oeo}, \varphi_{eoo}$ define the origin (o indicates odd, e even).

(h) From the theory summarized so far it is clear that a number of semindependent phases φ_{h_i} , equal to the dimension of the seminvariant vector ω_s , may be arbitrarily assigned in order to fix the origin. However, it is not always true that only one allowed origin compatible with the given phases exists. An additional condition is required such that only one permissible origin should lie at the intersection of the lattice planes corresponding to the origin-fixing reflections (or on the lattice plane $\mathbf{h}$ if one reflection is sufficient to define the origin). It may be shown that the condition is verified if the determinant formed with the vectors seminvariantly

associated with the origin reflections, reduced modulo ω_s , has the value ± 1 . In other words, such a determinant should be primitive modulo ω_s .

For example, in $P\bar{1}$ the three reflections

$$\mathbf{h}_1 = (345), \mathbf{h}_2 = (139), \mathbf{h}_3 = (784)$$

define the origin uniquely because

$$\begin{vmatrix} 3 & 4 & 5 \\ 1 & 3 & 9 \\ 7 & 8 & 4 \end{vmatrix} \xrightarrow{\text{reduced mod } (2, 2, 2)} \begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 0 \end{vmatrix} = -1.$$

Furthermore, in $P4mm$ [$\mathbf{h}_s = (h+k, l), \omega_s = (2, 0)$]

$$\mathbf{h}_1 = (5, 2, 0), \quad \mathbf{h}_2 = (6, 2, 1)$$

define the origin uniquely since

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Table 2.2.3.3. Allowed origin translations, seminvariant moduli and phases for centrosymmetric non-primitive space groups

	H-K group				
	$(h, l) \underline{C}(2, 2)$	$(k, l) \underline{I}(2, 2)$	$(h + k + l) \underline{F}(2)$	$(l) \underline{I}(2)$	$\underline{I}$
Space groups	$C \frac{2}{m}$ $C \frac{2}{c}$ $Cmcm$ $Cmca$ $Cmmm$ $Cccm$ $Cmma$ $Ccca$	$Immm$ $Ibam$ $Ibca$ $Imma$	$Fmmm$ $Fddd$ $Fm\bar{3}$ $Fd\bar{3}$ $Fm\bar{3}m$ $Fm\bar{3}c$ $Fd\bar{3}m$ $Fd\bar{3}c$	$I \frac{4}{m}$ $I \frac{4_1}{a}$ $I \frac{4}{m}mm$ $I \frac{4}{m}cm$ $I \frac{4_1}{a}md$ $I \frac{4_1}{a}cd$	$Im\bar{3}$ $Ia\bar{3}$ $Im\bar{3}m$ $Ia\bar{3}d$
Allowed origin translations	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, 0, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(0, \frac{1}{2}, 0)$ $(\frac{1}{2}, 0, 0)$	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	$(0, 0, 0)$
Vector $\mathbf{h}_s$ seminvariantly associated with $\mathbf{h} = (h, k, l)$	(h, l)	(k, l)	$(h + k + l)$	(l)	(h, k, l)
Seminvariant modulus ω_s	(2, 2)	(2, 2)	(2)	(2)	(1, 1, 1)
Seminvariant phases	φ_{eee}	φ_{eee}	φ_{eee}	$\varphi_{eoe}; \varphi_{eee}$ $\varphi_{ooe}; \varphi_{oeo}$	All
Number of semindependent phases to be specified	2	2	1	1	0

Table 2.2.3.4. Allowed origin translations, seminvariant moduli and phases for noncentrosymmetric non-primitive space groups

	H-K group					
	$(k, l)C(0, 2)$	$(h, l)C(0, 0)$	$(h, l)C(2, 0)$	$(h, l)C(2, 2)$	$(h, l)A(2, 0)$	$(h, l)I(2, 0)$
Space group	$C2$	Cm Cc	$Cmm2$ $Cmc2_1$ $Ccc2$	$C222$ $C222_1$	$Amm2$ $Abm2$ $Ama2$ $Aba2$	$Imm2$ $Iba2$ $Ima2$
Allowed origin translations	$(0, y, 0)$ $(0, y, \frac{1}{2})$	$(x, 0, z)$	$(0, 0, z)$ $(\frac{1}{2}, 0, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, 0)$ $(\frac{1}{2}, 0, \frac{1}{2})$	$(0, 0, z)$ $(\frac{1}{2}, 0, z)$	$(0, 0, z)$ $(\frac{1}{2}, 0, z)$
Vector $\mathbf{h}_s$ seminvariantly associated with $\mathbf{h} = (h, k, l)$	(k, l)	(h, l)	(h, l)	(h, l)	(h, l)	(h, l)
Seminvariant modulus ω_s	(0, 2)	(0, 0)	(2, 0)	(2, 2)	(2, 0)	(2, 0)
Seminvariant phases	φ_{e0e}	φ_{0e0}	φ_{ee0}	φ_{eee}	φ_{ee0}	φ_{ee0}
Allowed variations for the semindependent phases	$\ \infty\ ,$ $\ 2\ $ if $k = 0$	$\ \infty\ $	$\ \infty\ ,$ $\ 2\ $ if $l = 0$	$\ 2\ $	$\ \infty\ ,$ $\ 2\ $ if $l = 0$	$\ \infty\ ,$ $\ 2\ $ if $l = 0$
Number of semindependent phases to be specified	2	2	2	2	2	2

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$$\begin{vmatrix} 7 & 0 \\ 8 & 1 \end{vmatrix} \xrightarrow{\text{reduced mod } (2,0)} \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1.$$

(i) If an s.s. or an s.i. has a general value φ for a given structure, it will have a value $-\varphi$ for the enantiomorph structure. If $\varphi = 0, \pi$ the s.s. has the same value for both enantiomorphs. Once the origin has been assigned, in ncs. space groups the sign of a given s.s. $\varphi \neq 0, \pi$ can be assigned to fix the enantiomorph. In practice it is often advisable to use an s.s. or an s.i. whose value is as near as possible to $\pm\pi/2$.

2.2.4. Normalized structure factors

2.2.4.1. Definition of normalized structure factor

The normalized structure factors E (see also Chapter 2.1) are calculated according to (Hauptman & Karle, 1953)

$$|E_{\mathbf{h}}|^2 = |F_{\mathbf{h}}|^2 / \langle |F_{\mathbf{h}}|^2 \rangle, \quad (2.2.4.1)$$

where $|F_{\mathbf{h}}|^2$ is the squared observed structure-factor magnitude on the absolute scale and $\langle |F_{\mathbf{h}}|^2 \rangle$ is the expected value of $|F_{\mathbf{h}}|^2$.

$\langle |F_{\mathbf{h}}|^2 \rangle$ depends on the available *a priori* information. Often, but not always, this may be considered as a combination of several typical situations. We mention:

(a) No structural information. The atomic positions are considered random variables. Then

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} \sum_{j=1}^N f_j^2 = \varepsilon_{\mathbf{h}} \sum_N$$

so that

$$E_{\mathbf{h}} = \frac{F_{\mathbf{h}}}{(\varepsilon_{\mathbf{h}} \sum_N)^{1/2}}. \quad (2.2.4.2)$$

$\varepsilon_{\mathbf{h}}$ takes account of the effect of space-group symmetry (see Chapter 2.1).

(b) P atomic groups having a known configuration but with unknown orientation and position (Main, 1976). Then a certain number of interatomic distances $r_{j_1 j_2}$ are known and

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} \left(\sum_N + \sum_{i=1}^P \sum_{j_1 \neq j_2=1}^{M_i} f_{j_1} f_{j_2} \frac{\sin 2\pi q r_{j_1 j_2}}{2\pi q r_{j_1 j_2}} \right),$$

where M_i is the number of atoms in the i th molecular fragment and $q = |\mathbf{h}|$.

(c) P atomic groups with a known configuration, correctly oriented, but with unknown position (Main, 1976). Then a certain group of interatomic vectors $\mathbf{r}_{j_1 j_2}$ is fixed and

$$\langle |F_{\mathbf{h}}|^2 \rangle = \varepsilon_{\mathbf{h}} \left(\sum_N + \sum_{i=1}^P \sum_{j_1 \neq j_2=1}^{M_i} f_{j_1} f_{j_2} \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_{j_1 j_2} \right).$$

The above formula has been derived on the assumption that primitive positional random variables are uniformly distributed over the unit cell. Such an assumption may be considered unfavourable (Giacovazzo, 1988) in space groups for which the allowed shifts of origin, consistent with the chosen algebraic form for the symmetry operators $\mathbf{C}_s$, are arbitrary displacements along any polar axes. Thanks to the indeterminacy in the choice of origin, the first of the shifts $\boldsymbol{\tau}_i$ (to be applied to the i th fragment in order to translate atoms in the correct positions) may be restricted to a region which is smaller than the unit cell (e.g. in $P2$ we are free to specify

Table 2.2.3.4. (cont.)

H-K group							
$(h, l)I(2, 2)$	$(h+k+l)F(2)$	$(h+k+l)F(4)$	$(l)I(0)$	$(l)I(2)$	$(2k-l)I(4)$	$(l)F(0)$	I
$I222$ $I2_12_12_1$	$F432$ $F4_132$	$F222$ $F23$ $F\bar{4}3m$ $F\bar{4}3c$	$I4$ $I4_1$ $I4mm$ $I4cm$ $I4_1md$ $I4_1cd$	$I422$ $I4_122$ $I\bar{4}2m$ $I\bar{4}2d$	$I\bar{4}$ $I\bar{4}m2$ $I\bar{4}c2$	$Fmm2$ $Fdd2$	$I23$ $I2_13$ $I432$ $I4_132$ $I\bar{4}3m$ $I\bar{4}3d$
$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(0, \frac{1}{2}, 0)$ $(\frac{1}{2}, 0, 0)$	$(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(0, 0, 0)$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$	$(0, 0, z)$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$	$(0, 0, 0)$ $(0, 0, \frac{1}{2})$ $(\frac{1}{2}, 0, \frac{3}{4})$ $(\frac{1}{2}, 0, \frac{1}{4})$	$(0, 0, z)$	$(0, 0, 0)$
(h, l)	$(h+k+l)$	$(h+k+l)$	(l)	(l)	$(2k-l)$	(l)	(h, k, l)
$(2, 2)$	(2)	(4)	(0)	(2)	(4)	(0)	$(1, 1, 1)$
φ_{eee}	φ_{eee}	φ_{hkl} with $h+k+l \equiv 0$ (mod 4)	φ_{hk0}	φ_{hke}	φ_{hkl} with $(2k-l) \equiv 0$ (mod 4)	φ_{hk0}	All
$\ 2\ $	$\ 2\ $	$\ 2\ $ if $h+k+l \equiv 0$ (mod 2) $\ 4\ $ if $h+k+l$ $\equiv 1$ (mod 2)	$\ \infty\ $	$\ 2\ $	$\ 2\ $ if $h+k+l \equiv 0$ (mod 2) $\ 4\ $ if $2k-l \equiv$ 1 (mod 2)	$\ \infty\ $	All
2	1	1	1	1	1	1	0

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the origin along the diad axis by restricting τ_1 to the family of vectors $\{\tau_1\}$ of type $[x0z]$. The practical consequence is that $\langle |F_h|^2 \rangle$ is significantly modified in polar space groups if h satisfies

$$h \cdot \tau_1 = 0,$$

where τ_1 belongs to the family of restricted vectors $\{\tau_1\}$.

(d) Atomic groups correctly positioned. Then (Main, 1976; Giacovazzo, 1983a)

$$\langle |F_h|^2 \rangle = |F_{p,h}|^2 + \varepsilon_h \sum_q,$$

where $F_{p,h}$ is the structure factor of the partial known structure and q are the atoms with unknown positions.

(e) A pseudotranslational symmetry is present. Let $u_1, u_2, u_3, \dots$ be the pseudotranslation vectors of order $n_1, n_2, n_3, \dots$, respectively. Furthermore, let p be the number of atoms (symmetry equivalents included) whose positions are related by pseudotranslational symmetry and q the number of atoms (symmetry equivalents included) whose positions are not related by any pseudotranslation. Then (Cascarano *et al.*, 1985a,b)

$$\langle |F_h|^2 \rangle = \varepsilon_h (\zeta_h \sum_p + \sum_q),$$

where

$$\zeta_h = \frac{(n_1 n_2 n_3 \dots) \gamma_h}{m}$$

and γ_h is the number of times for which algebraic congruences

$$h \cdot R_s u_i \equiv 0 \pmod{1} \quad \text{for } i = 1, 2, 3, \dots$$

are simultaneously satisfied when s varies from 1 to m . If $\gamma_h = 0$ then F_h is said to be a *superstructure reflection*, otherwise it is a *substructure reflection*.

Often substructures are not ideal: *e.g.* atoms related by pseudotranslational symmetry are ideally located but of different type (replacive deviations from ideality); or they are equal but not ideally located (displacive deviations); or a combination of the two situations occurs. In these cases a correlation exists between the substructure and the superstructure. It has been shown (Mackay, 1953; Cascarano *et al.*, 1988a) that the scattering power of the substructural part may be estimated *via* a statistical analysis of diffraction data for ideal pseudotranslational symmetry or for displacive deviations from it, while it is not estimable in the case of replacive deviations.

2.2.4.2. Definition of quasi-normalized structure factor

When probability theory is not used, the *quasi-normalized structure factors* $\mathcal{E}_h$ and the *unitary structure factors* U_h are often used. $\mathcal{E}_h$ and U_h are defined according to

$$|\mathcal{E}_h|^2 = \varepsilon_h |E_h|^2$$

$$U_h = F_h / \left(\sum_{j=1}^N f_j \right).$$

Since $\sum_{j=1}^N f_j$ is the largest possible value for F_h , U_h represents the fraction of F_h with respect to its largest possible value. Therefore

$$0 \leq |U_h| \leq 1.$$

If atoms are equal, then $U_h = \mathcal{E}_h / N^{1/2}$.

2.2.4.3. The calculation of normalized structure factors

N.s.f.'s cannot be calculated by applying (2.2.4.1) to observed s.f.'s because: (a) the observed magnitudes I_h (already corrected for L_p factor, absorption, . . .) are on a relative scale; (b) $\langle |F_h|^2 \rangle$ cannot

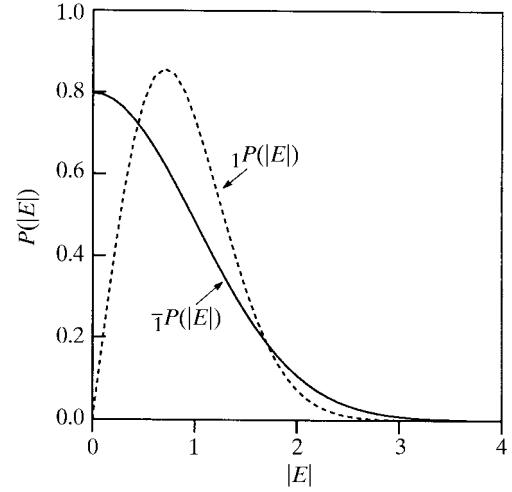


Fig. 2.2.4.1. Probability density functions for cs. and ncs. crystals.

be calculated without having estimated the vibrational motion of the atoms.

This is usually obtained by the well known Wilson plot (Wilson, 1942), according to which observed data are divided into ranges of $s^2 = \sin^2 \theta / \lambda^2$ and averages of intensity $\langle I_h \rangle$ are taken in each shell. Reflection multiplicities and other effects of space-group symmetry on intensities must be taken into account when such averages are calculated. The shells are symmetrically overlapped in order to reduce statistical fluctuations and are restricted so that the number of reflections in each shell is reasonably large. For each shell

$$K \langle I \rangle = \langle |F|^2 \rangle = \langle |F^o|^2 \rangle \exp(-2Bs^2) \quad (2.2.4.3)$$

should be obtained, where K is the scale factor needed to place X-ray intensities on the absolute scale, B is the overall thermal parameter and $\langle |F^o|^2 \rangle$ is the expected value of $|F|^2$ in which it is assumed that all the atoms are at rest. $\langle |F^o|^2 \rangle$ depends upon the structural information that is available (see Section 2.2.4.1 for some examples).

Equation (2.2.4.3) may be rewritten as

$$\ln \left\{ \frac{\langle I \rangle}{\langle |F^o|^2 \rangle} \right\} = -\ln K - 2Bs^2,$$

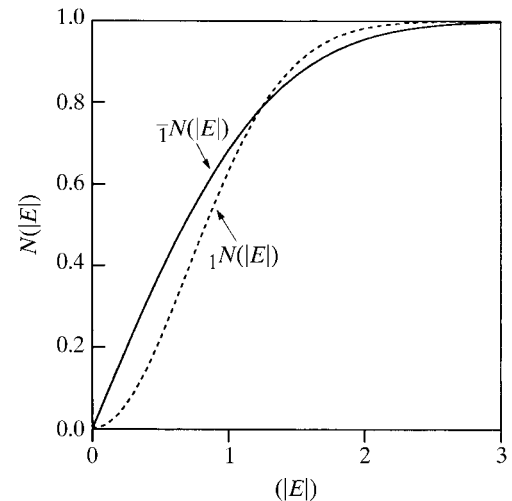


Fig. 2.2.4.2. Cumulative distribution functions for cs. and ncs. crystals.

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which plotted at various s^2 should be a straight line of which the slope ($2B$) and intercept ($\ln K$) on the logarithmic axis can be obtained by applying a linear least-squares procedure.

Very often molecular geometries produce perceptible departures from linearity in the logarithmic Wilson plot. However, the more extensive the available *a priori* information on the structure is, the closer, on the average, are the Wilson-plot curves to their least-squares straight lines.

Accurate estimates of B and K require good strategies (Rogers & Wilson, 1953) for:

(1) treatment of weak measured data. If weak data are set to zero, there will be bias in the statistics. Methods are, however, available (French & Wilson, 1978) that provide an *a posteriori* estimate of weak (even negative) intensities by means of Bayesian statistics.

(2) treatment of missing weak data (Rogers *et al.*, 1955; Vicković & Viterbo, 1979). All unobserved reflections may assume

$$\mu = |F_{o\min}|^2/3 \text{ for cs. space groups}$$

$$\mu = |F_{o\min}|^2/2 \text{ for ncs. space groups,}$$

where the subscript 'o min' refers to the minimum observed intensity.

Once K and B have been estimated, E_h values can be obtained from experimental data by

$$|E_h|^2 = \frac{KI_h}{\langle |F_h^o|^2 \rangle \exp(-2Bs^2)},$$

where $\langle |F_h^o|^2 \rangle$ is the expected value of $|F_h^o|^2$ for the reflection h on the basis of the available *a priori* information.

2.2.4.4. Probability distributions of normalized structure factors

Under some fairly general assumptions (see Chapter 2.1) probability distribution functions for the variable $|E|$ for cs. and ncs. structures are (see Fig. 2.2.4.1)

$${}_1P(|E|) d|E| = \sqrt{\frac{2}{\pi}} \exp\left(-\frac{E^2}{2}\right) d|E| \quad (2.2.4.4)$$

and

$${}_1P(|E|) d|E| = 2|E| \exp(-|E|^2) d|E|, \quad (2.2.4.5)$$

respectively. Corresponding cumulative functions are (see Fig. 2.2.4.2)

$${}_1N(|E|) = \sqrt{\frac{2}{\pi}} \int_0^{|E|} \exp\left(-\frac{t^2}{2}\right) dt = \operatorname{erf}\left(\frac{|E|}{\sqrt{2}}\right),$$

$${}_1N(|E|) = \int_0^{|E|} 2t \exp(-t^2) dt = 1 - \exp(-|E|^2).$$

Some moments of the distributions (2.2.4.4) and (2.2.4.5) are listed in Table 2.2.4.1. In the absence of other indications for a given crystal structure, a cs. or an ncs. space group will be preferred according to whether the statistical tests yield values closer to column 2 or to column 3 of Table 2.2.4.1.

For further details about the distribution of intensities see Chapter 2.1.

2.2.5. Phase-determining formulae

From the earliest periods of X-ray structure analysis several authors (Ott, 1927; Banerjee, 1933; Avrami, 1938) have tried to determine atomic positions directly from diffraction intensities. Significant

Table 2.2.4.1. Moments of the distributions (2.2.4.4) and (2.2.4.5)

$R(E_s)$ is the percentage of n.s.f.'s with amplitude greater than the threshold E_s .

Criterion	Centrosymmetric distribution	Noncentrosymmetric distribution
$\langle E \rangle$	0.798	0.886
$\langle E ^2 \rangle$	1.000	1.000
$\langle E ^3 \rangle$	1.596	1.329
$\langle E ^4 \rangle$	3.000	2.000
$\langle E ^5 \rangle$	6.383	3.323
$\langle E ^6 \rangle$	15.000	6.000
$\langle E^2 - 1 \rangle$	0.968	0.736
$\langle (E^2 - 1)^2 \rangle$	2.000	1.000
$\langle (E^2 - 1)^3 \rangle$	8.000	2.000
$\langle E^2 - 1 ^3 \rangle$	8.691	2.415
$R(1)$	0.320	0.368
$R(2)$	0.050	0.018
$R(3)$	0.003	0.0001

developments are the derivation of inequalities and the introduction of probabilistic techniques *via* the use of joint probability distribution methods (Hauptman & Karle, 1953).

2.2.5.1. Inequalities among structure factors

An extensive system of inequalities exists for the coefficients of a Fourier series which represents a positive function. This can restrict the allowed values for the phases of the s.f.'s in terms of measured structure-factor magnitudes. Harker & Kasper (1948) derived two types of inequalities:

Type 1. A modulus is bound by a combination of structure factors:

$$|U_h|^2 \leq \frac{1}{m} \sum_{s=1}^m a_s(-h) U_{h(I-R_s)}, \quad (2.2.5.1)$$

where m is the order of the point group and $a_s(-h) = \exp(-2\pi i h \cdot T_s)$.

Applied to low-order space groups, (2.2.5.1) gives

$$P1: |U_{h,k,l}|^2 \leq 1$$

$$P\bar{1}: U_{h,k,l}^2 \leq 0.5 + 0.5 U_{2h,2k,2l}$$

$$P2_1: |U_{h,k,l}|^2 \leq 0.5 + 0.5(-1)^k U_{2h,0,2l}.$$

The meaning of each inequality is easily understandable: in $P\bar{1}$, for example, $U_{2h,2k,2l}$ must be positive if $|U_{h,k,l}|$ is large enough.

Type 2. The modulus of the sum or of the difference of two structure factors is bound by a combination of structure factors:

$$|U_h \pm U_{h'}|^2 \leq \frac{1}{m} \left\{ \sum_{s=1}^m a_s(-h) U_{h(I-R_s)} + \sum_{s=1}^m a_s(-h') U_{h'(I-R_s)} \right. \\ \left. \pm 2 \operatorname{Re} \left[\sum_{s=1}^m a_s(-h') U_{h-h'(I-R_s)} \right] \right\} \quad (2.2.5.2)$$

where Re stands for 'real part of'. Equation (2.2.5.2) applied to $P1$ gives

$$|U_h \pm U_{h'}|^2 \leq 2 \pm 2|U_{h-h'}| \cos \varphi_{h-h'}.$$

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A variant of (2.2.5.2) valid for cs. space groups is

$$(U_{\mathbf{h}} \pm U_{\mathbf{h}'})^2 \leq (1 \pm U_{\mathbf{h}+\mathbf{h}'})(1 \pm U_{\mathbf{h}-\mathbf{h}'}).$$

After Harker & Kasper's contributions, several other inequalities were discovered (Gillis, 1948; Goedkoop, 1950; Okaya & Nitta, 1952; de Wolff & Bouman, 1954; Bouman, 1956; Oda *et al.*, 1961). The most general are the Karle–Hauptman inequalities (Karle & Hauptman, 1950):

$$D_m = \begin{vmatrix} U_0 & U_{-\mathbf{h}_1} & U_{-\mathbf{h}_2} & \dots & U_{-\mathbf{h}_n} \\ U_{\mathbf{h}_1} & U_0 & U_{\mathbf{h}_1-\mathbf{h}_2} & \dots & U_{\mathbf{h}_1-\mathbf{h}_n} \\ U_{\mathbf{h}_2} & U_{\mathbf{h}_2-\mathbf{h}_1} & U_0 & \dots & U_{\mathbf{h}_2-\mathbf{h}_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ U_{\mathbf{h}_n} & U_{\mathbf{h}_n-\mathbf{h}_1} & U_{\mathbf{h}_n-\mathbf{h}_2} & \dots & U_0 \end{vmatrix} \geq 0. \quad (2.2.5.3)$$

The determinant can be of any order but the leading column (or row) must consist of U 's with different indices, although, within the column, symmetry-related U 's may occur. For $n = 2$ and $\mathbf{h}_2 = 2\mathbf{h}_1 = 2\mathbf{h}$, equation (2.2.5.3) reduces to

$$D_3 = \begin{vmatrix} U_0 & U_{-\mathbf{h}} & U_{-2\mathbf{h}} \\ U_{\mathbf{h}} & U_0 & U_{-\mathbf{h}} \\ U_{2\mathbf{h}} & U_{\mathbf{h}} & U_0 \end{vmatrix} \geq 0,$$

which, for cs. structures, gives the Harker & Kasper inequality

$$U_{\mathbf{h}}^2 \leq 0.5 + 0.5U_{2\mathbf{h}}.$$

For $m = 3$, equation (2.2.5.3) becomes

$$D_3 = \begin{vmatrix} U_0 & U_{-\mathbf{h}} & U_{-\mathbf{k}} \\ U_{\mathbf{h}} & U_0 & U_{\mathbf{h}-\mathbf{k}} \\ U_{\mathbf{k}} & U_{\mathbf{k}-\mathbf{h}} & U_0 \end{vmatrix} \geq 0,$$

from which

$$1 - |U_{\mathbf{h}}|^2 - |U_{\mathbf{k}}|^2 - |U_{\mathbf{h}-\mathbf{k}}|^2 + 2|U_{\mathbf{h}}U_{\mathbf{k}}U_{\mathbf{h}-\mathbf{k}}| \cos \alpha_{\mathbf{h}, \mathbf{k}} \geq 0, \quad (2.2.5.4)$$

where

$$\alpha_{\mathbf{h}, \mathbf{k}} = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}.$$

If the moduli $|U_{\mathbf{h}}|$, $|U_{\mathbf{k}}|$, $|U_{\mathbf{h}-\mathbf{k}}|$ are large enough, (2.2.5.4) is not satisfied for all values of $\alpha_{\mathbf{h}, \mathbf{k}}$. In cs. structures the eventual check that one of the two values of $\alpha_{\mathbf{h}, \mathbf{k}}$ does not satisfy (2.2.5.4) brings about the unambiguous identification of the sign of the product $U_{\mathbf{h}}U_{\mathbf{k}}U_{\mathbf{h}-\mathbf{k}}$.

It was observed (Gillis, 1948) that 'there was a number of cases in which both signs satisfied the inequality, one of them by a comfortable margin and the other by only a relatively small margin. In almost all such cases it was the former sign which was the correct one. That suggests that the method may have some power in reserve in the sense that there are still fundamentally stronger inequalities to be discovered'. Today we identify this power in reserve in the use of probability theory.

2.2.5.2. Probabilistic phase relationships for structure invariants

For any space group (see Section 2.2.3) there are linear combinations of phases with cosines that are, in principle, fixed by the $|E|$ magnitudes alone (s.i.'s) or by the $|E|$ values and the trigonometric form of the structure factor (s.s.'s). This result greatly stimulated the calculation of conditional distribution functions

$$P(\Phi|\{\mathbf{R}\}), \quad (2.2.5.5)$$

where $R_{\mathbf{h}} = |E_{\mathbf{h}}|$, $\Phi = \sum A_i \varphi_{\mathbf{h}_i}$ is an s.i. or an s.s. and $\{\mathbf{R}\}$ is a

suitable set of diffraction magnitudes. The method was first proposed by Hauptman & Karle (1953) and was developed further by several authors (Bertaut, 1955a,b, 1960; Klug, 1958; Naya *et al.*, 1964, 1965; Giacovazzo, 1980a). From a probabilistic point of view the crystallographic problem is clear: the joint distribution $P(E_{\mathbf{h}_1}, \dots, E_{\mathbf{h}_n})$, from which the conditional distributions (2.2.5.5) can be derived, involves a number of normalized structure factors each of which is a linear sum of random variables (the atomic contributions to the structure factors). So, for the probabilistic interpretation of the phase problem, the atomic positions and the reciprocal vectors may be considered as random variables. A further problem is that of identifying, for a given Φ , a suitable set of magnitudes $|E|$ on which Φ primarily depends. The formulation of the *nested neighbourhood principle* first (Hauptman, 1975) fixed the idea of defining a sequence of sets of reflections each contained in the succeeding one and having the property that any s.i. or s.s. may be estimated *via* the magnitudes constituting the various neighbourhoods. A subsequent more general theory, the *representation method* (Giacovazzo, 1977a, 1980b), arranges for any Φ the set of intensities in a sequence of subsets in order of their expected effectiveness (in the statistical sense) for the estimation of Φ .

In the following sections the main formulae estimating low-order invariants and seminvariants or relating phases to other phases and diffraction magnitudes are given.

2.2.5.3. Triplet relationships

The basic formula for the estimation of the triplet phase $\Phi = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}$ given the parameter $G = 2\sigma_3\sigma_2^{-3/2} \times R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}-\mathbf{k}}$ is Cochran's (1955) formula

$$P(\Phi) = [2\pi I_0(G)]^{-1} \exp(G \cos \Phi), \quad (2.2.5.6)$$

where $\sigma_n = \sum_{j=1}^N Z_j^n$, Z_j is the atomic number of the j th atom and I_n is the modified Bessel function of order n . In Fig. 2.2.5.1 the distribution $P(\Phi)$ is shown for different values of G .

The conditional probability distribution for $\varphi_{\mathbf{h}}$, given a set of $(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})$ and $G_j = 2\sigma_3\sigma_2^{-3/2} R_{\mathbf{h}}R_{\mathbf{k}_j}R_{\mathbf{h}-\mathbf{k}_j}$, is given (Karle & Hauptman, 1956; Karle & Karle, 1966) by

$$P(\varphi_{\mathbf{h}}) = [2\pi I_0(\alpha)]^{-1} \exp[\alpha \cos(\varphi_{\mathbf{h}} - \beta_{\mathbf{h}})], \quad (2.2.5.7)$$

where

$$\alpha^2 = \left[\sum_{j=1}^r G_{\mathbf{h}, \mathbf{k}_j} \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j}) \right]^2 + \left[\sum_{j=1}^r G_{\mathbf{h}, \mathbf{k}_j} \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j}) \right]^2 \quad (2.2.5.8)$$

$$\tan \beta_{\mathbf{h}} = \frac{\sum_j G_{\mathbf{h}, \mathbf{k}_j} \sin(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})}{\sum_j G_{\mathbf{h}, \mathbf{k}_j} \cos(\varphi_{\mathbf{k}_j} + \varphi_{\mathbf{h}-\mathbf{k}_j})}. \quad (2.2.5.9)$$

$\beta_{\mathbf{h}}$ is the most probable value for $\varphi_{\mathbf{h}}$. The variance of $\varphi_{\mathbf{h}}$ may be obtained from (2.2.5.7) and is given by

$$V_{\mathbf{h}} = \frac{\pi^2}{3} + [I_0(\alpha)]^{-1} \sum_{n=1}^{\infty} \frac{I_{2n}(\alpha)}{n^2} - 4[I_0(\alpha)]^{-1} \sum_{n=0}^{\infty} \frac{I_{2n+1}(\alpha)}{(2n+1)^2}, \quad (2.2.5.10)$$

which is plotted in Fig. 2.2.5.2.

Equation (2.2.5.9) is the so-called *tangent formula*. According to (2.2.5.10), the larger is α the more reliable is the relation $\varphi_{\mathbf{h}} = \beta_{\mathbf{h}}$.

For an equal-atom structure $\sigma_3\sigma_2^{-3/2} = N^{-1/2}$.

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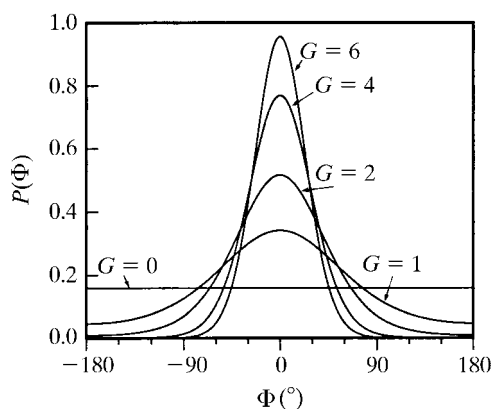


Fig. 2.2.5.1. Curves of (2.2.5.6) for some values of $G = 2\sigma_3\sigma_2^{-3/2}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|$.

The basic conditional formula for sign determination of $E_{\mathbf{h}}$ in cs. crystals is Cochran & Woolfson's (1955) formula

$$P^+ = \frac{1}{2} + \frac{1}{2} \tanh \left(\sigma_3 \sigma_2^{-3/2} |E_{\mathbf{h}}| \sum_{j=1}^r E_{\mathbf{k}_j} E_{\mathbf{h}-\mathbf{k}_j} \right), \quad (2.2.5.11)$$

where P^+ is the probability that $E_{\mathbf{h}}$ is positive and $\mathbf{k}$ ranges over the set of known values $E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$. The larger the absolute value of the argument of tanh, the more reliable is the phase indication.

An auxiliary formula exploiting all the $|E|$'s in reciprocal space in order to estimate a single Φ is the $B_{3,0}$ formula (Hauptman & Karle, 1958; Karle & Hauptman, 1958) given by

$$\begin{aligned} & |E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{-\mathbf{h}_1-\mathbf{h}_2}| \cos(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1+\mathbf{h}_2}) \\ & \simeq C \langle (|E_{\mathbf{k}}|^p - \overline{|E|^p})(|E_{\mathbf{h}_1+\mathbf{k}}|^p - \overline{|E|^p})(|E_{\mathbf{h}_1+\mathbf{h}_2+\mathbf{k}}|^p - \overline{|E|^p}) \rangle_{\mathbf{k}} \\ & - \frac{2\sigma_6}{\sigma_4^{3/2}} + \frac{\sigma_8^{1/2}}{\sigma_4} (|E_{\mathbf{h}_1}|^2 + |E_{\mathbf{h}_2}|^2 + |E_{\mathbf{h}_1+\mathbf{h}_2}|^2) \dots, \end{aligned} \quad (2.2.5.12)$$

where C is a constant which differs for cs. and ncs. crystals, $\overline{|E|^p}$ is the average value of $|E|^p$ and p is normally chosen to be some small number. Several modifications of (2.2.5.12) have been proposed (Hauptman, 1964, 1970; Karle, 1970a; Giacovazzo, 1977b).

A recent formula (Cascarano, Giacovazzo, Camalli *et al.*, 1984) exploits information contained within the second representation of Φ , that is to say, within the collection of special quintets (see Section 2.2.5.6):

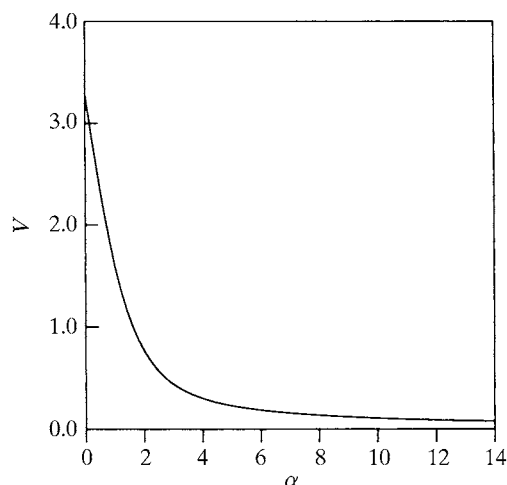


Fig. 2.2.5.2. Variance (in square radians) as a function of α .

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1+\mathbf{h}_2} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{k}},$$

where $\mathbf{k}$ is a free vector. The formula retains the same algebraic form as (2.2.5.6), but

$$G = \frac{2R_{\mathbf{h}_1}R_{\mathbf{h}_2}R_{\mathbf{h}_3}}{\sqrt{N}} (1 + Q), \quad (2.2.5.13)$$

where $[\mathbf{h}_3 = -(\mathbf{h}_1 + \mathbf{h}_2)]$,

$$Q = \sum_{\mathbf{k}} \frac{\sum_{i=1}^m A_{\mathbf{k},i}/N}{1 + (\varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2}\varepsilon_{\mathbf{h}_3} + \sum_{i=1}^m B_{\mathbf{k},i})/2N},$$

$$\begin{aligned} A_{\mathbf{k},i} &= \varepsilon_{\mathbf{k}} [\varepsilon_{\mathbf{h}_1+\mathbf{kR}_i} (\varepsilon_{\mathbf{h}_2-\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_3-\mathbf{kR}_i}) \\ &+ \varepsilon_{\mathbf{h}_2+\mathbf{kR}_i} (\varepsilon_{\mathbf{h}_1-\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_3-\mathbf{kR}_i}) \\ &+ \varepsilon_{\mathbf{h}_3+\mathbf{kR}_i} (\varepsilon_{\mathbf{h}_1-\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_2-\mathbf{kR}_i})], \\ B_{\mathbf{k},i} &= \varepsilon_{\mathbf{h}_1} [\varepsilon_{\mathbf{k}} (\varepsilon_{\mathbf{h}_1+\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_1-\mathbf{kR}_i}) \\ &+ \varepsilon_{\mathbf{h}_2+\mathbf{kR}_i} \varepsilon_{\mathbf{h}_3-\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_2-\mathbf{kR}_i} \varepsilon_{\mathbf{h}_3+\mathbf{kR}_i}] \\ &+ \varepsilon_{\mathbf{h}_2} [\varepsilon_{\mathbf{k}} (\varepsilon_{\mathbf{h}_2+\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_2-\mathbf{kR}_i}) \\ &+ \varepsilon_{\mathbf{h}_1+\mathbf{kR}_i} \varepsilon_{\mathbf{h}_3-\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_1-\mathbf{kR}_i} \varepsilon_{\mathbf{h}_3+\mathbf{kR}_i}] \\ &+ \varepsilon_{\mathbf{h}_3} [\varepsilon_{\mathbf{k}} (\varepsilon_{\mathbf{h}_3+\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_3-\mathbf{kR}_i}) \\ &+ \varepsilon_{\mathbf{h}_1+\mathbf{kR}_i} \varepsilon_{\mathbf{h}_2-\mathbf{kR}_i} + \varepsilon_{\mathbf{h}_1-\mathbf{kR}_i} \varepsilon_{\mathbf{h}_2+\mathbf{kR}_i}]; \end{aligned}$$

$\varepsilon = |E|^2 - 1$, $(\varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2}\varepsilon_{\mathbf{h}_3} + \sum_{i=1}^m B_{\mathbf{k},i})$ is assumed to be zero if it is experimentally negative. The prime to the summation warns the reader that precautions have to be taken in order to avoid duplications in the contributions.

G may be positive or negative. In particular, if $G < 0$ the triplet is estimated negative.

The accuracy with which the value of Φ is estimated strongly depends on $\varepsilon_{\mathbf{k}}$. Thus, in practice, only a subset of reciprocal space (the reflections $\mathbf{k}$ with large values of ε) may be used for estimating Φ .

(2.2.5.13) proved to be quite useful in practice. Positive triplet cosines are ranked in order of reliability by (2.2.5.13) markedly better than by Cochran's parameters. Negative estimated triplet cosines may be excluded from the phasing process and may be used as a figure of merit for finding the correct solution in a multisolution procedure.

2.2.5.4. Triplet relationships using structural information

A strength of direct methods is that no knowledge of structure is required for their application. However, when some *a priori* information is available, it should certainly be a weakness of the methods not to make use of this knowledge. The conditional distribution of Φ given $R_{\mathbf{h}}R_{\mathbf{k}}R_{\mathbf{h}-\mathbf{k}}$ and the first three of the five kinds of *a priori* information described in Section 2.2.4.1 is (Main, 1976; Heinemann, 1977a)

$$P(\Phi) \simeq \frac{\exp\{2QR_1R_2R_3 \cos(\Phi - q)\}}{2\pi I_0(2QR_1R_2R_3)}, \quad (2.2.5.14)$$

where

$$Q \exp(iq) = \frac{\sum_{i=1}^p g_i(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)}{\langle |F_{\mathbf{h}_1}|^2 \rangle^{1/2} \langle |F_{\mathbf{h}_2}|^2 \rangle^{1/2} \langle |F_{\mathbf{h}_3}|^2 \rangle^{1/2}}.$$

$\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ stand for $\mathbf{h}, -\mathbf{k}, -\mathbf{h} + \mathbf{k}$, and R_1, R_2, R_3 for $R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{h}-\mathbf{k}}$. The quantities $\langle |F_{\mathbf{h}_i}|^2 \rangle$ have been calculated in Section 2.2.4.1 according to different categories: $g_i(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$ is a suitable average of the product of three scattering factors for the i th atomic group, p is the number of atomic groups in the cell including those related by symmetry elements. We have the following categories.

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

(a) *No structural information*

(2.2.5.14) then reduces to (2.2.5.6).

(b) *Randomly positioned and randomly oriented atomic groups*
Then

$$g_i(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3) = \sum_{j,k,l} f_j f_k f_l \langle \exp[2\pi i(\mathbf{h}_1 \cdot \mathbf{r}_{kj} + \mathbf{h}_2 \cdot \mathbf{r}_{lj})] \rangle_R,$$

where $\langle \dots \rangle_R$ means rotational average. The average of the exponential term extends over all orientations of the triangle formed by the atoms j, k and l , and is given (Hauptman, 1965) by

$$B(z, t) = \langle \exp[2\pi i(\mathbf{h} \cdot \mathbf{r} + \mathbf{h}' \cdot \mathbf{r}')] \rangle \\ = \left(\frac{\pi}{2z}\right)^{1/2} \sum_{n=0}^{\infty} \frac{t^{2n}}{(n!)^2} J_{(4n+1)/2}(z),$$

where

$$z = 2\pi[q^2 r^2 + 2qrq'r' \cos \varphi_q \cos \varphi_r + q'^2 r'^2]^{1/2}$$

and

$$t = [2\pi^2 qrq'r' \sin \varphi_q \sin \varphi_r] / z;$$

q, q', r and r' are the magnitudes of $\mathbf{h}, \mathbf{h}', \mathbf{r}$ and $\mathbf{r}'$, respectively; φ_q and φ_r are the angles $(\mathbf{h}, \mathbf{h}')$ and $(\mathbf{r}, \mathbf{r}')$, respectively.

(c) *Randomly positioned but correctly oriented atomic groups*
Then

$$g_i(\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3) = \sum_{s=1}^m \sum_{j,k,l} f_j f_k f_l \\ \times \exp[2\pi i(\mathbf{h}_1 \cdot \mathbf{R}_s \mathbf{r}_{kj} + \mathbf{h}_2 \cdot \mathbf{R}_s \mathbf{r}_{lk})],$$

where the summations over j, k, l are taken over all the atoms in the i th group.

A modified expression for g_i has to be used in polar space groups for special triplets (Giacovazzo, 1988).

Translation functions [see Chapter 2.3; for an overview, see also Beurskens *et al.* (1987)] are also used to determine the position of a correctly oriented molecular fragment.

Such functions can work in direct space [expressed as Patterson convolutions (Buerger, 1959; Nordman, 1985) or electron-density convolutions (Rossmann *et al.*, 1964; Argos & Rossmann, 1980)] or in reciprocal space [expressed as correlation functions (Crowther & Blow, 1967; Karle, 1972; Langs, 1985) or residual functions (Rae, 1977)]. Both the probabilistic methods and the translation functions are quite efficient tools: the decision as to which one to use is often a personal choice.

(d) *Atomic groups correctly positioned*

Let p be the number of atoms with known position, q the number of atoms with unknown position, F_p and F_q the corresponding structure factors.

Tangent recycling methods (Karle, 1970b) may be used for recovering the complete crystal structure. The phase $\varphi_{p,h}$ is accepted in the starting set as a useful approximation of φ_h if $|F_{p,h}| > \eta |F_h|$, where η is the fraction of the total scattering power contained in the fragment and where $|F_h|$ is associated with $|E_h| > 1.5$.

Tangent recycling methods are applied (Beurskens *et al.*, 1979) with greater effectiveness to difference s.f.'s $\Delta F = (|F| - |F_p|) \exp(i\varphi_p)$. The weighted tangent formula uses ΔF_h values in order to convert them to more probable $F_{q,h}$ values.

From a probabilistic point of view (Giacovazzo, 1983a; Camalli *et al.*, 1985) the distribution of φ_h , given $E'_{p,h}$ and some products $(E'_k - E'_{p,k})(E'_{h-k} - E'_{p,h-k})$, is the von Mises function

$$P(\varphi_h | \dots) = [2\pi I_0(\alpha)]^{-1} \exp[\alpha \cos(\varphi_h - \theta_h)], \quad (2.2.5.15)$$

where θ_h , the most probable value of φ_h , is given by

$$\tan \theta_h \simeq \alpha'_2 / \alpha'_1, \quad (2.2.5.16) \\ \alpha^2 = \alpha_1'^2 + \alpha_2'^2$$

and

$$\alpha'_1 = 2R'_h \left\{ \mathcal{R} \left[E'_{p,h} + q^{-1/2} \sum_{\mathbf{k}} (E'_k - E'_{p,k}) \right. \right. \\ \left. \left. \times (E'_{h-k} - E'_{p,h-k}) \right] \right\} \\ \alpha'_2 = 2R'_h \left\{ \mathcal{I} \left[E'_{p,h} + q^{-1/2} \sum_{\mathbf{k}} (E'_k - E'_{p,k}) \right. \right. \\ \left. \left. \times (E'_{h-k} - E'_{p,h-k}) \right] \right\}.$$

$\mathcal{R}$ and $\mathcal{I}$ stand for 'real' and 'imaginary part of', respectively. Furthermore, $E' = F / \sum_q^{1/2}$ is a pseudo-normalized s.f. If no pair $(\varphi_k, \varphi_{h-k})$ is known, then

$$\alpha'_1 = 2R'_h R'_{p,h} \cos \varphi_{p,h} \\ \alpha'_2 = 2R'_h R'_{p,h} \sin \varphi_{p,h}$$

and (2.2.5.15) reduces to Sim's (1959) equation

$$P(\varphi_h) \simeq [2\pi I_0(G)]^{-1} \exp[G \cos(\varphi_h - \varphi_{p,h})], \quad (2.2.5.17)$$

where $G = 2R'_h R'_{p,h}$. In this case $\varphi_{p,h}$ is the most probable value of φ_h .

(e) *Pseudotranslational symmetry is present*

Substructure and superstructure reflections are then described by different forms of the structure-factor equation (Böhme, 1982; Gramlich, 1984; Fan *et al.*, 1983), so that probabilistic formulae estimating triplet cosines derived on the assumption that atoms are uniformly dispersed in the unit cell cannot hold. In particular, the reliability of each triplet also depends on, besides R_h, R_k, R_{h-k} , the actual $\mathbf{h}, \mathbf{k}, \mathbf{h} - \mathbf{k}$ indices and on the nature of the pseudotranslation. It has been shown (Cascarano *et al.*, 1985b; Cascarano, Giacovazzo & Luić, 1987) that (2.2.5.7), (2.2.5.8), (2.2.5.9) still hold provided G_{h,k_j} is replaced by

$$G'_{h,k_j} = \frac{2R_h R_{k_j} R_{h-k_j}}{\sqrt{N_{h,k}}},$$

where factors E and n_i are defined according to Section 2.2.4.1,

$$N_{h,k} = \frac{(\zeta_h[\sigma_2]_p + [\sigma_2]_q)(\zeta_k[\sigma_2]_p + [\sigma_2]_q)(\zeta_{h-k}[\sigma_2]_p + [\sigma_2]_q)}{\{(\beta/m)[\sigma_3]_p(n_1^2 n_2^2 n_3^2 \dots) + [\sigma_3]_q\}^2},$$

and β is the number of times for which

$$\begin{aligned} \mathbf{hR}_s \cdot \mathbf{u}_1 &\equiv 0 \pmod{1} & \mathbf{hR}_s \cdot \mathbf{u}_2 &\equiv 0 \pmod{1} & \mathbf{hR}_s \cdot \mathbf{u}_3 &\equiv 0 \pmod{1} \dots \\ \mathbf{kR}_s \cdot \mathbf{u}_1 &\equiv 0 \pmod{1} & \mathbf{kR}_s \cdot \mathbf{u}_2 &\equiv 0 \pmod{1} & \mathbf{kR}_s \cdot \mathbf{u}_3 &\equiv 0 \pmod{1} \dots \\ (\mathbf{h}-\mathbf{k})\mathbf{R}_s \cdot \mathbf{u}_1 &\equiv 0 \pmod{1} & (\mathbf{h}-\mathbf{k})\mathbf{R}_s \cdot \mathbf{u}_2 &\equiv 0 \pmod{1} & & \\ & & (\mathbf{h}-\mathbf{k})\mathbf{R}_s \cdot \mathbf{u}_3 &\equiv 0 \pmod{1} & \dots \end{aligned}$$

are simultaneously satisfied when s varies from 1 to m . The above formulae have been generalized (Cascarano *et al.*, 1988b) to the case in which deviations both of replacive and of displacive type from ideal pseudo-translational symmetry occur.

2.2.5.5. Quartet phase relationships

In early papers (Hauptman & Karle, 1953; Simerska, 1956) the phase

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$$\Phi = \varphi_h + \varphi_k + \varphi_l - \varphi_{h+k+l}$$

was always expected to be zero. Schenk (1973*a,b*) [see also Hauptman (1974)] suggested that Φ primarily depends on the seven magnitudes: R_h, R_k, R_l, R_{h+k+l} , called *basis magnitudes*, and $R_{h+k}, R_{h+l}, R_{k+l}$, called *cross magnitudes*.

The conditional probability of Φ in P_1 given seven magnitudes ($R_1 = R_h, \dots, R_4 = R_{h+k+l}, R_5 = R_{h+k}, R_6 = R_{h+l}, R_7 = R_{k+l}$) according to Hauptman (1975) is

$$P_7(\Phi) = \frac{1}{L} \exp(-2B \cos \Phi) I_0(2\sigma_3 \sigma_2^{-3/2} R_5 Y_5) \\ \times I_0(2\sigma_3 \sigma_2^{-3/2} R_6 Y_6) I_0(2\sigma_3 \sigma_2^{-3/2} R_7 Y_7),$$

where L is a suitable normalizing constant which can be derived numerically,

$$B = \sigma_2^{-3} (3\sigma_3^2 - \sigma_2 \sigma_4) R_1 R_2 R_3 R_4 \\ Y_5 = [R_1^2 R_2^2 + R_3^2 R_4^2 + 2R_1 R_2 R_3 R_4 \cos \Phi]^{1/2} \\ Y_6 = [R_3^2 R_1^2 + R_2^2 R_4^2 + 2R_1 R_2 R_3 R_4 \cos \Phi]^{1/2} \\ Y_7 = [R_2^2 R_3^2 + R_1^2 R_4^2 + 2R_1 R_2 R_3 R_4 \cos \Phi]^{1/2}.$$

For equal atoms $\sigma_2^{-3} (3\sigma_3^2 - \sigma_2 \sigma_4) = 2/N$. Denoting

$$C = R_1 R_2 R_3 R_4 / N, \\ Z_5 = 2Y_5 / \sqrt{N}, \quad Z_6 = 2Y_6 / \sqrt{N}, \quad Z_7 = 2Y_7 / \sqrt{N}$$

gives

$$P_7(\Phi) = \frac{1}{L} \exp(-4C \cos \Phi) \\ \times I_0(R_5 Z_5) I_0(R_6 Z_6) I_0(R_7 Z_7). \quad (2.2.5.18)$$

Fig. 2.2.5.3 shows the distribution (2.2.5.18) for three typical cases. It is clear from the figure that the cosine estimated near π or in the middle range will be in poorer agreement with the true values than the cosine near 0 because of the relatively larger values of the variance. In principle, however, the formula is able to estimate negative or enantiomorph-sensitive quartet cosines from the seven magnitudes.

In the cs. case (2.2.5.18) is replaced (Hauptman & Green, 1976) by

$$P^\pm \simeq \frac{1}{L} \exp(\mp 2C) \cosh(R_5 Z_5^\pm) \\ \times \cosh(R_6 Z_6^\pm) \cosh(R_7 Z_7^\pm), \quad (2.2.5.19) \quad \text{or}$$

where $P^\pm$ is the probability that the sign of $E_1 E_2 E_3 E_4$ is positive or negative, and

$$Z_5^\pm = \frac{1}{N^{1/2}} (R_1 R_2 \pm R_3 R_4), \\ Z_6^\pm = \frac{1}{N^{1/2}} (R_1 R_3 \pm R_2 R_4), \\ Z_7^\pm = \frac{1}{N^{1/2}} (R_1 R_4 \pm R_2 R_3).$$

The normalized probability may be derived by $P^+ / (P^+ + P^-)$. More simple probabilistic formulae were derived independently by Giacovazzo (1975, 1976):

$$P_7(\Phi) = [2\pi I_0(G)]^{-1} \exp(G \cos \Phi), \quad (2.2.5.20)$$

where

$$G = \frac{2C(1 + \varepsilon_5 + \varepsilon_6 + \varepsilon_7)}{1 + Q/(2N)} \quad (2.2.5.21)$$

$$Q = (\varepsilon_1 \varepsilon_2 + \varepsilon_3 \varepsilon_4) \varepsilon_5 + (\varepsilon_1 \varepsilon_3 + \varepsilon_2 \varepsilon_4) \varepsilon_6 + (\varepsilon_1 \varepsilon_4 + \varepsilon_2 \varepsilon_3) \varepsilon_7 \quad (2.2.5.22)$$

and $\varepsilon_i = (|E_i|^2 - 1)$. Q is never allowed to be negative.

According to (2.2.5.20) $\cos \Phi$ is expected to be positive or negative according to whether $(\varepsilon_5 + \varepsilon_6 + \varepsilon_7 + 1)$ is positive or negative: the larger is C , the more reliable is the phase indication. For $N \geq 150$, (2.2.5.18) and (2.2.5.20) are practically equivalent in all cases. If N is small, (2.2.5.20) is in good agreement with (2.2.5.18) for quartets strongly defined as positive or negative, but in poor agreement for enantiomorph-sensitive quartets (see Fig. 2.2.5.3).

In cs. cases the sign probability for $E_1 E_2 E_3 E_4$ is

$$P^+ = \frac{1}{2} + \frac{1}{2} \tanh(G/2), \quad (2.2.5.23)$$

where G is defined by (2.2.5.21).

All three cross magnitudes are not always in the set of measured reflections. From marginal distributions the following formulae arise (Giacovazzo, 1977*c*; Heinermann, 1977*b*):

(a) in the ncs. case, if R_7 , or R_6 and R_7 , or R_5 and R_6 and R_7 , are not in the measurements, then (2.2.5.18) is replaced by

$$P(\Phi | R_1, \dots, R_6) \simeq \frac{1}{L} \exp(-2C \cos \Phi) I_0(R_5 Z_5) I_0(R_6 Z_6),$$

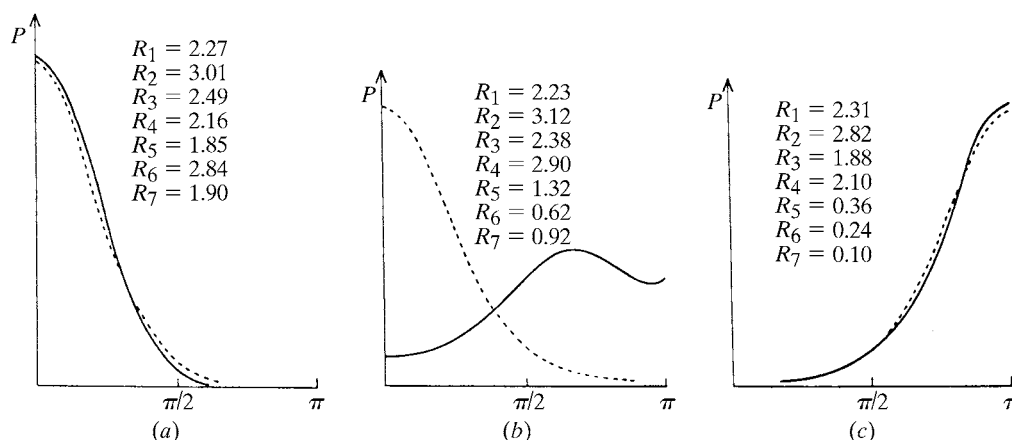


Fig. 2.2.5.3. Distributions (2.2.5.18) (—) and (2.2.5.20) (---) for the indicated $|E|$ values in three typical cases.

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Table 2.2.5.1. List of quartets symmetry equivalent to $\Phi = \Phi_1$ in the class mmm

Quartets	Basis vectors				Cross vectors		
Φ_1	(1, 2, 3)	($\bar{1}$, 5, $\bar{3}$)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, 7, 0)	(0, $\bar{3}$, 11)	($\bar{2}$, 0, 5)
Φ_2	($\bar{1}$, 2, 3)	(1, 5, $\bar{3}$)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, 7, 0)	($\bar{2}$, $\bar{3}$, 11)	(0, 0, 5)
Φ_3	(1, 2, $\bar{3}$)	($\bar{1}$, 5, 3)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, 7, 0)	(0, $\bar{3}$, 5)	($\bar{2}$, 0, 11)
Φ_4	($\bar{1}$, 2, $\bar{3}$)	(1, 5, 3)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, 7, 0)	($\bar{2}$, $\bar{3}$, 5)	(0, 0, 11)
Φ_5	($\bar{1}$, 2, 3)	($\bar{1}$, 5, $\bar{3}$)	(1, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	($\bar{2}$, 7, 0)	(0, $\bar{3}$, 11)	(0, 0, 5)
Φ_6	(1, 2, 3)	($\bar{1}$, 5, $\bar{3}$)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, $\bar{3}$, 0)	(0, 7, 11)	($\bar{2}$, 0, 5)
Φ_7	($\bar{1}$, 2, 3)	(1, 5, $\bar{3}$)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, $\bar{3}$, 0)	($\bar{2}$, 7, 11)	(0, 0, 5)
Φ_8	($\bar{1}$, 2, $\bar{3}$)	($\bar{1}$, 5, 3)	(1, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	($\bar{2}$, 7, 0)	(0, $\bar{3}$, 5)	(0, 0, 11)
Φ_9	(1, 2, $\bar{3}$)	($\bar{1}$, 5, 3)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, $\bar{3}$, 0)	(0, 7, 5)	($\bar{2}$, 0, 11)
Φ_{10}	($\bar{1}$, 2, $\bar{3}$)	(1, 5, 3)	($\bar{1}$, $\bar{5}$, 8)	(1, $\bar{2}$, $\bar{8}$)	(0, $\bar{3}$, 0)	($\bar{2}$, 7, 5)	(0, 0, 11)
Φ_{11}	($\bar{1}$, 2, 3)	($\bar{1}$, 5, $\bar{3}$)	(1, 5, 8)	(1, $\bar{2}$, $\bar{8}$)	($\bar{2}$, $\bar{3}$, 0)	(0, 7, 11)	(0, 0, 5)

$$P(\Phi|R_1, \dots, R_5) \simeq \frac{1}{L''} I_0(R_5 Z_5),$$

or

$$P(\Phi|R_1, \dots, R_4) \simeq \frac{1}{L'''} \exp(2C \cos \Phi),$$

respectively.

(b) in the same situations, we have for cs. cases

$$P^\pm \simeq \frac{1}{L'} \exp(\mp C) \cosh(R_5 Z_5^\pm) \cosh(R_6 Z_6^\pm),$$

or

$$P^\pm \simeq \frac{1}{L''} \cosh(R_5 Z_5^\pm)$$

or

$$P^\pm = \frac{1}{L'''} \exp(\pm C) \simeq 0.5 + 0.5 \tanh(\pm C),$$

respectively.

Equations (2.2.5.20) and (2.2.5.23) are easily modifiable when some cross magnitudes are not in the measurements. If R_i is not measured then (2.2.5.20) or (2.2.5.23) are still valid provided that in G it is assumed that $\varepsilon_i = 0$. For example, if R_7 and R_6 are not in the data then (2.2.5.21) and (2.2.5.22) become

$$G = \frac{2C(1 + \varepsilon_5)}{1 + Q/(2N)}, \quad Q = (\varepsilon_1 \varepsilon_2 + \varepsilon_3 \varepsilon_4) \varepsilon_5.$$

In space groups with symmetry higher than $P\bar{1}$ more symmetry-equivalent quartets can exist of the type

$$\psi = \varphi_{\mathbf{h}\mathbf{R}_\alpha} + \varphi_{\mathbf{k}\mathbf{R}_\beta} + \varphi_{\mathbf{l}\mathbf{R}_\gamma} + \varphi_{(\mathbf{h}+\mathbf{k}+\mathbf{l})\mathbf{R}_\delta},$$

where $\mathbf{R}_\alpha, \mathbf{R}_\beta, \mathbf{R}_\gamma, \mathbf{R}_\delta$ are rotation matrices of the space group. The set $\{\psi\}$ is called the *first representation* of Φ . In this case Φ primarily depends on more than seven magnitudes. For example, let us consider in $Pmmm$ the quartet

$$\Phi = \varphi_{123} + \varphi_{\bar{1}\bar{5}\bar{3}} + \varphi_{\bar{1}\bar{5}8} + \varphi_{1\bar{2}\bar{8}}.$$

Quartets symmetry equivalent to Φ and respective cross terms are given in Table 2.2.5.1.

Experimental tests on the application of the representation concept to quartets have recently been made (Busetta *et al.*, 1980). It was shown that quartets with more than three cross magnitudes are more accurately estimated than other quartets. Also, quartets with a cross reflection which is systematically absent were shown to be of significant importance in direct methods. In this

context it is noted that systematically absent reflections are not usually included in the set of diffraction data. This custom, not exceptionable when only triplet relations are used, can give rise to a loss of information when quartets are used. In fact the usual programs of direct methods discard quartets as soon as one of the cross reflections is not measured, so that systematic absences are dealt with in the same manner as those reflections which are outside the sphere of measurements.

2.2.5.6. Quintet phase relationships

A quintet phase

$$\Phi = \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} + \varphi_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}}$$

may be considered as the sum of three suitable triplets or the sum of a triplet and a quartet, *i.e.*

$$\begin{aligned} \Phi = & (\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}) + (\varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} - \varphi_{\mathbf{l}+\mathbf{m}}) \\ & + (\varphi_{\mathbf{h}+\mathbf{k}} + \varphi_{\mathbf{l}+\mathbf{m}} + \varphi_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}}) \end{aligned}$$

or

$$\Phi = (\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}+\mathbf{k}}) + (\varphi_{\mathbf{l}} + \varphi_{\mathbf{m}} + \varphi_{\overline{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}}} + \varphi_{\mathbf{h}+\mathbf{k}}).$$

It depends primarily on 15 magnitudes: the five *basis magnitudes*

$$R_{\mathbf{h}}, \quad R_{\mathbf{k}}, \quad R_{\mathbf{l}}, \quad R_{\mathbf{m}}, \quad R_{\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}},$$

and the ten *cross magnitudes*

$$\begin{aligned} & R_{\mathbf{h}+\mathbf{k}}, \quad R_{\mathbf{h}+\mathbf{l}}, \quad R_{\mathbf{h}+\mathbf{m}}, \quad R_{\mathbf{k}+\mathbf{l}+\mathbf{m}}, \quad R_{\mathbf{k}+\mathbf{l}}, \\ & R_{\mathbf{k}+\mathbf{m}}, \quad R_{\mathbf{h}+\mathbf{l}+\mathbf{m}}, \quad R_{\mathbf{l}+\mathbf{m}}, \quad R_{\mathbf{h}+\mathbf{k}+\mathbf{m}}, \quad R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}. \end{aligned}$$

In the following we will denote

$$R_1 = R_{\mathbf{h}}, \quad R_2 = R_{\mathbf{k}}, \quad \dots, \quad R_{15} = R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}.$$

Conditional distributions of Φ in $P1$ and $P\bar{1}$ given the 15 magnitudes have been derived by several authors and allow in favourable circumstances in ncs. space groups the quintets having Φ near 0 or near π or near $\pm\pi/2$ to be identified. Among others, we remember:

(a) the semi-empirical expression for $P_{15}(\Phi)$ suggested by Van der Putten & Schenk (1977):

$$P(\Phi|\dots) \simeq \frac{1}{L} \exp \left[\left(6 - \sum_{j=6}^{15} R_j^2 \right) 2C \cos \Phi \right] \prod_{j=6}^{15} I_0(2R_j Y_j),$$

where

$$C = N^{-3/2} R_1 R_2 R_3 R_4 R_5$$

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and Y_j is an expression related to the j th of the ten quartets connected with the quintet Φ ;

(b) the formula by Fortier & Hauptman (1977), valid in $P\bar{1}$, which is able to predict the sign of a quintet by means of an expression which involves a summation over 1024 sets of signs;

(c) the expression by Giacovazzo (1977d), according to which

$$P_{15}(\Phi) \simeq [2\pi I_0(G)]^{-1} \exp(G \cos \Phi), \quad (2.2.5.24)$$

where

$$G = \frac{2C}{1 + 6(N)^{1/2}} \left[\frac{1 + A + B}{1 + D/(2N)} \right] \quad (2.2.5.25)$$

and where

$$\begin{aligned} A &= \sum_{i=6}^{15} \varepsilon_i, \\ B &= \varepsilon_6\varepsilon_{13} + \varepsilon_6\varepsilon_{15} + \varepsilon_6\varepsilon_{14} + \varepsilon_7\varepsilon_{11} + \varepsilon_7\varepsilon_{15} + \varepsilon_7\varepsilon_{12} \\ &\quad + \varepsilon_8\varepsilon_{10} + \varepsilon_8\varepsilon_{14} + \varepsilon_8\varepsilon_{12} + \varepsilon_{10}\varepsilon_{15} + \varepsilon_{10}\varepsilon_9 + \varepsilon_{11}\varepsilon_{14} \\ &\quad + \varepsilon_{11}\varepsilon_9 + \varepsilon_{13}\varepsilon_9 + \varepsilon_{13}\varepsilon_{12}, \\ D &= \varepsilon_1\varepsilon_2\varepsilon_6 + \varepsilon_1\varepsilon_3\varepsilon_7 + \varepsilon_1\varepsilon_4\varepsilon_8 + \varepsilon_1\varepsilon_5\varepsilon_9 + \varepsilon_1\varepsilon_{10}\varepsilon_{15} \\ &\quad + \varepsilon_1\varepsilon_{11}\varepsilon_{14} + \varepsilon_1\varepsilon_{13}\varepsilon_{12} + \varepsilon_2\varepsilon_3\varepsilon_{10} + \varepsilon_2\varepsilon_4\varepsilon_{11} \\ &\quad + \varepsilon_2\varepsilon_5\varepsilon_{12} + \varepsilon_2\varepsilon_7\varepsilon_{15} + \varepsilon_2\varepsilon_8\varepsilon_{14} + \varepsilon_2\varepsilon_{13}\varepsilon_9 + \varepsilon_3\varepsilon_4\varepsilon_{13} \\ &\quad + \varepsilon_3\varepsilon_5\varepsilon_{14} + \varepsilon_3\varepsilon_6\varepsilon_{15} + \varepsilon_3\varepsilon_8\varepsilon_{12} + \varepsilon_3\varepsilon_{11}\varepsilon_9 + \varepsilon_4\varepsilon_5\varepsilon_{15} \\ &\quad + \varepsilon_4\varepsilon_6\varepsilon_{14} + \varepsilon_4\varepsilon_7\varepsilon_{12} + \varepsilon_4\varepsilon_{10}\varepsilon_9 + \varepsilon_5\varepsilon_6\varepsilon_{13} + \varepsilon_5\varepsilon_7\varepsilon_{11} \\ &\quad + \varepsilon_5\varepsilon_8\varepsilon_{10}. \end{aligned}$$

For cs. cases (2.2.5.24) reduces to

$$P^+ \simeq 0.5 + 0.5 \tanh(G/2). \quad (2.2.5.26)$$

Positive or negative quintets may be identified according to whether G is larger or smaller than zero.

If R_i is not measured then (2.2.5.24) and (2.2.5.25) are still valid provided that in (2.2.5.25) $\varepsilon_i = 0$.

If the symmetry is higher than in $P\bar{1}$ then more symmetry-equivalent quintets can exist of the type

$$\psi = \varphi_{\mathbf{h}\mathbf{R}_\alpha} + \varphi_{\mathbf{k}\mathbf{R}_\beta} + \varphi_{\mathbf{l}\mathbf{R}_\gamma} + \varphi_{\mathbf{m}\mathbf{R}_\delta} + \varphi_{(\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m})\mathbf{R}_\varepsilon},$$

where $\mathbf{R}_\alpha, \dots, \mathbf{R}_\varepsilon$ are rotation matrices of the space groups. The set $\{\psi\}$ is called the first representation of Φ . In this case Φ primarily depends on more than 15 magnitudes which all have to be taken into account for a careful estimation of Φ (Giacovazzo, 1980a).

A wide use of quintet invariants in direct methods procedures is prevented for two reasons: (a) the large correlation of positive quintet cosines with positive triplets; (b) the large computing time necessary for their estimation [quintets are phase relationships of order $1/(N\sqrt{N})$, so a large number of quintets have to be estimated in order to pick up a sufficient percentage of reliable ones].

2.2.5.7. Determinantal formulae

In a crystal structure with N identical atoms the joint probability distribution of n normalized s.f.'s $E_{\mathbf{h}_1+\mathbf{k}}, E_{\mathbf{h}_2+\mathbf{k}}, \dots, E_{\mathbf{h}_n+\mathbf{k}}$ under the following conditions:

(a) the structure is kept fixed whereas $\mathbf{k}$ is the primitive random variable;

(b) $E_{\mathbf{h}_i-\mathbf{h}_j}$, $i, j = 1, \dots, n$, have values which are known *a priori*; is given (Tsoucaris, 1970) [see also Castellano *et al.* (1973) and Heinermann *et al.* (1979)] by

$$P(E_1, E_2, \dots, E_n) = (2\pi)^{-n/2} D_n^{-1/2} \exp(-\frac{1}{2}Q_n) \quad (2.2.5.27)$$

for cs. structures and

$$P(E_1, E_2, \dots, E_n) = (2\pi)^{-n} D_n^{-1/2} \exp(-Q_n) \quad (2.2.5.28)$$

for ncs. structures. In (2.2.5.27) and (2.2.5.28) we have denoted

$$D_n = \lambda, \quad Q_n = \sum_{p, q=1}^n \Lambda_{pq} E_p E_q^*$$

$$E_j = E_{\mathbf{h}_j+\mathbf{k}}, \quad U_{pq} = U_{\mathbf{h}_p-\mathbf{h}_q}, \quad j, p, q = 1, \dots, n.$$

Λ_{pq} is an element of $\boldsymbol{\Lambda}^{-1}$, and $\boldsymbol{\Lambda}$ is the covariance matrix with elements

$$\boldsymbol{\Lambda} = \begin{pmatrix} \langle E_{\mathbf{h}_1+\mathbf{k}} E_{\mathbf{h}_1+\mathbf{k}} \rangle & U_{12} & \dots & U_{1n} \\ U_{21} & 1 & \dots & U_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ U_{p1} & U_{p2} & \dots & U_{pn} \\ \vdots & \vdots & \ddots & \vdots \\ U_{n1} & U_{n2} & \dots & 1 \end{pmatrix}.$$

λ is a K-H determinant: therefore $D_n \geq 0$. Let us call

$$\Delta_{n+1} = \frac{1}{N} \begin{vmatrix} 1 & U_{12} & \dots & U_{1n} & E_{\mathbf{h}_1+\mathbf{k}} \\ U_{21} & 1 & \dots & U_{2n} & E_{\mathbf{h}_2+\mathbf{k}} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ U_{n1} & U_{n2} & \dots & 1 & E_{\mathbf{h}_n+\mathbf{k}} \\ E_{-\mathbf{h}_1-\mathbf{k}} & E_{-\mathbf{h}_2-\mathbf{k}} & \dots & E_{-\mathbf{h}_n-\mathbf{k}} & N \end{vmatrix};$$

the K-H determinant obtained by adding to $\boldsymbol{\Lambda}$ the last column and line formed by $E_1, E_2, \dots, E_n$, and $E_1^*, E_2^*, \dots, E_n^*$, respectively. Then (2.2.5.27) and (2.2.5.28) may be written

$$\begin{aligned} P(E_1, E_2, \dots, E_n) \\ = (2\pi)^{-n/2} D_n^{-1/2} \exp \left[N \frac{\Delta_{n+1} - D_n}{2D_n} \right] \end{aligned} \quad (2.2.5.29)$$

and

$$\begin{aligned} P(E_1, E_2, \dots, E_n) \\ = (2\pi)^{-n} D_n^{-1/2} \exp \left[N \frac{\Delta_{n+1} - D_n}{D_n} \right], \end{aligned} \quad (2.2.5.30)$$

respectively. Because D_n is a constant, the maximum values of the conditional joint probabilities (2.2.5.29) and (2.2.5.30) are obtained when Δ_{n+1} is a maximum. Thus the *maximum determinant rule* may be stated (Tsoucaris, 1970; Lajz rowicz & Lajz rowicz, 1966): among all sets of phases which are compatible with the inequality

$$\Delta_{n+1}(E_1, E_2, \dots, E_n) \geq 0$$

the most probable one is that which leads to a maximum value of Δ_{n+1} .

If only one phase, *i.e.* φ_q , is unknown whereas all other phases and moduli are known then (de Rango *et al.*, 1974; Podjarny *et al.*, 1976) for cs. crystals

$$P^\pm(E_q) \simeq 0.5 + 0.5 \tanh \left\{ \pm |E_q| \sum_{\substack{p=1 \\ p \neq q}}^n \Lambda_{pq} E_p \right\}, \quad (2.2.5.31)$$

and for ncs. crystals

$$P(\varphi_q) = [2\pi I_0(G_q)]^{-1} \exp\{G_q \cos(\varphi_q - \theta_q)\}, \quad (2.2.5.32)$$

where

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$$G_q \exp(i\theta_q) = 2|E_q| \sum_{p \neq q=1}^n \Lambda_{pq} E_p.$$

Equations (2.2.5.31) and (2.2.5.32) generalize (2.2.5.11) and (2.2.5.7), respectively, and reduce to them for $n = 3$. Fourth-order determinantal formulae estimating triplet invariants in cs. and ncs. crystals, and making use of the entire data set, have recently been secured (Karle, 1979, 1980).

Advantages, limitations and applications of determinantal formulae can be found in the literature (Heinermann *et al.*, 1979; de Rango *et al.*, 1975, 1985). Taylor *et al.* (1978) combined K–H determinants with a magic-integer approach. The computing time, however, was larger than that required by standard computing techniques. The use of K–H matrices has been made faster and more effective by de Gelder *et al.* (1990) (see also de Gelder, 1992). They developed a phasing procedure (*CRUNCH*) which uses random phases as starting points for the maximization of the K–H determinants.

2.2.5.8. Algebraic relationships for structure seminvariants

According to the representations method (Giacovazzo, 1977a, 1980a,b):

- (i) any s.s. Φ may be estimated *via* one or more s.i.'s $\{\psi\}$, whose values differ from Φ by a constant arising because of symmetry;
- (ii) two types of s.s.'s exist, first-rank and second-rank s.s.'s, with different algebraic properties;
- (iii) conditions characterizing s.s.'s of first rank for any space group may be expressed in terms of seminvariant moduli and seminvariantly associated vectors. For example, for all the space groups with point group 422 [Hauptman–Karle group $(h+k, l)P(2, 2)$] the one-phase s.s.'s of first rank are characterized by

$$(h, k, l) \equiv 0 \pmod{(2, 2, 0) \text{ or } (2, 0, 2) \text{ or } (0, 2, 2)}$$

$$(h \pm k, l) \equiv 0 \pmod{(0, 2) \text{ or } (2, 0)}.$$

The more general expressions for the s.s.'s of first rank are

- (a) $\Phi = \varphi_{\mathbf{u}} = \varphi_{\mathbf{h}(\mathbf{I} - \mathbf{R}_{\alpha})}$ for one-phase s.s.'s;
- (b) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} = \varphi_{\mathbf{h}_1 - \mathbf{h}_2 \mathbf{R}_{\beta}} + \varphi_{\mathbf{h}_2 - \mathbf{h}_1 \mathbf{R}_{\alpha}}$ for two-phase s.s.'s;
- (c) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} = \varphi_{\mathbf{h}_1 - \mathbf{h}_2 \mathbf{R}_{\beta}} + \varphi_{\mathbf{h}_2 - \mathbf{h}_3 \mathbf{R}_{\gamma}} + \varphi_{\mathbf{h}_3 - \mathbf{h}_1 \mathbf{R}_{\alpha}}$ for three-phase s.s.'s;
- (d) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} + \varphi_{\mathbf{u}_3} + \varphi_{\mathbf{u}_4}$
 $= \varphi_{\mathbf{h}_1 - \mathbf{h}_2 \mathbf{R}_{\beta}} + \varphi_{\mathbf{h}_2 - \mathbf{h}_3 \mathbf{R}_{\gamma}} + \varphi_{\mathbf{h}_3 - \mathbf{h}_4 \mathbf{R}_{\delta}} + \varphi_{\mathbf{h}_4 - \mathbf{h}_1 \mathbf{R}_{\alpha}}$

for four-phase s.s.'s; *etc.*

In other words:

- (a) $\varphi_{\mathbf{u}}$ is an s.s. of first rank if at least one $\mathbf{h}$ and at least one rotation matrix $\mathbf{R}_{\alpha}$ exist such that $\mathbf{u} = \mathbf{h}(\mathbf{I} - \mathbf{R}_{\alpha})$. $\varphi_{\mathbf{u}}$ may be estimated *via* the special triplet invariants

$$\{\psi\} = \varphi_{\mathbf{u}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_{\alpha}}. \quad (2.2.5.33)$$

The set $\{\psi\}$ is called the *first representation* of $\varphi_{\mathbf{u}}$.

- (b) $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2}$ is an s.s. of first rank if at least two vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ and two rotation matrices $\mathbf{R}_{\alpha}$ and $\mathbf{R}_{\beta}$ exist such that

$$\begin{cases} \mathbf{u}_1 = \mathbf{h}_1 - \mathbf{h}_2 \mathbf{R}_{\beta} \\ \mathbf{u}_2 = \mathbf{h}_2 - \mathbf{h}_1 \mathbf{R}_{\alpha} \end{cases} \quad (2.2.5.34)$$

Φ may then be estimated *via* the special quartet invariants

$$\{\psi\} = \varphi_{\mathbf{u}_1 \mathbf{R}_{\alpha}} + \varphi_{\mathbf{u}_2} - \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_2 \mathbf{R}_{\beta} \mathbf{R}_{\alpha}} \quad (2.2.5.35a)$$

and

$$\{\psi\} = \{\varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2 \mathbf{R}_{\beta}} - \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_1 \mathbf{R}_{\alpha} \mathbf{R}_{\beta}}\}. \quad (2.2.5.35b)$$

For example, $\Phi = \varphi_{123} + \varphi_{\bar{7}2\bar{5}}$ in $P2_1$ may be estimated *via*

and

$$\{\psi\} = \varphi_{123} + \varphi_{\bar{7}2\bar{5}} - \varphi_{3K\bar{1}} + \varphi_{3K1}$$

$$\{\psi\} = \varphi_{123} + \varphi_{\bar{7}2\bar{5}} - \varphi_{4K4} + \varphi_{\bar{4}K\bar{4}},$$

where K is a free index.

The set of special quartets (2.2.5.35a) and (2.2.5.35b) constitutes the *first representations* of Φ .

Structure seminvariants of the second rank can be characterized as follows: suppose that, for a given seminvariant Φ , it is not possible to find a vectorial index $\mathbf{h}$ and a rotation matrix $\mathbf{R}_{\alpha}$ such that $\Phi - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_{\alpha}}$ is a structure invariant. Then Φ is a structure seminvariant of the second rank and a set of structure invariants ψ can certainly be formed, of type

$$\{\psi\} = \Phi + \varphi_{\mathbf{h}\mathbf{R}_p} - \varphi_{\mathbf{h}\mathbf{R}_q} + \varphi_{\mathbf{l}\mathbf{R}_i} - \varphi_{\mathbf{l}\mathbf{R}_j},$$

by means of suitable indices $\mathbf{h}$ and $\mathbf{l}$ and rotation matrices $\mathbf{R}_p, \mathbf{R}_q, \mathbf{R}_i$ and $\mathbf{R}_j$. As an example, for symmetry class 222, φ_{240} or φ_{024} or φ_{204} are s.s.'s of the first rank while φ_{246} is an s.s. of the second rank.

The procedure may easily be generalized to s.s.'s of any order of the first and of the second rank. So far only the role of one-phase and two-phase s.s.'s of the first rank in direct procedures is well documented (see references quoted in Sections 2.2.5.9 and 2.2.5.10).

2.2.5.9. Formulae estimating one-phase structure seminvariants of the first rank

Let $E_{\mathbf{H}}$ be our one-phase s.s. of the first rank, where

$$\mathbf{H} = \mathbf{h}(\mathbf{I} - \mathbf{R}_n). \quad (2.2.5.36)$$

In general, more than one rotation matrix $\mathbf{R}_n$ and more than one vector $\mathbf{h}$ are compatible with (2.2.5.36). The set of special triplets

$$\{\psi\} = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_n}\}$$

is the first representation of $E_{\mathbf{H}}$. In cs. space groups the probability that $E_{\mathbf{H}} > 0$, given $|E_{\mathbf{H}}|$ and the set $\{|E_{\mathbf{h}}|\}$, may be estimated (Hauptman & Karle, 1953; Naya *et al.*, 1964; Cochran & Woolfson, 1955) by

$$P^+(E_{\mathbf{H}}) \simeq 0.5 + 0.5 \tanh \sum_{\mathbf{h}, n} G_{\mathbf{h}, n} (-1)^{2\mathbf{h} \cdot \mathbf{T}_n}, \quad (2.2.5.37)$$

where

$$G_{\mathbf{h}, n} = |E_{\mathbf{H}}| \varepsilon_{\mathbf{h}} / (2\sqrt{N}), \text{ and } \varepsilon = |E|^2 - 1.$$

In (2.2.5.37), the summation over n goes within the set of matrices $\mathbf{R}_n$ for which (2.2.5.35a,b) is compatible, and $\mathbf{h}$ varies within the set of vectors which satisfy (2.2.5.36) for each $\mathbf{R}_n$. Equation (2.2.5.36) is actually a generalized way of writing the so-called $\sum_1$ relationships (Hauptman & Karle, 1953).

If $\varphi_{\mathbf{H}}$ is a phase restricted by symmetry to $\theta_{\mathbf{H}}$ and $\theta_{\mathbf{H}} + \pi$ in an ncs. space group then (Giacovazzo, 1978)

$$P(\varphi_{\mathbf{H}} = \theta_{\mathbf{H}}) \simeq 0.5 + 0.5 \tanh \left\{ \sum_{\mathbf{h}, n} G_{\mathbf{h}, n} \cos(\theta_{\mathbf{H}} - 2\pi \mathbf{h} \cdot \mathbf{T}_n) \right\}. \quad (2.2.5.38)$$

If $\varphi_{\mathbf{H}}$ is a general phase then $\varphi_{\mathbf{H}}$ is distributed according to

$$P(\varphi_{\mathbf{H}}) \simeq \frac{1}{L} \exp\{\alpha \cos(\varphi_{\mathbf{H}} - \theta_{\mathbf{H}})\},$$

where

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$$\tan \theta_{\mathbf{H}} = \frac{\left(\sum_{\mathbf{h}, n} G_{\mathbf{h}, n} \sin 2\pi \mathbf{h} \cdot \mathbf{T}_n \right)}{\left(\sum_{\mathbf{h}, n} G_{\mathbf{h}, n} \cos 2\pi \mathbf{h} \cdot \mathbf{T}_n \right)} \quad (2.2.5.39)$$

with a reliability measured by

$$\alpha = \left\{ \left(\sum_{\mathbf{h}, n} G_{\mathbf{h}, n} \sin 2\pi \mathbf{h} \cdot \mathbf{T}_n \right)^2 + \left(\sum_{\mathbf{h}, n} G_{\mathbf{h}, n} \cos 2\pi \mathbf{h} \cdot \mathbf{T}_n \right)^2 \right\}^{1/2}.$$

The second representation of $\varphi_{\mathbf{H}}$ is the set of special quintets

$$\{\psi\} = \{\varphi_{\mathbf{H}} - \varphi_{\mathbf{h}} + \varphi_{\mathbf{h}\mathbf{R}_n} + \varphi_{\mathbf{k}\mathbf{R}_j} - \varphi_{\mathbf{k}\mathbf{R}_j}\} \quad (2.2.5.40)$$

provided that $\mathbf{h}$ and $\mathbf{R}_n$ vary over the vectors and matrices for which (2.2.5.36) is compatible, $\mathbf{k}$ over the asymmetric region of the reciprocal space, and $\mathbf{R}_j$ over the rotation matrices in the space group. Formulae estimating $\varphi_{\mathbf{H}}$ via the second representation in all the space groups [all the base and cross magnitudes of the quintets (2.2.5.40) now constitute the *a priori* information] have recently been secured (Giacovazzo, 1978; Cascarano & Giacovazzo, 1983; Cascarano, Giacovazzo, Calabrese *et al.*, 1984). Such formulae contain, besides the contribution of order $N^{-1/2}$ provided by the first representation, a supplementary (not negligible) contribution of order $N^{-3/2}$ arising from quintets.

Denoting

$$E_1 = E_{\mathbf{H}}, E_2 = E_{\mathbf{h}}, E_3 = E_{\mathbf{k}}, \\ E_{4,j} = E_{\mathbf{h}+\mathbf{k}\mathbf{R}_j}, E_{5,j} = E_{\mathbf{H}+\mathbf{k}\mathbf{R}_j},$$

formulae (2.2.5.37), (2.2.5.38), (2.2.5.39) still hold provided that $\sum_{\mathbf{h}, n} G_{\mathbf{h}, n}$ is replaced by

$$\sum_{\mathbf{h}, n} G_{\mathbf{h}, n} + \sum'_{\mathbf{h}, \mathbf{k}, n} \frac{|E_{\mathbf{H}}|}{2N^{3/2}} \frac{A_{\mathbf{h}, \mathbf{k}, n}}{1 + B_{\mathbf{h}, \mathbf{k}, n}},$$

where

$$A_{\mathbf{h}, \mathbf{k}, n} = \left[(2|E_2|^2 - 1) \varepsilon_3 \left(\sum_{\substack{\mathbf{R}_j=\mathbf{R}_j \\ \mathbf{R}_j+\mathbf{R}_i\mathbf{R}_n=0}} \varepsilon_{4,i\varepsilon_{5,j}} + \sum_{\substack{\mathbf{R}_j=\mathbf{R}_j, \mathbf{R}_n \\ \mathbf{R}_i=\mathbf{R}_j\mathbf{R}_n}} \varepsilon_{4,i\varepsilon_{4,j}} \right) - \frac{\varepsilon_3}{2} \sum_{j=1}^m \varepsilon_{4,j} - \frac{1}{2} \sum_{\substack{\mathbf{R}_j=\mathbf{R}_i \\ \mathbf{R}_j+\mathbf{R}_i\mathbf{R}_n=0}} \varepsilon_{4,i\varepsilon_{5,j}} \right] / N, \\ B_{\mathbf{h}, \mathbf{k}, n} = \left[\varepsilon_1 \varepsilon_3 \sum_{j=1}^m \varepsilon_{5,j} + \varepsilon_1 \sum_{\substack{\mathbf{R}_j=\mathbf{R}_j, \mathbf{R}_n \\ \mathbf{R}_i=\mathbf{R}_j\mathbf{R}_n}} \varepsilon_{4,i\varepsilon_{4j}} + \varepsilon_2 \varepsilon_3 \sum_{j=1}^m \varepsilon_{4,j} + \varepsilon_2 \sum_{\substack{\mathbf{R}_j=\mathbf{R}_i \\ \mathbf{R}_j+\mathbf{R}_i\mathbf{R}_n=0}} \varepsilon_{4,i\varepsilon_{5,j}} + \frac{1}{4} \varepsilon_1 H_4(E_2) \right] / (2N).$$

m is the number of symmetry operators and $H_4(E) = E^4 - 6E^2 + 3$ is the Hermite polynomial of order four.

$B_{\mathbf{h}, \mathbf{k}, n}$ is assumed to be zero if it is computed negative. The prime to the summation warns the reader that precautions have to be taken in order to avoid duplication in the contributions.

2.2.5.10. Formulae estimating two-phase structure seminvariants of the first rank

Two-phase s.s.'s of the first rank were first evaluated in some cs. space groups by the method of coincidence by Grant *et al.* (1957); the idea was extended to ncs. space groups by Debaerdemaeker & Woolfson (1972), and in a more general way by Giacovazzo (1977*e,f*).

The technique was based on the combination of the two triplets

$$\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_1+\mathbf{h}_2} \\ \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2\mathbf{R}} \simeq \varphi_{\mathbf{h}_1+\mathbf{h}_2\mathbf{R}},$$

which, subtracted from one another, give

$$\varphi_{\mathbf{h}_1+\mathbf{h}_2\mathbf{R}} - \varphi_{\mathbf{h}_1+\mathbf{h}_2} \simeq \varphi_{\mathbf{h}_2\mathbf{R}} - \varphi_{\mathbf{h}_2} \simeq -2\pi \mathbf{h} \cdot \mathbf{T}.$$

If all four $|E|$'s are sufficiently large, an estimate of the two-phase seminvariant $\varphi_{\mathbf{h}_1+\mathbf{h}_2\mathbf{R}} - \varphi_{\mathbf{h}_1+\mathbf{h}_2}$ is available.

Probability distributions valid in $P2_1$ according to the neighbourhood principle have been given by Hauptman & Green (1978). Finally, the theory of representations was combined by Giacovazzo (1979*a*) with the joint probability distribution method in order to estimate two-phase s.s.'s in all the space groups.

According to representation theory, the problem is that of evaluating $\Phi = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2}$ via the special quartets (2.2.5.35*a*) and (2.2.5.35*b*). Thus, contributions of order N^{-1} will appear in the probabilistic formulae, which will be functions of the basis and of the cross magnitudes of the quartets (2.2.5.35). Since more pairs of matrices $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ can be compatible with (2.2.5.34), and for each pair ($\mathbf{R}_\alpha, \mathbf{R}_\beta$) more pairs of vectors $\mathbf{h}_1$ and $\mathbf{h}_2$ may satisfy (2.2.5.34), several quartets can in general be exploited for estimating Φ . The simplest case occurs in $P\bar{1}$ where the two quartets (2.2.5.35) suggest the calculation of the six-variate distribution function ($\mathbf{u}_1 = \mathbf{h}_1 + \mathbf{h}_2, \mathbf{u}_2 = \mathbf{h}_1 - \mathbf{h}_2$)

$$P(E_{\mathbf{h}_1}, E_{\mathbf{h}_2}, E_{\mathbf{h}_1+\mathbf{h}_2}, E_{\mathbf{h}_1-\mathbf{h}_2}, E_{2\mathbf{h}_1}, E_{2\mathbf{h}_2})$$

which leads to the probability formula

$$P^+ \simeq 0.5 + 0.5 \tanh \left(\frac{|E_{\mathbf{h}_1+\mathbf{h}_2} E_{\mathbf{h}_1-\mathbf{h}_2}|}{2N} \cdot \frac{A}{1+B} \right),$$

where P^+ is the probability that the product $E_{\mathbf{h}_1+\mathbf{h}_2} E_{\mathbf{h}_1-\mathbf{h}_2}$ is positive, and

$$A = \varepsilon_{\mathbf{h}_1} + \varepsilon_{\mathbf{h}_2} + 2\varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2} + \varepsilon_{\mathbf{h}_1}\varepsilon_{2\mathbf{h}_1} + \varepsilon_{\mathbf{h}_2}\varepsilon_{2\mathbf{h}_2} \\ B = (\varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2}\varepsilon_{\mathbf{u}_1} + \varepsilon_{\mathbf{h}_1}\varepsilon_{\mathbf{h}_2}\varepsilon_{\mathbf{u}_2} + \varepsilon_{\mathbf{u}_1}\varepsilon_{\mathbf{u}_2}\varepsilon_{2\mathbf{h}_1} + \varepsilon_{\mathbf{u}_1}\varepsilon_{\mathbf{u}_2}\varepsilon_{2\mathbf{h}_2}) / (2N).$$

It may be seen that in favourable cases $P^+ < 0.5$.

For the sake of brevity, the probabilistic formulae for the general case are not given and the reader is referred to the original papers.

2.2.6. Direct methods in real and reciprocal space: Sayre's equation

The statistical treatment suggested by Wilson for scaling observed intensities corresponds, in direct space, to the origin peak of the Patterson function, so it is not surprising that a general correspondence exists between probabilistic formulation in reciprocal space and algebraic properties in direct space.

For a structure containing atoms which are fully resolved from one another, the operation of raising $\rho(\mathbf{r})$ to the n th power retains

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the condition of resolved atoms but changes the shape of each atom. Let

$$\rho(\mathbf{r}) = \sum_{j=1}^N \rho_j(\mathbf{r} - \mathbf{r}_j),$$

where $\rho_j(\mathbf{r})$ is an atomic function and $\mathbf{r}_j$ is the coordinate of the 'centre' of the atom. Then the Fourier transform of the electron density can be written as

$$\begin{aligned} F_{\mathbf{h}} &= \sum_{j=1}^N \int_V \rho_j(\mathbf{r} - \mathbf{r}_j) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) dV \\ &= \sum_{j=1}^N f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j). \end{aligned} \quad (2.2.6.1)$$

If the atoms do not overlap

$$\rho^n(\mathbf{r}) = \left[\sum_{j=1}^N \rho_j(\mathbf{r} - \mathbf{r}_j) \right]^n \simeq \sum_{j=1}^N \rho_j^n(\mathbf{r} - \mathbf{r}_j)$$

and its Fourier transform gives

$$\begin{aligned} {}_n F_{\mathbf{h}} &= \int_V \rho^n(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) dV \\ &= \sum_{j=1}^N {}_n f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j). \end{aligned} \quad (2.2.6.2)$$

${}_n f_j$ is the scattering factor for the j th peak of $\rho^n(\mathbf{r})$:

$${}_n f_j(\mathbf{h}) = \int_V \rho_j^n(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d\mathbf{r}.$$

We now introduce the condition that all atoms are equal, so that $f_j \equiv f$ and ${}_n f_j \equiv {}_n f$ for any j . From (2.2.6.1) and (2.2.6.2) we may write

$$F_{\mathbf{h}} = \frac{f}{{}_n f} {}_n F_{\mathbf{h}} = \theta_n {}_n F_{\mathbf{h}}, \quad (2.2.6.3)$$

where θ_n is a function which corrects for the difference of shape of the atoms with electron distributions $\rho(\mathbf{r})$ and $\rho^n(\mathbf{r})$. Since

$$\begin{aligned} \rho^n(\mathbf{r}) &= \rho(\mathbf{r}) \dots \rho(\mathbf{r}) \\ &= \frac{1}{V^n} \sum_{\mathbf{h}_1, \dots, \mathbf{h}_n}^{+\infty} F_{\mathbf{h}_1} \dots F_{\mathbf{h}_n} \exp[-2\pi i (\mathbf{h}_1 + \dots + \mathbf{h}_n) \cdot \mathbf{r}], \end{aligned}$$

the Fourier transform of both sides gives

$$\begin{aligned} {}_n F_{\mathbf{h}} &= \frac{1}{V^n} \sum_{\mathbf{h}_1, \dots, \mathbf{h}_n}^{+\infty} F_{\mathbf{h}_1} \dots F_{\mathbf{h}_n} \int_V \exp[2\pi i (\mathbf{h} - \mathbf{h}_1 - \dots - \mathbf{h}_n) \cdot \mathbf{r}] dV \\ &= \frac{1}{V^{n-1}} \sum_{\mathbf{h}_1, \dots, \mathbf{h}_{n-1}}^{+\infty} F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h} - \mathbf{h}_1 - \mathbf{h}_2 - \dots - \mathbf{h}_{n-1}}, \end{aligned}$$

from which the following relation arises:

$$F_{\mathbf{h}} = \theta_n \frac{1}{V^{n-1}} \sum_{\mathbf{h}_1, \dots, \mathbf{h}_{n-1}}^{+\infty} F_{\mathbf{h}_1} F_{\mathbf{h}_2} \dots F_{\mathbf{h} - \mathbf{h}_1 - \mathbf{h}_2 - \dots - \mathbf{h}_{n-1}}. \quad (2.2.6.4)$$

For $n = 2$, equation (2.2.6.4) reduces to Sayre's (1952) equation [but see also Hughes (1953)]

$$F_{\mathbf{h}} = \theta_2 \frac{1}{V} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h} - \mathbf{k}}. \quad (2.2.6.5)$$

If the structure contains resolved isotropic atoms of two types, P and

Q , it is impossible to find a factor θ_2 such that the relation $F_{\mathbf{h}} = \theta_2 {}_2 F_{\mathbf{h}}$ holds, since this would imply values of θ_2 such that $({}_2 f)_P = \theta_2 ({}_2 f)_Q$ and $({}_2 f)_Q = \theta_2 ({}_2 f)_P$ simultaneously. However, the following relationship can be stated (Woolfson, 1958):

$$F_{\mathbf{h}} = \frac{A_s}{V} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h} - \mathbf{k}} + \frac{B_s}{V^2} \sum_{\mathbf{k}, \mathbf{l}} F_{\mathbf{k}} F_{\mathbf{l}} F_{\mathbf{h} - \mathbf{k} - \mathbf{l}}, \quad (2.2.6.6)$$

where A_s and B_s are adjustable parameters of $(\sin \theta)/\lambda$. Equation (2.2.6.6) can easily be generalized to the case of structures containing resolved atoms of more than two types (von Eller, 1973).

Besides the algebraic properties of the electron density, Patterson methods also can be developed so that they provide phase indications. For example, it is possible to find the reciprocal counterpart of the function

$$P_n(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_n) = \int_V \rho(\mathbf{r}) \rho(\mathbf{r} + \mathbf{u}_1) \dots \rho(\mathbf{r} + \mathbf{u}_n) dV. \quad (2.2.6.7)$$

For $n = 1$ the function (2.2.6.7) coincides with the usual Patterson function $P(\mathbf{u})$; for $n = 2$, (2.2.6.7) reduces to the double Patterson function $P_2(\mathbf{u}_1, \mathbf{u}_2)$ introduced by Sayre (1953). Expansion of $P_2(\mathbf{u}_1, \mathbf{u}_2)$ as a Fourier series yields

$$P_2(\mathbf{u}_1, \mathbf{u}_2) = \frac{1}{V^2} \sum_{\mathbf{h}_1, \mathbf{h}_2} E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3} \exp[-2\pi i (\mathbf{h}_1 \cdot \mathbf{u}_1 + \mathbf{h}_2 \cdot \mathbf{u}_2)]. \quad (2.2.6.8)$$

Vice versa, the value of a triplet invariant may be considered as the Fourier transform of the double Patterson.

Among the main results relating direct- and reciprocal-space properties it may be remembered:

(a) from the properties of $P_2(\mathbf{u}_1, \mathbf{u}_2)$ the following relationship may be obtained (Vaughan, 1958)

$$\begin{aligned} E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_1 + \mathbf{h}_2} - N^{-3/2} \\ \simeq A_1 (|E_{\mathbf{k}}|^2 - 1)(|E_{\mathbf{h}_1 + \mathbf{k}}|^2 - 1)(|E_{-\mathbf{h}_2 + \mathbf{k}}|^2 - 1)_{\mathbf{k}} - B_1, \end{aligned}$$

which is clearly related to (2.2.5.12);

(b) the zero points in the Patterson function provide information about the value of a triplet invariant (Anzenhofer & Hoppe, 1962; Allegra, 1979);

(c) the Hoppe sections (Hoppe, 1963) of the double Patterson provide useful information for determining the triplet signs (Krabbendam & Kroon, 1971; Simonov & Weissberg, 1970);

(d) one phase s.s.'s of the first rank can be estimated *via* the Fourier transform of single Harker sections of the Patterson (Ardito *et al.*, 1985), *i.e.*

$$F_{\mathbf{H}} \sim \frac{1}{L} \exp(2\pi i \mathbf{h} \cdot \mathbf{T}_n) \int_{HS(\mathbf{I}, \mathbf{C}_n)} P(\mathbf{u}) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}) d\mathbf{u}, \quad (2.2.6.9)$$

where (see Section 2.2.5.9) $\mathbf{H} = \mathbf{h}(\mathbf{I} - \mathbf{R}_n)$ is the s.s., $\mathbf{u}$ varies over the complete Harker section corresponding to the operator $\mathbf{C}_n$ [in symbols $HS(\mathbf{I}, \mathbf{C}_n)$] and L is a constant which takes into account the dimensionality of the Harker section.

If no spurious peak is on the Harker section, then (2.2.6.9) is an exact relationship. Owing to the finiteness of experimental data and to the presence of spurious peaks, (2.2.6.9) cannot be considered in practice an exact relation: it works better when heavy atoms are in the chemical formula.

More recently (Cascarano, Giacovazzo, Luić *et al.*, 1987), a special least-squares procedure has been proposed for discriminating spurious peaks among those lying on Harker sections and for improving positional and thermal parameters of heavy atoms.

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(e) translation and rotation functions (see Chapter 2.3), when defined in direct space, always have their counterpart in reciprocal space.

2.2.7. Scheme of procedure for phase determination

A traditional procedure for phase assignment may be schematically presented as follows:

Stage 1: *Normalization of s.f.'s*. See Section 2.2.4.

Stage 2: *(Possible) estimation of one-phase s.s.'s*. The computing program recognizes the one-phase s.s.'s and applies the proper formulae (see Section 2.2.5.9).

Each phase is associated with a reliability value, to allow the user to regard as known only those phases with reliability higher than a given threshold.

Stage 3: *Search of the triplets*. The reflections are listed for decreasing $|E|$ values and, related to each $|E|$ value, all possible triplets are reported (this is the so-called $\sum_2$ list). The value $G = 2|E_h E_k E_{h-k}|/\sqrt{N}$ is associated with every triplet for an evaluation of its efficiency. Usually reflections with $|E| < E_s$ (E_s may range from 1.2 to 1.6) are omitted from this stage onward.

Stage 4: *Definition of the origin and enantiomorph*. This stage is carried out according to the theory developed in Section 2.2.3. Phases chosen for defining the origin and enantiomorph, one-phase seminvariants estimated at stage 2, and symbolic phases described at stage 5 are the only phases known at the beginning of the phasing procedure. This set of phases is conventionally referred to as the *starting set*, from which iterative application of the tangent formula will derive new phase estimates.

Stage 5: *Assignment of one or more (symbolic or numerical) phases*. In complex structures the number of phases assigned for fixing the origin and the enantiomorph may be inadequate as a basis for further phase determination. Furthermore, only a few one-phase s.s.'s can be determined with sufficient reliability to make them qualify as members of the starting set. Symbolic phases may then be associated with some (generally from 1 to 6) high-modulus reflections (symbolic addition procedures). Iterative application of triplet relations leads to the determination of other phases which, in part, will remain expressed by symbols (Karle & Karle, 1966).

In other procedures (multisolution procedures) each symbol is assigned four phase values in turn: $\pi/4, 3\pi/4, 5\pi/4, 7\pi/4$. If p symbols are used, in at least one of the possible 4^p solutions each symbolic phase has unit probability of being within 45° of its true value, with a mean error of 22.5° .

To find a good starting set a *convergence method* (Germain *et al.*, 1970) is used according to which: (a)

$$\langle \alpha_h \rangle = \sum_j G_j I_1(G_j) / I_0(G_j)$$

is calculated for all reflections (j runs over the set of triplets containing h); (b) the reflection is found with smallest $\langle \alpha \rangle$ not already in the starting set; it is retained to define the origin if the origin cannot be defined without it; (c) the reflection is eliminated if it is not used for origin definition. Its $\langle \alpha \rangle$ is recorded and $\langle \alpha \rangle$ values for other reflections are updated; (d) the cycle is repeated from (b) until all reflections are eliminated; (e) the reflections with the smallest $\langle \alpha \rangle$ at the time of elimination go into the starting set; (f) the cycle from (a) is repeated until all reflections have been chosen.

Stage 6: *Application of tangent formula*. Phases are determined in reverse order of elimination in the convergence procedure. In order to ensure that poorly determined phases φ_{k_j} and φ_{h-k_j} have little effect in the determination of other phases a weighted tangent formula is normally used (Germain *et al.*, 1971):

$$\tan \varphi_h = \frac{\sum_j w_{k_j} w_{h-k_j} |E_{k_j} E_{h-k_j}| \sin(\varphi_{k_j} + \varphi_{h-k_j})}{\sum_j w_{k_j} w_{h-k_j} |E_{k_j} E_{h-k_j}| \cos(\varphi_{k_j} + \varphi_{h-k_j})}, \quad (2.2.7.1)$$

where

$$w_h = \min(0.2\alpha, 1).$$

Once a large number of contributions are available in (2.2.7.1) for a given φ_h , then the value of α_h quickly becomes greater than 5, and so assigns an unrealistic unitary weight to φ_h . In this respect a different weighting scheme may be proposed (Hull & Irwin, 1978) according to which

$$w = \psi \exp(-x^2) \int_0^x \exp(t^2) dt, \quad (2.2.7.2)$$

where $x = \alpha/\langle \alpha \rangle$ and $\psi = 1.8585$ is a constant chosen so that $w = 1$ when $x = 1$. Except for ψ , the right-hand side of (2.2.7.2) is the Dawson integral which assumes its maximum value at $x = 1$ (see Fig. 2.2.7.1): when $\alpha > \langle \alpha \rangle$ or $\alpha < \langle \alpha \rangle$ then $w < 1$ and so the agreement between α and $\langle \alpha \rangle$ is promoted.

Alternative weighting schemes for the tangent formula are frequently used [for example, see Debaerdemaeker *et al.* (1985)]. In one (Giacovazzo, 1979b), the values α_{k_j} and α_{h-k_j} (which are usually available in direct procedures) are considered as additional *a priori* information so that (2.2.7.1) may be replaced by

$$\tan \varphi_h \simeq \frac{\sum_j \beta_j \sin(\varphi_{k_j} + \varphi_{h-k_j})}{\sum_j \beta_j \cos(\varphi_{k_j} + \varphi_{h-k_j})}, \quad (2.2.7.3)$$

where β_j is the solution of the equation

$$D_1(\beta_j) = D_1(G_j) D_1(\alpha_{k_j}) D_1(\alpha_{h-k_j}). \quad (2.2.7.4)$$

In (2.2.7.4),

$$G_j = 2|E_h E_{k_j} E_{h-k_j}| \sqrt{N}$$

or the corresponding second representation parameter, and $D_1(x) = I_1(x)/I_0(x)$ is the ratio of two modified Bessel functions.

In order to promote (in accordance with the aims of Hull and Irwin) the agreement between α and $\langle \alpha \rangle$, the distribution of α may be used (Cascarano, Giacovazzo, Burla *et al.*, 1984; Burla *et al.*, 1987); in particular, the first two moments of the distribution: accordingly,

$$w = \left\{ \exp \left[\frac{-(\alpha - \langle \alpha \rangle)^2}{2\sigma_\alpha^2} \right] \right\}^{1/3}$$

may be used, where σ_α^2 is the estimated variance of α .

Stage 7: *Figures of merit*. The correct solution is found among several by means of figures of merit (FOMs) which are expected to be extreme for the correct solution. Largely used are (Germain *et al.*, 1970)

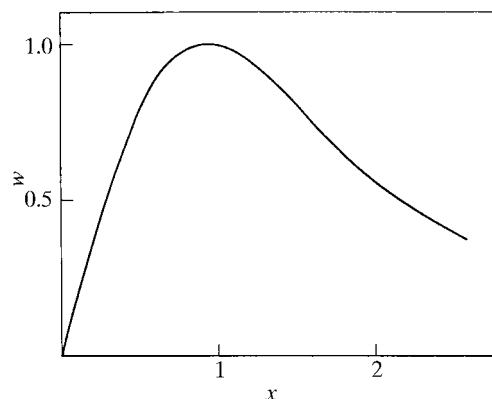


Fig. 2.2.7.1. The form of w as given by (2.2.7.2).

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$$(a) \quad \text{ABSFOM} = \sum_{\mathbf{h}} \alpha_{\mathbf{h}} / \sum_{\mathbf{h}} \langle \alpha_{\mathbf{h}} \rangle,$$

which is expected to be unity for the correct solution.

$$(b) \quad \text{PSIO} = \frac{\sum_{\mathbf{h}} |\sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|}{\sum_{\mathbf{h}} \left(\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|^2 \right)^{1/2}}.$$

The summation over $\mathbf{k}$ includes (Cochran & Douglas, 1957) the strong $|E|$'s for which phases have been determined, and indices $\mathbf{h}$ correspond to very small $|E_{\mathbf{h}}|$. Minimal values of PSIO (≤ 1.20) are expected to be associated with the correct solution.

$$(c) \quad R_{\alpha} = \frac{\sum_{\mathbf{h}} |\alpha_{\mathbf{h}} - \langle \alpha_{\mathbf{h}} \rangle|}{\sum_{\mathbf{h}} \langle \alpha_{\mathbf{h}} \rangle}.$$

That is, the Karle & Karle (1966) residual between the actual and the estimated α 's. After scaling of $\alpha_{\mathbf{h}}$ on $\langle \alpha_{\mathbf{h}} \rangle$ the correct solution should be characterized by the smallest R_{α} values.

$$(d) \quad \text{NQUEST} = \sum_j G_j \cos \Phi_j,$$

where G is defined by (2.2.5.21) and

$$\Phi = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}-\mathbf{k}-\mathbf{l}}$$

are quartet invariants characterized by large basis magnitudes and small cross magnitudes (De Titta *et al.*, 1975; Giacovazzo, 1976). Since G is expected to be negative as well as $\cos \Phi$, the value of NQUEST is expected to be positive and a maximum for the correct solution.

Figures of merit are then combined as

$$\begin{aligned} \text{CFOM} = & w_1 \frac{\text{ABSFOM} - \text{ABSFOM}_{\min}}{\text{ABSFOM}_{\max} - \text{ABSFOM}_{\min}} \\ & + w_2 \frac{\text{PSIO}_{\max} - \text{PSIO}}{\text{PSIO}_{\max} - \text{PSIO}_{\min}} \\ & + w_3 \frac{R_{\alpha_{\max}} - R_{\alpha}}{R_{\alpha_{\max}} - R_{\alpha_{\min}}} \\ & + w_4 \frac{\text{NQUEST} - \text{NQUEST}_{\min}}{\text{NQUEST}_{\max} - \text{NQUEST}_{\min}}, \end{aligned}$$

where w_i are empirical weights proportional to the confidence of the user in the various FOMs.

Different FOMs are often used by some authors in combination with those described above: for example, enantiomorph triplets and quartets are supplementary FOMs (Van der Putten & Schenk, 1977; Cascarano, Giacovazzo & Viterbo, 1987).

Different schemes of calculating and combining FOMs are also used: a recent scheme (Cascarano, Giacovazzo & Viterbo, 1987) uses

$$(a1) \quad \text{CPHASE} = \frac{\sum w_j G_j \cos(\Phi_j - \theta_j) + w_j G_j \cos \Phi_j}{\sum_{\text{s.i.}+\text{s.s.}} w_j G_j D_1(G_j)},$$

where the first summation in the numerator extends over symmetry-restricted one-phase and two-phase s.s.'s (see Sections 2.2.5.9 and 2.2.5.10), and the second summation in the numerator extends over negative triplets estimated *via* the second representation formula [equation (2.2.5.13)] and over negative quartets. The value of CPHASE is expected to be close to unity for the correct solution.

(a2) $\alpha_{\mathbf{h}}$ for strong triplets and $E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$ contributions for PSIO triplets may be considered random variables: the agreements

between their actual and their expected distributions are considered as criteria for identifying the correct solution.

(a3) correlation among some FOMs is taken into account.

According to this scheme, each FOM (as well as the CFOM) is expected to be unity for the correct solution. Thus one or more figures are available which constitute a sort of criterion (on an absolute scale) concerning the correctness of the various solutions: FOMs (and CFOM) $\simeq 1$ probably denote correct solutions, CFOMs $\ll 1$ should indicate incorrect solutions.

Stage 8: Interpretation of E maps. This is carried out in up to four stages (Koch, 1974; Main & Hull, 1978; Declercq *et al.*, 1973):

- (a) peak search;
- (b) separation of peaks into potentially bonded clusters;
- (c) application of stereochemical criteria to identify possible molecular fragments;
- (d) comparison of the fragments with the expected molecular structure.

2.2.8. Other multisolution methods applied to small molecules

In very complex structures a large initial set of known phases seems to be a basic requirement for a structure to be determined. This aim can be achieved, for example, by introducing a large number of permutable phases into the initial set. However, the introduction of every new symbol implies a fourfold increase in computing time, which, even in fast computers, quickly leads to computing-time limitations. On the other hand, a relatively large starting set is not in itself enough to ensure a successful structure determination. This is the case, for example, when the triplet invariants used in the initial steps differ significantly from zero. New strategies have therefore been devised to solve more complex structures.

(1) Magic-integer methods

In the classical procedure described in Section 2.2.7, the unknown phases in the starting set are assigned all combinations of the values $\pm\pi/4$, $\pm 3\pi/4$. For n unknown phases in the starting set, 4^n sets of phases arise by quadrant permutation; this is a number that increases very rapidly with n . According to White & Woolfson (1975), phases can be represented for a sequence of n integers by the equations

$$\varphi_i = m_i x \pmod{2\pi}, \quad i = 1, \dots, n. \quad (2.2.8.1)$$

The set of equations can be regarded as the parametric equation of a straight line in n -dimensional phase space. The nature and size of errors connected with magic-integer representations have been investigated by Main (1977) who also gave a recipe for deriving magic-integer sequences which minimize the r.m.s. errors in the represented phases (see Table 2.2.8.1). To assign a phase value, the variable x in equation (2.2.8.1) is given a series of values at equal intervals in the range $0 < x < 2\pi$. The enantiomorph is defined by exploring only the appropriate half of the n -dimensional space.

A different way of using the magic-integer method (Declercq *et al.*, 1975) is the *primary-secondary P-S method* which may be described schematically in the following way:

- (a) Origin- and enantiomorph-fixing phases are chosen and some one-phase s.s.'s are estimated.
- (b) Nine phases [this is only an example: very long magic-integer sequences may be used to represent primary phases (Hull *et al.*, 1981; Debaerdemaeker & Woolfson, 1983)] are represented with the approximated relationships:

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$$\begin{cases} \varphi_{i_1} = 3x \\ \varphi_{i_2} = 4x \\ \varphi_{i_3} = 5x \end{cases} \quad \begin{cases} \varphi_{j_1} = 3y \\ \varphi_{j_2} = 4y \\ \varphi_{j_3} = 5y \end{cases} \quad \begin{cases} \varphi_{p_1} = 3z \\ \varphi_{p_2} = 4z \\ \varphi_{p_3} = 5z. \end{cases}$$

Phases in (a) and (b) constitute the *primary set*.

(c) The phases in the *secondary set* are those defined through $\sum_2$ relationships involving pairs of phases from the primary set: they, too, can be expressed in magic-integer form.

(d) All the triplets that link together the phases in the combined primary and secondary set are now found, other than triplets used to obtain secondary reflections from the primary ones. The general algebraic form of these triplets will be

$$m_1x + m_2y + m_3z + b \equiv 0 \pmod{1},$$

where b is a phase constant which arises from symmetry translation. It may be expected that the 'best' value of the unknown x, y, z corresponds to a maximum of the function

$$\psi(x, y, z) = \sum |E_1 E_2 E_3| \cos 2\pi(m_1x + m_2y + m_3z + b),$$

with $0 \leq x, y, z < 1$. It should be noticed that ψ is a Fourier summation which can easily be evaluated. In fact, ψ is essentially a figure of merit for a large number of phases evaluated in terms of a small number of magic-integer variables and gives a measure of the internal consistency of $\sum_2$ relationships. The ψ map generally presents several peaks and therefore can provide several solutions for the variables.

(2) The random-start method

These are procedures which try to solve crystal structures by starting from random initial phases (Baggio *et al.*, 1978; Yao, 1981). They may be so described:

(a) A number of reflections (say $\text{NUM} \sim 100$ or larger) at the bottom of the CONVERGE map are selected. These, and the relationships which link them, form the system for which trial phases will be found.

(b) A pseudo-random number generator is used to generate M sets of NUM random phases. Each of the M sets is refined and extended by the tangent formula or similar methods.

(3) Accurate calculation of s.i.'s and s.s.'s with 1, 2, 3, 4, . . . , n phases

Having a large set of good phase relationships allows one to overcome difficulties in the early stages and in the refinement process of the phasing procedure. Accurate estimates of s.i.'s and s.s.'s may be achieved by the application of techniques such as the

representation method or the neighbourhood principle (Hauptman, 1975; Giacovazzo, 1977a, 1980b). So far, second-representation formulae are available for triplets and one-phase seminvariants; in particular, reliably estimated negative triplets can be recognized, which is of great help in the phasing process (Cascarano, Giacovazzo, Camalli *et al.*, 1984). Estimation of higher-order s.s.'s with upper representations or upper neighbourhoods is rather difficult, both because the procedures are time consuming and because the efficiency of the present joint probability distribution techniques deteriorates with complexity. However, further progress can be expected in the field.

(4) Modified tangent formulae and least-squares determination and refinement of phases

The problem of deriving the individual phase angles from triplet relationships is greatly overdetermined: indeed the number of triplets, in fact, greatly exceeds the number of phases so that any φ_h may be determined by a least-squares approach (Hauptman *et al.*, 1969). The function to be minimized may be

$$M = \frac{\sum_k w_k [\cos(\varphi_h - \varphi_k - \varphi_{h-k}) - C_k]^2}{\sum w_k},$$

where C_k is the estimate of the cosine obtained by probabilistic or other methods.

Effective least-squares procedures based on linear equations (Debaerdemaeker & Woolfson, 1983; Woolfson, 1977) can also be used. A triplet relationship is usually represented by

$$(\varphi_p \pm \varphi_q \pm \varphi_r + b) \approx 0 \pmod{2\pi}, \quad (2.2.8.2)$$

where b is a factor arising from translational symmetry. If (2.2.8.2) is expressed in cycles and suitably weighted, then it may be written as

$$w(\varphi_p \pm \varphi_q \pm \varphi_r + b) = wn,$$

where n is some integer. If the integers were known then the equation would appear (in matrix notation) as

$$A\Phi = C, \quad (2.2.8.3)$$

giving the least-squares solution

$$\Phi = (A^T A)^{-1} A^T C. \quad (2.2.8.4)$$

When approximate phases are available, the nearest integers may be found and equations (2.2.8.3) and (2.2.8.4) constitute the basis for further refinement.

Modified tangent procedures are also used, such as (Sint & Schenk, 1975; Busetta, 1976)

$$\tan \varphi_h \simeq \frac{\sum_j G_{h, k_j} \sin(\varphi_{k_j} + \varphi_{h-k_j} - \Delta_j)}{\sum_j G_{h, k_j} \cos(\varphi_{k_j} + \varphi_{h-k_j} - \Delta_j)},$$

where Δ_j is an estimate for the triplet phase sum $(\varphi_h - \varphi_{k_j} - \varphi_{h-k_j})$.

(5) Techniques based on the positivity of Karle-Hauptman determinants

(The main formulae have been briefly described in Section 2.2.5.7.) The maximum determinant rule has been applied to solve small structures (de Rango, 1969; Vermin & de Graaff, 1978) *via* determinants of small order. It has, however, been found that their use (Taylor *et al.*, 1978) is not of sufficient power to justify the

Table 2.2.8.1. Magic-integer sequences for small numbers of phases (n) together with the number of sets produced and the root-mean-square error in the phases

n	Sequence								No. of sets	R.m.s. error ($^\circ$)
1	1								4	26
2	2	3							12	29
3	3	4	5						20	37
4	5	7	8	9					32	42
5	8	11	13	14	15				50	45
6	13	18	21	23	24	25			80	47
7	21	29	34	37	39	40	41		128	48
8	34	47	55	60	63	65	66	67	206	49

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larger amount of computing time required by the technique as compared to that required by the tangent formula.

(6) *Tangent techniques using simultaneously triplets, quartets, . . .*

The availability of a large number of phase relationships, in particular during the first stages of a direct procedure, makes the phasing process easier. However, quartets are sums of two triplets with a common reflection. If the phase of this reflection (and/or of the other cross terms) is known then the quartet probability formulae described in Section 2.2.5.5 cannot hold. Similar considerations may be made for quintet relationships. Thus triplet, quartet and quintet formulae described in the preceding paragraphs, if used without modifications, will certainly introduce systematic errors in the tangent refinement process.

A method which takes into account correlation between triplets and quartets has been described (Giacovazzo, 1980c) [see also Freer & Gilmore (1980) for a first application], according to which

$$\tan \varphi_h \simeq \frac{\sum_{\mathbf{k}} G \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}) - \sum_{\mathbf{k}, \mathbf{l}} G' \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{h}-\mathbf{k}-\mathbf{l}})}{\sum_{\mathbf{k}} G \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}}) - \sum_{\mathbf{k}, \mathbf{l}} G' \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{h}-\mathbf{k}-\mathbf{l}})},$$

where G' takes into account both the magnitudes of the cross terms of the quartet and the fact that their phases may be known.

(7) *Integration of Patterson techniques and direct methods (Egert & Sheldrick, 1985) [see also Egert (1983, and references therein)]*

A fragment of known geometry is oriented in the unit cell by real-space Patterson rotation search (see Chapter 2.3) and its position is found by application of a translation function (see Section 2.2.5.4 and Chapter 2.3) or by maximizing the weighted sum of the cosines of a small number of strong translation-sensitive triple phase invariants, starting from random positions. Suitable FOMs rank the most reliable solutions.

(8) *Maximum entropy methods*

A common starting point for all direct methods is a stochastic process according to which crystal structures are thought of as being generated by randomly placing atoms in the asymmetric unit of the unit cell according to some *a priori* distribution. A non-uniform prior distribution of atoms $p(\mathbf{r})$ gives rise to a source of random atomic positions with entropy (Jaynes, 1957)

$$H(p) = - \int_V p(\mathbf{r}) \log p(\mathbf{r}) \, d\mathbf{r}.$$

The maximum value $H_{\max} = \log V$ is reached for a uniform prior $p(\mathbf{r}) = 1/V$.

The strength of the restrictions introduced by $p(\mathbf{r})$ is not measured by $H(p)$ but by $H(p) - H_{\max}$, given by

$$H(p) - H_{\max} = - \int_V p(\mathbf{r}) \log[p(\mathbf{r})/m(\mathbf{r})] \, d\mathbf{r},$$

where $m(\mathbf{r}) = 1/V$. Accordingly, if a prior prejudice $m(\mathbf{r})$ exists, which maximizes H , the revised relative entropy is

$$S(p) = - \int_V p(\mathbf{r}) \log[p(\mathbf{r})/m(\mathbf{r})] \, d\mathbf{r}.$$

The maximization problem was solved by Jaynes (1957). If $G_j(p)$ are linear constraint functionals defined by given constraint functions $C_j(\mathbf{r})$ and constraint values c_j , i.e.

$$G_j(p) = \int_V p(\mathbf{r}) C_j(\mathbf{r}) \, d\mathbf{r} = c_j,$$

the most unbiased probability density $p(\mathbf{r})$ under prior prejudice $m(\mathbf{r})$ is obtained by maximizing the entropy of $p(\mathbf{r})$ relative to $m(\mathbf{r})$. A standard variational technique suggests that the constrained maximization is equivalent to the unconstrained maximization of the functional

$$S(p) + \sum_j \lambda_j G_j(p),$$

where the λ_j 's are Lagrange multipliers whose values can be determined from the constraints.

Such a technique has been applied to the problem of finding good electron-density maps in different ways by various authors (Wilkins *et al.*, 1983; Bricogne, 1984; Navaza, 1985; Navaza *et al.*, 1983).

Maximum entropy methods are strictly connected with traditional direct methods: in particular it has been shown that:

(a) the maximum determinant rule (see Section 2.2.5.7) is strictly connected (Britten & Collins, 1982; Piro, 1983; Narayan & Nityananda, 1982; Bricogne, 1984);

(b) the construction of conditional probability distributions of structure factors amounts precisely to a reciprocal-space evaluation of the entropy functional $S(p)$ (Bricogne, 1984).

Maximum entropy methods are under strong development: important contributions can be expected in the near future even if a multipurpose robust program has not yet been written.

2.2.9. Some references to direct-methods packages

Some references for direct-methods packages are given below. Other useful packages using symbolic addition or multisolution procedures do exist but are not well documented.

CRUNCH: Gelder, R. de, de Graaff, R. A. G. & Schenk, H. (1993). *Automatic determination of crystal structures using Karle-Hauptman matrices*. *Acta Cryst.* **A49**, 287–293.

DIRDIF: Beurskens, P. T., Beurskens G., de Gelder, R., Garcia-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1999). *The DIRDIF-99 program system*. Crystallography Laboratory, University of Nijmegen, The Netherlands.

MITHRIL: Gilmore, C. J. (1984). *MITHRIL. An integrated direct-methods computer program*. *J. Appl. Cryst.* **17**, 42–46.

MULTAN88: Main, P., Fiske, S. J., Germain, G., Hull, S. E., Declercq, J.-P., Lessinger, L. & Woolfson, M. M. (1999). *Crystallographic software: teXsan for Windows*. <http://www.msc.com/brochures/teXsan/wintex.html>.

PATSEE: Egert, E. & Sheldrick, G. M. (1985). *Search for a fragment of known geometry by integrated Patterson and direct methods*. *Acta Cryst.* **A41**, 262–268.

SAPI: Fan, H.-F. (1999). *Crystallographic software: teXsan for Windows*. <http://www.msc.com/brochures/teXsan/wintex.html>.

SnB: Weeks, C. M. & Miller, R. (1999). *The design and implementation of SnB version 2.0*. *J. Appl. Cryst.* **32**, 120–124.

SHELX97: Sheldrick, G. M. (2000a). *The SHELX home page*. <http://shelx.uni-ac.gwdg.de/SHELX/>.

SHELXS: Sheldrick, G. M. (2000b). *SHELX*. <http://www.ucg.ie/cryst/shelx.htm>.

SIR97: Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *SIR97: a new tool for crystal structure determination and refinement*. *J. Appl. Cryst.* **32**, 115–119.

XTAL3.6.1: Hall, S. R., du Boulay, D. J. & Olthof-Hazekamp, R. (1999). *Xtal3.6 crystallographic software*. <http://www.crystal.uwa.edu.au/Crystal/xtal>.

2.2. DIRECT METHODS

2.2.10. Direct methods in macromolecular crystallography

2.2.10.1. Introduction

Protein structures cannot be solved *ab initio* by traditional direct methods (*i.e.*, by application of the tangent formula alone). Accordingly, the first applications were focused on two tasks:

- (a) improvement of the accuracy of the available phases (refinement process);
- (b) extension of phases from lower to higher resolution (phase-extension process).

The application of standard tangent techniques to (a) and (b) has not been found to be very satisfactory (Coulter & Dewar, 1971; Hendrickson *et al.*, 1973; Weinzierl *et al.*, 1969). Tangent methods, in fact, require atomicity and non-negativity of the electron density. Both these properties are not satisfied if data do not extend to atomic resolution ($d > 2 \text{ \AA}$). Because of series termination and other errors the electron-density map at $d > 2 \text{ \AA}$ presents large negative regions which will appear as false peaks in the squared structure. However, tangent methods use only a part of the information given by the Sayre equation (2.2.6.5). In fact, (2.2.6.5) express two equations relating the radial and angular parts of the two sides, so obtaining a large degree of overdetermination of the phases. To achieve this Sayre (1972) [see also Sayre & Toupin (1975)] suggested minimizing (2.2.10.1) by least squares as a function of the phases:

$$\sum_{\mathbf{h}} \left| a_{\mathbf{h}} F_{\mathbf{h}} - \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h}-\mathbf{k}} \right|^2. \quad (2.2.10.1)$$

Even if tests on rubredoxin (extensions of phases from 2.5 to 1.5 $\text{\AA}$ resolution) and insulin (Cutfield *et al.*, 1975) (from 1.9 to 1.5 $\text{\AA}$ resolution) were successful, the limitations of the method are its high cost and, especially, the higher efficiency of the least-squares method. Equivalent considerations hold for the application of determinantal methods to proteins [see Podjarny *et al.* (1981); de Rango *et al.* (1985) and literature cited therein].

A question now arises: why is the tangent formula unable to solve protein structures? Fan *et al.* (1991) considered the question from a first-principle approach and concluded that:

- (1) the triplet phase probability distribution is very flat for proteins (N is very large) and close to the uniform distribution;
- (2) low-resolution data create additional problems for direct methods since the number of available phase relationships per reflection is small.

Sheldrick (1990) suggested that direct methods are not expected to succeed if fewer than half of the reflections in the range 1.1–1.2 $\text{\AA}$ are observed with $|F| > 4\sigma(|F|)$ (a condition seldom satisfied by protein data).

The most complete analysis of the problem has been made by Giacovazzo, Guagliardi *et al.* (1994). They observed that the expected value of α (see Section 2.2.7) suggested by the tangent formula for proteins is comparable with the variance of the α parameter. In other words, for proteins the signal determining the phase is comparable with the noise, and therefore the phase indication is expected to be unreliable.

2.2.10.2. *Ab initio* direct phasing of proteins

Section 2.2.10.1 suggests that the mere use of the tangent formula or the Sayre equation cannot solve *ab initio* protein structures of usual size. However, even in an *ab initio* situation, there is a source of supplementary information which may be used. Good examples are the 'peaklist optimization' procedure (Sheldrick & Gould, 1995) and the SIR97 procedure (Altomare *et al.*, 1999) for refining and completing the trial structure offered by the first E map.

In both cases there are reasons to suspect that the correct structure is sometimes extracted from a totally incorrect direct-methods solution. These results suggest that a direct-space procedure can provide some form of structural information complementary to that used in reciprocal space by the tangent or similar formulae. The combination of real- and reciprocal-space techniques could therefore enlarge the size of crystal structures solvable by direct methods. The first program to explicitly propose the combined use of direct and reciprocal space was *Shake and Bake* (*SnB*), which inspired a second package, *half-bake* (*HB*). A third program, *SIR99*, uses a different algorithm.

The *SnB* method (DeTitta *et al.*, 1994; Weeks *et al.*, 1994; Hauptman, 1995) is the heir of the *cosine least-squares method* described in Section 2.2.8, point (4). The function

$$R(\Phi) = \frac{\sum_j G_j [\cos \Phi_j - D_1(G_j)]^2}{\sum_j G_j},$$

where Φ is the triplet phase, $G = 2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}|/(N)^{1/2}$ and $D_1(x) = I_1(x)/I_0(x)$.

$R(\Phi)$ is expected to have a global minimum, provided the number of phases involved is sufficiently large, when all the phases are equal to their true values for some choice of origin and enantiomorph. Thus the phasing problem reduces to that of finding the global minimum of $R(\Phi)$ (the *minimum principle*).

SnB comprises a *shake* step (phase refinement) and a *bake* step (electron-density modification), the second step aiming to impose phase constraints implicit in real space. Accordingly, the program requires two Fourier transforms per cycle, and numerous cycles. Thus it may be very time consuming and it is not competitive with other direct methods for the solution of the crystal structures of small molecules. However, it introduced into the field the tremendous usefulness of intensive computations for the direct solution of complex crystal structures.

Owing to Sheldrick (1997), *HB* does most of its work in direct space. Random atomic positions are generated, to which a modified *peaklist optimization* process is applied. A number of peaks are eliminated subject to the condition that $\sum |E_c|(|E_0|^2 - 1)$ remains as large as possible (only reflections with $|E_0| > |E_{\min}|$ are involved, where $|E_{\min}| \simeq 1.4$). The phases of a suitable subset of reflections are then used as input for a tangent expansion. Then an E map is calculated from which peaks are selected: these are submitted to the elimination procedure.

Typically 5–20 cycles of this internal loop are performed. Then a correlation coefficient (CC) between $|E_0|$ and $|E_c|$ is calculated for all the data. If the CC is good (*i.e.* larger than a given threshold), then a new loop is performed: a new E map is obtained, from which a list of peaks is selected for submission to the elimination procedure. The criterion now is the value of the CC, which is calculated for all the reflections. Typically two to five cycles of this external loop are performed.

The program works indefinitely, restarting from random atoms until interrupted. It may work either by applying the true space-group symmetry or after having expanded the data to $P1$.

The *SIR99* procedure (Burla *et al.*, 1999) may be divided into two distinct parts: the tangent section (*i.e.*, a double tangent process using triplet and quartet invariants) is followed by a real-space refinement procedure. As in *SIR97*, the reciprocal-space part is followed by the real-space refinement, but this time this last part is much more complex. It involves three different techniques: EDM (an electron-density modification process), the HAFR part (in which all the peaks are associated with the heaviest atomic species) and the DLSQ procedure (a least-squares Fourier refinement process). The atomicity is gradually introduced into the procedure. The entire process requires, for each trial, several cycles of EDM and HAFR:

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the real-space part is able to lead to the correct solution even when the tangent formula does not provide favourable phase values.

2.2.10.3. Integration of direct methods with isomorphous replacement techniques

The modulus of the isomorphous difference

$$\Delta F = |F_{PH}| - |F_P|$$

may be assumed at a first approximation as an estimate of the heavy-atom s.f. F_H . Normalization of $|\Delta F|$'s and application of the tangent formula may reveal the heavy-atom structure (Wilson, 1978).

The theoretical basis for integrating the techniques of direct methods and isomorphous replacement was introduced by Hauptman (1982a). According to his notation let us denote by f_j and g_j atomic scattering factors for the atom labelled j in a pair of isomorphous structures, and let E_h and G_h denote corresponding normalized structure factors. Then

$$E_h = |E_h| \exp(i\varphi_h) = \alpha_{20}^{-1/2} \sum_{j=1}^N f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j),$$

$$G_h = |G_h| \exp(i\psi_h) = \alpha_{02}^{-1/2} \sum_{j=1}^N g_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j),$$

where

$$\alpha_{mn} = \sum_{j=1}^N f_j^m g_j^n.$$

The conditional probability of the two-phase structure invariant $\Phi = \varphi_h - \psi_h$ given $|E_h|$ and $|G_h|$ is (Hauptman, 1982a)

$$P(\Phi | |E|, |G|) \simeq [2\pi I_0(Q)]^{-1} \exp(Q \cos \Phi),$$

where

$$Q = |EG| [2\alpha / (1 - \alpha^2)],$$

$$\alpha = \alpha_{11} / (\alpha_{20}^{1/2} \alpha_{02}^{1/2}).$$

Three-phase structure invariants were evaluated by considering that eight invariants exist for a given triple of indices $\mathbf{h}, \mathbf{k}, \mathbf{l}$ ($\mathbf{h} + \mathbf{k} + \mathbf{l} = 0$):

$$\begin{array}{ll} \Phi_1 = \varphi_h + \varphi_k + \varphi_l & \Phi_2 = \varphi_h + \varphi_k + \psi_l \\ \Phi_3 = \varphi_h + \psi_k + \varphi_l & \Phi_4 = \psi_h + \varphi_k + \varphi_l \\ \Phi_5 = \varphi_h + \psi_k + \psi_l & \Phi_6 = \psi_h + \varphi_k + \psi_l \\ \Phi_7 = \psi_h + \psi_k + \varphi_l & \Phi_8 = \psi_h + \psi_k + \psi_l. \end{array}$$

So, for the estimation of any Φ_j , the joint probability distribution

$$P(E_h, E_k, E_l, G_h, G_k, G_l)$$

has to be studied, from which eight conditional probability densities can be obtained:

$$P(\Phi_i | |E_h|, |E_k|, |E_l|, |G_h|, |G_k|, |G_l|)$$

$$\simeq [2\pi I_0(Q_j)]^{-1} \exp[Q_j \cos \Phi_j]$$

for $j = 1, \dots, 8$.

The analytical expressions of Q_j are too intricate and are not given here (the reader is referred to the original paper). We only say that Q_j may be positive or negative, so that reliable triplet phase estimates near 0 or near π are possible: the larger $|Q_j|$, the more reliable the phase estimate.

A useful interpretation of the formulae in terms of experimental parameters was suggested by Fortier *et al.* (1984): according to

them, distributions do not depend, as in the case of the traditional three-phase invariants, on the total number of atoms per unit cell but rather on the scattering difference between the native protein and the derivative (that is, on the scattering of the heavy atoms in the derivative).

Hauptman's formulae were generalized by Giacovazzo *et al.* (1988): the new expressions were able to take into account the resolution effects on distribution parameters. The formulae are completely general and include as special cases native protein and heavy-atom isomorphous derivatives as well as X-ray and neutron diffraction data. Their complicated algebraic forms are easily reduced to a simple expression in the case of a native protein heavy-atom derivative: in particular, the reliability parameter for Φ_1 is

$$Q_1 = 2[\sigma_3/\sigma_2^{3/2}]_P |E_h E_k E_l| + 2[\sigma_3/\sigma_2^{3/2}]_H \Delta_h \Delta_k \Delta_l, \quad (2.2.10.2)$$

where indices P and H warn that parameters have to be calculated over protein atoms and over heavy atoms, respectively, and

$$\Delta = (F_{PH} - F_P) / (\sum f_j^2)^{1/2}.$$

Δ is a pseudo-normalized difference (with respect to the heavy-atom structure) between moduli of structure factors.

Equation (2.2.10.2) may be compared with Karle's (1983) qualitative rule: if the sign of

$$[(F_h)_{PH} - (F_h)_P][(F_k)_{PH} - (F_k)_P][(F_l)_{PH} - (F_l)_P]$$

is plus then the value of Φ_1 is estimated to be zero; if its sign is minus then the expected value of Φ_1 is close to π . In practice Karle's rule agrees with (2.2.10.2) only if the Cochran-type term in (2.2.10.2) may be neglected. Furthermore, (2.2.10.2) shows that large reliability values do not depend on the triple product of structure-factor differences, but on the triple product of pseudo-normalized differences. A series of papers (Giacovazzo, Siliqi & Ralph, 1994; Giacovazzo, Siliqi & Spagna, 1994; Giacovazzo, Siliqi & Platas, 1995; Giacovazzo, Siliqi & Zanotti, 1995; Giacovazzo *et al.*, 1996) shows how equation (2.2.10.2) may be implemented in a direct procedure which proved to be able to estimate the protein phases correctly without any preliminary information on the heavy-atom substructure.

Combination of direct methods with the two-derivative case is also possible (Fortier *et al.*, 1984) and leads to more accurate estimates of triplet invariants provided experimental data are of sufficient accuracy.

2.2.10.4. Integration of anomalous-dispersion techniques with direct methods

If the frequency of the radiation is close to an absorption edge of an atom, then that atom will scatter the X-rays anomalously (see Chapter 2.4) according to $f = f' + if''$. This results in the breakdown of Friedel's law. It was soon realized that the Bijvoet difference could also be used in the determination of phases (Peerdeman & Bijvoet, 1956; Ramachandran & Raman, 1956; Okaya & Pepinsky, 1956). Since then, a great deal of work has been done both from algebraic (see Chapter 2.4) and from probabilistic points of view. In this section we are only interested in the second.

We will mention the following different cases:

- (1) The OAS (one-wavelength anomalous scattering) case, also called SAS (single-wavelength anomalous scattering).
- (2) The SIRAS (single isomorphous replacement combined with anomalous scattering) case. Typically, native protein and heavy-atom-derivative data are simultaneously available, with heavy atoms as anomalous scatterers.
- (3) The MIRAS case, which generalizes the SIRAS case.
- (4) The MAD case, a multiple-wavelength technique.

2.2. DIRECT METHODS

2.2.10.4.1. One-wavelength techniques

Probability distributions of diffraction intensities and of selected functions of diffraction intensities for dispersive structures have been given by various authors [Parthasarathy & Srinivasan (1964), see also Srinivasan & Parthasarathy (1976) and relevant literature cited therein]. We describe here some probabilistic formulae for estimating invariants of low order.

(a) *Estimation of two-phase structure invariants.* The conditional probability distribution of $\Phi = \varphi_{\mathbf{h}} + \varphi_{-\mathbf{h}}$ given $R_{\mathbf{h}}$ and $G_{\mathbf{h}}$ (normalized moduli of $F_{\mathbf{h}}$ and $F_{-\mathbf{h}}$, respectively) (Hauptman, 1982b; Giacovazzo, 1983b) is

$$P(\Phi|R_{\mathbf{h}}, G_{\mathbf{h}}) \simeq [2\pi I_0(Q)]^{-1} \exp[Q \cos(\Phi - q)], \quad (2.2.10.3)$$

where

$$\begin{aligned} Q &= \frac{2R_{\mathbf{h}}G_{\mathbf{h}}}{\sqrt{c}} [c_1^2 + c_2^2]^{1/2}, \\ \cos q &= \frac{c_1}{[c_1^2 + c_2^2]^{1/2}}, \quad \sin q = \frac{c_2}{[c_1^2 + c_2^2]^{1/2}}, \\ c_1 &= \sum_{j=1}^N (f_j'^2 - f_j''^2) / \sum, \\ c_2 &= 2 \sum_{j=1}^N f_j' f_j'' / \sum, \\ c &= [1 - (c_1^2 + c_2^2)]^2, \\ \sum &= \sum_{j=1}^N (f_j'^2 + f_j''^2). \end{aligned}$$

q is the most probable value of Φ : a large value of the parameter Q suggests that the phase relation $\Phi = q$ is reliable. Large values of Q are often available in practice: q , however, may be considered an estimate of $|\Phi|$ rather than of Φ because the enantiomorph is not fixed in (2.2.10.3). A formula for the estimation of Φ in centrosymmetric structures has recently been provided by Giacovazzo (1987).

If the positions of the p anomalous scatterers are known *a priori* [let $F_{p\mathbf{h}} = |F_{p\mathbf{h}}| \exp(i\varphi_{p\mathbf{h}})$ be the structure factor of the partial structure], then an estimate of $\Phi' = \varphi_{\mathbf{h}} - \varphi_{p\mathbf{h}}$ is given (Casarano & Giacovazzo, 1985) by

$$P(\Phi'|R_{\mathbf{h}}, R_{p\mathbf{h}}) \simeq [2\pi I_0(Q')]^{-1} \exp[Q' \cos \Phi'], \quad (2.2.10.4)$$

where

$$Q' = 2R^+ R_p^+ / \left(1 - \sum_p / \sum\right), \quad \sum_p = \sum_{j=1}^p (f_j'^2 + f_j''^2).$$

(2.2.10.4) may be considered the generalization of Sim's distribution (2.2.5.17) to dispersive structures.

(b) *Estimation of triplet invariants.* Kroon *et al.* (1977) first incorporated anomalous diffraction in order to estimate triplet invariants. Their work was based on an analysis of the complex double Patterson function. Subsequent probabilistic considerations (Heinermann *et al.*, 1978) confirmed their results, which can be so expressed:

$$\sin \bar{\Phi} = \frac{|\tau|^2 - |\bar{\tau}|^2}{4\tau''[\frac{1}{2}(|\tau|^2 + |\bar{\tau}|^2) - |\tau''|^2]^{1/2}}, \quad (2.2.10.5)$$

where $(\mathbf{h} + \mathbf{k} + \mathbf{l} = 0)$

$$\tau = E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{l}} = R_{\mathbf{h}} R_{\mathbf{k}} R_{\mathbf{l}} \exp(i\Phi_{\mathbf{h}, \mathbf{k}}),$$

$$\bar{\tau} = E_{-\mathbf{h}} E_{-\mathbf{k}} E_{-\mathbf{l}} = G_{\mathbf{h}} G_{\mathbf{k}} G_{\mathbf{l}} \exp(i\Phi_{\bar{\mathbf{h}}, \bar{\mathbf{k}}}),$$

$$\bar{\Phi} = \frac{1}{2}(\Phi_{\mathbf{h}, \mathbf{k}} - \Phi_{\bar{\mathbf{h}}, \bar{\mathbf{k}}}),$$

and τ'' is the contribution of the imaginary part of τ , which may be approximated in favourable conditions by

$$\begin{aligned} \tau'' &= 2f''[f_{\mathbf{h}}' f_{\mathbf{k}}' + f_{\mathbf{h}}' f_{\mathbf{l}}' + f_{\mathbf{k}}' f_{\mathbf{l}}'] \\ &\quad \times [1 + S(R_{\mathbf{h}}^2 + R_{\mathbf{k}}^2 + R_{\mathbf{l}}^2 - 3)], \end{aligned}$$

where S is a suitable scale factor.

Equation (2.2.10.5) gives two possible values for $\bar{\Phi}$ (Φ and $\pi - \Phi$). Only if $R_{\mathbf{h}} R_{\mathbf{k}} R_{\bar{\mathbf{h}} + \bar{\mathbf{k}}}$ is large enough may this phase ambiguity be resolved by choosing the angle nearest to zero.

The evaluation of triplet phases by means of anomalous dispersion has been further pursued by Hauptman (1982b) and Giacovazzo (1983b). Owing to the breakdown of Friedel's law there are eight distinct triplet invariants which can contemporaneously be exploited:

$$\begin{aligned} \Phi_1 &= \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}}, & \Phi_2 &= -\varphi_{-\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} \\ \Phi_3 &= \varphi_{\mathbf{h}} - \varphi_{-\mathbf{k}} + \varphi_{\mathbf{l}}, & \Phi_4 &= \varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} - \varphi_{-\mathbf{l}} \\ \Phi_5 &= \varphi_{-\mathbf{h}} + \varphi_{-\mathbf{k}} + \varphi_{-\mathbf{l}}, & \Phi_6 &= -\varphi_{\mathbf{h}} + \varphi_{-\mathbf{k}} + \varphi_{-\mathbf{l}} \\ \Phi_7 &= \varphi_{-\mathbf{h}} - \varphi_{\mathbf{k}} + \varphi_{-\mathbf{l}}, & \Phi_8 &= \varphi_{-\mathbf{h}} + \varphi_{-\mathbf{k}} - \varphi_{\mathbf{l}}. \end{aligned}$$

The conditional probability distribution for each of the eight triplet invariants, given $R_{\mathbf{h}}, R_{\mathbf{k}}, R_{\mathbf{l}}, G_{\mathbf{h}}, G_{\mathbf{k}}, G_{\mathbf{l}}$, is

$$P_j(\Phi_j) \simeq \frac{1}{L_j} \exp[A_j \cos(\Phi_j - \omega_j)].$$

The definitions of A_j, L_j and ω_j are rather extensive and so the reader is referred to the published papers. A_j and L_j are positive values, so ω_j is the expected value of Φ_j . It may lie anywhere between 0 and 2π .

An algebraic analysis of triplet phase invariants coupled with probabilistic considerations has been carried out by Karle (1984, 1985). The rules permit the qualitative selection of triple phase invariants that have values close to $\pi/2, -\pi/2, 0$, and other values in the range from $-\pi$ to π .

Let us now describe some practical aspects of the integration of direct methods with OAS techniques.

Anomalous difference structure factors

$$\Delta_{\text{iso}} = |F^+| - |F^-|$$

can be used for locating the positions of the anomalous scatterers (Mukherjee *et al.*, 1989). Tests prove that accuracy in the difference magnitudes is critical for the success of the phasing process.

Suppose now that the positions of the heavy atoms have been found. How do we estimate the phase values for the protein? The phase ambiguity strictly connected with OAS techniques can be overcome by different methods: we quote the Qs method by Hao & Woolfson (1989), the Wilson distribution method and the MPS method by Ralph & Woolfson (1991), and the Bijvoet–Ramachandran–Raman method by Peerdeman & Bijvoet (1956), Raman (1959) and Moncrief & Lipscomb (1966). More recently, a probabilistic method by Fan & Gu (1985) gained additional insight into the problem.

2.2.10.4.2. The SIRAS, MIRAS and MAD cases

Isomorphous replacement and anomalous scattering are discussed in Chapter 2.4 and in ITF (2001). We observe here only that the SIRAS case can lead algebraically to unambiguous phase determination provided the experimental data are sufficiently good.

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Thus, any probabilistic treatment must take into consideration errors in the measurements.

In the MIRAS and MAD cases the system is overconditioned: again any probabilistic treatment must consider errors in the measurements, but now overconditioning allows the reduction of the perverse effects of the experimental errors and (in MIRAS) of the lack of isomorphism.

A particular application of extreme relevance concerns the location of anomalous scatterers when selenomethionine-substituted proteins and MAD data are available (Hendrickson & Ogata, 1997; Smith, 1998). In this case, many selenium sites should be identified and usual Patterson-interpretation methods can be expected to fail. The successes of *SnB* and *HB* prove the essential role of direct methods in this important area.

2.3. Patterson and molecular-replacement techniques

BY M. G. ROSSMANN AND E. ARNOLD

2.3.1. Introduction

2.3.1.1. Background

Historically, the Patterson has been used in a variety of ways to effect the solutions of crystal structures. While some simple structures (Ketelaar & de Vries, 1939; Hughes, 1940; Speakman, 1949; Shoemaker *et al.*, 1950) were solved by direct analysis of Patterson syntheses, alternative methods have largely superseded this procedure. An early innovation was the heavy-atom method which depends on the location of a small number of relatively strong scatterers (Harker, 1936). Image-seeking methods and Patterson superposition techniques were first contemplated in the late 1930s (Wrinch, 1939) and applied sometime later (Beevers & Robertson, 1950; Clastre & Gay, 1950; Garrido, 1950*a*; Buerger, 1959). This experience provided the encouragement for computerized vector-search methods to locate individual atoms automatically (Mighell & Jacobson, 1963; Kraut, 1961; Hamilton, 1965; Simpson *et al.*, 1965) or to position known molecular fragments in unknown crystal structures (Nordman & Nakatsu, 1963; Huber, 1965). The Patterson function has been used extensively in conjunction with the isomorphous replacement method (Rossmann, 1960; Blow, 1958) or anomalous dispersion (Rossmann, 1961*a*) to determine the position of heavy-atom substitution. Pattersons have been used to detect the presence and relative orientation of multiple copies of a given chemical motif in the crystallographic asymmetric unit in the same or different crystals (Rossmann & Blow, 1962). Finally, the orientation and placement of known molecular structures ('molecular replacement') into unknown crystal structures can be accomplished *via* Patterson techniques.

The function, introduced by Patterson in 1934 (Patterson, 1934*a,b*), is a convolution of electron density with itself and may be defined as

$$P(\mathbf{u}) = \int_V \rho(\mathbf{x}) \cdot \rho(\mathbf{u} + \mathbf{x}) \, d\mathbf{x}, \quad (2.3.1.1)$$

where $P(\mathbf{u})$ is the 'Patterson' function at $\mathbf{u}$, $\rho(\mathbf{x})$ is the crystal's periodic electron density and V is the volume of the unit cell. The Patterson function, or F^2 series, can be calculated directly from the experimentally derived X-ray intensities as

$$P(\mathbf{u}) = \frac{2}{V^2} \sum_{\mathbf{h}}^{\text{hemisphere}} |\mathbf{F}_{\mathbf{h}}|^2 \cos 2\pi \mathbf{h} \cdot \mathbf{u}. \quad (2.3.1.2)$$

The derivation of (2.3.1.2) from (2.3.1.1) can be found in this volume (see Section 1.3.4.2.1.6) along with a discussion of the physical significance and symmetry of the Patterson function, although the principal properties will be restated here.

The Patterson can be considered to be a vector map of all the pairwise interactions between the atoms in a unit cell. The vectors in a Patterson correspond to vectors in the real (direct) crystal cell but translated to the Patterson origin. Their weights are proportional to the product of densities at the tips of the vectors in the real cell. The Patterson unit cell has the same size as the real crystal cell. The symmetry of the Patterson comprises the Laue point group of the crystal cell plus any additional lattice symmetry due to Bravais centring. The reduction of the real space group to the Laue symmetry is produced by the translation of all vectors to the Patterson origin and the introduction of a centre of symmetry. The latter is a consequence of the relationship between the vectors $\mathbf{AB}$ and $\mathbf{BA}$. The Patterson symmetries for all 230 space groups are tabulated in *IT A* (1983).

An analysis of Patterson peaks can be obtained by considering N atoms with form factors f_i in the unit cell. Then

$$\mathbf{F}_{\mathbf{h}} = \sum_{i=1}^N f_i \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_i).$$

Using Friedel's law,

$$\begin{aligned} |\mathbf{F}_{\mathbf{h}}|^2 &= \mathbf{F}_{\mathbf{h}} \cdot \mathbf{F}_{\mathbf{h}}^* \\ &= \left[\sum_{i=1}^N f_i \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_i) \right] \left[\sum_{j=1}^N f_j \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j) \right], \end{aligned}$$

which can be decomposed to

$$|\mathbf{F}_{\mathbf{h}}|^2 = \sum_{i=1}^N f_i^2 + \sum_{i \neq j}^N \sum_{j=1}^N f_i f_j \exp[2\pi i \mathbf{h} \cdot (\mathbf{x}_i - \mathbf{x}_j)]. \quad (2.3.1.3)$$

On substituting (2.3.1.3) in (2.3.1.2), we see that the Patterson consists of the sum of N^2 total interactions of which N are of weight f_i^2 at the origin and $N(N-1)$ are of weight $f_i f_j$ at $\mathbf{x}_i - \mathbf{x}_j$.

The weight of a peak in a real cell is given by

$$w_i = \int_U \rho_i(\mathbf{x}) \, d\mathbf{x} = Z_i \text{ (the atomic number),}$$

where U is the volume of the atom i . By analogy, the weight of a peak in a Patterson (form factor $f_i f_j$) will be given by

$$w_{ij} = \int_U P_{ij}(\mathbf{u}) \, d\mathbf{u} = Z_i Z_j.$$

Although the maximum height of a peak will depend on the spread of the peak, it is reasonable to assume that heights of peaks in a Patterson are proportional to the products of the atomic numbers of the interacting atoms.

There are a total of N^2 interactions in a Patterson due to N atoms in the crystal cell. These can be represented as an $N \times N$ square matrix whose elements $\mathbf{u}_{ij}$, w_{ij} indicate the position and weight of the peak produced between atoms i and j (Table 2.3.1.1). The N vectors corresponding to the diagonal of this matrix are located at the Patterson origin and arise from the convolution of each atom with itself. This leaves $N(N-1)$ vectors whose locations depend on the relative positions of all of the atoms in the crystal cell and whose weights depend on the atom types related by the vector. Complete specification of the unique non-origin Patterson vectors requires description of only the $N(N-1)/2$ elements in either the upper or the lower triangle of this matrix, since the two sets of vectors represented by the two triangles are related by a centre of symmetry [$\mathbf{u}_{ij} \equiv \mathbf{x}_i - \mathbf{x}_j = -\mathbf{u}_{ji} \equiv -(\mathbf{x}_j - \mathbf{x}_i)$]. Patterson vector positions are usually represented as $\langle uvw \rangle$, where u , v and w are expressed as fractions of the Patterson cell axes.

2.3.1.2. Limits to the number of resolved vectors

If we assume a constant number of atoms per unit volume, the number of atoms N in a unit cell increases in direct proportion with the volume of the unit cell. Since the number of non-origin peaks in the Patterson function is $N(N-1)$ and the Patterson cell is the same size as the real cell, the problem of overlapping peaks in the Patterson function becomes severe as N increases. To make matters worse, the breadth of a Patterson peak is roughly equal to the sum of the breadth of the original atoms. The effective width of a Patterson peak will also increase with increasing thermal motion, although this effect can be artificially reduced by sharpening techniques. Naturally, a loss of attainable resolution at high scattering angles

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.3.1.1. *Matrix representation of Patterson peaks*

The $N \times N$ matrix represents the position $\mathbf{u}_{ij}$ and weights w_{ij} of atomic interactions in a Patterson arising from N atoms at $\mathbf{x}_i$ and weight w_i in the real cell.

	$\mathbf{x}_1, w_1$	$\mathbf{x}_2, w_2$	$\dots$	$\mathbf{x}_N, w_N$
$\mathbf{x}_1, w_1$	$\mathbf{u}_{11} = \mathbf{x}_1 - \mathbf{x}_1,$ $w_{11} = w_1^2$	$\mathbf{u}_{12} = \mathbf{x}_1 - \mathbf{x}_2,$ $w_{12} = w_1 w_2$	$\dots$	$\mathbf{u}_{1N} = \mathbf{x}_1 - \mathbf{x}_N,$ $w_{1N} = w_1 w_N$
$\mathbf{x}_2, w_2$	$\mathbf{x}_2 - \mathbf{x}_1, w_2 w_1$	$0, w_2^2$	$\dots$	$\mathbf{x}_2 - \mathbf{x}_N, w_2 w_N$
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
$\mathbf{x}_N, w_N$	$\mathbf{x}_N - \mathbf{x}_1, w_N w_1$	$\mathbf{x}_N - \mathbf{x}_2, w_N w_2$	$\dots$	$0, w_N^2$

will affect the resolution of atomic peaks in the real cell as well as peaks in the Patterson cell. If U is the van der Waals volume per average atom, then the fraction of the cell occupied by atoms will be $f = NU/V$. Similarly, the fraction of the cell occupied by Patterson peaks will be $2UN(N-1)/V$ or $2f(N-1)$. With the reasonable assumption that $f \simeq 0.1$ for a typical organic crystal, then the cell can contain at most five atoms ($N \leq 5$) for there to be no overlap, other than by coincidence, of the peaks in the Patterson. As N increases there will occur a background of peaks on which are superimposed features related to systematic properties of the structure.

The contrast of selected Patterson peaks relative to the general background level can be enhanced by a variety of techniques. For instance, the presence of heavy atoms not only enhances the size of a relatively small number of peaks but ordinarily ensures a larger separation of the peaks due to the light-atom skeleton on which the heavy atoms are hung. That is, the factor f (above) is substantially reduced. Another example is the effect of systematic atomic arrangements (e.g. α -helices or aromatic rings) resulting in multiple peaks which stand out above the background. In the isomorphous replacement method, isomorphous difference Pattersons are utilized in which the contrast of the Patterson interactions between the heavy atoms is enhanced by removal of the predominant interactions which involve the rest of the structure.

2.3.1.3. *Modifications: origin removal, sharpening etc.*

A. L. Patterson, in his first in-depth exposition of his newly discovered F^2 series (Patterson, 1935), introduced the major modifications to the Patterson which are still in use today. He illustrated, with one-dimensional Fourier series, the techniques of removing the Patterson origin peak, sharpening the overall function and also removing peaks due to atoms in special positions. Each one of these modifications can improve the interpretability of Pattersons, especially those of simple structures. Whereas the recommended extent of such modifications is controversial (Buerger, 1966), most studies which utilize Patterson functions do incorporate some of these techniques [see, for example, Jacobson *et al.* (1961), Braun *et al.* (1969) and Nordman (1980a)]. Since Patterson's original work, other workers have suggested that the Patterson function itself might be modified; Fourier inversion of the modified Patterson then provides a new and perhaps more tractable set of structure factors (McLachlan & Harker, 1951; Simonov, 1965; Raman, 1966; Corfield & Rosenstein, 1966). Karle & Hauptman (1964) suggested that an improved set of structure factors could be obtained from an origin-removed Patterson modified such that it was everywhere non-negative and that Patterson density values less than a bonding distance from the origin were set to zero. Nixon (1978) was successful in solving a structure which had previously resisted solution by using a set of

structure factors which had been obtained from a Patterson in which the largest peaks had been attenuated.

The N origin peaks [see expression (2.3.1.3)] may be removed from the Patterson by using coefficients

$$|\mathbf{F}_{\mathbf{h}, \text{mod}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2 - \sum_{i=1}^N f_i^2.$$

A Patterson function using these modified coefficients will retain all interatomic vectors. However, the observed structure factors $\mathbf{F}_{\mathbf{h}}$ must first be placed on an absolute scale (Wilson, 1942) in order to match the scattering-factor term.

Analogous to origin removal, the vector interactions due to atoms in known positions can also be removed from the Patterson function. Patterson showed that non-origin Patterson peaks arising from known atoms 1 and 2 may be removed by using the expression

$$|\mathbf{F}_{\mathbf{h}, \text{mod}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2 - \sum_{i=1}^N f_i^2 t_i^2 - 2f_1 f_2 t_1 t_2 \cos 2\pi \mathbf{h} \cdot (\mathbf{x}_1 - \mathbf{x}_2),$$

where $\mathbf{x}_1$ and $\mathbf{x}_2$ are the positions of atoms 1 and 2 and t_1 and t_2 are their respective thermal correction factors. Using one-dimensional Fourier series, Patterson illustrated how interactions due to known atoms can obscure other information.

Patterson also introduced a means by which the peaks in a Patterson function may be artificially sharpened. He considered the effect of thermal motion on the broadening of electron-density peaks and consequently their Patterson peaks. He suggested that the F^2 coefficients could be corrected for thermal effects by simulating the atoms as point scatterers and proposed using a modified set of coefficients

$$|\mathbf{F}_{\mathbf{h}, \text{sharp}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2 / \bar{f}^2,$$

where $\bar{f}$, the average scattering factor per electron, is given by

$$\bar{f} = \sum_{i=1}^N f_i / \sum_{i=1}^N Z_i.$$

A common formulation for this type of sharpening expresses the atomic scattering factors at a given angle in terms of an overall isotropic thermal parameter B as

$$f(s) = f_0 \exp(-Bs^2).$$

The Patterson coefficients then become

$$\mathbf{F}_{\mathbf{h}, \text{sharp}} = \frac{Z_{\text{total}}}{\sum_{i=1}^N f(s)} \mathbf{F}_{\mathbf{h}}.$$

The normalized structure factors, E (see Chapter 2.2), which are used in crystallographic direct methods, are also a common source of sharpened Patterson coefficients ($E^2 - 1$). Although the centre positions and total contents of Patterson peaks are unaltered by sharpening, the resolution of individual peaks may be enhanced. The degree of sharpening can be controlled by adjusting the size of the assumed B factor; Lipson & Cochran (1966, pp. 165–170) analysed the effect of such a choice on Patterson peak shape.

All methods of sharpening Patterson coefficients aim at producing a point atomic representation of the unit cell. In this quest, the high-resolution terms are enhanced (Fig. 2.3.1.1). Unfortunately, this procedure must also produce a serious Fourier truncation error which will be seen as large ripples about each Patterson peak (Gibbs, 1898). Consequently, various techniques have been used (mostly unsuccessfully) in an attempt to balance the advantages of sharpening with the disadvantages of truncation errors.

Schomaker and Shoemaker [unpublished; see Lipson & Cochran (1966, p. 168)] used a function

2.3. PATTERSON AND MOLECULAR-REPLACEMENT TECHNIQUES

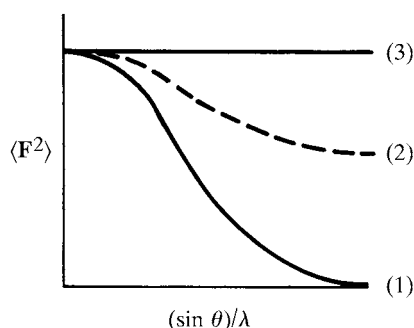


Fig. 2.3.1.1. Effect of 'sharpening' Patterson coefficients. (1) shows a mean distribution of $\langle F^2 \rangle$ values with resolution, $(\sin \theta)/\lambda$. The normal decline of this curve is due to increasing destructive interference between different portions within diffuse atoms at larger Bragg angles. (2) shows the distribution of 'sharpened' coefficients. (3) shows the theoretical distribution of $\langle F^2 \rangle$ produced by a point-atom structure. To represent such a structure with a Fourier series would require an infinite series in order to avoid large errors caused by truncation.

$$|F_{h, \text{sharp}}|^2 = \frac{|F_h|^2}{f^2} s^2 \exp \left[-\frac{\pi^2}{p} s^2 \right],$$

in which s is the length of the scattering vector, to produce a Patterson synthesis which is less sensitive to errors in the low-order terms. Jacobson *et al.* (1961) used a similar function,

$$|F_{h, \text{sharp}}|^2 = \frac{|F_h|^2}{f^2} (k + s^2) \exp \left[-\frac{\pi}{p} s^2 \right],$$

which they rationalize as the sum of a scaled exponentially sharpened Patterson and a gradient Patterson function (the value of k was empirically chosen as $\frac{2}{3}$). This approach was subsequently further developed and generalized by Wunderlich (1965).

2.3.1.4. Homometric structures and the uniqueness of structure solutions; enantiomorphic solutions

Interpretation of any Patterson requires some assumption, such as the existence of discrete atoms. A complete interpretation might also require an assumption of the number of atoms and may require other external information (*e.g.* bond lengths, bond angles, van der Waals separations, hydrogen bonding, positive density *etc.*). To what extent is the solution of a Patterson function unique? Clearly the greater is the supply of external information, the fewer will be the number of possible solutions. Other constraints on the significance of a Patterson include the error involved in measuring the observed coefficients and the resolution limit to which they have been observed. The larger the error, the larger the number of solutions. When the error on the amplitudes is infinite, it is only the other physical constraints, such as packing, which limit the structural solutions. Alternative solutions of the same Patterson are known as homometric structures.

During their investigation of the mineral bixbyite, Pauling & Shappell (1930) made the disturbing observation that there were two solutions to the structure, with different arrangements of atoms, which yielded the same set of calculated intensities. Specifically, atoms occupying equipoint set $24d$ in space group $I(2_1/a)\bar{3}$ can be placed at either $x, 0, \frac{1}{4}$ or $-x, 0, \frac{1}{4}$ without changing the calculated intensities. Yet the two structures were not chemically equivalent. These authors resolved the ambiguity by placing the oxygen atoms in question at positions which gave the most acceptable bonding distances with the rest of the structure.

Patterson interpreted the above ambiguity in terms of the F^2 series: the distance vector sets or Patterson functions of the two structures were the same since each yielded the same calculated intensities (Patterson, 1939). He defined such a pair of structures a homometric pair and called the degenerate vector set which they produced a homometric set. Patterson went on to investigate the likelihood of occurrence of homometric structures and, indeed, devoted a great deal of his time to this matter. He also developed algebraic formalisms for examining the occurrence of homometric pairs and multiplets in selected one-dimensional sets of points, such as cyclotomic sets, and also sets of points along a line (Patterson, 1944). Some simple homometric pairs are illustrated in Fig. 2.3.1.2.

Drawing heavily from Patterson's inquiries into the structural uniqueness allowed by the diffraction data, Hosemann, Bagchi and others have given formal definitions of the different types of homometric structures (Hosemann & Bagchi, 1954). They suggested a classification divided into pseudohomometric structures and homomorphs, and used an integral equation representing a convolution operation to express their examples of finite homometric structures. Other workers have chosen various means for describing homometric structures [Buerger (1959, pp. 41–50), Menzer (1949), Bullough (1961, 1964), Hoppe (1962)].

Since a Patterson function is centrosymmetric, the Pattersons of a crystal structure and of its mirror image are identical. Thus the enantiomeric ambiguity present in noncentrosymmetric crystal structures cannot be overcome by using the Patterson alone and represents a special case of homometric structures. Assignment of the correct enantiomorph in a crystal structure analysis is generally not possible unless a recognizable fragment of known chirality emerges (*e.g.* L-amino acids in proteins, D-ribose in nucleic acids, the known framework of steroids and other natural products, the right-handed twist of α -helices, the left-handed twist of successive strands in a β -sheet, the fold of a known protein subunit *etc.*) or anomalous-scattering information is available and can be used to resolve the ambiguity (Bijvoet *et al.*, 1951).

It is frequently necessary to select arbitrarily one enantiomorph over another in the early stages of a structure solution. Structure-factor phases calculated from a single heavy atom in space group $P1$, $P2$ or $P2_1$ (for instance) will be centrosymmetric and both enantiomorphs will be present in Fourier calculations based on these phases. In other space groups (*e.g.* $P2_12_12_1$), the selected heavy atom is likely to be near one of the planes containing the 2_1 axes and thus produce a weaker 'ghost' image of the opposite enantiomorph. The mixture of the two overlapped enantiomorphic solutions can cause interpretive difficulties. As the structure solution progresses, the 'ghosts' are exorcized owing to the dominance of the chosen enantiomorph in the phases.

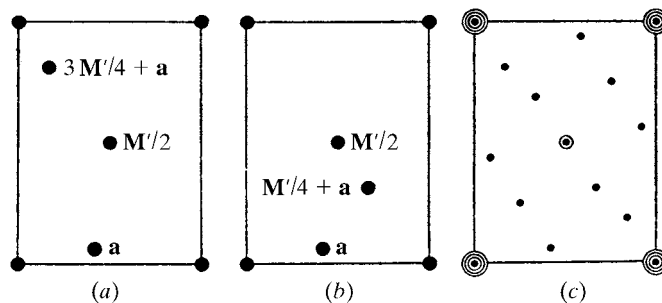


Fig. 2.3.1.2. (c) The point Patterson of the two homometric structures in (a) and (b). The latter are constructed by taking points at a and $\frac{1}{2}M'$, where M' is a cell diagonal, and adding a third point which is (a) at $\frac{3}{4}M' + a$ or (b) at $\frac{1}{4}M' + a$. [Reprinted with permission from Patterson (1944).]

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2.3.1.5. The Patterson synthesis of the second kind

Patterson also defined a second, less well known, function (Patterson, 1949) as

$$P_{\pm}(\mathbf{u}) = \int \rho(\mathbf{u} + \mathbf{x}) \cdot \rho(\mathbf{u} - \mathbf{x}) d\mathbf{x} \\ = \frac{2}{V^2} \sum_{\mathbf{h}}^{\text{hemisphere}} F_{\mathbf{h}}^2 \cos(2\pi 2\mathbf{h} \cdot \mathbf{u} - 2\alpha_{\mathbf{h}}).$$

This function can be computed directly only for centrosymmetric structures. It can be calculated for noncentrosymmetric structures when the phase angles are known or assumed. It will represent the degree to which the known or assumed structure has a centre of symmetry at $\mathbf{u}$. That is, the product of the density at $\mathbf{u} + \mathbf{x}$ and $\mathbf{u} - \mathbf{x}$ is large when integrated over all values $\mathbf{x}$ within the unit cell. Since atoms themselves have a centre of symmetry, the function will contain peaks at each atomic site roughly proportional in height to the square of the number of electrons in each atom plus peaks at the midpoint between atoms proportional in height to the product of the electrons in each atom. Although this function has not been found very useful in practice, it is useful for demonstrating the presence of weak enantiomorphic images in a given tentative structure determination.

2.3.2. Interpretation of Patterson maps

2.3.2.1. Simple solutions in the triclinic cell. Selection of the origin

A hypothetical one-dimensional centrosymmetric crystal structure containing an atom at x and at $-x$ and the corresponding Patterson is illustrated in Fig. 2.3.2.1. There are two different centres of symmetry which may be chosen as convenient origins. If the atoms are of equal weight, we expect Patterson vectors at positions $u = \pm 2x$ with weights equal to half the origin peak. There are two symmetry-related peaks, u_1 and u_2 (Fig. 2.3.2.1) in the Patterson. It is an arbitrary choice whether $u_1 = 2x$ or $u_2 = 2x$. This choice is equivalent to selecting the origin at the centre of symmetry I or II in the real structure (Fig. 2.3.2.1). Similarly in a three-dimensional $P\bar{1}$ cell, the Patterson will contain peaks at $\langle uvw \rangle$ which can be used to solve for the atom coordinates $\pm \langle 2x, 2y, 2z \rangle$. Solving for the same coordinates by starting from symmetric representations of the same vector will lead to alternate origin choices. For example, use of $\langle 1+u, 1+v, w \rangle$ will lead to translating the origin by $(+\frac{1}{2}, +\frac{1}{2}, 0)$ relative to the solution based on $\langle uvw \rangle$. There are eight distinct inversion centres in $P\bar{1}$, each one of which represents a valid origin choice. Although any choice of origin would be allowable, an inversion centre is

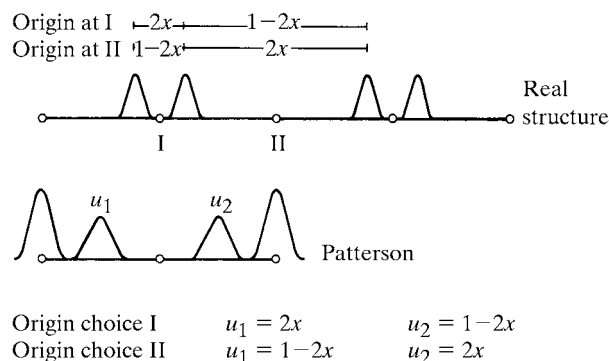


Fig. 2.3.2.1. Origin selection in the interpretation of a Patterson of a one-dimensional centrosymmetric structure.

convenient because then the structure factors are all real. Typically, one of the vector peaks closest to the Patterson origin is selected to start the solution, usually in the calculated asymmetric unit of the Patterson. Care must be exercised in selecting the same origin for all atomic positions by considering cross-vectors between atoms.

Examine, for example, the c -axis Patterson projection of a cuprous chloride azomethane complex ($\text{C}_2\text{H}_6\text{Cl}_2\text{Cu}_2\text{N}_2$) in $P\bar{1}$ as shown in Fig. 2.3.2.2. The largest Patterson peaks should correspond to vectors arising from Cu ($Z = 29$) and Cl ($Z = 17$) atoms. There will be copper atoms at $\mathbf{x}_{\text{Cu}}(x_{\text{Cu}}, y_{\text{Cu}})$ and $-\mathbf{x}_{\text{Cu}}(-x_{\text{Cu}}, -y_{\text{Cu}})$ as well as chlorine atoms at analogous positions. The interaction matrix is

	$\mathbf{x}_{\text{Cu}}, 29$	$\mathbf{x}_{\text{Cl}}, 17$	$-\mathbf{x}_{\text{Cu}}, 29$	$-\mathbf{x}_{\text{Cl}}, 17$
$\mathbf{x}_{\text{Cu}}, 29$	0, 841	$\mathbf{x}_{\text{Cu}} - \mathbf{x}_{\text{Cl}}, 493$	$2\mathbf{x}_{\text{Cu}}, 841$	$\mathbf{x}_{\text{Cu}} + \mathbf{x}_{\text{Cl}}, 493$
$\mathbf{x}_{\text{Cl}}, 17$		0, 289	$\mathbf{x}_{\text{Cl}} + \mathbf{x}_{\text{Cu}}, 493$	$2\mathbf{x}_{\text{Cl}}, 289$
$-\mathbf{x}_{\text{Cu}}, 29$			0, 841	$\mathbf{x}_{\text{Cu}} - \mathbf{x}_{\text{Cl}}, 493$
$-\mathbf{x}_{\text{Cl}}, 17$				0, 289

which shows that the Patterson should contain the following types of vectors:

Position	Weight	Multiplicity	Total weight
$2\mathbf{x}_{\text{Cu}}$	841	1	841
$2\mathbf{x}_{\text{Cl}}$	289	1	289
$\mathbf{x}_{\text{Cu}} - \mathbf{x}_{\text{Cl}}$	493	2	986
$\mathbf{x}_{\text{Cu}} + \mathbf{x}_{\text{Cl}}$	493	2	986

The coordinates of the largest Patterson peaks are given in Table 2.3.2.1 for an asymmetric half of the cell chosen to span $0 \rightarrow \frac{1}{2}$ in u and $0 \rightarrow 1$ in v . Since the three largest peaks are in the same ratio (7:7:6) as the three largest expected vector types (986:986:841), it is reasonable to assume that peak III corresponds to the copper-copper interaction at $2\mathbf{x}_{\text{Cu}}$. Hence, $x_{\text{Cu}} = 0.08$ and $y_{\text{Cu}} = 0.20$. Peaks I and II should be due to the double-weight Cu-Cl vectors at $\mathbf{x}_{\text{Cu}} - \mathbf{x}_{\text{Cl}}$ and $\mathbf{x}_{\text{Cu}} + \mathbf{x}_{\text{Cl}}$. Now suppose that peak I is at position $\mathbf{x}_{\text{Cu}} + \mathbf{x}_{\text{Cl}}$, then $x_{\text{Cl}} = 0.25$ and $y_{\text{Cl}} = 0.14$. Peak II should now check out as the remaining double-weight Cu-Cl interaction at $\mathbf{x}_{\text{Cu}} - \mathbf{x}_{\text{Cl}}$. Indeed, $\mathbf{x}_{\text{Cu}} - \mathbf{x}_{\text{Cl}} = \langle -0.17, 0.06 \rangle = -\langle 0.17, -0.06 \rangle$ which agrees tolerably well with the position of peak II. The chlorine position also predicts the position of a peak at $2\mathbf{x}_{\text{Cl}}$ with

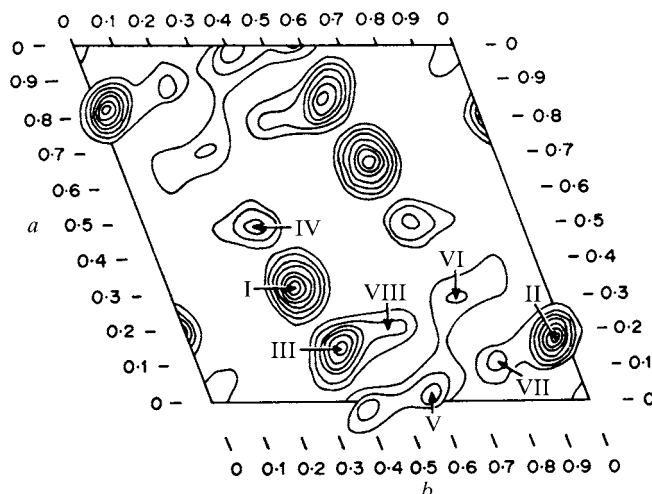


Fig. 2.3.2.2. The c -axis projection of cuprous chloride azomethane complex ($\text{C}_2\text{H}_6\text{Cl}_2\text{Cu}_2\text{N}_2$). The space group is $P\bar{1}$ with one molecule per unit cell. [Adapted from and reprinted with permission from Woolfson (1970, p. 321).]

2.3. PATTERSON AND MOLECULAR-REPLACEMENT TECHNIQUES

Table 2.3.2.1. *Coordinates of Patterson peaks for $C_2H_6Cl_2Cu_2N_2$ projection*

Height	u	v	Number in diagram (Fig. 2.3.2.2)
7	0.33	0.34	I
7	0.18	0.97	II
6	0.16	0.40	III
3	0.49	0.29	IV
3	0.02	0.59	V
2	0.30	0.75	VI
2	0.12	0.79	VII

weight 289; peak IV confirms the chlorine assignment. In fact, this Patterson can be solved also for the lighter nitrogen- and carbon-atom positions which account for the remainder of the vectors listed in Table 2.3.2.1. However, the simplest way to complete the structure determination is probably to compute a Fourier synthesis using phases calculated from the heavier copper and chlorine positions.

Consider now a real cell with M crystallographic asymmetric units, each of which contains N atoms. Let us define $\mathbf{x}_{mn}$, the position of the n th atom in the m th crystallographic unit, by

$$\mathbf{x}_{mn} = [\mathbf{T}_m]\mathbf{x}_{1n} + \mathbf{t}_m,$$

where $[\mathbf{T}_m]$ and $\mathbf{t}_m$ are the rotation matrix and translation vector, respectively, for the m th crystallographic symmetry operator. The Patterson of this crystal will contain vector peaks which arise from atoms interacting with other atoms both in the same and in different crystallographic asymmetric units. The set of $(MN)^2$ Patterson vector interactions for this crystal is represented in a matrix in Table 2.3.2.2. Upon dissection of this diagram we see that there are MN origin vectors, $M[(N-1)N]$ vectors from atom interactions with other atoms in the same crystallographic asymmetric unit and $[M(M-1)]N^2$ vectors involving atoms in separate asymmetric units. Often a number of vectors of special significance relating symmetry-equivalent atoms emerge from this milieu of Patterson

vectors and such 'Harker vectors' constitute the subject of the next section.

2.3.2.2. Harker sections

Soon after Patterson introduced the F^2 series, Harker (1936) recognized that many types of crystallographic symmetry result in a concentration of vectors at characteristic locations in the Patterson. Specifically, he showed that atoms related by rotation axes produce vectors in characteristic planes of the Patterson, and that atoms related by mirror planes or reflection glide planes produce vectors on characteristic lines. Similarly, noncrystallographic symmetry operators produce analogous concentrations of vectors. Harker showed how special sections through a three-dimensional function could be computed using one- or two-dimensional summations. With the advent of powerful computers, it is usual to calculate a full three-dimensional Patterson synthesis. Nevertheless, 'Harker' planes or lines are often the starting point for a structure determination. It should, however, be noted that non-Harker vectors (those not due to interactions between symmetry-related atoms) can appear by coincidence in a Harker section. Table 2.3.2.3 shows the position in a Patterson of Harker planes and lines produced by all types of crystallographic symmetry operators.

Buerger (1946) noted that Harker sections can be helpful in space-group determination. Concentrations of vectors in appropriate regions of the Patterson should be diagnostic for the presence of some symmetry elements. This is particularly useful where these elements (such as mirror planes) are not directly detected by systematic absences.

Buerger also developed a systematic method of interpreting Harker peaks which he called implication theory [Buerger (1959, Chapter 7)].

2.3.2.3. Finding heavy atoms

The previous two sections have developed some of the useful mechanics for interpreting Pattersons. In this section, we will consider finding heavy-atom positions, in the presence of numerous light atoms, from Patterson maps. The feasibility of structure solution by the heavy-atom method depends on a number of factors which include the relative size of the heavy atom and the extent and

Table 2.3.2.2. *Square matrix representation of vector interactions in a Patterson of a crystal with M crystallographic asymmetric units each containing N atoms*

Peak positions $\mathbf{u}_{m1n1, m2n2}$ correspond to vectors between the atoms $\mathbf{x}_{m1n1}$ and $\mathbf{x}_{m2n2}$ where $\mathbf{x}_{mn}$ is the n th atom in the m th crystallographic asymmetric unit. The corresponding weights are $w_{n1}w_{n2}$. The outlined blocks II and IM represent vector interactions between atoms in the same crystallographic asymmetric units (there are M such blocks). The off-diagonal blocks IIM1 and IIMM represent vector interactions between atoms in crystal asymmetric units 1 and M ; there are $M(M-1)$ blocks of this type. The significance of diagonal elements of block IIM1 is that they represent Harker-type interactions between symmetry-equivalent atoms (see Section 2.3.2.2).

	$\mathbf{x}_{11}, w_1$	$\mathbf{x}_{12}, w_2$	...	$\mathbf{x}_{1N}, w_N$	...	$\mathbf{x}_{M1}, w_1$	$\mathbf{x}_{M2}, w_2$	...	$\mathbf{x}_{MN}, w_N$
$\mathbf{x}_{11}, w_1$	$0, w_1^2$	$\mathbf{u}_{11, 12}, w_1w_2$	...	$\mathbf{u}_{11, 1N}, w_1w_N$	...				
$\mathbf{x}_{12}, w_2$		$0, w_2^2$	...	$\mathbf{u}_{12, 1N}, w_2w_N$	...				
$\vdots$		$\vdots$		$\vdots$					
$\mathbf{x}_{1N}, w_N$				$0, w_N^2$					
	Block II					Block IIM			
$\vdots$		$\vdots$					$\vdots$		
$\mathbf{x}_{M1}, w_1$	$\mathbf{u}_{M1, 11}, w_1^2$	$\mathbf{u}_{M1, 12}, w_1w_2$							
$\mathbf{x}_{M2}, w_2$	$\mathbf{u}_{M2, 11}, w_2w_1$	$\mathbf{u}_{M2, 12}, w_2^2$							
$\vdots$		$\vdots$							
$\mathbf{x}_{MN}, w_N$				$\mathbf{u}_{MN, 1N}, w_N^2$					
	Block IIM1					Block IM			

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Table 2.3.2.3. *Position of Harker sections within a Patterson*

Symmetry element	Form of $P(x, y, z)$
(a) Harker planes	
Axes parallel to the b axis: (i) 2, 3, $\bar{3}$, 4, $\bar{4}$, 6, $\bar{6}$ (ii) 2 ₁ , 4 ₂ , 6 ₃ (iii) 3 ₁ , 3 ₂ , 6 ₂ , 6 ₄ (iv) 4 ₁ , 4 ₃ (v) 6 ₁ , 6 ₅	$P(x, 0, z)$ $P(x, \frac{1}{2}, z)$ $P(x, \frac{1}{3}, z)$ $P(x, \frac{1}{4}, z)$ $P(x, \frac{1}{6}, z)$
(b) Harker lines	
Planes perpendicular to the b axis: (i) Reflection planes (ii) Glide plane, glide = $\frac{1}{2}a$ (iii) Glide plane, glide = $\frac{1}{2}c$ (iv) Glide plane, glide = $\frac{1}{2}(a + c)$ (v) Glide plane, glide = $\frac{1}{4}(a + c)$ (vi) Glide plane, glide = $\frac{1}{4}(3a + c)$	$P(0, y, 0)$ $P(\frac{1}{2}, y, 0)$ $P(0, y, \frac{1}{2})$ $P(\frac{1}{2}, y, \frac{1}{2})$ $P(\frac{1}{4}, y, \frac{1}{4})$ $P(\frac{3}{4}, y, \frac{1}{4})$
(c) Special Harker planes	
Axes parallel to or containing body diagonal (111), valid for cubic space groups only: Equation of plane $lx + my + nz - p = 0$ (i) 3 $l = m = n = \cos 54.73561^\circ = 0.57735$ $p = 0$ (ii) 3 ₁ $l = m = n = \cos 54.73561^\circ = 0.57735$ $p = \sqrt{3}/3$ Rhombohedral threefold axes produce analogous Harker planes whose description will depend on the interaxial angle.	

quality of the data. A useful rule of thumb is that the ratio

$$r = \frac{\sum_{\text{heavy}} Z^2}{\sum_{\text{light}} Z^2}$$

should be near unity if the heavy atom is to provide useful starting phase information (Z is the atomic number of an atom). The condition that $r > 1$ normally guarantees interpretability of the Patterson function in terms of the heavy-atom positions. This 'rule', arising from the work of Luzzati (1953), Woolfson (1956), Sim (1961) and others, is not inviolable; many ambitious determinations have been accomplished *via* the heavy-atom method for which r was well below 1.0. An outstanding example is vitamin B₁₂ with formula C₆₂H₈₈CoO₁₄P, which gave an $r = 0.14$ for the cobalt atom alone (Hodgkin *et al.*, 1957). One factor contributing to the success of such a determination is that the relative scattering power of Co is enhanced for higher scattering angles. Thus, the ratio, r , provides a conservative estimate. If the value of r is well above 1.0, the initial easier interpretation of the Patterson will come at the expense of poorly defined parameters of the lighter atoms.

A general strategy for determining heavy atoms from the Patterson usually involves the following steps.

- (1) List the number and type of atoms in the cell.
- (2) Construct the interaction matrix for the heaviest atoms to predict the positions and weights of the largest Patterson vectors. Group recurrent vectors and notice vectors with special properties, such as Harker vectors.

(3) Compute the Patterson using any desired modifications. Placing the map on an absolute scale [$P(000) = \sum Z^2$] is convenient but not necessary.

(4) Examine Harker sections and derive trial atom coordinates from vector positions.

(5) Check the trial coordinates using other vectors in the predicted set. Correlate enantiomorphic choice and origin choice for independent sites.

(6) Include the next-heaviest atoms in the interpretation if possible. In particular, use the cross-vectors with the heaviest atoms.

(7) Use the best heavy-atom model to initiate phasing.

Detailed and instructive examples of using Pattersons to find heavy-atom positions are found in almost every textbook on crystal structure analysis [see, for example, Buerger (1959), Lipson & Cochran (1966) and Stout & Jensen (1968)].

The determination of the crystal structure of cholesteryl iodide by Carlisle & Crowfoot (1945) provides an example of using the Patterson function to locate heavy atoms. There were two molecules, each of formula C₂₇H₄₅I, in the $P2_1$ unit cell. The ratio $r = 2.8$ is clearly well over the optimal value of unity. The $P(x, z)$ Patterson projection showed one dominant peak at $\langle 0.434, 0.084 \rangle$ in the asymmetric unit. The equivalent positions for $P2_1$ require that an iodine atom at x_1, y_1, z_1 generates another at $-x_1, \frac{1}{2} + y_1, z_1$ and thus produces a Patterson peak at $\langle 2x_1, \frac{1}{2}, 2z_1 \rangle$. The iodine position was therefore determined as 0.217, 0.042. The y coordinate of the iodine is arbitrary for $P2_1$ yet the value of $y_1 = 0.25$ is convenient, since an inversion centre in the two-atom iodine structure is then exactly at the origin, making all calculated phases 0 or π . Although the presence of this extra symmetry caused some initial difficulties in the interpretation of the steroid backbone, Carlisle and Crowfoot successfully separated the enantiomorphic images. Owing to the presence of the perhaps *too heavy* iodine atom, however, the structure of the carbon skeleton could not be defined very precisely. Nevertheless, all critical stereochemical details were adequately illuminated by this determination. In the cholesteryl iodide example, a number of different yet equivalent origins could have been selected. Alternative origin choices include all combinations of $x \pm \frac{1}{2}$ and $z \pm \frac{1}{2}$.

A further example of using the Patterson to find heavy atoms will be provided in Section 2.3.5.2 on solving for heavy atoms in the presence of noncrystallographic symmetry.

2.3.2.4. Superposition methods. Image detection

As early as 1939, Wrinch (1939) showed that it was possible, in principle, to recover a fundamental set of points from the vector map of that set. Unlike the Harker–Buerger implication theory (Buerger, 1946), the method that Wrinch suggested was capable of using all the vectors in a three-dimensional set, not those restricted to special lines or sections. Wrinch's ideas were developed for vector sets of points, however, and could not be directly applied to real, heavily overlapped Pattersons of a complex structure. These ideas seem to have lain dormant until the early 1950s when a number of independent investigators developed superposition methods (Beevers & Robertson, 1950; Clastre & Gay, 1950; Garrido, 1950a; Buerger, 1950a).

A Patterson can be considered as a sum of images of a molecule as seen, in turn, for each atom placed on the origin (Fig. 2.3.2.3). Thus, the deconvolution of a Patterson could proceed by superimposing each image of the molecule obtained onto the others by translating the Patterson origin to each imaging atom. For instance, let us take a molecule consisting of four atoms $ABCD$ arranged in the form of a quadrilateral (Fig. 2.3.2.3). Then the Patterson consists of the images of four identical quadrilaterals with atoms A, B, C and D placed on the origin in turn. The Pattersons can then be

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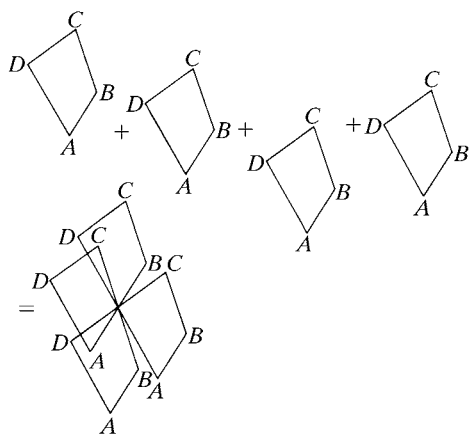


Fig. 2.3.2.3. Atoms $ABCD$, arranged as a quadrilateral, generate a Patterson which is the sum of the images of the quadrilateral when each atom is placed on the origin in turn.

deconvoluted by superimposing two of these Pattersons after translating these (without rotation) by, for instance, the vector $\mathbf{AB}$. A further improvement could be obtained by superimposing a third Patterson translated by $\mathbf{AC}$. This would have the additional advantage in that ABC is a noncentrosymmetric arrangement and, therefore, selects the enantiomorph corresponding to the hand of the atomic arrangement ABC [cf. Buerger (1951, 1959)].

A basic problem is that knowledge of the vectors $\mathbf{AB}$ and $\mathbf{AC}$ also implies some knowledge of the structure at a time when the structure is not yet known. In practice 'good-looking' peaks, estimated to be single peaks by assessing the absolute scale of the structure amplitudes with Wilson statistics, can be assumed to be the result of single interatomic vectors within a molecule. Superposition can then proceed and the result can be inspected for reasonable chemical sense. As many apparently single peaks can be tried systematically using a computer, this technique is useful for selecting and testing a series of reasonable Patterson interpretations (Jacobson *et al.*, 1961).

Three major methods have been used for the detection of molecular images of superimposed Pattersons. These are the sum, product and minimum 'image seeking' functions (Raman & Lipscomb, 1961). The concept of the sum function is to add the images where they superimpose, whereas elsewhere the summed Pattersons will have a lower value owing to lack of image superposition. Therefore, the sum function determines the average Patterson density for superimposed images, and is represented analytically as

$$S(\mathbf{x}) = \sum_{i=1}^N P(\mathbf{x} + \mathbf{u}_i),$$

where $S(\mathbf{x})$ is the sum function at $\mathbf{x}$ given by the superposition of the i th Patterson translated by $\mathbf{u}_i$, or

$$S(\mathbf{x}) = \sum_{\mathbf{h}} \left\{ F_{\mathbf{h}}^2 \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) \left[\sum_{i=1}^N \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_i) \right] \right\}.$$

Setting

$$m \exp(i\varphi_{\mathbf{h}}) = \sum_{i=1}^N \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_i)$$

(m and $\varphi_{\mathbf{h}}$ can be calculated from the translational vectors used for the superposition),

$$S(\mathbf{x}) = \sum_{\mathbf{h}} F_{\mathbf{h}}^2 m \exp(2\pi i \mathbf{h} \cdot \mathbf{x} + \varphi_{\mathbf{h}}).$$

Thus, the sum function is equivalent to a weighted 'heavy atom' method based on the known atoms assumed by the superposition translation vectors.

The product function is somewhat more vigorous in that the images are enhanced by the product. If an image is superimposed on no image, then the product should be zero.

The product function can be expressed as

$$Pr(\mathbf{x}) = \prod_{i=1}^N P(\mathbf{x} + \mathbf{u}_i).$$

When $N = 2$ ($\mathbf{h}$ and $\mathbf{p}$ are sets of Miller indices),

$$Pr(\mathbf{x}) = \sum_{\mathbf{h}} \sum_{\mathbf{p}} F_{\mathbf{h}}^2 F_{\mathbf{p}}^2 \exp[2\pi i (\mathbf{h} + \mathbf{p}) \cdot \mathbf{x}] \\ \times \exp[2\pi i (\mathbf{h} \cdot \mathbf{u}_1 + \mathbf{p} \cdot \mathbf{u}_2)].$$

Successive superpositions using the product functions will quickly be dominated by a few terms with very large coefficients.

Finally, the minimum function is a clever invention of Buerger (Buerger, 1950b, 1951, 1953a,b,c; Taylor, 1953; Rogers, 1951). If a superposition is correct then each Patterson must represent an image of the structure. Whenever there are two or more images that intersect in the Patterson, the Patterson density will be greater than a single image. When two different images are superimposed, it is a reasonable hope that at least one of these is a single image. Thus by taking the value of that Patterson which is the minimum, it should be possible to select a single image and eliminate noise from interfering images as far as possible. Although the minimum function is perhaps the most powerful algorithm for image selection of well sharpened Pattersons, it is not readily amenable to Fourier representation.

The minimum function was conceived on the basis of selecting positive images on a near-zero background. If it were desired to select negative images [e.g. the $(\mathbf{F}_1 - \mathbf{F}_2)^2$ correlation function discussed in Section 2.3.3.4], then it would be necessary to use a maximum function. In fact, normally, an image has finite volume with varying density. Thus, some modification of the minimum function is necessary in those cases where the image is large compared to the volume of the unit cell, as in low-resolution protein structures (Rossmann, 1961b). Nordman (1966) used the average of the Patterson values of the lowest 10 to 20 per cent of the vectors in comparing Pattersons with hypothetical point Pattersons. A similar criterion was used by High & Kraut (1966).

Image-seeking methods using Patterson superposition have been used extensively (Beevers & Robertson, 1950; Garrido, 1950b; Robertson, 1951). For a review the reader is referred to *Vector Space* (Buerger, 1959) and a paper by Fridrichsons & Mathieson (1962). However, with the advent of computerized direct methods (see Chapter 2.2), such techniques are no longer popular. Nevertheless, they provide the conceptual framework for the rotation and translation functions (see Sections 2.3.6 and 2.3.7).

2.3.2.5. Systematic computerized Patterson vector-search procedures. Looking for rigid bodies

The power of the modern digital computer has enabled rapid access to the large number of Patterson density values which can serve as a lookup table for systematic vector-search procedures. In the late 1950s, investigators began to use systematic searches for the placement of single atoms, of known chemical groups or fragments and of entire known structures. Methods for locating single atoms were developed and called variously: vector verification (Mighell & Jacobson, 1963), symmetry minimum function (Kraut, 1961; Simpson *et al.*, 1965; Corfield & Rosenstein, 1966) and consistency functions (Hamilton, 1965). Patterson superposition techniques using stored function values were often used to image the structure

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from the known portion. In such single-site search procedures, single atoms are placed at all possible positions in a crystal, using a search grid of the same fineness as for the stored Patterson function, preferably about one-third of the resolution of the Patterson map. Solutions are gauged to be acceptable if all expected vectors due to symmetry-related atoms are observed above a specified threshold in the Patterson.

Systematic computerized Patterson search procedures for orienting and positioning known molecular fragments were also developed in the early 1960s. These hierarchical procedures rely on first using the 'self'-vectors which depend only on the orientation of a molecular fragment. A search for the position of the fragment relative to the crystal symmetry elements then uses the cross-vectors between molecules (see Sections 2.3.6 and 2.3.7). Nordman constructed a weighted point representation of the predicted vector set for a fragment (Nordman & Nakatsu, 1963; Nordman, 1966) and successfully solved the structure of a number of complex alkaloids. Huber (1965) used the convolution molecule method of Hoppe (1957a) in three dimensions to solve a number of natural-product structures, including steroids. Various program systems have used Patterson search methods operating in real space to solve complex structures (Braun *et al.*, 1969; Egert, 1983).

Others have used reciprocal-space procedures for locating known fragments. Tollin & Cochran (1964) developed a procedure for determining the orientation of planar groups by searching for origin-containing planes of high density in the Patterson. General procedures using reciprocal-space representations for determining rotation and translation parameters have been developed and will be described in Sections 2.3.6 and 2.3.7, respectively.

Although as many functions have been used to detect solutions in these Patterson search procedures as there are programs, most rely on some variation of the sum, product and minimum functions (Section 2.3.2.4). The quality of the stored Patterson density representation also varies widely, but it is now common to use 16 or more bits for single density values. Treatment of vector overlap is handled differently by different investigators and the choice will depend on the degree of overlapping (Nordman & Schilling, 1970; Nordman, 1972). General Gaussian multiplicity corrections can be employed to treat coincidental overlap of independent vectors in general positions and overlap which occurs for symmetric peaks in the vicinity of a special position or mirror plane in the Patterson (G. Kamer, S. Ramakumar & P. Argos, unpublished results; Rossmann *et al.*, 1972).

2.3.3. Isomorphous replacement difference Pattersons

2.3.3.1. Introduction

One of the initial stages in the application of the isomorphous replacement method is the determination of heavy-atom positions. Indeed, this step of a structure determination can often be the most challenging. Not only may the number of heavy-atom sites be unknown, and have incomplete substitution, but the various isomorphous compounds may also lack isomorphism. To compound these problems, the error in the measurement of the isomorphous difference in structure amplitudes is often comparable to the differences themselves. Clearly, therefore, the ease with which a particular problem can be solved is closely correlated with the quality of the data-measuring procedure.

The isomorphous replacement method was used incidentally by Bragg in the solution of NaCl and KCl. It was later formalized by J. M. Robertson in the analysis of phthalocyanine where the coordination centre could be Pt, Ni and other metals (Robertson, 1935, 1936; Robertson & Woodward, 1937). In this and similar cases, there was no difficulty in finding the heavy-atom positions. Not only were the heavy atoms frequently in special positions, but

they dominated the total scattering effect. It was not until Perutz and his colleagues (Green *et al.*, 1954; Bragg & Perutz, 1954) applied the technique to the solution of haemoglobin, a protein of 68 000 Da, that it was necessary to consider methods for detecting heavy atoms. The effect of a single heavy atom, even uranium, can only have a very marginal effect on the structure amplitudes of a crystalline macromolecule. Hence, techniques had to be developed which were dependent on the difference of the isomorphous structure amplitudes rather than on the solution of the Patterson of the heavy-atom-derivative compound on its own.

2.3.3.2. Finding heavy atoms with centrosymmetric projections

Phases in a centrosymmetric projection will be 0 or π if the origin is chosen at the centre of symmetry. Hence, the native structure factor, $\mathbf{F}_N$, and the heavy-atom-derivative structure factor, $\mathbf{F}_{NH}$, will be collinear. It follows that the structure amplitude, $|\mathbf{F}_H|$, of the heavy atoms alone in the cell will be given by

$$|\mathbf{F}_H| = |(|\mathbf{F}_{NH}| \pm |\mathbf{F}_N|)| + \varepsilon,$$

where ε is the error on the parentetic sum or difference. Three different cases may arise (Fig. 2.3.3.1). Since the situation shown in Fig. 2.3.3.1(c) is rare, in general

$$|\mathbf{F}_H|^2 \simeq (|\mathbf{F}_{NH}| - |\mathbf{F}_N|)^2. \quad (2.3.3.1)$$

Thus, a Patterson computed with the square of the differences between the native and derivative structure amplitudes of a centrosymmetric projection will approximate to a Patterson of the heavy atoms alone.

The approximation (2.3.3.1) is valid if the heavy-atom substitution is small enough to make $|\mathbf{F}_H| \ll |\mathbf{F}_{NH}|$ for most reflections, but sufficiently large to make $\varepsilon \ll (|\mathbf{F}_{NH}| - |\mathbf{F}_N|)^2$. It is also assumed that the native and heavy-atom-derivative data have been placed on the same relative scale. Hence, the relation (2.3.3.1) should be re-written as

$$|\mathbf{F}_H|^2 \simeq (|\mathbf{F}_{NH}| - k|\mathbf{F}_N|)^2,$$

where k is an experimentally determined scale factor (see Section 2.3.3.7). Uncertainty in the determination of k will contribute further to ε , albeit in a systematic manner.

Centrosymmetric projections were used extensively for the determination of heavy-atom sites in early work on proteins such as haemoglobin (Green *et al.*, 1954), myoglobin (Bluhm *et al.*,

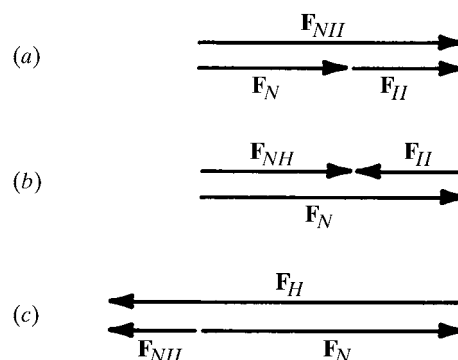


Fig. 2.3.3.1. Three different cases which can occur in the relation of the native, $\mathbf{F}_N$, and heavy-atom derivative, $\mathbf{F}_{NH}$, structure factors for centrosymmetric reflections. $\mathbf{F}_N$ is assumed to have a phase of 0, although analogous diagrams could be drawn when $\mathbf{F}_N$ has a phase of π . The crossover situation in (c) is clearly rare if the heavy-atom substitution is small compared to the native molecule, and can in general be neglected.

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1958) and lysozyme (Poljak, 1963). However, with the advent of faster data-collecting techniques, low-resolution (*e.g.* a 5 Å limit) three-dimensional data are to be preferred for calculating difference Pattersons. For noncentrosymmetric reflections, the approximation (2.3.3.1) is still valid but less exact (Section 2.3.3.3). However, the larger number of three-dimensional differences compared to projection differences will enhance the signal of the real Patterson peaks relative to the noise. If there are N terms in the Patterson synthesis, then the peak-to-noise ratio will be proportionally $\sqrt{N}$ and $1/\varepsilon$. With the subscripts 2 and 3 representing two- and three-dimensional syntheses, respectively, the latter will be more powerful than the former whenever

$$\frac{\sqrt{N_3}}{\varepsilon_3} > \frac{\sqrt{N_2}}{\varepsilon_2}.$$

Now, as $\varepsilon_3 \simeq \sqrt{2}\varepsilon_2$, it follows that N_3 must be greater than $2N_2$ if the three-dimensional noncentrosymmetric computation is to be more powerful. This condition must almost invariably be true.

2.3.3.3. Finding heavy atoms with three-dimensional methods

A Patterson of a native bio-macromolecular structure (coefficients F_N^2) can be considered as being, at least approximately, a vector map of all the light atoms (carbons, nitrogens, oxygens, some sulfurs, and also phosphorus for nucleic acids) other than hydrogen atoms. These interactions will be designated as LL . Similarly, a Patterson of the heavy-atom derivative will contain $HH + HL + LL$ interactions, where H represents the heavy atoms. Thus, a true difference Patterson, with coefficients $F_{NH}^2 - F_N^2$, will contain only the interactions $HH + HL$. In general, the carpet of HL vectors completely dominates the HH vectors except for very small proteins such as insulin (Adams *et al.*, 1969). Therefore, it would be preferable to compute a Patterson containing only HH interactions in order to interpret the map in terms of specific heavy-atom sites.

Blow (1958) and Rossmann (1960) showed that a Patterson with $(|\mathbf{F}_{NH}| - |\mathbf{F}_N|)^2$ coefficients approximated to a Patterson containing only HH vectors. If the phase angle between $\mathbf{F}_N$ and $\mathbf{F}_{NH}$ is φ (Fig. 2.3.3.2), then

$$|\mathbf{F}_H|^2 = |\mathbf{F}_N|^2 + |\mathbf{F}_{NH}|^2 - 2|\mathbf{F}_N||\mathbf{F}_{NH}|\cos\varphi.$$

In general, however, $|\mathbf{F}_H| \ll |\mathbf{F}_N|$. Hence, φ is small and

$$|\mathbf{F}_H|^2 \simeq (|\mathbf{F}_{NH}| - |\mathbf{F}_N|)^2,$$

which is the same relation as (2.3.3.1) for centrosymmetric approximations. Since the direction of $\mathbf{F}_H$ is random compared to $\mathbf{F}_N$, the root-mean-square projected length of $\mathbf{F}_H$ onto $\mathbf{F}_N$ will be $\mathbf{F}_H/\sqrt{2}$. Thus it follows that a better approximation is

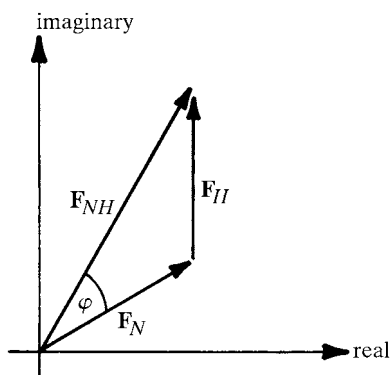


Fig. 2.3.3.2. Vector triangle showing the relationship between $\mathbf{F}_N$, $\mathbf{F}_{NH}$ and $\mathbf{F}_H$, where $\mathbf{F}_{NH} = \mathbf{F}_N + \mathbf{F}_H$.

$$|\mathbf{F}_H|^2 \simeq \sqrt{2}(|\mathbf{F}_{NH}| - |\mathbf{F}_N|)^2, \quad (2.3.3.2)$$

which accounts for the assumption (Section 2.3.3.2) that $\varepsilon_3 = \sqrt{2}\varepsilon_2$. The almost universal method for the initial determination of major heavy-atom sites in an isomorphous derivative utilizes a Patterson with $(|\mathbf{F}_{NH}| - |\mathbf{F}_N|)^2$ coefficients. Approximation (2.3.3.2) is also the basis for the refinement of heavy-atom parameters in a single isomorphous replacement pair (Rossmann, 1960; Cullis *et al.*, 1962; Terwilliger & Eisenberg, 1983).

2.3.3.4. Correlation functions

In the most general case of a triclinic space group, it will be necessary to select an origin arbitrarily, usually coincident with a heavy atom. All other heavy atoms (and subsequently also the macromolecular atoms) will be referred to this reference atom. However, the choice of an origin will be independent in the interpretation of each derivative's difference Patterson. It will then be necessary to correlate the various, arbitrarily chosen, origins. The same problem occurs in space groups lacking symmetry axes perpendicular to the primary rotation axis (*e.g.* $P2_1$, $P6$ etc.), although only one coordinate, namely parallel to the unique rotation axis, will require correlation. This problem gave rise to some concern in the 1950s. Bragg (1958), Blow (1958), Perutz (1956), Hoppe (1959) and Bodo *et al.* (1959) developed a variety of techniques, none of which were entirely satisfactory. Rossmann (1960) proposed the $(\mathbf{F}_{NH1} - \mathbf{F}_{NH2})^2$ synthesis and applied it successfully to the heavy-atom determination of horse haemoglobin. This function gives positive peaks ($H1 \cdot H1$) at the end of vectors between the heavy-atom sites in the first compound, positive peaks ($H2 \cdot H2$) between the sites in the second compound, and negative peaks between sites in the first and second compound (Fig. 2.3.3.3). It is thus the negative peaks which provide the necessary correlation. The function is unique in that it is a Patterson containing significant information in both positive and negative peaks. Steinrauf (1963) suggested using the coefficients $(|\mathbf{F}_{NH1}| - |\mathbf{F}_N|) \cdot (|\mathbf{F}_{NH2}| - |\mathbf{F}_N|)$ in order to eliminate the positive $H1 \cdot H1$ and $H2 \cdot H2$ vectors.

Although the problem of correlation was a serious concern in the early structural determination of proteins during the late 1950s and early 1960s, the problem has now been by-passed. Blow &

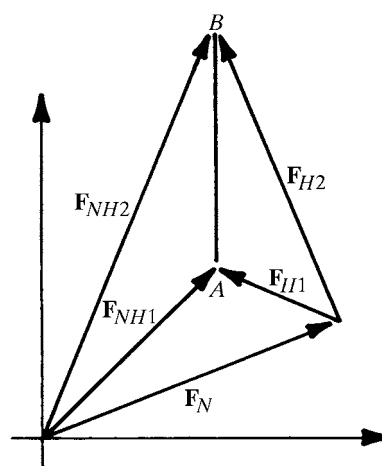


Fig. 2.3.3.3. A Patterson with coefficients $(\mathbf{F}_{NH1} - \mathbf{F}_{NH2})^2$ will be equivalent to a Patterson whose coefficients are $(AB)^2$. However, $AB = -\mathbf{F}_{H1} + \mathbf{F}_{H2}$. Thus, a Patterson with $(AB)^2$ coefficients is equivalent to having negative atomic substitutions in compound 1 and positive substitutions in compound 2, or *vice versa*. Therefore, the Patterson will contain positive peaks for vectors of the type $H1 \cdot H1$ and $H2 \cdot H2$, but negative vector peaks for vectors of type $H1 \cdot H2$.

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Rossmann (1961) and Kartha (1961) independently showed that it was possible to compute usable phases from a single isomorphous replacement (SIR) derivative. This contradicted the previously accepted notion that it was necessary to have at least two isomorphous derivatives to be able to determine a noncentrosymmetric reflection's phase (Harker, 1956). Hence, currently, the procedure used to correlate origins in different derivatives is to compute SIR phases from the first compound and apply them to a difference electron-density map of the second heavy-atom derivative. Thus, the origin of the second derivative will be referred to the arbitrarily chosen origin of the first compound. More important, however, the interpretation of such a 'feedback' difference Fourier is easier than that of a difference Patterson. Hence, once one heavy-atom derivative has been solved for its heavy-atom sites, the solution of other derivatives is almost assured. This concept is examined more closely in the following section.

2.3.3.5. Interpretation of isomorphous difference Pattersons

Difference Pattersons have usually been manually interpreted in terms of point atoms. In more complex situations, such as crystalline viruses, a systematic approach may be necessary to analyse the Patterson. That is especially true when the structure contains noncrystallographic symmetry (Argos & Rossmann, 1976). Such methods are in principle dependent on the comparison of the observed Patterson, $P_1(\mathbf{x})$, with a calculated Patterson, $P_2(\mathbf{x})$. A criterion, C_P , based on the sum of the Patterson densities at all test vectors within the unit-cell volume V , would be

$$C_P = \int_V P_1(\mathbf{x}) \cdot P_2(\mathbf{x}) d\mathbf{x}.$$

C_P can be evaluated for all reasonable heavy-atom distributions. Each different set of trial sites corresponds to a different P_2 Patterson. It is then easily shown that

$$C_P = \sum_{\mathbf{h}} \Delta_{\mathbf{h}}^2 E_{\mathbf{h}}^2,$$

where the sum is taken over all $\mathbf{h}$ reflections in reciprocal space, $\Delta_{\mathbf{h}}^2$ are the observed differences and $E_{\mathbf{h}}$ are the structure factors of the trial point Patterson. (The symbol E is used here because of its close relation to normalized structure factors.)

Let there be n noncrystallographic asymmetric units within the crystallographic asymmetric unit and m crystallographic asymmetric units within the crystal unit cell. Then there are L symmetry-related heavy-atom sites where $L = nm$. Let the scattering contribution of the i th site have a_i and b_i real and imaginary structure-factor components with respect to an arbitrary origin. Hence, for reflection $\mathbf{h}$

$$E_{\mathbf{h}}^2 \left(\sum_L a_{\mathbf{h}i} \right)^2 + \left(\sum_L b_{\mathbf{h}i} \right)^2 = L + \sum_{i \neq j}^N \sum_{j=1}^N (a_{\mathbf{h}i} a_{\mathbf{h}j} + b_{\mathbf{h}i} b_{\mathbf{h}j}).$$

Therefore,

$$C_P = \sum_{\mathbf{h}} \Delta_{\mathbf{h}}^2 \left[L + 2 \sum_{i \neq j} \sum_{j=1}^N (a_{\mathbf{h}i} a_{\mathbf{h}j} + b_{\mathbf{h}i} b_{\mathbf{h}j}) \right].$$

But $\sum_{\mathbf{h}} \Delta_{\mathbf{h}}^2$ must be independent of the number, L , of heavy-atom sites per cell. Thus the criterion can be re-written as

$$C'_P = \sum_{\mathbf{h}} \Delta_{\mathbf{h}}^2 \left[\sum_{i \neq j} \sum_{j=1}^N (a_{\mathbf{h}i} a_{\mathbf{h}j} + b_{\mathbf{h}i} b_{\mathbf{h}j}) \right]. \quad (2.3.3.3)$$

More generally, if some sites have already been tentatively determined, and if these sites give rise to the structure-factor components $A_{\mathbf{h}}$ and $B_{\mathbf{h}}$, then

$$E_{\mathbf{h}}^2 = \left(A_{\mathbf{h}} + \sum_N a_{\mathbf{h}i} \right)^2 + \left(B_{\mathbf{h}} + \sum_N b_{\mathbf{h}i} \right)^2. \quad (2.3.3.4)$$

Following the same procedure as above, it follows that

$$C'_P = \sum_{\mathbf{h}} \Delta_{\mathbf{h}}^2 \left[(A_{\mathbf{h}} a_{\mathbf{h}} + B_{\mathbf{h}} b_{\mathbf{h}}) + \sum_{i \neq j} \sum_{j=1}^N (a_{\mathbf{h}i} a_{\mathbf{h}j} + b_{\mathbf{h}i} b_{\mathbf{h}j}) \right], \quad (2.3.3.5)$$

where $a_{\mathbf{h}} = \sum_{i=1}^L a_{\mathbf{h}i}$ and $b_{\mathbf{h}} = \sum_{i=1}^L b_{\mathbf{h}i}$.

Expression (2.3.3.5) will now be compared with the 'feedback' method (Dickerson *et al.*, 1967, 1968) of verifying heavy-atom sites using SIR phasing. Inspection of Fig. 2.3.3.4 shows that the native phase, α , will be determined as $\alpha = \varphi + \pi$ (φ is the structure-factor phase corresponding to the presumed heavy-atom positions) when $|\mathbf{F}_N| > |\mathbf{F}_H|$ and $\alpha = \varphi$ when $|\mathbf{F}_N| \ll |\mathbf{F}_H|$. Thus, an SIR difference electron density, $\Delta\rho(\mathbf{x})$, can be synthesized by the Fourier summation

$$\begin{aligned} \Delta\rho(\mathbf{x}) &= \frac{1}{V} \sum m(|\mathbf{F}_{NH}| - |\mathbf{F}_N|) \cos(2\pi\mathbf{h} \cdot \mathbf{x} - \varphi_{\mathbf{h}}) \\ &\quad \text{from terms with } \Delta_{\mathbf{h}} = |\mathbf{F}_{NH}| - |\mathbf{F}_N| > 0 \\ &+ \frac{1}{V} \sum m(|\mathbf{F}_{NH}| - |\mathbf{F}_N|) \cos(2\pi\mathbf{h} \cdot \mathbf{x} - \varphi_{\mathbf{h}} - \pi) \\ &\quad \text{from terms with } \Delta_{\mathbf{h}} < 0 \\ &= \frac{1}{V} \sum m|\Delta_{\mathbf{h}}| \cos(2\pi\mathbf{h} \cdot \mathbf{x} - \varphi_{\mathbf{h}}), \end{aligned}$$

where m is a figure of merit of the phase reliability (Blow & Crick, 1959; Dickerson *et al.*, 1961). Now,

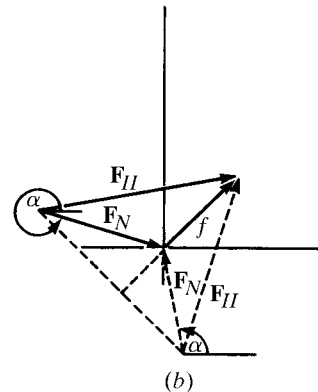
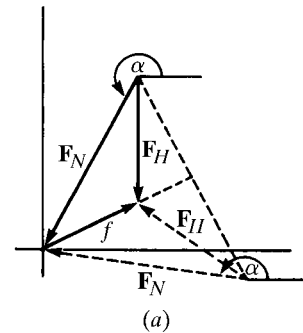


Fig. 2.3.3.4. The phase α of the native compound (structure factor $\mathbf{F}_N$) is determined either as being equal to, or 180° out of phase with, the presumed heavy-atom contribution when only a single isomorphous compound is available. In (a) is shown the case when $|\mathbf{F}_N| > |\mathbf{F}_{NH}|$ and $\alpha \simeq \varphi + \pi$. In (b) is shown the case when $|\mathbf{F}_N| < |\mathbf{F}_{NH}|$ and $\alpha = \varphi$, where φ is the phase of the heavy-atom structure factor $\mathbf{F}_H$.

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$$\mathbf{F}_h = A_h + iB_h = F_H \cos \varphi_h + iF_H \sin \varphi_h,$$

where A_h and B_h are the real and imaginary components of the presumed heavy-atom sites. Therefore,

$$\Delta\rho(\mathbf{x}) = \frac{1}{V} \sum \frac{m|\Delta_h|}{|\mathbf{F}_H|} (A_h \cos 2\pi\mathbf{h} \cdot \mathbf{x} + B_h \sin 2\pi\mathbf{h} \cdot \mathbf{x}).$$

If this SIR difference electron-density map shows significant peaks at sites related by noncrystallographic symmetry, then those sites will be at the position of a further set of heavy atoms. Hence, a suitable criterion for finding heavy-atom sites is

$$C_{\text{SIR}} = \sum_{j=1}^n \Delta\rho(\mathbf{x}_j),$$

or by substitution

$$C_{\text{SIR}} = \sum_{j=1}^n \frac{1}{V} \sum_h \frac{m|\Delta_h|}{|\mathbf{F}_H|} (A_h \cos 2\pi\mathbf{h} \cdot \mathbf{x}_j + B_h \sin 2\pi\mathbf{h} \cdot \mathbf{x}_j).$$

But

$$a_h = \sum_{j=1}^n \cos 2\pi\mathbf{h} \cdot \mathbf{x}_j \quad \text{and} \quad b_h = \sum_{j=1}^n \sin 2\pi\mathbf{h} \cdot \mathbf{x}_j.$$

Therefore,

$$C_{\text{SIR}} = \frac{1}{V} \sum_h \frac{m|\Delta_h|}{|\mathbf{F}_H|} (A_h a_h + B_h b_h). \quad (2.3.3.6)$$

This expression is similar to (2.3.3.5) derived by consideration of a Patterson search. It differs from (2.3.3.5) in two respects: the Fourier coefficients are different and expression (2.3.3.6) is lacking a second term. Now the figure of merit m will be small whenever $|\mathbf{F}_H|$ is small as the SIR phase cannot be determined well under those conditions. Hence, effectively, the coefficients are a function of $|\Delta_h|$, and the coefficients of the functions (2.3.3.5) and (2.3.3.6) are indeed rather similar. The second term in (2.3.3.5) relates to the use of the search atoms in phasing and could be included in (2.3.3.6), provided the actual feedback sites in each of the n electron-density functions tested by C_{SIR} are omitted in turn. Thus, a systematic Patterson search and an SIR difference Fourier search are very similar in character and power.

2.3.3.6. Direct structure determination from difference Pattersons

The difference Patterson computed with coefficients $F_{HN}^2 - F_N^2$ contains information on the heavy atoms (HH vectors) and the macromolecular structure (HL vectors) (Section 2.3.3.3). If the scaling between the $|\mathbf{F}_{HN}|$ and $|\mathbf{F}_N|$ data sets is not perfect there will also be noise. Rossmann (1961*b*) was partially successful in determining the low-resolution horse haemoglobin structure by using a series of superpositions based on the known heavy-atom sites. Nevertheless, Patterson superposition methods have not been used for the structure determination of proteins owing to the successful error treatment of the isomorphous replacement method in reciprocal space. However, it is of some interest here for it gives an alternative insight into SIR phasing.

The deconvolution of an arbitrary molecule, represented as '?', from an $(F_{HN}^2 - F_N^2)$ Patterson, is demonstrated in Fig. 2.3.3.5. The original structure is shown in Fig. 2.3.3.5(a) and the corresponding Patterson in Fig. 2.3.3.5(b). Superposition with respect to one of the heavy-atom sites is shown in Fig. 2.3.3.5(c) and the other in Fig. 2.3.3.5(d). Both Figs. 2.3.3.5(c) and (d) contain a centre of symmetry because the use of only a single HH vector implies a centre of symmetry half way between the two sites. The centre is

broken on combining information from all three sites (which together lack a centre of symmetry) by superimposing Figs. 2.3.3.5(c) and (d) to obtain either the original structure (Fig. 2.3.3.5a) or its enantiomorph. Thus it is clear, in principle, that there is sufficient information in a single isomorphous derivative data set, when used in conjunction with a native data set, to solve a structure completely. However, the procedure shown in Fig. 2.3.3.5 does not consider the accumulation of error in the selection of individual images when these intersect with another image. In this sense the reciprocal-space isomorphous replacement technique has greater elegance and provides more insight, whereas the alternative view given by the Patterson method was the original stimulus for the discovery of the SIR phasing technique (Blow & Rossmann, 1961).

Other Patterson functions for the deconvolution of SIR data have been proposed by Ramachandran & Raman (1959), as well as others. The principles are similar but the coefficients of the functions are optimized to emphasize various aspects of the signal representing the molecular structure.

2.3.3.7. Isomorphism and size of the heavy-atom substitution

It is insufficient to discuss Patterson techniques for locating heavy-atom substitutions without also considering errors of all kinds. First, it must be recognized that most heavy-atom labels are not a single atom but a small compound containing one or more heavy atoms. The compound itself will displace water or ions and locally alter the conformation of the protein or nucleic acid. Hence, a simple Gaussian approximation will suffice to represent individual heavy-atom scatterers responsible for the difference between native and heavy-atom derivatives. Furthermore, the heavy-atom compound often introduces small global structural changes which can be detected only at higher resolution. These problems were considered with some rigour by Crick & Magdoff (1956). In general, lack of isomorphism is exhibited by an increase in the size of the isomorphous differences with increasing resolution (Fig. 2.3.3.6).

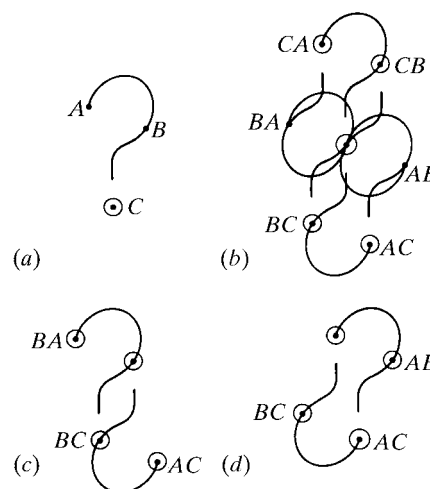


Fig. 2.3.3.5. Let (a) be the original structure which contains three heavy atoms ABC in a noncentrosymmetric configuration. Then a Fourier summation, with $(F_{NH}^2 - F_N^2)$ coefficients, will give the Patterson shown in (b). Displacement of the Patterson by the vector BC and selecting the common patterns yields (c). Similarly, displacement by AC gives (d). Finally, superposition of (c) on (d) gives the original figure or its enantiomorph. This series of steps demonstrates that, in principle, complete structural information is contained in an SIR derivative.

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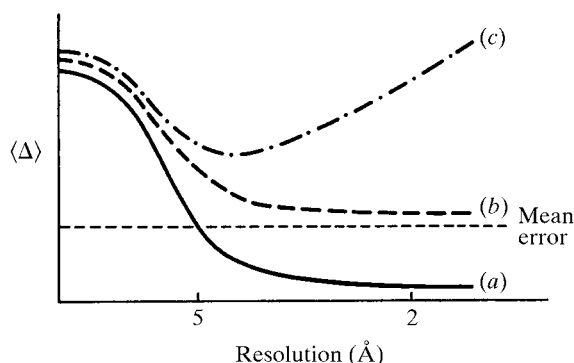


Fig. 2.3.3.6. A plot of mean isomorphous differences as a function of resolution. (a) The theoretical size of mean differences following roughly a Gaussian distribution. (b) The observed size of differences for a good isomorphous derivative where the smaller higher-order differences have been largely masked by the error of measurement. (c) Observed differences where 'lack of isomorphism' dominates beyond approximately 5 Å resolution.

Crick & Magdoff (1956) also derived the approximate expression

$$\sqrt{\frac{2N_H}{N_P}} \cdot \frac{f_H}{f_P}$$

to estimate the r.m.s. fractional change in intensity as a function of heavy-atom substitution. Here, N_H represents the number of heavy atoms attached to a protein (or other large molecule) which contains N_P light atoms. f_H and f_P are the scattering powers of the average heavy and protein atom, respectively. This function was tabulated by Eisenberg (1970) as a function of molecular weight (proportional to N_P). For instance, for a single, fully substituted, Hg atom the formula predicts an r.m.s. intensity change of around 25% in a molecule of 100 000 Da. However, the error of measurement of a reflection intensity is likely to be around 10% of I , implying perhaps an error of around 14% of I on a difference measurement. Thus, the isomorphous replacement difference measurement for almost half the reflections will be buried in error for this case.

Scaling of the different heavy-atom-derivative data sets onto a common relative scale is clearly important if error is to be reduced. Blundell & Johnson (1976, pp. 333–336) give a careful discussion of this subject. Suffice it to say here only that a linear scale factor is seldom acceptable as the heavy-atom-derivative crystals frequently suffer from greater disorder than the native crystals. The heavy-atom derivative should, in general, have a slightly larger mean value for the structure factors on account of the additional heavy atoms (Green *et al.*, 1954). The usual effect is to make $\sum |\mathbf{F}_{NH}|^2 / \sum |\mathbf{F}_N|^2 \simeq 1.05$ (Phillips, 1966).

As the amount of heavy atom is usually unknown in a yet unsolved heavy-atom derivative, it is usual practice either to apply a scale factor of the form $k \exp[-B(\sin \theta / \lambda)^2]$ or, more generally, to use local scaling (Matthews & Czerwinski, 1975). The latter has the advantage of not making any assumption about the physical nature of the relative intensity decay with resolution.

2.3.4. Anomalous dispersion

2.3.4.1. Introduction

The physical basis for anomalous dispersion has been well reviewed by Ramaseshan & Abrahams (1975), James (1965), Cromer (1974) and Bijvoet (1954). As the wavelength of radiation approaches the absorption edge of a particular element, then an atom will disperse X-rays in a manner that can be defined by the

complex scattering factor

$$f_0 + \Delta f' + i\Delta f'',$$

where f_0 is the scattering factor of the atom without the anomalous absorption and re-scattering effect, $\Delta f'$ is the real correction term (usually negative), and $\Delta f''$ is the imaginary component. The real term $f_0 + \Delta f'$ is often written as f' , so that the total scattering factor will be $f' + if''$. Values of $\Delta f'$ and $\Delta f''$ are tabulated in *IT IV* (Cromer, 1974), although their precise values are dependent on the environment of the anomalous scatterer. Unlike f_0 , $\Delta f'$ and $\Delta f''$ are almost independent of scattering angle as they are caused by absorption of energy in the innermost electron shells. Thus, the anomalous effect resembles scattering from a point atom.

The structure factor of index $\mathbf{h}$ can now be written as

$$\mathbf{F}_{\mathbf{h}} = \sum_{j=1}^N f'_j \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_j) + i \sum_{j=1}^N f''_j \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_j). \quad (2.3.4.1)$$

(Note that the only significant contributions to the second term are from those atoms that have a measurable anomalous effect at the chosen wavelength.)

Let us now write the first term as $A + iB$ and the second as $a + ib$. Then, from (2.3.4.1),

$$\mathbf{F} = (A + iB) + i(a + ib) = (A - b) + i(B + a). \quad (2.3.4.2)$$

Therefore,

$$|\mathbf{F}_{\mathbf{h}}|^2 = (A - b)^2 + (B + a)^2$$

and similarly

$$|\mathbf{F}_{\bar{\mathbf{h}}}|^2 = (A + b)^2 + (-B + a)^2,$$

demonstrating that Friedel's law breaks down in the presence of anomalous dispersion. However, it is only for noncentrosymmetric reflections that $|\mathbf{F}_{\mathbf{h}}| \neq |\mathbf{F}_{\bar{\mathbf{h}}}|$.

Now,

$$\rho(\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{h}}^{\text{sphere}} \mathbf{F}_{\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}).$$

Hence, by using (2.3.4.2) and simplifying,

$$\begin{aligned} \rho(\mathbf{x}) = \frac{2}{V} \sum_{\mathbf{h}}^{\text{hemisphere}} [(A \cos 2\pi \mathbf{h} \cdot \mathbf{x} - B \sin 2\pi \mathbf{h} \cdot \mathbf{x}) \\ + i(a \cos 2\pi \mathbf{h} \cdot \mathbf{x} - b \sin 2\pi \mathbf{h} \cdot \mathbf{x})]. \end{aligned} \quad (2.3.4.3)$$

The first term in (2.3.4.3) is the usual real Fourier expression for electron density, while the second term is an imaginary component due to the anomalous scattering of a few atoms in the cell.

2.3.4.2. The $P_s(\mathbf{u})$ function

Expression (2.3.4.3) gives the complex electron density expression in the presence of anomalous scatterers. A variety of Patterson-type functions can be derived from (2.3.4.3) for the determination of a structure. For instance, the $P_s(\mathbf{u})$ function gives vectors between the anomalous atoms and the 'normal' atoms.

From (2.3.4.1) it is easy to show that

$$\begin{aligned} \mathbf{F}_{\mathbf{h}} \mathbf{F}_{\mathbf{h}}^* &= |\mathbf{F}_{\mathbf{h}}|^2 \\ &= \sum_{i,j} (f'_i f'_j + f''_i f''_j) \cos 2\pi \mathbf{h} \cdot (\mathbf{x}_i - \mathbf{x}_j) \\ &\quad + \sum_{i,j} (f'_i f''_j - f''_i f'_j) \sin 2\pi \mathbf{h} \cdot (\mathbf{x}_i - \mathbf{x}_j). \end{aligned}$$

Therefore,

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$$|\mathbf{F}_{\mathbf{h}}|^2 + |\mathbf{F}_{\bar{\mathbf{h}}}|^2 = 2 \sum_{i,j} (f'_i f'_j + f''_i f''_j) \cos 2\pi \mathbf{h} \cdot (\mathbf{x}_i - \mathbf{x}_j)$$

and

$$|\mathbf{F}_{\mathbf{h}}|^2 - |\mathbf{F}_{\bar{\mathbf{h}}}|^2 = 2 \sum_{i,j} (f'_i f''_j - f''_i f'_j) \sin 2\pi \mathbf{h} \cdot (\mathbf{x}_i - \mathbf{x}_j).$$

Let us now consider the significance of a Patterson in the presence of anomalous dispersion. The normal Patterson definition is given by

$$\begin{aligned} P(\mathbf{u}) &= \int_V \rho^*(\mathbf{x}) \rho(\mathbf{x} + \mathbf{u}) d\mathbf{x} \\ &= \frac{1}{V^2} \sum_{\mathbf{h}}^{\text{sphere}} |\mathbf{F}_{\mathbf{h}}|^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{u}) \\ &\equiv P_c(\mathbf{u}) - iP_s(\mathbf{u}), \end{aligned}$$

where

$$P_c(\mathbf{u}) = \frac{2}{V} \sum_{\mathbf{h}}^{\text{hemisphere}} (|\mathbf{F}_{\mathbf{h}}|^2 + |\mathbf{F}_{\bar{\mathbf{h}}}|^2) \cos 2\pi \mathbf{h} \cdot \mathbf{u}$$

and

$$P_s(\mathbf{u}) = \frac{2}{V} \sum_{\mathbf{h}}^{\text{hemisphere}} (|\mathbf{F}_{\mathbf{h}}|^2 - |\mathbf{F}_{\bar{\mathbf{h}}}|^2) \sin 2\pi \mathbf{h} \cdot \mathbf{u}.$$

The $P_c(\mathbf{u})$ component is essentially the normal Patterson, in which the peak heights have been very slightly modified by the anomalous-scattering effect. That is, the peaks of $P_c(\mathbf{u})$ are proportional in height to $(f'_i f'_j + f''_i f''_j)$.

The $P_s(\mathbf{u})$ component is more interesting. It represents vectors between the normal atoms in the unit cell and the anomalous scatterers, proportional in height to $(f'_i f''_j - f''_i f'_j)$ (Okaya *et al.*, 1955). This function is antisymmetric with respect to the change of the direction of the diffraction vector. An illustration of the function is given in Fig. 2.3.4.1. In a unit cell containing N atoms, n of which are anomalous scatterers, the $P_s(\mathbf{u})$ function contains only $n(N - n)$ positive peaks and an equal number of negative peaks related to the former by anticosymmetry. The analysis of a $P_s(\mathbf{u})$ synthesis presents problems somewhat similar to those posed by a normal

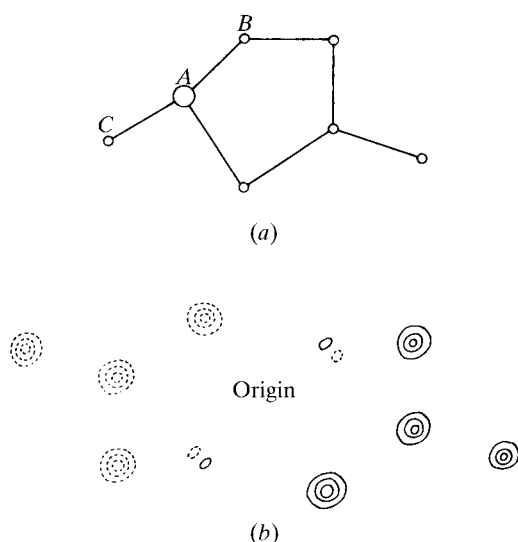


Fig. 2.3.4.1. (a) A model structure with an anomalous scatterer at A. (b) The corresponding $P_s(\mathbf{u})$ function showing positive peaks (full lines) and negative peaks (dashed lines). [Reprinted with permission from Woolfson (1970, p. 293).]

Patterson. The procedure has been used only rarely [cf. Moncrief & Lipscomb (1966) and Pepinsky *et al.* (1957)], probably because alternative procedures are available for small compounds and the solution of $P_s(\mathbf{u})$ is too complex for large biological molecules.

2.3.4.3. The position of anomalous scatterers

Anomalous scatterers can be used as an aid to phasing, when their positions are known. But the anomalous-dispersion differences (Bijvoet differences) can also be used to determine or confirm the heavy atoms which scatter anomalously (Rossmann, 1961a). Furthermore, the use of anomalous-dispersion information obviates the lack of isomorphism but, on the other hand, the differences are normally far smaller than those produced by a heavy-atom isomorphous replacement.

Consider a structure of many light atoms giving rise to the structure factor $\mathbf{F}_{\mathbf{h}}(N)$. In addition, it contains a few heavy atoms which have a significant anomalous-scattering effect. The non-anomalous component will be $\mathbf{F}_{\mathbf{h}}(H)$ and the anomalous component is $\mathbf{F}_{\mathbf{h}}''(H) = i(\Delta f''/f')\mathbf{F}_{\mathbf{h}}(H)$ (Fig. 2.3.4.2a). The total structure factor will be $\mathbf{F}_{\mathbf{h}}$. The Friedel opposite is constructed appropriately (Fig. 2.3.4.2a). Now reflect the Friedel opposite construction across the real axis of the Argand diagram (Fig. 2.3.4.2b). Let the difference in phase between $\mathbf{F}_{\mathbf{h}}$ and $\mathbf{F}_{\bar{\mathbf{h}}}$ be φ . Thus

$$4|\mathbf{F}_{\mathbf{h}}''(H)|^2 = |\mathbf{F}_{\mathbf{h}}|^2 + |\mathbf{F}_{\bar{\mathbf{h}}}|^2 - 2|\mathbf{F}_{\mathbf{h}}||\mathbf{F}_{\bar{\mathbf{h}}}| \cos \varphi,$$

but since φ is very small

$$|\mathbf{F}_{\mathbf{h}}''(H)|^2 \simeq \frac{1}{4}(|\mathbf{F}_{\mathbf{h}}| - |\mathbf{F}_{\bar{\mathbf{h}}}|)^2.$$

Hence, a Patterson with coefficients $(|\mathbf{F}_{\mathbf{h}}| - |\mathbf{F}_{\bar{\mathbf{h}}}|)^2$ will be

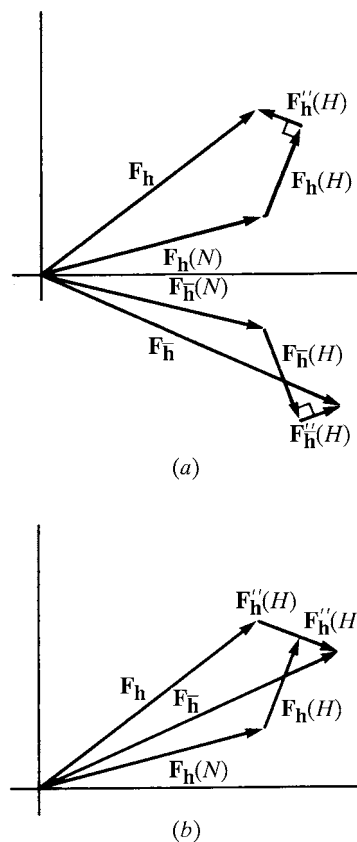


Fig. 2.3.4.2. Anomalous-dispersion effect for a molecule whose light atoms contribute $\mathbf{F}_{\mathbf{h}}(N)$ and heavy atom $\mathbf{F}_{\mathbf{h}}(H)$ with a small anomalous component of $\mathbf{F}_{\mathbf{h}}''(H)$, 90° ahead of the non-anomalous $\mathbf{F}_{\mathbf{h}}(H)$. In (a) is seen the construction for $\mathbf{F}_{\mathbf{h}}$ and $\mathbf{F}_{\bar{\mathbf{h}}}$. In (b) $\mathbf{F}_{\bar{\mathbf{h}}}$ has been reflected across the real axis.

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equivalent to a Patterson with coefficients $|\mathbf{F}_h''(H)|^2$ which is proportional to $|\mathbf{F}_h(H)|^2$. Such a Patterson (Rossmann, 1961a) will have vectors between all anomalous scatterers with heights proportional to the number of anomalous electrons $\Delta f''$. This 'anomalous dispersion' Patterson function has been used to find anomalous scatterers such as iron (Smith *et al.*, 1983; Strahs & Kraut, 1968) and sulfur atoms (Hendrickson & Teeter, 1981).

It is then apparent that a Patterson with coefficients

$$\Delta F_{\text{ANO}}^2 = (|\mathbf{F}_h| - |\mathbf{F}_{\bar{h}}|)^2$$

(Rossmann, 1961a), as well as a Patterson with coefficients

$$\Delta F_{\text{ISO}}^2 = (|\mathbf{F}_{NH}| - |\mathbf{F}_H|)^2$$

(Rossmann, 1960; Blow, 1958), represent Pattersons of the heavy atoms. The ΔF_{ANO}^2 Patterson suffers from errors which may be larger than the size of the Bijvoet differences, while the ΔF_{ISO}^2 Patterson may suffer from partial lack of isomorphism. Hence, Kartha & Parthasarathy (1965) have suggested the use of the sum of these two Pattersons, which would then have coefficients $(\Delta F_{\text{ANO}}^2 + \Delta F_{\text{ISO}}^2)$.

However, given both SIR and anomalous-dispersion data, it is possible to make an accurate estimate of the $|\mathbf{F}_H|^2$ magnitudes for use in a Patterson calculation [Blundell & Johnson (1976, p. 340), Matthews (1966), Singh & Ramaseshan (1966)]. In essence, the Harker phase diagram can be constructed out of three circles: the native amplitude and each of the two isomorphous Bijvoet differences, giving three circles in all (Blow & Rossmann, 1961) which should intersect at a single point thus resolving the ambiguity in the SIR data and the anomalous-dispersion data. Furthermore, the phase ambiguities are orthogonal; thus the two data sets are cooperative. It can be shown (Matthews, 1966; North, 1965) that

$$F_N^2 = F_{NH}^2 + F_H^2 \mp \frac{2}{k}(16k^2 F_P^2 F_H^2 - \Delta I^2)^{1/2},$$

where $\Delta I = F_{NH}^{+2} - F_{NH}^{-2}$ and $k = \Delta f''/f'$. The sign in the third-term expression is $-$ when $|(\alpha_{NH} - \alpha_H)| < \pi/2$ or $+$ otherwise. Since, in general, $|\mathbf{F}_H|$ is small compared to $|\mathbf{F}_N|$, it is reasonable to assume that the sign above is usually negative. Hence, the heavy-atom lower estimate (HLE) is usually written as

$$F_{\text{HLE}}^2 = F_{NH}^2 + F_H^2 - \frac{2}{k}(16k^2 F_P^2 F_H^2 - \Delta I^2)^{1/2},$$

which is an expression frequently used to derive Patterson coefficients useful in the determination of heavy-atom positions when both SIR and anomalous-dispersion data are available.

2.3.5. Noncrystallographic symmetry

2.3.5.1. Definitions

The interpretation of Pattersons can be helped by using various types of chemical or physical information. An obvious example is the knowledge that one or two heavy atoms per crystallographic asymmetric unit are present. Another example is the exploitation of a rigid chemical framework in a portion of a molecule (Nordman & Nakatsu, 1963; Burnett & Rossmann, 1971). One extremely useful constraint on the interpretation of Pattersons is noncrystallographic symmetry. Indeed, the structural solution of large biological assemblies such as viruses is only possible because of the natural occurrence of this phenomenon. The term 'molecular replacement' is used for methods that utilize noncrystallographic symmetry in the solution of structures [for earlier reviews see Rossmann (1972) and Argos & Rossmann (1980)]. These methods, which are only partially dependent on Patterson concepts, are discussed in Sections 2.3.6–2.3.8.

Crystallographic symmetry applies to the whole of the three-dimensional crystal lattice. Hence, the symmetry must be expressed both in the lattice and in the repeating pattern within the lattice. In contrast, noncrystallographic symmetry is valid only within a limited volume about the noncrystallographic symmetry element. For instance, the noncrystallographic twofold axes in the plane of the paper of Fig. 2.3.5.1 are true only in the immediate vicinity of each local dyad. In contrast, the crystallographic twofold axes perpendicular to the plane of the paper (Fig. 2.3.5.1) apply to every point within the lattice. Two types of noncrystallographic symmetry can be recognized: proper and improper rotations. A proper symmetry element is independent of the sense of rotation, as, for example, a fivefold axis in an icosahedral virus; a rotation either left or right by one-fifth of a revolution will leave all parts of a given icosahedral shell (but not the whole crystal) in equivalent positions. Proper noncrystallographic symmetry can also be recognized by the existence of a closed point group within a defined volume of the lattice. Improper rotation axes are found when two molecules are arbitrarily oriented relative to each other in the same asymmetric unit or when they occur in two entirely different crystal lattices. For instance, in Fig. 2.3.5.2, the object A_1B_1 can be rotated by $+\theta$ about the axis at P to orient it identically with A_2B_2 . However, the two objects will not be coincident after a rotation of A_1B_1 by $-\theta$ or of A_2B_2 by $+\theta$. The envelope around each noncrystallographic object must be known in order to define an improper rotation. In contrast, only the volume about the closed point group need be defined for proper noncrystallographic operations. Hence, the boundaries of the repeating unit need not correspond to chemically covalently linked units in the presence of proper rotations.

Translational components of noncrystallographic rotation elements are said to be 'precise' in a direction parallel to the axis and

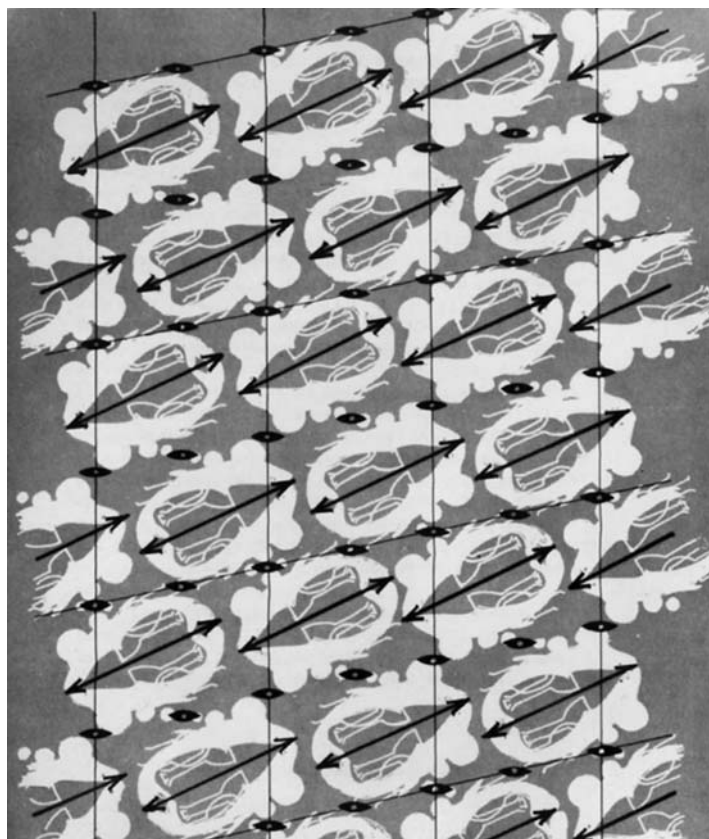


Fig. 2.3.5.1. The two-dimensional periodic design shows crystallographic twofold axes perpendicular to the page and local noncrystallographic rotation axes in the plane of the paper (design by Audrey Rossmann). [Reprinted with permission from Rossmann (1972, p. 8).]

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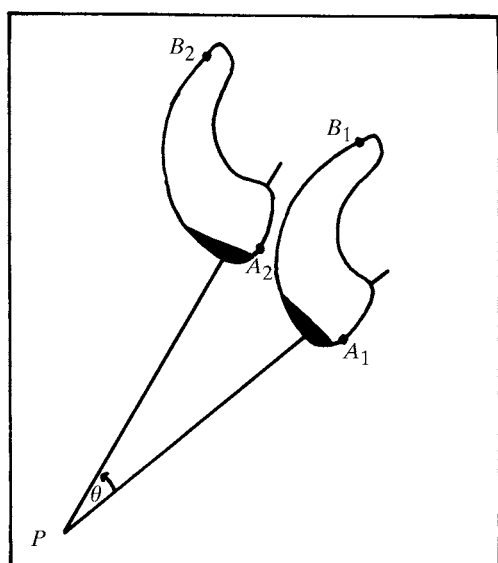


Fig. 2.3.5.2. The objects A_1B_1 and A_2B_2 are related by an improper rotation θ , since it is necessary to consider the sense of rotation to achieve superposition of the two objects. [Reprinted with permission from Rossmann (1972, p. 9).]

'imprecise' perpendicular to the axis (Rossmann *et al.*, 1964). The position, but not direction, of a rotation axis is arbitrary. However, a convenient choice is one that leaves the translation perpendicular to the axis at zero after rotation (Fig. 2.3.5.3).

Noncrystallographic symmetry has been used as a tool in structural analysis primarily in the study of biological molecules. This is due to the propensity of proteins to form aggregates with closed point groups, as, for instance, viruses with 532 symmetry. At best, only part of such a point group can be incorporated into the crystal lattice. Since biological materials cannot contain inversion elements, all studies of noncrystallographic symmetries have been limited to rotational axes. Reflection planes and inversion centres

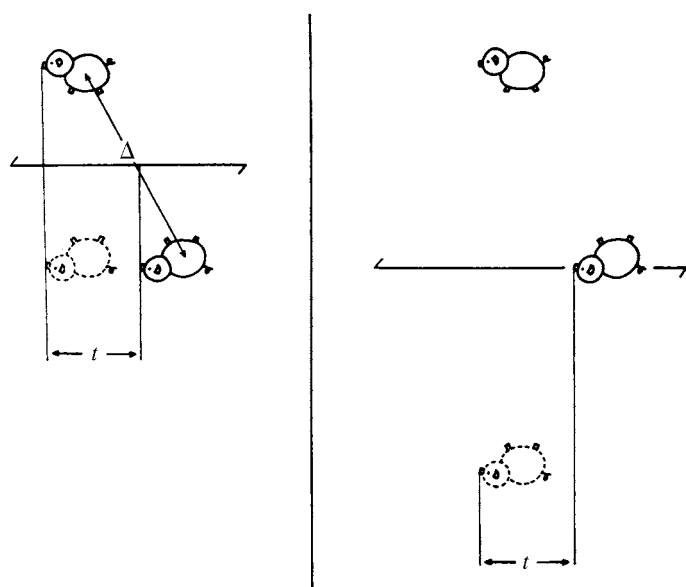


Fig. 2.3.5.3. The position of the twofold rotation axis which relates the two piglets is completely arbitrary. The diagram on the left shows the situation when the translation is parallel to the rotation axis. The diagram on the right has an additional component of translation perpendicular to the rotation axis, but the component parallel to the axis remains unchanged. [Reprinted from Rossmann *et al.* (1964).]

could also be considered in the application of molecular replacement to non-biological materials.

In this chapter, the relationship

$$\mathbf{x}' = [\mathbf{C}]\mathbf{x} + \mathbf{d}$$

will be used to describe noncrystallographic symmetry, where $\mathbf{x}$ and $\mathbf{x}'$ are position vectors, expressed as fractional coordinates, with respect to the crystallographic origin, $[\mathbf{C}]$ is a rotation matrix, and $\mathbf{d}$ is a translation vector. Crystallographic symmetry will be described as

$$\mathbf{x}' = [\mathbf{T}]\mathbf{x} + \mathbf{t},$$

where $[\mathbf{T}]$ and $\mathbf{t}$ are the crystallographic rotation matrix and translation vector, respectively. The noncrystallographic asymmetric unit will be defined as having n copies within the crystallographic asymmetric unit, and the unit cell will be defined as having m crystallographic asymmetric units. Hence, there are $L = nm$ noncrystallographic asymmetric units within the unit cell. Clearly, the n noncrystallographic asymmetric units cannot completely fill the volume of one crystallographic asymmetric unit. The remaining space must be assumed to be empty or to be occupied by solvent molecules which disobey the noncrystallographic symmetry.

2.3.5.2. Interpretation of Pattersons in the presence of noncrystallographic symmetry

If noncrystallographic symmetry is present, an atom at a general position within the relevant volume will imply the presence of others within the same crystallographic asymmetric unit. If the noncrystallographic symmetry is known, then the positions of equivalent atoms may be generated from a single atomic position. The additional vector interactions which arise from crystallographically and noncrystallographically equivalent atoms in a crystal may be predicted and exploited in an interpretation of the Patterson function.

An object in real space which has a closed point group may incorporate some of its symmetry in the crystallographic symmetry. If there are l such objects in the cell, then there will be mn/l equivalent positions within each object. The 'self-vectors' formed between these positions within the object will be independent of the position of the objects. This distinction is important in that the self-vectors arising from atoms interacting with other atoms within a single particle may be correctly predicted without the knowledge of the particle centre position. In fact, this distinction may be exploited in a two-stage procedure in which an atom may be first located relative to the particle centre by use of the self-vectors and subsequently the particle may be positioned relative to crystallographic symmetry elements by use of the 'cross-vectors' (Table 2.3.5.1).

The interpretation of a heavy-atom difference Patterson for the holo-enzyme of lobster glyceraldehyde-3-phosphate dehydrogenase (GAPDH) provides an illustration of how the known noncrystallographic symmetry can aid the solution (Rossmann *et al.*, 1972; Buehner *et al.*, 1974). The GAPDH enzyme crystallized in a $P2_12_12_1$ cell ($a = 149.0$, $b = 139.1$, $c = 80.7$ Å) containing one tetramer per asymmetric unit. A rotation-function analysis had indicated the presence of three mutually perpendicular molecular twofold axes which suggested that the tetramer had 222 symmetry, and a locked rotation function determined the precise orientation of the tetramer relative to the crystal axes (see Table 2.3.5.2). Packing considerations led to assignment of a tentative particle centre near $\frac{1}{2}, \frac{1}{4}, Z$.

An isomorphous difference Patterson was calculated for the K_2HgI_4 derivative of GAPDH using data to a resolution of 6.8 Å. From an analysis of the three Harker sections, a tentative first

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Table 2.3.5.1. Possible types of vector searches

Self-vectors	Cross-vectors	Dimension of search, n
(1) Locate single site relative to particle centre		$n = 3$
(2)	Use information from (1) to locate particle centre	$n \leq 3$
(3) Simultaneous search for both (1) and (2). In general this is a six-dimensional search but may be simplified when particle is on a crystallographic symmetry axis		$3 \leq n \leq 6$
(4) Given (1) for more than one site, find all vectors within particle		$n = 3$
(5) Given information from (3), locate additional site using complete vector set		$n = 3$

heavy-atom position was assigned (atom A_2 at x, y, z). At this juncture, the known noncrystallographic symmetry was used to obtain a full interpretation. From Table 2.3.5.2 we see that molecular axis 2 will generate a second heavy atom with co-ordinates roughly $\frac{1}{4} + y, -\frac{1}{4} + x, 2Z - z$ (if the molecular centre was assumed to be at $\frac{1}{2}, \frac{1}{4}, Z$). Starting from the tentative coordinates of site A_2 , the site A_1 related by molecular axis 1 was detected at about the predicted position and the second site A_1 generated acceptable cross-vectors with the earlier determined site A_2 . Further examination enabled the completion of the set of four noncrystallographically related heavy-atom sites, such that all predicted Patterson vectors were acceptable and all four sites placed the molecular centre in the same position. Following refinement of these four sites, the corresponding SIR phases were used to find an additional set of four sites in this compound as well as in a number of other derivatives. The multiple isomorphous replacement phases, in conjunction with real-space electron-density averaging of the noncrystallographically related units, were then sufficient to solve the GAPDH structure.

When investigators studied larger macromolecular aggregates such as the icosahedral viruses, which have 532 point symmetry, systematic methods were developed for utilizing the noncrystallographic symmetry to aid in locating heavy-atom sites in isomorphous heavy-atom derivatives. Argos & Rossmann (1974, 1976) introduced an exhaustive Patterson search procedure for a single heavy-atom site within the noncrystallographic asymmetric unit which has been successfully applied to the interpretation of both virus [satellite tobacco necrosis virus (STNV) (Lentz *et al.*, 1976), southern bean mosaic virus (Rayment *et al.*, 1978), alfalfa mosaic virus (Fukuyama *et al.*, 1983), cowpea mosaic virus

(Stauffer *et al.*, 1987)] and enzyme [catalase (Murthy *et al.*, 1981)] heavy-atom difference Pattersons. A heavy atom is placed in turn at all plausible positions within the volume of the noncrystallographic asymmetric unit and the corresponding vector set is constructed from the resulting constellation of heavy atoms. Argos & Rossmann (1976) found a spherical polar coordinate search grid to be convenient for spherical viruses. After all vectors for the current search position are predicted, the vectors are allocated to the nearest grid point and the list is sorted to eliminate recurring ones. The criterion used by Argos & Rossmann for selecting a solution is that the sum

$$S = \sum_{i=1}^N P_i - NP_{av}$$

of the lookup Patterson density values P_i achieves a high value for a correct heavy-atom position. The sum is corrected for the carpet of cross-vectors by the second term in the sum.

An additional criterion, which has been found useful for discriminating correct solutions, is a unit vector density criterion

$$U = \sum_{i=1}^N (P_i/n_i) / N,$$

where n_i is the number of vectors expected to contribute to the Patterson density value P_i (Arnold *et al.*, 1987). This criterion can be especially valuable for detecting correct solutions at special search positions, such as an icosahedral fivefold axis, where the number of vector lookup positions may be drastically reduced owing to the higher symmetry. An alternative, but equivalent, method for locating heavy-atom positions from isomorphous difference data is discussed in Section 2.3.3.5.

Even for a single heavy-atom site at a general position in the simplest icosahedral or ($T = 1$) virus, there are 60 equivalent heavy atoms in one virus particle. The number of unique vectors corresponding to this self-particle vector set will depend on the crystal symmetry but may be as many as $(60)(59)/2 = 1770$ for a virus particle at a general crystallographic position. Such was the case for the STNV crystals which were in space group $C2$ containing four virus particles at general positions. The method of Argos & Rossmann was applied successfully to a solution of the K_2HgI_4 derivative of STNV using a 10 Å resolution difference Patterson. Application of the noncrystallographic symmetry vector search procedure to a $K_2Au(CN)_2$ derivative of human rhinovirus 14 (HRV14) crystals (space group $P2_13, Z = 4$) has succeeded in establishing both the relative positions of heavy atoms within one particle and the positions of the virus particles relative to the crystal symmetry elements (Arnold *et al.*, 1987). The particle position was established by incorporating interparticle vectors in the search and varying the particle position along the crystallographic threefold axis until the best fit for the predicted vector set was achieved.

2.3.6. Rotation functions

2.3.6.1. Introduction

The rotation function is designed to detect noncrystallographic rotational symmetry (see Table 2.3.6.1). The normal rotation function definition is given as (Rossmann & Blow, 1962)

$$R = \int_U P_1(\mathbf{u}) \cdot P_2(\mathbf{u}') d\mathbf{u}, \quad (2.3.6.1)$$

where P_1 and P_2 are two Pattersons and U is an envelope centred at the superimposed origins. This convolution therefore measures the degree of similarity, or 'overlap', between the two Pattersons when P_2 has been rotated relative to P_1 by an amount defined by

Table 2.3.5.2. Orientation of the glyceraldehyde-3-phosphate dehydrogenase molecular twofold axis in the orthorhombic cell

Rotation axes	Polar coordinates (°)		Cartesian coordinates (direction cosines)		
	ψ	φ	u	v	w
1	45.0	-7.0	0.7018	0.7071	-0.0862
2	180.0-55.0	38.6	0.6402	-0.5736	0.5111
3	180.0-66.0	-70.6	0.3035	-0.4067	-0.8616

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Table 2.3.6.1. *Different types of uses for the rotation function*

Type of rotation function	Pattersons to be compared		Purpose
	P_1	P_2	
Self	Unknown structure	Unknown structure, same cell	Finds orientation of noncrystallographic axes
Cross	Unknown structure	Unknown structure in different cell	Finds relative orientation of unknown molecules
Cross	Unknown structure	Known structure in large cell to avoid overlap of self-Patterson vectors	Determines orientation of unknown structure as preliminary to positioning and subsequent phasing with known molecule

$$\mathbf{u}' = [\mathbf{C}]\mathbf{u}. \quad (2.3.6.2)$$

The elements of $[\mathbf{C}]$ will depend on three rotation angles $(\theta_1, \theta_2, \theta_3)$. Thus, R is a function of these three angles. Alternatively, the matrix $[\mathbf{C}]$ could be used to express mirror symmetry, permitting searches for noncrystallographic mirror or glide planes.

The basic concepts were first clearly stated by Rossmann & Blow (1962), although intuitive uses of the rotation function had been considered earlier. Hoppe (1957*b*) had also hinted at a convolution of the type given by (2.3.6.1) to find the orientation of known molecular fragments and these ideas were implemented by Huber (1965).

Consider a structure of two identical units which are in different orientations. The Patterson function of such a structure consists of three parts. There will be the self-Patterson vectors of one unit, being the set of interatomic vectors which can be formed within that unit, with appropriate weights. The set of self-Patterson vectors of the other unit will be identical, but they will be rotated away from the first due to the different orientation. Finally, there will be the cross-Patterson vectors, or set of interatomic vectors which can be formed from one unit to another. The self-Patterson vectors of the two units will all lie in a volume centred at the origin and limited by the overall dimensions of the units. Some or all of the cross-Patterson vectors will lie outside this volume. Suppose the Patterson function is now superposed on a rotated version of itself. There will be no particular agreement except when one set of self-Patterson vectors of one unit has the same orientation as the self-Patterson vectors from the other unit. In this position, we would expect a maximum of agreement or 'overlap' between the two. Similarly, the superposition of the molecular self-Patterson derived from different crystal forms can provide the relative orientation of the two crystals when the molecules are aligned.

While it would be possible to evaluate R by interpolating in P_2 and forming the point-by-point product with P_1 within the volume U for every combination of θ_1, θ_2 and θ_3 , such a process is tedious and requires large computer storage for the Pattersons. Instead, the process is usually performed in reciprocal space where the number of independent structure amplitudes which form the Pattersons is about one-thirtieth of the number of Patterson grid points. Thus, the computation of a rotation function is carried out directly on the structure amplitudes, while the overlap definition (2.3.6.1) simply serves as a physical basis for the technique.

The derivation of the reciprocal-space expression depends on the expansion of each Patterson either as a Fourier summation, the conventional approach of Rossmann & Blow (1962), or as a sum of spherical harmonics in Crowther's (1972) analysis. The conventional and mathematically easier treatment is discussed presently, but the reader is referred also to Section 2.3.6.5 for Crowther's elegant approach. The latter leads to a rapid technique for

performing the computations, about one hundred times faster than conventional methods.

Let, omitting constant coefficients,

$$P_1(\mathbf{u}) = \sum_{\mathbf{h}} |\mathbf{F}_{\mathbf{h}}|^2 \exp(2\pi i \mathbf{h} \cdot \mathbf{u})$$

and

$$P_2(\mathbf{u}') = \sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 \exp(2\pi i \mathbf{p} \cdot \mathbf{u}').$$

From (2.3.6.2) it follows that

$$P_2(\mathbf{u}') = \sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 \exp(2\pi i \mathbf{p} [\mathbf{C}] \cdot \mathbf{u}),$$

and, hence, by substitution in (2.3.6.1)

$$\begin{aligned} R(\theta_1, \theta_2, \theta_3) &= \int_U \left[\sum_{\mathbf{h}} |\mathbf{F}_{\mathbf{h}}|^2 \exp(2\pi i \mathbf{h} \cdot \mathbf{u}) \right] \\ &\quad \times \left[\sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 \exp(2\pi i \mathbf{p} [\mathbf{C}] \cdot \mathbf{u}) \right] d\mathbf{u} \\ &= U \sum_{\mathbf{h}} |\mathbf{F}_{\mathbf{h}}|^2 \left(\sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 G_{\mathbf{hp}} \right), \end{aligned} \quad (2.3.6.3)$$

where

$$UG_{\mathbf{hp}} = \int_U \exp\{2\pi i (\mathbf{h} + \mathbf{p}[\mathbf{C}]) \cdot \mathbf{u}\} d\mathbf{u}.$$

When the volume U is a sphere, $G_{\mathbf{hp}}$ has the analytical form

$$G_{\mathbf{hp}} = \frac{3(\sin \theta - \theta \cos \theta)}{\theta^3}, \quad (2.3.6.4)$$

where $\theta = 2\pi H R$ and $H = \mathbf{h} + \mathbf{p}[\mathbf{C}]$. G is a spherical interference function whose form is shown in Fig. 2.3.6.1

The expression (2.3.6.3) represents the rotation function in reciprocal space. If $\mathbf{h}' = [\mathbf{C}^T]\mathbf{p}$ in the argument of $G_{\mathbf{hp}}$, then $\mathbf{h}'$ can be seen as the point in reciprocal space to which $\mathbf{p}$ is rotated by $[\mathbf{C}]$. Only for those integral reciprocal-lattice points which are close to $\mathbf{h}'$ will $G_{\mathbf{hp}}$ be of an appreciable size (Fig. 2.3.6.1). Thus, the number of significant terms is greatly reduced in the summation over $\mathbf{p}$ for every value of $\mathbf{h}$, making the computation of the rotation function manageable.

The radius of integration R should be approximately equal to or a little smaller than the molecular diameter. If R were roughly equal to the length of a lattice translation, then the separation of reciprocal-lattice points would be about $1/R$. Hence, when H is equal to one reciprocal-lattice separation, $HR \simeq 1$, and G is thus

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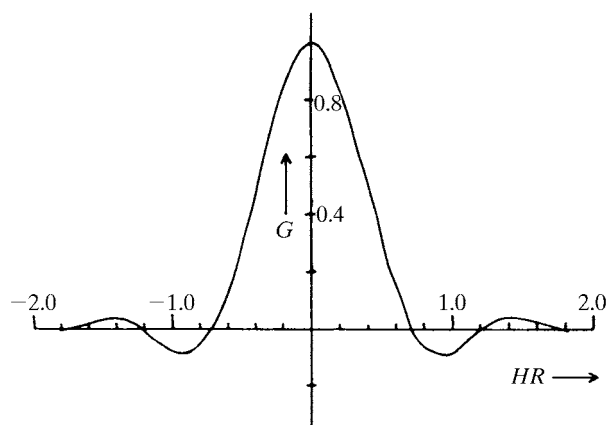


Fig. 2.3.6.1. Shape of the interference function G for a spherical envelope of radius R at a distance H from the reciprocal-space origin. [Reprinted from Rossmann & Blow (1962).]

quite small. Indeed, all terms with $HR > 1$ might well be neglected. Thus, in general, the only terms that need be considered are those where $-\mathbf{h}'$ is within one lattice point of $\mathbf{h}$. However, in dealing with a small molecular fragment for which R is small compared to the unit-cell dimensions, more reciprocal-lattice points must be included for the summation over $\mathbf{p}$ in the rotation-function expression (2.3.6.3).

In practice, the equation

$$\mathbf{h} + \mathbf{h}' = 0,$$

that is

$$[\mathbf{C}^T]\mathbf{p} = -\mathbf{h}$$

or

$$\mathbf{p} = [\mathbf{C}^T]^{-1}(-\mathbf{h}), \quad (2.3.6.5)$$

determines $\mathbf{p}$, given a set of Miller indices $\mathbf{h}$. This will give a non-integral set of Miller indices. The terms included in the inner summation of (2.3.6.3) will be integral values of $\mathbf{p}$ around the non-integral lattice point found by solving (2.3.6.5).

Details of the conventional program were given by Tollin & Rossmann (1966) and follow the principles outlined above. They discussed various strategies as to which crystal should be used to calculate the first ($\mathbf{h}$) and second ($\mathbf{p}$) Patterson. Rossmann & Blow (1962) noted that the factor $\sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 G_{\mathbf{h}\mathbf{p}}$ in expression (2.3.6.3) represents an interpolation of the squared transform of the self-Patterson of the second ($\mathbf{p}$) crystal. Thus, the rotation function is a sum of the products of the two molecular transforms taken over all the $\mathbf{h}$ reciprocal-lattice points. Lattman & Love (1970) therefore computed the molecular transform explicitly and stored it in the computer, sampling it as required by the rotation operation. A discussion on the suitable choice of variables in the computation of rotation functions has been given by Lifchitz (1983).

2.3.6.2. Matrix algebra

The initial step in the rotation-function procedure involves the orthogonalization of both crystal systems. Thus, if fractional coordinates in the first crystal system are represented by $\mathbf{x}$, these can be orthogonalized by a matrix $[\beta]$ to give the coordinates $\mathbf{X}$ in units of length (Fig. 2.3.6.2); that is,

$$\mathbf{X} = [\beta]\mathbf{x}.$$

If the point $\mathbf{X}$ is rotated to the point $\mathbf{X}'$, then

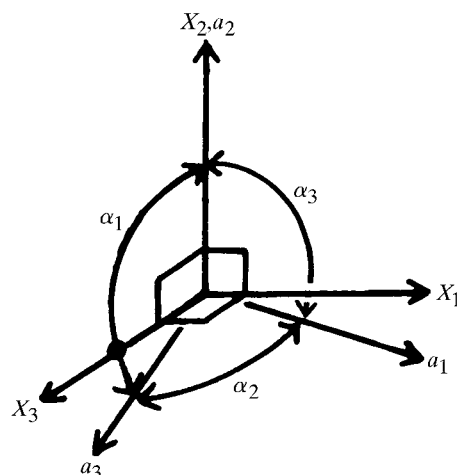


Fig. 2.3.6.2. Relationships of the orthogonal axes X_1, X_2, X_3 to the crystallographic axes a_1, a_2, a_3 . [Reprinted from Rossmann & Blow (1962).]

$$\mathbf{X}' = [\rho]\mathbf{X}, \quad (2.3.6.6)$$

where ρ represents the rotation matrix relating the two vectors in the orthogonal system. Finally, $\mathbf{X}'$ is converted back to fractional coordinates measured along the oblique cell dimension in the second crystal by

$$\mathbf{x}' = [\alpha]\mathbf{X}'.$$

Thus, by substitution,

$$\mathbf{x}' = [\alpha][\rho]\mathbf{X} = [\alpha][\rho][\beta]\mathbf{x}, \quad (2.3.6.7)$$

and by comparison with (2.3.6.2) it follows that

$$[\mathbf{C}] = [\alpha][\rho][\beta].$$

Fig. 2.3.6.2 shows the mode of orthogonalization used by Rossmann & Blow (1962). With their definition it can be shown that

$$[\alpha] = \begin{pmatrix} 1/(a_1 \sin \alpha_3 \sin \omega) & 0 & 0 \\ 1/(a_2 \tan \alpha_1 \tan \omega) & 1/a_2 & -1/(a_2 \tan \alpha_1) \\ -1/(a_2 \tan \alpha_3 \sin \omega) & 0 & 1/(a_3 \sin \alpha_1) \end{pmatrix}$$

and

$$[\beta] = \begin{pmatrix} a_1 \sin \alpha_3 \sin \omega & 0 & 0 \\ a_1 \cos \alpha_3 & a_2 & a_3 \cos \alpha_1 \\ a_1 \sin \alpha_3 \cos \omega & 0 & a_3 \sin \alpha_1 \end{pmatrix},$$

where $\cos \omega = (\cos \alpha_2 - \cos \alpha_1 \cos \alpha_3)/(\sin \alpha_1 \sin \alpha_3)$ with $0 \leq \omega < \pi$. For a Patterson compared with itself, $[\alpha] = [\beta]^{-1}$.

Both spherical (κ, ψ, φ) and Eulerian ($\theta_1, \theta_2, \theta_3$) angles are used in evaluating the rotation function. The usual definitions employed are given diagrammatically in Figs. 2.3.6.3 and 2.3.6.4. They give rise to the following rotation matrices.

(a) Matrix $[\rho]$ in terms of Eulerian angles $\theta_1, \theta_2, \theta_3$:

$$\begin{pmatrix} -\sin \theta_1 \cos \theta_2 \sin \theta_3 & \cos \theta_1 \cos \theta_2 \sin \theta_3 & \sin \theta_2 \sin \theta_3 \\ +\cos \theta_1 \cos \theta_3 & +\sin \theta_1 \cos \theta_3 & \\ -\sin \theta_1 \cos \theta_2 \cos \theta_3 & \cos \theta_1 \cos \theta_2 \cos \theta_3 & \sin \theta_2 \cos \theta_3 \\ -\cos \theta_1 \sin \theta_3 & -\sin \theta_1 \sin \theta_3 & \\ \sin \theta_1 \sin \theta_2 & -\cos \theta_1 \sin \theta_2 & \cos \theta_2 \end{pmatrix}$$

and (b) matrix $[\rho]$ in terms of rotation angle κ and the spherical polar coordinates ψ, φ :

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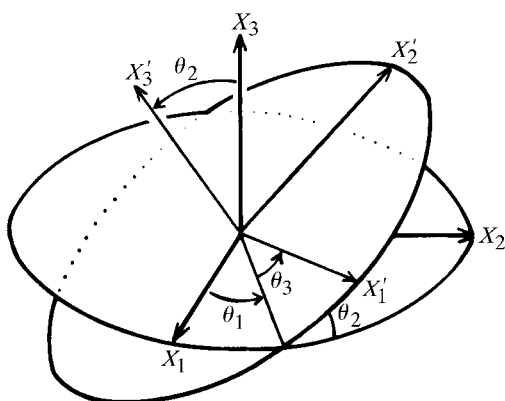


Fig. 2.3.6.3. Eulerian angles $\theta_1, \theta_2, \theta_3$ relating the rotated axes X'_1, X'_2, X'_3 to the original unrotated orthogonal axes X_1, X_2, X_3 . [Reprinted from Rossmann & Blow (1962).]

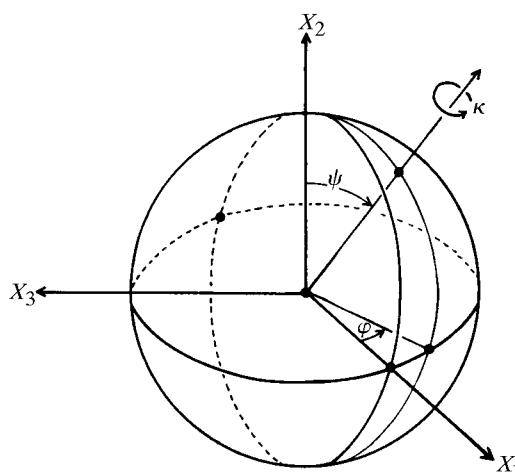


Fig. 2.3.6.4. Variables ψ and φ are polar coordinates which specify a direction about which the axes may be rotated through an angle κ . [Reprinted from Rossmann & Blow (1962).]

$$\begin{pmatrix} \cos \kappa + \sin^2 \psi \cos^2 \varphi (1 - \cos \kappa) & \sin \psi \cos \psi \cos \varphi (1 - \cos \kappa) \\ & + \sin \psi \sin \varphi \sin \kappa \\ \sin \psi \cos \psi \cos \varphi (1 - \cos \kappa) & \cos \kappa + \cos^2 \psi (1 - \cos \kappa) \\ & - \sin \psi \sin \varphi \sin \kappa \\ - \sin^2 \psi \sin \varphi \cos \varphi (1 - \cos \kappa) & - \sin \psi \cos \psi \sin \varphi (1 - \cos \kappa) \\ & - \cos \psi \sin \kappa \\ & + \sin \psi \cos \varphi \sin \kappa \\ & - \sin^2 \psi \cos \varphi \sin \varphi (1 - \cos \kappa) \\ & + \cos \psi \sin \kappa \\ & - \sin \psi \cos \psi \sin \varphi (1 - \cos \kappa) \\ & - \sin \psi \cos \varphi \sin \kappa \\ \cos \kappa + \sin^2 \psi \sin^2 \varphi (1 - \cos \kappa) \end{pmatrix}$$

Alternatively, (b) can be expressed as

$$\begin{pmatrix} \cos \kappa + u^2(1 - \cos \kappa) & uv(1 - \cos \kappa) - w \sin \kappa \\ vu(1 - \cos \kappa) + w \sin \kappa & \cos \kappa + v^2(1 - \cos \kappa) \\ wu(1 - \cos \kappa) - v \sin \kappa & wv(1 - \cos \kappa) + u \sin \kappa \\ & uw(1 - \cos \kappa) + v \sin \kappa \\ & uw(1 - \cos \kappa) - u \sin \kappa \\ & \cos \kappa + w^2(1 - \cos \kappa) \end{pmatrix},$$

where u, v and w are the direction cosines of the rotation axis given by

$$\begin{aligned} u &= \sin \psi \cos \varphi, \\ v &= \cos \psi, \\ w &= -\sin \psi \sin \varphi. \end{aligned}$$

This latter form also demonstrates that the trace of a rotation matrix is $2 \cos \kappa + 1$.

The relationship between the two sets of variables established by comparison of the elements of the two matrices yields

$$\begin{aligned} \cos(\kappa/2) &= \cos(\theta_2/2) \cos\left(\frac{\theta_1 + \theta_3}{2}\right), \\ \tan \varphi &= -\cot(\theta_2/2) \sin\left(\frac{\theta_1 + \theta_3}{2}\right) \sec\left(\frac{\theta_1 - \theta_3}{2}\right), \\ \cos \varphi \tan \psi &= \cot\left(\frac{\theta_1 - \theta_3}{2}\right). \end{aligned}$$

Since φ and ψ can always be chosen in the range 0 to π , these equations suffice to find (κ, ψ, φ) from any set $(\theta_1, \theta_2, \theta_3)$.

2.3.6.3. Symmetry

In analogy with crystal lattices, the rotation function is periodic and contains symmetry. The rotation function has a cell whose periodicity is 2π in each of its three angles. This may be written as

$$R(\theta_1, \theta_2, \theta_3) \equiv R(\theta_1 + 2\pi n_1, \theta_2 + 2\pi n_2, \theta_3 + 2\pi n_3)$$

or

$$R(\kappa, \psi, \varphi) \equiv R(\kappa + 2\pi n_1, \psi + 2\pi n_2, \varphi + 2\pi n_3),$$

where n_1, n_2 and n_3 are integers. A redundancy in the definition of either set of angles leads to the equivalence of the following points:

$$R(\theta_1, \theta_2, \theta_3) \equiv R(\theta_1 + \pi, -\theta_2, \theta_3 + \pi) \quad \text{in Eulerian space}$$

or

$$R(\kappa, \psi, \varphi) \equiv R(\kappa, 2\pi - \psi, \varphi + \pi) \quad \text{in polar space.}$$

These relationships imply an n glide plane perpendicular to θ_2 for Eulerian space or a φ glide plane perpendicular to ψ in polar space.

In addition, the Laue symmetry of the two Pattersons themselves must be considered. This problem was first discussed by Rossmann & Blow (1962) and later systematized by Tollin *et al.* (1966), Burdina (1970, 1971, 1973) and Rao *et al.* (1980). A closely related problem was considered by Hirshfeld (1968). The rotation function will have the same value whether the Patterson density at $\mathbf{X}$ or $[T_i]\mathbf{X}$ in the first crystal is multiplied by the Patterson density at $\mathbf{X}'$ or $[T_j]\mathbf{X}'$ in the second crystal. $[T_i]$ and $[T_j]$ refer to the i th and j th crystallographic rotations in the orthogonalized coordinate systems of the first and second crystal, respectively. Hence, from (2.3.6.6)

$$([T_j]\mathbf{X}') = [\rho]([T_i]\mathbf{X})$$

or

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Table 2.3.6.2. Eulerian symmetry elements for all possible types of space-group rotations

Axis	Direction	First crystal	Second crystal
1		$(\pi + \theta_1, -\theta_2, \pi + \theta_3)$	$(\pi + \theta_1, -\theta_2, \pi + \theta_3)$
2	[010]	$(\pi - \theta_1, \pi + \theta_2, \theta_3)$	$(\theta_1, \pi + \theta_2, \pi - \theta_3)$
2	[001]	$(\pi + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi + \theta_3)$
4	[001]	$(-\pi/2 + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi/2 + \theta_3)$
3	[001]	$(-2\pi/3 + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, 2\pi/3 + \theta_3)$
6	[001]	$(-\pi/3 + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi/3 + \theta_3)$
2*	[110]	$(3\pi/2 - \theta_1, \pi - \theta_2, \pi + \theta_3)$	$(\pi + \theta_1, \pi - \theta_2, -3\pi/2 - \theta_3)$

* This axis is not unique (that is, it can always be generated by two other unique axes), but is included for completeness.

$$\mathbf{X}' = [\mathbf{T}_j^T][\boldsymbol{\rho}][\mathbf{T}_i]\mathbf{X}.$$

Thus, it is necessary to find angular relationships which satisfy the relation

$$[\boldsymbol{\rho}] = [\mathbf{T}_j^T][\boldsymbol{\rho}][\mathbf{T}_i]$$

for given Patterson symmetries. Tollin *et al.* (1966) show that the Eulerian angular equivalences can be expressed in terms of the Laue symmetries of each Patterson (Table 2.3.6.2).

The example given by Tollin *et al.* (1966) is instructive in the use of Table 2.3.6.2. They consider the determination of the Eulerian space group when P_1 has symmetry $Pmmm$ and P_2 has symmetry $P2/m$. These Pattersons contain the proper rotation groups 222 and 2 (parallel to **b**), respectively. Inspection of Table 2.3.6.2 shows that these symmetries produce the following Eulerian relationships:

(a) In the first crystal ($Pmmm$):

- $\theta_1\theta_2\theta_3 \rightarrow \pi + \theta_1, -\theta_2, \pi + \theta_3$ (onefold axis)
- $\theta_1\theta_2\theta_3 \rightarrow \pi - \theta_1, \pi + \theta_2, \theta_3$ (twofold axis parallel to **b**)
- $\theta_1\theta_2\theta_3 \rightarrow \pi + \theta_1, \theta_2, \theta_3$ (twofold axis parallel to **c**).

(b) In the second crystal ($P2/m$):

- $\theta_1\theta_2\theta_3 \rightarrow \pi + \theta_1, -\theta_2, \pi + \theta_3$ (onefold axis)
- $\theta_1\theta_2\theta_3 \rightarrow \theta_1, \pi + \theta_2, \pi - \theta_3$ (twofold axis parallel to **b**).

When these symmetry operators are combined two cells result, each of which has the space group $Pbcb$ (Fig. 2.3.6.5). The asymmetric unit within which the rotation function need be evaluated is found

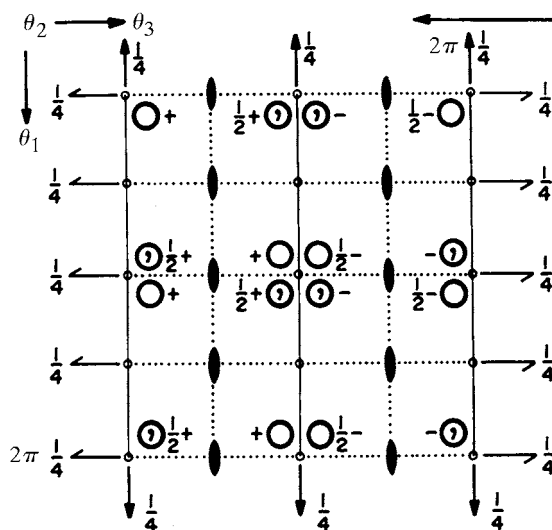


Fig. 2.3.6.5. Rotation space group diagram for the rotation function of a $Pmmm$ Patterson function (P_1) against a $P2/m$ Patterson function (P_2). The Eulerian angles $\theta_1, \theta_2, \theta_3$ repeat themselves after an interval of 2π . Heights above the plane are given in fractions of a revolution. [Reprinted from Tollin *et al.* (1966).]

from a knowledge of the Eulerian space group. In the above example, the limits of the asymmetric unit are $0 \leq \theta_1 \leq \pi/2$, $0 \leq \theta_2 \leq \pi$ and $0 \leq \theta_3 \leq \pi/2$.

Non-linear transformations occur when using Eulerian symmetries for threefold axes along [111] (as in the cubic system) or when using polar coordinates. Hence, Eulerian angles are far more suitable for a derivation of the limits of the rotation-function asymmetric unit. However, when searching for given molecular axes, where some plane of κ need be explored, polar angles are more useful.

Rao *et al.* (1980) have determined all possible rotation function Eulerian space groups, except for combinations with Pattersons of cubic space groups. They numbered these rotation groups 1 through 100 (Table 2.3.6.3) according to the combination of the Patterson Laue groups. The characteristics of each of the 100 groups are given in Table 2.3.6.4, including the limits of the asymmetric unit. In the 100 unique combinations of non-cubic Laue groups, there are only 16 basic rotation function space groups.

2.3.6.4. Sampling, background and interpretation

If the origins are retained in the Pattersons, their product will form a high but constant plateau on which the rotation-function

Table 2.3.6.3. Numbering of the rotation function space groups

The Laue group of the rotated Patterson map P_1 is chosen from the left column and the Laue group of P_2 is chosen from the upper row.

	1	2/m, b axis unique	2/m, c axis unique	mmm	4/m	4/mmm	3	3m	6/m	6/mmm
1	1	11	21	31	41	51	61	71	81	91
2/m, b axis unique	2	12	22	32	42	52	62	72	82	92
2/m, c axis unique	3	13	23	33	43	53	63	73	83	93
mmm	4	14	24	34	44	54	64	74	84	94
4/m	5	15	25	35	45	55	65	75	85	95
4/mmm	6	16	26	36	46	56	66	76	86	96
3	7	17	27	37	47	57	67	77	87	97
3m	8	18	28	38	48	58	68	78	88	98
6/m	9	19	29	39	49	59	69	79	89	99
6/mmm	10	20	30	40	50	60	70	80	90	100

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peaks are superimposed; this leads to a small apparent peak-to-noise ratio. The effect can be eliminated by removal of the origins through a modification of the Patterson coefficients. Irrespective of origin removal, a significant peak is one which is more than three r.m.s. deviations from the mean background.

As in all continuous functions sampled at discrete points, a convenient grid size must be chosen. Small intervals result in an excessive computing burden, while large intervals might miss peaks. Furthermore, equal increments of angles do not represent equal changes in rotation, which can result in distorted peaks (Lattman, 1972). In general, a crude idea of a useful sampling interval can be obtained by considering the angle necessary to move one reciprocal-lattice point onto its neighbour (separated by a^*) at the extremity of the resolution limit, R . This interval is given by

$$\Delta\theta = a^*/2(1/R) = \frac{1}{2}Ra^*.$$

Simple sharpening of the rotation function can be useful. This can be achieved by restricting the computations to a shell in reciprocal space or by using normalized structure factors. Useful limits are frequently 10 to 6 Å for an average protein or 6 to 5 Å for a virus structure determination.

When exploring the rotation function in polar coordinates, there is no significance to the latitude φ (Fig. 2.3.6.4) when $\psi = 0$. For small values of ψ , the rotation function will be quite insensitive to φ , which therefore needs to be explored only at coarse intervals (say 45°). As ψ approaches the equator at 90° , optimal increments of ψ and φ will be about equal. A similar situation exists with Eulerian angles. When $\theta_2 = 0$, the rotation function will be determined by $\theta_1 + \theta_3$, corresponding to $\psi = 0$ and varying κ in polar coordinates. There will be no dependence on $(\theta_1 - \theta_3)$. Thus Eulerian searches can often be performed more economically in terms of the variables $\eta = \theta_1 + \theta_3$ and $\Delta = \theta_1 - \theta_3$, where

$$[\rho] = \begin{pmatrix} \left[\cos \eta \cos^2 \left(\frac{\theta_2}{2} \right) \right. & \left[\sin \eta \cos^2 \left(\frac{\theta_2}{2} \right) \right. & \sin \theta_2 \sin(\eta - \Delta) \\ + \cos \Delta \sin^2 \left(\frac{\theta_2}{2} \right) & + \sin \Delta \sin^2 \left(\frac{\theta_2}{2} \right) & \\ \left[-\sin \eta \cos^2 \left(\frac{\theta_2}{2} \right) \right. & \left[\cos \eta \cos^2 \left(\frac{\theta_2}{2} \right) \right. & \sin \theta_2 \cos(\eta - \Delta) \\ + \sin \Delta \sin^2 \left(\frac{\theta_2}{2} \right) & - \cos \Delta \sin^2 \left(\frac{\theta_2}{2} \right) & \\ \sin \theta_2 \sin(\eta + \Delta) & - \sin \theta_2 \cos(\eta + \Delta) & \cos \theta_2 \end{pmatrix},$$

which reduces to the simple rotation matrix

$$[\rho] = \begin{pmatrix} \cos \eta & \sin \eta & 0 \\ -\sin \eta & \cos \eta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

when $\theta_2 = 0$.

The computational effort to explore carefully a complete asymmetric unit of the rotation-function Eulerian group can be considerable. However, unless improper rotations are under investigation (as, for example, cross-rotation functions between different crystal forms of the same molecule), it is not generally necessary to perform such a global search. The number of molecules per crystallographic asymmetric unit, or the number of subunits per molecule, are often good indicators as to the possible types of noncrystallographic symmetry element. For instance, in the early investigation of insulin, the rotation function was used to explore only the $\kappa = 180^\circ$ plane in polar coordinates as there were only two molecules per crystallographic asymmetric unit (Dodson *et al.*, 1966). Rotation functions of viruses, containing 532 icosahedral symmetry, are usually limited to exploration of the $\kappa = 180, 120, 72$ and 144° planes [*e.g.* Rayment *et al.* (1978) and Arnold *et al.* (1984)].

In general, the interpretation of the rotation function is straightforward. However, noise often builds up relative to the signal in high-symmetry space groups or if the data are limited or poor. One aid to a systematic interpretation is the locked rotation function (Rossmann *et al.*, 1972) for use when a molecule has more than one noncrystallographic symmetry axis. It is then possible to determine the rotation-function values for each molecular axis for a chosen molecular orientation (Fig. 2.3.6.6).

Another problem in the interpretation of rotation functions is the appearance of apparent noncrystallographic symmetry that relates the self-Patterson of one molecule to the self-Patterson of a crystallographically related molecule. For example, take the case of α -chymotrypsin (Blow *et al.*, 1964). The space group is $P2_1$ with a molecular dimer in each of the two crystallographic asymmetric units. The noncrystallographic dimer axis was found to be perpendicular to the crystallographic 2_1 axis. The product of the crystallographic twofold in the Patterson with the orthogonal twofold in the self-Patterson vectors around the origin creates a third twofold, orthogonal to both of the other twofolds. In real space this represents a twofold screw direction relating the two dimers in the cell. In other cases, the product of the crystallographic and noncrystallographic symmetry results in symmetry which only has meaning in terms of all the vectors in the vicinity of the Patterson origin, but not in real space. Rotation-function peaks arising from such products are called Klug peaks (Johnson *et al.*, 1975). Such peaks normally refer to the total symmetry of all the vectors around the Patterson origin and may, therefore, be much larger than the peaks due to noncrystallographic symmetry within one molecule alone. Hence the Klug peaks, if not correctly recognized, can lead to erroneous conclusions (Åkervall *et al.*, 1972). Litvin (1975) has shown how Klug peaks can be predicted. These usually occur only for special orientations of a particle with a given symmetry relative to the crystallographic symmetry axes. Prediction of Klug peaks requires the simultaneous consideration of the noncrystallographic point group, the crystallographic point group and their relative orientations.

2.3.6.5. The fast rotation function

Unfortunately, the rotation-function computations can be extremely time-consuming by conventional methods. Sasada (1964) developed a technique for rapidly finding the maximum of

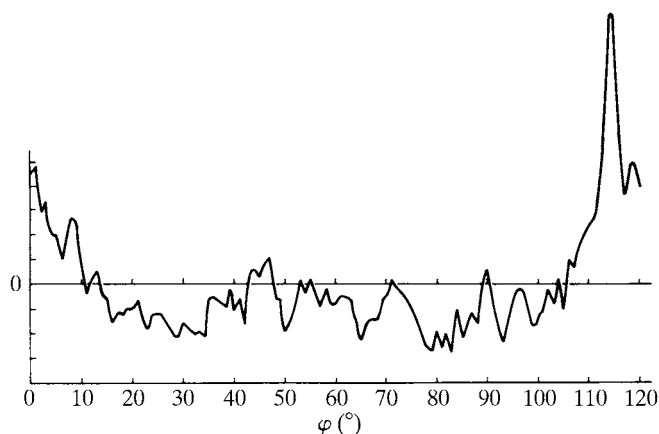


Fig. 2.3.6.6. The locked rotation function, L , applied to the determination of the orientation of the common cold virus (Arnold *et al.*, 1984). There are four virus particles per cubic cell with each particle sitting on a threefold axis. The locked rotation function explores all positions of rotation about this axis and, hence, repeats itself after 120° . The locked rotation function is determined from the individual rotation-function values of the noncrystallographic symmetry directions of a 532 icosahedron. [Reprinted with permission from Arnold *et al.* (1984).]

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Table 2.3.6.4. *Rotation function Eulerian space groups*

The rotation space groups are given in Table 2.3.6.3.

No. of the rotation space group	No. of equivalent positions ^(a)	Symbol ^(b)	Translation along the θ_1 axis ^(c)	Translation along the θ_3 axis ^(c)	Range of the asymmetric unit ^(d)		
1	2	<i>Pn</i>	2π	2π	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < 2\pi$
2	4	<i>Pbn</i> ₂	2π	2π	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
3	4	<i>Pc</i>	π	2π	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < 2\pi$
4	8	<i>Pbc</i> ₂	π	2π	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
5	8	<i>Pc</i>	$\pi/2$	2π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < 2\pi$
6	16	<i>Pbc</i> ₂	$\pi/2$	2π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
7	6	<i>Pn</i>	$2\pi/3$	2π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < 2\pi$
8	12	<i>Pbn</i> ₂	$2\pi/3$	2π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
9	12	<i>Pc</i>	$\pi/3$	2π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < 2\pi$
10	24	<i>Pbc</i> ₂	$\pi/3$	2π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
11	4	<i>P</i> ₂ <i>1nb</i>	2π	2π	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
12	8	<i>Pbnb</i>	2π	2π	$0 \leq \theta_1 \leq \pi/2$,	$0 \leq \theta_2 < \pi$,	$0 \leq \theta_3 < 2\pi$
13	8	<i>P</i> ₂ <i>cb</i>	π	2π	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
14	16	<i>Pbcb</i>	π	2π	$0 \leq \theta_1 \leq \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
15	16	<i>P</i> ₂ <i>cb</i>	$\pi/2$	2π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
16	32	<i>Pbcb</i>	$\pi/2$	2π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 < \pi$,	$0 \leq \theta_3 \leq \pi/2$
17	12	<i>P</i> ₂ <i>1nb</i>	$2\pi/3$	2π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
18	24	<i>Pbnb</i>	$2\pi/3$	2π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 < \pi$,	$0 \leq \theta_3 \leq \pi/2$
19	24	<i>P</i> ₂ <i>cb</i>	$\pi/3$	2π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < 2\pi$
20	48	<i>Pbcb</i>	$\pi/3$	2π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 < \pi$,	$0 \leq \theta_3 \leq \pi/2$
21	4	<i>Pa</i>	2π	π	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi$
22	8	<i>Pba</i> ₂	2π	π	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
23	8	<i>Pm</i>	π	π	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi$
24	16	<i>Pbm</i> ₂	π	π	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
25	16	<i>Pm</i>	$\pi/2$	π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi$
26	32	<i>Pbm</i> ₂	$\pi/2$	π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
27	12	<i>Pa</i>	$2\pi/3$	π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi$
28	24	<i>Pba</i> ₂	$2\pi/3$	π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
29	24	<i>Pm</i>	$\pi/3$	π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi$
30	48	<i>Pbm</i> ₂	$\pi/3$	π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
31	8	<i>P</i> ₂ <i>1ab</i>	2π	π	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
32	16	<i>Pbab</i>	2π	π	$0 \leq \theta_1 \leq \pi/2$,	$0 \leq \theta_2 < \pi$,	$0 \leq \theta_3 < \pi$
33	16	<i>P</i> ₂ <i>mb</i>	π	π	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
34	32	<i>Pbmb</i>	π	π	$0 \leq \theta_1 \leq \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
35	32	<i>P</i> ₂ <i>mb</i>	$\pi/2$	π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
36	64	<i>Pbmb</i>	$\pi/2$	π	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 \leq \pi/2$
37	24	<i>P</i> ₂ <i>1ab</i>	$2\pi/3$	π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
38	48	<i>Pbab</i>	$2\pi/3$	π	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 \leq \pi/2$
39	48	<i>P</i> ₂ <i>mb</i>	$\pi/3$	π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi$
40	96	<i>Pbmb</i>	$\pi/3$	π	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 \leq \pi/2$
41	8	<i>Pa</i>	2π	$\pi/2$	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi/2$
42	16	<i>Pba</i> ₂	2π	$\pi/2$	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$
43	16	<i>Pm</i>	π	$\pi/2$	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi/2$
44	32	<i>Pbm</i> ₂	π	$\pi/2$	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$
45	32	<i>Pm</i>	$\pi/2$	$\pi/2$	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi/2$
46	64	<i>Pbm</i> ₂	$\pi/2$	$\pi/2$	$0 \leq \theta_1 < \pi/2$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$
47	24	<i>Pa</i>	$2\pi/3$	$\pi/2$	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi/2$
48	48	<i>Pba</i> ₂	$2\pi/3$	$\pi/2$	$0 \leq \theta_1 < 2\pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$
49	48	<i>Pm</i>	$\pi/3$	$\pi/2$	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi$,	$0 \leq \theta_3 < \pi/2$
50	96	<i>Pbm</i> ₂	$\pi/3$	$\pi/2$	$0 \leq \theta_1 < \pi/3$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$
51	16	<i>P</i> ₂ <i>1ab</i>	2π	$\pi/2$	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$
52	32	<i>Pbab</i>	2π	$\pi/2$	$0 \leq \theta_1 < 2\pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 \leq \pi/4$
53	32	<i>P</i> ₂ <i>mb</i>	π	$\pi/2$	$0 \leq \theta_1 < \pi$,	$0 \leq \theta_2 \leq \pi/2$,	$0 \leq \theta_3 < \pi/2$

2.3. PATTERSON AND MOLECULAR-REPLACEMENT TECHNIQUES

Table 2.3.6.4. *Rotation function Eulerian space groups (cont.)*

No. of the rotation space group	No. of equivalent positions ^(a)	Symbol ^(b)	Translation along the θ_1 axis ^(c)	Translation along the θ_3 axis ^(c)	Range of the asymmetric unit ^(d)		
54	64	<i>Pbmb</i>	π	$\pi/2$	$0 \leq \theta_1 \leq \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/2$
55	64	<i>P2mb</i>	$\pi/2$	$\pi/2$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/2$
56	128	<i>Pbmb</i>	$\pi/2$	$\pi/2$	$0 \leq \theta_1 \leq \pi/4,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/2$
57	48	<i>P2₁ab</i>	$2\pi/3$	$\pi/2$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/2$
58	96	<i>Pbab</i>	$2\pi/3$	$\pi/2$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 \leq \pi/4$
59	96	<i>P2mb</i>	$\pi/3$	$\pi/2$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/2$
60	192	<i>Pbmb</i>	$\pi/3$	$\pi/2$	$0 \leq \theta_1 \leq \pi/6,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/2$
61	6	<i>Pn</i>	2π	$2\pi/3$	$0 \leq \theta_1 < 2\pi,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < 2\pi/3$
62	12	<i>Pbn2₁</i>	2π	$2\pi/3$	$0 \leq \theta_1 < 2\pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
63	12	<i>Pc</i>	π	$2\pi/3$	$0 \leq \theta_1 < \pi,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < 2\pi/3$
64	24	<i>Pbc2₁</i>	π	$2\pi/3$	$0 \leq \theta_1 < \pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
65	24	<i>Pc</i>	$\pi/2$	$2\pi/3$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < 2\pi/3$
66	48	<i>Pbc2₁</i>	$\pi/2$	$2\pi/3$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
67	18	<i>Pn</i>	$2\pi/3$	$2\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < 2\pi/3$
68	36	<i>Pbn2₁</i>	$2\pi/3$	$2\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
69	36	<i>Pc</i>	$\pi/3$	$2\pi/3$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < 2\pi/3$
70	72	<i>Pbc2₁</i>	$\pi/3$	$2\pi/3$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
71	12	<i>P2₁nb</i>	2π	$2\pi/3$	$0 \leq \theta_1 < 2\pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
72	24	<i>Pbnb</i>	2π	$2\pi/3$	$0 \leq \theta_1 \leq \pi/2,$	$0 \leq \theta_2 < \pi,$	$0 \leq \theta_3 < 2\pi/3$
73	24	<i>P2cb</i>	π	$2\pi/3$	$0 \leq \theta_1 < \pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
74	48	<i>Pbcb</i>	π	$2\pi/3$	$0 \leq \theta_1 \leq \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
75	48	<i>P2cb</i>	$\pi/2$	$2\pi/3$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
76	96	<i>Pbcb</i>	$\pi/2$	$2\pi/3$	$0 \leq \theta_1 \leq \pi/4,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
77	36	<i>P2₁nb</i>	$2\pi/3$	$2\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
78	72	<i>Pbnb</i>	$2\pi/3$	$2\pi/3$	$0 \leq \theta_1 \leq \pi/6,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < 2\pi/3$
79	72	<i>P2cb</i>	$\pi/3$	$2\pi/3$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
80	144	<i>Pbcb</i>	$\pi/3$	$2\pi/3$	$0 \leq \theta_1 \leq \pi/6,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < 2\pi/3$
81	12	<i>Pa</i>	2π	$\pi/3$	$0 \leq \theta_1 < 2\pi,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < \pi/3$
82	24	<i>Pba2</i>	2π	$\pi/3$	$0 \leq \theta_1 < 2\pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
83	24	<i>Pm</i>	π	$\pi/3$	$0 \leq \theta_1 < \pi,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < \pi/3$
84	48	<i>Pbm2</i>	π	$\pi/3$	$0 \leq \theta_1 < \pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
85	48	<i>Pm</i>	$\pi/2$	$\pi/3$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < \pi/3$
86	96	<i>Pbm2</i>	$\pi/2$	$\pi/3$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
87	36	<i>Pa</i>	$2\pi/3$	$\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < \pi/3$
88	72	<i>Pba2</i>	$2\pi/3$	$\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
89	72	<i>Pm</i>	$\pi/3$	$\pi/3$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi,$	$0 \leq \theta_3 < \pi/3$
90	144	<i>Pbm2</i>	$\pi/3$	$\pi/3$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
91	24	<i>P2₁ab</i>	2π	$\pi/3$	$0 \leq \theta_1 < 2\pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
92	48	<i>Pbab</i>	2π	$\pi/3$	$0 \leq \theta_1 \leq \pi/2,$	$0 \leq \theta_2 < \pi,$	$0 \leq \theta_3 < \pi/3$
93	48	<i>P2mb</i>	π	$\pi/3$	$0 \leq \theta_1 < \pi,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
94	96	<i>Pbmb</i>	π	$\pi/3$	$0 \leq \theta_1 \leq \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 \leq \pi/2$
95	96	<i>P2mb</i>	$\pi/2$	$\pi/3$	$0 \leq \theta_1 < \pi/2,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
96	192	<i>Pbmb</i>	$\pi/2$	$\pi/3$	$0 \leq \theta_1 \leq \pi/4,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
97	72	<i>P2₁ab</i>	$2\pi/3$	$\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
98	144	<i>Pbab</i>	$2\pi/3$	$\pi/3$	$0 \leq \theta_1 < 2\pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 \leq \pi/6$
99	144	<i>P2mb</i>	$\pi/3$	$\pi/3$	$0 \leq \theta_1 < \pi/3,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$
100	288	<i>Pbmb</i>	$\pi/3$	$\pi/3$	$0 \leq \theta_1 \leq \pi/6,$	$0 \leq \theta_2 \leq \pi/2,$	$0 \leq \theta_3 < \pi/3$

Notes: (a) This is the number of equivalent positions in the rotation unit cell. (b) Each symbol retains the order $\theta_1, \theta_2, \theta_3$. The monoclinic space groups have the b axis unique setting. (c) This is a translation symmetry: e.g. for the case of $\pi/2$ translation along the θ_1 axis, $\theta_1, \theta_2, \theta_3$ goes to $\pi/2 + \theta_1, \theta_2, \theta_3$ and $\pi + \theta_1, \theta_2, \theta_3$, and $3\pi/2 + \theta_1, \theta_2, \theta_3$. All other equivalent positions in the basic rotation space group are similarly translated. (d) Several consistent sets of ranges exist but the one with the minimum range of θ_2 is listed.

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

a given peak by looking at the slope of the rotation function. A major breakthrough came when Crowther (1972) recast the rotation function in a manner suitable for rapid computation. Only a brief outline of Crowther's fast rotation function is given here. Details are found in the original text (Crowther, 1972) and his computer program description.

Since the rotation function correlates spherical volumes of a given Patterson density with rotated versions of either itself or another Patterson density, it is likely that a more natural form for the rotation function will involve spherical harmonics rather than the Fourier components $|\mathbf{F}_h|^2$ of the crystal representation. Thus, if the two Patterson densities $P_1(r, \psi, \varphi)$ and $P_2(r, \psi, \varphi)$ are expanded within the spherical volume of radius less than a limiting value of a , then

$$P_1(r, \psi, \varphi) = \sum_{lmn} a_{lmn}^* \hat{j}_l(k_{ln}r) \hat{Y}_l^m(\psi, \varphi)$$

and

$$P_2(r, \psi, \varphi) = \sum_{l'm'n'} b_{l'm'n'} \hat{j}_{l'}(k_{l'n'}r) \hat{Y}_{l'}^{m'}(\psi, \varphi),$$

and the rotation function would then be defined as

$$R = \int_{\text{sphere}} P_1(r, \psi, \varphi) \mathcal{R} P_2(r, \psi, \varphi) r^2 \sin \psi \, dr \, d\psi \, d\varphi.$$

Here $\hat{Y}_l^m(\psi, \varphi)$ is the normalized spherical harmonic of order l ; $\hat{j}_l(k_{ln}r)$ is the normalized spherical Bessel function of order l ; a_{lmn} , b_{lmn} are complex coefficients; and $\mathcal{R} P_2(r, \psi, \varphi)$ represents the rotated second Patterson. The rotated spherical harmonic can then be expressed in terms of the Eulerian angles $\theta_1, \theta_2, \theta_3$ as

$$\mathcal{R}(\theta_1, \theta_2, \theta_3) \hat{Y}_l^m(\psi, \varphi) = \sum_{q=-l}^l D_{qm}^l(\theta_1, \theta_2, \theta_3) \hat{Y}_l^q(\psi, \varphi),$$

where

$$D_{qm}^l(\theta_1, \theta_2, \theta_3) = \exp(iq\theta_3) d_{qm}^l(\theta_2) \exp(im\theta_1)$$

and $d_{qm}^l(\theta_2)$ are the matrix elements of the three-dimensional rotation group. It can then be shown that

$$R(\theta_1, \theta_2, \theta_3) = \sum_{lmn} a_{lmn}^* b_{lm'n} D_{m'm}^l(\theta_1, \theta_2, \theta_3).$$

Since the radial summation over n is independent of the rotation,

$$c_{lmn} = \sum_n a_{lmn}^* b_{lmn},$$

and hence

$$R(\theta_1, \theta_2, \theta_3) = \sum_{lmn} c_{lmn} D_{m'm}^l(\theta_1, \theta_2, \theta_3)$$

or

$$R(\theta_1, \theta_2, \theta_3) = \sum_{mm'} \left[\sum_l c_{lmn} d_{m'm}^l(\theta_2) \right] \exp[i(m'\theta_3 + m\theta_1)].$$

The coefficients c_{lmn} refer to a particular pair of Patterson densities and are independent of the rotation. The coefficients $D_{m'm}^l$, containing the whole rotational part, refer to rotations of spherical harmonics and are independent of the particular Patterson densities. Since the summations over m and m' represent a Fourier synthesis, rapid calculation is possible.

As polar coordinates rather than Eulerian angles provide a more graphic interpretation of the rotation function, Tanaka (1977) has recast the initial definition as

$$\begin{aligned} R(\theta_1, \theta_2, \theta_3) &= \int_{\text{sphere}} [\mathcal{R}(\theta_1, \theta_2, \theta_3 = 0) P_1(r, \psi, \varphi)] \\ &\quad \times [\mathcal{R}(\theta_1, \theta_2, \theta_3) P_2(r, \psi, \varphi)] \, dV \\ &= \int_{\text{sphere}} [P_1(r, \psi, \varphi)] [\mathcal{R}^{-1}(\theta_1, \theta_2, \theta_3 = 0) \\ &\quad \times \mathcal{R}(\theta_1, \theta_2, \theta_3) P_2(r, \psi, \varphi)] \, dV. \end{aligned}$$

He showed that the polar coordinates are now equivalent to $\kappa = \theta_3$, $\psi = \theta_2$ and $\varphi = \theta_1 - \pi/2$. The rotation function can then be expressed as

$$\begin{aligned} R(\kappa, \psi, \varphi) &= \sum_{lmn} \left(\sum_n a_{lmn}^* b_{lm'n} \right) \sum_q \{ d_{qm}^l(\psi) d_{qm'}^l(\psi) (-1)^{(m'-m)} \\ &\quad \times \exp[i(\kappa q)] \exp[i(m' - m)\varphi] \}, \end{aligned}$$

permitting rapid calculation of the fast rotation function in polar coordinates.

Crowther (1972) uses the Eulerian angles α, β, γ which are related to those defined by Rossmann & Blow (1962) according to $\theta_1 = \alpha + \pi/2$, $\theta_2 = \beta$ and $\theta_3 = \gamma - \pi/2$.

2.3.7. Translation functions

2.3.7.1. Introduction

The problem of determining the position of a noncrystallographic symmetry element in space, or the position of a molecule of known orientation in a unit cell, has been reviewed by Rossmann (1972), Colman *et al.* (1976), Karle (1976), Argos & Rossmann (1980), Harada *et al.* (1981) and Beurskens (1981). All methods depend on the prior knowledge of the object's orientation implied by the rotation matrix $[\mathbf{C}]$. The various translation functions, T , derived below, can only be computed given this information.

The general translation function can be defined as

$$T(\mathbf{S}_x, \mathbf{S}_{x'}) = \int_U \rho_1(\mathbf{x}) \cdot \rho_2(\mathbf{x}') \, d\mathbf{x},$$

where T is a six-variable function given by each of the three components that define $\mathbf{S}_x$ and $\mathbf{S}_{x'}$. Here $\mathbf{S}_x$ and $\mathbf{S}_{x'}$ are equivalent reference positions of the objects, whose densities are $\rho_1(\mathbf{x})$ and $\rho_2(\mathbf{x}')$. The translation function searches for the optimal overlap of the two objects after they have been similarly oriented. Following the same procedure used for the rotation-function derivation, Fourier summations are substituted for $\rho_1(\mathbf{x})$ and $\rho_2(\mathbf{x}')$. It can then be shown that

$$\begin{aligned} T(\mathbf{S}_x, \mathbf{S}_{x'}) &= \int_U \left\{ \frac{1}{V_h} \sum_h |\mathbf{F}_h| \exp[i(\alpha_h - 2\pi \mathbf{h} \cdot \mathbf{x})] \right\} \\ &\quad \times \left\{ \frac{1}{V_p} \sum_p |\mathbf{F}_p| \exp[i(\alpha_p - 2\pi \mathbf{p} \cdot \mathbf{x}')] \right\} \, d\mathbf{x}. \end{aligned}$$

Using the substitution $\mathbf{x}' = [\mathbf{C}]\mathbf{x} + \mathbf{d}$ and simplifying leads to

$$\begin{aligned} T(\mathbf{S}_x, \mathbf{S}_{x'}) &= \frac{1}{V_h V_p} \sum_h \sum_p |\mathbf{F}_h| |\mathbf{F}_p| \\ &\quad \times \exp[i(\alpha_h + \alpha_p - 2\pi \mathbf{p} \cdot \mathbf{d})] \\ &\quad \times \int_U \exp\{-2\pi i(\mathbf{h} + [\mathbf{C}]^T \mathbf{p}) \cdot \mathbf{x}\} \, d\mathbf{x}. \end{aligned}$$

The integral is the diffraction function $G_{\mathbf{hp}}$ (2.3.6.4). If the integration is taken over the volume U , centred at $\mathbf{S}_x$ and $\mathbf{S}_{x'}$, it follows that

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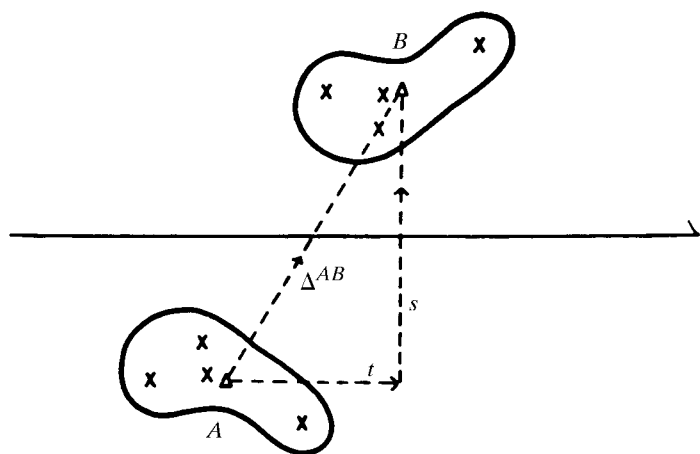


Fig. 2.3.7.1. Crosses represent atoms in a two-dimensional model structure. The triangles are the points chosen as approximate centres of molecules A and B. Δ^{AB} has components t and s parallel and perpendicular, respectively, to the screw rotation axis. [Reprinted from Rossmann *et al.* (1964).]

$$T(\mathbf{S}_x, \mathbf{S}_{x'}) = \frac{2}{V_h V_p} \sum_{\mathbf{h}} \sum_{\mathbf{p}} |\mathbf{F}_h| |\mathbf{F}_p| G_{\mathbf{h}\mathbf{p}} \times \cos[\alpha_h + \alpha_p - 2\pi(\mathbf{h} \cdot \mathbf{S}_x + \mathbf{p} \cdot \mathbf{S}_{x'})]. \quad (2.3.7.1)$$

2.3.7.2. Position of a noncrystallographic element relating two unknown structures

The function (2.3.7.1) is quite general. For instance, the rotation function corresponds to a comparison of Patterson functions P_1 and P_2 at their origins. That is, the coefficients are F^2 , phases are zero and $\mathbf{S}_x = \mathbf{S}_{x'} = 0$. However, the determination of the translation between two objects requires the comparison of cross-vectors away from the origin.

Consider, for instance, the determination of the precise translation vector parallel to a rotation axis between two identical

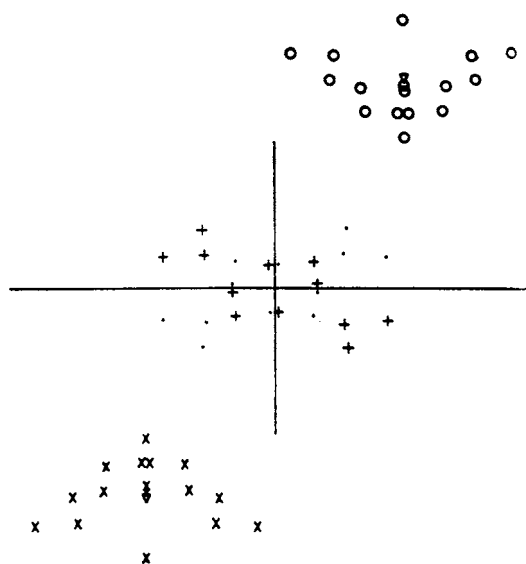


Fig. 2.3.7.2. Vectors arising from the structure in Fig. 2.3.7.1. The self-vectors of molecules A and B are represented by + and -; the cross-vectors from molecules A to B and B to A by x and o. Triangles mark the position of $+\Delta^{AB}$ and $-\Delta^{AB}$. [Reprinted from Rossmann *et al.* (1964).]

molecules of unknown structure. For simplicity, let the noncrystallographic axis be a dyad (Fig. 2.3.7.1). Fig. 2.3.7.2 shows the corresponding Patterson of the hypothetical point-atom structure. Opposite sets of cross-Patterson vectors in Fig. 2.3.7.2 are related by a twofold rotation and a translation equal to twice the precise vector in the original structure. A suitable translation function would then compare a Patterson at $\mathbf{S}$ with the rotated Patterson at $-\mathbf{S}$. Hence, substituting $\mathbf{S}_x = \mathbf{S}$ and $\mathbf{S}_{x'} = -\mathbf{S}$ in (2.3.7.1),

$$T(\mathbf{S}) = \frac{2}{V^2} \sum_{\mathbf{h}} \sum_{\mathbf{p}} |\mathbf{F}_h|^2 |\mathbf{F}_p|^2 G_{\mathbf{h}\mathbf{p}} \cos[2\pi(\mathbf{h} - \mathbf{p}) \cdot \mathbf{S}]. \quad (2.3.7.2)$$

The opposite cross-vectors can be superimposed only if an evenfold rotation between the unknown molecules exists. The translation function (2.3.7.2) is thus applicable only in this special situation. There is no published translation method to determine the interrelation of two unknown structures in a crystallographic asymmetric unit or in two different crystal forms. However, another special situation exists if a molecular evenfold axis is parallel to a crystallographic evenfold axis. In this case, the position of the noncrystallographic symmetry element can be easily determined from the large peak in the corresponding Harker section of the Patterson.

In general, it is difficult or impossible to determine the positions of noncrystallographic axes (or their intersection at a molecular centre). However, the position of heavy atoms in isomorphous derivatives, which usually obey the noncrystallographic symmetry, can often determine this information.

2.3.7.3. Position of a known molecular structure in an unknown unit cell

The most common type of translation function occurs when looking for the position of a known molecular structure in an unknown crystal. For instance, if the structure of an enzyme has previously been determined by the isomorphous replacement method, then the structure of the same enzyme from another species can often be solved by molecular replacement [*e.g.* Grau *et al.* (1981)]. However, there are some severe pitfalls when, for instance, there are gross conformational changes [*e.g.* Moras *et al.* (1980)]. This type of translation function could also be useful in the interpolation of E maps produced by direct methods. Here there may often be confusion as a consequence of a number of molecular images related by translations (Karle, 1976; Beurskens, 1981; Egert & Sheldrick, 1985).

Tollin's (1966) Q function and Crowther & Blow's (1967) translation function are essentially identical (Tollin, 1969) and depend on a prior knowledge of the search molecule as well as its orientation in the unknown cell. The derivation given here, however, is somewhat more general and follows the derivation of Argos & Rossmann (1980), and should be compared with the method of Harada *et al.* (1981).

If the known molecular structure is correctly oriented into a cell ($\mathbf{p}$) of an unknown structure and placed at $\mathbf{S}$ with respect to a defined origin, then a suitable translation function is

$$T(\mathbf{S}) = \sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}, \text{obs}}|^2 |\mathbf{F}_{\mathbf{p}}(\mathbf{S})|^2. \quad (2.3.7.3)$$

This definition is preferable to one based on an R -factor calculation as it is more amenable to computation and is independent of a relative scale factor.

The structure factor $\mathbf{F}_{\mathbf{p}}(\mathbf{S})$ can be calculated by modifying expression (2.3.8.9) (see below). That is,

$$\mathbf{F}_{\mathbf{p}}(\mathbf{S}) = \frac{U}{V_h} \sum_{n=1}^N \exp(2\pi i \mathbf{p} \cdot \mathbf{S}_n) \left[\sum_{\mathbf{h}} \mathbf{F}_h G_{\mathbf{h}\mathbf{p}_n} \exp(-2\pi i \mathbf{h} \cdot \mathbf{S}) \right],$$

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where V_h is the volume of cell ($\mathbf{h}$) and $\mathbf{S}_n$ is the position, in the n th crystallographic asymmetric unit, of cell ($\mathbf{p}$) corresponding to $\mathbf{S}$ in known cell ($\mathbf{h}$). Let

$$A_{p,n} \exp(i\gamma_n) = \sum_{\mathbf{h}} \mathbf{F}_h G_{h\mathbf{p}_n} \exp(-2\pi i \mathbf{h} \cdot \mathbf{S}),$$

which are the coefficients of the molecular transform for the known molecule placed into the n th asymmetric unit of the $\mathbf{p}$ cell. Thus

$$\mathbf{F}_p(\mathbf{S}) = \frac{U}{V_h} \sum_{n=1}^N A_{p,n} \exp[i(\gamma_n + 2\pi \mathbf{p} \cdot \mathbf{S}_n)]$$

or

$$\mathbf{F}_p(\mathbf{S}) = \frac{U}{V_h} \sum_{n=1}^N A_{p,n} \exp[i(\gamma_n + 2\pi \mathbf{p}_n \cdot \mathbf{S})],$$

where $\mathbf{p}_n = [\mathbf{C}_n^T] \mathbf{p}$ and $\mathbf{S} = \mathbf{S}_1$. Hence

$$|\mathbf{F}_p(\mathbf{S})|^2 = \left(\frac{U}{V_h} \right)^2 \sum_n \sum_m (A_{p,n} A_{p,m} \times \exp\{i[2\pi(\mathbf{p}_n - \mathbf{p}_m) \cdot \mathbf{S} + (\gamma_n - \gamma_m)]\}),$$

and then from (2.3.7.3)

$$T(\mathbf{S}) = \left(\frac{U}{V_h} \right)^2 \sum_{\mathbf{p}} \sum_n \sum_m \left(|\mathbf{F}_{p,\text{obs}}|^2 A_{p,n} A_{p,m} \times \exp\{i[2\pi(\mathbf{p}_n - \mathbf{p}_m) \cdot \mathbf{S} + (\gamma_n - \gamma_m)]\} \right), \quad (2.3.7.4)$$

which is a Fourier summation with known coefficients $\{|\mathbf{F}_{p,\text{obs}}|^2 A_{p,n} A_{p,m} \times \exp[i(\gamma_n - \gamma_m)]\}$ such that $T(\mathbf{S})$ will be a maximum at the correct molecular position.

Terms with $n = m$ in expression (2.3.7.4) can be omitted as they are independent of $\mathbf{S}$ and only contribute a constant to the value of $T(\mathbf{S})$. For terms with $n \neq m$, the indices take on special values. For instance, if the $\mathbf{p}$ cell is monoclinic with its unique axis parallel to $\mathbf{b}$ such that $\mathbf{p}_1 = (p, q, r)$ and $\mathbf{p}_2 = (\bar{p}, q, \bar{r})$, then $\mathbf{p}_1 - \mathbf{p}_2$ would be $(2p, 0, 2r)$. Hence, $T(\mathbf{S})$ would be a two-dimensional function consistent with the physical requirement that the translation component, parallel to the twofold monoclinic axis, is arbitrary.

Crowther & Blow (1967) show that if $\mathbf{F}_M$ are the structure factors of a known molecule correctly oriented within the cell of the unknown structure at an arbitrary molecular origin, then (altering the notation very slightly from above)

$$T(\mathbf{S}) = \sum_{\mathbf{p}} |\mathbf{F}_{\text{obs}}(\mathbf{p})|^2 \mathbf{F}_M(\mathbf{p}) \mathbf{F}_M^*(\mathbf{p}[\mathbf{C}]) \exp(-2\pi i \mathbf{p} \cdot \mathbf{S}),$$

where $[\mathbf{C}]$ is a crystallographic symmetry operator relative to which the molecular origin is to be determined. This is of the same form as (2.3.7.4) but concerns the special case where the $\mathbf{h}$ cell, into which the known molecule was placed, has the same dimensions as the $\mathbf{p}$ cell.

R -factor calculations are sometimes used to determine the position of a known molecular fragment in an unknown cell, particularly if only one parameter is being searched. Such calculations are computationally less convenient than the Fourier methods described above, but can be more sensitive. All these methods can be improved by simultaneous consideration of packing requirements of the molecular fragments (Harada *et al.*, 1981; Hendrickson & Ward, 1976; Rabinovich & Shakked, 1984). Indeed, packing considerations can frequently limit the search volume very considerably.

2.3.7.4. Position of a noncrystallographic symmetry element in a poorly defined electron-density map

If an initial set of poor phases, for example from an SIR derivative, are available and the rotation function has given the orientation of a noncrystallographic rotation axis, it is possible to search the electron-density map systematically to determine the translation axis position. The translation function must, therefore, measure the quality of superposition of the poor electron-density map on itself. Hence $\mathbf{S}_x = \mathbf{S}_y = \mathbf{S}$ and the function (2.3.7.1) now becomes

$$T(\mathbf{S}) = \frac{2}{V_h^2} \sum_{\mathbf{h}} \sum_{\mathbf{p}} |\mathbf{F}_h| |\mathbf{F}_p| G_{h\mathbf{p}} \cos[\alpha_h + \alpha_p - 2\pi(\mathbf{h} + \mathbf{p}) \cdot \mathbf{S}].$$

This real-space translation function has been used successfully to determine the intermolecular dyad axis for α -chymotrypsin (Blow *et al.*, 1964) and to verify the position of immunoglobulin domains (Colman & Fehllhammer, 1976).

2.3.8. Molecular replacement

2.3.8.1. Using a known molecular fragment

The most straightforward application of the molecular-replacement method occurs when the orientation and position of a known molecular fragment in an unknown cell have been previously determined. The simple procedure is to apply the rotation and translation operations to the known fragment. This will place it into one 'standard' asymmetric unit of the unknown cell. Then the crystal operators (assuming no further noncrystallographic operators are present in the unknown cell) are applied to generate the complete unit cell of the unknown structure. Structure factors can then be calculated from the rotated and translated known molecule into the unknown cell. The resultant model can be refined in numerous ways.

More generally, consider a molecule placed in any crystal cell ($\mathbf{h}$), within which coordinate positions shall be designated by $\mathbf{x}$. Let the corresponding structure factors be $\mathbf{F}_h$. It is then possible to compute the structure factors $\mathbf{F}_p$ for another cell ($\mathbf{p}$) into which the same molecule has been placed N times related by the crystallographic symmetry operators $[\mathbf{C}_1], \mathbf{d}_1; [\mathbf{C}_2], \mathbf{d}_2; \dots; [\mathbf{C}_N], \mathbf{d}_N$. Let the electron density at a point $\mathbf{y}_1$ in the first crystallographic asymmetric unit be spatially related to the point $\mathbf{y}_n$ in the n th asymmetric unit of the $\mathbf{p}$ crystal such that

$$\rho(\mathbf{y}_n) = \rho(\mathbf{y}_1), \quad (2.3.8.1)$$

where

$$\mathbf{y}_n = [\mathbf{C}_n] \mathbf{y}_1 + \mathbf{d}_n. \quad (2.3.8.2)$$

From the definition of a structure factor,

$$\mathbf{F}_p = \sum_{n=1}^N \int_U \rho(\mathbf{y}_n) \exp(2\pi i \mathbf{p} \cdot \mathbf{y}_n) d\mathbf{y}_n, \quad (2.3.8.3)$$

where the integral is taken over the volume U of one molecule. But since each molecule is identical as expressed in equation (2.3.8.1) and since (2.3.8.2) can be substituted in equation (2.3.8.3), we have

$$\mathbf{F}_p = \sum_{n=1}^N \int_U \rho(\mathbf{y}_1) \exp[2\pi i \mathbf{p} \cdot ([\mathbf{C}_n] \mathbf{y}_1 + \mathbf{d}_n)] d\mathbf{y}_1. \quad (2.3.8.4)$$

Now let the molecule in the $\mathbf{h}$ crystal be related to the molecule in the first asymmetric unit of the $\mathbf{p}$ crystal by the noncrystallographic symmetry operation

$$\mathbf{x} = [\mathbf{C}] \mathbf{y} + \mathbf{d}, \quad (2.3.8.5)$$

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which implies

$$\rho(\mathbf{x}) = \rho(\mathbf{y}_1) = \rho(\mathbf{y}_2) = \dots \quad (2.3.8.6)$$

Furthermore, in the $\mathbf{h}$ cell

$$\rho(\mathbf{x}) = \frac{1}{V_{\mathbf{h}}} \sum_{\mathbf{h}} \mathbf{F}_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \quad (2.3.8.7)$$

and thus, by combining with (2.3.8.5), (2.3.8.6) and (2.3.8.7),

$$\rho(\mathbf{y}_1) = \frac{1}{V_{\mathbf{h}}} \sum_{\mathbf{h}} \mathbf{F}_{\mathbf{h}} \exp[-2\pi i (\mathbf{h}[\mathbf{C}] \cdot \mathbf{y}_1 + \mathbf{h} \cdot \mathbf{d})]. \quad (2.3.8.8)$$

Now using (2.3.8.4) and (2.3.8.8) it can be shown that

$$\mathbf{F}_{\mathbf{p}} = \frac{U}{V_{\mathbf{h}}} \sum_{\mathbf{h}} \mathbf{F}_{\mathbf{h}} \sum_{n=1}^N G_{\mathbf{h}\mathbf{p}_n} \exp[2\pi i (\mathbf{p} \cdot \mathbf{S}_n - \mathbf{h} \cdot \mathbf{S})], \quad (2.3.8.9)$$

where

$$UG_{\mathbf{h}\mathbf{p}_n} = \int_U \exp[2\pi i (\mathbf{p}[\mathbf{C}_n] - \mathbf{h}[\mathbf{C}]) \cdot \mathbf{u}] \, d\mathbf{u}. \quad (2.3.8.10)$$

$\mathbf{S}$ is a chosen molecular origin in the $\mathbf{h}$ crystal and $\mathbf{S}_n$ is the corresponding molecular position in the n th asymmetric unit of the $\mathbf{p}$ crystal.

2.3.8.2. Using noncrystallographic symmetry for phase improvement

The use of noncrystallographic symmetry for phase determination was proposed by Rossmann & Blow (1962, 1963) and subsequently explored by Crowther (1967, 1969) and Main & Rossmann (1966). These methods were developed in reciprocal space and were primarily concerned with *ab initio* phase determination. Real-space averaging of electron density between noncrystallographically related molecules was used in the structure determination of deoxyhaemoglobin (Muirhead *et al.*, 1967) and of α -chymotrypsin (Matthews *et al.*, 1967). The improvement derived from the averaging between the two noncrystallographic units was, however, not clear in either case. The first obviously successful application was in the structure determination of lobster glyceraldehyde-3-phosphate dehydrogenase (Buehner *et al.*, 1974; Argos *et al.*, 1975), where the tetrameric molecule of symmetry 222 occupied one crystallographic asymmetric unit. The improvement in the essentially SIR electron-density map was considerable and the results changed from uninterpretable to interpretable. The uniqueness and validity of the solution lay in the obvious chemical correctness of the polypeptide fold and its agreement with known amino-acid-sequence data. In contrast to the earlier reciprocal-space methods, noncrystallographic symmetry was used as a method to improve poor phases rather than to determine phases *ab initio*.

Many other applications followed rapidly, aided greatly by the versatile techniques developed by Bricogne (1976). Of particular interest is the application to the structure determination of hexokinase (Fletterick & Steitz, 1976), where the averaging occurred both between different crystal forms and within the same crystal.

The most widely used procedure for real-space averaging is the 'double sorting' technique developed by Bricogne (1976) and also by Johnson (1978). An alternative method is to maintain the complete map stored in the computer (Nordman, 1980*b*). This avoids the sorting operation, but is only possible given a very large computer or a low-resolution map containing relatively few grid points.

Bricogne's double sorting technique involves generating real-space non-integral points (D_i) which are related to integral grid

points (I_i) in the cell asymmetric unit by the noncrystallographic symmetry operators. The elements of the set D_i are then brought back to their equivalent points in the cell asymmetric unit (D'_i) and sorted by their proximity to two adjacent real-space sections. The set I'_i , calculated on a finer grid than I_i and stored in the computer memory two sections at a time, is then used for linear interpolation to determine the density values at D'_i which are successively stored and summed in the related array I_i . A count is kept of the number of densities received at each I_i , resulting in a final averaged aggregate, when all real-space sections have been utilized. The density to be assigned outside the molecular envelope (defined with respect to the set I_i) is determined by averaging the density of all unused points in I_i . The grid interval for the set I'_i should be about one-sixth of the resolution to avoid serious errors from interpolation (Bricogne, 1976). The grid point separation in the set I_i need only be sufficient for representation of electron density, or about one-third of the resolution.

Molecular replacement in real space consists of the following steps (Table 2.3.8.1): (a) calculation of electron density based on a starting phase set and observed amplitudes; (b) averaging of this density among the noncrystallographic asymmetric units or molecular copies in several crystal forms, a process which defines a molecular envelope as the averaging is only valid within the range of the noncrystallographic symmetry; (c) reconstructing the unit cell based on averaged density in every noncrystallographic asymmetric unit; (d) calculating structure factors from the reconstructed cell; (e) combining the new phases with others to obtain a weighted best-phase set; and (f) returning to step (a) at the previous or an extended resolution. Decisions made in steps (b) and (e) determine the rate of convergence (see Table 2.3.8.1) to a solution (Arnold *et al.*, 1987).

The power of the molecular-replacement procedure for either phase improvement or phase extension depends on the number of

Table 2.3.8.1. *Molecular replacement: phase refinement as an iterative process*

(A)	$\mathbf{F}_{\text{obs}}, \alpha'_n, m'_n \rightarrow \rho_n$
(B)	$\rho_n \rightarrow \rho_n(\text{modified})$ (i) Use of noncrystallographic symmetry operators (ii) Definition of envelope limiting volume within which noncrystallographic symmetry is valid (iii) Adjustment of solvent density* (iv) Use of crystallographic operators to reconstruct modified density into a complete cell
(C)	$\rho_n(\text{modified}) \rightarrow \mathbf{F}_{\text{calc}, n+1}; \alpha_{\text{calc}, n+1}$
(D)	$(\mathbf{F}_{\text{calc}, n+1}, \alpha_{\text{calc}, n+1}) + (\mathbf{F}_{\text{obs}}, \alpha_0) \rightarrow \mathbf{F}_{\text{obs}}, \alpha'_{n+1}, m'_{n+1}$ (i) Assessment of reliability of new phasing set α_{n+1} in relation to original phasing set $\alpha_0(w)$ (ii) Use of figures of merit m_0, m_{n+1} and reliability w to determine modified phasing set α'_{n+1}, m'_{n+1} † (iii) Consideration of α_{n+1} and m_{n+1} where there was no prior knowledge of (a) $\mathbf{F}_{\text{obs}}$ (e.g. very low order reflections or uncollected data) (b) α_0 (e.g. no isomorphous information or phase extension)
(E)	Return to step (A) with α'_{n+1}, m'_{n+1} and a possibly augmented set of $\mathbf{F}_{\text{obs}}$.

* Wang (1985); Bhat & Blow (1982); Collins (1975); Schevitz *et al.* (1981); Hoppe & Gassmann (1968).

† Rossmann & Blow (1961); Hendrickson & Lattman (1970).

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noncrystallographic asymmetric units, the size of the excluded volume expressed in terms of the ratio $(V - UN)/V$ and the magnitude of the measurement error on the structure amplitudes. Crowther (1967, 1969) and Bricogne (1974) have investigated the dependence on the number of noncrystallographic asymmetric units and conclude that three or more copies are sufficient to ensure convergence of an iterative phase improvement procedure in the absence of errors on the structure amplitudes. As with the analogous case of isomorphous replacement in which three data sets ensure reasonable phase determination, additional copies will enhance the power of the method, although their usefulness is subject to the law of diminishing returns. Another example of this principle is the sign determination of the $h0l$ reflections of horse haemoglobin (Perutz, 1954) in which seven shrinkage stages constituted the sampling of the transform of a single copy.

Procedures for real-space averaging have been used extensively with great success. The interesting work of Wilson *et al.* (1981) is noteworthy for the continuous adjustment of molecular envelope with increased map definition. Furthermore, the analysis of complete virus structures has only been possible as a consequence of this technique (Bloomer *et al.*, 1978; Harrison *et al.*, 1978; Abad-Zapatero *et al.*, 1980; Liljas *et al.*, 1982). Although the procedure has been used primarily for phase improvement, apparently successful attempts have been made at phase extension (Nordman, 1980b; Gaykema *et al.*, 1984; Rossmann *et al.*, 1985). *Ab initio* phasing of glyceraldehyde-3-phosphate dehydrogenase (Argos *et al.*, 1975) was successfully attempted by initially filling the known envelope with uniform density to determine the phases of the innermost reflections and then gradually extending phases to 6.3 Å resolution. Johnson *et al.* (1976) used the same procedure to determine the structure of southern bean mosaic virus to 22.5 Å resolution. Particularly impressive was the work on polyoma virus (Rayment *et al.*, 1982; Rayment, 1983; Rayment *et al.*, 1983) where crude initial models led to an entirely unexpected breakdown of the Caspar & Klug (1962) concept of quasi-symmetry. *Ab initio* phasing has also been used by combining the electron-diffraction projection data of two different crystal forms of bacterial rhodopsin (Rossmann & Henderson, 1982).

2.3.8.3. Equivalence of real- and reciprocal-space molecular replacement

Let us proceed in reciprocal space doing exactly the same as is done in real-space averaging. Thus

$$\rho_{AV}(\mathbf{x}) = \frac{1}{N} \sum_{n=1}^N \rho(\mathbf{x}_n),$$

where

$$\mathbf{x}_n = [\mathbf{C}_n]\mathbf{x} + \mathbf{d}_n.$$

Therefore,

$$\rho_{AV}(\mathbf{x}) = \frac{1}{N} \sum_N \frac{1}{V} \left[\sum_{\mathbf{h}} \mathbf{F}_{\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_n) \right].$$

The next step is to perform the back-transform of the averaged electron density. Hence,

$$\mathbf{F}_{\mathbf{p}} = \int_U \rho_{AV}(\mathbf{x}) \exp(-2\pi i \mathbf{p} \cdot \mathbf{x}) d\mathbf{x},$$

where U is the volume within the averaged part of the cell. Hence, substituting for ρ_{AV} ,

$$\mathbf{F}_{\mathbf{p}} = \int_U \left[\frac{1}{NV} \sum_N \sum_{\mathbf{h}} \mathbf{F}_{\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_n) \right] \exp(-2\pi i \mathbf{p} \cdot \mathbf{x}) d\mathbf{x},$$

which is readily simplified to

$$\mathbf{F}_{\mathbf{p}} = \frac{U}{NV} \sum_{\mathbf{h}} \mathbf{F}_{\mathbf{h}} \sum_N G_{\mathbf{h}\mathbf{p}n} \exp(2\pi i \mathbf{h} \cdot \mathbf{d}_n).$$

Setting

$$\mathbf{B}_{\mathbf{h}\mathbf{p}} = \frac{U}{NV} \sum_N G_{\mathbf{h}\mathbf{p}n} \exp(2\pi i \mathbf{h} \cdot \mathbf{d}_n),$$

the molecular-replacement equations can be written as

$$\mathbf{F}_{\mathbf{p}} = \sum_{\mathbf{h}} \mathbf{B}_{\mathbf{h}\mathbf{p}} \mathbf{F}_{\mathbf{h}} \quad (2.3.8.11)$$

(Main & Rossmann, 1966), or in matrix form

$$\mathbf{F} = [\mathbf{B}]\mathbf{F},$$

which is the form of the equations used by Main (1967) and by Crowther (1967). Colman (1974) arrived at the same conclusions by an application of Shannon's sampling theorem. It should be noted that the elements of $[\mathbf{B}]$ are dependent only on knowledge of the noncrystallographic symmetry and the volume within which it is valid. Substitution of approximate phases into the right-hand side of (2.3.8.11) produces a set of calculated structure factors exactly analogous to those produced by back-transforming the averaged electron density in real space. The new phases can then be used in a renewed cycle of molecular replacement.

Computationally, it has been found more convenient and faster to work in real space. This may, however, change with the advent of vector processing in 'supercomputers'. Obtaining improved phases by substitution of current phases on the right-hand side of the molecular-replacement equations (2.3.8.1) seems less cumbersome than the repeated forward and backward Fourier transformation, intermediate sorting, and averaging required in the real-space procedure.

2.3.9. Conclusions

Complete interpretation of Patterson maps is no longer used frequently in structure analysis, although most determinations of heavy-atom positions of isomorphous pairs are based on Patterson analyses. Incorporation of the Patterson concept is crucial in many sophisticated techniques essential for the solution of complex problems, particularly in the application to biological macromolecular structures. Patterson techniques provide important physical insights in a link between real- and reciprocal-space formulation of crystal structures and diffraction data.

2.3.9.1. Update

This article was originally completed in January 1986. Since then, some advances have occurred. In particular, the use of real-space averaging between noncrystallographically related electron density within the crystallographic asymmetric unit has become an accepted way of extending phase information to higher resolution, particularly for complex structures such as viruses (Gaykema *et al.*, 1984; Rossmann *et al.*, 1985; Hogle *et al.*, 1985; Arnold *et al.*, 1987; Hosur *et al.*, 1987; Luo *et al.*, 1987; Acharya *et al.*, 1989). The power of this procedure has been examined theoretically by Arnold & Rossmann (1986).

The availability of fast computers with large random access memories and even larger disk storage also makes many of the techniques considered here commonplace and no longer subject to

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limitations of computer hardware. For instance, numerous rotation and translation functions can be evaluated rapidly, making it possible to explore many alternative interpretations of such functions in the anticipation that there must be one solution consistent with the available search models and the observed data. Such possibilities have encouraged the creation of powerful computer packages such as *MERLOT* (Fitzgerald, 1988), *BRUTE* (Fujinaga & Read, 1987), a package based on a generalized locked rotation function (Tong & Rossmann, 1990) and others. In addition, *ab initio* phase determination based on noncrystallographic redundancy has become a fairly common event (Rossmann, 1990).

Acknowledgements

As in other reviews, we are indebted to numerous authors for their writings and insights. In particular, however, we have borrowed extensively from the review by Argos & Rossmann (1980) on *Molecular Replacement*. We have been supported by a National Science Foundation grant and National Institutes of Health grants to MGR and a Damon Runyon–Walter Winchell Postdoctoral Fellowship to EA during the period when we prepared the manuscript. The manuscript was typed and brought to a readable form by Sharon Wilder to whom we are greatly indebted.

2.4. Isomorphous replacement and anomalous scattering

BY M. VIJAYAN AND S. RAMASESHAN

2.4.1. Introduction

Isomorphous replacement is among the earliest methods to be employed for crystal structure determination (Cork, 1927). The power of this method was amply demonstrated in the classical X-ray work of J. M. Robertson on phthalocyanine in the 1930s using centric data (Robertson, 1936; Robertson & Woodward, 1937). The structure determination of strychnine sulfate pentahydrate by Bijvoet and others provides an early example of the application of this method to acentric reflections (Bokhoven *et al.*, 1951). The usefulness of isomorphous replacement in the analysis of complex protein structures was demonstrated by Perutz and colleagues (Green *et al.*, 1954). This was closely followed by developments in the methodology for the application of isomorphous replacement to protein work (Harker, 1956; Blow & Crick, 1959) and rapidly led to the first ever structure solution of two related protein crystals, namely, those of myoglobin and haemoglobin (Kendrew *et al.*, 1960; Cullis *et al.*, 1961*b*). Since then isomorphous replacement has been the method of choice in macromolecular crystallography and most of the subsequent developments in and applications of this method have been concerned with biological macromolecules, mainly proteins (Blundell & Johnson, 1976; McPherson, 1982).

The application of anomalous-scattering effects has often developed in parallel with that of isomorphous replacement. Indeed, the two methods are complementary to a substantial extent and they are often treated together, as in this article. Although the most important effect of anomalous scattering, namely, the violation of Friedel's law, was experimentally observed as early as 1930 (Coster *et al.*, 1930), two decades elapsed before this effect was made use of for the first time by Bijvoet and his associates for the determination of the absolute configuration of asymmetric molecules as well as for phase evaluation (Bijvoet, 1949, 1954; Bijvoet *et al.*, 1951). Since then there has been a phenomenal spurt in the application of anomalous-scattering effects (Srinivasan, 1972; Ramaseshan & Abrahams, 1975; Vijayan, 1987). A quantitative formulation for the determination of phase angles using intensity differences between Friedel equivalents was derived by Ramachandran & Raman (1956), while Okaya & Pepinsky (1956) successfully developed a Patterson approach involving anomalous effects. The anomalous-scattering method of phase determination has since been used in the structure analysis of several structures, including those of a complex derivative of vitamin B₁₂ (Dale *et al.*, 1963) and a small protein (Hendrickson & Teeter, 1981). In the meantime, the effect of changes in the real component of the dispersion correction as a function of the wavelength of the radiation used, first demonstrated by Mark & Szillard (1925), also received considerable attention. This effect, which is formally equivalent to that of isomorphous replacement, was demonstrated to be useful in structure determination (Ramaseshan *et al.*, 1957; Ramaseshan, 1963). Protein crystallographers have been quick to exploit anomalous-scattering effects (Rossmann, 1961; Kartha & Parthasarathy, 1965; North, 1965; Matthews, 1966; Hendrickson, 1979) and, as in the case of the isomorphous replacement method, the most useful applications of anomalous scattering during the last two decades have been perhaps in the field of macromolecular crystallography (Kartha, 1975; Watenpaugh *et al.*, 1975; Vijayan, 1981). In addition to anomalous scattering of X-rays, that of neutrons was also found to have interesting applications (Koetzle & Hamilton, 1975; Sikka & Rajagopal, 1975). More recently there has been a further revival in the development of anomalous-scattering methods with the advent of synchrotron radiation, particularly in view of the possibility of choosing any desired wavelength from a synchrotron-radiation source (Helliwell, 1984).

It is clear from the foregoing that the isomorphous replacement and the anomalous-scattering methods have a long and distinguished history. It is therefore impossible to do full justice to them in a comparatively short presentation like the present one. Several procedures for the application of these methods have been developed at different times. Many, although of considerable historical importance, are not extensively used at present for a variety of reasons. No attempt has been made to discuss them in detail here; the emphasis is primarily on the state of the art as it exists now. The available literature on isomorphous replacement and anomalous scattering is extensive. The reference list given at the end of this part is representative rather than exhaustive.

During the past few years, rapid developments have taken place in the isomorphous replacement and anomalous-scattering methods, particularly in the latter, as applied to macromolecular crystallography. These developments will be described in detail in *International Tables for Crystallography*, Volume F (2001). Therefore, they have not been dealt with in this chapter. Significant developments in applications of direct methods to macromolecular crystallography have also occurred in recent years. A summary of these developments as well as the traditional direct methods on which the recent progress is based are presented in Chapter 2.2.

2.4.2. Isomorphous replacement method

2.4.2.1. Isomorphous replacement and isomorphous addition

Two crystals are said to be isomorphous if (a) both have the same space group and unit-cell dimensions and (b) the types and the positions of atoms in both are the same except for a replacement of one or more atoms in one structure with different types of atoms in the other (isomorphous replacement) or the presence of one or more additional atoms in one of them (isomorphous addition). Consider two crystal structures with identical space groups and unit-cell dimensions, one containing N atoms and the other M atoms. The N atoms in the first structure contain subsets P and Q whereas the M atoms in the second structure contain subsets P , Q' and R . The subset P is common to both structures in terms of atomic positions and atom types. The atomic positions are identical in subsets Q and Q' , but at any given atomic position the atom type is different in Q and Q' . The subset R exists only in the second structure. If $\mathbf{F}_N$ and $\mathbf{F}_M$ denote the structure factors of the two structures for a given reflection,

$$\mathbf{F}_N = \mathbf{F}_P + \mathbf{F}_Q \quad (2.4.2.1)$$

and

$$\mathbf{F}_M = \mathbf{F}_P + \mathbf{F}_{Q'} + \mathbf{F}_R, \quad (2.4.2.2)$$

where the quantities on the right-hand side represent contributions from different subsets. From (2.4.2.1) and (2.4.2.2) we have

$$\mathbf{F}_M - \mathbf{F}_N = \mathbf{F}_H = \mathbf{F}_{Q'} - \mathbf{F}_Q + \mathbf{F}_R. \quad (2.4.2.3)$$

The above equations are illustrated in the Argand diagram shown in Fig. 2.4.2.1. $\mathbf{F}_Q$ and $\mathbf{F}_{Q'}$ would be collinear if all the atoms in Q were of the same type and those in Q' of another single type, as in the replacement of chlorine atoms in a structure by bromine atoms.

We have a case of 'isomorphous replacement' if $\mathbf{F}_R = 0$ ($\mathbf{F}_H = \mathbf{F}_{Q'} - \mathbf{F}_Q$) and a case of 'isomorphous addition' if $\mathbf{F}_Q = \mathbf{F}_{Q'} = 0$ ($\mathbf{F}_H = \mathbf{F}_R$). Once $\mathbf{F}_H$ is known, in addition to the magnitudes of $\mathbf{F}_N$ and $\mathbf{F}_M$, which can be obtained experimentally, the two cases can be treated in an equivalent manner in reciprocal space. In deference to common practice, the term 'isomorphous

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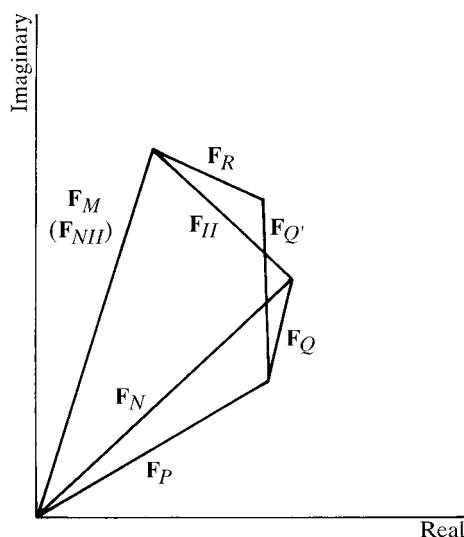


Fig. 2.4.2.1. Vector relationship between $\mathbf{F}_N$ and $\mathbf{F}_M (\equiv \mathbf{F}_{NH})$.

replacement' will be used to cover both cases. Also, in as much as $\mathbf{F}_M$ is the vector sum of $\mathbf{F}_N$ and $\mathbf{F}_H$, $\mathbf{F}_M$ and $\mathbf{F}_{NH}$ will be used synonymously. Thus

$$\mathbf{F}_M \equiv \mathbf{F}_{NH} = \mathbf{F}_N + \mathbf{F}_H. \quad (2.4.2.4)$$

2.4.2.2. Single isomorphous replacement method

The number of replaceable (or 'added') atoms is usually small and they generally have high atomic numbers. Their positions are often determined by a Patterson synthesis of one type or another (see Chapter 2.3). It will therefore be assumed in the following discussion that $\mathbf{F}_H$ is known. Then it can be readily seen by referring to Fig. 2.4.2.2 that

$$\alpha_N = \alpha_H - \cos^{-1} \frac{F_{NH}^2 - F_N^2 - F_H^2}{2F_N F_H} = \alpha_H \pm \varphi; \quad (2.4.2.5)$$

when φ is derived from its cosine function, it could obviously be positive or negative. Hence, there are two possible solutions for α_N . These two solutions are distributed symmetrically about $\mathbf{F}_H$. One of these would correspond to the correct value of α_N . Therefore, in general, the phase angle cannot be unambiguously determined using a pair of isomorphous crystals.

The twofold ambiguity in phase angle vanishes when the structures are centrosymmetric. $\mathbf{F}_{NH}$, $\mathbf{F}_N$ and $\mathbf{F}_H$ are all real in

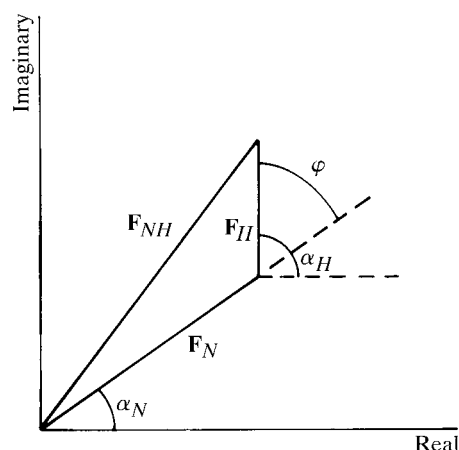


Fig. 2.4.2.2. Relationship between α_N , α_H and φ .

centric data and the corresponding phase angles are 0 or 180°. From (2.4.2.4)

$$F_{NH} \pm F_N = F_H. \quad (2.4.2.6)$$

The sign of F_H is already known and the signs of F_{NH} and F_N can be readily determined from (2.4.2.6) (Robertson & Woodward, 1937).

When the data are acentric, the best one can do is to use both the possible phase angles simultaneously in a Fourier synthesis (Bokhoven *et al.*, 1951). This double-phased synthesis, which is equivalent to the isomorphous synthesis of Ramachandran & Raman (1959), contains the structure and its inverse when the replaceable atoms have a centrosymmetric distribution (Ramachandran & Srinivasan, 1970). When the distribution is noncentrosymmetric, however, the synthesis contains peaks corresponding to the structure and general background. Fourier syntheses computed using the single isomorphous replacement method of Blow & Rossmann (1961) and Kartha (1961) have the same properties. In this method, the phase angle is taken to be the average of the two possible solutions of α_N , which is always α_H or $\alpha_H + 180^\circ$. Also, the Fourier coefficients are multiplied by $\cos \varphi$, following arguments based on the Blow & Crick (1959) formulation of phase evaluation (see Section 2.4.4.4). Although Blow & Rossmann (1961) have shown that this method could yield interpretable protein Fourier maps, it is rarely used as such in protein crystallography as the Fourier maps computed using it usually have unacceptable background levels (Blundell & Johnson, 1976).

2.4.2.3. Multiple isomorphous replacement method

The ambiguity in α_N in a noncentrosymmetric crystal can be resolved only if at least two crystals isomorphous to it are available (Bokhoven *et al.*, 1951). We then have two equations of the type (2.4.2.5), namely,

$$\alpha_N = \alpha_{H1} \pm \varphi_1 \quad \text{and} \quad \alpha_N = \alpha_{H2} \pm \varphi_2, \quad (2.4.2.7)$$

where subscripts 1 and 2 refer to isomorphous crystals 1 and 2, respectively. This is demonstrated graphically in Fig. 2.4.2.3 with the aid of the Harker (1956) construction. A circle is drawn with F_N as radius and the origin of the vector diagram as the centre. Two more circles are drawn with F_{NH1} and F_{NH2} as radii and the ends of vectors $-\mathbf{F}_{H1}$ and $-\mathbf{F}_{H2}$, respectively as centres. Each of these circles intersects the F_N circle at two points corresponding to the two possible solutions. One of the points of intersection is common and this point defines the correct value of α_N . With the assumption of perfect isomorphism and if errors are neglected, the phase circles corresponding to all the crystals would intersect at a common point if a number of isomorphous crystals were used for phase determination.

2.4.3. Anomalous-scattering method

2.4.3.1. Dispersion correction

Atomic scattering factors are normally calculated on the assumption that the binding energy of the electrons in an atom is negligible compared to the energy of the incident X-rays and the distribution of electrons is spherically symmetric. The transition frequencies within the atom are then negligibly small compared to the frequency of the radiation used and the scattering power of each electron in the atom is close to that of a free electron. When this assumption is valid, the atomic scattering factor is a real positive number and its value decreases as the scattering angle increases because of the finite size of the atom. When the binding energy of the electrons is appreciable, the atomic scattering factor at any given angle is given by

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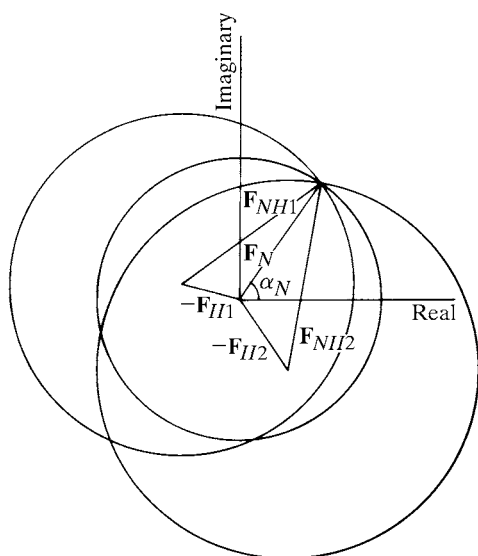


Fig. 2.4.2.3. Harker construction when two heavy-atom derivatives are available.

$$f_0 + f' + if'', \quad (2.4.3.1)$$

where f_0 is a real positive number and corresponds to the atomic scattering factor for a spherically symmetric collection of free electrons in the atom. The second and third terms are, respectively, referred to as the real and the imaginary components of the 'dispersion correction' (IT IV, 1974). f' is usually negative whereas f'' is positive. For any given atom, f'' is obviously 90° ahead of the real part of the scattering factor given by

$$f = f_0 + f'. \quad (2.4.3.2)$$

The variation of f' and f'' as a function of atomic number for two typical radiations is given in Fig. 2.4.3.1 (Srinivasan, 1972; Cromer, 1965). The dispersion effects are pronounced when an absorption edge of the atom concerned is in the neighbourhood of the wavelength of the incident radiation. Atoms with high atomic numbers have several absorption edges and the dispersion-correction terms in their scattering factors always have appreciable values. The values of f' and f'' do not vary appreciably with the angle of scattering as they are caused by core electrons confined to a very small volume around the nucleus. An atom is usually referred to as an anomalous scatterer if the dispersion-correction terms in its scattering factor have appreciable values. The effects on the structure factors or intensities of Bragg reflections resulting from dispersion corrections are referred to as anomalous-dispersion effects or anomalous-scattering effects.

2.4.3.2. Violation of Friedel's law

Consider a structure containing N atoms of which P are normal atoms and the remaining Q anomalous scatterers. Let $\mathbf{F}_P$ denote the contribution of the P atoms to the structure, and $\mathbf{F}_Q$ and $\mathbf{F}_Q''$ the real and imaginary components of the contribution of the Q atoms. The relation between the different contributions to a reflection $\mathbf{h}$ and its Friedel equivalent $-\mathbf{h}$ is illustrated in Fig. 2.4.3.2. For simplicity we assume here that all Q atoms are of the same type. The phase angle of $\mathbf{F}_Q''$ is then exactly 90° ahead of that of $\mathbf{F}_Q$. The structure factors of $\mathbf{h}$ and $-\mathbf{h}$ are denoted in the figure by $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$, respectively. In the absence of anomalous scattering, or when the imaginary component of the dispersion correction is zero, the magnitudes of the two structure factors are equal and Friedel's law is obeyed; the phase angles have equal magnitudes, but opposite signs. As can be seen from Fig. 2.4.3.2, this is no longer true when

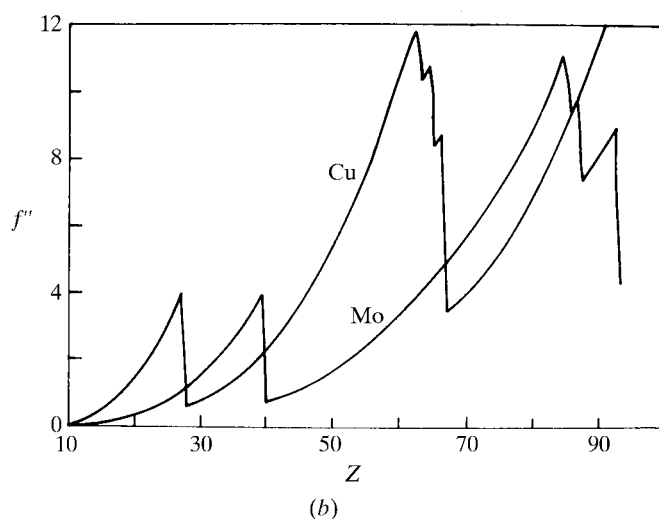
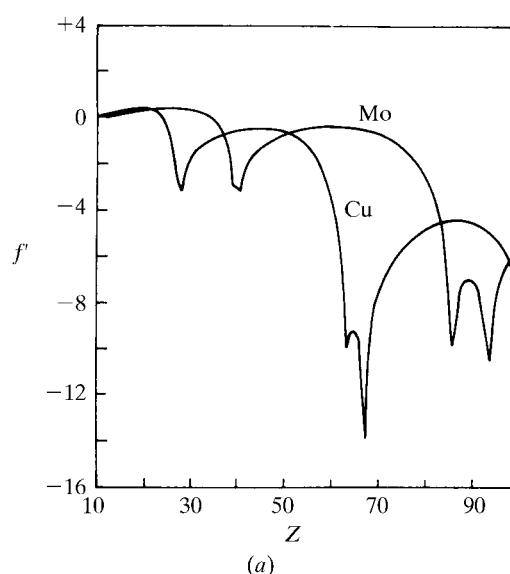


Fig. 2.4.3.1. Variation of (a) f' and (b) f'' as a function of atomic number for Cu $K\alpha$ and Mo $K\alpha$ radiations. Adapted from Fig. 3 of Srinivasan (1972).

$\mathbf{F}_Q''$ has a nonzero value. Friedel's law is then violated. A composite view of the vector relationship for $\mathbf{h}$ and $-\mathbf{h}$ can be obtained, as in Fig. 2.4.3.3, by reflecting the vectors corresponding to $-\mathbf{h}$ about the real axis of the vector diagram. $\mathbf{F}_P$ and $\mathbf{F}_Q$ corresponding to the two reflections superpose exactly, but $\mathbf{F}_Q''$ do not. $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$ then have different magnitudes and phases.

It is easily seen that Friedel's law is obeyed in centric data even when anomalous scatterers are present. $\mathbf{F}_P$ and $\mathbf{F}_Q$ are then parallel to the real axis and $\mathbf{F}_Q''$ perpendicular to it. The vector sum of the three components is the same for $\mathbf{h}$ and $-\mathbf{h}$. It may, however, be noted that the phase angle of the structure factor is then no longer 0 or 180° . Even when the structure is noncentrosymmetric, the effect of anomalous scattering in terms of intensity differences between Friedel equivalents varies from reflection to reflection. The difference between $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$ is zero when $\alpha_P = \alpha_Q$ or $\alpha_Q + 180^\circ$. The difference tends to the maximum possible value ($2F_Q''$) when $\alpha_P = \alpha_Q \pm 90^\circ$.

Intensity differences between Friedel equivalents depend also on the ratio (in terms of number and scattering power) between anomalous and normal scatterers. Differences obviously do not occur when all the atoms are normal scatterers. On the other hand, a structure containing only anomalous scatterers of the same type also

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2.4.3.3. Friedel and Bijvoet pairs

The discussion so far has been concerned essentially with crystals belonging to space groups $P1$ and $P\bar{1}$. In the centrosymmetric space group, the crystal and the diffraction pattern have the same symmetry, namely, an inversion centre. In $P1$, however, the crystals are noncentrosymmetric while the diffraction pattern has an inversion centre, in the absence of anomalous scattering. When anomalous scatterers are present in the structure ($\mathbf{F}_Q'' \neq 0$), Friedel's law breaks down and the diffraction pattern no longer has an inversion centre. Thus the diffraction pattern displays the same symmetry as that of the crystal in the presence of anomalous scattering. The same is true with higher-symmetry space groups also. For example, consider a crystal with space group $P222$, containing anomalous scatterers. The magnitudes of $\mathbf{F}_P$ are the same for all equivalent reflections; so are those of $\mathbf{F}_Q$ and $\mathbf{F}_Q''$. Their phase angles, however, differ from one equivalent to another, as can be seen from Table 2.4.3.1. When $\mathbf{F}_Q'' = 0$, the magnitudes of the vector sum of $\mathbf{F}_P$ and $\mathbf{F}_Q$ are the same for all the equivalent reflections. The intensity pattern thus has point-group symmetry $2/m\ 2/m\ 2/m$. When $\mathbf{F}_Q'' \neq 0$, the equivalent reflections can be grouped into two sets in terms of their intensities: $hkl, \bar{h}\bar{k}\bar{l}, \bar{h}k\bar{l}$ and $\bar{h}kl$; and $\bar{h}\bar{k}l, \bar{h}kl, h\bar{k}l$ and hkl . The equivalents belonging to the first group have the same intensity; so have the equivalents in the second group. But the two intensities are different. Thus the symmetry of the pattern is 222 , the same as that of the crystal.

In general, under conditions of anomalous scattering, equivalent reflections generated by the symmetry elements in the crystal have intensities different from those of equivalent reflections generated by the introduction of an additional inversion centre in normal scattering. There have been suggestions that a reflection from the first group and another from the second group should be referred to as a 'Bijvoet pair' instead of a 'Friedel pair', when the two reflections are not inversely related. Most often, however, the terms are used synonymously. The same practice will be followed in this article.

2.4.3.4. Determination of absolute configuration

The determination of the absolute configuration of chiral molecules has been among the most important applications of anomalous scattering. Indeed, anomalous scattering is the only effective method for this purpose and the method, first used in the early 1950s (Peerdeman *et al.*, 1951), has been extensively employed in structural crystallography (Ramaseshan, 1963; Vos, 1975).

Many molecules, particularly biologically important ones, are chiral in that the molecular structure is not superimposable on its mirror image. Chirality (handedness) arises primarily on account of the presence of asymmetric carbon atoms in the molecule. A tetravalent carbon is asymmetric when the four atoms (or groups) bonded to it are all different from one another. The substituents can then have two distinct arrangements which are mirror images of (or related by inversion to) each other. These optical isomers or enantiomers have the same chemical and physical properties except

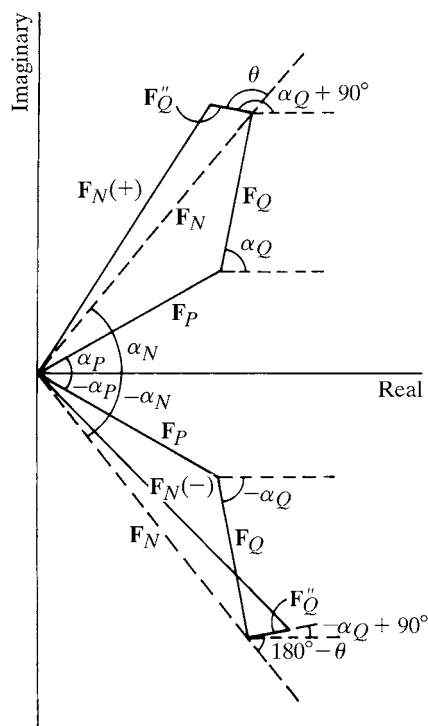


Fig. 2.4.3.2. Vector diagram illustrating the violation of Friedel's law when $\mathbf{F}_Q'' \neq 0$.

does not give rise to intensity differences. Expressions for intensity differences between Friedel equivalents have been derived by Zachariasen (1965) for the most general case of a structure containing normal as well as different types of anomalous scatterers. Statistical distributions of such differences under various conditions have also been derived (Parthasarathy & Srinivasan, 1964; Parthasarathy, 1967). It turns out that, with a single type of anomalous scatterer in the structure, the ratio

$$\frac{|F_N^2(+)-F_N^2(-)|}{F_N^2(+)+F_N^2(-)}$$

has a maximum mean value when the scattering powers of the anomalous scatterers and the normal scatterers are nearly the same (Srinivasan, 1972). Also, for a given ratio between the scattering powers, the smaller the number of anomalous scatterers, the higher is the mean ratio.

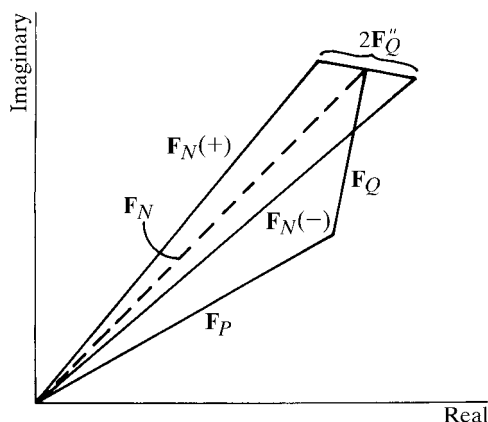


Fig. 2.4.3.3. A composite view of the vector relationship between $\mathbf{F}_N(+)$ and $\mathbf{F}_N(-)$.

Table 2.4.3.1. Phase angles of different components of the structure factor in space group $P222$

Reflection	Phase angle (°) of		
	$\mathbf{F}_P$	$\mathbf{F}_Q$	$\mathbf{F}_Q''$
$hkl, \bar{h}\bar{k}\bar{l}, \bar{h}k\bar{l}$	α_P	α_Q	$90 + \alpha_Q$
$\bar{h}\bar{k}l, \bar{h}kl, h\bar{k}l$	$-\alpha_P$	$-\alpha_Q$	$90 - \alpha_Q$

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that they rotate the plane of polarization in opposite directions when polarized light passes through them. It is not, however, possible to calculate the sign of optical rotation, given the exact spatial arrangement or the 'absolute configuration' of the molecule. Therefore, one cannot distinguish between the possible enantiomorphic configurations of a given asymmetric molecule from measurements of optical rotation. This is also true of molecules with chiralities generated by overall asymmetric geometry instead of the presence of asymmetric carbon atoms in them.

Normal X-ray scattering does not distinguish between enantiomers. Two structures $A(x_j, y_j, z_j)$ and $B(-x_j, -y_j, -z_j)$ ($j = 1, \dots, N$) obviously produce the same diffraction pattern on account of Friedel's law. The situation is, however, different when anomalous scatterers are present in the structure. The intensity difference between reflections $\mathbf{h}$ and $-\mathbf{h}$, or that between members of any Bijvoet pair, has the same magnitude, but opposite sign for structures A and B . If the atomic coordinates are known, the intensities of Bijvoet pairs can be readily calculated. The absolute configuration can then be determined, *i.e.* one can distinguish between A and B by comparing the calculated intensities with the observed ones for a few Bijvoet pairs with pronounced anomalous effects.

2.4.3.5. Determination of phase angles

An important application of anomalous scattering is in the determination of phase angles using Bijvoet differences (Ramachandran & Raman, 1956; Peerdeman & Bijvoet, 1956). From Figs. 2.4.3.2 and 2.4.3.3, we have

$$F_N^2(+) = F_N^2 + F_Q''^2 + 2F_N F_Q'' \cos \theta \quad (2.4.3.3)$$

and

$$F_N^2(-) = F_N^2 + F_Q''^2 - 2F_N F_Q'' \cos \theta. \quad (2.4.3.4)$$

Then

$$\cos \theta = \frac{F_N^2(+) - F_N^2(-)}{4F_N F_Q''}. \quad (2.4.3.5)$$

In the above equations F_N may be approximated to $[F_N(+) + F_N(-)]/2$. Then θ can be evaluated from (2.4.3.5) except for the ambiguity in its sign. Therefore, from Fig. 2.4.3.2, we have

$$\alpha_N = \alpha_Q + 90^\circ \pm \theta. \quad (2.4.3.6)$$

The phase angle thus has two possible values symmetrically distributed about F_Q'' . Anomalous scatterers are usually heavy atoms and their positions can most often be determined by Patterson methods. α_Q can then be calculated and the two possible values of α_N for each reflection evaluated using (2.4.3.6).

In practice, the twofold ambiguity in phase angles can often be resolved in a relatively straightforward manner. As indicated earlier, anomalous scatterers usually have relatively high atomic numbers. The 'heavy-atom' phases calculated from their positions therefore contain useful information. For any given reflection, that phase angle which is closer to the heavy-atom phase, from the two phases calculated using (2.4.3.6), may be taken as the correct phase angle. This method has been successfully used in several structure determinations including that of a derivative of vitamin B₁₂ (Dale *et al.*, 1963). The same method was also employed in a probabilistic fashion in the structure solution of a small protein (Hendrickson & Teeter, 1981). A method for obtaining a unique, but approximate, solution for phase angles from (2.4.3.6) has also been suggested (Srinivasan & Chacko, 1970). An accurate unique solution for phase angles can be obtained if one collects two sets of intensity data using two different wavelengths which have different dispersion-correction terms for the anomalous scatterers in the structure. Two

equations of the type (2.4.3.6) are then available for each reflection and the solution common to both is obviously the correct phase angle. Different types of Patterson and Fourier syntheses can also be employed for structure solution using intensity differences between Bijvoet equivalents (Srinivasan, 1972; Okaya & Pepinsky, 1956; Pepinsky *et al.*, 1957).

An interesting situation occurs when the replaceable atoms in a pair of isomorphous structures are anomalous scatterers. The phase angles can then be uniquely determined by combining isomorphous replacement and anomalous-scattering methods. Such situations normally occur in protein crystallography and are discussed in Section 2.4.4.5.

2.4.3.6. Anomalous scattering without phase change

The phase determination, and hence the structure solution, outlined above relies on the imaginary component of the dispersion correction. Variation in the real component can also be used in structure analysis. In early applications of anomalous scattering, the real component of the dispersion correction was made use of to distinguish between atoms of nearly the same atomic numbers (Mark & Szillard, 1925; Bradley & Rodgers, 1934). For example, copper and manganese, with atomic numbers 29 and 25, respectively, are not easily distinguishable under normal X-ray scattering. However, the real components of the dispersion correction for the two elements are -1.129 and -3.367 , respectively, when Fe $K\alpha$ radiation is used (IT IV, 1974). Therefore, the difference between the scattering factors of the two elements is accentuated when this radiation is used. The difference is more pronounced at high angles as the normal scattering factor falls off comparatively rapidly with increasing scattering angle whereas the dispersion-correction term does not.

The structure determination of KMnO₄ provides a typical example for the use of anomalous scattering without phase change in the determination of a centrosymmetric structure (Ramaseshan *et al.*, 1957; Ramaseshan & Venkatesan, 1957). f' and f'' for manganese for Cu $K\alpha$ radiation are -0.568 and 2.808 , respectively. The corresponding values for Fe $K\alpha$ radiation are -3.367 and 0.481 , respectively (IT IV, 1974). The data sets collected using the two radiations can now be treated as those arising from two perfectly isomorphous crystals. The intensity differences between a reflection in one set and the corresponding reflection in the other are obviously caused by the differences in the dispersion-correction terms. They can, however, be considered formally as intensity differences involving data from two perfectly isomorphous crystals. They can be used, as indeed they were, to determine the position of the manganese ion through an appropriate Patterson synthesis (see Section 2.4.4.2) and then to evaluate the signs of structure factors using (2.4.2.6) when the structure is centrosymmetric. When the structure is noncentrosymmetric, a twofold ambiguity exists in the phase angles in a manner analogous to that in the isomorphous replacement method. This ambiguity can be removed if the structure contains two different subsets of atoms Q_1 and Q_2 which, respectively, scatter radiations λ_{Q_1} and λ_{Q_2} anomalously. Data sets can then be collected with λ , which is scattered normally by all atoms, λ_{Q_1} and λ_{Q_2} . The three sets can be formally treated as those from three perfectly isomorphous structures and the phase determination effected using (2.4.2.7) (Ramaseshan, 1963).

2.4.3.7. Treatment of anomalous scattering in structure refinement

The effect of anomalous scattering needs to be taken into account in the refinement of structures containing anomalous scatterers, if accurate atomic parameters are required. The effect of the real part of the dispersion correction is largely confined to the thermal parameters of anomalous scatterers. This effect can be eliminated

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by simply adding f' to the normal scattering factor of the anomalous scatterers.

The effects of the imaginary component of the dispersion correction are, however, more complex. These effects could lead to serious errors in positional parameters when the space group is polar, if data in the entire diffraction sphere are not used (Ueki *et al.*, 1966; Cruickshank & McDonald, 1967). For example, accessible data in a hemisphere are normally used for X-ray analysis when the space group is $P1$. If the hemisphere has say h positive, the x coordinates of all the atoms would be in error when the structure contains anomalous scatterers. The situation in other polar space groups has been discussed by Cruickshank & McDonald (1967). In general, in the presence of anomalous scattering, it is desirable to collect data for the complete sphere, if accurate structural parameters are required (Srinivasan, 1972).

Methods have been derived to correct for dispersion effects in observed data from centrosymmetric and noncentrosymmetric crystals (Patterson, 1963). The methods are empirical and depend upon the refined parameters at the stage at which corrections are applied. This is obviously an unsatisfactory situation and it has been suggested that the measured structure factors of Bijvoet equivalents should instead be treated as independent observations in structure refinement (Ibers & Hamilton, 1964). The effect of dispersion corrections needs to be taken into account to arrive at the correct scale and temperature factors also (Wilson, 1975; Gilli & Cruickshank, 1973).

2.4.4. Isomorphous replacement and anomalous scattering in protein crystallography

2.4.4.1. Protein heavy-atom derivatives

Perhaps the most spectacular applications of isomorphous replacement and anomalous-scattering methods have been in the structure solution of large biological macromolecules, primarily proteins. Since its first successful application on myoglobin and haemoglobin, the isomorphous replacement method, which is often used in conjunction with the anomalous-scattering method, has been employed in the solution of scores of proteins. The application of this method involves the preparation of protein heavy-atom derivatives, *i.e.* the attachment of heavy atoms like mercury, uranium and lead, or chemical groups containing them, to protein crystals in a coherent manner without changing the conformation of the molecules and their crystal packing. This is only rarely possible in ordinary crystals as the molecules in them are closely packed. Protein crystals, however, contain large solvent regions and isomorphous derivatives can be prepared by replacing the disordered solvent molecules by heavy-atom-containing groups without disturbing the original arrangement of protein molecules.

2.4.4.2. Determination of heavy-atom parameters

For any given reflection, the structure factor of the native protein crystal ($\mathbf{F}_N$), that of a heavy-atom derivative ($\mathbf{F}_{NH}$), and the contribution of the heavy atoms in that derivative ($\mathbf{F}_H$) are related by the equation

$$\mathbf{F}_{NH} = \mathbf{F}_N + \mathbf{F}_H. \quad (2.4.4.1)$$

The value of $\mathbf{F}_H$ depends not only on the positional and thermal parameters of the heavy atoms, but also on their occupancy factors, because, at a given position, the heavy atom may not often be present in all the unit cells. For example, if the heavy atom is present at a given position in only half the unit cells in the crystal, then the occupancy factor of the site is said to be 0.5.

For the successful determination of the heavy-atom parameters, as also for the subsequent phase determination, the data sets from

the native and the derivative crystals should have the same relative scale. The different data sets should also have the same overall temperature factor. Different scaling procedures have been suggested (Blundell & Johnson, 1976) and, among them, the following procedure, based on Wilson's (1942) statistics, appears to be the most feasible in the early stages of structure analysis.

Assuming that the data from the native and the derivative crystals obey Wilson's statistics, we have, for any range of $\sin^2 \theta / \lambda^2$,

$$\ln \left\{ \frac{\sum f_{Nj}^2}{\langle F_N^2 \rangle} \right\} = \ln K_N + 2B_N \frac{\sin^2 \theta}{\lambda^2} \quad (2.4.4.2)$$

and

$$\ln \left\{ \frac{\sum f_{Nj}^2 + \sum f_{Hj}^2}{\langle F_{NH}^2 \rangle} \right\} = \ln K_{NH} + 2B_{NH} \frac{\sin^2 \theta}{\lambda^2}, \quad (2.4.4.3)$$

where f_{Nj} and f_{Hj} refer to the atomic scattering factors of protein atoms and heavy atoms, respectively. K_N and K_{NH} are the scale factors to be applied to the intensities from the native and the derivative crystals, respectively, and B_N and B_{NH} the temperature factors of the respective structure factors. Normally one would be able to derive the absolute scale factor and the temperature factor for both the data sets from (2.4.4.2) and (2.4.4.3) using the well known Wilson plot. The data from protein crystals, however, do not follow Wilson's statistics as protein molecules contain highly non-random features. Therefore, in practice, it is difficult to fit a straight line through the points in a Wilson plot, thus rendering the parameters derived from it unreliable. (2.4.4.2) and (2.4.4.3) can, however, be used in a different way. From the two equations we obtain

$$\begin{aligned} \ln \left\{ \frac{\sum f_{Nj}^2 + \sum f_{Hj}^2}{\sum f_{Nj}^2} \cdot \frac{\langle F_N^2 \rangle}{\langle F_{NH}^2 \rangle} \right\} \\ = \ln \left(\frac{K_{NH}}{K_N} \right) + 2(B_{NH} - B_N) \frac{\sin^2 \theta}{\lambda^2}. \end{aligned} \quad (2.4.4.4)$$

The effects of structural non-randomness in the crystals obviously cancel out in (2.4.4.4). When the left-hand side of (2.4.4.4) is plotted against $(\sin^2 \theta) / \lambda^2$, it is called a comparison or difference Wilson plot. Such plots yield the ratio between the scales of the derivative and the native data, and the additional temperature factor of the derivative data. Initially, the number and the occupancy factors of heavy-atom sites are unknown, and are roughly estimated from intensity differences to evaluate $\sum f_{Hj}^2$. These estimates usually undergo considerable revision in the course of the determination and the refinement of heavy-atom parameters.

At first, heavy-atom positions are most often determined by Patterson syntheses of one type or another. Such syntheses are discussed in some detail elsewhere in Chapter 2.3. They are therefore discussed here only briefly.

Equation (2.4.2.6) holds when the data are centric. F_H is usually small compared to F_N and F_{NH} , and the minus sign is then relevant on the left-hand side of (2.4.2.6). Thus the difference between the magnitudes of $\mathbf{F}_{NH}$ and $\mathbf{F}_N$, which can be obtained experimentally, normally gives a correct estimate of the magnitude of $\mathbf{F}_H$ for most reflections. Then a Patterson synthesis with $(F_{NH} - F_N)^2$ as coefficients corresponds to the distribution of vectors between heavy atoms, when the data are centric. But proteins are made up of L-amino acids and hence cannot crystallize in centrosymmetric space groups. However, many proteins crystallize in space groups with centrosymmetric projections. The centric data corresponding to these projections can then be used for determining heavy-atom positions through a Patterson synthesis of the type outlined above.

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The situation is more complex for three-dimensional acentric data. It has been shown (Rossmann, 1961) that

$$(F_{NH} - F_N)^2 \simeq F_H^2 \cos^2(\alpha_{NH} - \alpha_H) \quad (2.4.4.5)$$

when F_H is small compared to F_{NH} and F_N . Patterson synthesis with $(F_{NH} - F_N)^2$ as coefficients would, therefore, give an approximation to the heavy-atom vector distribution. An isomorphous difference Patterson synthesis of this type has been used extensively in protein crystallography to determine heavy-atom positions. The properties of this synthesis have been extensively studied (Ramachandran & Srinivasan, 1970; Rossmann, 1960; Phillips, 1966; Dodson & Vijayan, 1971) and it has been shown that this Patterson synthesis would provide a good approximation to the heavy-atom vector distribution even when F_H is large compared to F_N (Dodson & Vijayan, 1971).

As indicated earlier (see Section 2.4.3.1), heavy atoms are always anomalous scatterers, and the structure factors of any given reflection and its Friedel equivalent from a heavy-atom derivative have unequal magnitudes. If these structure factors are denoted by $F_{NH}(+)$ and $F_{NH}(-)$ and the real component of the heavy-atom contributions (including the real component of the dispersion correction) by F_H , then it can be shown (Kartha & Parthasarathy, 1965) that

$$\left(\frac{k}{2}\right)^2 [F_{NH}(+) - F_{NH}(-)]^2 = F_H^2 \sin^2(\alpha_{NH} - \alpha_H), \quad (2.4.4.6)$$

where $k = (f_H + f_H')/f_H''$. Here it has been assumed that all the anomalous scatterers are of the same type with atomic scattering factor f_H and dispersion-correction terms f_H' and f_H'' . A Patterson synthesis with the left-hand side of (2.4.4.6) as coefficients would also yield the vector distribution corresponding to the heavy-atom positions (Rossmann, 1961; Kartha & Parthasarathy, 1965). However, $F_{NH}(+) - F_{NH}(-)$ is a small difference between two large quantities and is liable to be in considerable error. Patterson syntheses of this type are therefore rarely used to determine heavy-atom positions.

It is interesting to note (Kartha & Parthasarathy, 1965) that addition of (2.4.4.5) and (2.4.4.6) readily leads to

$$(F_{NH} - F_N)^2 + \left(\frac{k}{2}\right)^2 [F_{NH}(+) - F_{NH}(-)]^2 \simeq F_H^2. \quad (2.4.4.7)$$

Thus, the magnitude of the heavy-atom contribution can be estimated if intensities of Friedel equivalents have been measured from the derivative crystal. F_{NH} is then not readily available, but to a good approximation

$$F_{NH} = [F_{NH}(+) + F_{NH}(-)]/2. \quad (2.4.4.8)$$

A different and more accurate expression for estimating F_H^2 from isomorphous and anomalous differences was derived by Matthews (1966). According to a still more accurate expression derived by Singh & Ramaseshan (1966),

$$\begin{aligned} F_H^2 &= F_{NH}^2 + F_N^2 - 2F_{NH}F_N \cos(\alpha_N - \alpha_{NH}) \\ &= F_{NH}^2 + F_N^2 \pm 2F_{NH}F_N \\ &\quad \times (1 - \{k[F_{NH}(+) - F_{NH}(-)]/2F_N\}^2)^{1/2}. \end{aligned} \quad (2.4.4.9)$$

The lower estimate in (2.4.4.9) is relevant when $|\alpha_N - \alpha_{NH}| < 90^\circ$ and the upper estimate is relevant when $|\alpha_N - \alpha_{NH}| > 90^\circ$. The lower and the upper estimates may be referred to as F_{HLE} and F_{HUE} , respectively. It can be readily shown (Dodson & Vijayan, 1971) that the lower estimate would represent the correct value of F_H for a vast majority of reflections. Thus, a Patterson synthesis with F_{HLE}^2 as coefficients would yield the vector distribution of heavy atoms in

the derivative. Such a synthesis would normally be superior to those with the left-hand sides of (2.4.4.5) and (2.4.4.6) as coefficients. However, when the level of heavy-atom substitution is low, the anomalous differences are also low and susceptible to large percentage errors. In such a situation, a synthesis with $(F_{NH} - F_N)^2$ as coefficients is likely to yield better results than that with F_{HLE}^2 as coefficients (Vijayan, 1981).

Direct methods employing different methodologies have also been used successfully for the determination of heavy-atom positions (Navia & Sigler, 1974). These methods, developed primarily for the analysis of smaller structures, have not yet been successful in *a priori* analysis of protein structures. The very size of protein structures makes the probability relations used in these methods weak. In addition, data from protein crystals do not normally extend to high enough angles to permit resolution of individual atoms in the structure and the feasibility of using many of the currently popular direct-method procedures in such a situation has been a topic of much discussion. The heavy atoms in protein derivative crystals, however, are small in number and are normally situated far apart from one another. They are thus expected to be resolved even when low-resolution X-ray data are used. In most applications, the magnitudes of the differences between F_{NH} and F_N are formally considered as the 'observed structure factors' of the heavy-atom distribution and conventional direct-method procedures are then applied to them.

Once the heavy-atom parameters in one or more derivatives have been determined, approximate protein phase angles, α_N 's, can be derived using methods described later. These phase angles can then be readily used to determine the heavy-atom parameters in a new derivative employing a difference Fourier synthesis with coefficients

$$(F_{NH} - F_N) \exp(i\alpha_N). \quad (2.4.4.10)$$

Such syntheses are also used to confirm and to improve upon the information on heavy-atom parameters obtained through Patterson or direct methods. They are obviously very powerful when centric data corresponding to centrosymmetric projections are used. The synthesis yields satisfactory results even when the data are acentric although the difference Fourier technique becomes progressively less powerful as the level of heavy-atom substitution increases (Dodson & Vijayan, 1971).

While the positional parameters of heavy atoms can be determined with a reasonable degree of confidence using the above-mentioned methods, the corresponding temperature and occupancy factors cannot. Rough estimates of the latter are usually made from the strength and the size of appropriate peaks in difference syntheses. The estimated values are then refined, along with the positional parameters, using the techniques outlined below.

2.4.4.3. Refinement of heavy-atom parameters

The least-squares method with different types of minimization functions is used for refining the heavy-atom parameters, including the occupancy factors. The most widely used method (Dickerson *et al.*, 1961; Muirhead *et al.*, 1967; Dickerson *et al.*, 1968) involves the minimization of the function

$$\varphi = \sum w(F_{NH} - |F_N + F_H|)^2, \quad (2.4.4.11)$$

where the summation is over all the reflections and w is the weight factor associated with each reflection. Here F_{NH} is the observed magnitude of the structure factor for the particular derivative and $F_N + F_H$ is the calculated structure factor. The latter obviously depends upon the protein phase angle α_N , and the magnitude and the phase angle of F_H which are in turn dependent on the heavy-atom parameters. Let us assume that we have three derivatives A, B and C, and that we have already determined the heavy-atom

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parameters HA_i , HB_i and HC_i . Then,

$$\begin{aligned} \mathbf{F}_{HA} &= \mathbf{F}_{HA}(HA_i) \\ \mathbf{F}_{HB} &= \mathbf{F}_{HB}(HB_i) \\ \mathbf{F}_{HC} &= \mathbf{F}_{HC}(HC_i). \end{aligned} \quad (2.4.4.12)$$

A set of approximate protein phase angles is first calculated, employing methods described later, making use of the unrefined heavy-atom parameters. These phase angles are used to construct $\mathbf{F}_N + \mathbf{F}_H$ for each derivative. (2.4.4.11) is then minimized, separately for each derivative, by varying HA_i for derivative A, HB_i for derivative B, and HC_i for derivative C. The refined values of HA_i , HB_i and HC_i are subsequently used to calculate a new set of protein phase angles. Alternate cycles of parameter refinement and phase-angle calculation are carried out until convergence is reached. The progress of refinement may be monitored by computing an R factor defined as (Kraut *et al.*, 1962)

$$R_K = \frac{\sum |\mathbf{F}_{NH} - |\mathbf{F}_N + \mathbf{F}_H||}{F_{NH}}. \quad (2.4.4.13)$$

The above method has been successfully used for the refinement of heavy-atom parameters in the X-ray analysis of many proteins. However, it has one major drawback in that the refined parameters in one derivative are dependent on those in other derivatives through the calculation of protein phase angles. Therefore, it is important to ensure that the derivative, the heavy-atom parameters of which are being refined, is omitted from the phase-angle calculation (Blow & Matthews, 1973). Even when this is done, serious problems might arise when different derivatives are related by common sites. In practice, the occupancy factors of the common sites tend to be overestimated compared to those of the others (Vijayan, 1981; Dodson & Vijayan, 1971). Yet another factor which affects the occupancy factors is the accuracy of the phase angles. The inclusion of poorly phased reflections tends to result in the underestimation of occupancy factors. It is therefore advisable to omit from refinement cycles reflections with figures of merit less than a minimum threshold value or to assign a weight proportional to the figure of merit (as defined later) to each term in the minimization function (Dodson & Vijayan, 1971; Blow & Matthews, 1973).

If anomalous-scattering data from derivative crystals are available, the values of F_H can be estimated using (2.4.4.7) or (2.4.4.9) and these can be used as the 'observed' magnitudes of the heavy-atom contributions for the refinement of heavy-atom parameters, as has been done by many workers (Watenpaugh *et al.*, 1975; Vijayan, 1981; Kartha, 1965). If (2.4.4.9) is used for estimating F_H , the minimization function has the form

$$\varphi = \sum w(F_{HLE} - F_H)^2. \quad (2.4.4.14)$$

The progress of refinement may be monitored using a reliability index defined as

$$R = \frac{\sum |F_{HLE} - F_H|}{\sum F_{HLE}}. \quad (2.4.4.15)$$

The major advantage of using F_{HLE} 's in refinement is that the heavy-atom parameters in each derivative can now be refined independently of all other derivatives. Care should, however, be taken to omit from calculations all reflections for which F_{HLE} is likely to be the correct estimate of F_H . This can be achieved in practice by excluding from least-squares calculations all reflections for which F_{HLE} has a value less than the maximum expected value of F_H for the given derivative (Vijayan, 1981; Dodson & Vijayan, 1971).

A major problem associated with this refinement method is concerned with the effect of experimental errors on refined

parameters. The values of $F_{NH}(+) - F_{NH}(-)$ are often comparable to the experimental errors associated with $F_{NH}(+)$ and $F_{NH}(-)$. In such a situation, even random errors in $F_{NH}(+)$ and $F_{NH}(-)$ tend to increase systematically the observed difference between them (Dodson & Vijayan, 1971). In (2.4.4.7) and (2.4.4.9), this difference is multiplied by k or $k/2$, a quantity much greater than unity, and then squared. This could lead to the systematic overestimation of F_{HLE} 's and the consequent overestimation of occupancy factors. The situation can be improved by employing empirical values of k , evaluated using the relation (Kartha & Parthasarathy, 1965; Matthews, 1966)

$$k = \frac{2 \sum |F_{NH} - F_N|}{\sum |F_{NH}(+) - F_{NH}(-)|}, \quad (2.4.4.16)$$

for estimating F_{HLE} or by judiciously choosing the weighting factors in (2.4.4.14) (Dodson & Vijayan, 1971). The use of a modified form of F_{HLE} , arrived at through statistical considerations, along with appropriate weighting factors, has also been advocated (Dodson *et al.*, 1975).

When the data are centric, (2.4.4.9) reduces to

$$F_H = F_{NH} \pm F_N. \quad (2.4.4.17)$$

Here, again, the lower estimate most often corresponds to the correct value of F_H . (2.4.4.17) does not involve $F_{NH}(+) - F_{NH}(-)$ which, as indicated earlier, is prone to substantial error. Therefore, F_H 's estimated using centric data are more reliable than those estimated using acentric data. Consequently, centric reflections, when available, are extensively used for the refinement of heavy-atom parameters. It may also be noted that in conditions under which F_{HLE} corresponds to the correct estimate of F_H , minimization functions (2.4.4.11) and (2.4.4.14) are identical for centric data.

A Patterson function correlation method with a minimization function of the type

$$\varphi = \sum w[(F_{NH} - F_N)^2 - F_H^2]^2 \quad (2.4.4.18)$$

was among the earliest procedures suggested for heavy-atom-parameter refinement (Rossmann, 1960). This procedure would obviously work well when centric reflections are used. A modified version of this procedure, in which the origins of the Patterson functions are removed from the correlation, and centric and acentric data are treated separately, has been proposed (Terwilliger & Eisenberg, 1983).

2.4.4.4. Treatment of errors in phase evaluation: Blow and Crick formulation

As shown in Section 2.4.2.3, ideally, protein phase angles can be evaluated if two isomorphous heavy-atom derivatives are available. However, in practice, conditions are far from ideal on account of several factors such as imperfect isomorphism, errors in the estimation of heavy-atom parameters, and the experimental errors in the measurement of intensity from the native and the derivative crystals. It is therefore desirable to use as many derivatives as are available for phase determination. When isomorphism is imperfect and errors exist in data and heavy-atom parameters, all the circles in a Harker diagram would not intersect at a single point; instead, there would be a distribution of intersections, such as that illustrated in Fig. 2.4.4.1. Consequently, a unique solution for the phase angle cannot be deduced.

The statistical procedure for computing protein phase angles using multiple isomorphous replacement (MIR) was derived by Blow & Crick (1959). In their treatment, Blow and Crick assume, for mathematical convenience, that all errors, including those arising from imperfect isomorphism, could be considered as residing in the magnitudes of the derivative structure factors only. They further assume that these errors could be described by a

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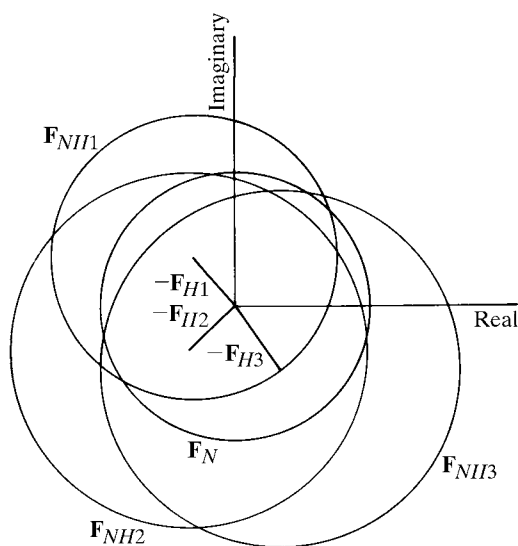


Fig. 2.4.4.1. Distribution of intersections in the Harker construction under non-ideal conditions.

Gaussian distribution. With these simplifying assumptions, the statistical procedure for phase determination could be derived in the following manner.

Consider the vector diagram, shown in Fig. 2.4.4.2, for a reflection from the i th derivative for an arbitrary value α for the protein phase angle. Then,

$$D_{Hi}(\alpha) = [F_N^2 + F_{Hi}^2 + 2F_N F_{Hi} \cos(\alpha_{Hi} - \alpha)]^{1/2}. \quad (2.4.4.19)$$

If α corresponds to the true protein phase angle α_N , then D_{Hi} coincides with F_{NHi} . The amount by which $D_{Hi}(\alpha)$ differs from F_{NHi} , namely,

$$\xi_{Hi}(\alpha) = F_{NHi} - D_{Hi}(\alpha), \quad (2.4.4.20)$$

is a measure of the departure of α from α_N . ξ is called the lack of closure. The probability for α being the correct protein phase angle could now be defined as

$$P_i(\alpha) = N_i \exp[-\xi_{Hi}^2(\alpha)/2E_i^2], \quad (2.4.4.21)$$

where N_i is the normalization constant and E_i is the estimated r.m.s. error. The methods for estimating E_i will be outlined later. When several derivatives are used for phase determination, the total probability of the phase angle α being the protein phase angle would be

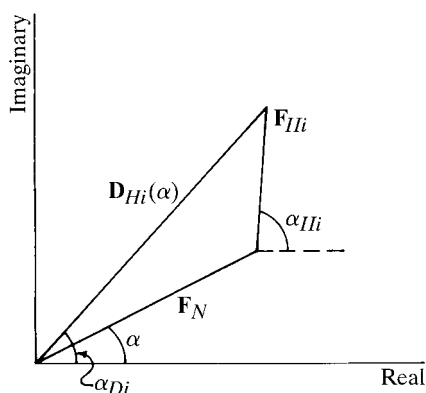


Fig. 2.4.4.2. Vector diagram indicating the calculated structure factor, $D_{Hi}(\alpha)$, of the i th heavy-atom derivative for an arbitrary value α for the phase angle of the structure factor of the native protein.

$$P(\alpha) = \prod P_i(\alpha) = N \exp\left\{-\sum_i [\xi_{Hi}^2(\alpha)/2E_i^2]\right\}, \quad (2.4.4.22)$$

where the summation is over all the derivatives. A typical distribution of $P(\alpha)$ plotted around a circle of unit radius is shown in Fig. 2.4.4.3. The phase angle corresponding to the highest value of $P(\alpha)$ would obviously be the most probable protein phase, α_M , of the given reflection. The most probable electron-density distribution is obtained if each F_N is associated with the corresponding α_M in a Fourier synthesis.

Blow and Crick suggested a different way of using the probability distribution. In Fig. 2.4.4.3, the centroid of the probability distribution is denoted by P . The polar coordinates of P are m and α_B , where m , a fractional positive number with a maximum value of unity, and α_B are referred to as the 'figure of merit' and the 'best phase', respectively. One can then compute a 'best Fourier' with coefficients

$$mF_N \exp(i\alpha_B).$$

The best Fourier is expected to provide an electron-density distribution with the lowest r.m.s. error. The figure of merit and the best phase are usually calculated using the equations

$$\begin{aligned} m \cos \alpha_B &= \sum_i P(\alpha_i) \cos(\alpha_i) / \sum_i P(\alpha_i) \\ m \sin \alpha_B &= \sum_i P(\alpha_i) \sin(\alpha_i) / \sum_i P(\alpha_i), \end{aligned} \quad (2.4.4.23)$$

where $P(\alpha_i)$ are calculated, say, at 5° intervals (Dickerson *et al.*, 1961). The figure of merit is statistically interpreted as the cosine of the expected error in the calculated phase angle and it is obviously a measure of the precision of phase determination. In general, m is high when α_M and α_B are close to each other and low when they are far apart.

2.4.4.5. Use of anomalous scattering in phase evaluation

When anomalous-scattering data have been collected from derivative crystals, $F_{NH}(+)$ and $F_{NH}(-)$ can be formally treated as arising from two independent derivatives. The corresponding Harker diagram is shown in Fig. 2.4.4.4. Thus, in principle, protein phase angles can be determined using a single derivative when anomalous-scattering effects are also made use of. It is interesting to note that the information obtained from isomorphous differences, $F_{NH} - F_N$, and that obtained from anomalous differences,

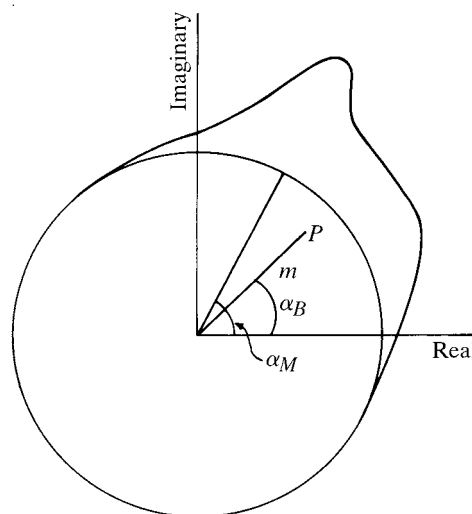


Fig. 2.4.4.3. The probability distribution of the protein phase angle. The point P is the centroid of the distribution.

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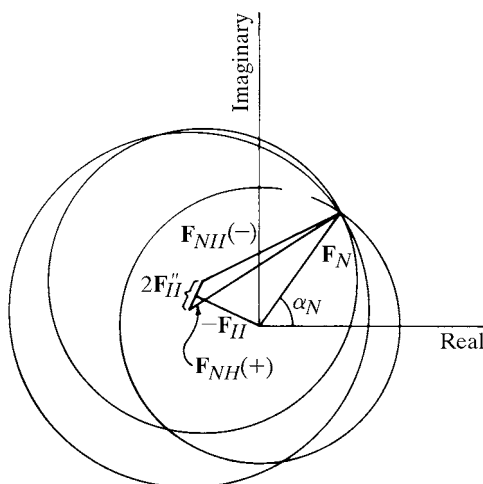


Fig. 2.4.4.4. Harker construction using anomalous-scattering data from a single derivative.

$F_{NH}(+) - F_{NH}(-)$, are complementary. The isomorphous difference for any given reflection is a maximum when F_N and F_H are parallel or antiparallel. The anomalous difference is then zero, if all the anomalous scatterers are of the same type, and α_N is determined uniquely on the basis of the isomorphous difference. The isomorphous difference decreases and the anomalous difference increases as the inclination between F_N and F_H increases. The isomorphous difference tends to be small and the anomalous difference tends to have the maximum possible value when F_N and F_H are perpendicular to each other. The anomalous difference then has the predominant influence in determining the phase angle.

Although isomorphous and anomalous differences have a complementary role in phase determination, their magnitudes are obviously unequal. Therefore, when $F_{NH}(+)$ and $F_{NH}(-)$ are treated as arising from two derivatives, the effect of anomalous differences on phase determination would be only marginal as, for any given reflection, $F_{NH}(+) - F_{NH}(-)$ is usually much smaller than $F_{NH} - F_N$. However, the magnitude of the error in the anomalous difference would normally be much smaller than that in the corresponding isomorphous difference. Firstly, the former is obviously free from the effects of imperfect isomorphism. Secondly, $F_{NH}(+)$ and $F_{NH}(-)$ are expected to have the same systematic errors as they are measured from the same crystal. These errors are eliminated in the difference between the two quantities. Therefore, as pointed out by North (1965), the r.m.s. error used for anomalous differences should be much smaller than that used for isomorphous differences. Denoting the r.m.s. error in anomalous differences by E' , the new expression for the probability distribution of protein phase angle may be written as

$$P_i(\alpha) = N_i \exp[-\xi_{Hi}^2(\alpha)/2E_i^2] \times \exp\{-[\Delta H_i - \Delta H_{ical}(\alpha)]^2/2E_i'^2\}, \quad (2.4.4.24)$$

where

$$\Delta H_i = F_{NH_i}(+) - F_{NH_i}(-)$$

and

$$\Delta H_{ical}(\alpha) = 2F_{Hi}'' \sin(\alpha_{Di} - \alpha_{Hi}).$$

Here α_{Di} is the phase angle of $D_{Hi}(\alpha)$ [see (2.4.4.19) and Fig. 2.4.4.2]. $\Delta H_{ical}(\alpha)$ is the anomalous difference calculated for the assumed protein phase angle α . F_{NH_i} may be taken as the average of $F_{NH_i}(+)$ and $F_{NH_i}(-)$ for calculating $\xi_{Hi}^2(\alpha)$ using (2.4.4.20).

2.4.4.6. Estimation of r.m.s. error

Perhaps the most important parameters that control the reliability of phase evaluation using the Blow and Crick formulation are the isomorphous r.m.s. error E_i and the anomalous r.m.s. error E'_i . For a given derivative, the sharpness of the peak in the phase probability distribution obviously depends upon the value of E and that of E' when anomalous-scattering data have also been used. When several derivatives are used, an overall underestimation of r.m.s. errors leads to artificially sharper peaks, the movement of α_B towards α_M , and deceptively high figures of merit. Opposite effects result when E 's are overestimated. Underestimation or overestimation of the r.m.s. error in the data from a particular derivative leads to distortions in the relative contribution of that derivative to the overall phase probability distributions. It is therefore important that the r.m.s. error in each derivative is correctly estimated.

Centric reflections, when present, obviously provide the best means for evaluating E using the expression

$$E^2 = \sum_n (|F_{NH} \pm F_N| - F_N)^2/n. \quad (2.4.4.25)$$

As suggested by Blow & Crick (1959), values of E thus estimated can be used for acentric reflections as well. Once a set of approximate protein phase angles is available, E_i can be calculated as the r.m.s. lack of closure corresponding to α_B [i.e. $\alpha = \alpha_B$ in (2.4.4.20)] (Kartha, 1976). E'_i can be similarly evaluated as the r.m.s. difference between the observed anomalous difference and the anomalous difference calculated for α_B [see (2.4.4.24)]. Normally, the value of E'_i is about a third of that of E_i (North, 1965).

A different method, outlined below, can also be used to evaluate E and E' when anomalous scattering is present (Vijayan, 1981; Adams, 1968). From Fig. 2.4.2.2, we have

$$\cos \psi = (F_{NH}^2 + F_H^2 - F_N^2)/2F_{NH}F_H \quad (2.4.4.26)$$

and

$$F_N^2 = F_{NH}^2 + F_H^2 - 2F_{NH}F_H \cos \psi, \quad (2.4.4.27)$$

where $\psi = \alpha_{NH} - \alpha_H$. Using arguments similar to those used in deriving (2.4.3.5), we obtain

$$\sin \psi = [F_{NH}^2(+) - F_{NH}^2(-)]/4F_{NH}F_H''. \quad (2.4.4.28)$$

If F_{NH} is considered to be equal to $[F_{NH}(+) + F_{NH}(-)]/2$, we obtain from (2.4.4.28)

$$F_{NH}(+) - F_{NH}(-) = 2F_H'' \sin \psi. \quad (2.4.4.29)$$

We obtain what may be called ψ_{iso} if the magnitude of ψ is determined from (2.4.4.26) and the quadrant from (2.4.4.28). Similarly, we obtain ψ_{ano} if the magnitude of ψ is determined from (2.4.4.28) and the quadrant from (2.4.4.26). Ideally, ψ_{iso} and ψ_{ano} should have the same value and the difference between them is a measure of the errors in the data. F_N obtained from (2.4.4.27) using ψ_{ano} may be considered as its calculated value (F_{Ncal}). Then, assuming all errors to lie in F_N , we may write

$$E^2 = \sum_n (F_N - F_{Ncal})^2/n. \quad (2.4.4.30)$$

Similarly, the calculated anomalous difference (ΔH_{cal}) may be evaluated from (2.4.4.29) using ψ_{iso} . Then

$$E'^2 = \sum_n [|F_{NH}(+) - F_{NH}(-)| - \Delta H_{cal}]^2/n. \quad (2.4.4.31)$$

If all errors are assumed to reside in F_H , E can be evaluated in yet another way using the expression

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$$E^2 = \sum_n (F_{HLE} - F_H)^2 / n. \quad (2.4.4.32)$$

2.4.4.7. Suggested modifications to Blow and Crick formulation and the inclusion of phase information from other sources

Modifications to the Blow and Crick procedure of phase evaluation have been suggested by several workers, although none represent a fundamental departure from the essential features of their formulation. In one of the modifications (Cullis *et al.*, 1961a; Ashida, 1976), all E_i 's are assumed to be the same, but the lack-of-closure error ξ_{Hi} for the i th derivative is measured as the distance from the mean of all intersections between phase circles to the point of intersection of the phase circle of that derivative with the phase circle of the native protein. Alternatively, individual values of E_i are retained, but the lack of closure is measured from the weighted mean of all intersections (Ashida, 1976). This is obviously designed to undo the effects of the unduly high weight given to F_N in the Blow and Crick formulation. In another modification (Raiz & Andreeva, 1970; Einstein, 1977), suggested for the same purpose, the F_N and F_{NHi} circles are treated as circular bands, the width of each band being related to the error in the appropriate structure factor. A comprehensive set of modifications suggested by Green (1979) treats different types of errors separately. In particular, errors arising from imperfect isomorphism are treated in a comprehensive manner.

Although the isomorphous replacement method still remains the method of choice for the *ab initio* determination of protein structures, additional items of phase information from other sources are increasingly being used to replace, supplement, or extend the information obtained through the application of the isomorphous replacement. Methods have been developed for the routine refinement of protein structures (Watenpaugh *et al.*, 1973; Huber *et al.*, 1974; Sussman *et al.*, 1977; Jack & Levitt, 1978; Isaacs & Agarwal, 1978; Hendrickson & Konner, 1980) and they provide a rich source of phase information. However, the nature of the problem and the inherent limitations of the Fourier technique are such that the possibility of refinement yielding misleading results exists (Vijayan, 1980a,b). It is therefore sometimes desirable to combine the phases obtained during refinement with the original isomorphous replacement phases. The other sources of phase information include molecular replacement (see Chapter 2.3), direct methods (Hendrickson & Karle, 1973; Sayre, 1974; de Rango *et al.*, 1975; see also Chapter 2.2) and different types of electron-density modifications (Hoppe & Gassmann, 1968; Collins, 1975; Schevitz *et al.*, 1981; Bhat & Blow, 1982; Agard & Stroud, 1982; Cannillo *et al.*, 1983; Raghavan & Tulinsky, 1979; Wang, 1985).

The problem of combining isomorphous replacement phases with those obtained by other methods was first addressed by Rossmann & Blow (1961). The problem was subsequently examined by Hendrickson & Lattman (1970) and their method, which involves a modification of the Blow and Crick formulation, is perhaps the most widely used for combining phase information from different sources.

The Blow and Crick procedure is based on an assumed Gaussian 'lumped' error in F_{NHi} which leads to a lack of closure, $\xi_{Hi}(\alpha)$, in F_{NHi} defined by (2.4.4.20). Hendrickson and Lattman make an equally legitimate assumption that the lumped error, again assumed to be Gaussian, is associated with F_{NHi}^2 . Then, as in (2.4.4.20), we have

$$\xi_{Hi}''(\alpha) = F_{NHi}^2 - D_{Hi}^2(\alpha), \quad (2.4.4.33)$$

where $\xi_{Hi}''(\alpha)$ is the lack of closure associated with F_{NHi}^2 for an assumed protein phase angle α . Then the probability for α being the

correct phase angle can be expressed as

$$P_i(\alpha) = N_i \exp[-\xi_{Hi}''(\alpha)/2E_i''^2], \quad (2.4.4.34)$$

where E_i'' is the r.m.s. error in F_{NHi}^2 , which can be evaluated using methods similar to those employed for evaluating E_i . Hendrickson and Lattman have shown that the exponent in the probability expression (2.4.4.34) can be readily expressed as a linear combination of five terms in the following manner.

$$-\xi_{Hi}''(\alpha)/2E_i''^2 = K_i + A_i \cos \alpha + B_i \sin \alpha + C_i \cos 2\alpha + D_i \sin 2\alpha, \quad (2.4.4.35)$$

where K_i, A_i, B_i, C_i and D_i are constants dependent on F_N, F_{Hi}, F_{NHi} and E_i'' . Thus, five constants are enough to store the complete probability distribution of any reflection. Expressions for the five constants have been derived for phase information from anomalous scattering, tangent formula, partial structure and molecular replacement. The combination of the phase information from all sources can then be achieved by simply taking the total value of each constant. Thus, the total probability of the protein phase angle being α is given by

$$P(\alpha) = \prod_s P_s(\alpha) = N \exp \left(\sum_s K_s + \sum_s A_s \cos \alpha + \sum_s B_s \sin \alpha + \sum_s C_s \cos 2\alpha + \sum_s D_s \sin 2\alpha \right), \quad (2.4.4.36)$$

where K_s, A_s etc. are the constants appropriate for the s th source and N is the normalization constant.

2.4.4.8. Fourier representation of anomalous scatterers

It is often useful to have a Fourier representation of only the anomalous scatterers in a protein. The imaginary component of the electron-density distribution obviously provides such a representation. When the structure is known and $F_N(+)$ and $F_N(-)$ have been experimentally determined, Chacko & Srinivasan (1970) have shown that this representation is obtained in a Fourier synthesis with $i[F_N(+) + F_N^*(-)]/2$ as coefficients, where $F_N^*(-)$, whose magnitude is $F_N(-)$, is the complex conjugate of $F_N(+)$. They also indicated a method for calculating the phase angles of $F_N(+)$ and $F_N^*(-)$. It has been shown (Hendrickson & Sheriff, 1987) that the Bijvoet-difference Fourier synthesis proposed earlier by Kraut (1968) is an approximation of the true imaginary component of the electron density. The imaginary synthesis can be useful in identifying minor anomalous-scattering centres when the major centres are known and also in providing an independent check on the locations of anomalous scatterers and in distinguishing between anomalous scatterers with nearly equal atomic numbers (Sheriff & Hendrickson, 1987; Kitagawa *et al.*, 1987).

2.4.5. Anomalous scattering of neutrons and synchrotron radiation. The multiwavelength method

The multiwavelength anomalous-scattering method (Ramaseshan, 1982) relies on the variation of dispersion-correction terms as a function of the wavelength used. The success of the method therefore depends upon the size of the correction terms and the availability of incident beams of comparable intensities at different appropriate wavelengths. Thus, although this method was used as early as 1957 (Ramaseshan *et al.*, 1957) as an aid to structure solution employing characteristic X-rays, it is, as outlined below, ideally suited in structural work employing neutrons and synchrotron radiation. In principle, γ -radiation can also be used for phase

2.4. ISOMORPHOUS REPLACEMENT AND ANOMALOUS SCATTERING

determination (Raghavan, 1961; Moon, 1961) as the anomalous-scattering effects in γ -ray scattering could be very large; the wavelength is also easily tunable. However, the intensity obtainable for γ -rays is several orders lower than that obtainable from X-ray and neutron sources, and hence γ -ray anomalous scattering is of hardly any practical value in structural analysis.

2.4.5.1. Neutron anomalous scattering

Apart from the limitations introduced by experimental factors, such as the need for large crystals and the comparatively low flux of neutron beams, there are two fundamental reasons why neutrons are less suitable than X-rays for the *ab initio* determination of crystal structures. First, the neutron scattering lengths of different nuclei have comparable magnitudes whereas the atomic form factors for X-rays vary by two orders of magnitude. Therefore, Patterson techniques and the related heavy-atom method are much less suitable for use with neutron diffraction data than with X-ray data. Secondly, neutron scattering lengths could be positive or negative and hence, in general, the positivity criterion (Karle & Hauptman, 1950) or the squarability criterion (Sayre, 1952) does not hold good for nuclear density. Therefore, the direct methods based on these criteria are not strictly applicable to structure analysis using neutron data, although it has been demonstrated that these methods could be successfully used in favourable situations in neutron crystallography (Sikka, 1969). The anomalous-scattering method is, however, in principle more powerful in the neutron case than in the X-ray case for *ab initio* structure determination.

Thermal neutrons are scattered anomalously at appropriate wavelengths by several nuclei. In a manner analogous to (2.4.3.1), the neutron scattering length of these nuclei can be written as

$$b_0 + b' + ib'' = b + ib'' \quad (2.4.5.1)$$

The correction terms b' and b'' are strongly wavelength-dependent. In favourable cases, b'/b_0 and b''/b_0 can be of the order of 10 whereas they are small fractions in X-ray anomalous scattering. In view of this pronounced anomalous effect in neutron scattering, Ramaseshan (1966) suggested that it could be used for structure solution. Subsequently, Singh & Ramaseshan (1968) proposed a two-wavelength method for unique structure analysis using neutron diffraction. The first part of the method is the determination of the positions of the anomalous scatterers from the estimated values of F_Q . The method employed for estimating F_Q is analogous to that using (2.4.4.9) except that data collected at two appropriate wavelengths are used instead of those from two isomorphous crystals. The second stage of the two-wavelength method involves phase evaluation. Referring to Fig. 2.4.3.2 and in a manner analogous to (2.4.3.5), we have

$$\sin \psi_1 = \frac{F_{N1}^2(+)-F_{N1}^2(-)}{4F_{N1}F_{Q1}'}, \quad (2.4.5.2)$$

where $\psi = \alpha_N - \alpha_Q$ and subscript 1 refers to data collected at wavelength λ_1 . Singh and Ramaseshan showed that $\cos \psi_1$ can also be determined when data are available at wavelength λ_1 and λ_2 . We may define

$$F_m^2 = [F_N^2(+) + F_N^2(-)]/2 \quad (2.4.5.3)$$

and we have from (2.4.3.3), (2.4.3.4) and (2.4.5.3)

$$F_N = (F_m^2 - F_Q^2)^{1/2}. \quad (2.4.5.4)$$

Then,

$$\cos \psi_1 = \frac{F_{m1}^2 - F_{m2}^2 - [(b_1^2 + b_1'^2) - (b_2^2 + b_2'^2)]x^2}{2(b_1 - b_2)F_{N1}x} + \frac{F_{Q1}}{F_{N1}}, \quad (2.4.5.5)$$

where x is the magnitude of the temperature-corrected geometrical part of F_Q . ψ_1 and hence α_{N1} can be calculated using (2.4.5.2) and (2.4.5.5). α_{N2} can also be obtained in a similar manner.

During the decade that followed Ramaseshan's suggestion, neutron anomalous scattering was used to solve half a dozen crystal structures, employing the multiple-wavelength methods as well as the methods developed for structure determination using X-ray anomalous scattering (Koetzle & Hamilton, 1975; Sikka & Rajagopal, 1975; Flook *et al.*, 1977). It has also been demonstrated that measurable Bijvoet differences could be obtained, in favourable situations, in neutron diffraction patterns from protein crystals (Schoenborn, 1975). However, despite the early promise held by neutron anomalous scattering, the method has not been as successful as might have been hoped. In addition to the need for large crystals, the main problem with using this method appears to be the time and expense involved in data collection (Koetzle & Hamilton, 1975).

2.4.5.2. Anomalous scattering of synchrotron radiation

The most significant development in recent years in relation to anomalous scattering of X-rays has been the advent of synchrotron radiation (Helliwell, 1984). The advantage of using synchrotron radiation for making anomalous-scattering measurements essentially arises out of the tunability of the wavelength. Unlike the characteristic radiation from conventional X-ray sources, synchrotron radiation has a smooth spectrum and the wavelength to be used can be finely selected. Accurate measurements have shown that values in the neighbourhood of 30 electrons could be obtained in favourable cases for f' and f'' (Templeton, Templeton, Phillips & Hodgson, 1980; Templeton, Templeton & Phizackerley, 1980; Templeton *et al.*, 1982). Schemes for the optimization of the wavelengths to be used have also been suggested (Narayan & Ramaseshan, 1981). Interestingly, the anomalous differences obtainable using synchrotron radiation are comparable in magnitude to the isomorphous differences normally encountered in protein crystallography. Thus, the use of anomalous scattering at several wavelengths would obviously eliminate the need for employing many heavy-atom derivatives. The application of anomalous scattering of synchrotron radiation for macromolecular structure analysis began to yield encouraging results in the 1980s (Helliwell, 1985). Intensity measurements from macromolecular X-ray diffraction patterns using synchrotron radiation at first relied primarily upon oscillation photography (Arndt & Wonacott, 1977). This method is not particularly suitable for accurately evaluating anomalous differences. Much higher levels of accuracy began to be achieved with the use of position-sensitive detectors (Arndt, 1986). Anomalous scattering, in combination with such detectors, has developed into a major tool in macromolecular crystallography (see IT F, 2001).

Acknowledgements

One of us (MV) acknowledges the support of the Department of Science & Technology, India.

2.5. Electron diffraction and electron microscopy in structure determination

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2.5.1. Foreword (J. M. COWLEY)

Given that electrons have wave properties and the wavelengths lie in a suitable range, the diffraction of electrons by matter is completely analogous to the diffraction of X-rays. While for X-rays the scattering function is the electron-density distribution, for electrons it is the potential distribution which is similarly peaked at the atomic sites. Hence, in principle, electron diffraction may be used as the basis for crystal structure determination. In practice it is used much less widely than X-ray diffraction for the determination of crystal structures but is receiving increasing attention as a means for obtaining structural information not readily accessible with X-ray- or neutron-diffraction techniques.

Electrons having wavelengths comparable with those of the X-rays commonly used in diffraction experiments have energies of the order of 100 eV. For such electrons, the interactions with matter are so strong that they can penetrate only a few layers of atoms on the surfaces of solids. They are used extensively for the study of surface structures by low-energy electron diffraction (LEED) and associated techniques. These techniques are not covered in this series of volumes, which include the principles and practice of only those diffraction and imaging techniques making use of high-energy electrons, having energies in the range of 20 keV to 1 MeV or more, in transmission through thin specimens.

For the most commonly used energy ranges of high-energy electrons, 100 to 400 keV, the wavelengths are about 50 times smaller than for X-rays. Hence the scattering angles are much smaller, of the order of 10^{-2} rad, the recording geometry is relatively simple and the diffraction pattern represents, to a useful first approximation, a planar section of reciprocal space.

The elastic scattering of electrons by atoms is several orders of magnitude greater than for X-rays. This fact has profound consequences, which in some cases are highly favourable and in other cases are serious hindrances to structure analysis work. On the one hand it implies that electron-diffraction patterns can be obtained from very small single-crystal regions having thicknesses equal to only a few layers of atoms and, with recently developed techniques, having diameters equivalent to only a few interatomic distances. Hence single-crystal patterns can be obtained from microcrystalline phases.

However, the strong scattering of electrons implies that the simple kinematical single-scattering approximation, on which most X-ray diffraction structure analysis is based, fails for electrons except for very thin crystals composed of light-atom materials. Strong dynamical diffraction effects occur for crystals which may be 100 Å thick, or less for heavy-atom materials. As a consequence, the theory of dynamical diffraction for electrons has been well developed, particularly for the particular special diffracting conditions relevant to the transmission of fast electrons (see Chapter 5.2), and observations of dynamical diffraction effects are commonly made and quantitatively interpreted. The possibility has thus arisen of using the observation of dynamical diffraction effects as the basis for obtaining crystal structure information. The fact that dynamical diffraction is dependent on the relative phases of the diffracted waves then implies that relative phase information can be deduced from the diffraction intensities and the limitations of kinematical diffraction, such as Friedel's law, do not apply. The most immediately practicable method for making use of this possibility is convergent-beam electron diffraction (CBED) as described in Section 2.5.3.

A further important factor, determining the methods for observing electron diffraction, is that, being charged particles, electrons can be focused by electromagnetic lenses. The irreducible

aberrations of cylindrical magnetic lenses have, to date, limited the resolution of electron microscopes to the extent that the least resolvable distances (or 'resolutions') are about 100 times the electron wavelength. However, with microscopes having a resolution of better than 2 Å it is possible to distinguish the individual rows of atoms, parallel to the incident electron beam, in the principal orientations of many crystalline phases. Thus 'structure images' can be obtained, sometimes showing direct representation of projections of crystal structures [see *IT C* (1999), Section 4.3.8]. However, the complications of dynamical scattering and of the coherent imaging processes are such that the image intensities vary strongly with crystal thickness and tilt, and with the defocus or other parameters of the imaging system, making the interpretation of images difficult except in special circumstances. Fortunately, computer programs are readily available whereby image intensities can be calculated for model structures [see *IT C* (1999), Section 4.3.6] Hence the means exist for deriving the projection of the structure if only by a process of trial and error and not, as would be desirable, from a direct interpretation of the observations.

The accuracy with which the projection of a structure can be deduced from an image, or series of images, improves as the resolution of the microscope improves but is not at all comparable with the accuracy attainable with X-ray diffraction methods. A particular virtue of high-resolution electron microscopy as a structural tool is that it may give information on individual small regions of the sample. Structures can be determined of 'phases' existing over distances of only a few unit cells and the defects and local disorders can be examined, one by one.

The observation of electron-diffraction patterns forms an essential part of the technique of structure imaging in high-resolution electron microscopy, because the diffraction patterns are used to align the crystals to appropriate axial orientations. More generally, for all electron microscopy of crystalline materials the image interpretation depends on knowledge of the diffraction conditions. Fortunately, the diffraction pattern and image of any specimen region can be obtained in rapid succession by a simple switching of lens currents. The ready comparison of the image and diffraction data has become an essential component of the electron microscopy of crystalline materials but has also been of fundamental importance for the development of electron-diffraction theory and techniques.

The individual specimen regions giving single-crystal electron-diffraction patterns are, with few exceptions, so small that they can be seen only by use of an electron microscope. Hence, historically, it was only after electron microscopes were commonly available that the direct correlations of diffraction intensities with crystal size and shape could be made, and a proper basis was available for the development of the adequate dynamical diffraction theory.

For the complete description of a diffraction pattern or image intensities obtained with electrons, it is necessary to include the effects of inelastic scattering as well as elastic scattering. In contrast to the X-ray diffraction case, the inelastic scattering does not produce just a broad and generally negligible background. The average energy loss for an inelastic scattering event is about 20 eV, which is small compared with the energy of about 100 keV for the incident electrons. The inelastically scattered electrons have a narrow angular distribution and are diffracted in much the same way as the incident or elastically scattered electrons in a crystal. They therefore produce a highly modulated contribution to the diffraction pattern, strongly peaked about the Bragg spot positions (see Chapter 4.3). Also, as a result of the inelastic scattering processes, including thermal diffuse scattering, an effective

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absorption function must be added in the calculation of intensities for elastically scattered electrons.

The inelastic scattering processes in themselves give information about the specimen in that they provide a measure of the excitations of both the valence-shell and the inner-shell electrons of the solid. The inner-shell electron excitations are characteristic of the type of atom, so that microanalysis of small volumes of specimen material (a few hundreds or thousands of atoms) may be achieved by detecting either the energy losses of the transmitted electrons or the emission of the characteristic X-ray [see *IT C* (1999), Section 4.3.4].

An adverse effect of the inelastic scattering processes, however, is that the transfer of energy to the specimen material results in radiation damage; this is a serious limitation of the application of electron-scattering methods to radiation-sensitive materials such as organic, biological and many inorganic compounds. The amount of radiation damage increases rapidly as the amount of information per unit volume, derived from the elastic scattering, is increased, *i.e.* as the microscope resolution is improved or as the specimen volume irradiated during a diffraction experiment is decreased. At the current limits of microscopic resolution, radiation damage is a significant factor even for the radiation-resistant materials such as semiconductors and alloys.

In the historical development of electron-diffraction techniques the progress has depended to an important extent on the level of understanding of the dynamical diffraction processes and this understanding has followed, to a considerable degree, from the availability of electron microscopes. For the first 20 years of the development, with few exceptions, the lack of a precise knowledge of the specimen morphology meant that diffraction intensities were influenced to an unpredictable degree by dynamical scattering and the impression grew that electron-diffraction intensities could not meaningfully be interpreted.

It was the group in the Soviet Union, led initially by Dr Z. G. Pinsker and later by Dr B. K. Vainshtein and others, which showed that patterns from thin layers of a powder of microcrystals could be interpreted reliably by use of the kinematical approximation. The averaging over crystal orientation reduced the dynamical diffraction effects to the extent that practical structure analysis was feasible. The development of the techniques of using films of crystallites having strongly preferred orientations, to give patterns somewhat analogous to the X-ray rotation patterns, provided the basis for the collection of three-dimensional diffraction data on which many structure analyses have been based [see Section 2.5.4 and *IT C* (1999), Section 4.3.5].

In recent years improvements in the techniques of specimen preparation and in the knowledge of the conditions under which dynamical diffraction effects become significant have allowed progress to be made with the use of high-energy electron diffraction patterns from thin single crystals for crystal structure analysis. Particularly for crystals of light-atom materials, including biological and organic compounds, the methods of structure analysis developed for X-ray diffraction, including the direct methods (see Section 2.5.7), have been successfully applied in an increasing number of cases. Often it is possible to deduce some structural information from high-resolution electron-microscope images and this information may be combined with that from the diffraction intensities to assist the structure analysis process [see *IT C* (1999), Section 4.3.8.8].

The determination of crystal symmetry by use of CBED (Section 2.5.3) and the accurate determination of structure amplitudes by use of methods depending on the observation of dynamical diffraction effects [*IT C* (1999), Section 4.3.7] came later, after the information on morphologies of crystals, and the precision electron optics associated with electron microscopes, became available.

In spite of the problem of radiation damage, a great deal of progress has been made in the study of organic and biological

materials by electron-scattering methods. In some respects these materials are very favourable because, with only light atoms present, the scattering from thin films can be treated using the kinematical approximation without serious error. Because of the problem of radiation damage, however, special techniques have been evolved to maximize the information on the required structural aspects with minimum irradiation of the specimen. Image-processing techniques have been evolved to take advantage of the redundancy of information from a periodic structure and the means have been devised for combining information from multiple images and diffraction data to reconstruct specimen structure in three dimensions. These techniques are outlined in Sections 2.5.5 and 2.5.6. They are based essentially on the application of the kinematical approximation and have been used very effectively within that limitation.

For most inorganic materials the complications of many-beam dynamical diffraction processes prevent the direct application of these techniques of image analysis, which depend on having a linear relationship between the image intensity and the value of the projected potential distribution of the sample. The smaller sensitivities to radiation damage can, to some extent, remove the need for the application of such methods by allowing direct visualization of structure with ultra-high-resolution images and the use of microdiffraction techniques.

2.5.2. Electron diffraction and electron microscopy

(J. M. COWLEY)

2.5.2.1. Introduction

The contributions of electron scattering to the study of the structures of crystalline solids are many and diverse. This section will deal only with the scattering of high-energy electrons (in the energy range of 10^4 to 10^6 eV) in transmission through thin samples of crystalline solids and the derivation of information on crystal structures from diffraction patterns and high-resolution images. The range of wavelengths considered is from about 0.122 Å (12.2 pm) for 10 kV electrons to 0.0087 Å (0.87 pm) for 1 MeV electrons. Given that the scattering amplitudes of atoms for electrons have much the same form and variation with $(\sin \theta)/\lambda$ as for X-rays, it is apparent that the angular range for strong scattering of electrons will be of the order of 10^{-2} rad. Only under special circumstances, usually involving multiple elastic and inelastic scattering from very thick specimens, are scattering angles of more than 10^{-1} rad of importance.

The strength of the interaction of electrons with matter is greater than that of X-rays by two or three orders of magnitude. The single-scattering, first Born approximation fails significantly for scattering from single heavy atoms. Diffracted beams from single crystals may attain intensities comparable with that of the incident beam for crystal thicknesses of 10^2 Å, rather than 10^4 Å or more. It follows that electrons may be used for the study of very thin samples, and that dynamical scattering effects, or the coherent interaction of multiply scattered electron waves, will modify the diffracted amplitudes in a significant way for all but very thin specimens containing only light atoms.

The experimental techniques for electron scattering are largely determined by the possibility of focusing electron beams by use of strong axial magnetic fields, which act as electron lenses having focal lengths as short as 1 mm or less. Electron microscopes employing such lenses have been produced with resolutions approaching 1 Å. With such instruments, images showing individual isolated atoms of moderately high atomic number may be obtained. The resolution available is sufficient to distinguish neighbouring rows of adjacent atoms in the projected structures of thin crystals viewed in favourable orientations. It is therefore

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possible in many cases to obtain information on the structure of crystals and of crystal defects by direct inspection of electron micrographs.

The electromagnetic electron lenses may also be used to form electron beams of very small diameter and very high intensity. In particular, by the use of cold field-emission electron guns, it is possible to obtain a current of 10^{-10} A in an electron beam of diameter 10 Å or less with a beam divergence of less than 10^{-2} rad, *i.e.* a current density of 10^4 A cm $^{-2}$ or more. The magnitudes of the electron scattering amplitudes then imply that detectable signals may be obtained in diffraction from assemblies of fewer than 10^2 atoms. On the other hand, electron beams may readily be collimated to better than 10^{-6} rad.

The cross sections for inelastic scattering processes are, in general, less than for the elastic scattering of electrons, but signals may be obtained by the observation of electron energy losses, or the production of secondary radiations, which allow the analysis of chemical compositions or electronic excited states for regions of the crystal 100 Å or less in diameter.

On the other hand, the transfer to the sample of large amounts of energy through inelastic scattering processes produces radiation damage which may severely limit the applicability of the imaging and diffraction techniques, especially for biological and organic materials, unless the information is gathered from large specimen volumes with low incident electron beam densities.

Structure analysis of crystals can be performed using electron diffraction in the same way as with X-ray or neutron diffraction. The mathematical expressions and the procedures are much the same. However, there are peculiarities of the electron-diffraction case which should be noted.

(1) Structure analysis based on electron diffraction is possible for thin specimens for which the conditions for kinematical scattering are approached, *e.g.* for thin mosaic single-crystal specimens, for thin polycrystalline films having a preferred orientation of very small crystallites or for very extensive, very thin single crystals of biological molecules such as membranes one or a few molecules thick.

(2) Dynamical diffraction effects are used explicitly in the determination of crystal symmetry (with no Friedel's law limitations) and for the measurement of structure amplitudes with high accuracy.

(3) For many radiation-resistant materials, the structures of crystals and of some molecules may be determined directly by imaging atom positions in projections of the crystal with a resolution of 2 Å or better. The information on atom positions is not dependent on the periodicity of the crystal and so it is equally possible to determine the structures of individual crystal defects in favourable cases.

(4) Techniques of microanalysis may be applied to the determination of the chemical composition of regions of diameter 100 Å or less using the same instrument as for diffraction, so that the chemical information may be correlated directly with morphological and structural information.

(5) Crystal-structure information may be derived from regions containing as few as 10^2 or 10^3 atoms, including very small crystals and single or multiple layers of atoms on surfaces.

2.5.2.2. The interactions of electrons with matter

(1) The *elastic* scattering of electrons results from the interaction of the charged electrons with the electrostatic potential distribution, $\varphi(\mathbf{r})$, of the atoms or crystals. An incident electron of kinetic energy eW gains energy $e\varphi(\mathbf{r})$ in the potential field. Alternatively it may be stated that an incident electron wave of wavelength $\lambda = h/mv$ is diffracted by a region of variable refractive index

$$n(\mathbf{r}) = k/K_0 = \{[W + \varphi(\mathbf{r})]/W\}^{1/2} \simeq 1 + \varphi(\mathbf{r})/2W.$$

(2) The most important *inelastic* scattering processes are:

(a) thermal diffuse scattering, with energy losses of the order of 2×10^{-2} eV, separable from the elastic scattering only with specially devised equipment; the angular distribution of thermal diffuse scattering shows variations with $(\sin \theta)/\lambda$ which are much the same as for the X-ray case in the kinematical limit;

(b) bulk plasmon excitation, or the excitation of collective energy states of the conduction electrons, giving energy losses of 3 to 30 eV and an angular range of scattering of 10^{-4} to 10^{-3} rad;

(c) surface plasmons, or the excitation of collective energy states of the conduction electrons at discontinuities of the structure, with energy losses less than those for bulk plasmons and a similar angular range of scattering;

(d) interband or intraband excitation of valence-shell electrons giving energy losses in the range of 1 to 10^2 eV and an angular range of scattering of 10^{-4} to 10^{-2} rad;

(e) inner-shell excitations, with energy losses of 10^2 eV or more and an angular range of scattering of 10^{-3} to 10^{-2} rad, depending on the energy losses involved.

(3) In the original treatment by Bethe (1928) of the elastic scattering of electrons by crystals, the Schrödinger equation is written for electrons in the periodic potential of the crystal; *i.e.*

$$\nabla^2 \psi(\mathbf{r}) + K_0^2 [1 + \varphi(\mathbf{r})/W] \psi(\mathbf{r}) = 0, \quad (2.5.2.1)$$

where

$$\begin{aligned} \varphi(\mathbf{r}) &= \int V(\mathbf{u}) \exp\{-2\pi i \mathbf{u} \cdot \mathbf{r}\} d\mathbf{u} \\ &= \sum_{\mathbf{h}} V_{\mathbf{h}} \exp\{-2\pi i \mathbf{h} \cdot \mathbf{r}\}, \end{aligned} \quad (2.5.2.2)$$

$\mathbf{K}_0$ is the wavevector in zero potential (outside the crystal) (magnitude $2\pi/\lambda$) and W is the accelerating voltage. The solutions of the equation are Bloch waves of the form

$$\psi(\mathbf{r}) = \sum_{\mathbf{h}} C_{\mathbf{h}}(\mathbf{k}) \exp\{-i(\mathbf{k}_0 + 2\pi \mathbf{h}) \cdot \mathbf{r}\}, \quad (2.5.2.3)$$

where $\mathbf{k}_0$ is the incident wavevector in the crystal and $\mathbf{h}$ is a reciprocal-lattice vector. Substitution of (2.5.2.2) and (2.5.2.3) in (2.5.2.1) gives the dispersion equations

$$(\kappa^2 - k_{\mathbf{h}}^2) C_{\mathbf{h}} + \sum_{\mathbf{g}}' V_{\mathbf{h}-\mathbf{g}} C_{\mathbf{g}} = 0. \quad (2.5.2.4)$$

Here κ is the magnitude of the wavevector in a medium of constant potential V_0 (the 'inner potential' of the crystal). The refractive index of the electron in the average crystal potential is then

$$n = \kappa/K = (1 + V_0/W)^{1/2} \simeq 1 + V_0/2W. \quad (2.5.2.5)$$

Since V_0 is positive and of the order of 10 V and W is 10^4 to 10^6 V, $n - 1$ is positive and of the order of 10^{-4} .

Solution of equation (2.5.2.4) gives the Fourier coefficients $C_{\mathbf{h}}^{(i)}$ of the Bloch waves $\psi^{(i)}(\mathbf{r})$ and application of the boundary conditions gives the amplitudes of individual Bloch waves (see Chapter 5.2).

(4) The experimentally important case of transmission of high-energy electrons through thin specimens is treated on the assumption of a plane wave incident in a direction almost perpendicular to an infinitely extended plane-parallel lamellar crystal, making use of the *small-angle scattering approximation* in which the forward-scattered wave is represented in the paraboloidal approximation to the sphere. The incident-beam direction, assumed to be almost parallel to the z axis, is unique and the z component of $\mathbf{k}$ is factored out to give

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$$\nabla^2 \psi + 2k\sigma \varphi \psi = \pm i2k \frac{\partial \psi}{\partial z}, \quad (2.5.2.6)$$

where $k = 2\pi/\lambda$ and $\sigma = 2\pi m_e \lambda / h^2$. [See Lynch & Moodie (1972), Portier & Gratiat (1981), Tournarie (1962), and Chapter 5.2.]

This equation is analogous to the time-dependent Schrödinger equation with z replacing t . Retention of the $\pm$ signs on the right-hand side is consistent with both ψ and ψ^* being solutions, corresponding to propagation in opposite directions with respect to the z axis. The double-valued solution is of importance in consideration of reciprocity relationships which provide the basis for the description of some dynamical diffraction symmetries. (See Section 2.5.3.)

(5) The integral form of the wave equation, commonly used for scattering problems, is written, for electron scattering, as

$$\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r}) + (\sigma/\lambda) \int \frac{\exp\{-i\mathbf{k}|\mathbf{r} - \mathbf{r}'|\}}{|\mathbf{r} - \mathbf{r}'|} \varphi(\mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}'. \quad (2.5.2.7)$$

The wavefunction $\psi(\mathbf{r})$ within the integral is approximated by using successive terms of a Born series

$$\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r}) + \psi^{(1)}(\mathbf{r}) + \psi^{(2)}(\mathbf{r}) + \dots \quad (2.5.2.8)$$

The first Born approximation is obtained by putting $\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r})$ in the integral and subsequent terms $\psi^{(n)}(\mathbf{r})$ are generated by putting $\psi^{(n-1)}(\mathbf{r})$ in the integral.

For an incident plane wave, $\psi^{(0)}(\mathbf{r}) = \exp\{-i\mathbf{k}_0 \cdot \mathbf{r}\}$ and for a point of observation at a large distance $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ from the scattering object ($|\mathbf{R}| \gg |\mathbf{r}'|$), the first Born approximation is generated as

$$\psi^{(1)}(\mathbf{r}) = \frac{i\sigma}{\lambda R} \exp\{-i\mathbf{k} \cdot \mathbf{R}\} \int \varphi(\mathbf{r}') \exp\{i\mathbf{q} \cdot \mathbf{r}'\} d\mathbf{r}',$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$ or, putting $\mathbf{u} = \mathbf{q}/2\pi$ and collecting the pre-integral terms into a parameter μ ,

$$\Psi(\mathbf{u}) = \mu \int \varphi(\mathbf{r}) \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}\} d\mathbf{r}. \quad (2.5.2.9)$$

This is the Fourier-transform expression which is the basis for the *kinematical scattering approximation*. It is derived on the basis that all $\psi^{(n)}(\mathbf{r})$ terms for $n \neq 0$ are very much smaller than $\psi^{(0)}(\mathbf{r})$ and so is a weak scattering approximation.

In this approximation, the scattered amplitude for an atom is related to the atomic structure amplitude, $f(\mathbf{u})$, by the relationship, derived from (2.5.2.8),

$$\begin{aligned} \psi(\mathbf{r}) &= \exp\{-i\mathbf{k}_0 \cdot \mathbf{r}\} + i \frac{\exp\{-i\mathbf{k} \cdot \mathbf{r}\}}{R\lambda} \sigma f(\mathbf{u}), \\ f(\mathbf{u}) &= \int \varphi(\mathbf{r}) \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}\} d\mathbf{r}. \end{aligned} \quad (2.5.2.10)$$

For centrosymmetrical atom potential distributions, the $f(\mathbf{u})$ are real, positive and monotonically decreasing with $|\mathbf{u}|$. A measure of the extent of the validity of the first Born approximation is given by the fact that the effect of adding the higher-order terms of the Born series may be represented by replacing $f(\mathbf{u})$ in (2.5.2.10) by the complex quantities $f(\mathbf{u}) = |\mathbf{f}| \exp\{i\eta(\mathbf{u})\}$ and for single heavy atoms the phase factor η may vary from 0.2 for $|\mathbf{u}| = 0$ to 4 or 5 for large $|\mathbf{u}|$, as seen from the tables of *IT C* (1999, Section 4.3.3).

(6) Relativistic effects produce appreciable variations of the parameters used above for the range of electron energies considered. The relativistic values are

$$m = m_0(1 - v^2/c^2)^{-1/2} = m_0(1 - \beta^2)^{-1/2}, \quad (2.5.2.11)$$

$$\lambda = h[2m_0 e |W(1 + |e|W/2m_0 c^2)|]^{-1/2} \quad (2.5.2.12)$$

$$= \lambda_c(1 - \beta^2)^{1/2}/\beta, \quad (2.5.2.13)$$

where λ_c is the Compton wavelength, $\lambda_c = h/m_0 c = 0.0242 \text{ \AA}$, and

$$\begin{aligned} \sigma &= 2\pi m_e \lambda / h^2 = (2\pi m_0 e / h^2)(\lambda_c / \beta) \\ &= 2\pi / \{\lambda W [1 + (1 - \beta^2)^{1/2}]\}. \end{aligned} \quad (2.5.2.14)$$

Values for these quantities are listed in *IT C* (1999, Section 4.3.2). The variations of λ and σ with accelerating voltage are illustrated in Fig. 2.5.2.1. For high voltages, σ tends to a constant value, $2\pi m_0 e \lambda_c / h^2 = e / \hbar c$.

2.5.2.3. Recommended sign conventions

There are two alternative sets of signs for the functions describing wave optics. Both sets have been widely used in the literature. There is, however, a requirement for internal consistency within a particular analysis, independently of which set is adopted. Unfortunately, this requirement has not always been met and, in fact, it is only too easy at the outset of an analysis to make errors in this way. This problem might have come into prominence somewhat earlier were it not for the fact that, for centrosymmetric crystals (or indeed for centrosymmetric projections in the case of planar diffraction), only the signs used in the transmission and propagation functions can affect the results. It is not until the origin is set away from a centre of symmetry that there is a need to be consistent in every sign used.

Signs for electron diffraction have been chosen from two points of view: (1) defining as positive the sign of the exponent in the structure-factor expression and (2) defining the forward propagating free-space wavefunction with a positive exponent.

The second of these alternatives is the one which has been adopted in most solid-state and quantum-mechanical texts.

The first, or *standard crystallographic* convention, is the one which could most easily be adopted by crystallographers accustomed to retaining a positive exponent in the structure-factor equation. This also represents a consistent *International Tables* usage. It is, however, realized that both conventions will continue to be used in crystallographic computations, and that there are by now a large number of operational programs in use.

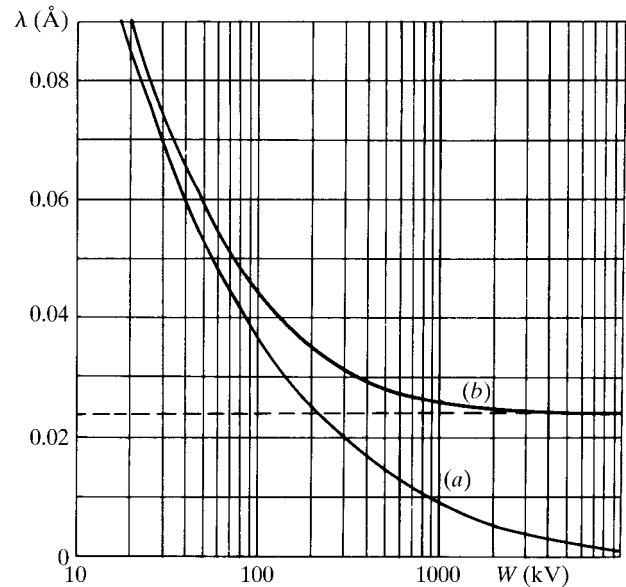


Fig. 2.5.2.1. The variation with accelerating voltage of electrons of (a) the wavelength, λ and (b) the quantity $\lambda[1 + (h^2/m_0^2 c^2 \lambda^2)] = \lambda_c / \beta$ which is proportional to the interaction constant σ [equation (2.5.2.14)]. The limit is the Compton wavelength λ_c (after Fujiwara, 1961).

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Table 2.5.2.1. *Standard crystallographic and alternative crystallographic sign conventions for electron diffraction*

	Standard	Alternative
Free-space wave	$\exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$	$\exp[+i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$
Fourier transforming from real space to reciprocal space	$\int \psi(\mathbf{r}) \exp[+2\pi i(\mathbf{u} \cdot \mathbf{r})] d\mathbf{r}$	$\int \psi(\mathbf{r}) \exp[-2\pi i(\mathbf{u} \cdot \mathbf{r})] d\mathbf{r}$
Fourier transforming from reciprocal space to real space	$\psi(\mathbf{r}) = \int \Psi(\mathbf{u}) \exp[-2\pi i(\mathbf{u} \cdot \mathbf{r})] d\mathbf{u}$	$\int \Psi(\mathbf{u}) \exp[+2\pi i(\mathbf{u} \cdot \mathbf{r})] d\mathbf{u}$
Structure factors	$V(\mathbf{h}) = (1/\Omega) \sum_j f_j(\mathbf{h}) \exp(+2\pi i\mathbf{h} \cdot \mathbf{r}_j)$	$(1/\Omega) \sum_j f_j(\mathbf{h}) \exp(-2\pi i\mathbf{h} \cdot \mathbf{r}_j)$
Transmission function (real space)	$\exp[-i\sigma\varphi(x, y)\Delta z]$	$\exp[+i\sigma\varphi(x, y)\Delta z]$
Phenomenological absorption	$\sigma\varphi(\mathbf{r}) - i\mu(\mathbf{r})$	$\sigma\varphi(\mathbf{r}) + i\mu(\mathbf{r})$
Propagation function $P(h)$ (reciprocal space) within the crystal	$\exp(-2\pi i\zeta_h\Delta z)$	$\exp(+2\pi i\zeta_h\Delta z)$
Iteration (reciprocal space)	$\Psi_{n+1}(\mathbf{h}) = [\Psi_n(\mathbf{h}) \cdot P(\mathbf{h})] * Q(\mathbf{h})$	
Unitarity test (for no absorption)	$T(\mathbf{h}) = Q(\mathbf{h}) * Q^*(-\mathbf{h}) = \delta(\mathbf{h})$	
Propagation to the image plane-wave aberration function, where $\chi(U) = \pi\lambda\Delta f U^2 + \frac{1}{2}\pi C_s\lambda^3 U^4$, $U^2 = u^2 + v^2$ and Δf is positive for overfocus	$\exp[i\chi(U)]$	$\exp[-i\chi(U)]$

σ = electron interaction constant = $2\pi me\lambda/h^2$; m = (relativistic) electron mass; λ = electron wavelength; e = (magnitude of) electron charge; h = Planck's constant; $k = 2\pi/\lambda$; Ω = volume of the unit cell; $\mathbf{u}$ = continuous reciprocal-space vector, components u, v ; $\mathbf{h}$ = discrete reciprocal-space coordinate; $\varphi(x, y)$ = crystal potential averaged along beam direction (positive); Δz = slice thickness; $\mu(\mathbf{r})$ = absorption potential [positive; typically $\leq 0.1\sigma\varphi(\mathbf{r})$]; Δf = defocus (defined as negative for underfocus); C_s = spherical aberration coefficient; ζ_h = excitation error relative to the incident-beam direction and defined as negative when the point h lies outside the Ewald sphere; $f_j(\mathbf{h})$ = atomic scattering factor for electrons, f_e , related to the atomic scattering factor for X-rays, f_X , by the Mott formula $f_e = (e/\pi U^2)(Z - f_X)$. $Q(\mathbf{h})$ = Fourier transform of periodic slice transmission function.

It is therefore recommended (a) that a particular sign usage be indicated as either *standard crystallographic* or *alternative crystallographic* to accord with Table 2.5.2.1, whenever there is a need for this to be explicit in publication, and (b) that either one or other of these systems be adhered to throughout an analysis in a self-consistent way, even in those cases where, as indicated above, some of the signs appear to have no effect on one particular conclusion.

2.5.2.4. Scattering of electrons by crystals; approximations

The forward-scattering approximation to the many-beam dynamical diffraction theory outlined in Chapter 5.2 provides the basis for the calculation of diffraction intensities and electron-microscope image contrast for thin crystals. [See Cowley (1995), Chapter 5.2 and *ITC* (1999) Sections 4.3.6 and 4.3.8.] On the other hand, there are various approximations which provide relatively simple analytical expressions, are useful for the determination of diffraction geometry, and allow estimates to be made of the relative intensities in diffraction patterns and electron micrographs in favourable cases.

(a) *The kinematical approximation*, derived in Section 2.5.2.2 from the first Born approximation, is analogous to the corresponding approximation of X-ray diffraction. It assumes that the scattering amplitudes are directly proportional to the three-dimensional Fourier transform of the potential distribution, $\varphi(\mathbf{r})$.

$$V(\mathbf{u}) = \int \varphi(\mathbf{r}) \exp\{2\pi i\mathbf{u} \cdot \mathbf{r}\} d\mathbf{r}, \quad (2.5.2.15)$$

so that the potential distribution $\varphi(\mathbf{r})$ takes the place of the charge-density distribution, $\rho(\mathbf{r})$, relevant for X-ray scattering.

The validity of the kinematical approximation as a basis for structure analysis is severely limited. For light-atom materials, such as organic compounds, it has been shown by Jap & Glaeser (1980) that the thickness for which the approximation gives reasonable accuracy for zone-axis patterns from single crystals is of the order of 100 Å for 100 keV electrons and increases, approximately as σ^{-1} , for higher energies. The thickness limits quoted for polycrystalline samples, having crystallite dimensions smaller than the sample thickness, are usually greater (Vainshtein, 1956). For heavy-atom

materials the approximation is more limited since it may fail significantly for single heavy atoms.

(b) *The phase-object approximation* (POA), or high-voltage limit, is derived from the general many-beam dynamical diffraction expression, equation (5.2.13.1), Chapter 5.2, by assuming the Ewald sphere curvature to approach zero. Then the scattering by a thin sample can be expressed by multiplying the incoming wave amplitude by the transmission function

$$q(xy) = \exp\{-i\sigma\varphi(xy)\}, \quad (2.5.2.16)$$

where $\varphi(xy) = \int \varphi(\mathbf{r}) dz$ is the projection of the potential distribution of the sample in the z direction, the direction of the incident beam. The diffraction-pattern amplitudes are then given by two-dimensional Fourier transform of (2.5.2.16).

This approximation is of particular value in relation to the electron microscopy of thin crystals. The thickness for its validity for 100 keV electrons is within the range 10 to 50 Å, depending on the accuracy and spatial resolution involved, and increases with accelerating voltage approximately as $\lambda^{-1/2}$. In computational work, it provides the starting point for the multi-slice method of dynamical diffraction calculations (*ITC*, 1999, Section 4.3.6.1).

(c) *The two-beam approximation* for dynamical diffraction of electrons assumes that only two beams, the incident beam and one diffracted beam (or two Bloch waves, each with two component amplitudes), exist in the crystal. This approximation has been adapted, notably by Hirsch *et al.* (1965), for use in the electron microscopy of inorganic materials.

It forms a convenient basis for the study of defects in crystals having small unit cells (metals, semiconductors *etc.*) and provides good preliminary estimates for the determination of crystal thicknesses and structure amplitudes for orientations well removed from principal axes, and for electron energies up to 200–500 keV, but it has decreasing validity, even for favourable cases, for higher energies. It has been used in the past as an ‘extinction correction’ for powder-pattern intensities (Vainshtein, 1956).

(d) *The Bethe second approximation*, proposed by Bethe (1928) as a means for correcting the two-beam approximation for the

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effects of weakly excited beams, replaces the Fourier coefficients of potential by the 'Bethe potentials'

$$U_{\mathbf{h}} = V_{\mathbf{h}} - 2k_0\sigma \sum_{\mathbf{g}} \frac{V_{\mathbf{g}} \cdot V_{\mathbf{h}-\mathbf{g}}}{\kappa^2 - k_{\mathbf{g}}^2}. \quad (2.5.2.17)$$

Use of these potentials has been shown to account well for the deviations of powder-pattern intensities from the predictions of two-beam theory (Horstmann & Meyer, 1965) and to predict accurately the extinctions of Kikuchi lines at particular accelerating voltages due to relativistic effects (Watanabe *et al.*, 1968), but they give incorrect results for the small-thickness limit.

2.5.2.5. Kinematical diffraction formulae

(1) *Comparison with X-ray diffraction.* The relations of real-space and reciprocal-space functions are analogous to those for X-ray diffraction [see equations (2.5.2.2), (2.5.2.10) and (2.5.2.15)]. For diffraction by crystals

$$\begin{aligned} \varphi(\mathbf{r}) &= \sum_{\mathbf{h}} V_{\mathbf{h}} \exp\{-2\pi i \mathbf{h} \cdot \mathbf{r}\}, \\ V_{\mathbf{h}} &= \int \varphi(\mathbf{r}) \exp\{2\pi i \mathbf{h} \cdot \mathbf{r}\} d\mathbf{r} \end{aligned} \quad (2.5.2.18)$$

$$= \frac{1}{\Omega} \sum_i f_i(\mathbf{h}) \exp\{2\pi i \mathbf{h} \cdot \mathbf{r}_i\}, \quad (2.5.2.19)$$

where the integral of (2.5.2.18) and the summation of (2.5.2.19) are taken over one unit cell of volume (see Dawson *et al.*, 1974).

Important differences from the X-ray case arise because

(a) the wavelength is relatively small so that the Ewald-sphere curvature is small in the reciprocal-space region of appreciable scattering amplitude;

(b) the dimensions of the single-crystal regions giving appreciable scattering amplitudes are small so that the 'shape transform' regions of scattering power around the reciprocal-lattice points are relatively large;

(c) the spread of wavelengths is small (10^{-5} or less, with no white-radiation background) and the degree of collimation is better (10^{-4} to 10^{-6}) than for conventional X-ray sources.

As a consequence of these factors, single-crystal diffraction patterns may show many simultaneous reflections, representing almost-planar sections of reciprocal space, and may show fine structure or intensity variations reflecting the crystal dimensions and shape.

(2) Kinematical diffraction-pattern intensities are calculated in a manner analogous to that for X-rays except that

(a) no polarization factor is included because of the small-angle scattering conditions;

(b) integration over regions of scattering power around reciprocal-lattice points cannot be assumed unless appropriate experimental conditions are ensured.

For a thin, flat, lamellar crystal of thickness H , the observed intensity is

$$I_{\mathbf{h}}/I_0 = |\sigma(V_{\mathbf{h}}/\Omega)(\sin \pi \zeta_{\mathbf{h}} H)/(\pi \zeta_{\mathbf{h}})|^2, \quad (2.5.2.20)$$

where $\zeta_{\mathbf{h}}$ is the excitation error for the $\mathbf{h}$ reflection and Ω is the unit-cell volume.

For a single-crystal diffraction pattern obtained by rotating a crystal or from a uniformly bent crystal or for a mosaic crystal with a uniform distribution of orientations, the intensity is

$$I_{\mathbf{h}} = I_0 \frac{\sigma^2 |V_{\mathbf{h}}|^2 V_c d_{\mathbf{h}}}{4\pi^2 \Omega^2}, \quad (2.5.2.21)$$

where V_c is the crystal volume and $d_{\mathbf{h}}$ is the lattice-plane spacing.

For a polycrystalline sample of randomly oriented small crystals, the intensity per unit length of the diffraction ring is

$$I_{\mathbf{h}} = I_0 \frac{\sigma^2 |V_{\mathbf{h}}|^2 V_c d_{\mathbf{h}}^2 M_{\mathbf{h}}}{8\pi^2 \Omega^2 L \lambda}, \quad (2.5.2.22)$$

where $M_{\mathbf{h}}$ is the multiplicity factor for the $\mathbf{h}$ reflection and L is the camera length, or the distance from the specimen to the detector plane. The special cases of 'oblique texture' patterns from powder patterns having preferred orientations are treated in *IT C* (1999, Section 4.3.5).

(3) *Two-beam dynamical diffraction formulae: complex potentials including absorption.* In the two-beam dynamical diffraction approximation, the intensities of the directly transmitted and diffracted beams for transmission through a crystal of thickness H , in the absence of absorption, are

$$I_0 = (1 + w^2)^{-1} \left[w^2 + \cos^2 \left\{ \frac{\pi H (1 + w^2)^{1/2}}{\xi_{\mathbf{h}}} \right\} \right] \quad (2.5.2.23)$$

$$I_{\mathbf{h}} = (1 + w^2)^{-1} \sin^2 \left\{ \frac{\pi H (1 + w^2)^{1/2}}{\xi_{\mathbf{h}}} \right\}, \quad (2.5.2.24)$$

where $\xi_{\mathbf{h}}$ is the extinction distance, $\xi_{\mathbf{h}} = (2\sigma |V_{\mathbf{h}}|)^{-1}$, and

$$w = \xi_{\mathbf{h}} \zeta_{\mathbf{h}} = \Delta\theta / (2\sigma |V_{\mathbf{h}}| d_{\mathbf{h}}), \quad (2.5.2.25)$$

where $\Delta\theta$ is the deviation from the Bragg angle.

For the case that $\zeta_{\mathbf{h}} = 0$, with the incident beam at the Bragg angle, this reduces to the simple *Pendellösung* expression

$$I_{\mathbf{h}} = 1 - I_0 = \sin^2 \{2\pi\sigma |V_{\mathbf{h}}| H\}. \quad (2.5.2.26)$$

The effects on the elastic Bragg scattering amplitudes of the inelastic or diffuse scattering may be introduced by adding an out-of-phase component to the structure amplitudes, so that for a centrosymmetric crystal, $V_{\mathbf{h}}$ becomes complex by addition of an imaginary component. Alternatively, an absorption function $\mu(\mathbf{r})$, having Fourier coefficients $\mu_{\mathbf{h}}$, may be postulated so that $\sigma V_{\mathbf{h}}$ is replaced by $\sigma V_{\mathbf{h}} + i\mu_{\mathbf{h}}$. The $\mu_{\mathbf{h}}$ are known as phenomenological absorption coefficients and their validity in many-beam diffraction has been demonstrated by, for example, Rez (1978).

The magnitudes $\mu_{\mathbf{h}}$ depend on the nature of the experiment and the extent to which the various inelastically or diffusely scattered electrons are included in the measurements being made. If measurements are made of purely elastic scattering intensities for Bragg reflections or of image intensity variations due to the interaction of the sharp Bragg reflections only, the main contributions to the absorption coefficients are as follows (Radi, 1970):

(a) from plasmon and single-electron excitations, μ_0 is of the order of $0.1 V_0$ and $\mu_{\mathbf{h}}$, for $\mathbf{h} \neq 0$, is negligibly small;

(b) from thermal diffuse scattering; $\mu_{\mathbf{h}}$ is of the order of $0.1 V_{\mathbf{h}}$ and decreasing more slowly than $V_{\mathbf{h}}$ with scattering angle.

Including absorption effects in (2.5.2.26) for the case $\zeta_{\mathbf{h}} = 0$ gives

$$\begin{aligned} I_0 &= \frac{1}{2} \exp\{-\mu_0 H\} [\cosh \mu_{\mathbf{h}} H + \cos(2\pi\sigma V_{\mathbf{h}} H)], \\ I_{\mathbf{h}} &= \frac{1}{2} \exp\{-\mu_0 H\} [\cosh \mu_{\mathbf{h}} H - \cos(2\pi\sigma V_{\mathbf{h}} H)]. \end{aligned} \quad (2.5.2.27)$$

The Borrmann effect is not very pronounced for electrons because $\mu_{\mathbf{h}} \ll \mu_0$, but can be important for the imaging of defects in thick crystals (Hirsch *et al.*, 1965; Hashimoto *et al.*, 1961).

Attempts to obtain analytical solutions for the dynamical diffraction equations for more than two beams have met with few successes. There are some situations of high symmetry, with incident beams in exact zone-axis orientations, for which the many-beam solution can closely approach equivalent two- or three-beam

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behaviour (Fukuhara, 1966). Explicit solutions for the three-beam case, which displays some aspects of many-beam character, have been obtained (Gjønnes & Høier, 1971; Hurley & Moodie, 1980).

2.5.2.6. Imaging with electrons

Electron optics. Electrons may be focused by use of axially symmetric magnetic fields produced by electromagnetic lenses. The focal length of such a lens used as a projector lens (focal points outside the lens field) is given by

$$f_p^{-1} = \frac{e}{8mW_r} \int_{-\infty}^{\infty} H_z^2(z) dz, \quad (2.5.2.28)$$

where W_r is the relativistically corrected accelerating voltage and H_z is the z component of the magnetic field. An expression in terms of experimental constants was given by Liebman (1955) as

$$\frac{1}{f} = \frac{A_0(NI)^2}{W_r(S+D)}, \quad (2.5.2.29)$$

where A_0 is a constant, NI is the number of ampere turns of the lens winding, S is the length of the gap between the magnet pole pieces and D is the bore of the pole pieces.

Lenses of this type have irreducible aberrations, the most important of which for the paraxial conditions of electron microscopy is the third-order spherical aberration, coefficient C_s , giving a variation of focal length of $C_s \alpha^2$ for a beam at an angle α to the axis. Chromatic aberration, coefficient C_c , gives a spread of focal lengths

$$\Delta f = C_c \left(\frac{\Delta W_0}{W_0} + 2 \frac{\Delta I}{I} \right) \quad (2.5.2.30)$$

for variations ΔW_0 and ΔI of the accelerating voltage and lens currents, respectively.

The objective lens of an electron microscope is the critical lens for the determination of image resolution and contrast. The action of this lens in a conventional transmission electron microscope (TEM) is described by use of the Abbe theory for coherent incident illumination transmitted through the object to produce a wavefunction $\psi_0(xy)$ (see Fig. 2.5.2.2).

The amplitude distribution in the back focal plane of the objective lens is written

$$\Psi_0(u, v) \cdot T(u, v), \quad (2.5.2.31)$$

where $\Psi_0(u, v)$ is the Fourier transform of $\psi_0(x, y)$ and $T(u, v)$ is the transfer function of the lens, consisting of an aperture function

$$A(u, v) = \begin{cases} 1 & \text{for } (u^2 + v^2)^{1/2} \leq A \\ 0 & \text{elsewhere} \end{cases} \quad (2.5.2.32)$$

and a phase function $\exp \{i\chi(u, v)\}$ where the phase perturbation $\chi(uv)$ due to lens defocus Δf and aberrations is usually approximated as

$$\chi(uv) = \pi \cdot \Delta f \cdot \lambda (u^2 + v^2) + \frac{\pi}{2} C_s \lambda^3 (u^2 + v^2)^2, \quad (2.5.2.33)$$

and u, v are the reciprocal-space variables related to the scattering angles φ_x, φ_y by

$$u = (\sin \varphi_x) / \lambda, \\ v = (\sin \varphi_y) / \lambda.$$

The image amplitude distribution, referred to the object coordinates, is given by Fourier transform of (2.5.2.31) as

$$\psi(xy) = \psi_0(xy) * t(xy), \quad (2.5.2.34)$$

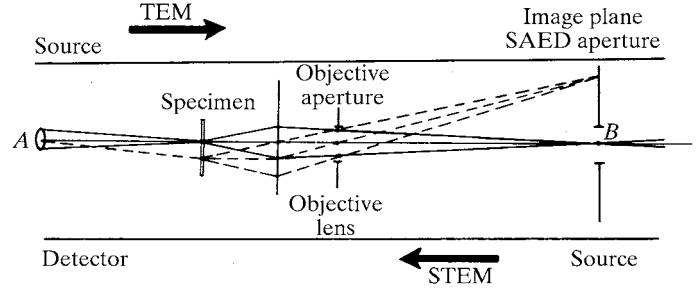


Fig. 2.5.2.2. Diagram representing the critical components of a conventional transmission electron microscope (TEM) and a scanning transmission electron microscope (STEM). For the TEM, electrons from a source A illuminate the specimen and the objective lens forms an image of the transmitted electrons on the image plane, B . For the STEM, a source at B is imaged by the objective lens to form a small probe on the specimen and some part of the transmitted beam is collected by a detector at A .

where $t(xy)$, given by Fourier transform of $T(u, v)$, is the spread function. The image intensity is then

$$I(xy) = |\psi(xy)|^2 = |\psi_0(xy) * t(xy)|^2. \quad (2.5.2.35)$$

In practice the coherent imaging theory provides a good approximation but limitations of the coherence of the illumination have appreciable effects under high-resolution imaging conditions.

The variation of focal lengths according to (2.5.2.30) is described by a function $G(\Delta f)$. Illumination from a finite incoherent source gives a distribution of incident-beam angles $H(u_1, v_1)$. Then the image intensity is found by integrating incoherently over Δf and u_1, v_1 :

$$I(xy) = \iint G(\Delta f) \cdot H(u_1 v_1) \\ \times |\mathcal{F}\{\Psi_0(u - u_1, v - v_1) \cdot T_{\Delta f}(u, v)\}|^2 d(\Delta f) \cdot du_1 dv_1, \quad (2.5.2.36)$$

where $\mathcal{F}$ denotes the Fourier-transform operation.

In the scanning transmission electron microscope (STEM), the objective lens focuses a small bright source of electrons on the object and directly transmitted or scattered electrons are detected to form an image as the incident beam is scanned over the object (see Fig. 2.5.2.2). Ideally the image amplitude can be related to that of the conventional transmission electron microscope by use of the 'reciprocity relationship' which refers to point sources and detectors for scalar radiation in scalar fields with elastic scattering processes only. It may be stated: 'The amplitude at a point B due to a point source at A is identical to that which would be produced at A for the identical source placed at B '.

For an axial point source, the amplitude distribution produced by the objective lens on the specimen is

$$\mathcal{F}[T(u, v)] = t(xy). \quad (2.5.2.37)$$

If this is translated by the scan to X, Y , the transmitted wave is

$$\psi_0(xy) = q(xy) \cdot t(x - X, y - Y). \quad (2.5.2.38)$$

The amplitude on the plane of observation following the specimen is then

$$\Psi(uv) = Q(u, v) * \{T(uv) \exp[2\pi i(uX + vY)]\}, \quad (2.5.2.39)$$

and the image signal produced by a detector having a sensitivity function $H(u, v)$ is

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$$I(X, Y) = \int H(u, v) |Q(u, v) * T(u, v)|^2 \exp\{2\pi i(uX + vY)\} du dv. \quad (2.5.2.40)$$

If $H(u, v)$ represents a small detector, approximated by a delta function, this becomes

$$I(x, y) = |q(xy) * t(xy)|^2, \quad (2.5.2.41)$$

which is identical to the result (2.5.2.35) for a plane incident wave in the conventional transmission electron microscope.

2.5.2.7. Imaging of very thin and weakly scattering objects

(a) *The weak-phase-object approximation.* For sufficiently thin objects, the effect of the object on the incident-beam amplitude may be represented by the transmission function (2.5.2.16) given by the phase-object approximation. If the fluctuations, $\varphi(xy) - \bar{\varphi}$, about the mean value of the projected potential are sufficiently small so that $\sigma[\varphi(xy) - \bar{\varphi}] \ll 1$, it is possible to use the *weak-phase-object approximation* (WPOA)

$$q(xy) = \exp\{-i\sigma\varphi(xy)\} = 1 - i\sigma\varphi(xy), \quad (2.5.2.42)$$

where $\varphi(xy)$ is referred to the average value, $\bar{\varphi}$. The assumption that only first-order terms in $\sigma\varphi(xy)$ need be considered is the equivalent of a single-scattering, or kinematical, approximation applied to the two-dimensional function, the projected potential of (2.5.2.16). From (2.5.2.42), the image intensity (2.5.2.35) becomes

$$I(xy) = 1 + 2\sigma\varphi(xy) * s(xy), \quad (2.5.2.43)$$

where the spread function $s(xy)$ is the Fourier transform of the imaginary part of $T(uv)$, namely $A(uv) \sin \chi(uv)$.

The optimum imaging condition is then found, following Scherzer (1949), by specifying that the defocus should be such that $|\sin \chi|$ is close to unity for as large a range of $U = (u^2 + v^2)^{1/2}$ as possible. This is so for a negative defocus such that $\chi(uv)$ decreases to a minimum of about $-2\pi/3$ before increasing to zero and higher as a result of the fourth-order term of (2.5.2.33) (see Fig. 2.5.2.3). This optimum, 'Scherzer defocus' value is given by

$$\frac{d\chi}{du} = 0 \quad \text{for} \quad \chi = -2\pi/3$$

or

$$\Delta f = -\left(\frac{4}{3} C_s \lambda\right)^{1/2}. \quad (2.5.2.44)$$

The resolution limit is then taken as corresponding to the value of $U = 1.51 C_s^{-1/4} \lambda^{-3/4}$ when $\sin \chi$ becomes zero, before it begins to oscillate rapidly with U . The resolution limit is then

$$\Delta x = 0.66 C_s^{1/4} \lambda^{3/4}. \quad (2.5.2.45)$$

For example, for $C_s = 1 \text{ mm}$ and $\lambda = 2.51 \times 10^{-2} \text{ \AA}$ (200 keV), $\Delta x = 2.34 \text{ \AA}$.

Within the limits of the WPOA, the image intensity can be written simply for a number of other imaging modes in terms of the Fourier transforms $c(\mathbf{r})$ and $s(\mathbf{r})$ of the real and imaginary parts of the objective-lens transfer function $T(\mathbf{u}) = A(\mathbf{u}) \exp\{i\chi(\mathbf{u})\}$, where $\mathbf{r}$ and $\mathbf{u}$ are two-dimensional vectors in real and reciprocal space, respectively.

For dark-field TEM images, obtained by introducing a central stop to block out the central beam in the diffraction pattern in the back-focal plane of the objective lens,

$$I(\mathbf{r}) = [\sigma\varphi(\mathbf{r}) * c(\mathbf{r})]^2 + [\sigma\varphi(\mathbf{r}) * s(\mathbf{r})]^2. \quad (2.5.2.46)$$

Here, as in (2.5.2.42), $\varphi(\mathbf{r})$ should be taken to imply the difference from the mean potential value, $\varphi(\mathbf{r}) - \bar{\varphi}$.

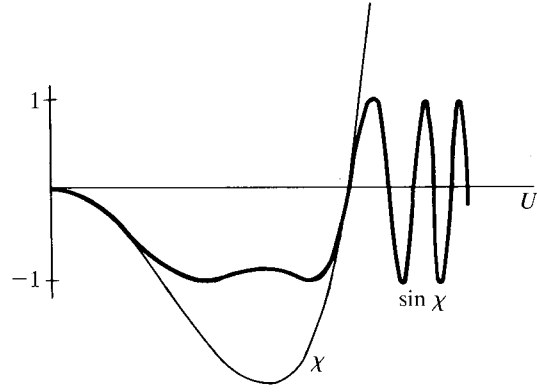


Fig. 2.5.2.3. The functions $\chi(U)$, the phase factor for the transfer function of a lens given by equation (2.5.2.33), and $\sin \chi(U)$ for the Scherzer optimum defocus condition, relevant for weak phase objects, for which the minimum value of $\chi(U)$ is $-2\pi/3$.

For bright-field STEM imaging with a very small detector placed axially in the central beam of the diffraction pattern (2.5.2.39) on the detector plane, the intensity, from (2.5.2.41), is given by (2.5.2.43).

For a finite axially symmetric detector, described by $D(\mathbf{u})$, the image intensity is

$$I(\mathbf{r}) = 1 + 2\sigma\varphi(\mathbf{r}) * \{s(\mathbf{r})[d(\mathbf{r}) * c(\mathbf{r})] - c(\mathbf{r})[d(\mathbf{r}) * s(\mathbf{r})]\}, \quad (2.5.2.47)$$

where $d(\mathbf{r})$ is the Fourier transform of $D(\mathbf{u})$ (Cowley & Au, 1978).

For STEM with an annular dark-field detector which collects all electrons scattered outside the central spot of the diffraction pattern in the detector plane, it can be shown that, to a good approximation (valid except near the resolution limit)

$$I(\mathbf{r}) = \sigma^2 \varphi^2(\mathbf{r}) * [c^2(\mathbf{r}) + s^2(\mathbf{r})]. \quad (2.5.2.48)$$

Since $c^2(\mathbf{r}) + s^2(\mathbf{r}) = |t(\mathbf{r})|^2$ is the intensity distribution of the electron probe incident on the specimen, (2.5.2.48) is equivalent to the incoherent imaging of the function $\sigma^2 \varphi^2(\mathbf{r})$.

Within the range of validity of the WPOA or, in general, whenever the zero beam of the diffraction pattern is very much stronger than any diffracted beam, the general expression (2.5.2.36) for the modifications of image intensities due to limited coherence may be conveniently approximated. The effect of integrating over the variables $\Delta f, u_1, v_1$, may be represented by multiplying the transfer function $T(u, v)$ by so-called 'envelope functions' which involve the Fourier transforms of the functions $G(\Delta f)$ and $H(u_1, v_1)$.

For example, if $G(\Delta f)$ is approximated by a Gaussian of width ε (at e^{-1} of the maximum) centred at Δf_0 and $H(u_1, v_1)$ is a circular aperture function

$$H(u_1, v_1) = \begin{cases} 1 & \text{if } u_1, v_1 < b \\ 0 & \text{otherwise,} \end{cases}$$

the transfer function $T_0(uv)$ for coherent radiation is multiplied by

$$\exp\{-\pi^2 \lambda^2 \varepsilon^2 (u^2 + v^2)/4\} \cdot J_1(\pi B \eta)/(\pi B \eta)$$

where

$$\eta = f_0 \lambda (u + v) + C_s \lambda^3 (u^3 + v^3) + \pi i \varepsilon^2 \lambda^2 (u^3 + u^2 v + u v^2 + v^3)/2. \quad (2.5.2.49)$$

(b) *The projected charge-density approximation.* For very thin specimens composed of moderately heavy atoms, the WPOA is

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inadequate. Within the region of validity of the phase-object approximation (POA), more complicated relations analogous to (2.5.2.43) to (2.5.2.47) may be written. A simpler expression may be obtained by use of the two-dimensional form of Poisson's equation, relating the projected potential distribution $\varphi(xy)$ to the projected charge-density distribution $\rho(xy)$. This is the PCDA (projected charge-density approximation) (Cowley & Moodie, 1960),

$$I(xy) = 1 + 2\Delta f \cdot \lambda \sigma \rho(xy). \quad (2.5.2.50)$$

This is valid for sufficiently small values of the defocus Δf , provided that the effects of the spherical aberration may be neglected, *i.e.* for image resolutions not too close to the Scherzer resolution limit (Lynch *et al.*, 1975). The function $\rho(xy)$ includes contributions from both the positive atomic nuclei and the negative electron clouds. For underfocus (Δf negative), single atoms give dark spots in the image. The contrast reverses with defocus.

2.5.2.8. Crystal structure imaging

(a) *Introduction.* It follows from (2.5.2.43) and (2.5.2.42) that, within the severe limitations of validity of the WPOA or the PCDA, images of very thin crystals, viewed with the incident beam parallel to a principal axis, will show dark spots at the positions of rows of atoms parallel to the incident beam. Provided that the resolution limit is less than the projected distances between atom rows (1–3 Å), the projection of the crystal structure may be seen directly.

In practice, theoretical and experimental results suggest that images may give a direct, although non-linear, representation of the projected potential or charge-density distribution for thicknesses much greater than the thicknesses for validity of these approximations, *e.g.* for thicknesses which may be 50 to 100 Å for 100 keV electrons for 3 Å resolutions and which increase for comparable resolutions at higher voltage but decrease with improved resolutions.

The use of high-resolution imaging as a means for determining the structures of crystals and for investigating the form of the defects in crystals in terms of the arrangement of the atoms has become a widely used and important branch of crystallography with applications in many areas of solid-state science. It must be emphasized, however, that image intensities are strongly dependent on the crystal thickness and orientation and also on the instrumental parameters (defocus, aberrations, alignment *etc.*). It is only when all of these parameters are correctly adjusted to lie within strictly defined limits that interpretation of images in terms of atom positions can be attempted [see *IT C* (1999, Section 4.3.8)].

Reliable interpretations of high-resolution images of crystals ('crystal structure images') may be made, under even the most favourable circumstances, only by the comparison of observed image intensities with intensities calculated by use of an adequate approximation to many-beam dynamical diffraction theory [see *IT C* (1999, Section 4.3.6)]. Most calculations for moderate or large unit cells are currently made by the multi-slice method based on formulation of the dynamical diffraction theory due to Cowley & Moodie (1957). For smaller unit cells, the matrix method based on the Bethe (1928) formulation is also frequently used (Hirsch *et al.*, 1965).

(b) *Fourier images.* For periodic objects in general, and crystals in particular, the amplitudes of the diffracted waves in the back focal plane are given from (2.5.2.31) by

$$\Psi_0(\mathbf{h}) \cdot T(\mathbf{h}). \quad (2.5.2.51)$$

For rectangular unit cells of the projected unit cell, the vector $\mathbf{h}$ has components h/a and k/b . Then the set of amplitudes (2.5.2.34), and hence the image intensities, will be identical for two different sets of defocus and spherical aberration values Δf_1 , C_{s1} and Δf_2 , C_{s2} if, for an integer N ,

$$\chi_1(h) = \chi_2(h) = 2N\pi;$$

i.e.

$$\pi\lambda\left(\frac{h^2}{a^2} + \frac{k^2}{b^2}\right)(\Delta f_1 - \Delta f_2) + \frac{1}{2}\pi\lambda^3\left(\frac{h^2}{a^2} + \frac{k^2}{b^2}\right)^2(C_{s1} - C_{s2}) = 2\pi N.$$

This relationship is satisfied for all h, k if a^2/b^2 is an integer and

$$\Delta f_1 - \Delta f_2 = 2na^2/\lambda$$

and

$$C_{s1} - C_{s2} = 4ma^4/\lambda^3, \quad (2.5.2.52)$$

where m, n are integers (Kuwabara, 1978). The relationship for Δf is an expression of the Fourier image phenomenon, namely that for a plane-wave incidence, the intensity distribution for the image of a periodic object repeats periodically with defocus (Cowley & Moodie, 1960). Hence it is often necessary to define the defocus value by observation of a non-periodic component of the specimen such as a crystal edge (Spence *et al.*, 1977).

For the special case $a^2 = b^2$, the image intensity is also reproduced exactly for

$$\Delta f_1 - \Delta f_2 = (2n + 1)a^2/\lambda, \quad (2.5.2.53)$$

except that in this case the image is translated by a distance $a/2$ parallel to each of the axes.

2.5.2.9. Image resolution

(1) *Definition and measurement.* The 'resolution' of an electron microscope or, more correctly, the 'least resolvable distance', is usually defined by reference to the transfer function for the coherent imaging of a weak phase object under the Scherzer optimum defocus condition (2.5.2.44). The resolution figure is taken as the inverse of the U value for which $\sin \chi(U)$ first crosses the axis and is given, as in (2.5.2.45), by

$$\Delta x = 0.66C_s^{1/4}\lambda^{3/4}. \quad (2.5.2.45)$$

It is assumed that an objective aperture is used to eliminate the contribution to the image for U values greater than the first zero crossing, since for these contributions the relative phases are distorted by the rapid oscillations of $\sin \chi(U)$ and the corresponding detail of the image is not directly interpretable in terms of the projection of the potential distribution of the object.

The resolution of the microscope in practice may be limited by the incoherent factors which have the effect of multiplying the WPOA transfer function by envelope functions as in (2.5.2.49).

The resolution, as defined above, and the effects of the envelope functions may be determined by Fourier transform of the image of a suitable thin, weakly scattering amorphous specimen. The Fourier-transform operation may be carried out by use of an optical diffractometer. A more satisfactory practice is to digitize the image directly by use of a two-dimensional detector system in the microscope or from a photographic recording, and perform the Fourier transform numerically.

For the optical diffractometer method, the intensity distribution obtained is given from (2.5.2.43) as a radially symmetric function of U ,

$$\begin{aligned} I(U) &= |\mathcal{F}I(xy)|^2 \\ &= \delta(U) + 4\sigma^2|\Phi(u)|^2 \cdot \sin^2 \chi(U) \cdot E^2(U), \end{aligned} \quad (2.5.2.54)$$

where $E(U)$ is the product of the envelope functions.

In deriving (2.5.2.54) it has been assumed that:

(a) the WPOA applies;

(b) the optical transmission function of the photographic record is linearly related to the image intensity, $I(xy)$;

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(c) the diffraction intensity $|\Phi(U)|^2$ is a radially symmetric, smoothly varying function such as is normally produced by a sufficiently large area of the image of an amorphous material;

(d) there is no astigmatism present and no drift of the specimen; either of these factors would remove the radial symmetry.

From the form of (2.5.2.54) and a preknowledge of $|\Phi(U)|^2$, the zero crossings of $\sin \chi$ and the form of $E(U)$ may be deduced. Analysis of a through-focus series of images provides more complete and reliable information.

(2) Detail on a scale much smaller than the resolution of the electron microscope, as defined above, is commonly seen in electron micrographs, especially for crystalline samples. For example, lattice fringes, having the periodicity of the crystal lattice planes, with spacings as small as 0.6 Å in one direction, have been observed using a microscope having a resolution of about 2.5 Å (Matsuda *et al.*, 1978), and two-dimensionally periodic images showing detail on the scale of 0.5 to 1 Å have been observed with a similar microscope (Hashimoto *et al.*, 1977).

Such observations are possible because

(a) for periodic objects the diffraction amplitude $\Psi_0(uv)$ in (2.5.2.31) is a set of delta functions which may be multiplied by the corresponding values of the transfer function that will allow strong interference effects between the diffracted beams and the zero beam, or between different diffracted beams;

(b) the envelope functions for the WPOA, arising from incoherent imaging effects, do not apply for strongly scattering crystals; the more general expression (2.5.2.36) provides that the incoherent imaging factors will have much less effect on the interference of some sets of diffracted beams.

The observation of finely spaced lattice fringes provides a measure of some important factors affecting the microscope performance, such as the presence of mechanical vibrations, electrical interference or thermal drift of the specimen. A measure of the fineness of the detail observable in this type of image may therefore be taken as a measure of 'instrumental resolution'.

2.5.2.10. Electron diffraction in electron microscopes

Currently most electron-diffraction patterns are obtained in conjunction with images, in electron microscopes of one form or another, as follows.

(a) Selected-area electron-diffraction (SAED) patterns are obtained by using intermediate and projector lenses to form an image of the diffraction pattern in the back-focal plane of the objective lens (Fig. 2.5.2.2). The area of the specimen from which the diffraction pattern is obtained is defined by inserting an aperture in the image plane of the objective lens. For parallel illumination of the specimen, sharp diffraction spots are produced by perfect crystals.

A limitation to the area of the specimen from which the diffraction pattern can be obtained is imposed by the spherical aberration of the objective lens. For a diffracted beam scattered through an angle α , the spread of positions in the object for which the diffracted beam passes through a small axial aperture in the image plane is $C_s \alpha^3$, e.g. for $C_s = 1$ mm, $\alpha = 5 \times 10^{-2}$ rad (10.0,0 reflection from gold for 100 keV electrons), $C_s \alpha^3 = 1250$ Å, so that a selected-area diameter of less than about 2000 Å is not feasible. For higher voltages, the minimum selected-area diameter decreases with λ^2 if the usual assumption is made that C_s increases for higher-voltage microscopes so that $C_s \lambda$ is a constant.

(b) Convergent-beam electron-diffraction (CBED) patterns are obtained when an incident convergent beam is focused on the specimen, as in an STEM instrument or an STEM attachment for a conventional TEM instrument.

For a large, effectively incoherent source, such as a conventional hot-filament electron gun, the intensities are added for each incident-beam direction. The resulting CBED pattern has an

intensity distribution

$$I(uv) = \int |\Psi_{u_1 v_1}(uv)|^2 du_1 dv_1, \quad (2.5.2.55)$$

where $\Psi_{u_1 v_1}(uv)$ is the Fourier transform of the exit wave at the specimen for an incident-beam direction u_1, v_1 .

(c) Coherent illumination from a small bright source such as a field emission gun may be focused on the specimen to give an electron probe having an intensity distribution $|t(xy)|^2$ and a diameter equal to the STEM dark-field image resolution [equation (2.5.2.47)] of a few Å. The intensity distribution of the resulting microdiffraction pattern is then

$$|\Psi(uv)|^2 = |\Psi_0(uv) * T(uv)|^2, \quad (2.5.2.56)$$

where $\Psi_0(uv)$ is the Fourier transform of the exit wave at the specimen. Interference occurs between waves scattered from the various incident-beam directions. The diffraction pattern is thus an in-line hologram as envisaged by Gabor (1949).

(d) Diffraction patterns may be obtained by using an optical diffractometer (or computer) to produce the Fourier transform squared of a small selected region of a recorded image. The optical diffraction-pattern intensity obtained under the ideal conditions specified under equation (2.5.2.54) is given, in the case of weak phase objects, by

$$I(uv) = \delta(uv) + 4\sigma^2 |\Phi(uv)|^2 \cdot \sin^2 \chi(uv) \cdot E^2(uv) \quad (2.5.2.57)$$

or, more generally, by

$$I(uv) = c\delta(uv) + |\Psi(uv) \cdot T(uv) * \Psi^*(uv) \cdot T^*(uv)|^2,$$

where $\Psi(uv)$ is the Fourier transform of the wavefunction at the exit face of the specimen and c is a constant depending on the characteristics of the photographic recording medium.

2.5.3. Space-group determination by convergent-beam electron diffraction* (P. GOODMAN)

2.5.3.1. Introduction

2.5.3.1.1. CBED

Convergent-beam electron diffraction, originating in the experiments of Kossel and Möllenstedt (Kossel & Möllenstedt, 1938) has been established over the past two decades as a powerful technique for the determination of space group in inorganic materials, with particular application when only microscopic samples are available. Relatively recently, with the introduction of the analytical electron microscope, this technique – abbreviated as CBED – has become available as a routine, so that there is now a considerable accumulation of data from a wide range of materials. A significant extension of the technique in recent times has been the introduction of LACBED (large-angle CBED) by Tanaka & Terauchi (1985). This technique allows an extensive angular range of single diffraction orders to be recorded and, although this method cannot be used for microdiffraction (since it requires an extensive single-crystal area), new LACBED applications appear regularly, particularly in the field of semiconductor research (see Section 2.5.3.6).

The CBED method relies essentially on two basic properties of transmission electron diffraction, namely the radical departure from Friedel's law and the formation of characteristic extinction bands

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within space-group-forbidden reflections. Departure from Friedel's law in electron diffraction was first noted experimentally by Miyake & Uyeda (1950). The prediction of space-group-forbidden bands (within space-group-forbidden reflections) by Cowley & Moodie (1959), on the other hand, was one of the first successes of N -beam theory. A detailed explanation was later given by Gjønnes & Moodie (1965). These are known variously as 'GM' bands (Tanaka *et al.*, 1983), or more simply and definitively as 'GS' (glide-screw) bands (this section). These extinctions have a close parallel with space-group extinctions in X-ray diffraction, with the reservation that only screw axes of order two are accurately extinctive under N -beam conditions. This arises from the property that only those operations which lead to identical *projections* of the asymmetric unit can have N -beam dynamical symmetries (Cowley *et al.*, 1961).

Additionally, CBED from perfect crystals produces high-order defect lines in the zero-order pattern, analogous to the defect Kikuchi lines of inelastic scattering, which provide a sensitive measurement of unit-cell parameters (Jones *et al.*, 1977; Fraser *et al.*, 1985; Tanaka & Terauchi, 1985).

The significant differences between X-ray and electron diffraction, which may be exploited in analysis, arise as a consequence of a much stronger interaction in the case of electrons (Section 2.5.2). Hence, thin, approximately parallel-sided crystal regions must be used in high-energy (100 kV–1 MV) electron transmission work, so that diffraction is produced from crystals effectively infinitely periodic in only two dimensions, leading to the relaxation of three-dimensional diffraction conditions known as 'excitation error' (Chapter 5.2). Also, there is the ability in CBED to obtain data from microscopic crystal regions of around 50 Å in diameter, with corresponding exposure times of several seconds, allowing a survey of a material to be carried out in a relatively short time.

In contrast, single-crystal X-ray diffraction provides much more limited symmetry information in a direct fashion [although statistical analysis of intensities (Wilson, 1949) will considerably supplement this information], but correspondingly gives much more direct three-dimensional geometric data, including the determination of unit-cell parameters and three-dimensional extinctions.

The relative strengths and weaknesses of the two techniques make it useful where possible to collect both convergent-beam and X-ray single-crystal data in a combined study. However, all parameters *can* be obtained from convergent-beam and electron-diffraction data, even if in a somewhat less direct form, making possible space-group determination from microscopic crystals and microscopic regions of polygranular material. Several reviews of the subject are available (Tanaka, 1994; Steeds & Vincent, 1983; Steeds, 1979). In addition, an atlas of characteristic CBED patterns for direct phase identification of metal alloys has been published (Mansfield, 1984), and it is likely that this type of procedure, allowing N -beam analysis by comparison with standard simulations, will be expanded in the near future.

2.5.3.1.2. Zone-axis patterns from CBED

Symmetry analysis is necessarily tied to examination of patterns near relevant zone axes, since the most intense N -beam interaction occurs amongst the zero-layer zone-axis reflections, with in addition a limited degree of upper-layer (higher-order Laue zone) interaction. There will generally be several useful zone axes accessible for a given parallel-sided single crystal, with the regions between axes being of little use for symmetry analysis. Only one such zone axis can be parallel to a crystal surface normal, and a microcrystal is usually chosen at least initially to have this as the principal symmetry axis. Other zone axes from that crystal may suffer mild symmetry degradation because the N -beam lattice component ('excitation error' extension) will not have the symmetry of the structure (Goodman, 1974; Eades *et al.*, 1983).

Upper-layer interactions, responsible for imparting three-dimensional information to the zero layer, are of two types: the first arising from 'overlap' of dynamic shape transforms and causing smoothly varying modulations of the zero-layer reflections, and the second, caused by direct interactions with the upper-layer, or higher-order Laue zone lines, leading to a sharply defined fine-line structure. These latter interactions are especially useful in increasing the accuracy of space-group determination (Tanaka *et al.*, 1983), and may be enhanced by the use of low-temperature specimen stages. The presence of these defect lines in convergent-beam discs, occurring especially in low-symmetry zone-axis patterns, allows symmetry elements to be related to the three-dimensional structure (Section 2.5.3.5; Fig. 2.5.3.4c).

To the extent that such three-dimensional effects can be ignored or are absent in the zero-layer pattern the *projection approximation* (Chapter 5.2) can be applied. This situation most commonly occurs in zone-axis patterns taken from relatively thin crystals and provides a useful starting point for many analyses, by identifying the projected symmetry.

2.5.3.2. Background theory and analytical approach

2.5.3.2.1. Direct and reciprocity symmetries: types I and II

Convergent-beam diffraction symmetries are those of Schrödinger's equation, *i.e.* of crystal potential, plus the diffracting electron. The appropriate equation is given in Section 2.5.2 [equation (2.5.2.6)] and Chapter 5.2 [equation (5.2.2.1)] in terms of the real-space wavefunction ψ . The symmetry elements of the crystal responsible for generating pattern symmetries may be conveniently classified as of two types (I and II) as follows.

I. The *direct* (type I: Table 2.5.3.1) symmetries imposed by this equation on the transmitted wavefunction given z -axis illumination ($\mathbf{k}_0$, the incident wavevector parallel to Z , the surface normal) are just the symmetries of φ whose operation leaves both crystal and z axis unchanged. These are also called 'vertical' symmetry elements, since they contain Z . These symmetries apply equally in real and reciprocal space, since the operator ∇^2 has circular symmetry in both spaces and does nothing to degrade the symmetry in

Table 2.5.3.1. Listing of the symmetry elements relating to CBED patterns under the classifications of 'vertical' (I), 'horizontal' (II) and combined or roto-inversionary axes

I. Vertical symmetry elements		
International symbols		
2, 3, 4, 6 (2 ₁ , 3 ₁ , ...)		
m (c)		
a, b (n)		
II. Horizontal symmetry elements		
	Diperic symbols	BESR symbols
	2'	m
	2' ₁	1 _R
	m'	2 _R
	a', b', n'	
	$\bar{1}'$	
I + II	$\bar{4}'$	4 _R
I × II	$\bar{3}' = 3 \times \bar{1}'$	6 _R = 3 · 2 _R
	$\bar{6}' = 3 \times m'$	31 _R

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transmission. Hence, for high-symmetry crystals (zone axis parallel to z axis), and to a greater or lesser degree for crystals of a more general morphology, these zone-axis symmetries apply both to electron-microscope lattice images and to convergent-beam patterns under z -axis-symmetrical illumination, and so impact also on space-group determination by means of high-resolution electron microscopy (HREM). In CBED, these elements lead to *whole pattern* symmetries, to which every point in the pattern contributes, regardless of diffraction order and Laue zone (encompassing ZOLZ and HOLZ reflections).

II. Reciprocity-induced symmetries, on the other hand, depend upon ray paths and path reversal, and in the present context have relevance only to the diffraction pattern. Crystal-inverting or horizontal crystal symmetry elements combine with reciprocity to yield *indirect* pattern symmetries lacking a one-to-one real-space correspondence, within individual diffraction discs or between disc pairs. Type II elements are assumed to lie on the central plane of the crystal, midway between surfaces, as symmetry operators; this assumption amounts to a 'central plane' approximation, which has a very general validity in space-group-determination work (Goodman, 1984a).

A minimal summary of basic theoretical points, otherwise found in Chapter 5.2 and numerous referenced articles, is given here.

For a specific zero-layer diffraction order g ($= h, k$) the incident and diffracted vectors are $\mathbf{k}_0$ and $\mathbf{k}_g$. Then the three-dimensional vector $\mathbf{K}_{0g} = \frac{1}{2}(\mathbf{k}_0 + \mathbf{k}_g)$ has the pattern-space projection, $\mathbf{K}_g = {}^p[\mathbf{K}_{0g}]$. The point $\mathbf{K}_g = \mathbf{0}$ gives the *symmetrical Bragg condition* for the associated diffraction disc, and $\mathbf{K}_g \neq \mathbf{0}$ is identifiable with the angular deviation of $\mathbf{K}_{0g}$ from the vertical z axis in three-dimensional space (see Fig. 2.5.3.1). $\mathbf{K}_g = \mathbf{0}$ also defines the symmetry centre within the two-dimensional disc diagram (Fig. 2.5.3.2); namely, the intersection of the lines S and G , given by the trace of excitation error, $\mathbf{K}_g = \mathbf{0}$, and the perpendicular line directed towards the reciprocal-space origin, respectively. To be definitive it is necessary to index diffracted amplitudes relating to a fixed crystal thickness and wavelength, with both crystallographic and momentum coordinates, as $\mathbf{u}_{g,K}$, to handle the continuous variation of $\mathbf{u}_g$ (for a particular diffraction order), with angles of incidence as determined by $\mathbf{k}_0$, and registered in the diffraction plane as the projection of $\mathbf{K}_{0g}$.

2.5.3.2.2. Reciprocity and Friedel's law

Reciprocity was introduced into the subject of electron diffraction in stages, the essential theoretical basis, through Schrödinger's equation, being given by Bilhorn *et al.* (1964), and the N -beam diffraction applications being derived successively by von Laue (1935), Cowley (1969), Pogany & Turner (1968), Moodie (1972), Buxton *et al.* (1976), and Gunning & Goodman (1992).

Reciprocity represents a reverse-incidence configuration reached with the reversed wavevectors $\bar{\mathbf{k}}_0 = -\mathbf{k}_g$ and $\bar{\mathbf{k}}_g = -\mathbf{k}_0$, so that the scattering vector $\Delta\mathbf{k} = \mathbf{k}_g - \mathbf{k}_0 = \bar{\mathbf{k}}_0 - \bar{\mathbf{k}}_g$ is unchanged, but $\bar{\mathbf{K}}_{0g} = \frac{1}{2}(\bar{\mathbf{k}}_0 + \bar{\mathbf{k}}_g)$ is changed in sign and hence reversed (Moodie, 1972). The reciprocity equation,

$$\mathbf{u}_{g,K} = \mathbf{u}_{\bar{g},\bar{K}}^* \quad (2.5.3.1)$$

is valid independently of crystal symmetry, but cannot contribute symmetry to the pattern unless a crystal-inverting symmetry element is present (since $\bar{\mathbf{K}}$ belongs to a reversed wavevector). The simplest case is centrosymmetry, which permits the right-hand side of (2.5.3.1) to be complex-conjugated giving the useful CBED pattern equation

$$\mathbf{u}_{g,K} = \mathbf{u}_{\bar{g},\bar{K}} \quad (2.5.3.2)$$

Since $\mathbf{K}$ is common to both sides there is a point-by-point identity

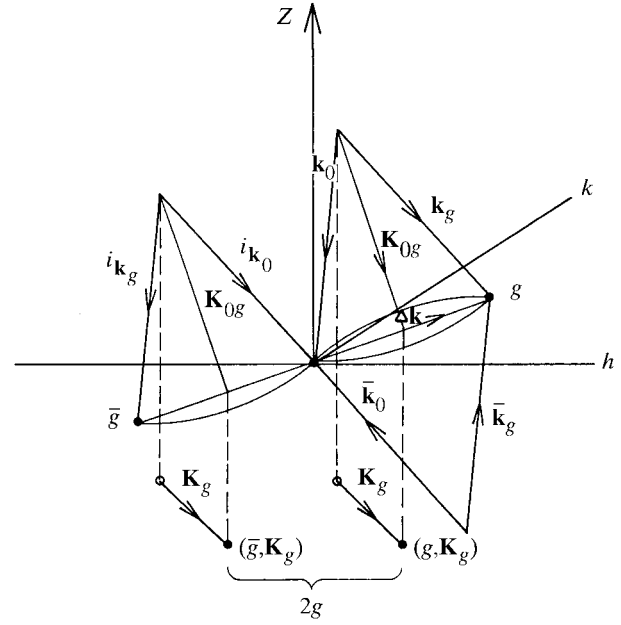


Fig. 2.5.3.1. Vector diagram in semi-reciprocal space, using Ewald-sphere constructions to show the 'incident', 'reciprocity' and 'reciprocity $\times$ centrosymmetry' sets of vectors. Dashed lines connect the full vectors $\mathbf{K}_{0g}$ to their projections $\mathbf{K}_g$ in the plane of observation.

between the related distributions, separated by $2g$ (the distance between g and $\bar{g}$ reflections). This invites an obvious analogy with *Friedel's law*, $F_g = F_g^*$, with the reservation that (2.5.3.2) holds only for centrosymmetric crystals. This condition (2.5.3.2) constitutes what has become known as the $\pm H$ symmetry and, incidentally, is the only reciprocity-induced symmetry so general as to not depend upon a disc symmetry-point or line, nor on a particular zone axis (*i.e.* it is not a point symmetry but a translational symmetry of the pattern intensity).

2.5.3.2.3. In-disc symmetries

(a) *Dark-field (diffracted-beam) discs.* Other reciprocity-generated symmetries which are available for experimental observation relate to a single (zero-layer) disc and its origin $\mathbf{K}_g = \mathbf{0}$, and are summarized here by reference to Fig. 2.5.3.2, and given in operational detail in Table 2.5.3.2. The notation subscript R , for reciprocity-induced symmetries, introduced by Buxton *et al.* (1976) is now adopted (and referred to as BESR notation). Fig.

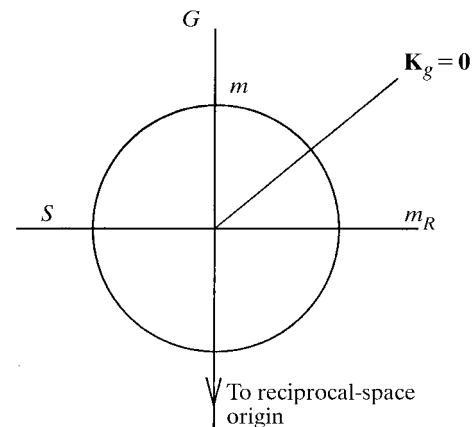


Fig. 2.5.3.2. Diagrammatic representation of a CBED disc with symmetry lines m, m_R (alternate labels G, S) and the central point $\mathbf{K}_g = \mathbf{0}$.

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2.5.3.2 shows a disc crossed by reference lines m and m_R . These will be mirror lines of intensity if: (a) g is parallel to a vertical mirror plane; and (b) g is parallel to a horizontal diad axis, respectively. The third possible point symmetry, that of disc centrosymmetry (1_R in BESR notation) will arise from the presence of a horizontal mirror plane. Lines m and m_R become the GS extinction lines G and S when glide planes and screw axes are present instead of mirror planes and diad axes.

(b) *Bright-field (central-beam) disc*. The central beam is a special case since the point $K_0 = 0$ is the centre of the whole pattern as well as of that particular disc. Therefore, both sets of rotational symmetry (types I and II) discussed above apply (see Table 2.5.3.3).

In addition, the central-beam disc is a source of three-dimensional lattice information from defect-line scattering. Given a sufficiently perfect crystal this fine-line structure overlays the more general intensity modulation, giving this disc a lower and more precisely recorded symmetry.

2.5.3.2.4. Zero-layer absences

Horizontal glides, a' , n' (diperiodic, primed notation), generate zero-layer absent rows, or centring, rather than GS bands (see Fig. 2.5.3.3). This is an example of the projection approximation in its most universally held form, *i.e.* in application to absences. Other examples of this are: (a) appearance of both G and S extinction bands near their intersection irrespective of whether glide or screw axes are involved; and (b) suppression of the influence of vertical, non-primitive translations with respect to observations in the zero

layer. It is generally assumed as a working rule that the zero-layer or ZOLZ pattern will have the rotational symmetry of the point-group component of the vertical screw axis (so that $2_1 \simeq 2$). Elements included in Table 2.5.3.1 on this pretext are given in parentheses. However, the presence of 2_1 rather than 2 (3_1 rather than 3 *etc.*) should be detectable as a departure from accurate twofold symmetry in the first-order-Laue-zone (FOLZ) reflection circle (depicted in Fig. 2.5.3.3). This has been observed in the cubic structure of $Ba_2Fe_2O_5Cl_2$, permitting the space groups $I23$ and $I2_13$ to be distinguished (Schwartzman *et al.*, 1996). A summary of all the symmetry components described in this section is given diagrammatically in Table 2.5.3.2.

2.5.3.3. Pattern observation of individual symmetry elements

The following guidelines, the result of accumulated experience from several laboratories, are given in an experimentally based sequence, and approximately in order of value and reliability.

(i) The value of X in an X -fold rotation axis is made immediately obvious in a zone-axis pattern, although a screw component is not detected in the pattern symmetry.

Roto-inversionary axes require special attention: $\bar{6}$ and $\bar{3}$ may be factorized, as in Tables 2.5.3.1, 2.5.3.3 and 2.5.3.4, to show better the additional CBED symmetries ($3/m'$ and $3 \times \bar{1}'$, respectively). $\bar{4}$ cannot be decomposed further (Table 2.5.3.1) and generates its own diffraction characteristics in non-projective patterns (see Section 2.5.3.5). This specific problem of observing the fourfold roto-

Table 2.5.3.2. Diagrammatic illustrations of the actions of five types of symmetry elements (given in the last column in Volume A diagrammatic symbols) on an asymmetric pattern component, in relation to the centre of the pattern at $K_{00} = 0$, shown as ' $\oplus$ ', or in relation to the centre of a diffraction order at $K_{0g} = 0$, shown as '+'

Type	Symmetry element	Observation and action	In combination	Interpretation
Vertical	4			
	$m; a$			
Horizontal	$2'; 2'_1$			
	$i(\bar{1}')$			
	$m'; a'$			

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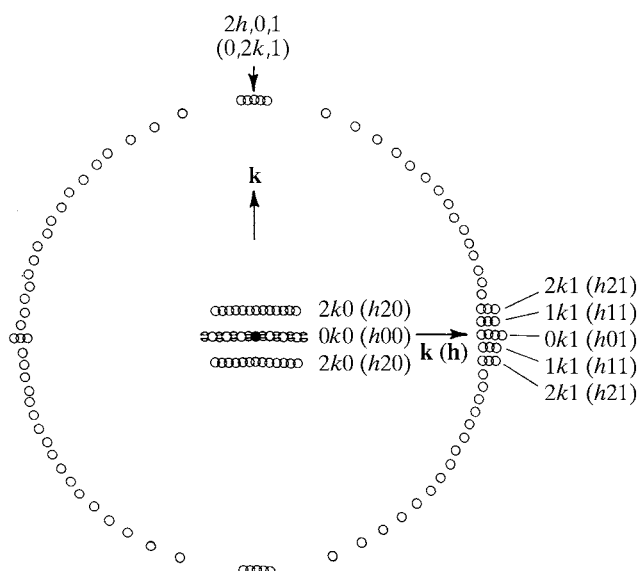


Fig. 2.5.3.3. Diagrammatic representation of the influence of non-symmorphic elements: (i) Alternate rows of the zero-layer pattern are absent owing to the horizontal glide plane. The pattern is indexed as for an 'a' glide; the alternative indices (in parentheses) apply for a 'b' glide. (ii) GS bands are shown along the central row of the zero layer, for odd-order reflections.

inversion symmetry has been resolved recently by Tanaka *et al.* (1994) using both CBED and LACBED techniques.

(ii) *Vertical mirror plane* determination may be the most accurate crystal point-symmetry test, given that it is possible to follow the symmetry through large crystal rotations (say 5 to 15°) about the mirror normal. It is also relatively unaffected by crystal surface steps as compared to (v) below.

(iii) *Horizontal glide planes* are determined unequivocally from zero-layer absences when the first Laue zone is recorded, either with the main pattern or by further crystal rotation; *i.e.* a section of this zone is needed to determine the lateral unit-cell parameters. This observation is illustrated diagrammatically in Fig. 2.5.3.3.

(iv) An extinction (GS) line or band through odd-order reflections of a zone-axis pattern indicates only a *projected glide line*. This is true because both $P2_1$ (No. 4) and Pa (No. 7) symmetries project into 'pg' in two dimensions. However, the projection approximation has only limited validity in CBED. For all crystal rotations *around* the 2_1 axis, or alternatively *about the glide-plane 'a' normal*, dynamic extinction conditions are retained. This is summarized by saying that the diffraction vector $\mathbf{K}_{0g}$ should be either normal to a screw axis or contained within a glide plane for the generation of the S or G bands, respectively. Hence $P2_1$ and Pa may be distinguished by these types of rotations away from the zone axis with the consequence that the element 2_1 in particular is characterized by extinctions close to the Laue circle for the tilted ZOLZ pattern (Goodman, 1984b), and that the glide a will generate extinction bands through both ZOLZ and HOLZ reflections for all orientations maintaining Laue-circle symmetry about the S band (Steeds *et al.*, 1978).

As a supplement to this, in a refined technique not universally applicable, Tanaka *et al.* (1983) have shown that fine-line detail from HOLZ interaction can be observed which will separately identify S - (2_1) and G -band symmetry from a single pattern (see Fig. 2.5.3.6).

(v) The centre-of-symmetry (or $\pm H$) test can be made very sensitive by suitable choice of diffraction conditions but requires a reasonably flat crystal since it involves a pair of patterns (the angular beam shift involved is very likely to be associated with

some lateral probe shift on the specimen). This test is best carried out at a low-symmetry zone axis, free from other symmetries, and preferably incorporating some fine-line HOLZ detail, in the following way. The hkl and $\bar{h}\bar{k}l$ reflections are successively illuminated by accurately exchanging the central-beam aperture with the diffracted-beam apertures, having first brought the zone axis on to the electron-microscope optic axis. This produces the symmetrical $\pm H$ condition.

(vi) In seeking internal m_R symmetry as a test for a horizontal diad axis it is as well to involve some distinctive detail in the mirror symmetry (*i.e.* simple two-beam-like fringes should be avoided), and also to rotate the crystal about the supposed diad axis, to avoid an m_R symmetry due to projection [for examples see Fraser *et al.* (1985) and Goodman & Whitfield (1980)].

(vii) The presence or absence of the in-disc centrosymmetry element 1_R formally indicates the presence or absence of a horizontal mirror element m' , either as a true mirror or as the mirror component of a horizontal glide plane g' . In this case the *absence* of symmetry provides more positive evidence than its presence, since absence is sufficient evidence for a lack of central-mirror crystal symmetry but an observed symmetry could arise from the operation of the projection approximation. If some evidence of the three-dimensional interaction is included in the observation or if three-dimensional interaction (from a large c axis parallel to the zone axis) is evident in the rest of the pattern, this latter possibility can be excluded. Interpretation is also made more positive by extending the angular aperture, especially by the use of LACBED.

These results are illustrated in Table 2.5.3.2 and by actual examples in Section 2.5.3.5.

2.5.3.4. Auxiliary tables

Space groups may very well be identified using CBED patterns from an understanding of the diffraction properties of real-space symmetry elements, displayed for example in Table 2.5.3.2. It is, however, of great assistance to have the symmetries tabulated in reciprocal space, to allow direct comparison with the pattern symmetries.

There are three generally useful ways in which this can be done, and these are set out in Tables 2.5.3.3 to 2.5.3.5. The simplest of these is by means of point group, following the procedures of Buxton *et al.* (1976). Next, the CBED pattern symmetries can be listed as diperiodic groups which are space groups in two dimensions, allowing identification with a restricted set of three-dimensional space groups (Goodman, 1984b). Finally, the dynamic extinctions (GS bands and zero-layer absences) can be listed for each non-symmorphic space group, together with the diffraction conditions for their observation (Tanaka *et al.*, 1983; Tanaka & Terauchi, 1985). Descriptions for these tables are given below.

Table 2.5.3.3. BESR symbols (Buxton *et al.*, 1976) incorporate the subscript R to describe reciprocity-related symmetry elements, R being the operator that rotates the disc pattern by 180° about its centre. The symbols formed in this way are $1_R, 2_R, 4_R, 6_R$, where X_R represents $2\pi/X$ rotation about the zone axis, followed by R . Of these, 2_R represents the $\pm H$ symmetry (two twofold rotations) described earlier [equation (2.5.3.2)] as a transformation of crystalline centrosymmetry; 6_R may be thought of as decomposing into $3 \cdot 2_R$ for purposes of measurement. The mirror line m_R (Fig. 2.5.3.2) is similarly generated by $m \cdot 1_R$.

Table 2.5.3.3 gives the BESR interrelation of pattern symmetries with point group (Buxton *et al.*, 1976; Steeds, 1983). Columns I and II of the table list the point symmetries of the whole pattern and bright-field pattern, respectively; column III gives the BESR diffraction groups. [Note: following the Pond & Vlachavas (1983) usage, '*' has been appended to the centrosymmetric groups.]

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Table 2.5.3.3. *Diffraction point-group tables, giving whole-pattern and central-beam pattern symmetries in terms of BESR diffraction-group symbols and diperiodic group symbols*

I	II	III	IV	V	
Whole pattern	Bright field (central beam)	BESR group	Diperiodic group (point group)	Cubic point groups	
				[100]	[110]
1	1	1	1		
1	2	<u>1_R</u>	<i>m'</i>		
2	2	2	2		
1	1	*2 _R	<u>1'</u>		
2	2	*2 <u>1_R</u>	2/ <i>m'</i>		
1	<i>m</i>	<i>m_R</i>	2'		23
<i>m</i>	<i>m</i>	<i>m</i>	<i>m</i>		
<i>m</i>	2 <i>mm</i>	<u><i>m</i>1_R</u>	2' <i>mm'</i>		<u>43<i>m</i></u>
2	2 <i>mm</i>	2 <i>m_Rm_R</i>	2'2'2	23	432
2 <i>mm</i>	2 <i>mm</i>	2 <i>mm</i>	<i>mm</i> 2		
<i>m</i>	<i>m</i>	*2 _R <i>mm_R</i>	2'/ <i>m</i>		<i>m</i> <u>3</u>
2 <i>mm</i>	2 <i>mm</i>	*2 <u><i>m</i>1_R</u>	<i>mmm'</i>	<i>m</i> <u>3</u>	<i>m</i> <u>3</u> <i>m</i>
4	4	4	4		
2	4	4 _R	<u>4'</u>		
4	4	*4 <u>1_R</u>	4/ <i>m'</i>		
4	4 <i>mm</i>	4 <i>m_Rm_R</i>	42'2'	<u>432</u>	
4 <i>mm</i>	4 <i>mm</i>	4 <i>mm</i>	4 <i>mm</i>		
2 <i>mm</i>	4 <i>mm</i>	4 _R <i>mm_R</i>	<u>4'</u> <i>m</i> 2'	<u>43<i>m</i></u>	
4 <i>mm</i>	4 <i>mm</i>	*4 <u><i>m</i>1_R</u>	4/ <i>m'</i> <i>mm</i>	<i>m</i> <u>3</u>	
3	3	3	3		
3	6	<u>3</u> 1 _R	<u>6'</u>		
3	3 <i>m</i>	3 <i>m_R</i>	32'		
3 <i>m</i>	3 <i>m</i>	3 <i>m</i>	3 <i>m</i>		
3 <i>m</i>	6 <i>mm</i>	<u>3</u> <i>m</i> 1 _R	<u>6'</u> <i>m</i> 2'		
6	6	6	6		
3	3	*6 _R	<u>3'</u>		
6	6	*6 <u>1_R</u>	6/ <i>m'</i>		
6	6 <i>mm</i>	6 <i>m_Rm_R</i>	62'2'		
6 <i>mm</i>	6 <i>mm</i>	6 <i>mm</i>	6 <i>mm</i>		
3 <i>m</i>	3 <i>m</i>	*6 _R <i>mm_R</i>	<u>3'</u> <i>m</i>		
6 <i>mm</i>	6 <i>mm</i>	*6 <u><i>m</i>1_R</u>	6/ <i>m'</i> <i>mm</i>		

Inspection of columns I and II shows that 11 of the 31 diffraction groups can be determined from a knowledge of the whole pattern and bright-field (central-beam disc) point symmetries alone. The remaining 10 pairs of groups need additional observation of the dark-field pattern for their resolution. Disc symmetries 1_R , m_R (Fig. 2.5.3.2; Table 2.5.3.2) are sought (a) in general zero-layer discs and (b) in discs having an m_R line perpendicular to a proposed twofold axis, respectively; the $\pm H$ test is applied for centrosymmetry, to complete the classification.

Column IV gives the equivalent diperiodic point-group symbol, which, unprimed, gives the corresponding three-dimensional symbol. This will always refer to a non-cubic point group. Column V gives the additional cubic point-group information indicating, where appropriate, how to translate the diffraction symmetry into [100] or [110] cubic settings, respectively.

Of the groups listed in column III, those representing the projection group of their class are underlined. These groups all contain 1_R , the BESR symbol for m' . When the projection

approximation is applicable, only those groups underlined will apply. The effect of this approximation is to add a horizontal mirror plane to the symmetry group.

Table 2.5.3.4. This lists possible space groups for each of the classified zero-layer CBED symmetries. Since the latter constitute the 80 diperiodic groups, it is first necessary to index the pattern in diperiodic nomenclature; the set of possible space groups is then given by the table.

A basic requirement for diperiodic group nomenclature has been that of compatibility with *IT A* and *I*. This has been met by the recent Pond & Vlachavas (1983) tabulation. For example, DG: (*)*pban'*, where * indicates centrosymmetry, becomes space group *Pban* when, in Seitz matrix description, the former group matrix is multiplied by the third primitive translation, a_3 . Furthermore, in textual reference the prime can be optionally omitted, since the lower-case lattice symbol is sufficient indication of a two-dimensional periodicity (as *pban*).

The three sections of Table 2.5.3.4 are:

I. Point-group entries, given in H–M and BESR symbols.

II. Pattern symmetries, in diperiodic nomenclature, have three subdivisions: (i) symmorphic groups: patterns without zero-layer absences or extinctions. Non-symmorphic groups are then given in two categories: (ii) patterns with zero-layer GS bands, and (iii) patterns with zero-layer absences resulting from a horizontal glide plane; where the pattern *also* contains dynamic extinctions (GS bands) and so is listed in column (ii), the column (iii) listing is given in parentheses.

The 'short' (Pond & Vlachavas) symbol has proved an adequate description for all but nine groups for which the screw-axis content was needed: here ($2'_1$), or ($2'_12'_1$), have been added to the symbol.

III. Space-group entries are given in terms of *IT A* numbers. The first column of each row gives the same-name space group as illustrated by the example *pban'* → *Pban* above. The groups following in the same row (which have the same zero-layer symmetry) complete an exhaustive listing of the *IIb* subgroups, given in *IT A*. Cubic space groups are underlined for the sake of clarity; hence, those giving rise to the zero-layer symmetry of the diffraction group in the [100] (cyclic) setting have a single underline: these are type I minimal supergroups in *IT A* nomenclature. The cubic groups are also given in the [110] setting, in underlined italics, since this is a commonly encountered high-symmetry setting. (Note: these then are no longer *minimal* supergroups and the relationship has to be found through a series of *IT A* listings.)

The table relates to maximal-symmetry settings. For monoclinic and orthorhombic systems there are three equally valid settings. For monoclinic groups, the oblique and rectangular settings appear separately; where rectangular C-centred groups appear in a second setting this is indicated by superscript '2'. For orthorhombic groups, superscripts correspond to the 'incident-beam' system adopted in Table 2.5.3.5, as follows: no superscript: [001] beam direction; superscript 1: [100] beam direction; superscript 2: [010] beam direction. The cubic system is treated specially as described above.

Table 2.5.3.5. This lists conditions for observation of GS bands for the 137 space groups exhibiting these extinctions. These are entered as 'G', 'S', or 'GS', indicating whether a glide plane, screw axis, or both is responsible for the GS band. All three possibilities will lead to a glide line (and hence to both extinction bands) in projection, and one of the procedures (a), (b), or (c) of Section 2.5.3.3(iv) above is needed to complete the three-dimensional interpretation. In addition, the presence of horizontal glide planes, which result in systematic absences in these particular cases in the zero-layer pattern, is indicated by the symbol '—'. Where these occur at the site of prospective 'G' or 'S' bands from other glide or

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screw elements the symbol of that element is given and the 'G' or 'S' symbol is omitted.

The following paragraphs give information on the real-space interpretation of GS band formation, and their specific extinction rules, considered useful in structural interpretation.

Real-space interpretation of extinction conditions. Dynamic extinctions (GS bands) are essentially a property of symmetry in reciprocal space. However, since diagrams from *ITI* and *A* are used there is a need to give an equivalent real-space description. These bands are associated with the half-unit-cell-translational glide planes and screw axes represented in these diagrams. Inconsistencies between 'conventional' and 'physical' real-space descriptions, however, become more apparent in dynamical electron diffraction, which is dependent upon three-dimensional scattering physics, than in X-ray diffraction. Also, the distinction between general (symmorphic) and specific (non-symmorphic) extinctions is more basic (in the former case). This is clarified by the following points:

(i) Bravais lattice centring restricts the conditions for observation of GS bands. For example, in space group *Abm2* (No. 39), 'A' centring prevents observation of the GS bands associated with the 'b' glide at the [001] zone-axis orientation; this observation, and hence verification of the *b* glide, must be made at the lower-symmetry zone axes [0*vw*] (see Table 2.5.3.5). In the exceptional cases of space groups *I212121* and *I213* (Nos. 24 and 199), conditions for the observation of the relevant GS bands are completely prevented by body centring; here the screw axes of the symmorphic groups *I222* and *I23* are parallel to the screw axes of their non-symmorphic derivatives. However, electron crystallographic methods also include direct structure imaging by HREM, and it is important to note here that while the indistinguishability encountered in data sets acquired in Fourier space applies to both X-ray diffraction and CBED (notwithstanding possible differences in HOLZ symmetries), this limitation does not apply to the HREM images (produced by dynamic scattering) yielding an approximate structure image for the (zone-axis) *projection*. This technique then becomes a powerful tool in space-group research by supplying phase information in a different form.

(ii) A different complication, relating to nomenclature, occurs in the space groups *P43n*, *Pn3n* and *Pm3n* (Nos. 218, 222 and 223) where 'c' glides parallel to a diagonal plane of the unit cell occur as primary non-symmorphic elements (responsible for reciprocal-space extinctions) but are not used in the Hermann-Mauguin symbol; instead the derivative 'n' glide planes are used as characters, resulting in an *apparent* lack of correspondence between the conventionally given real-space symbols and the reciprocal-space extinctions.

(Note: In *ITI* non-symmorphic reflection rules which duplicate rules given by lattice centring, or those which are a consequence of more general rules, are given in parentheses; in *IT A* this clarification by parenthesizing, helpful for electron-diffraction analysis, has been removed.)

(iii) Finally, diamond glides (symbol 'd') require special consideration since they are associated with translations $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, and so would appear not to qualify for GS bands; however, this translation is a result of the conventional cell being defined in real rather than reciprocal space where the extinction symmetry is formed. Hence 'd' glides occur only in *F*-centred lattices (most obviously Nos. 43, 70, 203, 277 and 228). These have correspondingly an *I*-centred reciprocal lattice for which the zero-layer two-dimensional unit cell has an edge of $a^{*'} = 2a^*$. Consequently, the first-order row reflection along the diamond glide retains the reciprocal-space anti-symmetry on the basis of this physical unit cell (halved in real space), and leads to the labelling of odd-order reflections as $4n + 2$ (instead of $2n + 1$ when the cell is not halved). Additionally, although seven space groups are *I*-centred in real

space with the conventional unit cell (Nos. 109, 110, 122, 141, 142, 220 and 230), these space groups are *F*-centred with the transformation $a'' = [110]$, $b'' = [\bar{1}\bar{1}0]$, and correspondingly *I*-centred in the reciprocal-space cell as before, but the directions [100], [010] and reflection rows *h*00, 0*k*0 become replaced by directions [110] (or $[\bar{1}\bar{1}0]$) and rows *hh*0, *hh*0, in the entries of Table 2.5.3.5.

Extinction rules for symmetry elements appearing in Table 2.5.3.5. Reflection indices permitting observation of *G* and *S* bands follow [here 'zero-layer' and 'out-of-zone' (i.e. HOLZ or alternative zone) serve to emphasize that these are zone-axis observations].

(i) *Vertical glide planes* lead to 'G' bands in reflections as listed ('a', 'b', 'c' and 'n' glides):

*h*0*l*, *hk*0, 0*kl* out-of-zone reflections (for glide planes having normals [010], [001] and [100]) having $h + l$, $h + k$, $k + l = 2n + 1$, respectively, in the case of 'n' glides, or h , k , l odd in the case of 'a', 'b' or 'c' glides, respectively;

*h*00, 0*k*0, 00*l* zero-layer reflections with h , k or l odd.

Correspondingly for 'd' glides:

(a) In *F*-centred cells:

*h*0*l*, *hk*0, 0*kl* out-of-zone reflections (for glide planes having normals [010], [100] and [001], having $h + l$, $k + l$, or $h + k = 4n + 2$, respectively, with h , k and l even; and (space group No. 43 only) zero-layer reflections *h*00, 0*k*0 with h , k even and $= 4n + 2$.

(b) In *I*-centred cells:

hhl (cyclic on h , k , l for cubic groups) out-of-zone reflections having $2h + l = 4n + 2$, with l even; and zero-layer reflections *hh*0, *hh*0 (cyclic on h , k , l for cubic groups) having h odd.

(ii) *Horizontal screw axes*, namely 2_1 or the 2_1 component of screw axes 4_1 , 4_3 , 6_1 , 6_3 , 6_5 , lead to 'S' bands in reflection rows parallel to the screw axis, i.e. either *h*00, 0*k*0 or 00*l*, with conventional indexing, for h , k or l odd.

(iii) *Horizontal glide planes* lead to zero-layer absences rather than GS bands. When these prevent observation of a specific GS band (by removing the two-dimensional conditions), the symbol '—' indicates a situation where, in general, there will simply be absences for the odd-order reflections. However, Ishizuka & Taftø (1982) were the first to observe finite-intensity narrow bands under these conditions, and it is now appreciated that with a sufficient crystal thickness and a certain minimum for the *z*-axis repeat distance, GS bands can be recorded by violating the condition for horizontal-mirror-plane (*m'*) extinction while satisfying the condition for *G* or *S*, achieved by appropriate tilts away from the exact zone-axis orientation [see Section 2.5.3.3(iv)].

2.5.3.5. Space-group analyses of single crystals; experimental procedure and published examples

2.5.3.5.1. Stages of procedure

(i) *Zone-axis patterns.* The first need is to record a principal zone-axis pattern. From this, the rotational order *X* of the vertical axis and associated mirror (including glide-line) components are readily observed (see all examples).

This pattern may include part of the higher-order Laue zone; in particular the closest or first-order Laue zone (FOLZ) should be included in order to establish the presence or absence of horizontal glide planes, as illustrated in Fig. 2.5.3.3. The projection approximation frequently applies to the zone-axis pattern, particularly when this is obtained from thin crystals (although this cannot apply by definition to the FOLZ). This is indicated by the absence of fine-line detail in the central beam particularly; identification of the projected symmetry is then straightforward.

(ii) *Laue circle patterns.* Next, it is usual to seek patterns in which discs around the Laue circle include the line m_R (Fig.

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2.5.3.2). The internal disc symmetries observed together with those from the zone-axis pattern will determine a diffraction group, classifying the zero-layer symmetry. [Fig. 6(c) of Goodman & Whitfield (1980) gives an example of Laue-circle symmetries.]

(iii) *Alternative zone axes or higher-order Laue zones.* Finally, alternative zone or higher-order Laue-zone patterns may be sought for additional three-dimensional data: (a) to determine the three-dimensional extinction rules, (b) to test for centrosymmetry, or (c) to test for the existence of mirror planes perpendicular to the principal rotation axis. These procedures are illustrated in the following examples.

2.5.3.5.2. Examples

(1) *Determination of centrosymmetry; examples from the hexagonal system.* Fig. 2.5.3.4(a) illustrates the allocation of planar point groups from [0001] zone-axis patterns of β - Si_3N_4 (left-hand side) and β -GaS (right-hand side); the patterns exhibit point symmetries of 6 and $6mm$, respectively, as indicated by the accompanying geometric figures, permitting point groups 6 or $6/m$, and $6mm$ or $6/mmm$, in three dimensions. Alternative zone axes are required to distinguish these possibilities, the actual test used (testing for the element m' or the centre of symmetry) being largely determined in practice by the type of crystal preparation.

Fig. 2.5.3.4(b) shows the CBED pattern from the [1120] zone axis of β - Si_3N_4 (Bando, 1981), using a crystal with the corresponding cleavage faces. The breakdown of Friedel's law between reflections 0002 and 000 $\bar{2}$ rules out the point group $6/m$ (the element m' from the first setting is not present) and establishes 6 as the correct point group.

Also, the GS bands in the 0001 and 000 $\bar{1}$ reflections are consistent with the space group $P6_3$. [Note: screw axes 6_1 , 6_3 and 6_5 are not distinguished from these data alone (Tanaka *et al.*, 1983).]

Fig. 2.5.3.4(c) shows CBED patterns from the vicinity of the [1102] zone axis of β -GaS, only 11.2° rotated from the [0001] axis and accessible using the same crystal as for the previous [0001] pattern. This shows a positive test for centrosymmetry using a conjugate reflection pair $1\bar{1}01/110\bar{1}$, and establishes the centrosymmetric point group $6/mmm$, with possible space groups Nos. 191, 192, 193 and 194. Rotation of the crystal to test the extinction rule for $hh2hl$ reflections with l odd (Goodman & Whitfield, 1980) establishes No. 194 ($P6_3/mmc$) as the space group.

Comment: These examples show two different methods for testing for centrosymmetry. The $\pm H$ test places certain requirements on the specimen, namely that it be reasonably accurately parallel-sided – a condition usually met by easy-cleavage materials like GaS, though not necessarily by the wedge-shaped refractory Si_3N_4 crystals. On the other hand, the 90° setting, required for direct observation of a possible perpendicular mirror plane, is readily available in these fractured samples, but not for the natural cleavage samples.

(2) *Point-group determination in the cubic system, using Table 2.5.3.3.* Fig. 2.5.3.5 shows [001] (cyclic) zone-axis patterns from two cubic materials, which serve to illustrate the ability to distinguish cubic point groups from single zone-axis patterns displaying detailed central-beam structures. The left-hand pattern, from the mineral gahnite (Ishizuka & Taftø, 1982) has $4mm$ symmetry in *both* the whole pattern and the central (bright-field) beam, permitting only the BESR group $4mm1_R$ for the cubic system (column III, Table 2.5.3.3); this same observation establishes the crystallographic point group as $m\bar{3}m$ (column V of Table 2.5.3.3). The corresponding pattern for the χ -phase precipitate of stainless steel (Steeds & Evans, 1980) has a whole-pattern symmetry of only $2mm$, lower than the central-beam (bright-field) symmetry of $4mm$ (this lower symmetry is made clearest from the innermost reflections bordering the central beam). This combination leads to

the BESR group $4mm_R$ (column III, Table 2.5.3.3), and identifies the cubic point group as $\bar{4}3m$.

(3) *Analysis of data from FeS_2 illustrating use of Tables 2.5.3.4 and 2.5.3.5.* FeS_2 has a cubic structure for which a complete set of data has been obtained by Tanaka *et al.* (1983); the quality of the data makes it a textbook example (Tanaka & Terauchi, 1985) for demonstrating the interpretation of extinction bands.

Figs. 2.5.3.6(a) and (b) show the [001] (cyclic) exact zone-axis pattern and the pattern with symmetrical excitation of the 100 reflection, respectively (Tanaka *et al.*, 1983).

(i) Using Table 2.5.3.4, since there are GS bands, the pattern group must be listed in column II(ii); since a horizontal ' b ' glide plane is present (odd rows are absent in the b^* direction), the symbol must contain a ' b ' (or ' d ') (cf. Fig. 2.5.3.3). The only possible cubic group from Table 2.5.3.4 is No. 205.

(ii) Again, a complete GS cross, with both G and S arms, is present in the 100 reflection (central in Fig. 2.5.3.6b), confirmed by mirror symmetries across the G and S lines. From Table 2.5.3.5 only space group No. 205 has the corresponding entry in the column for '[100] cyclic' with GS in the cubic system (space groups Nos. 198–230). Additional patterns for the [110] setting, appearing in the original paper (Tanaka *et al.*, 1983), confirm the cubic system, and also give additional extinction characteristics for 001 and 110 reflections (Tanaka *et al.*, 1983; Tanaka & Terauchi, 1985).

(4) *Determination of centrosymmetry and space group from extinction characteristics.* Especially in working with thin crystals used in conjunction with high-resolution lattice imaging, it is sometimes most practical to determine the point group (*i.e.* space-group class) from the dynamic extinction data. This is exemplified in the Moodie & Whitfield (1984) studies of orthorhombic materials. Observations on the zero-layer pattern for Ge_3SbSe_3 with a point symmetry of $2mm$, and with GS extinction bands along odd-order $h00$ reflections, together with missing reflection rows in the $0k0$ direction, permit identification from Table 2.5.3.4. This zone-axis pattern has the characteristics illustrated in Figs. 2.5.3.3 and hence (having both missing rows and GS bands) should be listed in both II(ii) and II(iii). Hence the diffraction group must be either No. 40 or 41. Here, the class mmm , and hence centrosymmetry, has been identified through non-symorphic elements.

This identification leaves seven possible space groups, Nos. 52, 54, 56, 57, 60, 61 and 62, to be distinguished by hkl extinctions.

The same groups are identified from Table 2.5.3.5 by seeking the entry GS '–' in one of the [001] (cyclic) entries for the orthorhombic systems. With the assumption that no other principal zone axis is readily available from the same sample (which will generally be true), Table 2.5.3.5, in the last three columns, indicates which *minor* zone axes should be sought in order to identify the space group, from the glide-plane extinctions of ' G ' bands. For example, space group 62 has no $h0l$ extinctions, but will give $0kl$ extinction bands ' G ' according to the rules for an ' n ' glide, *i.e.* in reflections for which $k+l=2n+1$. Again, if the alternative principal settings are available (from the alternative cleavages of the sample) the correct space group can be found from the first three columns of Table 2.5.3.5.

From the above discussions it will be clear that Tables 2.5.3.4 and 2.5.3.5 present information in a complementary way: in Table 2.5.3.4 the specific pattern group is indexed first with the possible space groups following, while in Table 2.5.3.5 the space group is indexed first, and the possible pattern symmetries are then given, in terms of the standard *International Tables* setting.

2.5.3.6. Use of CBED in study of crystal defects, twins and non-classical crystallography

(i) Certain crystal defects lend themselves to analysis by CBED and LACBED. In earlier work, use was made of the high sensitivity

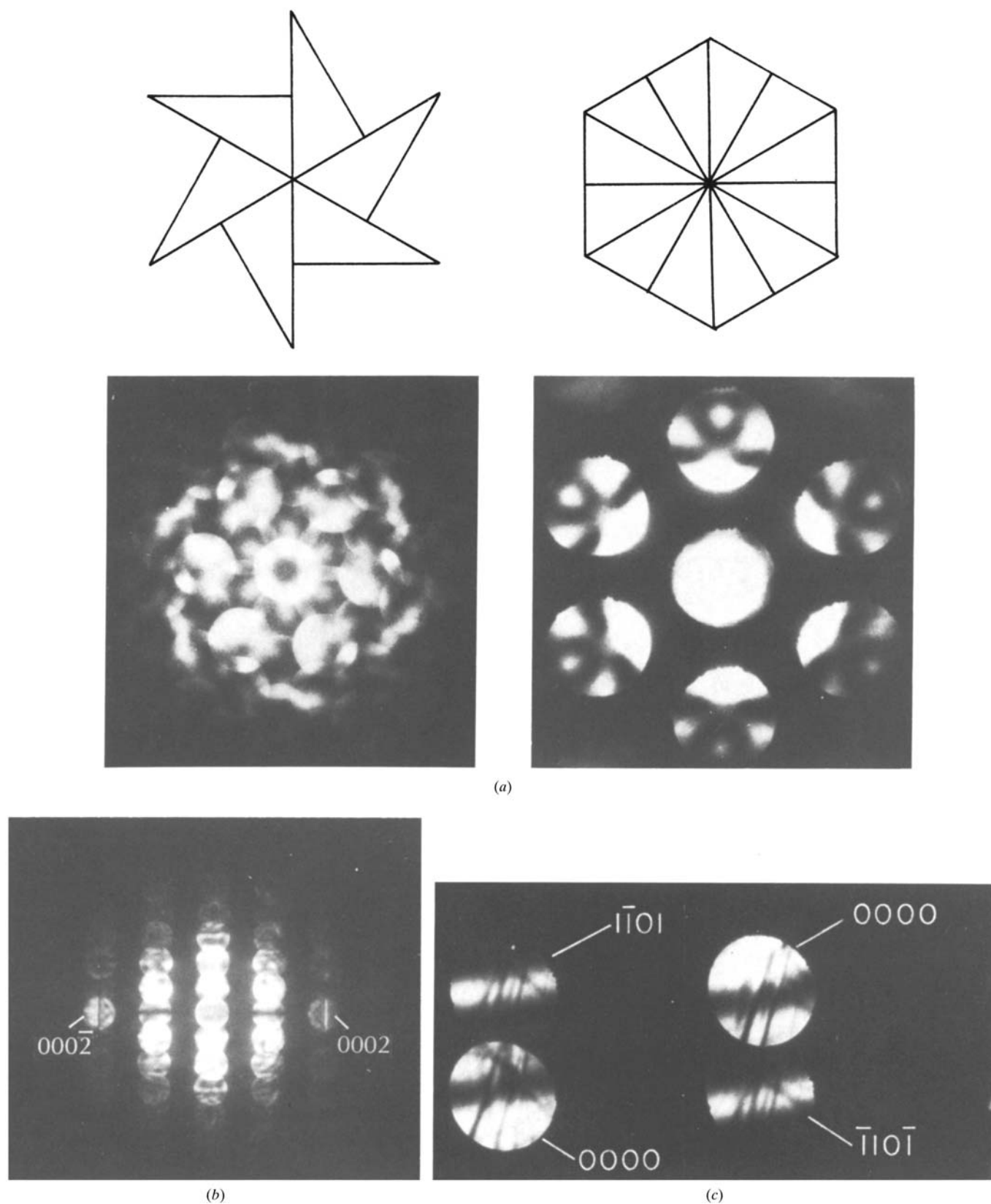


Fig. 2.5.3.4. (a) Zone-axis patterns from hexagonal structures $\beta\text{-Si}_3\text{N}_4$ (left) and $\beta\text{-GaS}$ (right) together with the appropriate planar figures for point symmetries 6 and $6mm$, respectively. (b) $[1210]$ zone-axis pattern from $\beta\text{-Si}_3\text{N}_4$, showing Friedel's law breakdown in symmetry between 0002 and $000\bar{2}$ reflections (Bando, 1981). (c) Conjugate pair of $1101/1101$ patterns from $\beta\text{-GaS}$, taken near the $[1102]$ zone axis, showing a translational symmetry associated with structural centrosymmetry.

of HOLZ line geometry to unit-cell parameters (Jones *et al.*, 1977). A computer program (Tanaka & Terauchi, 1985) is available for simulating relative line positions from lattice geometry, assuming kinematical scattering, which at least provides a valid starting point

since these spacings are mainly determined from geometric considerations. Fraser *et al.* (1985), for example, obtained a sensitivity of 0.03% in measurements of cubic-to-tetragonal distortions in this way, although the absolute accuracy was not established.

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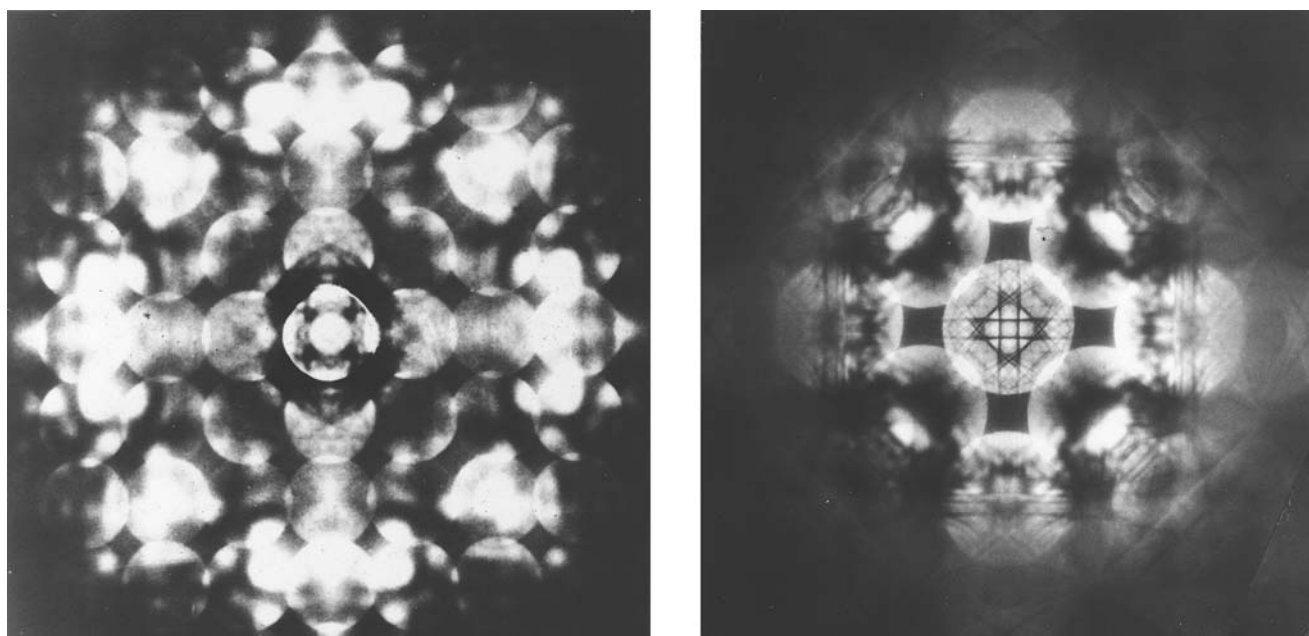


Fig. 2.5.3.5. Zone-axis patterns from cubic structures gahnite (left) (Ishizuka & Taftø, 1982) and χ -phase precipitate (right) (Steeds & Evans, 1980).

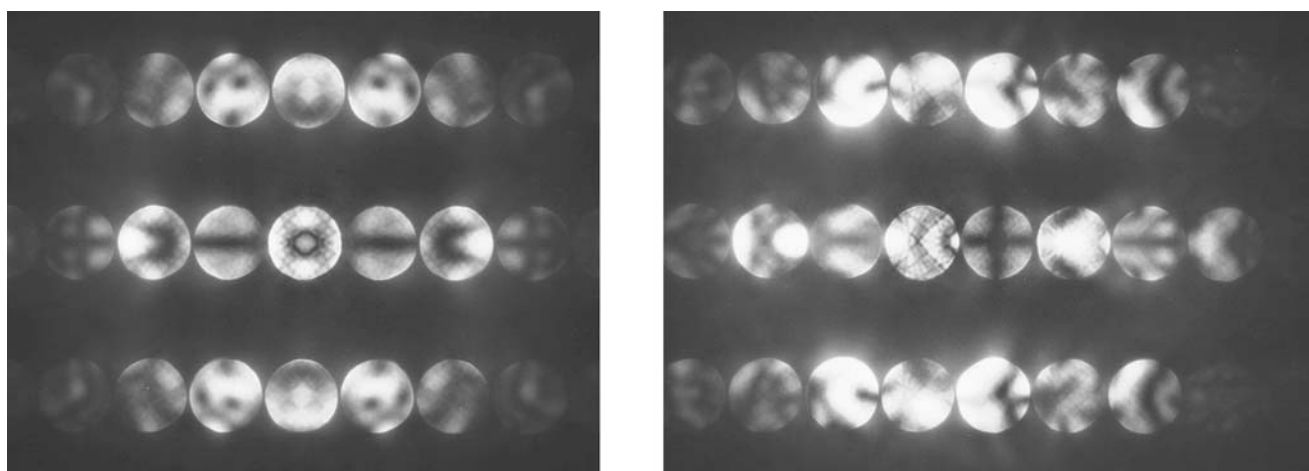


Fig. 2.5.3.6. (a) CBED pattern from the exact [001] (cyclic) zone-axis orientation of FeS_2 . (b) Pattern from the [001] zone axis oriented for symmetrical excitation of the 100 reflection (central in the printed pattern) [from the collection of patterns presented in Tanaka *et al.* (1983); originals kindly supplied by M. Tanaka].

(ii) By contrast, techniques have been devised for evaluating Bragg-line splitting caused by the action of a strain field within the single crystal. One method depends upon the observation of splitting in HOLZ lines (Carpenter & Spence, 1982). More recently, the use of LACBED has allowed quantitative evaluation of lattice distortions in semiconductor heterostructures (*e.g.* containing GaAs–InGaAs interfaces). This technique has been reviewed by Chou *et al.* (1994).

(iii) Quite distinct from this is the analysis of stacking faults between undistorted crystal domains (Johnson, 1972). Coherent twin boundaries with at least a two-dimensional coincidence site lattice can be considered in a similar fashion (Schapink *et al.*, 1983). In marked contrast to electron-microscopy image analysis these boundaries need to be parallel (or nearly so) to the crystal surfaces rather than inclined or perpendicular to them for analysis by CBED or LACBED.

The term ‘rigid-body displacement’ (RBD) is used when it is assumed that no strain field develops at the boundary. A classification of the corresponding bi-crystal symmetries was developed by Schapink *et al.* (1983) for these cases. Since experimental characterization of grain boundaries is of interest in metallurgy, this represents a new area for the application of LACBED and algorithms invoking reciprocity now make routine N -beam analysis feasible.

The original investigations, of a mid-plane stacking fault in graphite (Johnson, 1972) and of a mid-plane twin boundary in gold (Schapink *et al.*, 1983), represent classic examples of the influence of bi-crystal symmetry on CBED zone-axis patterns, whereby the changed central-plane symmetry is transformed through reciprocity into an exact diffraction symmetry. (a) In the graphite ($P6_3/mmc$) example, the hexagonal pattern of the unfaulted graphite is replaced by a trigonal pattern with mid-plane faulting. Here a mirror plane at

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the centre of the perfect crystal ($A-B-A$ stacking) is replaced by an inversion centre at the midpoint of the single rhombohedral cell $A-B-C$; the projected symmetry is also reduced from hexagonal to trigonal: both whole pattern and central beam then have the symmetry of $3m1$. The $2H$ polytype of TaS_2 ($P6_3/mmc$) (Tanaka & Terauchi, 1985) gives a second clear example. (b) In the case of a $[111]$ gold crystal, sectioning the f.c.c. structure parallel to $[111]$ preparatory to producing the twin already reduces the finite crystal symmetry to $R\bar{3}m$, i.e. a trigonal space group for which the central beam, and the HOLZ reflections in particular, exhibit the trigonal symmetry of $31m$ (rather than the $3m1$ of trigonal graphite). A central-plane twin boundary with no associated translation introduces a central horizontal mirror plane into the crystal. For the zone-axis pattern the only symmetry change will be in the central beam, which will become centrosymmetric, increasing its symmetry to $6mm$. Using diffraction-group terminology these cases are seen to be relative inverses. Unfaulted graphite has the BESR group $6mm1_R$ (central beam and whole pattern hexagonal); central-plane faulting results in a change to the group 6_Rmm_R . Unfaulted $[111]$ gold correspondingly has the BESR group symmetry 6_Rmm_R ; central-plane twinning results in the addition of the element 1_R (for a central mirror plane), leading to the group $6mm1_R$.

(iv) Finally, no present-day discussion of electron-crystallographic investigations of symmetry could be complete without reference to two aspects of non-classical symmetries widely discussed in the literature in recent years. The recent discovery of noncrystallographic point symmetries in certain alloys (Shechtman *et al.*, 1984) has led to the study of quasi-crystallinity. An excellent record of the experimental side of this subject may be found in the book *Convergent-beam electron diffraction III* by Tanaka *et al.* (1994), while the appropriate space-group theory has been developed by Mermin (1992). It would be inappropriate to comment further on this new subject here other than to state that this is clearly an area of study where combined HREM, CBED and selected-area diffraction (SAD) evidence is vital to structural elucidation.

The other relatively new topic is that of modulated structures. From experimental evidence, two distinct structural phenomena can be distinguished for structures exhibiting incommensurate superlattice reflections. Firstly, there are 'Vernier' phases, which exist within certain composition ranges of solid solutions and are composed of two extensive substructures, for which the super-space-group nomenclature developed by de Wolff *et al.* (1981) is structurally valid (e.g. Withers *et al.*, 1993). Secondly, there are structures essentially composed of random mixtures of two or more substructures existing as microdomains within the whole crystal (e.g. Grzinic, 1985). Here the SAD patterns will contain superlattice reflections with characteristic profiles and/or irregularities of spacings. A well illustrated review of incommensurate-structure analysis in general is given in the book by Tanaka *et al.* (1994), while specific discussions of this topic are given by Goodman *et al.* (1992), and Goodman & Miller (1993).

2.5.3.7. Present limitations and general conclusions

The list of examples given here must necessarily be regarded as unsatisfactory considering the vastness of the subject, although some attempt has been made to choose a diverse range of problems which will illustrate the principles involved. Some particular aspects, however, need further mention.

One of these concerns the problem of examining large-unit-cell materials with a high diffraction-pattern density. This limits the possible convergence angle, if overlap is to be avoided, and leaves numerous but featureless discs [for example Goodman (1984b)]. Technical advances which have been made to overcome this problem include the beam-rocking technique (Eades, 1980) and LACBED (Tanaka *et al.*, 1980), both of which are reviewed by

Tanaka & Terauchi (1985) and Eades *et al.* (1983). The disadvantage of these latter methods is that they both require a significantly larger area of specimen than does the conventional technique, and it may be that more sophisticated methods of handling the crowded conventional patterns are still needed.

Next, the matter of accuracy must be considered. There are two aspects of the subject where this is of concern. Firstly, there is a very definite limit to the sensitivity with which symmetry can be detected. In a simple structure of medium-light atoms, displacements of say 0.1 Å or less from a pseudomirror plane could easily be overlooked. An important aspect of CBED analysis, not mentioned above, is the N -beam computation of patterns which is required when something approaching a refinement (in the context of electron diffraction) is being attempted. Although this quantitative aspect has a long history [for example see Johnson (1972)], it has only recently been incorporated into symmetry studies as a routine (Creek & Spargo, 1985; Tanaka, 1994). Multi-slice programs which have been developed to produce computer-simulated pattern output are available (Section 2.5.3.8).

Next there is concern as to the allocation of a space group to structures which microscopically have a much lower symmetry (Goodman *et al.*, 1984). This arises because the volume sampled by the electron probe necessarily contains a large number of unit cells. Reliable microscopic interpretation of certain nonstoichiometric materials requires that investigations be accompanied by high-resolution microscopy. Frequently (especially in mineralogical samples), nonstoichiometry implies that a space group exists only on average, and that the concept of absolute symmetry elements is inapplicable.

From earlier and concluding remarks it will be clear that combined X-ray/CBED and CBED/electron-microscopy studies of inorganic materials represents the standard ideal approach to space-group analysis at present; given this approach, all the space-group problems of classical crystallography appear soluble. As has been noted earlier, it is important that HREM be considered jointly with CBED in determining space group by electron crystallography, and that only by this joint study can the so-called 'phase problem' be completely overcome. The example of the space-group pairs $I222/I2_12_12_1$ and $I23/I2_13$ has already been cited. Using CBED, it might be expected that FOLZ lines would show a break from twofold symmetry with the incident beam aligned with a 2_1 axis. However, a direct distinction should be made apparent from high-resolution electron micrographs. Other less clear-cut cases occur where the HREM images allow a space-group distinction to be made between possible space groups of the same arithmetic class, especially when only one morphology is readily obtained (e.g. $P222_1$, $P22_12_1$, $P2_12_12_1$).

The slightly more subtle problem of distinguishing enantiomorphic space-group pairs can be solved by one of two approaches: either the crystal must be rotated around an axis by a known amount to obtain two projections, or the required three-dimensional phase information can be deduced from specific three-beam-interaction data. This problem is part of the more general problem of solving handedness in an asymmetric structure, and is discussed in detail by Johnson & Preston (1994).

2.5.3.8. Computer programs available

(1) A FORTRAN source listing of program *TCBED* for simulating three-dimensional convergent-beam patterns with absorption by the Bloch-wave method: Zuo *et al.* (1989) [see also *Electron microdiffraction* (Spence & Zuo, 1992) for other useful programs and worked examples for the analysis of these diffraction

(continued on page 306)

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Table 2.5.3.4. *Tabulation of principal-axis CBED pattern symmetries against relevant space groups given as IT A numbers*

Three columns of diperiodic groups (central section) correspond to (i) symmorphic groups, (ii) non-symmorphic groups (GS bands) and (iii) non-symmorphic groups (zero-layer absences arising from horizontal glide planes). Cubic space groups are given underlined in the right-hand section with the code: underlining = [001](cyclic) setting; italics + underlining = [110](cyclic) setting. Separators ‘;’ and ‘:’ indicate change of Bravais lattice type and change of crystal system, respectively.

DG	I Point groups		II Diperiodic groups			SG	III Space groups
	H–M	BESR	(i)	(ii)	(iii)		Subgroups IIb (<u>Subgroups 1</u>)
Oblique						Triclinic	
1	1	1	$p1$			1	
2*	$\bar{1}$	2_R	$p\bar{1}'$			2	
						Monoclinic (Oblique)	
3	12	2	$p2$			3	4, 5
4	$1m$	1_R	pm'			6	8
5	$1m$				pb'	7	9
6*	$2/m$	21_R	$p2/m'$			10	11, 12
7*	$2/m$	21_R			$p2/b'$	13	14, 15
Rectangular						(Rectangular)	
8	21	m_R	$p2'$			3	5^2 : <u>195; 197, 199</u>
9	21	m_R		$p2'_1$		4	<u>198</u>
10	21	m_R	$c2'$			5	<u>196</u>
11	$m1$	m	pm			6 ²	7, 8 ²
12	$m1$	m		pa		7 ²	9 ²
13	$m1$	m	cm			8	9
14*	$12/m$	2_Rmm_R	$p2'/m$			10	13, 12 ² : <u>200, 201; 204</u>
15*	$12/m$	2_Rmm_R		$p2'_1/m$		11	14
16*	$12/m$	2_Rmm_R		$p2'/a$		13 ²	15 ² : <u>206</u>
17*	$12/m$	2_Rmm_R		$p2'_1/m$		14 ²	<u>205</u>
18*	$12/m$	2_Rmm_R	$c2'/m$			12	15: <u>202, 203</u>
						Orthorhombic	
19	222	$2m_Rm_R$	$p2'2'2$			16	17; 21 ² ; 22: <u>195; 196, 207, 206; 211, 214</u>
20	222	$2m_Rm_R$		$p2'_12'2$		17 ²	18 ² ; 20 ² : <u>212, 213</u>
21	222	$2m_Rm_R$		$p2'_12'_12$		18	19: <u>198</u>
22	222	$2m_Rm_R$	$c2'2'2$			21	20; 23, 24: <u>197, 199, 209, 210</u>
23	$mm2$	$2mm$	$pmm2$			25	26, 27; 38, 39; 42
24	$mm2$	$2mm$		$pbm2$		28	29, 30, 31 ² ; 40, 41
25	$mm2$	$2mm$		$pba2$		32	33, 34; 43
26	$mm2$	$2mm$	$cmm2$			35	36, 37; 44, 45, 46
27	$mm2$	$m1_R$	$p2'mm'$			25 ²	28 ¹ ; 35 ² , 42 ² ; 38 ² , 39 ² : <u>215; 217</u>
28	$mm2$	$m1_R$		$p2'_1m'a$		26 ¹	31 ¹ ; 36 ¹
29	$mm2$	$m1_R$		$p2'_1ab'$	$(p2'_1ab')$	29 ²	33 ²
30	$mm2$	$m1_R$			$p2'_1ma'$	26 ²	29 ¹ ; 36 ²
31	$mm2$	$m1_R$			$p2'_1mn'$	31 ²	33 ²
32	$mm2$	$m1_R$			$p2'mb'$	28 ²	32 ² , 40 ² , 41 ²
33	$mm2$	$m1_R$			$p2'aa'$	27 ²	30 ² ; 37 ²
34	$mm2$	$m1_R$			$pb2'n'$	30 ¹	34 ² ; 43 ² : <u>218; 219</u>
35	$mm2$	$m1_R$	$c2'mm'$			38 ¹	40 ¹ ; 44 ² , 46 ¹ : <u>216; 220</u>
36	$mm2$	$m1_R$			$c2'mb'$	39 ¹	41 ¹ ; 45 ² , 46 ²
37*	mmm	$2mm1_R$	$pmmm'$			47	49, 51 ¹ ; 65 ² , 67 ² ; 69: <u>200; 202, 221, 224, 226, 228, 229</u>
38*	mmm	$2mm1_R$		$p b m m' (2'_1)$		51 ²	53 ¹ , 57, 59 ² ; 63 ¹ , 64 ¹
39*	mmm	$2mm1_R$		$p b a m' (2'_1 2'_1)$		55	58, 62 ²
40*	mmm	$2mm1_R$		$p m a b' (2'_1 2'_1)$	$(p m a b')$	57 ¹	60 ² , 61, 62: <u>205</u>
41*	mmm	$2mm1_R$		$p b a a' (2'_1)$	$(p b a a')$	54 ²	52, 56 ² , 60 ¹

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Table 2.5.3.4. *Tabulation of principal-axis CBED pattern symmetries against relevant space groups given as IT A numbers (cont.)*

DG	I Point groups		II Dipericodic groups			SG	III Space groups
	H–M	BESR	(i)	(ii)	(iii)		Subgroups IIb (Subgroups 1)
42*	<i>mmm</i>	<i>2mm1_R</i>			<i>pmma'</i> (<i>2'</i> ₁)	51	54, 55 ² , 57 ² ; 63 ² , 64 ²
43*	<i>mmm</i>	<i>2mm1_R</i>			<i>pmmn'</i> (<i>2'</i> ₁ <i>2'</i> ₁)	59	56, 62 ¹
44*	<i>mmm</i>	<i>2mm1_R</i>			<i>pbmn'</i> (<i>2'</i> ₁)	53 ²	52 ¹ , 58 ¹ , 60
45*	<i>mmm</i>	<i>2mm1_R</i>			<i>pmaa'</i>	49 ²	50 ² , 53, 54 ¹ ; 66 ² , 68 ¹ : <u>222, 223</u>
46*	<i>mmm</i>	<i>2mm1_R</i>			<i>pban'</i>	50	52 ² , 48; 70: <u>201, 203, 230</u>
47*	<i>mmm</i>	<i>2mm1_R</i>	<i>cmmm'</i>			65	63, 66; 72, 74 ² , 71: <u>204, 225, 227</u>
48*	<i>mmm</i>	<i>2mm1_R</i>			<i>cmma'</i>	67	64, 68; 72 ¹ , 74, 73: <u>206</u>
Square						Tetragonal	
49	4	4	<i>p4</i>			75	77, 76, 78; 79, 80
50	4/ <i>m</i>	41 _R	<i>p4/m'</i>			83	84; 87
51	4/ <i>m</i>	41 _R			<i>p4/n'</i>	85	86, 88
52	422	4 <i>m_Rm_R</i>	<i>p42'2'</i>			89	93, 91, 95; 97, 98: <u>207, 208; 209, 210; 211, 214</u>
53	422	4 <i>m_Rm_R</i>		<i>p42'2'</i>		90	94, 92, 96: <u>212, 213</u>
54	4 <i>mm</i>	4 <i>mm</i>	<i>p4mm</i>			99	101, 103, 105; 107, 108
55	4 <i>mm</i>	4 <i>mm</i>		<i>p4bm</i>		100	102, 104, 106; 109, 110
56*	4/ <i>mmm</i>	4 <i>mm1_R</i>	<i>p4/m'mm</i>			123	124, 131, 132; 139, 140; <u>221, 223; 225, 226; 229</u>
57*	4/ <i>mmm</i>	4 <i>mm1_R</i>		<i>p4/m'bm</i> (<i>2'</i> ₁)		127	128, 135, 136
58*	4/ <i>mmm</i>	4 <i>mm1_R</i>			<i>p4/n'bm</i>	125	126, 133, 134; 141, 142: <u>222, 224; 227, 228; 230</u>
59*	4/ <i>mmm</i>	4 <i>mm1_R</i>			<i>p4/n'mm</i> (<i>2'</i> ₁)	129	130, 137, 138
60	$\bar{4}$	4 _R	<i>p4'</i>			81	82
61	$\bar{4}2m$	4 _R <i>mm_R</i>	<i>p4'm2'</i>			115	116; 119, 120
62	$\bar{4}2m$	4 _R <i>mm_R</i>		<i>p4b2'</i>		117	118; 122: <u>220</u>
63	$\bar{4}2m$	4 _R <i>mm_R</i>	<i>p4'2'm</i>			111	112; 121: <u>215; 216; 217; 218; 219</u>
64	$\bar{4}2m$	4 _R <i>mm_R</i>		<i>p4'2'm</i>		113	114
Hexagonal						Trigonal	
65	3	3	<i>p3</i>			143	144, 145; 146
66	$\bar{3}$	6 _R	<i>p3'</i>			147	148
67	32	3 <i>m_R</i>	<i>p312'</i>			149	151, 153
68	32	3 <i>m_R</i>	<i>p32'1</i>			150	152, 154; 155
69	3 <i>m</i>	3 <i>m</i>	<i>p31m</i>			157	159
70	3 <i>m</i>	3 <i>m</i>	<i>p3m1</i>			156	158; 160, 161
71*	$\bar{3}m$	6 _R <i>mm_R</i>	<i>p3'1m</i>			162	163
72*	$\bar{3}m$	6 _R <i>mm_R</i>	<i>p3'm1</i>			164	165; 166, 167
						Hexagonal	
73	6	6	<i>p6</i>			168	171, 172, 173, 169, 170
74	$\bar{6}$	31 _R	<i>p3/m'</i> (<i>p6'</i>)			174	
75	622	6 <i>m_Rm_R</i>	<i>p62'2'</i>			177	180, 181, 182, 178, 179
76	6 <i>mm</i>	6 <i>mm</i>	<i>p6mm</i>			183	184, 185, 186
77*	6/ <i>m</i>	61 _R	<i>p6/m'</i>			175	176
78*	6/ <i>mmm</i>	6 <i>mm1_R</i>	<i>p6/m'mm</i>			191	192, 193, 194
79	$\bar{6}m2$	3 <i>m1_R</i>	<i>p3/m'2'm</i> (<i>p6'm2'</i>)			189	190
80	$\bar{6}m2$	3 <i>m1_R</i>	<i>p3/m'm2'</i> (<i>p6'2'm</i>)			187	188

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions

Point groups 2, m , $2/m$ (2nd setting unique axis $\parallel b$)

Space group	Incident-beam direction	
	[$u0w$]	
4 $P2_1$	$0k0$ 2_1	S
7 Pc	$h0l$ c	G
9 Cc	$h0l$ c	G
11 $P2_1/m$	$0k0$ 2_1	S
13 $P2/c$	$h0l$ c	G
14 $P2_1/c$	$0k0$ 2_1	S
	$h0l$ c	G
15 $C2/c$	$h0l$ c	G

Point groups 222, $mm2$

Space group	Incident-beam direction					
	[100]	[010]	[001]	[$uv0$]	[$0vw$]	[$u0w$]
17 $P222_1$	$00l$ 2_1 S	$00l$ 2_1 S		$00l$ 2_1 S		
18 $P2_12_12$	$0k0$ 2_1 S	$h00$ 2_1 S	$h00, 0k0$ 2_1 S		$h00$ 2_1 S	$0k0$ 2_1 S
19 $P2_12_12_1$	$0k0, 00l$ 2_1 S	$h00, 00l$ 2_1 S	$h00, 0k0$ 2_1 S	$00l$ 2_1 S	$h00$ 2_1 S	$0k0$ 2_1 S
20 $C222_1$	$00l$ 2_1 S	$00l$ 2_1 S		$00l$ 2_1 S		
26 $Pmc2_1$	$00l$ $c + 2_1$ GS	$00l$ 2_1 $c' -$		$00l$ 2_1 S		$h0l$ c G
27 $Pcc2$	$00l$ c $c' -$	$00l$ c $c' -$			$0kl$ c G	$h0l$ c G
28 $Pma2$			$h00$ a G			$h0l$ a G
29 $Pca2_1$	$00l$ 2_1 $c' -$	$00l$ $c + 2_1$ GS	$h00$ a G	$00l$ 2_1 S	$0kl$ c G	$h0l$ a G
30 $Pnc2$	$00l$ c $n' -$	$00l$ n $c' -$	$0k0$ n G		$0kl$ n G	$h0l$ c G
31 $Pmn2_1$	$00l$ $n + 2_1$ GS	$00l$ 2_1 $n' -$	$h00$ n G	$00l$ 2_1 S		$h0l$ n G
32 $Pba2$			$h00, 0k0$ a b G		$0kl$ b G	$h0l$ a G

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Space group	Incident-beam direction					
	[100]	[010]	[001]	[uv0]	[0vw]	[u0w]
33 <i>Pna</i> 2 ₁	00l 2 ₁ n' –	00l n + 2 ₁ GS	h00, 0k0 a b G	00l 2 ₁ S	0kl n G	h0l a G
34 <i>Pnn</i> 2	00l n n' –	00l n n' –	h00, 0k0 n G		0kl n G	h0l n G
36 <i>Cmc</i> 2 ₁	00l c + 2 ₁ GS	00l 2 ₁ c' –		00l 2 ₁ S		h0l c G
37 <i>Ccc</i> 2	00l c c' –	00l c c' –			0kl c G	h0l c G
39 <i>Abm</i> 2					0kl b G	
40 <i>Ama</i> 2			h00 a G			h0l a G
41 <i>Aba</i> 2			h00 a G		0kl b G	h0l a G
43 <i>Fdd</i> 2	00l d' –	00l d d' –	h00, 0k0 d G		0kl d G	h0l d G
45 <i>Iba</i> 2		b' –	a' –		0kl b G	h0l a G
46 <i>Ima</i> 2			a' –			h0l a G

Point group *mmm*

Space group	Incident-beam direction					
	[100]	[010]	[001]	[uv0]	[0vw]	[u0w]
48 <i>P</i> 2/n 2/n 2/n	00l, 0k0 n n' –	00l, h00 n n' –	0k0, h00 n n' –	hk0 n G	0kl n G	h0l n G
49 <i>P</i> 2/c 2/c 2/m	00l c c' –	00l c c' –			0kl c G	h0l c G
50 <i>P</i> 2/b 2/a 2/n	0k0 n b' –	h00 n a' –	0k0, h00 b a n' –	hk0 n G	0kl b G	h0l a G
51 <i>P</i> 2 ₁ /m 2/m 2/a		h00 a + 2 ₁ GS	h00 2 ₁ a' –	hk0 a G	h00 2 ₁ S	
52 <i>P</i> 2/n 2 ₁ /n 2/a	00l, 0k0 n 2 ₁ a' –	00l, h00 n a n' –	0k0 n + 2 ₁ GS ----- h00 n n' –	hk0 a G	0kl n G	h0l n G ----- 0k0 2 ₁ S
53 <i>P</i> 2/m 2/n 2 ₁ /a	00l n + 2 ₁ GS	h00, 00l a 2 ₁ a' –	h00 n a' –	hk0 a G ----- 00l 2 ₁ S		h0l n G

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Space group	Incident-beam direction					
	[100]	[010]	[001]	[uv0]	[0vw]	[u0w]
54 $P 2_1/c 2_1/c 2/a$	$00l$ c c'	$h00$ $a + 2_1$ GS $00l$ c c'	$h00$ 2_1 a'	$hk0$ a G	$0kl$ c G $h00$ 2_1 S	$h0l$ c G
55 $P 2_1/b 2_1/a 2/m$	$0k0$ 2_1 b'	$h00$ 2_1 a'	$0k0, h00$ $b + 2_1, a + 2_1$ GS		$0kl$ b G $h00$ 2_1 S	$h0l$ a G $0k0$ 2_1 S
56 $P 2_1/c 2_1/c 2/n$	$0k0$ $n + 2_1$ GS $00l$ c c'	$h00$ $n + 2_1$ GS $00l$ c c'	$0k0, h00$ 2_1 n'	$hk0$ n G	$0kl$ c G $h00$ 2_1 S	$h0l$ c G $0k0$ 2_1 S
57 $P 2/b 2_1/c 2_1/m$	$00l$ $c + 2_1$ GS $0k0$ 2_1 b'	$00l$ 2_1 c'	$0k0$ $b + 2_1$ GS	$00l$ 2_1 S	$0kl$ b G	$h0l$ c G $0k0$ 2_1 S
58 $P 2_1/n 2_1/n 2/m$	$00l, 0k0$ $n 2_1$ n'	$00l, h00$ $n 2_1$ n'	$0k0, h00$ $n + 2_1$ GS		$0kl$ n G $h00$ 2_1 S	$h0l$ n G $0k0$ 2_1 S
59 $P 2_1/m 2_1/m 2/n$	$0k0$ $n + 2_1$ GS	$h00$ $n + 2_1$ GS	$0k0, h00$ 2_1 n'	$hk0$ n G	$h00$ 2_1 S	$0k0$ 2_1 S
60 $P 2_1/b 2/c 2_1/n$	$00l$ $c + 2_1$ GS $0k0$ n b'	$h00$ $n + 2_1$ GS $00l$ 2_1 c'	$0k0, h00$ $b 2_1$ n'	$hk0$ n G $00l$ 2_1 S	$0kl$ b G $h00$ 2_1 S	$h0l$ c G
61 $P 2_1/b 2_1/c 2_1/a$	$00l$ $c + 2_1$ GS $0k0$ 2_1 b'	$h00$ $a + 2_1$ GS $00l$ 2_1 c'	$0k0$ $b + 2_1$ GS $h00$ 2_1 a'	$hk0$ a G $00l$ 2_1 S	$0kl$ b G $h00$ 2_1 S	$h0l$ c G $0k0$ 2_1 S
62 $P 2_1/n 2_1/m 2_1/a$	$0k0, 00l$ 2_1 n'	$00l$ $n + 2_1$ GS $h00$ $a + 2_1$ GS	$0k0$ $n + 2_1$ GS $h00$ 2_1 a'	$hk0$ a G $00l$ 2_1 S	$0kl$ n G $h00$ 2_1 S	$0k0$ 2_1 S
63 $C 2/m 2/c 2_1/m$	$00l$ $c + 2_1$ GS	$00l$ 2_1 c'		$00l$ 2_1 S		$h0l$ c G
64 $C 2/m 2/c 2_1/a$	$00l$ $c + 2_1$ GS	$00l$ 2_1 c'		$hk0$ a G $00l$ 2_1 S		$h0l$ c G
66 $C 2/c 2/c 2/m$	$00l$ c c'	$00l$ c c'			$0kl$ c G	$h0l$ c G
67 $C 2/m 2/m 2/a$				$hk0$ a G		

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Space group	Incident-beam direction					
	[100]	[010]	[001]	[uv0]	[0vw]	[u0w]
68 $C 2/c 2/c 2/a$	$00l$ c $c' -$	$00l$ c $c' -$		$hk0$ a G	$0kl$ c G	$h0l$ c G
70 $F 2/d 2/d 2/d$	$00l, 0k0$ d $d' -$	$h00, 00l$ d $d' -$	$0k0, h00$ d $d' -$	$hk0$ d G	$0kl$ d G	$h0l$ d G
72 $I 2/b 2/a 2/m$	$b' -$	$d' -$			$0kl$ b G	$h0l$ a G
73 $I 2/b 2/c 2/a$	$b' -$	$c' -$	$d' -$	$hk0$ a G	$0kl$ b G	$h0l$ c G
74 $I 2/m 2/m 2/a$				$hk0$ a G		

Point groups $4, \bar{4}, 4/m$

Space group	Incident-beam direction	
	[uv0]	
76 $P4_1$	$00l$ 4_1	S
78 $P4_3$	$00l$ 4_3	S
85 $P4/n$	$hk0$ n	G
86 $P4_2/n$	$hk0$ n	G
88 $I4_1/a$	$hk0$ a	G

Point group 422

Space group	Incident-beam direction	
	[uv0]	[0vw]
90 $P4_2 2_1 2$		$h00$ 2_1 S
91 $P4_1 22$	$00l$ 4_1 S	
92 $P4_1 2_1 2$	$00l$ 4_1 S	$h00$ 2_1 S
94 $P4_2 2_1 2$		$h00$ 2_1 S
95 $P4_3 22$	$00l$ 4_3 S	
96 $P4_3 2_1 2$	$00l$ 4_3 S	$h00$ 2_1 S

Point group 4mm

Space group	Incident-beam direction				
	[100]	[001]	[110]	[u0w] and [0vw]*	[uūw]
100 $P4bm$		$h00, 0k0$ a b G		$h0l, 0kl$ a b G	
101 $P4_2 cm$	$00l$ c $c' -$			$h0l, 0kl$ c G	
102 $P4_2 nm$	$00l$ n $n' -$	$h00, 0k0$ n G		$h0l, 0kl$ n G	
103 $P4cc$	$00l$ c $c' -$		$00l$ c $c' -$	$h0l, 0kl$ c G	hhl c G
104 $P4nc$	$00l$ n $n' -$	$h00, 0k0$ n G	$00l$ c $c' -$	$h0l, 0kl$ n G	hhl c G
105 $P4_2 mc$			$00l$ c $c' -$		hhl c G

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Space group	Incident-beam direction				
	[100]	[001]	[110]	[u0w] and [0vw]*	[uūw]
106 $P4_2bc$		$h00, 0k0$ $a \ b$ G	$00l$ c $c' -$	$h0l, 0kl$ $a \ b$ G	hhl c G
108 $I4cm$				$h0l, 0kl$ c G	
109 $I3_1md$		$hh0$ $\bar{h}h0$ d G	$00l$ d $d' -$		hhl d G
110 $I4_1cd$		$hh0$ $\bar{h}h0$ d G	$00l$ d $d' -$	$h0l, 0kl$ c G	hhl d G

* Conditions in this column are cyclic on h and k .

Point groups $\bar{4}2m$, $4/mmm$

Space group	Incident-beam direction					
	[100]	[001]	[110]	[u0w] and [0vw]*	[uūw]	[uv0]
112 $P\bar{4}2c$			$00l$ c $c' -$		hhl c G	
113 $P\bar{4}2_1m$	$0k0$ 2_1 S	$h00, 0k0$ 2_1 S		$0k0, h00$ 2_1 S		
114 $P\bar{4}2_1c$	$0k0$ 2_1 S	$h00, 0k0$ 2_1 S	$00l$ c $c' -$	$0k0, h00$ 2_1 S	hhl c G	
116 $P4c2$	$00l$ c $c' -$			$h0l, 0kl$ c G		
117 $P\bar{4}b2$		$h00, 0k0$ $a \ b$ G		$h0l, 0kl$ $a \ b$ G		
118 $P\bar{4}n2$	$00l$ n $n' -$	$h00, 0k0$ n G		$h0l, 0kl$ n G		
120 $I\bar{4}c2$				$h0l, 0kl$ c G		
122 $I\bar{4}2d$		$hh0$ $\bar{h}h0$ d G	$00l$ d $d' -$		hhl d G	
124 $P 4/m 2/c 2/c$	$00l$ c $c' -$		$00l$ c $c' -$	$h0l, 0kl$ c G	hhl c G	
125 $P 4/n 2/b 2/m$	$0k0$ n $b' -$	$h00, 0k0$ $a \ b$ $n' -$		$h0l, 0kl$ $a \ b$ G		$hk0$ n G
126 $P 4/n 2/n 2/c$	$0k0$ n $n' -$ $00l$ n	$h00, 0k0$ n $n' -$	$00l$ c $c' -$	$h0l, 0kl$ n G	hhl c G	$hk0$ n G
127 $P 4/m 2_1/b 2/m$	$0k0$ 2_1 $b' -$	$h00$ $a + 2_1$ $0k0$ $b + 2_1$ GS		$h0l, 0kl$ $a \ b$ G		
				$0k0, h00$ 2_1 S		

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Space group	Incident-beam direction					
	[100]	[001]	[110]	[u0w] and [0vw]*	[uuv]	[uv0]
128 $P 4/m 2_1/n 2/c$	$00l, 0k0$ $n \quad 2_1$ $n'-$	$h00, 0k0$ $n + 2_1$ GS	$00l$ c $c'-$	$h0l, 0kl$ n G $0k0, h00$ 2_1 S	hhl c G	
129 $P 4/n 2_1/m 2/m$	$0k0$ $n + 2_1$ GS	$h00, 0k0$ 2_1 $n'-$		$0k0, h00$ 2_1 S		$hk0$ n G
130 $P 4/n 2_1/c 2/c$	$0k0$ $n + 2_1$ GS $00l$ c $c'-$	$h00, 0k0$ 2_1 $n'-$	$00l$ c $c'-$	$h0l, 0kl$ c G $0k0, h00$ 2_1 S	hhl c G	$hk0$ n G
131 $P 4_2/m 2/m 2/c$			$00l$ c $c-$		hhl c G	
132 $P 4_2/m 2/c 2/m$	$00l$ c $c'-$			$h0l, 0kl$ c G		
133 $P 4_2/n 2/b 2/c$	$0k0$ n $b'-$	$h00, 0k0$ $a \quad b$ $n'-$	$00l$ c $c'-$	$h0l, 0kl$ $a \quad b$ G	hhl c G	$hk0$ n G
134 $P 4_2/n 2/n 2/m$	$0k0, 00l$ n $n'-$	$h00, 0k0$ n $n'-$		$h0l, 0kl$ n G		$hk0$ n G
135 $P 4_2/m 2_1/b 2/c$	$0k0$ 2_1 $b'-$	$h00, 0k0$ $a + 2_1 \quad b + 2_1$ GS	$00l$ c $c'-$	$h0l, 0kl$ $a \quad b$ G $0k0, h00$ 2_1 S	hhl c G	
136 $P 4_2/m 2_1/n 2/m$	$00l, 0k0$ $n \quad 2$ $n'-$	$h00, 0k0$ $n + 2_1$ GS		$h0l, 0kl$ n G $0k0, h00$ 2_1 S		
137 $P 4_2/n 2_1/m 2/c$	$0k0$ $n + 2_1$ GS	$h00, 0k0$ 2_1 $n'-$	$00l$ c $c'-$	$0k0, h00$ 2_1 S	hhl c G	$hk0$ n G
138 $P 4_2/n 2_1/c 2/m$	$0k0$ $n + 2_1$ GS $00l$ c $c'-$	$h00, 0k0$ 2_1 $n'-$		$h0l, 0kl$ c G $0k0, h00$ 2_1 S		$hk0$ n G
140 $I 4/m 2/c 2/m$				$h0l, 0kl$ c G		
141 $I 4_1/a 2/m 2/d$		$hh0$ $\bar{h}h0$ d $d'-$	$00l, \bar{h}h0$ $d \quad a$ $d'-$		hhl d G	$hk0$ a G
142 $I 4_1/a 2/c 2/d$		$hh0$ $\bar{h}h0$ d $d'-$	$00l, \bar{h}h0$ $d \quad a$ $d'-$	$h0l, 0kl$ c G	hhl d G	$hk0$ a G

* Conditions in this column are cyclic on h and k .

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Point groups $3m$, $\bar{3}m$, 6 , $6/m$, 622 , $6mm$, $\bar{6}m2$, $6/mmm$

Space group	Incident-beam direction			
	[100]	[210]	$[2u\ u\ w]$	$[v0w]$
158 $P3c1$		$000l$ c G	$hh2\bar{h}l$ c G	
159 $P31c$	$000l$ c G			$h\bar{h}0l$ c G
161 $R3c$		$000l$ $l = 6n + 3$ G c	$hh2\bar{h}l$ c G	
163 $P\bar{3}1c$	$000l$ c G			$h\bar{h}0l$ c G
165 $P\bar{3}c1$		$000l$ c G	$hh2\bar{h}l$ c G	
167 $R\bar{3}c$		$000l$ $l = 6n + 3$ G c	$hh2\bar{h}l$ c G	
169 $P6_1$	$000l$ 6_1 S	$000l$ 6_1 S		
170 $P6_5$	$00l$ 6_5 S	$00l$ 6_5 S		
173 $P6_3$	$000l$ 6_3 S	$000l$ 6_3 S		
176 $P6_3/m$	$000l$ 6_3 S	$000l$ 6_3 S		
178 $P6_122$	$000l$ 6_1 S	$000l$ 6_1 S		
179 $P6_522$	$000l$ 6_5 S	$000l$ 6_5 S		
182 $P6_322$	$000l$ 6_3 S	$000l$ 6_3 S		
184 $P6cc$	$000l$ c $c' -$	$000l$ c $c' -$	$hh2\bar{h}l$ c G	$h\bar{h}0l$ c G
185 $P6_3cm$	$000l$ 6_3 $c' -$	$000l$ $c + 6_3$ GS	$hh2\bar{h}l$ c G	
186 $P6_3mc$	$000l$ $c + 6_3$ GS	$000l$ 6_3 $c' -$		$h\bar{h}0l$ c G
188 $P\bar{6}c2$		$000l$ c G	$hh2\bar{h}l$ c G	
190 $P\bar{6}c2$	$000l$ c G			$h\bar{h}0l$ c G
192 $P6/mcc$	$000l$ c $c' -$	$000l$ c $c' -$	$hh2\bar{h}l$ c G	$h\bar{h}0l$ c G
193 $P6_3/mcm$	$00l$ 6_3 $c' -$	$000l$ $c + 6_3$ GS	$hh2\bar{h}l$ c G	
194 $P6_3/mmc$	$000l$ $c + 6_3$ GS	$000l$ 6_3 $c' -$		$h\bar{h}0l$ c G

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Table 2.5.3.5. Conditions for observation of GS bands for the 137 space groups exhibiting these extinctions (cont.)

Point groups 23, $m\bar{3}$, 432 , $m\bar{3}m$

Space group	Incident-beam direction			
	[100] (cyclic)	[110] (cyclic)	[uv0] (cyclic)	[uuv] (cyclic)
198 $P2_13$	00l, 0k0 2 ₁ S	00l 2 ₁ S	00l 2 ₁ S	
201 $Pn\bar{3}$ $P2/n\bar{3}$	00l, 0k0 n n'—		$\bar{k}h0$ n G	
203 $Pd\bar{3}$ $F2/d\bar{3}$	00l, 0k0 d d'—		$\bar{k}h0$ d G	
205 $Pa\bar{3}$ $P2_1/a\bar{3}$	00l c + 2 ₁ GS	00l 2 ₁ S	00l 2 ₁ S	
	0k0 2 ₁ b'—	$\bar{h}h0$ a G	$\bar{k}h0$ a G	
206 $Ia\bar{3}$ $I2_1/a\bar{3}$		$\bar{h}h0$ a G	$\bar{k}h0$ a G	
212 $P4_332$			00l 4 ₃ S	
213 $P4_132$			00l 4 ₁ S	
218 $P\bar{4}3n$		00l c n—	hhl c G	
219 $F\bar{4}3c$			hhl c G	
220 $I\bar{4}3d$	0kk $0\bar{k}k$ d G	00l d d—	hhl d G	
222 $Pn\bar{3}n$	00l, 0k0 n n'—	00l c n—	hk0 n G	hhl c G
223 $Pm\bar{3}n$		00l c n'—		hhl c G
224 $Pn\bar{3}m$	00l, 0k0 n n'—		hk0 n G	
226 $Fm\bar{3}c$				hhl c G
227 $Fd\bar{3}m$	00l, 0k0 d d'—		hk0 d G	
228 $Fd\bar{3}c$	00l, 0k0 d d'—		hk0 d G	hhl c G
230 $Ia\bar{3}d$	0kk $0\bar{k}k$ d b'—	00l, $\bar{h}h0$ d a d'—	hk0 a G	hhl d G

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patterns]. Contact J. M. Zuo or J. C. H. Spence, Physics Department, Arizona State University, Tempe, Arizona, USA.

(2) A package for CBED pattern simulation by both Bloch-wave and multi-slice methods is available from P. Stadelmann (pierre.stadelmann@cime.uhd.edfl.ch), Lausanne, Switzerland, in UNIX for workstations [Silicon Graphics, Dec Alpha (OSF), IBM RISC 6000, SUN and HP-9000].

(3) HOLZ line simulations: Listing for PC 8801 (NEC): Tanaka & Terauchi (1985, pp. 174–175).

2.5.4. Electron-diffraction structure analysis (EDSA)

(B. K. VAINSHTEIN AND B. B. ZVYAGIN)

2.5.4.1. Introduction

Electron-diffraction structure analysis (EDSA) (Vainshtein, 1964) based on electron diffraction (Pinsker, 1953) is used for the investigation of the atomic structure of matter together with X-ray and neutron diffraction analysis. The peculiarities of EDSA, as compared with X-ray structure analysis, are defined by a strong interaction of electrons with the substance and by a short wavelength λ . According to the Schrödinger equation (see Section 5.2.2) the electrons are scattered by the electrostatic field of an object. The values of the atomic scattering amplitudes, f_e , are three orders higher than those of X-rays, f_x , and neutrons, f_n . Therefore, a very small quantity of a substance is sufficient to obtain a diffraction pattern. EDSA is used for the investigation of very thin single-crystal films, of ~ 5 – 50 nm polycrystalline and textured films, and of deposits of finely grained materials and surface layers of bulk specimens. The structures of many ionic crystals, crystal hydrates and hydro-oxides, various inorganic, organic, semiconducting and metallo-organic compounds, of various minerals, especially layer silicates, and of biological structures have been investigated by means of EDSA; it has also been used in the study of polymers, amorphous solids and liquids.

Special areas of EDSA application are: determination of unit cells; establishing orientational and other geometrical relationships between related crystalline phases; phase analysis on the basis of d_{hkl} and I_{hkl} sets; analysis of the distribution of crystallite dimensions in a specimen and inner strains in crystallites as determined from line profiles; investigation of the surface structure of single crystals; structure analysis of crystals, including atomic position determination; precise determination of lattice potential distribution and chemical bonds between atoms; and investigation of crystals of biological origin in combination with electron microscopy (Vainshtein, 1964; Pinsker, 1953; Zvyagin, 1967; Pinsker *et al.*, 1981; Dorset, 1976; Zvyagin *et al.*, 1979).

There are different kinds of electron diffraction (ED) depending on the experimental conditions: high-energy (HEED) (above 30–200 kV), low-energy (LEED) (10–600 V), transmission (THEED), and reflection (RHEED). In electron-diffraction studies use is made of special apparatus – electron-diffraction cameras in which the lens system located between the electron source and the specimen forms the primary electron beam, and the diffracted beams reach the detector without aberration distortions. In this case, high-resolution electron diffraction (HRED) is obtained. ED patterns may also be observed in electron microscopes by a selected-area method (SAD). Other types of electron diffraction are: MBD (microbeam), HDD (high-dispersion), CBD (convergent-beam), SMBD (scanning-beam) and RMBD (rocking-beam) diffraction (see Sections 2.5.2 and 2.5.3). The recent development of electron diffractometry, based on direct intensity registration and measurement by scanning the diffraction pattern against a fixed detector (scintillator followed by photomultiplier), presents a new improved level of EDSA which

provides higher precision and reliability of structural data (Avilov *et al.*, 1999; Tsipursky & Drits, 1977; Zhukhlistov *et al.*, 1997, 1998; Zvyagin *et al.*, 1996).

Electron-diffraction studies of the structure of molecules in vapours and gases is a large special field of research (Vilkov *et al.*, 1978). See also *Stereochemical Applications of Gas-Phase Electron Diffraction* (1988).

2.5.4.2. The geometry of ED patterns

In HEED, the electron wavelength λ is about 0.05 Å or less. The Ewald sphere with radius λ^{-1} has a very small curvature and is approximated by a plane. The ED patterns are, therefore, considered as plane cross sections of the reciprocal lattice (RL) passing normal to the incident beam through the point 000, to scale $L\lambda$ (Fig. 2.5.4.1). The basic formula is

$$r = |\mathbf{h}|L\lambda, \text{ or } rd = L\lambda, \quad (2.5.4.1)$$

where r is the distance from the pattern centre to the reflection, $\mathbf{h}$ is the reciprocal-space vector, d is the appropriate interplanar distance and L is the specimen-to-screen distance. The deviation of the Ewald sphere from a plane at distance h from the origin of the coordinates is $\delta_h = h^2\lambda/2$. Owing to the small values of λ and to the rapid decrease of f_e depending on $(\sin \theta)/\lambda$, the diffracted beams are concentrated in a small angular interval (≤ 0.1 rad).

Single-crystal ED patterns image one plane of the RL. They can be obtained from thin ideal crystalline plates, mosaic single-crystal films, or, in the RHEED case, from the faces of bulk single crystals. Point ED patterns can be obtained more easily owing to the following factors: the small size of the crystals (increase in the dimension of RL nodes) and mosaicity – the small spread of crystallite orientations in a specimen (tangential tension of the RL nodes). The crystal system, the parameters of the unit cell and the Laue symmetry are determined from point ED patterns; the probable space group is found from extinctions. Point ED patterns may be used for intensity measurements if the kinematic approximation holds true or if the contributions of the dynamic and secondary scattering are not too large.

The indexing of reflections and the unit-cell determination are carried out according to the formulae relating the RL to the DL (direct lattice) (Vainshtein, 1964; Pinsker, 1953; Zvyagin, 1967).

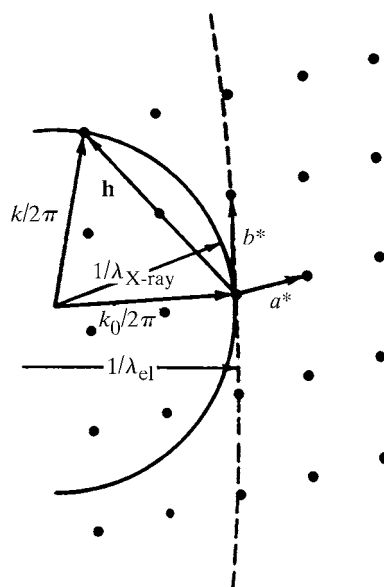


Fig. 2.5.4.1. Ewald spheres in reciprocal space. Dotted line: electrons, solid line: X-rays.

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Under electron-diffraction conditions crystals usually show a tendency to lie down on the substrate plane on the most developed face. Let us take this as (001). The vectors a and b are then parallel, while vector c^* is normal to this plane, and the RL points are considered as being disposed along direct lines parallel to the axis c^* with constant hk and variable l .

The interpretation of the point patterns as respective RL planes is quite simple in the case of orthogonal lattices. If the lattice is triclinic or monoclinic the pattern of the crystal in the position with the face (001) normal to the incident beam does not have to contain $hk0$ reflections with non-zero h and k because, in general, the planes ab and a^*b^* do not coincide. However, the intersection traces of direct lines hk with the plane normal to them (plane ab) always form a net with periods

$$(a \sin \gamma)^{-1}, (b \sin \gamma)^{-1}, \text{ and angle } \gamma' = \pi - \gamma \quad (2.5.4.2a)$$

(Fig. 2.5.4.2). The points hkl along these directions hk are at distances

$$\eta = ha^* \cos \beta^* + kb^* \cos \alpha^* + lc^* \quad (2.5.4.3)$$

from the ab plane.

By changing the crystal orientation it is possible to obtain an image of the a^*b^* plane containing $hk0$ reflections, or of other RL planes, with the exception of planes making a small angle with the axis c^* .

In the general case of an arbitrary crystal orientation, the pattern is considered as a plane section of the system of directions hk which makes an angle φ with the plane ab , intersecting it along a direction $[uv]$. It is described by two periods along directions $0h, 0k$;

$$(a \sin \gamma \cos \psi_h)^{-1}, (b \sin \gamma \cos \psi_k)^{-1}, \quad (2.5.4.2b)$$

with an angle γ'' between them satisfying the relation

$$\cos \gamma'' = \sin \psi_h \sin \psi_k - \cos \psi_h \cos \psi_k \cos \gamma, \quad (2.5.4.2c)$$

and by a system of parallel directions

$$p_h h + p_k k = l; \quad l = 0, \pm 1, \pm 2, \dots \quad (2.5.4.4)$$

The angles ψ_h, ψ_k are formed by directions $0h, 0k$ in the plane of the pattern with the plane ab . The coefficients p_h, p_k depend on the unit-cell parameters, angle φ and direction $[uv]$. These relations are used for the indexing of reflections revealed near the integer positions hkl in the pattern and for unit-cell calculations (Vainshtein, 1964; Zvyagin, 1967; Zvyagin *et al.*, 1979).

In RED patterns obtained with an incident beam nearly parallel to the plane ab one can reveal all the RL planes passing through c^* which become normal to the beam at different azimuthal orientations of the crystal.

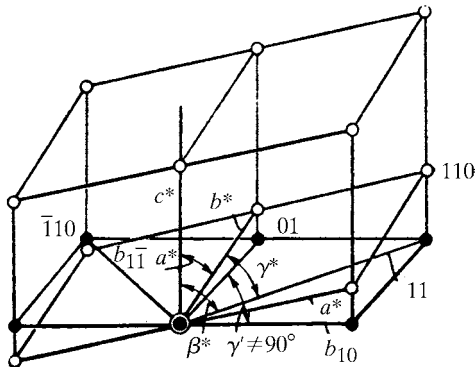


Fig. 2.5.4.2. Triclinic reciprocal lattice. Points: open circles, projection net; black circles.

With the increase of the thickness of crystals (see below, Chapter 5.1) the scattering becomes dynamical and Kikuchi lines and bands appear. Kikuchi ED patterns are used for the estimation of the degree of perfection of the structure of the surface layers of single crystals for specimen orientation in HREM (IT C, 1999, Section 4.3.8). Patterns obtained with a convergent beam contain Kossel lines and are used for determining the symmetry of objects under investigation (see Section 5.1.2).

Texture ED patterns are a widely used kind of ED pattern (Pinsker, 1953; Vainshtein, 1964; Zvyagin, 1967). Textured specimens are prepared by substance precipitation on the substrate, from solutions and suspensions, or from gas phase in vacuum. The microcrystals are found to be oriented with a common (developed) face parallel to the substrate, but they have random azimuthal orientations. Correspondingly, the RL also takes random azimuthal orientations, having c^* as the common axis, *i.e.* it is a rotational body of the point RL of a single crystal. Thus, the ED patterns from textures bear a resemblance, from the viewpoint of their geometry, to X-ray rotation patterns, but they are less complicated, since they represent a plane cross section of reciprocal space.

If the crystallites are oriented by the plane (hkl) , then the axis $[hkl]^*$ is the texture axis. For the sake of simplicity, let us assume that the basic plane is the plane (001) containing the axes a and b , so that the texture axis is $[001]^*$, *i.e.* the axis c^* . The matrices of appropriate transformations will define a transition to the general case (see IT A, 1995). The RL directions $hk = \text{constant}$, parallel to the texture axis, transform to cylindrical surfaces, the points with $\eta_{hkl} = \text{constant}$ are in planes perpendicular to the texture axis, while any 'tilted' lines transform to cones or hyperboloids of rotation. Each point hkl transforms to a ring lying on these surfaces. In practice, owing to a certain spread of c^* axes of single crystals, the rings are blurred into small band sections of a spherical surface with the centre at the point 000; the oblique cross section of such bands produces reflections in the form of arcs. The main interference curves for texture patterns are ellipses imaging oblique plane cross sections of the cylinders hk (Fig. 2.5.4.3).

At the normal electron-beam incidence (tilting angle $\varphi = 0^\circ$) the ED pattern represents a cross section of cylinders perpendicular to the axis c^* , *i.e.* a system of rings.

On tilting the specimen to an angle φ with respect to its normal position (usually $\varphi \simeq 60^\circ$) the patterns image an oblique cross section of the cylindrical RL, and are called oblique-texture (OT)

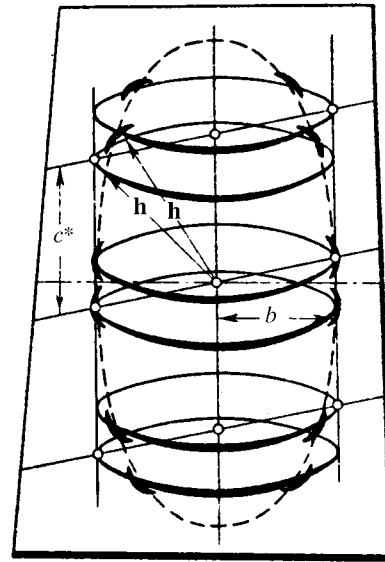


Fig. 2.5.4.3. Formation of ellipses on an electron-diffraction pattern from an oblique texture.

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ED patterns. The ellipses ($hk = \text{constant}$) and layer lines ($l = \text{constant}$) for orthogonal lattices are the main characteristic lines of ED patterns along which the reflections are arranged. The shortcoming of oblique-texture ED patterns is the absence of reflections lying inside the cone formed by rotation of the straight line coming from the point 000 at an angle $(90^\circ - \varphi)$ around the axis c^* and, in particular, of reflections 00 l . However, at $\varphi \lesssim 60\text{--}70^\circ$ the set of reflections is usually sufficient for structural determination.

For unit-cell determination and reflection indexing the values d (i.e. $|\mathbf{h}|$) are used, and the reflection positions defined by the ellipses hk to which they belong and the values η are considered. The periods a^*, b^* are obtained directly from h_{100} and h_{010} values. The period c^* , if it is normal to the plane a^*b^* (γ^* being arbitrary), is calculated as

$$c^* = \eta/l = (h_{hkl}^2 - h_{hk0}^2)^{1/2}/l. \quad (2.5.4.5a)$$

For oblique-angled lattices

$$c^* = [(h_{l+l}^2 + h_{l-l}^2 - 2h_l^2)/2]^{1/2}/l. \quad (2.5.4.5b)$$

In the general case of oblique-angled lattices the coaxial cylinders hk have radii

$$b_{hk} = (1/\sin \gamma)[(h^2/a^2) + (k^2/b^2) - (2hk \cos \gamma/ab)]^{1/2} \quad (2.5.4.6)$$

and it is always possible to use the measured or calculated values b_{hk} in (2.5.4.5a) instead of h_{hk0} , since

$$\eta = (h_{hkl}^2 - b_{hk}^2)^{1/2}. \quad (2.5.4.7)$$

In OT patterns the b_{hk} and η values are represented by the lengths of the small axes of the ellipses $B_{hk} = L\lambda b_{hk}$ and the distances of the reflections hkl from the line of small axes (equatorial line of the pattern)

$$D_{hkl} = L\lambda\eta/\sin \varphi = hp + ks + lq. \quad (2.5.4.8)$$

Analysis of the B_{hk} values gives a, b, γ , while p, s and q are calculated from the D_{hkl} values. It is essential that the components of the normal projections c_n of the axis c on the plane ab measured in the units of a and b are

$$\begin{aligned} x_n &= (c/a)(\cos \beta - \cos \alpha \cos \gamma)/\sin^2 \gamma \\ &= -p/q, \\ y_n &= (c/b)(\cos \alpha - \cos \beta \cos \gamma)/\sin^2 \gamma \\ &= -s/q. \end{aligned} \quad (2.5.4.9)$$

Obtaining x_n, y_n one can calculate

$$c_n = [(x_n a)^2 + (y_n b)^2 + 2x_n y_n ab \cos \gamma]^{1/2}.$$

Since

$$\begin{aligned} d_{001} &= L\lambda/q \sin \varphi, \\ c &= (c_n^2 + d_{001}^2)^{1/2}. \end{aligned} \quad (2.5.4.10)$$

The α, β values are then defined by the relations

$$\begin{aligned} \cos \alpha &= (x_n a \cos \gamma + y_n b)/c, \\ \cos \beta &= (x_n a + y_n b \cos \gamma)/c. \end{aligned} \quad (2.5.4.11)$$

Because of the small particle dimensions in textured specimens, the kinematic approximation is more reliable for OT patterns, enabling a more precise calculation of the structure amplitudes from the intensities of reflections.

Polycrystal ED patterns. In this case, the RL is a set of concentric spheres with radii h_{hkl} . The ED pattern, like an X-ray powder pattern, is a set of rings with radii

$$r_{hkl} = h_{hkl}L\lambda. \quad (2.5.4.12)$$

2.5.4.3. Intensities of diffraction beams

The intensities of scattering by a crystal are determined by the scattering amplitudes of atoms in the crystal, given by (see also Section 5.2.1)

$$\begin{aligned} f_e^{\text{abs}}(s) &= 4\pi K \int \varphi(r)r^2 \frac{\sin sr}{sr} dr, \\ K &= \frac{2\pi me}{h^2}; f_e = K^{-1}f_e^{\text{abs}}, \end{aligned} \quad (2.5.4.13)$$

where $\varphi(r)$ is the potential of an atom and $s = 4\pi(\sin \theta)/\lambda$. The absolute values of f_e^{abs} have the dimensionality of length L . In EDSA it is convenient to use f_e without K . The dimensionality of f_e is [potential L^3]. With the expression of f_e in $\text{V } \text{\AA}^3$ the value K^{-1} in (2.5.4.13) is $47.87 \text{ V } \text{\AA}^2$.

The scattering atomic amplitudes $f_e(s)$ differ from the respective $f_x(s)$ X-ray values in the following: while $f_x(0) = Z$ (electron shell charge), the atomic amplitude at $s = 0$

$$f_e(0) = 4\pi \int \varphi(r)r^2 dr \quad (2.5.4.14)$$

is the 'full potential' of the atom. On average, $f_e(0) \simeq Z^{1/3}$, but for small atomic numbers Z , owing to the peculiarities in the filling of the electron shells, $f_e(0)$ exhibits within periods of the periodic table of elements 'reverse motion', i.e. they decrease with Z increasing (Vainshtein, 1952, 1964). At large $(\sin \theta)/\lambda$, $f_e \simeq Z$. The atomic amplitudes and, consequently, the reflection intensities, are recorded, in practice, up to values of $(\sin \theta)/\lambda \simeq 0.8\text{--}1.2 \text{ \AA}^{-1}$, i.e. up to $d_{\min} \simeq 0.4\text{--}0.6 \text{ \AA}$.

The structure amplitude Φ_{hkl} of a crystal is determined by the Fourier integral of the unit-cell potential (see Chapter 1.2),

$$\Phi_{hkl} = \int_{\Omega} \varphi(\mathbf{r}) \exp\{2\pi i(\mathbf{r} \cdot \mathbf{h})\} d\mathbf{r}, \quad (2.5.4.15)$$

where Ω is the unit-cell volume. The potential of the unit cell can be expressed by the potentials of the atoms of which it is composed:

$$\varphi(\mathbf{r}) = \sum_{\text{cell}, i} \varphi_{\text{at}i}(\mathbf{r} - \mathbf{r}_i). \quad (2.5.4.16)$$

The thermal motion of atoms in a crystal is taken into account by the convolution of the potential of an atom at rest with the probability function $w(\mathbf{r})$ describing the thermal motion:

$$\varphi_{\text{at}} = \varphi_{\text{at}}(\mathbf{r}) * w(\mathbf{r}). \quad (2.5.4.17)$$

Accordingly, the atomic temperature factor of the atom in a crystal is

$$f_{eT}[(\sin \theta)/\lambda] = f_e f_T = f_e [(\sin \theta)/\lambda] \exp\{-B[(\sin \theta)/\lambda]^2\}, \quad (2.5.4.18)$$

where the Debye temperature factor is written for the case of isotropic thermal vibrations. Consequently, the structure amplitude is

$$\Phi_{hkl} = \sum_{\text{cell}, i} f_{eTi} \exp\{2\pi i(hx_i + ky_i + lz_i)\}. \quad (2.5.4.19)$$

This general expression is transformed (see IT I, 1952) according to the space group of a given crystal.

To determine the structure amplitudes in EDSA experimentally, one has to use specimens satisfying the kinematic scattering condition, i.e. those consisting of extremely thin crystallites. The

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limit of the applicability of the kinematic approximation (Blackman, 1939; Vainshtein, 1964) can be estimated from the formula

$$A = \lambda \left| \frac{\langle \Phi_{\mathbf{h}} \rangle}{\Omega} \right| t \lesssim 1, \quad (2.5.4.20)$$

where $\langle \Phi_{\mathbf{h}} \rangle$ is the averaged absolute value of $\Phi_{\mathbf{h}}$ (see also Section 5.2.1). Since $\langle \Phi_{\mathbf{h}} \rangle$ are proportional to $Z^{0.8}$, condition (2.5.4.20) is better fulfilled for crystals with light and medium atoms. Condition (2.5.4.20) is usually satisfied for textured and polycrystalline specimens. But for mosaic single crystals as well, the kinematic approximation limit is, in view of their real structure, substantially wider than estimated by (2.5.4.20) for ideal crystals. The fulfillment of the kinematic law for scattering can be, to a greater or lesser extent, estimated by comparing the decrease of experimental intensity $I_{\mathbf{h}}[(\sin \theta)/\lambda]$ averaged over definite angular intervals, and sums $\sum f_{\text{obs}}^2[(\sin \theta)/\lambda]$ calculated for the same angular intervals.

For mosaic single-crystal films the integral intensity of reflection is

$$I_{\mathbf{h}} = j_0 S \lambda^2 \left| \frac{\Phi_{\mathbf{h}}}{\Omega} \right|^2 \frac{t d_{\mathbf{h}}}{\alpha} \simeq \Phi_{\mathbf{h}}^2 d_{\mathbf{h}}; \quad (2.5.4.21)$$

for textures

$$I_{\mathbf{h}} = j_0 S \lambda^2 \left| \frac{\Phi_{\mathbf{h}}}{\Omega} \right|^2 \frac{t L \lambda p}{2 \pi R' \sin \varphi} \simeq \Phi_{\mathbf{h}}^2 p / R'. \quad (2.5.4.22)$$

Here j_0 is the incident electron-beam density, S is the irradiated specimen area, t is the thickness of the specimen, α is the average angular spread of mosaic blocks, R' is the horizontal coordinate of the reflection in the diffraction pattern and p is the multiplicity factor. In the case of polycrystalline specimens the local intensity in the maximum of the ring reflection

$$I_{\mathbf{h}} = j_0 S \lambda^2 \left| \frac{\Phi_{\mathbf{h}}}{\Omega} \right|^2 \frac{t d_{\mathbf{h}}^2 p \Delta S}{4 \pi L \lambda} \simeq \Phi_{\mathbf{h}}^2 d_{\mathbf{h}}^2 p \quad (2.5.4.23)$$

is measured, where ΔS is the measured area of the ring.

The transition from kinematic to dynamic scattering occurs at critical thicknesses of crystals when $A \geq 1$ (2.5.4.20). Mosaic or polycrystalline specimens then result in an uneven contribution of various crystallites to the intensity of the reflections. It is possible to introduce corrections to the experimental structure amplitudes of the first strong reflections most influenced by dynamic scattering by applying in simple cases the two-wave approximation (Blackman, 1939) or by taking into account multibeam theories (Fujimoto, 1959; Cowley, 1981; Avilov *et al.* 1984; see also Chapter 5.2).

The application of kinematic scattering formulae to specimens of thin crystals (5–20 nm) or dynamic corrections to thicker specimens (20–50 nm) permits one to obtain reliability factors between the calculated Φ^{calc} and observed Φ^{obs} structure amplitudes of $R = 5\text{--}15\%$, which is sufficient for structural determinations.

With the use of electron diffractometry techniques, reliability factors as small as $R = 2\text{--}3\%$ have been reached and more detailed data on the distribution of the inner-crystalline potential field have been obtained, characterizing the state and bonds of atoms, including hydrogen (Zhukhlistov *et al.*, 1997, 1998; Avilov *et al.*, 1999).

The applicability of kinematics formulae becomes poorer in the case of structures with many heavy atoms for which the atomic amplitudes also contain an imaginary component (Shoemaker & Glauber, 1952). The experimental intensity measurement is made by a photo method or by direct recording (Avilov, 1979). In some cases the amplitudes $\Phi_{\mathbf{hkl}}$ can be determined from dynamic

scattering patterns – the bands of equal thickness from a wedge-shaped crystal (Cowley, 1981), or from rocking curves.

2.5.4.4. Structure analysis

The unit cell is defined on the basis of the geometric theory of electron-diffraction patterns, and the space group from extinctions. It is also possible to use the method of converging beams (Section 5.2.2). The structural determination is based on experimental sets of values $|\Phi_{\mathbf{hkl}}|^2$ or $|\Phi_{\mathbf{hkl}}|$ (Vainshtein, 1964).

The trial-and-error method may be used for the simplest structures. The main method of determination is the construction of the Patterson functions

$$P(xyz) = \frac{1}{\Omega} \left[\Phi_{000}^2 + 2 \sum_{\mathbf{hkl} \neq 0} |\Phi_{\mathbf{hkl}}|^2 \cos 2\pi(hx + ky + lz) \right] \quad (2.5.4.24)$$

and their analysis on the basis of heavy-atom methods, superposition methods and so on (see Chapter 2.3). Direct methods are also used (Dorset *et al.*, 1979). Thus the phases of structure factors are calculated and assigned to the observed moduli

$$\Phi_{\mathbf{h}} = |\Phi_{\mathbf{h}, \text{obs}}| \exp\{i\alpha_{\text{calc}}\}. \quad (2.5.4.25)$$

The distribution of the potential in the unit cell, and, thereby, the arrangement in it of atoms (peaks of the potential) are revealed by the construction of three-dimensional Fourier series of the potential (see also Chapter 1.3)

$$\varphi(xyz) = \frac{1}{\Omega} \sum_{\mathbf{h}} \Phi_{\mathbf{hkl}} \exp\{-2\pi i(hx + ky + lz)\} \quad (2.5.4.26a)$$

or projections

$$\varphi'(xy) = \frac{1}{S} \sum_{\mathbf{h}} \Phi_{\mathbf{h}k0} \exp\{-2\pi i(hx + ky)\}. \quad (2.5.4.26b)$$

The general formulae (2.5.4.26a) and (2.5.4.26b) transform, according to known rules, to the expressions for each space group (see IT I, 1952). If $\Phi_{\mathbf{hkl}}$ are expressed in $\text{V } \text{\AA}^3$ and the volume Ω or the cell area S in $\text{\AA}^3$ and $\text{\AA}^2$, respectively, then the potential φ is obtained directly in volts, while the projection of the potential φ' is in $\text{V } \text{\AA}$. The amplitudes $|\Phi_{\mathbf{hkl}}|$ are reduced to an absolute scale either according to a group of strong reflections

$$\sum |\Phi_{\mathbf{h}}|^{\text{calc}} = \sum |\Phi_{\mathbf{h}}|^{\text{obs}} \quad (2.5.4.27)$$

or using the Parseval equality

$$\sum_{\mathbf{h}=-\infty}^{+\infty} |\Phi_{\mathbf{h}}|^2 = \Omega^2 \langle \varphi^2 \rangle = \Omega \sum_{i(\text{cell})} \frac{1}{2\pi^2} \int_0^\infty f_{eT_i}^2(s) s^2 ds \quad (2.5.4.28)$$

or Wilson's statistical method

$$\langle \Phi^2[(\sin \theta)/\lambda] \rangle = \sum_i f_{eT_i}^2[(\sin \theta)/\lambda]. \quad (2.5.4.29)$$

The term Φ_{000} defines the mean inner potential of a crystal, and is calculated from $f_e(0)$ [(2.5.4.13), (2.5.4.19)]

$$\langle \varphi_{\text{cr}} \rangle = \Phi_{000}/\Omega = \frac{1}{\Omega} \sum f_e(0). \quad (2.5.4.30)$$

The Fourier series of the potential in EDSA possess some peculiarities (Vainshtein, 1954, 1964) which make them different from the electron-density Fourier series in X-ray analysis. Owing to the peculiarities in the behaviour of the atomic amplitudes (2.5.4.13), which decrease more rapidly with increasing $(\sin \theta)/\lambda$ compared with f_x , the peaks of the atomic potential

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$$\varphi_{\text{at}}(r) = \frac{1}{2\pi^2} \int f_{eT}(s) \frac{\sin sr}{sr} s^2 ds \quad (2.5.4.31)$$

are more 'blurred' and exhibit a larger half-width than the electron-density peaks $\rho_{\text{at}}(r)$. On average, this half-width corresponds to the 'resolution' of an electron-diffraction pattern – about 0.5 Å or better. The potential in the maximum ('peak height') does not depend as strongly on the atomic number as in X-ray analysis:

$$\varphi(0) = \frac{1}{2\pi^2} \int f_{eT}(s) s^2 ds \sim Z^{0.75}, \quad (2.5.4.32)$$

while in X-ray diffraction $\rho(0) \sim Z^{1.2}$. In such a way, in EDSA the light atoms are more easily revealed in the presence of heavy atoms than in X-ray diffraction, permitting, in particular, hydrogen atoms to be revealed directly without resorting to difference syntheses as in X-ray diffraction. Typical values of the atomic potential $\varphi(0)$ (which depend on thermal motion) in organic crystals are: H ~ 35, C ~ 165, O ~ 215 V; in Al crystals 330 V, in Cu crystals 750 V.

The EDSA method may be used for crystal structure determination, depending on the types of electron-diffraction patterns, for crystals containing up to several tens of atoms in the unit cell. The accuracy in determination of atomic coordinates in EDSA is about 0.01–0.005 Å on average. The precision of EDSA makes it possible to determine accurately the potential distribution, to investigate atomic ionization, to obtain values for the potential between the atoms and, thereby, to obtain data on the nature of the chemical bond.

If the positions in the cell are occupied only partly, then the measurement of $\varphi_i(0)$ gives information on population percentage.

There is a relationship between the nuclear distribution, electron density and the potential as given by the Poisson equation

$$\nabla^2 \varphi(\mathbf{r}) = -4\pi e[\rho_+(\mathbf{r}) - \rho_-(\mathbf{r})]. \quad (2.5.4.33)$$

This makes it possible to interrelate X-ray diffraction, EDSA and neutron-diffraction data. Thus for the atomic amplitudes

$$f_e(s) = 4\pi Ke[Z - f_x(s)]s^{-2}, \quad (2.5.4.34)$$

where Z is the nuclear charge and f_x the X-ray atomic scattering amplitude, and for structure amplitudes

$$\Phi_{hkl} = \pi Ke[Z_{hkl} - F_{hkl}][h]^{-2}, \quad (2.5.4.35)$$

where F_{hkl} is the X-ray structure amplitude of the electron density of a crystal and Z_{hkl} is the amplitude of scattering from charges of nuclei in the cell taking into account their thermal motion. The values Z_{hkl} can be calculated easily from neutron-diffraction data, since the charges of the nuclei are known and the experiment gives the parameters of their thermal motion.

In connection with the development of high-resolution electron-microscopy methods (HREM) it has been found possible to combine the data from direct observations with EDSA methods. However, EDSA permits one to determine the atomic positions to a greater accuracy, since practically the whole of reciprocal space with 1.0–0.4 Å resolution is used and the three-dimensional arrangement of atoms is calculated. At the same time, in electron microscopy, owing to the peculiarities of electron optics and the necessity for an objective aperture, the image of the atoms in a crystal $\varphi'(\mathbf{x}) * A(\mathbf{x})$ is a convolution, with the aperture function blurring the image up to 1.5–2 Å resolution. In practice, in TEM one obtains only the images of the heaviest atoms of an object. However, the possibility of obtaining a direct image of a structure with all the defects in the atomic arrangement is the undoubted merit of TEM.

2.5.5. Image reconstruction* (B. K. VAINSHTEIN)

2.5.5.1. Introduction

In many fields of physical measurements, instrumental and informative techniques, including electron microscopy and computational or analogue methods for processing and transforming signals from objects investigated, find a wide application in obtaining the most accurate structural data. The signal may be radiation from an object, or radiation transmitted through the object, or reflected by it, which is transformed and recorded by a detector.

The image is the two-dimensional signal $I(xy)$ on the observation plane recorded from the whole three-dimensional volume of the object, or from its surface, which provides information on its structure. In an object this information may change owing to transformation of the scattered wave inside an instrument. The real image $J(xy)$ is composed of $I(xy)$ and noise $N(xy)$ from signal disturbances:

$$J(xy) = I(xy) + N(xy). \quad (2.5.5.1)$$

Image-reconstruction methods are aimed at obtaining the most accurate information on the structure of the object; they are subdivided into two types (*Picture Processing and Digital Filtering*, 1975; Rozenfeld, 1969):

(a) Image restoration – separation of $I(xy)$ from the image by means of compensation of distortions introduced in it by an image-forming system as well as by an account of the available quantitative data reflecting its structure.

(b) Image enhancement – maximum exclusion from the observed image $J(xy)$ (2.5.5.1) of all its imperfections $N(xy)$ from both accidental distortions in objects and various 'noise' in signals and detector, and obtaining $I(xy)$ as the result.

These two methods may be used separately or in combination.

The image should be represented in the form convenient for perception and analysis, e.g. in digital form, in lines of equal density, in points of different density, in half-tones or colour form and using, if necessary, a change or reversal of contrast.

Reconstructed images may be used for the three-dimensional reconstruction of the spatial structure of an object, e.g. of the density distribution in it (see Section 2.5.6).

This section is connected with an application of the methods of image processing in transmission electron microscopy (TEM). In TEM (see Section 2.5.2), the source-emitted electrons are transmitted through an object and, with the aid of a system of lenses, form a two-dimensional image subject to processing.

Another possibility for obtaining information on the structure of an object is structural analysis with the aid of electron diffraction – EDSA. This method makes use of information in reciprocal space – observation and measurement of electron-diffraction patterns and calculation from them of a two-dimensional projection or three-dimensional structure of an object using the Fourier synthesis. To do this, one has to find the relative phases of the scattered beams.

The wavefunction of an electron-microscopic image is written as

$$\psi_I = \mathcal{F}^{-1} T \mathcal{F} \psi_0. \quad (2.5.5.2)$$

Here ψ_0 is the incident plane wave. When the wave is transmitted through an object, it interacts with the electrostatic potential $\varphi(\mathbf{r})$ [$\mathbf{r}(xyz)$ is the three-dimensional vector in the space of the object]; this process is described by the Schrödinger equation (Section 2.5.2.1). As a result, on the exit surface of an object the wave takes the form $q\psi_0(\mathbf{x})$ where q is the transmission function and $\mathbf{x}$ is the two-dimensional vector $\mathbf{x}(xy)$. The diffraction of the wave $q\psi_0$ is

* Questions related to this section may be addressed to Dr D. L. Dorset (see list of contributing authors). Dr Dorset kindly checked the proofs of this section.

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described by the two-dimensional Fourier operator:

$$\mathcal{F}q = Q(\mathbf{u}) = \int q(\mathbf{x}) \exp[2\pi i(\mathbf{x}\mathbf{u})] d\mathbf{x}. \quad (2.5.5.3)$$

Here, we assume the initial wave amplitude to be equal to unity and the initial phase to be zero, so that $q\psi_0 = q$, which defines, in this case, the wavefunction in the back focal plane of an objective lens with the reciprocal-space coordinates $\mathbf{u}(u, v)$. The function Q is modified in reciprocal space by the lens transfer function $T(\mathbf{u})$. The scattered wave transformation into an image is described by the inverse Fourier operator $\mathcal{F}^{-1}TQ$.

The process of the diffraction $\mathcal{F}q\psi_0 = Q$, as seen from (2.5.5.1), is the same in both TEM and EDSA. Thus, in TEM under the lens actions $\mathcal{F}^{-1}TQ$ the image formation from a diffraction pattern takes place with an account of the phases, but these phases are modified by the objective-lens transfer function. In EDSA, on the other hand, there is no distorting action of the transfer function and the 'image' is obtained by computing the operation $\mathcal{F}^{-1}Q$.

The computation of projections, images and Fourier transformation is made by discretization of two-dimensional functions on a two-dimensional network of points – pixels in real space $\mathbf{x}(x_j, y_k)$ and in reciprocal space $\mathbf{u}(u_m, v_n)$.

2.5.5.2. Thin weak phase objects at optimal defocus

The intensity distribution $I(xy) \sim |\psi_I|^2$ of an electron wave in the image plane depends not only on the coherent and inelastic scattering, but also on the instrumental functions. The electron wave transmitted through an object interacts with the electrostatic potential $\varphi(\mathbf{r})$ which is produced by the nuclei charges and the electronic shells of the atoms. The scattering and absorption of electrons depend on the structure and thickness of a specimen, and the atomic numbers of the atoms of which it is composed. If an object with the three-dimensional distribution of potential $\varphi(\mathbf{r})$ is sufficiently thin, then the interaction of a plane electron wave ψ_0 with it can be described as the interaction with a two-dimensional distribution of potential projection $\varphi(\mathbf{x})$,

$$\varphi(\mathbf{x}) = \int_0^b \varphi(\mathbf{r}) dz, \quad (2.5.5.4)$$

where b is the specimen thickness. It should be noted that, unlike the three-dimensional function of potential $\varphi(\mathbf{r})$ with dimension $[M^{1/2}L^{3/2}T^{-1}]$, the two-dimensional function of potential projection $\varphi(\mathbf{x})$ has the potential-length dimension $[M^{1/2}L^{1/2}T^{-1}]$ which, formally, coincides with the charge dimension. The transmission function, in the general case, has the form $q(\mathbf{x}) = \exp[-i\sigma\varphi(\mathbf{x})]$ (2.5.2.42), and for weak phase objects the approximation $[\sigma\varphi \ll 1]$

$$q(\mathbf{x}) = 1 - i\sigma\varphi(\mathbf{x}) \quad (2.5.5.5)$$

is valid.

In the back focal plane of the objective lens the wave has the form

$$Q(uv) \cdot T(U) \quad (2.5.5.6)$$

$$T = A(U) \exp(i\chi U) \quad (2.5.5.7a)$$

$$\chi(U) = \pi\Delta f\lambda U^2 + \frac{\pi}{2}C_s\lambda^3 U^4, \quad (2.5.5.7b)$$

where $U = (u^2 + v^2)^{1/2}$; $\exp[i\chi(U)]$ is the Scherzer phase function (Scherzer, 1949) of an objective lens (Fig. 2.5.5.1), $A(U)$ is the aperture function, C_s the spherical aberration coefficient, and Δf the defocus value [(2.5.2.32)–(2.5.2.35)].

The bright-field image intensity (in object coordinates) is

$$I(xy) = |\psi_I(xy) * t(xy)|^2, \quad (2.5.5.8)$$

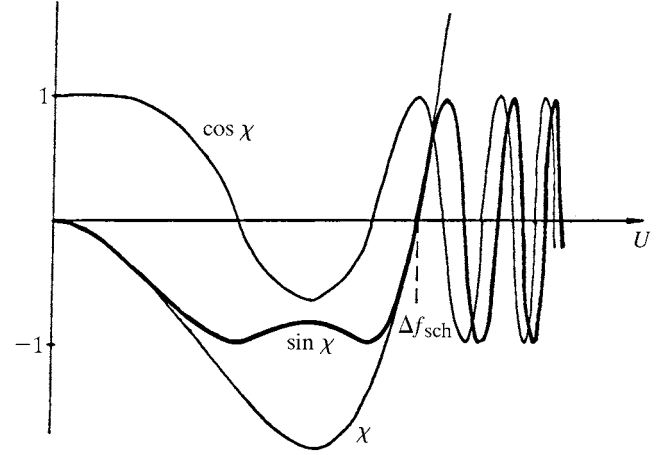


Fig. 2.5.5.1. The χ function and two components of the Scherzer phase function $\sin \chi(U)$ and $\cos \chi(U)$.

where $t = \mathcal{F}^{-1}[T]$. The phase function (2.5.5.7) depends on defocus, and for a weak phase object (Cowley, 1981)

$$I(xy) = 1 + 2\sigma\varphi(xy) * s(xy), \quad (2.5.5.9)$$

where $s = \mathcal{F}^{-1}[A(U)] \sin \chi$, which includes only an imaginary part of function (2.5.5.6). While selecting defocus in such a way that under the Scherzer defocus conditions [(2.5.2.44), (2.5.2.45)] $|\sin \chi| \simeq 1$, one could obtain

$$I(xy) = 1 + 2\sigma\varphi(xy) * a(xy). \quad (2.5.5.10)$$

In this very simple case the image reflects directly the structure of the object – the two-dimensional distribution of the projection of the potential convoluted with the spread function $a = \mathcal{F}^{-1}A$. In this case, no image restoration is necessary. Contrast reversal may be achieved by a change of defocus.

At high resolution, this method enables one to obtain an image of projections of the atomic structure of crystals and defects in the atomic arrangement – vacancies, replacements by foreign atoms, amorphous structures and so on; at resolution worse than atomic one obtains images of dislocations as continuous lines, inserted phases, inclusions *etc.* (Cowley, 1981). It is also possible to obtain images of thin biological crystals, individual molecules, biological macromolecules and their associations.

Image restoration. In the case just considered (2.5.5.10), the projection of potential $\varphi(xy)$, convoluted with the spread function, can be directly observed. In the general case (2.5.5.9), when the aperture becomes larger, the contribution to image formation is made by large values of spatial frequencies U , in which the function $\sin \chi$ oscillates, changing its sign. Naturally, this distorts the image just in the region of appropriate high resolution. However, if one knows the form of the function $\sin \chi$ (2.5.5.7), the true function $\varphi(xy)$ can be restored.

This could be carried out experimentally if one were to place in the back focal plane of an objective lens a zone plate transmitting only one-sign regions of $\sin \chi$ (Hoppe, 1971). In this case, the information on $\varphi(xy)$ is partly lost, but not distorted. To perform such a filtration in an electron microscope is a rather complicated task.

Another method is used (Erickson & Klug, 1971). It consists of a Fourier transformation $\mathcal{F}^{-1}$ of the measured intensity distribution TQ (2.5.5.6) and division of this transform, according to (2.5.5.7a,b), by the phase function $\sin \chi$. This gives

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$$\frac{TQ}{\sin \chi} = Q(uv)A(U). \quad (2.5.5.11a)$$

Then, the new Fourier transformation $\mathcal{F}QA$ yields (in the weak-phase-object approximation) the true distribution

$$\varphi(xy) * a(xy). \quad (2.5.5.11b)$$

The function $\sin \chi$ depending on defocus Δf should be known to perform this procedure. The transfer function can also be found from an electron micrograph (Thon, 1966). It manifests itself in a circular image intensity modulation of an amorphous substrate or, if the specimen is crystalline, in the 'noise' component of the image. The analogue method (optical Fourier transformation for obtaining the image $\sin \chi$) can be used (optical diffraction, see below); digitization and Fourier transformation can also be applied (Hoppe *et al.*, 1973).

The thin crystalline specimen implies that in the back focal objective lens plane the discrete kinematic amplitudes Φ_{hk} are arranged and, by the above method, they are corrected and released from phase distortions introduced by the function $\sin \chi$ (see below) (Unwin & Henderson, 1975).

For the three-dimensional reconstruction (see Section 2.5.6) it is necessary to have the projections of potential of the specimen tilted at different angles α to the beam direction (normal beam incidence corresponds to $\alpha = 0$). In this case, the defocus Δf changes linearly with increase of the distance l of specimen points from the rotation axis $\Delta f_\alpha = \Delta f_0(1 + l \sin \alpha)$. Following the above procedure for passing on to reciprocal space and correction of $\sin \chi$, one can find $\varphi_\alpha(xy)$ (Henderson & Unwin, 1975).

2.5.5.3. An account of absorption

Elastic interaction of an incident wave with a weak phase object is defined on its exit surface by the distribution of potential projection $\varphi(xy)$; however, in the general case, the electron scattering amplitude is a complex one (Glauber & Schomaker, 1953). In such a way, the image itself has the phase and amplitude contrast. This may be taken into account if one considers not only the potential projection $\varphi(xy)$, but also the 'imaginary potential' $\mu(xy)$ which describes phenomenologically the absorption in thin specimens. Then, instead of (2.5.5.5), the wave on the exit surface of a specimen can be written as

$$q(xy) = 1 - i\sigma\varphi(xy) - \mu(xy) \quad (2.5.5.12)$$

and in the back focal plane if $\Phi = \mathcal{F}\varphi$ and $M = \mathcal{F}\mu$

$$Q(uv) = \delta(uv) - i\sigma\Phi(uv) - M(uv). \quad (2.5.5.13)$$

Usually, μ is small, but it can, nevertheless, make a certain contribution to an image. In a sufficiently good linear approximation, it may be assumed that the real part $\cos \chi$ of the phase function (2.5.5.7a) affects $M(uv)$, while $\Phi(xy)$, as we know, is under the action of the imaginary part $\sin \chi$.

Thus, instead of (2.5.5.6), one can write

$$Q(\exp i\chi) = \delta(\mathbf{u}) - i\sigma\Phi(\mathbf{u}) \sin \chi - M(\mathbf{u}) \cos \chi, \quad (2.5.5.14)$$

and as the result, instead of (2.5.5.10),

$$I(xy) = 1 + 2\sigma\varphi(xy) * \mathcal{F}^{-1}(\sin \chi) * a(U) - 2\mu(xy) * \mathcal{F}^{-1}(\cos \chi) * a(U). \quad (2.5.5.15)$$

The functions $\varphi(xy)$ and $\mu(xy)$ can be separated by object imaging using the through-focus series method. In this case, using the Fourier transformation, one passes from the intensity distribution (2.5.5.15) in real space to reciprocal space. Now, at two different defocus values Δf_1 and Δf_2 [(2.5.5.6), (2.5.5.7a,b)] the

values $\Phi(\mathbf{u})$ and $M(\mathbf{u})$ can be found from the two linear equations (2.5.5.14). Using the inverse Fourier transformation, one can pass on again to real space which gives $\varphi(\mathbf{x})$ and $\mu(\mathbf{x})$ (Schiske, 1968). In practice, it is possible to use several through-focus series and to solve a set of equations by the least-squares method.

Another method for processing takes into account the simultaneous presence of noise $N(\mathbf{x})$ and transfer function zeros (Kirkland *et al.*, 1980). In this method the space frequencies corresponding to small values of the transfer function modulus are suppressed, while the regions where such a modulus is large are found to be reinforced.

2.5.5.4. Thick crystals

When the specimen thickness exceeds a certain critical value (~ 50 – 100 Å), the kinematic approximation does not hold true and the scattering is dynamic. This means that on the exit surface of a specimen the wave is not defined as yet by the projection of potential $\varphi(xy) = \int \varphi(\mathbf{r}) dz$ (2.5.5.3), but one has to take into account the interaction of the incident wave ψ_0 and of all the secondary waves arising in the whole volume of a specimen.

The dynamic scattering calculation can be made by various methods. One is the multi-slice (or phase-grating) method based on a recurrent application of formulae (2.5.5.3) for n thin layers Δz_i thick, and successive construction of the transmission functions q_i (2.5.5.4), phase functions $Q_i = \mathcal{F}q_i$, and propagation function $p_k = [k/2\pi i \Delta z] \exp[ik(x^2 + y^2)/2\Delta z]$ (Cowley & Moodie, 1957).

Another method – the scattering matrix method – is based on the solution of equations of the dynamic theory (Chapter 5.2). The emerging wave on the exit surface of a crystal is then found to diffract and experience the transfer function action [(2.5.5.6), (2.5.5.7a,b)].

The dynamic scattering in crystals may be interpreted using Bloch waves:

$$\Psi^j(\mathbf{r}) = \sum_H C_H^j \exp(-2\pi i \mathbf{k}_H^j \cdot \mathbf{r}). \quad (2.5.5.16)$$

It turns out that only a few (bound and valence Bloch waves) have strong excitation amplitudes. Depending on the thickness of a crystal, only one of these waves or their linear combinations (Kambe, 1982) emerges on the exit surface. An electron-microscopic image can be interpreted, at certain thicknesses, as an image of one of these waves [with a correction for the transfer function action (2.5.5.6), (2.5.5.7a,b)]; in this case, the identical images repeat with increasing thickness, while, at a certain thickness, the contrast reversal can be observed. Only the first Bloch wave which arises at small thickness, and also repeats with increasing thickness, corresponds to the projection of potential $\varphi(xy)$, *i.e.* the atom projection distribution in a thin crystal layer.

An image of other Bloch waves is defined by the function $\varphi(\mathbf{r})$, but their maxima or minima do not coincide, in the general case, with the atomic positions and cannot be interpreted as the projection of potential. It is difficult to reconstruct $\varphi(xy)$ from these images, especially when the crystal is not ideal and contains imperfections. In these cases one resorts to computer modelling of images at different thicknesses and defocus values, and to comparison with an experimentally observed pattern.

The imaging can be performed directly in an electron microscope not by a photo plate, but using fast-response detectors with digitized intensity output on line. The computer contains the necessary algorithms for Fourier transformation, image calculation, transfer function computing, averaging, and correction for the observed and calculated data. This makes possible the interpretation of the pattern observed directly in experiment (Herrmann *et al.*, 1980).

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2.5.5.5. Image enhancement

The real electron-microscope image is subdivided into two components:

$$J(xy) = I(xy) + N(xy). \quad (2.5.5.17)$$

The main of these, $I(xy)$, is a two-dimensional image of the 'ideal' object obtained in an electron microscope with instrumental functions inherent to it. However, in the process of object imaging and transfer of this information to the detector there are various sources of noise. In an electron microscope, these arise owing to emission-current and accelerating-voltage fluctuations, lens-supplying current (temporal fluctuations), or mechanical instabilities in a device, specimen or detector (spatial shifts). The two-dimensional detector (*e.g.* a photographic plate) has structural inhomogeneities affecting a response to the signal. In addition, the specimen is also unstable; during preparation or imaging it may change owing to chemical or some other transformations in its structure, thermal effects and so on. Biological specimens scatter electrons very weakly and their natural state is moist, while in the electron-microscope column they are under vacuum conditions. The methods of staining (negative or positive), *e.g.* of introducing into specimens substances containing heavy atoms, as well as the freeze-etching method, somewhat distort the structure of a specimen. Another source of structure perturbation is radiation damage, which can be eliminated at small radiation doses or by using the cryogenic technique. The structure of stained specimens is affected by stain graininess. We assume that all the deviations $\Delta I_k(xy)$ of a specimen image from the 'ideal' image $I_k(xy)$ are included in the noise term $N_k(xy)$. The substrate may also be inhomogeneous. All kinds of perturbations cannot be separated and they appear on an electron microscope image as the full noise content $N(xy)$.

The image enhancement involves maximum noise suppression $N(xy)$ and hence the most accurate separation of a useful signal $I(xy)$ from the real image $J(xy)$ (2.5.5.1). At the signal/noise ratio $I/N \simeq 1$ such a separation appears to be rather complicated. But in some cases the real image reflects the structure sufficiently well, *e.g.* during the atomic structure imaging of some crystals ($I/N > 10$). In other cases, especially of biological specimen imaging, the noise N distorts substantially the image, (I/N) $\sim$ 5–10. Here one should use the methods of enhancement. This problem is usually solved by the methods of statistical processing of sets of images J_k ($k = 1, \dots, n$). If one assumes that the informative signal $I_k(xy)$ is always the same, then the noise error $N(xy)$ may be reduced.

The image enhancement methods are subdivided into two classes:

- (a) image averaging in real space xy ;
- (b) Fourier analysis and filtration in reciprocal space.

These methods can be used separately or in combination. The enhancement can be applied to both the original and the restored images; there are also methods of simultaneous restoration and enhancement.

The image can be enhanced by analogue (mainly optical and photographic) methods or by computational methods for processing digitized functions in real and reciprocal space.

The cases where the image has translational symmetry, rotational symmetry, and where the image is asymmetric will be considered.

Periodic images. An image of the crystal structure with atomic or molecular resolution may be brought to self-alignment by a shift by a and b periods in a structure projection. This can be performed photographically by printing the shifted image on the same photographic paper or, *vice versa*, by shifting the paper (McLachlan, 1958).

The Fourier filtration method for a periodic image I_p with noise N is based on the fact that in Fourier space the components $\mathcal{F}I_p$ and $\mathcal{F}N$ are separated. Let us carry out the Fourier transformation of the

periodic signal I_p with the periods a, b and noise N :

$$\begin{aligned} \mathcal{F}J &= \mathcal{F}[I_p(xy) + N(xy)] \\ &= \int I_p(xy) \exp[2\pi i(hx + ky)] dx dy + \mathcal{F}N \\ &= \sum \Phi_{hk} \delta(\mathbf{u} - \mathbf{u}_{hk}) + \mathcal{F}N; \\ \mathbf{u}_{hk} &= h\mathbf{a}^* + k\mathbf{b}^*. \end{aligned} \quad (2.5.5.18)$$

The left part of (2.5.5.18) represents the Fourier coefficients Φ_{hk} distributed discretely with periods a^* and b^* in the plane $\mathbf{u}(uv)$. This is the two-dimensional reciprocal lattice. The right-hand side of (2.5.5.18) is the Fourier transform $\mathcal{F}N$ distributed continuously in the plane. Thus these parts are separated. Let us 'cut out' from distribution (2.5.5.18) only Φ_{hk} values using the 'window' function $w(uv)$. The window should match each of the real peaks Φ_{hk} which, owing to the finite dimensions of the initial periodic image, are not points, as this is written in an idealized form in (2.5.5.18) with the aid of δ functions. In reality, the 'windows' may be squares of about $a^*/10, b^*/10$ in size, or a circle. Performing the Fourier transformation of product (2.5.5.18) without $\mathcal{F}N$, and set of windows $w(\mathbf{u}) = w(uv) * \sum_{h,k} \delta(\mathbf{u} - h\mathbf{a}^* - k\mathbf{b}^*)$, we obtain:

$$\begin{aligned} J(xy) &= \mathcal{F}^{-1} \left\{ w(\mathbf{u}) \sum_{h,k} \Phi_{hk} \delta(\mathbf{u} - \mathbf{u}_{hk}) \right\} \\ &= W(xy) * I_p(\mathbf{x}), \end{aligned} \quad (2.5.5.19)$$

the periodic component without the background, $W(xy) = \mathcal{F}^{-1} w(\mathbf{u})$. The zero coefficient Φ_{00} in (2.5.5.19) should be decreased, since it is due, in part, to the noise. When the window w is sufficiently small, I_p in (2.5.5.19) represents the periodic distribution $\langle I \rangle$ (average over all the unit cells of the projection) included in I_p (2.5.5.18). Nevertheless, some error from noise in an image does exist, since with Φ_{hk} we also introduced into the inverse Fourier transformation the background transform values $\mathcal{F}^{-1} N_{hk}$ which are within the 'windows'.

This approach is realized by an analogue method [optical diffraction and filtering of electron micrographs in a laser beam (Klug & Berger, 1964)] and can also be carried out by computing.

As an example, Fig. 2.5.5.2(b) shows an electron micrograph of the periodic structure of a two-dimensional protein crystal, while Fig. 2.5.5.2(c) represents optical diffraction from this layer. In order to dissect the aperiodic component $\mathcal{F}N$ in a diffraction plane, according to the scheme in Fig. 2.5.5.2(a), one places a mask with windows covering reciprocal-lattice points. After such a filtration, only the I_p component makes a contribution during the image formation by means of a lens, while the component $\mathcal{F}N$ diffracted by the background is delayed. As a result, an optical pattern of the periodic structure is obtained (Fig. 2.5.5.2d).

Optical diffractometry also assists in determining the parameters of a two-dimensional lattice and its symmetry.

Using the same method, one can separate the superimposed images of two-dimensional structures with different periodicity and in different orientation, the images of the 'near' and 'far' sides of tubular periodic structures with monomolecular walls (Klug & DeRosier, 1966; Kiselev *et al.*, 1971), and so on.

Computer filtering involves measuring the image optical density J_{obs} , digitization, and Fourier transformation (Crowther & Amos, 1971). The sampling distance usually corresponds to one-third of the image resolution. When periodic weak phase objects are investigated, the transformation (2.5.5.18) yields the Fourier coefficients. If necessary, we can immediately make corrections in them using the microscope transfer function according to (2.5.5.6), (2.5.5.7a,b) and (2.5.5.11a), and thereby obtain the true kinematic amplitudes Φ_{hk} . The inverse transformation (2.5.5.16) gives a projection of the structure (Unwin & Henderson, 1975; Henderson & Unwin, 1975).

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

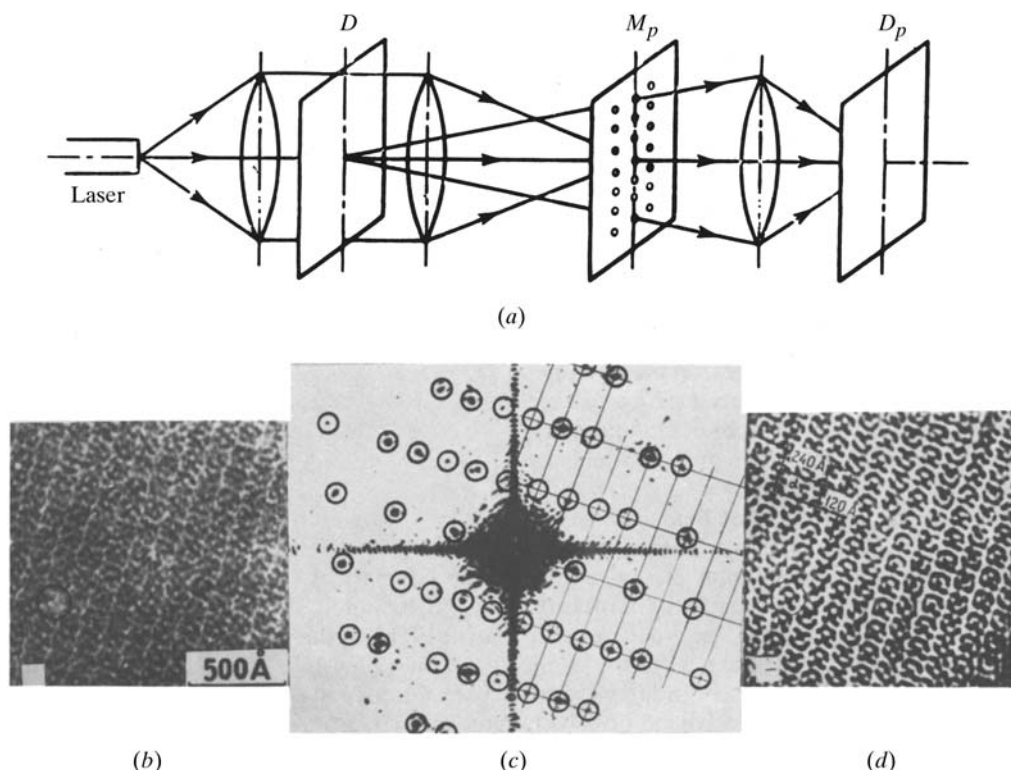


Fig. 2.5.5.2. (a) Diagram of an optical diffractometer. D is the object (an electron micrograph), M_p is the diffraction plane and a mask that transmits only Φ_{hk} , D_p is the plane of the (filtered) image; (b) an electron micrograph of a crystalline layer of the protein phosphorylase b ; (c) its optical diffraction pattern (the circles correspond to the windows in the mask that transmits only the Φ_{hk} diffracted beams from the periodic component of the image); (d) the filtered image. Parts (b)–(d) are based on the article by Kiselev *et al.* (1971).

Sometimes, an observed image $J(\mathbf{x})$ is ‘noised’ by the $N(\mathbf{x})$ to a great extent. Then, one may combine data on real and reciprocal space to construct a sufficiently accurate image. In this case, the electron-diffraction pattern is measured and structure-factor moduli from diffraction reflection intensities $I_{hk, \text{obs}}$ are obtained:

$$|\Phi_{hk, \text{obs}}| \sim \sqrt{I_{hk, \text{obs}}}. \quad (2.5.5.20)$$

At the same time, the structure factors

$$\Phi_{hk, \text{calc}} = |\Phi_{hk, \text{calc}}| \exp(i\alpha_{hk, \text{calc}}) \quad (2.5.5.21)$$

are calculated from the processed structure projection image by means of the Fourier transformation. However, owing to poor image quality we take from these data only the values of phases α_{hk} since they are less sensitive to scattering density distortions than the moduli, and construct the Fourier synthesis

$$I(xy) = \sum_{hk} |\Phi_{hk, \text{obs}}| \exp(i\alpha_{hk, \text{calc}}) \times \exp[2\pi i(hx + ky)]. \quad (2.5.5.22)$$

Here the possibilities of combining various methods open up, *e.g.* for obtaining the structure-factor moduli from X-ray diffraction, and phases from electron microscopy, and so on (Gurskaya *et al.*, 1971).

Images with point symmetry. If a projection of an object (and consequently, the object itself) has a rotational N -fold axis of symmetry, the structure coincides with itself on rotation through the angle $2\pi/N$. If the image is rotated through arbitrary angles and is aligned photographically with the initial image, then the best density coincidence will take place at a rotation through $\alpha = (k2\pi/N)$ ($k = 1, \dots, N$) which defines N . The pattern averaging over all the rotations will give the enhanced structure image with an $(N)^{1/2}$ times reduced background (Markham *et al.*, 1963).

Rotational filtering can be performed on the basis of the Fourier expansion of an image in polar coordinates over the angles (Crowther & Amos, 1971).

$$I(r, \psi) = \sum_{n=-\infty}^{+\infty} g_n(r) \exp(in\psi). \quad (2.5.5.23)$$

The integral over the radius from azimuthal components g_n gives their power

$$p_n \sim \int_0^a |g_n|^2 r dr, \quad (2.5.5.24)$$

where a is the maximum radius of the particle. A set p_n forms a spectrum, the least common multiple N of strong peaks defining the N -fold symmetry. The two-dimensional reconstructed image of a particle with rotational symmetry is defined by the synthesis (2.5.5.24) with $n = 0, N, 2N, 3N$.

Asymmetric images. In this case, a set of images is processed by computational or analogue methods. The initial selection of images involves the fulfillment of the maximum similarity condition.

The averaging of n images in real space gives

$$I_{\text{enh}} = (1/n) \sum_{k=1}^n J_k(xy) = \langle I_k \rangle(xy) + (1/n) \sum N_k(xy). \quad (2.5.5.25)$$

The signal/noise ratio on an average image is $(n)^{1/2}$ times enhanced.

The degree of similarity and accuracy of superposition of two images with an account both of translational and angular shifts is estimated by a cross-correlation function* of two selected images J_1 and J_2 (Frank, 1975, 1980).

* At $I_j = I_k$ this is the autocorrelation function, an analogue of the Patterson function used in crystallography.

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

$$\begin{aligned} k(\mathbf{x}') &= J_1 * J_2 = \int J_1(x) J_2(x + x') dx \\ &= k_{I_1 I_2} + k_{I_1 N_2} + k_{I_2 N_1} + k_{N_1 N_2}. \end{aligned} \quad (2.5.5.26)$$

The value $k(\mathbf{x}')$ is the measure of image similarity, the x' coordinate of the maximum indicates the shift of the images relative to each other. The first term of the resultant expression (2.5.5.26) is the cross-correlation function of noise-corrected images being compared, the second and third terms are approximately equal to zero, since the noise does not correlate with the signal; the last term is the autocorrelation function of the noise (Cramér, 1954; Frank, 1975, 1980).

The calculation of a correlation function is performed by means of Fourier transformation on the basis of the convolution theorem, since the Fourier transformation of the product of the Fourier transform of function J_1 and the conjugated Fourier transform function J_2 gives the cross-correlation function of the initial functions:

$$k = \mathcal{F}^{-1}[\mathcal{F}J_1 \cdot \mathcal{F}^*J_2]. \quad (2.5.5.27)$$

The probability density of samples for images has the form

$$\begin{aligned} p(J_1 J_2 \dots J_n) &= \frac{1}{(\sigma\sqrt{2\pi})^n} \\ &\times \exp\left[\frac{-1}{2\sigma^2} \sum \int [J_k(\mathbf{x} + \mathbf{x}_k) - J(\mathbf{x})]^2 dx\right]. \end{aligned} \quad (2.5.5.28)$$

Here J is the tentative image (as such, a certain 'best' image can first be selected, while at the repeated cycle an average image is obtained), $J_k(\mathbf{x})$ is the image investigated, σ is the standard deviation of the normal distribution of noises and x_k the relative shift of the image. This function is called a likelihood function; it has maxima relative to the parameters $J(x)$, x_k , σ . The average image and dispersion are

$$\begin{aligned} J(\mathbf{x}) &= (1/n) \sum [J_k(\mathbf{x} - \mathbf{x}_k)], \\ \sigma^2 &= (1/n) \sum [J_k(\mathbf{x} - \mathbf{x}_k) - J(\mathbf{x})]^2. \end{aligned} \quad (2.5.5.29)$$

This method is called the maximum-likelihood method (Cramér, 1954; Kosykh *et al.*, 1983).

It is convenient to carry out the image alignment, in turn, with respect to translational and angular coordinates. If we start with an angular alignment we first use autocorrelation functions or power spectra, which have the maximum and the symmetry centre at the origin of the coordinates. The angular correlation maximum

$$f(\theta') = \int f_k(\theta - \theta') f_e(\theta) d\theta \quad (2.5.5.30)$$

gives the mutual angle of rotation of two images.

Then we carry out the translational alignment of rotationally aligned images using the translational correlation function (2.5.5.26) (Langer *et al.*, 1970).

In the iteration alignment method, the images are first translationally aligned and then an angular shift is determined in image space in polar coordinates with the centre at the point of the best translational alignment. After the angular alignment the whole procedure may be repeated (Steinkilberg & Schramm, 1980).

The average image obtained may have false high-frequency components. They can be excluded by multiplying its Fourier components by some function and suppressing high-space frequencies, for instance by an 'artificial temperature factor' $\exp\{-B|\mathbf{u}|^2\}$.

For a set of similar images the Fourier filtration method can also be used (Ottensmeyer *et al.*, 1977). To do this, one should prepare from these images an artificial 'two-dimensional crystal', *i.e.* place

them in the same orientation at the points of the two-dimensional lattice with periods a , b .

$$J = \sum_{k=1}^n J_k(\mathbf{x} - \mathbf{t}_p); \mathbf{t} = p_1 \mathbf{a} + p_2 \mathbf{b}. \quad (2.5.5.31)$$

The processing is then performed according to (2.5.5.18), (2.5.5.19); as a result one obtains $\langle I(xy) \rangle$ with reduced background. Some translational and angular errors in the arrangement of the images at the artificial lattice points act as an artificial temperature factor. The method can be realized by computing or by optical diffraction.

2.5.6. Three-dimensional reconstruction*

(B. K. VAINSHTEIN)

2.5.6.1. The object and its projection

In electron microscopy we obtain a two-dimensional image $\varphi_2(\mathbf{x}_\tau)$ – a projection of a three-dimensional object $\varphi_3(\mathbf{r})$ (Fig. 2.5.6.1):

$$\varphi_2(\mathbf{x}_\tau) = \int \varphi_3(\mathbf{r}) d\tau \quad \boldsymbol{\tau} \perp \mathbf{x}. \quad (2.5.6.1)$$

The projection direction is defined by a unit vector $\boldsymbol{\tau}(\theta, \psi)$ and the projection is formed on the plane $\mathbf{x}$ perpendicular to $\boldsymbol{\tau}$. The set of various projections $\varphi_2(\mathbf{x}_\tau) = \varphi_{2i}(\mathbf{x}_i)$ may be assigned by a discrete or continuous set of points $\boldsymbol{\tau}_i(\theta_i, \psi_i)$ on a unit sphere $|\boldsymbol{\tau}| = 1$ (Fig. 2.5.6.2). The function $\varphi(\mathbf{x}_\tau)$ reflects the structure of an object, but gives information only on $\mathbf{x}_\tau$ coordinates of points of its projected density. However, a set of projections makes it possible to reconstruct from them the three-dimensional (3D) distribution $\varphi_3(xyz)$ (Radon, 1917; DeRosier & Klug, 1968; Vainshtein *et al.*, 1968; Crowther, DeRosier & Klug, 1970; Gordon *et al.*, 1970; Vainshtein, 1971a; Ramachandran & Lakshminarayanan, 1971; Vainshtein & Orlov, 1972, 1974; Gilbert, 1972a; Herman, 1980). This is the task of the three-dimensional reconstruction of the structure of an object:

$$\text{set } \varphi_2(\mathbf{x}_i) \rightarrow \varphi_3(\mathbf{r}). \quad (2.5.6.2)$$

Besides electron microscopy, the methods of reconstruction of a structure from its projections are also widely used in various fields, *e.g.* in X-ray and NMR tomography, in radioastronomy, and in various other investigations of objects with the aid of penetrating, back-scattered or their own radiations (Bracewell, 1956; Deans, 1983; Mersereau & Oppenheim, 1974).

In the general case, the function $\varphi_3(\mathbf{r})$ (2.5.6.1) (the subscript indicates dimension) means the distribution of a certain scattering density in the object. The function $\varphi_2(\mathbf{x})$ is the two-dimensional projection density; one can also consider one-dimensional projections $\varphi_1(x)$ of two- (or three-) dimensional distributions. In electron microscopy, under certain experimental conditions, by functions $\varphi_3(\mathbf{r})$ and $\varphi_2(\mathbf{x})$ we mean the potential and the projection of the potential, respectively [the electron absorption function μ (see Section 2.5.4) may also be considered as 'density']. Owing to a very large depth of focus and practical parallelism of the electron beam passing through an object, in electron microscopy the vector $\boldsymbol{\tau}$ is the same over the whole area of the irradiated specimen – this is the case of parallel projection.

The 3D reconstruction (2.5.6.2) can be made in the real space of an object – the corresponding methods are called the methods of direct three-dimensional reconstruction (Radon, 1917; Vainshtein

* Questions related to this section may be addressed to Professor J. M. Cowley (see list of contributing authors). Professor Cowley kindly checked the proofs for this section.

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

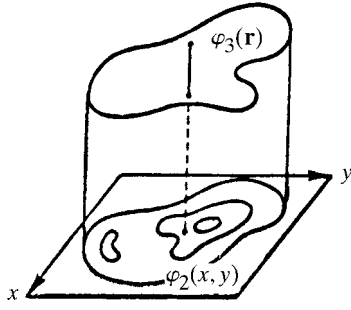


Fig. 2.5.6.1. A three-dimensional object φ_3 and its two-dimensional projection φ_2 .

et al., 1968; Gordon *et al.*, 1970; Vainshtein, 1971a; Ramachandran & Lakshminarayanan, 1971; Vainshtein & Orlov, 1972, 1974; Gilbert, 1972a).

On the other hand, three-dimensional reconstruction can be carried out using the Fourier transformation, *i.e.* by transition to reciprocal space. The Fourier reconstruction is based on the well known theorem: the Fourier transformation of projection φ_2 of a three-dimensional object φ_3 is the central (*i.e.* passing through the origin of reciprocal space) two-dimensional plane cross section of a three-dimensional transform perpendicular to the projection vector (DeRosier & Klug, 1968; Crowther, DeRosier & Klug, 1970; Bracewell, 1956). In Cartesian coordinates a three-dimensional transform is

$$\mathcal{F}_3[\varphi_3(\mathbf{r})] = \Phi_3(uvw) = \iiint \varphi_3(xyz) \times \exp\{2\pi i(ux + vy + wz)\} dx dy dz. \quad (2.5.6.3)$$

The transform of projection $\varphi_2(xy)$ along z is

$$\begin{aligned} \mathcal{F}_2[\varphi_2(xy)] &= \Phi_3(uv0) = \iiint \varphi_3(xyz) \\ &\times \exp\{2\pi i(ux + vy + 0z)\} dx dy dz \\ &= \iint \varphi_3(xyz) dz \exp\{2\pi i(ux + vy)\} dx dy \\ &= \iint \varphi_2(xy) \exp\{2\pi i(ux + vy)\} dx dy \\ &= \Phi_2(uv). \end{aligned} \quad (2.5.6.4)$$

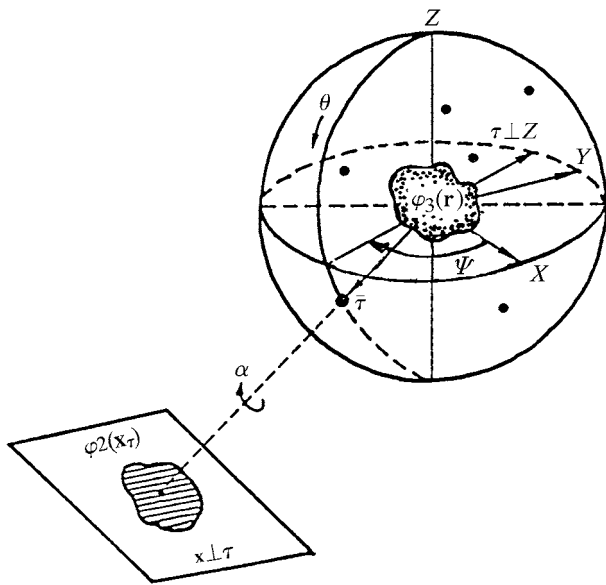


Fig. 2.5.6.2. The projection sphere and projection φ_2 of φ_3 along τ onto the plane $\mathbf{x} \perp \tau$. The case $\tau \perp z$ represents orthoaxial projection. Points indicate a random distribution of τ .

In the general case (2.5.6.1) of projecting the plane $\mathbf{x}(xy) \parallel \mathbf{u}(uv) \perp \tau$ along the vector τ

$$\mathcal{F}_2[\varphi_2(\mathbf{x}_\tau)] = \Phi_2(\mathbf{u}_\tau). \quad (2.5.6.5)$$

Reconstruction with Fourier transformation involves transition from projections φ_{2i} at various τ_i to cross sections Φ_{2i} , then to construction of the three-dimensional transform $\Phi_3(\mathbf{u})$ by means of interpolation between φ_{2i} in reciprocal space, and transition by the inverse Fourier transformation to the three-dimensional distribution $\varphi_3(\mathbf{r})$:

$$\begin{aligned} \text{set } \varphi_{2i}(\mathbf{x}_{\tau i}) &\rightarrow \text{set } \mathcal{F}_2(\varphi_2) \\ &\equiv \text{set } \Phi_{2i} \rightarrow \Phi_3 \rightarrow \mathcal{F}_3^{-1}(\Phi_3) \equiv \varphi_3(\mathbf{r}). \end{aligned} \quad (2.5.6.6)$$

Transition (2.5.6.2) or (2.5.6.6) from two-dimensional electron-microscope images (projections) to a three-dimensional structure allows one to consider the complex of methods of 3D reconstruction as three-dimensional electron microscopy. In this sense, electron microscopy is an analogue of methods of structure analysis of crystals and molecules providing their three-dimensional spatial structure. But in structure analysis with the use of X-rays, electrons, or neutrons the initial data are the data in reciprocal space $|\Phi_{2i}|$ in (2.5.6.6), while in electron microscopy this role is played by two-dimensional images $\varphi_{2i}(\mathbf{x})$ [(2.5.6.2), (2.5.6.6)] in real space.

In electron microscopy the 3D reconstruction methods are, mainly, used for studying biological structures (symmetric or asymmetric associations of biomacromolecules), the quaternary structure of proteins, the structures of muscles, spherical and rod-like viruses, bacteriophages, and ribosomes.

An exact reconstruction is possible if there is a continuous set of projections φ_τ corresponding to the motion of the vector $\tau(\theta, \psi)$ over any continuous line connecting the opposite points on the unit sphere (Fig. 2.5.6.2). This is evidenced by the fact that, in this case, the cross sections $\mathcal{F}_2$ which are perpendicular to τ in Fourier space (2.5.6.4) continuously fill the whole of its volume, *i.e.* give $\mathcal{F}_3(\varphi_3)$ (2.5.6.3) and thereby determine $\varphi_3(\mathbf{r}) = \mathcal{F}_3^{-1}(\Phi_3)$.

In reality, we always have a discrete (but not continuous) set of projections φ_{2i} . The set of φ_{2i} is, practically, obtained by the rotation of the specimen under the beam through various angles (Hoppe & Typke, 1979) or by imaging of the objects which are randomly oriented on the substrate at different angles (Kam, 1980; Van Heel, 1984). If the object has symmetry, one of its projections is equivalent to a certain number of different projections.

The object $\varphi_3(\mathbf{r})$ is finite in space. For function $\varphi_3(\mathbf{r})$ and any of its projections there holds the normalization condition

$$\Omega = \int \varphi_3(\mathbf{r}) dv_{\mathbf{r}} = \int \varphi_2(\mathbf{x}) d\mathbf{x} = \int \varphi_1(x) dx, \quad (2.5.6.7)$$

where Ω is the total 'weight' of the object described by the density distribution φ_3 . If one assumes that the density of an object is constant and that inside the object $\varphi = \text{constant} = 1$, and outside it $\varphi = 0$, then Ω is the volume of an object. The volume of an object, say, of molecules, viruses and so on, is usually known from data on the density or molecular mass.

2.5.6.2. Orthoaxial projection

In practice, an important case is where all the projection directions are orthogonal to a certain straight line: $\tau \perp z$ (Fig. 2.5.6.3). Here the axis of rotation or the axis of symmetry of an object is perpendicular to an electron beam. Then the three-dimensional problem is reduced to the two-dimensional one, since each cross section $\varphi_{2i}(\mathbf{x}, z = \text{constant})$ is represented by its one-dimensional projections. The direction of vector τ is defined by the rotational angle ψ of a specimen:

$$\varphi_1(x_{\psi i}) \equiv L^i(\psi_i) = \int \varphi_2(\mathbf{x}) d\tau_{\psi}; x_i \perp \tau_{\psi}. \quad (2.5.6.8)$$

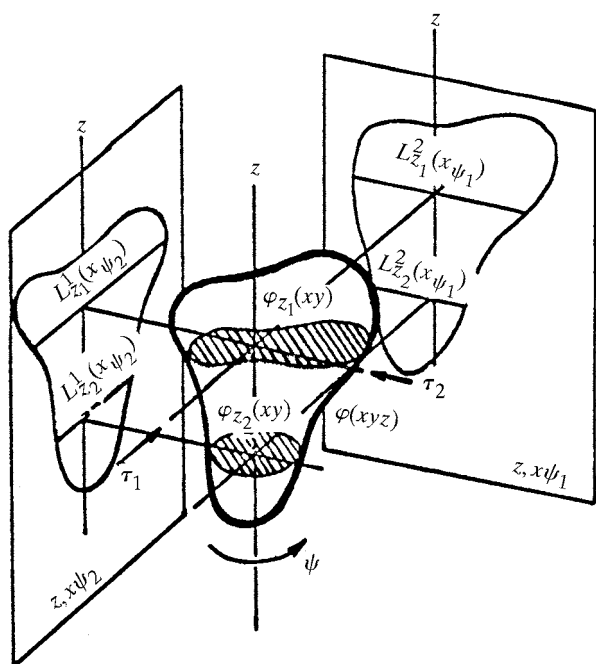


Fig. 2.5.6.3. Orthoaxial projection.

In this case, the reconstruction is carried out separately for each level z_l :

$$\text{set } \varphi_{1,z_l}(x\psi) \equiv \text{set } L^i_{z_l} \rightarrow \varphi_{2i}(xyz_l) \quad (2.5.6.9)$$

and the three-dimensional structure is obtained by superposition of layers $\varphi_{2i}(xy)\Delta z$ (Vainshtein *et al.*, 1968; Vainshtein, 1978).

2.5.6.3. Discretization

In direct methods of reconstruction as well as in Fourier methods the space is represented as a discrete set of points $\varphi(\mathbf{x}_{jk})$ on a two-dimensional net or $\varphi(\mathbf{r}_{jkl})$ on a three-dimensional lattice. It is sometimes expedient to use cylindrical or spherical coordinates. In two-dimensional reconstruction the one-dimensional projections are represented as a set of discrete values L^i , at a certain spacing in x_ψ . The reconstruction (2.5.6.9) is carried out over the discrete net with m^2 nodes φ_{jk} . The net side A should exceed the diameter of an object D , $A > D$; the spacing $a = A/m$. Then (2.5.6.8) transforms into the sum

$$L^i = \sum_k \varphi_{jk}. \quad (2.5.6.10)$$

For oblique projections the above sum is taken over all the points within the strips of width a along the axis τ_{ψ_i} (Fig. 2.5.6.4).

The resolution δ of the reconstructed function depends on the number h of the available projections. At approximately uniform angular distribution of projections, and diameter equal to D , the resolution at reconstruction is estimated as

$$\delta \simeq 2D/h. \quad (2.5.6.11)$$

The reconstruction resolution δ should be equal to or somewhat better than the instrumental resolution d of electron micrographs ($\delta < d$), the real resolution of the reconstructed structure being d . If the number of projections h is not sufficient, *i.e.* $\delta > d$, then the resolution of the reconstructed structure is δ (Crowther, DeRosier & Klug, 1970; Vainshtein, 1978).

In electron microscopy the typical instrumental resolution d of biological macromolecules for stained specimens is about 20 Å; at the object with diameter $D \simeq 200$ Å the sufficient number h of projections is about 20. If the projections are not uniformly

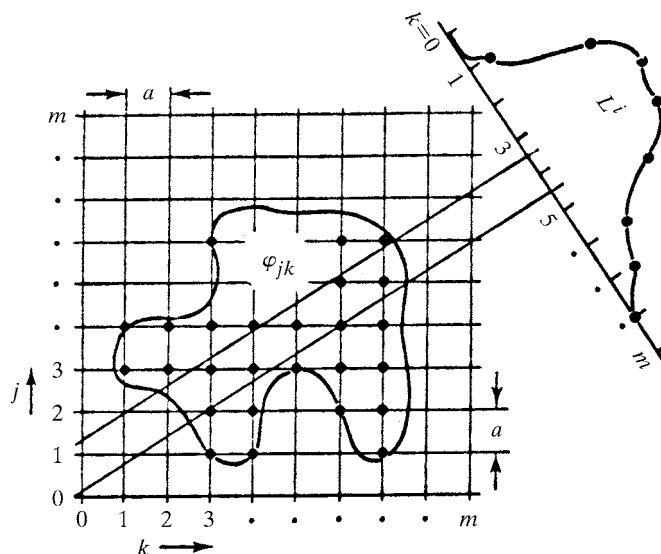


Fig. 2.5.6.4. Discretization and oblique projection.

distributed in projection angles, the resolution decreases towards $\mathbf{x} \perp \boldsymbol{\tau}$ for such $\boldsymbol{\tau}$ in which the number of projections is small.

Properties of projections of symmetric objects. If the object has an N -fold axis of rotation, its projection has the same symmetry. At orthoaxial projection perpendicular to the N -fold axis the projections which differ in angle at $j(2\pi/N)$ are identical:

$$\varphi_2(\mathbf{x}_\psi) = \varphi_2[\mathbf{x}_{\psi+j(2\pi/N)}] \quad (j = 1, 2, \dots, N). \quad (2.5.6.12)$$

This means that one of its projections is equivalent to N projections. If we have h independent projections of such a structure, the real number of projections is hN (Vainshtein, 1978). For a structure with cylindrical symmetry ($N = \infty$) one of its projections fully determines the three-dimensional structure.

Many biological objects possess helical symmetry – they transform into themselves by the screw displacement operation $s_{p/q}$, where p is the number of packing units in the helical structure per q turns of the continuous helix. In addition, the helical structures may also have the axis of symmetry N defining the pitch of the helix. In this case, a single projection is equivalent to $h = pN$ projections (Cochran *et al.*, 1952).

Individual protein molecules are described by point groups of symmetry of type N or $N/2$. Spherical viruses have icosahedral symmetry 532 with two-, three- and fivefold axes of symmetry. The relationship between vectors $\boldsymbol{\tau}$ of projections is determined by the transformation matrix of the corresponding point group (Crowther, Amos *et al.*, 1970).

2.5.6.4. Methods of direct reconstruction

Modelling. If several projections are available, and, especially, if the object is symmetric, one can, on the basis of spatial imagination, recreate approximately the three-dimensional model of the object under investigation. Then one can compare the projections of such a model with the observed projections, trying to draw them as near as possible. In early works on electron microscopy of biomolecules the tentative models of spatial structure were constructed in just this way; these models provide, in the case of the quaternary structure of protein molecules or the structure of viruses, schemes for the arrangement of protein subunits. Useful subsidiary information in this case can be obtained by the method of optical diffraction and filtration.

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

2.5.6.5. The method of back-projection

This method is also called the synthesis of projection functions. Let us consider a two-dimensional case and stretch along τ_{ψ_i} each one-dimensional projection L^i (Fig. 2.5.6.5) by a certain length b ; thus, we obtain the projection function

$$L^i(\mathbf{x}) = \frac{1}{b} L^i(x_i) \cdot 1(\tau_i). \quad (2.5.6.13)$$

Let us now superimpose h functions L^i

$$\sum_{i=1}^h L^i(\mathbf{x}) = \Sigma_2(\mathbf{x}). \quad (2.5.6.14)$$

The continuous sum over the angles of projection synthesis is

$$\begin{aligned} \Sigma_2(\mathbf{x}) &= \int_0^\pi L(\psi, \mathbf{x}) d\psi = \rho_2(\mathbf{x}) * |\mathbf{x}|^{-1} \\ &\simeq \sum_{i=1}^h L^i = \rho_2(\mathbf{x}) + B(1); \end{aligned} \quad (2.5.6.15)$$

this is the convolution of the initial function with a rapidly falling function $|\mathbf{x}|^{-1}$ (Vainshtein, 1971b). In (2.5.6.15), the approximation for a discrete set of h projections is also written. Since the function $|\mathbf{x}|^{-1}$ approaches infinity at $x = 0$, the convolution with it will reproduce the initial function $\rho(\mathbf{x})$, but with some background B decreasing around each point according to the law $|\mathbf{x}|^{-1}$. At orthoaxial projection the superposition of cross sections $\varphi_2(\mathbf{x}, z_k)$ arranged in a pile gives the three-dimensional structure φ_3 .

Radon operator. Radon (1917; see also Deans, 1983) gave the exact solution of the problem of reconstruction. However, his mathematical work was for a long time unknown to investigators engaged in reconstruction of a structure from images; only in the early 1970s did some authors obtain results analogous to Radon's (Ramachandran & Lakshminarayanan, 1971; Vainshtein & Orlov, 1972, 1974; Gilbert, 1972a).

The convolution in (2.5.6.15) may be eliminated using the Radon integral operator, which modifies projections by introducing around each point the negative values which annihilate on superposition the positive background values. The one-dimensional projection modified with the aid of the Radon operator has the form

$$\tilde{L}(x_\psi) = \frac{1}{2\pi^2} \int_0^\infty \frac{2L(x_\psi) - L(x_\psi + x'_\psi) - L(x_\psi - x'_\psi)}{x'^2_\psi} dx'_\psi. \quad (2.5.6.16)$$

Now $\varphi_2(\mathbf{x})$ is calculated analogously to (2.5.6.14), not from the initial projections L but from the modified projection $\tilde{L}$:

$$\varphi_2(\mathbf{x}) = \int_0^\pi \tilde{L}(\psi, \mathbf{x}) d\psi \simeq \sum_{i=1}^k \tilde{L}_i(\psi_i, \mathbf{x}). \quad (2.5.6.17)$$

The reconstruction of high-symmetry structures, in particular helical ones, by the direct method is carried out from one projection making use of its equivalence to many projections. The Radon formula in discrete form can be obtained using the double Fourier transformation and convolution (Ramachandran & Lakshminarayanan, 1971).

2.5.6.6. The algebraic and iteration methods

These methods have been derived for the two-dimensional case; consequently, they can also be applied to three-dimensional reconstruction in the case of orthoaxial projection.

Let us discretize $\varphi_2(\mathbf{x})$ by a net m^2 of points φ_{jk} ; then we can construct the system of equations (2.5.6.10).

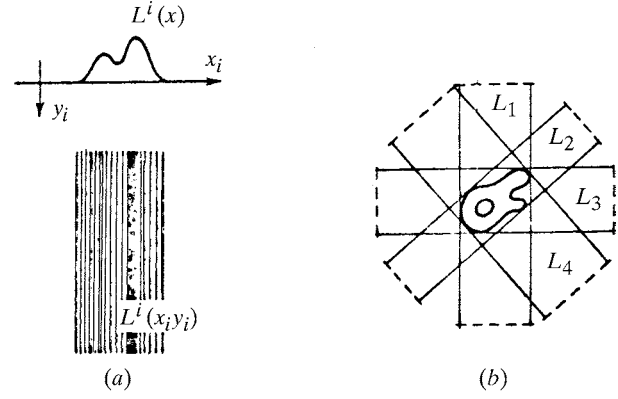


Fig. 2.5.6.5. (a) Formation of a projection function; (b) superposition of these functions.

When h projections are available the condition of unambiguous solution of system (2.5.6.10) is: $h \geq m$. At $m \simeq (3-5)h$ we can, in practice, obtain sufficiently good results (Vainshtein, 1978).

Methods of reconstruction by iteration have also been derived that cause some initial distribution to approach one $\varphi_2(\mathbf{x})$ satisfying the condition that its projection will resemble the set L^i . Let us assign on a discrete net φ_{jk} as a zero-order approximation the uniform distribution of mean values (2.5.6.7)

$$\varphi_{jk}^0 = \langle \varphi \rangle = \Omega/m^2. \quad (2.5.6.18)$$

The projection of the q th approximation φ_{jk}^q at the angle φ_i (used to account for discreteness) is L_n^{iq} .

The next approximation φ_{jk}^{q+1} for each point jk is given in the method of 'summation' by the formula

$$\varphi_{jk}^{q+1} = \max[\varphi_{jk}^q + (L_n^i - L_n^{i,q})/N_{L_n}^i; 0], \quad (2.5.6.19)$$

where $N_{L_n^i}$ is the number of points in a strip of the projection L_n^i . One cycle of iterations involves running φ_{jk}^q around all of the angles ψ_j (Gordon *et al.*, 1970).

When carrying out iterations, we may take into account the contribution not only of the given projection, but also of all others. In this method the process of convergence improves. Some other iteration methods have been elaborated (Gordon & Herman, 1971; Gilbert, 1972b; Crowther & Klug, 1974; Gordon, 1974).

2.5.6.7. Reconstruction using Fourier transformation

This method is based on the Fourier projection theorem [(2.5.6.3)–(2.5.6.5)]. The reconstruction is carried out according to scheme (2.5.6.6) (DeRosier & Klug, 1968; Crowther, DeRosier & Klug, 1970; Crowther, Amos *et al.* 1970; DeRosier & Moore, 1970; Orlov, 1975). The three-dimensional Fourier transform $\mathcal{F}_3(\mathbf{u})$ is found from a set of two-dimensional cross sections $\mathcal{F}_2(\mathbf{u})$ on the basis of the Whittaker–Shannon interpolation. If the object has helical symmetry (which often occurs in electron microscopy of biological objects, *e.g.* on investigating bacteriophage tails, muscle proteins) cylindrical coordinates are used. Diffraction from such structures with c periodicity and scattering density $\varphi(r, \psi, z)$ is defined by the Fourier–Bessel transform:

$$\begin{aligned} \Phi(R, \Psi, Z) &= \sum_{n=-\infty}^{+\infty} \exp\left[in\left(\Psi + \frac{\pi}{2}\right)\right] \int_0^\infty \int_0^{2\pi} \int_0^l \varphi(r, \psi, z) \\ &\quad \times J_n(2\pi r R) \exp[-i(n\psi + 2\pi z Z)] r dr d\psi dz \\ &= \sum_n G_n(R, Z) \exp\left[in\left(\Psi + \frac{\pi}{2}\right)\right]. \end{aligned} \quad (2.5.6.20)$$

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The inverse transformation has the form

$$\rho(r, \psi, z) = \sum_n \int g_n(r, Z) \exp(in\psi) \exp(2\pi izZ) dZ, \quad (2.5.6.21)$$

so that g_n and G_n are the mutual Bessel transforms

$$G_n(R, Z) = \int_0^\infty g_n(rZ) J_n(2\pi rR) 2\pi r dr \quad (2.5.6.22)$$

$$g_n(r, Z) = \int_0^\infty G_n(R, Z) J_n(2\pi rR) 2\pi R dR. \quad (2.5.6.23)$$

Owing to helical symmetry, (2.5.6.22), (2.5.6.23) contain only those of the Bessel functions which satisfy the selection rule (Cochran *et al.*, 1952)

$$l = mp + (nq/N), \quad (2.5.6.24)$$

where N , q and p are the helix symmetry parameters, $m = 0, \pm 1, \pm 2, \dots$. Each layer l is practically determined by the single function J_n with the lowest n ; the contribution of other functions is neglected. Thus, the Fourier transformation of one projection of a helical structure, with an account of symmetry and phases, gives the three-dimensional transform (2.5.6.23). We can introduce into this transform the function of temperature-factor type filtering the 'noise' from large spatial frequencies.

2.5.6.8. Three-dimensional reconstruction in the general case

In the general case of 3D reconstruction $\varphi_3(\mathbf{r})$ from projections $\varphi_2(\mathbf{x}_\tau)$ the projection vector τ occupies arbitrary positions on the projection sphere (Fig. 2.5.6.2). Then, as in (2.5.6.15), we can construct the three-dimensional spatial synthesis. To do this, let us transform the two-dimensional projections $\varphi_{2i}[\mathbf{x}, \tau(\theta, \psi)_i]$ by extending them along τ as in (2.5.6.13) into three-dimensional projection functions $\varphi_3(\mathbf{r}_{\tau_i})$.

Analogously to (2.5.6.15), such a three-dimensional synthesis is the integral over the hemisphere (Fig. 2.5.6.2)

$$\begin{aligned} \Sigma_3(\mathbf{r}) &= \int_\omega \varphi_3(\mathbf{r}, \tau_i) d\omega_\tau = \varphi(\mathbf{r}) * |\mathbf{r}|^{-2} \\ &\simeq \Sigma \varphi_{3i}[\mathbf{r}_{\tau(\theta, \psi)_i}] \simeq \varphi_3(\mathbf{r}) + B; \end{aligned} \quad (2.5.6.25)$$

this is the convolution of the initial function with $|\mathbf{r}|^{-2}$ (Vainshtein, 1971b).

To obtain the exact reconstruction of $\varphi_3(\mathbf{r})$ we find, from each $\varphi_2(\mathbf{x}_\tau)$, the modified projection (Vainshtein & Orlov, 1974; Orlov, 1975)

$$\tilde{\varphi}_2(\mathbf{x}_\tau) = \int \frac{\varphi_2(\mathbf{x}_\tau) - \varphi_2(\mathbf{x}'_\tau)}{|\mathbf{x}_\tau - \mathbf{x}'_\tau|^3} ds_{\mathbf{x}'}. \quad (2.5.6.26)$$

By extending $\varphi_2(\mathbf{x}_\tau)$ along τ we transform them into $\tilde{\varphi}_3(\mathbf{r}_\tau)$. Now the synthesis over the angles $\omega_\tau = (\theta, \psi, \alpha)_\tau$ gives the three-dimensional function

$$\varphi_3(\mathbf{r}) = \frac{1}{4\pi^3} \int \tilde{\varphi}_3(\mathbf{r}_\tau) d\omega_\tau \simeq \sum_i \tilde{\varphi}_{3i}[\mathbf{r}_{\tau(\theta, \psi, \alpha)_i}]. \quad (2.5.6.27)$$

The approximation for a discrete set of angles is written on the right. In this case we are not bound by the coaxial projection condition which endows the experiment with greater possibilities; the use of object symmetry also profits from this. To carry out the 3D reconstruction (2.5.6.25) or (2.5.6.27) one should know all three Euler's angles ψ, θ, α (Fig. 2.5.6.2).

The projection vectors τ_i should be distributed more or less uniformly over the sphere (Fig. 2.5.6.2). This can be achieved by using special goniometric devices.

Another possibility is the investigation of particles which, during the specimen preparation, are randomly oriented on the substrate. This, in particular, refers to asymmetric ribosomal particles. In this case the problem of determining these orientations arises.

The method of spatial correlation functions may be applied if a large number of projections with uniformly distributed projection directions is available (Kam, 1980). The space correlation function is the averaged characteristic of projections over all possible directions which is calculated from the initial projections or the corresponding sections of the Fourier transform. It can be used to find the coefficients of the object density function expansion over spherical harmonics, as well as to carry out the 3D reconstruction in spherical coordinates.

Another method (Van Heel, 1984) involves the statistical analysis of image types, subdivision of images into several classes and image averaging inside the classes. Then, if the object is rotated around some axis, the 3D reconstruction is carried out by the iteration method.

If such a specimen is inclined at a certain angle with respect to the beam, then the images of particles in the preferred orientation make a series of projections inclined at an angle β and having a random azimuth. The azimuthal rotation is determined from the image having zero inclination.

If particles on the substrate have a characteristic shape, they may acquire a preferable orientation with respect to the substrate, their azimuthal orientation α being random (Radermacher *et al.*, 1987).

In the general case, the problem of determining the spatial orientations of randomly distributed identical three-dimensional particles $\varphi_3(\mathbf{r})$ with an unknown structure may be solved by measuring their two-dimensional projections $p(\mathbf{x}_\tau)$ (Fig. 2.5.6.1)

$$p(\mathbf{x}_{\tau_i}) \equiv \varphi_2(\mathbf{x}_{\tau_i}) \simeq \int \varphi_3(\mathbf{r}) d\tau_i \quad \mathbf{x} \perp \tau_i; \quad (2.5.6.1a)$$

if the number i of such projections is not less than three, $i \geq 3$ (Vainshtein & Goncharov, 1986a,b; Goncharov *et al.* 1987; Goncharov, 1987). The direction of the vector τ_i along which the projection $p(\tau_i)$ is obtained is set by the angle $\omega_i(\theta_i, \psi_i)$ (Fig. 2.5.6.2).

The method is based on the analysis of one-dimensional projections q_α of two-dimensional projections $p(\mathbf{x}_{\tau_i})$

$$q(x_{\perp\alpha}) = \int p(\mathbf{x}_{\tau_i}) dx_{\parallel\alpha}, \quad (2.5.6.28)$$

where α is the angle of the rotation about vector τ in the p plane.

Lemma 1. Any two projections $p_1(\mathbf{x}_{\tau_1})$ and $p_2(\mathbf{x}_{\tau_2})$ (Fig. 2.5.6.6) have common (identical) one-dimensional projections $q_{12}(x_{12})$:

$$q_{12}(x_{12}) = q_{1, \alpha_{1j}}(x_{\perp\alpha_{1j}}) = q_{2, \alpha_{2k}}(x_{\perp\alpha_{2k}}). \quad (2.5.6.29)$$

Vectors τ_1 and τ_2 (Fig. 2.5.6.3) determine plane h in which they are both lying. Vector $m_{12} = \langle \tau_1 \tau_2 \rangle$ is normal to plane h and parallel to axis x_{12} of the one-dimensional projection q_{12} ; both $x_{\perp\alpha_{1j}}$ and $x_{\perp\alpha_{2k}}$ axes along which the projections q_1 and q_2 are constructed are perpendicular to x_{12} .

The corresponding lemma in the Fourier space states:

Lemma 2. Any two plane transforms, $\Phi_2(\mathbf{u}_{\tau_1}) = \mathcal{F}_2 p_1$ and $\Phi_2(\mathbf{u}_{\tau_2}) = \mathcal{F}_2 p_2$ intersect along the straight line v_{12} (Fig. 2.5.6.7); the one-dimensional transform $Q(v_{12})$ is the transform of $q_{12} : Q(v_{12}) = \mathcal{F}_1 q_{12}$.

Thus in order to determine the orientations $\omega_i(\theta_i, \psi_i, \alpha_i)$ of a three-dimensional particle $\varphi_{3, \omega_i}(\mathbf{r})$ it is necessary either to use projections p_i in real space or else to pass to the Fourier space (2.5.6.5).

Now consider real space. The projections p_i are known and can be measured but angles α_{ij} of their rotation about vector τ_i (Fig. 2.5.6.8) are unknown and should be determined. Let us choose any two projections p_1 and p_2 and construct a set of one-dimensional projections $q_{1, \alpha_{1j}}$ and $q_{2, \alpha_{2k}}$ by varying angles α_{1j} and α_{2k} . In

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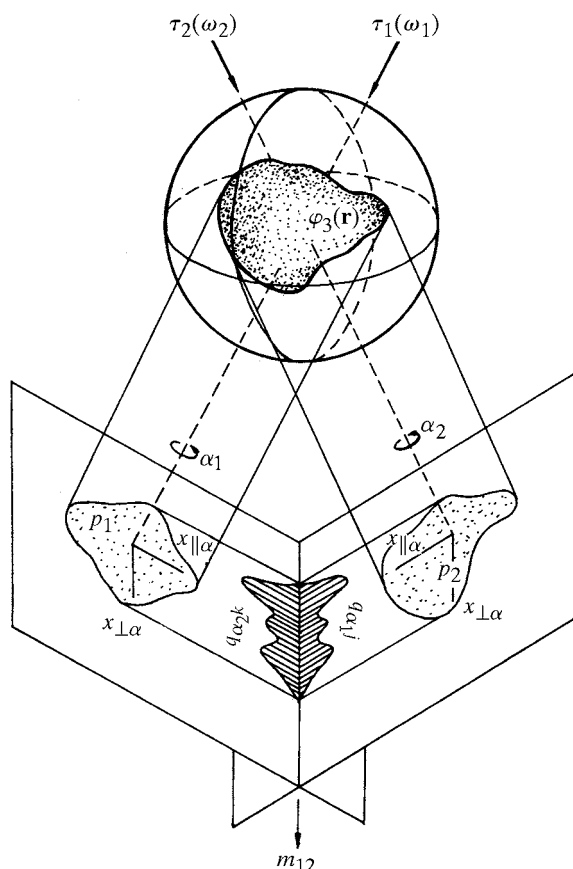


Fig. 2.5.6.6. Relative position of the particle and planes of projection.

accordance with *Lemma 1*, there exists a one-dimensional projection, common for both p_1 and p_2 , which determines angles α_{1j} and α_{2k} along which p_1 and p_2 should be projected for obtaining the identical projection q_{12} (Fig. 2.5.6.5). Comparing $q_{1, \alpha_{1j}}$ and $q_{2, \alpha_{2k}}$ and using the minimizing function

$$D(1, 2) = |q_{1, \alpha_{1j}} - q_{2, \alpha_{2k}}|^2 \quad (2.5.6.30)$$

it is possible to find such a common projection q_{12} . (A similar consideration in Fourier space yields Q_{12} .)

The mutual spatial orientations of any three non-coplanar projection vectors τ_1, τ_2, τ_3 can be found from three different two-dimensional projections p_1, p_2 and p_3 by comparing the following pairs of projections: p_1 and p_2 , p_1 and p_3 , and p_2 and

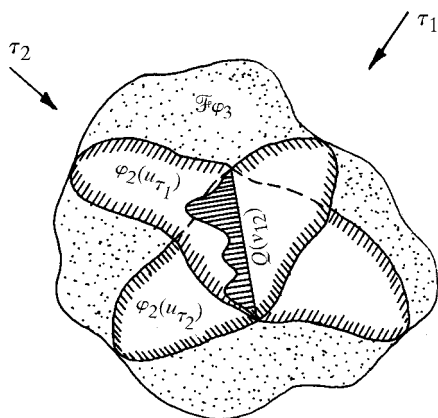


Fig. 2.5.6.7. Section of a three-dimensional Fourier transform of the density of the particles, corresponding to plane projections of this density.

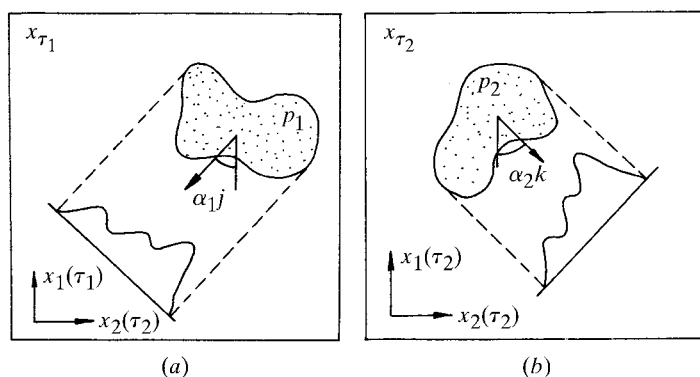


Fig. 2.5.6.8. Plane projections of a three-dimensional body. The systems of coordinates in planes (a) and (b) are chosen independently of one another.

p_3 , and by determining the corresponding q_{12}, q_{13} and q_{23} . The determination of angles ω_1, ω_2 and ω_3 reduces to the construction of a trihedral angle formed by planes h_{12}, h_{13} and h_{23} . Then the projections $p_i(\omega_i)$ with the known ω_i ($i = 1, 2, 3$) can be complemented with other projections ($i = 4, 5, \dots$) and the corresponding values of ω can be determined. Having a sufficient number of projections and knowing the orientations ω_i , it is possible to carry out the 3D reconstruction of the object [see (2.5.6.27); Orlov, 1975; Vainshtein & Goncharov, 1986a; Goncharov *et al.*, 1987].

2.5.7. Direct phase determination in electron crystallography (D. L. DORSET)

2.5.7.1. Problems with 'traditional' phasing techniques

The concept of using experimental electron-diffraction intensities for quantitative crystal structure analyses has already been presented in Section 2.5.4. Another aspect of quantitative structure analysis, employing high-resolution images, has been presented in Sections 2.5.5 and 2.5.6. That is to say, electron micrographs can be regarded as an independent source of crystallographic phases.

Before direct methods (Chapter 2.2) were developed as the standard technique for structure determination in small-molecule X-ray crystallography, there were two principal approaches to solving the crystallographic phase problem. First, 'trial and error' was used, finding some means to construct a reasonable model for the crystal structure *a priori*, e.g. by matching symmetry properties shared by the point group of the molecule or atomic cluster and the unit-cell space group. Secondly, the autocorrelation function of the crystal, known as the Patterson function (Chapter 2.3), was calculated (by the direct Fourier transform of the available intensity data) to locate salient interatomic vectors within the unit cell.

The same techniques had been used for electron-diffraction structure analysis (nowadays known as *electron crystallography*). In fact, advocacy of the first method persists. Because of the perturbations of diffracted intensities by multiple-beam dynamical scattering (Chapter 5.2), it has often been suggested that trial and error be used to construct the scattering model for the unit crystal in order to test its convergence to observed data after simulation of the scattering events through the crystal. This indirect approach assumes that no information about the crystal structure can be obtained directly from observed intensity data. Under more favourable scattering conditions nearer to the kinematical approximation, *i.e.* for experimental data from thin crystals made up of light atoms, trial and error modelling, simultaneously minimizing an atom-atom nonbonded potential function with the crystal-

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lographic residual, has enjoyed widespread use in electron crystallography, especially for the determination of linear polymer structures (Brisse, 1989; Pérez & Chanzy, 1989).

Interpretation of Patterson maps has also been important for structure analysis in electron crystallography. Applications have been discussed by Vainshtein (1964), Zvyagin (1967) and Dorset (1994a). In face of the dynamical scattering effects for electron scattering from heavy-atom crystals realized later (*e.g.* Cowley & Moodie, 1959), attempts had also been made to modify this autocorrelation function by using a power series in $|F_h|$ to sharpen the peaks (Cowley, 1956). (Here $F_h \equiv \Phi_h$, replacing the notation for the kinematical electron-diffraction structure factor employed in Section 2.5.4.) More recently, Vincent and co-workers have selected first-order-Laue-zone data from inorganics to minimize the effect of dynamical scattering on the interpretability of their Patterson maps (Vincent & Exelby, 1991, 1993; Vincent & Midgley, 1994). Vainshtein & Klechkovskaya (1993) have also reported use of the Patterson function to solve the crystal structure of a lead soap from texture electron-diffraction intensity data.

It is apparent that trial-and-error techniques are most appropriate for *ab initio* structure analysis when the underlying crystal structures are reasonably easy to model. The requisite positioning of molecular (or atomic) groups within the unit cell may be facilitated by finding atoms that fit a special symmetry position [see IT A (1995)]. Alternatively, it is helpful to know the molecular orientation within the unit cell (*e.g.* provided by the Patterson function) to allow the model to be positioned for a conformational or translational search. [Examples would include the polymer-structure analyses cited above, as well as the layer-packing analysis of some phospholipids (Dorset, 1987).] While attempts at *ab initio* modelling of three-dimensional crystal structures, by searching an n -dimensional parameter space and seeking a global internal energy minimum, has remained an active research area, most success so far seems to have been realized with the prediction of two-dimensional layers (Scaringe, 1992). In general, for complicated unit cells, determination of a structure by trial and error is very difficult unless adequate constraints can be placed on the search.

Although Patterson techniques have been very useful in electron crystallography, there are also inherent difficulties in their use, particularly for locating heavy atoms. As will be appreciated from comparison of scattering-factor tables for X-rays [IT C (1999) Chapter 6.1] with those for electrons, [IT C (1999) Chapter 4.3] the relative values of the electron form factors are more compressed with respect to atomic number than are those for X-ray scattering. As discussed in Chapter 2.3, it is desirable that the ratio of summed scattering factor terms, $r = \sum_{\text{heavy}} Z^2 / \sum_{\text{light}} Z^2$, where Z is the scattering factor value at $\sin \theta / \lambda = 0$, be near unity. A practical comparison would be the value of r for copper (DL-alaninate) solved from electron-diffraction data by Vainshtein *et al.* (1971). For electron diffraction, $r = 0.47$ compared to the value 2.36 for X-ray diffraction. Orientation of salient structural features, such as chains and rings, would be equally useful for light-atom moieties in electron or X-ray crystallography with Patterson techniques. As structures become more complicated, interpretation of Patterson maps becomes more and more difficult unless an automated search can be carried out against a known structural fragment (Chapter 2.3).

2.5.7.2. Direct phase determination from electron micrographs

The 'direct method' most familiar to the electron microscopist is the high-resolution electron micrograph of a crystalline lattice. Retrieval of an average structure from such a micrograph assumes that the experimental image conforms adequately to the 'weak phase object' approximation, as discussed in Section 2.5.5. If this is

so, the use of image-averaging techniques, *e.g.* Fourier filtration or correlational alignment, will allow the unit-cell contents to be visualized after the electron-microscope phase contrast transfer function is deconvoluted from the average image, also discussed in Section 2.5.5. Image analyses can also be extended to three dimensions, as discussed in Section 2.5.6, basically by employing tomographic reconstruction techniques to combine information from the several tilt projections taken from the crystalline object. The potential distribution of the unit cell to the resolution of the imaging experiment can then be used, *via* the Fourier transform, to obtain crystallographic phases for the electron-diffraction amplitudes recorded at the same resolution. This method for phase determination has been the mainstay of protein electron crystallography.

Once a set of phases is obtained from the Fourier transform of the deconvoluted image, they must, however, be referred to an allowed crystallographic origin. For many crystallographic space groups, this choice of origin may coincide with the location of a major symmetry element in the unit cell [see IT A (1995)]. Hence, since the Fourier transform of translation is a phase term, if an image shift $[\delta(\mathbf{r} + \mathbf{r}_0)]$ is required to translate the origin of the repeating mass unit $\varphi(\mathbf{r})$ from the arbitrary position in the image to a specific site allowed by the space group,

$$g(\mathbf{r}) = \varphi(\mathbf{r}) \otimes \delta(\mathbf{r} + \mathbf{r}_0) = \varphi(\mathbf{r} + \mathbf{r}_0),$$

where the operation ' $\otimes$ ' denotes convolution. The Fourier transform of this shifted density function will be

$$G(\mathbf{s}) = F(\mathbf{s}) \exp(2\pi i \mathbf{s} \cdot \mathbf{r}_0) = |F(\mathbf{s})| \exp[i(\phi_s + 2\pi i \mathbf{s} \cdot \mathbf{r}_0)].$$

In addition to the crystallographic phases ϕ_s , it will, therefore, be necessary to find the additional phase-shift term $2\pi i \mathbf{s} \cdot \mathbf{r}_0$ that will access an allowed unit-cell origin. Such origin searches are carried out automatically by some commercial image-averaging computer-software packages.

In addition to applications to thin protein crystals (*e.g.* Henderson *et al.*, 1990; Jap *et al.*, 1991; Kühlbrandt *et al.*, 1994), there are numerous examples of molecular crystals that have been imaged to a resolution of 3–4 Å, many of which have been discussed by Fryer (1993). For π -delocalized compounds, which are the most stable in the electron beam against radiation damage, the best results (2 Å resolution) have been obtained at 500 kV from copper perchlorophthalocyanine epitaxially crystallized onto KCl. As shown by Uyeda *et al.* (1978–1979), the averaged images clearly depict the positions of the heavy Cu and Cl atoms, while the positions of the light atoms in the organic residue are not resolved. (The utility of image-derived phases as a basis set for phase extension will be discussed below.) A number of aromatic polymer crystals have also been imaged to about 3 Å resolution, as reviewed recently (Tsuji, 1989; Dorset, 1994b).

Aliphatic molecular crystals are much more difficult to study because of their increased radiation sensitivity. Nevertheless, monolamellar crystals of the paraffin n -C₄₄H₉₀ have been imaged to 2.5 Å resolution with a liquid-helium cryomicroscope (Zemlin *et al.*, 1985). Similar images have been obtained at room temperature from polyethylene (Revol & Manley, 1986) and also a number of other aliphatic polymer crystals (Revol, 1991).

As noted by J. M. Cowley in Section 2.5.1, dynamical scattering can pose a significant barrier to the direct interpretation of high-resolution images from many inorganic materials. Nevertheless, with adequate control of experimental conditions (limiting crystal thickness, use of high-voltage electrons) some progress has been made. Pan & Crozier (1993) have described 2.0 Å images from zeolites in terms of the phase-grating approximation. A three-dimensional structural study has been carried out on an aluminosilicate by Wenk *et al.* (1992) with thin samples that

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conform to the weak-phase-object approximation at the 800 kV used for the imaging experiment. Heavy and light (*e.g.* oxygen) atoms were located in the micrographs in good agreement with an X-ray crystal structure. Heavy-atom positions from electron microscopic and X-ray structure analyses have also been favourably compared for two heavy-metal oxides (Hovmöller *et al.*, 1984; Li & Hovmöller, 1988).

2.5.7.3. Probabilistic estimate of phase invariant sums

Conventional direct phasing techniques, as commonly employed in X-ray crystallography (*e.g.* see Chapter 2.2), have also been used for *ab initio* electron-crystallographic analyses. As in X-ray crystallography, probabilistic estimates of a linear combination of phases (Hauptman & Karle, 1953; Hauptman, 1972) are made after normalized structure factors are calculated *via* electron form factors, *i.e.*

$$|E_{\mathbf{h}}^2| = I_{\text{obs}}/\varepsilon \sum_i f_i^2, \text{ where } \langle |E|^2 \rangle = 1.000.$$

(Here, an overall temperature factor can be found from a Wilson plot. Because of multiple scattering, the value of B may be found occasionally to lie close to $0.0 \text{ \AA}^2$.) The phase invariant sums

$$\psi = \phi_{\mathbf{h}_1} + \phi_{\mathbf{h}_2} + \phi_{\mathbf{h}_3} + \dots$$

can be particularly effective for structure analysis. Of particular importance historically have been the Σ_2 -triple invariants where $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0$ and $\mathbf{h}_1 \neq \mathbf{h}_2 \neq \mathbf{h}_3$. The probability of predicting $\psi = 0$ is directly related to the value of

$$A = (2\sigma_3/\sigma_2^{3/2})|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|,$$

where $\sigma_{\mathbf{h}} = \sum_{j=1}^N Z_j^n$ and Z is the value of the scattering factor at $\sin \theta/\lambda = 0$. Thus, the values of the phases are related to the measured structure factors, just as they are found to be in X-ray crystallography. The normalization described above imposes the point-atom structure (compensating for the fall-off of an approximately Gaussian form factor) often assumed in deriving the joint probability distributions. Especially for van der Waals structures, the constraint of positivity also holds in electron crystallography. (It is also quite useful for charged atoms so long as the reflections are not measured at very low angles.) Other useful phase invariant sums are the Σ_1 triples, where $\mathbf{h}_1 = \mathbf{h}_2 = -1/2\mathbf{h}_3$, and the quartets, where $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 + \mathbf{h}_4 = 0$ and $\mathbf{h}_1 \neq \mathbf{h}_2 \neq \mathbf{h}_3 \neq \mathbf{h}_4$. The prediction of a correct phase for an invariant is related in each case to the normalized structure-factor magnitudes.

The procedure for phase determination, therefore, is identical to the one used in X-ray crystallography (see Chapter 2.2). Using vectorial combinations of Miller indices, one generates triple and quartet invariants from available measured data and ranks them according to parameters such as A , defined above, which, as shown in Chapter 2.2, are arguments of the Cochran formula. The invariants are thus listed in order of their reliability. This, in fact, generates a set of simultaneous equations in crystallographic phase. In order to begin solving these equations, it is permissible to define arbitrarily the phase values of a limited number of reflections (three for a three-dimensional primitive unit cell) for reflections with Miller-index parity $hkl \neq ggg$ and $\sum_i h_i k_i l_i \neq ggg$, where g is an even number. This defines the origin of a unit cell. For noncentrosymmetric unit cells, the condition for defining the origin, which depends on the space group, is somewhat more complicated and an enantiomorph-defining reflection must be added.

In the evaluation of phase-invariant sums above a certain probability threshold, phase values are determined algebraically after origin (and enantiomorph) definition until a large enough set is obtained to permit calculation of an interpretable potential map (*i.e.*

where atomic positions can be seen). There may be a few invariant phase sums above this threshold probability value which are incorrectly predicted, leading either to false phase assignments or at least to phase assignments inconsistent with those found from other invariants. A small number of such errors can generally be tolerated. Another problem arises when an insufficient quantity of new phase values is assigned directly from the phase invariants after the origin-defining phases are defined. This difficulty may occur for small data sets, for example. If this is the case, it is possible that a new reflection of proper index parity can be used to define the origin. Alternatively, $\phi_n = a, b, c \dots$ algebraic unknowns can be used to establish the phase linkage among certain reflections. If the structure is centrosymmetric, and when enough reflections are given at least symbolic phase assignments, 2^n maps are calculated and the correct structure is identified by inspection of the potential maps. When all goes well in this so-called 'symbolic addition' procedure, the symbols are uniquely determined and there is no need to calculate more than a single map. If algebraic values are retained for certain phases because of limited vectorial connections in the data set, then a few maps may need to be generated so that the correct structure can be identified using the chemical knowledge of the investigator. The atomic positions identified can then be used to calculate phases for all observed data (*via* the structure-factor calculation) and the structure can be refined by Fourier (or, sometimes, least-squares) techniques to minimize the crystallographic R factor.

The first actual application of direct phasing techniques to experimental electron-diffraction data, based on symbolic addition procedures, was to two methylene subcell structures (an n -paraffin and a phospholipid; Dorset & Hauptman, 1976). Since then, evaluation of phase invariants has led to numerous other structures. For example, early texture electron-diffraction data sets obtained in Moscow (Vainshtein, 1964) were shown to be suitable for direct analysis. The structure of diketopiperazine (Dorset, 1991a) was determined from these electron-diffraction data (Vainshtein, 1955) when directly determined phases allowed computation of potential maps such as the one shown in Fig. 2.5.7.1. Bond distances and angles are in good agreement with the X-ray structure, particularly after least-squares refinement (Dorset & McCourt, 1994a). In addition, the structures of urea (Dorset, 1991b), using data published by Lobachev & Vainshtein (1961), paraelectric thiourea (Dorset, 1991b), using data published by Dvoryankin & Vainshtein (1960), and three mineral structures (Dorset, 1992a), from data published by Zvyagin (1967), have been determined, all using the original texture (or mosaic single-crystal) diffraction data. The most recent determination based on such texture diffraction data is that of basic copper chloride (Voronova & Vainshtein, 1958; Dorset, 1994c).

Symbolic addition has also been used to assign phases to selected-area diffraction data. The crystal structure of boric acid (Cowley, 1953) has been redetermined, adding an independent low-temperature analysis (Dorset, 1992b). Additionally, a direct structure analysis has been reported for graphite, based on high-voltage intensity data (Ogawa *et al.*, 1994). Two-dimensional data from several polymer structures have also been analysed successfully (Dorset, 1992c) as have three-dimensional intensity data (Dorset, 1991c,d; Dorset & McCourt, 1993).

Phase information from electron micrographs has also been used to aid phase determination by symbolic addition. Examples include the epitaxially oriented paraffins n -hexatriacontane (Dorset & Zemlin, 1990), n -tritriacontane (Dorset & Zhang, 1991) and a 1:1 solid solution of $n\text{-C}_{32}\text{H}_{66}/n\text{-C}_{36}\text{H}_{74}$ (Dorset, 1990a). Similarly, lamellar electron-diffraction data to *ca* $3 \text{ \AA}$ resolution from epitaxially oriented phospholipids have been phased by analysis of Σ_1 and Σ_2 -triplet invariants (Dorset, 1990b, 1991e,f), in one case combined with values from a $6 \text{ \AA}$ resolution electron

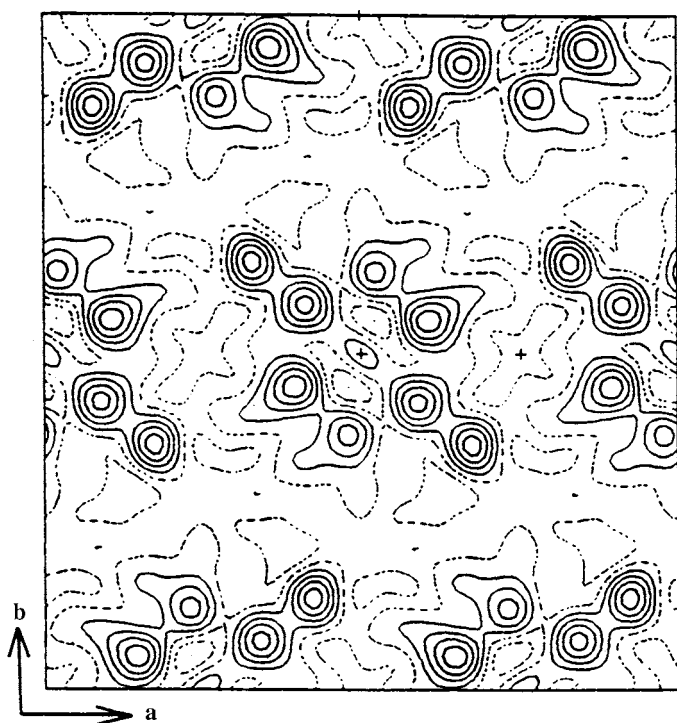


Fig. 2.5.7.1. Potential map for diketopiperazine ([001] projection) after a direct phase determination with texture electron-diffraction intensity data obtained originally by Vainshtein (1955).

microscope image (Dorset *et al.*, 1990, 1993). Most recently, such data have been used to determine the layer packing of a phospholipid binary solid solution (Dorset, 1994d).

An *ab initio* direct phase analysis was carried out with zonal electron-diffraction data from copper perchlorophthalocyanine. Using intensities from a *ca* 100 Å thick sample collected at 1.2 MeV, the best map from a phase set with symbolic unknowns retrieves the positions of all the heavy atoms, equivalent to the results of the best images (Uyeda *et al.*, 1978–1979). Using these positions to calculate an initial phase set, the positions of the remaining light C, N atoms were found by Fourier refinement so that the final bond distances and angles were in good agreement with those from X-ray structures of similar compounds (Dorset *et al.*, 1991). A similar analysis has been carried out for the perbromo analogue (Dorset *et al.*, 1992). Although dynamical scattering and secondary scattering significantly perturb the observed intensity data, the total molecular structure can be visualized after a Fourier refinement. Most recently, a three-dimensional structure determination was reported for C₆₀ buckminsterfullerene based on symbolic addition with results most in accord with a rotationally disordered molecular packing (Dorset & McCourt, 1994b).

2.5.7.4. The tangent formula

Given a triple phase relationship

$$\phi_{\mathbf{h}} \simeq \phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}},$$

where $\mathbf{h}$, $\mathbf{k}$ and $\mathbf{h} - \mathbf{k}$ form a vector sum, it is often possible to find a more reliable estimate of $\phi_{\mathbf{h}}$ when all the possible vectorial contributions to it within the observed data set $\mathbf{k}_r$ are considered as an average, *viz.*:

$$\phi_{\mathbf{h}} \simeq \langle \phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_r}.$$

For actual phase determination, this can be formalized as follows. After calculating normalized structure-factor magnitudes $|E_{\mathbf{h}}|$ from

the observed $|F_{\mathbf{h}}|$ to generate all possible phase triples within a reasonably high $A_{\mathbf{h}}$ threshold, new phase values can be estimated after origin definition by use of the tangent formula (Karle & Hauptman, 1956):

$$\tan \phi_{\mathbf{h}} = \frac{\sum_{\mathbf{k}_r} W_{\mathbf{h}} |E_{\mathbf{k}}| |E_{\mathbf{h}-\mathbf{k}}| \sin(\phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}_r} W_{\mathbf{h}} |E_{\mathbf{k}}| |E_{\mathbf{h}-\mathbf{k}}| \cos(\phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}})}.$$

The reliability of the phase estimate depends on the variance $V(\phi_{\mathbf{h}})$, which is directly related to the magnitude of $\alpha_{\mathbf{h}}$, *i.e.*

$$\alpha_{\mathbf{h}}^2 = \left[\sum_{\mathbf{k}_r} A_{\mathbf{h}, \mathbf{k}} \cos(\phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}}) \right]^2 + \left[\sum_{\mathbf{k}_r} A_{\mathbf{h}, \mathbf{k}} \sin(\phi_{\mathbf{k}} + \phi_{\mathbf{h}-\mathbf{k}}) \right]^2;$$

$A_{\mathbf{h}, \mathbf{k}}$ is identical to the A value defined in the previous section. In the initial stages of phase determination $\alpha_{\mathbf{h}}$ is replaced by an expectation value α_E until enough phases are available to permit its calculation.

The phase solutions indicated by the tangent formula can thus be ranked according to the phase variance and the determination of phases can be made symbolically from the most probable triple-product relationships. This procedure is equivalent to the one described above for the evaluation of phase-invariant sums by symbolic addition. This procedure may allow determination of a large enough basis phase set to produce an interpretable map.

An alternative procedure is to use an automatic version of the tangent formula in a multisolution process. This procedure is described in Chapter 2.2. After origin definition, enough algebraic unknowns are defined (two values if centrosymmetric and four values, cycling through phase quadrants, if noncentrosymmetric) to access as many of the unknown phases as possible. These are used to generate a number of trial phase sets and the likelihood of identifying the correct solution is based on the use of some figure of merit.

Multisolution approaches employing the tangent formula include *MULTAN* (Germain *et al.*, 1971), *QTAN* (Langs & DeTitta, 1975) and *RANTAN* (Yao, 1981). *RANTAN* is a version of *MULTAN* that allows for a larger initial random phase set (with suitable control of weights in the tangent formula). *QTAN* utilizes the α_{hest} definition, where

$$\alpha_{\text{hest}} = \left\{ \sum_{\mathbf{k}} A_{\mathbf{h}, \mathbf{k}}^2 + 2 \sum_{\mathbf{k} \neq \mathbf{k}'} A_{\mathbf{h}, \mathbf{k}} A'_{\mathbf{h}, \mathbf{k}} \frac{I_1(A_{\mathbf{h}, \mathbf{k}}) I_1(A'_{\mathbf{h}, \mathbf{k}})}{I_0(A_{\mathbf{h}, \mathbf{k}}) I_0(A'_{\mathbf{h}, \mathbf{k}})} \right\}^{1/2},$$

for evaluating the phase variance. (Here I_0 , I_1 are modified Bessel functions.) After multiple solutions are generated, it is desirable to locate the structurally most relevant phase sets by some figure of merit. There are many that have been suggested (Chapter 2.2). The most useful figure of merit in *QTAN* has been the NQUEST (De Titta *et al.*, 1975) estimate of negative quartet invariants (see Chapter 2.2). More recently, this has been superseded by the minimal function (Hauptman, 1993):

$$R(\phi) = \frac{\sum_{\mathbf{h}, \mathbf{k}} A_{\mathbf{h}, \mathbf{k}} (\cos \phi_{\mathbf{h}, \mathbf{k}} - t_{\mathbf{h}, \mathbf{k}})^2}{\sum_{\mathbf{h}, \mathbf{k}} A_{\mathbf{h}, \mathbf{k}}},$$

where $t_{\mathbf{h}, \mathbf{k}} = I_1(A_{\mathbf{h}, \mathbf{k}})/I_0(A_{\mathbf{h}, \mathbf{k}})$ and $\phi_{\mathbf{h}, \mathbf{k}} = \phi_{\mathbf{h}} + \phi_{\mathbf{k}} + \phi_{-\mathbf{h}-\mathbf{k}}$.

In the first application (Dorset *et al.*, 1979) of multisolution phasing to electron-diffraction data (using the program *QTAN*), *n*-beam dynamical structure factors generated for cytosine and disodium 4-oxypyrimidine-2-sulfinate were used to assess the effect of increasing crystal thickness and electron accelerating voltage on the success of the structure determination. At 100 kV samples at least 80 Å thickness were usable for data collection and at 1000 kV this sample thickness limit could be pushed to 300 Å – or, perhaps, 610 Å if a partial structure were accepted for later Fourier

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refinement. NQUEST identified the best phase solutions. Later QTAN was used to evaluate the effect of elastic crystal bend on the structure analysis of cytosine (Moss & Dorset, 1982).

In actual experimental applications, two forms of thiourea were investigated with QTAN (Dorset, 1992*d*), using published three-dimensional electron-diffraction intensities (Dvoryankin & Vainshstein, 1960, 1962). Analysis of the centrosymmetric paraelectric structure yielded results equivalent to those found earlier by symbolic addition (Dorset, 1991*b*). Analysis of the noncentrosymmetric ferroelectric form was also quite successful (Dorset, 1992*d*). In both cases, the correct structure was found at the lowest value of NQUEST. Re-analysis of the diketopiperazine structure with QTAN also found the correct structure (Dorset & McCourt, 1994*a*) within the four lowest values of NQUEST, but not the one at the lowest value. The effectiveness of this figure of merit became more questionable when QTAN was used to solve the noncentrosymmetric crystal structure of a polymer (Dorset, McCourt, Kopp *et al.*, 1994). The solution could not be found readily when NQUEST was used but was easily identified when the minimal function $R(\phi)$ was employed instead.

MULTAN has been used to phase simulated data from copper perchlorophthalocyanine (Fan *et al.*, 1985). Within the 2 Å resolution of the electron-microscope image, if one seeks phases for diffraction data in reciprocal-space regions where the objective lens phase contrast transfer function $|C(s)| \leq 0.2$, the method proves to be successful. The method is also quite effective for phase extension from 2 Å to 1 Å diffraction resolution, where the low-angle data serve as a large initial phase set for the tangent formula. However, no useful results were found from an *ab initio* phase determination carried out solely with the electron-diffraction structure-factor magnitudes. Similar results were obtained when RANTAN was used to phase experimental data from this compound (Fan *et al.*, 1991), *i.e.* the multisolution approach worked well for phase extension but not for *ab initio* phase determination. Additional tests were subsequently carried out with QTAN on an experimental *hk0* electron-diffraction data set collected at 1200 kV (Dorset, McCourt, Fryer *et al.*, 1994). Again, *ab initio* phase determination is not possible by this technique. However, if a basis set was constructed from the Fourier transform of a 2.4 Å image, a correct solution could be found, but not at the lowest value of NQUEST. This figure of merit was useful, however, when the basis set was taken from the symbolic addition determination mentioned in the previous section.

2.5.7.5. Density modification

Another method of phase determination, which is best suited to refining or extending a partial phase set, is the Hoppe–Gassmann density modification procedure (Hoppe & Gassmann, 1968; Gassmann & Zechmeister, 1972; Gassmann, 1976). The procedure is very simple but also very computer-intensive. Starting with a small set of (phased) F_h , an initial potential map $\varphi(\mathbf{r})$ is calculated by Fourier transformation. This map is then modified by some real-space function, which restricts peak sizes to a maximum value and removes all negative density regions. The modified map $\varphi'(\mathbf{r})$ is then Fourier-transformed to produce a set of phased structure factors. Phase values are accepted *via* another modification function in reciprocal space, *e.g.* $E_{\text{calc}}/E_{\text{obs}} \geq p$, where p is a threshold quantity. The new set is then transformed to obtain a new $\varphi(\mathbf{r})$ and the phase refinement continues iteratively until the phase solution converges (judged by lower crystallographic R values).

The application of density modification procedures to electron-crystallographic problems was assessed by Ishizuka *et al.* (1982), who used simulated data from copper perchlorophthalocyanine within the resolution of the electron-microscope image. The method was useful for finding phase values in reciprocal-space regions

where the transfer function $|C(s)| \leq 0.2$. As a technique for phase extension, density modification was acceptable for test cases where the resolution was extended from 1.67 to 1.0 Å, or 2.01 to 1.21 Å, but it was not very satisfactory for a resolution enhancement from 2.5 to 1.67 Å. There appear to have been no tests of this method yet with experimental data. However, the philosophy of this technique will be met again below in the description of the the maximum entropy and likelihood procedure.

2.5.7.6. Convolution techniques

One of the first relationships ever derived for phase determination is the Sayre (1952) equation:

$$F_h = \frac{\theta}{V} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h}-\mathbf{k}},$$

which is a simple convolution of phased structure factors multiplied by a function of the atomic scattering factors. For structures with non-overlapping atoms, consisting of one atomic species, it is an exact expression. Although the convolution term resembles part of the tangent formula above, no statistical averaging is implied (Sayre, 1980). In X-ray crystallography this relationship has not been used very often, despite its accuracy. Part of the reason for this is that it requires relatively high resolution data for it to be useful. It can also fail for structures comprised of different atomic species.

Since, relative to X-ray scattering factors, electron scattering factors span a narrower range of magnitudes at $\sin \theta/\lambda = 0$, it might be thought that the Sayre equation would be particularly useful in electron crystallography. In fact, Liu *et al.* (1988) were able to extend phases for simulated data from copper perchlorophthalocyanine starting at the image resolution of 2 Å and reaching the 1 Å limit of an electron-diffraction data set. This analysis has been improved with a 2.4 Å basis set obtained from the Fourier transform of an electron micrograph of this material at 500 kV and extended to the 1.0 Å limit of a 1200 kV electron-diffraction pattern (Dorset *et al.*, 1995). Using the partial phase sets for zonal diffraction data from several polymers by symbolic addition (see above), the Sayre equation has been useful for extending into the whole *hk0* set, often with great accuracy. The size of the basis set is critical but the connectivity to access all reflections is more so. Fan and co-workers have had considerable success with the analysis of incommensurately modulated structures. The average structure (basis set) is found by high-resolution electron microscopy and the ‘superlattice’ reflections, corresponding to the incommensurate modulation, are assigned phases in hyperspace by the Sayre convolution. Examples include a high T_c superconductor (Mo *et al.*, 1992) and the mineral ankangite (Xiang *et al.*, 1990). Phases of regular inorganic crystals have also been extended from the electron micrograph to the electron-diffraction resolution by this technique (Hu *et al.*, 1992).

In an investigation of how direct methods might be used for phase extension in protein electron crystallography, low-resolution phases from two proteins, bacteriorhodopsin (Henderson *et al.*, 1986) and halorhodopsin (Havelka *et al.*, 1993) were extended to higher resolution with the Sayre equation (Dorset *et al.*, 1995). For the noncentrosymmetric bacteriorhodopsin *hk0* projection a 10 Å basis set was used, whereas a 15 Å set was accepted for the centrosymmetric halorhodopsin projection. In both cases, extensions to 6 Å resolution were reasonably successful. For bacteriorhodopsin, for which data were available to 3.5 Å, problems with the extension were encountered near 5 Å, corresponding to a minimum in a plot of average intensity *versus* resolution. Suggestions were made on how a multisolution procedure might be successful beyond this point.

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2.5.7.7. Maximum entropy and likelihood

Maximum entropy has been applied to electron crystallography in several ways. In the sense that images are optimized, the entropy term

$$S = -\sum_i P_i \ln P_i,$$

where $P_i = p_i / \sum_i p_i$ and p_i is a pixel density, has been evaluated for various test electron-microscope images. For crystals, the true projected potential distribution function is thought to have the maximum value of S . If the phase contrast transfer function used to obtain a micrograph is unknown, test images (*i.e.* trial potential maps) can be calculated for different values of Δf_{trial} . The value that corresponds to the maximum entropy would be near the true defocus. In this way, the actual objective lens transfer function can be found for a single image (Li, 1991) in addition to the other techniques suggested by this group.

Another use of the maximum-entropy concept is to guide the progress of a direct phase determination (Bricogne & Gilmore, 1990; Gilmore *et al.*, 1990). Suppose that there is a small set H of known phases $\phi_{\mathbf{h} \in H}$ (corresponding either to origin definition, or the Fourier transform of an electron micrograph, or both) with associated unitary structure-factor amplitudes $|U_{\mathbf{h} \in H}|$. [The unitary structure factor is defined as $|U_{\mathbf{h}}| = |E_{\mathbf{h}}|/(N)^{1/2}$.] As usual, the task is to expand into the unknown phase set K to solve the crystal structure. From Bayes' theorem, the procedure is based on an operation where $p(\text{map}|\text{data}) \propto p(\text{map})p(\text{data}|\text{map})$. This means that the probability of successfully deriving a potential map, given diffraction data, is estimated. This so-called posterior probability is approximately proportional to the product of the probability of generating the map (known as the prior) and the probability of generating the data, given the map (known as the likelihood). The latter probability consults the observed data and can be used as a figure of merit.

Beginning with the basis set H , a trial map is generated from the limited number of phased structure factors. As discussed above, the map can be immediately improved by removing all negative density. The map can be improved further if its entropy is maximized using the equation given above for S . This produces the so-called maximum-entropy prior $q^{\text{ME}}(X)$.

So far, it has been assumed that all $|U_{\mathbf{h} \in K}| = 0$. If large reflections from the K set are now added and their phase values are permuted, then a number of new maps can be generated and their entropies can be maximized as before. This creates a phasing 'tree' with many possible solutions; individual branch points can have further reflections added *via* permutations to produce further sub-branches, and so on. Obviously, some figure of merit is needed to 'prune' the tree, *i.e.* to find likely paths to a solution.

The desired figure of merit is the likelihood $L(H)$. First a quantity

$$\Lambda_{\mathbf{h}} = 2NR \exp[-N(r^2 + R^2)]I_o(2NrR),$$

where $r = |U_{\mathbf{h}}^{\text{ME}}|$ (the calculated unitary structure factors) and $R = |U_{\mathbf{h}}^o|$ (the observed unitary structure factors), is defined. From this one can calculate

$$L(H) = \sum_{\mathbf{h} \notin H} \ln \Lambda_{\mathbf{h}}.$$

The null hypothesis $L(H_o)$ can also be calculated from the above when $r = 0$, so that the likelihood gain

$$Lg = L(H) - L(H_o)$$

ranks the nodes of the phasing tree in order of the best solutions.

Applications have been made to experimental electron-crystallographic data. A small-molecule structure starting with phases from an electron micrograph and extending to electron-diffraction

resolution has been reported (Dong *et al.*, 1992). Other experimental electron-diffraction data sets used in other direct phasing approaches (see above) also have been assigned phases by this technique (Gilmore, Shankland & Bricogne, 1993). These include intensities from diketopiperazine and basic copper chloride. An application of this procedure in protein structure analysis has been published by Gilmore *et al.* (1992) and Gilmore, Shankland & Fryer (1993). Starting with 15 Å phases, it was possible to extend phases for bacteriorhodopsin to the limits of the electron-diffraction pattern, apparently with greater accuracy than possible with the Sayre equation (see above).

2.5.7.8. Influence of multiple scattering on direct electron crystallographic structure analysis

The aim of electron-crystallographic data collection is to minimize the effect of dynamical scattering, so that the unit-cell potential distribution or its Fourier transform is represented significantly in the recorded signal. It would be a mistake, however, to presume that these data ever conform strictly to the kinematical approximation, for there is always some deviation from this ideal scattering condition that can affect the structure analysis. Despite this fact, some direct phasing procedures have been particularly 'robust', even when multiple scattering perturbations to the data are quite obvious (*e.g.* as evidenced by large crystallographic residuals).

The most effective direct phasing procedures seem to be those based on the Σ_2 triple invariants. These phase relationships will not only include the symbolic addition procedure, as it is normally carried out, but also the tangent formula and the Sayre equation (since it is well known that this convolution can be used to derive the functional form of the three-phase invariant). The strict ordering of $|E_{\mathbf{h}}|$ magnitudes is, therefore, not critically important so long as there are no major changes from large to small values (or *vice versa*). This was demonstrated in direct phase determinations of simulated n -beam dynamical diffraction data from a sulfur-containing polymer (Dorset & McCourt, 1992). Nevertheless, there is a point where measured data cannot be used. For example, intensities from *ca* 100 Å-thick epitaxially oriented copper perchlorophthalocyanine crystals become less and less representative of the unit-cell transform at lower electron-beam energies (Tivol *et al.*, 1993) and, accordingly, the success of the phase determination is compromised (Dorset, McCourt, Fryer *et al.*, 1994). The similarity between the Sayre convolution and the interactions of structure-factor terms in, *e.g.*, the multislice formulation of n -beam dynamical scattering was noted by Moodie (1965). It is interesting to note that dynamical scattering interactions observed by direct excitation of Σ_2 and Σ_1 triples in convergent-beam diffraction experiments can actually be exploited to determine crystallographic phases to very high precision (Spence & Zuo, 1992, pp. 56–63).

While the evaluation of positive quartet invariant sums (see Chapter 2.2) seems to be almost as favourable in the electron diffraction case as is the evaluation of Σ_2 triples, negative quartet invariants seem to be particularly sensitive to dynamical diffraction. If dynamical scattering can be modelled crudely by a convolutional smearing of the diffraction intensities, then the lowest structure-factor amplitudes, and hence the estimates of lowest $|E_{\mathbf{h}}|$ values, will be the ones most compromised. Since the negative-quartet relationships require an accurate prediction of small 'cross-term' $|E_{\mathbf{h}}|$ values, multiple scattering can, therefore, limit the efficacy of this invariant for phase determination. In initial work, negative quartets have been mostly employed in the NQUEST figure of merit, and analyses (Dorset, McCourt, Fryer *et al.*, 1994; Dorset & McCourt, 1994a) have shown how the degradation of weak kinematical $|E_{\mathbf{h}}|$ terms effectively reduced its effectiveness for

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locating correct structure solutions *via* the tangent formula, even though the tangent formula itself (based on triple phase estimates) was quite effective for phase determination. Substitution of the minimal function $R(\phi)$ for NQUEST seems to have overcome this difficulty. [It should be pointed out, though, that only the Σ_2 -triple contribution to $R(\phi)$ is considered.]

Structure refinement is another area where the effects of dynamical scattering are also problematic. For example, in the analysis of the paraelectric thiourea structure (Dorset, 1991*b*) from published texture diffraction data (Dvoryankin & Vainshtein, 1960), it was virtually impossible to find a chemically reasonable structure geometry by Fourier refinement, even though the direct phase determination itself was quite successful. The best structure was found only when higher-angle intensities (*i.e.* those least affected by dynamical scattering) were used to generate the potential map. Later analyses on heavy-atom-containing organics (Dorset *et al.*, 1992) found that the lowest kinematical R -factor value did not correspond to the chemically correct structure geometry. This observation was also made in the least-squares refinement of diketopiperazine (Dorset & McCourt, 1994*a*). It is

obvious that, if a global minimum is sought for the crystallographic residual, then dynamical structure factors, rather than kinematical values, should be compared to the observed values (Dorset *et al.*, 1992). Ways of integrating such calculations into the refinement process have been suggested (Sha *et al.*, 1993). Otherwise one must constrain the refinement to chemically reasonable bonding geometry in a search for a local R -factor minimum.

Corrections for such deviations from the kinematical approximation are complicated by the presence of other possible data perturbations, especially if microareas are being sampled, *e.g.* in typical selected-area diffraction experiments. Significant complications can arise from the diffraction incoherence observed from elastically deformed crystals (Cowley, 1961) as well as secondary scattering (Cowley *et al.*, 1951). These complications were also considered for the larger (*e.g.* millimeter diameter) areas sampled in an electron-diffraction camera when recording texture diffraction patterns (Turner & Cowley, 1969), but, because of the crystallite distributions, it is sometimes found that the two-beam dynamical approximation is useful (accounting for a number of successful structure analyses carried out in Moscow).

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2.1

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3.1. Distances, angles, and their standard uncertainties

BY D. E. SANDS

3.1.1. Introduction

A crystal structure analysis provides information from which it is possible to compute distances between atoms, angles between interatomic vectors, and the uncertainties in these quantities. In Cartesian coordinate systems, these geometric computations require the Pythagorean theorem and elementary trigonometry. The natural coordinate systems of crystals, though, are determined by symmetry, and only in special cases are the basis vectors (or coordinate axes) of these systems constrained to be of equal lengths or mutually perpendicular.

It is possible, of course, to transform the positional parameters of the atoms to a Cartesian system and perform the subsequent calculations with the transformed coordinates. Along with the coordinates, the transformations must be applied to anisotropic thermal factors, variance–covariance matrices and other important quantities. Moreover, leaving the natural coordinate system of the crystal sacrifices the simplified relationships imposed by translational and point symmetry; for example, if an atom has fractional coordinates x^1, x^2, x^3 , an equivalent atom will be at $1 + x^1, x^2, x^3$, etc.

Fortunately, formulation of the calculations in generalized rectilinear coordinate systems is straightforward, and readily adapted to computer languages (Section 3.1.12 illustrates the use of Fortran for such calculations). The techniques for these computations are those of tensor analysis, which provides a compact and elegant notation. While an effort will be made to be self-sufficient in this chapter, some proficiency in vector algebra is assumed, and the reader not familiar with the basics of tensor analysis should refer to Chapter 1.1 and Sands (1982a).

3.1.2. Scalar product

The scalar product of vectors $\mathbf{u}$ and $\mathbf{v}$ is defined as

$$\mathbf{u} \cdot \mathbf{v} = uv \cos \varphi, \quad (3.1.2.1)$$

where u and v are the lengths of the vectors and φ is the angle between them. In terms of components,

$$\mathbf{u} \cdot \mathbf{v} = (u^i \mathbf{a}_i) \cdot (v^j \mathbf{a}_j) \quad (3.1.2.2)$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j \mathbf{a}_i \cdot \mathbf{a}_j \quad (3.1.2.3)$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j g_{ij}. \quad (3.1.2.4)$$

In all equations in this chapter, the convention is followed that summation is implied over an index that is repeated once as a subscript and once as a superscript in an expression; thus, the right-hand side of (3.1.2.4) implies the sum of nine terms

$$u^1 v^1 g_{11} + u^1 v^2 g_{12} + \dots + u^3 v^3 g_{33}.$$

The g_{ij} in (3.1.2.4) are the components of the metric tensor [see Chapter 1.1 and Sands (1982a)]

$$g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j. \quad (3.1.2.5)$$

Subscripts are used for quantities that transform the same way as the basis vectors $\mathbf{a}_i$; such quantities are said to transform covariantly. Superscripts denote quantities that transform the same way as coordinates x^i ; these quantities are said to transform contravariantly (Sands, 1982a).

Equation (3.1.2.4) is in a form convenient for computer evaluation, with indices i and j taking successively all values from 1 to 3. The matrix form of (3.1.2.4) is useful both for symbolic manipulation and for computation,

$$\mathbf{u} \cdot \mathbf{v} = \mathbf{u}^T \mathbf{g} \mathbf{v}, \quad (3.1.2.6)$$

where the superscript italic T following a matrix symbol indicates a transpose. Written out in full, (3.1.2.6) is

$$\mathbf{u} \cdot \mathbf{v} = (u^1 u^2 u^3) \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} \begin{pmatrix} v^1 \\ v^2 \\ v^3 \end{pmatrix}. \quad (3.1.2.7)$$

If $\mathbf{u}$ is the column vector with components u^1, u^2, u^3 , $\mathbf{u}^T$ is the corresponding row vector shown in (3.1.2.7).

3.1.3. Length of a vector

By (3.1.2.1), the scalar product of a vector with itself is

$$\mathbf{v} \cdot \mathbf{v} = (v)^2. \quad (3.1.3.1)$$

The length of $\mathbf{v}$ is, therefore, given by

$$v = (v^i v^j g_{ij})^{1/2}. \quad (3.1.3.2)$$

Computation of lengths in a generalized rectilinear coordinate system is thus simply a matter of evaluating the double summation $v^i v^j g_{ij}$ and taking the square root.

3.1.4. Angle between two vectors

By (3.1.2.1) and (3.1.2.4), the angle φ between vectors $\mathbf{u}$ and $\mathbf{v}$ is given by

$$\varphi = \cos^{-1} [u^i v^j g_{ij} / (uv)]. \quad (3.1.4.1)$$

An even more concise expression of equations such as (3.1.4.1) is possible by making use of the ability of the metric tensor $\mathbf{g}$ to convert components from contravariant to covariant (Sands, 1982a). Thus,

$$v_i = g_{ij} v^j, \quad u_j = g_{ij} u^i, \quad (3.1.4.2)$$

and (3.1.2.4) may be written succinctly as

$$\mathbf{u} \cdot \mathbf{v} = u^i v_i \quad (3.1.4.3)$$

or

$$\mathbf{u} \cdot \mathbf{v} = u_i v^i. \quad (3.1.4.4)$$

With this notation, the angle calculation of (3.1.4.1) becomes

$$\varphi = \cos^{-1} [u^i v_i / (uv)] = \cos^{-1} [u_i v^i / (uv)]. \quad (3.1.4.5)$$

The summations in (3.1.4.3), (3.1.4.4) and (3.1.4.5) include only three terms, and are thus equivalent in numerical effort to the computation in a Cartesian system, in which the metric tensor is represented by the unit matrix and there is no numerical distinction between covariant components and contravariant components.

Appreciation of the elegance of tensor formulations may be enhanced by noting that corresponding to the metric tensor $\mathbf{g}$ with components g_{ij} there is a contravariant metric tensor $\mathbf{g}^*$ with components

$$g^{ij} = \mathbf{a}^i \cdot \mathbf{a}^j. \quad (3.1.4.6)$$

The $\mathbf{a}^i$ are contravariant basis vectors, known to crystallographers as reciprocal axes. Expressions parallel to (3.1.4.2) may be written, in which $\mathbf{g}^*$ plays the role of converting covariant components to contravariant components. These tensors thus express mathematically the crystallographic notions of crystal space and reciprocal space [see Chapter 1.1 and Sands (1982a)].

3.1. DISTANCES, ANGLES, AND THEIR STANDARD UNCERTAINTIES

3.1.5. Vector product

The scalar product defined in Section 3.1.2 is one multiplicative operation of two vectors that may be defined; another is the vector product, which is denoted as $\mathbf{u} \wedge \mathbf{v}$ (or $\mathbf{u} \times \mathbf{v}$ or $[\mathbf{uv}]$). The vector product of vectors $\mathbf{u}$ and $\mathbf{v}$ is defined as a vector of length $uv \sin \varphi$, where φ is the angle between the vectors, and of direction perpendicular to both $\mathbf{u}$ and $\mathbf{v}$ in the sense that $\mathbf{u}$, $\mathbf{v}$ and $\mathbf{u} \wedge \mathbf{v}$ form a right-handed system; $\mathbf{u} \wedge \mathbf{v}$ is generated by rotating $\mathbf{u}$ into $\mathbf{v}$ and advancing in the direction of a right-handed screw. The magnitude of $\mathbf{u} \wedge \mathbf{v}$, given by

$$|\mathbf{u} \wedge \mathbf{v}| = uv \sin \varphi \quad (3.1.5.1)$$

is equal to the area of the parallelogram defined by $\mathbf{u}$ and $\mathbf{v}$.

It follows from the definition that

$$\mathbf{u} \wedge \mathbf{v} = -\mathbf{v} \wedge \mathbf{u}. \quad (3.1.5.2)$$

3.1.6. Permutation tensors

Many relationships involving vector products may be expressed compactly and conveniently in terms of the permutation tensors, defined as

$$\varepsilon_{ijk} = \mathbf{a}_i \cdot \mathbf{a}_j \wedge \mathbf{a}_k \quad (3.1.6.1)$$

$$\varepsilon^{ijk} = \mathbf{a}^i \cdot \mathbf{a}^j \wedge \mathbf{a}^k. \quad (3.1.6.2)$$

Since $\mathbf{a}_i \cdot \mathbf{a}_j \wedge \mathbf{a}_k$ represents the volume of the parallelepiped defined by vectors $\mathbf{a}_i, \mathbf{a}_j, \mathbf{a}_k$, it follows that ε_{ijk} vanishes if any two indices are equal to each other. The same argument applies, of course, to ε^{ijk} . That is,

$$\varepsilon_{ijk} = 0, \quad \varepsilon^{ijk} = 0, \quad \text{if } j = i \text{ or } k = i \text{ or } k = j. \quad (3.1.6.3)$$

If the indices are all different,

$$\varepsilon_{ijk} = PV, \quad \varepsilon^{ijk} = PV^* \quad (3.1.6.4)$$

for even permutations of ijk (123, 231, or 312), and

$$\varepsilon_{ijk} = -PV, \quad \varepsilon^{ijk} = -PV^* \quad (3.1.6.5)$$

for odd permutations (132, 213, or 321). Here, $P = +1$ for right-handed axes, $P = -1$ for left-handed axes, V is the unit-cell volume, and $V^* = 1/V$ is the volume of the reciprocal cell defined by the reciprocal basis vectors $\mathbf{a}^i, \mathbf{a}^j, \mathbf{a}^k$.

A discussion of the properties of the permutation tensors may be found in Sands (1982a). In right-handed Cartesian systems, where $P = 1$, and $V = V^* = 1$, the permutation tensors are equivalent to the permutation symbols denoted by e_{ijk} .

3.1.7. Components of vector product

As is shown in Sands (1982a), the components of the vector product $\mathbf{u} \wedge \mathbf{v}$ are given by

$$\mathbf{u} \wedge \mathbf{v} = \varepsilon_{ijk} u^i v^j \mathbf{a}^k, \quad (3.1.7.1)$$

where again $\mathbf{a}^k$ is a reciprocal basis vector (some writers use $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ to represent the reciprocal axes). A special case of (3.1.7.1) is

$$\mathbf{a}_i \wedge \mathbf{a}_j = \varepsilon_{ijk} \mathbf{a}^k, \quad (3.1.7.2)$$

which may be taken as a defining equation for the reciprocal basis vectors. Similarly,

$$\mathbf{a}^i \wedge \mathbf{a}^j = \varepsilon^{ijk} \mathbf{a}_k, \quad (3.1.7.3)$$

which completes the characterization of the dual vector system with basis vectors $\mathbf{a}_i$ and $\mathbf{a}^j$ obeying

$$\mathbf{a}_i \cdot \mathbf{a}^j = \delta_i^j. \quad (3.1.7.4)$$

In (3.1.7.4), δ_i^j is the Kronecker delta, which equals 1 if $i = j$, 0 if $i \neq j$. The relationships between these quantities are explored at some length in Sands (1982a).

3.1.8. Some vector relationships

The results developed above lead to several useful relationships between vectors; for derivations, see Sands (1982a).

3.1.8.1. Triple vector product

$$\mathbf{u} \wedge (\mathbf{v} \wedge \mathbf{w}) = (\mathbf{u} \cdot \mathbf{w})\mathbf{v} - (\mathbf{u} \cdot \mathbf{v})\mathbf{w} \quad (3.1.8.1)$$

$$(\mathbf{u} \wedge \mathbf{v}) \wedge \mathbf{w} = -(\mathbf{v} \cdot \mathbf{w})\mathbf{u} + (\mathbf{u} \cdot \mathbf{w})\mathbf{v}. \quad (3.1.8.2)$$

3.1.8.2. Scalar product of vector products

$$(\mathbf{u} \wedge \mathbf{v}) \cdot (\mathbf{w} \wedge \mathbf{z}) = (\mathbf{u} \cdot \mathbf{w})(\mathbf{v} \cdot \mathbf{z}) - (\mathbf{u} \cdot \mathbf{z})(\mathbf{v} \cdot \mathbf{w}). \quad (3.1.8.3)$$

A derivation of this result may be found also in Shmueli (1974).

3.1.8.3. Vector product of vector products

$$(\mathbf{u} \wedge \mathbf{v}) \wedge (\mathbf{w} \wedge \mathbf{z}) = (\mathbf{u} \cdot \mathbf{w} \wedge \mathbf{z})\mathbf{v} - (\mathbf{v} \cdot \mathbf{w} \wedge \mathbf{z})\mathbf{u} \quad (3.1.8.4)$$

$$(\mathbf{u} \wedge \mathbf{v}) \wedge (\mathbf{w} \wedge \mathbf{z}) = (\mathbf{u} \cdot \mathbf{v} \wedge \mathbf{z})\mathbf{w} - (\mathbf{u} \cdot \mathbf{v} \wedge \mathbf{w})\mathbf{z}. \quad (3.1.8.5)$$

3.1.9. Planes

Among several ways of characterizing a plane in a general rectilinear coordinate system is a description in terms of the coordinates of three non-collinear points that lie in the plane. If the points are U, V and W , lying at the ends of vectors $\mathbf{u}, \mathbf{v}$ and $\mathbf{w}$, the vectors $\mathbf{u} - \mathbf{v}, \mathbf{v} - \mathbf{w}$ and $\mathbf{w} - \mathbf{u}$ are in the plane. The vector

$$\mathbf{z} = (\mathbf{u} - \mathbf{v}) \wedge (\mathbf{v} - \mathbf{w}) \quad (3.1.9.1)$$

is normal to the plane. Expansion of (3.1.9.1) yields

$$\mathbf{z} = (\mathbf{u} \wedge \mathbf{v}) + (\mathbf{v} \wedge \mathbf{w}) + (\mathbf{w} \wedge \mathbf{u}). \quad (3.1.9.2)$$

Making use of (3.1.7.1),

$$\mathbf{z} = \varepsilon_{ijk}(u^j v^k + v^j w^k + w^j u^k) \mathbf{a}^i. \quad (3.1.9.3)$$

If now $\mathbf{x}$ is any vector from the origin to the plane, $\mathbf{x} - \mathbf{u}$ is in the plane, and

$$(\mathbf{x} - \mathbf{u}) \cdot \mathbf{z} = 0. \quad (3.1.9.4)$$

From (3.1.9.2),

$$\mathbf{u} \cdot \mathbf{z} = \mathbf{u} \cdot \mathbf{v} \wedge \mathbf{w}. \quad (3.1.9.5)$$

Rearrangement of (3.1.9.4) with $\mathbf{x} \cdot \mathbf{z}$ on the left and $\mathbf{u} \cdot \mathbf{z}$ on the right, and using (3.1.9.3) for $\mathbf{z}$ on the left leads to

$$\varepsilon_{ijk} x^i (u^j v^k + v^j w^k + w^j u^k) = \varepsilon_{ijk} u^i v^j w^k. \quad (3.1.9.6)$$

If, in particular, the points are on the coordinate axes, their designations are $[u^1, 0, 0]$, $[0, v^2, 0]$ and $[0, 0, w^3]$, and (3.1.9.6) becomes

$$x^1/u^1 + x^2/v^2 + x^3/w^3 = 1, \quad (3.1.9.7)$$

which may be written

$$x^i h_i = 1 \quad (3.1.9.8)$$

or

$$\mathbf{x} \cdot \mathbf{h} = 1 \quad (3.1.9.9)$$

in which the vector $\mathbf{h}$ has coordinates

3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

$$\mathbf{h} = (1/u^1, 1/v^2, 1/w^3). \quad (3.1.9.10)$$

That is, the covariant components of $\mathbf{h}$ are given by the reciprocals of the intercepts of the plane on the axes. The vector $\mathbf{h}$ is normal to the plane it describes (Sands, 1982a) and the length of $\mathbf{h}$ is the reciprocal of the distance d of the plane from the origin; i.e.,

$$h = 1/d. \quad (3.1.9.11)$$

If the indices h_i are relatively prime integers, the theory of numbers tells us that the Diophantine equation (3.1.9.8) has solutions x^i that are integers. Points whose contravariant components are integers are lattice points, and such a plane passes through an infinite number of lattice points and is called a *lattice plane*. Thus, the h_i for lattice planes are the familiar Miller indices of crystallography.

Calculations involving planes become quite manageable when the normal vector $\mathbf{h}$ is introduced. Thus, the distance l from a point P with coordinates p^i to a plane characterized by $\mathbf{h}$ is

$$l = (1 - \mathbf{p} \cdot \mathbf{h})/h, \quad (3.1.9.12)$$

where a negative sign indicates that the point is on the opposite side of the plane from the origin.

The dihedral angle τ between planes with normals $\mathbf{h}$ and $\mathbf{h}'$ is

$$\tau = \cos^{-1}[-\mathbf{h} \cdot \mathbf{h}'/(hh')]. \quad (3.1.9.13)$$

A variation of (3.1.9.13) expresses τ in terms of vector $\mathbf{u}$ in the first plane, vector $\mathbf{w}$ in the second plane, and vector $\mathbf{v}$, the intersection of the planes, as (Shmueli, 1974)

$$\tau = \cos^{-1}[(\mathbf{u} \wedge \mathbf{v}) \cdot (\mathbf{v} \wedge \mathbf{w})/|\mathbf{u} \wedge \mathbf{v}||\mathbf{v} \wedge \mathbf{w}|]. \quad (3.1.9.14)$$

A similar calculation gives angles of torsion. Let $\mathbf{t}_h$ and $\mathbf{u}_h$ be, respectively, the projections of vectors $\mathbf{t}$ and $\mathbf{u}$ onto the plane with normal $\mathbf{h}$.

$$\mathbf{t}_h = \mathbf{t} - (\mathbf{t} \cdot \mathbf{h})\mathbf{h}/h^2 \quad (3.1.9.15)$$

$$\mathbf{u}_h = \mathbf{u} - (\mathbf{u} \cdot \mathbf{h})\mathbf{h}/h^2. \quad (3.1.9.16)$$

The angle between $\mathbf{t}_h$ and $\mathbf{u}_h$ represents a torsion about $\mathbf{h}$ (Sands, 1982b). Another approach to the torsion angle, which gives equivalent results (Shmueli, 1974), is to compute the angle between $\mathbf{t} \wedge \mathbf{h}$ and $\mathbf{u} \wedge \mathbf{h}$ using (3.1.8.3).

3.1.10. Variance-covariance matrices

Refinement of a crystal structure yields both the parameters that describe the structure and estimates of the uncertainties of those parameters. Refinement by the method of least squares minimizes a weighted sum of squares of residuals. In the matrix notation of Hamilton's classic book (Hamilton, 1964), values of the m parameters to be determined are expressed by the $m \times 1$ column vector $\mathbf{X}$ given by

$$\mathbf{X} = (\mathbf{A}^T \mathbf{P} \mathbf{A})^{-1} \mathbf{A}^T \mathbf{P} \mathbf{F}, \quad (3.1.10.1)$$

where $\mathbf{F}$ is an $n \times 1$ matrix representing the observations (structure factors or squares of structure factors), $\mathbf{P}$ is an $n \times n$ weight matrix that is proportional to the variance-covariance matrix of the observed $\mathbf{F}$, $\mathbf{A}$ is an $n \times m$ design matrix consisting of the derivatives of each element of $\mathbf{F}$ with respect to each of the parameters and $\mathbf{A}^T$ is the transpose of $\mathbf{A}$. The variance-covariance matrix of the parameters is then given by

$$\mathbf{M} = \mathbf{V}^T \mathbf{P} \mathbf{V} (\mathbf{A}^T \mathbf{P} \mathbf{A})^{-1} / (n - m). \quad (3.1.10.2)$$

Here, $\mathbf{V}$ is the $n \times 1$ matrix of residuals, consisting of the differences between the observed and calculated values of the elements of $\mathbf{F}$. Since $\mathbf{V}^T \mathbf{P} \mathbf{V} / (n - m)$ is just a single number, $\mathbf{M}$ is proportional to the inverse least-squares matrix $(\mathbf{A}^T \mathbf{P} \mathbf{A})^{-1}$.

Once the variance-covariance matrix of the parameters is known, the variances and covariances of any quantities derived from these parameters can be computed. The variance of a single function f is given by

$$\sigma^2(f) = \frac{\partial f}{\partial x^i} \frac{\partial f}{\partial x^j} \text{cov}(x^i, x^j), \quad (3.1.10.3)$$

where, as usual, we are using the summation convention and summing over all parameters included in f . A generalization of (3.1.10.3) for two functions is

$$\text{cov}(f_1, f_2) = \frac{\partial f_1}{\partial x^i} \frac{\partial f_2}{\partial x^j} \text{cov}(x^i, x^j). \quad (3.1.10.4)$$

[The covariance of two quantities is, of course, just the variance if the two quantities are the same. For an elementary discussion of statistical covariance and correlation, see Sands (1977).] Equation (3.1.10.4) may now be extended to any number of functions (Sands, 1966); the $k \times k$ variance-covariance matrix $\mathbf{C}$ of k functions of m parameters is given in terms of the $m \times m$ variance-covariance matrix of the parameters by

$$\mathbf{C} = \mathbf{D} \mathbf{M} \mathbf{D}^T, \quad (3.1.10.5)$$

in which the ij th element of the $k \times m$ matrix $\mathbf{D}$ is the derivative of function f_i with respect to parameter j . Element C_{II} (no summation implied over I) is the variance of function f_I , and C_{IJ} is the covariance of functions f_I and f_J .

The calculation of $\mathbf{C}$ must, of course, include the contributions of all sources of error, so $\mathbf{M}$ in (3.1.10.5) should include the variances and covariances of the unit-cell dimensions and of any other relevant parameters with non-negligible uncertainties.

It may be easier, in some cases, to carry out calculations of variances and covariances in steps. For example, the variance-covariance matrix of a set of distances may be computed and then other quantities may be determined as functions of the distances. It is imperative that all non-vanishing covariances be included in every stage of the calculation; only in special cases are the covariances negligible, and often they are large enough to affect the results seriously (Sands, 1977).

These principles may be used to explore the effects of symmetry or of transformations on the variance-covariance matrices of atomic parameters and derived quantities. Using the notation of Sands (1966), with x_A^i and x_B^j the positional parameters i of atoms A and B , respectively, we define $\mathbf{M}_{AA}$, $\mathbf{M}_{AB}$, $\mathbf{M}_{BA}$ and $\mathbf{M}_{BB}$ as 3×3 matrices with ij th elements $\text{cov}(x_A^i, x_A^j)$, $\text{cov}(x_A^i, x_B^j)$, $\text{cov}(x_B^i, x_A^j)$ and $\text{cov}(x_B^i, x_B^j)$, respectively. If atom B' is generated from atom B by symmetry operator $\mathbf{S}$, such that

$$\mathbf{x}_{B'} = \mathbf{S} \mathbf{x}_B \quad (3.1.10.6)$$

$$x_{B'}^i = S_j^i x_B^j, \quad (3.1.10.7)$$

it is shown in Sands (1966) that the variance-covariance matrices involving atom B' are

$$\mathbf{M}_{AB'} = \mathbf{M}_{AB} \mathbf{S}^T \quad (3.1.10.8)$$

$$\mathbf{M}_{B'A} = \mathbf{S} \mathbf{M}_{BA} \quad (3.1.10.9)$$

$$\mathbf{M}_{B'B'} = \mathbf{S} \mathbf{M}_{BB} \mathbf{S}^T. \quad (3.1.10.10)$$

If symmetry operator $\mathbf{S}$ is applied to both atoms A and B to generate atoms A' and B' , the corresponding matrices may be expressed by the matrix equation

$$\begin{pmatrix} \mathbf{M}_{A'A'} & \mathbf{M}_{A'B'} \\ \mathbf{M}_{B'A'} & \mathbf{M}_{B'B'} \end{pmatrix} = \begin{pmatrix} \mathbf{S} \mathbf{M}_{AA} \mathbf{S}^T & \mathbf{S} \mathbf{M}_{AB} \mathbf{S}^T \\ \mathbf{S} \mathbf{M}_{BA} \mathbf{S}^T & \mathbf{S} \mathbf{M}_{BB} \mathbf{S}^T \end{pmatrix}. \quad (3.1.10.11)$$

3.1. DISTANCES, ANGLES, AND THEIR STANDARD UNCERTAINTIES

If $\mathbf{G}$ is a matrix that transforms to a new set of axes,

$$\mathbf{a}' = \mathbf{Ga}, \quad (3.1.10.12)$$

the transformed variance–covariance matrix of the atomic parameters is

$$\mathbf{M}' = (\mathbf{G}^T)^{-1} \mathbf{M} \mathbf{G}^{-1}. \quad (3.1.10.13)$$

To apply these formulae to calculations of the errors and covariances of interatomic distances and angles, consider the triangle of atoms A, B, C with edges $l_1 = AB, l_2 = BC, l_3 = CA$, and angles $\alpha_1, \alpha_2, \alpha_3$ at A, B, C , respectively. If the atoms are not related by symmetry,

$$\sigma^2(l_1) = \mathbf{l}_1^T \mathbf{g}(\mathbf{M}_{AA} - \mathbf{M}_{AB} - \mathbf{M}_{BA} + \mathbf{M}_{BB}) \mathbf{g} \mathbf{l}_1 / l_1^2 \quad (3.1.10.14)$$

$$\text{cov}(l_1, l_2) = \mathbf{l}_1^T \mathbf{g}(\mathbf{M}_{AB} - \mathbf{M}_{AC} - \mathbf{M}_{BB} + \mathbf{M}_{BC}) \mathbf{g} \mathbf{l}_2 / l_1 l_2. \quad (3.1.10.15)$$

If atom B is generated from atom A by symmetry matrix $\mathbf{S}$, the results, as derived in Sands (1966), are

$$\begin{aligned} \sigma^2(l_1) = & \mathbf{l}_1^T \mathbf{g}(\mathbf{M}_{AA} - \mathbf{S} \mathbf{M}_{AA} - \mathbf{M}_{AA} \mathbf{S}^T \\ & + \mathbf{S} \mathbf{M}_{AA} \mathbf{S}^T) \mathbf{g} \mathbf{l}_1 / l_1^2 \end{aligned} \quad (3.1.10.16)$$

$$\begin{aligned} \sigma^2(l_2) = & \mathbf{l}_2^T \mathbf{g}(\mathbf{S} \mathbf{M}_{AA} \mathbf{S}^T - \mathbf{M}_{AC} \mathbf{S}^T \\ & - \mathbf{S} \mathbf{M}_{AC} + \mathbf{M}_{CC}) \mathbf{g} \mathbf{l}_2 / l_2^2 \end{aligned} \quad (3.1.10.17)$$

$$\begin{aligned} \sigma^2(l_3) = & \mathbf{l}_3^T \mathbf{g}(\mathbf{M}_{AA} - \mathbf{M}_{AC} - \mathbf{M}_{CA} \\ & + \mathbf{M}_{CC}) \mathbf{g} \mathbf{l}_3 / l_3^2 \end{aligned} \quad (3.1.10.18)$$

$$\begin{aligned} \text{cov}(l_1, l_2) = & \mathbf{l}_1^T \mathbf{g}(\mathbf{M}_{AA} \mathbf{S}^T - \mathbf{S} \mathbf{M}_{AA} \mathbf{S}^T \\ & - \mathbf{M}_{AC} + \mathbf{S} \mathbf{M}_{AC}) \mathbf{g} \mathbf{l}_2 / l_1 l_2 \end{aligned} \quad (3.1.10.19)$$

$$\begin{aligned} \text{cov}(l_1, l_3) = & \mathbf{l}_1^T \mathbf{g}(-\mathbf{M}_{AA} + \mathbf{S} \mathbf{M}_{AA} \\ & + \mathbf{M}_{AC} - \mathbf{S} \mathbf{M}_{AC}) \mathbf{g} \mathbf{l}_3 / l_1 l_3 \end{aligned} \quad (3.1.10.20)$$

$$\begin{aligned} \text{cov}(l_2, l_3) = & \mathbf{l}_2^T \mathbf{g}(-\mathbf{S} \mathbf{M}_{AA} + \mathbf{M}_{CA} \\ & + \mathbf{S} \mathbf{M}_{AC} - \mathbf{M}_{CC}) \mathbf{g} \mathbf{l}_3 / l_2 l_3. \end{aligned} \quad (3.1.10.21)$$

In equations (3.1.10.14)–(3.1.10.21), $\mathbf{l}_i$ is a column vector with components the differences of the coordinates of the atoms connected by the vector. Representative formulae involving the angles $\alpha_1, \alpha_2, \alpha_3$ are

$$\begin{aligned} \sigma^2(\alpha_1) = & [\cos^2 \alpha_2 \sigma^2(l_1) - 2 \cos \alpha_2 \text{cov}(l_1, l_2) \\ & + 2 \cos \alpha_2 \cos \alpha_3 \text{cov}(l_1, l_3) + \sigma^2(l_2) \\ & - 2 \cos \alpha_3 \text{cov}(l_2, l_3) \\ & + \cos^2 \alpha_3 \sigma^2(l_3)] (l_2 / l_1 l_3 \sin \alpha_1)^2 \end{aligned} \quad (3.1.10.22)$$

$$\begin{aligned} \text{cov}(\alpha_1, \alpha_2) = & [\cos \alpha_1 \cos \alpha_2 \sigma^2(l_1) \\ & + (\cos \alpha_2 \cos \alpha_3 - \cos \alpha_1) \text{cov}(l_1, l_2) \\ & + (\cos \alpha_1 \cos \alpha_3 - \cos \alpha_2) \text{cov}(l_1, l_3) \\ & - \cos \alpha_3 \sigma^2(l_2) + (1 + \cos^2 \alpha_3) \text{cov}(l_2, l_3) \\ & - \cos \alpha_3 \sigma^2(l_3)] / (l_1^2 \sin \alpha_1 \sin \alpha_2) \end{aligned} \quad (3.1.10.23)$$

$$\begin{aligned} \text{cov}(\alpha_1, l_1) = & [-\cos \alpha_2 \sigma^2(l_1) + \text{cov}(l_1, l_2) \\ & - \cos \alpha_3 \text{cov}(l_1, l_3)] (l_2 / l_1 l_3 \sin \alpha_1) \end{aligned} \quad (3.1.10.24)$$

$$\begin{aligned} \text{cov}(\alpha_1, l_2) = & [-\cos \alpha_2 \text{cov}(l_1, l_2) + \sigma^2(l_2) \\ & - \cos \alpha_3 \text{cov}(l_2, l_3)] (l_2 / l_1 l_3 \sin \alpha_1). \end{aligned} \quad (3.1.10.25)$$

If any of the angles approach 0 or 180°, the denominators in (3.1.10.22)–(3.1.10.25) will become very small, necessitating high-precision arithmetic. Indeterminacies resulting from special relationships between atomic positions may require rederivation

of the equations for variances and covariances, to take the relationships into account explicitly and avoid the indeterminacies. A true symmetry condition requiring, for example, a linear bond should cause little problem, and the corresponding variance will be zero. It is the indeterminacies not originating from crystal symmetry that demand caution, in recognizing them and in coping with them correctly.

A general expression for the variance of a dihedral angle, in terms of the variances and covariances of the coordinates of the four atoms, is (Shmueli, 1974)

$$\sigma^2(\tau) = \sum_k \sum_n \frac{\partial \tau}{\partial x_{(k)}^i} \frac{\partial \tau}{\partial x_{(n)}^j} \text{cov}[x_{(k)}^i, x_{(n)}^j], \quad (3.1.10.26)$$

where, in addition to the usual tensor summation over i and j from 1 to 3, summation must be carried out over the four atoms (*i.e.*, k and n vary from 1 to 4). Special cases of (3.1.10.26), corresponding to various levels of approximation of diagonal matrices and isotropic errors, are given in Shmueli (1974). Formulae in dyadic notation are given in Waser (1973) for the variances and covariances of dihedral angles, of best planes, of torsion angles, and of other molecular parameters.

3.1.11. Mean values

The weighted mean of a set of quantities X_i is

$$\langle X \rangle = \sum w_i X_i / \sum w_i, \quad (3.1.11.1)$$

where the weights are typically chosen to minimize the variance of $\langle X \rangle$. The variance may be computed from the variance–covariance matrix $\mathbf{M}$ of the X_i by

$$\sigma^2(\langle X \rangle) = \mathbf{w}^T \mathbf{M} \mathbf{w} / (\sum w_i)^2. \quad (3.1.11.2)$$

Minimization of $\sigma^2(\langle X \rangle)$ leads to weights given by

$$\mathbf{w} = \mathbf{M}^{-1} \mathbf{v}, \quad (3.1.11.3)$$

where the components of vector $\mathbf{v}$ are all equal ($v_i = v_j$ for all i and j); since (3.1.11.1) and (3.1.11.2) require only relative weights, we can assign $v_i = 1$ for all i . Placing these weights in (3.1.11.2) yields

$$\sigma^2(\langle X \rangle) = 1 / \sum w_i. \quad (3.1.11.4)$$

For the case of uncorrelated X_i , the weights are inversely proportional to the corresponding variances

$$w_i = 1 / \sigma^2(X_i). \quad (3.1.11.5)$$

For the case of two correlated variables,

$$w_i = 1 / [\sigma^2(X_i) - \text{cov}(X_1, X_2)]. \quad (3.1.11.6)$$

Derivation and discussion of these equations may be found in Sands (1966, 1982b).

The presence of systematic errors in the experimental data often results in these formulae producing estimates of the standard uncertainties of molecular dimensions that are too small; it has been suggested that such error estimates should be multiplied by 1.5 to make them more realistic (Taylor & Kennard, 1983). It is essential also that averages be computed only of similar quantities, and interatomic distances corresponding to different bond orders or different environments may not represent the same physical quantities; that is, there are reasons for the discrepancies, and averaging may obscure important information. Another source of error in molecular geometry parameters determined from crystallographic measurements is thermal motion, and distances should be corrected for such effects before making comparisons (Busing & Levy, 1964; Johnson, 1970, 1980).

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A discussion of the appropriateness of weighted and unweighted means may be found in Taylor & Kennard (1985), which suggests that the unweighted mean might even be preferable if environmental effects are large.

3.1.12. Computation

It has been mentioned that the tensor formulation used in this chapter is particularly amenable to machine computation. As a simple illustration of this point, the following Fortran program will compute the lengths of vectors **X** and **Y** and the angle between them.

```
DIMENSION X(3),Y(3),G(3,3),SUM(3)
READ (5,10)(X(I),I = 1,3)
READ (5,10)(Y(I),I = 1,3)
```

```
      READ (5,10)((G(I,J),J = 1,3),I = 1,3)
10 FORMAT (3F10.5)
      DO 20 I = 1,3
20 SUM(I) = 0
      DO 30 I = 1,3
      DO 30 J = 1,3
      SUM(1) = SUM(1) + X(I) * X(J) * G(I,J)
      SUM(2) = SUM(2) + Y(I) * Y(J) * G(I,J)
      SUM(3) = SUM(3) + X(I) * Y(J) * G(I,J)
30 CONTINUE
      DIST1 = SQRT(SUM(1))
      DIST2 = SQRT(SUM(2))
      ANGLE = 57.296 * ACOS(SUM(3)/(DIST1 * DIST2))
      WRITE (6,10) DIST1,DIST2,ANGLE
      END
```

3.2. The least-squares plane

BY R. E. MARSH AND V. SCHOMAKER

3.2.1. Introduction

By way of introduction, we remark that in earlier days of crystal structure analysis, before the advent of high-speed computers and routine three-dimensional analyses, molecular planarity was often assumed so that atom coordinates along the direction of projection could be estimated from two-dimensional data [see, *e.g.*, Robertson (1948)]. Today, the usual aim in deriving the coefficients of a plane is to investigate the degree of planarity of a group of atoms as found in a full, three-dimensional structure determination. We further note that, for such purposes, a crystallographer will often be served just as well by establishing the plane in an almost arbitrary fashion as by resorting to the most elaborate, nit-picking and pretentious least-squares treatment. The approximate plane and the associated perpendicular distances of the atoms from it will be all he needs as scaffolding for his geometrical and structural imagination; reasonable common sense will take the place of explicit attention to error estimates.

Nevertheless, we think it appropriate to lay out in some detail the derivation of the ‘best’ plane, in a least-squares sense, through a group of atoms and of the standard uncertainties associated with this plane. We see two cases: (1) The weights of the atoms in question are considered to be isotropic and uncorrelated (*i.e.* the weight matrix for the positions of all the atoms is diagonal, when written in terms of Cartesian axes, and for each atom the three diagonal elements are equal). In such cases the weights may have little or nothing to do with estimates of random error in the atom positions (they may have been assigned merely for convenience or convention), and, therefore, no one should feel that the treatment is proper in respect to the theory of errors. Nevertheless, it may be desired to incorporate the error estimates (variances) of the atom positions into the *results* of such calculations, whereupon these variances (which may be anisotropic, with correlation between atoms) need to be propagated. In this case the distinction between *weights* (or their inverses) and *variances* must be kept very clear. (2) The weights are anisotropic and are presumably derived from a variance–covariance matrix, which may include correlation terms between different atoms; the objective is to achieve a truly proper Gaussian least-squares result.

3.2.2. Least-squares plane based on uncorrelated, isotropic weights

This is surely the most common situation; it is not often that one will wish to take the trouble, or be presumptive enough, to assign anisotropic or correlated weights to the various atoms. And one will sometimes, perhaps even often, not be genuinely interested in the hypothesis that the atoms actually are rigorously coplanar; for instance, one might be interested in examining the best plane through such a patently non-planar molecule as cyclohexane. Moreover, the calculation is simple enough, given the availability of computers and programs, as to be a practical realization of the off-the-cuff treatment suggested in our opening paragraph. The problem of deriving the plane’s coefficients is intrinsically nonlinear in the way first discussed by Schomaker *et al.* (1959; SWMB). Any formulation other than as an eigenvalue–eigenvector problem (SWMB), as far as we can tell, will sometimes go astray. As to the propagation of errors, numerous treatments have been given, but none that we have seen is altogether satisfactory.

We refer all vectors and matrices to Cartesian axes, because that is the most convenient in calculation. However, a more elegant formulation can be written in terms of general axes [*e.g.*, as in Shmueli (1981)].

The notation is troublesome. Indices are needed for atom number and Cartesian direction, and the exponent 2 is needed as well, which is difficult if there are superscript indices. The best way seems to be to write all the indices as subscripts and distinguish among them by context – *i, j, 1, 2, 3* for directions; *k, l, p* (and sometimes *K, . . .*) for atoms. In any case, *atom* first then *direction* if there are two subscripts; *direction*, if only one index for a vector component, but *atom* (in this section at least) if for a weight or a vector. And σ_{d_1} , *e.g.*, for the standard uncertainty of the distance of atom 1 from a plane. For simplicity in practice, we use Cartesian coordinates throughout.

The first task is to find the plane, which we write as

$$0 = \mathbf{m} \cdot \mathbf{r} - d \equiv \mathbf{m}^T \mathbf{r} - d,$$

where $\mathbf{r}$ is here the vector from the origin to any point on the plane (but usually represents the measured position of an atom), $\mathbf{m}$ is a unit vector parallel to the normal from the origin to the plane, d is the length of the normal, and $\mathbf{m}$ and $\mathbf{r}$ are the column representations of $\mathbf{m}$ and $\mathbf{r}$. The least-squares condition is to find the stationary values of $S \equiv [w_k(\mathbf{m}^T \mathbf{r}_k - d)^2]$ subject to $\mathbf{m}^T \mathbf{m} = 1$, with $\mathbf{r}_k$, $k = 1, \dots, n$, the vector from the origin to atom k and with weights, w_k , isotropic and without interatomic correlations for the n atoms of the plane. We also write S as $S \equiv [w(\mathbf{m}^T \mathbf{r} - d)^2]$, the subscript for atom number being implicit in the Gaussian summations ($[\dots]$) over all atoms, as it is also in the angle-bracket notation for the weighted average over all atoms, for example in $\langle \mathbf{r} \rangle$ – the weighted centroid of the groups of atoms – just below.

First solve for d , the origin-to-plane distance.

$$0 = -\frac{1}{2} \frac{\partial S}{\partial d} = [w(\mathbf{m}^T \mathbf{r} - d)] = 0,$$

$$d = [w\mathbf{m}^T \mathbf{r}] / [w] \equiv \mathbf{m}^T \langle \mathbf{r} \rangle.$$

Then

$$S \equiv [w(\mathbf{m}^T \mathbf{r} - d)^2] = [w\{\mathbf{m}^T (\mathbf{r} - \langle \mathbf{r} \rangle)\}^2]$$

$$\equiv [w(\mathbf{m}^T \mathbf{s})^2] \equiv \mathbf{m}^T [w\mathbf{s}\mathbf{s}^T] \mathbf{m} \equiv \mathbf{m}^T \mathbf{A} \mathbf{m}.$$

Here $\mathbf{s}_k \equiv \mathbf{r}_k - \langle \mathbf{r} \rangle$ is the vector from the centroid to atom k . Then solve for $\mathbf{m}$. This is the eigenvalue problem – to diagonalize $\mathbf{A}$ (bear in mind that $\mathbf{A}_{ij}$ is just $[w s_i s_j]$) by rotating the coordinate axes, *i.e.*, to find the 3×3 arrays $\mathbf{M}$ and $\mathbf{L}$, $\mathbf{L}$ diagonal, to satisfy

$$\mathbf{M}^T \mathbf{A} \mathbf{M} = \mathbf{L}, \quad \mathbf{M}^T \mathbf{M} = \mathbf{I}.$$

$\mathbf{A}$ and $\mathbf{M}$ are symmetric; the columns $\mathbf{m}$ of $\mathbf{M}$ are the direction cosines of, and the diagonal elements of $\mathbf{L}$ are the sums of weighted squares of residuals from, the best, worst and intermediate planes, as discussed by SWMB.

3.2.2.1. Error propagation

Waser *et al.* (1973; WMC) carefully discussed how the random errors of measurement of the atom positions propagate into the derived quantities in the foregoing determination of a least-squares plane. This section presents an extension of their discussion. To begin, however, we first show how standard first-order perturbation theory conveniently describes the propagation of error into $\mathbf{M}$ and $\mathbf{L}$ when the positions $\mathbf{r}_k$ of the atoms are incremented by the amounts $\delta \mathbf{r}_k \equiv \xi_k$ and the corresponding quantities $\mathbf{s}_k \equiv \mathbf{r}_k - \langle \mathbf{r} \rangle$ (the vectors from the centroid to the atoms) by the amounts η_k , ($\mathbf{s} \rightarrow \mathbf{s} + \eta$), $\eta_k \equiv \xi_k - \langle \xi \rangle$. (The need to account for the variation in position of the centroid, *i.e.* to distinguish between η_k and ξ_k , was overlooked by WMC.) The consequent increments in $\mathbf{A}$, $\mathbf{M}$ and $\mathbf{L}$ are

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$$\begin{aligned}\delta\mathbf{A} &= [w\eta\mathbf{s}^T] + [w\mathbf{s}\eta^T] \equiv \alpha, \\ \delta\mathbf{M} &= \mathbf{M}\mu, \\ \delta\mathbf{L} &\equiv \lambda.\end{aligned}$$

Here the columns of μ are expressed as linear combinations of the columns of $\mathbf{M}$. Note also that both perturbations, μ and λ , which are the adjustments to the orientations and associated eigenvalues of the principal planes, will depend on the reduced coordinates $\mathbf{s}$ and the perturbing influences ξ by way of α , which in turn depends only on the reduced coordinates and the reduced shifts η_k . In contrast,

$$\delta\mathbf{d} = \delta(\mathbf{m}^T \langle \mathbf{r} \rangle) = (\delta\mathbf{m}^T) \langle \mathbf{r} \rangle + \mathbf{m}^T \langle \xi \rangle;$$

the change in the origin-to-plane distance for the plane defined by the column vectors $\mathbf{m}$ of $\mathbf{M}$, depends on the $\langle \mathbf{r} \rangle$ and $\langle \xi \rangle$ directly as well as on the $\mathbf{s}$ and η by way of the $\delta\mathbf{m}$.

The first-order results arising from the standard conditions, $\mathbf{M}^T \mathbf{M} = \mathbf{I}$, $\mathbf{L}$ diagonal, and $\mathbf{M}^T \mathbf{A} \mathbf{M} = \mathbf{L}$, are

$$\mu^T + \mu = 0, \lambda \text{ diagonal},$$

and

$$\mu^T \mathbf{M}^T \mathbf{A} \mathbf{M} + \mathbf{M}^T \alpha \mathbf{M} + \mathbf{M}^T \mathbf{A} \mathbf{M} \mu = \mu^T \mathbf{L} + \mathbf{L} \mu + \mathbf{M}^T \alpha \mathbf{M} = \lambda.$$

Stated in terms of the matrix components λ_{ij} and μ_{ij} , the first condition is $\mu_{ij} = -\mu_{ji}$, hence $\mu_{ii} = 0$, $i, j = 1, 2, 3$, and the second is $\lambda_{ij} = 0$, $i \neq j$. With these results the third condition then reads

$$\begin{aligned}\lambda_{jj} &= (\mathbf{M}^T \alpha \mathbf{M})_{jj}, & j &= 1, 2, 3 \\ \mu_{ij} &= (\mathbf{M}^T \alpha \mathbf{M})_{ij} / (L_{jj} - L_{ii}), & i &\neq j, \quad i, j = 1, 2, 3.\end{aligned}$$

All this is analogous to the usual first-order perturbation theory, as, for example, in elementary quantum mechanics.

Now rotate to the coordinates defined by WMC, with axes parallel to the original eigenvectors [$\mathbf{M} = \mathbf{I}$, $A_{ij} = L_{ij} \delta_{ij}$, $(\mathbf{M}^T \alpha \mathbf{M})_{ij} = \alpha_{ij}$], restrict attention to the best plane ($M_{13} \equiv m_1 = 0, M_{23} \equiv m_2 = 0, M_{33} \equiv m_3 = 1$), and define ε^T as $(\delta m_1, \delta m_2, \delta d_c)$, keeping in mind $\delta m_3 = \mu_{33} = 0$; d_c itself, the original plane-to-centroid distance, of course vanishes. One then finds

$$\begin{aligned}\delta m_i &\equiv \varepsilon_i = \alpha_{i3} / (L_{33} - L_{ii}) \\ &= [w(s_i \eta_3 + s_3 \eta_i)] / ([ws_3^2] - [ws_i^2]), \quad i = 1, 2, \\ \delta d_c &\equiv \varepsilon_3 = [w\xi_3] / [w] \equiv \langle \xi_3 \rangle, \quad \xi_k \equiv \delta r_k,\end{aligned}$$

and also

$$\delta d = \varepsilon_1 \langle r_1 \rangle + \varepsilon_2 \langle r_2 \rangle + \varepsilon_3.$$

These results have simple interpretations. The changes in direction of the plane normal (the δm_i) are rotations, described by ε_1 and ε_2 , in response to changes in moments acting against effective torsion force constants. For ε_2 , for example, the contribution of atom k to the total relevant moment, about direction 1, is $-w_k s_{k3} s_{k2}$ ($w_k s_{k3}$ the 'force' and s_{k2} the lever arm), and its nominally first-order change has two parts, $-w_k s_{k2} \eta_3$ from the change in force and $-w_k s_{k3} \eta_2$ from the change in lever arm; the resisting torsion constant is $[ws_2^2] - [ws_3^2]$, which, reflection will show, is qualitatively reasonable if not quantitatively obvious. The perpendicular displacement of the plane from the original centroid $\langle \mathbf{r} \rangle$ is ε_3 , but there are two further contributions to δd , the change in distance from origin to plane along the plane normal, that arise from the two components of out-of-plane rotation of the plane about its centroid. Note that ε_3 is not given by $[w\eta_3]/[w] = [w(\xi_3 - \langle \xi_3 \rangle)]/[w]$, which vanishes identically.

There is a further, somewhat delicate point: If the group of atoms is indeed essentially coplanar, the s_{k3} are of the same order of

magnitude as the η_{ki} , unlike the s_{ki} , $i \neq 3$, which are in general about as big as the lateral extent of the group. It is then appropriate to drop all terms in η_i or ξ_i , $i \neq 3$, and, in the denominators, the terms in s_{k3}^2 .

The covariances of the derived quantities (by *covariances* we mean here both variances and covariances) can now be written out rather compactly by extending the implicit designation of atom numbers to double sums, the first of each of two similar factors referring to the first atom index and the second to the second, *e.g.*, $\sum_{kl} ww(s_i s_j) \dots \equiv \sum_{kl} w_k w_l (s_{ki} s_{lj}) \dots$. Note that the various covariances, *i.e.* the averages over the presumed population of random errors of replicated measurements, are indicated by overlines, angle brackets having been pre-empted for averages over sets of atoms.

$$\begin{aligned}\text{cov}(m_i, m_j) &\equiv \overline{\varepsilon_i \varepsilon_j} \\ &= \frac{\sum_{kl} ww(s_i s_j \overline{\eta_3 \eta_3} + s_3 s_3 \overline{\eta_i \eta_j} + s_i s_3 \overline{\eta_3 \eta_j} + s_3 s_j \overline{\eta_i \eta_3})}{\{[w(s_3^2 - s_i^2)]\} \{[w(s_3^2 - s_j^2)]\}}, \quad i, j = 1, 2 \\ \text{cov}(m_i, d_c) &\equiv \overline{\varepsilon_i \varepsilon_3} = \frac{\sum_{kl} ww(s_{ki} \overline{\eta_3 \xi_3} + s_{kj} \overline{\eta_i \xi_3})}{\{[w(s_3^2 - s_i^2)]\} [w]}, \quad i, j = 1, 2 \\ \sigma^2(d_c) &\equiv \overline{\varepsilon_3^2} = \frac{\sum_{kl} ww \overline{\xi_3 \xi_3}}{[w]^2} \\ \sigma^2(d) &\equiv \langle (\delta d)^2 \rangle = \langle r_1 \rangle^2 \overline{\varepsilon_1^2} + \langle r_2 \rangle^2 \overline{\varepsilon_2^2} + \overline{\varepsilon_3^2} + 2\langle r_1 \rangle \langle r_2 \rangle \overline{\varepsilon_1 \varepsilon_2} \\ &\quad + 2\langle r_1 \rangle \overline{\varepsilon_1 \varepsilon_3} + 2\langle r_2 \rangle \overline{\varepsilon_2 \varepsilon_3}.\end{aligned}$$

Interatomic covariance (*e.g.*, $\overline{\eta_{k3} \eta_{l3}}$, $k \neq l$) thus presents no formal difficulty, although actual computation may be tedious. Nonzero covariance for the η 's may arise explicitly from interatomic covariance (*e.g.*, $\overline{\xi_{ki} \xi_{lj}}$, $k \neq l$) of the errors in the atomic positions r_k , and it will *always* arise implicitly because $\langle \xi \rangle$ in $\eta_k = \xi_k - \langle \xi \rangle$ includes all the ξ_k and therefore has nonzero covariance with all of them and with itself, even if there is no interatomic covariance among the ξ_i 's.

If both types of interatomic covariance (explicit and implicit) are negligible, the ε covariances simplify a great deal, the double summations reducing to single summations. [The formal expression for $\sigma^2(d)$ does not change, so it will not be repeated.]

$$\begin{aligned}\text{cov}(m_i, m_j) &\equiv \overline{\varepsilon_i \varepsilon_j} \\ &= \frac{[w^2(s_i s_j \overline{\eta_3^2} + s_3^2 \overline{\eta_i \eta_j} + s_i s_3 \overline{\eta_3 \eta_j} + s_3 s_j \overline{\eta_i \eta_3})]}{\{[w(s_3^2 - s_i^2)]\} \{[w(s_3^2 - s_j^2)]\}}, \quad i, j = 1, 2 \\ \text{cov}(m_i, d_c) &\equiv \overline{\varepsilon_i \varepsilon_3} = \frac{[w^2(s_i \overline{\eta_3 \xi_3} + s_3 \overline{\eta_i \xi_3})]}{\{[w(s_3^2 - s_i^2)]\} [w]}, \quad i, j = 1, 2 \\ \sigma^2(d_c) &\equiv \overline{\varepsilon_3^2} = \frac{[w^2 \overline{\xi_3^2}]}{[w]^2}.\end{aligned}$$

When the variances are the same for ξ as for η (*i.e.* $\overline{\xi_i \xi_j} = \overline{\eta_i \eta_j}$, all i, j) and the covariances all vanish ($\overline{\xi_i \xi_j} = 0$, $i \neq j$), the $\overline{\varepsilon_i \varepsilon_j}$ simplify further. If the variances are also isotropic ($\overline{\xi_i^2} = \overline{\xi_j^2} = \sigma^2$, all i, j), there is still further simplification to

$$\begin{aligned}\sigma^2(m_i) &\equiv \overline{\varepsilon_i^2} = \frac{[w^2 \sigma^2 (s_i^2 + s_3^2)]}{\{[w(s_3^2 - s_i^2)]\}^2}, \quad i = 1, 2 \\ \sigma^2(d_c) &\equiv \overline{\varepsilon_3^2} = [w^2 \sigma^2] / [w]^2 \\ \text{cov}(m_1, m_2) &\equiv \overline{\varepsilon_1 \varepsilon_2} = \frac{[w^2 \sigma^2 s_1 s_2]}{\{[w(s_3^2 - s_1^2)]\} \{[w(s_3^2 - s_2^2)]\}} \\ \text{cov}(m_i, d_c) &\equiv \overline{\varepsilon_i \varepsilon_3} = \frac{[w^2 \sigma^2 s_i]}{\{[w(s_3^2 - s_i^2)]\} [w]}, \quad i = 1, 2.\end{aligned}$$

If allowance is made for the difference in definition between ε_3 and

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δd , these expressions are equivalent to the ones (equations 7–9) given by WMC, who, however, do not appear to have been aware of the distinction between η and ξ and the possible consequences thereof.

If, finally, w^{-1} for each atom is taken equal to its $\overline{\eta_j^2} = \sigma^2$, all j , there is still further simplification.

$$\begin{aligned}\sigma^2(m_i) &\equiv \overline{\varepsilon_i^2} = \frac{[w(s_3^2 + s_i^2)]}{\{[w(s_3^2 - s_i^2)]\}^2}, \quad i = 1, 2 \\ \sigma^2(d_c) &\equiv \overline{\varepsilon_3^2} = [w]/[w]^2 = 1/[w] \\ \text{cov}(m_1, m_2) &\equiv \overline{\varepsilon_1 \varepsilon_2} = \frac{[ws_1 s_2]}{\{[w(s_3^2 - s_1^2)]\}\{[w(s_3^2 - s_2^2)]\}} \\ \text{cov}(m_i, d_c) &\equiv \overline{\varepsilon_i \varepsilon_3} = \frac{[ws_i]}{\{[w(s_3^2 - s_i^2)]\}[w]}, \quad i = 1, 2.\end{aligned}$$

For the earlier, more general expressions for the components of $\varepsilon \varepsilon^T$ it is still necessary to find $\overline{\eta_{ki} \eta_{lj}}$ and $\overline{\eta_{ki} \xi_{lj}}$ in terms of $\xi_{ki} \xi_{lj}$, with $\eta_{ki} \equiv \delta s_{ki} = \delta(r_{ki} - \langle r_{ki} \rangle) = \xi_{ki} - \langle \xi_i \rangle = \sum_l w_l (\xi_{ki} - \xi_{li})/[w]$.

$$\begin{aligned}\overline{\eta_{ki} \eta_{pj}} &= \sum_{l, q} w_l w_q (\xi_{ki} - \xi_{li})(\xi_{pj} - \xi_{qj})/[w]^2 \\ &= (\xi_{ki} - \langle \xi_i \rangle)(\xi_{pj} - \langle \xi_j \rangle) \\ \overline{\eta_{ki} \xi_{p3}} &= \sum_l w_l (\xi_{ki} - \xi_{li}) \xi_{p3} / [w] = \overline{\xi_{ki} \xi_{p3}} - \langle \xi_i \rangle \xi_{p3}.\end{aligned}$$

In the isotropic, ‘no-correlation’ case, for example, these reduce to

$$\begin{aligned}\overline{\eta_{ki} \eta_{pi}} &= -w_k \overline{\xi_{ki}^2} / [w] - w_p \overline{\xi_{pi}^2} / [w] \\ &\quad + [w^2 \overline{\xi_i^2}] / [w]^2, \quad k \neq p; i = 1, 2 \\ \overline{\eta_{ki}^2} &= (1 - 2w_k / [w]) \overline{\xi_{ki}^2} + [w^2 \overline{\xi_i^2}] / [w]^2, \quad i = 1, 2 \\ \overline{\eta_{k3} \eta_{p3}} &= -w_p \overline{\xi_{p3}^2} / [w],\end{aligned}$$

and

$$\overline{\eta_{k3}^2} = \overline{\xi_{k3}^2} - w_k \overline{\xi_{k3}^2} / [w] = \overline{\xi_{k3}^2} (1 - w_k / [w]).$$

Here the difference between the correct covariance values and the values obtained on ignoring the variation in $\langle r \rangle$ may be important if the number of defining atoms is small, say, 5 or 4 or, in the extreme, 3.

3.2.2.2. The standard uncertainty of the distance from an atom to the plane

There are two cases, as has been pointed out, *e.g.*, by Ito (1982).

(1) The atom (atom K) was *not* included in the specification of the plane.

$$\begin{aligned}d_K &= \mathbf{m}^T (\mathbf{r}_K - \langle \mathbf{r} \rangle) = r_{k3} - \langle r_3 \rangle \\ \delta d_K &= \xi_{k3} + s_{K1} \varepsilon_1 + s_{K2} \varepsilon_2 - \varepsilon_3 \\ \sigma_{d_K}^2 &= \overline{\xi_{k3}^2} + s_{K1}^2 \overline{\varepsilon_1^2} + s_{K2}^2 \overline{\varepsilon_2^2} + \overline{\varepsilon_3^2} \\ &\quad + 2s_{K1} s_{K2} \overline{\varepsilon_1 \varepsilon_2} - 2s_{K1} \overline{\varepsilon_1 \varepsilon_3} - 2s_{K2} \overline{\varepsilon_2 \varepsilon_3} \\ &\quad + 2s_{K1} \overline{\xi_{k3} \varepsilon_1} + 2s_{K2} \overline{\xi_{k3} \varepsilon_2} - 2\overline{\xi_{k3} \varepsilon_3}.\end{aligned}$$

In the isotropic, ‘no-correlation’ case the last three terms, *i.e.* the terms in $\varepsilon_i \xi_{K3}$, are all negligible or zero.

In either case the value for $\overline{\xi_{k3}^2}$ and the appropriate $\overline{\varepsilon_i \varepsilon_j}$ values from the least-squares-plane calculation need to be inserted.

(2) Atom K was included in the specification of the plane. The expression for $\sigma_{d_K}^2$ remains the same, but the averages in it may be importantly different.

For example, consider a plane defined by only three atoms, one of overwhelmingly great w at $(0, 0, 0)$, one at $(1, 0, 0)$ and one at $(0, 1, 0)$. The centroid is at $(0, 0, 0)$ and we take $K = 2$, *i.e.* σ_{d_2} is the item of interest. Of course, it is obvious without calculation that the standard uncertainties vanish for the distances of the three atoms from the plane they alone define; the purpose here is only to show, in one case for one of the atoms, that the calculation gives the same result, partly, it will be seen, because the change in orientation of the plane is taken into account. If the only variation in the atom positions is described by $\overline{\xi_{23}^2} = \sigma^2$, one has $s_{21} = 1, \varepsilon_3 = \varepsilon_2 = 0, \varepsilon_1 = -\xi_{23}$, and $\overline{\xi_{K3} \varepsilon_1} = \sigma^2$. The non-vanishing terms in the desired variance are then

$$\begin{aligned}\sigma_{d_2}^2 &= \overline{\xi_{23}^2} + s_{21}^2 \overline{\varepsilon_1^2} + 2s_{21} \overline{\xi_{23} \varepsilon_1} \\ &= (1 + 1 - 2)\sigma^2 = 0.\end{aligned}$$

If, however, the problem concerns the same plane and a fourth atom at position $(1, 0, r_{43})$, *not* included in the specification of the plane and uncertain only in respect to r_{43} (which is arbitrary) with $\overline{\xi_{43}^2} = \sigma^2$ (the same mean-square variation in direction 3 as for atom 2) and $\overline{\xi_{43} \xi_{23}} = 0$, the calculation for $\sigma_{d_4}^2$ runs the same as before, except for the third term:

$$\sigma_{d_4}^2 = (1 + 1 - 0)\sigma^2 = 2\sigma^2.$$

Extreme examples of this kind show clearly enough that variation in the direction of the plane normal or in the normal component of the centroid position will sometimes be important, the remarks to the contrary by Shmueli (1981) and, for the centroid, the omission by WMC notwithstanding. If only a few atoms are used to define the plane (*e.g.*, three or, as is often the case, a very few more), both the covariance with the centroid position and uncertainty in the direction of the normal are likely to be important. The uncertainty in the normal may still be important, even if a goodly number of atoms are used to define the plane, whenever the test atom lies near or beyond the edge of the lateral domain defined by the other atoms.

3.2.3. The proper least-squares plane, with Gaussian weights

If it is desired to weight the points to be fitted by a plane in the sense of Gaussian least squares, then two items different from what we have seen in the crystallographic literature have to be brought into view: (1) the weights may be anisotropic and include interatomic correlations, because the error matrix of the atom coordinates may in general be anisotropic and include interatomic correlations; and (2) it has to be considered that the atoms truly lie on a plane and that their observed positions are to be adjusted to lie precisely on that plane, whatever its precise position may turn out to be and no matter what the direction, in response to the anisotropic weighting, of their approach to the plane.

An important consequence of (1), the non-diagonal character of the weight matrix, even with Cartesian coordinates, is that the problem is no longer an ordinary eigenvalue problem as treated by SWMB (1959),* not even if there is no interatomic correlation and

* A simple two-dimensional problem illustrates the point. A regular polygon of n atoms is to define a ‘best’ line (always a *central* line). If the error matrix (the same for each atom) is isotropic, the weighted sum of squares of deviations from the line is independent of its orientation for $n > 2$, *i.e.* the problem is a degenerate eigenvalue problem, with two equal eigenvalues. However, if the error ellipsoids are not isotropic and are all oriented radially or all tangentially (these are merely the two orientations tried), the sum has $n/2$ equal minima for even n and 2 equal minima for odd n , in the one- π range of possible orientations of the line.

Possibly similar peculiarities might be imagined if the anisotropic weights were more complicated (*e.g.*, ‘star’ shaped) than can be described by a non-singular matrix, or by any matrix. Such are of course excluded here.

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the anisotropy is the same for each atom. On this last case the contrary remark in SWMB at the beginning of the footnote, p. 601, is incorrect, and the treatments in terms of the eigenvector–eigenvalue problem by Hamilton (1961, 1964, pp. 174–177) and Ito (1981a)* evade us. At best the problem is still not a genuine eigenvalue problem if the anisotropies of the atoms are not all alike.

Hypothesis (2), of perfect planarity, may be hard to swallow. It has to be tested, and for any set of atoms the conclusion may be that they probably do not lie on a plane. But if the hypothesis is provisionally adopted (and it has to be decided beforehand which of the following alternatives is to be followed), the adjusted positions are obtained by moving the atoms onto the plane

(a) along paths normal to the plane, or

(b) along the *proper* paths of ‘least resistance’ – that is, paths with, in general, both normal and lateral components differently directed for each atom so as to minimize the appropriately weighted quadratic form of differences between the observed and adjusted coordinates. The lateral motions (and the anisotropic weights that induce them) may change the relative weights of different atoms in accordance with the orientation of the plane; change the perpendicular distance of origin-to-plane; and change the orientation of the plane in ways that may at first give surprise.

Our first example of this has already been given.† A second, which actually inspired our first, is to be found in Hamilton (1964; example 5-8-1, p. 177), who discusses a rectangle of four points with identical error ellipsoids elongated in the long direction of the rectangle. The unweighted best line bisects the pattern along this direction, but the weighted best line is parallel to the short direction, if the elongation of the ellipsoids is sufficient. A third example (it is severely specialized so that a precise result can be attained without calculation) has three atoms *ABC* arranged like a C_{2v} –*mm* molecule with bond angle 90°. The central atom, *B*, has overwhelming isotropic weight; *A* and *C* have parallel extremely elongated error ellipsoids, aligned parallel to the *A*–*B* bond. The unweighted best line passes through *B* parallel to *A*–*C*; the weighted best line passes through *B* and through *C*. Our last example is of a plane defined by a number of atoms of which one lies a considerable distance above the plane and at a distance from the normal through the centroid, but with the downward semi-axis of its extremely elongated prolate error ellipsoid intersecting that normal before it intersects the plane. If this atom is moved at right angles to the plane and further away from it, the centroid normal tips toward the atom, whereas it would tip away if the atom’s weight function were isotropic or if the calculation were the usual one and in effect constrained the adjusted position of the atom to move at right angles to the plane.

The lead notion here – that the observed points are to be adjusted individually to fit a curve (surface) of required type exactly, rather than that the curve should simply be constructed to fit the observed points as well as possible in the sense of minimizing the weighted sum of squares of the distances along some preordained direction (perhaps normal to the plane, but perhaps as in ordinary curve fitting parallel to the *y* axis) – we first learned from the book by Deming (1943), *Statistical Adjustment of Data*, but it is to be found in Whittaker & Robinson (1929), Arley & Buch (1950), Hamilton (1964, our most used reference), and doubtless widely throughout the least-squares literature. It has recently been strongly emphasized by Lybanon (1984), who gives a number of modern references. It is the only prescription that properly satisfies the least-squares

conditions, whereas (a) and other analogous prescriptions are only arbitrary regressions, in (a) a normal regression onto the plane.‡

We have explored the problem of least-squares *adjustment* of observed positions subject to anisotropic weights with the help of three Fortran programs, one for the straight line and two for the plane. In the first plane program an approximate plane is derived, coordinates are rotated as in WMC (1973), and the parameters of the plane are adjusted and the atoms moved onto it, either normally or in full accord with the least-squares condition, but in either case subject to independent anisotropic weight matrices. The other plane program, described in Appendix 3.2.1, proceeds somewhat more directly, with the help of the method of Lagrange multipliers. However, neither program has been brought to a satisfactory state for the calculation of the variances and covariances of the derived quantities.

3.2.3.1. Formulation and solution of the general Gaussian plane

We conclude with an outline for a complete feasible solution, including interatomic weight-matrix elements. Consider atoms at observed vector positions $\mathbf{r}_k$, $k = 1, \dots, n$, designated in the following equations by $\mathbf{R}$, an n -by-3 array, with $R_{ki} = r_{ki}$; the corresponding adjusted positions denoted by the array $\mathbf{R}_a$; n constraints (each adjusted position $\mathbf{r}_a - a$ for ‘adjusted’ – must be on the plane), and $3n + 3$ adjustable parameters ($3n$ $\mathbf{R}_a$ components and the 3 components of the vector $\mathbf{b}$ of reciprocal intercepts of the plane), so that the problem has $n - 3$ degrees of freedom. The $3n$ -by- $3n$ weight matrix $\mathbf{P}$ may be anisotropic for the separate atoms, and may include interatomic elements; it is symmetric in the sense $P_{kij} = P_{lji}$, but P_{kij} will not in general be equal to P_{kji} . The array $\mathbf{A}$ denotes n Lagrange multipliers, one for each atom and unrelated to the λ ’s of Section 3.2.2; m and d still represent the direction cosines of the plane normal and the perpendicular origin-to-plane distance.

For a linear least-squares problem we know (see, e.g., Hamilton, 1964, p. 143) that the proper weight matrix is the reciprocal of the atomic error matrix ($\mathbf{P} = \mathbf{M}^{-1}$);§ note that ‘ $\mathbf{M}$ ’ is unrelated to the ‘ $\mathbf{M}$ ’ of Section 3.2.2. The least-squares sum is now

$$S = (\mathbf{R} - \mathbf{R}_a)\mathbf{P}(\mathbf{R} - \mathbf{R}_a),$$

and the augmented sum for applying the method of Lagrange multipliers is

$$\Phi = S/2 - \mathbf{A}\mathbf{b}\mathbf{R}_a.$$

‡ Ito’s second method (Ito, 1981b), of ‘substitution’, is also a regression, essentially like the regression along *z* at fixed *x* and *y* used long ago by Clews & Cochran (1949, p. 52) and like the regressions of *y* on fixed *x* that – despite the fact that both *x* and *y* are afflicted with random errors – are commonly taught or practised in schools, universities and laboratories nearly 200 years after Gauss, to the extent that Deming, Lybanon and other followers of Gauss have so far had rather little influence. Kalantar’s (1987) short note is a welcome but still rare exception.

§ Is this statement firm for a nonlinear problem? We use it, assuming that at convergence the problem has become effectively linear. But in fact this will depend on how great the nonlinearity is, in comparison with the random errors (variances) that eventually have to be considered. Another caveat may be in order in regard to our limited knowledge of Gauss’s second derivation of the method of least squares, the one he preferred [see Whittaker & Robinson (1929)] and which establishes for a linear system that the best *linear combination* of a set of observations, afflicted by random errors, for estimating any arbitrary derived quantity – best in the sense of being unbiased and having minimal mean-square error – is given by the method of least squares with the weight matrix set equal to the inverse error matrix of the observations. Hamilton, and Whittaker & Robinson, prove this only for the case that the derived parameters are not constrained, whereas here they are. We believe, however, that the best choice of weights is a question concerning only the observations, and that it cannot be affected by the method used for minimizing *S* subject to any constraints, whether by eliminating some of the parameters by invoking the constraints directly or by the use of Lagrange multipliers.

* Ito observes that his method fails when there are only three points to define the plane, his least-squares normal equations becoming singular. But the situation is worse: his equations are singular for any number of points, if the points fit a plane exactly.

† See first footnote.

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Here the summation brackets ($\dots$) have been replaced by matrix products, but the simplified notation is not matrix notation. It has to be regarded as only a useful mnemonic in which all the indices and their clutter have been suppressed in view of their inconveniently large number for some of the arrays. If the dimensions of each are kept in mind, it is easy to recall the indices, and if the indices are resupplied at any point, it is not difficult to discover what is really meant by any of the expressions or whether evaluations have to be executed in a particular order.

The conditions to be satisfied are

$$\begin{aligned} 0 &= \frac{-\partial\Phi}{\partial\mathbf{R}_a} = \mathbf{P}(\mathbf{R} - \mathbf{R}_a) + \mathbf{A}\mathbf{b}, \\ 0 &= \frac{-\partial\Phi}{\partial\mathbf{b}} = \mathbf{A}\mathbf{R}_a, \\ \mathbf{1} &= \mathbf{b}\mathbf{R}_a. \end{aligned}$$

That the partial derivatives of $S/2$ should be represented by $\mathbf{P}(\mathbf{R} - \mathbf{R}_a)$ depends upon the above-mentioned symmetry of $\mathbf{P}$. Note that each of the n unit elements of $\mathbf{1}$ expresses the condition that its $\mathbf{r}_a$ should indeed lie on the plane, and that $\mathbf{A}\mathbf{b}$ is just the same as $\mathbf{b}\mathbf{A}$. The perpendicular origin-to-plane distance and the direction cosines of the plane normal are $d^2 = 1/\mathbf{b}^T\mathbf{b}$ and $\mathbf{m} = \mathbf{b}/\sqrt{\mathbf{b}^T\mathbf{b}}$.

On multiplication by $\mathbf{M}$ the first condition solves for $\mathbf{R}_a$, and that expression combined separately with the second condition and with the third gives highly nonlinear equations (there is further mention of this nonlinearity in Appendix 3.2.1) that have to be solved for $\mathbf{b}$ and $\mathbf{A}$:

$$\begin{aligned} \mathbf{R}_a &= \mathbf{R} + \mathbf{M}\mathbf{A}\mathbf{b} = \mathbf{R} + \mathbf{M}\mathbf{b}\mathbf{A} \\ 0 &= \mathbf{F} \equiv (\mathbf{A}\mathbf{M}\mathbf{A})\mathbf{b} + \mathbf{A}\mathbf{R} \\ 0 &= \mathbf{G} \equiv (\mathbf{b}\mathbf{M}\mathbf{b})\mathbf{A} - (\mathbf{1} - \mathbf{b}\mathbf{R}). \end{aligned}$$

The best way of handling these equations, at least if it is desired to find their solutions both for $\mathbf{R}_a$, $\mathbf{A}$, and $\mathbf{b}$ and for the error matrix of these derived quantities in terms of the error matrix for $\mathbf{R}$, seems to be to find an approximate solution by one means or another, to make sure that it is the desired solution, if (as may be) there is ambiguity, and to shift the origin to a point far enough from the plane and close enough to the centroid normal to avoid the difficulties discussed by SWMB. Then linearize the first and second equations by differentiation and solve the results first iteratively to fit the current residuals $\mathbf{F}_0$ and $\mathbf{G}_0$ and then for nominally infinitesimal increments $\delta\mathbf{b}$ and $\delta\mathbf{A}$. In effect, one deals with equations $\mathbf{Q}\mathbf{X} = \mathbf{Y}$, where $\mathbf{Q}$ is the $(n+3) \times (n+3)$ matrix of coefficients of the following set of equations, $\mathbf{X}$ is the $(n+3)$ -dimensional vector of increments $\delta\mathbf{b}$ and $\delta\mathbf{A}$, and $\mathbf{Y}$ is the vector either of the first terms or of the second terms on the right-hand side of the equations.

$$\begin{aligned} (\mathbf{A}\mathbf{M}\mathbf{A})\delta\mathbf{b} + (\mathbf{M}\mathbf{A}\mathbf{b} + \mathbf{A}\mathbf{M}\mathbf{b} + \mathbf{R})\delta\mathbf{A} &= -\mathbf{F}_0 - \mathbf{A}\delta\mathbf{R} \\ (\mathbf{M}\mathbf{b}\mathbf{A} + \mathbf{b}\mathbf{M}\mathbf{A} + \mathbf{R})\delta\mathbf{b} + (\mathbf{b}\mathbf{M}\mathbf{b})\delta\mathbf{A} &= -\mathbf{G}_0 - \mathbf{b}\delta\mathbf{R}. \end{aligned}$$

When $\mathbf{X}$ becomes the vector ε of errors in $\mathbf{b}$ and $\mathbf{A}$ as induced by errors $\eta \equiv \delta\mathbf{R}$ in the measured atom positions, these equations become, in proper matrix notation, $\mathbf{Q}\varepsilon = \mathbf{Z}\eta$, with solution $\varepsilon = \mathbf{Q}^{-1}\mathbf{Z}\eta$, where $\mathbf{Z}$ is the $(n+3)$ -dimensional vector of components, first of $\mathbf{b}$ then of $\mathbf{A}$. The covariance matrix $\overline{\varepsilon\varepsilon^T}$, from which all the covariances of $\mathbf{b}$, $\mathbf{R}_a$, and $\mathbf{R}$ (including for the latter any atoms that were not included for the plane) can be derived, is then given by

$$\overline{\varepsilon\varepsilon^T} = \mathbf{Q}^{-1}\mathbf{Z}\overline{\eta\eta^T}\mathbf{Z}^T(\mathbf{Q}^{-1})^T.$$

This is not as simple as the familiar expression for propagation of errors for a least-squares problem solved without the use of

Lagrange multipliers, i.e. $\overline{\varepsilon\varepsilon^T} = \mathbf{B}^{-1}$, where $\mathbf{B}$ is the matrix of the usual normal equations, both because $\mathbf{B} = \mathbf{B}^T$ is no longer valid and because the middle factor $\mathbf{Z}\overline{\eta\eta^T}\mathbf{Z}^T$ is no longer equal to $\mathbf{B}^{-1}$.

It is easy to verify that $\mathbf{A}$ consists of a set of coefficients for combining the n row vectors of $\mathbf{M}\mathbf{b}$, in the expression for $\mathbf{R}_a$, into corrections to $\mathbf{R}$ such that each adjusted position lies exactly on the plane:

$$\begin{aligned} \mathbf{b}\mathbf{R}_a &= \mathbf{b}\mathbf{R} + \mathbf{b}\mathbf{M}\mathbf{b}(\mathbf{b}\mathbf{M}\mathbf{b})^{-1}(\mathbf{I} - \mathbf{b}\mathbf{R}) \\ &= \mathbf{b}\mathbf{R} + \mathbf{I} - \mathbf{b}\mathbf{R} = \mathbf{I}. \end{aligned}$$

At the same time one can see how the lateral shifts occur in response to the anisotropy of $\mathbf{M}$, especially if, now, only the anisotropic case without interatomic correlations is considered. For atom k write $\mathbf{b}$ in terms of its components along the principal axes of $\mathbf{M}_k$, associated with the eigenvalues α, β and γ ; the shifts are then proportional to $\mathbf{M}_{\alpha\alpha}b_\alpha^2$, $\mathbf{M}_{\beta\beta}b_\beta^2$ and $\mathbf{M}_{\gamma\gamma}b_\gamma^2$, each along its principal axis, and the sums of the contributions of these shift components to the total displacement along the plane normal or along either of two orthogonal directions in the plane can readily be visualized. In effect $\mathbf{M}_k$ is the compliance matrix for these shifts of atom k . Similarly, it can be seen that in the isotropic case with interatomic correlations a pair of equally weighted atoms located, for example, at some distance apart and at about the same distance from the plane, will have different shifts (and different influences on d and $\mathbf{m}$) depending on whether the covariance between the errors in the perpendicular components of their observed positions relative to the plane is small, or, if large, whether it is positive or is negative. If the covariance is large and positive, the adjusted positions will both be pulled toward the plane, strongly resisting, however, the apparent necessity that both reach the plane by moving by different amounts; in consequence, there will be a strong tendency for the plane to tilt toward the more distant atom, and possibly even away from the nearer one. But if the covariance is large and negative, the situation is reversed: the more distant atom can readily move more than the nearer one, while it is very difficult to move them together; the upshot is then that the plane will move to meet the original midpoint of the two atoms while they tilt about that midpoint to accommodate the plane.

It is attractive to solve our problem with the 'normal' formulation of the plane, $\mathbf{m}\mathbf{r} = d$, and so directly avoid the problems that arise for $d \approx 0$. The solution in terms of the reciprocal intercepts $\mathbf{b}$ has been given first, however, because reducing by two (d and a Lagrange multiplier) the number of parameters to be solved for may more than make up for the nuisance of having to move the origin. The solution in terms of d follows.

The augmented variation function is now

$$\Phi = (\mathbf{R} - \mathbf{R}_a)\mathbf{P}(\mathbf{R} - \mathbf{R}_a)/2 - \mathbf{A}(\mathbf{m}\mathbf{R}_a - d\mathbf{I}) + \mu\mathbf{m}\mathbf{m}/2,$$

the term in the new Lagrange multiplier, μ , and the term in $d\mathbf{I}$ having been added to the previous expression. The $\mathbf{I}$, an n -vector of 1's, is needed to express the presence of n terms in the $\mathbf{A}$ sum. There are then five equations to be satisfied – actually $n+1+3n+3+1 = 4n+5$ ordinary equations – in the $3n$ $\mathbf{R}_a$ components, the n $\mathbf{A}$'s, the 3 $\mathbf{m}$ components, μ , and $d - 4n+5$ unknowns in all, as required. These equations are as follows:

$$\begin{aligned} \mathbf{m}\mathbf{R}_a &= d\mathbf{I} \\ \mathbf{m}\mathbf{m} &= 1 \\ 0 &= -\left(\frac{\partial\Phi}{\partial\mathbf{R}_a}\right) = \mathbf{P}(\mathbf{R} - \mathbf{R}_a) + \mathbf{A}\mathbf{m} \\ 0 &= \frac{\partial\Phi}{\partial\mathbf{m}} = -\mathbf{A}\mathbf{R}_a + \mu\mathbf{m} \end{aligned}$$

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$$0 = \frac{\partial \Phi}{\partial d} = \mathbf{A}\mathbf{I}.$$

As before, multiply the third equation by $\mathbf{M}$ and solve for $\mathbf{R}_a$. Then substitute the result into the first and fourth equations to obtain

$$\begin{aligned} \mathbf{m}\mathbf{R} + \mathbf{m}\mathbf{M}\mathbf{m}\mathbf{A} &= d\mathbf{I}, \\ \mathbf{m}\mathbf{m} &= 1, \\ \mathbf{A}\mathbf{R} + \mathbf{A}\mathbf{M}\mathbf{A}\mathbf{m} &= \mu\mathbf{m}, \\ \mathbf{A}\mathbf{I} &= 0 \end{aligned}$$

as the $n + 5$ mostly nonlinear equations to be solved for $\mathbf{m}$, $\mathbf{A}$, d and μ by linearizing (differentiation), solving for increments, and iterating, in the pattern described more fully above. An approximate solution for $\mathbf{m}$ and d has first to be obtained somehow, perhaps by the method of SWMB (with isotropic uncorrelated weights), checked for suitability, and extended to a full complement of first approximations by

$$\begin{aligned} \mathbf{A} &= (\mathbf{m}\mathbf{M}\mathbf{m})^{-1}(d\mathbf{I} - \mathbf{m}\mathbf{R}) \\ \mu &= \mathbf{m}\mathbf{A}\mathbf{R} + \mathbf{m}\mathbf{A}\mathbf{M}\mathbf{A}\mathbf{m}, \end{aligned}$$

which readily follow from the previous equations. As in the 'intercepts' solution the linearized expression for the increments in μ , $\mathbf{A}$, d and $\mathbf{m}$ can be used together with the equation for $\mathbf{R}_a$ to obtain all the covariances needed in the treatment described in Section 3.2.2.

3.2.3.2. Concluding remarks

Proper tests of statistical significance of this or that aspect of a least-squares plane can be made if the plane has been based on a proper weight matrix as discussed in Section 3.2.3; if it can be agreed that the random errors of observation are normally distributed; and if an agreeable test (*null*) hypothesis can be formulated. For example, one may ask for the probability that a degree of fit of the observed positions to the least-squares plane at least as poor as the fit that was found might occur if the atoms in truth lie precisely on a plane. The χ^2 test answers this question: a table of probabilities displayed as a function of χ^2 and ν provides the answer. Here χ^2 is just our minimized

$$S = \mathbf{b}\mathbf{A}\mathbf{M}\mathbf{P}\mathbf{M}\mathbf{A}\mathbf{b} = \mathbf{b}\mathbf{A}\mathbf{M}\mathbf{A}\mathbf{b},$$

and

$$\begin{aligned} \nu &= n_{\text{observations}} - n_{\text{adjusted parameters}} - n_{\text{constraints}} \\ &= 3n - (n + 3) - n = n - 3, \end{aligned}$$

is the number of degrees of freedom for the problem of the plane (erroneously cited in at least one widely used crystallographic system of programs as $3n - 3$). There will not usually be any reason to believe that the atoms are exactly coplanar in any case; nevertheless, this test may well give a satisfying indication of whether or not the atoms are, in the investigator's judgment, essentially coplanar. It must be emphasized that χ^2 as calculated in Section 3.2.3 will include proper allowance for uncertainties in the d and orientation of the plane with greater reliability than the estimates of Section 3.2.2, which are based on nominally arbitrary weights. Both, however, will allow for the large variations in d and *tilt* that can arise in either case if n is small. Some of the earlier, less complete discussions of this problem have been mentioned in Section 3.2.2.

Among the problems not considered here are ones of fitting more than one plane to a set of observed positions, *e.g.* of two planes fitted to three sets of atoms associated, respectively, with the first plane, the second plane, and both planes, and of the angle between the two planes. For the atoms common to both planes there will be a

fundamental point of difference between existing programs (in which, in effect, the positions of the atoms in common are inconsistently adjusted to one position on the first plane and, in general, a different position on the second) and what we would advocate as the proper procedure of requiring the adjusted positions of such atoms to lie on the line of intersection of the two planes. As to the dihedral angle there is a difficulty, noted by WMC (1973, p. 2705), that the usual formulation of $\sigma^2(\theta_0)$ in terms of the cosine of the dihedral angle reduces to 0/0 at $\theta_0 = 0$. However, this variance is obviously well defined if the plane normals and their covariances are well defined. The essential difficulty lies with the ambiguity in the direction of the line of intersection of the planes in the limit of zero dihedral angle. For the torsion angle about a line defined by two atoms, there should be no such difficulty. It seems likely that for the two-plane problem proposed above, the issue that decides whether the dihedral angle will behave like the standard dihedral angle or, instead, like the torsion angle, will be found to be whether or not two or more atoms are common to both planes.

All that we have tried to bring out about the covariances of derived quantities involving the plane requires that the covariances of the experimental atom positions (reduced in our formulations to Cartesian coordinates) be included. However, such covariances of derived quantities are often not available in practice, and are usually left unused even if they are. The need to use the covariances, not just the variances, has been obvious from the beginning. It has been emphasized in another context by Schomaker & Marsh (1983) and much more strongly and generally by Waser (1973), whose pleading seems to have been generally ignored, by now, for about thirty years.

Appendix 3.2.1.

Consider n atoms at observed vector positions $\mathbf{r}$ (expressed in Cartesians), n constraints (each adjusted position $\mathbf{r}_a - \mathbf{a}$ for 'adjusted' – must be on the plane) and $3n + 3$ adjustable parameters ($3n$ $\mathbf{r}_a$ components and the 3 components of the vector $\mathbf{a}$ of reciprocal intercepts of the plane), so that the problem has $n - 3$ degrees of freedom. The weight matrices $\mathbf{P}$ may be differently anisotropic for each atom, but there are no interatomic correlations. As before, square brackets, '[...]', represent the Gaussian sum over all atoms, usually suppressing the atom indices. We also write λ , *not* the λ of Section 3.2.2, for the Lagrange multipliers (one for each atom); $\mathbf{m}$ for the direction cosines of the plane normal; and d for the perpendicular origin-to-plane distance.

As before, $\mathbf{P}_k$ is the reciprocal of the atomic error matrix: $\mathbf{P}_k = \mathbf{M}_k^{-1}$ (correspondingly, $\mathbf{P} \equiv \mathbf{M}^{-1}$) but ' $\mathbf{M}$ ' is no longer the ' $\mathbf{M}$ ' of Section 3.2.2. The appropriate least-squares sum is

$$S = [(\mathbf{r} - \mathbf{r}_a)^T \mathbf{P}(\mathbf{r} - \mathbf{r}_a)]$$

and the augmented sum for applying the method of Lagrange multipliers is

$$\Phi = S/2 - [\lambda \mathbf{a}^T \mathbf{r}_a].$$

Φ is to be minimized with respect to variations of the adjusted atom positions $\mathbf{r}_{ka}$ and plane reciprocal intercepts b_i , leading to the equations

$$\begin{aligned} 0 &= \frac{-\partial \phi}{\partial \mathbf{r}_a^T} = \mathbf{P}(\mathbf{r} - \mathbf{r}_a) + \lambda \mathbf{b} \text{ and} \\ 0 &= \frac{-\partial \Phi}{\partial \mathbf{b}^T} = [\lambda \mathbf{r}_a], \end{aligned}$$

subject to the plane conditions $\mathbf{b}^T \mathbf{r}_a = 1$, each atom, with $d^2 = 1/(\mathbf{b}^T \mathbf{b})$, $\mathbf{m} = \mathbf{b}/\sqrt{\mathbf{b}^T \mathbf{b}}$. These equations are nonlinear.

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A convenient solution runs as follows: first multiply the first equation by $\mathbf{M}$ and solve for the adjusted atom positions in terms of the Lagrange multipliers λ and the reciprocal intercepts $\mathbf{b}$ of the plane; then multiply *that* result by $\mathbf{b}^T$ applying the plane conditions, and solve for the λ 's

$$\begin{aligned} \mathbf{r}_a &= \mathbf{r} + \lambda \mathbf{M} \mathbf{b}, \quad \mathbf{M} \equiv \mathbf{P}^{-1} \\ 1 &= \mathbf{b}^T \mathbf{r} + \lambda \mathbf{b}^T \mathbf{M} \mathbf{b}, \\ \lambda &= (1 - \mathbf{b}^T \mathbf{r}) / (\mathbf{b}^T \mathbf{M} \mathbf{b}). \end{aligned}$$

Next insert these values for the λ 's and $\mathbf{r}_a$'s into the second equation:

$$0 = \frac{\partial \Phi}{\partial \mathbf{b}^T} = [\lambda \mathbf{r}_a] = \left[\frac{1 - \mathbf{b}^T \mathbf{r}}{\mathbf{b}^T \mathbf{M} \mathbf{b}} \left(\mathbf{r} + \frac{1 - \mathbf{b}^T \mathbf{r}}{\mathbf{b}^T \mathbf{M} \mathbf{b}} \mathbf{M} \mathbf{b} \right) \right].$$

This last equation, $F(\mathbf{b}) = 0$, is to be solved for $\mathbf{b}$. It is highly nonlinear: $F(\mathbf{b}) = O(\mathbf{b}^3)/O(\mathbf{b}^4)$. One can proceed to a first approximation by writing $0 = [(1 - \mathbf{b}^T \mathbf{r})\mathbf{r}]$; i.e., $[\mathbf{r}\mathbf{r}] \cdot \mathbf{b} = [\mathbf{r}]$, in dyadic notation. $[\mathbf{M} = \mathbf{I}$, all atoms; $1 - \mathbf{b}^T \mathbf{r} = 0$ in the multiplier of $\mathbf{M}\mathbf{b}/(\mathbf{b}^T \mathbf{M} \mathbf{b})$.] A linear equation in $\mathbf{b}$, this approximation usually works well.* We have also used the iterative Frazer, Duncan & Collar eigenvalue solution as described by SWMB (1959), which works even when the plane passes exactly through the origin. To continue the solution of the nonlinear equations, by linearizing and iterating, write $F(\mathbf{b}) = 0$ in the form

$$\begin{aligned} 0 &= [\lambda \mathbf{r} + \lambda^2 \mathbf{M} \mathbf{b}] \\ &\approx \left[\mathbf{r} \frac{\partial \lambda}{\partial \mathbf{b}} + 2 \mathbf{M} \mathbf{b} \lambda \frac{\partial \lambda}{\partial \mathbf{b}} + \lambda^2 \mathbf{M} \right] \delta \mathbf{b} + [\lambda(\mathbf{r} + \lambda \mathbf{M} \mathbf{b})]_0, \end{aligned}$$

solve for $\delta \mathbf{b}$, reset $\mathbf{b}$ to $\mathbf{b} + \delta \mathbf{b}$, etc., until the desired degree of convergence of $|\delta \mathbf{b}|/|\mathbf{b}|$ toward zero has been attained. By $\partial \lambda / \partial \mathbf{b}$ is meant the partial derivative of the above expression for λ with respect to $\mathbf{b}$, as detailed in the next paragraph.

In the Fortran program *DDLELSP* (double precision Deming Lagrange, with error estimates, least-squares plane, written to explore this solution) the preceding equation is recast as

$$\begin{aligned} \mathbf{B} \delta \mathbf{b} &\equiv \left[\lambda^2 \mathbf{M} + (\mathbf{r} + 2\lambda \mathbf{M} \mathbf{b}) \frac{\partial \lambda}{\partial \mathbf{b}} \right] \delta \mathbf{b} \\ &\equiv \mathbf{Y} = -[\lambda(\mathbf{r} + \lambda \mathbf{M} \mathbf{b})]_0, \end{aligned}$$

* We do not fully understand the curious situation of this equation. It arises immediately if the isotropic problem is formulated as one of minimizing $[(1 - \mathbf{b}^T \mathbf{r})^2]$ by varying $\mathbf{b}$, and it fails then [SWMB (1959) referred to it as 'an incorrect method'], as it obviously must – observe the denominator – if the plane passes too close to the origin. However, it fails in other circumstances also. The main point about it is perhaps that it is linear in $\mathbf{b}$ and is obtained as the supposedly exact and *unique* solution of the isotropic problem, whereas the problem has no unique solution but three solutions instead (SWMB, 1959). From the point of view of Gaussian least squares, the essential fault in minimizing $S_{\text{lin}} = [(1 - \mathbf{b}^T \mathbf{r})^2]$ may be that the apparently simple weighting function in it, i.e. the identity, is actually complicated and unreasonable. In terms of distance deviations from the plane, we have $S_{\text{lin}} = [w(d - \mathbf{m}^T \mathbf{r})^2]$, with $w = \mathbf{b}^T \mathbf{b} = d^{-2}$. Prudence requires that the origin be shifted to a point sufficiently far from the plane and close enough to the centroid normal to avoid the difficulties discussed by SWMB. Note that for the one-dimensional problem of fitting a constant to a set of measurements of a single entity the Deming–Lagrange treatment with the condition $1 = c x_a$ and weights w reduces immediately to the standard result $1/c = [wx]/[w]$.

with

$$\begin{aligned} \frac{\partial \lambda}{\partial \mathbf{b}} &= \mathbf{r}^T / \mathbf{b}^T \mathbf{M} \mathbf{b} - [2(1 - \mathbf{b}^T \mathbf{r}) / (\mathbf{b}^T \mathbf{M} \mathbf{b})^2] \\ &= -(\mathbf{r}^T + 2\lambda \mathbf{b}^T \mathbf{M}) / \mathbf{b}^T \mathbf{M} \mathbf{b}. \end{aligned}$$

The usual goodness of fit, GOF2 in *DDLELSP*, evaluates to

$$\begin{aligned} \text{GOF2} &= \left(\frac{S_{\text{min}}}{n-3} \right)^{1/2} = \left(\frac{1}{n-3} [\lambda^2 \mathbf{b}^T \mathbf{M} \mathbf{P} \mathbf{M} \mathbf{b}] \right)^{1/2} \\ &= \left(\frac{1}{n-3} [\lambda^2 \mathbf{b}^T \mathbf{M} \mathbf{b}] \right)^{1/2} \\ &= \left(\frac{1}{n-3} \left[\frac{(1 - \mathbf{b}^T \mathbf{r})^2}{\mathbf{b}^T \mathbf{M} \mathbf{b}} \right] \right)^{1/2}. \end{aligned}$$

This is only an approximation, because the residuals $1 - \mathbf{b}^T \mathbf{r}$ are not the differences between the observations and appropriate linear functions of the parameters, nor are their variances (the $\mathbf{b}^T \mathbf{M} \mathbf{b}$'s) independent of the parameters (or, in turn, the errors in the observations).

We ask also about the perpendicular distances, e , of atoms to plane and the mean-square deviation $(\delta e)^2$ to be expected in e .

$$\begin{aligned} e &= (1 - \mathbf{b}^T \mathbf{r}) / \sqrt{\mathbf{b}^T \mathbf{b}} = d(1 - \mathbf{b}^T \mathbf{r}) \\ \delta e &= -d(\mathbf{b}^T \eta + \mathbf{r}^T \varepsilon) + O(\eta^2). \end{aligned}$$

Here η and ε are the errors in $\mathbf{r}$ and $\mathbf{b}$. Neglecting ' $O(\eta^2)$ ' then leads to

$$\overline{(\delta e)^2} = d^2 (\mathbf{b}^T \overline{\eta \eta^T} \mathbf{b} + 2 \mathbf{b}^T \overline{\eta \varepsilon^T} \mathbf{r} + \mathbf{r}^T \overline{\varepsilon \varepsilon^T} \mathbf{r}).$$

We have $\overline{\eta \eta^T} = \mathbf{M} = \mathbf{P}^{-1}$, but $\overline{\eta \varepsilon^T}$ and $\overline{\varepsilon \varepsilon^T}$ perhaps still need to be evaluated.

3.3. Molecular modelling and graphics

BY R. DIAMOND

3.3.1. Graphics

3.3.1.1. Coordinate systems, notation and standards

3.3.1.1.1. Cartesian and crystallographic coordinates

It is usual, for purposes of molecular modelling and of computer graphics, to adopt a Cartesian coordinate system using mutually perpendicular axes in a right-handed system using the ångström unit or the nanometre as the unit of distance along such axes, and largely to ignore the existence of crystallographic coordinates expressed as fractions of unit-cell edges. Transformations between the two are thus associated, usually, with the input and output stages of any software concerned with modelling and graphics, and it will be assumed after this section that all coordinates are Cartesian using the chosen unit of distance as the unit of coordinates. For a discussion of coordinate transformations and rotations without making this assumption see Chapter 1.1 in which formulations using co- and contravariant forms are presented.

The relationship between these systems may be written

$$\mathbf{X} = \mathbf{M}\mathbf{x} \quad \mathbf{x} = \mathbf{M}^{-1}\mathbf{X}$$

in which $\mathbf{X}$ and $\mathbf{x}$ are position vectors in direct space, written as column vectors, with $\mathbf{x}$ expressed in crystallographic fractional coordinates (dimensionless) and $\mathbf{X}$ in Cartesian coordinates (dimension of length).

There are two forms of $\mathbf{M}$ in common use. The first of these sets the first component of $\mathbf{X}$ parallel to $\mathbf{a}^*$ and the third parallel to $\mathbf{c}$ and is

$$\mathbf{M} = \begin{pmatrix} a\varphi/\sin\alpha & 0 & 0 \\ a(\cos\gamma - \cos\alpha\cos\beta)/\sin\alpha & b\sin\alpha & 0 \\ a\cos\beta & b\cos\alpha & c \end{pmatrix}$$

$$\mathbf{M}^{-1} = \begin{pmatrix} \sin\alpha/a\varphi & 0 & 0 \\ (\cos\alpha\cos\beta - \cos\gamma)/b\varphi\sin\alpha & 1/b\sin\alpha & 0 \\ (\cos\alpha\cos\gamma - \cos\beta)/c\varphi\sin\alpha & -1/c\tan\alpha & 1/c \end{pmatrix}$$

in which

$$\varphi = \sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

$$= \sin\alpha\sin\beta\sin\gamma^*.$$

φ is equal to the volume of the unit cell divided by abc , and is unchanged by cyclic permutation of α, β and γ and of α^*, β^* and γ^* . The Cartesian and crystallographic axes have the same chirality if the positive square root is taken.

The second form sets the first component of $\mathbf{X}$ parallel to $\mathbf{a}$ and the third component of $\mathbf{X}$ parallel to $\mathbf{c}^*$ and is

$$\mathbf{M} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & c(\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma \\ 0 & 0 & c\varphi/\sin\gamma \end{pmatrix}$$

$$\mathbf{M}^{-1} = \begin{pmatrix} 1/a & -1/a\tan\gamma & (\cos\alpha\cos\gamma - \cos\beta)/a\varphi\sin\gamma \\ 0 & 1/b\sin\gamma & (\cos\beta\cos\gamma - \cos\alpha)/b\varphi\sin\gamma \\ 0 & 0 & \sin\gamma/c\varphi \end{pmatrix}.$$

A third form, suitable only for rhombohedral cells, is

$$\mathbf{M} = \frac{a}{3} \begin{pmatrix} p+2q & p-q & p-q \\ p-q & p+2q & p-q \\ p-q & p-q & p+2q \end{pmatrix}$$

$$\mathbf{M}^{-1} = \frac{1}{3a} \begin{pmatrix} \frac{1}{p} + \frac{2}{q} & \frac{1}{p} - \frac{1}{q} & \frac{1}{p} - \frac{1}{q} \\ \frac{1}{p} - \frac{1}{q} & \frac{1}{p} + \frac{2}{q} & \frac{1}{p} - \frac{1}{q} \\ \frac{1}{p} - \frac{1}{q} & \frac{1}{p} - \frac{1}{q} & \frac{1}{p} + \frac{2}{q} \end{pmatrix}$$

in which

$$p = \pm\sqrt{1 + 2\cos\alpha} \quad q = \pm\sqrt{1 - \cos\alpha},$$

which preserves the equivalence of axes. Here the chiralities of the Cartesian and crystallographic axes are the same if p is chosen positive, and different otherwise, and the two sets of axes coincide in projection along the triad if q is chosen positive and are π out of phase otherwise.

3.3.1.1.2. Homogeneous coordinates

Homogeneous coordinates have found wide application in computer graphics. For some equipment their use is essential, and they are of value analytically even if the available hardware does not require their use.

Homogeneous coordinates employ four quantities, X, Y, Z and W , to define the position of a point, rather than three. The fourth coordinate has a scaling function so that it is the quantity X/W (as delivered to the display hardware) which controls the left-right positioning of the point within the picture. A point with $|X/W| < 1$ is in the picture, normally, and those with $|X/W| > 1$ are outside it, but see Section 3.3.1.3.5.

There are many reasons why homogeneous coordinates may be adopted, among them the following:

(i) X, Y, Z and W may be held as integers, thus enabling fast arithmetic whilst offering much of the flexibility of floating-point working. A single W value may be common to a whole array of X, Y, Z values.

(ii) Perspective transformations can be implemented without the need for any division. Only high-speed matrix multiplication using integer arithmetic is necessary, provided only that the drawing hardware can provide displacements proportional to the ratio of two signals, X and W or Y and W . Rotation, translation, scaling and the application of perspective are all affected by operations of the same form, namely multiplication of a four-vector by a 4×4 matrix. The hardware may thus be kept relatively simple since only one type of operation needs to be provided for.

(iii) Since kX, kY, kZ, kW represents the same point as X, Y, Z, W , the hardware may be arranged to maximize resolution without risk of integer overflow.

For analytical purposes it is convenient to regard homogeneous transformations in terms of partitioned matrices

$$\begin{pmatrix} \mathbf{M} & \mathbf{V} \\ \mathbf{U} & N \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix},$$

where $\mathbf{M}$ is a 3×3 matrix, $\mathbf{V}$ and $\mathbf{X}$ are three-element column vectors, $\mathbf{U}$ is a three-element row vector and N and W are scalars.

Matrices and vectors which are equivalent under the considerations of (iii) above will be related by the sign $\simeq$ in what follows.

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Hardware systems which use true floating-point representations have less need of homogeneous coordinates and for these N and W may normally be set to unity.

3.3.1.1.3. Notation

In this chapter the conventions of matrix algebra will be adhered to except where it is convenient to show operations on elements of vectors, matrices and tensors, where a subscript notation will be used with a modified summation convention in which summation is over lower-case subscripts *only*. Thus the equation

$$x_i = A_{ij}X_j$$

is to be read 'For any i , x_i is $A_{ij}X_j$ summed over j '.

Subscripts using the letter i or later in the alphabet will relate to the usual three dimensions and imply a three-term summation. Subscripts a to h are not necessarily so limited, and, in particular, the subscript a is used to imply summation over atoms of which there may be an arbitrary number.

We shall use the superscript T to denote a transpose, and also use the Kronecker delta, δ_{IJ} , which is 1 if $I = J$ and zero otherwise, and the tensor ε_{IJK} which is 1 if I, J and K are a cyclic permutation of 1, 2, 3, -1 if an anticyclic permutation, and zero otherwise.

$$\varepsilon_{IJK} = (I - J)(J - K)(K - I)/2 \quad 1 \leq I, J, K \leq 3.$$

A useful identity is then

$$\varepsilon_{iJK}\varepsilon_{iLM} = \delta_{JL}\delta_{KM} - \delta_{JM}\delta_{KL}.$$

Single modulus signs surrounding the symbol for a square matrix denote its determinant, and around a vector denote its length.

The symbol $\simeq$ is defined in the previous section.

3.3.1.1.4. Standards

The sections of this chapter concerned with graphics are primarily concerned with the mathematical aspects of graphics programming as they confront the applications programmer. The implementations outlined in the final section have all, so far as the author is aware, been developed *ab initio* by their inventors to deal with these aspects using their own and unrelated techniques and protocols. It is clear, however, that standards are now emerging, and it is to be hoped that future developments in applications software will handle the graphics aspects through one or other of these standards.

First among these standards is the Graphical Kernel System, GKS, defined in *American National Standards Institute, American National Standard for Information Processing Systems – Computer Graphics – Graphical Kernel System (GKS) Functional Description* (1985) and described and illustrated by Hopgood *et al.* (1986) and Enderle *et al.* (1984). GKS became a full International Standards Organization (ISO) standard in 1985, and its purpose is to standardize the interface between application software and the graphics system, thus enhancing portability of software. Specifications for Fortran, Pascal and Ada formulations are at an advanced stage of development. Its value to crystallographers is limited by the fact that it is only two-dimensional. A three-dimensional extension known as GKS-3D, defined in *International Standards Organisation, International Standard Information Processing Systems – Computer Graphics – Graphical Kernel System for Three Dimensions (GKS-3D), Functional Description* (1988) became an ISO standard in 1988. Perhaps of greatest interest to crystallographers, however, is the Programmers' Hierarchical Interactive Graphics System (PHIGS) (Brown, 1985; Abi-Ezzi & Bunshaft, 1986) since this allows hierarchical segmentation of picture content to exist in both the applications software and the graphics device in a related manner, which GKS does not. Some graphics devices now

available support this type of working and its exploitation indicates the choice of PHIGS. Furthermore, Fortran implementations of GKS and GKS-3D require points to be stored in arrays dimensioned as $X(N)$, $Y(N)$, $Z(N)$ which may be equivalenced (in the Fortran sense) to $XYZ(N, 3)$ but not to $XYZ(3, N)$, which may not be convenient. PHIGS also became an International Standard in 1988: *American National Standards Institute, American National Standard for Information Processing Systems – Computer Graphics – Programmer's Hierarchical Graphics System (PHIGS) Functional Description, Archive File Format, Clear-Text Encoding of Archive File* (1988). PHIGS has also been extended to support the capability of raster-graphics machines to represent reflections, shadows, see-through effects *etc.* in a version known as PHIGS+ (van Dam, 1988).

Increasingly, manufacturers of graphics equipment are orienting their products towards one or other of these standards. While these standards are not the subject of this chapter it is recommended that they be studied before investing in equipment.

In addition to these standards, related standards are evolving under the auspices of the ISO for defining images in a file-storage, or metafile, form, and for the interface between the device-independent and device-dependent parts of a graphics package. Arnold & Bono (1988) describe the ANSI and ISO Computer Graphics Metafile standard which provides for the definition of (two-dimensional) images. The definition of three-dimensional scenes requires the use of (PHIGS) archive files.

3.3.1.2. Orthogonal (or rotation) matrices

It is a basic requirement for any graphics or molecular-modelling system to be able to control and manipulate the orientation of the structures involved and this is achieved using orthogonal matrices which are the subject of these sections.

3.3.1.2.1. General form

If a vector $\mathbf{v}$ is expressed in terms of its components resolved onto an axial set of vectors $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ which are of unit length and mutually perpendicular and right handed in the sense that $(\mathbf{X} \times \mathbf{Y}) \cdot \mathbf{Z} = +1$, and if these components are v_i , and if a second set of axes $\mathbf{X}', \mathbf{Y}', \mathbf{Z}'$ is similarly established, with the same origin and chirality, and if $\mathbf{v}$ has components v'_i on these axes then

$$v'_i = a_{ij}v_j,$$

in which a_{ij} is the cosine of the angle between the i th primed axis and the j th unprimed axis. Evidently the elements a_{ij} comprise a matrix $\mathbf{R}$, such that any row represents one of the primed axial vectors, such as $\mathbf{X}'$, expressed as components on the unprimed axes, and each column represents one of the unprimed axial vectors expressed as components on the primed axes. It follows that $\mathbf{R}^T = \mathbf{R}^{-1}$ since elements of the product $\mathbf{R}^T \mathbf{R}$ are scalar products among perpendicular unit vectors.

A real matrix whose transpose equals its inverse is said to be *orthogonal*.

Since $\mathbf{X}, \mathbf{Y}$ and $\mathbf{Z}$ can simultaneously be superimposed on $\mathbf{X}', \mathbf{Y}'$ and $\mathbf{Z}'$ without deformation or change of scale the relationship is one of rotation, and orthogonal matrices are often referred to as rotation matrices. The operation of replacing the vector $\mathbf{v}$ by $\mathbf{R}\mathbf{v}$ corresponds to rotating the axes from the unprimed to the primed set with $\mathbf{v}$ itself unchanged. Equally, the same operation corresponds to retaining fixed axes and rotating the vector in the opposite sense. The second interpretation is the one more frequently helpful since conceptually it corresponds more closely to rotational operations on objects, and it is primarily in this sense that the following is written.

If three vectors $\mathbf{u}, \mathbf{v}$ and $\mathbf{w}$ form the edges of a parallelepiped, then its volume V is

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$$V = \mathbf{u} \cdot (\mathbf{v} \times \mathbf{w}) = \varepsilon_{ijk} u_i v_j w_k$$

and if these vectors are transformed by the matrix $\mathbf{R}$ as above, then the transformed volume V' is

$$V' = \varepsilon_{lmn} u'_l v'_m w'_n = \varepsilon_{lmn} a_{li} a_{mj} a_{nk} u_i v_j w_k.$$

But the determinant of $\mathbf{R}$ is given by

$$|\mathbf{R}| \varepsilon_{IJK} = \varepsilon_{lmn} a_{li} a_{mj} a_{nk}$$

so that

$$V' = |\mathbf{R}| V$$

and the determinant of $\mathbf{R}$ must therefore be +1 for a transformation which is a pure rotation. Nevertheless orthogonal matrices with determinant -1 exist though these do not describe a pure rotation. They may always be described as the product of a pure rotation and inversion through the origin and are referred to here as improper rotations. In what follows all references to orthogonal matrices refer to those with positive determinant only, unless stated otherwise.

An important general form of an orthogonal matrix in three dimensions was derived as equation (1.1.4.32) and is

$$\mathbf{R} = \begin{pmatrix} l^2 + (m^2 + n^2) \cos \theta & lm(1 - \cos \theta) - n \sin \theta & nl(1 - \cos \theta) + m \sin \theta \\ lm(1 - \cos \theta) + n \sin \theta & m^2 + (n^2 + l^2) \cos \theta & mn(1 - \cos \theta) - l \sin \theta \\ nl(1 - \cos \theta) - m \sin \theta & mn(1 - \cos \theta) + l \sin \theta & n^2 + (l^2 + m^2) \cos \theta \end{pmatrix}$$

or

$$R_{IJ} = (1 - \cos \theta) l_I l_J + \delta_{IJ} \cos \theta - \varepsilon_{IJK} l_K \sin \theta,$$

in which l, m and n are the direction cosines of the axis of rotation (which are the same when referred to either set of axes under either interpretation) and θ is the angle of rotation. In this form, and with $\mathbf{R}$ operating on column vectors on the right, the sign of θ is such that, when viewed along the rotation axis from the origin towards the point lmn , the object is rotated clockwise for positive θ with a fixed right-handed axial system. If, under the same viewing conditions, the axes are to be rotated clockwise through θ with the object fixed then the components of vectors in the object, on the new axes, are given by $\mathbf{R}$ with the same lmn and with θ negated. This is the transpose of $\mathbf{R}$, and if $\mathbf{R}$ is constructed from a product, as below, then each factor matrix in the product must be transposed and their order reversed to achieve this. Note that if, for a given rotation, the viewing direction from the origin is reversed, l, m, n and θ are all reversed and the matrix is unchanged.

Any rotation about a reference axis such that two of the direction cosines are zero is termed a *primitive rotation*, and it is frequently a requirement to generate or to interpret a general rotation as a product of primitive rotations.

A second important general form is based on Eulerian angles and is the product of three such primitives. It is

$$\mathbf{R} = \begin{pmatrix} \cos \varphi_3 & -\sin \varphi_3 & 0 \\ \sin \varphi_3 & \cos \varphi_3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \varphi_2 & 0 & \sin \varphi_2 \\ 0 & 1 & 0 \\ -\sin \varphi_2 & 0 & \cos \varphi_2 \end{pmatrix} \begin{pmatrix} \cos \varphi_1 & -\sin \varphi_1 & 0 \\ \sin \varphi_1 & \cos \varphi_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} (\cos \varphi_3 \cos \varphi_2 \cos \varphi_1 - (\cos \varphi_3 \cos \varphi_2 \sin \varphi_1 \cos \varphi_3 \sin \varphi_2) - \sin \varphi_3 \sin \varphi_1) & + \sin \varphi_3 \cos \varphi_1 \\ (\sin \varphi_3 \cos \varphi_2 \cos \varphi_1 - \sin \varphi_3 \cos \varphi_2 \sin \varphi_1 \sin \varphi_3 \sin \varphi_2) & + \cos \varphi_3 \sin \varphi_1 \\ -\sin \varphi_2 \cos \varphi_1 & \sin \varphi_2 \sin \varphi_1 & \cos \varphi_2 \end{pmatrix}$$

which is commonly employed in four-circle diffractometers for which $\varphi = -\varphi_1$, $\chi = \varphi_2$ and $\omega = -\varphi_3$. In terms of the fixed-axes-moving-object conceptualization this corresponds to a rotation φ_1 about Z followed by φ_2 about Y followed by φ_3 about Z . In the familiar diffractometer example, when $\chi = 0$ the φ and ω axes are both vertical and equivalent. If φ is altered first, then the χ axis is

still in the direction of a fixed Y axis, but if ω is altered first it is not. Since all angles are to be rotations about fixed axes to describe a rotating object it follows that it is φ rather than ω which corresponds to φ_1 . In general, when rotating parts are mounted on rotating parts the rotation closest to the moved object must be applied first, forming the right-most factor in any multiple transformation, with the rotation closest to the fixed part as the left-most factor, assuming data supplied as column vectors on the right.

Given an orthogonal matrix, in either numerical or analytical form, it may be required to discover θ and the axis of rotation, or to factorize it as a product of primitives. From the first form we see that the vector

$$v_I = \varepsilon_{Ijk} a_{jk},$$

consisting of the antisymmetric part of $\mathbf{R}$, has elements $-2 \sin \theta$ times the direction cosines l, m, n , which establishes the direction immediately, and normalization using $l^2 + m^2 + n^2 = 1$ determines $\sin \theta$. Furthermore, the trace is $1 + 2 \cos \theta$ so that the quadrant of θ is also fixed. This method fails, however, if the matrix is symmetrical, which occurs if $\theta = \pi$. In this case only the direction of the axis is required, which is given by

$$l : m : n = (a_{23})^{-1} : (a_{31})^{-1} : (a_{12})^{-1}$$

for non-zero elements, or $l = \sqrt{\frac{1}{2}(a_{11} + 1)}$ etc., with the signs chosen to satisfy $a_{12} = 2lm$ etc.

The Eulerian form may be factorized by noting that $\tan \varphi_1 = -a_{32}/a_{31}$, $\tan \varphi_3 = a_{23}/a_{13}$, $\cos \varphi_2 = a_{33}$. There is then freedom to choose the sign of $\sin \varphi_2$, but the choice then fixes the quadrants of φ_1 and φ_3 through the elements in the last row and column, and the primitives may then be constructed. These expressions for φ_1 and φ_3 fail if $\sin \varphi_2 = 0$, in which case the rotation reduces to a primitive rotation about Z with angle $(\varphi_1 + \varphi_3)$, $\varphi_2 = 0$, or $(\varphi_3 - \varphi_1)$, $\varphi_2 = \pi$.

Eulerian angles are unlikely to be the best choice of primitive angles unless they are directly related to the parameters of a system, as with the diffractometer. It is often more important that the changes to primitive angles should be quasi-linearly related to θ for any small rotations, which is not the case with Eulerian angles when the required rotation axis is close to the X axis. In such a case linearized techniques for solving for the primitive angles will fail. Furthermore, if the required rotation is about Z only $(\varphi_1 + \varphi_3)$ is determinate.

Quasi-linear relationships between θ and the primitive rotations arise if the primitives are one each about X, Y and Z . Any order of the three factors may be chosen, but the choice must then be adhered to since these factors do not commute. For sufficiently small rotations the primitive rotations are then $l\theta, m\theta$ and $n\theta$, whilst for larger θ linearized iterative techniques for finding the primitive rotations are likely to be convergent and well conditioned.

The three-dimensional space of the angles φ_1, φ_2 and φ_3 in either case is non-linearly related to θ . In the Eulerian case the worst non-linearities occur at the origin of φ -space. Equally severe non-linearities occur in the quasi-linear case also but are 90° away from the origin and less likely to be troublesome.

Neither of the foregoing general forms of orthogonal matrix has ideally convenient properties. The first is inconvenient because it uses four non-equivalent variables l, m, n and θ , with a linking equation involving l, m and n , so that they cannot be treated as independent variables for analytical purposes. The second form (the product of primitives) is not ideal because the three angles, though independent, are not equivalent, the non-equivalence arising from the non-commutation of the primitive factors. In the remainder of this section we give two further forms of orthogonal matrix which each use three variables which are independent and strictly equivalent, and a third form using four whose squares sum to unity.

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The first of these is based on the diagonal and uses the three independent variables p, q, r , from which we construct the auxiliary variables

$$P = \pm\sqrt{1+p-q-r}, \quad Q = \pm\sqrt{1-p+q-r}, \\ R = \pm\sqrt{1-p-q+r}, \quad S = \pm\sqrt{1+p+q+r},$$

then

$$\mathbf{R} = \begin{pmatrix} p & \frac{1}{2}[PQ - RS] & \frac{1}{2}[PR + QS] \\ \frac{1}{2}[PQ + RS] & q & \frac{1}{2}[QR - PS] \\ \frac{1}{2}[PR - QS] & \frac{1}{2}[QR + PS] & r \end{pmatrix}$$

is orthogonal with positive determinant for any of the sixteen sign combinations. The signs of P, Q, R and S are, respectively, the signs of the direction cosines of the rotation axis and of $\sin \theta$. Using also $T = \sqrt{4 - S^2}$, which may be deemed positive without loss of generality,

$$l = P/T, m = Q/T, n = R/T, \sin \theta = ST/2, \\ \cos \theta = 1 - T^2/2 = S^2/2 - 1.$$

Although p, q and r are independent, the point $[pqr]$ is bound, by the requirement that P, Q, R and S be real, to lie within a tetrahedron whose vertices are the points $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}11]$ and $[1\bar{1}\bar{1}]$, corresponding to the identity and to 180° rotations about each of the axes. The facts that the identity occurs at a vertex of the feasible region and that $(1 - \cos \theta)$, rather than $\sin \theta$, is linear on p, q and r in this vicinity make this form suitable only for substantial rotations.

The second form consists in defining a rotation vector $\mathbf{r}$ with components u, v, w such that $u = lt, v = mt, w = nt$ with $t = \tan(\theta/2)$ and $\mathbf{r} \cdot \mathbf{r} = t^2$. Then the matrix

$$\mathbf{R} = \begin{pmatrix} \frac{1+u^2-v^2-w^2}{1+t^2} & \frac{2(uv-w)}{1+t^2} & \frac{2(uw+v)}{1+t^2} \\ \frac{2(uv+w)}{1+t^2} & \frac{1-u^2+v^2-w^2}{1+t^2} & \frac{2(vw-u)}{1+t^2} \\ \frac{2(uw-v)}{1+t^2} & \frac{2(vw+u)}{1+t^2} & \frac{1-u^2-v^2+w^2}{1+t^2} \end{pmatrix} \\ R_{IJ} = (1+t^2)^{-1}[\delta_{IJ}(1-u_k u_k) + 2(u_I u_J - \varepsilon_{IJK} u_k)]$$

is orthogonal and the variables u, v, w are independent, equivalent and unbounded, and, unlike the previous form, small rotations are quasi-linear on these variables. As examples, $\mathbf{r} = [100]$ gives 90° about X , $\mathbf{r} = [111]$ gives 120° about $[111]$.

$\mathbf{R}$ then transforms a vector $\mathbf{d}$ according to

$$\mathbf{R}\mathbf{d} = \mathbf{d} + \frac{2}{1+t^2} \{(\mathbf{r} \times \mathbf{d}) + [\mathbf{r} \times (\mathbf{r} \times \mathbf{d})]\}.$$

Multiplying two such matrices together allows us to establish the manner in which the rotation vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ combine.

$$\mathbf{r} = \frac{\mathbf{r}_2 + \mathbf{r}_1 + \mathbf{r}_2 \times \mathbf{r}_1}{1 - \mathbf{r}_2 \cdot \mathbf{r}_1}$$

for a rotation $\mathbf{r}_1$ followed by $\mathbf{r}_2$, so that rotations expressed in terms of rotation angles and axes may be compounded into a single such rotation without the need to form and decompose a product matrix.

Note that if $\mathbf{r}_1$ and $\mathbf{r}_2$ are parallel this reduces to the formula for the tangent of the sum of two angles, and that if $\mathbf{r}_1 \cdot \mathbf{r}_2 = 1$ the combined rotation is always 180° . Note, too, that reversing the order of application of the rotations reverses only the vector product.

If three rotations $\mathbf{r}_1, \mathbf{r}_2$ and $\mathbf{r}_3$ are applied successively, $\mathbf{r}_1$ first, then their combined rotation is

$$\mathbf{r} = [\mathbf{r}_3(1 - \mathbf{r}_1 \cdot \mathbf{r}_2) + \mathbf{r}_2(1 + \mathbf{r}_3 \cdot \mathbf{r}_1) + \mathbf{r}_1(1 - \mathbf{r}_3 \cdot \mathbf{r}_2) \\ + \mathbf{r}_3 \times \mathbf{r}_2 + \mathbf{r}_3 \times \mathbf{r}_1 + \mathbf{r}_2 \times \mathbf{r}_1] \\ \times [1 - \mathbf{r}_1 \cdot \mathbf{r}_2 - \mathbf{r}_2 \cdot \mathbf{r}_3 - \mathbf{r}_3 \cdot \mathbf{r}_1 - \mathbf{r}_3 \cdot (\mathbf{r}_2 \times \mathbf{r}_1)]^{-1}.$$

Note the irregular pattern of signs in the numerator.

Similar ideas, using a vector of magnitude $\sin(\theta/2)$, are developed in Aharonov *et al.* (1977).

The third form of orthogonal matrix uses four variables, λ, μ, ν and σ , which comprise a four-dimensional vector $\boldsymbol{\rho}$, such that $\lambda = ls, \mu = ms, \nu = ns$ with $s = \sin(\theta/2)$ and $\sigma = \cos(\theta/2)$. In terms of these variables

$$\mathbf{R} = \begin{pmatrix} (\lambda^2 - \mu^2 - \nu^2 + \sigma^2) & 2(\lambda\mu - \nu\sigma) & 2(\lambda\nu + \mu\sigma) \\ 2(\mu\lambda + \nu\sigma) & (-\lambda^2 + \mu^2 - \nu^2 + \sigma^2) & 2(\mu\nu - \lambda\sigma) \\ 2(\lambda\nu - \mu\sigma) & 2(\mu\nu + \lambda\sigma) & (-\lambda^2 - \mu^2 + \nu^2 + \sigma^2) \end{pmatrix}.$$

Two further matrices $\mathbf{S}$ and $\mathbf{T}$ may be defined (Diamond, 1988),

$$\mathbf{S} = \begin{pmatrix} -\sigma & \nu & -\mu & \lambda \\ -\nu & -\sigma & \lambda & \mu \\ \mu & -\lambda & -\sigma & \nu \\ \lambda & \mu & \nu & \sigma \end{pmatrix} \text{ and } \mathbf{T} = \begin{pmatrix} \sigma & -\nu & \mu & \lambda \\ \nu & \sigma & -\lambda & \mu \\ -\mu & \lambda & \sigma & \nu \\ -\lambda & -\mu & -\nu & \sigma \end{pmatrix},$$

which are themselves orthogonal (though $\mathbf{S}$ has determinant -1) and which have the property that

$$\mathbf{S}^2 = \begin{pmatrix} \mathbf{R} & \mathbf{0} \\ \mathbf{0}^T & \mathbf{1} \end{pmatrix}$$

so that, for example, if homogeneous coordinates are being employed (Section 3.3.1.1.2)

$$\begin{pmatrix} x' \\ y' \\ z' \\ w \end{pmatrix} = \begin{pmatrix} -\sigma & \nu & -\mu & \lambda \\ -\nu & -\sigma & \lambda & \mu \\ \mu & -\lambda & -\sigma & \nu \\ \lambda & \mu & \nu & \sigma \end{pmatrix} \begin{pmatrix} -\sigma & \nu & -\mu & \lambda \\ -\nu & -\sigma & \lambda & \mu \\ \mu & -\lambda & -\sigma & \nu \\ \lambda & \mu & \nu & \sigma \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ w \end{pmatrix}$$

is a rotation of (x, y, z, w) through the angle θ about the axis (l, m, n) . With suitably pipelined hardware this forms an efficient means of applying rotations since the 'overhead' of establishing $\mathbf{S}$ is so trivial.

$\mathbf{T}$ has the property that the rotation vector $\boldsymbol{\rho}$ arising from a concatenation of n rotations is

$$\boldsymbol{\rho} = \mathbf{T}_n \mathbf{T}_{n-1} \dots \mathbf{T}_1 \boldsymbol{\rho}_0,$$

in which $\boldsymbol{\rho}_0^T$ is the vector $(0, 0, 0, 1)$ which defines a null rotation. This equation may be used as a basis for factorizing a given rotation into a concatenation of rotations about designated axes (Diamond, 1990a).

Finally, an exact rotation of the vector $\mathbf{d}$ may be obtained without using matrices at all by writing

$$\mathbf{d} = \sum_{n=0}^{\infty} \mathbf{d}_n$$

in which

$$\mathbf{d}_n = \frac{1}{n} (\boldsymbol{\theta} \times \mathbf{d}_{n-1})$$

and $\mathbf{d}_0$ is the initial position which is to be rotated. Here $\boldsymbol{\theta}$ is a vector with direction cosines l, m and n , and magnitude equal to the required rotation angle in radians (Diamond, 1966). This method is particularly efficient when $|\boldsymbol{\theta}| \ll 1$ or when the number of vectors to be transformed is small since the overhead of establishing $\mathbf{R}$ is eliminated and the process is simple to program. It is the three-dimensional analogue of the power series for $\sin \theta$ and $\cos \theta$ and has the same convergence properties.

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3.3.1.2.2. Measurement of rotations and strains from coordinates

Given the coordinates of a molecular fragment it is often a requirement to relate the fragment to its image in some standard orientation by a transformation which may be required to be a pure rotation, or may be required to be a combination of rotation and strain. Of the methods reviewed in this section all except (iv) are concerned with pure rotation, ignoring any strain that may be present, and give the best rigid-body superposition. In all these methods, unless inhomogeneous strain is being considered, the best possible superposition is obtained if the centroids of the two images are first brought into coincidence by translation and treated as the origin.

Methods (i) to (v) seek transformations which perform the superposition and impose on these, in various ways, the requirements of orthogonality for the rotational part. All these methods therefore need some defence against indeterminacy that arises in the general transformation if one or both of the fragments is planar, and, if improper rotations are to be excluded, need a defence against these also if the fragment and its image are of opposite chirality. Methods (vi) and (vii) pay no attention to the general transformation and work with variables which are intrinsically rotational in character, and always produce an orthogonal transformation with positive determinant, with no degeneracy arising from planar fragments which need no special attention. Even collinear atoms cause no problem, the superposition being performed correctly but with an arbitrary rotation about the length of the line being present in the result. These methods are therefore to be preferred over the earlier ones unless the purpose of the operation is to detect differences of chirality, although this, too, can be detected with a simple test.

In this review we adopt the same notation for all the methods which, unavoidably, means that symbols are used in ways which differ from the original publications. We use the symbol $\mathbf{x}$ for the vector set which is to be rotated and $\mathbf{X}$ for the vector set whose orientation is not to be altered, and write the residuals as

$$e_{IA} = D_{Ij}x_{jA} - X_{IA}$$

and, by choice of origin,

$$W_a x_{Ia} = W_a X_{Ia} = 0_I$$

for weights W . The quadratic residual to be minimized is

$$E = W_a e_{ia} e_{ia}$$

and we define the matrix $M_{IJ} = W_a x_{Ia} X_{Ja}$ and use $\mathbf{l}$ for the direction cosines of the rotation axis.

(i) McLachlan's first method (McLachlan, 1972, 1982) is iterative and conceptually the simplest. It sets

$$D_{IJ} = A_{Ik} R_{kJ}$$

in which $\mathbf{A}$ and $\mathbf{R}$ are both orthogonal with $\mathbf{R}$ being a current estimate of $\mathbf{D}$ and $\mathbf{A}$ being an adjustment which, at the beginning of each cycle, has a zero angle associated with it. One iterative cycle estimates a non-trivial $\mathbf{A}$, after which the product $\mathbf{AR}$ replaces $\mathbf{R}$.

$$A_{IJ} = (1 - \cos \theta) l_I l_J + \delta_{IJ} \cos \theta - \varepsilon_{IJK} l_k \sin \theta$$

and

$$\left(\frac{\partial A_{IJ}}{\partial \theta} \right)_{\theta=0} = -\varepsilon_{IJK} l_k,$$

therefore

$$\begin{aligned} \left(\frac{\partial E}{\partial \theta} \right)_{\theta=0} &= 2W_a \left(\frac{\partial A_{ij}}{\partial \theta} \right)_{\theta=0} R_{jk} x_{ka} (A_{il} R_{lm} x_{ma} - X_{ia}) \\ &= 2\varepsilon_{ijl} R_{jk} M_{kl} l_l. \end{aligned}$$

For this to vanish for all possible rotation axes $\mathbf{l}$ the vector

$$g_L = \varepsilon_{ijl} R_{jk} M_{kl}$$

must vanish, *i.e.* at the end of the iteration $\mathbf{R}$ must be such that the matrix

$$N_{JI} = R_{Jk} M_{kl}$$

is symmetrical. The vector $\mathbf{g}$ represents the couple exerted on the rotating body by forces $2W_a(R_{Ij}x_{jA} - X_{IA})$ acting at the atoms. Choosing

$$l_L = g_L / |\mathbf{g}|$$

gives the greatest $|\partial E / \partial \theta|_{\theta=0}$ and $(\partial E / \partial \theta)$ vanishes when

$$\tan \theta = \frac{\varepsilon_{ijk} N_{ji} l_k}{N_{pq} (l_p l_q - \delta_{pq})}$$

in which N is constructed from the current $\mathbf{R}$ matrix. $\mathbf{A}$ is then constructed from $\mathbf{l}$ and this θ and $\mathbf{AR}$ replaces $\mathbf{R}$. The process is iterative because a couple about some new axis can appear when rotation about $\mathbf{g}$ eliminates the couple about $\mathbf{g}$.

Note that for each rotation axis $\mathbf{l}$ there are two values of θ , differing by π , which reduce $|\mathbf{g}|$ to zero, corresponding to maximum and minimum values of E . The minimum is that which makes

$$\frac{\partial^2 E}{\partial \theta^2} = 2(\text{tr } N - l_i N_{ij} l_j)$$

positive. Adding π to θ alters $\mathbf{R}$ and N and negates this quantity.

Note, too, that the process is essentially characterized as that which makes the product $\mathbf{RM}$ symmetrical with $\mathbf{R}$ orthogonal. We return to this point in (iii).

(ii) Kabsch's method (Kabsch, 1976, 1978) minimizes E with respect to the nine elements of $\mathbf{D}$, subject to the six constraints

$$D_{kl} D_{kj} - \delta_{IJ} = 0_{IJ},$$

by using an auxiliary function

$$F = L_{ij} (D_{ki} D_{kj} - \delta_{ij})$$

in which $\mathbf{L}$ is symmetric containing six Lagrange multipliers. The Lagrangian function

$$G = E + F$$

then has minima with respect to the elements of $\mathbf{D}$ at locations which are dependent, *inter alia*, on the elements of $\mathbf{L}$. By suitably choosing $\mathbf{L}$ a minimum of G may be brought into coincidence with the constrained minimum of E . A minimum of G occurs where

$$\frac{\partial G}{\partial D_{IJ}} = 2D_{Ik} (S_{Jk} + L_{Jk}) - 2M_{JI} = 0_{IJ}$$

and the 9×9 matrix

$$\frac{\partial^2 G}{\partial D_{MK} \partial D_{IJ}} = 2\delta_{MI} (S_{JK} + L_{JK})$$

is positive definite, block diagonal, and has

$$S_{JK} = W_a x_{Ja} x_{Ka}$$

which is symmetrical. Thus $\mathbf{L}$ must be chosen so as to make the symmetric matrix $(\mathbf{S} + \mathbf{L})$ such that

$$\mathbf{D}(\mathbf{S} + \mathbf{L})^T = \mathbf{M}^T$$

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with D orthogonal, or $RN = M^T$ with R replacing D since we are now confined to the orthogonal case, and N is symmetric and positive definite.

(iii) Comparison of the Kabsch and McLachlan methods. Using the initials of these authors as subscripts, we have seen that the Kabsch solution involves solving

$$R_{WK}N_{WK} = M^T$$

for an orthogonal matrix R_{WK} given that N_{WK} is symmetrical and positive definite. Thus

$$MM^T = N_{WK}^T R_{WK}^T R_{WK} N_{WK} = N_{WK}^2$$

and

$$R_{WK} = M^T (MM^T)^{-1/2}.$$

By comparison, the McLachlan treatment leads to an orthogonal R matrix satisfying

$$R_{ADM} = N_{ADM} M^{-1}$$

in which N_{ADM} is also symmetric and positive definite, which similarly leads to

$$R_{ADM} = (M^T M)^{1/2} M^{-1}.$$

These seemingly different expressions for R_{WK} and R_{ADM} are, in fact, equal, as the following shows

$$R_{WK} = R_{ADM} R_{ADM}^{-1} R_{WK} = R_{ADM} M N_{ADM}^{-1} M^T N_{WK}^{-1},$$

therefore

$$\begin{aligned} R_{WK}^T R_{WK} &= I \\ &= N_{WK}^{-1} M N_{ADM}^{-1} M^T R_{ADM}^T R_{ADM} M N_{ADM}^{-1} M^T N_{WK}^{-1}. \end{aligned}$$

Multiplying on both sides by N_{WK} gives

$$N_{WK}^2 = (M N_{ADM}^{-1} M^T)^2,$$

and since both N matrices are positive definite

$$N_{WK} = M N_{ADM}^{-1} M^T$$

and conversely

$$N_{ADM} = M^T N_{WK}^{-1} M,$$

therefore

$$R_{WK} = M^T M^{T-1} N_{ADM} M^{-1} = R_{ADM}.$$

(iv) Diamond's first method. This method (Diamond, 1976a) differs from the previous ones in that the transformation D is allowed to be a general transformation which is then factorized into the product of an orthogonal matrix R and a symmetrical matrix T . The transformation of x to fit X is thus interpreted as the combination of homogeneous strain and pure rotation in which x is subjected to strain and the result is rotated.

$$D = RT$$

$$T^2 = D^T D$$

$$T = (D^T D)^{1/2}$$

$$R = D(D^T D)^{-1/2}.$$

Furthermore, the solution for D is

$$D = M^T S^{-1}$$

(in the notation of Kabsch), so that

$$R = M^T S^{-1} (S^{-1} M M^T S^{-1})^{-1/2}$$

which may be compared with the results of the previous paragraph.

Although this R matrix by itself (*i.e.* applied without T) does not produce the best rotational superposition (*i.e.* smallest E), it is the one which *exactly* superposes the only three vectors in x whose mutual dispositions are conserved, on their equivalents in X , so that the rotation so found is arguably the best defined one.

Alternatives based on $D = TR$, $D^{-1} = RT$, $D^{-1} = TR$ are all easily developed, and these ideas are developed by Diamond (1976a) to include non-homogeneous strains also.

(v) McLachlan's second method. This method (McLachlan, 1979) is based on the properties of the 6×6 matrix

$$\begin{pmatrix} 0 & M \\ M^T & 0 \end{pmatrix}$$

and is immune to singularity of M . If p and q are three-dimensional vectors such that (p^T, q^T) is an eigenvector of this matrix then

$$\begin{pmatrix} 0 & M \\ M^T & 0 \end{pmatrix} \begin{pmatrix} p \\ q \end{pmatrix} = \begin{pmatrix} Mq \\ M^T p \end{pmatrix} = \begin{pmatrix} p\lambda \\ q\lambda \end{pmatrix}.$$

If q is negated the second equality is maintained provided λ is also negated. Therefore an orthogonal 6×6 matrix

$$\begin{pmatrix} H & H \\ K & -K \end{pmatrix}$$

(consisting of 3×3 partitions) exists for which

$$\begin{pmatrix} H^T & K^T \\ H^T & -K^T \end{pmatrix} \begin{pmatrix} 0 & M \\ M^T & 0 \end{pmatrix} \begin{pmatrix} H & H \\ K & -K \end{pmatrix} = \begin{pmatrix} \Lambda & 0 \\ 0 & -\Lambda \end{pmatrix}$$

in which Λ is diagonal and contains non-negative eigenvalues. The reverse transformation shows that

$$M = 2H\Lambda K^T$$

and multiplying the eigenvectors together gives

$$H^T H = K^T K = \frac{1}{2} I = H H^T = K K^T.$$

Therefore

$$2KH^T M = 4KH^T H\Lambda K^T = 2K\Lambda K^T,$$

but $2KH^T$ is orthogonal and $2K\Lambda K^T$ is symmetrical, therefore [by paragraphs (i) and (iii) above] $2KH^T$ is the required rotation. Similarly, forming

$$M^T = 2K\Lambda H^T$$

$$2M^T H\Lambda^{-1} H^T = 4K\Lambda H^T H\Lambda^{-1} H^T = 2KH^T$$

corresponds to the Kabsch formulation [paragraphs (ii) and (iii)] since $2H\Lambda^{-1} H^T$ is symmetrical and the same rotation, $2KH^T$, appears.

Note that the determinant of the orthogonal matrix so found is twice the product of the determinants of H and of K , and since the positive eigenvalues are collected into Λ it follows that the sign of the determinant of M is the same as the sign of the determinant of the resulting orthogonal matrix. If this is negative it means that the best superposition is obtained if one vector set is inverted and that x and X are of opposite chirality.

Expanding the expression for E , the weighted sum of squares of errors, for an orthogonal transformation shows that this is least when the trace of the product RM is greatest. In this treatment

$$\text{tr}(RM) = \text{tr}(2KH^T \cdot 2H\Lambda K^T) = \text{tr}(2K\Lambda K^T) = \text{tr}(\Lambda).$$

Hence, if the eigenvalues in Λ and $-\Lambda$ are arranged in decreasing

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order of modulus, and if the determinant of $\mathbf{M}$ is negative, then exchanging the third and sixth columns of

$$\begin{pmatrix} \mathbf{H} & \mathbf{H} \\ \mathbf{K} & -\mathbf{K} \end{pmatrix}$$

produces a product $2\mathbf{KH}^T$ with positive determinant (*i.e.* a proper rotation) at minimum cost in residual. Similarly, if $\mathbf{M}$ is singular and one or more eigenvalues in $\mathbf{\Lambda}$ vanishes it is necessary only to complete an orthonormal set of eigenvectors such that the determinants of $\mathbf{H}$ and $\mathbf{K}$ have the same sign.

(vi) MacKay's method. MacKay (1984) was the first to consider the rotational superposition problem in terms of the vector $\mathbf{r}$ of Section 3.3.1.2.1. Using quaternion algebra he showed that if a vector $\mathbf{x}$ is rotated to $\mathbf{X} = \mathbf{R}\mathbf{x}$ then

$$(\mathbf{X} - \mathbf{x}) = \mathbf{r} \times (\mathbf{X} + \mathbf{x}),$$

where $|\mathbf{r}| = \tan(\theta/2)$ and the direction of $\mathbf{r}$ is the axis of rotation, as may also be shown from elementary considerations. MacKay then solves this for the vector $\mathbf{r}$ by least squares given the vector pairs $\mathbf{X}$ and $\mathbf{x}$. The individual errors are

$$e_{IA} = \varepsilon_{Ijk} r_j (X_{ka} + x_{ka}) - (X_{IA} - x_{IA})$$

and

$$E = W_a e_{ia} e_{ia}.$$

Setting $\partial E / \partial r_p = 0_p$ gives

$$\begin{aligned} W_a \varepsilon_{ipk} \varepsilon_{ilm} r_l (X_{ka} + x_{ka}) (X_{ma} + x_{ma}) \\ = W_a \varepsilon_{ipk} (X_{ka} + x_{ka}) (X_{ia} - x_{ia}) \end{aligned}$$

which reduces to

$$2\mathbf{V} = -(\mathbf{Q} + \mathbf{Q}_0)\mathbf{r}$$

in which

$$\begin{aligned} \mathbf{Q} &= \mathbf{M} + \mathbf{M}^T - 2\mathbf{I} \text{tr } \mathbf{M} \\ \mathbf{Q}_0 &= \mathbf{S} + \mathbf{S}' - \mathbf{I}(\text{tr } \mathbf{S} + \text{tr } \mathbf{S}') \\ V_I &= \varepsilon_{Ijk} M_{jk} \\ S_{IJ} &= W_a x_{Ia} x_{Ja} \\ S'_{IJ} &= W_a X_{Ia} X_{Ja}. \end{aligned}$$

Thus a direct solution for $\mathbf{r}$ is obtained,

$$\mathbf{r} = -2(\mathbf{Q}_0 + \mathbf{Q})^{-1}\mathbf{V},$$

the elements of which are u , v and w , and may be used to construct the orthogonal matrix as in Section 3.3.1.2.1. $\mathbf{Q} + \mathbf{Q}_0$ may be obtained directly from $\mathbf{X} + \mathbf{x}$.

If the requisite rotation is 180° , $(\mathbf{Q}_0 + \mathbf{Q})$ is singular and cannot be inverted. In this case any row or column of the adjoint of $(\mathbf{Q}_0 + \mathbf{Q})$ is a vector in the direction of the axis. Normalizing this vector to unity, giving $\mathbf{I}$, gives the requisite orthogonal matrix as

$$\mathbf{R} = 2\mathbf{I}\mathbf{I}^T - \mathbf{I}.$$

Note that MacKay's residual E is quadratic in $\mathbf{r}$. E therefore has one minimum and no maximum, and the minimum is reached on the first cycle of least squares. By contrast, the objective function E that is minimized in methods (i), (ii), (v) and (vii) has one minimum, one maximum and two saddle points in the space of the vector $\mathbf{r}$, as shown in (vii).

It may be shown (Diamond, 1989) that if MacKay's solution vector $\mathbf{r}$ is denoted by $\mathbf{r}_M$ and that given by the other methods [except (iv)] by $\mathbf{r}_O$ then

$$\mathbf{r}_M = \mathbf{r}_O - \mathbf{A}^{-1}\mathbf{B}\mathbf{r}_O$$

in which $\mathbf{A}$ and $\mathbf{B}$ are real symmetric, positive semi-definite. $\mathbf{A}$ is positive definite unless all the individual vector sums $(\mathbf{X} + \mathbf{x})$ are parallel, as can happen when the best rotation is 180° . Thus the MacKay method only gives the same result as the other methods if:

(a) the initial orientation is optimal, for then $\mathbf{r}_O = \mathbf{0}$, or

(b) perfect fitting is possible, for then $\mathbf{B} = \mathbf{0}$, or

(c) all the residual vectors (after fitting by $\mathbf{r}_O$) are parallel to $\mathbf{r}_O$, for then $\mathbf{B}$ is singular such that $\mathbf{B}\mathbf{r}_O = \mathbf{0}$. In general, $|\mathbf{r}_M| \leq |\mathbf{r}_O|$. $\mathbf{r}_O$ may be found by iterating $\mathbf{r}_M$, but $\mathbf{x}$ must be replaced by $\mathbf{R}\mathbf{x}$ on each iteration.

(vii) Diamond's second method. This is closely related to MacKay's method, but uses a four-dimensional vector $\boldsymbol{\rho}$ with components λ , μ , ν and σ in which λ , μ and ν are the direction cosines of the rotation axis multiplied by $\sin(\theta/2)$ and σ is $\cos(\theta/2)$. In terms of such a vector Diamond (1988) showed that

$$E = E_0 - 2\boldsymbol{\rho}^T \mathbf{P} \boldsymbol{\rho}$$

in which E is the weighted sum of squares of coordinate differences, as before, E_0 is its value before any rotation is applied and $\mathbf{P}$ is the matrix

$$\mathbf{P} = \begin{pmatrix} \mathbf{Q} & \mathbf{V} \\ \mathbf{V}^T & 0 \end{pmatrix}.$$

The rotation matrix $\mathbf{R}$ corresponding to the vector $\boldsymbol{\rho}$ is then the last of the forms for $\mathbf{R}$ given in Section 3.3.1.2.1.

The minimum E is therefore E_0 minus twice the largest eigenvalue of $\mathbf{P}$ since $\boldsymbol{\rho}^T \boldsymbol{\rho} = 1$, and a stationary value of E occurs when $\boldsymbol{\rho}$ is any of the four eigenvectors of $\mathbf{P}$. E thus has a maximum, a minimum and two saddle points, in general, and its value may be determined before any coordinates are transformed. Diamond also showed that the orientations giving these stationary values are related by the operations of 222 symmetry. Equivalent results have also been obtained by Kearsley (1989).

As an alternative to solving a 4×4 eigenproblem, Diamond also showed that the vector $\mathbf{r}$, as in MacKay's solution, may be obtained by iterating

$$\begin{aligned} \alpha_0 &= E_0/2 \\ \mathbf{r}_n &= (\alpha_n \mathbf{I} - \mathbf{Q})^{-1} \mathbf{V} \\ \alpha_{n+1} &= \frac{\mathbf{V} \cdot \mathbf{r}_n + \alpha_n r_n^2}{1 + r_n^2} \end{aligned}$$

which has the property that if $\mathbf{X}$ and $\mathbf{x}$ are exactly superposable then α_0 is the exact solution and no iteration is necessary. If $\mathbf{X}$ and $\mathbf{x}$ are similar but not exactly superposable then a small number of iterations may be required to reach a stable $\mathbf{r}$ vector, though the matrix $\mathbf{Q}_0$ is not required. As in MacKay's solution, $(\alpha \mathbf{I} - \mathbf{Q})$ is singular at the end of the iteration if the required rotation is 180° , but the MacKay and Diamond methods both have the advantage that improper rotations are never generated by these means, and methods based on $\mathbf{P}$ and $\boldsymbol{\rho}$ rather than $\mathbf{Q}$ and $\mathbf{r}$ are trouble-free for 180° rotations. The iterative loop in this method does not require $\mathbf{R}\mathbf{x}$ to be redetermined on each cycle.

Finally, it may be shown that if p_1, p_2, p_3, p_4 are the eigenvalues of $\mathbf{P}$ arranged in descending order and

$$p_1 - p_2 - p_3 + p_4$$

is negative, then a closer superposition may be obtained by reversing the chirality of one of the vector sets, and the $\mathbf{R}$ matrix constructed from $\boldsymbol{\rho}_4$ optimally superimposes $\mathbf{R}\mathbf{x}$ onto $-\mathbf{X}$, the enantiomer of $\mathbf{X}$ (Diamond, 1990b).

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3.3.1.2.3. Orthogonalization of impure rotations

There are several ways of deriving a strictly orthogonal matrix from a given approximately orthogonal matrix, among them the following.

(i) The Gram–Schmidt process. This is probably the simplest and the easiest to compute. If the given matrix consists of three column vectors $\mathbf{v}_1, \mathbf{v}_2$ and $\mathbf{v}_3$ (later referred to as primers) which are to be replaced by three column vectors $\mathbf{u}_1, \mathbf{u}_2$ and $\mathbf{u}_3$ then the process is

$$\begin{aligned}\mathbf{u}_1 &= \mathbf{v}_1/|\mathbf{v}_1| \\ \mathbf{u}_2 &= \mathbf{v}_2 - (\mathbf{u}_1 \cdot \mathbf{v}_2)\mathbf{u}_1 \\ \mathbf{u}_2 &= \mathbf{u}_2/|\mathbf{u}_2| \\ \mathbf{u}_3 &= \mathbf{v}_3 - (\mathbf{u}_1 \cdot \mathbf{v}_3)\mathbf{u}_1 - (\mathbf{u}_2 \cdot \mathbf{v}_3)\mathbf{u}_2 \\ \mathbf{u}_3 &= \mathbf{u}_3/|\mathbf{u}_3|.\end{aligned}$$

As successive vectors are established, each vector $\mathbf{v}$ has subtracted from it its components in the directions of established vectors, and the remainder is normalized. The method will fail at the normalization step if the vectors $\mathbf{v}$ are not linearly independent. Otherwise, the process may be extended to any number of dimensions.

The weakness of the method is that, though $\mathbf{u}_1$ differs from $\mathbf{v}_1$ only in scale, $\mathbf{u}_N$ may differ grossly from $\mathbf{v}_N$ as the various columns are not treated equivalently.

(ii) A preferable method which treats all vectors equivalently is to iteratively replace the matrix $\mathbf{M}$ by $\frac{1}{2}(\mathbf{M} + \mathbf{M}^T)$.

Defining the residual matrix $\mathbf{E}$ as

$$\mathbf{E} = \mathbf{M}\mathbf{M}^T - \mathbf{I},$$

then on each iteration $\mathbf{E}$ is replaced by

$$\mathbf{E}^2(\mathbf{M}\mathbf{M}^T)^{-1}/4$$

and convergence necessarily ensues.

(iii) A third method resolves $\mathbf{M}$ into its symmetric and antisymmetric parts

$$\mathbf{S} = \frac{1}{2}(\mathbf{M} + \mathbf{M}^T), \quad \mathbf{A} = \frac{1}{2}(\mathbf{M} - \mathbf{M}^T), \quad \mathbf{M} = \mathbf{S} + \mathbf{A}$$

and constructs an orthogonal matrix for which only $\mathbf{S}$ is altered. $\mathbf{A}$ determines l, m, n and θ as shown in Section 3.3.1.2.1, and from these a new $\mathbf{S}$ may be constructed.

(iv) A fourth method is to treat the general matrix $\mathbf{M}$ as a combination of pure strain and pure rotation. Setting

$$\mathbf{M} = \mathbf{R}\mathbf{T}$$

with $\mathbf{R}$ orthogonal and $\mathbf{T}$ symmetrical gives

$$\mathbf{T} = (\mathbf{M}^T\mathbf{M})^{1/2}, \quad \mathbf{R} = \mathbf{M}(\mathbf{M}^T\mathbf{M})^{-1/2}.$$

The rotation so found is the one which exactly superposes those three mutually perpendicular directions which remain mutually perpendicular under the transformation $\mathbf{M}$.

$\mathbf{T} - \mathbf{I}$ is then the strain tensor of an unrotated body.

Writing $\mathbf{M} = \mathbf{R}\mathbf{T}$, $\mathbf{T} = (\mathbf{M}\mathbf{M}^T)^{1/2}$, $\mathbf{R} = (\mathbf{M}\mathbf{M}^T)^{-1/2}\mathbf{M}$ may also be useful, in which $\mathbf{T} - \mathbf{I}$ is the strain tensor of a rotated body. See also Section 3.3.1.2.2 (iv).

3.3.1.2.4. Eigenvalues and eigenvectors of orthogonal matrices

If $\mathbf{R}$ is the orthogonal matrix given in Section 3.3.1.2.1 in terms of the direction cosines l, m and n of the axis of rotation, then it is clear that (l, m, n) is an eigenvector of $\mathbf{R}$ with eigenvalue unity because

$$\mathbf{R} \begin{pmatrix} l \\ m \\ n \end{pmatrix} = \begin{pmatrix} l \\ m \\ n \end{pmatrix}.$$

Consideration of the determinant $|\mathbf{R} - \lambda\mathbf{I}| = 0$ shows that the sum of the three eigenvalues is $1 + 2\cos\theta$ and that their product is unity. Hence the three eigenvalues are $1, e^{i\theta}$ and $e^{-i\theta}$. Since $\mathbf{R}$ is real, its product with any real vector is also real, yet its product with an eigenvector must, in general, be complex. Thus the eigenvectors must themselves be complex.

The remaining two eigenvectors $\mathbf{u}$ may be found using the results of Section 3.3.1.2.1 (*q.v.*) according to

$$\mathbf{R}\mathbf{u} = \mathbf{u} + \frac{2}{1+t^2} \{(\mathbf{r} \times \mathbf{u}) + [\mathbf{r} \times (\mathbf{r} \times \mathbf{u})]\} = \mathbf{u}e^{\pm i\theta} = \mathbf{u} \frac{1 \pm it}{1 \mp it},$$

which is solved by any vector of the form

$$\mathbf{u} = \mathbf{l} \times \mathbf{v} \mp i\mathbf{l} \times (\mathbf{l} \times \mathbf{v})$$

for any real vector $\mathbf{v}$, where $\mathbf{l}$ is the normalized axis vector, $\mathbf{l} = \mathbf{r}/|\mathbf{r}|$, $|\mathbf{l}| = 1$, $t = \tan(\theta/2)$. Eigenvectors for the two eigenvalues may have unrelated $\mathbf{v}$ vectors though the sign choices are coupled. If the vector $\mathbf{v}$ is rotated about $\mathbf{l}$ through an angle φ the corresponding vector $\mathbf{u}$ is multiplied by $e^{-i\varphi}$ and remains an eigenvector. Using superscript signs to denote the sign of θ in the eigenvalue with which each vector is associated, the matrix

$$\mathbf{U} = (\mathbf{l}, \mathbf{u}^+, \mathbf{u}^-)$$

has the properties that

$$\mathbf{R}\mathbf{U} = \mathbf{U} \begin{pmatrix} 1 & 0 & 0 \\ 0 & e^{i\theta} & 0 \\ 0 & 0 & e^{-i\theta} \end{pmatrix}$$

and

$$\mathbf{U}^{*T}\mathbf{U} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2|\mathbf{l} \times \mathbf{v}^+|^2 & 0 \\ 0 & 0 & 2|\mathbf{l} \times \mathbf{v}^-|^2 \end{pmatrix}$$

which places restrictions on $\mathbf{v}$ if this is to be the identity. Note that the 23 element vanishes even in the absence of any relationship between $\mathbf{v}^+$ and $\mathbf{v}^-$.

A convenient form for $\mathbf{U}$, symmetrical in the elements of $\mathbf{l}$, is obtained by setting $\mathbf{v}^+ = \mathbf{v}^- = [111]$ and is

$$\mathbf{U} = \begin{pmatrix} l & \{(m-n) - i[l(l+m+n)-1]\}/d & \{(m-n) + i[l(l+m+n)-1]\}/d \\ m & \{(n-l) - i[m(l+m+n)-1]\}/d & \{(n-l) + i[m(l+m+n)-1]\}/d \\ n & \{(l-m) - i[n(l+m+n)-1]\}/d & \{(l-m) + i[n(l+m+n)-1]\}/d \end{pmatrix}$$

in which the normalizing denominator is given by

$$d = 2\sqrt{1 - lm - mn - nl}.$$

3.3.1.3. Projection transformations and spaces

In the following section we address the question of the relationship between the coordinates of a molecular model and the corresponding coordinates on the screen of the graphics device. A good introduction to this topic is given by Newman & Sproull (1973), and Foley *et al.* (1990) give a comprehensive account of the field, including recent developments, especially those arising from the development of raster-graphics technologies.

3.3.1.3.1. Definitions

Typically, the coordinates, $\mathbf{X}$, of points in an object to be drawn are held in homogeneous Cartesian form as described in Section 3.3.1.1.2. Such coordinates are said to be in *data space* or *world*

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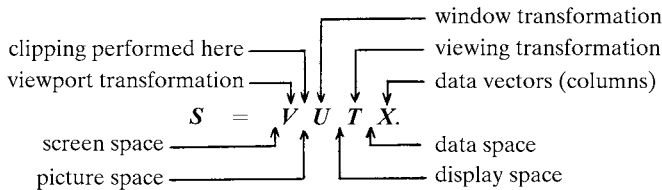
coordinates and this coordinate system is generally a constant aspect of the problem.

In order to view these data in convenient ways such coordinates may be subjected to a 4×4 *viewing transformation* T , affecting orientation, scale *etc.*, the resulting coordinates TX being then in *display space*. Here, and throughout what follows, we treat position vectors as columns with transformation matrices as factors on the left, though some writers do the reverse.

In general, only some portion of display space which lies inside a certain frustum of a pyramid is required to fall within the picture. The pyramid may be thought of as having the observer's eye at its vertex, with a rectangular base corresponding to the picture area. This volume is called a *window*. A transformation, U , which takes *display-space* coordinates as input and generates vectors (X, Y, Z, W) for which X/W and $Y/W = \pm 1$ for points on the left, right, top and bottom boundaries of the window and for which Z/W takes particular values on the front and back planes of the window, is said to be a *windowing transformation*. In machines for which Z/W controls intensity depth cueing, the range of Z/W corresponding to the window is likely to be 0 to 1 rather than -1 to 1. Coordinates obtained by multiplying display-space coordinates by U are termed *picture-space* coordinates. Mathematically, U is a 4×4 matrix like any other, but functionally it is special. Declaring a transformation to be a windowing transformation implies that only resulting points having $|X|, |Y| < W$ and positive $Z < W$ are to be plotted. Machines with clipping hardware to truncate lines which run out of the picture perform clipping on the output from the windowing transformation.

Finally, the picture has to be drawn in some rectangular portion of the screen which is allocated for the purpose. Such an area is termed a *viewport* and is defined in terms of *screen coordinates* which are defined absolutely for the hardware in question as $\pm n$ for full-screen deflection, where n is declared by the manufacturer. *Screen coordinates* are obtained from picture coordinates with a *viewport transformation*, V .*

To summarize, screen coordinates, S , are given by



3.3.1.3.2. Translation

The transformation

$$\begin{pmatrix} NI & \mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix} = \begin{pmatrix} \mathbf{X}N + \mathbf{V}W \\ NW \end{pmatrix} \simeq \begin{pmatrix} \mathbf{X} + \mathbf{V}W/N \\ W \end{pmatrix} \simeq \begin{pmatrix} \mathbf{X}/W + \mathbf{V}/N \\ 1 \end{pmatrix}$$

evidently corresponds to the addition of the vector $\mathbf{V}W/N$ to the components of $\mathbf{X}$ or of $\mathbf{V}/N$ to the components of $\mathbf{X}/W$. (I is the identity.) Displacements may thus be affected by expressing the required displacement vector in homogeneous coordinates with any suitable choice of N (commonly, $N = W$), with $\mathbf{V}$ scaled to correspond to this choice, and loading the 4×4 transformation matrix as indicated above.

* In recent years it has become increasingly common, especially in two-dimensional work, to apply the term 'window' to what is here called a viewport, but in this chapter we use these terms in the manner described in the text.

3.3.1.3.3. Rotation

Rotation about the origin is achieved by

$$\begin{pmatrix} NR & \mathbf{0} \\ \mathbf{0}^T & N \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix} = \begin{pmatrix} NR\mathbf{X} \\ NW \end{pmatrix} \simeq \begin{pmatrix} R\mathbf{X} \\ W \end{pmatrix},$$

in which R is an orthogonal 3×3 matrix. R necessarily has elements not exceeding one in modulus. For machines using integer arithmetic, therefore, N would be chosen large enough (usually half the largest possible integer) for the product NR to be well represented in the available word length. Characteristically, N affects resolution but not scale.

3.3.1.3.4. Scale

The transformation

$$\begin{pmatrix} SN & \mathbf{0} \\ \mathbf{0}^T & N \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix} = \begin{pmatrix} SN\mathbf{X} \\ NW \end{pmatrix} \simeq \begin{pmatrix} S\mathbf{X} \\ W \end{pmatrix}$$

scales the vector $(\mathbf{X}, W)$ by the factor S . For integer working and $|S| < 1$, N should be set to the largest representable integer. For $|S| > 1$ the product SN should be the largest representable integer, N being reduced accordingly.

3.3.1.3.5. Windowing and perspective

It is necessary at this point to relate the discussion to the axial system inherent in the graphics device employed. One common system adopts X horizontal and to the right when viewing the screen, Y vertically upwards in the plane of the screen, and Z normal to X and Y with $+Z$ into the screen. This is, unfortunately, a left-handed system in that $(\mathbf{X} \times \mathbf{Y}) \cdot \mathbf{Z}$ is negative. Since it is usual in crystallographic work to use right-handed axial systems it is necessary to incorporate a matrix of the form

$$\begin{pmatrix} W & 0 & 0 & 0 \\ 0 & W & 0 & 0 \\ 0 & 0 & -W & 0 \\ 0 & 0 & 0 & W \end{pmatrix}$$

either as the left-most factor in the matrix T or as the right-most factor in the windowing transformation U (see Section 3.3.1.3.1). The latter choice is to be preferred and is adopted here. The former choice leads to complications if transformations in display space will be required. Display-space coordinates are necessarily referred to this axial system.

Let L, R, T, B, N and F be the left, right, top, bottom, near and far boundaries of the windowed volume ($L < R, T > B, N < F$), S be the Z coordinate of the screen, and C, D and E be the coordinates of the observer's eye position, all ten of these parameters being referred to the origin of display space as origin, which may be anywhere in relation to the hardware. L, R, T and B are to be evaluated in the screen plane. All ten parameters may be referred to their own fourth coordinate, V , meaning that the point (X, Y, Z, W) in display space will be on the left boundary of the picture if $X/W = L/V$ when $Z/W = S/V$. V may be freely chosen so that all eleven quantities and all elements of U suit the word length of the machine. These relationships are illustrated in Fig. 3.3.1.1.

Since

$$(X, Y, Z, W) \simeq \left(\frac{XV}{W}, \frac{YV}{W}, \frac{ZV}{W}, V \right),$$

XV/W is a display-space coordinate on the same scale as the window parameters. This must be plotted on the screen at an X coordinate (on the scale of the window parameters) which is the weighted mean of XV/W and C , the weights being $(S - E)$ and

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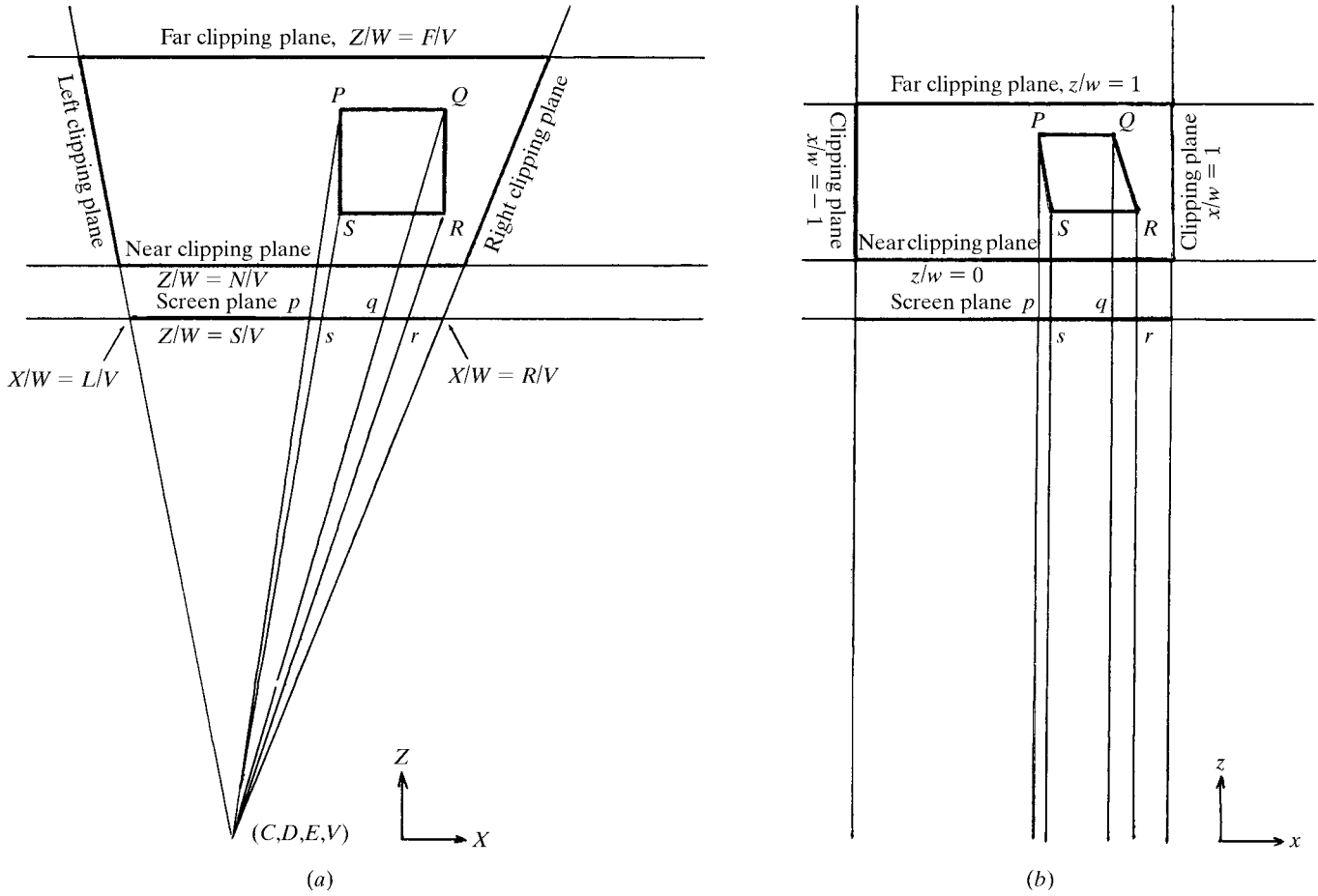


Fig. 3.3.1.1. The relationship between display-space coordinates (X, Y, Z, W) and picture-space coordinates (x, y, z, w) derived from them by the window transformation, U . (a) Display space (in X, Z projection) showing a square object P, Q, R, S for display viewed from the position (C, D, E, V) . The bold trapezium is the window (volume) and the bold line is the viewport portion of the screen. The points P, Q, R and S must be plotted at p, q, r and s to give the correct impression of the object. (b) Picture space (in x, z projection). The window is mapped to a rectangle and all sight lines are parallel to the z axis, but the object P, Q, R, S is no longer square. The distribution of p, q, r and s is identical in the two cases. Note that z/w values are not linear on Z/W , and that the origin of picture space arises at the midpoint of the near clipping plane, regardless of the location of the origin of display space. The figure is accurately to scale for coincident viewport positions. The words 'Left clipping plane', if part of the scene in display space, would currently be obscured, but would come into view if the eye moved to the right, increasing C , as the left clipping plane would pivot about the point L/V in the screen plane.

($ZV/W - S$), respectively. This provides perspective because the weighted mean is at the point where the straight line from (X, Y, Z, W) to the eye intersects the screen. This then has to be mapped into the L -to- R interval, so that picture-space coordinates (x, y, z, w) are given by

$$\begin{pmatrix} x \\ y \\ z \\ w \end{pmatrix} = \begin{pmatrix} \frac{2(S-E)V}{(R-L)} & 0 & \frac{(2C-R-L)V}{(R-L)} & \frac{(R+L)E-2SC}{(R-L)} \\ 0 & \frac{2(S-E)V}{(T-B)} & \frac{(2D-T-B)V}{(T-B)} & \frac{(T+B)E-2SD}{(T-B)} \\ 0 & 0 & \frac{(F-E)V}{(F-N)} & \frac{-N(F-E)}{(F-N)} \\ 0 & 0 & V & -E \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \\ W \end{pmatrix}$$

which provides for $|x/w|$ and $|y/w|$ to be unity on the picture boundaries, which is usually a requirement of the clipping hardware, and for $0 < z/w < 1$, zero being for the near-plane boundary. Even though z/w is not linear on Z/W , straight lines and planes in display space transform to straight lines and planes in picture space,

the non-linearity affecting only distances. Thus vector-drawing machines are not disadvantaged by the introduction of perspective.

Note that the dimensionality of X/W must equal that of S/V and that this may be regarded as length or as a pure number, but that in either case x/w is dimensionless, consistent with the stipulation that the picture boundaries be defined by the pure number ± 1 .

The above matrix is U and is suited to left-handed hardware systems. Note that only the last column of U (the translational part) is sensitive to the location of the origin of display space and that if the eye is on the normal to the picture centre then $C = \frac{1}{2}(R+L)$, $D = \frac{1}{2}(T+B)$ and simplifications result. If C, D and E can be continuously monitored then dynamic parallax as well as perspective may be obtained (Diamond *et al.*, 1982).

If data space is referred to right-handed axes, the viewing transformation T involves only proper rotations and the hardware uses a left-handed axial system then elements in the third column of U should be negated, as explained in the opening paragraph.

To provide for orthographic projection, multiply every element of U by $-K/E$ and then let $E \rightarrow -\infty$, choosing some positive K to suit the word length of the machine [see Section 3.3.1.1.2 (iii)]. The

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result is

$$\mathbf{U}' \simeq \begin{pmatrix} \frac{2KV}{(R-L)} & 0 & 0 & \frac{-K(R+L)}{(R-L)} \\ 0 & \frac{2KV}{(T-B)} & 0 & \frac{-K(T+B)}{(T-B)} \\ 0 & 0 & \frac{KV}{(F-N)} & \frac{-KN}{(F-N)} \\ 0 & 0 & 0 & K \end{pmatrix},$$

which is the orthographic window.

It may be convenient in some applications to separate the functions of windowing and the application of perspective, and to write

$$\mathbf{U} = \mathbf{U}'\mathbf{P},$$

where $\mathbf{U}$ and $\mathbf{U}'$ are as above and $\mathbf{P}$ is a perspective transformation given by

$$\mathbf{P} = (\mathbf{U}')^{-1}\mathbf{U} \simeq \begin{pmatrix} S-E & 0 & C & -SC/V \\ 0 & S-E & D & -SD/V \\ 0 & 0 & F-E+N & -NF/V \\ 0 & 0 & V & -E \end{pmatrix},$$

which involves F and N but not R, L, T or B . In this form the action of $\mathbf{P}$ may be thought of as compressing distant parts of display space prior to an orthographic projection by $\mathbf{U}'$ into picture space.

Other factorizations of $\mathbf{U}$ are possible, for example

$$\mathbf{U} = \mathbf{U}''\mathbf{P}'$$

with

$$\mathbf{U}'' \simeq \begin{pmatrix} \frac{2KV}{R-L} & 0 & 0 & \frac{-K(R+L)}{(R-L)} \\ 0 & \frac{2KV}{T-B} & 0 & \frac{-K(T+B)}{(T-B)} \\ 0 & 0 & \frac{KV(N-E)(F-E)}{E^2(F-N)} & \frac{KN(F-E)}{E(F-N)} \\ 0 & 0 & 0 & K \end{pmatrix}$$

$$\mathbf{P}' \simeq \begin{pmatrix} S-E & 0 & C & -SC/V \\ 0 & S-E & D & -SD/V \\ 0 & 0 & -E & 0 \\ 0 & 0 & V & -E \end{pmatrix},$$

which renders $\mathbf{P}'$ independent of all six boundary planes, but $\mathbf{U}''$ is no longer independent of E . It is not possible to factorize $\mathbf{U}$ so that the left factor is a function only of the boundary planes and the right factor a function only of eye and screen positions.

Note that as $E \rightarrow -\infty$, $\mathbf{U}'' \rightarrow \mathbf{U}'$, $\mathbf{P}$ and $\mathbf{P}' \rightarrow -\mathbf{I}E \simeq \mathbf{I}$.

3.3.1.3.6. Stereoviews

Assuming that left- and right-eye views are to be presented through the same viewport (next section) or that their viewports are to be superimposed by an external optical system, *e.g.* Ortony mirrors, then stereopairs are obtained by using appropriate eye coordinates in the $\mathbf{U}$ matrix of the previous section. However, $\mathbf{U}$ may be factorized according to

$$\mathbf{U} = \mathbf{U}'''\mathbf{S}$$

in which $\mathbf{U}'''$ is the matrix $\mathbf{U}$ obtained by setting (C, D, E, V) to correspond to the point midway between the viewer's eyes and

$$\mathbf{S} = \begin{pmatrix} 1 & 0 & c/(S-E) & -cS/(S-E)V \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\simeq \begin{pmatrix} V & 0 & cV/(S-E) & -cS/(S-E) \\ 0 & V & 0 & 0 \\ 0 & 0 & V & 0 \\ 0 & 0 & 0 & V \end{pmatrix}$$

in which $(c, 0, 0, V)$ is the position of the right eye relative to the mean eye position, and the left-eye view is obtained by negating c .

Stereo is often approximated by introducing a rotation about the Y axis of $\pm \sin^{-1}[c/(S-E)]$ to the views or $\sin^{-1}[2c/(S-E)]$ to one of them. The first corresponds to

$$\mathbf{S} = \begin{pmatrix} \sqrt{1-\sigma^2} & 0 & \sigma & 0 \\ 0 & 1 & 0 & 0 \\ -\sigma & 0 & \sqrt{1-\sigma^2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

with $\sigma = c/(S-E)$. The main difference is in the resulting Z value, which only affects depth cueing and z clipping. The X translation which arises if $S \neq 0$ is also suppressed, but this is not likely to be noticeable. σ is often treated as a constant, such as $\sin 3^\circ$.

The distinction in principle between the true $\mathbf{S}$ and the rotational approximation is that with the true $\mathbf{S}$ the eye moves relative to the screen and the displayed object, whereas with the approximation the eye and the screen are moved relative to the displayed object, in going from one view to the other.

Strobing of left and right images may conveniently be accomplished with an electro-optic liquid-crystal shutter as described by Harris *et al.* (1985). The shutter is switched by the display itself, thus solving the synchronization problem in a manner free of inertia.

A further discussion of stereopairs may be found in Johnson (1970) and in Thomas (1993), the second of which generalizes the treatment to allow for the possible presence of an optical system.

3.3.1.3.7. Viewports

The window transformation of the previous two sections has been constructed to yield picture coordinates (X, Y, Z, W) (formerly called x, y, z, w) such that a point having X/W or $Y/W = \pm 1$ is on the boundary of the picture, and the clipping hardware operates on this basis. However, the edges of the picture need not be at the edges of the screen and a viewport transformation, $\mathbf{V}$, is therefore needed to position the picture in the requisite part of the screen.

$$\mathbf{V} = \begin{pmatrix} (r-l)/2 & 0 & 0 & (r+l)/2 \\ 0 & (t-b)/2 & 0 & (t+b)/2 \\ 0 & 0 & n & 0 \\ 0 & 0 & 0 & n \end{pmatrix},$$

where r, l, t and b are now the right, left, top and bottom boundaries of the picture area, or viewport, expressed in screen coordinates, and n is the full-screen deflection value. Thus a point with $X/W = 1$ in picture space plots on the screen with an X coordinate which is a fraction r/n of full-screen deflection to the right. Z/W is unchanged

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by $\mathbf{V}$ and is used only to control intensity in a technique known as depth cueing.

It is necessary, of course, to arrange for the aspect ratio of the viewport, $(r-l)/(t-b)$, to equal that of the window otherwise distortions are introduced.

3.3.1.3.8. Compound transformations

In this section we consider the viewing transformation $\mathbf{T}$ of Section 3.3.1.3.1 and its construction in terms of translation, rotation and scaling, Sections 3.3.1.3.2–4. We use $\mathbf{T}'$ to denote a new transformation in terms of the prevailing transformation $\mathbf{T}$.

We note first that any 4×4 matrix of the form

$$\begin{pmatrix} UR & \mathbf{V} \\ \mathbf{0}^T & W \end{pmatrix},$$

with U a scalar, may be factorized according to

$$\begin{pmatrix} UR & \mathbf{V} \\ \mathbf{0}^T & W \end{pmatrix} \simeq \begin{pmatrix} UI & \mathbf{0} \\ \mathbf{0}^T & W \end{pmatrix} \begin{pmatrix} UI & \mathbf{V} \\ \mathbf{0}^T & U \end{pmatrix} \begin{pmatrix} UR & \mathbf{0} \\ \mathbf{0}^T & U \end{pmatrix}$$

and also that multiplying

$$\begin{pmatrix} UR & \mathbf{V} \\ \mathbf{0}^T & W \end{pmatrix}$$

by an isotropic scaling matrix, a rotation, or a translation, either on the left or on the right, yields a product matrix of the same form, and its inverse

$$\begin{pmatrix} WR^T & -R^T\mathbf{V} \\ \mathbf{0}^T & U \end{pmatrix}$$

is also of this form, *i.e.* any combination of these three operations in any order may be reduced by the above factorization to a rotation about the original origin, a translation (which defines a new origin) and an expansion or contraction about the new origin, applied in that order.

If

$$\begin{pmatrix} NR & \mathbf{0} \\ \mathbf{0}^T & N \end{pmatrix}$$

is a rotation matrix as in Section 3.3.1.3.3, its application produces a rotation about an axis through the origin defined only in the space in which it is applied. For example, if

$$\mathbf{R} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathbf{T}' \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix} = \mathbf{T} \begin{pmatrix} NR & \mathbf{0} \\ \mathbf{0}^T & N \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix}$$

rotates the image about the z axis of data space, whatever the prevailing viewing transformation, $\mathbf{T}$.

Forming

$$\begin{pmatrix} NR & \mathbf{0} \\ \mathbf{0}^T & N \end{pmatrix} \mathbf{T} \begin{pmatrix} \mathbf{X} \\ W \end{pmatrix}$$

rotates the image about the z axis of display space, *i.e.* the normal to the tube face under the usual conventions, whatever the prevailing $\mathbf{T}$. Furthermore, if this rotation is to appear to be about some chosen position in the picture, *e.g.* the centre, then the window transformation $\mathbf{U}$, Section 3.3.1.3.5, must place the origin of display space there by setting $F > S = R + L = T + B = 0 > N$, in the notation of that section.

If a rotation is to be about a point

$$\begin{pmatrix} \mathbf{V} \\ N \end{pmatrix}$$

then

$$\mathbf{T}' = \begin{pmatrix} NI & \mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix} \begin{pmatrix} N'R & \mathbf{0} \\ \mathbf{0}^T & N' \end{pmatrix} \begin{pmatrix} NI & -\mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix} \mathbf{T}$$

$$\simeq \begin{pmatrix} NR & \mathbf{V} - R\mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix} \mathbf{T}$$

or

$$\mathbf{T}' = \mathbf{T} \begin{pmatrix} NI & \mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix} \begin{pmatrix} N'R & \mathbf{0} \\ \mathbf{0}^T & N' \end{pmatrix} \begin{pmatrix} NI & -\mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix}$$

$$\simeq \mathbf{T} \begin{pmatrix} NR & \mathbf{V} - R\mathbf{V} \\ \mathbf{0}^T & N \end{pmatrix}$$

according to whether $\mathbf{R}$ and $\mathbf{V}$ are both defined in display space or both in data space. If the rotation is defined in display space and the position of the centre of rotation is defined in data space, then the first form of $\mathbf{T}'$ must be used, in which $\mathbf{V}$ is first computed from

$$\begin{pmatrix} \mathbf{V} \\ N \end{pmatrix} = \mathbf{T} \begin{pmatrix} \mathbf{U} \\ W \end{pmatrix}$$

for a rotation centre at

$$\begin{pmatrix} \mathbf{U} \\ W \end{pmatrix}$$

in data space.

For continuous rotations defined in display space it is usually worthwhile to bring the centre of rotation to the origin of display space and leave it there, *i.e.* to omit the left-most factor in the first expression for $\mathbf{T}'$. Incremental rotations can then be made by further rotational factors on the left without further attention to $\mathbf{V}$. When continuous rotations are implemented by repeated multiplication of $\mathbf{T}$ by a rotation matrix, say thirty times a second for a minute or so, the orthogonality of the top-left partition of $\mathbf{T}$ may become degraded by accumulation of round-off error and this should be corrected occasionally by one of the methods of Section 3.3.1.2.3.

It is sometimes a requirement, depending on hardware capabilities, to affect a transformation in display space when access to data space is all that is readily available. In such a case

$$\mathbf{T}' = \mathbf{T}_1 \mathbf{T} = \mathbf{T} \mathbf{T}_2,$$

where $\mathbf{T}_1$ is the required alteration to the prevailing viewing transformation $\mathbf{T}$ and $\mathbf{T}_2$ is the data-space equivalent,

$$\mathbf{T}_2 = \mathbf{T}^{-1} \mathbf{T}_1 \mathbf{T} = \begin{pmatrix} UR & \mathbf{V} \\ \mathbf{0}^T & W \end{pmatrix}^{-1} \begin{pmatrix} U_1 \mathbf{R}_1 & \mathbf{V}_1 \\ \mathbf{0}^T & W_1 \end{pmatrix} \begin{pmatrix} UR & \mathbf{V} \\ \mathbf{0}^T & W \end{pmatrix}$$

$$\simeq \begin{pmatrix} UU_1 R^T R_1 R & R^T (U_1 \mathbf{R}_1 \mathbf{V} + W \mathbf{V}_1 - W_1 \mathbf{V}) \\ \mathbf{0}^T & UW_1 \end{pmatrix}.$$

An important special case is when $\mathbf{T}_1$ is to effect a rotation about the origin of display space without change of scale, so that $\mathbf{V}_1 = 0, U_1 = W_1 = W$, for then

$$\mathbf{T}_2 \simeq \begin{pmatrix} UR^T R_1 R & R^T (R_1 - I) \mathbf{V} \\ \mathbf{0}^T & U \end{pmatrix}.$$

If $\mathbf{r}$ is the required axis of rotation of $\mathbf{R}_1$ in display space then the axis of rotation of $\mathbf{R}^T R_1 R$ in data space is $\mathbf{s} = R^T \mathbf{r}$ since $R^T R_1 R \mathbf{s} = \mathbf{s}$. This gives a particularly simple result if $\mathbf{R}_1$ is to be a primitive rotation for then $\mathbf{s}$ is the relevant row of $\mathbf{R}$, and $R^T R_1 R$

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can be constructed directly from this and the required angle of rotation.

3.3.1.3.9. Inverse transformations

It is frequently a requirement to be able to identify a feature or position in data space from its position on the screen. Facilities for identifying an existing feature on the screen are in many instances provided by the manufacturer as a 'hit' function which correlates the position indicated on the screen by the user (with a tablet or light pen) with the action of drawing and flags the corresponding item in the drawing internally as having been hit. In other instances it may be necessary to be able to indicate a position in data space independently of any drawn feature and this may be done by setting two or more non-parallel sight lines through the displayed volume and finding their best point of intersection in data space.

In Section 3.3.1.3.1 the relationship between data-space co-ordinates and screen-space coordinates was given as

$$\mathbf{S} = \mathbf{VUTX};$$

hence data-space coordinates are given by

$$\mathbf{X} = \mathbf{T}^{-1}\mathbf{U}^{-1}\mathbf{V}^{-1}\mathbf{S}.$$

A line of sight through the displayed volume passing through the point

$$\begin{pmatrix} x \\ y \end{pmatrix}$$

on the screen is the line joining the two position vectors

$$\mathbf{S} = \begin{pmatrix} x & x \\ y & y \\ o & n \\ n & n \end{pmatrix}$$

in screen-space coordinates, as in Section 3.3.1.3.7, from which the corresponding two points in data space may be obtained using

$$\mathbf{V}^{-1} \simeq \begin{pmatrix} \frac{2n}{r-l} & 0 & 0 & \frac{-(r+l)}{(r-l)} \\ 0 & \frac{2n}{t-b} & 0 & -\frac{(t+b)}{(t-b)} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

and

$$\mathbf{U}^{-1} \simeq \begin{pmatrix} \frac{R-L}{2(S-E)} & 0 & \frac{-C(F-N)}{(F-E)(N-E)} & \frac{(R+L)(N-E)-2C(N-S)}{2(N-E)(S-E)} \\ 0 & \frac{T-B}{2(S-E)} & \frac{-D(F-N)}{(F-E)(N-E)} & \frac{(T+B)(N-E)-2D(N-S)}{2(N-E)(S-E)} \\ 0 & 0 & \frac{-E(F-N)}{(F-E)(N-E)} & \frac{N}{(N-E)} \\ 0 & 0 & \frac{-V(F-N)}{(F-E)(N-E)} & \frac{V}{(N-E)} \end{pmatrix}$$

in the notation of Section 3.3.1.3.5, and $\mathbf{T}^{-1}$ was given in Section 3.3.1.3.8. If orthographic projection is being used ($E = -\infty$) then $\mathbf{U}^{-1}$ simplifies to

$$\mathbf{U}^{-1} \simeq \begin{pmatrix} \frac{R-L}{2} & 0 & 0 & \frac{R+L}{2} \\ 0 & \frac{T-B}{2} & 0 & \frac{T+B}{2} \\ 0 & 0 & F-N & N \\ 0 & 0 & 0 & V \end{pmatrix}.$$

Each of these inverse matrices may be suitably scaled to suit the word length of the machine [Section 3.3.1.1.2 (iii)].

Having determined the end points of one sight line in data space the viewing transformation $\mathbf{T}$ may then be changed and the required position marked again through the screen in the new orientation. Each such operation generates a pair of points in data space, expressed in homogeneous form, with a variety of values for the fourth coordinate. Each such point must then be converted to three dimensions in the form $(X/W, Y/W, Z/W)$, and for each sight line any (three-dimensional) point $\mathbf{p}_A$ on the line and the direction $\mathbf{q}_A$ of the line are established. For each sight line a rank 2 projector matrix $\mathbf{M}_A$ of order 3 is formed as

$$\mathbf{M}_A = \mathbf{I} - \mathbf{q}_A \mathbf{q}_A^T / \mathbf{q}_A^T \mathbf{q}_A$$

and the best point of intersection of the sight lines is given by

$$\left(\sum_a \mathbf{M}_a \right)^{-1} \left(\sum_a \mathbf{M}_a \mathbf{p}_a \right),$$

to which three-vector a fourth coordinate of unity may be applied.

3.3.1.3.10. The three-axis joystick

The three-axis joystick is a device which depends on compound transformations for its exploitation. As it is usually mounted it consists of a vertical shaft, mounted at its lower end, which can rotate about its own length (the Y axis of display space, Section 3.3.1.3.1), its angular setting, φ , being measured by a shaft encoder in its mounting. At the top of this shaft is a knee-joint coupling to a second shaft. The first angle φ is set to zero when the second shaft is in some selected direction, *e.g.* normal to the screen and towards the viewer, and goes positive if the second shaft is moved clockwise when seen from above. The knee joint itself contains a shaft encoder, providing an angle, ψ , which may be set to zero when the second shaft is horizontal and goes positive when its free end is raised. A knob on the tip of the second shaft can then rotate about an axis along the second shaft, driving a third shaft encoder providing an angle θ . The device may then be used to produce a rotation of the object on the screen about an axis parallel to the second shaft through an angle given by the knob. The necessary transformation is then

$$\mathbf{R} = \begin{pmatrix} \cos \varphi & 0 & -\sin \varphi \\ 0 & 1 & 0 \\ \sin \varphi & 0 & \cos \varphi \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \psi & \sin \psi \\ 0 & -\sin \psi & \cos \psi \end{pmatrix} \\ \times \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \psi & -\sin \psi \\ 0 & \sin \psi & \cos \psi \end{pmatrix} \\ \times \begin{pmatrix} \cos \varphi & 0 & \sin \varphi \\ 0 & 1 & 0 \\ -\sin \varphi & 0 & \cos \varphi \end{pmatrix}$$

which is

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$$\begin{pmatrix} c^2\psi s^2\varphi + (1 - c^2\psi s^2\varphi)c\theta & -s\psi c\psi s\varphi(1 - c\theta) - c\psi c\varphi s\theta \\ -s\psi c\psi s\varphi(1 - c\theta) + c\psi c\varphi s\theta & s^2\psi + c^2\psi c\theta \\ -c^2\psi s\varphi c\varphi(1 - c\theta) - s\psi s\theta & s\psi c\psi c\varphi(1 - c\theta) - c\psi s\varphi s\theta \\ & -c^2\psi s\varphi c\varphi(1 - c\theta) + s\psi s\theta \\ & s\psi c\psi c\varphi(1 - c\theta) + c\psi s\varphi s\theta \\ & c^2\psi c^2\varphi + (1 - c^2\psi c^2\varphi)c\theta \end{pmatrix}$$

in which $\cos$ and $\sin$ are abbreviated to c and s , which is the standard form with $l = -\cos \psi \sin \varphi$, $m = \sin \psi$, $n = \cos \psi \cos \varphi$.

3.3.1.3.11. Other useful rotations

If rotations in display space are to be controlled by trackerball or tablet then there are two measures available, an x and a y , which can define an axis of rotation in the plane of the screen and an angle θ . If x and y are suitably scaled coordinates of a pen on a tablet then the rotation

$$\begin{pmatrix} \frac{y^2 + x^2 c}{x^2 + y^2} & \frac{-xy(1 - c)}{x^2 + y^2} & x\sqrt{x^2 + y^2} \\ \frac{-xy(1 - c)}{x^2 + y^2} & \frac{x^2 + y^2 c}{x^2 + y^2} & y\sqrt{x^2 + y^2} \\ -x\sqrt{x^2 + y^2} & -y\sqrt{x^2 + y^2} & c \end{pmatrix}$$

with $c = \sqrt{1 - (x^2 + y^2)^2}$ is about an axis in the xy plane (*i.e.* the screen face) normal to (x, y) and with $\sin \theta = x^2 + y^2$. Applied repetitively this gives a quadratic velocity characteristic. Similarly, if an atom at (x, y, z, w) in display space is to be brought onto the z axis by a rotation with its axis in the xy plane the necessary matrix, in homogeneous form, is

$$\begin{pmatrix} \frac{x^2 z + y^2 r}{x^2 + y^2} & \frac{-xy(r - z)}{x^2 + y^2} & -x & 0 \\ \frac{-xy(r - z)}{x^2 + y^2} & \frac{x^2 r + y^2 z}{x^2 + y^2} & -y & 0 \\ x & y & z & 0 \\ 0 & 0 & 0 & r \end{pmatrix}$$

with $r = \sqrt{x^2 + y^2 + z^2}$.

3.3.1.3.12. Symmetry

In Section 3.3.1.1.1 it was pointed out that it is usual to express coordinates for graphical purposes in Cartesian coordinates in ångström units or nanometres. Symmetry, however, is best expressed in crystallographic fractional coordinates. If a molecule, with Cartesian coordinates, is being displayed, and a symmetry-related neighbour is also to be displayed, then the data-space coordinates must be multiplied by

$$\begin{pmatrix} \mathbf{W} & \mathbf{T} \\ \mathbf{0}^T & W \end{pmatrix} \begin{pmatrix} \mathbf{M} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} \mathcal{P} \begin{pmatrix} \mathbf{M}^{-1} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} \begin{pmatrix} \mathbf{W} & -\mathbf{T} \\ \mathbf{0}^T & W \end{pmatrix},$$

where

$$\begin{pmatrix} \mathbf{T} \\ W \end{pmatrix}$$

are the data-space coordinates of the crystallographic origin, $\mathbf{M}$ and $\mathbf{M}^{-1}$ are as in Section 3.3.1.1.1 and $\mathcal{P}$ is a crystallographic symmetry operator in homogeneous coordinates, expressed relative to the same crystallographic origin.

For example, in $P2_1$ with the origin on the screw dyad along $\mathbf{b}$,

$$\mathcal{P} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

and

$$\begin{pmatrix} \mathbf{M} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} \mathcal{P} \begin{pmatrix} \mathbf{M}^{-1} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2}b \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

$\mathcal{P}$ comprises a proper or improper rotational partition, $\mathbf{S}$, in the upper-left 3×3 in the sense that $\mathbf{MSM}^{-1}$ is orthogonal, and with the associated fractional lattice translation in the last column, with the last row always consisting of three zeros and 1 at the 4, 4 position. See *IT A* (1983, Chapters 5.3 and 8.1) for a fuller discussion of symmetry using augmented (*i.e.* 4×4) matrices.

3.3.1.4. Modelling transformations

The two sections under this heading are concerned only with the graphical aspects of conformational changes. Determination of such changes is considered under Section 3.3.2.2.

3.3.1.4.1. Rotation about a bond

It is a common requirement in molecular modelling to be able to rotate part of a molecule relative to the remainder about a bond between two atoms.

If four atoms are bonded 1–2–3–4 then the dihedral angle in the bond 2–3 is zero if the four atoms are *cis* planar, and a rotation in the 2–3 bond is, by convention (IUPAC–IUB Commission on Biochemical Nomenclature, 1970), positive if, when looking along the 2–3 bond, the far end rotates clockwise relative to the near end. This is valid for either viewing direction. This sign convention, when applied to the $\mathbf{R}$ matrix of Section 3.3.1.2.1, leads to the following statement.

If one of the two atoms is selected as the near atom and the direction cosines are those of the vector from the near atom to the far atom, and if the matrix is to rotate material attached to the far atom (with the reference axes fixed), then a positive rotation in the foregoing sense is generated by a positive θ .

Rotation about a bond normally involves compounding $\mathbf{R}$ with translations in the manner of Section 3.3.1.3.8.

3.3.1.4.2. Stacked transformations

A flexible molecule may require to be drawn in any of a number of conformations which are related to one another by, for example, rotations about single bonds, changes of bond angles or changes of bond lengths, all of which changes may be brought about by the application of suitable homogeneous transformations during the drawing of the molecule (Section 3.3.1.3.8). With suitable organization, this may be done without necessarily altering the coordinates of the atoms in the coordinate list, only the transformations being manipulated during drawing.

The use of transformations in the manner shown below is straightforward for simply connected structures or structures containing only rigid rings. Flexible rings may be similarly handled provided that the matrices employed are consistent with the consequential constraints as described in Section 3.3.2.2.1, though this requirement may make real-time folding of flexible rings difficult.

Any simply connected structure may be organized as a tree with a node at each branch point and with an arbitrary number of sites of

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conformational change between one node and the next. We shall call such sites and their associated matrices 'conformons'. The technique then depends on the stacking technique in which matrices are stored and later recovered in the reverse order of their storage.

One begins at some reference point deemed to be fixed in data space and at this point one stacks the prevailing viewing transformation. From this reference point one advances through the molecule along the structural tree and as each conformon is encountered its matrix is calculated. The product of the prevailing matrix with the conformon matrix is formed and stacked, and this product becomes the prevailing matrix. This product is constructed with the conformon matrix as a factor on the right, *i.e.* in data space as defined in Section 3.3.1.3.1, and is calculated using the coordinates of the molecule in their unmodified form, *i.e.* before any shape changes are brought about.

This progression leads eventually to an extremity of the tree. At this point drawing is commenced using the prevailing matrix and working backwards towards the fixed root, unstacking (or 'popping') a matrix as each conformon is passed until a node is reached, which, in general, will occur only part way back to the root. On reaching such a node drawing is suspended and one advances along the newly found branch as before, stacking matrices, until another extremity is reached when drawing towards the root is resumed. This alternation of stacking matrices while moving away from the root and drawing and unstacking matrices while moving towards the root is continued until the whole tree is traversed.

This process is illustrated schematically in Fig. 3.3.1.2 for a simple tree with one node, numbered 1, and three conformons at *a*, *b* and *c*. One enters the tree with a current viewing transformation *T* and progresses upwards from the fixed lower extremity. When the conformon at *a* is encountered, *T* is stacked and the product TM_a is formed. Continuing up the tree, at node 1 either branch may be chosen; we choose the left and, on reaching *b*, TM_a is stacked and TM_aM_b is formed. On reaching the tip drawing down to *b* is done with this transformation, TM_a is then unstacked and drawing continues with this matrix until node 1 is reached. The other branch is then followed to *c* whereupon TM_a is again stacked and the product TM_aM_c is formed. From the tip down as far as *c* is drawn with this matrix, whereupon TM_a is unstacked and drawing continues down to *a*, where *T* is unstacked before drawing the section nearest the root.

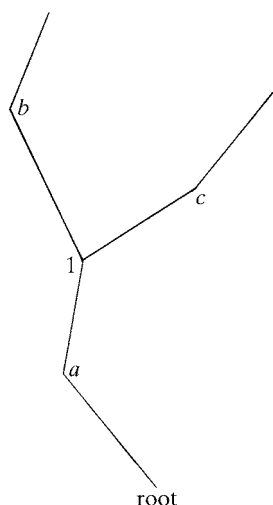


Fig. 3.3.1.2. Schematic representation of a simple branched-chain molecule with a stationary root and two extremities. The positions marked *a*, *b* and *c* are the loci of possible conformational change, here called conformons, and there is a single, numbered branch point.

With this organization the matrices associated with *b* and *c* are unaffected by changes in the conformation at *a*, notwithstanding the fact that changes at *a* alter the direction of the axis of rotation at *b* or *c*.

Two other approaches are also possible. One of these is to start at the tip of the left branch, replace the coordinates of atoms between *b* and the tip by M_bX , and later replace all coordinates between the tip and *a* by M_aX , with a similar treatment for the other branch. The advantage of this is that no storage is required for stacked matrices, but the disadvantage is that atoms near the tips of the tree have to be reprocessed for every conformon. It also modifies the stored coordinates, which may or may not be desirable.

The second alternative is to draw upwards from the root using *T* until *a* is reached, then using TM_a until *b* is reached, then using TM'_bM_a to the tip, but in this formulation M'_b must be based on the geometry that exists at *b* after the transformation M_a has been applied to this region of the molecule, *i.e.* M'_b is characteristic of the final conformation rather than the initial one.

3.3.1.5. Drawing techniques

3.3.1.5.1. Types of hardware

There are two main types of graphical hardware in use for interactive work, in addition to plotters used for batch work. These main types are raster and vector. In raster equipment the screen is scanned as in television, with a grid of points, called pixels, addressed sequentially as the scan proceeds. Associated with each pixel is a word of memory, usually containing something in the range of 1 to 24 bits per pixel, which controls the colour and intensity to be displayed. Many computer terminals have one bit per pixel (said to be 'single-plane' systems) and these are essentially monochrome and have no grey scale. Four-plane systems are cheap and popular and commonly provide 4-bit by 4-bit look-up tables between the pixel memory and the monitor with one such table for each of the colours red, green and blue. If these tables are each loaded identically then 16 levels of monochrome grey scale are available, but if they are loaded differently 16 different colours are available simultaneously chosen from a total of 4096 possibilities. Four-plane systems are adequate for many applications where colour is used for coding, but are inadequate if colour is intended also to provide realism, where brilliance and saturation must be varied as well as hue. For these applications eight-plane systems are commonly used which permit 256 colours chosen from 16 million using three look-up tables, though the limitations of these can also be felt and full colour is only regarded as being available in 24-plane systems.

Raster-graphics devices are ideal for drawing objects represented by opaque surfaces which can be endowed with realistic reflecting properties (Max, 1984) and they have been successfully used to give effects of transparency. They are also capable of representing shadows, though these are generally difficult to calculate (see Section 3.3.1.5.5). Many devices of this type provide vectorization, area fill and anti-aliasing. Vectorization provides automatically for the loading of relevant pixels on a straight line between specified points. Area fill automatically fills any irregular pre-defined polygon on the screen with a uniform colour with the user specifying only the colour and one point within the polygon. Anti-aliasing is the term used for a technique which softens the staircase effect that may be seen on a line which runs at a small angle to a vertical or horizontal row of pixels.

The main drawback with this type of equipment is that it is slow compared to vector machines. Only relatively simple objects can be displayed with smooth rotation in real time as transformed coordinates have to be converted to pixel addresses and the

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previous frame needs to be deleted with each new frame unless it is known that each new frame will specify every pixel. However, the technology is advancing rapidly and these restrictions are already disappearing.

Vector machines, on the other hand, are specialized to drawing straight lines between specified points by driving the electron beam along such lines. No time is wasted on blank areas of the screen. Dots may be drawn with arbitrary coordinates, in any order, but areas, if they are to be filled, must be done with a ruling technique which is very seldom done. Images produced by vector machines are naturally transparent in that foreground does not obscure background, which makes them ideal for seeing into representations of molecular structure.

3.3.1.5.2. Optimization of line drawings

A line drawing consisting of n line segments may be specified by anything from $(n + 1)$ to $2n$ position vectors depending on whether the lines are end-to-end connected or independent. Appreciable gains in both processing time and storage requirements may be made in complicated drawings by arranging for line segments to be end-to-end connected as far as possible, and an algorithm for doing this is outlined below. For further details see Diamond (1984a).

Supposing that a list of nodal points (atoms if a covalent skeleton is being drawn) exists within a computer with each node appearing only once and that the line segments to be drawn between them are already determined, then at each node there are, generally, both forward and backward connections, forward connections being those to nodes further down the list. A quantity D is calculated at each node which is the number of forward connections minus the number of backward connections. At the commencement of drawing, the first connected node in the list must have a positive D , the last must have a negative D , the sum of all D values must be zero and the sum of the positive ones is the number of strokes required to draw the drawing, a 'stroke' being a sequence of end-to-end connected line segments drawn without interruption. The total number of position vectors required to specify the drawing is then the number of nodes plus the number of strokes plus the number of rings minus one.

Drawing should then be done by scanning the list of nodes from the top looking for a positive D (usually found at the first node), commencing a stroke at this node and decrementing its D value by 1. This stroke is continued from node to node using the specified connections until a negative D is encountered, at which point the stroke is terminated and the D value at the terminating node is incremented by 1. This is done even though this terminating node may also possess some forward connections, as the total number of strokes required is not minimized by keeping a stroke going as far as possible, but by terminating a stroke as soon as it reaches a node at which some stroke is bound to terminate.

The next stroke is initiated by resuming the scan for positive D values at the point in the node list where the previous stroke began. If this scan encounters a zero D value at a node which has not hitherto been drawn to, or drawn from, then the node concerned is isolated and not connected to any other, and such nodes may require to be drawn with some special symbol. The expression already given for the number of vectors required is valid in the presence of isolated nodes if drawing an isolated node is allowed one position vector, this vector not being counted as a stroke.

The number of strokes generated by this algorithm is sensitive to the order in which the nodes are listed, but if this resembles a natural order then the number of strokes generated is usually close to the minimum, which is half the number of nodes having an odd number of connections. For example, the letter E has six nodes, four of which have an odd number of connections, so it may be drawn with two strokes.

3.3.1.5.3. Representation of surfaces by lines

The commonest means of representing surfaces, especially contour surfaces, is to consider evenly spaced serial sections and to perform two-dimensional contouring on each section. Repeating this on serial sections in two other orientations then provides a good representation of the surface in three dimensions when all such contours are displayed. The density is normally cited on a grid with submultiples of **a**, **b** and **c** as grid vectors, inverse linear interpolation being used between adjacent grid points to locate points on the contour. For vector-graphics applications it is expedient to connect such points with straight lines; some equipment may be capable of connecting them with splines though this is burdensome or impossible if real-time rotation of the scene is required. Precalculation of splines stored as short vectors is always possible if the proliferation of vectors is acceptable. For efficient drawing it is necessary for the line segments of a contour to be end-to-end connected, which means that it is necessary to contour by following contours wherever they go and not by scanning the grid. Algorithms which function in this way have been given by Heap & Pink (1969) and Diamond (1982a). Contouring by grid scanning followed by line connection by the methods of the previous section would be possible but less efficient. Further contouring methods are described by Sutcliffe (1980) and Cockrell (1983).

For raster-graphics devices there is little disadvantage in using curved contours though many raster devices now have vectorizing hardware for loading a line of pixels given only the end points. For these devices well shaped contours may be computed readily, using only linear arithmetic and a grid-scanning approach (Gossling, 1967). Others have colour-coded each pixel according to the density, which provides a contoured visual impression without performing contouring (Hubbard, 1983).

3.3.1.5.4. Representation of surfaces by dots

Connolly (Langridge *et al.*, 1981; Connolly, 1983a,b) represents surfaces by placing dots on the surface with an approximately uniform superficial density. Connolly's algorithm was developed to display solvent-accessible surfaces of macromolecules and provides for curved concave portions where surface atoms meet. Pearl & Honegger (1983) have developed a similar algorithm, based on a grid, which generates only convex portions which meet in cusps, but is faster to compute than the Connolly surface. Bash *et al.* (1983) have produced a van der Waals surface algorithm fast enough to permit real-time changes to the structure without tearing the surface.

It has become customary to use a dot representation to display computed surfaces, such as the surface at a van der Waals radius from atomic centres, and to use lines to represent experimentally determined surfaces, especially density contours.

3.3.1.5.5. Representation of surfaces by shading

Many techniques have been developed, mainly for raster-graphics devices, for representing molecular surfaces and these have been very well reviewed by Max (1984).

The simplest technique in this class consists in representing each atom by a uniform disc, or high polygon, which can be colour-coded and area-filled by the firmware of the device. If such atoms are sorted on their z coordinate and drawn in order, furthest ones first, so that nearer ones partly or completely overwrite the further ones then the result is a simple representation of the molecule as seen from the front. This technique is fast and has its uses when a rapid schematic is all that is required. In one sense it is wasteful to process distant atoms when they are going to be overwritten by foreground atoms, but front-to-back processing requires the boundaries of visible parts

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of partially obscured atoms near the front to be determined before they can be painted or, alternatively, every pixel must be tested before loading to see if it is already loaded. Not only does this approach give a uniform rendering over the whole area of one atom, it also gives a boundary between overlapping atoms with almost equal z values which completes the circle of the nearer atom, though it should be an arc of an ellipse when the atoms are drawn with radii exceeding their covalent radii.

Greater realism is achieved by establishing a z buffer, which is an additional area of memory with one word per pixel, in which is stored the z value of the currently loaded feature in each pixel. Treatments which take account of the sphericity are then possible and correct arcs of intersection for interpenetrating spheres and more complicated entities arise naturally through loading a colour value into a pixel only if the z coordinate is less than that of the currently loaded value. This z buffer and the associated x , y coordinates should be in picture space or screen space rather than display space since only after the application of perspective can points with the same x/w and y/w coordinates obscure one another.

It is usual in such systems to vary the intensity of colour within one atom by darkening it towards the circumference on the basis of the z coordinate. Some systems augment this impression of sphericity by highlighting. The simplest form of highlighting is an extension of the uniform disc treatment in which additional, brighter discs, possibly off centre, are associated with each atom. More general highlighting (Phong, 1975) is computed from four unit vectors, these being the normal to the surface, the direction to a light source, the direction to the viewer and the normalized vector sum of these last two. Intensity levels may then be set as the sum of three terms: a constant, a term proportional to the scalar product of the first two vectors (if positive) and a term proportional to a high power of the scalar product of the first and last vectors; the higher the power the glossier the surface appears to be. This final term normally adds a white term, rather than the surface colour, supposing the light source to be white.

Shadows may also be rendered to give even greater realism. In addition to the z buffer and (x, y) frame buffer a second z buffer for z' values associated with x' and y' is also required. These coordinates are then related by $x' = x + \alpha z$, $y' = y + \beta z$, $z' = z$. The second buffer is a ray buffer since $x'y'$ are the coordinates with which an illuminating ray passing through (xyz) passes through the $z = 0$ plane, and z' , stored at x' , y' , records the depth at which this ray encounters material. Thus any two pixels $(x_1y_1z_1)$ and $(x_2y_2z_2)$ are on the same illuminating ray if their x' and y' values are equal and the one with smaller z' shadows the other. Processing a pixel at $(x_1y_1z_1)$ therefore involves first determining its visibility on the basis of the z buffer, as before, then, whether or not it is visible, setting $z'_1 = z_1$ and considering the value of z' currently stored at $x'y'$, which we call z'_2 .

If $z'_1 < z'_2$ then $x_1y_1z_1$ is in light and must be loaded accordingly. From z'_2 we find the previously processed pixel $(x_2y_2z_2)$ which is now in shade and which was in light when originally processed, so that the colour value stored at x_2y_2 needs to be altered *unless* the pixel at x_2y_2 is now $(x_2y_2z_3)$ with $z_3 < z_2$, in which case the pixel $(x_2y_2z_2)$ which has now become shadowed by $(x_1y_1z_1)$ has, in the meantime, been obscured by $(x_2y_2z_3)$ which is not shadowed by $(x_1y_1z_1)$ and no change is therefore needed. In either event z'_1 then replaces z'_2 .

If $z'_1 > z'_2$ then $(x_1y_1z_1)$, if visible, is in shade and must be coloured accordingly, and in this case z'_2 is not superseded.

This shadowing scheme corresponds to illumination by a light source at infinity in picture space or, equivalently, with a z coordinate equal to that of the eye in display space. For its implementation x , y and z may be in any convenient coordinate system, e.g. pixel addresses, but if x and y are expressed with the range -1 to 1 and z with the range 0 to 1 corresponding to the

window then they may be identified as the quantities x/w , y/w and z/w of picture space (Section 3.3.1.3.1).

If, in the notation of Section 3.3.1.3.5, the light source is placed at (P, Q, E, V) in display space and a ray leaves it in the direction (p, q, r, V) then

$$x' = \frac{p}{r} \cdot \frac{2(S-E)}{(R-L)} + \frac{2(S-E)(P-C)}{(N-E)(R-L)} + \frac{2C-R-L}{R-L},$$

which varies only with beam direction,

$$\alpha = \frac{2(S-E)(F-N)(P-C)}{(F-E)(N-E)(R-L)}$$

and similarly for y' and β .

3.3.1.5.6. Advanced hidden-line and hidden-surface algorithms

Hidden surfaces may be handled quite generally with the z -buffer technique described in the previous section but this technique becomes very inefficient with very complicated scenes. Faster techniques have been developed to handle computations in real time (e.g. 25 frames s^{-1}) on raster machines when both the viewpoint and parts of the environment are moving and substantial complexity is required. These techniques generally represent surfaces by a number of points in the surface, connected by lines to form panels. Many algorithms require these panels to be planar and some require them to be triangular. Of those that permit polygonal panels, most require the polygons to be convex with no re-entrant angles. Yet others are limited to cases where the objects themselves are convex. Some can handle interpenetrating surfaces, others exclude these. Some make enormous gains in efficiency if the objects in the scene are separable by the insertion of planes between them and degrade to lower efficiency if required, for example, to draw a chain. Some are especially suited to vector machines and others to raster machines, the latter capitalizing on the finite resolution of such systems. In all of these the basic entities for consideration are entire panels or edges, and in some cases vertices, point-by-point treatment of the entire surface being avoided until after all decisions are made concerning what is or is not visible.

All of these algorithms strive to derive economies from the notion of 'coherence'. The fact that, in a cine context, one frame is likely to be similar to the previous frame is referred to as 'frame coherence'. In raster scans line coherence also exists, and other kinds of coherence can also be identified. The presence of any form of coherence may enable the computation to be concerned primarily with changes in the situation, rather than with the totality of the situation so that, for example, computation is required where one edge crosses in front of another, but only trivial actions are involved so long as scan lines encounter the projections of edges in the same order.

The choice of technique from among many possibilities may even depend on the viewpoint if the scene has a statistical anisotropy. For example, the depiction of a city seen from a viewpoint near ground level involves many hidden surfaces. Distant buildings may be hidden many times over. The same scene depicted from an aerial viewpoint shows many more surfaces and fewer overlaps. This difference may swing the balance of advantage between an algorithm which sorts first on z or one which leaves that till last.

These advanced techniques have, so far, found little application in crystallography, but this may change. Ten such techniques are critically reviewed and compared by Sutherland *et al.* (1974), and three of these are described in detail by Newman & Sproull (1973).

3.3.2. Molecular modelling, problems and approaches

This section is concerned with software techniques which permit a set of atomic coordinates for a molecule to be generated *ab initio*, or to be modified, by reference to some chosen criterion, usually the electron density. Software that can change the shape of a molecule must be cognizant of the connectivity of the molecule and the bonding characteristics of atom types. It must also have means of regaining good stereochemistry if current coordinates are poor in this respect, or of performing its manipulations in ways which conserve essential stereochemical features. Approaches to some of these problems are outlined below. Many of the issues involved, including the topics outlined in Section 3.3.1.4 above, have been excellently reviewed by Hermans (1985), though with little reference to graphical aspects, and a comprehensive treatment of modelling methods based on energies is given by Burkert & Allinger (1982).

3.3.2.1. Connectivity

It is necessary to distinguish three different kinds of connectivity, namely structural, logical and drawing connectivities. Structural connectivity consists of the specification of the chemical bonding of the molecule and, as such, is an absolute property of the molecule. Logical connectivity consists of the specification of what part or parts of a molecule are moved, and in what way, if some stereochemical feature is altered. Logical and structural connectivity are closely related and in simple cases coincide, but the distinction is apparent, for example, if the puckering of a five-membered ring is being modelled by permitting folding of the pentagon about a line connecting non-adjacent corners. This line is then a logical connection between two moving parts, but it is not a feature of the structural connectivity.

Drawing connectivity consists of a specification of the lines to be drawn to represent the molecule and often coincides with the structural connectivity. However, stylized drawings, such as those showing the α -carbon atoms of a protein, require to be drawn with lines which are features neither of the logical nor of the structural connectivity.

3.3.2.1.1. Connectivity tables

The simplest means of storing connectivity information is by means of tables in which, for each atom, a list of indices of other atoms to which it is connected is stored. This approach is quite general; it may serve any type of molecular structure and permits structures to be traversed in a variety of ways. In this form, however, it is extravagant on storage because every connection is stored twice, once at each of the nodes it connects. It may, however, provide the starting material for the algorithm of Section 3.3.1.5.2 and its generality may justify its expense.

From such a list, lists of bonds, bond angles and dihedral angles may readily be derived in which each entry points to two, three or four atoms in the atom list. Lists of these three types form the basis of procedures which adjust the shape of a molecule to reduce its estimated potential energy (Levitt & Lifson, 1969; Levitt, 1974), and of search-and-retrieval techniques (Allen *et al.*, 1979).

Katz & Levinthal (1972) discuss the explicit specification of structural connectivity in terms of a tree structure in which, for each atom, is stored a single pointer to the connected atom nearer to the root, virtual atoms being used to allow ring structures to be treated as trees. An algorithm is also presented which allows such a tree specification to be redetermined if an atom in the tree is newly chosen as the root atom or if the tree itself is modified.

Cohen *et al.* (1981) have developed methods of handling connectivity in complicated fused- and bridged-ring systems.

3.3.2.1.2. Implied connectivity

In cases where software is required to deal only with a certain class of molecule, it may be possible to exploit the characteristics of that class to define an ordering for lists of atoms such that connectivity is implied by the ordering of items in the list. Such an ordering may successfully define one of the three types of connectivity defined in Section 3.3.2.1 but it is unlikely to be able to meet the needs of all three simultaneously. It may also be at a disadvantage when required to deal with structures not part of the class for which it is designed. Within these limitations, however, it may be exceedingly efficient. Both proteins and nucleic acids are of a class which permits their logical connectivity to be specified entirely by list ordering, and the software described in Section 3.3.3.2.6 uses no connectivity tables for this purpose. The ordering rules concerned are given by Diamond (1976b).

Drawing connectivity needs explicit specification in such a case; this may be done using only one 16-bit integer per atom, which may be stored as part of the atom list without the need of a separate table. This integer consists of two signed bytes which act as relative pointers in the list, positive pointers implying draw-to, negative pointers implying move-to. As each atom is encountered during drawing the right byte is read and utilized, and the two bytes are swapped before proceeding. This allows up to two bonds drawn to an atom and two bonds drawn from it, four in all, with a minimum of storage (Diamond, 1984a).

Brandenburg *et al.* (1981) handle drawing connectivity by enlarging the molecular list with duplicate atoms such that each is connected to the next in the list, but moves and draws still need to be distinguished.

Levitt (1971) has developed a syntax for specifying structural connectivity implicitly from a list structure which is very general, though designed with biopolymers in mind, and the work of Katz & Levinthal (1972) includes something similar.

3.3.2.2. Modelling methods

Fundamental to the design of any software for molecular modelling are the choices of modelling criteria, and of parameterization. Criteria which may be adopted might include the fitting of electron density, the minimization of an energy estimate or the matching of complementary surfaces between a pair of molecules. Parameterizations which may be adopted include the use of Cartesian coordinates of atoms as independent variables, or of internal coordinates, such as dihedral angles, as independent variables with atomic positions being dependent on these. Systems designed to suit energetic criteria usually use Cartesian coordinates since all aspects of the structure, including bond lengths, must be treated as variables and be allowed to contribute to the energy estimate. Systems designed to fit a model to observed electron density, however, may adequately meet the stereochemical requirements of modelling on either parameterization, and examples of both types appear below.

Inputs to modelling systems vary widely. Systems intended for use mainly with proteins or other polymeric structures usually work with a library of monomers which the software may develop into a polymer. Systems intended for smaller molecules usually develop the molecular structure atom-by-atom rather than a residue at a time, and systems of this kind require a very general form of input. They may accept a list of atom types and coordinates if measurement and display of a known molecule is the objective, or they may accept 'sketch-pad' input in the form of a hand-drawn two-dimensional sketch of the type conventional in chemistry, if the objective is the design of a molecule. Sketch-pad input is a feature of some systems with quantum-mechanical capabilities.

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3.3.2.2.1. Methods based on conformational variables

Suppose that $\mathbf{t}$ represents a vector from the current position of an atom in the model to a target position then (see Section 3.3.1.1.3), to first order, the observational equations are

$$t_{IA} = D_{IP} \theta_P + v_{IA}$$

in which θ represents changes to conformational variables which may include dihedral angles, bond angles, bond lengths, and parameters determining overall position and orientation of the molecule as a whole. If every such parameter is included the model acquires $3n$ degrees of freedom for n atoms, in which case the methods of the next section are more appropriate, but if bond lengths and some or all bond angles are being treated as constants then the above equation becomes the basis of the treatment.

$$D_{IP} = \frac{\partial r_{IA}}{\partial \theta_P} = \varepsilon_{ijk} n_{jP} (r_{kA} - r_{kP})$$

in which $\mathbf{n}_P$ is a unit vector defining the axis of rotation for an angular variable θ_P , $\mathbf{r}_A$ and $\mathbf{r}_P$ are position vectors of the atom A and the site of the parameter P , and $\mathbf{v}_A$ represents a residual vector.

$\sigma = v_{ia} v_{ia}$ is minimized by

$$\theta = \mathbf{M}^{-1} \mathbf{V}$$

in which

$$M_{PQ} = D_{IP} D_{IQ}$$

$$V_P = D_{IP} t_{ia}$$

More generally, if σ represents any scalar quantity which is to be minimized, e.g. an energy, then

$$V_P = -\frac{1}{2} \frac{\partial \sigma}{\partial \theta_P}$$

$$M_{PQ} = \frac{1}{2} \frac{\partial^2 \sigma}{\partial \theta_P \partial \theta_Q}$$

It is beyond the scope of this chapter to review the methods available for evaluating θ from these equations. Difficulties may arise from two sources:

(i) Inversion of $\mathbf{M}$ may be difficult if $\mathbf{M}$ is large or ill conditioned and impossible if $\mathbf{M}$ is singular.

(ii) Successful evaluation of $\mathbf{M}^{-1} \mathbf{V}$ will not minimize σ in one step if $\mathbf{t}$ is not linearly dependent on θ or, equivalently, $\partial^2 \sigma / \partial \theta_P \partial \theta_Q$ is not constant, and substantial changes θ are involved. Iteration is then necessary.

Difficulties of the first kind may be overcome by gradient methods, for example the conjugate gradient method without searches if $\mathbf{M}$ is available or with searches if it is not available, or they may be overcome by methods based on eigenvalue decompositions. If non-linearity is serious less dependence should be placed on $\mathbf{M}$ and gradient methods using searches are more valuable. In this connection Diamond (1966) introduced a sliding filter technique which produced rapid convergence in extreme conditions of non-linearity. These topics have been reviewed elsewhere (Diamond, 1981, 1984b) and are the subject of many textbooks (Walsh, 1975; Gill *et al.*, 1981; Luenberger, 1984).

Warne *et al.* (1972) have developed a similar system using dihedral angles as variables and a variety of alternative optimization algorithms.

The modelling of flexible rings or lengths of chain with two or more fixed parts is sometimes held to be a difficulty in methods using conformational variables, although a simple two-stage solution does exist. The principle involved is the sectioning of the space of the variables into two orthogonal subspaces of which the

first is used to satisfy the constraints and the second is used to perform the optimization subject to those constraints.

The algebra of the method may be outlined as follows, and is given in more detail by Diamond (1971, 1980a,b). Parametric shifts θ_1 which satisfy the constraints are solutions of

$$\mathbf{V}_1 = \mathbf{M}_1 \theta_1$$

in which $\mathbf{V}_1$ and $\mathbf{M}_1$ depend only on the target vectors, $\mathbf{t}_1$, of the atoms with constrained positions and on the corresponding derivatives. We then find a partitioned orthogonal matrix $(\mathbf{A}_1 \mathbf{B}_1)$ satisfying

$$(\mathbf{A}_1 \mathbf{B}_1) = (\mathbf{E}_\lambda \mathbf{E}_0) \begin{pmatrix} \mathbf{R}_\lambda & \mathbf{0} \\ \mathbf{0} & \mathbf{R}_0 \end{pmatrix}$$

in which $\mathbf{E}_\lambda$ are the eigenvectors of $\mathbf{M}_1$ having positive eigenvalues, $\mathbf{E}_0$ are those having zero eigenvalues, and $\mathbf{R}_\lambda$ and $\mathbf{R}_0$ are arbitrary orthogonal matrices. Then

$$\begin{pmatrix} \mathbf{A}_1^T \\ \mathbf{B}_1^T \end{pmatrix} \mathbf{V}_1 = \begin{pmatrix} \mathbf{A}_1^T \\ \mathbf{B}_1^T \end{pmatrix} \mathbf{M}_1 (\mathbf{A}_1 \mathbf{B}_1) \begin{pmatrix} \mathbf{A}_1^T \\ \mathbf{B}_1^T \end{pmatrix} \theta_1$$

$$= \begin{pmatrix} \mathbf{A}_1^T \mathbf{M}_1 \mathbf{A}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{A}_1^T \\ \mathbf{B}_1^T \end{pmatrix} \theta_1$$

$$\mathbf{A}_1^T \theta_1 = (\mathbf{A}_1^T \mathbf{M}_1 \mathbf{A}_1)^{-1} \mathbf{A}_1^T \mathbf{V}_1$$

in which the matrix to be inverted is positive definite. $\mathbf{A}_1$, however, is rectangular so that multiplying on the left by $\mathbf{A}_1$ does not necessarily serve to determine θ_1 , but we may write

$$\theta_1 = (\mathbf{A}_1 \mathbf{B}_1) \begin{pmatrix} \varphi_1 \\ \psi_1 \end{pmatrix}$$

giving

$$\begin{pmatrix} \mathbf{A}_1^T \\ \mathbf{B}_1^T \end{pmatrix} \mathbf{V}_1 = \begin{pmatrix} \mathbf{A}_1^T \mathbf{M}_1 \mathbf{A}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \psi_1 \end{pmatrix}$$

$$\varphi_1 = (\mathbf{A}_1^T \mathbf{M}_1 \mathbf{A}_1)^{-1} \mathbf{A}_1^T \mathbf{V}_1$$

and ψ_1 is indeterminate and free to adopt any value. We therefore adopt

$$\theta_1 = \mathbf{A}_1 \varphi_1 = \mathbf{A}_1 (\mathbf{A}_1^T \mathbf{M}_1 \mathbf{A}_1)^{-1} \mathbf{A}_1^T \mathbf{V}_1,$$

which is the smallest vector of parametric shifts which will satisfy the constraints, and allow ψ_1 to be determined by the remaining observational equations in which the target vectors, $\mathbf{t}$, are now modified to $\mathbf{t}_2$ according to

$$\mathbf{t}_2 = \mathbf{t} - \mathbf{D}_2 \theta_1,$$

$\mathbf{D}_2$ and $\mathbf{t}_2$ being the derivatives and effective target vectors for the unconstrained atoms. We then solve

$$\mathbf{V}_2 = \mathbf{M}_2 \theta_2$$

in which θ_2 is required to be of the form

$$\theta_2 = \mathbf{B}_1 \psi_1$$

giving

$$\theta_2 = \mathbf{B}_1 (\mathbf{B}_1^T \mathbf{M}_2 \mathbf{B}_1)^{-1} \mathbf{B}_1^T \mathbf{V}_2$$

and apply the total shifts

$$\Theta = \theta_1 + \theta_2$$

to obtain a structure which is optimized within the restrictions imposed by the constraints.

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It may happen that $\mathbf{B}_1^T \mathbf{M}_2 \mathbf{B}_1$ is itself singular because there are insufficient data in the vector $\mathbf{t}_2$ to control the structure and the parametric shifts contained in $\boldsymbol{\theta}_2$ fully. In this event the same process may be applied again, basing the solution for $\boldsymbol{\theta}_2$ on

$$\begin{pmatrix} \mathbf{A}_2^T \\ \mathbf{B}_2^T \end{pmatrix} \mathbf{B}_1^T \mathbf{M}_2 \mathbf{B}_1 (\mathbf{A}_2 \mathbf{B}_2)$$

so that the vectors in $\mathbf{B}_2$ represent the degrees of freedom which remain uncommitted. This method of application of constraints by subspace sectioning may be nested to any depth and is completely general.

A valid matrix $\mathbf{A}_1$ may be found from $\mathbf{M}_1$ by using the fact that the columns of $\mathbf{M}_1$ are all linear combinations of the columns of $\mathbf{E}_\lambda$ and are void of any contribution from $\mathbf{E}_0$. It follows that $\mathbf{A}_1$ may be found by using the columns of $\mathbf{M}_1$ as priming vectors in the Gram-Schmidt process [Section 3.3.1.2.3 (i)] until the normalizing step involves division by zero. $\mathbf{A}_1$ is then complete if all the columns of $\mathbf{M}_1$ have been tried. $(\mathbf{A}_1 \mathbf{B}_1)$ may then be completed by using arbitrary vectors as primers.

Manipulation of a ring of n atoms may be achieved by treating it as a chain of $(n+2)$ atoms [having $(n+1)$ bond lengths, n bond angles and $(n-1)$ dihedral angles] in which atom 1 is required to coincide with atom $(n+1)$ and atom 2 with $(n+2)$. $\mathbf{t}_1$ then contains two vectors, namely the lack-of-closure vectors at these points, and is typically zero. $\mathbf{A}_1$ is then found to have five columns corresponding to the five degrees of freedom of two points of fixed separation; $\boldsymbol{\theta}_1$ contains only zeros if the ring is initially closed, and contains ring-closure corrections if, through non-linearity or otherwise, the ring has opened. $\mathbf{B}_1$ contains $(p-5)$ columns if the chain of $(n+2)$ points has p variable parameters. It follows, if bond lengths and bond angles are treated as constants, that the seven-membered ring is the smallest ring which is flexible, that the six-membered ring (if it can be closed with the given bond angles) has no flexibility (though it may have discrete alternatives) and that it may be impossible to close a five-membered ring. Therefore some variation of bond angles and/or bond lengths is essential for the modelling of flexible five- and six-membered rings. Treating the ring as a chain of $(n+1)$ atoms is less satisfactory as there is then no control over the bond angle at the point of ring closure.

A useful concept for the modelling of flexible five-membered rings with near-constant bond angles is the concept of the pseudorotation angle P , and amplitude θ_m , for which the j th dihedral angle is given by

$$\theta_j = \theta_m \cos \left(P + \frac{4\pi j}{5} \right).$$

This formulation has the property $\sum_{j=0}^4 \theta_j = 0$, which is not exactly true; nevertheless, θ_j values measured from observed conformations comply with this formulation within a degree or so (Altona & Sundaralingam, 1972).

Software specialized to the handling of condensed ring systems has been developed by van der Lieth *et al.* (1984) (Section 3.3.3.3.1) and by Cohen *et al.* (1981) (Section 3.3.3.3.2).

3.3.2.2.2. Methods based on positional coordinates

Modelling methods in which atomic coordinates are the independent variables are mathematically simpler than those using angular variables especially if the function to be minimized is a quadratic function of interatomic distances or of distances between atoms and fixed points. The method of Dodson *et al.* (1976) is representative of this class and it may be outlined as follows. If $\mathbf{d}$ is a column vector containing ideal values of the scalar distances from atoms to fixed target points or to other atoms, and if $\mathbf{l}$

is a column vector containing the prevailing values of these quantities obtained from the model, then

$$\mathbf{d} = \mathbf{l} + \mathbf{D}\delta\mathbf{x} + \boldsymbol{\varepsilon}$$

in which the column matrix $\delta\mathbf{x}$ contains alterations to the atomic coordinates, $\boldsymbol{\varepsilon}$ contains residual discrepancies and $\mathbf{D}$ is a large sparse rectangular matrix containing values of $\partial l / \partial x$, of which there are not more than six non-zero values on any row, consisting of direction cosines of the line of which $\mathbf{l}$ is the length. $\boldsymbol{\varepsilon}^T \mathbf{W} \boldsymbol{\varepsilon}$ is then minimized by setting

$$\mathbf{D}^T \mathbf{W} (\mathbf{d} - \mathbf{l}) = \mathbf{D}^T \mathbf{W} \mathbf{D} \delta\mathbf{x},$$

which they solve by the method of conjugate gradients without searches. This places reliance on the linearity of the observational equations (Diamond, 1984b). It also works entirely with the sparse matrix $\mathbf{W}^{1/2} \mathbf{D}$, the dense matrix $\mathbf{D}^T \mathbf{W} \mathbf{D}$, and its inverse, being never calculated.

The method is extremely efficient in annealing a model structure for which an initial position for every atom is available, especially if the required shifts are within the quasi-linear region, but is less effective when large dihedral-angle changes are involved or when many atoms are to be placed purely by interpolation between a few others for which target positions are available. Interbond angles are controlled by assigning d values to second-nearest-neighbour distances; this is effective except for bond angles near 180° so that, in particular, planar groups require an out-of-plane dummy atom to be included which has no target position of its own but does have target values of distances between itself and atoms in the planar group. The method requires a d value to be supplied for every type of nearest- and next-nearest-neighbour distance in the structure, of which there are many, together with W values which are the inverse variances of the distances concerned as assessed by surveys of the corresponding distances in small-molecule structures, or from estimates of their accuracy, or from estimates of accuracy of the target positions.

Hermans & McQueen (1974) published a similar method which differs in that it moves only one atom at a time, in the environment of its neighbours, these being considered fixed while the central atom is under consideration. This is inefficient in the sense that in any one cycle one atom moves only a small fraction ($\sim 3\%$) of the distance it will ultimately be required to move, but individual atom cycles are so cheap and simple that many cycles can be afforded. The method was selected for inclusion in *Frodo* by Jones (1978) (Section 3.3.3.2.7) and is an integral part of the *GRIP* system (Tsernoglou *et al.*, 1977; Girling *et al.*, 1980) (Section 3.3.3.2.2) for which it was designed.

3.3.2.2.3. Approaches to the problem of multiple minima

Modelling methods which operate by minimizing an objective function of the coordinates (whether conformational or positional) suffer from the fact that any realistic objective function representing the potential energy of the structure is likely to have many minima in the space of the variables for any but the simplest problems. No general system has yet been devised that can ensure that the global minimum is always found in such cases, but we indicate here two approaches to this problem.

The first approach uses dynamics to escape from potential-energy minima. Molecular-mechanics simulations allow each atom to possess momentum as well as position and integrate the equations of motion, conserving the total energy. By progressively removing energy from the simulation by scaling down the momentum vectors some potential-energy minimum may be found. Conversely, a minimization of potential energy which has led to a minimum thought not to be the global minimum may be continued by introducing atomic momenta sufficient to overcome potential-

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energy barriers between minima, and subsequently attenuate the momenta again. In this way a number of minima may be found (Levitt & Warshel, 1975). It is equivalent to initializing a potential-energy minimization from a number of different conformations but it has the property that the minima so found are separated by energy barriers for which an upper limit is known so that the possibility exists of exploring transition pathways.

A second approach (Purisma & Scheraga, 1986) is relatively new. If the objective function to be minimized can be expressed in terms of interatomic distances, and if each atom is given coordinates in a space of $n - 1$ dimensions for n atoms, then a starting structure may be postulated for which the interatomic distances *all* take their ideal values and the objective function is then necessarily at an absolute minimum. This multidimensional structure is then projected into a space of fewer dimensions, within which it is again optimized with respect to the objective function. The dimensionality of the model is thus progressively reduced until a three-dimensional model is attained at a low energy. This means that the minimum so attained in three dimensions is approached *from beneath*, having previously possessed a lower value in a higher-dimensional space. This, in itself, does not guarantee that the three-dimensional minimum-energy structure so found is at the global minimum, but it is not affected by energy barriers between minima in the same way, and it does appear to reach very low minima, and frequently the global one. Because it is formulated entirely in terms of interatomic distances it offers great promise for modelling molecules on the basis of data from nuclear magnetic resonance.

3.3.3. Implementations

In this section the salient characteristics of a number of systems are described. Regrettably, it cannot claim to be a complete guide to all existing systems, but it probably describes a fairly representative sample. Some of these systems have arisen in academia and these are freely described. Some have arisen in or been adopted by companies which now market them, and these are described by reference to the original publications. Other marketed systems for which originators' published descriptions have not been found are not described. Yet other systems have been developed, for example, by companies within the chemical and pharmaceutical industries for their own use, and these have generally not been described in what follows since it is assumed that they are not generally available, even where published descriptions exist.

Software concerned especially with molecular dynamics has not been included unless it also provides static modelling capability, since this is a rapidly growing field and it has been considered to be beyond the intended scope of this chapter. Systems for which outline descriptions have already been given (Levitt & Lifson, 1969; Levitt, 1974; Diamond, 1966; Warne *et al.*, 1972; Dodson *et al.*, 1976; Hermans & McQueen, 1974) are not discussed further.

For some of the earliest work Levinthal (1966) still makes interesting reading and Feldmann (1976) is still an excellent review of the technical issues involved. The issues have not changed, the algorithms there described are still valuable, only the manner of their implementation has moved on as hardware has developed. A further review of the computer generation of illustrations has been given by Johnson (1980). Excellent bibliographies relating to these sections have been given by Morffew (1983, 1984), which together contain over 250 references including their titles.

The following material is divided into three sections. The first is concerned primarily with display rather than modelling though some of these systems can modify a model, the second is concerned with molecular modelling with reference to electron density and can develop a model *ab initio*, and the third is concerned with modelling with reference to other criteria.

Where software names are known to be acronyms constructed from initial letters, or where the original authors have used capitals, the names are capitalized here. Otherwise names are lower case with an initial capital.

While it is recognised that many of the systems here described are now of mainly historical interest, most have been retained for the second edition, some have been updated and some new paragraphs have been added.

3.3.3.1. Systems for the display and modification of retrieved data

One of the earliest systems designed for information retrieval and display was that described by Meyer (1970, 1971) which used television raster technology and enabled the contents of the Brookhaven Protein Data Bank (Meyer, 1974; Bernstein *et al.*, 1977) to be studied visually by remote users. It also enabled a rigid two-ring molecule to be solved from packing considerations alone (Hass *et al.*, 1975; Willoughby *et al.*, 1974). Frames for display were written digitally on a disk and the display rate was synchronized to the disk rotation. With the reduction in the cost of core storage, contemporary systems use large frame buffer memories thus avoiding synchronization problems and permitting much richer detail than was possible in 1970. A majority of the systems in this section use raster techniques which preclude real-time rotation except for relatively simple drawings, though *GRAMPS* is an exception (O'Donnell & Olson, 1981; Olson, 1982) (Section 3.3.3.1.4).

3.3.3.1.1. ORTEP

This program, the Oak Ridge Thermal Ellipsoid Program, due to Johnson (1970, 1976) was developed originally for the preparation of line drawings on paper though versions have since been developed to suit raster devices with interactive capability.

The program draws molecules in correct perspective with each atom represented by an ellipsoid which is the equi-probability surface for the atomic centre, as determined by anisotropic temperature factor refinement, the principal axes of which are displayed. Bonds are represented by cylindrical rods connecting the atoms which in the drawing are tapered by the perspective.

In line-drawing versions the problem of hidden-line suppression is solved analytically, whereas the later versions for raster devices draw the furthest elements of the picture first and either overwrite these with nearer features of the scene if area painting is being done or use the nearer features as erase templates if line drawings are being made.

3.3.3.1.2. Feldmann's system

R. J. Feldmann and co-workers (Feldmann, 1983) at the National Institutes of Health, Bethesda, Maryland, USA, were among the first to develop a suite of programs to display molecular structure using colour raster-graphics techniques. Their system draws with coloured shaded spheres, usually with one sphere to represent each atom, but alternatively the spheres may represent larger moieties like amino acids or whole proteins if lower-resolution representations are required. These workers have made very effective use of colour. Conventionally, oxygens have been modelled in red, but this system allows charged oxygens to be red and uncharged ones to be pink, with a similar treatment in blue for charged and uncharged nitrogens. By such means they have been able to give immediacy to the hydrophobic and electrostatic properties of molecular surfaces, and have used these characteristics effectively in studies of the binding possibilities of benzamidine derivatives to trypsin (Feldmann *et al.*, 1978).

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The algorithm developed by Porter (1978) for shading spheres to be darkened near their peripheries also computes the proper appearance of the line of intersection of two spheres wherever interpenetration occurs, in contrast to some simpler systems which draw a complete disc for whichever sphere is forward of the other. Provided that all opaque spheres are drawn first, the system is also capable of representing transparent spheres by darkening the colour of the existing background inside, and especially near the edge of, discs representing transparent foreground spheres.

Other systems that produce space-filling pictures of a similar general character have been produced by Motherwell (1978), by Sundaram & Radhakrishnan (1979) and by Lesk (next section).

3.3.3.1.3. *Lesk & Hardman software*

The complexity of macromolecules is a formidable obstacle to perceiving the basic features of their construction and the stylized drawings produced by this software following the artistry of Richardson (1977, 1981, 1985) enables the internal organization of such molecules to be appreciated readily. The software is capable of mixing several styles of representation, among them the Richardson style of cylinders for α -helices, arrows for β -strands and ribbons for less-organized regions, or the creased-ribbon technique for the whole chain, or a ball-and-stick representation of atoms and bonds, or space-filling spheres. All these styles are available simultaneously in a single picture with depth cueing, colour and shading, and hidden-feature suppression as appropriate. It is also able to show a stylized drawing of a complete molecule together with a magnified part of it in a more detailed style. See Lesk & Hardman (1982, 1985).

3.3.3.1.4. *GRAMPS*

This system, due to O'Donnell & Olson (O'Donnell & Olson, 1981; Olson, 1982) provides a high-level graphics language and its associated interpretive software. It provides a general means of defining objects, drawable by line drawings, in such a way that these may be logically connected in groups or trees using a simple command language. Such a system may, for example, define a subunit protein of an icosahedral virus and define icosahedral symmetry, in such a way that modification of one subunit is expressed simultaneously in all subunits whilst preserving the symmetry, and simultaneously allowing the entire virus particle to be rotated. Such logical and functional relationships are established by the user through the medium of the *GRAMPS* language at run time, and a great diversity of such relationships may be created. The system is thus not limited to any particular type of structure, such as linear polymers, and has proved extremely effective as a means of providing animation for the production of cine film depicting viral and other structures. *GRAMPS* runs on all Silicon Graphics workstations under IRIX 4.0 or above.

3.3.3.1.5. *Takenaka & Sasada's system*

Takenaka & Sasada (1980) have described a system for the manipulation and display of molecular structures, including packing environments in the crystal, using a minicomputer loosely coupled to a mainframe. Their system is also capable of model building by the addition of groups of one or more atoms with a facility for monitoring interaction distances while doing so.

3.3.3.1.6. *MIDAS*

This system, due to Langridge and co-workers (Gallo *et al.*, 1983; Ferrin *et al.*, 1984) is primarily concerned with the display of existing structures rather than with the establishment of new ones, but it may modify such structures by bond rotations under manual control. It is of particular value in the study of molecular

interactions since two or more molecules may be manipulated simultaneously and independently. Visual docking of molecules is greatly facilitated by the display of van der Waals surfaces, which may be computed in real time so that the turning of a bond in the underlying structure does not tear the surface (Bash *et al.*, 1983).

3.3.3.1.7. *Insight*

This system, originally due to Dayringer *et al.* (1986), has a functionality similar to *MIDAS*. It has been replaced by *Insight II* (current version 2.3.5). It appears to be well suited to the study of intermolecular relationships in docking and in structural comparisons, and it is able to make modifications to structures. Objects for display may be molecular or non-molecular, the former having an atomic substructure and the latter consisting of a vector list which may not be subdivided into referable components. Map fitting with the current version has been reported.

3.3.3.1.8. *PLUTO*

PLUTO was developed by Motherwell (1978) at the Cambridge Crystallographic Data Centre (CCDC) for the display of molecular structures and crystal-packing diagrams, including an option for space-filling model style with shadowing. The emphasis was on a free format command and data structure, and the ability to produce ball-and-spoke drawings with line shadowing suitable for reproduction in journal publication. Many variant versions have been produced, with essentially the 1978 functionality, its popularity deriving from its ease of use and the provision of default options for establishing connectivity using standard bonding radii. It was distributed as part of the CCDC software associated with the Cambridge Structural Database, with an interface for reading entries from the database.

In 1993 Motherwell and others at the CCDC added an interactive menu and introduced colour and PostScript output. New features were introduced to allow interactive examination of intermolecular contacts, particularly hydrogen-bonded networks, and sections through packing diagrams (Cambridge Structural Database, 1994).

3.3.3.1.9. *MDKINO*

This system, due to Swanson *et al.* (1989), provides for the extraction and visualization of selected regions from molecular-dynamics simulations. It permits stereo viewing, interactive geometric interrogation and both forwards and backwards display of motion.

3.3.3.2. *Molecular-modelling systems based on electron density*

Systems described in this section require real-time rotation of complicated transparent scenes and all used vector-graphics technology in their original implementations for that reason, though many are now available for raster machines. In every case the graphics are the means of communication between the user and software possessing high functionality, capable of building a representation of a molecule *ab initio* and to alter it, change its shape and position it optimally in relation to an electron-density map, with due attention being paid to stereochemical considerations, by one or more of several approaches.

3.3.3.2.1. *CHEMGRAF*

Katz & Levinthal (1972) have developed a powerful modelling and display system for macromolecules known as *CHEMGRAF*. This system permits the definition of many atom types which includes bonding specifications, so that, for example, four types of carbon atom are included in the basic list and others may be added.

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A molecular fragment with an unsatisfied valency (by which it might later be attached to another such group) would have that feature represented by a 'vanishing virtual' atom which removes the need for any organizational distinction between such fragments and complete molecules. Fragments, such as amino-acid residues, may be assembled from atoms, and molecules may be assembled from atoms and/or from such fragments invoked by name, by the superposition and elimination of the relevant vanishing virtuals. The assembly process includes the development of a connectivity tree for the molecule and provision is made for the 'turning' or reconstruction of such trees if the combination of such fragments redefines the root atom of one or more of the fragments. The system also provides for ring closure. Model building initially uses fixed bond lengths and angles, varying only the dihedral angles in single bonds, but has a library of preformed rings which could not otherwise be modelled on the simple basis. The results of such modelling may then be subjected to an energy-minimization routine using a steepest-descent method in the space of the dihedral angles and referring to the Lennard-Jones potential for non-bonded atom pairs. Atoms are first sorted into contiguous cubes so that all neighbours of any atom may be found by searching not more than 27 cubes.

The system is also capable of modelling by reference to electron density either by the translation and rotation of molecular fragments and the rotation of rotatable bonds within them or by the automatic linking of peaks in an electron-density map which are separated by less than, say, 1.8 Å, which is an important aid to interpretation when the resolution is sufficiently high.

3.3.3.2.2. *GRIP*

This system, developed by Professor F. P. Brooks, Dr W. V. Wright and associates at the University of North Carolina, Chapel Hill, NC, USA, was designed for biopolymers and was the first to enable a protein electron-density map to be interpreted *ab initio* without the aid of mechanical models (Tsernoglou *et al.*, 1977). Girling *et al.* (1980) give a more recent example of its use.

In its 1975 version *GRIP* is a three-machine system. Centrally there is a minicomputer which receives inputs from the user and controls a vector display with high-speed matrix-multiplication capability. The third machine is a mainframe computer with high-speed communication with the minicomputer.

The system develops a polymer chain from a library of monomers and manipulates it through bond rotations or free rotations of fragments explicitly specified by the user, with the aid of dials which may be coupled to bonds for the purpose. Bond rotations in the main chain either rotate part of the molecule relative to the remainder, which may have undesirable long-range effects, or the scope of the rotation is artificially limited with consequential discontinuities arising in the chain. Such discontinuities are removed or alleviated by the mainframe computer using the method of Hermans & McQueen (1974), which treats atomic position vectors, rather than bond rotations, as independent variables.

The system made pioneering use of a two-axis joystick to control orientation and a three-translation joystick to control position.

3.3.3.2.3. *Barry, Denson & North's systems*

These systems (Barry & North, 1971; North *et al.*, 1981; North, 1982) are examples of pioneering work done with minicomputers before purpose-built graphics installations became widespread; examples of their use are given by Ford *et al.* (1974), Potterton *et al.* (1983) and Dodson *et al.* (1982). They have the ability to develop a polymer chain in sections of several residues, each of which may subsequently be adjusted to remove any misfit errors where the sections overlap. Manipulations are by rotation and translation of sections and by bond rotations within sections. These movements

are directly controlled by the user, who may simultaneously observe on the screen the agreement with electron density, or calculated estimates of potential or interaction energy, or a volume integral of the product of observed and model densities, or predicted shifts of proton magnetic resonance spectra. Thus models which are optimal by various criteria may be constructed, but there is no optimizer directly controlling the rotational adjustments which are determined by the user.

One of the earliest applications of them (Beddell, 1970) was in the fitting of substrate molecules to the active site of lysozyme using difference electron densities; however, the systems also permitted the enzyme-substrate interaction to be studied simultaneously and to be taken into account in adjusting the model.

3.3.3.2.4. *MMS-X*

The Molecular Modelling System-X (*MMS-X*) is a system of purpose-built hardware developed by Barry, Marshall and others at Washington University, St Louis. Associated with it are several sets of software. The St Louis software consists of a suite of programs rather than one large one and provides for the construction of a polymer chain in helical segments which may be adjusted bodily to fit the electron density, and internally also if the map requires this too. Non-helical segments are built helically initially and unwound by user-controlled rotations in single bonds. The fitting is done to visual criteria. An example of the use of this system is given by Lederer *et al.* (1981).

Miller *et al.* (1981) have described an alternative software system for the same equipment. Functions invoked from a keyboard allow dials to be coupled to dihedral angles in the structure. Their system communicates with a mainframe computer which can deliver small blocks of electron density to be contoured and stored locally by the graphics system; this provides freedom of choice of contour level at run time. An example of the use of this system is given by Abad-Zapatero *et al.* (1980).

3.3.3.2.5. *Texas A&M University system*

This system (Morimoto & Meyer, 1976), a development of Meyer's earlier system (Section 3.3.3.1), uses vector-graphics technology and a minicomputer and is free of the timing restrictions of the earlier system. The system allows control dials to be dynamically coupled by software to rotations or translations of parts of the structure, thus permitting the re-shaping or re-positioning of the model to suit an electron-density map which may be contoured and managed by the minicomputer host. The system may be used to impose idealized geometry, such as planar peptides in proteins, or it may work with non-idealized coordinates.

The system was successfully applied to the structures of rubredoxin and the extracellular nuclease of *Staphylococcus aureus* (Collins *et al.*, 1975) and to binding studies of sulfonamides to carbonic anhydrase (Vedani & Meyer, 1984). In addition, two of the first proteins to be constructed without the aid of a 'Richards' Box' were modelled on this system: monoclinic lysozyme in 1976 (Hogle *et al.*, 1981) and arabinose binding protein in 1978 (Gilliland & Quiocho, 1981).

3.3.3.2.6. *Bilder*

This system (Diamond, 1980a,c, 1982b) runs on a minicomputer independent of any mainframe. It builds a polymer chain from a library of residues and adapts it by internal rotations and overall positioning in much the same way as previous systems described in this section. Like them, it can provide user-controlled bond rotations, but its distinctive feature is that it has an optimizer within the minicomputer which will determine optimal combinations of bond rotations needed to meet the user's declared

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objectives. Such objectives are normally target positions for atoms set by the user by visual reference to the density, using the method of Section 3.3.1.3.9, but they may include target values for angles. These latter may either declare a required shape that is to take precedence over positional requirements, which are then achieved as closely as the declared shape allows, or they may be in least-squares competition with the positional requests. The optimizer also recognizes the constraints imposed by chain continuity and enables an internal section of the main chain to be modified without breaking its connection to the rest of the molecule. Similar techniques also allow ring systems to adopt various conformations, by bond rotation, without breaking the ring, simultaneously permitting the ring to have target positions. The optimizer is unperturbed by under-determined situations, providing a minimum-disturbance result in such cases. All these properties of the optimizer are generated without recourse to any 'special cases' by a generalization of the subspace section technique which was used to maintain chain continuity in a 'real-space-refinement' program (Diamond, 1971). This is based entirely on the rank of the normal matrix that arises during optimization, which may serve to satisfy a constraint such as chain continuity or ring closure and simultaneously to establish what degrees of freedom remain to be controlled by other criteria. In *Bilder* this is achieved without establishing eigenvalues or eigenvectors. The method is described in outline in Section 3.3.2.2.1 and in detail by Diamond (1980*a,b*).

The angular variables used normally comprise all single bonds but may include others, such as the peptide bond with or without a target of 180°. Thus this bond may be completely rigid, elastic, or completely free. Any interbond angles may also be parameterized but at some cost in storage. The normal mode of working is to develop a single chain for the entire length of the molecule, but if cumulative error makes fitting difficult a fresh chain may be started at any stage. *Bilder* may itself reconnect such chains at a later stage.

Construction and manipulation operates on a few residues at a time within the context of a polymer chain, but any or all of the rest of the molecule, or other molecules, may be displayed simultaneously.

Contouring is done in advance to produce a directoried file of contoured bricks of space, each brick containing up to 20 independently switchable elements which need not all be from the same map. Choice of contour level and displayed volume is thus instantaneous within the choices prepared.

The system is menu driven from a tablet, only file assignments and the like requiring the keyboard, and it offers dynamic parallax as an aid to 3D perception (Diamond *et al.*, 1982). Bloomer *et al.* (1978), Phillips (1980), and Evans *et al.* (1981) give examples of its use.

3.3.3.2.7. *Frodo*

This system, due to Jones (Jones, 1978, 1982, 1985; Jones & Liljas, 1984), in its original implementation was a three-machine system comprising graphics display, minicomputer and mainframe, though more recent implementations combine the last two functions in a 'midi'. Its capabilities are similar to those of *Bilder* described above, but its approach to stereochemical questions is very different. Where *Bilder* does not allow an atom to be moved out of context (unless it comprises a 'chain' of one atom) *Frodo* will permit an atom or group belonging to a chain to be moved independently of the other members of the chain and then offers regularization procedures based on the method of Hermans & McQueen (1974) to regain good stereochemistry. During this regularization, selected atoms may be fixed, remaining atoms then adjusting to these. A peptide, for example, may be inverted by moving the carbonyl oxygen across the peptide and fixing it, relying on the remaining atoms to rearrange themselves. (*Bilder* would do

the equivalent operation by cutting the chain nearby, turning the peptide explicitly, reconnecting the chain and optimizing to regain chain continuity.) The *Frodo* approach is easy to use especially when large displacements of an existing structure are called for, but requires that ideal values be specified for all bond lengths, angles and fixed dihedrals since the system may need to regain such values in a distorted situation. *Bilder*, in contrast, never changes such features and so need not know their ideal values.

Frodo may work either with consecutive residues of a polymer chain, useful for initial building, or with a volume centred on a chosen position, which is ideal for adjusting interacting side chains which are close in space but remote in sequence.

In recent implementations *Frodo* can handle maps both in density grid form and in contour form and permits on-line contouring. It has also been developed (Jones & Liljas, 1984) to allow the automatic adjustment of the position and orientation of small rigid groupings by direct reference to electron density in the manner of Diamond (1971) but without the maintenance of chain continuity, which is subsequently reintroduced by regularization.

Horjales and Cambillau (Cambillau & Horjales, 1987; Cambillau *et al.*, 1984) have also provided a development of *Frodo* which allows the optimization of the interaction of a ligand and a substrate with both molecules being treated as flexible.

3.3.3.2.8. *Guide*

Brandenburg *et al.* (1981) have described a system which enables representations of macromolecules to be modified with reference to electron density. Such modifications include rotation about single bonds under manual control, or the movement with six degrees of freedom, also under manual control, of any part or parts of the molecule relative to the remainder. The latter operation may necessitate subsequent regularization of the structure if the moved and unmoved parts are chemically connected, and this is done as a separate operation on a different machine. The system also has the capability of displaying several molecules and of manually superimposing these on each other for comparison purposes.

3.3.3.2.9. *HYDRA*

This program, due to Hubbard (1985) (and, more recently, to Molecular Simulations) has several functional parts, referred to as 'heads', which all use the same data structure. The addition of further heads may be accomplished, knowing the data structure, without the need to know anything of the internal workings of existing heads.

The program contains extensive features for the display, analysis and modelling of molecular structure with particular emphasis on proteins. Display options include dotted surfaces, molecular skeletons, protein cartoons and a variety of van der Waals, ball-and-stick, and other raster-graphics display techniques such as ray tracing and shaded molecular surfaces. Protein analysis features include the analysis of hydrogen bonding, and of secondary and domain structure, as well as computational assessment of deviations from accepted protein structural characteristics such as abnormal main-chain or side-chain conformations and solvent exposure of hydrophobic amino acids. A full set of protein modelling facilities are provided including homology modelling and the 'docking' of substrate molecules. The program contains extensive tools for interactive modelling of structures from NMR or X-ray crystallographic data, and provides interfaces to molecular-mechanics and dynamics calculations. There are also database searching facilities to analyse and compare features of protein structure, and it is well suited to the making of cine films.

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3.3.3.2.10. *O*

Jones *et al.* (1991) have developed a modelling system for proteins with a radically different approach to any of the foregoing, in that they begin by reducing the available electron-density map to a skeletal representation (Greer, 1974; Williams, 1982) which consists of a line running through the density close to its maximal values, this being the basis of a chain trace. Provisional α -carbon positions are also estimated at this stage. A database of known structures is then scanned for pentapeptides which may be superimposed on five successive positions in the chain trace, the best fit so found being taken to provide coordinates for the three central residues of the developing model. The process advances by three residues at each step, the first and last residues of the pentapeptide being used only to ensure that the central residues are built in a manner compatible with what precedes and follows.

The process ensures that conformations so built are free from improbable conformations, and the whole forms an adequate starting structure for molecular-dynamics procedures, even though some imperfect geometry is to be expected where each tripeptide joins the next.

3.3.3.3. *Molecular-modelling systems based on other criteria*

Systems described within this section mostly have some form of energy minimization as their objective but some are purely geometrical. The optimization of molecules through empirical force fields has been reviewed by Allinger (1976), Burkert & Allinger (1982) and Boyd & Lipkowitz (1982). Some of these systems are in the academic domain, others are commercial. Most have capabilities exceeding the features referred to here and, of necessity, the list cannot be complete. No attempt at comparative evaluations is attempted or implied.

3.3.3.3.1. *Molbuild, Rings, PRXBLD and MM2/MMP2*

Liljefors (1983) has described a system for constructing representations of organic molecules. The system develops the molecule with plausible geometry and satisfied valencies at all stages of the development with explicit recognition of lone pairs and the various possible hybridization states. Growth is generally by substitution in which a substituent and the atom it is to replace are both nominated from the screen. The bond which is reconstructed in a substitution is generally a single bond. Double and triple bonds are introduced by the substitution of moieties containing them. Atom types may be changed after incorporation in the growing molecule, so that although the menu of substituents includes $-\text{CH}_3$ but not $-\text{NH}_2$ the latter may be obtained by incorporating $-\text{CH}_3$, then changing C to N and one of the hydrogens to a lone pair. Facilities are also provided for cyclization and acyclization.

van der Lieth *et al.* (1984) have described an extension to this that is specialized to the construction of fused-ring systems. It permits the joining of rings by fusion of a bond, in which two adjacent atoms in one ring are superposed on two in another. It also permits the construction of spiro links in which one atom is common to two rings, or the construction of bridges, or the polymerization of ring systems to form, for example, oligosaccharides. Again the satisfaction of valencies is maintained during building and the geometry of the result is governed by superposition of relevant atoms in the moieties involved.

PRXBLD is a molecular model-building program which accepts two-dimensional molecular drawings in a manner similar to *Script* (Section 3.3.3.3.2) and constructs approximate three-dimensional coordinates from these. It is the model-building component of *SECS* (Simulation and Evaluation of Chemical Synthesis) (Wipke *et al.*, 1977; Wipke & Dyott, 1974; Wipke, 1974). See also Anderson (1984).

All three of these programs produce output which is acceptable as input to *MM2(82)/MMP2* which are developments of Allinger's geometrical optimization based on molecular mechanics (Allinger, 1976).

3.3.3.3.2. *Script*

This system, described by Cohen *et al.* (1981), is specialized for fused-ring systems, especially steroids, but is not limited to these classes. The system allows the user to draw on the screen (with a light pen or equivalent) a two-dimensional representation of a molecule using single lines for single bonds, double lines for double bonds, and wedges to indicate out-of-plane substituents. The software can then enumerate the possible distinct conformers, each of which is expected to be near an energy minimum on the conformational potential surface. Each conformer may then be annealed to reach an energy minimum using an energy estimate based on bond lengths, bond angles, torsion angles and van der Waals, electrostatic and hydrogen-bonding terms. An example is given of the identification of an unusual conformer as the most stable one from twelve possibilities for a four-ring system.

The program is a development of similar work by Cohen (1971) in which the molecule was defined in terms of a tree structure and an optimizer based on search techniques rather than gradient vectors was used. The method included van der Waals terms and hence estimated energy differences between stereoisomers in condensed ring systems arising from steric hindrance.

3.3.3.3.3. *CHARMM*

This system, due to Brooks *et al.* (1983), is primarily concerned with molecular dynamics but it includes the capability of model-building proteins and nucleic acids from sequence information and values of internal coordinates (bond lengths, bond angles and dihedral angles). The resulting structure (or a given structure) may then be optimized by minimizing an empirical energy function which may include electrostatic and hydrogen-bonding terms as well as the usual van der Waals energy and a Hookean treatment of the covalent skeleton. Hydrogen atoms need not be handled explicitly, groups such as $-\text{CH}_2-$ being treated as single pseudo atoms, and this may be advisable for large structures. For small or medium proteins hydrogens may be treated explicitly and their initial positions may be determined by *CHARMM* if they are not otherwise known.

3.3.3.3.4. *Commercial systems*

A number of very powerful molecular-modelling systems are now available commercially and we mention a few of these here. Typically, each consists of a suite of programs sharing a common data structure so that the components of a system may be acquired selectively.

The *Chem-X* system, from Chemical Design Ltd, enables models to be developed from sketch-pad input, provides for their geometrical optimization and interfaces the result to *Gaussian80* for quantum-mechanical calculations.

MACCS, from Molecular Design Ltd, and related software (Allinger, 1976; Wipke *et al.*, 1977; Potenzzone *et al.*, 1977) has similar features and also has extensive database-maintenance facilities including data on chemical reactions.

Sybyl, from Tripos Associates (van Opdenbosch *et al.*, 1985), also builds from sketches with a standard fragment library, and provides interfaces to quantum-mechanical routines, to various databases and to *MACCS*.

Insight II (Section 3.3.3.1.7) is available from Biosym and *GRAMPS* (Section 3.3.3.1.4) is available from T. J. O'Donnell Associates.

3.4. Accelerated convergence treatment of R^{-n} lattice sums

BY D. E. WILLIAMS

3.4.1. Introduction

The electrostatic energy of an ionic crystal is often represented by taking a pairwise sum between charge sites interacting *via* Coulomb's law (the $n = 1$ sum). The individual terms may be positive or negative, depending on whether the pair of sites have charges of the same or different signs. The Coulombic energy is very long-range, and it is well known that convergence of the Coulombic lattice-energy sum is extremely slow. For simple structure types Madelung constants have been calculated which represent the Coulombic energy in terms of the cubic lattice constant or a nearest-neighbour distance. Glasser & Zucker (1980) give tables of Madelung constants and review the subject giving references dating back to 1884. If the ionic crystal structure is not of a simple type usually no Madelung constant will be available and the Coulombic energy must be obtained for the specific crystal structure being considered. In carrying out this calculation, accelerated-convergence treatment of the Coulombic lattice sum is indispensable to achieve accuracy with a reasonable amount of computational effort. A model of a molecular crystal may include partial net atomic charges or other charge sites such as lone-pair electrons. The ($n = 1$) sum also applies between these site charges.

The dispersion energy of ionic or molecular crystals may be represented by an ($n = 6$) sum over atomic sites, with possible inclusion of ($n = 8, 10, \dots$) terms for higher accuracy. The dispersion-energy sum has somewhat better convergence properties than the Coulombic sum. Nevertheless, accelerated-convergence treatment of the dispersion sum is strongly recommended since its use can yield at least an order of magnitude improvement in accuracy for a given calculation effort. The repulsion energy between non-bonded atoms in a crystal may be represented by an exponential function of short range, or possibly by an ($n = 12$) function of short range. The convergence of the repulsion energy is fast and no accelerated-convergence treatment is normally required.

3.4.2. Definition and behaviour of the direct-space sum

This pairwise sum is taken between atoms (or sites) in the reference unit cell and all other atoms (or sites) in the crystal, excluding the self terms. Thus, the second atom (or site) is taken to range over the entire crystal, with elimination of self-energy terms. If V_n represents an energy, each atom is assigned one half of the pair energy. Therefore, the energy per unit cell is

$$V_n = (1/2) \sum_j^{\text{one cell}} \sum_k^{\text{all cells}} Q_{jk} R_{jk}^{-n},$$

where Q_{jk} is a given coefficient, R_{jk} is an interatomic distance, and the prime on the second sum indicates that self terms are omitted. In the case of the Coulombic sum, $n = 1$ and $Q_{jk} = q_j q_k$ is the product of the site charges.

Table 3.4.2.1 gives an example of the convergence behaviour of the untreated ($n = 1$) Coulombic sum for sodium chloride. Even at the rather large summation limit of 20 Å the Coulombic lattice sum has not converged and is incorrect by about 8%. The 20 Å sum included 832 molecules and 2494 individual distances. At various smaller summation limits the truncation error fluctuates wildly and can be either positive or negative. Note that the results shown in the table always refer to summation over whole molecules, that is, over neutral charge units.

If the Coulombic summation is not carried out over neutral charge units the truncation error is even larger. These considerations support the conclusion that accelerated-convergence treatment of

the Coulombic lattice sum should be regarded as mandatory. Table 3.4.2.2 gives an example of the convergence behaviour of the untreated ($n = 6$) dispersion sum for benzene. In obtaining this sum it is not necessary to consider whole molecules as in the Coulombic case. The exclusion of atoms (or sites) in the portions of molecules outside the summation limit greatly reduces the number of terms to be considered. At the summation limit of 20 Å, 439 benzene molecules and 22 049 individual distances are considered; the dispersion-sum truncation error is 0.4%. Thus, if sufficient computer time is available it may be possible to obtain a moderately accurate dispersion sum without the use of accelerated convergence. However, as shown below, the use of accelerated convergence will greatly speed up the calculation, and is in practice necessary if higher accuracy is required.

3.4.3. Preliminary description of the method

Ewald (1921) developed a method which modified the mathematical representation of the Coulombic lattice sum to improve the rate of convergence. This method was based on partially transforming the lattice sum into reciprocal space. Bertaut (1952) presented another method for derivation of the Ewald result which used the concept of the crystallographic structure factor. His formula extended the Ewald treatment to a composite lattice with more than one atom per lattice point. Nijboer & DeWette (1957) developed a general Fourier transform method for the evaluation of R^{-n} sums in simple lattices. Williams (1971) extended this treatment to a composite lattice and gave general formulae for the R^{-n} sums for any crystal. A review article, on which this chapter is based, appeared later (Williams, 1989).

Consider a function, $W(R)$, which is unity at $R = 0$ and smoothly declines to zero as R approaches infinity. If each term of the lattice sum is multiplied by $W(R)$, the rate of convergence is increased. However, the rate of convergence of the remainder of the original sum, which contains the difference terms, is not increased.

$$V_n = (1/2) \sum_j^{\text{one cell}} \sum_k^{\text{all cells}} Q_{jk} R_{jk}^{-n} W(R) \\ + (1/2) \sum_j^{\text{one cell}} \sum_k^{\text{all cells}} Q_{jk} R_{jk}^{-n} [1 - W(R)].$$

In the accelerated-convergence method the difference terms are expressed as an integral of the product of two functions. According

Table 3.4.2.1. *Untreated lattice-sum results for the Coulombic energy ($n = 1$) of sodium chloride (kJ mol^{-1} , Å); the lattice constant is taken as 5.628 Å*

Truncation limit	Number of molecules	Number of terms	Calculated energy
6.0	23	67	−696.933
8.0	59	175	−597.371
10.0	108	322	−915.152
12.0	201	601	−773.475
14.0	277	829	−796.248
16.0	426	1276	−826.502
18.0	587	1759	−658.995
20.0	832	2494	−794.619
Converged value			−862.825

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Table 3.4.2.2. *Untreated lattice-sum results for the dispersion energy ($n = 6$) of crystalline benzene ($\text{kJ mol}^{-1}, \text{\AA}$)*

Truncation limit	Number of molecules	Number of terms	Calculated energy
6.0	26	524	-69.227
8.0	51	1313	-76.007
10.0	77	2631	-78.179
12.0	126	4718	-79.241
14.0	177	7531	-79.726
16.0	265	11274	-80.013
18.0	344	15904	-80.178
20.0	439	22049	-80.295
Converged value			-80.589

to Parseval's theorem (described below) this integral is equal to an integral of the product of the two Fourier transforms of the functions. Finally, the integral over the Fourier transforms of the functions is converted to a sum in reciprocal (or Fourier-transform) space. The choice of the convergence function $W(R)$ is not unique; an obvious requirement is that the relevant Fourier transforms must exist and have correct limiting behaviour. Nijboer and DeWette suggested using the incomplete gamma function for $W(R)$. More recently, Fortuin (1977) showed that this choice of convergence function leads to optimal convergence of the sums in both direct and reciprocal space:

$$W(R) = \Gamma(n/2, \pi w^2 R^2) / \Gamma(n/2),$$

where $\Gamma(n/2)$ and $\Gamma(n/2, \pi w^2 R^2)$ are the gamma function and the incomplete gamma function, respectively:

$$\Gamma(n/2, \pi w^2 R^2) = \int_{\pi w^2 R^2}^{\infty} t^{(n/2)-1} \exp(-t) dt$$

and

$$\Gamma(n/2) = \Gamma(n/2, 0).$$

The complement of the incomplete gamma function is

$$\gamma(n/2, \pi w^2 R^2) = \Gamma(n/2) - \Gamma(n/2, \pi w^2 R^2).$$

3.4.4. Preliminary derivation to obtain a formula which accelerates the convergence of an R^{-n} sum over lattice points $\mathbf{X}(\mathbf{d})$

The three-dimensional direct-space crystal lattice is specified by the origin vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. A general vector in direct space is defined as

$$\mathbf{X}(\mathbf{x}) = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3,$$

where x_1, x_2, x_3 are the fractional cell coordinates of $\mathbf{X}$. A lattice vector in direct space is defined as

$$\mathbf{X}(\mathbf{d}) = d_1 \mathbf{a}_1 + d_2 \mathbf{a}_2 + d_3 \mathbf{a}_3,$$

where d_1, d_2, d_3 are integers (specifying particular values of x_1, x_2, x_3) designating a lattice point. V_d is the direct-cell volume which is equal to $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$. A general point in the direct lattice is $\mathbf{X}(\mathbf{x})$; the contents of the lattice are by definition identical as the components of $\mathbf{x}$ are increased or decreased by integer amounts.

The reciprocal-lattice vectors are defined by the relations

$$\begin{aligned} \mathbf{a}_j \cdot \mathbf{b}_k &= 1 & j &= k \\ &= 0 & j &\neq k. \end{aligned}$$

A general vector in reciprocal space $\mathbf{H}(\mathbf{r})$ is defined as

$$\mathbf{H}(\mathbf{r}) = r_1 \mathbf{b}_1 + r_2 \mathbf{b}_2 + r_3 \mathbf{b}_3.$$

A reciprocal-lattice vector $\mathbf{H}(\mathbf{h})$ is defined by the integer triplet h_1, h_2, h_3 (specifying particular values of r_1, r_2, r_3) so that

$$\mathbf{H}(\mathbf{h}) = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3.$$

In other sections of this volume a shortened notation $\mathbf{h}$ is used for the reciprocal-lattice vector. In this section the symbol $\mathbf{H}(\mathbf{h})$ is used to indicate that it is a particular value of $\mathbf{H}(\mathbf{r})$.

The three-dimensional Fourier transform $g(\mathbf{t})$ of a function $f(\mathbf{x})$ is defined by

$$g(\mathbf{t}) = FT_3[f(\mathbf{x})] = \int f(\mathbf{x}) \exp(2\pi i \mathbf{x} \cdot \mathbf{t}) d\mathbf{x}.$$

The Fourier transform of the set of points defining the direct lattice is the set of points defining the reciprocal lattice, scaled by the direct-cell volume. It is useful for our purpose to express the lattice transform in terms of the Dirac delta function $\delta(\mathbf{x} - \mathbf{x}_o)$ which is defined so that for any function $f(\mathbf{x})$

$$f(\mathbf{x}_o) = \int \delta(\mathbf{x} - \mathbf{x}_o) f(\mathbf{x}) d\mathbf{x}.$$

We then write

$$FT_3\{\sum_{\mathbf{d}} \delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})]\} = V_d^{-1} \sum_{\mathbf{h}} \delta[\mathbf{H}(\mathbf{r}) - \mathbf{H}(\mathbf{h})].$$

First consider the lattice sum over the direct-lattice points $\mathbf{X}(\mathbf{d})$, relative to a particular point $\mathbf{X}(\mathbf{x}) = \mathbf{R}$, with omission of the origin lattice point.

$$S'(n, \mathbf{R}) = \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n}.$$

The special case with $\mathbf{R} = 0$ will also be needed:

$$S'(n, 0) = \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d})|^{-n}.$$

Now define a sum of Dirac delta functions

$$f'[\mathbf{X}(\mathbf{d})] = \sum_{\mathbf{d} \neq 0} \delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})].$$

Then S' can be represented as an integral

$$S'(n, \mathbf{R}) = \int f'[\mathbf{X}(\mathbf{d})] |\mathbf{X} - \mathbf{R}|^{-n} d\mathbf{X},$$

in which a term is contributed to S' whenever the direct-space vector $\mathbf{X}$ coincides with the lattice vector $\mathbf{X}(\mathbf{d})$, except for $\mathbf{d} = 0$. Now apply the convergence function to S' :

$$\begin{aligned} S'(n, \mathbf{R}) &= [\Gamma(n/2)]^{-1} \int f'[\mathbf{X}(\mathbf{d})] |\mathbf{X} - \mathbf{R}|^{-n} \\ &\quad \times \Gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) d\mathbf{X} \\ &\quad + [\Gamma(n/2)]^{-1} \int f'[\mathbf{X}(\mathbf{d})] |\mathbf{X} - \mathbf{R}|^{-n} \\ &\quad \times \gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) d\mathbf{X}. \end{aligned}$$

The first integral is shown here only for the purpose of giving a consistent representation of S' ; in fact, the first integral will be reconverted back into a sum and evaluated in direct space. The second integral will be transformed to reciprocal space using Parseval's theorem [see, for example, Arfken (1970)], which states that

$$\int f(\mathbf{X}) g^*(\mathbf{X}) d\mathbf{X} = \int FT_3[f(\mathbf{X})] FT_3[g^*(\mathbf{X})] d\mathbf{H}.$$

3.4. ACCELERATED CONVERGENCE TREATMENT OF R^{-n} LATTICE SUMS

Considering only the second integral in the formula for S' and explicitly introducing the $\mathbf{d} = 0$ term we have

$$[\Gamma(n/2)]^{-1} \int f[\mathbf{X}(\mathbf{d})] |\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) d\mathbf{X} \\ - [\Gamma(n/2)]^{-1} \int \delta(\mathbf{X}) |\mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{R}|^2) d\mathbf{X},$$

where the unprimed f includes the $\mathbf{h} = 0$ term which was earlier omitted from f' :

$$f(\mathbf{X}) = \sum_{\mathbf{d}} \delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})].$$

Using Parseval's theorem, and evaluating the origin term, we have

$$[\Gamma(n/2)]^{-1} \int FT_3 \{f[\mathbf{X}(\mathbf{d})]\} FT_3 \\ \times [|\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2)] d\mathbf{H} \\ - [\Gamma(n/2)]^{-1} |\mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{R}|^2).$$

The Fourier transform of the complement of the incomplete gamma function divided by $|\mathbf{X}|^n$ is (Nijboer & DeWette, 1957)

$$FT_3 [\gamma(n/2, \pi w^2 |\mathbf{X}|^2) |\mathbf{X}|^{-n}] \\ = \pi^{n-(3/2)} |\mathbf{H}|^{n-3} \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2].$$

If there is a change of origin and the point $(\mathbf{X} - \mathbf{R})$ is used instead of $\mathbf{X}$ the transform is

$$FT_3 [\gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) |\mathbf{X} - \mathbf{R}|^{-n}] \\ = \pi^{n-(3/2)} |\mathbf{H}|^{n-3} \Gamma[(-n/2) \\ + (3/2), \pi w^{-2} |\mathbf{H}|^2] \exp(2\pi i \mathbf{H} \cdot \mathbf{R}).$$

Evaluation of the two Fourier transforms in the first term gives

$$[\Gamma(n/2)]^{-1} \int V_d^{-1} \sum_{\mathbf{h}} \delta[\mathbf{H}(\mathbf{h}) - \mathbf{H}] \pi^{n-(3/2)} |\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2] \exp(2\pi i \mathbf{H} \cdot \mathbf{R}) d\mathbf{H}.$$

Because of the presence of the Dirac delta function in each integral, we can convert the integrals with $\mathbf{h}$ unequal to zero into a sum

$$[\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n-(3/2)} \sum_{\mathbf{h} \neq 0} |\mathbf{H}(\mathbf{h})|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}].$$

The $\mathbf{h} = 0$ term needs to be evaluated in the limit. Clearly, the complex exponential goes to unity. If n is greater than 3 the limit of the indeterminate form infinity/infinity is needed:

$$\lim_{|\mathbf{H}| \rightarrow 0} \frac{\Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2]}{|\mathbf{H}|^{3-n}} \\ = \lim_{|\mathbf{H}| \rightarrow 0} \frac{\int_{\pi w^{-2} |\mathbf{H}|^2}^{\infty} t^{(-n/2)+(1/2)} \exp(-t) dt}{|\mathbf{H}|^{3-n}}.$$

The limit can be found by L'Hospital's rule [see, for example, Widder (1961)] which states that if $f(x)$ and $g(x)$ both approach infinity as x approaches a constant, c , and the limit of the ratio of the first derivatives $f'(x)$ and $g'(x)$ exists, that limit is also true for the limit of the ratio of the functions:

$$\lim_{x \rightarrow c} \frac{f(x)}{g(x)} = \lim_{x \rightarrow c} \frac{f'(x)}{g'(x)}.$$

To differentiate the definite integral function, Leibnitz's formula may be used [see, for example, Arfken (1970)]. This formula states that

$$\frac{d}{dx} \int_{g(x)}^{h(x)} f(t, x) dt = \int_{g(x)}^{h(x)} \frac{df(t, x)}{dx} dt \\ + f[h(x)] \frac{dh(x)}{dx} - f[g(x)] \frac{dg(x)}{dx}.$$

In our case, x becomes $|\mathbf{H}|$; f becomes $t^{(-n/2)+(1/2)} \exp(-t)$ which is independent of $|\mathbf{H}|$; g becomes $\pi w^{-2} |\mathbf{H}|^2$; and h is infinite. Thus only the last term of Leibnitz's formula is nonzero and we obtain for the ratio of the first derivatives

$$\lim_{|\mathbf{H}| \rightarrow 0} \frac{-(\pi w^{-2} |\mathbf{H}|^2)^{(-n/2)+(1/2)} \exp(-\pi w^2 |\mathbf{H}|^2) 2\pi w^{-2} |\mathbf{H}|}{(3-n) |\mathbf{H}|^{2-n}} \\ = \pi^{(-n/2)+(3/2)} w^{n-3} [2/(n-3)],$$

so that the limiting value for the $\mathbf{h} = 0$ term for n greater than 3 is

$$+ [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} [2/(n-3)].$$

The final result for S' is

$$S'(n, \mathbf{R}) = [\Gamma(n/2)]^{-1} \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n} \\ \times \Gamma(n/2, \pi w^2 |\mathbf{X}(\mathbf{d}) - \mathbf{R}|^2) \\ - [\Gamma(n/2)]^{-1} |\mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{R}|^2) \\ + [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n-(3/2)} \sum_{\mathbf{h} \neq 0} |\mathbf{H}(\mathbf{h})|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \\ \times \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}] \\ + [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} 2(n-3)^{-1}.$$

The significance of the terms is as follows. The first term represents the convergence-accelerated direct sum, which does not include the origin term; the next term, also in direct space, corrects for the remainder resulting from the subtraction of the origin term; the third term comes from Parseval's theorem and is a sum over the nonzero $\mathbf{h}$ reciprocal-lattice points; and the last term is the reciprocal-lattice $\mathbf{h} = 0$ term.

If $\mathbf{R} = 0$ the second term becomes an indeterminate form 0/0. The limit can be found with use of L'Hospital's rule again, this time for the 0/0 form. We need the limit of $f(x)/g(x)$, where $f(R) = \gamma(n/2, \pi w^2 R^2)$ and $g(R) = R^n$. To differentiate the incomplete gamma function, we can again use Leibnitz's formula. In this case only the second term of the formula is nonzero and we obtain for the ratio of the first derivatives

$$\frac{2\pi^{n/2} w^n |\mathbf{R}|^{n-1} \exp(-\pi w^2 |\mathbf{R}|^2)}{n |\mathbf{R}|^{n-1}},$$

so that the limiting value for this term as $|\mathbf{R}|$ approaches zero is

$$-[\Gamma(n/2)]^{-1} 2\pi^{n/2} w^n n^{-1}.$$

Therefore, the value of the sum when $\mathbf{R} = 0$ is

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$$\begin{aligned}
 S'(n, 0) = & [\Gamma(n/2)]^{-1} \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d})|^{-n} \Gamma(n/2, \pi w^2 |\mathbf{X}(\mathbf{d})|^2) \\
 & - [\Gamma(n/2)]^{-1} 2\pi^{n/2} w^n n^{-1} \\
 & + [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n-(3/2)} \sum_{\mathbf{h} \neq 0} |\mathbf{H}(\mathbf{h})|^{n-3} \\
 & \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \\
 & + [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} 2(n-3)^{-1} \sum_j Q_{jj}.
 \end{aligned}
 \tag{8}$$

3.4.5. Extension of the method to a composite lattice

Define a general lattice sum over direct-space points $\mathbf{R}_j$ which interact with pairwise coefficients Q_{jk} , where $Q_{jk} = Q_{kj}$:

$$V(n, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n},$$

where the prime indicates that when $\mathbf{d} = 0$ the self-terms with $j = k$ are omitted. For convenience the terms may be divided into three groups: the first group of terms has $\mathbf{d} = 0$, where j is unequal to k ; the second group has $\mathbf{d}$ not zero and j not equal to k ; and the third group has $\mathbf{d}$ not zero and $j = k$. (A possible fourth group with $\mathbf{d} = 0$ and $j = k$ is omitted, as defined.)

$$\begin{aligned}
 V(n, \mathbf{R}_j) = & (1/2) \sum_{j \neq k} Q_{jk} |\mathbf{R}_k - \mathbf{R}_j|^{-n} \\
 & + (1/2) \sum_{j \neq k} Q_{jk} S'(n, |\mathbf{R}_j - \mathbf{R}_k|) + (1/2) \sum_j Q_{jj} S'(n, 0).
 \end{aligned}$$

By expanding this expression we obtain

$$\begin{aligned}
 V(n, \mathbf{R}_j) = & (1/2) \sum_{j \neq k} Q_{jk} |\mathbf{R}_k - \mathbf{R}_j|^{-n} \\
 & + \left\{ [1/2\Gamma(n/2)] \sum_{j \neq k} Q_{jk} \sum_{\mathbf{d} \neq 0} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n} \right. \\
 & \times \Gamma(n/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2) \left. \right\} \\
 & - \left\{ [1/2\Gamma(n/2)] \sum_{j \neq k} Q_{jk} |\mathbf{R}_k - \mathbf{R}_j|^{-n} \right. \\
 & \times \gamma(n/2, \pi w^2 |\mathbf{R}_k - \mathbf{R}_j|^2) \left. \right\} \\
 & + \left\{ [1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \sum_{j \neq k} Q_{jk} \sum_{\mathbf{h} \neq 0} |\mathbf{H}(\mathbf{h})|^{n-3} \right. \\
 & \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \\
 & \times \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)] \left. \right\} \\
 & + [1/2\Gamma(n/2)] V_d^{-1} \pi^{n/2} w^{n-3} 2(n-3)^{-1} \sum_{j \neq k} Q_{jk} \\
 & + \left\{ [1/2\Gamma(n/2)] \sum_j Q_{jj} \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d})|^{-n} \right. \\
 & \times \Gamma(n/2, \pi w^2 |\mathbf{X}(\mathbf{d})|^2) \left. \right\} \\
 & - [1/\Gamma(n/2)] \pi^{n/2} w^n n^{-1} \sum_j Q_{jj}
 \end{aligned}
 \tag{1}$$

$$\begin{aligned}
 (1) \quad & (1) + (2) + (3) + (6) = [1/2\Gamma(n/2)] \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n} \\
 & \times \Gamma[n/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2].
 \end{aligned}
 \tag{2}$$

Now let us combine terms (4) and (8), carrying out the $\mathbf{h}$ summation first:

$$\begin{aligned}
 (4) + (8) = & [1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \sum_{\mathbf{h}} |\mathbf{H}(\mathbf{h})|^{n-3} \\
 & \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \\
 & \times \sum_j \sum_k Q_{jk} \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)].
 \end{aligned}
 \tag{3}$$

Terms (5) and (9) may be combined:

$$(5) + (9) = [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} (n-3)^{-1} \left(\sum_j Q_{jj} + \sum_{j \neq k} Q_{jk} \right).
 \tag{4}$$

The final formula is shown below. The significance of the four terms is: (1) the treated direct-lattice sum; (2) a correction for the difference resulting from the removal of the origin term in direct space; (3) the reciprocal-lattice sum, except $\mathbf{h} = 0$; and (4) the $\mathbf{h} = 0$ term of the reciprocal-lattice sum.

$$\begin{aligned}
 V(n, \mathbf{R}_j) = & [1/2\Gamma(n/2)] \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n} \\
 & \times \Gamma(n/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2)
 \end{aligned}
 \tag{5}$$

$$- [1/\Gamma(n/2)] \pi^{n/2} w^n n^{-1} \sum_j Q_{jj}
 \tag{6}$$

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$$+ [1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}}|\mathbf{H}(\mathbf{h})|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2] \\ \times \sum_j \sum_k Q_{jk} \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)] \quad (3)$$

$$+ [\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n/2}w^{n-3}(n-3)^{-1} \left(\sum_j \sum_k Q_{jk} \right). \quad (4)$$

3.4.6. The case of $n = 1$ (Coulombic lattice energy)

As taken above, the limit of the reciprocal-lattice $\mathbf{h} = 0$ term of $S'(n, \mathbf{R})$ or $S'(n, 0)$ existed only if n was greater than 3. The corresponding contributions to $V(n, \mathbf{R}_j)$ were terms (5) and (9) of Section 3.4.5. To extend the method to $n = 1$ we will show in this section that these $\mathbf{h} = 0$ terms vanish if conditions of unit-cell neutrality and zero dipole moment are satisfied.

The integral representation of the term (5) is

$$[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_{j \neq k} Q_{jk} \int \delta(0)|\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}|^2] \\ \times \exp[2\pi i \mathbf{H} \cdot (\mathbf{R}_k - \mathbf{R}_j)] d\mathbf{H}$$

and for term (9) is

$$[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_j Q_{jj} \int \delta(0)|\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}|^2] d\mathbf{H}.$$

Combining these two sums of integrals into one integral sum gives

$$[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)} \int \delta(0)|\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}|^2] \sum_j \sum_k Q_{jk} \\ \times \exp[2\pi i \mathbf{H} \cdot (\mathbf{R}_k - \mathbf{R}_j)] d\mathbf{H}.$$

For $n = 1$, suppose q_j are net atomic charges so that the geometric combining law holds for $Q_{jk} = q_j q_k$. Then the double sum over j and k can be factored so that the limit that needs to be considered is

$$\lim_{|\mathbf{H}| \rightarrow 0} \frac{\left[\sum_k q_k \exp(2\pi i \mathbf{H} \cdot \mathbf{R}_k) \right] \left[\sum_j q_j \exp(-2\pi i \mathbf{H} \cdot \mathbf{R}_j) \right]}{|\mathbf{H}|^2}.$$

If the unit cell does not have a net charge, the sum over the q 's goes to zero in the limit and this is a 0/0 indeterminate form. Let $|\mathbf{H}|$ approach zero along the polar axis so that $\mathbf{H} \cdot \mathbf{R}_k = H_3 R_{3k}$, where subscript 3 indicates components along the polar axis. To find the limit with L'Hospital's rule the numerator and denominator are differentiated twice with respect to H_3 . Represent the numerator of the limit by the product (uv) and note that

$$\frac{d^2(uv)}{dx^2} = u \frac{d^2v}{dx^2} + v \frac{d^2u}{dx^2} + 2 \frac{du}{dx} \frac{dv}{dx}.$$

It is seen that in addition to cell neutrality the product of the first derivatives of the sums must exist. These sums are

$$\left[2\pi i \sum_k q_k R_{3k} \exp(2\pi i H_3 R_{3k}) \right]$$

and

$$\left[-2\pi i \sum_j q_j R_{3j} \exp(-2\pi i H_3 R_{3j}) \right],$$

which vanish if the unit cell has no dipole moment in the polar direction, that is, if $\sum q_j R_{3j} = 0$. Since the second derivative of the denominator is a constant, the desired limit is zero under the specified conditions. Now the polar direction can be chosen arbitrarily, so the unit cell must not have a dipole moment in any direction for the limit of the numerator to be zero. Thus we have the formula for the Coulombic lattice sum

$$V(1, \mathbf{R}_j) = [1/2\Gamma(1/2)] \sum_j \sum_k Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-1} \\ \times \Gamma(1/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2) \\ + [1/2\Gamma(1/2)] V_d^{-1} \pi^{-1/2} \sum_{\mathbf{h}} |\mathbf{H}(\mathbf{h})|^{-2} \\ \times \Gamma(1/2, \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2) \sum_j \sum_k Q_{jk} \\ \times \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)] \\ - [1/\Gamma(1/2)] \pi^{1/2} w \sum_j q_j^2,$$

which holds on conditions that the unit cell be electrically neutral and have no dipole moment. If the unit cell has a dipole moment, the limiting value discussed above depends on the direction of $\mathbf{H}$. For methods of obtaining the Coulombic lattice sum where the unit cell does have a dipole moment, the reader is referred to the literature (DeWette & Schacher, 1964; Cummins *et al.*, 1976; Bertaut, 1978; Massidda, 1978).

3.4.7. The cases of $n = 2$ and $n = 3$

If $n = 2$ the denominator considered for the limit in the preceding section is linear in $|\mathbf{H}|$ so that only one differentiation is needed to obtain the limit by L'Hospital's method. Since a term of the type $\sum q_j \exp(2\pi i \mathbf{H} \cdot \mathbf{R}_j)$ is always a factor, the requirement that the unit cell have no dipole moment can be relaxed. For $n = 2$ the zero-charge condition is still required: $\sum q_j = 0$. When $n = 3$ the expression becomes determinate and no differentiation is required to obtain a limit. In addition, factoring the Q_{jk} sums into q_j sums is not necessary so that the only remaining requirement for this term to be zero is $\sum \sum Q_{jk} = 0$, which is a further relaxation beyond the requirement of cell neutrality.

3.4.8. Derivation of the accelerated convergence formula via the Patterson function

The structure factor with generalized coefficients q_j is defined by

$$F[\mathbf{H}(\mathbf{h})] = \sum_j q_j \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}_j].$$

The corresponding Patterson function is defined by

$$P(\mathbf{X}) = V_d^{-1} \sum_{\mathbf{h}} |F[\mathbf{H}(\mathbf{h})]|^2 \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{X}].$$

The physical interpretation of the Patterson function is that it is nonzero only at the intersite vector points $\mathbf{R}_k + \mathbf{X}(\mathbf{h}) - \mathbf{R}_j$. If the origin point is removed, the lattice sum may be expressed as an integral over the Patterson function. This origin point in the Patterson function corresponds to intersite vectors with $j = k$ and $\mathbf{H}(\mathbf{h}) = 0$:

$$S_n = (1/2V_d) \int |\mathbf{X}|^{-n} [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})] d\mathbf{X}.$$

Using the incomplete gamma function as a convergence function, this formula expands into two integrals

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$$S_n = [1/2V_d\Gamma(n/2)] \int |\mathbf{X}|^{-n} \\ \times [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})]\Gamma(n/2, \pi w^2|\mathbf{X}|^2) d\mathbf{X} \\ + [1/2V_d\Gamma(n/2)] \int |\mathbf{X}|^{-n} \\ \times [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})]\gamma(n/2, \pi w^2|\mathbf{X}|^2) d\mathbf{X}.$$

The first integral is shown only for a consistent representation; actually it will be reconverted to a sum and evaluated in direct space. The first part of the second integral will be evaluated with Parseval's theorem and the second part in the limit as $|\mathbf{X}|$ approaches zero:

$$[1/2V_d\Gamma(n/2)] \int FT_3[P(\mathbf{X})] \\ \times FT_3[|\mathbf{X}|^{-n}\gamma(n/2, \pi w^2|\mathbf{X}|^2)] d\mathbf{H} \\ - \lim_{\mathbf{X} \rightarrow 0} [1/2V_d\Gamma(n/2)][P(0)|\mathbf{X}|^{-n}\gamma(n/2, \pi w^2|\mathbf{X}|^2)].$$

The first Fourier transform (of the Patterson function) is the set of amplitudes of the structure factors and the second Fourier transform has already been discussed above; the method for obtaining the limit (for n equal to or greater than 1) was also discussed above. The result obtained is

$$[1/2V_d\Gamma(n/2)]\pi^{n-(3/2)} \int |F[\mathbf{H}(\mathbf{h})]|^2 |\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}|^2] d\mathbf{H} \\ - [1/2V_d\Gamma(n/2)][F(0)]^2 2\pi^{n/2} w^n n^{-1}.$$

The integral can be converted into a sum, since $|F[\mathbf{H}(\mathbf{h})]|$ is nonzero only at the reciprocal-lattice points:

$$[1/2V_d\Gamma(n/2)]\pi^{n-(3/2)} \sum_{\mathbf{h}} |F[\mathbf{H}(\mathbf{h})]|^2 |\mathbf{H}(\mathbf{h})|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2].$$

The term with $\mathbf{H}(\mathbf{h}) = 0$ is evaluated in the limit, for n greater than 3, as

$$[\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} (n-3)^{-1} |F(0)|^2.$$

Since $|F(0)|^2 = \sum_j \sum_k q_j q_k$, this term is identical with the third term of $V(n, \mathbf{R}_j)$ as derived earlier. The case of $n = 1$ is handled in the same way as previously discussed, where the limit of this term is zero provided the unit cell has no net charge or dipole moment.

3.4.9. Evaluation of the incomplete gamma function

The incomplete gamma function may be expressed in terms of commonly available functions such as the exponential integral and the complement of the error function. The definition of the exponential integral is

$$E_1(x^2) = \int_{x^2}^{\infty} t^{-1} \exp(-t) dt = \Gamma(0, x^2).$$

The definition of the complement of the error function is

$$\operatorname{erfc}(x) = \int_x^{\infty} \exp(-t^2) dt = \pi^{-1/2} \Gamma(1/2, x^2).$$

Numerical approximations to these functions are given, for example, by Hastings (1955). The recursion formula for the incomplete gamma function (Davis, 1972)

$$\Gamma(n+1, x^2) = n\Gamma(n, x^2) + x^{2n} \exp(-x^2)$$

may be used to obtain working formulae starting from the special values of $\Gamma(0, x^2)$ and $\Gamma(1/2, x^2)$ which are defined above. Also we note that $\Gamma(1, x^2) = \exp(-x^2)$.

3.4.10. Summation over the asymmetric unit and elimination of intramolecular energy terms

Let us consider the case where the unit cell contains Z molecules which are related by Z symmetry operations, and it is desired to include only intermolecular distances in the summation. In the direct sum (1) the indices j and k will then run only over the asymmetric unit, and all terms with $\mathbf{d} = 0$ are eliminated. The calculated energy refers then to one molecule (or mole) rather than to one unit cell. The correction term (2) also refers to one molecule according to the range of j and k . Since the reciprocal-lattice sum refers to the entire unit cell, terms (3) and (4) need to be divided by Z to refer the energy to one molecule.

Both the direct and reciprocal sums must be corrected for the elimination of intramolecular terms. Using the convergence function $W(R)$, we have

$$V(n, \mathbf{R}_j) = \sum_{\text{inter}} |\mathbf{R}|^{-n} W(R) + \sum_{\text{intra}} |\mathbf{R}|^{-n} W(R) \\ + \sum_{\text{inter}} |\mathbf{R}|^{-n} [1 - W(R)] + \sum_{\text{intra}} |\mathbf{R}|^{-n} [1 - W(R)].$$

As mentioned above, the second summation term, which is the intramolecular term in direct space, is simply left out of the calculation. When using the accelerated-convergence method the third and fourth summation terms are always obtained, evaluated in reciprocal space. The undesired inclusion of the intramolecular term (fourth term above) in the reciprocal-space sum may be compensated for by explicit subtraction of this term from the sum.

3.4.11. Reference formulae for particular values of n

In this section let $a^2 = \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2$ and $b^2 = \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2$. Let $T_0 = \sum Q_{jj} = \sum q_j^2$; $T_1 = \sum_j \sum_{k \neq j} Q_{jk} = T_0 + 2 \sum_j \sum_{k > j} Q_{jk}$. If the geometric mean combining law holds, $T_1 = (\sum_j q_j)^2$; let

$$T_2(h) = \sum_j \sum_k Q_{jk} \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)] \\ = T_0 + 2 \sum_j \sum_{k > j} Q_{jk} \cos[2\pi \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)].$$

Then

$$T_2(\mathbf{h}) = |F(\mathbf{h})|^2 = |\sum_j q_j \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}_j]|^2 = A(\mathbf{h})^2 + B(\mathbf{h})^2,$$

where

$$A(\mathbf{h}) = \sum_j q_j \cos[2\pi \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}_j]$$

and

$$B(\mathbf{h}) = \sum_j q_j \sin[2\pi \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}_j].$$

The formulae below describe $V(n, \mathbf{R}_j)$ in terms of T_0 , T_1 and T_2 ; the distance $|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|$ is simply represented by R_{jkd} .

$$V(1, \mathbf{R}_j) = (1/2) \sum_j \sum_k' q_j q_k \sum_{\mathbf{d}} R_{jkd}^{-1} \operatorname{erfc}(a) \\ + (1/2\pi V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^{-2} \exp(-b^2) - wT_0$$

$$V(2, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-2} \exp(-a^2) \\ + (\pi/2V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^{-1} \operatorname{erfc}(b) - (\pi/2)w^2 T_0$$

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$$V(3, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-3} [\operatorname{erfc}(a) + 2a\pi^{-1/2} \exp(-a^2)] \\ + (\pi/V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) E_1(b^2) - (2\pi/3) w^3 T_0$$

$$V(4, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-4} (1 + a^2) \exp(-a^2) \\ + (\pi^{5/2}/V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})| \\ \times [-\pi^{1/2} \operatorname{erfc}(b) + b^{-1} \exp(-b^2)] \\ + (\pi^2/V_d) w T_1 - (\pi^2/4) w^4 T_0$$

$$V(5, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-5} \\ \times [\operatorname{erfc}(a) + 2\pi^{-1/2} a (1 + 2a^2/3) \exp(-a^2)] \\ + (2\pi^3/3V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^2 \\ \times [b^{-2} \exp(-b^2) - E_1(b^2)] \\ + (2\pi^2/3V_d) w^2 T_1 - (4\pi^2/15) w^5 T_0$$

$$V(6, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-6} [1 + a^2 + (a^4/2)] \exp(-a^2) \\ + (\pi^{9/2}/3V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^3 \\ \times [\pi^{1/2} \operatorname{erfc}(b) + [(1/2b^3) - (1/b)] \exp(-b^2)] \\ + (\pi^3/6V_d) w^3 T_1 - (\pi^3/12) w^6 T_0$$

$$V(7, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-7} \\ \times [\operatorname{erfc}(a) + 2\pi^{-1/2} a [1 + (2/3)a^2 + (4/15)a^4] \\ \times \exp(-a^2)] \\ + (2\pi^5/15V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^4 \\ \times [(-b^{-2} + b^{-4}) \exp(-b^2) + E_1(b^2)] \\ + (2\pi^3/15V_d) w^4 T_1 - (8\pi^3/105) w^7 T_0$$

$$V(8, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-8} \\ \times [1 + a^2 + (a^4/2) + (a^6/6)] \exp(-a^2) \\ + (2\pi^{13/2}/45V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^5 \\ \times [-\pi^{1/2} \operatorname{erfc}(b) + [(1/b) - (1/2b^3) + (3/4b^5)] \\ \times \exp(-b^2)] \\ + (\pi^4/30V_d) w^5 T_1 - (\pi^4/48) w^8 T_0$$

$$V(9, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-9} \\ \times [\operatorname{erfc}(a) + 2\pi^{-1/2} a [1 + (2/3)a^2 + (4/15)a^4 \\ + (8/105)a^6] \exp(-a^2)] \\ + (4\pi^7/315V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^6 \\ \times [(b^{-2} - b^{-4} + 2b^{-6}) \exp(-b^2) - E_1(b^2)] \\ + (8\pi^4/315V_d) w^6 T_1 - (16\pi^4/945) w^9 T_0$$

$$V(10, \mathbf{R}_j) = (1/2) \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} R_{jkd}^{-10} \\ \times [1 + a^2 + (a^4/2) + (a^6/6) + (a^8/24)] \exp(-a^2) \\ + (\pi^{17/2}/315V_d) \sum_{\mathbf{h} \neq 0} T_2(\mathbf{h}) |\mathbf{H}(\mathbf{h})|^7 \\ \times [\pi^{1/2} \operatorname{erfc}(b) + [(-1/b) + (1/2b^3) - (3/4b^5) \\ + (15/8b^7)] \exp(-b^2)] \\ + (\pi^5/168V_d) w^7 T_1 - (\pi^5/240) w^{10} T_0.$$

3.4.12. Numerical illustrations

Consider the case of the sodium chloride crystal structure (a face-centred cubic structure) as a simple example for evaluation of the Coulombic sum. The sodium ion can be taken at the origin, and the chloride ion halfway along an edge of the unit cell. The results can easily be generalized for this structure type by using the unit-cell edge length, a , as a scaling constant.

First, consider the nearest neighbours. Each sodium and each chloride ion is surrounded by six ions of opposite sign at a distance of $a/2$. The Coulombic energy for the first coordination sphere is $-(1/2)(12)(2/a)(1389.3654) = -16672.385/a \text{ kJ mol}^{-1}$. Table 3.4.2.1 shows that the converged value of the lattice energy is $-4855.979/a$. Thus the nearest-neighbour energy is over three times more negative than the total lattice energy. In the second coordination sphere each ion is surrounded by 12 similar ions at a distance of $a/2^{1/2}$. The energy contribution of the second sphere is $+(1/2)(24)(2^{1/2}/a)(1389.3654) = +23578.313/a$. Thus, major cancellation occurs and the net energy for the first two coordination spheres is $+6905.928/a$ which actually has the wrong sign for a stable crystal. The third coordination sphere again makes a negative contribution. Each ion is surrounded by eight ions of opposite sign at a distance of $a/3^{1/2}$. The energy contribution is $-(1/2)(16)(3^{1/2}/a)(1389.3654) = -19251.612/a$, now giving a total so far of $-12345.684/a$. In the fourth coordination sphere each ion is surrounded by six others of the same sign at a distance of a . The energy contribution is $+(1/2)(12)(1/a)(1389.3654) = +8336.19/a$ to yield a total of $-4009.491/a$.

It is seen immediately by examining the numbers that the Coulombic sum is converging very slowly in direct space. Madelung (1918) devised a method for accurate evaluation of the sodium chloride lattice sum. However, his method is not generally applicable for more complex lattice structures. Evjen (1932) emphasized the importance of summing over a neutral domain, and replaced the sum with an integral outside of the first few shells of nearest neighbours. But the method of Ewald remained as the

Table 3.4.12.1. Accelerated-convergence results for the Coulombic sum ($n = 1$) of sodium chloride ($\text{kJ mol}^{-1}, \text{\AA}$): the direct sum plus the constant term

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
6.0	-779.087	-838.145	-860.393	-924.275	-1125.372
8.0	-818.549	-860.194	-863.764	-924.282	-1125.372
10.0	-865.323	-862.818	-863.811	-924.282	
12.0	-861.183	-862.824	-863.811		
14.0	-862.717	-862.828			
16.0	-862.792	-862.828			
18.0	-862.810				
20.0	-862.825				

3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

Table 3.4.12.2. *The reciprocal-lattice results ($\text{kJ mol}^{-1}, \text{\AA}$) for the Coulombic sum ($n = 1$) of sodium chloride*

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
0.0	-277.872	-416.806	-555.742	-833.613	-1111.483
0.4	0.000	0.003	0.986	61.451	261.042
0.5		0.003	0.986	61.451	261.042
0.6				61.457	262.542
0.7				61.457	262.542
0.8					262.547
0.9					262.547

Table 3.4.12.3. *Accelerated-convergence results for the dispersion sum ($n = 6$) of crystalline benzene ($\text{kJ mol}^{-1}, \text{\AA}$); the figures shown are the direct-lattice sum plus the two constant terms*

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
6.0	-73.452	-77.761	-79.651	-61.866	76.645
8.0	-79.029	-80.374	-80.256	-61.870	76.645
10.0	-80.217	-80.571	-80.265	-61.870	
12.0	-80.527	-80.585	-80.265		
14.0	-80.578	-80.585			
16.0	-80.588				
18.0	-80.589				
20.0	-80.589				

only completely general and accurate method of evaluating the Coulombic sum for a general lattice. Although it was derived in a somewhat different way, Ewald's method is equivalent to accelerated convergence for the special case of $n = 1$.

In the reciprocal lattice of sodium chloride only points with indices (hkl) all even or all odd are permitted by the face-centred symmetry. The reciprocal cell has edge length $1/a$ and the reciprocal-axis directions coincide with the direct-lattice axis directions. The closest points to the origin are the eight (111) forms at a distance of $(1/a)/3^{1/2}$. For sodium chloride this distance is $0.3078 \text{\AA}^{-1}$.

Table 3.4.12.1 shows the effect of convergence acceleration on the direct-space portion of the ($n = 1$) sum for the sodium chloride structure. The constant term $-w \sum q_j^2$ is included in the values given. This constant term is always large if w is not zero; for instance, when $w = 0.1$ this term is -277.872 (Table 3.4.12.2). For $w = 0.1$ the reciprocal-lattice sum is zero to six figures. Thus, only the direct sum (plus the constant term) is needed, evaluated out to $20 \text{\AA}$ in direct space, to obtain six-figure accuracy. As shown in Table 3.4.2.1 above, the same summation effort without the use of accelerated convergence gave 8% error, or only slightly better than one-figure accuracy. The accelerated-convergence technique therefore yielded nearly five orders of magnitude improvement in accuracy, even without evaluation of the reciprocal-lattice sum.

The column showing $w = 0.15$ shows an example of how the reciprocal-lattice sum can also be neglected if lower accuracy is required. Table 3.4.12.2 shows that the reciprocal-lattice sum is still only 0.003. But now the direct-lattice sum only needs to be evaluated out to $14 \text{\AA}$, with further savings in calculation effort. For w values larger than 0.15 the reciprocal sum is needed. For $w = 0.4$

Table 3.4.12.4. *The reciprocal-lattice results ($\text{kJ mol}^{-1}, \text{\AA}$) for the dispersion sum ($n = 6$) of crystalline benzene*

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
0.0	-5.547	-16.706	-32.326	-43.681	80.947
0.3	0.000	-0.004	-0.321	-16.792	-117.106
0.4	0.000	-0.004	-0.324	-18.656	-152.651
0.5			-0.324	-18.716	-155.940
0.6				-18.719	-157.102
0.7				-18.719	-157.227
0.8					-157.233
0.9					-157.234
1.0					-157.234

Table 3.4.12.5. *Approximate time (s) required to evaluate the dispersion sum ($n = 6$) for crystalline benzene within $0.001 \text{ kJ mol}^{-1}$ truncation error*

w	Direct terms	Reciprocal terms	Time, direct	Time, reciprocal	Total time
0.0	(not yet converged at $20 \text{\AA}$ summation limit)				>107
0.1	15904	0	77	0	77
0.15	4718	34	23	6	29
0.2	2631	78	13	14	27
0.3	1313	246	7	46	53
0.4	524	804	3	149	152

this sum must be evaluated out to $0.8 \text{\AA}^{-1}$ to obtain six-figure accuracy.

Table 3.4.12.3 illustrates an application for the ($n = 6$) dispersion sum. When $w = 0.1 \text{\AA}^{-1}$ five figures of accuracy can be obtained without consideration of the reciprocal sum. The direct sum is required out to $18 \text{\AA}$. If $w = 0.15$, better than four-figure accuracy can still be obtained without evaluating the reciprocal-lattice sum. In this case, the direct lattice needs to be summed only to $12 \text{\AA}$, and there is a saving of an order of magnitude in the length of the calculation. As with the Coulombic sum, if w is greater than 0.15 the reciprocal-lattice summation is needed; Table 3.4.12.4 shows the values.

The time required to obtain a lattice sum of given accuracy will vary depending on the particular structure considered and of course on the computer and program which are used. An example of timing for the benzene dispersion sum is given in Table 3.4.12.5 for the PCK83 program (Williams, 1984) running on a VAX-11/750 computer. In this particular case direct terms were evaluated at a rate of about 200 terms s^{-1} and reciprocal terms, being a sum themselves, were evaluated at a slower rate of about 5 terms s^{-1} .

Table 3.4.12.5 shows the time required for evaluation of the dispersion sum using various values of the convergence constant, w . The timing figures show that there is an optimum choice for w ; for the PCK83 program the optimum value indicated is $0.15\text{--}0.2 \text{\AA}^{-1}$. In the program of Pietila & Rasmussen (1984) values in the range $0.15\text{--}0.2 \text{\AA}^{-1}$ are also suggested. For the WMIN program (Busing, 1981) a slightly higher value of $0.25 \text{\AA}^{-1}$ is suggested. Trial calculations can be used to determine the optimum value of w for the situation of a particular crystal structure, program and computer.

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4.1. Thermal diffuse scattering of X-rays and neutrons

BY B. T. M. WILLIS

4.1.1. Introduction

Thermal motion of the atoms in a crystal gives rise to a reduction in the intensities of the Bragg reflections and to a diffuse distribution of non-Bragg scattering in the rest of reciprocal space. This distribution is known as thermal diffuse scattering (TDS). Measurement and analysis of TDS gives information about the lattice dynamics of the crystal, *i.e.* about the small oscillatory displacements of the atoms from their equilibrium positions which arise from thermal excitations. Lattice-dynamical models form the basis for interpreting many physical properties – for example, specific heat and thermal conductivity – which cannot be explained by a static model of the crystal.

Reference to a lattice-dynamical model is found in Newton's *Principia*, which contains a discussion of the vibrations of a linear chain of equidistant mass points connected by springs. The model was used to estimate the speed of sound in air. The vibrational properties of a one-dimensional crystal treated as a linear chain of atoms provide the starting point for several modern treatises on the lattice dynamics of crystals.

The classical theory of the dynamics of three-dimensional crystals is based on the treatment of Born & von Kármán (1912, 1913). In this theory, the restoring force on an atom is determined not by the displacement of the atom from its equilibrium position, but by its displacement relative to its neighbours. The atomic motion is then considered in terms of travelling waves, or 'lattice vibrations', extending throughout the whole crystal. These waves are the normal modes of vibration, in which each mode is characterized by a wavevector $\mathbf{q}$, an angular frequency $\omega(\mathbf{q})$ and certain polarization properties.

For twenty years after its publication the Born–von Kármán treatment was eclipsed by the theory of Debye (1912). In the Debye theory the crystal is treated as a continuous medium instead of a discrete array of atoms. The theory gives a reasonable fit to the integral vibrational properties (for example, the specific heat or the atomic temperature factor) of simple monatomic crystals. It fails to account for the form of the frequency distribution function which relates the number of modes and their frequency.

An even simpler model than Debye's is due to Einstein (1907), who considered the atoms in the crystal to be vibrating independently of each other and with the same frequency ω_E . By quantizing the energy of each atom in units of $\hbar\omega_E$, Einstein showed that the specific heat falls to zero at $T = 0$ K and rises asymptotically to the Dulong and Petit value for T much larger than $\hbar\omega_E/k_B$. ($\hbar$ is Planck's constant divided by 2π and k_B is Boltzmann's constant.) His theory accounts satisfactorily for the breakdown of equipartition of energy at low temperatures, but it predicts a more rapid fall-off of specific heat with decreasing temperature than is observed.

Deficiencies in the Debye theory were noted by Blackman (1937), who showed that they are overcome satisfactorily using the more rigorous Born–von Kármán theory. Extensive X-ray studies of Laval (1939) on simple structures such as sylvine, aluminium and diamond showed that the detailed features of the TDS could only be explained in terms of the Born–von Kármán theory. The X-ray work on aluminium was developed further by Olmer (1948) and by Walker (1956) to derive the phonon dispersion relations (see Section 4.1.5) along various symmetry directions in the crystal.

It is possible to measure the vibrational frequencies directly with X-rays, but such measurements are very difficult as lattice vibrational energies are many orders of magnitude less than X-ray energies. The situation is much more favourable with thermal neutrons because their wavelength is comparable with interatomic spacings and their energy is comparable with a quantum of

vibrational energy (or phonon). The neutron beam is scattered inelastically by the lattice vibrations, exchanging energy with the phonons. By measuring the energy change for different directions of the scattered beam, the dispersion relations $\omega(\mathbf{q})$ can be determined. Brockhouse & Stewart (1958) reported the first dispersion curves to be derived in this way; since then the neutron technique has become the principal experimental method for obtaining detailed information about lattice vibrations.

In this chapter we shall describe briefly the standard treatment of the lattice dynamics of crystals. There follows a section on the theory of the scattering of X-rays by lattice vibrations, and a similar section on the scattering of thermal neutrons. We then refer briefly to experimental work with X-rays and neutrons. The final section is concerned with the measurement of elastic constants: these constants are required in calculating the TDS correction to measured Bragg intensities (see Section 7.4.2 of *IT C*, 1999).

4.1.2. Dynamics of three-dimensional crystals

For modes of vibration of very long wavelength, the crystal can be treated as a homogeneous elastic continuum without referring to its crystal or molecular structure. The theory of the propagation of these elastic waves is based on Hooke's law of force and on Newton's equations of motion. As the wavelength of the vibrations becomes shorter and shorter and approaches the separation of adjacent atoms, the calculation of the vibrational properties requires a knowledge of the crystal structure and of the nature of the forces between adjacent atoms. The three-dimensional treatment is based on the formulation of Born and von Kármán, which is discussed in detail in the book by Born & Huang (1954) and in more elementary terms in the books by Cochran (1973) and by Willis & Pryor (1975).

Before setting up the equations of motion, it is necessary to introduce three approximations:

(i) *The harmonic approximation.* When an atom is displaced from its equilibrium position, the restoring force is assumed to be proportional to the displacement, measured relative to the neighbouring atoms. The approximation implies no thermal expansion and other properties not possessed by real crystals; it is a reasonable assumption in the lattice-dynamical theory provided the displacements are not too large.

(ii) *The adiabatic approximation.* We wish to set up a potential function for the crystal describing the binding between the atoms. However, the binding involves electronic motions whereas the dynamics involve nuclear motions. The adiabatic approximation, known as the Born–Oppenheimer approximation in the context of molecular vibrations, provides the justification for adopting the same potential function to describe both the binding and the dynamics. Its essence is that the electronic and nuclear motions may be considered separately. This is possible if the nuclei move very slowly compared with the electrons: the electrons can then instantaneously take up a configuration appropriate to that of the displaced nuclei without changing their quantum state. The approximation holds well for insulators, where electronic transition energies are high owing to the large energy gap between filled and unfilled electron states. Surprisingly, it even works for metals, because (on account of the Pauli principle) only a few electrons near the Fermi level can make transitions.

(iii) *Periodic boundary conditions.* These are introduced to avoid problems associated with the free surface. The system is treated as an infinite crystal made up of contiguous, repeating blocks of the actual crystal. The periodic (or cyclic) boundary conditions require that the displacements of corresponding atoms in different blocks are identical. The validity of the conditions was challenged by

4.1. THERMAL DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

Raman (1941), but these objections were safely disposed of by Ledermann (1944).

4.1.2.1. Equations of motion

As a result of thermal fluctuations, the atoms vibrate about their equilibrium positions, so that the actual position of the κ th atom in the l th primitive cell is given by

$$\mathbf{R}(\kappa l) = \mathbf{r}(\kappa l) + \mathbf{u}(\kappa l)$$

with $\mathbf{r}$ representing the equilibrium position and $\mathbf{u}$ the thermal displacement. (In lattice-dynamical theory it is advantageous to deal with the primitive cell, as it possesses the fewest degrees of freedom.) The kinetic energy of the vibrating crystal is

$$(1/2) \sum_{\kappa l \alpha} m(\kappa) \dot{u}_{\alpha}^2(\kappa l),$$

where $m(\kappa)$ is the mass of atom κ and the index α ($\alpha = 1, 2, 3$) refers to the Cartesian components of the displacement. (The dot denotes the time derivative.)

If the adiabatic approximation is invoked, the potential energy V of the crystal can be expressed as a function of the instantaneous atomic positions. Expanding V in powers of $\mathbf{u}(\kappa l)$, using the three-dimensional form of Taylor's series, we have

$$V = V^{(0)} + V^{(1)} + V^{(2)} + V^{(3)} + \dots,$$

where $V^{(0)}$ is the static (equilibrium) potential and $V^{(1)}$, $V^{(2)}$ are given by

$$V^{(1)} = \sum_{\kappa l \alpha} \left. \frac{\partial V}{\partial u_{\alpha}(\kappa l)} \right|_0 u_{\alpha}(\kappa l)$$

$$V^{(2)} = \frac{1}{2} \sum_{\kappa l \alpha} \sum_{\kappa' l' \alpha'} \left. \frac{\partial^2 V}{\partial u_{\alpha}(\kappa l) \partial u_{\alpha'}(\kappa' l')} \right|_0 u_{\alpha}(\kappa l) u_{\alpha'}(\kappa' l').$$

The subscript zero indicates that the derivatives are to be evaluated at the equilibrium configuration. In the harmonic approximation, $V^{(3)}$ and all higher terms in the expansion are neglected.

At equilibrium the forces on an atom must vanish, so that

$$V^{(1)} = 0.$$

Ignoring the static potential $V^{(0)}$, the quadratic term $V^{(2)}$ only remains and the Hamiltonian for the crystal (the sum of the kinetic and potential energies) is then

$$H = \frac{1}{2} \sum_{\kappa l \alpha} m(\kappa) \dot{u}_{\alpha}^2(\kappa l) + \frac{1}{2} \sum_{\kappa l \alpha} \sum_{\kappa' l' \alpha'} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha}(\kappa l) u_{\alpha'}(\kappa' l'),$$

(4.1.2.1)

where $\Phi_{\alpha \alpha'}$ is an element of the 3×3 'atomic force-constant matrix' and is defined (for distinct atoms κl , $\kappa' l'$) by

$$\Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} = \left. \frac{\partial^2 V}{\partial u_{\alpha}(\kappa l) \partial u_{\alpha'}(\kappa' l')} \right|_0.$$

It is the negative of the force in the α direction imposed on the atom (κl) when atom ($\kappa' l'$) is displaced unit distance along α' with all the remaining atoms fixed at their equilibrium sites. $\Phi_{\alpha \alpha'}$ is defined differently for the self-term with $\kappa = \kappa'$ and $l = l'$:

$$\Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa \\ l & l \end{pmatrix} = - \sum_{\substack{\kappa l \\ \kappa l' \neq \kappa l}} \sum_{\substack{\kappa' l' \\ \kappa' l' \neq \kappa l}} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix}.$$

Thus the self-matrix describes the force on (κl) when the atom itself is displaced with all the remaining atoms kept stationary.

There are restrictions on the number of distinct force constants $\Phi_{\alpha \alpha'}$: these are imposed by symmetry and by the requirement that the potential energy is invariant under infinitesimal translations and rotations of the rigid crystal. Such constraints are discussed in the book by Venkataraman *et al.* (1975).

Applying Hamilton's equations of motion to equation (4.1.2.1) now gives

$$m(\kappa) \ddot{u}_{\alpha}(\kappa l) = - \sum_{\kappa' l' \alpha'} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha'}(\kappa' l').$$

(4.1.2.2)

These represent $3nN$ coupled differential equations, where n is the number of atoms per primitive cell ($\kappa = 1, \dots, n$) and N is the number of cells per crystal ($l = 1, \dots, N$).

By applying the periodic boundary conditions, the solutions of equation (4.1.2.2) can be expressed as running, or travelling, plane waves extending throughout the entire crystal. The number of independent waves (or normal modes) is $3nN$. Effectively, we have transferred to a new coordinate system: instead of specifying the motion of the individual atoms, we describe the thermal motion in terms of normal modes, each of which contributes to the displacement of each atom. The general solution for the α component of the displacement of (κl) is then given by the superposition of the displacements from all modes:

$$u_{\alpha}(\kappa l) = [m(\kappa)]^{-1/2} \sum_{j \mathbf{q}} |A_j(\mathbf{q})| e_{\alpha}(\kappa | j \mathbf{q}) \times \exp\{i[\mathbf{q} \cdot \mathbf{r}(\kappa l) - \omega_j(\mathbf{q})t]\}.$$

(4.1.2.3)

Here $\mathbf{q}$ is the wavevector of a mode (specifying both its wavelength and direction of propagation in the crystal) and $\omega_j(\mathbf{q})$ its frequency. There are N distinct wavevectors, occupying a uniformly distributed mesh of N points in the Brillouin zone (reciprocal cell); each wavevector is shared by $3n$ modes which possess, in general, different frequencies and polarization properties. Thus an individual mode is conveniently labelled ($j \mathbf{q}$), where j is an index ($j = 1, \dots, 3n$) indicating the *branch*. The scalar quantity $|A_j(\mathbf{q})|$ in equation (4.1.2.3) is the amplitude of excitation of ($j \mathbf{q}$) and $e_{\alpha}(\kappa | j \mathbf{q})$ is the element of the eigenvector $\mathbf{e}(j \mathbf{q})$ referring to the displacement in the α direction of the atom κ . The eigenvector itself, with dimensions $n \times 1$, determines the pattern of atomic displacements in the mode ($j \mathbf{q}$) and its magnitude is fixed by the orthonormality and closure conditions

$$\sum_{\alpha \kappa} e_{\alpha}^*(\kappa | j \mathbf{q}) e_{\alpha}(\kappa | j' \mathbf{q}) = \delta_{jj'}$$

and

$$\sum_j e_{\alpha}(\kappa | j \mathbf{q}) e_{\alpha'}^*(\kappa' | j \mathbf{q}) = \delta_{\alpha \alpha'} \delta_{\kappa \kappa'}$$

with $*$ indicating complex conjugate and δ the Kronecker delta.

The pre-exponential, or amplitude, terms in (4.1.2.3) are independent of the cell number. This follows from Bloch's (1928) theorem which states that, for corresponding atoms in different cells, the motions are identical as regards their amplitude and direction and differ only in phase. The theorem introduces an enormous simplification as it allows us to restrict attention to the $3n$ equations of motion of the n atoms in just one cell, rather than the $3nN$ equations of motion for all the atoms in the crystal.

Substitution of (4.1.2.3) into (4.1.2.2) gives the equations of motion in the form

$$\omega_j^2(\mathbf{q}) e_{\alpha}(\kappa | j \mathbf{q}) = \sum_{\alpha' \kappa'} D_{\alpha \alpha'}(\kappa \kappa' | \mathbf{q}) e_{\alpha'}(\kappa' | j \mathbf{q}),$$

(4.1.2.4)

in which $D_{\alpha \alpha'}$ is an element of the dynamical matrix $\mathbf{D}(\mathbf{q})$. $D_{\alpha \alpha'}$ is

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defined by

$$D_{\alpha\alpha'}(\kappa\kappa'|\mathbf{q}) = [m(\kappa)m(\kappa')]^{-1/2} \exp\{i\mathbf{q}[r(\kappa') - r(\kappa)]\} \\ \times \sum \Phi_{\alpha\alpha'} \begin{pmatrix} \kappa & \kappa' \\ 0 & L \end{pmatrix} \exp[i\mathbf{q} \cdot \mathbf{r}(L)], \quad (4.1.2.5)$$

where $\mathbf{r}(\kappa)$ is the position of atom κ with respect to the cell origin, L is $l' - l$ and $\mathbf{r}(L)$ is the separation between cells l and l' . The element $D_{\alpha\alpha'}$ is obtained by writing down the $\alpha\alpha'$ component of the force constant between atoms κ, κ' which are L cells apart and multiplying by the phase factor $\exp[i\mathbf{q} \cdot \mathbf{r}(L)]$; this term is then summed over those values of L covering the range of interaction of κ and κ' .

The dynamical matrix is Hermitian and has dimensions $3n \times 3n$. Its eigenvalues are the squared frequencies $\omega_j^2(\mathbf{q})$ of the normal modes and its eigenvectors $\mathbf{e}(\mathbf{q})$ determine the corresponding pattern of atomic displacements. The frequencies of the modes in three of the branches, j , go to zero as $\mathbf{q}$ approaches zero: these are the acoustic modes. The remaining $3n - 3$ branches contain the optic modes. There are N distinct $\mathbf{q}$ vectors, and so, in all, there are $3N$ acoustic modes and $(3n - 3)N$ optic modes. Thus copper has acoustic modes but no optic modes, silicon and rock salt have an equal number of both, and lysozyme possesses predominantly optic modes.

4.1.2.2. Quantization of normal modes. Phonons

Quantum concepts are not required in solving the equations of motion (4.1.2.4) to determine the frequencies and displacement patterns of the normal modes. The only place where quantum mechanics is necessary is in calculating the energy of the mode, and from this the amplitude of vibration $|A_j(\mathbf{q})|$.

It is possible to discuss the theory of lattice dynamics from the beginning in the language of quantum mechanics (Donovan & Angress, 1971). Instead of treating the modes as running waves, they are conceived as an assemblage of indistinguishable quasi-particles called phonons. Phonons obey Bose–Einstein statistics and are not limited in number. The number of phonons, each with energy $\hbar\omega_j(\mathbf{q})$ in the vibrational state specified by $\mathbf{q}$ and j , is given by

$$n_j(\mathbf{q}) = \{\exp[\hbar\omega_j(\mathbf{q})/k_B T] - 1\}^{-1} \quad (4.1.2.6)$$

and the mode energy $E_j(\mathbf{q})$ by

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})[n_j(\mathbf{q}) + (1/2)]. \quad (4.1.2.7)$$

Thus the quantum number $n_j(\mathbf{q})$ describes the degree of excitation of the mode ($j\mathbf{q}$). The relation between $E_j(\mathbf{q})$ and the amplitude $|A_j(\mathbf{q})|$ is

$$E_j(\mathbf{q}) = N\omega_j^2(\mathbf{q})|A_j(\mathbf{q})|^2. \quad (4.1.2.8)$$

Equations (4.1.2.6) to (4.1.2.8) together determine the value of $|A_j(\mathbf{q})|$ to be substituted into equation (4.1.2.3) to give the atomic displacement in terms of the absolute temperature and the properties of the normal modes.

In solving the lattice-dynamical problem using the Born–von Kármán analysis, the first step is to set up a force-constant matrix describing the interactions between all pairs of atoms. This is followed by the assembly of the dynamical matrix $\mathbf{D}$, whose eigenvalues give the frequencies of the normal modes and whose eigenvectors determine the patterns of atomic displacement for each mode.

Before considering the extension of this treatment to molecular crystals, we shall comment briefly on the less rigorous treatments of Einstein and Debye.

4.1.2.3. Einstein and Debye models

In the Einstein model it is assumed that each atom vibrates in its private potential well, entirely unaffected by the motion of its neighbours. There is no correlation between the motion of different atoms, whereas correlated motion – in the form of collective modes propagating throughout the crystal – is a central feature in explaining the characteristics of the TDS. Nevertheless, the Einstein model is occasionally used to represent modes belonging to flat optic branches of the dispersion relations, with the frequency written symbolically as $\omega(\mathbf{q}) = \omega_E$ (constant).

In the Debye model the optic branches are ignored. The dispersion relations for the remaining three acoustic branches are assumed to be the same and represented by

$$\omega(\mathbf{q}) = \mathbf{v}_s \mathbf{q}, \quad (4.1.2.9)$$

where $\mathbf{v}_s$ is a mean sound velocity. The Brillouin zone is replaced by a sphere with radius q_D chosen to ensure the correct number of modes. The linear relationship (4.1.2.9) holds right up to the boundary of the spherical zone. In an improved version of the Debye model, (4.1.2.9) is replaced by the expression

$$\omega(\mathbf{q}) = \mathbf{v}_s(2q_D/\pi) \sin(\pi\mathbf{q}/2q_D), \quad (4.1.2.10)$$

which is the same as (4.1.2.9) at $q = 0$ but gives a sinusoidal dispersion relation with zero slope at the zone boundary.

4.1.2.4. Molecular crystals

The full Born–von Kármán treatment becomes excessively cumbersome when applied to most molecular crystals. For example, for naphthalene with two molecules or 36 atoms in the primitive cell, the dynamical matrix has dimensions 108×108 . Moreover, the physical picture of molecules or of groups of atoms, vibrating in certain modes as quasi-rigid units, is lost in the full treatment.

To simplify the setting up of the dynamical matrix, it is assumed that the molecules vibrate as rigid units in the crystal with each molecule possessing three translational and three rotational (librational) degrees of freedom. The motion of these rigid groups as a whole is described by the *external modes* of motion, whereas the *internal modes* arise from distortions within an individual group. The frequencies of these internal modes, which are largely determined by the strong intramolecular forces, are unaffected by the phase of the oscillation between neighbouring cells: the modes are taken, therefore, to be equivalent to those of the free molecule. The remaining external modes are calculated by applying the Born–von Kármán procedure to the crystal treated as an assembly of rigid molecules.

The dynamical matrix $\mathbf{D}(\mathbf{q})$ now has dimensions $6n' \times 6n'$, where n' is the number of molecules in the primitive cell: for naphthalene, $\mathbf{D}$ is reduced to 12×12 . The elements of $\mathbf{D}$ can be expressed in the same form as equation (4.1.2.5) for an atomic system. κ, κ' refer to molecules which are L cells apart and the indices α, α' ($= 1, \dots, 6$) label the six components of translation and rotation. $m(\kappa)$ in equation (4.1.2.5) is replaced by $m_\alpha(\kappa)$ where m_α represents the 3×3 molecular-mass matrix for $\alpha = 1, 2, 3$ and the 3×3 moment-of-inertia matrix referred to the principal axes of inertia for $\alpha = 4, 5, 6$. The 6×6 force-torque constant matrices $\Phi_{\alpha\alpha'}$ are derived by taking the second derivative of the potential energy of the crystal with respect to the coordinates of translation and rotation.

4.1.3. Scattering of X-rays by thermal vibrations

The change of frequency, or energy, of X-rays on being scattered by thermal waves is extremely small. The differential scattering cross section, $d\sigma/d\Omega$, giving the probability that X-rays are scattered into the solid angle $d\Omega$ is then

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$$\frac{d\sigma}{d\Omega} = \langle |Y(Q)|^2 \rangle,$$

where

$$Y(Q) = \sum_{\kappa l} f_{\kappa}(\mathbf{Q}) \exp\{i\mathbf{Q} \cdot [\mathbf{r}(\kappa l) + \mathbf{u}(\kappa l)]\}. \quad (4.1.3.1)$$

The angled brackets indicate an average value over a period of time much longer than the period of oscillation of an atom. $\mathbf{Q}$ is the 'scattering vector' defined by

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}_0,$$

where $\mathbf{k}$ and $\mathbf{k}_0$ are the wavevectors (each of magnitude $2\pi/\lambda$) of the scattered and incident beams, respectively. The magnitude of $\mathbf{Q}$ is $4\pi(\sin \theta)/\lambda$, where 2θ is the angle between $\mathbf{k}$ and $\mathbf{k}_0$. $f_{\kappa}(\mathbf{Q})$ is the scattering factor of the κ th atom in the unit cell.

The cross section $d\sigma/d\Omega$ can be expanded as a power series:

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)^{(0)} + \left(\frac{d\sigma}{d\Omega}\right)^{(1)} + \left(\frac{d\sigma}{d\Omega}\right)^{(2)} + \dots \quad (4.1.3.2)$$

The individual terms on the right-hand side refer to the cross sections for zero-order, first-order, second-order scattering . . . , *i.e.* for processes involving no exchange of energy between the incident radiation and the crystal (Bragg scattering), the exchange of one quantum of lattice vibrational energy (one-phonon scattering), the exchange of two quanta (two-phonon scattering) . . .

The instantaneous thermal displacement $\mathbf{u}(\kappa l)$ of the atom (κl) can be expressed, using equations (4.1.2.3), (4.1.2.6), (4.1.2.7) and (4.1.2.8), as a superposition of the displacements of the $3nN$ ($\sim 10^{23}$) independent normal modes of vibration:

$$\begin{aligned} \mathbf{u}(\kappa l) = [Nm(\kappa)]^{-1/2} \sum_{j\mathbf{q}} \frac{E_j^{-1/2}(\mathbf{q})}{\omega_j^2(\mathbf{q})} \mathbf{e}(\kappa|j\mathbf{q}) \\ \times \exp\{i[\mathbf{q} \cdot \mathbf{r}(\kappa l) - \omega_j(\mathbf{q})t]\}. \end{aligned} \quad (4.1.3.3)$$

Explicit expressions can now be given for the partial cross sections in equation (4.1.3.2). The cross section for Bragg scattering is

$$\left(\frac{d\sigma}{d\Omega}\right)^{(0)} = N|F(\mathbf{Q})|^2 \frac{(2\pi)^3}{v} \sum_{\mathbf{h}} \delta(\mathbf{Q} - \mathbf{Q}_{\mathbf{h}}), \quad (4.1.3.4)$$

where v is the cell volume. The delta function requires that

$$\mathbf{Q} = \mathbf{Q}_{\mathbf{h}},$$

where $\mathbf{Q}_{\mathbf{h}}$ is a reciprocal-lattice vector, so that scattering is restricted to the points $\mathbf{h}$ of the reciprocal lattice. The structure factor $F(\mathbf{Q})$ is

$$F(\mathbf{Q}) = \sum_{\kappa} f_{\kappa}(\mathbf{Q}) \exp[i\mathbf{Q} \cdot \mathbf{r}(\kappa)] \exp(-W_{\kappa}),$$

where the exponent W_{κ} of the temperature factor of the atom κ is calculated by summing over the normal modes:

$$W_{\kappa} = \frac{1}{2Nm(\kappa)} \sum_{j\mathbf{q}} |\mathbf{Q}_{\mathbf{h}} \cdot \mathbf{e}(\kappa|j\mathbf{q})|^2 \frac{E_j(\mathbf{q})}{\omega_j^2(\mathbf{q})}. \quad (4.1.3.5)$$

The last equation shows that the acoustic modes, with frequencies approaching zero as $\mathbf{q} \rightarrow 0$, make the largest contribution to the temperature factor.

The one-phonon cross section is

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)^{(1)} = \frac{(2\pi)^3}{v} \sum_{j\mathbf{q}} \frac{|G_j(\mathbf{Q}, \mathbf{q})|^2 E_j(\mathbf{q})}{\omega_j^2(\mathbf{q})} \\ \times \sum_{\mathbf{h}} \delta(\mathbf{Q} \pm \mathbf{q} - \mathbf{Q}_{\mathbf{h}}), \end{aligned} \quad (4.1.3.6)$$

where $G_j(\mathbf{Q}, \mathbf{q})$ is the 'structure factor for one-phonon scattering' by the mode ($j\mathbf{q}$) and is given by

$$\begin{aligned} G_j(\mathbf{Q}, \mathbf{q}) = \sum_{\kappa} \frac{\mathbf{Q} \cdot \mathbf{e}(\kappa|j\mathbf{q})}{[m(\kappa)]^{1/2}} \cdot f_{\kappa}(\mathbf{Q}) \\ \times \exp[i\mathbf{Q} \cdot \mathbf{r}(\kappa)] \exp(-W_{\kappa}). \end{aligned}$$

The delta function in equation (4.1.3.6) implies that

$$\mathbf{Q} = \mathbf{Q}_{\mathbf{h}} \pm \mathbf{q}, \quad (4.1.3.7)$$

so that the scattering from the $3n$ modes with the same wavevector $\mathbf{q}$ is restricted to pairs of points in reciprocal space which are displaced by $\pm\mathbf{q}$ from the reciprocal-lattice points. (These satellite reflections are analogous to the pairs of 'ghosts' near the principal diffraction maxima in a grating ruled with a periodic error.) There is a huge number, N , of $\mathbf{q}$ vectors which are uniformly distributed throughout the Brillouin zone, and each of these vectors gives a cross section in accordance with equation (4.1.3.6). Thus the one-phonon TDS is spread throughout the whole of reciprocal space, rising to a maximum at the reciprocal-lattice points where $\omega \rightarrow 0$ for the acoustic modes.

For two-phonon scattering, involving modes with wavevectors $\mathbf{q}_1$ and $\mathbf{q}_2$, the scattering condition becomes

$$\mathbf{Q} = \mathbf{Q}_{\mathbf{h}} \pm \mathbf{q}_1 \pm \mathbf{q}_2. \quad (4.1.3.8)$$

The intensity at any point in reciprocal space is now contributed by a very large number of pairs of elastic waves with wavevectors satisfying equation (4.1.3.8). These vectors span the entire Brillouin zone, and so the variation of the two-phonon intensity with location in reciprocal space is less pronounced than for one-phonon scattering.

Expressions for $(d\sigma/d\Omega)^{(2)}$ and for higher terms in equation (4.1.3.2) will not be given, but a rough estimate of their relative magnitudes can be derived by using the Einstein model of the crystal. All frequencies are the same, $\omega_j(\mathbf{q}) = \omega_E$, and for one atom per cell ($n = 1$) the exponent of the temperature factor, equation (4.1.3.5), becomes

$$W = \frac{Q^2 k_B T}{2m\omega_E^2}, \quad (4.1.3.9)$$

assuming classical equipartition of energy between modes: $E_j(\mathbf{q}) = k_B T$. The cross sections for zero-order, first-order, second-order . . . scattering are then

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)^{(0)} &= Nf^2 \exp(-2W) \\ \left(\frac{d\sigma}{d\Omega}\right)^{(1)} &= Nf^2 \exp(-2W) 2W \\ \left(\frac{d\sigma}{d\Omega}\right)^{(2)} &= Nf^2 \exp(-2W) \frac{1}{2} (2W)^2 \\ &\vdots \end{aligned}$$

and the total cross section is

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$$\frac{d\sigma}{d\Omega} = Nf^2 \exp(-2W) \left\{ 1 + 2W + \frac{1}{2}(2W)^2 + \frac{1}{6}(2W)^3 + \dots \right\}.$$

The expression in curly brackets is the expansion of $\exp(2W)$. The n th term in the expansion, associated with the n th-order (n -phonon) process, is proportional to W^n or to $Q^{2n}T^n$. The higher-order processes are more important, therefore, at higher values of $(\sin \theta)/\lambda$ and at higher temperatures.

Our treatment so far applies to the TDS from single crystals. It can be extended to cover the TDS from polycrystalline samples, but the calculations are more complicated as the first-order scattering at a fixed value of $(\sin \theta)/\lambda$ is contributed by phonon wavevectors extending over the whole of the Brillouin zone. For a fuller discussion of the TDS from powders see Section 7.4.2 in *IT C* (1999).

4.1.4. Scattering of neutrons by thermal vibrations

The amplitude of the X-ray beam scattered by a single atom is denoted by the form factor or atomic scattering factor $f(\mathbf{Q})$. The corresponding quantity in neutron scattering is the scattering amplitude or scattering length b of an atom. b is independent of scattering angle and is also independent of neutron wavelength apart from for a few isotopes (e.g. ^{113}Cd , ^{149}Sm) with resonances in the thermal neutron region.

The scattering amplitude for atoms of the same chemical element can vary randomly from one atom to the next, as different amplitudes are associated with different isotopes. If the nucleus has a nonzero spin, even a single isotope has two different amplitudes, dependent on whether the nuclear spin is parallel or antiparallel to the spin of the incident neutron. If there is a variation in the amplitude associated with a particular type of atom, some of the waves scattered by the atom will interfere with one another and some will not. The first part is called coherent scattering and the second incoherent scattering. The amplitude of the coherent scattering is determined by the mean atomic scattering amplitude, averaged over the various isotopes and spin states of the atom, and is known as the coherent scattering length, $\bar{b}$.

A crucial difference between neutrons and X-rays concerns their energies:

$$\begin{aligned} E &= \hbar^2 k^2 / 2m_n & (\text{neutrons}) \\ &= c\hbar k & (\text{X-rays}), \end{aligned}$$

where m_n is the neutron mass and c the velocity of light. At $\lambda = 1 \text{ \AA}$, neutrons have an energy of 0.08 eV or a temperature of about 800 K; for X-rays of this wavelength the corresponding temperature exceeds 10^8 K ! Thermal neutrons have energies comparable with phonon energies, and so inelastic scattering processes, involving the exchange of energy between neutrons and phonons, produce appreciable changes in neutron energy. (These changes are readily determined from the change in wavelength or velocity of the scattered neutrons.) It is customary to refer to the thermal diffuse scattering of neutrons as ‘inelastic neutron scattering’ to draw attention to this energy change.

For a scattering process in which energy is exchanged with just one phonon, energy conservation gives

$$E_0 - E = \varepsilon \hbar \omega_j(\mathbf{q}), \quad (4.1.4.1)$$

where E_0 and E are the energies of the neutron before and after scattering. If $\varepsilon = +1$ the neutron loses energy by creating a phonon (‘phonon emission’), and if $\varepsilon = -1$ it gains energy by annihilating a phonon (‘phonon absorption’).

The partial differential scattering cross section $d^2\sigma/d\Omega d\omega$ gives the probability that neutrons will be scattered into a small solid angle $d\Omega$ about the direction $\mathbf{k}$ with a change of energy between $\hbar\omega$ and $\hbar(\omega + d\omega)$. This cross section can be split into two terms, known as the coherent and incoherent cross sections:

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}} + \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{incoh}}.$$

The coherent cross section depends on the correlation between the positions of all the atoms at different times, and so gives interference effects. The incoherent cross section depends only on the correlation between the positions of the same atom at different times, giving no interference effects. Incoherent inelastic scattering is the basis of a powerful technique for studying the dynamics of molecular crystals containing hydrogen (Boutin & Yip, 1968).

The coherent scattering cross section $(d^2\sigma/d\Omega d\omega)_{\text{coh}}$ can be expanded, as in the X-ray case [equation (4.1.3.2)], into terms representing the contributions from zero-phonon, one-phonon, two-phonon . . . scattering. To determine phonon dispersion relations, we measure the one-phonon contribution and this arises from both phonon emission and phonon absorption:

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}}^{(1)} = \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}+1}^{(1)} + \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}-1}^{(1)}.$$

The superscript (1) denotes a one-phonon process, and the subscript +1 (−1) indicates emission (absorption).

The emission cross section is given by (Squires, 1978)

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}+1}^{(1)} &= \frac{\hbar k}{k_0} \frac{4\pi^3}{\mathbf{v}} \sum_{\mathbf{q}} \sum_{\mathbf{Q}_h} \frac{[n_j(\mathbf{q}) + 1]}{\omega_j(\mathbf{q})} \\ &\times \left| \frac{b_\kappa}{[m(\kappa)]^{1/2}} \exp[i\mathbf{Q} \cdot \mathbf{r}(\kappa)] \right. \\ &\times \left. \mathbf{Q} \cdot \mathbf{e}(\kappa|\mathbf{q}) \exp(-W_\kappa) \right|^2 \\ &\times \delta[\omega - \omega_j(\mathbf{q})] \delta(\mathbf{Q} - \mathbf{Q}_h + \mathbf{q}), \end{aligned} \quad (4.1.4.2)$$

whereas for phonon absorption

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}-1}^{(1)} &= \frac{\hbar k}{k_0} \frac{4\pi^3}{\mathbf{v}} \sum_{\mathbf{q}} \sum_{\mathbf{Q}_h} \frac{[n_j(\mathbf{q})]}{\omega_j(\mathbf{q})} \\ &\times \left| \frac{b_\kappa}{[m(\kappa)]^{1/2}} \exp[i\mathbf{Q} \cdot \mathbf{r}(\kappa)] \right. \\ &\times \left. \mathbf{Q} \cdot \mathbf{e}(\kappa|\mathbf{q}) \exp(-W_\kappa) \right|^2 \\ &\times \delta[\omega + \omega_j(\mathbf{q})] \delta(\mathbf{Q} - \mathbf{Q}_h - \mathbf{q}). \end{aligned} \quad (4.1.4.3)$$

The first delta function in these two expressions embodies energy conservation,

$$\hbar\omega \equiv \frac{\hbar^2}{2m_n} (k_0^2 - k^2) = \varepsilon \hbar \omega_j(\mathbf{q}),$$

and the second embodies conservation of momentum,

$$\mathbf{Q} \equiv \mathbf{k} - \mathbf{k}_0 = \mathbf{Q}_h - \varepsilon \mathbf{q}. \quad (4.1.4.4)$$

The phonon population number, $n_j(\mathbf{q})$, tends to zero as $T \rightarrow 0$ [see equation (4.1.2.6)], so that the one-phonon absorption cross

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section is very small at low temperatures where there are few phonons for the radiation to absorb. Comparison of equations (4.1.4.2) and (4.1.4.3) shows that there is always a greater probability that the neutrons are scattered with energy loss rather than with energy gain.

Normally it is not possible in X-ray experiments to distinguish between phonon emission and phonon absorption, and the measured cross section is obtained by summing over all energy transfers. The cross section for X-rays can be derived from the neutron formulae, equations (4.1.4.2) and (4.1.4.3), by putting $k = k_0$ and by replacing b_k with $f_k(\mathbf{Q})$. Integration over ω and addition of the parts for emission and absorption gives the X-ray formula (4.1.3.6).

The theory of neutron scattering can also be formulated in terms of thermal averages known as Van Hove correlation functions (Van Hove, 1954). For example, the partial differential cross section for coherent scattering is

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}} = \frac{k}{k_0} S(\mathbf{Q}, \omega),$$

where

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar} \int G(\mathbf{r}, t) \exp[i(\mathbf{Q} \cdot \mathbf{r} - \omega t)] d\mathbf{r} dt.$$

$S(\mathbf{Q}, \omega)$ is the Fourier transform in space and time of $G(\mathbf{r}, t)$, the time-dependent pair-correlation function. The classical interpretation of $G(\mathbf{r}, t)$ is that it is the probability of finding any atom at time t in a volume $d\mathbf{r} = d^3r$, if there is an atom at the origin at time zero.

4.1.5. Phonon dispersion relations

Both X-rays and neutrons are used for determining crystal structures, but the X-ray method plays the dominant role. The reverse is true for the measurement of phonon dispersion relations: the experimental determination of $\omega(\mathbf{q})$ versus $\mathbf{q}$ was first undertaken with X-rays, but the method has been superseded by the technique of coherent inelastic neutron scattering (or neutron spectroscopy). For phonon wavevectors lying anywhere within the first Brillouin zone, it is necessary to employ radiation of wavelength comparable with interatomic distances and of energy comparable with lattice vibrational energies. X-rays satisfy the first of these conditions, but not the second, whereas the opposite holds for infrared radiation. Thermal neutrons satisfy both conditions simultaneously.

4.1.5.1. Measurement with X-rays

Frequencies can be derived indirectly with X-rays from the intensity of the thermal diffuse scattering. For a monatomic crystal with one atom per primitive cell, there are no optic modes and the one-phonon TDS intensity, equation (4.1.3.6), reduces to

$$\frac{d\sigma}{d\Omega} = Q^2 f^2 e^{-2W} \sum_{j=1}^3 \frac{E_j(\mathbf{q})}{\omega^2(\mathbf{q})} \cos^2 \alpha_j(\mathbf{q}) \delta(\mathbf{Q} \pm \mathbf{q} - \mathbf{Q}_h), \quad (4.1.5.1)$$

where $\alpha_j(\mathbf{q})$ is the angle between $\mathbf{Q}$ and the direction of polarization of the mode ($j\mathbf{q}$). There are three acoustic modes associated with each wavevector $\mathbf{q}$, but along certain directions of $\mathbf{Q}$ it is possible to isolate the intensities contributed by the individual modes by choosing $\alpha_j(\mathbf{q})$ to be close to 0 or 90°. Equation (4.1.5.1) can then be employed to derive the frequency $\omega_j(\mathbf{q})$ for just one mode. The measured intensity must be corrected for multi-phonon and Compton scattering, both of which can exceed the intensity of the one-phonon scattering. The correction for two-phonon scattering involves an integration over the entire Brillouin zone, and this in turn requires an approximate knowledge of the dispersion relations.

The correction for Compton scattering can be made by repeating the measurements at low temperature.

The X-ray method is hardly feasible for systems with several atoms in the primitive cell. It comes into its own for those few materials which cannot be examined by neutrons. These include boron, cadmium and samarium with high absorption cross sections for thermal neutrons, and vanadium with a very small coherent (and a large incoherent) cross section for the scattering of neutrons. An important feature of TDS measurements with X-rays is in providing an independent check on interatomic or intermolecular force constants derived from measurements with inelastic neutron scattering. The force model is used to generate phonon frequencies and eigenvectors, which are then employed to compute the one-phonon and multi-phonon contributions to the X-ray TDS. Any discrepancy between calculated and observed X-ray intensities might be ascribed to such features as ionic deformation (Buyers *et al.*, 1968) or anharmonicity (Schuster & Weymouth, 1971).

4.1.5.2. Measurement with neutrons

The inelastic scattering of neutrons by phonons gives rise to changes of energy which are readily measured and converted to frequencies $\omega_j(\mathbf{q})$ using equation (4.1.4.1). The corresponding wavevector $\mathbf{q}$ is derived from the momentum conservation relation (4.1.4.4). Nearly all phonon dispersion relations determined to date have been obtained in this way. Well over 200 materials have been examined, including half the chemical elements, a large number of alloys and diatomic compounds, and rather fewer molecular crystals (Dolling, 1974; Bilz & Kress, 1979). Phonon dispersion curves have been determined in crystals with up to ten atoms in the primitive cell, for example, tetracyanoethylene (Chaplot *et al.*, 1983).

The principal instrument for determining phonon dispersion relations with neutrons is the triple-axis spectrometer, first designed and built by Brockhouse (Brockhouse & Stewart, 1958). The modern instrument is unchanged apart from running continuously under computer control. A beam of thermal neutrons falls on a single-crystal monochromator, which Bragg reflects a single wavelength on to the sample in a known orientation. The magnitude of the scattered wavevector, and hence the change of energy on scattering by the sample, is found by measuring the Bragg angle at which the neutrons are reflected by the crystal analyser. The direction of $\mathbf{k}$ is defined by a collimator between the sample and analyser.

In the 'constant $\mathbf{Q}$ ' mode of operating the triple-axis spectrometer, the phonon wavevector is kept fixed while the energy transfer $\hbar\omega$ is varied. This allows the frequency spectrum to be determined for all phonons sharing the same $\mathbf{q}$; the spectrum will contain up to $3n$ frequencies, corresponding to the $3n$ branches of the dispersion relations.

In an inelastic neutron scattering experiment, where the TDS intensity is of the order of one-thousandth of the Bragg intensity, it is necessary to use a large sample with a volume of 1 cm³, or more. The sample should have a high cross section for coherent scattering as compared with the cross sections for incoherent scattering and for true absorption. Crystals containing hydrogen should be deuterated.

Dolling (1974) has given a comprehensive review of the measurement of phonon dispersion relations by neutron spectroscopy.

4.1.5.3. Interpretation of dispersion relations

The usual procedure for analysing dispersion relations is to set up the Born-von Kármán formalism with interatomic force constants Φ . The calculated frequencies $\omega_j(\mathbf{q})$ are then derived from the eigenvalues of the dynamical matrix $\mathbf{D}$ (Section 4.1.2.1) and the force constants fitted, by least squares, to the observed frequencies. Several sets of force constants may describe the frequencies equally

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well, and to decide which set is preferable it is necessary to compare eigenvectors as well as eigenvalues (Cochran, 1971).

The main interest in the curves is in testing different models of interatomic potentials, whose derivatives are related to the measured force constants. For the solid inert gases the curves are reproduced reasonably well using a two-parameter Lennard-Jones 6-12 potential, although calculated frequencies are systematically higher than the experimental points near the Brillouin-zone boundary (Fujii *et al.*, 1974). To reproduce the dispersion relations in metals it is necessary to use a large number of interatomic force constants, extending to at least fifth neighbours. The number of independent constants is then too large for a meaningful analysis with the Born-von Kármán theory, but in the pseudo-potential approximation (Harrison, 1966) only two parameters are required to give good agreement between calculated and observed frequencies of simple metals such as aluminium. In the rigid-ion model for ionic crystals, the ions are treated as point charges centred on the nuclei and polarization of the outermost electrons is ignored. This is unsatisfactory at high frequencies. In the shell model, polarization is accounted for by representing the ion as a rigid core connected by a flexible spring to a polarizable shell of outermost electrons. There are many variants of this model – extended shell, overlap shell, deformation dipole, breathing shell . . . (Bilz & Kress, 1979). For molecular crystals the contributions to the force constants from the intermolecular forces can be derived from the non-bonded atomic pair potential of, say, the 6-exponential type:

$$\varphi(r) = -\frac{A_{ij}}{r^6} + B_{ij} \exp(-C_{ij}r).$$

Here, i, j label atoms in different molecules. The values of the parameters A, B, C depend on the pair of atomic species i, j only. For hydrocarbons they have been tabulated for different atom pairs by Kitaigorodskii (1966) and Williams (1967). The 6-exponential potential is applicable to molecular crystals that are stabilized mainly by London-van der Waals interactions; it is likely to fail when hydrogen bonds are present.

4.1.6. Measurement of elastic constants

There is a close connection between the theory of lattice dynamics and the theory of elasticity. Acoustic modes of vibration of long wavelength propagate as elastic waves in a continuous medium, with all the atoms in one unit cell moving in phase with one another. These vibrations are sound waves with velocities which can be calculated from the macroscopic elastic constants and from the density. The sound velocities are also given by the slopes, at $q = 0$, of the acoustic branches of the phonon dispersion relations. A knowledge of the velocities, or of the elastic constants, is necessary in estimating the TDS contribution to measured Bragg intensities.

The elastic constants relate the nine components of stress and nine components of strain, making 81 constants in all. This large

number is reduced to 36, because there are only six independent components of stress and six independent components of strain. An economy of notation is now possible, replacing the indices 11 by 1, 22 by 2, 33 by 3, 23 by 4, 31 by 5 and 12 by 6, so that the elastic constants are represented by c_{ij} with $i, j = 1, \dots, 6$. Applying the principle of conservation of energy gives

$$c_{ij} = c_{ji}$$

and the number of constants is reduced further to 21. Crystal symmetry effects yet a further reduction. For cubic crystals there are just three independent constants (c_{11}, c_{12}, c_{44}) and the 6×6 matrix of elastic constants is

$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix}.$$

In principle, the elastic constants can be derived from static measurements of the four quantities – compressibility, Poisson's ratio, Young's modulus and rigidity modulus. The measurements are made along different directions in the crystal: at least six directions are needed for the orthorhombic system. The accuracy of the static method is limited by the difficulty of measuring small strains.

Dynamic methods are more accurate as they depend on measuring a frequency or velocity. For a cubic crystal, the three elastic constants can be derived from the three sound velocities propagating along the single direction [110]; for non-cubic crystals the velocities must be measured along a number of non-equivalent directions.

Sound velocities can be determined in a number of ways. In the ultrasonic pulse technique, a quartz transducer sends a pulse through the crystal; the pulse is reflected from the rear surface back to the transducer, and the elapsed time for the round trip of several cm is measured. Brillouin scattering of laser light is also used (Vacher & Boyer, 1972). Fluctuations in dielectric constant caused by (thermally excited) sound waves give rise to a Doppler shift of the light frequency. The sound velocity is readily calculated from this shift, and the elastic constants are then obtained from the velocities along several directions, using the Christoffel relations (Hearmon, 1956). The Brillouin method is restricted to transparent materials. This restriction does not apply to neutron diffraction methods, which employ the inelastic scattering of neutrons (Willis, 1986; Schofield & Willis, 1987; Popa & Willis, 1994).

Tables of elastic constants of cubic and non-cubic crystals have been compiled by Hearmon (1946, 1956) and by Huntingdon (1958).

4.2. Disorder diffuse scattering of X-rays and neutrons

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4.2.1. Scope of this chapter

Diffuse scattering of X-rays, neutrons and other particles is an accompanying effect in all diffraction experiments aimed at structure analysis with the aid of so-called elastic scattering. In this case the momentum exchange of the scattered photon (or particle) includes the crystal as a whole; the energy transfer involved becomes negligibly small and need not be considered in diffraction theory. Inelastic scattering processes, however, are due to excitation processes, such as ionization, phonon scattering *etc.* Distortions as a consequence of structural changes cause typical elastic or inelastic diffuse scattering. All these processes contribute to scattering, and a general theory has to include all of them. Hence, the exact treatment of diffuse scattering becomes very complex. Fortunately, approximations treating the phenomena independently are possible in most cases, but it should be kept in mind that difficulties may occasionally arise.

A separation of elastic from inelastic diffuse scattering may be made if detectors sensitive to the energy of radiation are used. Difficulties may sometimes result from small energy exchanges, which cannot be resolved for experimental reasons. The latter is true for scattering of X-rays by phonons which have energies of the order of 10^{-2} – 10^{-3} eV, a value which is considerably smaller than 10 keV, a typical value for X-ray quanta. Another equivalent explanation, frequently forwarded in the literature, is the high speed of X-ray photons, such that the rather slow motion of atoms cannot be ‘observed’ by them during diffraction. Hence, all movements appear as static displacement waves of atoms, and temperature diffuse scattering is pseudo-elastic for X-rays. This is not true in the case of thermal neutrons, which have energies comparable to those of phonons. Since thermal diffuse scattering is discussed in Chapter 4.1, this chapter is mainly concerned with the elastic (or pseudo-elastic other than thermal) part of diffuse scattering.

The full treatment of the complicated theoretical background for all other kinds of diffuse scattering lies beyond the scope of this article. It is also impossible to refer to all papers in this wide and complicated field. Different theoretical treatments of one and the same subject are often developed, but only some are given here, in most cases those which may be understood most easily – at least to the authors’ feeling. As shown in this chapter, electron-density fluctuations and distribution functions of defects play an important role for the complete interpretation of diffraction patterns. Both quantities may best be studied in the low-angle scattering range, which occasionally represents the only Bragg peak dealing with the full information of the distribution function of the defects. Hence, many problems cannot be solved without a detailed interpretation of low-angle diffraction.

Disorder phenomena in magnetic structures are not specifically discussed here. Magnetic diffuse neutron scattering and special experimental techniques themselves constitute a large subject. Many aspects, however, may be analysed along similar lines as given here. For this particular topic the reader is referred to textbooks of neutron scattering, where the theory of diffraction by magnetic materials is generally included (see, *e.g.*, Lovesey, 1984).

Glasses, liquids or liquid crystals show typical diffuse diffraction phenomena. Particle-size effects and strains have an important influence on the diffuse scattering. The same is true for dislocations and point defects such as interstitials or vacancies. These defects are mainly described by their strain field which influences the intensities of sharp reflections like an artificial temperature factor: the Bragg peaks diminish in intensity, while the diffuse scattering increases predominantly close to them. These phenomena are less important from a structural point of view, at least in the case of

metals or other simple structures. This statement is true as long as the structure of the ‘kernel’ of defects may be neglected when compared with the influence of the strain field. Whether dislocations in more complicated structures meet this condition is not yet known.

Radiation damage in crystals represents another field of diffuse scattering which cannot be treated here explicitly. As long as point defects only are generated, the strain field around these defects is the most important factor governing diffuse scattering. Particles with high energy, such as fast neutrons, protons and others, generate complicated defect structures which have to be treated with the aid of the cluster method described below, but no special reference is given here because of the complexity of these phenomena.

Diffuse scattering related to phase transitions, in particular the critical diffuse scattering observed at or close to the transition temperature, cannot be discussed here. In simple cases a satisfactory description may be given with the aid of a ‘soft phonon’, which freezes at the critical temperature, thus generating typical temperature-dependent diffuse scattering. If the geometry of the lattice is maintained during the transformation (no breakdown into crystallites of different cell geometry), the diffuse scattering is very similar to diffraction phenomena described in this article. Sometimes, however, very complicated interim stages (ordered or disordered) are observed demanding a complicated theory for their full explanation (see, *e.g.*, Dorner & Comes, 1977).

Commensurate and incommensurate modulated structures as well as quasicrystals are frequently accompanied by a typical diffuse scattering, demanding an extensive experimental and theoretical study in order to arrive at a satisfactory explanation. A reliable structure determination becomes very difficult in cases where the interpretation of diffuse scattering has not been incorporated. Many erroneous structural conclusions have been published in the past. The solution of problems of this kind needs careful thermodynamical consideration as to whether a plausible explanation of the structural data can be given.

Obviously, there is a close relationship between thermodynamics and diffuse scattering in disordered systems, representing a stable or metastable thermal equilibrium. From the thermodynamical point of view the system is then characterized by its grand partition function, which is intimately related to the correlation functions used in the interpretation of diffuse scattering. The latter is nothing other than a kind of ‘partial partition function’ where two atoms, or two cell occupations, are fixed such that the sum of all partial partition functions represents the grand partition function. This fact yields the useful correlation between thermodynamics and diffuse scattering mentioned above, which may well be used for a determination of thermodynamical properties of the crystal. This subject could not be included here for the following reason: real three-dimensional crystals generally exhibit diffuse scattering by defects and/or disordering effects which are not in thermal equilibrium. They are created during crystal growth, or are frozen-in defects formed at higher temperatures. Hence, a thermodynamical interpretation of diffraction data needs a careful study of diffuse scattering as a function of temperature or some other thermodynamical parameters. This can be done in very rare cases only, so the omission of this subject seems justified.

For all of the reasons mentioned above, this article cannot be complete. It is hoped, however, that it will provide a useful guide for those who need the information for the full understanding of the crystal chemistry of a given structure.

There is no comprehensive treatment of all aspects of diffuse scattering. Essential parts are treated in the textbooks of James (1954), Wilson (1962), Wooster (1962) and Schwartz & Cohen (1977); handbook articles are written by Jagodzinski (1963,

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1964a,b, 1987), Schulz (1982), Welberry (1985); and a series of interesting papers is collected by Collongues *et al.* (1977).

Many differences are caused by different symbols and by different 'languages' used in the various diffraction methods. Quite a few of the new symbols in use are not really necessary, but some are caused by differences in the experimental techniques. For example, the neutron scattering length b may usually be equated with the atomic form factor f in X-ray diffraction. The differential cross section introduced in neutron diffraction represents the intensity scattered into an angular range $d\Omega$ and an energy range dE . The famous scattering law in neutron work corresponds to the square of an (extended) structure factor; the 'static structure factor', a term used by neutron diffractionists, is nothing other than the conventional Patterson function. The complicated resolution functions in neutron work correspond to the well known Lorentz factors in X-ray diffraction. These have to be derived in order to include all techniques used in diffuse-scattering work.

4.2.2. Summary of basic scattering theory

Diffuse scattering results from deviations from the identity of translational invariant scattering objects and from long-range correlations in space and time. Fluctuations of scattering amplitudes and/or phase shifts of the scattered wavetrains reduce the maximum capacity of interference (leading to Bragg reflections) and are responsible for the diffuse scattering, *i.e.* scattering parts which are not located in reciprocal space in distinct spots. Unfortunately, the terms 'coherent' and 'incoherent' scattering used in this context are not uniquely defined in the literature. Since all scattering processes are correlated in space and time, there is no incoherent scattering at all in its strict sense. (A similar relationship exists for 'elastic' and 'inelastic' scattering. Here pure inelastic scattering would take place if the momentum and the energy were transferred to a single scatterer; on the other hand, an elastic scattering process would demand a uniform exchange of momentum and energy with the whole crystal.) Obviously, both cases are idealized and the truth lies somewhere in between. In spite of this, a great many authors use the term 'incoherent' systematically for the diffuse scattering away from the Bragg peaks, even if some diffuse maxima or minima, other than those due to structure factors of molecules or atoms, are observed. Although this definition is unequivocal as such, it is physically incorrect. Other authors use the term 'coherent' for Bragg scattering only; all diffuse contributions are then called 'incoherent'. This definition is clear and unique since it considers space and time, but it does not differentiate between incoherent and inelastic. In the case of neutron scattering both terms are essential and cannot be abandoned.

In neutron diffraction the term 'incoherent' scattering is generally used in cases where no correlation between spin orientations or between isotopes of the same element exists. Hence, another definition of 'incoherence' is proposed for scattering processes that are uncorrelated in space and time. In fact there may be correlations between the spins *via* their magnetic field, but the correlation length in space (and time) may be very small, such that the scattering process appears to be incoherent. Even in these cases the nuclei contribute to coherent (average structure) and incoherent scattering (diffuse background). Hence, the scattering process cannot really be understood by assuming nuclei which scatter independently. For this reason, it seems to be useful to restrict the term 'incoherent' to cases where a random contribution to scattering is realized or, in other words, a continuous function exists in reciprocal space. This corresponds to a δ function in real four-dimensional space. The randomness may be attributed to a nucleus (neutron diffraction) or an atom (molecule). It follows from this definition that the scattering need not be continuous, but

may be modulated by structure factors of molecules. In this sense we shall use the term 'incoherent', remembering that it is incorrect from a physical point of view.

As mentioned in Chapter 4.1 the theory of thermal neutron scattering must be treated quantum mechanically. (In principle this is true also in the X-ray case.) In the classical limit, however, the final expressions have a simple physical interpretation. Generally, the quantum-mechanical nature of the scattering function of thermal neutrons is negligible at higher temperatures and in those cases where energy or momentum transfers are not too large. In almost all disorder problems this classical interpretation is sufficient for interpretation of diffuse scattering phenomena. This is not quite true in the case of orientational disorder (plastic crystals) where H atoms are involved.

The basic formulae given below are valid in either the X-ray or the neutron case: the atomic form factor f replaces the coherent scattering length b_{coh} (abbreviated to b). The formulation in the frame of the van Hove correlation function $G(\mathbf{r}, t)$ (classical interpretation, coherent part) corresponds to a treatment by a four-dimensional Patterson function $P(\mathbf{r}, t)$.

The basic equations for the differential cross sections are:

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d(\hbar\omega)} = N \frac{|\mathbf{k}|}{|\mathbf{k}_0|} \frac{\langle b \rangle^2}{2\pi\hbar} \int_{\mathbf{r}} \int_t G(\mathbf{r}, t) \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.1a)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d(\hbar\omega)} = N \frac{|\mathbf{k}|}{|\mathbf{k}_0|} \frac{\langle b^2 \rangle - \langle b \rangle^2}{2\pi\hbar} \int_{\mathbf{r}} \int_t G_s(\mathbf{r}, t) \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.1b)$$

(N = number of scattering nuclei of same chemical species; $\mathbf{k}$, $\mathbf{k}_0$ = wavevectors after/before scattering).

The integrations over space may be replaced by summations in disordered crystals except for cases where structural elements exhibit a liquid-like behaviour. Then the van Hove correlation functions are:

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_j, \mathbf{r}_{j'}} \delta\{\mathbf{r} - [\mathbf{r}_{j'}(t) - \mathbf{r}_j(0)]\} \quad (4.2.2.2a)$$

$$G_s(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_j} \delta\{\mathbf{r} - [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\}. \quad (4.2.2.2b)$$

$G(\mathbf{r}, t)$ gives the probability that if there is an atom j at $\mathbf{r}_j(0)$ at time zero, there is an *arbitrary* atom j' at $\mathbf{r}_{j'}(t)$ at *arbitrary* time t , while $G_s(\mathbf{r}, t)$ refers to the *same* atom j at $\mathbf{r}_j(t)$ at time t .

Equations (4.2.2.1) may be rewritten by use of the four-dimensional Fourier transforms of G , and G_s , respectively:

$$S_{\text{coh}}(\mathbf{H}, \omega) = \frac{1}{2\pi} \int_{\mathbf{r}} \int_t G(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.3a)$$

$$S_{\text{inc}}(\mathbf{H}, \omega) = \frac{1}{2\pi} \int_{\mathbf{r}} \int_t G_s(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.3b)$$

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d(\hbar\omega)} = N \frac{k}{k_0} \langle b \rangle^2 S_{\text{coh}}(\mathbf{H}, \omega) \quad (4.2.2.4a)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d(\hbar\omega)} = N \frac{k}{k_0} [\langle b^2 \rangle - \langle b \rangle^2] S_{\text{inc}}(\mathbf{H}, \omega). \quad (4.2.2.4b)$$

Incoherent scattering cross sections [(4.2.2.3b), (4.2.2.4b)] refer to one and the same particle (at different times). In particular, plastic crystals (see Section 4.2.4.5) may be studied by means of this

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incoherent scattering. It should be emphasized, however, that for reasons of intensity only disordered crystals with strong incoherent scatterers can be investigated by this technique. In practice, mostly samples with hydrogen atoms were investigated. This topic will not be treated further in this article (see, *e.g.*, Springer, 1972; Lechner & Riekel, 1983). The following considerations are restricted to *coherent* scattering only.

Essentially the same formalism as given by equations (4.2.2.1a)–(4.2.2.4a) may be described by the use of a generalized Patterson function, which is more familiar to crystallographers,

$$P(\mathbf{r}, t) = \int_{\mathbf{r}'} \int_{t'=0}^{\tau} \rho(\mathbf{r}', t') \rho(\mathbf{r}' + \mathbf{r}, t' + t) d\mathbf{r}' dt', \quad (4.2.2.5)$$

where τ denotes the time of observation. The only difference between $G(\mathbf{r}, t)$ and $P(\mathbf{r}, t)$ is the inclusion of the scattering weight (f or b) in $P(\mathbf{r}, t)$. $P(\mathbf{r}, t)$ is an extension of the usual spatial Patterson function $P(\mathbf{r})$.

$$\begin{aligned} P(\mathbf{r}, t) &\leftrightarrow 2\pi S(\mathbf{H}, \omega) \equiv |F(\mathbf{H}, \omega)|^2 \\ &= \int_{\mathbf{r}} \int_t P(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt. \end{aligned} \quad (4.2.2.6)$$

One difficulty arises from neglecting the time of observation. Just as $S(\mathbf{H})$ ($\sim |F(\mathbf{H})|^2$) is always proportional to the scattering volume V , in the frame of a kinematical theory or within Born's first approximation [*cf.* equation (4.2.2.1a)], so $S(\mathbf{H}, \omega)$ [$\sim |F(\mathbf{H}, \omega)|^2$] is proportional to volume *and* observation time. Generally one does not make S proportional to V , but one normalizes S to be independent of τ as $\tau \rightarrow \infty$: $2\pi S = (1/\tau)|F|^2$. Averaging over time τ gives therefore

$$\begin{aligned} S(\mathbf{H}, \omega) &= \frac{1}{2\pi} \int_{\mathbf{r}} \int_t \left\langle \int_{\mathbf{r}'} \rho(\mathbf{r}', t') \rho(\mathbf{r}' + \mathbf{r}, t' + t) d\mathbf{r}' \right\rangle_t \\ &\quad \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt. \end{aligned} \quad (4.2.2.7)$$

Special cases (see, *e.g.*, Cowley, 1981):

(1) *Pure elastic measurement*

$$\begin{aligned} I_e \sim S(\mathbf{H}, 0) &= \int_{\mathbf{r}} \left[\int_t P(\mathbf{r}, t) dt \right] \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}\} d\mathbf{r} \\ &= \left| \sum_j f_j \langle \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}_j(t)\} \rangle_t \right|^2. \end{aligned} \quad (4.2.2.8)$$

In this type of measurement the time-averaged 'structure' is determined:

$$\langle \rho(\mathbf{r}, t) \rangle_t = \int_{\mathbf{H}} |F(\mathbf{H}, 0)| \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}\} d\mathbf{H}.$$

The projection along the time axis in real (Patterson) space gives a section in Fourier space at $\omega = 0$. True elastic measurement is a domain of neutron scattering. For a determination of the time-averaged structure of a statistically disordered crystal dynamical disorder (phonon scattering) may be separated. For liquids or liquid-like systems this kind of scattering technique is rather ineffective as the time-averaging procedure gives a uniform particle distribution only.

(2) *Integration over frequency (or energy)*

$$\begin{aligned} I_{\text{tot}} &\sim \int_{\omega} |F(\mathbf{H}, \omega)|^2 d\omega = \int_{\omega} \int_{\mathbf{r}} \int_t P(\mathbf{r}, t) \\ &\quad \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt d\omega \\ &= \int_{\mathbf{r}} P(\mathbf{r}, 0) \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}\} d\mathbf{r} \end{aligned} \quad (4.2.2.9)$$

(*cf.* properties of δ functions). In such an experiment one determines

the Patterson function for $t = 0$, *i.e.* the instantaneous structure ('snapshot' of the correlation function): a projection in Fourier space along the energy axis gives a section in direct (Patterson) space at $t = 0$. An energy integration is automatically performed in a conventional X-ray diffraction experiment ($|\mathbf{k}| \sim |\mathbf{k}_0|$). One should keep in mind that in a real experiment there is, of course, an average over both the sample volume and the time of observation.

In most practical cases averaging over time is equivalent to averaging over space: the total diffracted intensity may be regarded as the sum of intensities from a large number of independent regions due to the limited coherence of a beam. At any time these regions take all possible configurations. Therefore, this sum of intensities is equivalent to the sum of intensities from any one region at different times:

$$\begin{aligned} \langle I_{\text{tot}} \rangle_t &= \left\langle \sum_j \sum_{j'} f_j f_{j'} \exp\{2\pi i\mathbf{H} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})\} \right\rangle_t \\ &= \sum_{j, j'} f_j f_{j'} \langle \exp\{2\pi i\mathbf{H} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})\} \rangle_t. \end{aligned} \quad (4.2.2.9a)$$

From the basic formulae one also derives the well known results of X-ray or neutron scattering by a periodic arrangement of particles in space [*cf.* equation (4.1.3.2) of Chapter 4.1]:

$$\frac{d\sigma}{d\Omega} = N \frac{(2\pi)^3}{V_c} \sum_{\mathbf{h}} |F(\mathbf{H})|^2 \delta(\mathbf{H} - \mathbf{h}) \quad (4.2.2.10)$$

$$F(\mathbf{H}) = \sum_j f_j(\mathbf{H}) \exp\{-W_j\} \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}_j\}. \quad (4.2.2.11)$$

$F(\mathbf{H})$ denotes the Fourier transform of one cell (structure factor); the f_j 's are assumed to be real.

The evaluation of the intensity expressions (4.2.2.6), (4.2.2.8) or (4.2.2.9), (4.2.2.9a) for a disordered crystal must be performed in terms of statistical relationships between scattering factors and/or atomic positions.

From these basic concepts the generally adopted method in a disorder problem is to try to separate the scattering intensity into two parts, namely one part $\langle \rho \rangle$ from an average periodic structure where formulae (4.2.2.10), (4.2.2.11) apply and a second part $\Delta\rho$ resulting from fluctuations from this average (see, *e.g.*, Schwartz & Cohen, 1977). One may write formally:

$$\rho = \langle \rho \rangle + \Delta\rho, \quad (4.2.2.12a)$$

where $\langle \rho \rangle$ is defined to be time independent and periodic in space and $\langle \Delta\rho \rangle = 0$. Because cross terms $\langle \rho \rangle * \Delta\rho$ vanish by definition, the Patterson function is

$$\begin{aligned} [\langle \rho(\mathbf{r}) \rangle + \Delta\rho(\mathbf{r})] * [\langle \rho(-\mathbf{r}) \rangle + \Delta\rho(-\mathbf{r})] \\ = [\langle \rho(\mathbf{r}) \rangle * \langle \rho(-\mathbf{r}) \rangle] + [\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})]. \end{aligned} \quad (4.2.2.12b)$$

Fourier transformation gives

$$I \approx |\langle F \rangle|^2 + |\Delta F|^2 \quad (4.2.2.13a)$$

$$|\Delta F|^2 = \langle |F|^2 \rangle - |\langle F \rangle|^2. \quad (4.2.2.13b)$$

Since $\langle \rho \rangle$ is periodic, the first term in (4.2.2.13) describes Bragg scattering where $\langle F \rangle$ plays the normal role of a structure factor of one cell of the averaged structure. The second term corresponds to diffuse scattering. In many cases diffuse interferences are centred exactly at the positions of the Bragg reflections. It is then a serious experimental problem to decide whether the observed intensity distribution is Bragg scattering obscured by crystal-size limitations or other scattering phenomena.

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If disordering is time dependent exclusively, $\langle \rho \rangle$ represents the time average, whereas $\langle F \rangle$ gives the pure elastic scattering part [cf. equation (4.2.2.8)] and ΔF refers to inelastic scattering only.

4.2.3. General treatment

4.2.3.1. Qualitative interpretation of diffuse scattering

Any structure analysis of disordered structures should start with a qualitative interpretation of diffuse scattering. This problem may be facilitated with the aid of Fourier transforms and their algebraic operations (see, e.g., Patterson, 1959). For simplicity the following modified notation is used in this section: functions in real space are represented by small letters, e.g. $a(\mathbf{r})$, $b(\mathbf{r})$, . . . except for $F(\mathbf{r})$ and $P(\mathbf{r})$ which are used as general symbols for a structure and the Patterson function, respectively; functions in reciprocal space are given by capital letters $A(\mathbf{H})$, $B(\mathbf{H})$; $\mathbf{r}$ and $\mathbf{H}$ are general vectors in real and reciprocal space, respectively, $Hx + Ky + Lz$ is the scalar product $\mathbf{H} \cdot \mathbf{r}$; $d\mathbf{r}$ and $d\mathbf{H}$ indicate integrations in three dimensions in real and reciprocal space, respectively. Even for X-rays the electron density $\rho(\mathbf{r})$ will generally be replaced by the scattering potential $a(\mathbf{r})$. Consequently, anomalous contributions to scattering may be included if complex functions $a(\mathbf{r})$ are admitted. In the neutron case $a(\mathbf{r})$ refers to a quasi-potential. Using this notation we obtain the scattered amplitude and phase $A(\mathbf{H}) \exp i\varphi$

$$A(\mathbf{H}) = \int_{\mathbf{r}} a(\mathbf{r}) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}\} d\mathbf{r} \quad (4.2.3.1a)$$

$$a(\mathbf{r}) = \int_{\mathbf{H}} A(\mathbf{H}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{r}\} d\mathbf{H} \quad (4.2.3.1b)$$

(constant factors are omitted).

$a(\mathbf{r})$ and $A(\mathbf{H})$ are reversibly and uniquely determined by Fourier transformation. Consequently equations (4.2.3.1) may simply be replaced by $a(\mathbf{r}) \leftrightarrow A(\mathbf{H})$, where the double-headed arrow represents the two integrations given by (4.2.3.1) and means: $A(\mathbf{H})$ is the Fourier transform of $a(\mathbf{r})$, and *vice versa*. The following relations may easily be derived from (4.2.3.1):

$$a(\mathbf{r}) + b(\mathbf{r}) \leftrightarrow A(\mathbf{H}) + B(\mathbf{H}) \quad (\text{law of addition}) \quad (4.2.3.2)$$

$$\beta a(\mathbf{r}) \leftrightarrow \beta A(\mathbf{H}) \quad (\text{law of scalar multiplication}) \quad (4.2.3.3)$$

(β = scalar quantity).

On the other hand, the multiplication of two functions does not yield a relation of similar symmetrical simplicity:

$$\begin{aligned} a(\mathbf{r})b(\mathbf{r}) &\leftrightarrow \int A(\mathbf{H}')B(\mathbf{H}-\mathbf{H}') d\mathbf{H}' \\ &= A(\mathbf{H}) * B(\mathbf{H}) \end{aligned} \quad (4.2.3.4a)$$

$$\begin{aligned} a(\mathbf{r}) * b(\mathbf{r}) &= \int a(\mathbf{r}')b(\mathbf{r}-\mathbf{r}') d\mathbf{r}' \\ &\leftrightarrow A(\mathbf{H})B(\mathbf{H}) \end{aligned} \quad (4.2.3.4b)$$

(laws of convolution and multiplication).

Since $a(\mathbf{r})b(\mathbf{r}) = b(\mathbf{r})a(\mathbf{r})$:

$$\int A(\mathbf{H}')B(\mathbf{H}-\mathbf{H}') d\mathbf{H}' = \int B(\mathbf{H}')A(\mathbf{H}-\mathbf{H}') d\mathbf{H}'$$

and *vice versa*. The convolution operation is commutative in either space.

For simplicity the symbol $a(\mathbf{r}) * b(\mathbf{r})$ instead of the complete convolution integral is used. The distribution law $a(b+c) = ab+ac$ is valid for the convolution as well:

$$a(\mathbf{r}) * [b(\mathbf{r}) + c(\mathbf{r})] = a(\mathbf{r}) * b(\mathbf{r}) + a(\mathbf{r}) * c(\mathbf{r}). \quad (4.2.3.5)$$

The associative law of multiplication does not hold if mixed products (convolution and multiplication) are used:

$$a(\mathbf{r}) * [b(\mathbf{r})c(\mathbf{r})] \neq [a(\mathbf{r}) * b(\mathbf{r})]c(\mathbf{r}). \quad (4.2.3.6)$$

From equations (4.2.3.1) one has:

$$\begin{aligned} a(\mathbf{r} - \mathbf{r}_0) &\leftrightarrow A(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_0) \\ A(\mathbf{H} - \mathbf{H}_0) &\leftrightarrow a(\mathbf{r}) \exp(-2\pi i \mathbf{H}_0 \cdot \mathbf{r}) \end{aligned} \quad (4.2.3.7)$$

(law of displacements).

Since symmetry operations are well known to crystallographers in reciprocal space also, the law of inversion is mentioned here only:

$$a(-\mathbf{r}) \leftrightarrow A(-\mathbf{H}). \quad (4.2.3.8)$$

Consequently, if $a(\mathbf{r}) = a(-\mathbf{r})$, then $A(\mathbf{H}) = A(-\mathbf{H})$. In order to calculate the intensity the complex conjugate $A^+(\mathbf{H})$ is needed:

$$a^+(\mathbf{r}) \leftrightarrow A^+(-\mathbf{H}) \quad (4.2.3.9a)$$

$$a^+(-\mathbf{r}) \leftrightarrow A^+(\mathbf{H}). \quad (4.2.3.9b)$$

Equations (4.2.3.9) yield the relationship $A^+(-\mathbf{H}) = A(\mathbf{H})$ ('Friedel's law') if $a(\mathbf{r})$ is a *real* function. The multiplication of a function with its conjugate is given by:

$$a(\mathbf{r}) * a^+(-\mathbf{r}) \leftrightarrow |A(\mathbf{H})|^2,$$

with

$$a(\mathbf{r}) * a^+(-\mathbf{r}) = \int a(\mathbf{r}')a(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = P(\mathbf{r}). \quad (4.2.3.10)$$

Note that $P(\mathbf{r}) = P(-\mathbf{r})$ is not valid if $a(\mathbf{r})$ is complex. Consequently $|A(-\mathbf{H})|^2 \neq |A(\mathbf{H})|^2$. This is shown by evaluating $A(-\mathbf{H})A^+(-\mathbf{H})$

$$A(-\mathbf{H})A^+(-\mathbf{H}) \leftrightarrow a(-\mathbf{r}) * a^+(\mathbf{r}) = P(-\mathbf{r}). \quad (4.2.3.11)$$

Equation (4.2.3.11) is very useful for the determination of the contribution of anomalous scattering to diffuse reflections.

Most of the diffuse diffraction phenomena observed may be interpreted qualitatively or even semi-quantitatively in a very simple manner using a limited number of important Fourier transforms, given below.

4.2.3.1.1. Fourier transforms

(1) Normalized Gaussian function

$$(\pi^{3/2}\alpha\beta\gamma)^{-1} \exp\{-(x/\alpha)^2 - (y/\beta)^2 - (z/\gamma)^2\}. \quad (4.2.3.12)$$

This plays an important role in statistics. Its Fourier transform is again a Gaussian:

$$\exp\{-\pi^2(\alpha^2 H^2 + \beta^2 K^2 + \gamma^2 L^2)\}. \quad (4.2.3.12a)$$

The three parameters α , β , γ determine the width of the curve. Small values of α , β , γ represent a broad maximum in reciprocal space but a narrow one in real space, and *vice versa*. The constant has been chosen such that the integral of the Gaussian is unity in real space. The product of two Gaussians in reciprocal space

$$\begin{aligned} &\exp\{-\pi^2(\alpha_1^2 H^2 + \beta_1^2 K^2 + \gamma_1^2 L^2)\} \\ &\times \exp\{-\pi^2(\alpha_2^2 H^2 + \beta_2^2 K^2 + \gamma_2^2 L^2)\} \\ &= \exp\{-\pi^2[(\alpha_1^2 + \alpha_2^2)H^2 + (\beta_1^2 + \beta_2^2)K^2 \\ &\quad + (\gamma_1^2 + \gamma_2^2)L^2]\} \end{aligned} \quad (4.2.3.12b)$$

again represents a Gaussian of the same type, but with a sharper profile. Consequently its Fourier transform given by the convolution of the transforms of the two Gaussians is itself a Gaussian with a broader maximum. It may be concluded from this discussion that the Gaussian with $\alpha, \beta, \gamma \rightarrow 0$ is a δ function in real space, and its Fourier transform is unity in reciprocal space. The convolution of two δ functions is again a δ function.

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(2) Lattices

Lattices in real and reciprocal space may be described by δ functions

$$l(\mathbf{r}) = \sum_{\mathbf{n}} \delta(\mathbf{r} - \mathbf{n})$$

and

$$L(\mathbf{H}) = \sum_{\mathbf{h}} \delta(\mathbf{H} - \mathbf{h}),$$

where $\mathbf{n}$, $\mathbf{h}$ represent the components of the displacement vectors in real and reciprocal space, respectively. The Fourier transforms of lattices with orthogonal basis vectors of unit length and an infinite number of points in all three dimensions correspond to each other. In the following the relation $l(\mathbf{r}) \leftrightarrow L(\mathbf{H})$ is used in this generalized sense.

The Fourier transforms of *finite* lattices are given by

$$\frac{\sin \pi N_1 H}{\sin \pi H} \frac{\sin \pi N_2 K}{\sin \pi K} \frac{\sin \pi N_3 L}{\sin \pi L}, \quad (4.2.3.13)$$

which is a periodic function in reciprocal space, but, strictly speaking, non-periodic in real space. It should be pointed out that the correspondence of lattices in either space is valid only if the origin coincides with a δ function. This fact may easily be understood by applying the law of displacement given in equation (4.2.3.7).

(3) Box functions

The Fourier transform of a box function $b(\mathbf{r})$ with unit height is:

$$b(\mathbf{r}) \leftrightarrow \frac{\sin \pi \alpha H}{\pi H} \frac{\sin \pi \beta K}{\pi K} \frac{\sin \pi \gamma L}{\pi L}. \quad (4.2.3.14)$$

α , β , γ describe its extension in the three dimensions. This function is real as long as the centre of symmetry is placed at the origin, otherwise the law of displacement has to be used. The convolution of the box function is needed for the calculation of intensities:

$$t(\mathbf{r}) = b(\mathbf{r}) * b(-\mathbf{r}) \\ \leftrightarrow \left(\frac{\sin \pi \alpha H}{\pi H} \right)^2 \left(\frac{\sin \pi \beta K}{\pi K} \right)^2 \left(\frac{\sin \pi \gamma L}{\pi L} \right)^2. \quad (4.2.3.15)$$

$t(\mathbf{r})$ is a generalized three-dimensional 'pyramid' of doubled basal length when compared with the corresponding length of the box function. The top of the pyramid has a height given by the number of unit cells covered by the box function. Obviously, the box function generates a particle size in real space by multiplying the infinite lattice $l(\mathbf{r})$ by $b(\mathbf{r})$. Fourier transformation yields a particle-size effect well known in diffraction. Correspondingly, the termination effect of a Fourier synthesis is caused by multiplication by a box function in reciprocal space, which causes a broadening of maxima in real space.

(4) Convolutions

It is often very useful to elucidate the convolution given in equations (4.2.3.4) by introducing the corresponding pictures in real or reciprocal space. Since $1 \cdot f(\mathbf{r}) = f(\mathbf{r})$, $\delta(\mathbf{H}) * F(\mathbf{H}) = F(\mathbf{H})$ the convolution with a δ function must result in an identical picture of the second function, although the function is used as $f(-\mathbf{r})$ in the integrals of equations (4.2.3.4), $f(\mathbf{r} - \mathbf{r}')$ with $\mathbf{r}'$ as variable in the integral of convolution. The convolution with $f(-\mathbf{r})$ brings the integral into the form

$$\int f(\mathbf{r}') f(\mathbf{r}' - \mathbf{r}) d\mathbf{r}', \quad (4.2.3.16)$$

which is known as the Patterson function (or self- or auto-

convolution) and represents the generalized Patterson function including anomalous scattering [cf. equation (4.2.3.10)].

The change of the variable in the convolution integral may sometimes lead to confusion if certain operations are applied to the arguments of the functions entering the integral. Hence, it seems to be useful to mention the invariance of the convolution integral with respect to a change of sign, or a displacement, respectively, if applied to $\mathbf{r}'$ in both functions. Consequently, the convolution with the inverted function $a(\mathbf{r}) * b(-\mathbf{r})$ may be determined as follows:

$$b'(\mathbf{r}) = b(-\mathbf{r}) \\ a(\mathbf{r}) * b(-\mathbf{r}) = a(\mathbf{r}) * b'(\mathbf{r}) = \int a(\mathbf{r}') b'(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \\ = \int a(\mathbf{r}') b(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = P'(\mathbf{r}). \quad (4.2.3.17)$$

This equation means that the second function is displaced into the positive direction by $\mathbf{r}$, then multiplied by the first function and integrated. In the original meaning of the convolution the operation represents a displacement of the second function into the positive direction and an inversion at the displaced origin before multiplication and subsequent integration. On comparing both operations it may be concluded that $P'(\mathbf{r}) \neq P'(-\mathbf{r})$ if the second function is acentric. For real functions both have to be acentric. In a similar way it may be shown that the convolution of

$$a(\mathbf{r} - \mathbf{m}) * b(\mathbf{r} - \mathbf{m}') = \int_{\mathbf{r}'} a(\mathbf{r}' - \mathbf{m}) b(\mathbf{r} - \mathbf{m}' - \mathbf{r}') d\mathbf{r}' \\ = \int_{\mathbf{r}''} a(\mathbf{r}'') b(\mathbf{r} - \mathbf{m}' - \mathbf{m} - \mathbf{r}'') d\mathbf{r}'' \quad (4.2.3.18)$$

Equation (4.2.3.18) indicates a displacement by $\mathbf{m}' + \mathbf{m}$ with respect to the convolution of the undisplaced functions. Consequently

$$\delta(\mathbf{r} - \mathbf{m}) * \delta(\mathbf{r} - \mathbf{m}') = \delta(\mathbf{r} - \mathbf{m} - \mathbf{m}'). \quad (4.2.3.19)$$

Obviously, the commutative law of convolution is obeyed; on the other hand, the convolution with the inverted function yields

$$\delta(\mathbf{r} - \mathbf{m}' + \mathbf{m}),$$

indicating that the commutative law (interchange of $\mathbf{m}$ and $\mathbf{m}'$) is violated because of the different signs of $\mathbf{m}$ and $\mathbf{m}'$.

The effectiveness of the method outlined above may be greatly improved by introducing further Fourier transforms of useful functions in real and reciprocal space (Patterson, 1959).

4.2.3.1.2. Applications

(1) Clusters in a periodic lattice (low concentrations)

The exsolution of clusters of equal sizes is considered. The lattice of the host is undistorted and the clusters have the same lattice but a different structure. A schematic drawing is shown in Fig. 4.2.3.1. Two different structures are introduced by

$$F_1(\mathbf{r}) = \sum_{\nu} \delta(\mathbf{r} - \mathbf{r}_{\nu}) * F_{\nu}(\mathbf{r}) \\ F_2(\mathbf{r}) = \sum_{\mu} \delta(\mathbf{r} - \mathbf{r}_{\mu}) * F_{\mu}(\mathbf{r}).$$

Their Fourier transforms are the structure factors $F_1(\mathbf{H})$, $F_2(\mathbf{H})$. The bold lines in Fig. 4.2.3.1 indicate the clusters, which may be represented by box functions $b(\mathbf{r})$ in the simplest case. It should be pointed out, however, that a more complicated shape means nothing other than a replacement of $b(\mathbf{r})$ by another shape function $b'(\mathbf{r})$ and its Fourier transform $B'(\mathbf{H})$. The distribution of clusters is represented by

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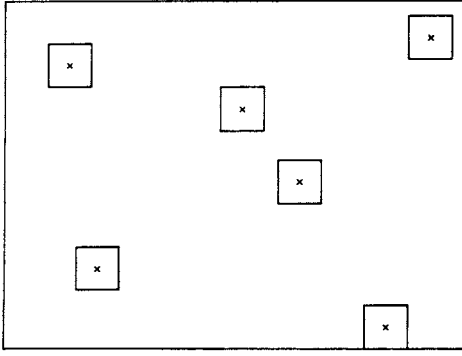


Fig. 4.2.3.1. Model of the two-dimensional distribution of point defects, causing changes in the surroundings.

$$d(\mathbf{r}) = \sum_{\mathbf{m}} \delta(\mathbf{r} - \mathbf{m}),$$

where $\mathbf{m}$ refers to the centres (crosses in Fig. 4.2.3.1) of the box functions. The problem is therefore defined by:

$$l(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b(\mathbf{r})] * [F_2(\mathbf{r}) - F_1(\mathbf{r})] * d(\mathbf{r}). \quad (4.2.3.20a)$$

The incorrect addition of $F_1(\mathbf{r})$ to the areas of clusters $F_2(\mathbf{r})$ is compensated by subtracting the same contribution from the second term in equation (4.2.3.20a). In order to determine the diffuse scattering the Fourier transformation of (4.2.3.20a) is performed:

$$L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}). \quad (4.2.3.20b)$$

The intensity is given by

$$|L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2. \quad (4.2.3.20c)$$

Evaluation of equation (4.2.3.20c) yields three terms (c.c. means complex conjugate):

- (i) $|L(\mathbf{H})F_1(\mathbf{H})|^2$
- (ii) $\{[L(\mathbf{H})F_1(\mathbf{H})][L(\mathbf{H}) * B(\mathbf{H})] \times [F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}) + \text{c.c.}\}$
- (iii) $|[L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2$.

The first two terms represent modulated lattices [multiplication of $L(\mathbf{H})$ by $F_1(\mathbf{H})$]. Consequently, they cannot contribute to diffuse scattering which is completely determined by the third term. Fourier transformation of this term gives $[l(\mathbf{r}) = l(-\mathbf{r}); b(\mathbf{r}) = b(-\mathbf{r}); \Delta F = F_2 - F_1]$:

$$\begin{aligned} & [l(\mathbf{r})b(\mathbf{r})] * \Delta F(\mathbf{r}) * d(\mathbf{r}) * [l(\mathbf{r})b(\mathbf{r})] * \Delta F^+(-\mathbf{r}) * d(-\mathbf{r}) \\ &= [l(\mathbf{r})b(\mathbf{r})] * [l(\mathbf{r})b(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}) \\ &= [l(\mathbf{r})t(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}). \end{aligned} \quad (4.2.3.21a)$$

According to equation (4.2.3.15) and its subsequent discussion the convolution of the two expressions in square brackets was replaced by $l(\mathbf{r})t(\mathbf{r})$, where $t(\mathbf{r})$ represents the 'pyramid' of n -fold height discussed above and n is the number of unit cells within $b(\mathbf{r})$. $d(\mathbf{r}) * d(-\mathbf{r})$ is the Patterson function of the distribution function $d(\mathbf{r})$. Its usefulness may be recognized by considering the two possible extreme solutions, namely the random and the strictly periodic distribution.

If no fluctuations of domain sizes are admitted the minimum distance between two neighbouring domains is equal to the length of the domain in the corresponding direction. This means that the distribution function cannot be completely random. In one

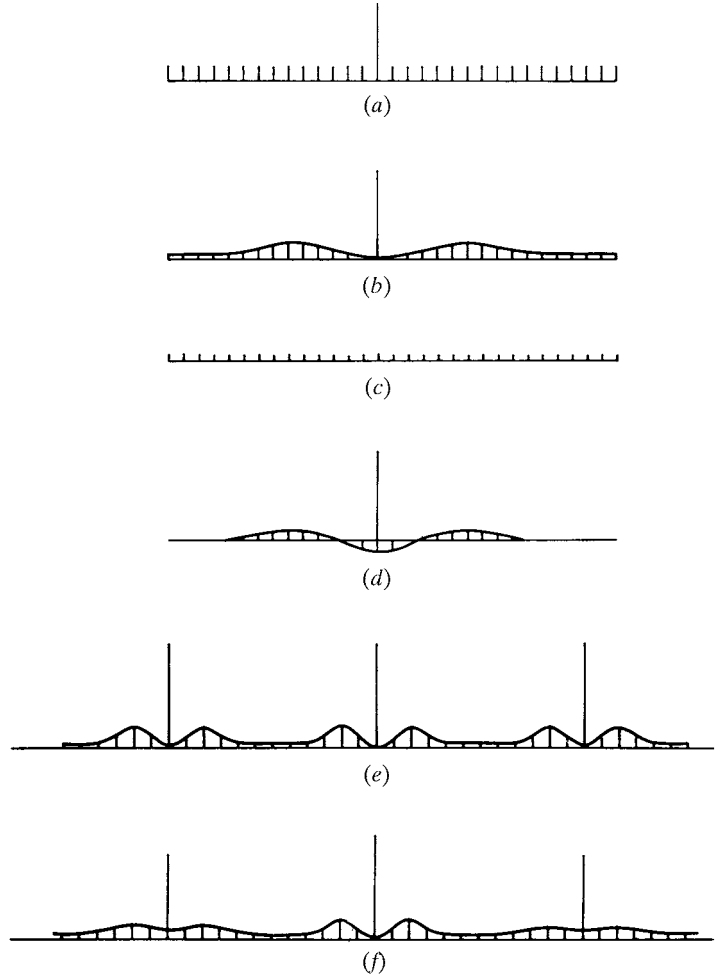


Fig. 4.2.3.2. One-dimensional Patterson functions of various point-defect distributions: (a) random distribution; (b) influence of finite volume of defects on the distribution function; (c), (d) decomposition of (b) into a periodic (c) and a convergent (d) part; (e) Fourier transform of (c) + (d); (f) changes of (e), if the centres of the defects show major deviations from the origins of the lattice.

dimension the solution of a random distribution of particles of a given size on a finite length shows that the distribution functions exhibit periodicities depending on the average free volume of one particle (Zernike & Prins, 1927). Although the problem is more complicated in three dimensions, there should be no fundamental difference in the exact solutions.

On the other hand, it may be shown that the convolution of a pseudo-random distribution may be obtained if the average free volume is large. This is shown in Fig. 4.2.3.2(a) for the particular case of a cluster smaller than one unit cell. A strictly periodic distribution function (superstructure) may result, however, if the volume of the domain and the average free volume are equal. Obviously, the practical solution for the self-convolution of the distribution function (= Patterson function) lies somewhere in between, as shown in Fig. 4.2.3.2(b). If a harmonic periodicity damped by a Gaussian is assumed, this self-convolution of the distribution in real space may be considered to consist of two parts, as shown in Figs. 4.2.3.2(c), (d). Note that the two different solutions result in completely different diffraction patterns:

(i) The geometrically perfect lattice extends to distances which are large when compared with the correlation length of the distribution function. Then the Patterson function of the distribution function concentrates at the positions of the basic lattice, which is

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given by multiplication by the lattice $l(\mathbf{r})$. The corresponding convolution in reciprocal space gives the same contribution to all Bragg reflections (Fig. 4.2.3.2e).

(ii) There is no perfect lattice geometry. In this case a continuous Patterson function results. Fourier transformation yields an influence which is now restricted primarily to the reflection 000, i.e. to the low-angle diffraction range.

Figs. 4.2.3.2(e), (f) show the different diffraction patterns of the diffuse scattering which is concentrated around the Bragg maxima. Although the discussion of the diffuse scattering was restricted to the case of identical domains, the introduction of a distribution of domain sizes does not influence the diffraction pattern essentially, as long as the fluctuation of sizes is small compared with the average volume of domain sizes and no strong correlation exists between domains of any size (size-independent random distribution).

The complete qualitative discussion of the diffraction pattern may be made by investigating the Fourier transform of (4.2.3.21a):

$$[L(\mathbf{H}) * T(\mathbf{H})] |\Delta F(\mathbf{H})|^2 |D(\mathbf{H})|^2. \quad (4.2.3.21b)$$

The first factor in (4.2.3.21b) describes the particle-size effect of a domain containing the influence of a surrounding strain field and the new structure of the domains precipitated from the bulk. $D(\mathbf{H})$ has its characteristic variation near the Bragg peaks (Figs. 4.2.3.2e, f), and is less important in between. For structure determination of domains, intensities near the Bragg peaks should be avoided. Note that equation (4.2.3.21b) may be used for measurements applying anomalous scattering in both the centric and the acentric case.

Solution of the diffraction problem. In equation (4.2.3.21b) $\Delta F(\mathbf{H})$ is replaced by its average

$$\langle \Delta F(\mathbf{H}) \rangle = \sum_{\mu} p_{\mu} \Delta F_{\mu}(\mathbf{H}),$$

where p_{μ} represents the *a priori* probability of a domain of type μ . This replacement becomes increasingly important if small clusters (domains) have to be considered. Applications of the formulae to Guinier–Preston zones are given by Guinier (1942) and Gerold (1954); a similar application to clusters of vacancies in spinels with an excess in Al_2O_3 was outlined by Jagodzinski & Haefner (1967).

Although refinement procedures are possible in principle, the number of parameters entering the diffraction problem becomes increasingly large if more clusters or domains (different sizes) have to be introduced. Another difficulty results from the large number of diffraction data which must be collected to perform a reliable structure determination. There is no need to calculate the first two terms in equation (4.2.3.20c) which do contribute to the sharp Bragg peaks only, because their intensity is simply described by the averaged structure factor $|\langle F(\mathbf{H}) \rangle|^2$. These terms may therefore be replaced by

$$|L(\mathbf{H})|^2 |\langle F(\mathbf{H}) \rangle|^2$$

with

$$|\langle F(\mathbf{H}) \rangle|^2 = \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2 \quad (4.2.3.21c)$$

where p_{μ} is the *a priori* probability of the structure factor $F_{\mu}(\mathbf{H})$. It should be emphasized here that (4.2.3.21c) is independent of the distribution function $d(\mathbf{r})$, or its Fourier transform $D(\mathbf{H})$.

(2) Periodic lamellar domains

Here $d(\mathbf{r})$ is one-dimensional, and can easily be calculated: a periodic array of two types of lamellae having the same basic lattice $l(\mathbf{r})$, but a different structure, is shown in Fig. 4.2.3.3. The size of the

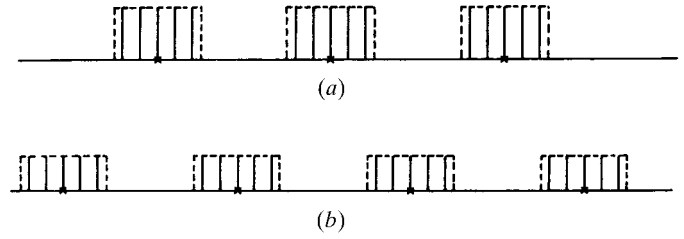


Fig. 4.2.3.3. Periodic array of domains consisting of two different atoms, represented by different heights. (a) Distribution of domain type 1, (b) distribution of domain type 2.

two types of lamellae may be different. The structure of the first domain type is given by a convolution with $F_1(\mathbf{r})$ (Fig. 4.2.3.3a) and that of the second domain type by $F_2(\mathbf{r})$ (Fig. 4.2.3.3b). Introducing $\langle F(\mathbf{r}) \rangle$ and $\Delta F(\mathbf{r})$, the structure in real space is described by:

$$\begin{aligned} & [l(\mathbf{r})b_1(\mathbf{r})] * d(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b_2(\mathbf{r})] * d(\mathbf{r}) * F_2(\mathbf{r}) \\ &= \{ [l(\mathbf{r})b_1(\mathbf{r}) + l(\mathbf{r})b_2(\mathbf{r})] * d(\mathbf{r}) \} * \langle F(\mathbf{r}) \rangle \\ &+ [l(\mathbf{r})b_1(\mathbf{r}) - l(\mathbf{r})b_2(\mathbf{r})] * d(\mathbf{r}) * \Delta F(\mathbf{r}). \end{aligned} \quad (4.2.3.22a)$$

Obviously the first term in curly brackets in equation (4.2.3.22a) is no more than $l(\mathbf{r})$ itself and $d(\mathbf{r})$ is strictly periodic. $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$ are box functions, mutually displaced by $\pm(n_1 + n_2)/2$ unit cells in the $\mathbf{c}$ direction [n_1, n_2 are the numbers of cells covered by $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$, respectively].

Fourier transformation of equation (4.2.3.22a) yields

$$L(\mathbf{H}) \langle F(\mathbf{H}) \rangle + \{ L(\mathbf{H}) * [B_1(\mathbf{H}) - B_2(\mathbf{H})] \} D(\mathbf{H}) \Delta F(\mathbf{H}). \quad (4.2.3.22b)$$

The first term in equation (4.2.3.22b) gives the normal sharp reflections of the average structure, while the second describes superlattice reflections [sublattice $L_s(\mathbf{H}) = D(\mathbf{H})$ in reciprocal space], multiplied by $\Delta F(\mathbf{H})$ and another 'structure factor' generated by the convolution of the reciprocal lattice $L(\mathbf{h})$ with $[B_1(\mathbf{H}) - B_2(\mathbf{H})]$ (cf. Fig. 4.2.3.3b). Since the centres of $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$ are mutually displaced, the expression in square brackets includes extinctions if $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$ represent boxes equal in size. These extinctions are discussed below. It should be pointed out that $L_s(\mathbf{H})$ and its Fourier transform $l_s(\mathbf{r})$ are commensurate with the basic lattice, as long as no change of the translation vector at the interface of the lamellae occurs. Obviously, $L_s(\mathbf{H})$ becomes incommensurate in the general case of a slightly distorted interface. Considerations of this kind play an important role in the discussion of modulated structures.

No assumption has been made so far for the position of the interface. This point is meaningless only in the case of a strictly periodic array of domains (no diffuse scattering). Therefore it seems to be convenient to introduce two basic vectors parallel to the interface in real space which demand a new reciprocal vector perpendicular to them defined by $(\mathbf{a}' \times \mathbf{b}')/V'$, where $\mathbf{a}', \mathbf{b}'$ are the new basic vectors and V' is the volume of the supercell. As long as the new basic vectors are commensurate with the original lattice, the direction of the new reciprocal vector $\mathbf{c}^*$, perpendicular to $\mathbf{a}', \mathbf{b}'$, passes through the Bragg points of the original reciprocal lattice and the reciprocal lattice of the superlattice remains commensurate as long as V' is a multiple of V ($V' = mV$, $m = \text{integer}$). Since the direction of $\mathbf{c}$ is arbitrary to some extent, there is no clear rule about the assignment of superlattice reflections to the original Bragg peaks. This problem becomes very important if extinction rules of the basic lattice and the superlattice have to be described together.

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Example. We consider a b.c.c. structure with two kinds of atoms (1, 2) with a strong tendency towards superstructure formation (CsCl-type ordering). According to equations (4.2.3.21b,c) and (4.2.3.22b) we obtain, in the case of negligible short-range order, the following expressions for sharp and diffuse scattering (c = concentration):

$$I_s = |cF_1(\mathbf{H}) + (1-c)F_2(\mathbf{H})|^2 \quad \text{for } h+k+l=2n$$

$$I_d = c(1-c)|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2 \quad \text{elsewhere.}$$

With increasing short-range order the sharp reflections remain essentially unaffected, while the diffuse ones concentrate into diffuse maxima at $\mathbf{h}$ with $h+k+l=2n+1$. This process is treated more extensively below. As long as the domains exhibit no clear interface, it is useful to describe the ordering process with the two possible cell occupations of a pair of different atoms; then contributions of equal pairs may be neglected with increasing short-range order. Now the two configurations 1, 2 and 2, 1 may be given with the aid of the translation $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$. Hence the two structure factors are

$$F_1 \text{ and } F_2 = F_1 \exp\{\pi i(h+k+l)\}.$$

Since both structure factors occur with the same probability, the equations for sharp and diffuse reflections become

$$I_s = \frac{1}{4}|F_1(\mathbf{H})|^2[1 + \exp\{\pi i(h+k+l)\}]^2$$

$$I_d = \frac{1}{4}|F_1(\mathbf{H})|^2[1 - \exp\{\pi i(h+k+l)\}]^2.$$

It is well recognized that no sharp reflections may occur for $h+k+l=2n+1$, and the same holds for the diffuse scattering if $h+k+l=2n$. This extinction rule for diffuse scattering is due to suppression of contributions of equal pairs. The situation becomes different for lamellar structures. Let us first consider the case of lamellae parallel to (100). The ordered structure is formed by an alternating sequence of monoatomic layers, consisting of atoms of types 1 and 2, respectively. Hence, the interface between two neighbouring domains is a pair of equal layers 1,1 or 2,2 which are not equivalent. Each interface of type 1 (2) may be described by an inserted layer of type 1 (2), and the chemical composition differs from 1:1 if one type of interface is preferred. Since the contribution of equal pairs has been neglected in deriving the extinction rule of diffuse scattering (see above) this rule is no longer valid. Because of the lamellar structure the diffuse intensity is concentrated into streaks parallel to (00 l). Starting from the diffuse maximum (010), the diffuse streak passes over the sharp reflection 011 to the next diffuse one 012 *etc.*, and the extinction rule is violated as long as one of the two interfaces is predominant. Hence, the position of the interface determines the extinction rule in this orientation.

A completely different behaviour is observed for lamellae parallel to (110). This structure is described by a sequence of equal layers containing 1 and 2 atoms. The interface between two domains (exchange of the two different atoms) is now nothing other than the displacement parallel to the layer of the original one in the ordered sequence. Calculation of the two structure factors would involve displacements $\pm\frac{1}{2}(\mathbf{a} - \mathbf{b})$. Starting from the diffuse reflection 001, the diffuse streak parallel to ($HH0$) passes through (111), (221), (331), . . . ; *i.e.* through diffuse reflections only. On the other hand, rows ($HH2$) going through (002), (112), (222), . . . do not show any diffuse scattering. Hence, we have a new extinction rule for diffuse scattering originating from the orientation of interfaces. This fact is rather important in structure determination. For various reasons, lamellar interfaces show a strong tendency towards a periodic arrangement. In diffraction the diffuse streak then concentrates into more or less sharp superstructure reflections. These are not observed on those rows of the reciprocal lattice which are free from diffuse scattering. The same extinction law is not valid

in the case of the (100) orientation of the interfaces. Summarizing, we may state that three types of extinction rules have to be considered:

- (a) Normal extinctions for the average structure.
- (b) Extinction of the difference structure factors for diffuse scattering.
- (c) Extinctions caused by the ordering process itself.

(3) *Lamellar system with two different structures, where $\langle F(\mathbf{H}) \rangle$ and $\Delta F(\mathbf{H})$ do not obey any systematic extinction law*

The convolution of the second term in equation (4.2.3.22b) (*cf.* Fig. 4.2.3.3) may be represented by a convolution of the Fourier transform of a box function $B_1(\mathbf{H})$ with the reciprocal superlattice. Since $B_1(\mathbf{H})$ is given by $\sin(\pi m_s H)/(\pi H)$, where m_s = number of cells of the supercell, the reader might believe that the result of the convolution may easily be determined quantitatively: this assumption is not correct because of the slow convergence of $B_1(\mathbf{H})$. The systematic coincidences of the maxima, or minima, of $B_1(\mathbf{H})$ with the points of the superlattice in the commensurate case cause considerable changes in intensities especially in the case of a small thickness of the domains. For this reason an accurate calculation of the amplitudes of satellites is necessary (Jagodzinski & Penzkofer, 1981):

- (a) Bragg peaks of the basic lattice

$$I \sim |\langle F(\mathbf{H}) \rangle|^2; \quad (4.2.3.23a)$$

- (b) satellites: $\nu = 2n$ (n = integer except 0)

$$I \sim |2 \sin \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2; \quad (4.2.3.23b)$$

- (c) satellites: $\nu = 2n + 1$

$$I \sim |2 \cos \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2. \quad (4.2.3.23c)$$

ν = order of satellites, $C = \frac{1}{2}(N_1 - N_2)/(N_1 + N_2)$, N_1, N_2 = number of cells within $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$, respectively.

Obviously, there is again a systematic extinction rule for even satellites if $N_1 = N_2$.

Equation (4.2.3.23b) indicates an increasing intensity of first even-order satellites with increasing C . Intensities of first even and odd orders become nearly equal if $N_2 \simeq \frac{1}{2}N_1$. Smaller values of N_2 result in a decrease of intensities of both even and odd orders (no satellites if $N_2 = 0$). The denominators in equations (4.2.3.23b,c) indicate a decrease in intensity with increasing order of satellites. The quantitative behaviour of the intensities needs a more detailed discussion of the numerator in equations (4.2.3.23a,b) with increasing order of satellites. Obviously, there are two kinds of extinction rules to be taken into account: systematic absences for the various orders of satellites, and the usual extinctions for $\langle F(\mathbf{H}) \rangle$ and $\Delta F(\mathbf{H})$. Both have to be considered separately in order to arrive at reliable conclusions. This different behaviour of the superlattice reflections (satellites) and that of the basic lattice may well be represented by a multi-dimensional group-theoretical representation as has been shown by de Wolff (1974), Janner & Janssen (1980), de Wolff *et al.* (1981), and others.

(4) *Non-periodic system (qualitative discussion)*

Following the discussion of equations (4.2.3.21) one may conclude that the fluctuations of domain sizes cause a broadening of satellites, if the periodic distribution function has to be replaced by a statistical one. In this case the broadening effect increases with the order of satellites. The intensities, however, are completely determined by the distribution function and can be estimated by calculating the intensities of the perfectly ordered array, as approximated by the distribution function.

A careful check of $\langle F(\mathbf{H}) \rangle$ and $\Delta F(\mathbf{H})$ in equations (4.2.3.23) shows that the position of the interface plays an important role for

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the intensities of satellites. Since this position determines the origin of the unit cells in the sublattice, we have to choose this origin for the calculation of $F(\mathbf{H})$ and $\Delta F(\mathbf{H})$. This involves phase factors which are meaningless for integral values of $\mathbf{H}$, (i) if the average $\langle F(\mathbf{H}) \rangle$ refers to different structures with arbitrary origin, or (ii), which is important for practical cases, where no change occurs in the origin of related structures for neighbouring domains which are bound to an origin by general convention (e.g. a centre of symmetry). This statement is no longer true for non-integral values of $\mathbf{H}$ which are needed for the calculation of intensities of satellites. The intensities of satellites become different for different positions of the interface, even in the absence of a relative displacement between neighbouring domains with respect to an origin by convention. This statement may be extended to non-periodic distribution functions. Consequently, one may conclude that the study of diffuse scattering yields information on the interfacial scattering. For slightly different structures at the interface two cases are important:

- (i) the two structures are related by symmetry (e.g. by a twin law); and
- (ii) the difference between the two structures cannot be described by a symmetry operation.

In structures based on the same sublattice, the first case seems to be more important, because two different structures with the same sublattice are improbable. In the first case there is an identical sublattice if the symmetry operation in question does not influence the plane of intergrowth, e.g. a mirror plane should coincide with the plane of intergrowth. Since we have two inequivalent mirror planes in any sublattice, there are two such planes. It is assumed that no more than one unit cell of both domains at the interface has a slightly different structure without any change of geometry of the unit cell, and the number of unit cells is equal because of the equivalence of both domain structures (twins). Fig. 4.2.3.4(a) shows a picture of this model; Figs. 4.2.3.4(b), (c) explain that this structure may be described by two contributions:

- (i) The first term is already given by equation (4.2.3.23) for $N_1 = N_2$, consequently odd orders of satellites only are observed.
- (ii) The second term may be described by a superlattice containing $2N_1$ cells with an alternating arrangement of interfaces, correlated by the relevant plane of symmetry.

In real space the second term may be constructed by convolution of the one-dimensional superlattice with two difference structures displaced by $\mp N_1/2$ units of the sublattice; its Fourier transformation yields

$$L_s(\mathbf{H}) \{ \Delta F_i(\mathbf{H}) \exp\{2\pi i N_1 H/2\} + \Delta F'_i(\mathbf{H}) \exp\{-2\pi i N_1 H/2\} \}, \quad (4.2.3.24)$$

where $\Delta F_i, \Delta F'_i$ correspond to the Fourier transforms of the contributions shown in Fig. 4.2.3.4(c). Since $H = \nu/N_1$ there are alternating contributions to the ν th satellite, which may be calculated more accurately by taking into account the symmetry operations. The important difference between equations (4.2.3.23) and (4.2.3.24) is the missing decrease in intensity with increasing order of satellites. Consequently one may conclude that the interface contributes to low- and high-order satellites as well, but its influence prevails for high-order satellites. Similar considerations may be made for two- and three-dimensional distributions of domains. A great variety of extinction rules may be found depending on the type of order approximated by the distribution under investigation.

(5) Two kinds of lamellar domains with variable size distribution

Obviously the preceding discussion of the diffuse scattering from domains is restricted to more or less small fluctuations of domain sizes. This is specifically valid if the most probable domain size

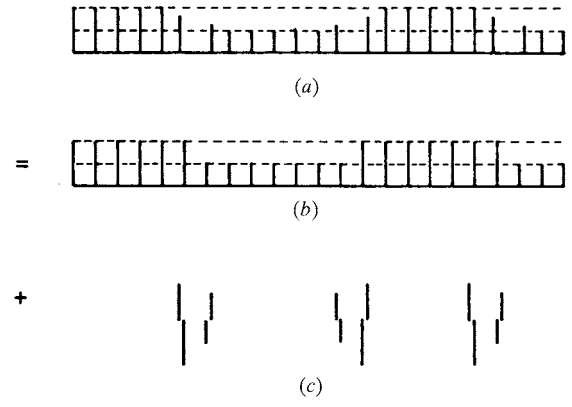


Fig. 4.2.3.4. Influence of distortions at the boundary of domains, and separation into two parts; for discussion see text.

does not differ markedly from the average size. The condition is violated in the case of order-disorder phenomena. It may happen that the smallest ordered area is the most probable one, although the average is considerably larger. This may be shown for a lamellar structure of two types of layers correlated by a (conditional) pair probability $p_{\mu\mu'}(\mathbf{1})$. As shown below, a pair at distance $\mathbf{m}$ occurs with the probability $p_{\mu}p_{\mu'}(\mathbf{m})$ which may be derived from the pair-probability of nearest neighbours $p_{\mu}p_{\mu'}(\mathbf{1})$. (In fact only one component of vector $\mathbf{m}$ is relevant in this context.) The problem will be restricted to two kinds of layers ($\mu, \mu' = 1, 2$). Furthermore, it will be symmetric in the sense that the pair probabilities obey the following rules

$$p_{11}(\mathbf{m}) = p_{22}(\mathbf{m}), \quad p_{12}(\mathbf{m}) = p_{21}(\mathbf{m}). \quad (4.2.3.25)$$

It may be derived from equation (4.2.3.25) that the *a priori* probabilities p_{μ} of a single layer are $\frac{1}{2}$ and

$$p_{11}(\mathbf{0}) = p_{22}(\mathbf{0}) = 1, \quad p_{12}(\mathbf{0}) = p_{21}(\mathbf{0}) = 0.$$

With these definitions and the general relation

$$p_{11}(\mathbf{m}) + p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) + p_{21}(\mathbf{m}) = 1$$

the *a priori* probability of a domain containing m layers of type 1 may be calculated with the aid of $p_{11}(\mathbf{1})$ [$0 \leq p_{11}(\mathbf{1}) \leq 1$]:

$$p_{\mu} = \frac{1}{2} p_{11}(\mathbf{1})^{m-1} [1 - p_{11}(\mathbf{1})]. \quad (4.2.3.26)$$

Hence the most probable size of domains is a single layer because a similar relation holds for layers of type 2. Since the average thickness of domains is strongly dependent on $p_{11}(\mathbf{1})$ [infinite for $p_{11}(\mathbf{1}) = 1$, and one layer for $p_{11}(\mathbf{1}) = 0$] it may become very large in the latter case. Consequently there are extremely large fluctuations if $p_{11}(\mathbf{1})$ is small, but different from zero.

It may be concluded from equation (4.2.3.26) that the function $p_{11}(\mathbf{m})$ decreases monotonically with increasing $\mathbf{m}$, approaching $\frac{1}{2}$ with $\mathbf{m} \rightarrow \infty$. Apparently this cannot be true for a finite crystal if $p_{11}(\mathbf{m})$ is unity (structure of two types of domains) or zero (superstructure of alternating layers). In either case the crystal should consist of a single domain of type 1 or 2, or one of the possible superstructures 1212..., 2121..., respectively. Hence one has to differentiate between long-range order, where two equivalent solutions have to be considered, and short-range order, where $p_{11}(\mathbf{m})$ approaches the *a priori* probability $\frac{1}{2}$ for large m . This behaviour of $p_{11}(\mathbf{m})$ and $p_{12}(\mathbf{m})$, which may also be expressed by equivalent correlation functions, is shown in Figs. 4.2.3.5(a) (short-range order) and 4.2.3.5(b) (long-range order). $p_{11}(\mathbf{m})$ approaches $\frac{1}{2} + s$ for large m with $s = 0$ in the case of short-range order, while $p_{12}(\mathbf{m})$ becomes $\frac{1}{2} - s$. Obviously a strict correlation between $p_{11}(\mathbf{1})$ and s exists which has to be calculated. For a qualitative

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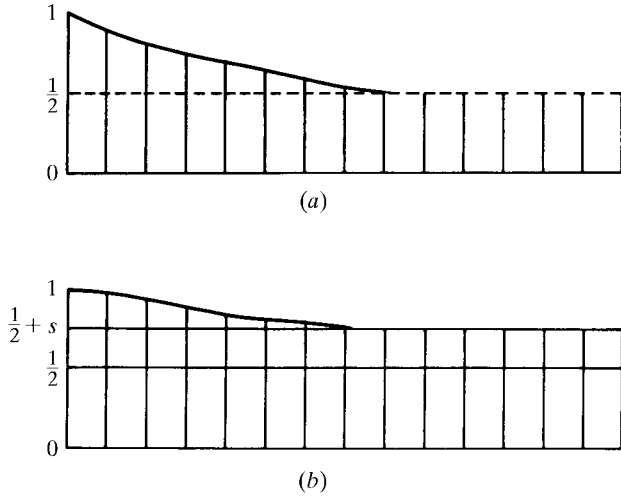


Fig. 4.2.3.5. Typical distributions of mixed crystals (unmixing): (a) upper curve: short-range order only; (b) lower curve: long-range order.

interpretation of the diffraction pictures this correlation may be derived from the diffraction pattern itself. The $p_{\mu\mu'}(\mathbf{m})$ are separable into a strictly periodic and a monotonically decreasing term approaching zero in both cases. This behaviour is shown in Figs. 4.2.3.6(a), (b). The periodic term contributes to sharp Bragg scattering. In the case of short-range order the symmetry relations given in equation (4.2.3.25) are valid. The convolution in real space yields with factors $t(\mathbf{r})$ (equations 4.2.3.21):

$$\begin{aligned} & \frac{1}{2} t(\mathbf{r}) \left[\sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{11}(\mathbf{m}) \right] * F_1(\mathbf{r}) * F_1(-\mathbf{r}) \\ & + \frac{1}{2} t(\mathbf{r}) \left[\sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{12}(\mathbf{m}) \right] * F_1(\mathbf{r}) * F_2(-\mathbf{r}) \\ & + \frac{1}{2} t(\mathbf{r}) \left[\sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{21}(\mathbf{m}) \right] * F_2(\mathbf{r}) * F_1(-\mathbf{r}) \\ & + \frac{1}{2} t(\mathbf{r}) \left[\sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{22}(\mathbf{m}) \right] * F_2(\mathbf{r}) * F_2(-\mathbf{r}), \end{aligned}$$

where $p'_{\mu\mu'}(\mathbf{m})$ are factors attached to the δ functions:

$$\begin{aligned} p'_{11}(\mathbf{m}) &= p_{11}(\mathbf{m}) - \frac{1}{2} = p'_{22}(\mathbf{m}) \\ p'_{12}(\mathbf{m}) &= p'_{21}(\mathbf{m}) = -p'_{11}(\mathbf{m}). \end{aligned}$$

The positive sign of n in the δ functions results from the convolution with the inverted lattice [cf. Patterson (1959, equation 32)]. Fourier

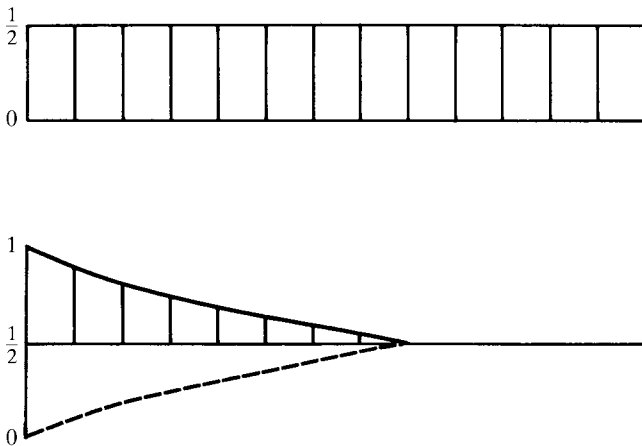


Fig. 4.2.3.6. Decomposition of Fig. 4.2.3.5(a) into a periodic and a rapidly convergent part.

transformation of the four terms given above yields the four corresponding expressions (μ, μ'):

$$\frac{1}{2} [T(\mathbf{H}) * \sum_{\mathbf{m}} p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{m}\}] F_{\mu}(\mathbf{H}) F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27a)$$

Now the summation over $\mathbf{m}$ may be replaced by an integral if the factor $l(\mathbf{m})$ is added to $p'_{\mu\mu'}(\mathbf{m})$, which may then be considered as the smoothest continuous curve passing through the relevant integer values of $\mathbf{m}$:

$$\sum \rightarrow \int l(\mathbf{m}) p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{m}\} d\mathbf{m}$$

since both $l(\mathbf{m})$ and $p'_{\mu\mu'}(\mathbf{m})$ are symmetric in our special case we obtain

$$\sum = L(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H}).$$

Insertion of the sum in equation (4.2.3.27a) results in

$$\frac{1}{2} [L(\mathbf{H}) * T(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H})] F_{\mu}(\mathbf{H}) F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27b)$$

Using all symmetry relations for $p'_{\mu\mu'}(\mathbf{m})$ and $P'_{\mu\mu'}(\mathbf{H})$, respectively, we obtain for the diffuse scattering after summing over μ, μ'

$$I_d \approx [L(\mathbf{H}) * T(\mathbf{H}) * P'_{11}(\mathbf{H})] |\Delta F(\mathbf{H})|^2 \quad (4.2.3.28)$$

with $\Delta F(\mathbf{H}) = \frac{1}{2} [F_1(\mathbf{H}) - F_2(\mathbf{H})]$.

It should be borne in mind that $P'_{11}(\mathbf{H})$ decreases rapidly if $p'_{11}(\mathbf{r})$ decreases slowly and *vice versa*. It is interesting to compare the different results from equations (4.2.3.21b) and (4.2.3.28). Equation (4.2.3.28) indicates diffuse maxima at the positions of the sharp Bragg peaks, while the multiplication by $D(\mathbf{H})$ causes satellite reflections in the neighbourhood of Bragg maxima. Both equations contain the factor $|\Delta F(\mathbf{H})|^2$ indicating the same influence of the two structures. More complicated formulae may be derived for several cell occupations. In principle, a result similar to equation (4.2.3.28) will be obtained, but more interdependent correlation functions $p_{\mu\mu'}(\mathbf{r})$ have to be introduced. Consequently, the behaviour of diffuse intensities becomes more differentiated in so far as all $p'_{\mu\mu'}(\mathbf{r})$ are now correlated with the corresponding $\Delta F_{\mu}(\mathbf{r}), \Delta F_{\mu'}(-\mathbf{r})$. Hence the method of correlation functions becomes increasingly ineffective with increasing number of correlation functions. Here the cluster method seems to be more convenient and is discussed below.

(6) *Lamellar domains with long-range order: tendency to exsolution*

The Patterson function of a disordered crystal exhibiting long-range order is shown in Fig. 4.2.3.5(b). Now $p_{11}(\infty)$ converges against $\frac{1}{2} + s$, the *a priori* probability changes correspondingly. Since $p_{12}(\infty)$ becomes $\frac{1}{2} - s$, the symmetry relation given in equation (4.2.3.25) is violated: $p_{11}(\mathbf{r}) \neq p_{22}(\mathbf{r})$ for a finite crystal; it is evident that another crystal shows long-range order with the inverted correlation function, $p_{22}(\infty) = \frac{1}{2} + s$, $p_{21}(\infty) = \frac{1}{2} - s$, respectively, such that the symmetry $p_{11}(\mathbf{r}) = p_{22}(\mathbf{r})$ is now valid for an assembly of finite crystals only. According to Fig. 4.2.3.5(b) there is a change in the intensities of the Bragg peaks.

$$\begin{aligned} I_1 &\sim |(\frac{1}{2} + s) F_1(\mathbf{H}) + (\frac{1}{2} - s) F_2(\mathbf{H})|^2 \\ I_2 &\sim |(\frac{1}{2} + s) F_2(\mathbf{H}) + (\frac{1}{2} - s) F_1(\mathbf{H})|^2, \end{aligned} \quad (4.2.3.29)$$

where I_1, I_2 represent the two solutions discussed for the assembly of crystals which have to be added with the probability $\frac{1}{2}$; the intensities of sharp reflections become

$$I = (I_1 + I_2)/2. \quad (4.2.3.30)$$

Introducing equation (4.2.3.29) into (4.2.3.30) we obtain

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$$I \sim \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 + s^2[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2. \quad (4.2.3.31a)$$

$s = 0$ corresponds to the well known behaviour of sharp reflections, $s = \frac{1}{2}$ (maximum long-range order) gives

$$I \sim \frac{1}{2}[F_1(\mathbf{H})]^2 + [F_2(\mathbf{H})]^2. \quad (4.2.3.31b)$$

This result reveals some difficulties for structure determination of the averaged structure as long as s is different from zero or $\frac{1}{2}$, since in the former case the use of integrated sharp Bragg intensities yields a correct average structure. If $s = \frac{1}{2}$, a correct structure determination can only be performed with a refinement allowing for an incoherent superposition of two different structures. Having subtracted all periodic contributions to $p_{\mu\mu'}(\mathbf{r})$, new functions which describe the remaining non-periodic parts have to be introduced (Fig. 4.2.3.6b). In order to obtain a clear overview of intensities, $p'_{\mu\mu'}(\mathbf{r})$ is again defined:

$$p'_{\mu\mu'}(\mathbf{r}) = cp_{\mu\mu'}(\mathbf{r}) - p_{\mu\mu'}(\infty),$$

where c should be chosen such that $p_{\mu\mu'}(\mathbf{0}) = 1$. By this definition a very simple behaviour of the diffuse scattering is obtained:

$$\begin{aligned} p'_{11}(\mathbf{r}) &: \frac{1}{2} - s; & p'_{12}(\mathbf{r}) &: -(\frac{1}{2} - s); \\ p'_{22}(\mathbf{r}) &: \frac{1}{2} + s; & p'_{21}(\mathbf{r}) &: -(\frac{1}{2} + s). \end{aligned}$$

With the definitions introduced above it is found that:

$$p'_{11}(\mathbf{r}) = p'_{22}(\mathbf{r}).$$

The diffuse scattering is given by:

$$I_d(\mathbf{H}) = (\frac{1}{4} - s^2)[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2 [P'_{11}(\mathbf{H}) * L(\mathbf{H})]. \quad (4.2.3.32)$$

Since equation (4.2.3.32) is symmetrical with respect to an interchange of F_1 and F_2 , the same result is obtained for I_2 . Diffuse reflections occur in the positions of the sharp ones; the integrated intensities of sharp and diffuse reflections are independent of the special shape of $P'_{11}(\mathbf{H})$: $p_{11}(\mathbf{0}) = 1$; hence

$$1 = \int P'_{11}(\mathbf{H}) \exp\{2\pi i \mathbf{0} \cdot \mathbf{H}\} d\mathbf{H} = \int P'_{11}(\mathbf{H}) d\mathbf{H}.$$

(7) *Lamellar domains with long-range order: tendency to superstructure*

So far it has been tacitly assumed that the crystal shows a preference for equal neighbours. If there is a reversed tendency (pairs of unequal neighbours are more probable) the whole procedure outlined above may be repeated as shown in Fig. 4.2.3.7 for the one-dimensional example. With the same probability of an unlike pair as used for the equal pair in the preceding example, the order process approaches an alternating structure such that the even-order neighbours have the same pair probabilities, while the odd ones are complementary for equal pairs (Fig. 4.2.3.7). In order to calculate intensities, it is necessary to introduce a new lattice with the doubled lattice constant and the corresponding reciprocal lattice with $b^{*'} = b^*/2$. In order to describe the probability $p_{\mu\mu'}(\mathbf{r})$, one has to introduce two lattices in real space – the normal lattice with the

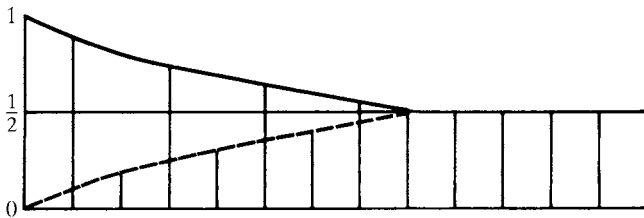


Fig. 4.2.3.7. The same distribution (cf. Fig. 4.2.3.5) in the case of superstructure formation.

undisplaced origin and the displaced one. Fourier transformation of the new functions yields the following very similar results:

Sharp Bragg reflections

(a) $k' = \text{even}$

$$I = \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 \quad (4.2.3.33a)$$

(b) $k' = \text{odd}$

$$I = s^2 \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2 \quad (4.2.3.33b)$$

Diffuse reflections

(c) $k' = \text{odd}$

$$I = (\frac{1}{4} - s^2) \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2. \quad (4.2.3.33c)$$

Obviously, there is a better situation for determination of the averaged structure which may be performed without any difficulty, regardless of whether s is different from zero or not. For this purpose even reflections (or reflections in the old setting) may be used. The inclusion of odd reflections in the structure determination of the superstructure is also possible if convenient $\mathbf{H}$ -independent scaling factors are introduced in order to compensate for the loss in intensity which is unavoidable for the integration of the diffuse scattering.

A few comments should be made on the physical meaning of the formulae derived above. All formulae may be applied to the general three-dimensional case, where long-range and short-range order is a function of the relevant thermodynamical parameters. In practice, long-range order will never be realized in a real crystal consisting of mosaic blocks which may behave as small subunits in order-disorder transitions. Another reason to assume partly incoherent areas in single crystals is the presence of possible strains or other distortions at the interfaces between domains which should cause a decrease of the averaged areas of coherent scattering. All these effects may lead to diffuse scattering in the neighbourhood of Bragg peaks, similar to the diffuse scattering caused by domain structures. For this reason an incoherent treatment of domains is probably more efficient, although considerable errors in intensity measurements may occur. A very careful study of line profiles is generally useful in order to decide between the various possibilities.

(8) *Order-disorder in three dimensions*

Correlation functions in three dimensions may have very complicated periodicities; hence a careful study is necessary as to whether or not they may be interpreted in terms of a superlattice. If so, extinction rules have to be determined in order to obtain information on the superspace group. In the literature these are often called modulated structures because a sublattice, as determined by the basic lattice, and a superlattice may well be defined in reciprocal space: reflections of a sublattice including (000) are formally described by a multiplication by a lattice having larger lattice constants (superlattice) in reciprocal space; in real space this means a convolution with the Fourier transform of this lattice (sublattice). In this way the averaged structure is generated in each of the subcells (superposition or 'projection' of all subcells into a single one). Obviously, the Patterson function of the averaged structure contains little information in the case of small subcells. Hence it is advisable to include the diffuse scattering of the superlattice reflections at the beginning of any structure determination.

N subcells in real space are assumed, each of them representing a kind of a complicated 'atom' which may be equal by translation or other symmetry operation. Once a superspace group has been determined, the usual extinction rules of space groups may be applied, remembering that the 'atoms' themselves may have systematic extinctions. Major difficulties arise from the existence of different symmetries of the subgroup and the supergroup. Since the symmetry of the supergroup is lower in general, all missing

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symmetry elements may cause domains, corresponding to the missing symmetry element: translations cause antiphase domains in their generalized sense, other symmetry elements cause twins generated by rotations, mirror planes or the centre of symmetry. If all these domains are small enough to be detected by a careful study of line profiles, using diffraction methods with a high resolution power, the structural study may be facilitated by a reasonable explanation of scaling factors to be introduced for groups of reflections affected by the possible domain structures.

(9) Density modulations

A density modulation of a structure in real space leads to pairs of satellites in reciprocal space. Each main reflection is accompanied by a pair of satellites in the directions $\mp\Delta\mathbf{H}$ with phases $\mp 2\pi\varphi$. The reciprocal lattice may then be written in the following form ($0 \leq \alpha \leq 1$):

$$L(\mathbf{H}) + \frac{\alpha}{2}L(\mathbf{H} + \Delta\mathbf{H})\exp\{2\pi i\Phi\} + \frac{\alpha}{2}L(\mathbf{H} - \Delta\mathbf{H})\exp\{2\pi i(-\Phi)\}.$$

Fourier transformation yields

$$l(\mathbf{r}) \left[1 + \frac{\alpha}{2}\exp\{2\pi i(\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)\} + \frac{\alpha}{2}\exp\{-2\pi i(\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)\} \right] = l(\mathbf{r})[1 + \alpha \cos(2\pi\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)]. \quad (4.2.3.34)$$

Equation (4.2.3.34) describes the lattice modulated by a harmonic density wave. Since phases cannot be determined by intensity measurements, there is no possibility of obtaining any information on the phase relative to the sublattice. From (4.2.3.34) it is obvious that the use of higher orders of harmonics does not change the situation. If $\Delta\mathbf{H}$ is not rational such that $n\Delta\mathbf{H}$ ($n = \text{integer}$) does not coincide with a main reflection in reciprocal space, the modulated structure is incommensurate with the basic lattice, and the phase of the density wave becomes meaningless. The same is true for the relative phases of the various orders of harmonic modulations of the density. This uncertainty even remains valid for commensurate density modulations of the sublattice, because coinciding higher-order harmonics in reciprocal space cause the same difficulty; higher-order coefficients cannot uniquely be separated from lower ones, consequently structure determination becomes impossible unless phase-determination methods are applied. Fortunately, density modulations of pure harmonic character are impossible for chemical reasons; they may be approximated by disorder phenomena for the averaged structure only. If diffuse scattering is taken into account the situation is changed considerably: A careful study of the diffuse scattering alone, although difficult in principle, will yield the necessary information about the relative phases of density waves (Korekawa, 1967).

(10) Displacement modulations

Displacement modulations are more complicated, even in a primitive structure. The Fourier transform of a longitudinal or a transverse displacement wave has to be calculated and this procedure does not result in a function of similar simplicity. A set of satellites is generated whose amplitudes are described by Bessel functions of ν th order, where ν represents the order of the satellites. With α as amplitude of the displacement wave the intensity of the satellites increases with the magnitude of the product $H\alpha$. This means that a single harmonic displacement causes an infinite number of satellites. They may be unobservable at low diffraction angles as long as the amplitudes are small. If the displacement

modulation is incommensurate there are no coincidences with reflections of the sublattice. Consequently, the reciprocal space is completely covered with an infinite number of satellites, or, in other words, with diffuse scattering. This is a clear indication that incommensurate displacement modulations belong to the category of disordered structures. Statistical fluctuations of amplitudes of the displacement waves cause additional diffuse scattering, regardless of whether the period is commensurate or incommensurate (Overhauser, 1971; Axe, 1980). Fluctuations of 'phases' (= periods) cause a broadening of satellites in reciprocal space, but no change of their integrated intensities as long as the changes are not correlated with fluctuation periods. The broadening of satellite reflections increases with the order of satellites and $(\mathbf{H} \cdot \mathbf{a})$. Obviously, there is no fundamental difference in the calculation of diffuse scattering with an ordered supercell of sufficient size.

The use of optical transforms has been revived recently, although its efficiency is strongly dependent on the availability of a useful computer program capable of producing masks for optical diffraction. An atlas of optical transforms is available (Wooster, 1962; Harburn *et al.*, 1975), but the possibility cannot be excluded that the diffuse scattering observed does not fit well into one of the diffraction pictures shown. Yet one of the major advantages of this optical method is the simple experimental setup and the high brilliance owing to the use of lasers. This method is specifically useful in disordered molecular structures where only a few orientations of the molecules have to be considered. It should be borne in mind, however, that all optical masks must correspond to projections of the disorder model along one specific direction which generates the two-dimensional diffraction picture under consideration. An important disadvantage is caused by the difficulty in simulating the picture of an atom. This situation may be improved by using computer programs with a high-resolution matrix printer representing electron densities by point densities of the printer. This latter method seems to be very powerful because of the possibility of avoiding 'ghosts' in the diffraction picture.

4.2.3.2. Guideline to solve a disorder problem

Generally, structure determination of a disordered crystal should start in the usual way by solving the average structure. The effectiveness of this procedure strongly depends on the distribution of integrated intensities of sharp and diffuse reflections. In cases where the integrated intensities of Bragg peaks is predominant, the maximum information can be drawn from the averaged structure. The observations of fractional occupations of lattice sites, split positions and anomalous temperature factors are indications of the disorder involved. Since these aspects of disorder phenomena in the averaged structure may be interpreted very easily, a detailed discussion of this matter is not given here (see any modern textbook of X-ray crystallography).

Difficulties may arise from the intensity integration which should be carried out using a high-resolution diffraction method. The importance of this may be understood from the following argument. The averaged structure is determined by the coherent superposition of different structure factors. This interpretation is true if there is a strictly periodic subcell with long-range order which allows for a clear separation of sharp and diffuse scattering. There are important cases, however, where this procedure cannot be applied without loss of information.

(a) The diffuse scattering is concentrated near the Bragg peaks for a large number of reflections. Because of the limited resolution power of conventional single-crystal methods the separation of sharp and diffuse scattering is impossible. Hence, the conventional study of integrated intensities does not really lead to an averaged structure. In this case a refinement should be tried using an incoherent superposition of different structure factors. Application

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of this procedure is subject to conditions which have to be checked very carefully before starting the refinement: first, it is necessary to estimate the amount of diffuse scattering not covered by intensity integration of the 'sharp' reflections. Since loss in intensity, hidden in the background scattering, is underestimated very frequently, it should be checked whether nearly coinciding sharp and diffuse maxima are modulated by the same structure factor. It may be difficult to meet this condition in some cases; *e.g.* this condition is fulfilled for antiphase domains, but the same is not true for twin domains.

(b) The concentration of diffuse maxima near Bragg peaks is normally restricted to domain structures with a strictly periodic sublattice. Cases deviating from this rule are possible. Since they are rare, they are omitted here. Even structures with small deviations from the average structure do not lead to structure factors for diffuse scattering which are proportional to that of the average structure. This has been shown in the case of a twin structure correlated by a mirror plane where the reflections of a zone only have equal structure factors (Cowley & Au, 1978). This effect causes even more difficulties for orthogonal lattices where the two twins have reflections in exactly the same positions, although differing in their structure factors. In this particular case, the incoherent or coherent treatment in refinements may be seriously hampered by strains originating from the boundary. Unsatisfactory refinements may be explained in this way but this does not improve their reliability.

The integrated intensity of any structure is independent of atomic positions if the atomic form factors remain unchanged by structural fluctuations. Small deviations of atomic form factors owing to electron-density changes of valence electrons are neglected. Consequently, the integrated diffuse intensities remain unchanged if the average structure is not altered by the degree of order. The latter condition is obeyed in cases where a geometrical long-range order of the lattice is independent of the degree of order, and no long-range order in the structure exists. This law is extremely useful for the interpretation of diffuse scattering. Unfortunately, intensity integration over coinciding sharp and diffuse maxima does not necessarily lead to a structure determination of the corresponding undistorted structure. This integration may be useful for antiphase domains without major structural changes at the boundaries. In all other cases the deviations of domains (or clusters) from the averaged structure determine the intensities of maxima which are no longer correlated with those of the average structure.

If the integrated intensity of diffuse scattering is comparable with, or even larger than, those of the Bragg peaks it is useful to begin the interpretation with a careful statistical study of the diffuse intensities. Intensity statistics can be applied in a way similar to the intensity statistics in classical structure determination. The following rules are briefly discussed in order to enable a semi-quantitative interpretation of the essential features of disorder to be realized.

(1) First, it is recommended that the integrated intensities be studied in certain areas of reciprocal space.

(2) Since low-angle scattering is very sensitive to fluctuations of densities, the most important information can be drawn from its intensity behaviour. If there is at least a one-dimensional sublattice in reciprocal space without diffuse scattering, it may often be concluded that there is no important low-angle scattering either. This law is subject to the condition of a sufficient number of reflections obeying this extinction rule without any exception.

(3) If the diffuse scattering shows maxima and minima, it should be checked whether the maxima observed may be approximately assigned to a lattice in reciprocal space. Obviously, this condition can hardly be met exactly if these maxima are modulated by a kind of structure factor, which causes displacements of maxima proportional to the gradient of this structure factor. Hence this

influence may well be estimated from a careful study of the complete diffuse diffraction pattern.

It should then be checked whether the corresponding lattice represents a sub- or a superlattice of the structure. An increase of the width of reflections as a function of growing $|\mathbf{H}|$ indicates strained clusters of sub- or superlattice.

(4) The next step is the search for extinction rules of diffuse scattering. The simplest is the lack of low-angle scattering which has already been mentioned above. Since diffuse scattering is generally given by equation (4.2.2.13)

$$I_d(\mathbf{H}) = \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \\ = \sum_{\mu} p_{\mu} |F_{\mu}(\mathbf{H})|^2 - \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2,$$

it may be concluded that this condition is fulfilled in cases where all structural elements participating in disorder differ by translations only (stacking faults, antiphase domains *etc.*). They add phase factors to the various structure factors, which may become $n2\pi$ (n = integer) for specific values of the reciprocal vector $\mathbf{H}$. If all p_{μ} are equivalent by symmetry:

$$p \sum_{\mu} |F_{\mu}(\mathbf{H})|^2 - [p \sum_{\mu} F_{\mu}(\mathbf{H})][p \sum_{\mu} F_{\mu}^*(\mathbf{H})] = 0.$$

Other possibilities of vanishing diffuse scattering may be derived in a similar manner for special reflections if glide operations are responsible for disorder. Since we are concerned with disordered structures, these glide operations need not necessarily be a symmetry operation of the lattice. It should be pointed out, however, that all these extinction rules of diffuse scattering are a kind of 'anti'-extinction rule, because they are valid for reflections having maximum intensity for the sharp reflections unless the structure factor itself vanishes.

(5) Furthermore, it is important to plot the integrated intensities of sharp and diffuse scattering as a function of the reciprocal coordinates at least in a semi-quantitative way. If the ratio of integrated intensities remains constant in the statistical sense, we are predominantly concerned with a density phenomenon. It should be pointed out, however, that a particle-size effect of domains behaves like a density phenomenon (density changes at the boundary!).

If the ratio of 'diffuse' to 'sharp' intensities increases with diffraction angle, we have to take into account atomic displacements. A careful study of this ratio yields very important information on the number of displaced atoms. The result has to be discussed separately for domain structures if the displacements are equal in the subcells of a single domain, but different for the various domains. In the case of two domains with displacements of all atoms the integrated intensities of sharp and diffuse reflections become statistically equal for large $|\mathbf{H}|$. Other rules may be derived from statistical considerations.

(6) The next step of a semi-quantitative interpretation is the check of the intensity distribution of diffuse reflections in reciprocal space. Generally this modulation is simpler than that of the sharp reflections. Hence it is frequently possible to start a structure determination with diffuse scattering. This method is extremely helpful for one- and two-dimensional disorder where partial structure determinations yield valuable information, even for the evaluation of the average structure.

(7) In cases where no sub- or superlattice belonging to diffuse scattering can be determined, a careful check of integrated intensities in the surroundings of Bragg peaks should again be performed. If systematic absences are found, the disorder is most probably restricted to specific lattice sites which may also be found in the average structure. The accuracy, however, is much lower here. If no such effects correlated with the average structure are

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observed, the disorder problem is related to a distribution of molecules or clusters with a structure differing from the average structure. As pointed out in Section 4.2.3.1 the problem of the representative structure(s) of the molecule(s) or the cluster(s) should be solved. Furthermore their distribution function(s) is (are) needed. In this particular case it is very useful to start with a study of diffuse intensity at low diffraction angles in order to acquire the information about density effects. Despite the contribution to sharp reflections, one should remember that the information derived from the average structure may be very low (e.g. small displacements, low concentrations *etc.*).

(8) As pointed out above, a Patterson picture – or strictly speaking a difference Patterson ($|\Delta F|^2$ -Fourier synthesis) – may be very useful in this case. This method is promising in the case of disorder in molecular structures where the molecules concerned are at least partly known. Hence the interpretation of the difference Patterson may start with some internal molecular distances. Non-molecular structures show some distances of the average structure. Consequently a study of the important distances will yield information on displacements or replacements in the average structure. For a detailed study of this matter the reader is referred to the literature (Schwartz & Cohen, 1977).

Although it is highly improbable that exactly the same diffraction picture will really be found, the use of an atlas of optical transforms (Wooster, 1962; Harburn *et al.*, 1975; Welberry & Withers, 1987) may be very helpful at the beginning of any study of diffuse scattering. The most important step is the separation of the distribution function from the molecular scattering. Since this information may be derived from a careful comparison of low-angle diffraction with the remaining sharp reflections, this task is not too difficult. If the influence of the distribution function is unknown, the reader is strongly advised to disregard the immediate neighbourhood of Bragg peaks in the first step of the interpretation. Obviously information may be lost in this way but, as has been shown in the past, much confusion caused by the attempt to interpret the scattering near the Bragg peaks with specific structural properties of a cluster or molecular model is avoided. The inclusion of this part of diffuse scattering can be made after the complete interpretation of the change of the influence of the distribution function on diffraction in the far-angle region.

4.2.4. Quantitative interpretation

4.2.4.1. Introduction

In these sections quantitative interpretations of the elastic part of diffuse scattering (X-rays and neutrons) are outlined. Although similar relations are valid, magnetic scattering of neutrons is excluded. Obviously, all disorder phenomena are strongly temperature dependent if thermal equilibrium is reached. Consequently, the interpretation of diffuse scattering should include a statistical thermodynamical treatment. Unfortunately, no quantitative theory for the interpretation of structural phenomena is so far available: all quantitative solutions introduce formal order parameters such as correlation functions or distributions of defects. At low temperatures (low concentration of defects) the distribution function plays the dominant role in diffuse scattering. With increasing temperature the number of defects increases with corresponding strong interactions between them. Therefore, correlations become increasingly important, and phase transformations of first or higher order may occur which need a separate theoretical treatment. In many cases large fluctuations of structural properties occur which are closely related to the dynamical properties of the crystal. Theoretical approximations are possible

but their presentation is far beyond the scope of this article. Hence we restrict ourselves to formal parameters in the following.

Point defects or limited structural units, such as molecules, clusters of finite size *etc.*, may only be observed in diffraction for a sufficiently large number of defects. This statement is no longer true in high-resolution electron diffraction where single defects may be observed either by diffraction or by optical imaging if their contrast is high enough. Hence, electron microscopy and diffraction provide valuable methods for the interpretation of disorder phenomena.

The arrangement of a finite assembly of structural defects is described by its structure and its three-dimensional (3D) distribution function. Structures with a strict 1D periodicity (chain-like structures) need a 2D distribution function, while for structures with a 2D periodicity (layers) a 1D distribution function is sufficient. Since the distribution function is the dominant factor in statistics with correlations between defects, we define the dimensionality of disorder as that of the corresponding distribution function. This definition is more effective in diffraction problems because the dimension of the disorder problem determines the dimension of the diffuse scattering: 1D diffuse streaks, 2D diffuse layers, or a general 3D diffuse scattering.

Strictly speaking, completely random distributions cannot be realized as shown in Section 4.2.3. They occur approximately if the following conditions are satisfied.

(1) The average volume of all defects including their surrounding strain fields NcV_d (N = number of unit cells, c = concentration of defects, V_d = volume of the defect with $V_d > V_c$, V_c = volume of the unit cell) is small in comparison with the total volume NV_c of the crystal, or $V_c \gg cV_d$.

(2) Interactions between the defects are negligible. These conditions, however, are valid in very rare cases only, *i.e.* where small concentrations and vanishing strain fields are present. Remarkable exceptions from this rule are real point defects without interactions, such as isotope distribution (neutron diffraction!), or the system AuAg at high temperature.

As already mentioned, disorder phenomena may be observed in thermal equilibrium. Two completely different cases have to be considered.

(1) The concentration of defects is given by the chemical composition, *i.e.* impurities in a closed system.

(2) The number of defects increases with temperature and also depends on pressure or other parameters, *i.e.* interstitials, voids, static displacements of atoms, stacking faults, dislocations *etc.*

In many cases the defects do not occur in thermal equilibrium. Nevertheless, their diffuse scattering is temperature dependent because of the anomalous thermal movements at the boundary of the defect. Hence, the observation of a temperature-dependent behaviour of diffuse scattering cannot be taken as a definite criterion of thermal equilibrium without further careful interpretation.

Ordering of defects may take place in a very anisotropic manner. This is demonstrated by the huge number of examples of 1D disorder. As shown by Jagodzinski (1963) this type of disorder cannot occur in thermal equilibrium for the infinite crystal. This type of disorder is generally formed during crystal growth or mechanical deformation. Similar arguments may be applied to 2D disorder. This is a further reason why the so-called Ising model can hardly be used in order to obtain interaction energies of structural defects. From these remarks it becomes clear that order parameters are more or less formal parameters without strict thermodynamical meaning.

The following section is organized as follows: first we discuss the simple case of 1D disorder where reliable solutions of the diffraction problem are available. Intensity calculations of diffuse scattering of 2D disorder by chain-like structures follow. Finally, the 3D case is treated, where formal solutions of the diffraction

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problem have been tried and applied successfully to metallic systems to some extent. A short concluding section concerns the special phenomenon of orientational disorder.

4.2.4.2. One-dimensional disorder of ordered layers

As has been pointed out above, it is often useful to start the interpretation of diffuse scattering by checking the diffraction pattern with respect to the dimensionality of the disorder concerned. Since each disordered direction in the crystal demands a violation of the corresponding Laue condition, this question may easily be answered by looking at the diffuse scattering. Diffuse streaks in reciprocal space are due to a one-dimensional violation of the Laue conditions, and will be called one-dimensional disorder. This kind of order is typical for layer structures, but it is frequently observed in cases where several sequences of layers do not differ in the interactions of next-nearest neighbours. Typical examples are structures which may be described in terms of close packing, *e.g.* hexagonal and cubic close packing.

For a quantitative interpretation of diffuse streaks we need one-dimensional correlation functions, which may uniquely be determined if a single independent correlation function is active. According to equation (4.2.3.28) Fourier transformation yields the information required. In all other cases a specific model has to be suggested for a full interpretation of diffuse streaks. Another comment seems to be necessary: disorder parameters can be defined uniquely only if the diffraction pattern allows for a differentiation between long-range and short-range order. This question can at least partly be answered by studying the line width of sharp reflections with a very good resolution. Since integrated intensities of sharp reflections have to be separated from the diffuse scattering, this question is of outstanding importance in most cases. Inclusion of diffuse parts in the diffraction pattern during intensity integration of sharp reflections may lead to serious errors in the interpretation of the average structure.

The existence of diffuse streaks in more than one direction of reciprocal space means that the diffraction problem is no longer one-dimensional. Sometimes the problem may be treated independently, if the streaks are sharp, and no interference effects may be observed in the diffraction pattern in areas where the diffuse streaks do overlap. In all other cases there are correlations between the various directions of one-dimensional disorder which may be determined with the aid of a model covering more than one of the pertinent directions of disorder.

Before starting the discussion of the quantitative solution of the one-dimensional problem, some remarks should be made on the usefulness of quantitative disorder parameters. It is well known from statistical thermodynamics that a one-dimensional system cannot show long-range order above $T = 0$ K. Obviously, this statement is in contradiction with many experimental observations where long-range order is realized even in layer structures. The reason for this behaviour is given by the following arguments which are valid for any structure. Let us assume a structure with strong interactions at least in two directions. From the theoretical treatment of the two-dimensional Ising model it is known that such a system shows long-range order below a critical temperature T_c . This statement is true even if the layer is finite, although the strict thermodynamic behaviour is not really critical in the thermodynamical sense. A three-dimensional crystal can be constructed by adding layer after layer. Since each layer has a typical two-dimensional free energy, the full statistics of the three-dimensional crystal may be calculated by introducing a specific free energy for the various stackings of layers. Obviously, this additional energy has to include terms describing potential and entropic energies as well. They may be formally developed into contributions of next, overnext *etc.* nearest neighbours. Apparently, the contribution to

entropy must include configurational and vibrational parts which are strongly coupled. As long as the layers are finite, there is a finite probability of a fault in the stacking sequence of layers which approaches zero with increasing extension of the layers. Consequently, the free energy of a change in the favourite stacking sequence becomes infinite quadratically with the size of the layer. Therefore, the crystal should be either completely ordered or disordered; the latter case can only be realized if the free energies of one or more stacking sequences are exactly equal (very rare, but possible over a small temperature range of phase transformations). An additional positive entropy associated with a deviation from the periodic stacking sequence may lead to a kind of competition between entropy and potential energy, in such a way that periodic sequences of faults result. Obviously, this situation occurs in the transition range of two structures differing only in their stacking sequence. On the other hand, one must assume that defects in the stacking sequence may be realized if the size of the layers is small. This situation occurs during crystal growth, but one should remember that the number of stacking defects should decrease with increasing size of the growing crystal. Apparently, this rearrangement of layers may be suppressed as a consequence of relaxation effects. The growth process itself may influence the propagation of stacking defects and, consequently, the determination of stacking-fault probabilities, aiming at an interpretation of the chemical bonding seems to be irrelevant in most cases.

The quantitative solution of the diffraction problem of one-dimensional disorder follows a method similar to the Ising model. As long as next-nearest neighbours alone are considered, the solution is very simple only if two possibilities of structure factors are to be taken into account. Introducing the probability of equal pairs 1 and 2, α , one arrives at the known solution for the *a priori* probability p_μ and *a posteriori* probabilities $p_{\mu\mu'}(\mathbf{m})$, respectively. In the one-dimensional Ising model with two spins and the interaction energies $(U \mp \Delta U)/k_B T$, defining the pair probability $[\alpha = p_{11}(\mathbf{1})]$

$$\alpha = \frac{\exp\{\pm \Delta U/k_B T\}}{[\exp\{+\Delta U/k_B T\} + \exp\{-\Delta U/k_B T\}]}$$

the full symmetry is $p_1 = p_2 = \frac{1}{2}$, and $p_{11}(\mathbf{m}) = p_{22}(\mathbf{m})$.

Consequently:

$$p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) = 1 - p_{11}(\mathbf{m}).$$

The scattered intensity is given by

$$I(\mathbf{H}) = L(h, k) \sum_{\mathbf{m}} \langle FF_m^+ \rangle (N - |\mathbf{m}|) \exp\{-2\pi i \mathbf{m} \cdot \mathbf{l}\}, \quad (4.2.4.1)$$

where $\mathbf{m} = \mathbf{m}\mathbf{c}$, N = number of unit cells in the $\mathbf{c}$ direction and $\langle FF_m^+ \rangle$ depends on λ_1, λ_2 which are the eigenvalues of the matrix

$$\begin{pmatrix} \alpha & 1 - \alpha \\ 1 - \alpha & \alpha \end{pmatrix}.$$

From the characteristic equation

$$\lambda^2 - 2\alpha\lambda - 1 + 2\alpha = 0 \quad (4.2.4.2)$$

one has

$$\lambda_1 = 1; \quad \lambda_2 = 2\alpha - 1. \quad (4.2.4.2a)$$

λ_1 describes a sharp Bragg reflection (average structure) which need not be calculated. Its intensity is simply proportional to $\langle F(\mathbf{H}) \rangle$. The second characteristic value yields a diffuse reflection in the same position if the sign is positive ($\alpha > 0.5$), and in a position displaced by $\frac{1}{2}$ in reciprocal space if the sign is negative ($\alpha < 0.5$). Because of the symmetry conditions $p_{11}(\mathbf{m})$ only is needed; it may be determined with the aid of the boundary conditions

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$$p_{11}(\mathbf{0}) = 1, \quad p_{11}(\mathbf{1}) = \alpha,$$

and the general relation that $p_{\mu\mu'}(\mathbf{m})$ is given by

$$p_{\mu\mu'}(\mathbf{m}) = c'_{\mu\mu'}\lambda_1^m + c''_{\mu\mu'}\lambda_2^m.$$

The final solution of our problem yields simply:

$$p_{11}(\mathbf{m}) = \frac{1}{2} + \frac{1}{2}\lambda_2^m = p_{22}(\mathbf{m}),$$

$$p_{12}(\mathbf{m}) = \frac{1}{2} - \frac{1}{2}\lambda_2^m = p_{21}(\mathbf{m}).$$

The calculation of the scattered intensity is now performed with the general formula

$$I(\mathbf{H}) = L(h, k) \sum_m \sum_{\mu, \mu'} p_{\mu\mu'}(\mathbf{m}) F_{\mu} F_{\mu'}^+ (N - |m|) \times \exp\{-2\pi i m l\}. \quad (4.2.4.3)$$

Evaluation of this expression yields

$$I(\mathbf{H}) = L(h, k) \sum_m (N - |m|) \exp\{-2\pi i m l\} \times [|\frac{1}{2}(F_1 + F_2)|^2 \lambda_1^m + |\frac{1}{2}(F_1 - F_2)|^2 \lambda_2^m]. \quad (4.2.4.4)$$

Since the characteristic solutions of the problem are real:

$$I(\mathbf{H}) = L(\mathbf{h}) |(F_1 + F_2)/2|^2 + L(h, k) |(F_1 - F_2)/2|^2 \times \frac{1 - |\lambda_2|^2}{1 - 2\lambda_2 \cos 2\pi l + |\lambda_2|^2}. \quad (4.2.4.5)$$

This particle size effect has been neglected in (4.2.4.5). This result confirms the fact mentioned above that the sharp Bragg peaks are determined by the averaged structure factor and the diffuse one by its mean-square deviation.

For the following reason there are no examples for quantitative applications: two different structures generally have different lattice constants; hence the original assumption of an undisturbed lattice geometry is no longer valid. The only case known to the authors is the typical lamellar structure of plagioclases, reported by Jagodzinski & Korekawa (1965). The authors interpret the well known 'Schiller effect' as a consequence of optical diffraction. Hence, the size of the lamellae is of the order of 2000 Å. This long-period superstructure cannot be explained in terms of next-nearest-neighbour interactions. In principle, however, the diffraction effects are similar: instead of the diffuse peak as described by the second term in equation (4.2.4.5), satellites of first and second order, etc. accompanying the Bragg peaks are observed. The study of this phenomenon (Korekawa & Jagodzinski, 1967) has not so far resulted in a quantitative interpretation.

Obviously, the symmetry relation used in the formulae discussed above is only valid if the structures described by the F_{μ} are related by symmetries such as translations, rotations or combinations of both. The type of symmetry has an important influence on the diffraction pattern.

(1) Translation parallel to the ordered layers

If the translation vector between the two layers in question is such that $2\Delta\mathbf{r}$ is a translation vector parallel to the layer, there are two relevant structure factors

$$F_1, F_2 = F_1 \exp(2\pi i \mathbf{H} \cdot \Delta\mathbf{r}).$$

$\mathbf{H} \cdot \Delta\mathbf{r}$ may be either an integer or an integer + $\frac{1}{2}$. Since any integer may be neglected because of the translation symmetry parallel to the layer, we have $F_1 = F_2$ in the former case, and $F_1 = -F_2$ in the latter. As a consequence either the sharp reflections given in equation (4.2.4.4) vanish, or the same is true for the diffuse ones.

Hence, the reciprocal lattice may be described in terms of two kinds of lattice rows, sharp and diffuse, parallel to the reciprocal coordinate l .

Disorder of this type is observed very frequently. One of the first examples was wollastonite, CaSiO_3 , published by Jefferey (1953). Here the reflections with $k = 2n$ are sharp Bragg peaks without any diffuse scattering. Diffuse streaks parallel to $(h00)$, however, are detected for $k = 2n + 1$. In the light of the preceding discussion, the translation vector is $\frac{1}{2}\mathbf{b}$, and the plane of ordered direction (plane of intergrowth of the two domains) is (100) . Hence the displacement is parallel to the said plane. Since the intensity of the diffuse lines does not vary according to the structure factor involved, the disorder cannot be random. The maxima observed are approximately in the position of a superstructure, generated by large domains without faults in the stacking sequence, mutually displaced by $\frac{1}{2}\mathbf{b}$ (antiphase domains). This complicated ordering behaviour is typical for 1D order and may easily be explained by the above-mentioned fact that an infinitely extended interface between two domains causes an infinite unfavourable energy (Jagodzinski, 1964b, p. 188). Hence, a growing crystal should become increasingly ordered. This consideration explains why the agreement between a 1D disorder theory and experiment is often so poor.

Examples where more than one single displacement vector occur are common. If these are symmetrically equivalent all symmetries have to be considered. The most important cases of displacements differing only by translation are the well known close-packed structures (see below). A very instructive example is the mineral maucherite (approximately Ni_4As_3). According to Jagodzinski & Laves (1947) the structure has the following disorder parameters: interface (001) , displacement vectors $[000]$, $[\frac{1}{2}00]$, $[0\frac{1}{2}0]$, $[\frac{1}{2}\frac{1}{2}0]$. From equation (4.2.4.5) we obtain:

$$\langle F(\mathbf{H}) \rangle = [1 + \exp\{\pi i h\} + \exp\{\pi i k\} + \exp\{\pi i(h+k)\}]/4.$$

Hence there are sharp reflections for $h, k = \text{even}$, and diffuse ones otherwise. Further conclusions may be drawn from the average structure.

(2) Translation perpendicular to the ordered layers

If the translation is $\mathbf{c}/2$ the structure factors are:

$$F_2 = F_1 \exp\{2\pi i l\}$$

$$F_1 = F_2 \text{ for } l = \text{even}$$

$$F_1 = -F_2 \text{ for } l = \text{odd}.$$

There are sharp ($l = 2n$) and diffuse ($l = 2n + 1$) reflections on all reciprocal-lattice rows discussed above.

Since the sharp and diffuse reflections occur on the same reciprocal line there is a completely different behaviour compared with the preceding case. In general, a component of any displacement vector perpendicular to the interface gives rise to a change in chemical composition as shown in the next example: in a binary system consisting of A and B atoms with a tendency towards an alternating arrangement of A and B layers, any fault in the sequence $BABAB|BABAB|B$ increases the number of B atoms (or A atoms). Generally such kinds of defects will lead to an interface with a different lattice constant, at least in the direction perpendicular to the interface. Consequently the exact displacement vectors of $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ are rare. Since ordered structures should be realized in the 1D case, incommensurate superstructures will occur which are very abundant during ordering processes. An interesting example has been reported and interpreted by Cowley (1976) where the displacement vector has a translational period of $\frac{1}{4}$ perpendicular to the plane of intergrowth. Reflections $00l$ and $22l$ with $l = 4n$ are sharp, all remaining reflections more or less diffuse. Since the maxima $(111), (133)$ show a systematically different

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behaviour, there is also a displacement component parallel to the plane of intergrowth in question. The semi-quantitative interpretation has been given in his paper.

(3) Rotations

The discussion concerning layers related by a twofold rotation parallel to $\mathbf{c}$ may easily be made by simply considering their structure factors. Since the layers do not obey the twofold symmetry their structure factors are generally different; unless they equalize accidentally there are sharp and diffuse reflections according to the values of $\langle F \rangle$ and ΔF , respectively. Obviously, $F_1 = F_2$ is valid only if $h = k = 0$; consequently there is just one reciprocal-lattice row free from diffuse scattering.

(4) Asymmetric case

In the asymmetric case the symmetry conditions used above are no longer valid:

$$p_1 \neq p_2, p_{12} \neq p_{21}, p_{11} \neq p_{22}.$$

But there is one condition which may be derived from the invariance of the numbers of pairs in the relevant and its opposite direction:

$$p_{\mu} p_{\mu\mu'}(\mathbf{m}) = p_{\mu'} p_{\mu'\mu}(-\mathbf{m}).$$

This equation requires that $p_{\mu\mu'}(\mathbf{m})$ is not necessarily symmetric in $\mathbf{m}$. The calculation of characteristic values yields

$$\lambda_1 = 1, \quad \lambda_2 = (\alpha_1 + \alpha_2) - 1. \quad (4.2.4.6)$$

The *a priori* probabilities are now different from $\frac{1}{2}$, and may be calculated by considering $p_{\mu\mu'}(\mathbf{m}) \rightarrow p_{\mu'}(\mathbf{m} \rightarrow \infty)$:

$$p_1 = \alpha_1 / (\alpha_1 + \alpha_2); \quad p_2 = \alpha_2 / (\alpha_1 + \alpha_2).$$

The intensity is given by an expression very similar to (4.2.4.5):

$$\begin{aligned} I(\mathbf{H}) &= L(\mathbf{h}) [[\alpha_1 / (\alpha_1 + \alpha_2)] F_1 + [\alpha_2 / (\alpha_1 + \alpha_2)] F_2]^2 \\ &\quad + L(h, k) [[\alpha_1 / (\alpha_1 + \alpha_2)] F_1 - [\alpha_2 / (\alpha_1 + \alpha_2)] F_2]^2 \\ &\quad \times (1 - |\lambda_2|^2) / (1 - 2\lambda_2 \cos 2\pi l + |\lambda_2|^2). \end{aligned} \quad (4.2.4.7)$$

Again there are sharp Bragg reflections and diffuse ones in the same positions, or in a displaced position depending on the sign of λ_2 .

From a discussion of the next-nearest-neighbour Ising model one may conclude that the detailed study of the qualitative behaviour of sharp and diffuse reflections may give additional information on the symmetry of the layers involved.

In the case of translations between neighbouring layers not fulfilling the condition $\mathbf{h} \cdot \mathbf{r} = \text{integer}$, where $\mathbf{r}$ is parallel to the layer, more than two structure factors have to be taken into account. If $n\mathbf{h} \cdot \mathbf{r} = \text{integer}$, where n is the smallest integer fulfilling the said condition, n different structure factors have to be considered. The characteristic equation has formally to be derived with the aid of an $n \times n$ matrix containing internal symmetries which may be avoided by adding the phase factors $\varepsilon = \exp\{2\pi i \mathbf{H} \cdot \mathbf{r} / n\}$, $\varepsilon^+ = \exp\{-2\pi i \mathbf{H} \cdot \mathbf{r} / n\}$ to the probability of pairs. The procedure is allowed if the displacements $\mathbf{r}$ and $-\mathbf{r}$ are admitted only for neighbouring layers. The matrix yielding the characteristic values may then be reduced to

$$\begin{pmatrix} \alpha_1 \varepsilon & (1 - \alpha_1) \varepsilon^+ \\ (1 - \alpha_2) \varepsilon & \alpha_2 \varepsilon^+ \end{pmatrix}$$

and yields the characteristic equation

$$\lambda^2 - \lambda(\alpha_1 \varepsilon + \alpha_2 \varepsilon^+) - 1 + \alpha_1 + \alpha_2 = 0. \quad (4.2.4.8)$$

Equation (4.2.4.8) gives sharp Bragg reflections for $\mathbf{H} \cdot \mathbf{r} / n = \text{integer}$; the remaining diffuse reflections are displaced

corresponding to the phase of the complex characteristic value. Equation (4.2.4.8) has been used in many cases. Qualitative examples are the mixed-layer structures published by Hendricks & Teller (1942). An example of a four-layer-type structure is treated by Dubernat & Pezerat (1974). A first quantitative treatment with good agreement between theory and experimental data (powder diffraction) has been given by Dorner & Jagodzinski (1972) for the binary system $\text{TiO}_2\text{-SnO}_2$. In the range of the so-called spinodal decomposition the chemical composition of the two domains and the average lengths of the two types of domains could be determined. Another quantitative application was reported by Jagodzinski & Hellner (1956) for the transformation of RhSn_2 into a very complicated mixed-layer type. A good agreement of measured and calculated diffuse scattering (asymmetric line profiles, displacement of maxima) could be found over a wide angular range of single-crystal diffraction.

4.2.4.2.1. Stacking disorder in close-packed structures

From an historical point of view stacking disorder in close-packed systems is most important. The three relevant positions of ordered layers are represented by the atomic coordinates $|0, 0|, |\frac{1}{3}, \frac{2}{3}|, |\frac{2}{3}, \frac{1}{3}|$ in the hexagonal setting of the unit cell, or simply by the figures 1, 2, 3 in the same sequence. Structure factors F_1, F_2, F_3 refer to the corresponding positions of the same layer:

$$\begin{aligned} F_2 &= F_1 \exp\{2\pi i(h - k)/3\}, \\ F_3 &= F_1 \exp\{-2\pi i(h - k)/3\}, \end{aligned}$$

hence

$$F_1 = F_2 = F_3 \quad \text{if } h - k \equiv 0 \pmod{3}.$$

According to the above discussion the said indices define the reciprocal-lattice rows exhibiting sharp reflections only, as long as the distances between the layers are exactly equal. The symmetry conditions caused by the translation are normally:

$$\begin{aligned} p_1 &= p_2 = p_3, & p_{11} &= p_{22} = p_{33}, \\ p_{12} &= p_{23} = p_{31}, & p_{13} &= p_{21} = p_{32}. \end{aligned}$$

For the case of close packing of spheres and some other problems any configuration of $\mathbf{m}$ layers determining the *a posteriori* probability $p_{\mu\mu'}(\mathbf{m})$, $\mu = \mu'$, has a symmetrical counterpart where μ is replaced by $\mu' + 1$ (if $\mu' = 3, \mu' + 1 = 1$).

In this particular case $p_{12}(\mathbf{m}) = p_{13}(\mathbf{m})$, and equivalent relations generated by translation.

Nearest-neighbour interactions do not lead to an ordered structure if the principle of close packing is obeyed (no pairs in equal positions) (Hendricks & Teller, 1942; Wilson, 1942). Extension of the interactions to next-but-one or more neighbours may be carried out by introducing the method of matrix multiplication developed by Kakinoki & Komura (1954, 1965), or the method of overlapping clusters (Jagodzinski, 1954). The latter procedure is outlined in the case of interactions between four layers. A given set of three layers may occur in the following 12 combinations:

$$\begin{aligned} &123, 231, 312; \quad 132, 213, 321; \\ &121, 232, 313; \quad 131, 212, 323. \end{aligned}$$

Since three of them are equivalent by translation, only four representatives have to be introduced:

$$123; \quad 132; \quad 121; \quad 131.$$

In the following the new indices 1, 2, 3, 4 are used for these four representatives for the sake of simplicity.

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In order to construct the statistics layer by layer the next layer must belong to a triplet starting with the same two symbols with which the preceding one ended, *e.g.* 123 can only be followed by 231, or 232. In a similar way 132 can only be followed by 321 or 323. Since both cases are symmetrically equivalent the probabilities α_1 and $1 - \alpha_1$ are introduced. In a similar way 121 may be followed by 212 or 213 *etc.* For these two groups the probabilities α_2 and $1 - \alpha_2$ are defined. The different translations of groups are considered by introducing the phase factors as described above. Hence, the matrix for the characteristic equation may be set up as follows. As representative cluster of each group is chosen that one having the number 1 at the centre, *e.g.* 312 is representative for the group 123, 231, 312; in a similar way 213, 212 and 313 are the remaining representatives. Since this arrangement of three layers is equivalent by translation, it may be assumed that the structure of the central layer is not influenced by the statistics to a first approximation. The same arguments hold for the remaining three groups. On the other hand, the groups 312 and 213 are equivalent by rotation only. Consequently their structure factors may differ if the influence of the two neighbours has to be taken into account. A different situation exists for the groups 212 and 313 which are correlated by a centre of symmetry, which causes different corresponding structure factors. It should be pointed out, however, that the structure factor is invariant as long as there is no influence of neighbouring layers on the structure of the central layer. The latter is often observed in close-packed metal structures, or in compounds like ZnS, SiC and others. For the calculation of intensities $p_\mu p_{\mu\mu'}, F_\mu F_{\mu'}^+$ is needed.

According to the following scheme of sequences any sequence of pairs is correlated with the same phase factor for FF^+ due to translation, if both members of the pair belong to the same group. Consequently the phase factor may be attached to the sequence probability such that FF^+ remains unchanged, and the group may be treated as a single element in the statistics. In this way the reduced matrix for the solution of the characteristic equation is given by

F_μ	$F_{\mu'}^+$	(1) 312, 123(ε^+), 231(ε)	(2) 212, 323(ε^+), 131(ε)	(3) 213, 321(ε^+), 132(ε)	(4) 313, 121(ε^+), 232(ε)
(1) 312, 123(ε), 231(ε^+)		$\alpha_1 \varepsilon^+$	0	0	$(1 - \alpha_1) \varepsilon^+$
(2) 212, 323(ε), 131(ε^+)		$(1 - \alpha_2) \varepsilon^+$	0	0	$\alpha_2 \varepsilon^+$
(3) 213, 321(ε), 132(ε^+)		0	$(1 - \alpha_2) \varepsilon$	$\alpha_1 \varepsilon$	0
(4) 313, 121(ε), 232(ε^+)		0	$\alpha_2 \varepsilon$	$(1 - \alpha_2) \varepsilon$	0

There are three solutions of the diffraction problem:

(1) If $h - k = 0 \pmod{3}$, $\varepsilon = +1$, there are two quadratic equations:

$$\begin{aligned} \lambda^2 - (\alpha_1 + \alpha_2)\lambda - 1 + \alpha_1 + \alpha_2 &= 0 \\ \lambda^2 - (\alpha_1 - \alpha_2)\lambda + 1 - \alpha_1 - \alpha_2 &= 0 \end{aligned} \quad (4.2.4.9)$$

with solutions

$$\begin{aligned} \lambda_1 &= 1, \quad \lambda_2 = \alpha_1 + \alpha_2 - 1 \\ \lambda_{3/4} &= \frac{\alpha_1 - \alpha_2}{2} \pm \left[\frac{(\alpha_1 - \alpha_2)^2}{4} - 1 + \alpha_1 - \alpha_2 \right]^{1/2}. \end{aligned} \quad (4.2.4.10)$$

λ_1 and λ_2 are identical with the solution of the asymmetric case of two kinds of layers [*cf.* equation (4.2.4.6)]. They yield sharp

reflections for $l = \text{integer}$, and diffuse ones in a position determined by the sequence probabilities α_1 and α_2 (position either $l = \text{integer}$, $l = \frac{1}{2} + \text{integer}$, respectively). The remaining two characteristic values may be given in the form $\lambda = |\lambda| \exp\{2\pi i \varphi\}$, where φ determines the position of the reflection. If the structure factors of the layers are independent of the cluster, $\lambda_2, \lambda_3, \lambda_4$ become irrelevant because of the new identity of the F 's (no diffuse scattering). Weak diffuse intensities on the lattice rows $k - k = 0 \pmod{3}$ may be explained in terms of this influence.

(2) The remaining two solutions for $\varepsilon = \exp\{\pm 2\pi i(h - k)/3\}$ are equivalent, and result in the same characteristic values. They have been discussed explicitly in the literature; the reader is referred to the papers of Jagodzinski (1949*a,b,c*, 1954).

In order to calculate the intensities one has to reconsider the symmetry of the clusters, which is different from the symmetry of the layers. Fortunately, a threefold rotation axis is invariant against the translations, but this is not true for the remaining symmetry operations in the layer if there are any more. Since we have two pairs of inequivalent clusters, namely 312, 213 and 212, 313, there are only two different *a priori* probabilities $p_1 = p_3$ and $p_2 = p_4 = \frac{1}{2}(1 - 2p_1)$.

The symmetry conditions of the new clusters may be determined by means of the so-called 'probability trees' described by Wilson (1942) and Jagodzinski (1949*b*, pp. 208–214). For example: $p_{11} = p_{33}$, $p_{22} = p_{44}$, $p_{13} = p_{31}$, $p_{24} = p_{42}$ *etc.*

It should be pointed out that clusters 1 and 3 describe a cubic arrangement of three layers in the case of simple close packing, while clusters 2 and 4 represent the hexagonal close packing. There may be a small change in the lattice constant c perpendicular to the layers. Additional phase factors then have to be introduced in the matrix for the characteristic equation, and a recalculation of the constants is necessary. As a consequence, the reciprocal-lattice rows $(h - k) \equiv 0 \pmod{3}$ become diffuse if $l \neq 0$, and the diffuseness increases with l . A similar behaviour results for the remaining reciprocal-lattice rows.

The final solution of the diffraction problem results in the following general intensity formula:

$$\begin{aligned} I(\mathbf{H}) &= L(h, k) N \sum_{\nu} \{A_{\nu}(\mathbf{H})(1 - |\lambda_{\nu}|^2) \\ &\quad \times [1 - 2|\lambda_{\nu}| \cos 2\pi(l - \varphi_{\nu}) + |\lambda_{\nu}|^2]^{-1} \\ &\quad - 2B_{\nu}(\mathbf{H})|\lambda_{\nu}| \sin 2\pi(l - \varphi_{\nu}) \\ &\quad \times [1 - 2|\lambda_{\nu}| \cos 2\pi(l - \varphi_{\nu}) + |\lambda_{\nu}|^2]^{-1}\}. \end{aligned} \quad (4.2.4.11)$$

Here A_{ν} and B_{ν} represent the real and imaginary part of the constants to be calculated with the aid of the boundary conditions of the problem. The first term in equation (4.2.4.11) determines the symmetrical part of a diffuse reflection with respect to the maximum, and is completely responsible for the integrated

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intensity. The second term causes an antisymmetrical contribution to intensity profiles but does not influence the integrated intensities. These general relations enable a semi-quantitative interpretation of the sharp and diffuse scattering in any case, without performing the time-consuming calculations of the constants which may only be done in more complicated disorder problems with the aid of a computer program evaluating the boundary conditions of the problem.

This can be carried out with the aid of the characteristic values and a linear system of equations (Jagodzinski, 1949a,b,c), or with the aid of matrix formalism (Kakinoki & Komura, 1954; Takaki & Sakurai, 1976). As long as only the line profiles and positions of the reflections are required, these quantities may be determined experimentally and fitted to characteristic values of a matrix. The size of this matrix is given by the number of sharp and diffuse maxima observed, while $|\lambda_\nu|$ and $\exp\{2\pi i\varphi_\nu\}$ may be found by evaluating the line width and the position of diffuse reflections. Once this matrix has been found, a semi-quantitative model of the disorder problem can be given. If a system of sharp reflections is available, the averaged structure can be solved as described in Section 4.2.3.2. The determination of the constants of the diffraction problem is greatly facilitated by considering the intensity modulation of diffuse scattering, which enables a phase determination of structure factors to be made under certain conditions.

The theory of closed-packed structures with three equivalent translation vectors has been applied very frequently, even to systems which do not obey the principle of close-packing. The first quantitative explanation was published by Halla *et al.* (1953). It was shown there that single crystals of $C_{18}H_{24}$ from the same synthesis may have a completely different degree of order. This was true even within the same crystal. Similar results were found for C, Si, CdI_2 , CdS_2 , mica and many other compounds. Quantitative treatments are less abundant [*e.g.* CdI_2 : Martorana *et al.* (1986); MX_3 structures: Conradi & Müller (1986)]. Special attention has been paid to the quantitative study of polytypic phase transformations in order to gain information about the thermodynamical stability or the mechanism of layer displacements, *e.g.* Co (Edwards & Lipson, 1942; Frey & Boysen, 1981), SiC (Jagodzinski, 1972; Pandey *et al.*, 1980), ZnS (Müller, 1952; Mardix & Steinberger, 1970; Frey *et al.*, 1986) and others.

Certain laws may be derived for the reduced integrated intensities of diffuse reflections. 'Reduction' in this context means a division of the diffuse scattering along l by the structure factor, or the difference structure factor if $\langle F \rangle \neq 0$. This procedure is valuable if the number of stacking faults rather than the complete solution of the diffraction problem is required.

The discussion given above has been made under the assumption that the full symmetry of the layers is maintained in the statistics. Obviously, this is not necessarily true if external lower symmetries influence the disorder. An important example is the generation of stacking faults during plastic deformation. Problems of this kind need a complete reconsideration of symmetries. Furthermore, it should be pointed out that a treatment with the aid of an extended Ising model as described above is irrelevant in most cases. Simplified procedures describing the diffuse scattering of intrinsic, extrinsic, twin stacking faults and others have been described in the literature. Since their influence on *structure determination* can generally be neglected, the reader is referred to the literature for additional information.

4.2.4.3. Two-dimensional disorder of chains

In this section disorder phenomena are considered which are related to chain-like structural elements in crystals. This topic includes the so-called '1D crystals' where translational symmetry

(in direct space) exists in one direction only – crystals in which highly anisotropic binding forces are responsible for chain-like atomic groups, *e.g.* compounds which exhibit a well ordered 3D framework structure with tunnels in a unique direction in which atoms, ions or molecules are embedded. Examples are compounds with platinum, iodine or mercury chains, urea inclusion compounds with columnar structures (organic or inorganic), 1D ionic conductors, polymers *etc.* Diffuse-scattering studies of 1D conductors have been carried out in connection with investigations of stability/instability problems, incommensurate structures, phase transitions, dynamic precursor effects *etc.* These questions are not treated here. For general reading of diffuse scattering in connection with these topics see, *e.g.*, Comes & Shirane (1979, and references therein). Also excluded are specific problems related to polymers or liquid crystals (mesophases) (see Chapter 4.4) and magnetic structures with chain-like spin arrangements.

Trivial diffuse scattering occurs as 1D Bragg scattering (diffuse layers) by internally ordered chains. Diffuse phenomena in reciprocal space are due to 'longitudinal' disordering within the chains (along the unique direction) as well as to 'transverse' correlations between different chains over a restricted volume. Only static aspects are considered; diffuse scattering resulting from collective excitations or diffusion-like phenomena which are of inelastic or quasielastic origin are not treated here.

4.2.4.3.1. Scattering by randomly distributed collinear chains

As found in any elementary textbook of diffraction the simplest result of scattering by a chain with period c

$$l(\mathbf{r}) = l(z) = \sum_{n_3} \delta(z - n_3 c) \quad (4.2.4.12)$$

is described by one of the Laue equations:

$$G(L) = |L(L)|^2 = \sin^2 \pi N L / \sin^2 \pi L \quad (4.2.4.13)$$

which gives broadened profiles for small N . In the context of phase transitions the Ornstein–Zernike correlation function is frequently used, *i.e.* (4.2.4.13) is replaced by a Lorentzian:

$$1/\{\xi^2 + 4\pi^2(L - l)^2\}, \quad (4.2.4.14)$$

where ξ denotes the correlation length.

In the limiting case $N \rightarrow \infty$, (4.2.4.13) becomes

$$\sum_l \delta(L - l). \quad (4.2.4.15)$$

The scattering by a real chain $a(\mathbf{r})$ consisting of molecules with structure factor F_M is therefore determined by

$$F_M(\mathbf{H}) = \sum_j f_j \exp\{2\pi i(Hx_j + Ky_j + Lz_j)\}. \quad (4.2.4.16)$$

The Patterson function is:

$$\begin{aligned} P(\mathbf{r}) = & (1/c) \int \int |F_0(H, K)|^2 \cos 2\pi(Hx + Ky) dH dK \\ & + (2/c) \sum_l \int \int |F_l|^2 \exp\{2\pi i(Hx + Ky)\} \\ & \times \exp\{-2\pi i l z\} dH dK, \end{aligned} \quad (4.2.4.17)$$

where the index l denotes the only relevant position $L = l$ (the subscript M is omitted).

The intensity is concentrated in diffuse layers perpendicular to $\mathbf{c}^*$ from which the structural information may be extracted. Projections are:

$$\int a(\mathbf{r}) dz = \int \int F_0(H, K) \exp\{2\pi i(Hx + Ky)\} dH dK \quad (4.2.4.18)$$

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$$\int \int a(\mathbf{r}) \, dx \, dy = (2/c) \sum_l F_l(00l) \exp(-2\pi i l z). \quad (4.2.4.19)$$

Obviously the z parameters can be determined by scanning along a meridian (00L) through the diffuse sheets (diffractometer recording). Owing to intersection of the Ewald sphere with the set of planes the meridian cannot be recorded on *one* photograph; successive equi-inclination photographs are necessary. Only in the case of large c spacings is the meridian well approximated in one photograph.

There are many examples where a tendency to cylindrical symmetry exists: chains with p -fold rotational or screw symmetry around the preferred direction or assemblies of chains (or domains) with statistical orientational distribution around the texture axis. In this context it should be mentioned that symmetry operations with rotational parts belonging to the 1D rod groups actually occur, *i.e.* not only $p = 2, 3, 4, 6$.

In all these cases a treatment in the frame of cylindrical coordinates is advantageous (see, *e.g.*, Vainshtein, 1966):

Direct space	Reciprocal space
$x = r \cos \psi$	$H = H_r \cos \Psi$
$y = r \sin \psi$	$K = H_r \sin \Psi$
$z = z$	$L = L$

$$a(r, \psi, z) = \int \int \int F(\mathbf{H}) \exp\{-2\pi i [H_r r \cos(\psi - \Psi) + Lz]\} \times H_r \, dH_r \, d\Psi \, dL \quad (4.2.4.20)$$

$$F(\mathbf{H}) = \int \int \int a(r, \psi, z) \exp\{2\pi i [H_r r \cos(\psi - \Psi) + Lz]\} \times r \, dr \, d\psi \, dz. \quad (4.2.4.21)$$

The integrals may be evaluated by the use of Bessel functions:

$$J_n(u) = \frac{1}{2\pi i^n} \int \exp\{i(u \cos \varphi + n\varphi)\} \, d\varphi$$

($u = 2\pi r H_r$; $\varphi = \psi - \Psi$).

The 2D problem $a = a(r, \psi)$ is treated first; an extension to the general case $a(r, \psi, z)$ is easily made afterwards.

Along the theory of Fourier series one has:

$$\begin{aligned} a(r, \psi) &= \sum_n a_n(r) \exp\{in\psi\} \\ a_n(r) &= \frac{1}{2\pi} \int a(r, \psi) \exp\{-in\psi\} \, d\psi \end{aligned} \quad (4.2.4.22)$$

or with:

$$\begin{aligned} \alpha_n &= \frac{1}{2\pi} \int a(r, \psi) \cos(n\psi) \, d\psi \\ \beta_n &= \frac{1}{2\pi} \int a(r, \psi) \sin(n\psi) \, d\psi \\ a_n(r) &= |a_n(r)| \exp\{-i\psi_n(r)\} \\ |a_n(r)| &= \sqrt{\alpha_n^2 + \beta_n^2} \\ \psi_n(r) &= \arctan \beta_n / \alpha_n. \end{aligned}$$

If contributions to anomalous scattering are neglected $a(r, \psi)$ is a real function:

$$a(r, \psi) = \sum_n |a_n(r)| \cos[n\psi - \psi_n(r)]. \quad (4.2.4.23)$$

Analogously, one has

$$F(H_r, \Psi) = \sum_n |F_n(H_r)| \exp(in\Psi). \quad (4.2.4.24)$$

$F(H_r, \Psi)$ is a complex function; $F_n(H_r)$ are the Fourier coefficients which are to be evaluated from the $a_n(r)$:

$$\begin{aligned} F_n(H_r) &= \frac{1}{2\pi} \int F(H_r, \Psi) \exp\{-in\Psi\} \, d\Psi \\ &= \exp\{in\pi/2\} \int a_n(r) J_n(2\pi r H_r) 2\pi r \, dr \\ F(H_r, \Psi) &= \sum_n \exp\{in[\Psi + (\pi/2)]\} \int a_n(r) \\ &\quad \times J_n(2\pi r H_r) 2\pi r \, dr \end{aligned} \quad (4.2.4.25)$$

$$\begin{aligned} a(r, \psi) &= \sum_n \exp\{in[\Psi - (\pi/2)]\} \int F_n(H_r) \\ &\quad \times J_n(2\pi r H_r) 2\pi H_r \, dH_r. \end{aligned} \quad (4.2.4.26)$$

The formulae may be used for calculation of diffuse intensity distribution within a diffuse sheet, in particular when the chain molecule is projected along the unique axis [*cf.* equation (4.2.4.18)].

Special cases are:

(a) *Complete cylinder symmetry*

$$F(H_r) = 2\pi \int a(r) J_0(2\pi r H_r) r \, dr \quad (4.2.4.27)$$

$$a(r) = 2\pi \int F(H_r) J_0(2\pi r H_r) H_r \, dH_r. \quad (4.2.4.28)$$

(b) *p-fold symmetry of the projected molecule* $a(r, \psi) = a[r, \psi + (2\pi/p)]$

$$\begin{aligned} F_p(H_r, \Psi) &= \sum_n \exp\{inp[\Psi + (\pi/2)]\} \\ &\quad \times \int a_{np}(r) J_{np}(2\pi r H_r) 2\pi r \, dr \end{aligned} \quad (4.2.4.29)$$

$$a_p(r, \psi) = \sum_n |a_{np}(r)| \cos[np\psi - \psi_{np}(r)]. \quad (4.2.4.30)$$

Only Bessel functions $J_0, J_p, J_{2p}, \dots$ occur. In most cases J_{2p} and higher orders may be neglected.

(c) *Vertical mirror planes*

Only cosine terms occur, *i.e.* all $\beta_n = 0$ or $\psi_n(r) = 0$.

The *general 3D expressions* valid for extended chains with period c [equation (4.2.4.12)] are found in an analogous way:

$$a(r, \psi, z) = a_M(r, \psi, z) * l(z)$$

$$\begin{aligned} F(\mathbf{H}) &= F_l(H_r, \Psi, L) = F_M(\mathbf{H}) L(L) \\ &= \int \int \int a_M(r, \psi, z) \exp\{2\pi i [H_r r \cos(\psi - \Psi) + Lz]\} \\ &\quad \times 2\pi r \, dr \, d\psi \, dz \end{aligned} \quad (4.2.4.31)$$

using a series expansion analogous to (4.2.4.23) and (4.2.4.24):

$$a_{nl}(r) = \frac{1}{2\pi} \int \int a_M \exp\{-i(n\psi - 2\pi l z)\} \, d\psi \, dz \quad (4.2.4.32)$$

$$F_{nl}(H_r) = \exp\{in\pi/2\} \int a_{nl}(r) J_n(2\pi H_r r) 2\pi r \, dr \quad (4.2.4.33)$$

one has:

$$F_l(\mathbf{H}) = \sum_n \exp\{in[\Psi + (\pi/2)]\} \int a_{nl}(r) J_n(2\pi H_r r) 2\pi r \, dr. \quad (4.2.4.34)$$

In practice the integrals are often replaced by discrete summation of j atoms at positions: $r = r_j$, $\psi = \psi_j$, $z = z_j$ ($0 \leq z_j < c$):

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$$F_l(\mathbf{H}) = \sum_j \sum_n f_j J_n(2\pi H_r r_j) \exp\{-in\psi_j\} \times \exp(2\pi i l z_j) \exp\{in[\Psi + (\pi/2)]\} \quad (4.2.4.35)$$

or

$$F_l(\mathbf{H}) = \sum_n (\alpha_n + i\beta_n) \exp\{in\Psi\}$$

$$\alpha_n = \sum_j f_j J_n(2\pi H_r r_j) \cos\{n[(\pi/2) - \psi_j] + 2\pi l z_j\}$$

$$\beta_n = \sum_j f_j J_n(2\pi H_r r_j) \sin\{n[(\pi/2) - \psi_j] + 2\pi l z_j\}.$$

Intensity in the l th diffuse layer is given by

$$I_l = \sum_n \sum_{n'} [(\alpha_n \alpha_{n'} + \beta_n \beta_{n'}) + i(\alpha_{n'} \beta_n - \alpha_n \beta_{n'})] \times \exp\{i(n - n')\Psi\}. \quad (4.2.4.36)$$

(a) *Cylinder symmetry* (free rotating molecules around the chain axis or statistical averaging with respect to ψ over an assembly of chains). Only component F_{0l} occurs:

$$F_{0l}(H_r, L) = 2\pi \int \langle a_M \rangle J_0(2\pi H_r r) \exp\{2\pi i l z\} r \, dr \, dz$$

or

$$F_{0l}(H_r, L) = \sum_j f_j J_0(2\pi H_r r_j) \exp\{2\pi i l z_j\}.$$

In particular, $F_{00}(H_r)$ determines the radial component of the molecule projected along z :

$$F_{00}(H_r) = \sum_j f_j J_0(2\pi H_r r_j).$$

(b) *p-fold symmetry* of a plane molecule (or projected molecule) as outlined previously: only components np instead of n occur. Bessel functions J_0 and J_p are sufficient in most cases.

(c) *Vertical mirror plane*: see above.

(d) *Horizontal mirror plane* (perpendicular to the chain): Exponentials $\exp\{2\pi i l z\}$ in equation (4.2.4.32) may be replaced by $\cos 2\pi l z$.

(e) *Twofold symmetry axis* perpendicular to the chain axis (at positions $\psi = 0, 2\pi/p, \dots$). Exponentials in equation (4.2.4.32), $\exp\{-i(np\psi - 2\pi l z)\}$, are replaced by the corresponding cosine term $\cos(np\psi + 2\pi l z)$.

Formulae concerning the reverse method (Fourier synthesis) are not given here (see, e.g., Vainshtein, 1966). Usually there is no practical use in diffuse-scattering work because it is very difficult to separate out a single component F_{nl} . Every diffuse layer is affected by *all* components F_{nl} . There is a chance if *one* diffuse layer corresponds predominantly to *one* Bessel function.

4.2.4.3.2. Disorder within randomly distributed collinear chains

Deviations from strict periodicities in the z direction within one chain may be due to loss of translational symmetry of the centres of the molecules along z and/or due to varying orientations of the molecules with respect to different axes, such as azimuthal misorientation, tilting with respect to the z axis or combinations of both types. As in 3D crystals, there may or may not exist 1D structures in an averaged sense.

4.2.4.3.2.1. General treatment

All formulae given in this section are only special cases of a 3D treatment (see, e.g., Guinier, 1963). The 1D lattice (4.2.4.12) is

replaced by a distribution:

$$d(z) = \sum_\nu \delta(z - z_\nu)$$

$$D(L) = \sum_\nu \exp\{2\pi i L z_\nu\} \quad (4.2.4.37)$$

$$F(\mathbf{H}) = F_M(\mathbf{H})D(L).$$

The Patterson function is given by

$$P(\mathbf{r}) = [a_M(\mathbf{r}) * a_M - (\mathbf{r})] * [d(z) * d - (z)]. \quad (4.2.4.38)$$

Because the autocorrelation function $w = d * d$ is centrosymmetric

$$w(z) = N\delta(z) + \sum_\nu \sum_\mu \delta[z - (z_\nu - z_\mu)] + \sum_\nu \sum_\mu \delta[z + (z_\nu - z_\mu)], \quad (4.2.4.39)$$

the interference function $W(L) (= |D(L)|^2)$ is given by

$$W(L) = N + 2 \sum_\nu \sum_\mu \cos 2\pi [L(z_\nu - z_\mu)] \quad (4.2.4.40)$$

$$I(\mathbf{H}) = |F_M(\mathbf{H})|^2 W(L). \quad (4.2.4.41)$$

Sometimes, e.g. in the following example of orientational disorder, there is an order only within domains. As shown in Section 4.2.3, this may be treated by a box or shape function $b(z) = 1$ for $z \leq z_N$ and 0 elsewhere.

$$d(z) = d_\infty b(z)$$

$$a(\mathbf{r}) = a_M(\mathbf{r}) * [d_\infty b(z)] \quad (4.2.4.42)$$

$$F(\mathbf{H}) = F_M(\mathbf{H})[D_\infty * B(L)]$$

with

$$b(z) * b - (z) \leftrightarrow |B(L)|^2$$

$$I = |F_M(\mathbf{H})|^2 |D_\infty * B(L)|^2. \quad (4.2.4.43)$$

If the order is perfect within one domain one has $D_\infty(L) \simeq \sum \delta(L - l)$; $(D_\infty * B) = \sum D(L - l)$; i.e. each reflection is affected by the shape function.

4.2.4.3.2.2. Orientational disorder

A misorientation of the chain molecules with respect to one another is taken into account by different structure factors F_M .

$$I(\mathbf{H}) = \sum_\nu \sum_\mu F_\nu(\mathbf{H}) F_\mu(\mathbf{H})^+ \exp\{2\pi i L(z_\nu - z_\mu)\}. \quad (4.2.4.44)$$

A further discussion follows the same arguments outlined in Section 4.2.3. For example, a very simple result is found in the case of uncorrelated orientations. Averaging over all pairs $F_\nu F_\mu^+$ yields

$$I(\mathbf{H}) = N(\langle |F|^2 \rangle - \langle |F| \rangle^2) + \langle |F| \rangle^2 L(L), \quad (4.2.4.44a)$$

where

$$\langle |F| \rangle^2 = 1/N^2 \langle F_\nu F_\mu^+ \rangle$$

$$= \sum_\nu \alpha_\nu F_\nu(\mathbf{H}) \sum_\mu \alpha_\mu F_\mu^+(\mathbf{H}) \quad (\nu \neq \mu)$$

$$\langle |F|^2 \rangle = 1/N \langle F_\nu F_\nu^+ \rangle = \sum_\nu \alpha_\nu |F_\nu(\mathbf{H})|^2.$$

Besides the diffuse layer system there is a diffuse background modulated by the $\mathbf{H}$ dependence of $[\langle |F(\mathbf{H})|^2 \rangle - \langle |F(\mathbf{H})| \rangle^2]$.

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4.2.4.3.2.3. Longitudinal disorder

In this context the structure factor of a chain molecule is neglected. Irregular distances between the molecules within a chain occur owing to the shape of the molecules, intrachain interactions and/or interaction forces *via* a surrounding matrix. A general discussion is given by Guinier (1963). It is convenient to reformulate the discrete Patterson function, *i.e.* the correlation function (4.2.4.39).

$$w(z) = N\delta(z) + \sum_{\nu} \delta[z \pm (z_{\nu} - z_{\nu+1})] + \sum_{\nu} \delta[z \pm (z_{\nu} - z_{\nu+2})] + \dots \quad (4.2.4.39a)$$

in terms of continuous functions $a_{\mu}(z)$ which describe the probability of finding the μ th neighbour within an arbitrary distance

$$w'(z) = w(z)/N = \delta(z) + a_1(z) + a_{-1}(z) + \dots + a_{\mu}(z)a_{-\mu}(z) + \dots \quad (4.2.4.45)$$

$$[\int a_{\mu}(z) dz = 1, a_{\mu}(z) = a_{-\mu}(-z)].$$

There are two principal ways to define $a_{\mu}(z)$. The first is the case of a well defined one-dimensional lattice with positional fluctuations of the molecules around the lattice points, *i.e.* long-range order is retained: $a_{\mu}(z) = \mu c_0 + z_{\mu}$, where z_{μ} denotes the displacement of the μ th molecule in the chain. Frequently used are Gaussian distributions:

$$c' \exp\{-(z - \mu c_0)^2/2\Delta^2\}$$

(c' = normalizing constant; Δ = standard deviation). Fourier transformation [equation (4.2.4.45)] gives the well known result

$$I_d \sim (1 - \exp\{-L^2\Delta^2\}),$$

i.e. a monotonically increasing intensity with L (modulation due to a molecular structure factor neglected). This result is quite analogous to the treatment of the scattering of independently vibrating atoms. If (short-range) correlations exist between the molecules the Gaussian distribution is replaced by a multivariate normal distribution where correlation coefficients κ^{μ} ($0 < \kappa < 1$) between a molecule and its μ th neighbour are incorporated. κ^{μ} is defined by the second moment: $\langle z_0 z_{\mu} \rangle / \Delta^2$.

$$a_{\mu}(z) = c'' \exp\{-(z - \mu c_0)^2/2\Delta^2(1 - \kappa^{\mu})\}.$$

Obviously the variance increases if the correlation diminishes and reaches an upper bound of twice the single site variance. Fourier transformation gives an expression for diffuse intensity (Welberry, 1985):

$$I_d(L) \sim \exp\{-L^2\Delta^2\} \sum_j (-L^2\Delta^2)^j/j! \times (1 - \kappa^{2j})/(1 + \kappa^{2j} - 2\kappa^j \cos 2\pi L c_0). \quad (4.2.4.46)$$

For small Δ , terms with $j > 1$ are mostly neglected. The terms become increasingly important with higher values of L . On the other hand, κ^j becomes smaller with increasing j , each additional term in equation (4.2.4.46) becomes broader and, as a consequence, the diffuse planes in reciprocal space become broader with higher L .

In a different way – in the paracrystal method – the position of the second and subsequent molecules with respect to some reference zero point depends on the *actual* position of the predecessor. The variance of the position of the μ th molecule relative to the first becomes unlimited. There is a continuous transition to a fluid-like behaviour of the chain molecules. This 1D paracrystal (sometimes called distortions of second kind) is only a special case of the 3D paracrystal concept (see Hosemann & Bagchi, 1962; Wilke, 1983). Despite some difficulties with this

concept (Brämer, 1975; Brämer & Ruland, 1976) it is widely used as a theoretical model for describing diffraction of highly distorted lattices. One essential development is to limit the size of a paracrystalline grain so that fluctuations never become too large (Hosemann, 1975).

If this concept is used for the 1D case, $a_{\mu}(z)$ is defined by convolution products of $a_1(z)$. For example, the probability of finding the next-nearest molecule is given by

$$a_2(z) = \int a_1(z') a_1(z - z') dz' = a_1(z) * a_1(z)$$

and, generally:

$$a_{\mu}(z) = a_1(z) * a_1(z) * a_1(z) * \dots * a_1(z)$$

(μ -fold convolution).

The mean distance between next-nearest neighbours is

$$\langle c \rangle = \int z' a_1(z') dz'$$

and between neighbours of the μ th order: $\mu\langle c \rangle$. The average value of $a_{\mu} = 1/\langle c \rangle$, which is also the value of $w(z)$ for $z > z_k$, where the distribution function is completely smeared out. The general expression for the interference function $G(L)$ is

$$G(L) = 1 + \sum_{\mu} \{F^{\mu} + F^{+\mu}\} = \text{Re}\{(1 + F)/(1 - F)\} \quad (4.2.4.47)$$

with $F(L) \leftrightarrow a_1(z)$, $F^{\mu}(L) \leftrightarrow a_{\mu}(z)$.

With $F = |F|e^{i\chi}$ ($\chi = L\langle c \rangle$), equation (4.2.4.47) is written:

$$G(L) = [1 - |F(L)|^2]/[1 - 2|F(L)|\cos\chi + |F(L)|^2]. \quad (4.2.4.47a)$$

[Note the close similarity to the diffuse part of equation (4.2.4.5), which is valid for 1D disorder problems.]

This function has maxima of height $(1 + |F|)/(1 - |F|)$ and minima of height $(1 - |F|)/(1 + |F|)$ at positions lc^* and $(l + \frac{1}{2})c^*$, respectively. With decreasing $|F|$ the oscillations vanish; a critical L value (corresponding to z_k) may be defined by $G_{\max}/G_{\min} \lesssim 1.2$. Actual values depend strongly on $F(\mathbf{H})$.

The paracrystal method is substantiated by the choice $a_1(z)$, *i.e.* the disorder model. Again, frequently used is a Gaussian distribution:

$$a_1(z) = 1/\sqrt{2\pi}\Delta \cdot \exp\{-(z - \langle c \rangle)^2/2\Delta^2\}$$

$$a_{\mu}(z) = 1/\sqrt{\mu} \cdot 1/\sqrt{2\pi}\Delta \cdot \exp\{-(z - \mu\langle c \rangle)^2/2\mu\Delta^2\}$$

$$(4.2.4.48)$$

with the two parameters $\langle c \rangle$, Δ .

There are peaks of height $1/[\pi^2 L^2 (\Delta/\langle c \rangle)^2]$ which obviously decrease with L^2 and $(\Delta/\langle c \rangle)^2$. The oscillations vanish for $|F| \simeq 0.1$, *i.e.* $1/\langle c \rangle \simeq 0.25/\Delta$. The width of the m th peak is $\Delta_m = \sqrt{m}\Delta$. The integral reflectivity is approximately $1/\langle c \rangle [1 - \pi^2 L^2 (\Delta/\langle c \rangle)^2]$ and the integral width (defined by integral reflectivity divided by peak reflectivity) (background subtracted!) $1/\langle c \rangle \pi^2 L^2 (\Delta/\langle c \rangle)^2$ which, therefore, increases with L^2 . In principle the same results are given by Zernike & Prins (1927). In practice a single Gaussian distribution is not fully adequate and modified functions must be used (Rosshirt *et al.*, 1985).

A final remark concerns the normalization [equation (4.2.4.39)]. Going from (4.2.4.39) to (4.2.4.45) it is assumed that N is a large number so that the correct normalization factors $(N - |\mu|)$ for each $a_{\mu}(z)$ may be approximated by a uniform N . If this is not true then

$$G(L) = N + \sum_{\mu} (N - |\mu|)(F^{\mu} + F^{+\mu}) = N \text{Re} \{(1 + |F|)/(1 - |F|)\} - 2 \text{Re} \{|F|(1 - |F|^N)/(1 - |F|^2)\}. \quad (4.2.4.49)$$

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The correction term may be important in the case of relatively small (1D) domains. As mentioned above, the structure factor of a chain molecule was neglected. The $\mathbf{H}$ dependence of F_m , of course, obscures the intensity variation of the diffuse layers as described by (4.2.4.47a).

The matrix method developed for the case of planar disorder was adapted to 2D disorder by Scaringe & Ibers (1979). Other models and corresponding expressions for diffuse scattering are developed from specific microscopic models (potentials), *e.g.* in the case of $\text{Hg}_{3-6}\text{AsF}_6$ (Emery & Axe, 1978; Radons *et al.*, 1983), hollandites (Beyeler *et al.*, 1980; Ishii, 1983), iodine chain compounds (Endres *et al.*, 1982) or urea inclusion compounds (Forst *et al.*, 1987).

4.2.4.3.3. Correlations between different almost collinear chains

In real cases there are more or less strong correlations between different chains at least within small domains. Deviations from a strict (3D) order of chain-like structural elements are due to several reasons: shape and structure of the chains, varying binding forces, thermodynamical or kinetic considerations.

Many types of disorder occur. (1) Relative shifts parallel to the common axis while projections along this axis give a perfect 2D ordered net ('axial disorder'). (2) Relative fluctuations of the distances between the chains (perpendicular to the unique axis) with short-range order along the transverse $\mathbf{a}$ and/or $\mathbf{b}$ directions. The net of projected chains down to the ab plane is distorted ('net distortions'). Disorder of types (1) and (2) is sometimes correlated owing to non-uniform cross sections of the chains. (3) Turns, twists and torsions of chains or parts of chains. This azimuthal type of disorder may be treated similarly to the case of azimuthal disorder of single-chain molecules. Correlations between axial shifts and torsions produce 'screw shifts' (helical structures). Torsion of chain parts may be of dynamic origin (rotational vibrations). (4) Tilting or bending of the chains in a uniform or non-uniform way ('conforming/non-conforming'). Many of these types and a variety of combinations between them are found in polymer and liquid crystals and are treated therefore separately. Only some simple basic ideas are discussed here in brief.

For the sake of simplicity the paracrystal concept in combination with Gaussians is used again. Distribution functions are given by convolution products of next-nearest-neighbour distribution functions. As long as averaged lattice directions and lattice constants in a plane perpendicular to the chain axis exist, only two functions $a_{100} = a_1(xyz)$ and $a_{010} = a_2(xyz)$ are needed to describe the arrangement of next-nearest chains. Longitudinal disorder is treated as before by a third distribution function $a_{001} = a_3(xyz)$. The phenomena of chain bending or tilting may be incorporated by an x and y dependence of a_3 . Any general fluctuation in the spatial arrangement of chains is given by

$$a_{mpq} = a_1 * \dots * a_1 * a_2 * \dots * a_2 * a_3 * \dots * a_3. \quad (4.2.4.50)$$

(m -fold, p -fold, q -fold self-convolution of a_1, a_2, a_3 , respectively.)

$$w(\mathbf{r}) = \delta(\mathbf{r}) \sum_m \sum_p \sum_q [a_{mpq}(\mathbf{r}) + a_{-mpq}(\mathbf{r})]. \quad (4.2.4.51)$$

a_ν ($\nu = 1, 2, 3$) are called fundamental functions. If an averaged lattice cannot be defined, more fundamental functions a_ν are needed to account for correlations between them.

By Fourier transformations the interference function is given by

$$G(\mathbf{H}) = \sum_m \sum_p \sum_q F_1^m F_2^p F_3^q = G_1 G_2 G_3; \quad (4.2.4.52)$$

$$G_\nu = \text{Re}\{(1 + |F_\nu|)/(1 - |F_\nu|)\}.$$

If Gaussian functions are assumed, simple pictures are derived. For example:

$$a_1(\mathbf{r} + \langle \mathbf{a} \rangle) = 1/(2\pi)^{3/2} \cdot 1/(\Delta_{11}\Delta_{12}\Delta_{13}) \times \exp\{-\frac{1}{2}[(x^2/\Delta_{11}^2) + (y^2/\Delta_{12}^2) + (z^2/\Delta_{13}^2)]\} \quad (4.2.4.53)$$

describes the distribution of neighbours in the x direction (mean distance $\langle a \rangle$). Parameter Δ_{13} concerns axial, Δ_{11} and Δ_{12} radial and tangential fluctuations, respectively. Pure axial distribution along $\mathbf{c}$ is given by projection of a_1 on the z axis, pure net distortions by projection on the $x - y$ plane. If the chain-like structure is neglected the interference function

$$G_1(\mathbf{H}) = \exp\{-2\pi^2(\Delta_{11}^2 H^2 + \Delta_{12}^2 K^2 + \Delta_{13}^2 L^2)\} \quad (4.2.4.54)$$

describes a set of diffuse planes perpendicular to $\mathbf{a}^*$ with mean distance $1/\langle a \rangle$. These diffuse layers broaden along H with $m\Delta_{11}$ and decrease in intensity along K and L monotonically. There is an ellipsoidal-shaped region in reciprocal space defined by main axes of length $1/\Delta_{11}, 1/\Delta_{12}, 1/\Delta_{13}$ with a limiting surface given by $|F| \simeq 0.1$, beyond which the diffuse intensity is completely smeared out. The influence of a_2 may be discussed in an analogous way.

If the chain-like arrangement parallel to $\mathbf{c}$ [equation (4.2.4.12)] is taken into consideration,

$$l(z) = \sum_{n_3} \delta(z - n_3 c);$$

the set of planes perpendicular to $\mathbf{a}^*$ (and/or $\mathbf{b}^*$) is subdivided in the L direction by a set of planes located at $l \cdot 1/c$ [equation (4.2.4.15)].

Longitudinal disorder is given by $a_3(z)$ [equation (4.2.4.48), $\Delta_{33} = \Delta$] and leads to two intersecting sets of broadened diffuse layer systems.

Particular cases like pure axial distributions ($\Delta_{11}, \Delta_{12} \sim 0$), pure tangential distributions (net distortions: $\Delta_{11}, \Delta_{13} \sim 0$), uniform bending of chains or combinations of these effects are discussed in the monograph of Vainshtein (1966).

4.2.4.4. Disorder with three-dimensional correlations (defects, local ordering and clustering)

4.2.4.4.1. General formulation (elastic diffuse scattering)

In this section general formulae for diffuse scattering will be derived which may best be applied to crystals with a well ordered average structure, characterized by (almost) sharp Bragg peaks. Textbooks and review articles concerning defects and local ordering are by Krivoglaз (1969), Dederichs (1973), Peisl (1975), Schwartz & Cohen (1977), Schmatz (1973, 1983), Bauer (1979), and Kitaigorodsky (1984). A series of interesting papers on local order is given by Young (1975) and also by Cowley *et al.* (1979). Expressions for polycrystalline sample material are given by Warren (1969) and Fender (1973).

Two general methods may be applied:

(a) the average difference cluster method, where a representative cluster of scattering differences between the average structure and the cluster is used; and

(b) the method of short-range-order correlation functions where formal parameters are introduced.

Both methods are equivalent in principle. The cluster method is generally more convenient in cases where a single average cluster is a good approximation. This holds for small concentrations of clusters with sufficient space in between. The method of short-range-order parameters is optimal in cases where isolated clusters are not realized and the correlations do not extend to long distances. Otherwise periodic solutions are more convenient in most cases.

In any case, the first step towards the solution of the diffraction problem is the accurate determination of the average structure. As

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described in Section 4.2.3.2 important information on fractional occupations, interstitials and displacements (unusual thermal parameters) of atoms may be derived. Unfortunately all defects contribute to diffuse scattering; hence one has to start with the assumption that the disorder to be interpreted is predominant. Fractional occupancy of certain lattice sites by two or more kinds of atoms plays an important role in the literature, especially in metallic or ionic structures. Since vacancies may be treated as atoms with zero scattering amplitude, structures containing vacancies may be formally treated as multi-component systems.

Since the solution of the diffraction problem should not be restricted to metallic systems with a simple (primitive) structure, we have to consider the structure of the unit cell – as given by the average structure – and the propagation of order according to the translation group separately. In simple metallic systems this difference is immaterial. It is well known that the thermodynamic problem of propagation of order in a three-dimensional crystal can hardly be solved analytically in a general way. Some solutions have been published with the aid of the so-called Ising model using next-nearest-neighbour interactions. They are excellent for an understanding of the principles of order–disorder phenomena, but they can scarcely be applied quantitatively in practical problems. Hence, methods have been developed to derive the propagation of order from the diffraction pattern by means of Fourier transformation. This method has been described qualitatively in Section 4.2.3.1, and will be used here for a quantitative application. In a first approximation the assumption of a small number of different configurations of the unit cell is made, represented by the corresponding number of structure factors. Displacements of atoms caused by the configurations of the neighbouring cells are excluded. This problem will be treated subsequently.

The finite number of structures of the unit cell in the disordered crystal is given by

$$F_\nu(\mathbf{r}) = \sum_j \sum_\mu \pi_{j\mu}^\nu f_\mu(\mathbf{r} - \mathbf{r}_j). \quad (4.2.4.55)$$

Note that $F_\nu(\mathbf{r})$ is defined in real space, and $\mathbf{r}_j$ gives the position vector of site j ; $\pi_{j\mu}^\nu = 1$ if in the ν th structure factor the site j is occupied by an atom of kind μ , and 0 elsewhere.

In order to apply the laws of Fourier transformation adequately, it is useful to introduce the distribution function of F_ν

$$\pi_\nu(\mathbf{r}) = \sum_{\mathbf{n}} \pi_{\mathbf{n}\nu} \delta(\mathbf{r} - \mathbf{n}) \quad (4.2.4.56)$$

with $\pi_{\mathbf{n}\nu} = 1$, if the cell $\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ has the F_ν structure, and $\pi_{\mathbf{n}\nu} = 0$ elsewhere.

In the definitions given above $\pi_{\mathbf{n}\nu}$ are numbers (scalars) assigned to the cell. Since all these are occupied we have

$$\sum_\nu \pi_\nu(\mathbf{r}) = l(\mathbf{r})$$

with $l(\mathbf{r}) =$ lattice in real space.

The structure of the disordered crystal is given by

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}). \quad (4.2.4.57)$$

$\pi_\nu(\mathbf{r})$ consists of $\alpha_\nu N$ points, where $N = N_1 N_2 N_3$ is the total (large) number of unit cells and α_ν denotes the *a priori* probability (concentration) of the ν th cell occupation.

It is now useful to introduce

$$\Delta\pi_\nu(\mathbf{r}) = \pi_\nu(\mathbf{r}) - \alpha_\nu l(\mathbf{r}) \quad (4.2.4.58)$$

with

$$\sum_\nu \Delta\pi_\nu(\mathbf{r}) = \sum_\nu \pi_\nu(\mathbf{r}) - l(\mathbf{r}) \sum_\nu \alpha_\nu = l(\mathbf{r}) - l(\mathbf{r}) = 0.$$

Introducing (4.2.4.58) into (4.2.4.57):

$$\begin{aligned} \sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r}) \sum_\nu \alpha_\nu F_\nu(\mathbf{r}) \\ &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r}) \langle F(\mathbf{r}) \rangle. \end{aligned} \quad (4.2.4.59)$$

Similarly:

$$\Delta F_\nu(\mathbf{r}) = F_\nu(\mathbf{r}) - \langle F(\mathbf{r}) \rangle \quad (4.2.4.60)$$

$$\sum_\nu \alpha_\nu \Delta F_\nu(\mathbf{r}) = \sum_\nu \alpha_\nu F_\nu(\mathbf{r}) - \sum_\nu \alpha_\nu \langle F(\mathbf{r}) \rangle = 0.$$

Using (4.2.4.60) it follows from (4.2.4.58) that

$$\begin{aligned} \sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) \\ &\quad + \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \langle F(\mathbf{r}) \rangle + l(\mathbf{r}) * \langle F(\mathbf{r}) \rangle \\ &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) + l(\mathbf{r}) * \langle F(\mathbf{r}) \rangle. \end{aligned} \quad (4.2.4.61)$$

Comparison with (4.2.4.59) yields

$$\sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}).$$

Fourier transformation of (4.2.4.61) gives

$$\sum_\nu \Pi_\nu(\mathbf{H}) F_\nu(\mathbf{H}) = \sum_\nu \Delta\Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) + L(\mathbf{H}) \langle F(\mathbf{H}) \rangle$$

with

$$\sum_\nu \Delta\Pi_\nu(\mathbf{H}) = 0; \quad \sum_\nu \Delta F_\nu(\mathbf{H}) = 0.$$

The expression for the scattered intensity is therefore

$$\begin{aligned} I(\mathbf{H}) &= \left| \sum_\nu \Delta\Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) \right|^2 + |L(\mathbf{H}) \langle F(\mathbf{H}) \rangle|^2 \\ &\quad + L(\mathbf{H}) \left\{ \langle F^+(\mathbf{H}) \rangle \sum_\nu \Delta\Pi_\nu(\mathbf{H}) F_\nu(\mathbf{H}) \right. \\ &\quad \left. + \langle F^+(\mathbf{H}) \rangle \sum_\nu \Delta\Pi_\nu^+(\mathbf{H}) F_\nu^+(\mathbf{H}) \right\}. \end{aligned} \quad (4.2.4.62)$$

Because of the multiplication by $L(\mathbf{H})$ the third term in (4.2.4.62) contributes to sharp reflections only. Since they are correctly given by the second term in (4.2.4.62), the third term vanishes. Hence, the diffuse part is given by

$$I_d(\mathbf{H}) = \left| \sum_\nu \Delta\Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) \right|^2. \quad (4.2.4.63)$$

For a better understanding of the behaviour of diffuse scattering it is useful to return to real space:

$$\begin{aligned} i_d(\mathbf{r}) &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \sum_{\nu'} \Delta\pi_{\nu'}(-\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) \\ &= \sum_\nu \sum_{\nu'} \Delta\pi_\nu(\mathbf{r}) * \Delta\pi_{\nu'}(-\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) \end{aligned} \quad (4.2.4.64)$$

and with (4.2.4.58):

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$$i_d(\mathbf{r}) = \sum_{\nu} \sum_{\nu'} [\pi_{\nu}(\mathbf{r}) - \alpha_{\nu} l(\mathbf{r})] * [\pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \quad (4.2.4.65)$$

Evaluation of this equation for a single term yields

$$[\pi_{\nu}(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu} l(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu'} l(\mathbf{r}) * \pi_{\nu}(\mathbf{r}) + \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r}) * l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \quad (4.2.4.66)$$

Since $l(\mathbf{r})$ is a periodic function of points, all convolution products with $l(\mathbf{r})$ are also periodic. For the final evaluation the decrease of a number of overlapping points (maximum N) in the convolution products with increasing displacements of the functions is neglected (no particle-size effect). Then (4.2.4.66) becomes

$$[\pi_{\nu}(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r}) + N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) = [\pi_{\nu}(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \quad (4.2.4.67)$$

If the first term in (4.2.4.67) is considered, the convolution of the two functions for a given distance $\mathbf{n}$ counts the number of coincidences of the function $\pi_{\nu}(\mathbf{r})$ with $\pi_{\nu'}(-\mathbf{r})$. This quantity is given by $Nl(\mathbf{r})\alpha_{\nu}p_{\nu\nu'}(-\mathbf{r})$, where $\alpha_{\nu}p_{\nu\nu'}(\mathbf{r})$ is the probability of a pair occupation in the $\mathbf{r}$ direction.

Equation (4.2.4.67) then reads:

$$[Nl(\mathbf{r})\alpha_{\nu}p_{\nu\nu'}(-\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) = N \alpha_{\nu} [p'_{\nu\nu'}(-\mathbf{r})l(\mathbf{r})] * [\Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \quad (4.2.4.68)$$

with $p'_{\nu\nu'}(\mathbf{r}) = p_{\nu\nu'}(\mathbf{r}) - \alpha_{\nu'}$. The function $\alpha_{\nu}p'_{\nu\nu'}(\mathbf{r})$ is usually called the pair-correlation function $g \leftrightarrow \alpha_{\nu\nu'}|_{\mathbf{nn}'}$ in the physical literature.

The following relations hold:

$$\sum_{\nu} \alpha_{\nu} = 1 \quad (4.2.4.69a)$$

$$\sum_{\nu'} \alpha_{\nu} p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'}; \quad \sum_{\nu'} \alpha_{\nu} p'_{\nu\nu'}(\mathbf{r}) = 0 \quad (4.2.4.69b)$$

$$\sum_{\nu} \alpha_{\nu} p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu}; \quad \sum_{\nu} \alpha_{\nu} p'_{\nu\nu'}(\mathbf{r}) = 0 \quad (4.2.4.69c)$$

$$\alpha_{\nu} p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'} p_{\nu'\nu}(-\mathbf{r}). \quad (4.2.4.69d)$$

Also, functions normalized to unity are in use. Obviously the following relation is valid: $p'_{\nu\nu'}(0) = \delta_{\nu\nu'} - \alpha_{\nu'}$.

Hence:

$$\alpha_{\nu\nu'}|_{\mathbf{nn}'} = \alpha_{\nu} p'_{\nu\nu'}(\mathbf{r}) / (\delta_{\nu\nu'} - \alpha_{\nu'})$$

is unity for $\mathbf{r} = 0$ ($\mathbf{n} = \mathbf{n}'$). This property is especially convenient in binary systems.

With (4.2.4.68), equation (4.2.4.64) becomes

$$i_d(\mathbf{r}) = N \sum_{\nu} \sum_{\nu'} [\alpha_{\nu} p'_{\nu\nu'}(-\mathbf{r})l(\mathbf{r})] * [\Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \quad (4.2.4.70)$$

and Fourier transformation yields

$$I_d(\mathbf{H}) = N \sum_{\nu} \sum_{\nu'} [\alpha_{\nu} p'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})] \Delta F_{\nu}(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}). \quad (4.2.4.71)$$

It may be concluded from equations (4.2.4.69) that all functions $p'_{\nu\nu'}(\mathbf{r})$ may be expressed by $p'_{11}(\mathbf{r})$ in the case of two structure factors F_1, F_2 . Then all $p'_{\nu\nu'}(\mathbf{r})$ are symmetric in $\mathbf{r}$; the same is true for the $P'_{\nu\nu'}(\mathbf{H})$. Consequently, the diffuse reflections described by (4.2.4.71) are all symmetric. The position of the diffuse peak depends strongly on the behaviour of $p'_{\nu\nu'}(\mathbf{r})$; in the case of cluster formation Bragg peaks and diffuse peaks coincide. Diffuse superstructure reflections are observed if the $p'_{\nu\nu'}(\mathbf{r})$ show some damped periodicities.

It should be emphasized that the condition $p'_{\nu\nu'}(\mathbf{r}) = p'_{\nu\nu'}(-\mathbf{r})$ may be violated for $\nu \neq \nu'$ if more than two cell occupations are involved. As shown below, the possibly asymmetric functions may be split into symmetric and antisymmetric parts. From equation (4.2.3.8) it follows that the Fourier transform of the antisymmetric part of $p'_{\nu\nu'}(\mathbf{r})$ is also antisymmetric. Hence, the convolution in the two terms in square brackets in (4.2.4.71) yields an antisymmetric contribution to each diffuse peak, generated by the convolution with the reciprocal lattice $L(\mathbf{h})$.

Obviously, equation (4.2.4.71) may also be applied to primitive lattices, occupied by two or more kinds of atoms. Then the structure factors F_{ν} are merely replaced by the atomic scattering factors f_{ν} and the α_{ν} are equivalent to the concentrations of atoms c_{ν} . In terms of the $\alpha_{\nu\nu'}|_{\mathbf{nn}'}$ (Warren short-range-order parameters) equation (4.2.4.71) reads

$$I_d(\mathbf{H}) = N(\bar{f}^2 - \bar{f}^2) \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \alpha_{\nu\nu'}|_{\mathbf{nn}'} \exp\{2\pi i \mathbf{H}(\mathbf{n} - \mathbf{n}')\}. \quad (4.2.4.71a)$$

In the simplest case of a binary system A, B

$$\alpha_{\mathbf{nn}'} = (1 - p_{AB|\mathbf{nn}'})/c_B = (1 - p_{BA|\mathbf{nn}'})/c_A; \\ c_A p_{AB} = c_B p_{BA}; \quad p_{AA} = 1 - p_{AB};$$

$$I_d(\mathbf{H}) = N c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \alpha_{\mathbf{nn}'} \times \exp\{2\pi i \mathbf{H}(\mathbf{n} - \mathbf{n}')\}. \quad (4.2.4.71b)$$

[The exponential in (4.2.4.71b) may even be replaced by a cosine term owing to the centrosymmetry of this particular case.]

It should be mentioned that the formulations of the problem in terms of pair probabilities, pair correlation functions, short-range-order parameters or concentration waves (Krivoglaz, 1969) are equivalent. Using continuous electron (or nuclear) density functions where site occupancies are implied, the Patterson function may be used, too (Cowley, 1981).

4.2.4.4.2. Random distribution

As shown above in the case of random distributions all $p'_{\nu\nu'}(\mathbf{r})$ are zero, except for $\mathbf{r} = 0$. Consequently, $p'_{\nu\nu'}(\mathbf{r})l(\mathbf{r})$ may be replaced by

$$\alpha_{\nu} p'_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu} \delta_{\nu\nu'} - \alpha_{\nu} \alpha_{\nu'}. \quad (4.2.4.72)$$

According to (4.2.4.59) and (4.2.4.61) the diffuse scattering can be given by the Fourier transformation of

$$\sum_{\nu} \sum_{\nu'} \Delta \pi_{\nu}(\mathbf{r}) * \Delta \pi_{\nu'}(-\mathbf{r}) * F_{\nu}(\mathbf{r}) * F_{\nu'}(-\mathbf{r}) = \sum_{\nu} \sum_{\nu'} p'_{\nu\nu'}(\mathbf{r}) * F_{\nu}(\mathbf{r}) * F_{\nu'}(-\mathbf{r})$$

or with (4.2.4.72):

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$$i_d(\mathbf{r}) = N \sum_{\nu} \sum_{\nu'} [\alpha_{\nu} \delta_{\nu\nu'} - \alpha_{\nu} \alpha_{\nu'}] * F_{\nu}(\mathbf{r}) * F_{\nu'}(-\mathbf{r}).$$

Fourier transformation gives

$$I_d(\mathbf{H}) = N \left\{ \sum_{\nu} \alpha_{\nu} |F_{\nu}(\mathbf{H})|^2 - \sum_{\nu} \alpha_{\nu} F_{\nu}(\mathbf{H}) \sum_{\nu'} \alpha_{\nu'} F_{\nu'}^+(\mathbf{H}) \right\} \\ = N \{ \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \}. \quad (4.2.4.73)$$

This is the most general form of any diffuse scattering of systems ordered randomly ('Laue scattering'). Occasionally it is called 'incoherent scattering' (see Section 4.2.2).

4.2.4.4.3. Short-range order in multi-component systems

The diffuse scattering of a disordered binary system without displacements of the atoms has already been discussed in Section 4.2.4.4.1. It could be shown that all distribution functions $p'_{\nu\nu'}(\mathbf{r})$ are mutually dependent and may be replaced by a single function [cf. (4.2.4.69)]. In that case $p'_{\nu\nu'}(\mathbf{r}) = p'_{\nu\nu'}(-\mathbf{r})$ was valid for all. This condition, however, may be violated in multi-component systems. If a tendency towards an $F_1 F_2 F_3$ order in a ternary system is assumed, for example, $p_{12}(\mathbf{r})$ is apparently different from $p_{12}(-\mathbf{r})$. In this particular case it is useful to introduce

$$\langle p'_{\nu\nu'}(\mathbf{r}) \rangle = \frac{1}{2} [p'_{\nu\nu'}(\mathbf{r}) + p'_{\nu\nu'}(-\mathbf{r})]; \\ \Delta p'_{\nu\nu'}(\mathbf{r}) = \frac{1}{2} [p'_{\nu\nu'}(\mathbf{r}) - p'_{\nu\nu'}(-\mathbf{r})]$$

and their Fourier transforms $\langle P'_{\nu\nu'}(\mathbf{H}) \rangle$, $\Delta P'_{\nu\nu'}(\mathbf{H})$, respectively.

The asymmetric correlation functions are therefore expressed by

$$p'_{\nu\nu'}(\mathbf{r}) = \langle p'_{\nu\nu'}(\mathbf{r}) \rangle + \Delta p'_{\nu\nu'}(\mathbf{r}); \\ p'_{\nu\nu'}(-\mathbf{r}) = \langle p'_{\nu\nu'}(\mathbf{r}) \rangle - \Delta p'_{\nu\nu'}(\mathbf{r}); \\ \Delta p'_{\nu\nu}(\mathbf{r}) = 0.$$

Consequently, $i_d(\mathbf{r})$ (4.2.4.70) and $I_d(\mathbf{H})$ (4.2.4.71) may be separated according to the symmetric and antisymmetric contributions. The final result is:

$$I_d(\mathbf{H}) = N \left\{ \sum_{\nu} \alpha_{\nu} [P'_{\nu\nu}(\mathbf{H}) * L(\mathbf{H})] |F_{\nu}(\mathbf{H})|^2 \right. \\ + \sum_{\nu > \nu'} \alpha_{\nu} [\langle P'_{\nu\nu'}(\mathbf{H}) \rangle * L(\mathbf{H})] \\ \times [\Delta F_{\nu}(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}) + \Delta F_{\nu}^+(\mathbf{H}) \Delta F_{\nu'}(\mathbf{H})] \\ + \sum_{\nu > \nu'} \alpha_{\nu} [\Delta P'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})] \\ \times [\Delta F_{\nu}(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}) - \Delta F_{\nu}^+(\mathbf{H}) \Delta F_{\nu'}(\mathbf{H})] \left. \right\}. \quad (4.2.4.74)$$

Obviously, antisymmetric contributions to line profiles will only occur if structure factors of acentric cell occupations are involved. This important property may be used to draw conclusions with respect to structure factors involved in the statistics. It should be mentioned here that the Fourier transform of the antisymmetric function $\Delta p'_{\nu\nu'}(\mathbf{r})$ is imaginary and antisymmetric. Since the last term in (4.2.4.74) is also imaginary, the product of the two factors in brackets is real, as it should be.

4.2.4.4.4. Displacements: general remarks

Even small displacements may have an important influence on the problem of propagation of order. Therefore, no structural treatments other than the introduction of formal parameters (*e.g.* Landau's theory) have been published in the literature. Most of the

examples with really reliable results refer to binary systems, and even these represent very crude approximations, as will be shown below. For this reason we shall restrict ourselves here to binary systems, although general formulae where displacements are included may be developed in a formal way.

Two kinds of atoms, $f_1(\mathbf{r})$ and $f_2(\mathbf{r})$, are considered. Obviously, the position of any given atom is determined by its surroundings. Their extension depends on the forces acting on the atom under consideration. These may be very weak in the case of metals (repulsive forces, so-called 'size effect'), but long-range effects have to be expected in ionic crystals. For the development of formulae authors have assumed that small displacements $\Delta_{\nu\nu'}(\mathbf{r})$ may be assigned to the pair correlation functions $p'_{\nu\nu'}(\mathbf{r})$ by adding a phase factor $\exp\{2\pi i \mathbf{H} \cdot \Delta_{\nu\nu'} \mathbf{r}\}$ which is then expanded in the usual way:

$$\exp\{2\pi i \mathbf{H} \cdot \Delta_{\nu\nu'} \mathbf{r}\} \simeq 1 + 2\pi i \mathbf{H} \cdot \Delta_{\nu\nu'} \mathbf{r} - 2[\pi \mathbf{H} \cdot \Delta_{\nu\nu'} \mathbf{r}]^2. \quad (4.2.4.75)$$

The displacements and correlation probabilities are separable if the change of atomic scattering factors in the angular range considered may be neglected. The formulae in use are given in the next section. As shown below, this method represents nothing other than a kind of average over certain sets of displacements. For this purpose the correct solution of the problem has to be discussed. In the simplest model the displacements are due to next-nearest neighbours only. It is assumed further that the configurations rather than the displacements determine the position of the central atom and a general displacement of the centre of the first shell does not occur (no influence of a strain field). Obviously, the formal correlation function of pairs is not independent of displacements. This difficulty may be avoided either by assuming that the pair correlation function has already been separated from the diffraction data, or by theoretical calculations of the correlation function (mean-field method) (Moss, 1966; de Fontaine, 1972, 1973). The validity of this procedure is subject to the condition that the displacements have no influence on the correlation functions themselves.

The observation of a periodic average structure justifies the definition of a periodic array of origins which normally depends on the degree of order. Local deviations of origins may be due to fluctuations in the degree of order and due to the surrounding atoms of a given site occupation. For example, a b.c.c. lattice with eight nearest neighbours is considered. It is assumed that only these have an influence on the position of the central atom owing to different forces of the various configurations. With two kinds of atoms, there are $2^9 = 512$ possible configurations of the cluster (central atom plus 8 neighbours). Symmetry considerations reduce this number to 28. Each is characterized by a displacement vector. Hence, their *a priori* probabilities and the propagation of 28 different configurations have to be determined. Since each atom has to be considered as the centre once, this problem may be treated by introducing 28 different atomic scattering factors as determined from the displacements: $f_{\nu}(\mathbf{r}) \exp\{2\pi i \mathbf{H} \cdot \Delta \mathbf{r}_{\nu\nu'}\}$. The diffraction problem has to be solved with the aid of the propagation of order of overlapping clusters. This is demonstrated by a two-dimensional model with four nearest neighbours (Fig. 4.2.4.1). Here the central and the neighbouring cluster (full and broken lines) overlap with two sites in the, *e.g.*, $\mathbf{x}$ direction. Hence, only neighbouring clusters with the same overlapping pairs are admitted. These restrictions introduce severe difficulties into the problem of propagation of cluster ordering which determines the displacement field. Since it was assumed that the problem of pair correlation had been solved, the cluster probabilities may be derived by calculating

$$\alpha_{\nu} l(\mathbf{r}) \prod_{\mathbf{n} \neq 0} p'_{\nu\nu'}(\mathbf{r} - \mathbf{n}). \quad (4.2.4.76)$$

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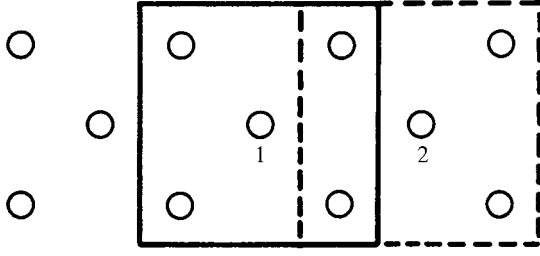


Fig. 4.2.4.1. Construction of the correlation function in the method of overlapping clusters.

In the product only next-nearest neighbours have to be included. This must be performed for the central cluster ($\mathbf{r} = 0$) and for the reference cluster at $\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, because all are characterized by different displacements. So far, possible displacement of the centre has not been considered; this may also be influenced by the problem of propagation of cluster ordering. These displacement factors should best be attached to the function describing the propagation of order which determines, in principle, the local fluctuations of the lattice constants (strain field *etc.*). This may be understood by considering a binary system with a high degree of order but with atoms of different size. Large fluctuations of lattice constants are involved in the case of exsolution of the two components because of their different lattice parameters, but they become small in the case of superstructure formation where a description in terms of antiphase domains is reasonable (equal lattice constants). This example demonstrates the mutual dependence of ordering and displacements which is mostly neglected in the literature.

The method of assigning phase factors to the pair correlation function is now discussed. Pair correlation functions average over all pairs of clusters having the same central atom. An analogous argument holds for displacements: using pair correlations for the determination of displacements means nothing other than averaging over all displacements caused by various clusters around the same central atom. There remains the general strain field due to the propagation of order, whereas actual displacements of atoms are realized by fluctuations of configurations. Since large fluctuations of this type occur in highly disordered crystals, the displacements become increasingly irrelevant. Hence, the formal addition of displacement factors to the pair correlation function does not yield too much information about the structural basis of the displacements. This situation corresponds exactly to the relationship between a Patterson function and a real structure: the structure has to be found which explains the more or less complicated function completely, and its unique solution is rather difficult. These statements seem to be necessary because in most publications related to this subject these considerations are not taken into account adequately. Displacements usually give rise to antisymmetric contributions to diffuse reflections. As pointed out above, the influence of displacements has to be considered as phase factors which may be attached either to the structure factors or to the Fourier transforms $P'_{\nu\nu'}(\mathbf{H})$ of the correlation functions in equation (4.2.4.71). As has been mentioned in the context of equation (4.2.4.74) antisymmetric contributions will occur if acentric structure factors are involved. Apparently, this condition is met by the phase factors of displacements. In consequence, antisymmetric contributions to diffuse reflections may also originate from the displacements. This fact can also be demonstrated if the assignment of phase factors to the Fourier transforms of the correlation functions is advantageous. In this case equations (4.2.4.69a,b) are no longer valid because the functions $p'_{\nu\nu'}(\mathbf{r})$ become complex. The most important change is the relation corresponding to (4.2.4.69):

$$\alpha_{\nu} p'_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu} p'_{\nu\nu'}^+(-\mathbf{r}) \leftrightarrow \alpha_{\nu} P'_{\nu\nu'}(\mathbf{H}) = \alpha_{\nu} P'_{\nu\nu'}^+(\mathbf{H}). \quad (4.2.4.77)$$

Strictly speaking we have to replace the *a priori* probabilities α_{ν} by complex numbers $\alpha_{\nu} \exp(2\pi i \Delta \mathbf{r}_{\nu} \cdot \mathbf{H})$ which are determined by the position of the central atom. In this way all correlations between displacements may be included with the aid of the clusters mentioned above. To a rough approximation it may be assumed that no correlations of this kind exist. In this case the complex factors may be assigned to the structure factors involved. Averaging over all displacements results in diffraction effects which are very similar to a static Debye–Waller factor for all structure factors. On the other hand, the thermal motion of atoms is treated similarly. Obviously both factors affect the sharp Bragg peaks. Hence, this factor can easily be determined by the average structure which contains a Debye–Waller factor including static and thermal displacements. It should be pointed out, however, that these static displacements cause elastic diffuse scattering which cannot be separated by inelastic neutron scattering techniques.

A careful study of the real and imaginary parts of

$$\langle p'_{\nu\nu'}(\mathbf{r}) \rangle = \langle p'_{\nu\nu'}(\mathbf{r}) \rangle_R + \langle p'_{\nu\nu'}(\mathbf{r}) \rangle_I$$

and

$$\Delta p'_{\nu\nu'}(\mathbf{r}) = \Delta p'_{\nu\nu'}(\mathbf{r})_R + \Delta p'_{\nu\nu'}(\mathbf{r})_I$$

and their Fourier transforms results, after some calculations, in the following relation for diffuse scattering:

$$\begin{aligned} I_d \simeq N \sum_{\nu} \alpha_{\nu} |\Delta F_{\nu}(\mathbf{H})|^2 \{ [\langle P'_{\nu\nu'}(\mathbf{H}) \rangle - \Delta P'_{\nu\nu'}(\mathbf{H})] * L(\mathbf{H}) \} \\ + 2N \sum_{\nu > \nu'} \alpha_{\nu} (\Delta F_{\nu} \Delta F_{\nu'}^+)_R \\ \times \{ [\langle P'_{\nu\nu'}(\mathbf{H}) \rangle_R - \Delta P'_{\nu\nu'}(\mathbf{H})_I] * L(\mathbf{H}) \} \\ + 2N \sum_{\nu > \nu'} \alpha_{\nu} (\Delta F_{\nu} \Delta F_{\nu'}^+)_I \\ \times \{ [\langle P'_{\nu\nu'}(\mathbf{H}) \rangle_I - \Delta P'_{\nu\nu'}(\mathbf{H})_R] * L(\mathbf{H}) \}. \end{aligned} \quad (4.2.4.78)$$

It should be noted that all contributions are real. This follows from the properties of Fourier transforms of symmetric and antisymmetric functions. All $\Delta P'_{\nu\nu'}(\mathbf{H})$ are antisymmetric; hence they generate antisymmetric contributions to the line profiles. In contrast to equation (4.2.4.75), the real and the imaginary parts of the structure factors contribute to the asymmetry of the line profiles.

4.2.4.4.5. Distortions in binary systems

In substitutional binary systems (primitive cell with only one sublattice) the Borie–Sparks method is widely used (Sparks & Borie, 1966; Borie & Sparks, 1971). The method is formulated in the short-range-order-parameter formalism. The diffuse scattering may be separated into two parts (a) owing to short-range order and (b) owing to static displacements.

Corresponding to the expansion (4.2.4.75), $I_d = I_{\text{sro}} + I_2 + I_3$, where I_{sro} is given by equation (4.2.4.71b) and the correction terms I_2 and I_3 relate to the linear and the quadratic term in (4.2.4.75). The intensity expression will be split into terms of A–A, A–B, . . . pairs. More explicitly $\Delta_{\nu\nu'}\mathbf{r} = \mathbf{u}_{\nu\nu'} - \mathbf{u}_{\nu'\nu}$ and with the following abbreviations:

$$\delta_{\mathbf{nn}'|AA} = \mathbf{u}_{\mathbf{n}|A} - \mathbf{u}_{\mathbf{n}'|A} = x_{\mathbf{nn}'|AA}\mathbf{a} + y_{\mathbf{nn}'|AA}\mathbf{b} + z_{\mathbf{nn}'|AA}\mathbf{c}$$

$$\delta_{\mathbf{nn}'|AB} = \mathbf{u}_{\mathbf{n}|A} - \mathbf{u}_{\mathbf{n}'|B} = \dots$$

$$F_{\mathbf{nn}'|AA} = f_A^2 / (f_A - f_B)^2 \cdot [(c_A/c_B) + \alpha_{\mathbf{nn}'}]$$

$$F_{\mathbf{nn}'|BB} = f_B^2 / (f_A - f_B)^2 \cdot [(c_B/c_A) + \alpha_{\mathbf{nn}'}]$$

$$F_{\mathbf{nn}'|AB} = 2f_A f_B / (f_A - f_B)^2 \cdot (1 - \alpha_{\mathbf{nn}'}) = F_{\mathbf{nn}'|BA}$$

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one finds (where the short-hand notation is self-explanatory):

$$I_2 = 2\pi i c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{ H \cdot [F_{\mathbf{nn}'}|AA \langle x_{\mathbf{nn}'}|AA \rangle + F_{\mathbf{nn}'}|BB \langle x_{\mathbf{nn}'}|BB \rangle + F_{\mathbf{nn}'}|AB \langle x_{\mathbf{nn}'}|AB \rangle] + K \cdot [y'] + L \cdot [z'] \} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\} \quad (4.2.4.79)$$

$$I_3 = c_A c_B (f_A - f_B)^2 (-2\pi)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{ H^2 [F_{\mathbf{nn}'}|AA \langle x_{\mathbf{nn}'}^2|AA \rangle + F_{\mathbf{nn}'}|BB \langle x_{\mathbf{nn}'}^2|BB \rangle + F_{\mathbf{nn}'}|AB \langle x_{\mathbf{nn}'}^2|AB \rangle] + K^2 \cdot [y'^2] + L^2 \cdot [z'^2] + HK [F_{\mathbf{nn}'}|AA \langle (xy)_{\mathbf{nn}'}|AA \rangle + F_{\mathbf{nn}'}|BB \langle (xy)_{\mathbf{nn}'}|BB \rangle + F_{\mathbf{nn}'}|AB \langle (xy)_{\mathbf{nn}'}|AB \rangle] + KL [y'z'] + LH [z'x'] \} \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}. \quad (4.2.4.80)$$

With further abbreviations

$$\begin{aligned} \gamma_{\mathbf{nn}'}|x &= 2\pi (F_{\mathbf{nn}'}|AA \langle x_{\mathbf{nn}'}|AA \rangle + F_{\mathbf{nn}'}|BB \langle x_{\mathbf{nn}'}|BB \rangle + F_{\mathbf{nn}'}|AB \langle x_{\mathbf{nn}'}|AB \rangle) \\ \gamma_{\mathbf{nn}'}|y &= \dots \\ \gamma_{\mathbf{nn}'}|z &= \dots \\ \delta_{\mathbf{nn}'}|x &= (-2\pi^2) (F_{\mathbf{nn}'}|AA \langle x_{\mathbf{nn}'}^2|AA \rangle + F_{\mathbf{nn}'}|BB \langle x_{\mathbf{nn}'}^2|BB \rangle + F_{\mathbf{nn}'}|AB \langle x_{\mathbf{nn}'}^2|AB \rangle) \\ \delta_{\mathbf{nn}'}|y &= \dots \\ \delta_{\mathbf{nn}'}|z &= \dots \\ \epsilon_{\mathbf{nn}'}|xy &= (-4\pi^2) (F_{\mathbf{nn}'}|AA \langle (xy)_{\mathbf{nn}'}|AA \rangle + F_{\mathbf{nn}'}|BB \langle (xy)_{\mathbf{nn}'}|BB \rangle + F_{\mathbf{nn}'}|AB \langle (xy)_{\mathbf{nn}'}|AB \rangle) \\ \epsilon_{\mathbf{nn}'}|yz &= \dots \\ \epsilon_{\mathbf{nn}'}|zx &= \dots \\ I_2 &= c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} i (\gamma_{\mathbf{nn}'}|x + \gamma_{\mathbf{nn}'}|y + \gamma_{\mathbf{nn}'}|z) \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\} \\ I_3 &= c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} (\delta_{\mathbf{nn}'}|x H^2 + \delta_{\mathbf{nn}'}|y K^2 + \delta_{\mathbf{nn}'}|z L^2 + \epsilon_{\mathbf{nn}'}|xy HK + \epsilon_{\mathbf{nn}'}|yz KL + \epsilon_{\mathbf{nn}'}|zx LH \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}). \end{aligned}$$

If the $F_{\mathbf{nn}'}|AA, \dots$ are independent of $|\mathbf{H}|$ in the range of measurement which is better fulfilled with neutrons than with X-rays (see below), γ, δ, ϵ are the coefficients of the Fourier series:

$$\begin{aligned} Q_x &= \sum_{\mathbf{n}} \sum_{\mathbf{n}'} i \gamma_{\mathbf{nn}'}|x \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}; \\ Q_y &= \dots; \quad Q_z = \dots; \\ R_x &= \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \delta_{\mathbf{nn}'}|x \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}; \\ R_y &= \dots; \quad R_z = \dots; \\ S_{xy} &= \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \epsilon_{\mathbf{nn}'}|xy \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}; \\ S_{yz} &= \dots; \quad S_{zx} = \dots \end{aligned}$$

The functions Q, R, S are then periodic in reciprocal space.

The double sums over $\mathbf{n}, \mathbf{n}'$ may be replaced by $N \sum_{m,n,p}$ where m, n, p are the coordinates of the interatomic vectors $(\mathbf{n} - \mathbf{n}')$ and I_2 becomes

$$I_2 = -N c_A c_B (f_A - f_B)^2 \sum_m \sum_n \sum_p (H \gamma_{lmn|x} + \dots + \dots) \times \sin 2\pi (Hm + Kn + Lp). \quad (4.2.4.81)$$

The intensity is therefore modulated sinusoidally and increases with scattering angle. The modulation gives rise to an asymmetry in the intensity around a Bragg peak. Similar considerations for I_3 reveal an intensity contribution h_i^2 times a sum over cosine terms which is symmetric around the Bragg peaks. This term shows quite an analogous influence of local static displacements and thermal movements: an increase of diffuse intensity around the Bragg peaks and a reduction of Bragg intensities, which is not discussed here. The second contribution I_2 has no analogue owing to the non-vanishing average displacement. The various diffuse intensity contributions may be separated by symmetry considerations. Once they are separated, the single coefficients may be determined by Fourier inversion. Owing to the symmetry constraints there are relations between the displacements $\langle x \dots \rangle$ and, in turn, between the γ and Q components. The same is true for the δ, ϵ , and R, S components. Consequently, there are symmetry conditions for the individual contributions of the diffuse intensity which may be used to distinguish them. Generally the total diffuse intensity may be split into only a few independent terms. The single components of Q, R, S may be expressed separately by combinations of diffuse intensities which are measured in definite selected volumes in reciprocal space. Only a minimum volume must be explored in order to reveal the behaviour over the whole reciprocal space. This minimum repeat volume is different for the single components: I_{stro}, Q, R, S or combinations of them.

The Borie–Sparks method has been applied very frequently to binary and even ternary systems; some improvements have been communicated by Bardhan & Cohen (1976). The diffuse scattering of the historically important metallic compound Cu_3Au has been studied by Cowley (1950*a,b*), and the pair correlation parameters could be determined. The typical fourfold splitting was found by Moss (1966) and explained in terms of atomic displacements. The same splitting has been found for many similar compounds such as Cu_3Pd (Ohshima *et al.*, 1976), Au_3Cu (Bessière *et al.*, 1983), and $\text{Ag}_{1-x}\text{Mg}_x$ ($x = 0.15-0.20$) (Ohshima & Harada, 1986). Similar pair correlation functions have been determined. In order to demonstrate the disorder parameters in terms of structural models, computer programs were used (*e.g.* Gehlen & Cohen, 1965). A similar microdomain model was proposed by Hashimoto (1974, 1981, 1983, 1987). According to approximations made in the theoretical derivation the evaluation of diffuse scattering is generally restricted to an area in reciprocal space where the influence of displacements is of the same order of magnitude as that of the pair correlation function. The agreement between calculation and measurement is fairly good but it should be remembered that the amount and quality of the experimental information used is low. No residual factors are so far available; these would give an idea of the reliability of the results.

The more general case of a multi-component system with several atoms per lattice point was treated similarly by Hayakawa & Cohen (1975). Sources of error in the determination of the short-range-order coefficients are discussed by Gragg *et al.* (1973). In general the assumption of constant $F_{\mathbf{nn}'}|AA, \dots$ produces an incomplete separation of the order- and displacement-dependent components of diffuse scattering. By an alternative method, by separation of the form factors from the Q, R, S functions and solving a large array of linear relationships by least-squares methods, the accuracy of the separation of the various contributions is improved (Tibbals, 1975;

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Georgopoulos & Cohen, 1977; Wu *et al.*, 1983). The method does not work for neutron diffraction. Also, the case of planar short-range order with corresponding diffuse intensity along rods in reciprocal space may be treated along the Borie & Sparks method (Ohshima & Moss, 1983).

Multi-wavelength methods taking advantage of the variation of the structure factor near an absorption edge (anomalous dispersion) are discussed by Cenedese *et al.* (1984). The same authors show that in some cases the neutron method allows for a contrast variation by using samples with different isotope substitution.

4.2.4.4.6. Powder diffraction

Evaluation of diffuse-scattering data from powder diffraction follows the same theoretical formulae developed for the determination of the radial distribution function for glasses and liquids (Debye & Menke, 1931; Warren & Gingrich, 1934). The final formula for random distributions may be given as (Fender, 1973)

$$I_d^p = \{ \langle |F(\mathbf{H})|^2 \rangle - \langle |F(\mathbf{H})| \rangle^2 \} \sum_i s_i \sin(2\pi H r_i) / (2\pi H r_i). \quad (4.2.4.82)$$

s_i represents the number of atoms at distance r_i from the origin. An equivalent expression for a substitutional binary alloy is

$$I_d^p = \alpha(1 - \alpha) \{ |f_2(\mathbf{H}) - f_1(\mathbf{H})|^2 \} \sum_i s_i \sin(2\pi H r_i) / (2\pi H r_i). \quad (4.2.4.83)$$

4.2.4.4.7. Small concentrations of defects

In the literature small concentrations are treated in terms of fluctuations of the functions $\pi_{\mathbf{H}}$ as defined in equation (4.2.4.56). Generally we prefer the introduction of the distribution function of the defects or clusters. Since this problem has already been treated in Section 4.2.4.4.3 only some very brief remarks are given here. The most convenient way to derive the distribution function correctly from experimental data is the use of low-angle scattering which generally shows one or more clear maxima caused by partly periodic properties of the distribution function. For the deconvolution of the distribution function, received by Fourier transformation of the corrected diffused low-angle scattering, the reader is referred to the relevant literature. Since deconvolutions are not unique some reasonable assumptions are necessary for the final solution. Anomalous scattering may be very helpful if applicable.

4.2.4.4.8. Cluster method

As mentioned above, the cluster method may be useful for the interpretation of disorder problems. In the general formula of diffuse scattering of random distributions equation (4.2.2.13) may be used. Here $\langle |F(\mathbf{H})|^2 \rangle$ describes the sharp Bragg maxima, while $|\Delta F(\mathbf{H})|^2 = \langle |F(\mathbf{H})|^2 \rangle - \langle |F(\mathbf{H})| \rangle^2$ represents the contribution to diffuse scattering. Correlation effects can also be taken into account by using clusters of sufficient size if their distribution may be considered as random in good approximation. The diffuse intensity is then given by

$$I_d(\mathbf{H}) = \sum_{\nu} p_{\nu} |F_{\nu}(\mathbf{H})|^2 - \left| \sum_{\nu} p_{\nu} F_{\nu}(\mathbf{H}) \right|^2, \quad (4.2.4.84)$$

where $F_{\nu}(\mathbf{H})$ represents the difference structure factor of the ν th cluster and p_{ν} is its *a priori* probability. Obviously equation (4.2.4.84) is of some use in two cases only. (1) The number of clusters is sufficiently small and meets the condition of nearly random distribution. In principle, its structure may then be determined with the aid of refinement methods according to

equation (4.2.4.84). Since the second term is assumed to be known from the average structure, the first term may be evaluated by introducing as many parameters as there are clusters involved. A special computer program for incoherent refinement has to be used if more than one representative cluster has to be introduced. In the case of more clusters, constraints are necessary. (2) The number of clusters with similar structures is not limited. It may be assumed that their size distribution may be expressed by well known analytical expressions, *e.g.* Gaussians or Lorentzians. The distribution is still assumed to be random.

An early application of the cluster method was the calculation of the diffuse intensity of Guinier–Preston zones, where a single cluster is sufficient (see, *e.g.*, Gerold, 1954; Bubeck & Gerold, 1984). Unfortunately no refinements of cluster structures have so far been published. The full theory of the cluster method was outlined by Jagodzinski & Haefner (1967).

Some remarks on the use of residual factors should be added here. Obviously the diffuse scattering may be used for refinements in a similar way as in conventional structure determination. For this purpose a sufficiently small reciprocal lattice has to be defined. The size of the reciprocal cell has to be chosen with respect to the maximum gradient of diffuse scattering. Then the diffuse intensity may be described by a product of the real intensity distribution and the small reciprocal lattice. Fourier transformation yields the convolution of the real disordered structure and a large unit cell. In other words, the disordered structure is subdivided into large units and subsequently superimposed ('projected') in a single cell. In cases where a clear model of the disorder could be determined, a refinement procedure for atomic and other relevant parameters can be started. In this way a residual factor may be determined. A first approach has been elaborated by Epstein & Welberry (1983) in the case of substitutional disorder of two molecules.

The outstanding limiting factor is the collection of weak intensity data. The amount increases rapidly with the complexity of the structure and could even exceed by far the amount which is needed in the case of protein structure refinement. Hence, it seems to be reasonable to restrict the measurement to distinct areas in reciprocal space. Most of these publications, however, use too little information when compared with the minimum of data which would be necessary for the confirmation of the proposed model. Hence, physical and chemical considerations should be used as an additional source of information.

4.2.4.4.9. Comparison between X-ray and neutron methods

Apart from experimental arguments in favour of either method, there are some specific points which should be mentioned in this context. The diffuse scattering in question must be separated from Bragg scattering and from other diffuse-scattering contributions. Generally both methods are complementary: neutrons are preferable in cases where X-rays show only a small scattering contrast: (heavy) metal hydrides, oxides, carbides, Al–Mg distribution *etc.* In favourable cases it is possible to suppress (nuclear) Bragg scattering of neutrons when isotopes are used so that $\sum_{\nu} c_{\nu} f_{\nu} = 0$ for all equivalent positions. Another way to separate Bragg peaks is to record the diffuse intensity, if possible, at low $|\mathbf{H}|$ values. This can be achieved either by measurement at low θ angles or by using long wavelengths. For reasons of absorption the latter point is the domain of neutron scattering. Exceeding the Bragg cut-off, Bragg scattering is ruled out. In this way 'diffuse' background owing to multiple Bragg scattering is avoided. Other diffuse-scattering contributions which increase with the $|\mathbf{H}|$ value are thus also minimized: thermal diffuse scattering (TDS) and scattering due to long-range static displacements. On the other hand, lattice distortions, Huang scattering, ... should be measured at large values of $|\mathbf{H}|$. TDS

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can be separated by purely elastic neutron methods within the limits given by the energy resolution of an instrument. This technique is of particular importance at higher temperatures where TDS becomes remarkably strong. Neutron scattering is a good tool only in cases where (isotope/spin-)incoherent scattering is not too strong. In the case of magnetic materials confusion with paramagnetic diffuse scattering could occur. This is also important when electrons are trapped by defects which themselves act as paramagnetic centres.

As mentioned in Section 4.2.4.4 the evaluations of the γ , δ , ε depend on the assumption that the f 's do not depend on $|\mathbf{H}|$ strongly within the range of measurement. Owing to the atomic form factor, this is not always well approximated in the X-ray case and is one of the main sources of error in the determination of the short-range-order parameters.

4.2.4.4.10. Dynamic properties of defects

Some brief remarks concerning the dynamic properties of defects as discussed in the previous sections now follow. Mass defects (impurity atoms), force-constant defects *etc.* influence the dynamic properties of the undistorted lattice and one could think of a modified TDS as discussed in Chapter 4.1. In the case of low defect concentrations special vibrational modes characterized by large amplitudes at the defect with frequency shifts and reduced lifetimes (resonant modes) or vibrational modes localized in space may occur. Other modes with frequencies near these particular modes may also be affected. Owing to the very low intensity of these phenomena their influence on the normal TDS is negligible and may be neglected in diffuse-scattering work. Theoretical treatments of crystals with higher defect concentrations are extremely difficult and not developed so far. For further reading see Böttger (1983).

4.2.4.5. Orientational disorder

Molecular crystals show in principle disorder phenomena similar to those discussed in previous sections (substitutional or displacement disorder). Here we have to replace the structure factors $F_\nu(\mathbf{H})$, used in the previous sections, by the molecular structure factors in their various orientations. Usually these are rapidly varying functions in reciprocal space which may obscure the disorder diffuse scattering. Disorder in molecular crystals is treated by Guinier (1963), Amorós & Amorós (1968), Flack (1970), Epstein *et al.* (1982), Welberry & Siripitayananon (1986, 1987), and others.

A particular type of disorder is very common in molecular and also in ionic crystals: the centres of masses of molecules or ionic complexes form a perfect 3D lattice but their orientations are disordered. Sometimes these solids are called plastic crystals. For comparison, the liquid-crystalline state is characterized by an orientational order in the absence of long-range positional order of the centres of the molecules. A clear-cut separation is not possible in cases where translational symmetry occurs in low dimension, *e.g.* in sheets or parallel to a few directions in crystal space. For discussion of these mesophases see Chapter 4.4.

An orientationally disordered crystal may be imagined in a static picture by freezing molecules in different sites in one of several orientations. Local correlations between neighbouring molecules and correlations between position and orientation may be responsible for orientational short-range order. Often thermal reorientations of the molecules are related to an orientationally disordered crystal. Thermal vibrations of the centres of masses of the molecules, librational or rotational excitations around one or more axes of the molecules, jumps between different equilibrium positions or diffusion-like phenomena are responsible for diffuse scattering of dynamic origin. As mentioned above the complexity of molecular structures and the associated large number of thermal modes complicate a separation from static disorder effects.

Generally high Debye–Waller factors are typical for scattering of orientationally disordered crystals. Consequently only a few Bragg reflections are observable. A large amount of structural information is stored in the diffuse background. It has to be analysed with respect to an incoherent and coherent part, elastic, quasielastic or inelastic nature, short-range correlations within one and the same molecule and between orientations of different molecules, and cross correlations between positional and orientational disorder scattering. Combined X-ray and neutron methods are therefore highly recommended.

4.2.4.5.1. General expressions

On the assumption of a well ordered 3D lattice, a general expression for the scattering by an orientationally disordered crystal with one molecule per unit cell may be given. This is a very common situation. Moreover, orientational disorder is frequently related to molecules with an overall ‘globular’ shape and consequently to crystals of high (in particular, averaged) spherical symmetry. In the following the relevant equations are given for this situation; these are discussed in some detail in a review article by Fouret (1979). The orientation of a molecule is characterized by a parameter ω_l , *e.g.* the set of Eulerian angles of three molecular axes with respect to the crystal axes: $\omega_l = 1, \dots, D$ (D possible different orientations). The equilibrium position of the centre of mass of a molecule in orientation ω_l is given by $\mathbf{r}_l$, the equilibrium position of atom k within a molecule l in orientation ω_l by $\mathbf{r}_{lk}$ and a displacement from this equilibrium position by $\mathbf{u}_{lk}$. Averaging over a long time, *i.e.* supposing that the lifetime of a discrete configuration is long compared with the period of atomic vibrations, the observed intensity may be deduced from the intensity expression corresponding to a given configuration at time t :

$$I(\mathbf{H}, t) = \sum_l \sum_{\nu'} F_l(\mathbf{H}, t) F_{\nu'}^+(\mathbf{H}, t) \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{\nu'})\} \quad (4.2.4.85)$$

$$F_l(\mathbf{H}, t) = \sum_k f_k \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} + \mathbf{u}_{lk})\}. \quad (4.2.4.86)$$

Averaging procedures must be carried out with respect to the thermal vibrations (denoted by an overbar) and over all configurations (symbol $\langle \rangle$). The centre-of-mass translational vibrations and librations of the molecules are most important in this context. (Internal vibrations of the molecules are assumed to be decoupled and remain unconsidered.)

$$I(\mathbf{H}, t) = \sum_l \sum_{\nu'} \overline{\langle F_l(\mathbf{H}, t) F_{\nu'}^+(\mathbf{H}, t) \rangle} \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{\nu'})\}. \quad (4.2.4.85a)$$

Thermal averaging gives (*cf.* Chapter 4.1)

$$I = \sum_l \sum_{\nu'} \overline{F_l F_{\nu'}^+} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{\nu'})\} \\ \overline{F_l F_{\nu'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{\nu'k'})\} \\ \times \overline{\exp\{2\pi i \mathbf{H} \cdot (\mathbf{u}_{lk} - \mathbf{u}_{\nu'k'})\}}. \quad (4.2.4.87)$$

In the harmonic approximation $\exp\{2\pi i \mathbf{H} \cdot \Delta \mathbf{u}\}$ is replaced by $\exp\{\frac{1}{2} [2\pi i \mathbf{H} \cdot \Delta \mathbf{u}]^2\}$. This is, however, a more or less crude approximation because strongly anharmonic vibrations are quite common in an orientationally disordered crystal. In this approximation $F_l F_{\nu'}^+$ becomes

$$\overline{F_l F_{\nu'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{-B_k(\omega_l)\} \\ \times \exp\{-B_{k'}(\omega_{\nu'})\} \exp\{D_{lk, \nu'k'}\}. \quad (4.2.4.88)$$

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B_k is equal to $\frac{1}{2}(2\pi\mathbf{H} \cdot \mathbf{u}_{lk})^2$ (Debye–Waller factor) and depends on the specific configuration ω_l . $D_{lk;l'k'} = (2\pi\mathbf{H} \cdot \mathbf{u}_{lk})(2\pi\mathbf{H} \cdot \mathbf{u}_{l'k'})$ includes all the correlations between positions, orientations and vibrations of the molecules.

Averaging over different configurations demands a knowledge of the orientational probabilities. The probability of finding molecule l in orientation ω_l is given by $p(\omega_l)$. The double probability $p(\omega_l, \omega_{l'})$ gives the probability of finding two molecules l, l' in different orientations ω_l and $\omega_{l'}$, respectively. In the absence of correlations between the orientations we have: $p(\omega_l, \omega_{l'}) = p(\omega_l)p(\omega_{l'})$. If correlations exist: $p(\omega_l, \omega_{l'}) = p'(\omega_l|\omega_{l'})$ where $p'(\omega_l|\omega_{l'})$ defines the conditional probability that molecule l' has the orientation ω_l if molecule l has the orientation $\omega_{l'}$. For long distances between l and l' $p'(\omega_l|\omega_{l'})$ tends to $p(\omega_{l'})$.

The difference $\Delta(\omega_l|\omega_{l'}) = p'(\omega_l|\omega_{l'}) - p(\omega_{l'})$ characterizes, therefore, the degree of short-range orientational correlation. Note that this formalism corresponds fully to the $p_\mu, p_{\mu\mu'}$ used in the context of translational disorder.

The average structure factor, sometimes called averaged form factor, of the molecule is given by

$$\langle F_l \rangle = \sum_{\omega_l} p(\omega_l) F_l(\omega_l). \quad (4.2.4.89)$$

(a) Negligible correlations between vibrations of different molecules (Einstein model):

$$D_{lk;l'k'} = 0 \text{ for } l \neq l'.$$

From (4.2.4.88) it follows (the prime symbol takes the Debye–Waller factor into account):

$$\begin{aligned} \overline{\langle I \rangle} &= N^2 |\langle F' \rangle|^2 L(\mathbf{H}) \\ &+ N \left\{ \sum_k \sum_{k'} \sum_{\omega_l} p(\omega_l) f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \right. \\ &\times \exp\{D_{lk;l'k'}\} - |\langle F' \rangle|^2 \Big\} \\ &+ N \sum_{\Delta l \neq 0} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l) \Delta(\omega_l|\omega_{l'}) \\ &\times F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \end{aligned} \quad (4.2.4.90)$$

$L(\mathbf{H})$ is the reciprocal lattice of the well defined ordered lattice. The first term describes Bragg scattering from an averaged structure. The second term governs the diffuse scattering in the absence of short-range orientational correlations. The last term takes the correlation between the orientations into account.

If rigid molecules with centre-of-mass translational displacements and negligible librations are assumed, which is a first approximation only, $|\langle F \rangle|^2$ is no longer affected by a Debye–Waller factor.

In this approximation the diffuse scattering may therefore be separated into two parts:

$$N(\langle F^2 \rangle - |\langle F' \rangle|^2) = N(F^2 - |\langle F \rangle|^2) + N(|\langle F \rangle|^2 - |\langle F' \rangle|^2) \quad (4.2.4.91)$$

with

$$\begin{aligned} \langle F^2 \rangle &= \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} f_k(\omega_l) f_{k'}(\omega_{l'}) p(\omega_l) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}. \end{aligned} \quad (4.2.4.92)$$

The first term in (4.2.4.91) gives the scattering from equilibrium fluctuations in the scattering from individual molecules (diffuse scattering without correlations), the second gives the contribution from the centre-of-mass thermal vibrations of the molecules.

(b) If intermolecular correlations between the molecules cannot be neglected, the final intensity expression for diffuse scattering is very complicated. In many cases these correlations are caused by dynamical processes (see Chapter 4.1). A simplified treatment assumes the molecule to be a rigid body with a centre-of-mass displacement $\mathbf{u}_l$ and neglects vibrational–librational and librational–librational correlations: $D_{l;l'} = (2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})$ ($l \neq l'$). The following expression approximately holds:

$$\begin{aligned} \overline{\langle I \rangle} &= N^2 |\langle F' \rangle|^2 L(\mathbf{H}) \\ &+ \left\langle \sum_l \sum_{l'} F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \exp\{D_{l;l'}\} \right\rangle \{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \\ &+ N \left\{ \sum_{\omega_l} \sum_{k, k'} p(\omega_l) f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \right. \\ &\times \exp\{D_{lk;l'k'}\} - \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} p(\omega_l) p(\omega_{l'}) f_k f_{k'} \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \\ &\times \exp\{D_{lk;l'k'}\} \Big\} + \sum_{l \neq l'} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l) \Delta(\omega_l|\omega_{l'}) \\ &\times F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \exp\{D_{l;l'}\}. \end{aligned} \quad (4.2.4.93)$$

Again the first term describes Bragg scattering and the second corresponds to the average thermal diffuse scattering in the disordered crystal. Because just one molecule belongs to one unit cell only acoustic waves contribute to this part. To an approximation, the result for an ordered crystal may be used by replacing F by $\langle F' \rangle$ [Chapter 4.1, equation (4.1.3.4)]. The third term corresponds to random-disorder diffuse scattering. If librations are neglected this term may be replaced by $N(\langle F^2 \rangle - \langle F \rangle^2)$. The last term in (4.2.4.93) describes space correlations. Omission of $\exp\{D_{l;l'}\}$ or expansion to $\sim (1 + D_{l;l'})$ are further simplifying approximations.

In either (4.2.4.90) or (4.2.4.93) the diffuse-scattering part depends on a knowledge of the conditional probability $\Delta(\omega_l|\omega_{l'})$ and the orientational probability $p(\omega_l)$. The latter may be found, at least in principle, from the average structure factor.

4.2.4.5.2. Rotational structure (form) factor

In certain cases and with simplifying assumptions, $\langle F \rangle$ [equation (4.2.4.89)] and $\langle \Delta F^2 \rangle$ [equation (4.2.4.92)] may be calculated. Assuming only one molecule per unit cell and treating the molecule as a rigid body, one derives from the structure factor of an ordered crystal F_l

$$\langle F \rangle = \sum_k f_k \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \quad (4.2.4.94)$$

and

$$\begin{aligned} \langle \Delta F^2 \rangle &= \sum_k \sum_{k'} f_k f_{k'} [\langle \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \rangle \\ &- \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{l'k'}\} \rangle]. \end{aligned} \quad (4.2.4.95)$$

If the molecules have random orientation in space the following expressions hold [see, e.g., Dolling *et al.* (1979)]:

$$\langle F \rangle = \sum_k f_k j_0(\mathbf{H} \cdot \mathbf{r}_k) \quad (4.2.4.96)$$

$$\begin{aligned} \langle |\Delta F|^2 \rangle &= \sum_k \sum_{k'} f_k f_{k'} \{ j_0(\mathbf{H} \cdot (\mathbf{r}_k - \mathbf{r}_{k'})) \\ &- j_0(\mathbf{H} \cdot \mathbf{r}_k) j_0(\mathbf{H} \cdot \mathbf{r}_{k'}) \}. \end{aligned} \quad (4.2.4.97)$$

$j_0(z)$ is the zeroth order of the spherical Bessel functions and describes an atom k uniformly distributed over a shell of radius r_k .

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In practice the molecules perform more or less finite librations about the main orientation. The structure factor may then be found by the method of symmetry-adapted functions [see, *e.g.*, Press (1973), Press & Hüller (1973), Dolling *et al.* (1979), Prandl (1981, and references therein)].

$$\langle F \rangle = \sum_k f_k 4\pi \sum_{\nu} \sum_{\mu=-\nu}^{+\nu} i^{\nu} j_{\nu}(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{(k)} Y_{\nu\mu}(\theta, \varphi). \quad (4.2.4.98)$$

$j_{\nu}(z)$ is the ν th order of spherical Bessel functions, the coefficients $C_{\nu\mu}^{(k)}$ characterize the angular distribution of $\mathbf{r}_k$, $Y(\theta, \varphi)$ are the spherical harmonics where $|\mathbf{H}|, \theta, \varphi$ denote polar coordinates of $\mathbf{H}$.

The general case of an arbitrary crystal, site and molecular symmetry and the case of several symmetrically equivalent orientationally disordered molecules per unit cell are treated by Prandl (1981); an example is given by Hohlwein *et al.* (1986). As mentioned above, cubic plastic crystals are common and therefore mostly studied up to now. The expression for $\langle F \rangle$ may then be formulated as an expansion in cubic harmonics, $K_{\nu\mu}(\theta, \varphi)$:

$$\langle F \rangle = \sum_k f_k 4\pi \sum_{\nu} \sum_{\mu} i^{\nu} j_{\nu}(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}' K_{\nu\mu}(\theta, \varphi). \quad (4.2.4.99)$$

($C_{\nu\mu}'$ are modified expansion coefficients.)

Taking into account isotropic centre-of-mass translational displacements, which are not correlated with the librations, we obtain:

$$\langle F' \rangle = \langle F \rangle \exp\left\{-\frac{1}{6} H^2 \langle U^2 \rangle\right\}. \quad (4.2.4.100)$$

U is the mean-square translational displacement of the molecule. Correlations between translational and vibrational displacements are treated by Press *et al.* (1979).

Equivalent expressions for crystals with symmetry other than cubic may be found from the same concept of symmetry-adapted functions [tables are given by Bradley & Cracknell (1972)].

4.2.4.5.3. Short-range correlations

The final terms in equations (4.2.4.90) and (4.2.4.93) concern correlations between the orientations of different molecules. Detailed evaluations need a knowledge of a particular model. Examples are compounds with nitrate groups (Wong *et al.*, 1984; Lefebvre *et al.*, 1984), CBr_4 (More *et al.*, 1980, 1984), and many others (see Sherwood, 1979). The situation is even more complicated when a modulation wave with respect to the occupation of different molecular orientations is superimposed. A limiting case would be a box-like function describing a pattern of domains. Within one domain all molecules have the same orientation. This situation is common in ferroelectrics where molecules exhibit a permanent dipole moment. The modulation may occur in one or more directions in space. The observed intensity in this type of orientationally disordered crystal is characterized by a system of more or less diffuse satellite reflections. The general scattering theory of a crystal with occupational modulation waves follows the same lines as outlined in Section 4.2.3.1.

4.2.5. Measurement of diffuse scattering

To conclude this chapter experimental aspects are summarized which are specifically important in diffuse-scattering work. The summary is restricted to film methods commonly used in laboratories and (X-ray or neutron) diffractometer measurements. Sophisticated special techniques and instruments at synchrotron facilities and reactors dedicated to diffuse-scattering work are not described here. The full merit of these machines may be assessed

after inspection of corresponding user handbooks which are available upon request. Also excluded from this section are instruments and methods related to diffuse scattering at low angles, *i.e.* small-angle scattering techniques. Although no fundamental differences exist between an X-ray experiment in a laboratory and at a synchrotron facility, some specific points have to be considered in the latter case. These are discussed by Matsubara & Georgopoulos (1985), Oshima & Harada (1986), and Ohshima *et al.* (1986).

Generally, diffuse scattering is weak in comparison with Bragg scattering, anisotropically and inhomogeneously distributed in reciprocal space, elastic, inelastic, or quasi-elastic in origin. It is frequently related to more than one structural element, which means that different parts may show different behaviour in reciprocal space and/or on an energy scale. Therefore special care has to be taken concerning the following points: (1) type of experiment: X-rays or neutrons, film or diffractometer/spectrometer, single crystal or powder; (2) strong sources; (3) best choice of wavelength (or energy) of incident radiation if no 'white' technique is used; (4) monochromatic and focusing techniques; (5) sample environment and background reduction; (6) resolution and scanning procedure in diffractometer or densitometer recording.

On undertaking an investigation of a disorder problem by an analysis of the diffuse scattering an overall picture should first be recorded by X-ray diffraction experiments. Several sections through reciprocal space help to define the problem. For this purpose film methods are preferable. Cameras with relatively short crystal-film distances avoid long exposure times. Unfortunately, there are some disorder problems which cannot be tackled by X-ray methods. X-rays are rather insensitive for the elucidation of disorder problems where light atoms in the presence of heavy atoms play the dominant role, or when elements are involved which scarcely differ in X-ray scattering amplitudes (*e.g.* Al/Si/Mg). In these cases neutrons have to be used at an early stage. If a significant part of the diffuse scattering is suspected not to be of static origin concomitant purely elastic, quasi-elastic or inelastic neutron experiments have to be planned from the very beginning.

Because diffuse scattering is usually weak, intense radiation sources are needed, whereas the background level should be kept as low as possible. Coming to the background problem later, we should make some brief remarks concerning sources. Even a normal modern X-ray tube is a stronger source, defined by the flux density from an anode (number of photons $\text{cm}^{-2} \text{s}^{-1}$), than a reactor with the highest available flux. For this reason most experimental work which can be performed with X-rays should be. Generally the characteristic spectrum will be used, but special methods have been developed where the white X-ray spectrum is of interest (see below). A most powerful source in this respect is a modern synchrotron storage ring (see, *e.g.*, Kunz, 1979). With respect to rotating anodes one should bear in mind not only the power but also the flux density, because there is little merit for a broad focus in diffuse-scattering work (separation of sharp and diffuse scattering). One can suppose that synchrotron radiation in the X-ray range will also play an important role in the field of monochromatic diffraction methods, owing to the extremely high brilliance of these sources (number of quanta $\text{cm}^{-2} \text{sr}^{-1} \text{s}^{-1}$ and wavelength interval). Diffuse neutron-diffraction work may only be performed on a high- or medium-flux reactor. Highly efficient monochromator systems are necessary. In combination with time-of-flight neutron methods pulsed sources are nowadays equivalent to reactors (Windsor, 1982).

If film and (X-ray) diffractometer methods are compared, film techniques are highly recommended at an early stage to give a general survey of the disorder problem. Routine X-ray techniques such as rotation photographs, Weissenberg or precession techniques may be used. The Weissenberg method is preferred to the

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precession method in most cases because of the comparatively larger coverage of reciprocal space (with the same wavelength). The drawback of a distorted image of the reciprocal space may be compensated by digitizing the film blackening *via* a densitometer recording and subsequent plotting. With this procedure a distorted section through the reciprocal lattice may be transformed into a form suitable for easy interpretation (Welberry, 1983).

Frequently used are standing-crystal techniques in combination with monochromatic radiation, usually called monochromatic Laue techniques (see, *e.g.*, Flack, 1970). The Noromosaic technique (Jagodzinski & Korekawa, 1973) is characterized by a convergent monochromatic beam which simulates an oscillation photograph over a small angular range. Heavily overexposed photographs, with respect to Bragg scattering, allow for sampling of diffuse intensity if a crystal is oriented in such a way that there is a well defined section between the Ewald sphere and the diffuse phenomenon under consideration. By combining single Noromosaic photographs, Weissenberg patterns can be simulated. This relatively tedious way of comparison with a true Weissenberg photograph is often unavoidable because the heavily overexposed Bragg peaks obscure weak diffuse phenomena over a considerable area of a photograph. Furthermore, standing pictures are pointwise measurements in comparison with the normal continuous pattern with respect to the crystal setting. Long-exposure Weissenberg photographs are therefore not equivalent to a smaller set of standing photographs. In this context it should be mentioned that a layer-line screen has not only the simple function of a selecting diaphragm, but the gap width determines the resolution volume within which diffuse intensity is collected (Welberry, 1983). For further discussion of questions of resolution see below. Single-crystal diffractometer measurements, either in the X-ray or in the neutron case, are frequently adopted for quantitative measurements of diffuse intensities. Microdensitometer recording of X-ray films is an equivalent method, incorporating corrections for background and other factors into this procedure. A comparison of Weissenberg and diffractometer methods for the measurement of diffuse scattering is given by Welberry & Glazer (1985).

In the case of powder-diffractometer experiments preferred orientations/textures could lead to a complete misidentification of the problem. Single-crystal experiments are preferable in some respect, because diffuse phenomena in a powder diagram may be analysed only after an idea about the disorder has been obtained and only in special cases. Nevertheless, high-resolution powder investigations give quick supporting information, *e.g.* about superlattice peaks, split reflections, lattice strains, domain size effects, lattice-constant change related to a disorder effect *etc.*

Before starting an experiment of any kind, one should specify the optimum wavelength. This is important with respect to the problem to be solved: *e.g.*, point defects cause diffuse scattering to fall off with increasing scattering vector; short-range ordering between clusters causes broad peaks corresponding to large d spacings; lattice-relaxation processes induce a broadening of the interferences (Huang scattering); or static modulation waves with long periods give rise to satellite scattering close to Bragg peaks. In all these cases a long wavelength is preferable. On the other hand, a shorter wavelength is needed if diffuse phenomena are structured in a sense that broad peaks are observable up to large reciprocal vectors, or diffuse streaks or planes have to be recorded up to high values of the scattering vector in order to decide between different models. The λ^3 -dependence of the scattered intensity, in the framework of the kinematical theory, is a crucial point for exposure or data-acquisition times. Moreover, the accuracy with which an experiment can be carried out suffers from a short wavelength: generally, momentum as well as energy resolution are lower. For a quantitative estimate detailed considerations of resolution in reciprocal (and energy) space are needed. Special attention must

be paid to absorption phenomena, in particular when (in the X-ray case) an absorption edge of an element of the sample is close to the wavelength used. $\lambda \sim 0.91 \text{ \AA}$ must be avoided in combination with film methods owing to the K edge of Br. Strong fluorescence scattering may completely obscure weak diffuse-scattering phenomena. In comparison with X-rays, the generally lower absorption coefficients of neutrons of any wavelength makes absolute measurements easier. This also allows the use of larger sample volumes, which is not true in the X-ray case. An extinction problem does not exist in diffuse-scattering work. In particular, the use of a long wavelength is profitable when the main diffuse contributions can be recorded within an Ewald sphere as small as the Bragg cut-off of the sample: $\lambda = 2d_{\max}$; a contamination by Bragg scattering can then be avoided.

This is also advantageous from a different point of view: because the contribution of thermal diffuse scattering increases with increasing scattering vector $\mathbf{H}$, the relative amount of this component becomes negligibly small within the first reciprocal cell.

Highly monochromatic radiation should be used in order to eliminate broadening effects due to the wavelength distribution. Focusing monochromators help to overcome the lack of luminosity. A focusing technique, in particular a focusing camera geometry, is very helpful for deciding between geometrical broadening and 'true' diffuseness. With good success a method is used where in a monochromatic divergent beam the sample is placed with its selected axis lying in the scattering plane of the monochromator (Jagodzinski, 1968). The specimen is fully embedded in the incident beam which is focused onto the film. By this procedure the influence of the sample size is suppressed in one dimension. In an oscillation photograph a high resolution perpendicular to the diffuse layer lines may thus be achieved.

A serious problem is a careful suppression of background scattering. Incoherent X-ray scattering as an inherent property of a sample occurs as continuous blackening in the case of fluorescence, or as scattering at high 2θ angles owing to Compton scattering or 'incoherent' inelastic effects. Protecting the film by a thin Al or Ni foil is of some help against fluorescence, but also attenuates the diffuse intensity. Scratching the film emulsion after the exposure from the 'front' side of the film is another possibility for reducing the relative amount of the lower-energy fluorescence radiation. Obviously, energy-dispersive counter methods are highly efficient in this case (see below). Air scattering produces a background at low 2θ angles which may easily be avoided by special slit systems and evacuation of the camera.

In X-ray or neutron diffractometer measurements incoherent and multiple scattering contribute to a background which varies only slowly with 2θ and can be subtracted by linear interpolation or fitting a smooth curve, or can even be calculated quantitatively and then subtracted. In neutron diffraction there are rare cases when monoisotopic and 'zero-spin' samples are available and, consequently, the corresponding incoherent scattering part vanishes completely. In some cases a separation of coherent and incoherent neutron scattering is possible by polarization analysis (Gerlach *et al.*, 1982). An 'empty' scan can take care of instrumental background contributions. Evacuation or controlled-atmosphere studies need a chamber which may give rise to spurious scattering. This can be avoided if no part of the vacuum chamber is hit by the primary beam. The problem is less serious in neutron work. Mounting a specimen, *e.g.*, on a silica fibre with cement, poorly aligned collimators or beam catchers are further sources. Sometimes a specimen has to be enclosed in a capillary which will always be hit by the incident beam. Careful and tedious experimental work is necessary in the case of low- and high-temperature (or -pressure) investigations which have to be carried out in many disorder problems. Whereas the experimental situation is again less serious in neutron scattering, there are large problems with scattering from

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walls and containers in X-ray work. Most of the X-ray investigations have therefore been made on quenched samples. Because TDS is dominating at high temperatures, also in the presence of a static disorder problem, the quantitative separation can hardly be carried out in the case of high experimental background. Calculation and subtraction of the TDS is possible in principle, but difficult in practice.

A quantitative analysis of diffuse-scattering data is essential for a definite decision about a disorder model. By comparison of calculated and corrected experimental data the magnitudes of the parameters of the structural disorder model may be derived. A careful analysis of the data requires, therefore, corrections for polarization (X-ray case), absorption and resolution. These may be performed in the usual way for polarization and absorption. Very detailed considerations, however, are necessary for the question of instrumental resolution which depends, in addition to other factors, on the scattering angle and implies intensity corrections analogous to the Lorentz factor used in structure analysis from sharp Bragg reflections.

Resolution is conveniently described by a function, $R(\mathbf{H} - \mathbf{H}_0)$, which is defined as the probability of detecting a photon or neutron with momentum transfer $\hbar\mathbf{H} = \hbar(\mathbf{k} - \mathbf{k}_0)$ when the instrument is set to measure $\mathbf{H}_0$. This function R depends on the instrumental parameters (collimations, mosaic spread of monochromator, scattering angle) and the spectral width of the source. Fig. 4.2.5.1 shows a schematic sketch of a diffractometer setting. Detailed considerations of resolution volume in X-ray diffractometry are given by Sparks & Borie (1966). If a triple-axis (neutron) instrument is used, for example in a purely elastic configuration, the set of instrumental parameters is extended by the mosaic of the analyser and the collimations between analyser and detector (see Chapter 4.1).

If photographic (X-ray) techniques are used, the detector aperture is controlled by the slit width of the microdensitometer. A general formulation of R in neutron diffractometry is given by Cooper & Nathans (1968):

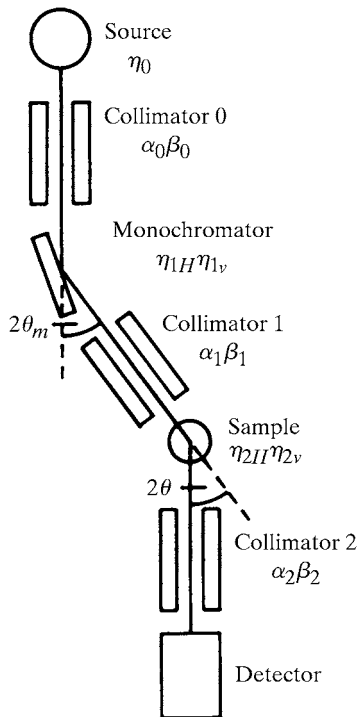


Fig. 4.2.5.1. Schematic sketch of a diffractometer setting.

$$R'(\mathbf{H} - \mathbf{H}_0) = R'_0 \exp \left\{ -\frac{1}{2} \sum_k \sum_l M'_{kl} \Delta H_k \Delta H_l \right\}. \quad (4.2.5.1)$$

Gaussians are assumed for the mosaic distributions and for the transmission functions the parameters are involved in the coefficients R'_0 and M'_{kl} .

The general assumption of Gaussians is not too serious in the X-ray case (Iizumi, 1973). Restrictions are due to absorption which makes the profiles asymmetric. Box-like functions are considered to be better for the spectral distribution or for large apertures (Boysen & Adlhart, 1987). These questions are treated in some detail by Klug & Alexander (1954). The main features, however, may also be derived by the Gaussian approximation. In practice the function R may be obtained either by calculation from the known instrumental parameters or by measuring Bragg peaks of a perfect unstrained crystal. In the latter case [cf. equation (4.2.5.2)] the intensity profile is given solely by the resolution function. A normalization with the Bragg intensities is also useful in order to place the diffuse-scattering intensity on an absolute scale.

In single-crystal diffractometry the measured intensity is given by the convolution product of $d\sigma/d\Omega$ with R ,

$$I(\mathbf{H}_0) = \int \frac{d\sigma}{d\Omega}(\mathbf{H}) \cdot R(\mathbf{H} - \mathbf{H}_0) d\mathbf{H}, \quad (4.2.5.2)$$

where $d\sigma/d\Omega$ describes the scattering cross section for the disorder problem. In more accurate form the mosaic of the sample has to be included:

$$\begin{aligned} I(\mathbf{H}_0) &= \int \frac{d\sigma}{d\Omega}(\mathbf{H} - \Delta\mathbf{k}) \cdot \eta(\Delta\mathbf{k}) R(\mathbf{H} - \mathbf{H}_0) d\mathbf{H} d(\Delta\mathbf{k}) \\ &= \int \frac{d\sigma}{d\Omega}(\mathbf{H}') \cdot R'(\mathbf{H}' - \mathbf{H}_0) d\mathbf{H}'. \end{aligned} \quad (4.2.5.2a)$$

$R'(\mathbf{H}' - \mathbf{H}_0) = \int \eta(\Delta\mathbf{k}) R(\mathbf{H}' + \Delta\mathbf{k} - \mathbf{H}_0) d(\Delta\mathbf{k})$. $\eta(\Delta\mathbf{k})$ describes the mosaic block distribution around a most probable vector $\mathbf{k}_0$; $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}_0$; $\mathbf{H}' = \mathbf{H} - \Delta\mathbf{k}$.

In formulae (4.2.5.1) and (4.2.5.2) all factors independent of 2θ are neglected. All intensity expressions have to be calculated from equations (4.2.5.2) or (4.2.5.2a). In the case of a dynamical disorder problem, i.e. when the differential cross section also depends on energy transfer $\hbar\omega$, the integration must be extended over energy.

The intensity variation of diffuse peaks with 2θ was studied in detail by Yessik *et al.* (1973). In principle all special cases are included there. In practice, however, some important simplifications can be made if $d\sigma/d\Omega$ is either very broad or very sharp compared with R , i.e. for Bragg peaks, sharp streaks, 'thin' diffuse layers or extended 3D diffuse peaks (Boysen & Adlhart, 1987).

In the latter case the cross section $d\sigma/d\Omega$ may be treated as nearly constant over the resolution volume so that the corresponding 'Lorentz' factor is independent of 2θ :

$$L_{3D} = 1. \quad (4.2.5.3)$$

For a diffuse plane within the scattering plane with very small thickness and slowly varying cross section within the plane, one derives for a point measurement in the plane:

$$L_{2D, \parallel} = (\beta_1'^2 + \beta_2'^2 + \eta_{2v}^2 - \sin^2 \theta)^{-1/2}, \quad (4.2.5.4)$$

exhibiting an explicit dependence on θ ($\beta_1', \beta_2', \eta_{2v}$ determining an effective vertical divergence before the sample, the divergence before the detector and the vertical mosaic spread of the sample, respectively).

In the case of *relaxed* vertical collimations $\beta_1', \beta_2' \gg \eta_{2v}$

$$L_{2D, \parallel} = (\beta_1'^2 + \beta_2'^2)^{-1/2}, \quad (4.2.5.4a)$$

i.e. again independent of θ .

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Scanning across the diffuse layer in a direction perpendicular to it one obtains an integrated intensity which is also independent of 2θ . This is even true if approximations other than Gaussians are used.

If, on the other hand, an equivalent diffuse plane is positioned perpendicular to the scattering plane, the equivalent expression for $L_{2D, \perp}$ of a point measurement is given by

$$\begin{aligned} L_{2D, \perp} \simeq & [4\eta_{2H}^2 \sin^2 \theta \cos^2 \psi + \alpha_2^2 \sin^2(\psi - \theta) \\ & + \sin^2(\psi + \theta) + 4\eta_0' \sin^2 \theta \sin^2 \psi \\ & - 4\alpha_1'' \sin \theta \sin \psi \sin(\theta + \psi)], \end{aligned} \quad (4.2.5.5)$$

where ψ gives the angle between the line of intersection between the diffuse and the scattering plane and the vector $\mathbf{H}_0$. The coefficients η_{2H} , α_2 , α_1' , α_1'' , η are either instrumental parameters or functions of them, defining horizontal collimations and mosaic spreads. In the case of a (sharp) X-ray line (produced, for example, by filtering) the last two terms in equation (4.2.5.5) vanish.

The use of integrated intensities from individual scans perpendicular to the diffuse plane, now carried out within the scattering plane, again gives a Lorentz factor independent of 2θ .

In the third fundamental special case, diffuse streaking along one reciprocal direction within the scattering plane (narrow cross section, slowly varying intensity along the streak), the Lorentz factor for a point measurement may be expressed by the product

$$L_{1D, \parallel} \simeq L_{2D, \parallel} L_{2D, \perp}, \quad (4.2.5.6)$$

where ψ now defines the angle between the streak and $\mathbf{H}_0$. The integrated intensity taken from an H scan perpendicular to the streak has to be corrected by a Lorentz factor which is equal to $L_{2D, \parallel}$ [equation (4.2.5.4)]. In the case of a diffuse streak perpendicular to the scattering plane a relatively complicated equation holds for the corresponding Lorentz factor (Boysen & Adlhart, 1987). Again more simple expressions hold for integrated intensities from H scans perpendicular to the streaks. Such scans may be performed in the radial direction (corresponding to a θ - 2θ scan):

$$L_{1D, \perp, \text{rad}} = (4\eta_{2H}^2 + \alpha_2^2 + \alpha_1'^2)^{-1/2} \cdot 1/\sin \theta \quad (4.2.5.7)$$

or perpendicular to the radial direction (within the scattering plane) (corresponding to an ω scan):

$$L_{1D, \perp, \text{per}} = (\alpha_2^2 + \alpha_1'^2 + 4\eta_0' \tan^2 \theta - 4\alpha_1'' \tan \theta)^{-1/2} \cdot 1/\cos \theta \quad (4.2.5.8)$$

Note that only the radial scan yields a simple θ dependence ($\sim 1/\sin \theta$).

From these considerations it is recommended that integrated intensities from scans perpendicular to a diffuse plane or a diffuse streak should be used in order to extract the disorder cross sections. For other scan directions, which make an angle α with the intersection line (diffuse plane) or with a streak, the L factors are simply: $L_{2D, \perp}/\sin \alpha$ and $L_{1D, \perp}/\sin \alpha$, respectively.

One point should be emphasized: since in a usual experiment the integration is performed over an angle $\Delta\omega$ via a general $\delta\omega$: ($g\delta 2\theta$) scan, an additional correction factor arises:

$$\Delta\omega/\Delta\mathbf{H}_\beta = \sin(\beta + \theta)/(\mathbf{k}_0 \sin 2\theta). \quad (4.2.5.9)$$

β is the angle between $\mathbf{H}_0$ and the scan direction $\mathbf{H}_\beta$; $g = (\tan \beta + \tan \theta)/(2 \tan \theta)$ defines the coupling ratio between the rotation of the crystal around a vertical axis and the rotation of the detector shaft. Most frequently used are the so-called 1:2 and ω -scan techniques where $\beta = 0$ and 90° , respectively.

It should be mentioned that the results in the neutron case are restricted to the elastic diffuse part, since in a diffractometer measurement the inelastic part deserves special attention concerning the integration over energy by the detector (Tucciarone *et al.*,

1971; Grabcev, 1974). If a triple-axis instrument is used, the collimations α_2 and β_2 have to be replaced by effective values after the sample owing to the analyser system.

In order to optimize a single-crystal experiment, the scan direction and also the instrumental collimations should be carefully chosen according to the anisotropy of the diffuse phenomenon. If the variation of $d\sigma/d\Omega$ is appreciable along a streak, the resolution should be held narrow in one direction and relaxed in the other to gain intensity and the scans should be performed perpendicular to that direction. If the variation is smooth the sharpest signal is measured by a scan perpendicular to the streak. In any case, a good knowledge of the resolution and its variation with 2θ is helpful.

Even the diffuse background in powder diagrams contains valuable information about disorder. Only in very simple cases can a model be deduced from a powder pattern alone; however, a refinement of a known disorder model can favourably be carried out, *e.g.* the temperature dependence may be studied. On account of the intensity integration the ratio of diffuse intensity to Bragg intensity is enhanced in a powder pattern. Moreover, a powder pattern contains, in principle, all the information about the sample and might thus reveal more than single-crystal work.

The quantitative calculation of a diffuse background is also helpful in combination with Rietveld's (1969) method for refining an averaged structure by fitting (powder) Bragg reflections. In particular, for highly anisotropic diffuse phenomena characteristic asymmetric line shapes occur.

The calculation of these line shapes is treated in the literature, mostly neglecting the instrumental resolution (see, *e.g.*, Warren, 1941; Wilson, 1949; Jones, 1949; and de Courville-Brenasin *et al.*, 1981). This is not justified if the variation of the diffuse intensity becomes comparable with that of the resolution function as is often the case in neutron diffraction. It may be incorporated by taking advantage of a resolution function of a powder instrument (Caglioti *et al.*, 1958). A detailed analysis of diffuse peaks is given by Yessik *et al.* (1973), the equivalent considerations for diffuse planes and streaks by Boysen (1985). The case of 3D random disorder (incoherent neutron scattering, monotonous Laue scattering, averaged TDS, multiple scattering or short-range-order modulations) is treated by Sabine & Clarke (1977).

In polycrystalline samples the cross section has to be averaged over all orientations (n_c = number of crystallites in the sample):

$$\frac{d\sigma_p}{d\Omega}(\mathbf{H}') = \frac{n_c}{H^2} \int \frac{d\sigma}{d\Omega}(\mathbf{H}') R'(|\mathbf{H}'| - |\mathbf{H}_0|) d\mathbf{H}' \quad (4.2.5.10)$$

and this averaged cross section enters the relevant expressions for the convolution product with the resolution function.

A general intensity expression may be written as (Yessik *et al.*, 1973):

$$I_n(\mathbf{H}_0) = P \sum_{\tau} m(\tau) A_n \Phi_n(\mathbf{H}_0, \tau). \quad (4.2.5.11)$$

P denotes a scaling factor depending on the instrumental luminosity, τ the shortest distance to the origin of the reciprocal lattice, $m(\tau)$ the corresponding symmetry-induced multiplicity, A_n contains the structure factor of the structural units and the type of disorder, and Φ_n describes the characteristic modulation of the diffuse phenomenon of dimension n in the powder pattern. These expressions are given below with the assumption of Gaussian line shapes of width D for the narrow extension(s). The formulae depend on a factor $M = A_{1/2}(4k_1^2 - H_0^2)/(32 \ln 2)$, where $A_{1/2}$ describes the dependence of the Bragg peaks on the instrumental parameters U , V , W (see Caglioti *et al.*, 1958),

$$A_{1/2}^2 = U \tan^2 \theta + V \tan \theta + W. \quad (4.2.5.12)$$

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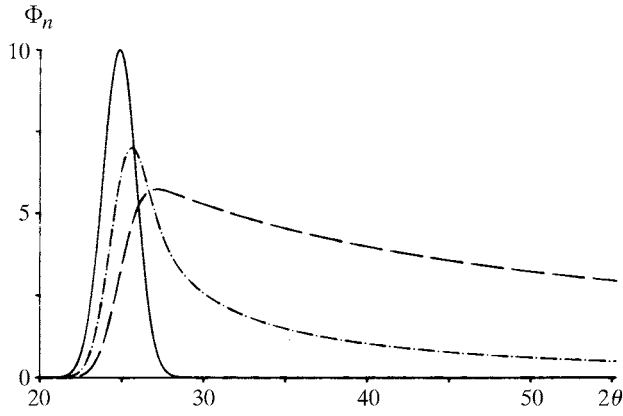


Fig. 4.2.5.2. Line profiles in powder diffraction for sharp and diffuse reflections; peaks (full line), continuous streaks (dot-dash lines) and continuous planes (broken lines). For explanation see text.

(a) Isotropic diffuse peak around τ

$$\Phi_0 = [2\pi(M^2 + D^2)]^{-1/2} \cdot 1/\tau^2 \times \exp\{-(\mathbf{H}_0 - \tau)^2/2(M^2 + D^2)\}. \quad (4.2.5.13)$$

The moduli $|\mathbf{H}_0|$ and $|\tau|$ enter the exponential, *i.e.* the variation of $d\sigma/d\Omega$ along $|\mathbf{H}_0|$ is essential. For broad diffuse peaks ($M \ll D$) the angular dependence is due to $1/\tau^2$, *i.e.* proportional to $1/\sin^2 \theta$. This result is valid for diffuse peaks of any shape.

(b) Diffuse streak

$$\Phi_1 = 2\pi(M^2 + D^2)^{-1/2} \int (\tau^2 + q^2)^{-1/2} \times \exp\{-\mathbf{H}_0 - \sqrt{\tau^2 + q^2}/2(M^2 + D^2)\} dq. \quad (4.2.5.14)$$

The integral has to be evaluated numerically. If $(M^2 + D^2)$ is not too large, the term $1/k_0^2 = 1/(\tau^2 + q^2)$ varies only slowly compared to the exponential term and may be kept outside the integral, setting it approximately to $1/H_0^2$.

(c) Diffuse plane (with $r^2 = q_x^2 + q_y^2$)

$$\Phi_2 = (M^2 + D^2)^{-1/2} \int r^2/(\tau^2 + r^2) \times \exp\{-\mathbf{H}_0 - \sqrt{\tau^2 + r^2}/2(M^2 + D^2)\} dr. \quad (4.2.5.15)$$

With the same approximation as in (b) the expression may be

simplified to

$$\Phi_2 = \pi/\mathbf{H}_0 [1 - \text{erf}\{(\tau - \mathbf{H}_0)/\sqrt{2(M^2 + D^2)}\} + 1/\mathbf{H}_0^2 \sqrt{2\pi(M^2 + D^2)} \times \exp\{-(\mathbf{H}_0 - \tau)^2/2(M^2 + D^2)\}]. \quad (4.2.5.16)$$

(d) Slowly varying diffuse scattering in three dimensions

$\Phi_3 = \text{constant}$.

Consequently, the intensity is directly proportional to the cross section. The characteristic functions Φ_0 , Φ_1 and Φ_2 are shown in Fig. 4.2.5.2 for equal values of τ and D . Note the relative peak shifts and the high-angle tail.

Techniques for the measurement of diffuse scattering using a *white* spectrum are common in neutron diffraction. Owing to the relatively low velocity of thermal or cold neutrons, time-of-flight (TOF) methods in combination with time-resolving detector systems, placed at a fixed angle 2θ , allow for a simultaneous recording along a radial direction through the origin of reciprocal space (see, *e.g.*, Turberfield, 1970; Bauer *et al.*, 1975). The scan range is limited by the Ewald spheres corresponding to λ_{max} and λ_{min} , respectively. With several such detector systems placed at different angles, several scans may be carried out simultaneously during one neutron pulse. There is a renaissance of these methods in combination with high-flux pulsed neutron sources.

An analogue of neutron TOF diffractometry in the X-ray case is a combination of a white source of X-rays and an energy-dispersive detector. This technique, which has been known in principle for a long time, suffered from relatively weak white sources. With the development of high-power X-ray generators or the powerful synchrotron source this method has become highly interesting in recent times. Its use in diffuse-scattering work (in particular, resolution effects) is discussed by Harada *et al.* (1984).

Valuable developments with a view to diffuse-scattering work are multidetectors (see, *e.g.*, Haubold, 1975) and position-sensitive detectors for X-rays (Arndt, 1986a) and neutrons (Convert & Forsyth, 1983). A linear position-sensitive detector allows one to record a large amount of data at the same time, which is very favourable in powder work and also in diffuse scattering with single crystals. By combining a linear position-sensitive detector and the TOF method a whole area in reciprocal space is accessible simultaneously (Niimura *et al.*, 1982; Niimura, 1986). At present, area detectors are mainly used in combination with low-angle scattering techniques, but are also of growing interest for diffuse-scattering work (Arndt, 1986b).

4.3. Diffuse scattering in electron diffraction

BY J. M. COWLEY AND J. K. GJØNNES

4.3.1. Introduction

The origins of diffuse scattering in electron-diffraction patterns are the same as in the X-ray case: inelastic scattering due to electronic excitations, thermal diffuse scattering (TDS) from atomic motions, scattering from crystal defects or disorder. For diffraction by crystals, the diffuse scattering can formally be described in terms of a nonperiodic deviation $\Delta\varphi$ from the periodic, average crystal potential, $\bar{\varphi}$:

$$\varphi(\mathbf{r}, t) = \bar{\varphi}(\mathbf{r}) + \Delta\varphi(\mathbf{r}, t), \quad (4.3.1.1)$$

where $\Delta\varphi$ may have a static component from disorder in addition to time-dependent fluctuations of the electron distribution or atomic positions.

In the kinematical case, the diffuse scattering can be treated separately. The intensity I_d as a function of the scattering variable $\mathbf{u}$ ($|\mathbf{u}| = 2 \sin \theta / \lambda$) and energy transfer $h\nu$ is then given by the Fourier transform $\mathcal{F}$ of $\Delta\varphi$

$$I(\mathbf{u}, \nu) = |\Delta\Phi(\mathbf{u}\nu)|^2 = |\mathcal{F}\{\Delta\varphi(\mathbf{r}, t)\}|^2 = \mathcal{F}\{P_d(\mathbf{r}, \nu)\} \quad (4.3.1.2)$$

and may also be written as the Fourier transform of a correlation function P_d representing fluctuations in space and time (see Cowley, 1981). When the energy transfers are small – as with TDS – and hence not measured, the observed intensity corresponds to an integral over ν :

$$\begin{aligned} I(\mathbf{u}) &= I_d(\mathbf{u}) + I_{av}(\mathbf{u}) \\ I_d(\mathbf{u}) &= \int I_d(\mathbf{u}, \nu) d\nu = \mathcal{F}\{P_d(\mathbf{r}, 0)\} \end{aligned}$$

and also

$$I_d(\mathbf{u}) = \langle |\Phi(\mathbf{u})|^2 \rangle - |\langle \Phi(\mathbf{u}) \rangle|^2, \quad (4.3.1.3)$$

where the brackets may indicate a time average, an expectation value, or a spatial average over the periodicity of the lattice in the case of static deviations from a periodic structure.

The considerations of TDS and static defects and disorder of Chapters 4.1 and 4.2 thus may be applied directly to electron diffraction in the kinematical approximation when the differences in experimental conditions and diffraction geometry are taken into account.

The most prominent contribution to the diffuse background in electron diffraction, however, is the inelastic scattering at low angles arising mainly from the excitation of outer electrons. This is quite different from the X-ray case where the inelastic ('incoherent') scattering, $S(\mathbf{u})$, goes to zero at small angles and increases to a value proportional to Z for high values of $|\mathbf{u}|$. The difference is due to the Coulomb nature of electron scattering, which leads to the kinematical intensity expression S/u^4 , emphasizing the small-angle region. At high angles, the inelastic scattering from an atom is then proportional to Z/u^4 , which is considerably less than the corresponding elastic scattering $(Z - f)^2/u^4$ which approaches Z^2/u^4 (Section 2.5.2) (see Fig. 4.3.1.1).

The kinematical description can be used for electron scattering only when the crystal is very thin (10 nm or less) and composed of light atoms. For heavy atoms such as Au or Pb, crystals of thickness 1 nm or more in principal orientations show strong deviations from kinematical behaviour. With increasing thickness, dynamical scattering effects first modify the sharp Bragg reflections and then have increasingly significant effects on the diffuse scattering. Bragg scattering of the diffuse scattering produces Kikuchi lines and other effects. Multiple diffuse scattering broadens the distribution and smears out detail. As the thickness increases further, the diffuse

scattering increases and the Bragg beams are reduced in intensity until there is only a diffuse 'channelling pattern' where the features depend in only a very indirect way on the incident-beam direction or on the sources of the diffuse scattering (Uyeda & Nonoyama, 1968).

The multiple-scattering effects make the quantitative interpretation of diffuse scattering more difficult and complicate the extraction of particular components, *e.g.* disorder scattering. Much of the multiple scattering involves inelastic scattering processes. However, electrons that have lost energy of the order of 1 eV or more can be subtracted experimentally by use of electron energy filters (Krahl *et al.*, 1990; Krivanek *et al.*, 1992) which are commercially available. Measurement can be made also of the complete scattering function $I(\mathbf{u}, \nu)$, but such studies have been rare. Another significant improvement to quantitative measurement of diffuse electron scattering is offered by new recording devices: slow-scan charge-couple-device cameras (Krivanek & Mooney, 1993) and imaging plates (Mori *et al.*, 1990).

There are some advantages in the use of electrons which make it uniquely valuable for particular applications.

(1) Diffuse-scattering distributions can be recorded from very small specimen regions, a few nm in diameter and a few nm thick. The diameter of the specimen area may be varied readily up to several μm .

(2) Diffraction information on defects or disorder may be correlated with high-resolution electron-microscope imaging of the same specimen area [see Section 4.3.8 in *IT C* (1999)].

(3) The electron-diffraction pattern approximates to a planar section of reciprocal space, so that complicated configurations of diffuse scattering may be readily visualized (see Fig. 4.3.1.2).

(4) Dynamical effects may be exploited to obtain information about localization of sources of the diffuse scattering within the unit cell.

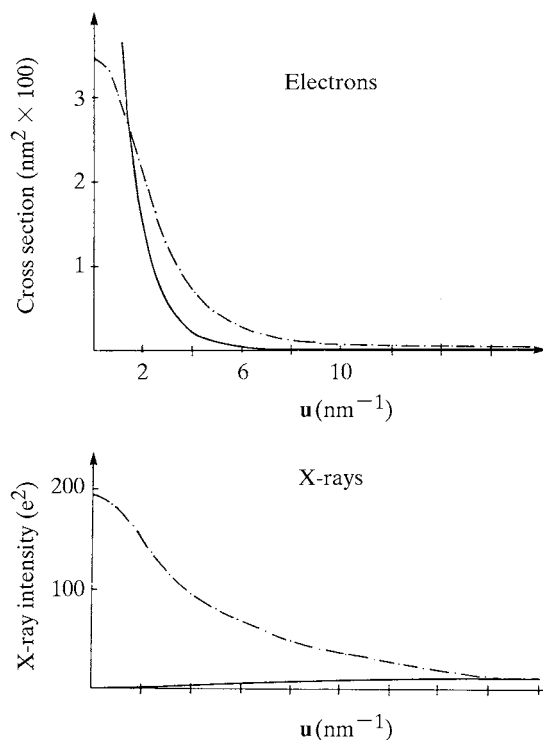


Fig. 4.3.1.1. Comparison between the kinematical inelastic scattering (full line) and elastic scattering (broken) for electrons and X-rays. Values for silicon [Freeman (1960) and *IT C* (1999)].

4. DIFFUSE SCATTERING AND RELATED TOPICS

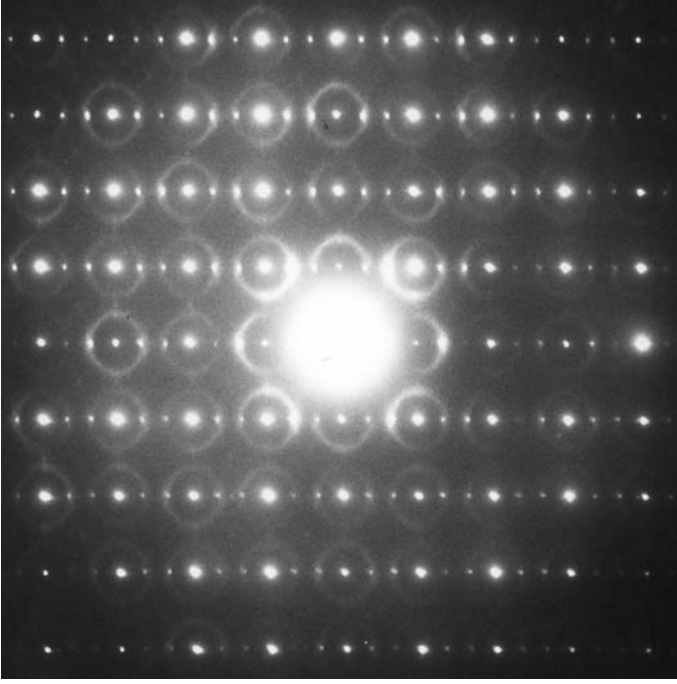


Fig. 4.3.1.2. Electron-diffraction pattern from a disordered crystal of $17\text{Nb}_2\text{O}_5.48\text{WO}_3$ close to the [001] orientation of the tetragonal tungsten-bronze-type structure (Iijima & Cowley, 1977).

These experimental and theoretical aspects of electron diffraction have influenced the ways in which it has been applied in studies of diffuse scattering.

In general, we may distinguish three different approaches to the interpretation of diffuse scattering:

(a) The crystallographic way, in which the Patterson- or correlation-function representation of the local order is emphasized, *e.g.* by use of short-range-order parameters.

(b) The physical model in terms of excitations. These are usually described in reciprocal (momentum) space: phonons, plasmons *etc.*

(c) Structure models in direct space. These must be derived by trial or by chemical considerations of bonds, coordinates *etc.*

Owing to the difficulties of separating the different components in the diffuse scattering, most work on diffuse scattering of electrons has followed one or both of the two last approaches, although Patterson-type interpretation, based upon kinematical scattering including some dynamical corrections, has also been tried.

4.3.2. Inelastic scattering

In the kinematical approximation, a general expression which includes inelastic scattering can be written in the form quoted by Van Hove (1954)

$$I(\mathbf{u}, \nu) = \frac{m^3 k}{2^2 h^6 k_o} \times W(\mathbf{u}) \sum_{\eta} P_{n_o} \sum_{j=1}^Z |\langle n_o | \exp\{2\pi i \mathbf{u} \cdot \mathbf{R}_j\} | n \rangle|^2 \times \delta\left(\nu + \frac{E_n - E_{n_o}}{h}\right) \quad (4.3.2.1)$$

for the intensity of scattering as function of energy transfer and momentum transfer from a system of Z identical particles, $\mathbf{R}_j$. Here m and h have their usual meanings; k_o and k , E_{n_o} and E_n are

wavevectors and energies before and after the scattering between object states n_o and n ; P_{n_o} are weights of the initial states; $W(\mathbf{u})$ is a form factor (squared) for the individual particle.

In equation (4.3.2.1), $\mathbf{u}$ is essentially momentum transfer. When the energy transfer is small ($\Delta E/E \ll \theta$), we can still write $|\mathbf{u}| = 2 \sin \theta / \lambda$, then the sum over final states n is readily performed and an expression of the Waller–Hartree type is obtained for the total inelastic scattering as a function of angle:

$$I_{\text{inel}}(\mathbf{u}) \propto \frac{S}{u^4},$$

where

$$S(u) = Z - \sum_{j=1}^Z |f_{jj}(u)|^2 - \sum_j \sum_{k \neq j}^Z |f_{jk}(u)|^2, \quad (4.3.2.2)$$

and where the one-electron f 's for Hartree–Fock orbitals, $f_{jk}(\mathbf{u}) = \langle j | \exp(2\pi i \mathbf{u} \cdot \mathbf{r}) | k \rangle$, have been calculated by Freeman (1959, 1960) for atoms up to $Z = 30$. The last sum is over electrons with the same spin only.

The Waller–Hartree formula may be a very good approximation for Compton scattering of X-rays, where most of the scattering occurs at high angles and multiple scattering is no problem. With electrons, it has several deficiencies. It does not take into account the electronic structure of the solid, which is most important at low values of u . It does not include the energy distribution of the scattering. It does not give a finite cross section at zero angle, if u is interpreted as an angle. In order to remedy this, we should go back to equation (4.3.1.2) and decompose $\mathbf{u}$ into two components, one tangential part which is associated with angle in the usual way and one normal component along the beam direction, u_n , which may be related to the excitation energy $\Delta E = E_n - E_{n_o}$ by the expression $u_n = \Delta E_k / 2E$. This will introduce a factor $1/(u^2 + u_n^2)$ in the intensity at small angles, often written as $1/(\theta^2 + \theta_E^2)$, with ΔE estimated from ionization energies *etc.* (Strictly speaking, ΔE is not a constant, not even for scattering from one shell. It is a weighted average which will vary with u .)

Calculations beyond this simple adjustment of the Waller–Hartree-type expression are few. Plasmon scattering has been treated on the basis of a nearly free electron model by Ferrel (1957):

$$\frac{d^2 \sigma}{d(\Delta E) d\Omega} = (1/\pi^2 a_H m v^2 N) (-\text{Im}\{1/\varepsilon\}) / (\theta^2 + \theta_E^2), \quad (4.3.2.3)$$

where m , v are relativistic mass and velocity of the incident electron, N is the density of the valence electrons and $\varepsilon(\Delta E, \theta)$ their dielectric constant. Upon integration over ΔE :

$$\frac{d\sigma}{d\Omega} = \frac{E_p}{2\pi a_H m v N} [1/(\theta^2 + \theta_E^2) G(\theta, \theta_c)], \quad (4.3.2.4)$$

where $G(\theta, \theta_c)$ takes account of the cut-off angle θ_c . Inner-shell excitations have been studied because of their importance to spectroscopy. The most realistic calculations may be those of Leapman *et al.* (1980) where one-electron wavefunctions are determined for the excited states in order to obtain ‘generalized oscillator strengths’ which may then be used to modify equation (4.3.1.2).

At high energies and high momentum transfer, the scattering will approach that of free electrons, *i.e.* a maximum at the so-called Bethe ridge, $E = h^2 u^2 / 2m$.

A complete and detailed picture of inelastic scattering of electrons as a function of energy and angle (or scattering variable) is lacking, and may possibly be the least known area of diffraction by solids. It is further complicated by the dynamical scattering, which involves the incident and diffracted electrons and also the ejected atomic electron (see *e.g.* Maslen & Rossouw, 1984).

4.3. DIFFUSE SCATTERING IN ELECTRON DIFFRACTION

4.3.3. Kinematical and pseudo-kinematical scattering

Kinematical expressions for TDS or defect and disorder scattering according to equation (4.3.1.3) can be obtained by inserting the appropriate atomic scattering factors in place of the X-ray scattering factors in Chapter 4.1. The complications introduced by dynamical diffraction are considerable (see Section 4.3.4). In the most general case, a complete specification of the disordered structure may be needed. However, for thin specimens, approximate treatments of the deviations from kinematical scattering may lead to relatively simple forms. Two such cases are treated in this section, both relying on the small-angle nature of electron scattering. The first is based upon the phase-object approximation, which applies to small angles and thin specimens.

The amplitude at the exit surface of a specimen can always be written as a sum of a periodic and a nonperiodic part, and may in analogy with the kinematical case [equation (4.3.1.1)] be written

$$\psi(\mathbf{r}) = \bar{\psi}(\mathbf{r}) + \Delta\psi(\mathbf{r}), \quad (4.3.3.1)$$

where $\mathbf{r}$ is a vector in two dimensions. The intensities can be separated in the same way [cf. equation (4.3.1.3)].

When the phase-object approximation applies (Chapter 2.1)

$$\begin{aligned} \psi(\mathbf{r}) &= \exp\{-i\sigma\varphi(\mathbf{r})\} \\ &= \exp\{-i\sigma\bar{\varphi}(\mathbf{r})\}[1 - i\sigma\Delta\varphi(\mathbf{r}) - \dots]. \end{aligned} \quad (4.3.3.2)$$

Then the Bragg reflections are given by Fourier transform of the periodic part, *viz*:

$$\langle \exp\{-i\sigma\varphi(\mathbf{r})\} \rangle = \exp\{-i\sigma\bar{\varphi}(\mathbf{r})\} \exp\left\{-\frac{1}{2}\sigma^2 \langle \Delta\varphi^2(\mathbf{r}) \rangle\right\}; \quad (4.3.3.3)$$

note that an absorption function is introduced.

The diffuse scattering derives from

$$-i\sigma\Delta\varphi(\mathbf{r}) \exp\{-i\sigma\bar{\varphi}(\mathbf{r})\}, \quad (4.3.3.4)$$

so that

$$I_d(\mathbf{u}) = \sigma^2 |\Delta\Phi(\mathbf{u}) * \Phi_{av}(\mathbf{u})|^2. \quad (4.3.3.5)$$

Thus, the kinematical diffuse-scattering amplitude is convoluted with the amplitude function for the average structure, *i.e.* the set of sharp Bragg beams. When the direct beam, $\Phi_{av}(0)$, is relatively strong, the kinematical diffuse scattering will be modified to only a limited extent by convolution with the Bragg reflections. To the extent that the diffuse scattering is periodic in reciprocal space, the effect will be to modify the intensity by a slowly varying function. Thus the shapes of local diffuse maxima will not be greatly affected.

The electron-microscope image contrast derived from the diffuse scattering will be obtained by inserting equation (4.3.3.4) in the appropriate intensity expressions of Section 4.3.8 of *IT C* (1999).

Another approach may be used for extended crystal defects in thin films, *e.g.* faults normal or near-normal to the film surface. Often, an average periodic structure may not readily be defined, as in the case of a set of incommensurate stacking faults. Kinematically, the projection of the structure in the simplest case may be described by convoluting the projection of a unit-cell structure with a nonperiodic set of delta functions which constitute a distribution function:

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) * \sum_n \delta(\mathbf{r} - \mathbf{r}_n) = \varphi_0(\mathbf{r}) * d(\mathbf{r}). \quad (4.3.3.6)$$

Then the diffraction-pattern intensity is

$$I(\mathbf{u}) = |\Phi_0(\mathbf{u})|^2 |D(\mathbf{u})|^2. \quad (4.3.3.7)$$

Here, $\Phi_0(\mathbf{u})$ is the scattering amplitude of the unit whereas the function $|D(\mathbf{u})|^2$, where $D(\mathbf{u}) = \mathcal{F}\{d(\mathbf{r})\}$, gives the configuration

of spots, streaks or other diffraction maxima corresponding to the faulted structure (see *e.g.* Marks, 1985).

In the projection (column) approximation to dynamical scattering, the wavefunction at the exit surface may be given by an expression identical to (4.3.3.6), but with a wavefunction, $\psi_0(\mathbf{r})$, for the unit in place of the projected potential, $\varphi_0(\mathbf{r})$.

An intensity expression of the same form as (4.3.3.7) then applies, with a dynamical scattering amplitude Ψ_0 for the scattering unit substituted for the kinematical amplitude Φ_0 .

$$I(\mathbf{u}) = |\Psi_0(\mathbf{u})|^2 |D(\mathbf{u})|^2, \quad (4.3.3.8)$$

which in the simplest case describes a diffraction pattern with the same features as in the kinematical case. Note that $\Psi_0(\mathbf{u})$ may have different symmetries when the incident beam is tilted away from a zone axis, leading to diffuse streaks *etc.* appearing also in positions where the kinematical diffuse scattering is zero. More complicated cases have been considered by Cowley (1976a) who applied this type of analysis to the case of nonperiodic faulting in magnesium fluorogermanate (Cowley, 1976b).

4.3.4. Dynamical scattering: Bragg scattering effects

The distribution of diffuse scattering is modified by higher-order terms in essentially two ways: Bragg scattering of the incident and diffuse beams or multiple diffuse scattering, or by a combination.

Theoretical treatment of the Bragg scattering effects in diffuse scattering has been given by many authors, starting with Kainuma's (1955) work on Kikuchi-line contrast (Howie, 1963; Fujimoto & Kainuma, 1963; Gjønnes, 1966; Rez *et al.*, 1977; Maslen & Rossouw, 1984; Wang, 1995; Allen *et al.*, 1997). Mathematical formalism may vary but the physical pictures and results are essentially the same. They may be discussed with reference to a Born-series expansion, *i.e.* by introducing the potential φ in the integral equation, as a sum of a periodic and a nonperiodic part [cf. equation (4.3.1.1)] and arranging the terms by orders of $\Delta\varphi$.

$$\begin{aligned} \psi &= \psi_0 + G\varphi\psi \\ &= [1 + G\varphi + (G\varphi)^2 + \dots]\psi_0 \\ &= [1 + G\bar{\varphi} + (G\bar{\varphi})^2 + \dots]\psi_0 \\ &\quad + [1 + G\bar{\varphi} + (G\bar{\varphi})^2 + \dots] \\ &\quad \times G(\Delta\varphi)[1 + G\bar{\varphi} + (G\bar{\varphi})^2 + \dots]\psi_0 \\ &\quad + \text{higher-order terms.} \end{aligned} \quad (4.3.4.1)$$

Some of the higher-order terms contributing to the Bragg scattering can be included by adding the essentially imaginary term $\langle \Delta\varphi G(\Delta\varphi) \rangle$ to the static potential $\bar{\varphi}$.

Theoretical treatments have mostly been limited to the first-order diffuse scattering. With the usual approximation to forward scattering, the expression for the amplitude of diffuse scattering in a direction $\mathbf{k}_0 + \mathbf{u} + \mathbf{g}$ can be written as

$$\begin{aligned} \psi(\mathbf{u} + \mathbf{g}) &= \sum_g \sum_f \int_0^z S_{hg}(\mathbf{k}_0 + \mathbf{u}, z - z_1) \\ &\quad \times \Delta\Phi(\mathbf{u} + \mathbf{g} - \mathbf{f}) S_{f0}(\mathbf{k}_0, z_1) dz_1 \end{aligned} \quad (4.3.4.2)$$

and read (from right to left): S_{f0} , Bragg scattering of the incident beam above the level z_1 ; $\Delta\Phi$, diffuse scattering within a thin layer dz_1 through the Fourier components $\Delta\Phi$ of the nonperiodic potential $\Delta\Phi$; S_{hg} , Bragg scattering between diffuse beams in the lower part of the crystal. It is commonly assumed that diffuse scattering at different levels can be treated as independent (Gjønnes, 1966), then the intensity expression becomes

4. DIFFUSE SCATTERING AND RELATED TOPICS

$$I(\mathbf{u} + \mathbf{g}) = \sum_h \sum_{h'} \sum_f \sum_{f'} \int_0^z S_{gh}(2) S_{gh'}^*(2) \times \langle \Delta\Phi(\mathbf{u} + \mathbf{h} - \mathbf{f}) \Delta\Phi^*(\mathbf{u} + \mathbf{h}' - \mathbf{f}') \rangle \times S_{f0}(1) S_{f'0}^*(1) dz_1, \quad (4.3.4.3)$$

where (1) and (2) refer to the regions above and below the diffuse-scattering layer. This expression can be manipulated further, *e.g.* by introducing Bloch-wave expansion of the scattering matrices, *viz*

$$I(\mathbf{u} + \mathbf{g}) = \sum_{hh'} \sum_{ff'} \sum_{jj'} C_g^j(2) C_g^{j*}(2) C_h^{j'}(2) C_h^{j'*}(2) \times \frac{\exp[i(\gamma^i - \gamma^{j'})z] - \exp[i(\gamma^j - \gamma^{j'})z]}{\gamma^i - \gamma^{j'} - \gamma^j + \gamma^{j'}} \times \langle f(\mathbf{u} + \mathbf{h} - \mathbf{f}) f^*(\mathbf{u} + \mathbf{h}' - \mathbf{f}') \rangle \times C_f^{i*}(1) C_{f'}^{j'}(1) C_0^i(1) C_0^{i*}(1), \quad (4.3.4.4)$$

which may be interpreted as scattering by $\Delta\varphi$ between Bloch waves belonging to the same branch (intraband scattering) or different branches (interband scattering). Another alternative is to evaluate the scattering matrices by multislice calculations (Section 4.3.5).

Expressions such as (4.3.4.2) contain a large number of terms. Unless very detailed calculations relating to a precisely defined model are to be carried out, attention should be focused on the most important terms.

In Kikuchi-line contrast, the scattering in the upper part of the crystal is usually not considered and frequently the angular variation of the $\Phi(\mathbf{u})$ is also neglected. In diffraction contrast from small-angle inelastic scattering, it may be sufficient to consider the intraband terms [$i = i'$, $j = j'$ in (4.3.4.3)].

In studies of diffuse-scattering distribution, the factor $\langle \Phi(\mathbf{u} + \mathbf{h}) \Phi(\mathbf{u} + \mathbf{h}') \rangle$ will produce two types of terms: Those with $\mathbf{h} = \mathbf{h}'$ result only in a redistribution of intensity between corresponding points in the Brillouin zones, with the same total intensity. Those with $\mathbf{h} \neq \mathbf{h}'$ lead to enhancement or reduction of the total diffuse intensity and hence absorption from the Bragg beam and enhanced/reduced intensity of secondary radiation, *i.e.* anomalous absorption and channelling effects. They arise through interference between different Fourier components of the diffuse scattering and carry information about position of the sources of diffuse scattering, referred to the projected unit cell. This is exploited in channelling experiments, where beam direction is used to determine atom reaction (Taftø & Spence, 1982; Taftø & Lehmpfuhl, 1982).

Gjønnes & Høier (1971) expressed this information in terms of the Fourier transform R of the generalized or Kikuchi-line form factor;

$$\langle \Delta\Phi(\mathbf{u}) \Delta\Phi^*(\mathbf{u} + \mathbf{h}) \rangle \mathbf{u}^2(\mathbf{u} + \mathbf{h})^2 = Q(\mathbf{u} + \mathbf{h}) = \mathcal{F}\{R(\mathbf{r}, \mathbf{g})\} \quad (4.3.4.5)$$

includes information both about correlations between sources of diffuse scattering and about their position in the projected unit cell. It is seen that $Q(\mathbf{u}, 0)$ represents the kinematical intensity, hence $\int R(\mathbf{r}, \mathbf{g}) d\mathbf{g}$ is the Patterson function. The integral of $Q(\mathbf{u}, \mathbf{h})$ in the plane gives the anomalous absorption (Yoshioka, 1957) which is related to the distribution $R(\mathbf{r}, 0)$ of scattering centres across the unit cell.

The scattering factor $\langle \Delta\Phi(\mathbf{u}) \Delta\Phi^*(\mathbf{u} - \mathbf{h}) \rangle$ can be calculated for different modes. For one-electron excitations as an extension of the Waller-Hartree expression (Gjønnes, 1962; Whelan, 1965):

$$\langle \Delta\Phi(\mathbf{u}) \Delta\Phi^*(\mathbf{u} - \mathbf{h}) \rangle = \sum_i \frac{f_{ii}(\mathbf{h}) - f_{ii}(\mathbf{u}) f_{ii}(|\mathbf{h} - \mathbf{u}|)}{u^2(\mathbf{h} - \mathbf{u})^2} - \sum_i \sum_{i \neq j} \frac{f_{ij}(\mathbf{u}) f_{ij}(|\mathbf{h} - \mathbf{u}|)}{u^2(\mathbf{h} - \mathbf{u})^2}, \quad (4.3.4.6)$$

where f_{ij} are the one-electron amplitudes (Freeman, 1959).

A similar expression for scattering by phonons is obtained in terms of the scattering factors $G_j(\mathbf{u}, \mathbf{g})$ for the branch j , wavevector $\mathbf{g}$ and a polarization vector $\mathbf{l}_{j,q}$ (see Chapter 4.1):

$$\langle \Delta\Phi(\mathbf{u}) \Delta\Phi^*(\mathbf{u} - \mathbf{h}) \rangle = G_j(\mathbf{u}, \mathbf{q}) G_j^*(\mathbf{u} - \mathbf{h}, \mathbf{q}), \quad (4.3.4.7)$$

independent phonons being assumed.

For scattering from substitutional order in a binary alloy with ordering on one site only, we obtain simply

$$\Delta\Phi(\mathbf{u}) \Delta\Phi^*(\mathbf{u} - \mathbf{h}) = |\Delta\varphi(\mathbf{u})|^2 \frac{f_A(|\mathbf{u} - \mathbf{h}|) - f_B(|\mathbf{u} - \mathbf{h}|)}{f_A(\mathbf{u}) - f_B(\mathbf{u})}, \quad (4.3.4.8)$$

where $f_{A,B}$ are atomic scattering factors. It is seen that $Q(\mathbf{u})$ then does not contain any new information; the location of the site involved in the ordering is known.

When several sites are involved in the ordering, the dynamical scattering factor becomes less trivial, since scattering factors for the different ordering parameters (for different sites) will include a factor $\exp(2\pi i \mathbf{r}_m \cdot \mathbf{h})$ (see Andersson *et al.*, 1974).

From the above expressions, it is found that the Bragg scattering will affect diffuse scattering from different sources differently: Diffuse scattering from substitutional order will usually be enhanced at low and intermediate angles, whereas scattering from thermal and electronic fluctuations will be reduced at low angles and enhanced at higher angles. This may be used to study substitutional order and displacement order (size effect) separately (Andersson, 1979).

The use of such expressions for quantitative or semiquantitative interpretation raises several problems. The Bragg scattering effects occur in all diffuse components, in particular the inelastic scattering, which thus may no longer be represented by a smooth, monotonic background. It is best to eliminate this experimentally. When this cannot be done, the experiment should be arranged so as to minimize Kikuchi-line excess/deficient terms, by aligning the incident beam along a not too dense zone. In this way, one may optimize the diffuse-scattering information and minimize the dynamical corrections, which then are used partly as guides to conditions, partly as refinement in calculations.

The multiple scattering of the background remains as the most serious problem. Theoretical expressions for multiple scattering in the absence of Bragg scattering have been available for some time (Moliere, 1948), as a sum of convolution integrals

$$I(\mathbf{u}) = [(\mu t) I_1(\mathbf{u}) + (1/2)(\mu t)^2 I_2(\mathbf{u}) + \dots] \exp(-\mu t), \quad (4.3.4.9)$$

where $I_2(\mathbf{u}) = I_1(\mathbf{u}) * I_1(\mathbf{u}) \dots$ etc., and $I_1(\mathbf{u})$ is normalized.

A complete description of multiple scattering in the presence of Bragg scattering should include Bragg scattering between diffuse scattering at all levels $z_1, z_2, \dots$ etc. This quickly becomes unwieldy. Fortunately, the experimental patterns seem to indicate that this is not necessary: The Kikuchi-line contrast does not appear to be very sensitive to the exact Bragg condition of the incident beam. Høier (1973) therefore introduced Bragg scattering only in the last part of the crystal, *i.e.* between the level z_n and the final thickness z for n -times scattering. He thus obtained the formula:

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$$I(\mathbf{u} + \mathbf{h}) = \sum_j |C_h^j|^2 \left\{ A_1^j \sum_{g \neq g'} \sum F_1(\mathbf{u}, \mathbf{g}, \mathbf{g}') C_g^j C_{g'}^{j*} + \sum_n \sum_g A_{ng}^j F_n(\mathbf{u}, \mathbf{g}) |C_g^j|^2 \right\}, \quad (4.3.4.10)$$

where F_n are normalized scattering factors for n th-order multiple diffuse scattering and A_n^j are multiple-scattering coefficients which include absorption.

When the thickness is increased, the variation of $F_n(\mathbf{u}, \mathbf{g})$ with angle becomes slower, and an expression for intensity of the channelling pattern is obtained (Gjønnes & Taftø, 1976):

$$I(\mathbf{u} + \mathbf{h}) = \sum_j \sum_g \sum_n |C_h^j|^2 |C_g^j|^2 A_n^j \\ = \sum_j |C_h^j|^2 \sum_n A_n^j \rightarrow |C_h^j|^2 / \mu^j(\mathbf{u}). \quad (4.3.4.11)$$

Another approach is the use of a modified diffusion equation (Ohtsuki *et al.*, 1976).

These expressions seem to reproduce the development of the general background with thickness over a wide range of thicknesses. It may thus appear that the contribution to the diffuse background from known sources can be treated adequately – and that such a procedure must be included together with adequate filtering of the inelastic component in order to improve the quantitative interpretation of diffuse scattering.

4.3.5. Multislice calculations for diffraction and imaging

The description of dynamical diffraction in terms of the progression of a wave through successive thin slices of a crystal (Chapter 5.2) forms the basis for the multislice method for the calculation of electron-diffraction patterns and electron-microscope images [see Section 4.3.6.1 in *IT C* (1999)]. This method can be applied directly to the calculations of diffuse scattering in electron diffraction due to thermal motion and positional disorder and for calculating the images of defects in crystals.

It is essentially an amplitude calculation based on the formulation of equation (4.3.4.1) [or (4.3.4.2)] for first-order diffuse scattering. The Bragg scattering in the first part of the crystal is calculated using a standard multislice method for the set of beams $\mathbf{h}$. In the n th slice of the crystal, a diffuse-scattering amplitude $\Psi_d(\mathbf{u})$ is convoluted with the incident set of Bragg beams. For each $\mathbf{u}$, propagation of the set of beams $\mathbf{u} + \mathbf{h}$ is then calculated through the remaining slices of the crystal. The intensities for the exit wave at the set of points $\mathbf{u} + \mathbf{h}$ are then calculated by adding either amplitudes or intensities. Amplitudes are added if there is correlation between the defects in successive slices. Intensities are added if there are no such correlations. The process is repeated for all $\mathbf{u}$ values to obtain a complete mapping of the diffuse scattering.

Calculations have been made in this way, for example, for short-range order in alloys (Fisher, 1969) and also for TDS on the assumption of both correlated and uncorrelated atomic motions (Doyle, 1969). The effects of the correlations were shown to be small.

This computing method is not practical for electron-microscope images in which individual defects are to be imaged. The perturbations of the exit wavefunction due to individual defects (vacancies, replaced atoms, displaced atoms) or small groups of defects may then be calculated with arbitrary accuracy by use of the 'periodic continuation' form of the multislice computer programs in which an artificial, large, superlattice unit cell is assumed [Section

4.3.6.1 in *IT C* (1999)]. The corresponding images and micro-diffraction patterns from the individual defects or clusters may then be calculated (Fields & Cowley, 1978). A more recent discussion of the image calculations, particularly in relation to thermal diffuse scattering, is given by Cowley (1988).

In order to calculate the diffuse-scattering distributions from disordered systems or from a crystal with atoms in thermal motion by the multislice method with periodic continuation, it would be necessary to calculate for a number of different defect configurations sufficiently large to provide an adequate representation of the statistics of the disordered system. However, it has been shown by Cowley & Fields (1979) that, if the single-diffuse-scattering approximation is made, the perturbations of the exit wave due to individual defects are characteristic of the defect type and of the slice number and may be added, so that a considerable simplification of the computing process is possible. Methods for calculating diffuse scattering in electron-diffraction patterns using the multislice approach are described by Tanaka & Cowley (1987) and Cowley (1989). Loane *et al.* (1991) introduced the concept of 'frozen phonons' for multislice calculations of thermal scattering.

4.3.6. Qualitative interpretation of diffuse scattering of electrons

Quantitative interpretation of the intensity of diffuse scattering by calculation of *e.g.* short-range-order parameters has been the exception. Most studies have been directed to qualitative features and their variation with composition, treatment *etc.* Many features in the scattering which pass unrecognized in extensive X-ray or neutron investigations will be observed readily with electrons, frequently inviting other ways of interpretation.

Most such studies have been concerned with substitutional disorder, but the extensive investigations of thermal streaks by Honjo and co-workers should be mentioned (Honjo *et al.*, 1964). Diffuse spots and streaks from disorder have been observed from a wide range of substances. The most frequent may be streaks due to planar faults, one of the most common objects studied by electron microscopy. Diffraction patterns are usually sufficient to determine the orientation and the fault vector; the positions and distribution of faults are more easily seen by dark-field microscopy, whereas the detailed atomic arrangement is best studied by high-resolution imaging of the structure [Section 4.3.8 in *IT C* (1999)].

This combination of diffraction and different imaging techniques cannot be applied in the same way to the study of the essentially three-dimensional substitutional local order. Considerable effort has therefore been made to interpret the details of diffuse scattering, leaving the determination of the short-range-order (SRO) parameters usually to X-ray or neutron studies.

Frequently, characteristic shapes or splitting of the diffuse spots from *e.g.* binary alloys are observed. They reflect order extending over many atomic distances, and have been assumed to arise from forces other than the near-neighbour pair forces invoked in the theory of local order. A relationship between the diffuse-scattering distribution and the Fourier transform of the effective atom-pair-interaction potential is given by the ordering theory of Clapp & Moss (1968). An interpretation in terms of long-range forces carried by the conduction electrons was proposed by Krivoglaz (1969). Extensive studies of alloy systems (Ohshima & Watanabe, 1973) show that the separations, m , observed in split diffuse spots from many alloys follow the predicted variation with the electron/atom ratio e/a :

$$m = \left[\frac{12}{\pi} (e/a) \right]^{1/3} t - \sqrt{2},$$

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where m is measured along the $[110]$ direction in units of $2a^*$ and t is a truncation factor for the Fermi surface.

A similarity between the location of diffuse maxima and the shape of the Fermi surface has been noted also for other structures, notably some defect rock-salt-type structures. Although this may offer a clue to the forces involved in the ordering, it entails no description of the local structure. Several attempts have been made to formulate principles for building the disordered structure, from small ordered domains embedded in less ordered regions (Hashimoto, 1974), by a network of antiphase boundaries, or by building the structure from clusters with the average composition and coordination (De Ridder *et al.*, 1976). Evidence for such models may be sought by computer simulations, in the details of the SRO scattering as seen in electron diffraction, or in images.

The cluster model is most directly tied to the location of diffuse scattering, noting that a relation between order parameters derived from clusters consistent with the ordered state can be used to predict the position of diffuse scattering in the form of surfaces in reciprocal space, *e.g.* the relation $\cos h + \cos k + \cos l = 0$ for ordering of octahedral clusters in the rock-salt-type structure (Sauvage & Parthé, 1974).

Some of the models imply local fluctuations in order which may be observable either by diffraction from very small regions or by imaging. Microdiffraction studies (Tanaka & Cowley, 1985) do indeed show that spots from 1–1.5 nm regions in disordered LiFeO_2 appear on the locus of diffuse maxima observed in diffraction from larger areas.

Imaging of local variations in the SRO structure has been pursued with different techniques (De Ridder *et al.*, 1976; Tanaka & Cowley, 1985; De Meulenaere *et al.*, 1998), *viz.*: dark field using diffuse spots only; bright field with the central spot *plus* diffuse spots; lattice image. With domains of about 3 nm or more, high-resolution images seem to give clear indication of their presence and form. For smaller ordered regions, the interpretation becomes increasingly complex: Since the domains will then usually not extend through the thickness of the foil, they cannot be imaged separately. Since image-contrast calculations essentially demand complete specification of the local structure, a model beyond the statistical description must be constructed in order to be compared with observations. On the other hand, these models of the local structure should be consistent with the statistics derived from diffraction patterns collected from a larger volume.

4.4. Scattering from mesomorphic structures

BY P. S. PERSHAN

4.4.1. Introduction

The term mesomorphic is derived from the prefix ‘meso-’, which is defined in the dictionary as ‘a word element meaning middle’, and the term ‘-morphic’, which is defined as ‘an adjective termination corresponding to morph or form’. Thus, mesomorphic order implies some ‘form’, or order, that is ‘in the middle’, or intermediate between that of liquids and crystals. The name liquid crystalline was coined by researchers who found it to be more descriptive, and the two are used synonymously. It follows that a mesomorphic, or liquid-crystalline, phase must have more symmetry than any one of the 230 space groups that characterize crystals.

A major source of confusion in the early liquid-crystal literature was concerned with the fact that many of the molecules that form liquid crystals also form true three-dimensional crystals with diffraction patterns that are only subtly different from those of other liquid-crystalline phases. Since most of the original mesomorphic phase identifications were performed using a ‘miscibility’ procedure, which depends on optically observed changes in textures accompanying variation in the sample’s chemical composition, it is not surprising that some three-dimensional crystalline phases were mistakenly identified as mesomorphic. Phases were identified as being either the same as, or different from, phases that were previously observed (Liebert, 1978; Gray & Goodby, 1984), and although many of the workers were very clever in deducing the microscopic structure responsible for the microscopic textures, the phases were labelled in the order of discovery as smectic-A, smectic-B *etc.* without any attempt to develop a systematic nomenclature that would reflect the underlying order. Although different groups did not always assign the same letters to the same phases, the problem is now resolved and the assignments used in this article are commonly accepted (Gray & Goodby, 1984).

Fig. 4.4.1.1 illustrates the way in which increasing order can be assigned to the series of mesomorphic phases in three dimensions listed in Table 4.4.1.1. Although the phases in this series are the most thoroughly documented mesomorphic phases, there are others not included in the table which we will discuss below.

The progression from the completely symmetric isotropic liquid through the mesomorphic phases into the crystalline phases can be described in terms of three separate types of order. The first, or the molecular orientational order, describes the fact that the molecules have some preferential orientation analogous to the spin orientational order of ferromagnetic materials. In the present case, the molecular quantity that is oriented is a symmetric second-rank tensor, like the moment of inertia or the electric polarizability, rather than a magnetic moment. This is the only type of long-range order in the nematic phase and as a consequence its physical properties are those of an anisotropic fluid; this is the origin of the name liquid crystal. Fig. 4.4.1.2(a) is a schematic illustration of the nematic order if it is assumed that the molecules can be represented by oblong ellipses. The average orientation of the ellipses is aligned; however, there is no long-range order in the relative positions of the ellipses. Nematic phases are also observed for disc-shaped molecules and for clusters of molecules that form micelles. These all share the common properties of being optically anisotropic and fluid-like, without any long-range positional order.

The second type of order is referred to as bond orientational order. Consider, for example, the fact that for dense packing of spheres on a flat surface most of the spheres will have six neighbouring spheres distributed approximately hexagonally around it. If a perfect two-dimensional triangular lattice of indefinite size were constructed of these spheres, each hexagon on the lattice would be oriented in the same way. Within the last few years, we have come to recognize that this type of order, in which the hexagons are everywhere parallel to one another, is possible even when there is no lattice. This type of order is referred to as bond orientational order, and bond orientational order in the absence of a lattice is the essential property defining the hexatic phases (Halperin & Nelson, 1978; Nelson & Halperin, 1979; Young, 1979; Birgeneau & Litster, 1978).

Table 4.4.1.1. Some of the symmetry properties of the series of three-dimensional phases described in Fig. 4.4.1.1

The terms LRO and SRO imply long-range or short-range order, respectively, and QLRO refers to ‘quasi-long-range order’ as explained in the text.

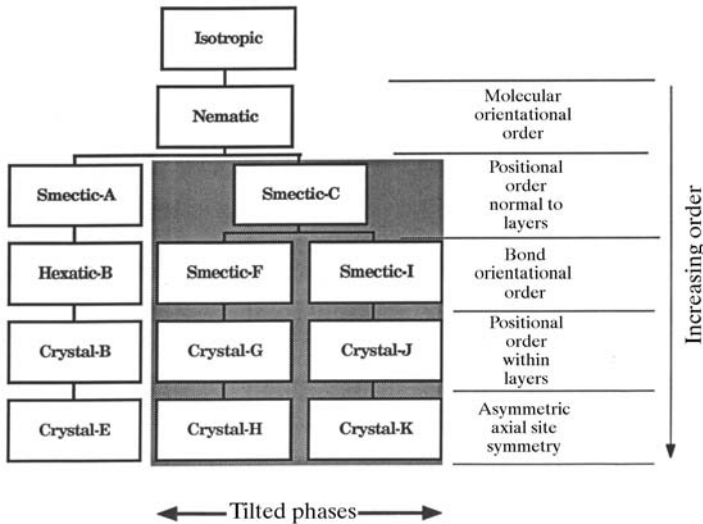


Fig. 4.4.1.1. Illustration of the progression of order throughout the sequence of mesomorphic phases that are based on ‘rod-like’ molecules. The shaded section indicates phases in which the molecules are tilted with respect to the smectic layers.

Phase	Molecular orientation order within layer	Bond orientation order	Positional order	
			Normal to layer	Within layer
Smectic-A (SmA)	SRO	SRO	SRO	SRO
Smectic-C (SmC)	LRO	LRO*	SRO	SRO
Hexatic-B	LRO*	LRO	QLRO	SRO
Smectic-F (SmF)	LRO	LRO	QLRO	SRO
Smectic-I (SmI)	LRO	LRO	QLRO	SRO
Crystalline-B (CrB)	LRO	LRO	LRO	LRO
Crystalline-G (CrG)	LRO	LRO	LRO	LRO
Crystalline-J (CrJ)	LRO	LRO	LRO	LRO
Crystalline-E (CrE)	LRO	LRO	LRO	LRO
Crystalline-H (CrH)	LRO	LRO	LRO	LRO
Crystalline-K (CrK)	LRO	LRO	LRO	LRO

* Theoretically, the existence of LRO in the molecular orientation, or tilt, implies that there must be some LRO in the bond orientation and *vice versa*.

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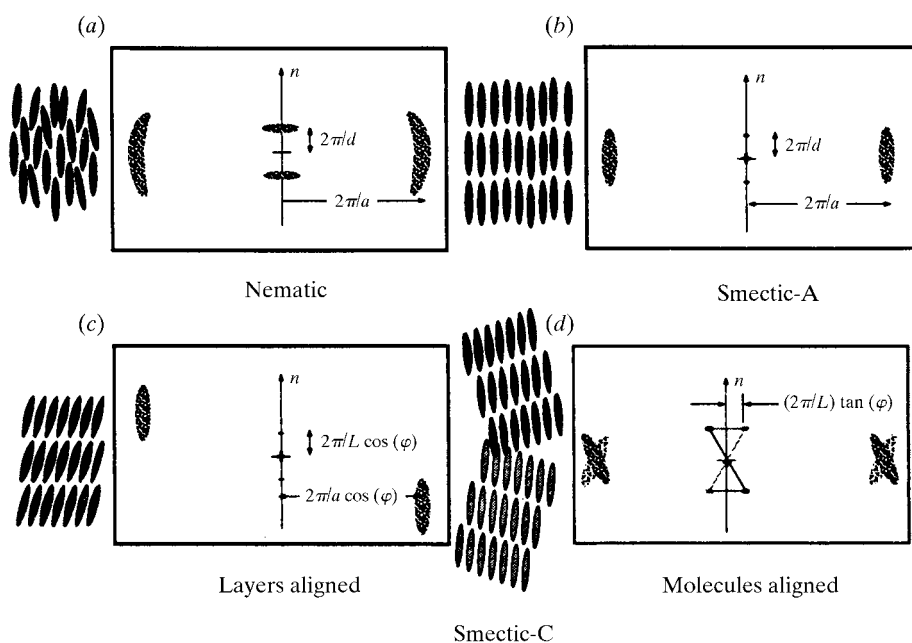


Fig. 4.4.1.2. Schematic illustration of the real-space molecular order and the scattering cross sections in reciprocal space for the: (a) nematic; (b) smectic-A; and (c), (d) smectic-C phases. The scattering cross sections are enclosed in the boxes. Part (c) indicates the smectic-C phase for an oriented monodomain and (d) indicates a polydomain smectic-C structure in which the molecular axes are aligned.

The third type of order is the positional order of an indefinite lattice of the type that defines the 230 space groups of conventional crystals. In view of the fact that some of the mesomorphic phases have a layered structure, it is convenient to separate the positional order into the positional order along the layer normal and perpendicular to it, or within the layers.

Two of the symmetries listed in Tables 4.4.1.1 and 4.4.1.2 are short-range order (SRO), implying that the order is only correlated over a finite distance such as for a simple liquid, and long-range order (LRO) as in either the spin orientation of a ferromagnet or the positional order of a three-dimensional crystal. The third type of symmetry, 'quasi-long-range order' (QLRO), will be explained below. In any case, the progressive increase in symmetry from the isotropic liquid to the crystalline phases for this series of

mesomorphic phases is illustrated in Fig. 4.4.1.1. One objective of this chapter is to describe the reciprocal-space structure of the phases listed in the tables and the phase transitions between them.

Finally, in most of the crystalline phases that we wish to discuss, the molecules have considerable amounts of rotational disorder. For example, one series of molecules that form mesomorphic phases consists of long thin molecules which might be described as 'blade shaped'. Although the cross section of these molecules is quite anisotropic, the site symmetry of the molecule is often symmetric, as though the molecule is rotating freely about its long axis. On cooling, many of the mesomorphic systems undergo transitions to the phases, listed at the bottom of Fig. 4.4.1.1, for which the site symmetry is anisotropic as though some of the rotational motions about the molecular axis have been frozen out. A similar type of transition, in which rotational motions are frozen out, occurs on cooling systems such as succinonitrile ($\text{NCCH}_2\text{CH}_2\text{CN}$) that form optically isotropic 'plastic crystals' (Springer, 1977).

There are two broad classes of liquid-crystalline systems, the thermotropic and the lyotropic, and, since the former are much better understood, this chapter will emphasize results on thermotropic systems (Liebert, 1978). The historical difference between these two, and also the origin of their names, is that the lyotropic are always mixtures, or solutions, of unlike molecules in which one is a normal, or non-mesogenic, liquid. Solutions of soap and water are prototypical examples of lyotropics, and their mesomorphic phases appear as a function of either concentration or temperature. In contrast, the thermotropic systems are usually formed from a single chemical component, and the mesomorphic phases appear primarily as a function of temperature changes. The molecular distinction between the two is that one of the molecules in the lyotropic solution always has a hydrophilic part, often called the 'head group', and one or more hydrophobic alkane chains called 'tails'. These molecules will often form mesomorphic phases as single-component or neat systems; however, the general belief is that in solution with either water or oil most of the phases are the result of competition between the hydrophilic and hydrophobic interactions, as well as other factors such as packing and steric constraints (Pershan, 1979; Safran & Clark, 1987). To the extent that molecules

Table 4.4.1.2. *The symmetry properties of the two-dimensional hexatic and crystalline phases*

Phase	Molecular orientation order within layer	Bond orientation order	Positional order within layer
Smectic-A (SmA)	SRO	SRO	SRO
Smectic-C (SmC)	QLRO	QLRO	SRO
Hexatic-B	QLRO	QLRO	SRO
Smectic-F (SmF)	QLRO	QLRO	SRO
Smectic-I (SmI)	QLRO	QLRO	SRO
Crystalline-B (CrB)	LRO	LRO	QLRO
Crystalline-G (CrG)	LRO	LRO	QLRO
Crystalline-J (CrJ)	LRO	LRO	QLRO
Crystalline-E (CrE)	LRO	LRO	QLRO
Crystalline-H (CrH)	LRO	LRO	QLRO
Crystalline-K (CrK)	LRO	LRO	QLRO

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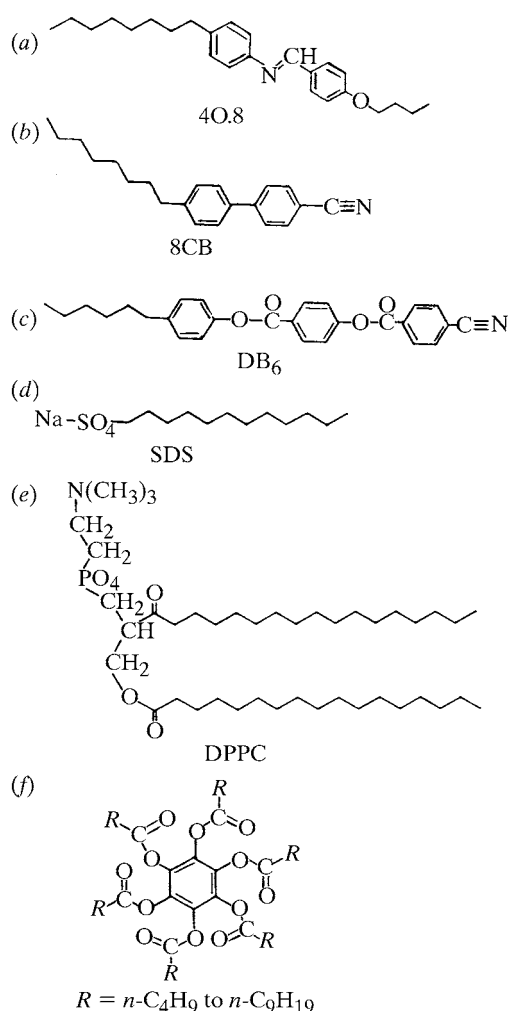


Fig. 4.4.1.3. Chemical formulae for some of the molecules that form thermotropic liquid crystals: (a) *N*-[4-(*n*-butyloxy)benzylidene]-4-*n*-octylaniline (4O.8), (b) 4'-*n*-octylbiphenyl-4-carbonitrile (8CB), (c) 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB₆); lyotropic liquid crystals: (d) sodium dodecyl sulfate, (e) 1,2-dipalmitoyl-L-phosphatidylcholine (DPPC); and a discotic liquid crystal: (f) benzenehexyl hexa-*n*-alkanoates.

that form thermotropic liquid-crystalline phases have hydrophilic and hydrophobic parts, the disparity in the affinity of these parts for either water or oil is much less and most of these molecules are relatively insoluble in water. These molecules are called thermotropic because their phase transformations are primarily studied only as a function of temperature. This is not to say that there are not numerous examples of interesting studies of the concentration dependence of phase diagrams involving mixtures of thermotropic liquid crystals.

Fig. 4.4.1.3 displays some common examples of molecules that form lyotropic and thermotropic phases. In spite of the above remarks, it is interesting to observe that different parts of typical thermotropic molecules do have some of the same features as the lyotropic molecules. For example, although the rod-like thermotropic molecules always have an alkane chain at one or both ends of a more rigid section, the chain lengths are rarely as long as those of the lyotropic molecules, and although the solubility of parts of the thermotropic molecules, when separated, are not as disparate as those of the lyotropic molecules, they are definitely different. We suspect that this may account for the subtler features of the phase transformations between the mesomorphic phases to be discussed

below. On the other hand, the inhomogeneity of the molecule is probably not important for the nematic phase.

4.4.2. The nematic phase

The nematic phase is a fluid for which the molecules have long-range orientational order. The phase as well as its molecular origin can be most simply illustrated by treating the molecules as long thin rods. The orientation of each molecule can be described by a symmetric second-rank tensor $s_{i,j} = (n_i n_j - \delta_{i,j}/3)$, where $\mathbf{n}$ is a unit vector along the axis of the rod (De Gennes, 1974). For disc-like molecules, such as that shown in Fig. 4.4.1.3(f), or for micellar nematic phases, $\mathbf{n}$ is along the principal symmetry axis of either the molecule or the micelle (Lawson & Flautt, 1967). Since physical quantities such as the molecular polarizability, or the moment of inertia, transform as symmetric second-rank tensors, either one of these could be used as specific representations of the molecular orientational order. The macroscopic order, however, is given by the statistical average $S_{i,j} = \langle s_{i,j} \rangle = S(\langle n_i \rangle \langle n_j \rangle - \delta_{i,j}/3)$, where $\langle \mathbf{n} \rangle$ is a unit vector along the macroscopic symmetry axis and S is the order parameter of the nematic phase.

The microscopic origin of the phase can be understood in terms of steric constraints that occur on filling space with highly asymmetric objects such as long rods or flat discs. Maximizing the density requires some degree of short-range orientational order, and theoretical arguments can be invoked to demonstrate long-range order. Onsager presented quantitative arguments of this type to explain the nematic order observed in concentrated solutions of the long thin rods of tobacco mosaic viruses (Onsager, 1949; Lee & Meyer, 1986), and qualitatively similar ideas explain the nematic order for the shorter thermotropic molecules (Maier & Saupe, 1958, 1959).

The existence of nematic order can also be understood in terms of a phenomenological mean-field theory (De Gennes, 1969b, 1971; Fan & Stephen, 1970). If the free-energy difference ΔF between the isotropic and nematic phases can be expressed as an analytic function of the nematic order parameter $S_{i,j}$, one can expand $\Delta F(S_{i,j})$ as a power series in which the successive terms all transform as the identity representation of the point group of the isotropic phase, i.e. as scalars. The most general form is given by:

$$\Delta F(S_{i,j}) = \frac{A}{2} \sum_{ij} S_{ij} S_{ji} + \frac{B}{3} \sum_{ijk} S_{ij} S_{jk} S_{ki} + \frac{D}{4} \left| \sum_{ij} S_{ij} S_{ji} \right|^2 + \frac{D'}{4} \sum_{ijkl} S_{ij} S_{jk} S_{kl} S_{li}. \quad (4.4.2.1)$$

The usual mean-field treatment assumes that the coefficient of the leading term is of the form $A = a(T - T^*)$, where T is the absolute temperature and T^* is the temperature at which $A = 0$. Taking a , D and $D' > 0$, one can show that for either positive or negative values of B , but for sufficiently large T , the minimum value of $\Delta F = 0$ occurs for $S_{i,j} = 0$, corresponding to the isotropic phase. For $T < T^*$, ΔF can be minimized, at some negative value, for a nonzero $S_{i,j}$ corresponding to nematic order. The details of how this is derived for a tensorial order parameter can be found in the literature (De Gennes, 1974); however, the basic idea can be understood by treating $S_{i,j}$ as a scalar. If we write

$$\Delta F = \frac{1}{2} A S^2 + \frac{1}{3} B S^3 + \frac{1}{4} D S^4 = \left\{ \frac{A}{2} - \frac{B^2}{9D} \right\} S^2 + \frac{D}{4} \left(S + \frac{2B}{3D} \right)^2 \quad (4.4.2.2)$$

and if T_{NI} is defined by the condition $A = a(T_{\text{NI}} - T^*) = 2B^2/9D$, then $\Delta F = 0$ for both $S = 0$ and $S = -2B/3D$. This value for T_{NI}

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marks the transition temperature from the isotropic phase, when $A > 2B^2/9D$ and the only minimum is at $S = 0$ with $\Delta F = 0$, to the nematic case when $A < 2B^2/9D$ and the absolute minimum with $\Delta F < 0$ is slightly shifted from $S = -2B/3D$. The symmetry properties of second-rank tensors imply that there will usually be a nonvanishing value for B , and this implies that the transition from the isotropic to nematic transition will be first order with a discontinuous jump in the nematic order parameter $S_{i,j}$. Although most nematic systems are uniaxial, biaxial nematic order is theoretically possible (Freiser, 1971; Alben, 1973; Lubensky, 1987) and it has been observed in certain lyotropic nematic liquid crystals (Neto *et al.*, 1985; Hendriks *et al.*, 1986; Yu & Saupe, 1980) and in one thermotropic system (Malthête *et al.*, 1986).

The X-ray scattering cross section of an oriented monodomain sample of the nematic phase with rod-like molecules usually exhibits a diffuse spot like that illustrated in Fig. 4.4.1.2(a), where the maximum of the cross section is along the average molecular axis $\langle \mathbf{n} \rangle$ at a value of $|\mathbf{q}| \approx 2\pi/d$, where $d \approx 20.0$ to 40.0 Å is of the order of the molecular length L . This is a precursor to the smectic-A order that develops at lower temperatures for many materials. In addition, there is a diffuse ring along the directions normal to $\langle \mathbf{n} \rangle$ at $|\mathbf{q}| \approx 2\pi/a$, where $a \approx 4.0$ Å is comparable to the average radius of the molecule. In some nematic systems, the near-neighbour correlations favour antiparallel alignment and molecular centres tend to form pairs such that the peak of the scattering cross section can actually have values anywhere in the range from $2\pi/L$ to $2\pi/2L$. There are also other cases where there are two diffuse peaks, corresponding to both $|\mathbf{q}_1| \approx 2\pi/L$ and $|\mathbf{q}_2| \approx |\mathbf{q}_1|/2$ which are precursors of a richer smectic-A morphology (Prost & Barois, 1983; Prost, 1984; Sigaud *et al.*, 1979; Wang & Lubensky, 1984; Hardouin *et al.*, 1983; Chan, Pershan *et al.*, 1985). In some cases, $|\mathbf{q}_2| \approx \frac{1}{2}|\mathbf{q}_1|$ and competition between the order parameters at incommensurate wavevectors gives rise to modulated phases. For the moment, we will restrict the discussion to those systems for which the order parameter is characterized by a single wavevector.

On cooling, many nematic systems undergo a second-order phase transition to a smectic-A phase and as the temperature approaches the nematic to smectic-A transition the widths of these diffuse peaks become infinitesimally small. De Gennes (1972) demonstrated that this phenomenon could be understood by analogy with the transitions from either normal fluidity to superfluidity in liquid helium or normal conductivity to superconductivity in metals. Since the electron density of the smectic-A phase is (quasi-)periodic in one dimension, he represented it by the form:

$$\rho(\mathbf{r}) = \langle \rho \rangle + \text{Re}\{\Psi \exp[i(2\pi/d)z]\},$$

where d is the thickness of the smectic layers lying in the xy plane. The complex quantity $\psi = |\psi| \exp(i\varphi)$ is similar to the superfluid wavefunction except that in this analogy the amplitude $|\psi|$ describes the electron-density variations normal to the smectic layers, and the phase φ describes the position of the layers along the z axis. De Gennes proposed a mean-field theory for the transition in which the free-energy difference between the nematic and smectic-A phase $\Delta F(\Psi)$ was represented by

$$\Delta F(\psi) = \frac{A}{2} |\psi|^2 + \frac{D}{4} |\psi|^4 + \frac{E}{2} \left[\left\{ \frac{\partial}{\partial z} - i \left(\frac{2\pi}{d} \right) \right\} \psi \right]^2 + \left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2. \quad (4.4.2.3)$$

This mean-field theory differs from the one for the isotropic to nematic transition in that the symmetry for the latter allowed a term that was cubic in the order parameter, while no such term is allowed for the nematic to smectic-A transition. In both cases, however, the

coefficient of the leading term is taken to have the form $a(T - T^*)$. If $D > 0$, without the cubic term the free energy has only one minimum when $T > T^*$ at $|\psi| = 0$, and two equivalent minima at $|\psi| = \{a(T^* - T)/D\}^{0.5}$ for $T < T^*$. On the basis of this free energy, the nematic to smectic-A transition can be second order with a transition temperature $T_{\text{NA}} = T^*$ and an order parameter that varies as the square root of $(T_{\text{NA}} - T)$. There are conditions that we will not discuss in detail when D can be negative. In that case, the nematic to smectic-A transition will be first order (McMillan, 1972, 1973a,b,c). McMillan pointed out that, by allowing coupling between the smectic and nematic order parameters, a more general free energy can be developed in which D is negative. McMillan's prediction that for systems in which the difference $T_{\text{IN}} - T_{\text{NA}}$ is small the nematic to smectic-A transition will be first order is supported by experiment (Ocko, Birgeneau & Litster, 1986; Ocko *et al.*, 1984; Thoen *et al.*, 1984). Although the mean-field theory is not quantitatively accurate, it does explain the principal qualitative features of the nematic to smectic-A transition.

The differential scattering cross section for X-rays can be expressed in terms of the Fourier transform of the density-density correlation function $\langle \rho(\mathbf{r}) \rho(0) \rangle$. The expectation value is calculated from the thermal average of the order parameter that is obtained from the free-energy density $\Delta F(\psi)$. If one takes the transform

$$\Psi(\mathbf{Q}) \equiv \frac{1}{(2\pi)^3} \int d^3\mathbf{r} \exp[i(\mathbf{Q} \cdot \mathbf{r})] \rho(\mathbf{r}), \quad (4.4.2.4)$$

the free-energy density in reciprocal space has the form

$$\Delta F(\psi) = \frac{A}{2} |\psi|^2 + \frac{D}{4} |\psi|^4 + \frac{E}{2} \{ [Q_z - (2\pi/d)]^2 + Q_x^2 + Q_y^2 \} |\psi|^2 \quad (4.4.2.5)$$

and one can show that for $T > T_{\text{NA}}$ the cross section obtained from the above form for the free energy is

$$\frac{d\sigma}{d\Omega} \approx \frac{\sigma_0}{A + E\{[Q_z - (2\pi/d)]^2 + Q_x^2 + Q_y^2\}}, \quad (4.4.2.6)$$

where the term in $|\psi|^4$ has been neglected. The mean-field theory predicts that the peak intensity should vary as $\sigma_0/A \approx 1/(T - T_{\text{NA}})$ and that the half width of the peak in any direction should vary as $(A/E)^{1/2} \approx (T - T_{\text{NA}})^{1/2}$. The physical interpretation of the half width is that the smectic fluctuations in the nematic phase are correlated over lengths $\xi = (E/A)^{1/2} \sim (T - T_{\text{NA}})^{-1/2}$.

One of the major shortcomings of all mean-field theories is that they do not take into account the difference between the average value of the order parameter $\langle \psi \rangle$ and the instantaneous value $\psi = \langle \psi \rangle + \delta\psi$, where $\delta\psi$ represents the thermal fluctuations (Ma, 1976). The usual effect expected from theories for this type of critical phenomenon is a 'renormalization' of the various terms in the free energy such that the temperature dependence of correlation length has the form $\xi(t) \propto t^{-\nu}$, where $t \equiv (T - T^*)/T^*$, $T^* = T_{\text{NA}}$ is the second-order transition temperature, and ν is expected to have some universal value that is generally not equal to 0.5. One of the major unsolved problems of the nematic to smectic-A phase transition is that the width along the scattering vector $\mathbf{q}$ varies as $1/\xi_{\parallel} \propto t^{\nu_{\parallel}}$ with a temperature dependence different from that of the width perpendicular to $\mathbf{q}$, $1/\xi_{\perp} \propto t^{\nu_{\perp}}$; also, neither $\nu_{\parallel}$ nor $\nu_{\perp}$ have the expected universal values (Lubensky, 1983; Nelson & Toner, 1981).

The correlation lengths are measured by fitting the differential scattering cross sections to the empirical form:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{1 + (\mathbf{Q}_z - |\mathbf{q}|)^2 \xi_{\parallel}^2 + \mathbf{Q}_{\perp}^2 \xi_{\perp}^2 + c(\mathbf{Q}_{\perp}^2 \xi_{\perp}^2)^2}. \quad (4.4.2.7)$$

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Table 4.4.2.1. Summary of critical exponents from X-ray scattering studies of the nematic to smectic-A phase transition

Molecule	γ	$\nu_{\parallel}$	$\nu_{\perp}$	Reference
4O.7	1.46	0.78	0.65	(a)
8S5	1.53	0.83	0.68	(b), (g)
CBOOA	1.30	0.70	0.62	(c), (d)
4O.8	1.31	0.70	0.57	(e)
8OCB	1.32	0.71	0.58	(d), (f)
9S5	1.31	0.71	0.57	(b), (g)
8CB	1.26	0.67	0.51	(h), (i)
10S5	1.10	0.61	0.51	(b), (g)
9CB	1.10	0.57	0.39	(g), (j)

References: (a) Garland *et al.* (1983); (b) Brisbin *et al.* (1979); (c) Djurek *et al.* (1974); (d) Litster *et al.* (1979); (e) Birgeneau *et al.* (1981); (f) Kasting *et al.* (1980); (g) Ocko *et al.* (1984); (h) Thoen *et al.* (1982); (i) Davidov *et al.* (1979); (j) Thoen *et al.* (1984).

The amplitude $\sigma \propto t^{-\gamma}$, where the measured values of γ are empirically found to be very close to the measured values for the sum $\nu_{\parallel} + \nu_{\perp}$. Most of the systems that have been measured to date have values for $\nu_{\parallel} > 0.66 > \nu_{\perp}$ and $\nu_{\parallel} - \nu_{\perp} \approx 0.1$ to 0.2. Table 4.4.2.1 lists sources of the observed values for γ , $\nu_{\parallel}$ and $\nu_{\perp}$. The theoretical and experimental studies of this pretransition effect account for a sizeable fraction of all of the liquid-crystal research in the last 15 or 20 years, and as of this writing the explanation for these two different temperature dependences remains one of the major unresolved theoretical questions in equilibrium statistical physics.

It is very likely that the origin of the problem is the QLRO in the position of the smectic layers. Lubensky attempted to deal with this by introducing a gauge transformation in such a way that the thermal fluctuations of the transformed order parameter did not have the logarithmic divergence. While this approach has been informative, it has not yet yielded an agreed-upon understanding. Experimentally, the effect of the phase can be studied in systems where there are two competing order parameters with wavevectors that are at $\mathbf{q}_2$ and $\mathbf{q}_1 \approx 2\mathbf{q}_2$ (Sigaud *et al.*, 1979; Hardouin *et al.*, 1983; Prost & Barois, 1983; Wang & Lubensky, 1984; Chan, Pershan *et al.*, 1985). On cooling, mixtures of 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB₆) and *N,N'*-(1,4-phenylenedimethylene)bis(4-butylaniline) (also known as terephthal-bis-butylaniline, TBBA) first undergo a second-order transition from the nematic to a phase that is designated as smectic-A₁. The various smectic-A and smectic-C morphologies will be described in more detail in the following section; however, the smectic-A₁ phase is characterized by a single peak at $q_1 = 2\pi/d$ owing to a one-dimensional density wave with wavelength d of the order of the molecular length L . In addition, however, there are thermal fluctuations of a second-order parameter with a period of $2L$ that give rise to a diffuse peak at $q_2 = \pi/L$. On further cooling, this system undergoes a second second-order transition to a smectic-A₂ phase with QLRO at $q_2 \approx \pi/L$, with a second harmonic that is exactly at $q = 2q_2 \approx 2\pi/L$. The critical scattering on approaching this transition is similar to that of the nematic to smectic-A₁, except that the pre-existing density wave at $q_1 = 2\pi/L$ quenches the phase fluctuations of the order parameter at the subharmonic $q_2 = \pi/L$. The measured values of $\nu_{\parallel} = \nu_{\perp} \approx 0.74$ (Chan, Pershan *et al.*, 1985) agree with those expected from the appropriate theory (Huse, 1985). A mean-field theory that describes this effect is discussed in Section 4.4.3.2 below.

It is interesting to note that even those systems for which the nematic to smectic-A transition is first order show some pretransitional lengthening of the correlation lengths $\xi_{\parallel}$ and $\xi_{\perp}$. In these cases, the apparent T^* at which the correlation lengths would diverge is lower than T_{NA} and the divergence is truncated by the first-order transition (Ocko *et al.*, 1984).

4.4.3. Smectic-A and smectic-C phases

4.4.3.1. Homogeneous smectic-A and smectic-C phases

In the smectic-A and smectic-C phases, the molecules organize themselves into layers, and from a naive point of view one might describe them as forming a one-dimensional periodic lattice in which the individual layers are two-dimensional liquids. In the smectic-A phase, the average molecular axis $\langle \mathbf{n} \rangle$ is normal to the smectic layers while for the smectic-C it makes a finite angle. It follows from this that the smectic-C phase has lower symmetry than the smectic-A, and the phase transition from the smectic-A to smectic-C can be considered as the ordering of a two-component order parameter, *i.e.* the two components of the projection of the molecular axis on the smectic layers (De Gennes, 1973). Alternatively, Chen & Lubensky (1976) have developed a mean-field theory in which the transition is described by a free-energy density of the Lifshitz form. This will be described in more detail below; however, it corresponds to replacing equation (4.4.2.5) for the free energy $\Delta F(\psi)$ by an expression for which the minimum is obtained when the wavevector $\mathbf{q}$, of the order parameter $\psi \propto \exp[i\mathbf{q} \cdot \mathbf{r}]$, tilts away from the molecular axis.

The X-ray cross section for the prototypical aligned monodomain smectic-A sample is shown in Fig. 4.4.1.2(b). It consists of a single sharp spot along the molecular axis at $|\mathbf{q}|$ somewhere between $2\pi/2L$ and $2\pi/L$ that reflects the QLRO along the layer normal, and a diffuse ring in the perpendicular direction at $|\mathbf{q}| \approx 2\pi/a$ that reflects the SRO within the layer. The scattering cross section for an aligned smectic-C phase is similar to that of the smectic-A except that the molecular tilt alters the intensity distribution of the diffuse ring. This is illustrated in Fig. 4.4.1.2(c) for a monodomain sample. Fig. 4.4.1.2(d) illustrates the scattering pattern for a polydomain smectic-C sample in which the molecular axis remains fixed, but where the smectic layers are randomly distributed azimuthally around the molecular axis.

The naivety of describing these as periodic stacks of two-dimensional liquids derives from the fact that the sharp spot along the molecular axis has a distinct temperature-dependent shape indicative of QLRO that distinguishes it from the Bragg peaks due to true LRO in conventional three-dimensional crystals. Landau and Peierls discussed this effect for the case of two-dimensional crystals (Landau, 1965; Peierls, 1934) and Caillé (1972) extended the argument to the mesomorphic systems.

The usual treatment of thermal vibrations in three-dimensional crystals estimates the Debye-Waller factor by integrating the thermal expectation value for the mean-square amplitude over reciprocal space (Kittel, 1963):

$$W \simeq \frac{k_B T}{c^3} \int_0^{k_D} \frac{k^{(d-1)}}{k^2} dk, \quad (4.4.3.1)$$

where c is the sound velocity, $\omega_D \equiv ck_D$ is the Debye frequency and $d = 3$ for three-dimensional crystals. In this case, the integral converges and the only effect is to reduce the integrated intensity of the Bragg peak by a factor proportional to $\exp(-2W)$. For two-dimensional crystals $d = 2$, and the integral, of the form of dk/k , obtains a logarithmic divergence at the lower limit (Fleming *et al.*, 1980). A more precise treatment of thermal vibrations, necessitated by this divergence, is to calculate the relative phase of X-rays

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scattered from two points in the sample a distance $|\mathbf{r}|$ apart. The appropriate integral that replaces the Debye–Waller integral is

$$\langle [u(\mathbf{r}) - u(0)]^2 \rangle \simeq \frac{k_B T}{c^3} \int \sin^2(\mathbf{k} \cdot \mathbf{r}) \frac{dk}{k} d\{\cos(\mathbf{k} \cdot \mathbf{r})\} \quad (4.4.3.2)$$

and the divergence due to the lower limit is cut off by the fact that $\sin^2(\mathbf{k} \cdot \mathbf{r})$ vanishes as $k \rightarrow 0$. More complete analysis obtains $\langle [u(\mathbf{r}) - u(0)]^2 \rangle \simeq (k_B T/c^2) \ln(|\mathbf{r}|/a)$, where $a \approx$ atomic size. If this is exponentiated, as for the Debye–Waller factor, the density–density correlation function can be shown to have the form $\langle \rho(\mathbf{r})\rho(0) \rangle \simeq |\mathbf{r}/a|^{-\eta}$, where $\eta \simeq |\mathbf{q}|^2(k_B T/c^2)$ and $|\mathbf{q}| \simeq 2\pi/a$. In place of the usual periodic density–density correlation function of three-dimensional crystals, the periodic correlations of two-dimensional crystals decay as some power of the distance. This type of positional order, in which the correlations decay as some power of the distance, is the quasi-long-range order (QLRO) that appears in Tables 4.4.1.1 and 4.4.1.2. It is distinguished from true long-range order (LRO) where the correlations continue indefinitely, and short-range order (SRO) where the positional correlations decay exponentially as in either a simple fluid or a nematic liquid crystal.

The usual prediction of Bragg scattering for three-dimensional crystals is obtained from the Fourier transform of the three-dimensional density–density correlation function. Since the correlation function is made up of periodic and random parts, it follows that the scattering cross section is made up of a δ function at the Bragg condition superposed on a background of thermal diffuse scattering from the random part. In principle, these two types of scattering can be separated empirically by using a high-resolution spectrometer that integrates all of the δ -function Bragg peak, but only a small part of the thermal diffuse scattering. Since the two-dimensional lattice is not strictly periodic, there is no formal way to separate the periodic and random parts, and the Fourier transform for the algebraic correlation function obtains a cross section that is described by an algebraic singularity of the form $|\mathbf{Q} - \mathbf{q}|^{\eta-2}$ (Gunther *et al.*, 1980). In 1972, Caillé (Caillé, 1972) presented an argument that the X-ray scattering line shape for the one-dimensional periodicity of the smectic-A system in three dimensions has an algebraic singularity that is analogous to the line shapes from two-dimensional crystals.

In three-dimensional crystals, both the longitudinal and the shear sound waves satisfy linear dispersion relations of the form $\omega = ck$. In simple liquids, and also for nematic liquid crystals, only the longitudinal sound wave has such a linear dispersion relation. Shear sound waves are overdamped and the decay rate $1/\tau$ is given by the imaginary part of a dispersion relation of the form $\omega = i(\eta/\rho)k^2$, where η is a viscosity coefficient and ρ is the liquid density. The intermediate order of the smectic-A mesomorphic phase, between the three-dimensional crystal and the nematic, results in one of the modes for shear sound waves having the curious dispersion relation $\omega^2 = c^2 k_\perp^2 k_z^2 / (k_\perp^2 + k_z^2)$, where $k_\perp$ and k_z are the magnitudes of the components of the acoustic wavevector perpendicular and parallel to $\langle \mathbf{n} \rangle$, respectively (De Gennes, 1969a; Martin *et al.*, 1972). More detailed analysis, including terms of higher order in $k_\perp^2$, obtains the equivalent of the Debye–Waller factor for the smectic-A as

$$W \simeq k_B T \int_0^{k_D} \frac{k_\perp dk_\perp dk_z}{Bk_z^2 + Kk_\perp^4}, \quad (4.4.3.3)$$

where B and K are smectic elastic constants, $k_\perp^2 = k_x^2 + k_y^2$, and k_D is the Debye wavevector. On substitution of $u^2 = (K/B)k_\perp^2 + k_z^2$, the integral can be manipulated into the form $\int du/u$, which diverges logarithmically at the lower limit in exactly the same way as the integral for the Debye–Waller factor of the two-dimensional crystal. The result is that the smectic-A phase has a sharp peak,

described by an algebraic cusp, at the place in reciprocal space where one would expect a true δ -function Bragg cross section from a truly periodic one-dimensional lattice. In fact, the lattice is not truly periodic and the smectic-A system has only QLRO along the direction $\langle \mathbf{n} \rangle$.

X-ray scattering experiments to test this idea were carried out on one thermotropic smectic-A system, but the results, while consistent with the theory, were not adequate to provide an unambiguous proof of the algebraic cusp (Als-Nielsen *et al.*, 1980). One of the principal difficulties was due to the fact that, when thermotropic samples are oriented in an external magnetic field in the higher-temperature nematic phase and then gradually cooled through the nematic to smectic-A phase transition, the smectic-A samples usually have mosaic spreads of the order of a fraction of a degree and this is not sufficient for detailed line-shape studies near to the peak. A second difficulty is that, in most of the thermotropic smectic-A phases that have been studied to date, only the lowest-order peak is observed. It is not clear whether this is due to a large Debye–Waller-type effect or whether the form factor for the smectic-A layer falls off this rapidly. Nevertheless, since the factor η in the exponent of the cusp $|\mathbf{Q} - \mathbf{q}|^{\eta-2}$ depends quadratically on the magnitude of the reciprocal vector $|\mathbf{q}|$, the shape of the cusp for the different orders would constitute a severe test of the theory.

Fortunately, it is common to observe multiple orders for lyotropic smectic-A systems and such an experiment, carried out on the lyotropic smectic-A system formed from a quaternary mixture of sodium dodecyl sulfate, pentanol, water and dodecane, confirmed the theoretical predictions for the Landau–Peierls effect in the smectic-A phase (Safinya, Roux *et al.*, 1986). The problem of sample mosaic was resolved by using a three-dimensional powder. Although the conditions on the analysis are delicate, Safinya *et al.* demonstrated that for a perfect powder, for which the microcrystals are sufficiently large, the powder line shape does allow unambiguous determination of all of the parameters of the anisotropic line shape.

The only other X-ray study of a critical property on the smectic-A side of the transition has been a measurement of the temperature dependence of the integrated intensity of the peak. For three-dimensional crystals, the integrated intensity of a Bragg peak can be measured for samples with poor mosaic distributions, and because the differences between QLRO and true LRO are only manifest at long distances in real space, or at small wavevectors in reciprocal space, the same is true for the ‘quasi-Bragg peak’ of the smectic-A phase. Chan *et al.* measured the temperature dependence of the integrated intensity of the smectic-A peak across the nematic to smectic-A phase transition for a number of liquid crystals with varying exponents $\nu_\parallel$ and $\nu_\perp$ (Chan, Deutsch *et al.*, 1985). For the Landau–De Gennes free-energy density (equation 4.4.2.5), the theoretical prediction is that the critical part of the integrated intensity should vary as $|t|^x$, where $x = 1 - \alpha$ when the critical part of the heat capacity diverges according to the power law $|t|^{-\alpha}$. Six samples were measured with values of α varying from 0 to 0.5. Although for samples with $\alpha \approx 0.5$ the critical intensity did vary as $x \approx 0.5$, there were systematic deviations for smaller values of α , and for $\alpha \approx 0$ the measured values of x were in the range 0.7 to 0.76. The origin of this discrepancy is not at present understood.

Similar integrated intensity measurements in the vicinity of the first-order nematic to smectic-C transition cannot easily be made in smectic-C samples since the magnetic field aligns the molecular axis $\langle \mathbf{n} \rangle$, and when the layers form at some angle φ to $\langle \mathbf{n} \rangle$ the layer normals are distributed along the full 2π of azimuthal directions around $\langle \mathbf{n} \rangle$, as shown in Fig. 4.4.1.2(d). The X-ray scattering pattern for such a sample is a partial powder with a peak-intensity distribution that forms a ring of radius $|\mathbf{q}| \sin(\varphi)$. The opening of the single spot along the average molecular axis $\langle \mathbf{n} \rangle$ into a ring can be used to study either the nematic to smectic-C or the smectic-A to smectic-C transition (Martinez-Miranda *et al.*, 1986).

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The statistical physics in the region of the phase diagram surrounding the triple point, where the nematic, smectic-A and smectic-C phases meet, has been the subject of considerable theoretical speculation (Chen & Lubensky, 1976; Chu & McMillan, 1977; Benguigui, 1979; Huang & Lien, 1981; Grinstein & Toner, 1983). The best representation of the observed X-ray scattering structure near the nematic to smectic-A, the nematic to smectic-C and the nematic/smectic-A/smectic-C (NAC) multicritical point is obtained from the mean-field theory of Chen and Lubensky, the essence of which is expressed in terms of an energy density of the form

$$\Delta F(\psi) = \frac{A}{2} |\psi|^2 + \frac{D}{4} |\psi|^4 + \frac{1}{2} [E_{\parallel} (Q_{\parallel}^2 - Q_0^2)^2 + E_{\perp} Q_{\perp}^2 + E_{\perp\perp} Q_{\perp}^4 + E_{\perp\parallel} Q_{\perp}^2 (Q_{\parallel}^2 - Q_0^2)] |\psi(\mathbf{Q})|^2, \quad (4.4.3.4)$$

where $\psi = \psi(\mathbf{Q})$ is the Fourier component of the electron density:

$$\psi(\mathbf{Q}) \equiv \frac{1}{(2\pi)^3} \int d^3\mathbf{r} \exp[i(\mathbf{Q} \cdot \mathbf{r})] \rho(\mathbf{r}). \quad (4.4.3.5)$$

The quantities $E_{\parallel}$, $E_{\perp\perp}$, and $E_{\perp\parallel}$ are all positive definite; however, the sign of A and $E_{\perp}$ depends on temperature. For $A > 0$ and $E_{\perp} > 0$, the free energy, including the higher-order terms, is minimized by $\psi(\mathbf{Q}) = 0$ and the nematic is the stable phase. For $A < 0$ and $E_{\perp} > 0$, the minimum in the free energy occurs for a nonvanishing value for $\psi(\mathbf{Q})$ in the vicinity of $Q_{\parallel} \approx Q_0$, corresponding to the uniaxial smectic-A phase; however, for $E_{\perp} < 0$, the free-energy minimum occurs for a nonvanishing $\psi(\mathbf{Q})$ with a finite value of $Q_{\perp}$, corresponding to smectic-C order. The special point in the phase diagram where two terms in the free energy vanish simultaneously is known as a 'Lifshitz point' (Hornreich *et al.*, 1975). In the present problem, this occurs at the triple point where the nematic, smectic-A and smectic-C phases coexist. Although there have been other theoretical models for this transition, the best agreement between the observed and theoretical line shapes for the X-ray scattering cross sections is based on the Chen–Lubensky model. Most of the results from light-scattering experiments in the vicinity of the NAC triple point also agree with the main features predicted by the Chen–Lubensky model; however, there are some discrepancies that are not explained (Solomon & Litster, 1986).

The nematic to smectic-C transition in the vicinity of this point is particularly interesting in that, on approaching the nematic to smectic-C transition temperature from the nematic phase, the X-ray scattering line shapes first appear to be identical to the shapes usually observed on approaching the nematic to smectic-A phase transition; however, within approximately 0.1 K of the transition, they change to shapes that clearly indicate smectic-C-type fluctuations. Details of this crossover are among the strongest evidence supporting the Lifshitz idea behind the Chen–Lubensky model.

4.4.3.2. Modulated smectic-A and smectic-C phases

Previously, we mentioned that, although the reciprocal-lattice spacing $|\mathbf{q}|$ for many smectic-A phases corresponds to $2\pi/L$, where L is the molecular length, there are a number of others for which $|\mathbf{q}|$ is between π/L and $2\pi/L$ (Leadbetter, Frost, Gaughan, Gray & Mosley, 1979; Leadbetter *et al.*, 1977). This suggests the possibility of different types of smectic-A phases in which the bare molecular length is not the sole determining factor of the period d . In 1979, workers at Bordeaux optically observed some sort of phase transition between two phases that both appeared to be of the smectic-A type (Sigaud *et al.*, 1979). Subsequent X-ray studies indicated that in the nematic phase these materials simultaneously displayed critical fluctuations with two separate periods (Levelut *et al.*, 1981; Hardouin *et al.*, 1980, 1983; Ratna *et al.*, 1985, 1986; Chan, Pershan *et al.*, 1985, 1986; Safinya, Varady *et al.*, 1986; Fontes *et al.*, 1986) and confirmed phase transitions between phases that have been designated smectic-A₁ with period $d \approx L$, smectic-A₂ with period $d \approx 2L$ and smectic-A_d with period $L < d < 2L$. Stimulated by the experimental results, Prost and co-workers generalized the De Gennes mean-field theory by writing

$$\rho(\mathbf{r}) = \langle \rho \rangle + \text{Re} \{ \Psi_1 \exp(i\mathbf{q}_1 \cdot \mathbf{r}) + \Psi_2 \exp(i\mathbf{q}_2 \cdot \mathbf{r}) \},$$

where 1 and 2 refer to two different density waves (Prost, 1979; Prost & Barois, 1983; Barois *et al.*, 1985). In the special case that $\mathbf{q}_1 \approx 2\mathbf{q}_2$ the free energy represented by equation (4.4.2.3) must be generalized to include terms like

$$(\Psi_2^*)^2 \Psi_1 \exp[i(\mathbf{q}_1 - 2\mathbf{q}_2) \cdot \mathbf{r}] + \text{c.c.}$$

that couple the two order parameters. Suitable choices for the relative values of the phenomenological parameters of the free energy then result in minima that correspond to any one of these three smectic-A phases. Much more interesting, however, was the observation that even if $|\mathbf{q}_1| < 2|\mathbf{q}_2|$ the two order parameters could still be coupled together if $\mathbf{q}_1$ and $\mathbf{q}_2$ were not collinear, as illustrated in Fig. 4.4.3.1(a), such that $2\mathbf{q}_1 \cdot \mathbf{q}_2 = |\mathbf{q}_1|^2$. Prost *et al.* predicted the existence of phases that are modulated in the direction perpendicular to the average layer normal with a period $4\pi/|\mathbf{q}_2| \sin(\varphi) = 2\pi/|\mathbf{q}_m|$. Such a modulated phase has been observed and is designated as the smectic-A (Hardouin *et al.*, 1981). Similar considerations apply to the smectic-C phases and the modulated phase is designated smectic-C̄; (Hardouin *et al.*, 1982; Huang *et al.*, 1984; Safinya, Varady *et al.*, 1986).

4.4.3.3. Surface effects

The effects of surfaces in inducing macroscopic alignment of mesomorphic phases have been important both for technological applications and for basic research (Sprokel, 1980; Gray & Goodby, 1984). Although there are a variety of experimental techniques that are sensitive to mesomorphic surface order (Beaglehole, 1982; Faetti & Palleschi, 1984; Faetti *et al.*, 1985; Gannon & Faber, 1978; Miyano, 1979; Mada & Kobayashi, 1981; Guyot-Sionnest *et al.*,

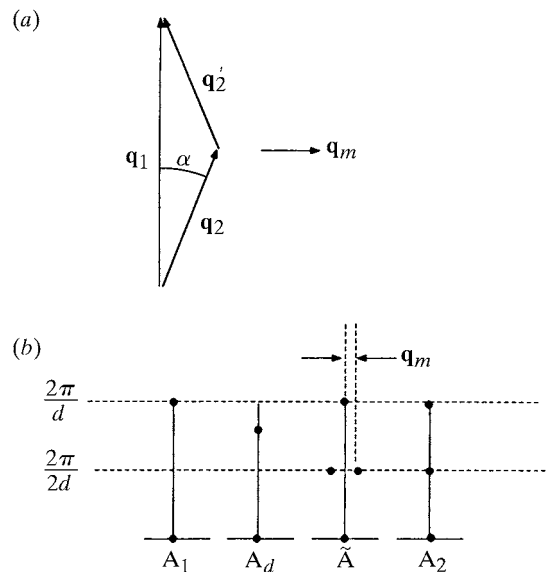


Fig. 4.4.3.1. (a) Schematic illustration of the necessary condition for coupling between order parameters when $|\mathbf{q}_2| < 2|\mathbf{q}_1|$; $|\mathbf{q}| = (|\mathbf{q}_2|^2 - |\mathbf{q}_1|^2)^{1/2} = |\mathbf{q}_1| \sin(\alpha)$. (b) Positions of the principal peaks for the indicated smectic-A phases.

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1986), it is only recently that X-ray scattering techniques have been applied to this problem. In one form or another, all of the techniques for obtaining surface specificity in an X-ray measurement make use of the fact that the average interaction between X-rays and materials can be treated by the introduction of a dielectric constant $\varepsilon \approx 1 - (4\pi\rho e^2/m\omega^2) = 1 - \rho r_e \lambda^2/\pi$, where ρ is the electron density, r_e is the classical radius of the electron, and ω and λ are the angular frequency and the wavelength of the X-ray. Since $\varepsilon < 1$, X-rays that are incident at a small angle to the surface θ_0 will be refracted in the material toward a smaller angle $\theta_T \approx (\theta_0^2 - \theta_c^2)^{1/2}$, where the 'critical angle' $\theta_c \approx (\rho r_e \lambda^2/\pi)^{1/2} \approx 0.003$ rad ($\approx 0.2^\circ$) for most liquid crystals (Warren, 1968). Although this is a small angle, it is at least two orders of magnitude larger than the practical angular resolution available in modern X-ray spectrometers (Als-Nielsen *et al.*, 1982; Pershan & Als-Nielsen, 1984; Pershan *et al.*, 1987). One can demonstrate that for many conditions the specular reflection $R(\theta_0)$ is given by

$$R(\theta_0) \approx R_F(\theta_0) |\rho^{-1} \int dz \exp(-iQz) \langle \partial\rho/\partial z \rangle|^2,$$

where $Q \equiv (4\pi/\lambda) \sin(\theta_0)$, $\langle \partial\rho/\partial z \rangle$ is the normal derivative of the electron density averaged over a region in the surface that is defined by the coherence area of the incident X-ray, and

$$R_F(\theta_0) \approx \left(\frac{\theta_0 - \sqrt{\theta_0^2 - \theta_c^2}}{\theta_0 + \sqrt{\theta_0^2 - \theta_c^2}} \right)^2$$

is the Fresnel reflection law that is calculated from classical optics for a flat interface between the vacuum and a material of dielectric constraint ε . Since the condition for specular reflection, that the incident and scattered angles are equal and in the same plane, requires that the scattering vector $\mathbf{Q} = \hat{z}(4\pi/\lambda) \sin(\theta_0)$ be parallel to the surface normal, it is quite practical to obtain, for flat surfaces, an unambiguous separation of the specular reflection signal from all other scattering events.

Fig. 4.4.3.2(a) illustrates the specular reflectivity from the free nematic–air interface for the liquid crystal 4'-octyloxybiphenyl-4-carbonitrile (8OCB) 0.050 K above the nematic to smectic-A phase-transition temperature (Pershan & Als-Nielsen, 1984). The dashed line is the Fresnel reflection $R_F(\theta_0)$ in units of $\sin(\theta_0)/\sin(\theta_c)$,

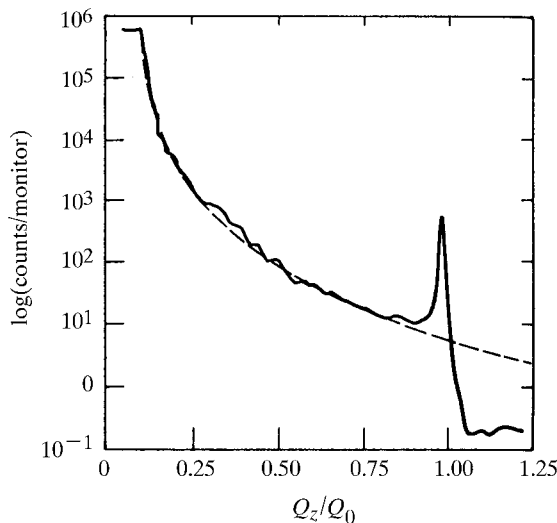


Fig. 4.4.3.2. Specular reflectivity of ~ 8 keV X-rays from the air–liquid interface of the nematic liquid crystal 8OCB 0.05 K above the nematic to smectic-A transition temperature. The dashed line is the Fresnel reflection law as described in the text.

where the peak at $\theta_c = 1.39^\circ$ corresponds to surface-induced smectic order in the nematic phase: *i.e.* the selection rule for specular reflection has been used to separate the specular reflection from the critical scattering from the bulk. Since the full width at half maximum is exactly equal to the reciprocal of the correlation length for critical fluctuations in the bulk, $2/\xi_{\parallel}$ at all temperatures from $T - T_{NA} \approx 0.006$ K up to values near to the nematic to isotropic transition, $T - T_{NA} \approx 3.0$ K, it is clear this is an example where the gravitationally induced long-range order in the surface position has induced mesomorphic order that has long-range correlations parallel to the surface. Along the surface normal, the correlations have only the same finite range as the bulk critical fluctuations. Studies on a number of other nematic (Gransbergen *et al.*, 1986; Ocko *et al.*, 1987) and isotropic surfaces (Ocko, Braslau *et al.*, 1986) indicate features that are specific to local structure of the surface.

4.4.4. Phases with in-plane order

Although the combination of optical microscopy and X-ray scattering studies on unoriented samples identified most of the mesomorphic phases, there remain a number of subtle features that were only discovered by spectra from well oriented samples (see the extensive references contained in Gray & Goodby, 1984). Nematic phases are sufficiently fluid that they are easily oriented by either external electric or magnetic fields, or surface boundary conditions, but similar alignment techniques are not generally successful for the more ordered phases because the combination of strains induced by thermal expansion and the enhanced elasticity that accompanies the order creates defects that do not easily anneal. Other defects that might have been formed during initial growth of the phase also become trapped and it is difficult to obtain well oriented samples by cooling from a higher-temperature aligned phase. Nevertheless, in some cases it has been possible to obtain crystalline-B samples with mosaic spreads of the order of a fraction of a degree by slowing cooling samples that were aligned in the nematic phase. In other cases, mesomorphic phases were obtained by heating and melting single crystals that were grown from solution (Benattar *et al.*, 1979; Leadbetter, Mazid & Malik, 1980).

Moncton & Pindak (1979) were the first to realize that X-ray scattering studies could be carried out on the freely suspended films that Friedel (1922) described in his classical treatise on liquid crystals. These samples, formed across a plane aperture (*i.e.* approximately 1 cm in diameter) in the same manner as soap bubbles, have mosaic spreads that are an order of magnitude smaller. The geometry is illustrated in Fig. 4.4.4.1(a). The substrate in which the aperture is cut can be glass (*e.g.* a microscope cover slip), steel or copper sheeting, *etc.* A small amount of the material, usually in the high-temperature region of the smectic-A phase, is spread around the outside of an aperture that is maintained at the necessary temperature, and a wiper is used to drag some of the material across the aperture. If a stable film is successfully drawn, it is detected optically by its finite reflectivity. In particular, against a dark background and with the proper illumination it is quite easy to detect the thinnest free films.

In contrast to conventional soap films that are stabilized by electrostatic effects, smectic films are stabilized by their own layer structure. Films as thin as two molecular layers can be drawn and studied for weeks (Young *et al.*, 1978). Thicker films of the order of thousands of layers can also be made and, with some experience in depositing the raw material around the aperture and the speed of drawing, it is possible to draw films of almost any desired thickness (Moncton *et al.*, 1982). For films thinner than approximately 20 to 30 molecular layers (*i.e.* 600 to 1000 Å), the thickness is determined from the reflected intensity of a small helium–neon laser. Since the

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

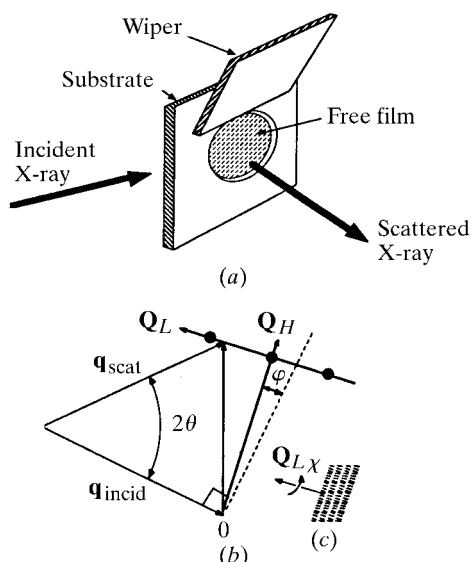


Fig. 4.4.4.1. (a) Schematic illustration of the geometry and (b) kinematics of X-ray scattering from a freely suspended smectic film. The insert (c) illustrates the orientation of the film in real space corresponding to the reciprocal-space kinematics in (b). If the angle $\varphi = \theta$, the film is oriented such that the scattering vector is parallel to the surface of the film, *i.e.* parallel to the smectic layers. A ' Q_L scan' is taken by simultaneous adjustment of φ and 2θ to keep $(4\pi/\lambda) \sin(\theta) \cos(\theta - \varphi) = (4\pi/\lambda) \sin(\theta_{100})$, where θ_{100} is the Bragg angle for the 100 reflection. The different in-plane Bragg reflections can be brought into the scattering plane by rotation of the film by the angle χ around the film normal.

reflected intensities for films of 2, 3, 4, 5, . . . layers are in the ratio of 4, 9, 16, 25, . . . , the measurement can be calibrated by drawing and measuring a reasonable number of thin films. The most straightforward method for thick films is to measure the ellipticity of the polarization induced in laser light transmitted through the film at an oblique angle (Collett, 1983; Collett *et al.*, 1985); however, a subtler method that makes use of the colours of white light reflected from the films is also practical (Sirota, Pershan, Sorensen & Collett, 1987). In certain circumstances, the thickness can also be measured using the X-ray scattering intensity in combination with one of the other methods.

Fig. 4.4.4.1 illustrates the scattering geometry used with these films. Although recent unpublished work has demonstrated the possibility of a reflection geometry (Sorensen, 1987), all of the X-ray scattering studies to be described here were performed in transmission. Since the in-plane molecular spacings are typically between 4 and 5 Å, while the layer spacing is closer to 30 Å, it is difficult to study the 00L peaks in this geometry.

Fig. 4.4.4.2 illustrates the difference between X-ray scattering spectra taken on a bulk crystalline-B sample of *N*-[4-(*n*-butyloxy)-benzylidene]-4-*n*-octylaniline (4O.8) that was oriented in an external magnetic field while in the nematic phase and then cooled through the smectic-A phase into the crystalline-B phase (Aeppli *et al.*, 1981), and one taken on a thick freely suspended film of *N*-[4-(*n*-heptyloxy)benzylidene]-4-*n*-heptylaniline (7O.7) (Collett *et al.*, 1982, 1985). Note that the data for 7O.7 are plotted on a semi-logarithmic scale in order to display simultaneously both the Bragg peak and the thermal diffuse background. The scans are along the Q_L direction, at the appropriate value of Q_H to intersect the peaks associated with the intralayer periodicity. In both cases, the widths of the Bragg peaks are essentially determined by the sample mosaicity and as a result of the better alignment the ratio of the

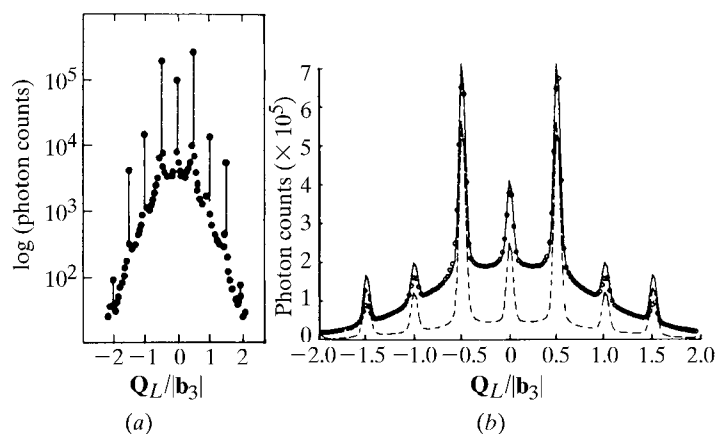


Fig. 4.4.4.2. Typical Q_L scans from the crystalline-B phases of (a) a free film of 7O.7, displayed on a logarithmic scale to illustrate the reduced level of the diffuse scattering relative to the Bragg reflection and (b) a bulk sample of 4O.8 oriented by a magnetic field.

thermal diffuse background to the Bragg peak is nearly an order of magnitude smaller for the free film sample.

4.4.4.1. Hexatic phases in two dimensions

The hexatic phase of matter was first proposed independently by Halperin & Nelson (Halperin & Nelson 1978; Nelson & Halperin 1979) and Young (Young, 1979) on the basis of theoretical studies of the melting process in two dimensions. Following work by Kosterlitz & Thouless (1973), they observed that since the interaction energy between pairs of dislocations in two dimensions decreases logarithmically with their separation, the enthalpy and the entropy terms in the free energy have the same functional dependence on the density of dislocations. It follows that the free-energy difference between the crystalline and hexatic phase has the form $\Delta F = \Delta H - T\Delta S \approx T_c S(\rho) - TS(\rho) = S(\rho)(T_c - T)$, where $S(\rho) \approx \rho \log(\rho)$ is the entropy as a function of the density of dislocations ρ and T_c is defined such that $T_c S(\rho)$ is the enthalpy. Since the prefactor of the enthalpy term is independent of temperature while that of the entropy term is linear, there will be a critical temperature, T_c , at which the sign of the free energy changes from positive to negative. For temperatures greater than T_c , the entropy term will dominate and the system will be unstable against the spontaneous generation of dislocations. When this happens, the two-dimensional crystal, with positional QLRO, but true long-range order in the orientation of neighbouring atoms, can melt into a new phase in which the positional order is short range, but for which there is QLRO in the orientation of the six neighbours surrounding any atom. The reciprocal-space structures for the two-dimensional crystal and hexatic phases are illustrated in Figs. 4.4.4.3(b) and (c), respectively. That of the two-dimensional solid consists of a hexagonal lattice of sharp rods (*i.e.* algebraic line shapes in the plane of the crystal). For a finite size sample, the reciprocal-space structure of the two-dimensional hexatic phase is a hexagonal lattice of diffuse rods and there are theoretical predictions for the temperature dependence of the in-plane line shapes (Aeppli & Bruinsma, 1984). If the sample were of infinite size, the QLRO of the orientation would spread the six spots continuously around a circular ring, and the pattern would be indistinguishable from that of a well correlated liquid, *i.e.* Fig. 4.4.4.3(a). The extent of the patterns along the rod corresponds to the molecular form factor. Figs. 4.4.4.3(a), (b) and (c) are drawn on the assumption that the molecules are normal to the two-

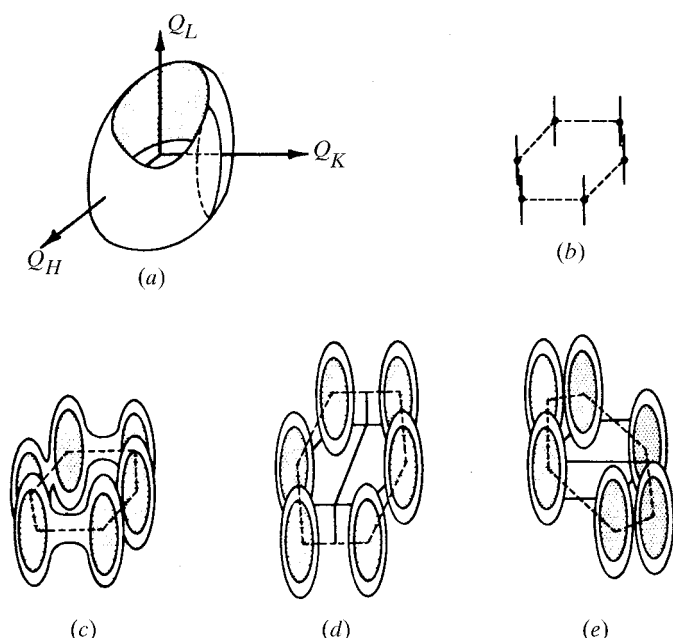


Fig. 4.4.4.3. Scattering intensities in reciprocal space from two-dimensional: (a) liquid; (b) crystal; (c) normal hexatic; and tilted hexatics in which the tilt is (d) towards the nearest neighbours as for the smectic-I or (e) between the nearest neighbours as for the smectic-F. The thin rods of scattering in (b) indicate the singular cusp for peaks with algebraic line shapes in the HK plane.

dimensional plane of the phase. If the molecules are tilted, the molecular form factor for long thin rod-like molecules will shift the intensity maxima as indicated in Figs. 4.4.4.3(d) and (e). The phase in which the molecules are normal to the two-dimensional plane is the two-dimensional *hexatic-B* phase. If the molecules tilt towards the position of their nearest neighbours (in real space), or in the direction that is between the lowest-order peaks in reciprocal space, the phase is the two-dimensional *smectic-I*, Fig. 4.4.4.3(d). The other tilted phase, for which the tilt direction is between the nearest neighbours in real space or in the direction of the lowest-order peaks in reciprocal space, is the *smectic-F*, Fig. 4.4.4.3(e).

Although theory (Halperin & Nelson, 1978; Nelson & Halperin, 1979; Young, 1979) predicts that the two-dimensional crystal can melt into a hexatic phase, it does not say that it must happen, and the crystal can melt directly into a two-dimensional liquid phase. Obviously, the hexatic phases will also melt into a two-dimensional liquid phase. Fig. 4.4.4.3(a) illustrates the reciprocal-space structure for the two-dimensional liquid in which the molecules are normal to the two-dimensional surface. Since the longitudinal (*i.e.* radial) width of the hexatic spot could be similar to the width that might be expected in a well correlated fluid, the direct X-ray proof of the transition from the hexatic-B to the normal liquid requires a hexatic sample in which the domains are sufficiently large that the sample is not a two-dimensional powder. On the other hand, the elastic constants must be sufficiently large that the QLRO does not smear the six spots into a circle. The radial line shape of the powder pattern of the hexatic-B phase can also be subtly different from that of the liquid and this is another possible way that X-ray scattering can detect melting of the hexatic-B phase (Aeppli & Bruinsma, 1984).

Changes that occur on the melting of the tilted hexatics, *i.e.* smectic-F and smectic-I, are usually easier to detect and this will be discussed in more detail below. On the other hand, there is a fundamental theoretical problem concerning the way of understanding the melting of the tilted hexatics. These phases actually

have the same symmetry as the two-dimensional tilted fluid phase, *i.e.* the smectic-C. In two dimensions they all have QLRO in the tilt orientation, and since the simplest phenomenological argument says that there is a linear coupling between the tilt order and the near-neighbour positional order (Nelson & Halperin, 1980; Bruinsma & Nelson, 1981), it follows that the QLRO of the smectic-C tilt should induce QLRO in the near-neighbour positional order. Thus, by the usual arguments, if there is to be a phase transition between the smectic-C and one of the tilted hexatic phases, the transition must be a first-order transition (Landau & Lifshitz, 1958). This is analogous to the three-dimensional liquid-to-vapour transition which is first order up to a critical point, and beyond the critical point there is no real phase transition.

4.4.4.2. Hexatic phases in three dimensions

Based on both this theory and the various X-ray scattering patterns that had been reported in the literature (Gray & Goodby, 1984), Litster & Birgeneau (Birgeneau & Litster, 1978) suggested that some of the three-dimensional systems that were previously identified as mesomorphic were actually three-dimensional hexatic systems. They observed that it is not theoretically consistent to propose that the smectic phases are layers of two-dimensional crystals randomly displaced with respect to each other since, in thermal equilibrium, the interactions between layers of two-dimensional crystals must necessarily cause the layers to lock together to form a three-dimensional crystal.* On the other hand, if the layers were two-dimensional hexatics, then the interactions would have the effect of changing the QLRO of the hexagonal distribution of neighbours into the true long-range-order orientational distribution of the three-dimensional hexatic. In addition, interactions between layers in the three-dimensional hexatics can also result in interlayer correlations that would sharpen the width of the diffuse peaks in the reciprocal-space direction along the layer normal.

4.4.4.2.1. Hexatic-B

Although Leadbetter, Frost & Mazid (1979) had remarked on the different types of X-ray structures that were observed in materials identified as 'smectic-B', the first proof for the existence of the hexatic-B phase of matter was the experiment by Pindak *et al.* (1981) on thick freely suspended films of the liquid crystal *n*-hexyl 4'-pentyloxybiphenyl-4-carboxylate (65OBC). A second study on free films of the liquid crystal *n*-butyl 4'-*n*-hexyloxybiphenyl-4-carboxylate (46OBC) demonstrated that, as the hexatic-B melts into the smectic-A phase, the position and the in-plane width of the X-ray scattering peaks varied continuously. In particular, the in-plane correlation length evolved continuously from 160 Å, nearly 10 K below the hexatic to smectic-A transition, to only 17 Å, a few degrees above. Similar behaviour was also observed in a film only two layers thick (Davey *et al.*, 1984). Since the observed width of the peak along the layer normal corresponded to the molecular form factor, these systems have negligible interlayer correlations.

4.4.4.2.2. Smectic-F, smectic-I

In contrast to the hexatic-B phase, the principal reciprocal-space features of the smectic-F phase were clearly determined before the theoretical work that proposed the hexatic phase. Demus *et al.* (1971) identified a new phase in one material, and subsequent X-ray studies by Leadbetter and co-workers (Leadbetter, Mazid & Richardson, 1980; Leadbetter, Gaughan *et al.*, 1979; Gane &

* Prior to the paper by Birgeneau & Litster, it was commonly believed that some of the smectic phases consisted of uncorrelated stacks of two-dimensional crystals.

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

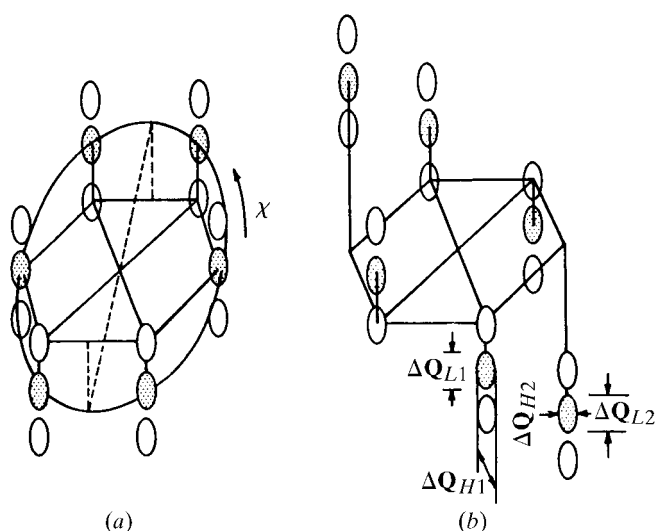


Fig. 4.4.4.4. Scattering intensities in reciprocal space from three-dimensional tilted hexatic phases: (a) the smectic-I and (b) the smectic-F. The variation of the intensity along the Q_L direction indicates interlayer correlations that are absent in Figs. 4.4.4.1(d) and (e). The peak widths $\Delta Q_{L1,2}$ and $\Delta Q_{H1,2}$ correspond to the four inequivalent widths in the smectic-F phase. Similar inequivalent widths exist for the smectic-I phase. The circle through the shaded points in (a) indicates the reciprocal-space scan that directly measures the hexatic order. A similar scan in the smectic-C phase would have intensity independent of χ .

Leadbetter, 1981) and by Benattar and co-workers (Benattar *et al.*, 1978, 1980, 1983; Guillon *et al.*, 1986) showed it to have the reciprocal-space structure illustrated in Fig. 4.4.4.4(b). There are interlayer correlations in the three-dimensional smectic-F phases, and as a consequence the reciprocal-space structure has maxima along the diffuse rods. Benattar *et al.* (1979) obtained monodomain smectic-F samples of the liquid crystal N,N' -(1,4-phenylenedimethylene)bis(4-*n*-pentylaniline) by melting a single crystal that was previously precipitated from solution. One of the more surprising results of this work was the demonstration that the near-neighbour packing was very close to what would be expected from a model in which rigid closely packed rods were simply tilted away from the layer normal. In view of the facts that the molecules are clearly not cylindrical, and that the molecular tilt indicates that the macroscopic symmetry has been broken, it would have been reasonable to expect significant deviations from local hexagonal symmetry when the system is viewed along the molecular axis. The fact that this is not the case indicates that this phase has a considerable amount of rotational disorder around the long axis of the molecules.

Other important features of the smectic-F phase are, firstly, that the local molecular packing is identical to that of the tilted crystalline-G phase (Benattar *et al.*, 1979; Sirota *et al.*, 1985; Guillon *et al.*, 1986). Secondly, there is considerable temperature dependence of the widths of the various diffuse peaks. Fig. 4.4.4.4(b) indicates the four inequivalent line widths that Sirota and co-workers measured in freely suspended films of the liquid crystal N -[4-(*n*-heptyloxy)benzylidene]-4-*n*-heptyl aniline (70.7). Parenthetically, bulk samples of this material do not have a smectic-F phase; however, the smectic-F is observed in freely suspended films as thick as ~ 200 layers. Fig. 4.4.4.5 illustrates the thickness-temperature phase diagram of 70.7 between 325 and 342 K (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987). Bulk samples and thick films have a first-order transition from the crystalline-B to the smectic-C at 342 K. Thinner films indicate a surface phase above

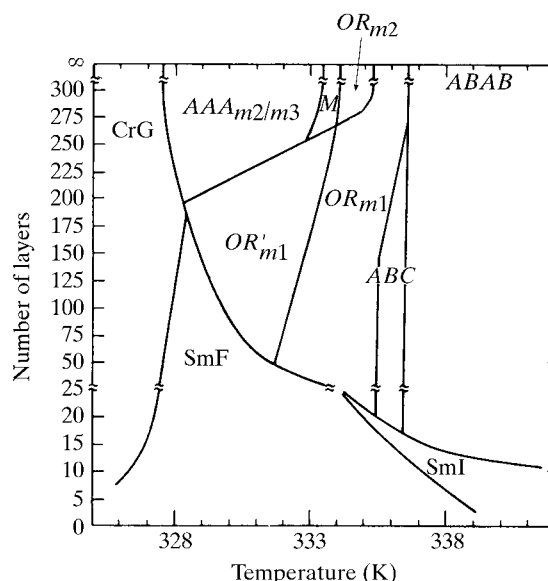


Fig. 4.4.4.5. The phase diagram for free films of 70.7 as a function of thickness and temperature. The phases ABAB, AAA, OR_{m1} , OR_{m2} , OR'_{m1} , M and ABAB are all crystalline-B with varying interlayer stacking, or long-wavelength modulations; CrG, SmF and SmI are crystalline-G, smectic-F and smectic-I, respectively (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987; Sirota, Pershan, Sorensen & Collett, 1987).

342 K that will be discussed below. Furthermore, although there is a strong temperature dependence of the widths of the diffuse scattering peaks, the widths are independent of film thickness. This demonstrates that, although the free film boundary conditions have stabilized the smectic-F phase, the properties of the phase are not affected by the boundaries. Finally, the fact that the widths ΔQ_{L1} and ΔQ_{L2} along the L direction and ΔQ_{H1} and ΔQ_{H2} along the in-plane directions are not equal indicates that the correlations are very anisotropic (Brock *et al.*, 1986; Sirota *et al.*, 1985). We will discuss one possible model for these properties after presenting other data on thick films of 70.7. From the fact that the positions of the intensity maxima for the diffuse spots of the smectic-F phase of 70.7 correspond exactly to the positions of the Bragg peaks in the crystalline-G phase, we learn that the local molecular packing must be identical in the two phases. The major difference between the crystalline-G and the tilted hexatic smectic-F phase is that, in the latter, defects destroy the long-range positional order of the former (Benattar *et al.*, 1979; Sirota *et al.*, 1985). Although this is consistent with the existing theoretical model that attributes hexatic order to a proliferation of unbounded dislocations, it is not obvious that the proliferation is attributable to the same Kosterlitz-Thouless mechanism that Halperin & Nelson and Young discussed for the transition from the two-dimensional crystal to the hexatic phase. We will say more on this point below.

The only identified difference between the two tilted hexatic phases, the smectic-F and the smectic-I, is the direction of the molecular tilt relative to the near-neighbour positions. For the smectic-I, the molecules tilt towards one of the near neighbours, while for the smectic-F they tilt between the neighbours (Gane & Leadbetter, 1983). There are a number of systems that have both smectic-I and smectic-F phases, and in all cases of which we are aware the smectic-I is the higher-temperature phase (Gray & Goodby, 1984; Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987).

Optical studies of freely suspended films of materials in the nO_m series indicated tilted surface phases at temperatures for which the bulk had uniaxial phases (Farber, 1985). As mentioned above,

4. DIFFUSE SCATTERING AND RELATED TOPICS

X-ray scattering studies of 7O.7 demonstrated that the smectic-F phase set in for a narrow temperature range in films as thick as 180 layers, and that the temperature range increases with decreasing layer number. For films of the order of 25 layers thick, the smectic-I phase is observed at approximately 334 K, and with decreasing thickness the temperature range for this phase also increases. Below approximately 10 to 15 layers, the smectic-I phase extends up to ~ 342 K where bulk samples undergo a first-order transition from the crystalline-B to the smectic-C phase. Synchrotron X-ray scattering experiments show that, in thin films (five layers for example), the homogeneous smectic-I film undergoes a first-order transition to one in which the two surface layers are smectic-I and the three interior layers are smectic-C (Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987). The fact that two phases with the same symmetry can coexist in this manner tells us that in this material there is some important microscopic difference between them. This is reaffirmed by the fact that the phase transition from the surface smectic-I to the homogeneous smectic-C phase has been observed to be first order (Sorensen *et al.*, 1987).

In contrast to 7O.7, Birgeneau and co-workers found that in racemic 4-(2-methylbutyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (8OSI) (Brock *et al.*, 1986), the X-ray structure of the smectic-I phase evolves continuously into that of the smectic-C. By applying a magnetic field to a thick freely suspended sample, Brock *et al.* were able to obtain a large monodomain sample. They measured the X-ray scattering intensity around the circle in the reciprocal-space plane shown in Fig. 4.4.4.4(b) that passes through the peaks. For higher temperatures, when the sample is in the smectic-C phase, the intensity is essentially constant around the circle; however, on cooling, it gradually condenses into six peaks, separated by 60° . The data were analysed by expressing the intensity as a Fourier series of the form

$$S(\chi) = I_0 \left[\frac{1}{2} + \sum_{n=1}^{\infty} C_{6n} \cos 6n(90^\circ - \chi) \right] + I_B,$$

where I_0 fixes the absolute intensity and I_B fixes the background. The temperature variation of the coefficients scaled according to the relation $C_{6n} = C_6^{\sigma_n}$ where the empirical relation $\sigma_n = 2.6(n-1)$ is in good agreement with a theoretical form predicted by Aharony *et al.* (1986). The only other system in which this type of measurement has been made was the smectic-C phase of 7O.7 (Collett, 1983). In that case, the intensity around the circle was constant, indicating the absence of any tilt-induced bond orientational order (Aharony *et al.*, 1986).

It would appear that the near-neighbour molecular packing of the smectic-I and the crystalline-J phases is the same, in just the same way as for the packing of the smectic-F and the crystalline-G phases. The four smectic-I widths analogous to those illustrated in Fig. 4.4.4.4(a) are, like that of the smectic-F, both anisotropic and temperature dependent (Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987; Brock *et al.*, 1986; Benattar *et al.*, 1979).

4.4.4.3. Crystalline phases with molecular rotation

4.4.4.3.1. Crystal-B

Recognition of the distinction between the hexatic-B and crystalline-B phases provided one of the more important keys to understanding the ordered mesomorphic phases. There are a number of distinct phases called crystalline-B that are all true three-dimensional crystals, with resolution-limited Bragg peaks (Moncton & Pindak, 1979; Aeppli *et al.*, 1981). The feature common to them all is that the average molecular orientation is normal to the layers, and within each layer the molecules are distributed on a triangular lattice. In view of the 'blade-like' shape of the molecule, the hexagonal site symmetry implies that the

molecules must be rotating rapidly (Levelut & Lambert, 1971; Levelut, 1976; Richardson *et al.*, 1978). We have previously remarked that this apparent rotational motion characterizes all of the phases listed in Table 4.4.1.1 except for the crystalline-E, -H and -K. In the most common crystalline-B phase, adjacent layers have ABAB-type stacking (Leadbetter, Gaughan *et al.*, 1979; Leadbetter, Mazid & Kelly, 1979). High-resolution studies on well oriented samples show that in addition to the Bragg peaks the crystalline-B phases have rods of relatively intense diffuse scattering distributed along the 10L Bragg peaks (Moncton & Pindak, 1979; Aeppli *et al.*, 1981). The widths of these rods in the reciprocal-space direction, parallel to the layers, are very sharp, and without a high-resolution spectrometer their widths would appear to be resolution limited. In contrast, along the reciprocal-space direction normal to the layers, their structure corresponds to the molecular form factor.

If the intensity of the diffuse scattering can be represented as proportional to $(\mathbf{Q} \cdot \mathbf{u})^2$, where $\mathbf{u}$ describes the molecular displacement, the fact that there is no rod of diffuse scattering through the 00L peaks indicates that the rods through the 10L peaks originate from random disorder in 'sliding' displacements of adjacent layers. It is likely that these displacements are thermally excited phonon vibrations; however, we cannot rule out some sort of non-thermal static defect structure. In any event, assuming this diffuse scattering originates in a thermal vibration for which adjacent layers slide over one another with some amplitude $\langle \mathbf{u}^2 \rangle^{1/2}$, and assuming strong coupling between this shearing motion and the molecular tilt, we can define an angle $\varphi = \tan^{-1}(\langle \mathbf{u}^2 \rangle^{1/2}/d)$, where d is the layer thickness. The observed diffuse intensity corresponds to angles φ between 3 and 6° (Aeppli *et al.*, 1981).

Leadbetter and co-workers demonstrated that in the *nO.m* series various molecules undergo a series of restacking transitions and that crystalline-B phases exist with ABC and AAA stacking as well as the more common ABAB (Leadbetter, Mazid & Richardson 1980; Leadbetter, Mazid & Kelly, 1979). Subsequent high-resolution studies on thick freely suspended films revealed that the restacking transitions were actually subtler, and in 7O.7, for example, on cooling the hexagonal ABAB phase one observes an orthorhombic and then a monoclinic phase before the hexagonal AAA (Collett *et al.*, 1982, 1985). Furthermore, the first transition from the hexagonal ABAB to the monoclinic phase is accompanied by the appearance of a relatively long wavelength modulation within the plane of the layers. The polarization of this modulation is along the layer normal, or orthogonal to the polarization of the displacements that gave rise to the rods of thermal diffuse scattering (Gane & Leadbetter, 1983).

It is also interesting to note that the AAA simple hexagonal structure does not seem to have been observed outside liquid-crystalline materials and, were it not for the fact that the crystalline-B hexagonal AAA is always accompanied by long wavelength modulations, it would be the only case of which we are aware.

Figs. 4.4.4.6(a) and (b) illustrate the reciprocal-space positions of the Bragg peaks (dark dots) and modulation-induced side bands (open circles) for the unmodulated hexagonal ABAB and the modulated orthorhombic phase (Collett *et al.*, 1984). For convenience, we only display one 60° sector. Hirth *et al.* (1984) explained how both the reciprocal-space structure and the modulation of the orthorhombic phase could result from an ordered array of partial dislocations. They were not, however, able to provide a specific model for the microscopic driving force for the transition. Sirota, Pershan & Deutsch (1987) proposed a variation of the Hirth model in which the dislocations pair up to form a wall of dislocation dipoles such that within the wall the local molecular packing is essentially identical to the packing in the crystalline-G phase that appears at temperatures just below the crystalline-B phase. This model explains: (1) the macroscopic symmetry of the

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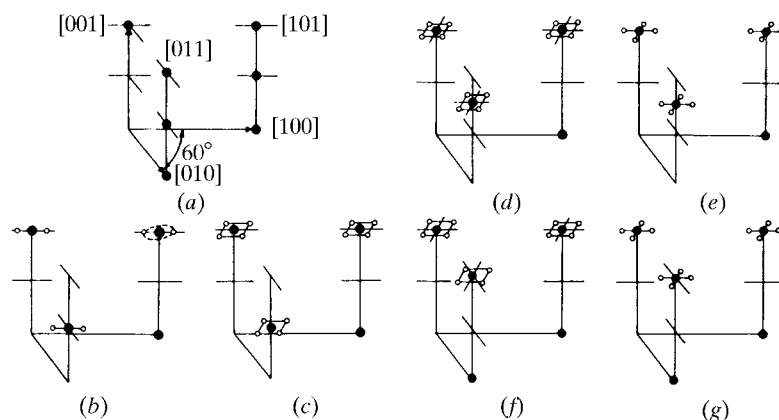


Fig. 4.4.4.6. Location of the Bragg peaks in one 60° section of reciprocal space for the three-dimensional crystalline-B phases observed in thick films of 7O.7. (a) The normal hexagonal crystalline-B phase with ABAB stacking. (b) The one-dimensional modulated phase with orthorhombic symmetry. The closed circles are the principal Bragg peaks and the open circles indicate side bands associated with the long-wavelength modulation. (c) The two-dimensional modulated phase with orthorhombic symmetry. Only the lowest-order side bands are shown. They are situated on the corners of squares surrounding the Bragg peak. The squares are oriented as shown and the amplitude of the square diagonal is equal to the distance between the two side bands illustrated in (b). (d) The two-dimensional modulated phase with monoclinic symmetry. Note that the L position of one of the peaks has shifted relative to (c). (e) A two-dimensional modulated phase with orthorhombic symmetry that is only observed on heating the quenched phase illustrated in (g). (f) The two-dimensional modulated phase with hexagonal symmetry and AAA layer stacking. (g) A two-dimensional hexagonal phase with AAA layer stacking that is only observed on rapid cooling from the phase shown in (c).

phase; (2) the period of the modulation; (3) the polarization of the modulation; and (4) the size of the observed deviations of the reciprocal-space structure from the hexagonal symmetry of the ABAB phase and suggests a microscopic driving mechanism that we will discuss below.

On further cooling, there is a first-order transition in which the one-dimensional modulation that appeared at the transition to orthorhombic symmetry is replaced by a two-dimensional modulation as shown in Fig. 4.4.4.6(c). On further cooling, there is another first-order transition in which the positions of the principal Bragg spots change from having orthorhombic to monoclinic symmetry as illustrated in Fig. 4.4.4.6(d). On further cooling, the Bragg peaks shift continually until there is one more first-order transition to a phase with hexagonal AAA positions as illustrated in Fig. 4.4.4.6(f). On further cooling, the AAA symmetry remains unchanged, and the modulation period is only slightly dependent on temperature, but the modulation amplitude increases dramatically. Eventually, as indicated in the phase diagram shown in Fig. 4.4.4.5, the system undergoes another first-order transition to the tilted crystalline-G phase. The patterns in Figs. 4.4.4.6(e) and (g) are observed by rapid quenching from the temperatures at which the patterns in Fig. 4.4.4.6(b) are observed.

Although there is not yet an established theoretical explanation for the origin of the 'restacking-modulation' effects, there are a number of experimental facts that we can summarize, and which indicate a probable direction for future research. Firstly, if one ignores the long wavelength modulation, the hexagonal ABAB phase is the only phase in the diagram for 7O.7 for which there are two molecules per unit cell. There must be some basic molecular effect that determines this particular coupling between every other layer. In addition, it is particularly interesting that it only manifests itself for a small temperature range and then vanishes as the sample is cooled. Secondly, any explanation for the driving force of the restacking transition must also explain the modulations that accompany it. In particular, unless one cools rapidly, the same modulation structures with the same amplitudes always appear at the same temperature, regardless of the sample history, *i.e.* whether heating or cooling. No significant hysteresis is observed and Sirota argued that the structures are in thermal equilibrium.

There are a number of physical systems for which the development of long-wavelength modulations is understood, and

in each case they are the result of two or more competing interaction energies that cannot be simultaneously minimized (Blinic & Levanyuk, 1986; Safinya, Varady *et al.*, 1986; Lubensky & Ingersent, 1986; Winkor & Clarke, 1986; Moncton *et al.*, 1981; Fleming *et al.*, 1980; Villain, 1980; Frank & van der Merwe, 1949; Bak *et al.*, 1979; Pokrovsky & Talapov, 1979). The easiest to visualize is epitaxial growth of one crystalline phase on the surface of another when the two lattice vectors are slightly incommensurate. The first atomic row of adsorbate molecules can be positioned to minimize the attractive interactions with the substrate. This is slightly more difficult for the second row, since the distance that minimizes the interaction energy between the first and second rows of adsorbate molecules is not necessarily the same as the distance that would minimize the interaction energy between the first row and the substrate. As more and more rows are added, the energy price of this incommensurability builds up, and one possible configuration that minimizes the global energy is a modulated structure.

In all known cases, the very existence of modulated structures implies that there must be competing interactions, and the only real question about the modulated structures in the crystalline-B phases is the identification of the competing interactions. It appears that one of the more likely possibilities is the difficulty in packing the 7O.7 molecules within a triangular lattice while simultaneously optimizing the area per molecule of the alkane tails and the conjugated rings in the core (Carlson & Sethna, 1987; Sadoc & Charvolin, 1986). Typically, the mean cross-sectional area for a straight alkane in the all-*trans* configuration is between 18 and $19 \text{ \AA}^2$, while the mean area per molecule in the crystalline-B phase is closer to $24 \text{ \AA}^2$. While these two could be reconciled by assuming that the alkanes are tilted with respect to the conjugated core, there is no reason why the angle that reconciles the two should also be the same angle that minimizes the internal energy of the molecule. Even if it were the correct angle at some temperature by accident, the average area per chain is certainly temperature dependent. Even without attempting to include the rotational dynamics that are necessary to understanding the axial site symmetry, it is obvious that there can be a conflict in the packing requirements of the two different parts of the molecule.

A possible explanation of these various structures might be as follows: at high temperatures, both the alkane chain, as well as the

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other degrees of freedom, have considerable thermal motions that make it possible for the conflicting packing requirements to be simultaneously reconciled by one or another compromise. On the other hand, with decreasing temperature, some of the thermal motions become frozen out, and the energy cost of the reconciliation that was possible at higher temperatures becomes too great. At this point, the system must find another solution, and the various modulated phases represent the different compromises. Finally, all of the compromises involving inhomogeneities, like the modulations or grain boundaries, become impossible and the system transforms into a homogeneous crystalline-G phase.

If this type of argument could be made more specific, it would also provide a possible explanation for the molecular origin of the three-dimensional hexatic phases. The original suggestion for the existence of hexatic phases in two dimensions was based on the fact that the interaction energy between dislocations in two dimensions was logarithmic, such that the entropy and the enthalpy had the same functional dependence on the density of dislocations. This gave rise to the observation that above a certain temperature two-dimensional crystals would be unstable against thermally generated dislocations. Although Litster and Birgeneau's suggestion that some of the observed smectic phases might be stacks of two-dimensional hexatics is certainly correct, it is not necessary that the observed three-dimensional hexatics originate from entropy-driven thermally excited dislocations. For example, the temperature–layer-number phase diagram for 7O.7 that is shown in Fig. 4.4.4.5 has the interesting property that the temperature region over which the tilted hexatic phases exist in thin films is almost the same as the temperature region for which the modulated phases exist in thick films and in bulk samples.

From the fact that molecules in the *nO.m* series that only differ by one or two $-\text{CH}_2-$ groups have different sequences of mesomorphic phases, we learn that within any one molecule the difference in chemical potentials between the different mesomorphic phases must be very small (Leadbetter, Mazid & Kelly, 1979; Doucet & Levelut, 1977; Leadbetter, Frost & Mazid, 1979; Leadbetter, Mazid & Richardson, 1980; Smith *et al.*, 1973; Smith & Garland, 1973). For example, although in 7O.7 the smectic-F phase is only observed in finite-thickness films, both 5O.6 and 9O.4 have smectic-F phase in bulk. Thus, in bulk 7O.7 the chemical potential for the smectic-F phase must be only slightly larger than that of the modulated crystalline-B phases, and the effect of the surfaces must be sufficient to reverse the order in samples of finite thickness.

As far as the appearance of the smectic-F phase in 7O.7 is concerned, it is well known that the interaction energy between dislocation pairs is very different near a free surface from that in the bulk (Pershan, 1974; Pershan & Prost, 1975). The origin of this is that the elastic properties of the surface will usually cause the stress field of a dislocation near to the surface either to vanish or to be considerably smaller than it would in the bulk. Since the interaction energy between dislocations depends on this stress field, the surface significantly modifies the dislocation–dislocation interaction. This is a long-range effect, and it would not be surprising if the interactions that stabilized the dislocation arrays to produce the long-wavelength modulations in the thick samples were sufficiently weaker in the samples of finite thickness that the dislocation arrays are disordered. Alternatively, there is evidence that specific surface interactions favour a finite molecular tilt at temperatures where the bulk phases are uniaxial (Farber, 1985). Incommensurability between the period of the tilted surface molecules and the crystalline-B phases below the surface would increase the density of dislocations, and this would also modify the dislocation–dislocation interactions in the bulk.

Sirota *et al.* (1985) and Sirota, Pershan, Sorensen & Collett (1987) demonstrated that, while the correlation lengths of the smectic-F phase have a significant temperature dependence, the

lengths are independent of film thickness, and this supports the argument that although the effects of the surface are important in stabilizing the smectic-F phase in 7O.7, once the phase is established it is essentially no different from the smectic-F phases observed in bulk samples of other materials. Brock *et al.* (1986) observed anisotropies in the correlation lengths of thick samples of 8OSI that are similar to those observed by Sirota.

These observations motivate the hypothesis that the dislocation densities in the smectic-F phases are determined by the same incommensurability that gives rise to the modulated crystalline-B structures. Although all of the experimental evidence supporting this hypothesis was obtained from the smectic-F tilted hexatic phase, there is no reason why this speculation could not apply to both the tilted smectic-I and the untilted hexatic-B phase.

4.4.4.3.2. Crystal-G, crystal-J

The crystalline-G and crystalline-J phases are the ordered versions of the smectic-F and smectic-I phases, respectively. The positions of the principal peaks illustrated in Fig. 4.4.4.4 for the smectic-F(I) are identical to the positions in the smectic-G(J) phase if small thermal shifts are discounted. In both the hexatic and the crystalline phases, the molecules are tilted with respect to the layer normals by approximately 25 to 30° with nearly hexagonal packing around the tilted axis (Doucet & Levelut, 1977; Levelut *et al.*, 1974; Levelut, 1976; Leadbetter, Mazid & Kelly, 1979; Sirota, Pershan, Sorensen & Collett, 1987). The interlayer molecular packing appears to be end to end, in an AAA type of stacking (Benattar *et al.*, 1983; Benattar *et al.*, 1981; Levelut, 1976; Gane *et al.*, 1983). There is only one molecule per unit cell and there is no evidence for the long-wavelength modulations that are so prevalent in the crystalline-B phase that is the next higher temperature phase above the crystalline-G in 7O.7.

4.4.4.4. Crystalline phases with herringbone packing

4.4.4.4.1. Crystal-E

Fig. 4.4.4.7 illustrates the intralayer molecular packing proposed for the crystalline-E phase (Levelut, 1976; Doucet, 1979; Levelut *et al.*, 1974; Doucet *et al.*, 1975; Leadbetter *et al.*, 1976; Richardson *et al.*, 1978; Leadbetter, Frost, Gaughan & Mazid, 1979; Leadbetter, Frost & Mazid, 1979). The molecules are, on average, normal to the

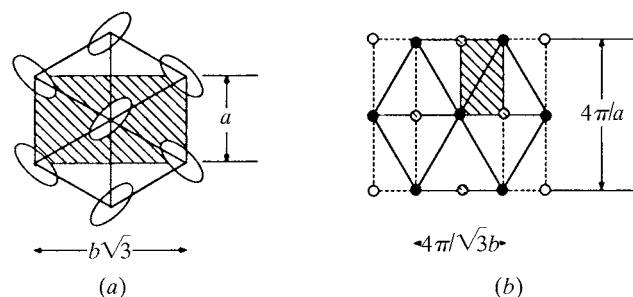


Fig. 4.4.4.7. (a) The 'herringbone' stacking suggested for the crystalline-E phase in which molecular rotation is partially restricted. The primitive rectangular unit cell containing two molecules is illustrated by the shaded region. The lattice has rectangular symmetry and $a \neq b$. (b) The position of the Bragg peaks in the plane in reciprocal space that is parallel to the layers. The dark circles indicate the principal Bragg peaks that would be the only ones present if all molecules were equivalent. The open circles indicate additional peaks that are observed for the model illustrated in (a). The cross-hatched circles indicate peaks that are missing because of the glide plane in (a).

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layers; however, from the optical birefringence it is apparent that the site symmetry is not uniaxial. X-ray diffraction studies on single crystals by Doucet and co-workers demonstrated that the biaxiality was not attributable to molecular tilt and subsequent work by a number of others resulted in the arrangement shown in Fig. 4.4.4.7(a). The most important distinguishing reciprocal-space feature associated with the intralayer 'herringbone' packing is the appearance of Bragg peaks at $\sin(\theta)$ equal to $\sqrt{7}/2$ times the value for the lowest-order in-plane Bragg peak for the triangular lattice (Pindak *et al.*, 1981). These are illustrated by the open circles in Fig. 4.4.4.7(b). The shaded circles correspond to peaks that are missing because of the glide plane that relates the two molecules in the rectangular cell.

Leadbetter, Mazid & Malik (1980) carried out detailed studies on both the crystalline-E phase of isobutyl 4-(4-phenylbenzylidene-amino)cinnamate (IBPBAC) and the crystalline phase immediately below the crystalline-E phase. Partially ordered samples of the crystalline-E phase were obtained by melting the lower-temperature crystalline phase. Although the data for the crystalline-E phase left some ambiguity, they argued that the phase they were studying might well have had molecular tilts of the order of 5 or 6°. This is an important distinction, since the crystalline-H and crystalline-J phases are essentially tilted versions of the crystalline-E. Thus, one important symmetry difference that might distinguish the crystalline-E from the others is the presence of a mirror plane parallel to the layers. In view of the low symmetry of the individual molecules, the existence of such a mirror plane would imply residual molecular motions. In fact, using neutron diffraction Leadbetter *et al.* (1976) demonstrated for a different liquid crystal that, even though the site symmetry is not axially symmetric, there is considerable residual rotational motion in the crystalline-E phase about the long axis of the molecules. Since the in-plane spacing is too small for neighbouring molecules to be rotating independently of each other, they proposed what might be interpreted as large partially hindered rotations.

4.4.4.4.2. Crystal-H, crystal-K

The crystalline-H and crystalline-K phases are tilted versions of the crystalline-E. The crystalline-H is tilted in the direction between the near neighbours, with the convenient mnemonic that on cooling the sequence of phases with the same relative orientation of tilt to near-neighbour position is $F \rightarrow G \rightarrow H$. Similarly, the tilt direction for the crystalline-K phase is similar to that of the smectic-I and crystalline-J so that the expected phase sequence on cooling might be $I \rightarrow J \rightarrow K$. In fact, both of these sequences are only intended to indicate the progression in lower symmetry; the actual transitions vary from material to material.

4.4.5. Discotic phases

In contrast to the long thin rod-like molecules that formed most of the other phases discussed in this chapter, the discotic phases are formed by molecules that are more disc-like [see Fig. 4.4.1.3(f), for example]. There was evidence that mesomorphic phases were formed from disc-like molecules as far back as 1960 (Brooks & Taylor, 1968); however, the first identification of a discotic phase was by Chandrasekhar *et al.* (1977) with benzenhexyl hexa-*n*-alkanoate compounds. Disc-like molecules can form either a fluid nematic phase in which the disc normals are aligned, without any particular long-range order at the molecular centre of mass, or more-ordered 'columnar' (Helfrich, 1979) or 'discotic' (Billard *et al.*, 1981) phases in which the molecular positions are correlated such that the discs stack on top of one another to form columns. Some of the literature designates this nematic phase as N_D to distinguish it from the phase formed by 'rod-like' molecules

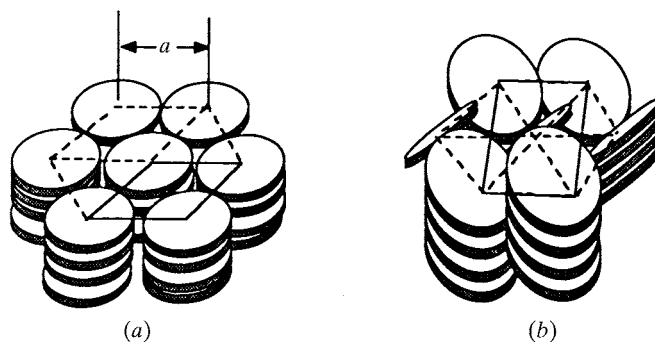


Fig. 4.4.5.1. Schematic illustration of the molecular stacking for the discotic (a) D_2 and (b) D_1 phases. In neither of these two phases is there any indication of long-range positional order along the columns. The hexagonal symmetry of the D_1 phase is broken by 'herringbone-like' correlations in the molecular tilt from column to column.

(Destrade *et al.*, 1983). In the same way that the appearance of layers characterizes order in smectic phases, the order for the discotic phases is characterized by the appearance of columns. Chandrasekhar (1982, 1983) and Destrade *et al.* (1983) have reviewed this area and have summarized the several notations for various phases that appear in the literature. Levelut (1983) has also written a review and presented a table listing the space groups for columnar phases formed by 18 different molecules. Unfortunately, it is not absolutely clear which of these are mesomorphic phases and which are crystals with true long-range positional order.

Fig. 4.4.5.1 illustrates the molecular packing in two of the well identified discotic phases that are designated as D_1 and D_2 (Chandrasekhar, 1982). The phase D_2 consists of a hexagonal array of columns for which there is no intracolumnar order. The system is uniaxial and, as originally proposed, the molecular normals were supposed to be along the column axis. However, recent X-ray scattering studies on oriented free-standing fibres of the D_2 phase of triphenylene hexa-*n*-dodecanoate indicate that the molecules are tilted with respect to the layer normal (Safinya *et al.*, 1985, 1984). The D_1 phase is definitely a tilted phase, and consequently the columns are packed in a rectangular cell. According to Safinya *et al.*, the D_1 to D_2 transition corresponds to an order-disorder transition in which the molecular tilt orientation is ordered about the column axis in the D_1 phase and disordered in the D_2 phase. The reciprocal-space structure of the D_1 phase is similar to that of the crystalline-E phase shown in Fig. 4.4.4.7(b).

Other discotic phases that have been proposed would have the molecules arranged periodically along the column, but disordered between columns. This does not seem physically realistic since it is well known that thermal fluctuations rule out the possibility of a one-dimensional periodic structure even more strongly than for the two-dimensional lattice that was discussed above (Landau, 1965; Peierls, 1934). On the other hand, in the absence of either more high-resolution studies on oriented fibres or further theoretical studies, we prefer not to speculate on the variety of possible true discotic or discotic-like crystalline phases that might exist. This is a subject for future research.

4.4.6. Other phases

We have deliberately chosen not to discuss the properties of the cholesteric phase in this chapter because the length scales that characterize the long-range order are of the order of micrometres and are more easily studied by optical scattering than by X-rays (De Gennes, 1974; De Vries, 1951). Nematic phases formed from chiral

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molecules develop long-range order in which the orientation of the director $\langle \mathbf{n} \rangle$ varies in a plane-wave-like manner that can be described as $\mathbf{x} \cos(2\pi z/\lambda) + \mathbf{y} \sin(2\pi z/\lambda)$, where $\mathbf{x}$ and $\mathbf{y}$ are unit vectors and $\lambda/2$ is the cholesteric ‘pitch’ that can be anywhere from 0.1 to 10 μm depending on the particular molecule. Even more interesting is that for many cholesteric systems there is a small temperature range, of the order of 1 K, between the cholesteric and isotropic phases for which there is a phase known as the ‘blue phase’ (Coates & Gray, 1975; Stegemeyer & Bergmann, 1981; Meiboom *et al.*, 1981; Bensimon *et al.*, 1983; Hornreich & Shtrikman, 1983; Crooker, 1983). In fact, there is more than one ‘blue phase’ but they all have the property that the cholesteric twist forms a three-dimensional lattice twisted network rather than the plane-wave-like twist of the cholesteric phase. Three-dimensional Bragg scattering from blue phases using laser light indicates cubic lattices; however, since the optical cholesteric interactions are much stronger than the usual interactions between X-rays and atoms, interpretation of the results is subtler.

Gray and Goodby discuss a ‘smectic-D’ phase that is otherwise omitted from this chapter (Gray & Goodby, 1984). Gray and co-workers first observed this phase in the homologous series of 4'-*n*-alkoxy-3'-nitrobiphenyl-4-carboxylic acids (Gray *et al.*, 1957). In the hexadecyloxy compound, this phase exists for a region of about 26 K between the smectic-C and smectic-A phases: smectic-C (444.2 K) smectic-D (470.4 K) smectic-A. It is optically isotropic and X-ray studies by Diele *et al.* (1972) and by Tardieu & Billard (1976) indicate a number of similarities to the ‘cubic-isotropic’ phase observed in lyotropic systems (Luzzati & Riess-Husson, 1966; Tardieu & Luzzati, 1970). More recently, Etherington *et al.* (1986) studied the ‘smectic-D’ phase of 3'-cyano-4'-*n*-octadecyloxy-biphenyl-4-carboxylic acid. Since this material appears to be more stable than some of the others that were previously studied, they were able to perform sufficient measurements to determine that the space group is cubic $P2_13$ or $Pm\bar{3}$ with a lattice parameter of 86 Å. Etherington *et al.* suggested that the ‘smectic-D’ phase that they studied is a true three-dimensional cubic crystal of micelles and noted that the designation of ‘smectic-D’ is not accurate. Guillon & Skoulios (1987) have proposed a molecular model for this and related phases.

Fontell (1974) has reviewed the literature on the X-ray diffraction studies of lyotropic mesomorphic systems and the reader is referred there for more extensive information on those cubic systems. The mesomorphic structures of lyotropic systems are much richer than those of the thermotropic and, in addition to all structures mentioned here, there are lyotropic systems in which the smectic-A lamellae seem to break up into cylindrical rods which seem to have the same macroscopic symmetry as some of the discotic phases. On the other hand, it is also much more difficult to prepare a review for the lyotropic systems in the same type of detail as for the thermotropic. The extra complexity associated with the need to control water concentration as well as temperature has made both theoretical and experimental progress more difficult, and, since there has not been very much experimental work on well oriented samples, detailed knowledge of many of these phases is also limited. Aside from the simpler lamellae systems, which seem to have the same symmetry as the thermotropic smectic-A phase, it is not at all clear which of the other phases are three-dimensional crystals and which are true mesomorphic structures. For example, dipalmitoylphosphatidylcholine has an L_β phase that appears for temperatures and (or) water content that is lower than that of the smectic-A L_α phase (Shipley *et al.*, 1974; Small, 1967; Chapman *et al.*, 1967). The diffraction pattern for this phase contains sharp large-angle reflections that may well correspond to a phase that is like one of the crystalline phases listed in Tables 4.4.1.1 and 4.4.1.2, and Fig. 4.4.1.1. On the other hand, this phase could also be hexatic and we do not have sufficient information to decide. The interested

reader is referred to the referenced articles for further detailed information.

4.4.7. Notes added in proof to first edition

4.4.7.1. Phases with intermediate molecular tilt: smectic-L, crystalline-M,N

Following the completion of this manuscript, Smith and co-workers [G. S. Smith, E. B. Sirota, C. R. Safinya & N. A. Clark (1988). *Phys. Rev. Lett.* **60**, 813–816; E. B. Sirota, G. S. Smith, C. R. Safinya, R. J. Plano & N. A. Clark (1988). *Science*, **242**, 1406–1409] published an X-ray scattering study of the structure of a freely suspended multilayer film of hydrated phosphatidylcholine in which the phase that had been designated L_β' in the literature on lipid phases [M. J. Janiak, D. M. Small & G. G. Shipley (1979). *J. Biol. Chem.* **254**, 6068–6078; V. Luzzati (1968). In *Biological Membranes: Physical Fact and Function*, Vol. 1, edited by D. Chapman, pp. 71–123; A. Tardieu, V. Luzzati & F. C. Reman (1973). *J. Mol. Biol.* **75**, 711–733] was shown to consist of three separate two-dimensional phases in which the positional order in adjacent layers is uncoupled. The three phases are distinguished by the direction of the alkane-chain tilt relative to the nearest neighbours, and in one of these phases the orientation varies continuously with increasing hydration. At the lowest hydration, they observe a phase in which the tilt is towards the second-nearest neighbour; in analogy to the smectic-F phase, they designate this phase $L_{\beta F}$. On increasing hydration, they observe a phase in which the tilt direction is intermediate between the nearest- and next-nearest-neighbour directions, and which varies continuously with hydration. This is a new phase that was not previously known and they designate it $L_{\beta L}$. On further hydration, they observe a phase in which the molecular tilt is towards a nearest neighbour and this is designated $L_{\beta I}$. At maximum hydration, they observe the phase with long-wavelength modulation that was previously designated P_β [M. J. Janiak, D. M. Small & G. G. Shipley (1979). *J. Biol. Chem.* **254**, 6068–6078]. J. V. Selinger & D. R. Nelson [*Phys. Rev. Lett.* (1988), **61**, 416–419] have subsequently developed a theory for the phase transitions between phases with varying tilt orientation and have rationalized the existence of phases with intermediate tilt. To be complete, both Fig. 4.4.1.1 and Table 4.4.1.1 should be amended to include this type of hexatic order which is now referred to as the smectic-L. Extension of the previous logic suggests that the crystalline phases with intermediate tilt should be designated M and N, where N has ‘herringbone’ type of intermolecular order.

4.4.7.2. Nematic to smectic-A phase transition

At the time this manuscript was prepared, there was a fundamental discrepancy between theoretical predictions for the details of the critical properties of the second-order nematic to smectic-A phase transition. This has been resolved. W. G. Bouwan & W. H. de Jeu [*Phys. Rev. Lett.* (1992), **68**, 800–803] reported an X-ray scattering study of the critical properties of octyloxy-phenylcyanobenzoyloxybenzoate in which the data were in good agreement with predictions of the three-dimensional xy model [T. C. Lubensky (1983). *J. Chim. Phys.* **80**, 31–43; J. C. Le Guillou & J. Zinn-Justin (1985). *J. Phys. Lett.* **52**, L-137–L-141]. The differences between this experiment and others that were discussed previously, and which did not agree with theory, are firstly that this material is much further from the tricritical point that appears to be ubiquitous for most liquid-crystalline materials and, secondly, that they used the Landau–De Gennes theory to argue that the critical temperature dependence for the $Q_\perp^4$ term in the differential cross section given in equation (4.4.2.7) is not that of the $c\xi_\perp^4$ term but

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rather should vary as $[(T - T_{\text{NA}})/T]^{-\gamma/4}$, where γ is the exponent that describes the critical-temperature dependence of the smectic order parameter $|\Psi|^2 \simeq [(T - T_{\text{NA}})/T]^{-\gamma}$. The experimental results are in good agreement with the Monte Carlo simulation of the N-S_A transition that was reported by C. Dasgupta [*Phys. Rev. Lett.* (1985), **55**, 1771–1774; *J. Phys. (Paris)*, (1987), **48**, 957–970].

4.5. Polymer crystallography

BY R. P. MILLANE AND D. L. DORSET

4.5.1. Overview (R. P. MILLANE AND D. L. DORSET)

Linear polymers from natural or synthetic sources are actually polydisperse aggregates of high-molecular-weight chains. Nevertheless, many of these essentially infinite-length molecules can be prepared as solid-state specimens that contain ordered molecular segments or crystalline inclusions (Vainshtein, 1966; Tadokoro, 1979; Mandelkern, 1989; Barham, 1993). In general, ordering can occur in a number of ways. Hence an oriented and/or somewhat ordered packing of chain segments might be found in a stretched fibre, or in the chain-folded arrangement of a lamellar crystallite. Lamellae themselves may exist as single plates or in the more complex array of a spherulite (Geil, 1963). Diffraction data can be obtained from these various kinds of specimens and used to determine molecular and crystal structures.

There are numerous reasons why crystallography of polymers is important. Although it may be possible to crystallize small constituent fragments of these large molecules and determine their crystal structures, one often wishes to study the intact (and biologically or functionally active) polymeric system. The molecular conformations and intermolecular interactions are determinants of parameters such as persistence length which affect, for example, solution conformations (random or worm-like coils) which determine viscosity. Molecular conformations also influence intermolecular interactions, which determine physical properties in gels and melts. Molecular conformations are, of course, of critical importance in many biological recognition processes. Knowledge of the stereochemical constraints that are placed on the molecular packing to maximize unit-cell density is particularly relevant to the fact that many linear molecules (as well as monodisperse substances with low molecular weight) can adopt several different allomorphic forms, depending on the crystallization conditions employed or the biological origin. Since different allomorphs can behave quite differently from one another, it is clear that the mode of chain packing is related to the bulk properties of the polymer (Grubb, 1993). The three-dimensional geometry of the chain packing obtained from a crystal structure analysis can be used to investigate other phenomena such as the possible inclusion of disordered material in *chain-fold* regions (Mandelkern, 1989; Lotz & Wittmann, 1993), the ordered interaction of crystallite sectors across grain boundaries where tight interactions are found between domains, or the specific interactions of polymer chains with another substance in a composite material (Lotz & Wittmann, 1993).

The two primary crystallographic techniques used for studying polymer structure are described in this chapter. The first is X-ray fibre diffraction analysis, described in Section 4.5.2; and the second is polymer electron crystallography, described in Section 4.5.3.

Crystallographic studies of polymers were first performed using X-ray diffraction from oriented fibre specimens. Early applications were to cellulose and DNA from the 1930s to the 1950s, and the technique has subsequently been applied to hundreds of biological and synthetic polymers (Arnott, 1980; Millane, 1988). This technique is now referred to as *X-ray fibre diffraction analysis*. In fact, fibre diffraction analysis can be employed not only for polymers, but for any system that can be oriented. Indeed, one of the first applications of the technique was to tobacco mosaic virus (Franklin, 1955). Fibre diffraction analysis has also utilized, in some cases, neutrons instead of X-rays (*e.g.* Stark *et al.*, 1988; Forsyth *et al.*, 1989). X-ray fibre diffraction analysis is particularly suitable for biological polymers that form natural fibrous superstructures and even for many synthetic polymers that exist in either a fibrous or a liquid-crystalline state. Fibre diffraction has played an important role in structural studies of polynucleotides, polysacchar-

ides, polypeptides and polyesters, as well as rod-like helical viruses, bacteriophages, microtubules and muscle fibres (Arnott, 1980; French & Gardner, 1980; Hall, 1984; Millane, 1988; Atkins, 1989). The common, and unique, feature of these systems is that the molecules (or their aggregates) are randomly rotated about an axis of preferred orientation. As a result, the measured diffraction is the cylindrical average of that from a single molecule or aggregate. The challenge for the structural scientist, therefore, is that of structure determination from cylindrically averaged diffraction intensities. Since a wide range of types and degrees of order (or disorder) occur in fibrous specimens, as well as a wide range of sizes of the repeating units, a variety of methods are used for structure determination.

The second technique used for structural studies of polymers is *polymer electron crystallography*. This involves measuring electron intensity data from individual crystalline regions or lamellae in the diffraction plane of an electron microscope. This is possible because a narrow electron beam can be focused on a single thin microcrystal and because of the enhanced scattering cross section of matter for electrons. By tilting the specimen, three-dimensional diffraction intensities from a single microcrystal can be collected. This means that the unit-cell dimensions and symmetry can be obtained unambiguously in electron-diffraction experiments on individual chain-folded lamellae, and the data can be used for actual single-crystal structure determinations. One of the first informative electron-diffraction studies of crystalline polymer films was made by Storks (1938), who formulated the concept of chain folding in polymer lamellae. Among the first quantitative structure determinations from electron-diffraction intensities was that of Tatarinova & Vainshtein (1962) on the α form of poly- γ -methyl-L-glutamate. Quantitative interpretation of the intensity data may benefit from the assumption of *quasi-kinematical* scattering (Dorset, 1995a), as long as the proper constraints are placed on the experiment. Structure determination may then proceed using the traditional techniques of X-ray crystallography. While molecular-modelling approaches (in which atomic level molecular and crystal structure models are constructed and refined) have been employed with single-crystal electron-diffraction data (Brissette, 1989), the importance of *ab initio* structure determination has been established in recent years (Dorset, 1995b), demonstrating that no initial assumptions about the molecular geometry need be made before the determination is begun. In some cases too, high-resolution electron micrographs of the polymer crystal structure can be used as an additional means for determining crystallographic phases and/or to visualize lattice defects.

Each of the two techniques described above has its own advantages and disadvantages. While specimen disorder can limit the application of X-ray fibre diffraction analysis, polymer electron diffraction is limited to materials that can be prepared as crystalline lamellae and that can withstand the high vacuum environment of an electron microscope (although the latter restriction can now be largely overcome by the use of low-temperature specimen holders and/or environmental chambers).

4.5.2. X-ray fibre diffraction analysis (R. P. MILLANE)

4.5.2.1. Introduction

X-ray fibre diffraction analysis is a collection of crystallographic techniques that are used to determine molecular and crystal structures of molecules, or molecular assemblies, that form specimens (often fibres) in which the molecules, assemblies or

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crystallites are approximately parallel but not otherwise ordered (Arnott, 1980; French & Gardner, 1980; Hall, 1984; Vibert, 1987; Millane, 1988; Atkins, 1989; Stubbs, 1999). These are usually long, slender molecules and they are often inherently flexible, which usually precludes the formation of regular three-dimensional crystals suitable for conventional crystallographic analysis. X-ray fibre diffraction therefore provides a route for structure determination for certain kinds of specimens that cannot be crystallized. Although it may be possible to crystallize small *fragments* or *subunits* of these molecules, and determine the crystal structures of these, X-ray fibre diffraction provides a means for studying the intact, and often the biologically or functionally active, system. Fibre diffraction has played an important role in the determination of biopolymers such as polynucleotides, polysaccharides (both linear and branched), polypeptides and a wide variety of synthetic polymers (such as polyesters), as well as larger assemblies including rod-like helical viruses, bacteriophages, microtubules and muscle fibres (Arnott, 1980; Arnott & Mitra, 1984; Millane, 1990c; Squire & Vibert, 1987).

Specimens appropriate for fibre diffraction analysis exhibit rotational disorder (of the molecules, aggregates or crystallites) about a preferred axis, resulting in cylindrical averaging of the diffracted intensity in reciprocal space. Therefore, fibre diffraction analysis can be thought of as 'structure determination from cylindrically averaged diffraction intensities' (Millane, 1993). In a powder specimen the crystallites are completely (spherically) disordered, so that structure determination by fibre diffraction can be considered to be intermediate between structure determination from single crystals and from powders.

This section is a review of the theory and techniques of structure determination by X-ray fibre diffraction analysis. It includes descriptions of fibre specimens, the theory of diffraction by these specimens, intensity data collection and processing, and the variety of structure determination methods used for the various kinds of specimens studied by fibre diffraction. It does not include descriptions of specimen preparation (those can be found in the references given for specific systems), or of applications of X-ray diffraction to determining polymer morphology (*e.g.* particle or void sizes and shapes, texture, domain structure *etc.*).

4.5.2.2. Fibre specimens

A wide variety of kinds of fibre specimen exist. All exhibit preferred orientation; the variety results from variability in the degree of order (crystallinity) in the lateral plane (the plane perpendicular to the axis of preferred orientation). This leads to categorization of three kinds of fibre specimen: *noncrystalline fibres*, in which there is no order in the lateral plane; *polycrystalline fibres*, in which there is near-perfect crystallinity in the lateral plane; and *disordered fibres*, in which there is disorder either within the molecules or in their crystalline packing (or both). The kind of fibre specimen affects the kind of diffraction pattern obtained, the relationships between the molecular and crystal structures and the diffraction data, methods of data collection, and methods of structure determination.

Noncrystalline fibres are made up of a collection of molecules that are *oriented*. This means that there is a common axis in each molecule (referred to here as the *molecular axis*), the axes being parallel in the specimen. The direction of preferred orientation is called the *fibre axis*. The molecule itself is usually considered to be a rigid body. There is no other ordering within the specimen. The molecules are therefore randomly positioned in the lateral plane and are randomly rotated about their molecular axes. Furthermore, if the molecule does not have a twofold rotation axis normal to the molecular axis, then the molecular axis has a *direction* associated with it, and the molecular axes are oriented randomly parallel or

antiparallel to each other. This is often called *directional disorder*, or the molecules are said to be oriented *randomly up and down*. The average length of the ordered molecular segments in a noncrystalline fibre is referred to as the *coherence length*.

Polycrystalline fibres are characterized by molecular segments packing together to form well ordered microcrystallites within the specimen. The crystallites effectively take the place of the molecules in a noncrystalline specimen as described above. The crystallites are oriented, and since the axis within each crystallite that is aligned parallel to those in other crystallites usually corresponds to the long axes of the constituent molecules, it is also referred to here as the molecular axis. The crystallites are randomly positioned in the lateral plane, randomly rotated about the molecular axis, and randomly oriented up or down. The size of the crystalline domains can be characterized by their average dimensions in the directions of the **a**, **b** and **c** unit-cell vectors. However, because of the rotational disorder of the crystallites, any differences between crystallite dimensions in different directions normal to the fibre axis tend to be smeared out in the diffraction pattern, and the crystallite size is usefully characterized by the average dimensions of the crystallites normal and parallel to the fibre axis.

The molecules or crystallites in a fibre specimen are not perfectly oriented, and the variation in inclinations of the molecular axes to the fibre axis is referred to as *disorientation*. Assuming that the orientation is axisymmetric, then it can be described by an *orientation density function* $\Omega(\alpha)$ such that $\Omega(\alpha) d\omega$ is the fraction of molecules in an element of solid angle $d\omega$ inclined at an angle α to the fibre axis. The exact form of $\Omega(\alpha)$ is generally not known for any particular fibre and it is often sufficient to assume a Gaussian orientation density function, so that

$$\Omega(\alpha) = \frac{1}{2\pi\alpha_0^2} \exp\left(-\frac{\alpha^2}{2\alpha_0^2}\right), \quad (4.5.2.1)$$

where α_0 is a measure of the degree of disorientation.

Fibre specimens often exhibit various kinds of disorder. The disorder may be within the molecules or in their packing. Disorder affects the relationship between the molecular and crystal structure and the diffracted intensities. Disorder within the molecules may result from a degree of randomness in the chemical sequence of the molecule or from variability in the interactions between the units that make up the molecule. Such molecules may (at least in principle) form noncrystalline, polycrystalline or partially crystalline (described below) fibres. Disordered packing of molecules within crystallites can result from a variety of ways in which the molecules can interact with each other. Fibre specimens made up of disordered crystallites are referred to here as partially crystalline fibres.

4.5.2.3. Diffraction by helical structures

Molecules or assemblies studied by fibre diffraction are usually made up of a large number of identical, or nearly identical, residues, or subunits, that in an oriented specimen are distributed along an axis; this leads naturally to helical symmetry. Since a periodic structure with no helix symmetry can be treated as a onefold helix, the assumption of helix symmetry is not restrictive.

4.5.2.3.1. Helix symmetry

The presence of a unique axis about which there is rotational disorder means that it is convenient to use cylindrical polar coordinate systems in fibre diffraction. We denote by (r, φ, z) a cylindrical polar coordinate system in real space, in which the z axis is parallel to the molecular axes. The molecule is said to have u_v helix symmetry, where u and v are integers, if the electron density

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$f(r, \varphi, z)$ satisfies

$$f(r, \varphi + (2\pi mv/u), z + (mc/u)) = f(r, \varphi, z), \quad (4.5.2.2)$$

where m is any integer. The constant c is the period along the z direction, which is referred to variously as the *molecular repeat distance*, the *crystallographic repeat*, or the *c repeat*. The helix pitch P is equal to c/v . Helix symmetry is easily interpreted as follows. There are u subunits, or *helix repeat units*, in one c repeat of the molecule. The helix repeat units are repeated by integral rotations of $2\pi v/u$ about, and translations of c/u along, the molecular (or helix) axis. The helix repeat units may therefore be referenced to a helical lattice that consists of points at a fixed radius, with relative rotations and translations as described above. These points lie on a helix of pitch P , there are v turns (or pitch-lengths) of the helix in one c repeat, and there are u helical lattice points in one c repeat. A u , v helix is said to have ' u residues in v turns'.

Since the electron density is periodic in φ and z , it can be decomposed into a Fourier series as

$$f(r, \varphi, z) = \sum_{l=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} g_{nl}(r) \exp(i[n\varphi - (2\pi lz/c)]), \quad (4.5.2.3)$$

where the coefficients $g_{nl}(r)$ are given by

$$g_{nl}(r) = (c/2\pi) \int_0^{2\pi} \int_0^c f(r, \varphi, z) \exp(i[-n\varphi + (2\pi lz/c)]) d\varphi dz. \quad (4.5.2.4)$$

Assume now that the electron density has helical symmetry. Denote by $g(r, \varphi, z)$ the electron density in the region $0 < z < c/u$; the electron density being zero outside this region, i.e. $g(r, \varphi, z)$ is the electron density of a single helix repeat unit. It follows that

$$f(r, \varphi, z) = \sum_{m=-\infty}^{\infty} g[r, \varphi + (2\pi mv/u), z + (mc/u)]. \quad (4.5.2.5)$$

Substituting equation (4.5.2.5) into equation (4.5.2.4) shows that $g_{nl}(r)$ vanishes unless $(l - nv)$ is a multiple of u , i.e. unless

$$l = um + vn \quad (4.5.2.6)$$

for any integer m . Equation (4.5.2.6) is called the *helix selection rule*. The electron density in the helix repeat unit is therefore given by

$$g(r, \varphi, z) = \sum_l \sum_n g_{nl}(r) \exp(i[n\varphi - (2\pi lz/c)]), \quad (4.5.2.7)$$

where

$$g_{nl}(r) = (c/2\pi) \int \int g(r, \varphi, z) \exp(i[-n\varphi + (2\pi lz/c)]) d\varphi dz, \quad (4.5.2.8)$$

and where in equation (4.5.2.7) (and in the remainder of this section) the sum over l is over all integers, the sum over n is over all integers satisfying the helix selection rule and the integral in equation (4.5.2.8) is over one helix repeat unit. The effect of helix symmetry, therefore, is to restrict the number of Fourier coefficients $g_{nl}(r)$ required to represent the electron density to those whose index n satisfies the selection rule. Note that the selection rule is usually derived using a rather more complicated argument by considering the convolution of the Fourier transform of a continuous filamentary helix with a set of planes in reciprocal space (Cochran *et al.*, 1952). The approach described above, which follows that of Millane (1991), is much more straightforward.

4.5.2.3.2. Diffraction by helical structures

Denote by (R, ψ, Z) a cylindrical polar coordinate system in reciprocal space (with the Z and z axes parallel), and by $F(R, \psi, Z)$ the Fourier transform of $f(r, \varphi, z)$. Since $f(r, \varphi, z)$ is periodic in z with period c , its Fourier transform is nonzero only on the *layer planes* $Z = l/c$ where l is an integer. Denote $F(R, \psi, l/c)$ by $F_l(R, \psi)$; using the cylindrical form of the Fourier transform shows that

$$F_l(R, \psi) = \int_0^c \int_0^{2\pi} \int_0^\infty f(r, \varphi, z) \exp(i2\pi[Rr \cos(\psi - \varphi) + (lz/c)]) r dr d\varphi dz. \quad (4.5.2.9)$$

It is convenient to rewrite equation (4.5.2.9) making use of the Fourier decomposition described in Section 4.5.2.3.1, since this allows utilization of the helix selection rule. The *Fourier-Bessel structure factors* (Klug *et al.*, 1958), $G_{nl}(R)$, are defined as the Hankel transform of the Fourier coefficients $g_{nl}(r)$, i.e.

$$G_{nl}(R) = \int_0^\infty g_{nl}(r) J_n(2\pi Rr) 2\pi r dr, \quad (4.5.2.10)$$

and the inverse transform is

$$g_{nl}(r) = \int_0^\infty G_{nl}(R) J_n(2\pi Rr) 2\pi R dR. \quad (4.5.2.11)$$

Using equations (4.5.2.7) and (4.5.2.11) shows that equation (4.5.2.9) can be written as

$$F_l(R, \psi) = \sum_n G_{nl}(R) \exp(in[\psi + (\pi/2)]), \quad (4.5.2.12)$$

where, as usual, the sum is over only those values of n that satisfy the helix selection rule. Using equations (4.5.2.8) and (4.5.2.10) shows that the Fourier-Bessel structure factors may be written in terms of the atomic coordinates as

$$G_{nl}(R) = \sum_j f_j(\rho) J_n(2\pi Rr_j) \exp(i[-n\varphi_j + (2\pi lz_j/c)]), \quad (4.5.2.13)$$

where $f_j(\rho)$ is the (spherically symmetric) atomic scattering factor (usually including an isotropic temperature factor) of the j th atom and $\rho = (R^2 + l^2/Z^2)^{1/2}$ is the spherical radius in reciprocal space. Equations (4.5.2.12) and (4.5.2.13) allow the complex diffracted amplitudes for a helical molecule to be calculated from the atomic coordinates, and are analogous to expressions for the structure factors in conventional crystallography.

The significance of the selection rule is now more apparent. On a particular layer plane l , not all Fourier-Bessel structure factors $G_{nl}(R)$ contribute; only those whose Bessel order n satisfies the selection rule for that value of l contribute. Since any molecule has a maximum radius, denoted here by $r_{\max}$, and since $J_n(x)$ is small for $x < |n| - 2$ and diffraction data are measured out to only a finite value of R , reference to equation (4.5.2.10) [or equation (4.5.2.13)] shows that there is a maximum Bessel order that contributes significant value to equation (4.5.2.12) (Crowther *et al.*, 1970; Makowski, 1982), so that the infinite sum over n in equation (4.5.2.12) can be replaced by a finite sum. On each layer plane there is also a minimum value of $|n|$, denoted by $n_{\min}$, that satisfies the helix selection rule, so that the region $R < R_{\min}$ is devoid of diffracted amplitude where

$$R_{\min} = \frac{n_{\min} - 2}{2\pi r_{\max}}. \quad (4.5.2.14)$$

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The selection rule therefore results in a region around the Z axis of reciprocal space that is devoid of diffraction, the shape of the region depending on the helix symmetry.

4.5.2.3.3. Approximate helix symmetry

In some cases the nature of the subunits and their interactions results in a structure that is not exactly periodic. Consider a helical structure with $u + x$ subunits in v turns, where x is a small ($x \ll 1$) real number; *i.e.* the structure has approximate, but not exact, u_v helix symmetry. Since the molecule has an *approximate* repeat distance c , only those layer planes close to those at $Z = l/c$ show significant diffraction. Denoting by Z_{mn} the Z coordinate of the n th Bessel order and its associated value of m , and using the selection rule shows that

$$Z_{mn} = [(um + vn)/c] + (mx/c) = (l/c) + (mx/c), \quad (4.5.2.15)$$

so that the positions of the Bessel orders are shifted by mx/c from their positions if the helix symmetry is exactly u_v . At moderate resolution m is small so the shift is small. Hence Bessel orders that would have been coincident on a particular layer plane are now separated in reciprocal space. This is referred to as *layer-plane splitting* and was first observed in fibre diffraction patterns from tobacco mosaic virus (TMV) (Franklin & Klug, 1955). Splitting can be used to advantage in structure determination (Section 4.5.2.6.6).

As an example, TMV has approximately 49_3 helix symmetry with a c repeat of 69 Å. However, close inspection of diffraction patterns from TMV shows that there are actually about 49.02 subunits in three turns (Stubbs & Makowski, 1982). The virus is therefore more accurately described as a 2451_{150} helix with a c repeat of 3450 Å. The layer lines corresponding to this larger repeat distance are not observed, but the effects of layer-plane splitting are detectable (Stubbs & Makowski, 1982).

4.5.2.4. Diffraction by fibres

The kind of diffraction pattern obtained from a fibre specimen made up of helical molecules depends on the kind of specimen as described in Section 4.5.2.2. This section is divided into four parts. The first two describe diffraction patterns obtained from noncrystalline and polycrystalline fibres (which are the most common kinds used for structural analysis), and the last two describe diffraction by partially crystalline fibres.

4.5.2.4.1. Noncrystalline fibres

A noncrystalline fibre is made up of a collection of helical molecules that are oriented parallel to each other, but are otherwise randomly positioned and rotated relative to each other. The recorded intensity, $I_l(R)$, is therefore that diffracted by a single molecule cylindrically averaged about the Z axis in reciprocal space *i.e.*

$$I_l(R) = (1/2\pi) \int_0^{2\pi} |F_l(R, \psi)|^2 d\psi; \quad (4.5.2.16)$$

using equation (4.5.2.12) shows that

$$I_l(R) = \sum_n |G_{nl}(R)|^2, \quad (4.5.2.17)$$

where, as usual, the sum is over the values of n that satisfy the helix selection rule. On the diffraction pattern, reciprocal space (R, ψ, Z) collapses to the two dimensions (R, Z) . The R axis is called the *equator* and the Z axis the *meridian*. The layer planes collapse to *layer lines*, at $Z = l/c$, which are indexed by l . Equation (4.5.2.17) gives a rather simple relationship between the recorded intensity and the Fourier–Bessel structure factors.

Coherence length and disorientation, as described in Section 4.5.2.2, also affect the form of the diffraction pattern. These effects are described here, although they also apply to other than noncrystalline fibres. A finite coherence length leads to smearing of the layer lines along the Z direction. If the average coherence length of the molecules is l_c , the intensity distribution $I_l(R, Z)$ about the l th layer line can be approximated by

$$I_l(R, Z) = I_l(R) \exp(-\pi l_c^2 [Z - (l/c)]^2). \quad (4.5.2.18)$$

It is convenient to express the effects of disorientation on the intensity distribution of a fibre diffraction pattern by writing the latter as a function of the polar coordinates (ρ, σ) (where σ is the angle with the Z axis) in (R, Z) space. Assuming a Gaussian orientation density function [equation (4.5.2.1)], if α_0 is small and the effects of disorientation dominate over those of coherence length (which is usually the case except close to the meridian), then the distribution of intensity about one layer line can be approximated by (Holmes & Barrington Leigh, 1974; Stubbs, 1974)

$$I(\rho, \sigma) \simeq \frac{I_l(R)}{2\pi\alpha_0 l_c \rho} \exp\left[-\frac{(\sigma - \sigma_l)^2}{2\beta^2}\right], \quad (4.5.2.19)$$

where (Millane & Arnott, 1986; Millane, 1989c)

$$\beta^2 = \alpha_0^2 + (1/2\pi l_c^2 \rho^2 \sin^2 \sigma_l) \quad (4.5.2.20)$$

and σ_l is the polar angle at the centre of the layer line, *i.e.* $R = \rho \sin \sigma_l$. The effect of disorientation, therefore, is to smear each layer line about the origin of reciprocal space.

4.5.2.4.2. Polycrystalline fibres

A polycrystalline fibre is made up of crystallites that are oriented parallel to each other, but are randomly positioned and randomly rotated about their molecular axes. The recorded diffraction pattern is the intensity diffracted by a single crystallite, cylindrically averaged about the Z axis. On a fibre diffraction pattern, therefore, the Bragg reflections are cylindrically projected onto the (R, Z) plane and their positions are described by the cylindrically projected reciprocal lattice (Finkenstadt & Millane, 1998).

The molecules are periodic and are therefore usually aligned with one of the unit-cell vectors. Since the z axis is defined as the fibre axis, it is usual in fibre diffraction to take the $\mathbf{c}$ lattice vector as the unique axis and as the lattice vector parallel to the molecular axes. It is almost always the case that the fibre is rotationally disordered about the molecular axes, *i.e.* about $\mathbf{c}$. Consider first the case of a monoclinic unit cell ($\alpha = \beta = 90^\circ$) so that the reciprocal lattice is cylindrically projected about $\mathbf{c}^*$. The cylindrical coordinates of the projected reciprocal-lattice points are then given by

$$R_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + 2hka^*b^* \cos \gamma^* \quad (4.5.2.21)$$

and

$$Z_{hkl} = lc^*, \quad (4.5.2.22)$$

so that R depends only on h and k , and Z depends only on l . Reflections with fixed h and k lie on straight *row lines*. Certain sets of distinct reciprocal-lattice points will have the same value of R_{hkl} and therefore superimpose in cylindrical projection. For example, for an orthorhombic system ($\gamma = 90^\circ$) the reciprocal-lattice points (hkl) , $(\bar{h}kl)$, $(h\bar{k}l)$ and $(\bar{h}\bar{k}l)$ superimpose. Furthermore, the crystallites in a fibre specimen are usually oriented randomly up and down so that the reciprocal-lattice points (hkl) and $(h\bar{k}\bar{l})$ superimpose, so that in the orthorhombic case eight reciprocal-lattice points superimpose. Also, as described below, reciprocal-lattice points that have similar values of R can effectively superimpose.

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If the unit cell is either triclinic, or is monoclinic with $\alpha \neq 90^\circ$ or $\beta \neq 90^\circ$, then $\mathbf{c}^*$ is inclined to $\mathbf{c}$ and the Z axis, and the reciprocal lattice is not cylindrically projected about $\mathbf{c}^*$. Equation (4.5.2.22) for Z_{hkl} still applies, but the cylindrical radius is given by

$$R_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 [c^{*2} - (1/c^2)] + 2hka^*b^* \cos \gamma^* + 2hla^*c^* \cos \beta^* + 2klb^*c^* \cos \alpha^* \quad (4.5.2.23)$$

and the row lines are curved (Finkenstadt & Millane, 1998).

The most complicated situation arises if the crystallites are rotationally disordered about an axis that is inclined to $\mathbf{c}$. Reciprocal space is then rotated about an axis that is inclined to the normal to the a^*b^* plane, R_{hkl} and Z_{hkl} are both functions of h, k and l , equation (4.5.2.23) does not apply, and reciprocal-lattice points for fixed l do not lie on layer lines of constant Z . Although this situation is rather unusual, it does occur (Daubeny *et al.*, 1954), and is described in detail by Finkenstadt & Millane (1998).

The observed fibre diffraction pattern consists of reflections at the projected reciprocal-lattice points whose intensities are equal to the sums of the intensities of the contributing structure factors. The observed intensity, denoted by $I_l(R_{hk})$, at a projected reciprocal-lattice point on the l th layer line and with $R = R_{hk}$ is therefore given by (assuming, for simplicity, a monoclinic system)

$$I_l(R_{hk}) = \sum_{h', k' \in \mathcal{J}(h, k)} |F_{h'k'l}|^2, \quad (4.5.2.24)$$

where $\mathcal{J}(h, k)$ denotes the set of indices (h', k') such that $R_{h'k'} = R_{hk}$. The number of independent reflections contributing in equation (4.5.2.24) depends on the space-group symmetry of the crystallites, because of either systematic absences or structure factors whose values are related.

The effect of a finite crystallite size is to smear what would otherwise be infinitely sharp reflections into broadened reflections of a finite size. If the average crystallite dimensions normal and parallel to the z axis are l_{lat} (i.e. in the 'lateral' direction) and l_{axial} (i.e. in the 'axial' direction), respectively, the profile of the reflection centred at $(R_{hk}, Z = l/c)$ can be written as (Fraser *et al.*, 1984; Millane & Arnott, 1986; Millane, 1989c)

$$I(R, Z) = I_l(R_{hk})S(R - R_{hk}, Z - l/c), \quad (4.5.2.25)$$

where the profile function $S(R, Z)$ can be approximated by

$$S(R, Z) = \exp[-\pi(l_{\text{lat}}^2 R^2 + l_{\text{axial}}^2 Z^2)]. \quad (4.5.2.26)$$

The effect of crystallite disorientation is to smear the reflections given by equation (4.5.2.26) about the origin of the projected reciprocal space. If the effects of disorientation dominate over those of crystallite size, then the profile of a reflection can be approximated by (Fraser *et al.*, 1984; Millane & Arnott, 1986; Millane, 1989c)

$$I(\rho, \sigma) \simeq \frac{I_l(R_{hk})}{2\pi\alpha_0 l_{\text{lat}} l_{\text{axial}} \rho} \times \exp\left(-\left[\frac{(\rho - \rho_{hkl})^2}{2\beta_\rho^2} + \frac{(\sigma - \sigma_{hkl})^2}{2\beta_\sigma^2}\right]\right), \quad (4.5.2.27)$$

where $(\rho_{hkl}, \sigma_{hkl})$ are the polar coordinates of the reflection,

$$\beta_\rho^2 = \frac{l_{\text{lat}}^2 l_{\text{axial}}^2}{2\pi(l_{\text{lat}}^2 \sin^2 \sigma_{hkl} + l_{\text{axial}}^2 \cos^2 \sigma_{hkl})} \quad (4.5.2.28)$$

and

$$\beta_\sigma^2 = \alpha_0 + \frac{l_{\text{lat}}^2 l_{\text{axial}}^2}{2\pi\rho_{hkl}^2(l_{\text{axial}}^2 \sin^2 \sigma_{hkl} + l_{\text{lat}}^2 \cos^2 \sigma_{hkl})}. \quad (4.5.2.29)$$

Reflections that have similar enough (R, Z) coordinates overlap severely with each other and are also included in the sum in equation (4.5.2.24). This is quite common in practice because a number of sets of reflections may have similar values of R_{hk} .

4.5.2.4.3. Random copolymers

Random copolymers are made up of a small number of different *kinds* of monomer, whose sequence along the polymer chain is not regular, but is random, or partially random. A particularly interesting class are synthetic polymers such as copolyesters that form a variety of liquid-crystalline phases and have useful mechanical properties (Biswas & Blackwell, 1988a). The structures of these materials have been studied quite extensively using X-ray fibre diffraction analysis. Because the molecules do not have an average c repeat, their diffraction patterns do not consist of equally spaced layer lines. However, as a result of the small number of distinct spacings associated with the monomers, diffracted intensity is concentrated about layer lines, but these are irregularly spaced (along Z) and are *aperiodic*. Since the molecule is not periodic, the basic theory of diffraction by helical molecules described in Section 4.5.2.3.2 does not apply in this case. Cylindrically averaged diffraction from random copolymers is described here. Related approaches have been described independently by Hendricks & Teller (1942) and Blackwell *et al.* (1984). Hendricks & Teller (1942) considered the rather general problem of diffraction by layered structures made up of different kinds of layers, the probability of a layer at a particular level depending on the layers present at adjacent levels. This is a one-dimensional disordered structure that can be used to describe a random copolymer. Blackwell and co-workers have developed a similar theory in terms of a one-dimensional paracrystalline model (Hosemann & Bagchi, 1962) for diffraction by random copolymers (Blackwell *et al.*, 1984; Biswas & Blackwell, 1988a), and this is the theory described here.

Consider a random copolymer made up of monomer units (residues) of N different types. Since the disorder is along the length of the polymer, some of the main characteristics of diffraction from such a molecule can be elucidated by studying the diffraction along the meridian of the diffraction pattern. The meridional diffraction is the intensity of the Fourier transform of the polymer chain projected onto the z axis and averaged over all possible monomer sequences. The diffraction pattern depends on the monomer (molar) compositions, denoted by p_i , the statistics of the monomer sequence (described by the probability of the different possible monomer pairs in this model) and the Fourier transform of the monomer units. Development of this model shows that the meridional diffracted intensity $I(Z)$ can be written in the form (Blackwell *et al.*, 1984; Biswas & Blackwell, 1988a; Schneider *et al.*, 1991)

$$I(Z) = \sum_i p_i |F_i(Z)|^2 + 2 \sum_i \sum_{j \neq i} \Re\{F_i(Z)F_j^*(Z)T_{ij}(Z)\}, \quad (4.5.2.30)$$

where the summations are over the different monomer types and $F_i(Z)$ is the axial Fourier transform of the i th monomer unit (each referenced to a common origin). The $T_{ij}(Z)$ are most conveniently described by defining them as the ij th element of an $N \times N$ matrix $\mathbf{T}$, which is given by

$$\mathbf{T} = \frac{\mathbf{PMX}(Z)}{\mathbf{I} - \mathbf{MX}(Z)}, \quad (4.5.2.31)$$

where $\mathbf{P}, \mathbf{M}, \mathbf{X}(Z)$ and $\mathbf{I}$ are $N \times N$ matrices. $\mathbf{I}$ is the unit matrix and $\mathbf{P}$ is a diagonal matrix with elements p_i . The elements M_{ij} of $\mathbf{M}$ are the probabilities of forming ij monomer pairs and can be generated for different kinds of random sequence (e.g. chemical restrictions on the occurrence of particular monomer pairs, random chains,

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varying degrees of blockiness, tendency towards alternating sequences *etc.*) (Schneider *et al.*, 1991). The matrix $\mathbf{X}(Z)$ is diagonal with elements equal to $\langle \exp(i2\pi Z\zeta_i) \rangle$ where the ζ_i are the projected monomer lengths and the average is over all chain conformations.

Equation (4.5.2.30) can be used to calculate the meridional diffraction for a particular random copolymer. The most important result of such a calculation is that intensity maxima are spaced irregularly along the meridian. The positions of the maxima depend on the monomer proportions, the sequence statistics and the projected monomer lengths.

The full cylindrically averaged diffraction pattern, denoted by $I(R, Z)$, from a noncrystalline specimen containing oriented random copolymer chains can be calculated by replacing $F_i(Z)$ in equation (4.5.2.30) by $F_i(R, Z)$, *i.e.*

$$I(R, Z) = \sum_i p_i |F_i(R, Z)|^2 + 2 \sum_i \sum_{j \neq i} \Re \{ F_i(R, Z) F_j^*(R, Z) T_{ij}(Z) \} \quad (4.5.2.32)$$

(Biswas & Blackwell, 1988a). Note that we write $I(R, Z)$ rather than $I_l(Z)$ since the pattern cannot be indexed on the basis of regularly spaced layer lines. The $F_i(R, Z)$ in equation (4.5.2.32) depend on the chain conformation, since this affects the range of monomer orientations and hence their average diffraction. Chivers & Blackwell (1985) have considered two extreme cases, one corresponding to fixed conformations between monomers and the other corresponding to completely random conformations between monomers, and have derived expressions for the diffracted intensity in both cases. Equation (4.5.2.32) allows one to calculate the fibre diffraction pattern from an array of parallel random copolymers that exhibit no lateral ordering. The diffraction pattern consists of irregularly spaced layer lines whose spacings (in Z) are the same as those described above for the meridional maxima. Measurement of layer-line spacings and intensities and comparison with calculations based on the constituent monomers allows chain conformations to be estimated (Biswas & Blackwell, 1988a).

Diffraction patterns from liquid-crystalline random copolymers often contain sharp Bragg maxima on the layer lines. This indicates that, despite the random sequence and the possible dissimilarity of the component monomers, the chains are able to pack together in a regular way (Biswas & Blackwell, 1988b,c). Expressions that allow calculation of diffraction patterns for arrays of polymers with minimal registration, in which short, non-identical sequences form layers, have been derived (Biswas & Blackwell, 1988b,c). Calculation of diffracted intensities, coupled with molecular-mechanics modelling, allows chain conformations and packing to be investigated (Hofmann *et al.*, 1994).

4.5.2.4.4. Partially crystalline fibres

In this section we address disorder in the packing of the molecules in a polycrystalline fibre. The presence of disorder within the crystallites modifies the intensities of the Bragg reflections, as well as introducing continuous diffraction. The dominant effect, sometimes seen on fibre diffraction patterns (Stroud & Millane, 1995a), is for Bragg reflections to remain at low resolution but to be replaced by continuous diffraction at high resolution. There are two distinct cases to consider. The first is where the distortions at different lattice points in the crystallite are uncorrelated, and the second is where they are correlated.

Disorder within a crystallite in a polycrystalline fibre may consist of (1) deviations in the positions of the molecules (which are treated as rigid bodies) from their positions in a regular lattice, (2) rotations of the molecules about their molecular axes from their rotational positions in an ordered crystal, and (3) random orientations (up or

down) of the molecules. The first of these is called *lattice disorder*, and the second and third are components of *substitution disorder*.

Uncorrelated disorder has been treated by a number of authors (Clark & Muus, 1962; Tanaka & Naya, 1969; Fraser & MacRae, 1973; Arnott, 1980). A rather complete model has been described by Millane & Stroud (1991) and Stroud & Millane (1995b), which is presented here. If the lattice and substitution disorders are independent, and the lattice and substitution distortions at different lattice sites are uncorrelated, then the cylindrically averaged layer-line intensities $I_l(R)$ diffracted from a fibre can be written as a sum of Bragg and diffuse (continuous) intensities (Tanaka & Naya, 1969):

$$I_l(R) = I_l^B(R) + I_l^D(R). \quad (4.5.2.33)$$

The profiles of the Bragg reflections are independent of the position of the reflection in reciprocal space. If the Cartesian components of the lattice distortions are independent, normally distributed, and the x and y components have equal variances, cylindrical averaging of the diffracted intensity can be performed analytically.

The lattice disorder consists of distortions of the two-dimensional lattice (in the lateral plane) into three-dimensional space, and in the *absence* of substitution disorder the Bragg component is given by (Stroud & Millane, 1995b)

$$I_l^B(R) = I_l(R_{hk}) w_{\text{lattice}}(R_{hk}, l/c) \quad (4.5.2.34)$$

where $I_l(R_{hk})$ is given by equation (4.5.2.24), the *lattice disorder weight*, $w_{\text{lattice}}(R, Z)$, is given by

$$w_{\text{lattice}}(R, Z) = \exp[-4\pi^2(R^2\sigma_{\text{lat}}^2 + Z^2\sigma_{\text{axial}}^2)], \quad (4.5.2.35)$$

where σ_{lat}^2 and σ_{axial}^2 are the variances of the lattice distortions normal ('lateral') and parallel ('axial') to the z axis, respectively. The diffuse component is given by

$$I_l^D(R) = (1/A_{\text{cryst}}) I_l(R) [1 - w_{\text{lattice}}(R, l/c)], \quad (4.5.2.36)$$

where $I_l(R)$ is given by equation (4.5.2.17) and A_{cryst} is the average cross-sectional area of the crystallites. Inspection of equations (4.5.2.34) and (4.5.2.36) shows that the effect of the lattice disorder is to weight the amplitudes of the Bragg reflections down with increasing R and l , and to introduce a continuous intensity component whose amplitude increases with R and Z . Furthermore, the amplitude of the diffuse component relative to the Bragg component is inversely proportional to A_{cryst} , and therefore is not significant unless the crystallites are small.

If substitution disorder is also present, then equation (4.5.2.33) still applies but equations (4.5.2.34) and (4.5.2.36) are replaced by

$$I_l^B(R) = \left| \sum_n w_{nl} G_{nl}^2(R_{hk}) \exp[in(\psi_{hk} + \pi/2)] \right|^2 w_{\text{lattice}}(R_{hk}, l/c) \quad (4.5.2.37)$$

and

$$I_l^D(R) = (1/A_{\text{cryst}}) \sum_n |G_{nl}(R)|^2 [1 - |w_{nl}|^2 w_{\text{lattice}}(R, l/c)], \quad (4.5.2.38)$$

respectively, where the *substitution disorder weight*, w_{nl} , is given by

$$w_{nl} = \int_0^{c/2u} \int_0^{2\pi} p(\varphi, z) \exp[i(2\pi z l/c - n\varphi)] d\varphi dz. \quad (4.5.2.39)$$

In equation (4.5.2.39), $p(\varphi, z)$ is the probability density function (p.d.f.) that describes the substitution disorder, *i.e.* the p.d.f. for a molecule being rotated by φ about and translated by z along the

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molecular axis relative to its position in the undistorted lattice. Inspection of equations (4.5.2.37) and (4.5.2.38) shows that the substitution disorder weights the different contributing Bessel terms differently. This can lead to quite complicated effects on the diffraction pattern for various kinds of substitution disorder, resulting in different distributions and amplitudes of Bragg and diffuse diffraction over the diffraction pattern (Stroud & Millane, 1995b). If one assumes either uniform or normal distributions for φ and z , then expressions can be obtained for the w_{nl} in terms of the variances of the distributions of φ and z (Stroud & Millane, 1995b). The cases where distortions in φ are correlated with distortions in z (e.g. 'screw disorder'), and directional (up and down) disorder, can also be accommodated. This model has been shown to be capable of predicting diffraction patterns which are in good agreement with those measured from some disordered polycrystalline fibres (Stroud & Millane, 1995a).

We consider now the case of correlated packing disorder. As a result of intermolecular contacts within a polycrystalline specimen, it is possible that distortions at one lattice site will affect the degree of distortion at neighbouring sites. Coupling between distortions at different lattice sites can be included in the model of disorder by allowing the distortions at different lattice sites to be correlated. The effect of correlated distortions on diffraction patterns is that the diffracted intensity does not separate into Bragg and diffuse components as it does in the case of uncorrelated distortions [equation (4.5.2.33)]. The intensity can be described as being diffuse on the whole diffraction pattern, with (often broad) maxima occurring at some of the reciprocal-lattice points, but with no significant maxima at other reciprocal-lattice points. The widths of the profiles of the maxima generally increase with increasing resolution, whereas the widths of the Bragg maxima resulting from uncorrelated disorder as described above are independent of resolution. A broadening of diffraction maxima with increasing resolution and blending into continuous diffraction is sometimes seen on diffraction patterns from polycrystalline fibres, indicating the presence of correlated disorder (Stroud & Millane, 1996b).

Correlated lattice disorder consists of correlated distortions of the two-dimensional lattice into three-dimensional space. A flexible model of crystalline disorder is that based on the perturbed lattice approach (Welberry *et al.*, 1980). While formulating perturbed lattices with only nearest-neighbour interactions is complicated, a more tractable approach is to base the statistics on an imposed correlation field (de Graaf, 1989; Stroud & Millane, 1996a). This approach has been used to describe cylindrically averaged diffraction from polycrystalline fibres that contain correlated lattice disorder and uncorrelated substitution disorder (Stroud & Millane, 1996a,b), and is presented here.

To develop a flexible and tractable theory for diffraction from crystallites with correlated disorder, it is necessary to formulate the problem in real space. The size and shape of a crystallite in the xy (lateral) plane is described by a *shape function* $s_{\text{lat}}(\mathbf{r})$, where $\mathbf{r}$ denotes the position vector in real space, which is equal to unity inside the crystallite and zero outside. The autocorrelation of the shape function, $t(\mathbf{r})$, is given by

$$t(\mathbf{r}) = \int s(\mathbf{r}')s(\mathbf{r} + \mathbf{r}') d\mathbf{r}'. \quad (4.5.2.40)$$

The correlations between the x components, and between the y components, of the distortions at any two lattice sites are taken to be identical. The correlations between distortion vectors are defined in terms of lateral, $\rho_{\text{lat}}(\mathbf{r})$, and axial, $\rho_{\text{axial}}(\mathbf{r})$, correlation fields such that the correlation coefficients between components of the distortions in the x (or y) and z directions, respectively, are equal to the correlation field evaluated for $\mathbf{r}$ equal to the inter-site vector. Various functional forms for the correlation fields are possible, but exponential correlation functions are usually used (Stroud & Millane, 1996a). If $t(\mathbf{r})$ and the correlation fields are circularly

symmetric, then cylindrical averaging of the diffracted intensity can be performed analytically.

For a polycrystalline fibre with correlated lattice disorder and uncorrelated substitution disorder, the diffracted intensity is given by (Stroud & Millane, 1996b)

$$I_l(R) = \sum_{j,k} t(r_{jk}) w_{\text{lat}}(R, r_{jk}) w_{\text{axial}}(l/c, r_{jk}) \times \sum_{m,n} J_{n-m}(2\pi R r_{jk}) \Re\{w_{ml} w_{nl}^* G_{ml}(R) G_{nl}^*(R)\} \times \exp[i(m-n)\varphi_{jk}] \quad (4.5.2.41)$$

where $r = |\mathbf{r}|$, the sum over (j, k) is over all the sites of the undistorted lattice within the region occupied by the autocorrelation function, (r_{jk}, φ_{jk}) are the polar coordinates of the lattice sites, and the lateral and axial lattice disorder weights are given by

$$w_{\text{lat}}(R, r) = \exp(-4\pi^2 R^2 \sigma_{\text{lat}}^2 [1 - \rho_{\text{lat}}(r)]) \quad (4.5.2.42)$$

and

$$w_{\text{axial}}(Z, r) = \exp(-4\pi^2 Z^2 \sigma_{\text{axial}}^2 [1 - \rho_{\text{axial}}(r)]). \quad (4.5.2.43)$$

Equation (4.5.2.41) is an expression for the continuous intensity distribution along the layer lines and does not separate into Bragg and continuous components as in the case of uncorrelated disorder. However, calculations using these expressions show that the continuous intensity is sharply peaked around the projected reciprocal-lattice points at low resolution, the peaks broadening with increasing resolution until they have the character of continuous diffraction at high resolution (Stroud & Millane, 1996a). This is consistent with the character of diffraction patterns from some disordered polycrystalline fibres. A detailed study of the effects of correlated disorder on fibre diffraction patterns, and analysis of such disorder, can be found in Stroud & Millane (1996a) and Stroud & Millane (1996b).

4.5.2.5. Processing diffraction data

Since the diffraction pattern from a fibre is two-dimensional, it can be collected with a single exposure of a stationary specimen. Diffraction data are collected either on film, which is subsequently scanned by a two-dimensional microdensitometer to obtain a digitized representation of the diffracted intensity, or using an electronic area detector (imaging plate, CCD camera, wire detector *etc.*) (Fraser *et al.*, 1976; Namba, Yamashita & Vonderviszt, 1989; Lorenz & Holmes, 1993). We assume here that the diffraction pattern is recorded on a flat film (or detector) that is normal to the incident X-ray beam, although other film geometries are easily accommodated (Fraser *et al.*, 1976). The fibre specimen is usually oriented with its axis normal to the incident X-ray beam, although, as is described below, it is sometimes tilted by a small angle to the normal in order to better access reciprocal space close to the meridian. The diffraction and camera geometry are shown in Fig. 4.5.2.1. Referring to this figure, P and S denote the intersections of the diffracted beam with the sphere of reflection and the film, respectively. The fibre, and therefore reciprocal space, is tilted by an angle β to the normal to the incident beam. The angles μ and χ define the direction of the diffracted beam and θ is the Bragg angle. Cartesian and polar coordinates on the film are denoted by (u, v) and (r, φ) , respectively, and D denotes the film-to-specimen distance.

Inspection of Fig. 4.5.2.1 shows that the cylindrical (R, ψ, Z) and spherical (ρ, ψ, σ) polar coordinates in reciprocal space are related to μ and χ by

$$\rho = (1/\lambda)[2(1 - \cos \mu - \cos \chi)]^{1/2}, \quad (4.5.2.44)$$

$$Z = (1/\lambda)[\sin \beta(1 - \cos \mu \cos \chi) + \cos \beta \sin \chi]^{1/2}, \quad (4.5.2.45)$$

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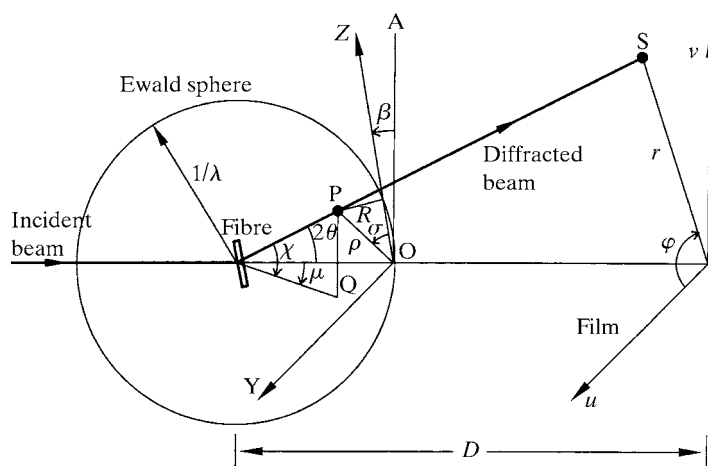


Fig. 4.5.2.1. Fibre diffraction geometry (see text). **O** is the origin of reciprocal space and **OA** is normal to the incident X-ray beam. Reciprocal space is rotated about **OY** so that the Z axis is inclined at an angle β to **OA**. **Q** is the projection of **P** onto the plane containing the incident beam and **OY**.

$$R = (\rho^2 - Z^2)^{1/2}, \quad (4.5.2.46)$$

$$\sin \psi = \frac{\sin \mu \cos \chi}{R \lambda} \quad (4.5.2.47)$$

and

$$\tan \sigma = R/Z. \quad (4.5.2.48)$$

The coordinates on the film are related to μ and χ by

$$u = D \tan \mu \quad (4.5.2.49)$$

and

$$v = D \cos \mu \tan \chi, \quad (4.5.2.50)$$

and we also have that

$$r = D \tan 2\theta. \quad (4.5.2.51)$$

Use of the above equations allows the reciprocal-space coordinates to be calculated from film-space coordinates, and *vice versa*. The film coordinates (u, v) represent a relatively undistorted map of reciprocal space (R, Z) , except near the v (vertical) axis of the diffraction pattern. The meridian of reciprocal space does not map onto the film. Inspection of Fig. 4.5.2.1 shows that the only point on the meridian that does appear on the film is at $Z = \lambda^{-1} \sin \beta$. The region *close* to the meridian that appears on the film can therefore be manipulated by adjusting the fibre tilt.

The film-to-specimen distance can be determined by including with the specimen a crystalline power that gives a diffraction ring of known spacing and adjusting the film-to-specimen distance so that the calculated and observed rings coincide. A nonzero fibre tilt leads to differences between the upper and lower halves of the diffraction pattern, and these differences can be used to determine the tilt. This can be done by either calculating the ρ and χ values for several sets of the same reflection above and below the equator and using the relationship

$$\tan \beta = \frac{\sin \chi_U + \sin \chi_L}{\lambda^2 \rho^2}, \quad (4.5.252)$$

where χ_U and χ_L refer to the upper and lower ($\chi < 0$) reflections (Millane & Arnott, 1986; Lorenz & Holmes, 1993), or by finding the tilt that minimizes the differences between optical densities at the same reciprocal-space coordinates above and below the equator

(Fraser *et al.*, 1976). The optical densities may also be corrected for the effects of film (or detector) nonlinearity (Fraser *et al.*, 1976) and the effects of variable absorption owing to the oblique passage of the beam through the film using expressions given by Fraser *et al.* (1976) and Lorenz & Holmes (1993).

Accurate subtraction of background diffraction is important in order to obtain accurate intensity measurements. One approach to estimating background diffraction is to fit a global background function, usually expanded as a polynomial (Lorenz & Holmes, 1993) or a Fourier-Bessel (Millane & Arnott, 1985) series, to optical densities at a set of points on the diffraction pattern that represent background alone. The background function may or may not be circularly symmetric. The background function is subtracted from the whole diffraction pattern. Another approach, suitable only for Bragg diffraction patterns, is to fit a plane under each reflection, either to the peripheral regions of the reflection or as part of a profile-fitting procedure (Fraser *et al.*, 1976). A different plane is required for each reflection. A third approach, more suitable for continuous diffraction patterns, is to fit a one-dimensional polynomial in angle, for each value of r on the film, possibly as part of a deconvolution procedure (Makowski, 1978). Recently, Ivanova & Makowski (1998) have described an iterative low-pass filtering technique for estimating the background on diffraction patterns from poorly oriented specimens in which there is little space between the layer lines for sampling the background.

A polarization correction is applied to the diffraction pattern, where for unpolarized X-rays (laboratory sources) the polarization factor p is given by (Fraser *et al.*, 1976)

$$p = (1 + \cos^2 2\theta)/2. \quad (4.5.2.53)$$

The diffraction pattern is usually mapped into reciprocal space (R, Z) for subsequent analysis. The mapping is performed by assigning to the intensity $I(R, Z)$ at position (R, Z) in reciprocal space the value given by (Fraser *et al.*, 1976)

$$I(R, Z) = \frac{I(u(R, Z); v(R, Z))}{\cos^3 \mu \cos^3 \chi}, \quad (4.5.2.54)$$

where $I(u; v)$ denotes the intensity on the film. The functions $u(R, Z)$ and $v(R, Z)$ can be derived from the equations given above. Note that equation (4.5.2.54) includes, implicitly, the Lorentz factor.

Subsequent processing depends on whether the diffraction pattern is continuous (*i.e.* from a noncrystalline specimen) or Bragg (*i.e.* from a polycrystalline specimen). Diffraction patterns from partially crystalline specimens that contain both components have been analysed using a combination of both approaches (Arnott *et al.*, 1986; Park *et al.*, 1987).

For a diffraction pattern containing continuous diffraction on layer lines, one usually extracts the cylindrically averaged transform $I_l(R)$ from the intensity $I(R, Z)$ on the diffraction pattern mapped into reciprocal space. This involves correcting for the effects of coherence length and disorientation expressed by equation (4.5.2.19), and for the overlap of the smeared layer lines that results from their increasing width with increasing R . The diffracted intensity $I(\rho, \sigma)$ in polar coordinates in reciprocal space is equal to the sum of the diffraction $I_l(\rho, \sigma)$ due to each (overlapping) layer line so that

$$I(\rho, \sigma) = \sum_l I_l(\rho, \sigma). \quad (4.5.2.55)$$

Referring to equations (4.5.2.55), (4.5.2.19) and (4.5.2.20) shows that if the smearing due to disorientation dominates over that due to coherence length, then for fixed ρ , equation (4.5.2.55) represents a convolution along σ of the layer-line intensities $I_l(\rho \sin \sigma_l)$ with the Gaussian angular profile in equation (4.5.2.19). By mapping the

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intensity $I(R, Z)$ into polar coordinates as $I(\rho, \sigma)$, or by simply sampling $I(R, Z)$ for fixed ρ and equally spaced samples of σ , $I_l(R)$ can be calculated from $I(\rho, \sigma)$ by deconvolution, usually by some appropriate solution of the resulting system of linear equations (Makowski, 1978). If the effects of coherence length are significant, as they often are, then equation (4.5.2.55) does not represent a convolution since the width of the Gaussian smearing function depends on σ through equation (4.5.2.20). However, the problem can still be posed as the solution of a system of linear equations and becomes one of profile fitting rather than deconvolution (Millane & Arnott, 1986). This allows the layer-line intensities to be extracted from the data beyond the resolution where they overlap, although there is a limiting resolution, owing to excessive overlap, beyond which reliable data cannot be obtained (Makowski, 1978; Millane & Arnott, 1986). This procedure requires that α_0 and l_c be known; these parameters can be estimated from the angular profiles at low resolution where there is no overlap, or they can be determined as part of the profile-fitting procedure.

For a diffraction pattern from a polycrystalline specimen containing Bragg reflections, the intensities $I_l(R_{hk})$ given by equation (4.5.2.24) need to be extracted from the intensity $I(R, Z)$ on the diffraction pattern mapped into reciprocal space. Each composite reflection $I_l(R_{hk})$ is smeared into a spot whose intensity profile is given by equation (4.5.2.27), and adjacent reflections may overlap. The intensity $I_l(R_{hk})$ is equal to the intensity $I(R, Z)$ integrated over the region of the spot, and the intensity at the centre of a spot is reduced, relative to $I_l(R_{hk})$, by a factor that increases with the degree of smearing.

The c repeat can be obtained immediately from the layer-line spacing. Initial estimates of the remaining cell constants can be made from inspection of the (R, Z) coordinates of low-order reflections. These values are refined by minimizing the difference between the calculated and measured (R, Z) coordinates of all the sharp reflections on the pattern.

One approach to measuring the intensities of Bragg reflections is to estimate the boundary of each spot (or a fixed proportion of the region occupied by each spot) and integrate the intensity over that region (Millane & Arnott, 1986; Hall *et al.*, 1987). For spots that overlap, an integration region that is the union of the region occupied by each contributing spot can be used, allowing the intensities for composite spots to be calculated (Millane & Arnott, 1986). This is more accurate than methods based on the measurement of the peak intensity followed by a correction for smearing. Integration methods suffer from problems associated with determining accurate spot boundaries and they are not capable of separating weakly overlapping spots. A more effective approach is one based on profile fitting. The intensity distribution on the diffraction pattern can be written as

$$I(R, Z) = \sum_l \sum_{h, k} I_l(R_{hk}, R, Z), \quad (4.5.2.56)$$

where $I_l(R_{hk}, R, Z)$ denotes the intensity distribution of the spot $I_l(R_{hk})$, and the sums are over all spots on the diffraction pattern. Using equation (4.5.2.27) shows that equation (4.5.2.56) can be written as

$$I(R, Z) = \sum_l \sum_{h, k} I_l(R_{hk}) S(R_{hk}; l/c; R; Z), \quad (4.5.2.57)$$

where $S(R_{hk}; l/c; R; Z)$ denotes the profile of the spot centred at $(R_{hk}, l/c)$ [which can be derived from equation (4.5.2.27)]. Given estimates of the parameters l_{lat} , l_{axial} and α_0 , equation (4.5.2.57) can be written as a system of linear equations that can be solved for the intensities $I_l(R_{hk})$ from the data $I(R, Z)$ on the diffraction pattern. The parameters l_{lat} , l_{axial} and α_0 , as well as the cell constants and

possibly other parameters, can also be refined as part of the profile-fitting procedure using nonlinear optimization.

A suite of programs for processing fibre diffraction data is distributed (and often developed) by the Collaborative Computational Project for Fibre and Polymer Diffraction (CCP13) in the UK (www.dl.ac.uk/SRS/CCP13) (Shotton *et al.*, 1998).

4.5.2.6. Structure determination

4.5.2.6.1. Overview

Structure determination in fibre diffraction is concerned with determining atomic coordinates or some other structural parameters, from the measured cylindrically averaged diffraction data. Fibre diffraction analysis suffers from the phase problem and low resolution (diffraction data rarely extend beyond 3 Å resolution), but this is no worse than in protein crystallography where phases derived from, say, isomorphous replacement or molecular replacement, coupled with the considerable stereochemical information usually available on the molecule under study, together contribute enough information to lead to precise structures. What makes structure determination by fibre diffraction more difficult is the loss of information owing to the cylindrical averaging of the diffraction data. However, in spite of these difficulties, fibre diffraction has been used to determine, with high precision, the structures of a wide variety of biological and synthetic polymers, and other macromolecular assemblies. Because of the size of the repeating unit and the resolution of the diffraction data, methods for structure determination in fibre diffraction tend to mimic those of macromolecular (protein) crystallography, rather than small-molecule crystallography (direct methods).

For a noncrystalline fibre one can determine only the molecular structure from the continuous diffraction data, whereas for a polycrystalline fibre one can determine crystal structures from the Bragg diffraction data. However, there is little fundamental difference between methods used for structure determination with noncrystalline and polycrystalline fibres. For partially crystalline fibres, little has so far been attempted with regard to rigorous structure determination.

As is the case with protein crystallography, the precise methods used for structure determination by fibre diffraction depend on the particular problem at hand. A variety of tools are available and one selects from these those that are appropriate given the data available in a particular case. For example, the structure of a polycrystalline polynucleotide might be determined by using Patterson functions to determine possible packing arrangements, molecular model building to define, refine and arbitrate between structures, difference Fourier synthesis to locate ions or solvent molecules, and finally assessment of the reliability of the structure. As a second example, to determine the structure of a helical virus, one might use isomorphous replacement to obtain phase estimates, calculate an electron-density map, fit a preliminary model and refine it using simulated annealing alternating with difference Fourier analysis, and assess the results. The various tools available, together with indications of where and how they are used, are described in the following sections.

Although a variety of techniques are used to solve structures using fibre diffraction, most of the methods do fall broadly into one of three classes that depend primarily on the size of the helical repeat unit. The first class applies to molecules whose repeating units are small, *i.e.* are represented by a relatively small number of independent parameters or degrees of freedom (after all stereochemical constraints have been incorporated). The structure can then be determined by an exhaustive exploration of the parameter space using molecular model building. The first example above would belong to this class. The second class of methods is appropriate when the size of the helical repeating unit is such that

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its structure is described by too many variable parameters for the parameter space to be explored *a priori*. It is then necessary to phase the fibre diffraction data and construct an electron-density map into which the molecular structure can be fitted and then refined. The second example above would belong to this class. The second class of methods therefore mimics conventional protein crystallography quite closely. The third class of problems applies when the structure is large, but there are too few diffraction data to attempt phasing and the usual determination of atomic coordinates. The solution to such problems varies from case to case and usually involves modelling and optimization of some kind.

An important parameter in structure determination by fibre diffraction is the degree of overlap (that results from the cylindrical averaging) in the data. This parameter is equal to the number of significant terms in equation (4.5.2.17) or the number of independent terms in equation (4.5.2.24), and depends on the position in reciprocal space and, for a polycrystalline fibre, the space-group symmetry. The number of degrees of freedom in a particular datum is equal to twice this number (since each structure factor generally has real and imaginary parts), and is denoted in this section by m . Determination of the $G_{nl}(R)$ from the cylindrically averaged data $I_l(R)$ therefore involves separating the $m/2$ amplitudes $|G_{nl}(R)|$ and assigning phases to each. The electron density can be calculated from the $G_{nl}(R)$ using equations (4.5.2.7) and (4.5.2.11).

4.5.2.6.2. Helix symmetry, cell constants and space-group symmetry

The first step in analysis of any fibre diffraction pattern is determination of the molecular helix symmetry u_v . Only the zero-order Bessel term contributes diffracted intensity on the meridian, and referring to equation (4.5.2.6) shows that the zero-order term occurs only on layer lines for which l is a multiple of u . Therefore, inspection of the distribution of diffraction along the meridian allows the value of u to be inferred. This procedure is usually effective, but can be difficult if u is large, because the first meridional maximum may be on a layer line that is difficult to measure. This difficulty was overcome in one case by Franklin & Holmes (1958) by noting that the second Bessel term on the equator is $n = u$, estimating $G_{00}(R)$ using data from a heavy-atom derivative (see Section 4.5.2.6.6), subtracting this from $I_0(R)$, and using the behaviour of the remaining intensity for small R to infer the order of the next Bessel term [using equation (4.5.2.14)] and thence u .

Referring to equations (4.5.2.6) and (4.5.2.14) shows that the distribution of $R_{\min}$ for $0 < l < u$ depends on the value of v . Therefore, inspection of the intensity distribution close to the meridian often allows v to be inferred. Note, however, that the distribution of $R_{\min}$ does not distinguish between the helix symmetries u_v and u_{u-v} . Any remaining ambiguities in the helix symmetry need to be resolved by steric considerations, or by detailed testing of models with the different symmetries against the available data.

For a polycrystalline system, the cell constants are determined from the (R, Z) coordinates of the spots on the diffraction pattern as described in Section 4.5.2.6.4. Space-group assignment is based on analysis of systematic absences, as in conventional crystallography. However, in some cases, because of possible overlap of systematic absences with other reflections, there may be some ambiguity in space-group assignment. However, the space group can always be limited to one of a few possibilities, and ambiguities can usually be resolved during structure determination (Section 4.5.2.6.4).

4.5.2.6.3. Patterson functions

In fibre diffraction, the conventional Patterson function cannot be calculated since the individual structure-factor intensities are not

available. However, MacGillavry & Bruins (1948) showed that the cylindrically averaged Patterson function can be calculated from fibre diffraction data. Consider the function $\hat{Q}(r, z)$ defined by

$$\hat{Q}(r, z) = \sum_{l=0}^{\infty} \int \varepsilon_l I_l(R) J_0(2\pi Rr) \cos(2\pi lz/c) 2\pi R \, dR, \quad (4.5.2.58)$$

where $\varepsilon_l = 1$ for $l = 0$ and 2 for $l > 0$, which can be calculated from the intensity distribution on a continuous fibre diffraction pattern. Using equations (4.5.2.7), (4.5.2.10), (4.5.2.17) and (4.5.2.58) shows that $\hat{Q}(r, z)$ is the cylindrical average of the Patterson function, $\hat{P}(r, \varphi, z)$, of one molecule, *i.e.*

$$\hat{Q}(r, z) = (1/2\pi) \int_0^{2\pi} \hat{P}(r, \varphi, z) \, d\varphi. \quad (4.5.2.59)$$

The $\hat{}$ symbols on $\hat{P}(r, \varphi, z)$ and $\hat{Q}(r, z)$ indicate that these are Patterson functions of a single molecule, as distinct from the usual Patterson function of a crystal, which contains intermolecular interatomic vectors and is periodic with the same periodicity as the crystal. $\hat{P}(r, \varphi, z)$ is periodic only along z and is therefore, strictly, a Patterson function along z and an autocorrelation function along x and y (Millane, 1990b). The cylindrically averaged Patterson contains information on interatomic separations along the axial direction and in the lateral plane, but no information on orientations of the vectors in the lateral plane.

For a polycrystalline system; consider the function $Q(r, z)$ given by

$$Q(r, z) = \sum_l \sum_{h,k} R_{hk} I_l(R_{hk}) J_0(2\pi R_{hk} r) \cos(2\pi lz/c), \quad (4.5.2.60)$$

where the sums are over all the overlapped reflections $I_l(R_{hk})$ on the diffraction pattern, given by equation (4.5.2.24). It is easily shown that $Q(r, z)$ is related to the Patterson function $P(r, \varphi, z)$ by

$$Q(r, z) = (1/2\pi) \int_0^{2\pi} P(r, \varphi, z) \, d\varphi, \quad (4.5.2.61)$$

where, in this case, $P(r, \varphi, z)$ is the usual Patterson function (expressed in cylindrical polar coordinates), *i.e.* it contains all intermolecular (both intra- and inter-unit cell) interatomic vectors and has the same translational symmetry as the unit cell. The cylindrically averaged Patterson function for polycrystalline fibres therefore contains the same information as it does for noncrystalline fibres (*i.e.* no angular information in the lateral plane), except that it also contains information on intermolecular separations.

Low resolution and cylindrical averaging, in addition to the usual difficulties with interpretation of Patterson functions, has resulted in the cylindrically averaged Patterson function not playing a major role in structure determination by fibre diffraction. However, information provided by the cylindrically averaged Patterson function has, in a number of instances, been a useful component in fibre diffraction analyses. A good review of the application of Patterson functions in fibre diffraction is given by Stubbs (1987). Removing data from the low-resolution part (or all) of the equator when calculating the cylindrically averaged Patterson function removes the strong vectors related to axially invariant (or cylindrically symmetric) parts of the map, and can aid interpretation (Namba *et al.*, 1980; Stubbs, 1987). It is also important when calculating cylindrically averaged Patterson functions to use data only at a resolution that is appropriate to the size and spacings of features one is looking for (Stubbs, 1987).

Cylindrically averaged Patterson functions were used in early applications of fibre diffraction analysis (Franklin & Gosling, 1953; Franklin & Klug, 1955). The intermolecular peaks that usually dominate in a cylindrically averaged Patterson function can help to define the locations of multiple molecules in the unit cell.

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Depending on the space-group symmetry, it is sometimes possible to calculate the complete three-dimensional Patterson function (or certain projections of it). This comes about because of the equivalence of the amplitudes of overlapping reflections in some high-symmetry space groups. The intensity of each reflection can then be determined and a full three-dimensional Patterson map calculated (Alexeev *et al.*, 1992). The only difficulty is that non-systematic overlaps are often present, although these are usually relatively few in number and the intensity can be apportioned equally amongst them, the resulting errors usually being small relative to the level of detail present in the Patterson map. For lower space-group symmetries, it may not be possible to calculate a three-dimensional Patterson map, but it may be possible to calculate certain projections of the map. For example, if the overlapped $hk0$ reflections have the same intensities, a projection of the Patterson map down the c axis can be calculated. Since such a projection is along the polymer axes, it gives the relative positions of the molecules in the ab plane. If the combined helix and space-group symmetry is high, an estimate of the electron density can be obtained by averaging appropriate copies of the three-dimensional Patterson function (Alexeev *et al.*, 1992).

4.5.2.6.4. Molecular model building

The majority of the structures determined by X-ray fibre diffraction analysis have been determined by molecular model building (Campbell Smith & Arnott, 1978; Arnott, 1980; Millane, 1988). Most applications of molecular model building have been to polycrystalline systems, although there have been a number of applications to noncrystalline systems (Park *et al.*, 1987; Millane *et al.*, 1988). The approach is to use spacings and symmetry information derived directly from the diffraction pattern, coupled with the primary structure and stereochemical information on the molecule under study, to construct models of all *kinds* of possible molecular or crystal structure. These models are each refined (optimized) against the diffraction data, as well as stereochemical restraints, to produce the best model of each kind. The optimized models can be compared using various figures of merit, and in favourable cases one model will be sufficiently superior to the remainder for it to represent unequivocally the correct structure. The principle of this approach is that by making use of stereochemical constraints, the molecular and crystal structure have few enough degrees of freedom that the parameter space has a sufficiently small number of local minima for these to be identified and individually examined to find the global minimum. The X-ray phases are therefore not determined explicitly.

There are three steps involved in structure determination by molecular model building: (1) construction of all possible molecular and crystal structure models, (2) refinement of each model against the X-ray data and stereochemical restraints, and (3) adjudication among the refined models. The overall procedure for determining polymer structures using molecular model building is summarized by the flow chart in Fig. 4.5.2.2, and is described below.

The helix symmetry of the molecule, or one of a few helix symmetries, can be determined as described in Section 4.5.2.6.2. Different kinds of molecular model may correspond to one of a few different helix symmetries, usually corresponding to different values of v . For example, helix symmetries u_v and u_{u-v} , which correspond to the left- and right-handed helices, cannot be distinguished on the basis of the overall intensity distribution alone. Other examples of different kinds of molecular model may include single, double or multiple helices, parallel or antiparallel double helices, different juxtapositions of chains within multiple helices and different conformational domains within the molecule. For polycrystalline systems, in addition to different kinds of

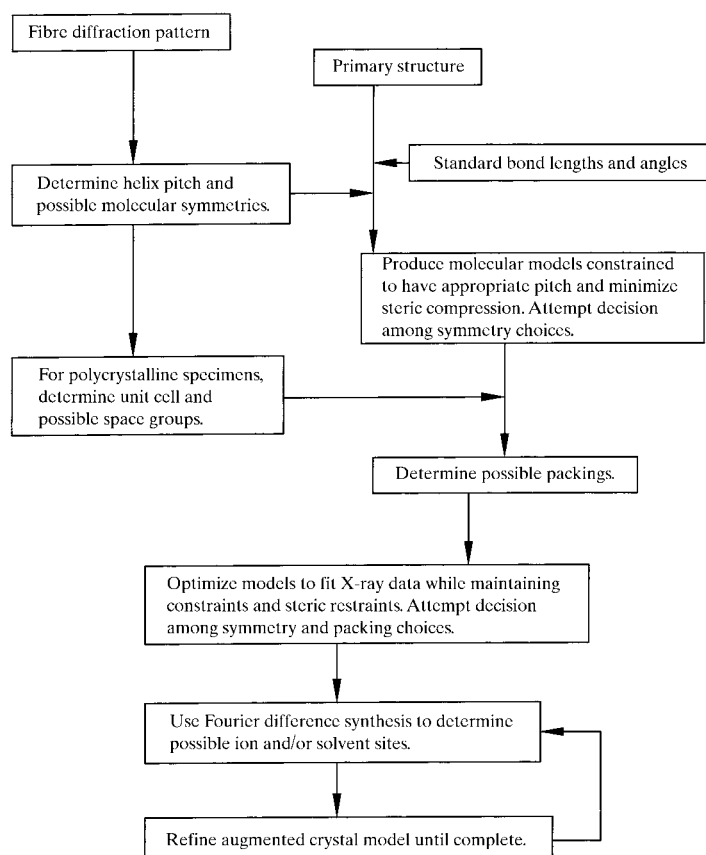


Fig. 4.5.2.2. Flow chart of the molecular-model-building approach to structure determination (Arnott, 1980).

molecular structures, there are often different kinds of possible packing arrangements within the unit cell. There may be a number of possible packings which correspond to different arrangements within the crystallographic asymmetric unit, and there may be more than one space group that needs to be considered.

Despite the apparent large number of potential starting models implied by the above discussion, in practice the number of feasible models is usually quite small, and many of these are often eliminated at an early stage. Definition and refinement of helical polymers [steps (1) and (2) above] are carried out using computer programs, the most popular and versatile being the *linked-atom least-squares* (LALS) system (Campbell Smith & Arnott, 1978; Millane *et al.*, 1985), originally developed by Arnott and co-workers in the early 1960s (Arnott & Wonacott, 1966). This system has been used to determine the structures of a wide variety of polynucleotides, polysaccharides, polyesters and polypeptides (Arnott, 1980; Arnott & Mitra, 1984; Chandrasekaran & Arnott, 1989; Millane, 1990c). Other refinement systems exist (Zugenmaier & Sarko, 1980; Iannelli, 1994), but the principles are essentially the same and the following discussion is in terms of the LALS system. The atomic coordinates are defined, using a linked-atom description, in terms of bond lengths, bond angles and conformation (torsion) angles (Campbell Smith & Arnott, 1978). Stereochemical constraints are imposed, and the number of parameters reduced, by fixing the bond lengths, often (but not always) the bond angles, and possibly some of the conformation angles. The molecular conformation is then defined by the remaining parameters. For polycrystalline systems, there are usually additional variable parameters that define the packing of the molecule(s) in the unit cell. A further source of stereochemical data is the requirement that a model exhibit no over-short nonbonded interatomic distances. These are incorporated by a quadratic nonbonded potential that is

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matched to a Buckingham potential (Campbell Smith & Arnott, 1978). A variety of other restraints can also be incorporated.

In the *LALS* system, the quantity Ω given by

$$\Omega = \sum_m \omega_m \Delta F_m^2 + \sum_m k_m \Delta d_m^2 + \sum_m \lambda_m G_m = X + C + L \quad (4.5.2.62)$$

is minimized by varying a set of chosen parameters consisting of conformation angles, possibly bond angles, and packing parameters. The term X involves the differences ΔF_m between the model and experimental X-ray amplitudes – Bragg and/or continuous. The term C involves restraints to ensure that over-short nonbonded interatomic distances are driven beyond acceptable minimum values, that conformations are within desired domains, that hydrogen-bond and coordination geometries are close to the expected configurations, and a variety of other relationships are satisfied (Campbell Smith & Arnott, 1978). The ω_m and k_m are weights that are inversely proportional to the estimated variances of the data. The term L involves constraints which are relationships that are to be satisfied exactly ($G_m = 0$) and the λ_m are Lagrange multipliers. Constraints are used, for example, to ensure connectivity from one helix pitch to the next and to ensure that chemical ring systems are closed. The cost function Ω is minimized using full-matrix nonlinear least squares and singular value decomposition (Campbell Smith & Arnott, 1978).

Structure determination usually involves first using equation (4.5.2.62) with the terms C and L only, to establish the stereochemical viability of each kind of possible molecular model and packing arrangement. It is worth emphasizing that it is usually advantageous if the specimen is polycrystalline, even though the continuous diffraction contains, in principle, more information than the Bragg reflections (since the latter are sampled). This is because the molecule in a noncrystalline specimen must be refined in steric isolation, whereas for a polycrystalline specimen it is refined while packed in the crystal lattice. The extra information provided by the intermolecular contacts can often help to eliminate incorrect models. This can be particularly significant if the molecule has flexible sidechains. The initial models that survive the steric optimization are then optimized also against the X-ray data, by further refinement with X included in equation (4.5.2.62). The ratios $(\Omega_P/\Omega_Q)^{1/2}$ and $(X_P/X_Q)^{1/2}$ can be used in Hamilton's test (Hamilton, 1965) to evaluate the differences between models P and Q . On the basis of these statistical tests, one can decide if one model is superior to the others at an acceptable confidence level. In the final stages of refinement, bond angles may be varied in a 'stiffly elastic' fashion from their mean values if there are sufficient data to justify the increase in the number of degrees of freedom.

If sufficient X-ray data are available, it is sometimes possible to locate additional ordered molecules such as counterions or solvent molecules by difference Fourier synthesis as described in Section 4.5.2.6.5. Their positions can then be co-refined with the polymer structure while hydrogen bonds and coordination geometries are optimized. The resulting structure can then be used to compute improved phases to search for additional molecules. Since the signal-to-noise ratio in fibre difference syntheses is usually low, difference maps must be interpreted with caution. The assignment of counterions or solvent molecules to peaks in the difference synthesis must be supported by plausible interactions with the rest of the structure and, following refinement of the structure, by elimination of the peak in the difference map and by a significant improvement in the agreement between the calculated and measured X-ray amplitudes.

4.5.2.6.5. Difference Fourier synthesis

Difference Fourier syntheses are widely used in both protein and small-molecule crystallography to detect structural errors or to

complete partial structures (Drenth, 1994). The difficulty in applying difference Fourier techniques in fibre diffraction is that the individual observed amplitudes $|F_o|$ are not available. However, difference syntheses have found wide use in fibre diffraction analysis, one of the earliest applications being to polycrystalline fibres of polynucleotides (e.g. Arnott *et al.*, 1967). Calculation of a three-dimensional difference map (for the unit cell) from Bragg fibre diffraction data requires that the observed intensity $I_l(R_{hk}) = I_o$ be apportioned among the contributing intensities $|F_{hkl}|^2 = |F_o|^2$. There are two ways of doing this. The intensities may be divided equally among the contributing $(m/2)$ reflections [i.e. $|F_o| = (2I_o/m)^{1/2}$], or they may be divided in the same proportions as those in the model, i.e.

$$|F_o| = \left(\frac{I_o}{\sum |F_c|^2} \right)^{1/2} |F_c|. \quad (4.5.2.63)$$

The advantage of the former is that it is unbiased, and the advantage of the latter is that it may be more accurate but is biased towards the model. Equal division of the intensities is often (but not always) used to minimize model bias. Once the observed amplitudes have been apportioned, an $|F_o| - |F_c|$ map can be calculated as in conventional crystallography, although noise levels will be higher owing to errors in apportioning the amplitudes. As a result of overlapping of the reflections, a synthesis based on coefficients $m|F_o| - (m-1)|F_c|$ gives a more accurate estimate of the true density than does one based on $2|F_o| - |F_c|$, as is described below. Difference syntheses for polycrystalline specimens calculated in this way have been used, for example, to locate cations and water molecules in polynucleotide and polysaccharide structures (e.g. Cael *et al.*, 1978), to help position molecules in the unit cell (e.g. Chandrasekaran *et al.*, 1994) and to help position side chains, and have also been applied in neutron fibre diffraction studies of polynucleotides (Forsyth *et al.*, 1989).

Sim (1960) has shown that the mean-squared error in difference syntheses can be minimized by weighting the coefficients based on the agreement between the calculated and observed structure amplitudes. Such an analysis has recently been conducted for fibre diffraction, and shows that the optimum difference synthesis is obtained by using coefficients (Millane & Baskaran, 1997; Baskaran & Millane, 1999a)

$$\left[w_m \frac{|F_c|(I_o)^{1/2}}{(\sum |F_c|^2)^{1/2}} - |F_c| \right] \exp(i\alpha_c), \quad (4.5.2.64)$$

where m is the number of degrees of freedom as defined in Section 4.5.2.6.1. If the reflections contributing to I_o are either all centric or all acentric, then the weights are given by

$$w_m = \frac{I_{m/2}(X)}{I_{m/2-1}(X)}, \quad (4.5.2.65)$$

where $I_m(\cdot)$ denotes the modified Bessel function of the first kind of order m , and X is given by

$$X = \frac{\kappa(I_o)^{1/2}(\sum |F_c|^2)^{1/2}}{\sum f_j^2}, \quad (4.5.2.66)$$

where $\kappa = 1$ for centric reflections and 2 for acentric reflections. The form of the weighting function is more complicated if both centric and acentric reflections contribute, but it can be approximated as w' given by

$$w' = (w_{2N_a} + w_{N_c})/2, \quad (4.5.2.67)$$

where N_a and N_c are the number of acentric and centric reflections,

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respectively, contributing. Use of the weighted maps reduces bias towards the model (Baskaran & Millane, 1999b).

For continuous diffraction data from noncrystalline specimens, the situation is essentially identical except that one works in cylindrical coordinates. Referring to equations (4.5.2.7) and (4.5.2.10), the desired difference synthesis, $\Delta g(r, \varphi, z)$, is the Fourier–Bessel transform of $G_o - G_c$ where G_o and G_c denote the observed and calculated, respectively, Fourier–Bessel structure factors $G_{nl}(R)$. Since G_o is not known, the synthesis is based on the Fourier–Bessel transform of $(|G_o| - |G_c|) \exp(i\alpha_c)$, where α_c is the phase of G_c . As in the polycrystalline case, the individual $|G_o|$ need to be estimated from the data $I_o^{1/2}$ given by equation (4.5.2.17), and can be based on either equal division of the data, or division in the same proportion as the amplitudes from the model.

Namba & Stubbs (1987a) have shown that the peak heights in a difference synthesis are $1/m$ times their true value, as opposed to half their true value in a conventional difference synthesis. The best estimate of the true map is therefore provided by a synthesis based on the coefficients $[m|F_o| - (m-1)|F_c|] \exp(i\alpha_c)$, rather than on $(2|F_o| - |F_c|) \exp(i\alpha_c)$. Test examples showed that the noise in the synthesis can be reduced by using a value for m that is fixed over the diffraction pattern and approximately equal to the average value of m over the pattern (Namba & Stubbs, 1987a). Difference Fourier maps for noncrystalline systems have been used in studies of helical viruses to locate heavy atoms, to correct errors in atomic models and to locate water molecules (Mandelkow *et al.*, 1981; Lobert *et al.*, 1987; Namba, Pattanayek & Stubbs, 1989; Wang & Stubbs, 1994).

4.5.2.6.6. Multidimensional isomorphous replacement

At low enough resolution, only one Fourier–Bessel structure factor contributes on each layer line of a fibre diffraction pattern, so that only the phase needs to be determined and the situation is no different to that in protein crystallography. If heavy-atom-derivative specimens can be prepared, the usual method of multiple isomorphous replacement (MIR) (Drenth, 1994) can be applied, which in principle requires only two heavy-atom derivatives. At higher resolution, however, more than one Fourier–Bessel structure factor contributes on each layer line. A generalized form of isomorphous replacement which involves using diffraction data from several heavy-atom derivatives to determine the real and imaginary components of each contributing $G_{nl}(R)$ is referred to as *multidimensional isomorphous replacement* (MDIR) (Namba & Stubbs, 1985). MDIR was first described and used to determine the structure of TMV at 6.7 Å resolution (Stubbs & Diamond, 1975; Holmes *et al.*, 1975), and has since been used to extend the resolution to 2.9 Å (Namba, Pattanayek & Stubbs, 1989). A consequence of cylindrical averaging is that large numbers of heavy-atom derivatives are required: at least two for each Bessel term to be separated. The theory of MDIR is outlined here.

The first step in MDIR is location of the heavy atoms in the derivative structures. The radial coordinate of a heavy atom can be determined by analysis of the intensity distribution in the low-resolution region of the equator where only the $G_{00}(R)$ Bessel term contributes. Since $G_{00}(R)$ is real, and $I_l(R)$ can be measured continuously in R , inspection of the positions of the minima and maxima in the low-resolution region of the equator generally allows the sign of $G_{00}(R)$ to be assigned to $I_0^{1/2}(R)$, i.e. $G_{00}(R)$ can be determined from $I_0(R)$. If the sign is determined for both the native and a heavy-atom derivative, referring to equation (4.5.2.13) shows that

$$G_{00}^D(R) - G_{00}(R) = o_h f_h J_0(2\pi R r_h), \quad (4.5.2.68)$$

where $G_{00}^D(R)$ is the value derived from the derivative data, o

denotes the occupancy and the subscript h denotes values for the heavy atom. The parameters o_h and r_h on the right-hand side of equation (4.5.2.68) can be searched in a trial-and-error fashion to obtain the best agreement with the left-hand side (calculated from the data) to determine the radial coordinate r_h of the heavy atom (Mandelkow & Holmes, 1974). Lobert *et al.* (1987) applied the same method to cucumber green mottle mosaic virus (CGMMV), except that the sign of $G_{00}(R)$ was taken from that of TMV.

Two approaches have been used to determine the angular and axial coordinates of the heavy atom. Mandelkow & Holmes (1974) and Holmes *et al.* (1975) used a search procedure in which the quantity $\Phi = -n\varphi_h + 2\pi l z_h / c$ is varied and used to calculate the intensity of the Fourier–Bessel structure factor for the heavy atom alone. This is compared to $I_l^D(R) - I_l(R)$ on each layer line, where only one Bessel order contributes, and Φ chosen to minimize the mean-square difference. The values of Φ found for each layer line can then be combined to determine φ_h and z_h . In the case of CGMMV, Lobert *et al.* (1987) used the phases and Bessel-order separations from TMV to calculate Fourier–Bessel difference maps between the native and derivative data to determine the heavy-atom coordinates (r_h, φ_h, z_h) .

Consider a set of isomorphous heavy-atom derivatives indexed by j . Since the analysis is applied at any point (l, R) on the fibre diffraction pattern, the symbol G_n will be used for $G_{nl}(R)$ where no confusion arises. Denote by $G_{n,j}$ the value of G_n for the j th derivative, so that

$$G_{n,j} = G_n + g_{n,j}, \quad (4.5.2.69)$$

where $g_{n,j}$ denotes the Fourier–Bessel structure factor of a structure containing the heavy atom only. Denote by A_n and B_n the real and imaginary parts, respectively, of G_n (for the native structure), and by $a_{n,j}$ and $b_{n,j}$ the real and imaginary parts of $g_{n,j}$, i.e. for the j th heavy-atom structure alone. Equation (4.5.2.17) can then be written as

$$I = \sum_n (A_n^2 + B_n^2) \quad (4.5.2.70)$$

for the native and

$$I_j = \sum_n [(A_n + a_{n,j})^2 + (B_n + b_{n,j})^2] \quad (4.5.2.71)$$

for the j th derivative. If intensity data are available from J heavy-atom derivatives, $a_{n,j}$ and $b_{n,j}$ can be calculated from the heavy-atom positions, and equations (4.5.2.70) and (4.5.2.71) represent a system of $J + 1$ second-order equations for the m unknowns A_n and B_n . If $J + 1 > m$, then the system of equations is overdetermined and can be solved for the A_n and B_n . The solution of this nonlinear system can be eased by deriving a system of linear equations by substituting from (4.5.2.70) into (4.5.2.71), giving

$$\sum_n (A_n a_{n,j} + B_n b_{n,j}) = (1/2) \left[I_j - I - \sum_n (a_{n,j}^2 + b_{n,j}^2) \right]. \quad (4.5.2.72)$$

Equation (4.5.2.72) is a system of linear equations for the unknowns A_n and B_n , the solution being subject to the constraint equation (4.5.2.70). However, since the original problem is second-order, there may be up to m local minima. Stubbs & Diamond (1975) describe a numerical procedure for locating *all* the local minima and selecting the best of these based on ‘continuity’ of the $G_{nl}(R)$. This method was used to determine the structure of TMV at 6.7 Å resolution (Holmes *et al.*, 1975) and 4 Å resolution (Stubbs *et al.*, 1977). In current applications of MDIR a more direct solution technique is used in which the phase-determining equations (4.5.2.70) and (4.5.2.71) are solved by first solving the linear equations (4.5.2.72) by linear least squares to obtain an approximate

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solution, which is then refined by solving the quadratic equations (4.5.2.70) and (4.5.2.71) directly using nonlinear least squares (Namba & Stubbs, 1985).

The number of heavy-atom derivatives required can be quite demanding experimentally, although phasing with fewer heavy-atom derivatives is possible, particularly if additional information is available, such as from a related structure. The different Bessel terms may be assumed to contribute the same amplitude each, or, if the structure of a related molecule is known, the ratios of the amplitudes can be taken as being the same as those for the related molecule. Using the amplitude estimates derived using either of these two approaches, applied to both native and derivative data, the phases of the Bessel terms can be estimated using conventional MIR and data from at least two heavy-atom derivatives, allowing an initial electron-density map to be calculated. If only one heavy-atom derivative is available then two phase solutions are obtained, but the method of conventional single isomorphous replacement (SIR) (Drenth, 1994) can be used to obtain an estimate of the electron density. The electron density obtained by MIR, and particularly by SIR, in this way tends to be noisy and low contrast as a result of inaccurate division of the intensities, as well as the usual sources of errors in MIR. The electron density can, however, be improved using solvent levelling. If *no* heavy-atom derivatives are available, both the relative amplitudes *and* the phases can be based on those of a related structure. Model bias can, however, be more serious than in conventional crystallography since both the phases and the relative amplitudes are based on the model.

The feasibility of structure determination with a limited number of heavy-atom derivatives was first demonstrated by Namba & Stubbs (1987*b*) using data from TMV at 4 Å resolution. The structure of CGMMV has been determined at 5 Å resolution using data from two heavy-atom derivatives and the techniques described above (Lobert *et al.*, 1987; Lobert & Stubbs, 1990). Structure determination at this resolution using MDIR would theoretically require six heavy-atom derivatives. Initial separation of the Bessel-term amplitudes was based on the equal-amplitude assumption and also on the relative amplitudes for (homologous) TMV.

In general, the equal-amplitude assumption appears to produce reliable electron-density maps where only two or three Bessel terms contribute. The corresponding resolution depends on the helix symmetry and the molecular diameter, but can be relatively high for molecules with high helix symmetry. At higher resolution where more Bessel terms contribute, use of related or partial structures can be used to calculate initial Bessel-term amplitudes and can lead to successful phasing.

If the molecule has only approximate helix symmetry, then layer-line splitting (Section 4.5.2.3.3) can provide additional information which reduces the number of heavy-atom derivatives required. The degree of splitting is usually significantly less than the breadth of the layer lines so that the different Bessel terms within a (split) layer line overlap. The effect of splitting can be observed, however, since the centre of a layer line, at a particular value of R , is shifted towards the position of the stronger Bessel term contributing at that radius. The shift depends on the relative magnitudes of the contributing Bessel terms, and can be measured and used in phase determination as detailed by Stubbs & Makowski (1982). If P of the heavy-atom derivatives (in addition to the native) give accurate splitting information, then an additional P linear equations [analogous to equation (4.5.2.72)] and one quadratic equation [analogous to equation (4.5.2.70)] are available for solution of the phase problem, and the number of heavy-atom derivatives required is reduced by a factor of up to two. The value of layer-line splitting was first demonstrated by recalculating an electron-density map of TMV at 6.7 Å resolution using only two derivatives, rather than using six derivatives without the use of splitting data (Stubbs & Makowski, 1982). Layer-line splitting was subsequently used in a

structure determination of TMV at 3.6 Å resolution (Namba & Stubbs, 1985).

Macromolecular fibre structures that have been built into an electron-density map have been refined using both restrained least-squares (RLS) and molecular-dynamics (MD) refinements. Restrained least squares has been used to refine the structure of TMV at 2.9 Å resolution (Namba, Pattanayek & Stubbs, 1989); however, Wang & Stubbs (1993) have shown that a larger radius of convergence is obtained using MD refinement (as in protein crystallography).

Molecular-dynamics refinement in fibre diffraction has been implemented by adding a fibre diffraction option (Wang & Stubbs, 1993) to the *X-PLOR* program (Brünger, 1992). This involves including the cylindrically averaged fibre diffraction intensities in the energy term and taking account of the inter-helical subunit contacts and covalent connections in the same way as described above for RLS refinement. The effective potential-energy function E used is

$$E = E_e + S \sum_l \sum_i w_{li} \{ [I_l^o(R_i)]^{1/2} - k [I_l^c(R_i)]^{1/2} \}^2, \quad (4.5.2.73)$$

where E_e is the empirical energy function (which typically includes bond-length, bond-angle and torsion-angle distortions, van der Waals and electrostatic interactions, and other terms such as ring planarity), $I_l^o(R_i)$ and $I_l^c(R_i)$ are the observed and calculated, respectively, cylindrically averaged diffraction intensities sampled at $R = R_i$, the w_{li} are weights for the observed intensities $I_l^o(R_i)$ and k is a scale factor between the calculated and observed data. The quantity S is a weight to make the gradients of the two terms in equation (4.5.2.73) comparable (Wang & Stubbs, 1993), and can be estimated using the method of Brünger (1992). Molecular-dynamics refinement has been successfully used to refine the structure of CGMMV at 3.4 Å resolution (Wang & Stubbs, 1994). In the case of ribgrass mosaic virus (RMV), the close isomorphism with TMV (identical helix symmetry, similar repeat distance, significant sequence homology and similar diffraction pattern) allowed an initial model to be built based on the TMV structure, and a solution obtained at 2.9 Å by alternating molecular-dynamics refinement with difference-map and omit-map calculations (Wang *et al.*, 1997).

4.5.2.6.7. Other techniques

Aside from the techniques for structure determination described in the previous sections, a variety of other techniques have been applied to specific problems where the methods described above are not suitable. This situation usually arises where the diffraction data available are far too few, by themselves, to determine the individual atomic coordinates of a structure, even with the usual stereochemical constraints. Often only relatively low-resolution data are available, but they can be supplemented by either a low-resolution or high-resolution model of either a whole molecule or relatively large subunits. Structure determination often amounts to positioning the molecules or subunits within a larger assembly. The results can be quite precise, depending on the information available. The problem is almost always one of refinement or optimization, since it invariably involves optimizing some kind of model directly against the fibre diffraction data. The problem is usually twofold: (1) parameterizing the model with few enough parameters to obtain a usable data-to-parameter ratio, but retaining enough degrees of freedom to represent the important structural features; and (2) devising an optimization procedure that will locate the global minimum of the resulting complicated cost function. There have been numerous such applications in fibre diffraction, and rather than attempt to be exhaustive or detailed, I will briefly mention a few of the more prominent applications and techniques.

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The structure of the bacteriophage Pf1 was determined at 7 Å resolution using a model in which the α -helical segments of the structure were represented by rods of electron density of appropriate dimensions and spacings (Makowski *et al.*, 1980). The positions and orientations of the rods were refined in an iterative procedure that alternated between real space and reciprocal space and also incorporated solvent levelling. Neutron fibre diffraction data have been collected from specifically deuterated phages and, starting with a model of the kind described above, iterative application of difference maps (between the deuterated and native data) was used to locate 15 (of the 46) residues, allowing construction of a model of the coat protein (Stark *et al.*, 1988; Nambudripad *et al.*, 1991).

Pf1 undergoes a temperature-induced structural transition that involves a small change in the helix symmetry. The low-temperature form has 71_{13} helix symmetry with a c repeat of 216.5 Å, and the high-temperature form (that discussed in the previous paragraph) has 27_5 helix symmetry and a c repeat of 78.3 Å. These two symmetries are very similar since $71/3 \approx 27/5$ and $216.5/71 \approx 78.3/27$, *i.e.* the rotations and translations from one subunit to the next are very similar in both structures.

The structure of the low-temperature form of Pf1 has been determined at 3.3 Å resolution by starting with an α -helical polyalanine model (Marvin *et al.*, 1987) and alternating rounds of molecular-dynamics refinement and model rebuilding based on $(2F_o - F_c)$ maps and omit maps (Gonzalez *et al.*, 1995). The structure of the high-temperature form of Pf1 was determined using data to 3 Å resolution, starting with a model based on the low-temperature form, making small adjustments to satisfy the slightly different helix symmetry, and refining the model using molecular dynamics (Welsh *et al.*, 2000).

The bacteriophage Pf3 is related to Pf1 but does not undergo a structural transition, and fibre diffraction patterns are similar to those from the high-temperature form of Pf1. An α -helical polyalanine model of Pf3 based on the Pf1 structure was used to separate and phase the Bessel terms, which were then used to calculate $(5F_o - 4F_c)$ maps. These maps were used to align and position the polypeptide chain, and the resulting model was refined by molecular dynamics (Welsh *et al.*, 1998).

The R-type bacterial flagellar filament structure (that has a very high molecular weight subunit) has been determined at 9 Å resolution by X-ray fibre diffraction (Yamashita *et al.*, 1998). Accurate intensities were taken from high-quality X-ray diffraction patterns and combined with phases obtained from electron cryomicroscopy, and solvent levelling was used to refine the phases.

Some studies of muscle provide a good example of the use of low-resolution fibre diffraction data, coupled with high-resolution crystal structures of some of the component molecules, to determine the structure of a complex. Holmes *et al.* (1990) constructed a model of F-actin based on the crystal structure of the monomer, G-actin, and 8 Å fibre diffraction data, by either treating the monomer as a rigid body or dividing it into four separate rigid domains, and using a search procedure followed by least-squares refinement. The results gave the orientation of the actin monomer in the actin helix. This structure has since been refined using a genetic algorithm (Lorenz *et al.*, 1993) and normal-mode analysis (Tirion *et al.*, 1995). The genetic algorithm involved a Monte Carlo method of selecting subdomains to be refined and nonlinear least squares to obtain the best fit for the selected domains. In the normal-mode analysis, the model was parameterized in terms of its low-frequency vibrational modes to allow low-energy conformational changes and reduce the number of parameters which were optimized against the fibre diffraction data using nonlinear least squares.

Squire *et al.* (1993) have refined a low-resolution model of the muscle thin-filament structure that consists of four spheres representing each of the F-actin monomer subdomains and five spheres (fixed relative to each other) representing tropomyosin.

Steric restraints were placed on the actin subdomain and thin-filament structures. The positions of the actin subdomains and the orientation of the tropomyosin were refined using a search procedure against fibre diffraction data from both 'resting' and 'activated' muscle at 25 Å resolution. More recent work has used a low-resolution model of the myosin head (based on the single-crystal atomic structure), a search procedure and simulated-annealing refinements to study myosin head configuration (Hudson *et al.*, 1997) and myosin rod packing (Squire *et al.*, 1998).

4.5.2.6.8. Reliability

As with structure determination in any area of crystallography, assessment of the reliability or precision of a structure is critically important. The most commonly used measure of reliability in fibre diffraction is the R factor, calculated as

$$R = \frac{\sum_i ||F|_i^o - |F|_i^c|}{\sum_i |F|_i^o}, \quad (4.5.2.74)$$

where $|F|_i^o$ and $|F|_i^c$ denote the observed (measured) and calculated, respectively, amplitude of either the samples (along R) of the cylindrically averaged intensity $I_l^{1/2}(R)$ (for a noncrystalline specimen) or the cylindrically averaged structure factors $I_l^{1/2}(R_{hk})$ (for a polycrystalline specimen). One way of assessing the significance of the R factor obtained in a particular structure determination is by comparing it with the 'largest likely R factor' (Wilson, 1950), *i.e.* the expected value of the R factor for a random distribution of atoms. Wilson (1950) showed that the largest likely R factor is 0.83 for a centric crystal and 0.59 for an acentric crystal. Although it does not provide a quantitative measure of structural reliability, the largest likely R factor does provide a useful yardstick for evaluating the significance of R factors obtained in structure determinations.

The largest likely R factor for fibre diffraction can be calculated from the amplitude statistics, which depend on the number of degrees of freedom, m , in the measured intensity (Stubbs, 1989; Millane, 1990a). Making use of these statistics shows that the largest likely R factor, R_m , for m components is given by (Stubbs, 1989; Millane, 1989a)

$$R_m = 2 - 2^{2-m} m \binom{2m-1}{m} B_{1/2} \left(\frac{m+1}{2}, \frac{m}{2} \right), \quad (4.5.2.75)$$

where $\binom{m}{n}$ is the binomial coefficient and $B_x(m, n)$ the incomplete beta function. The beta function in equation (4.5.2.75) can be replaced by a finite series that is easy to evaluate (Millane, 1989a). The expression in equation (4.5.2.75) for R_m can be written in various approximate forms (Millane, 1990d, 1992a), the simplest being

$$R_m \simeq (2/\pi m)^{1/2} \quad (4.5.2.76)$$

(Millane, 1990d), which shows that the largest likely R factor falls off approximately as $m^{-1/2}$ with increasing m . This is because it is easier to match the sum of a number of structure amplitudes than to match each of them individually. The important conclusion is that the largest likely R factor is smaller in fibre diffraction than in conventional crystallography (where $m = 1$ or 2), and it is smaller when there are more overlapping reflections. This means that for equivalent precision, the R factor must be smaller for a structure determined by fibre diffraction than for one determined by conventional crystallography. How much smaller depends on the number of overlapping reflections on the diffraction pattern.

In a structure determination, the data have different values of m at different positions on the diffraction pattern. Using the definition of the R factor, equation (4.5.2.74), shows that the largest likely R factor for a structure determination is given by (Millane, 1989b)

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$$R = \frac{\sum_m N_m R_m S_m}{\sum_m N_m S_m}, \quad (4.5.2.77)$$

where the sums are over the values of m on the diffraction pattern, N_m is the number of data that have m components, R_m is given by equation (4.5.2.75) and S_m is given by

$$S_m = \frac{\Gamma((m/2) + (1/2))}{\Gamma(m/2)}, \quad (4.5.2.78)$$

where $\Gamma(\cdot)$ is the gamma function. The quantities on the right-hand side of equation (4.5.2.77) are easily determined for a particular data set. The largest likely R factor decreases (since m increases) with increasing resolution of the data, increasing diameter of the molecule and decreasing order u of the helix symmetry. For example, for TMV at 5 Å resolution the largest likely R factor is 0.37, and at 3 Å resolution it is 0.31, whereas for a tenfold nucleic acid structure at 3 Å resolution it is 0.40 (Millane, 1989b, 1992b). This underlines the importance of comparing R factors obtained in a fibre diffraction analysis with the largest likely R factor; an R factor of 0.25 that may indicate a good protein structure may, or may not, indicate a well determined fibre structure.

Using approximations for R_m , S_m and m allows the following approximation for the largest likely R factor for a noncrystalline fibre to be derived (Millane, 1992b):

$$R \simeq 0.261(ud_{\max}/r_{\max})^{1/2}, \quad (4.5.2.79)$$

where $d_{\max}$ is the resolution of the data. The approximation (4.5.2.79) is generally not good enough for calculating accurate largest likely R factors, but it does show the general behaviour with helix symmetry, molecular diameter and diffraction-data resolution. Other approximations to largest likely R factors have been derived that are quite accurate and also include the effect of a minimum resolution for the data (Millane, 1992b).

Largest likely R factors in fibre diffraction studies are typically between about 0.3 and 0.5, depending on the particular structure (Millane, 1989b, 1992b; Millane & Stubbs, 1992). Although the largest likely R factor does not give a quantitative assessment of the significance of an R factor obtained in a particular structure determination, it can be used as a guide to the significance. R factors obtained for well determined protein structures are typically between about one-third and one-half of the corresponding largest likely R factor, depending on the resolution. It is therefore reasonable to expect the R factor for a well determined fibre structure to be between one-third and one-half of the largest likely R factor calculated for the structure. R factors should, therefore, generally be less than 0.15 to 0.25, depending on the particular structure and the resolution as illustrated by the examples presented in Millane & Stubbs (1992).

The free R factor (Brünger, 1997) has become popular in single-crystal crystallography as a tool for validation of refinements. The free R factor is more difficult to implement (but is probably even more important) in fibre diffraction studies because of the smaller data sets, but has been used to advantage in recent studies (Hudson *et al.*, 1997; Welsh *et al.*, 1998, 2000).

4.5.3. Electron crystallography of polymers

(D. L. DORSET)

4.5.3.1. Is polymer electron crystallography possible?

As a crystallographic tool, the electron microscope has also made an important impact in polymer science. Historically, single-crystal electron diffraction information has been very useful for the interpretation of cylindrically averaged fibre X-ray patterns (Atkins,

1989), particularly when there is an extensive overlap of diffracted intensities. An electron diffraction pattern aids indexing of the fibre pattern and facilitates measurement of unit-cell constants, and the observation of undistorted plane-group symmetry similarly places important constraints on the identification of the space group (Geil, 1963; Wunderlich, 1973).

The concept of using electron diffraction intensities by themselves for the quantitative determination of crystal structures of polymers or other organics often has been met with scepticism (Lipson & Cochran, 1966). Difficulties experienced in the quantitative interpretation of images and diffraction intensities from 'hard' materials composed of heavy atoms (Hirsch *et al.*, 1965; Cowley, 1981), for example, has adversely affected the outlook for polymer structure analysis, irrespective of whether these reservations are important or not for 'soft' materials comprising light atoms. Despite the still commonly held opinion that no new crystal structures will be determined that are solely based on data collected in the electron microscope, it can be shown that this extremely pessimistic outlook is unwarranted. With proper control of crystallization (*i.e.* crystal thickness) and data collection, the electron microscope can be used quite productively for the direct determination of macromolecular structures at atomic resolution, not only to verify some of the previous findings of fibre X-ray diffraction analysis, but, more importantly, to determine new structures, even of crystalline forms that cannot be studied conveniently by X-rays as drawn fibres (Dorset, 1995b). The potential advantages of electron crystallography are therefore clear. The great advantage in scattering cross section of matter for electrons over X-rays permits much smaller samples to be examined by electron diffraction as single-crystalline preparations (Vainshstein, 1964). (Typical dimensions are given below.)

Electron crystallography can be defined as the quantitative use of electron micrographs and electron diffraction intensities for the determination of crystal structures. In the electron microscope, an electron beam illuminates a semitransparent object and the microscope objective lens produces an enlarged representation of the object as an image. If the specimen is thin enough and/or the electron energy is high enough, the weak-phase-object or 'kinematical' approximation is valid (Cowley, 1981), see Chapter 2.5. That is to say, there is an approximate one-to-one mapping of density points between the object mass distribution and the image, within the resolution limits of the instrument (as set by the objective lens aberrations and electron wavelength). The spatial relationships between diffraction and image planes of an electron microscope objective lens are reciprocal and related by Fourier transform operations (Cowley, 1988). While it is easy to transform from the image to the diffraction pattern, the reverse Fourier transform of the diffraction pattern to a high-resolution image requires solution of the famous crystallographic phase problem (as discussed for electron diffraction in Section 2.5.7).

Certainly, in electron diffraction studies, one must still be cognizant of the limitations imposed by the underlying scattering theory. An approximate 'quasi-kinematical' data set is often sufficient for the analysis (Dorset, 1995a). However (Dorset, 1995b), there are other important perturbations to diffraction intensities which should be minimized. For example, the effects of radiation damage while recording a high-resolution image are minimized by so-called 'low-dose' procedures (Tsuji, 1989).

4.5.3.2. Crystallization and data collection

The success of electron crystallographic determinations relies on the possibility of collecting data from *thin* single microcrystals. These can be grown by several methods, including self-seeding, epitaxial orientation, *in situ* polymerization on a substrate, in a Langmuir–Blodgett layer, *in situ* polymerization within a thin layer

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and polymerization in dilute solution. If these preparations do not provide sufficient information, then data can also be collected from microfibrils. Thin cast films have also been examined after stretching.

Self-seeding (Blundell *et al.*, 1966) has been one of the most important techniques for growing single chain-folded lamellae. The technique is very simple. A dilute suspension of the polymer is made in a poor solvent. The temperature is raised to cause total solubilization of the macromolecule and then lowered to room temperature to crystallize ill-formed particles (mostly dendrites). The temperature is then elevated again until the suspension just clears, leaving small seeds of the polymer crystals behind. Upon lowering to a suitable temperature above ambient, which is then fixed, isothermal crystallization of well formed lamellae is allowed to occur over time. When the crystallization procedure is complete, the suspension can be cooled again to room temperature and the lamellae harvested. These lamellae are typically less than 10 nm thick, with lateral dimensions between 1.0 and 10.0 μm .

Epitaxial orientation techniques, to give alternative projections of the chain packing, have become increasingly important in recent years. While inorganic substrates have been described (Mauritz *et al.*, 1978), the use of organic layers for this purpose (Wittmann & Lotz, 1990; Lotz & Wittmann, 1993) has been more promising because these substrates are less easily contaminated by adsorbed gases and water vapour, and because the nucleation is anisotropic. Often the crystallization can be carried out from a cooled co-melt, *i.e.* a dilute solution of the polymer in the organic small molecule. When the liquidus curve of the eutectic phase diagram is crossed, the diluent crystals form first. Since these have a surface lattice spacing closely resembling that of the polymer-chain packing, the polymer chains can be directed to lie *along* the substrate surface, rather than normal to it, as the solidus line of the phase diagram is crossed. The substrate can then be removed by some suitable technique (sublimation, selective solvation) to permit the investigation of the oriented film. Variations of this procedure include crystallization of polymer-chain segments from the vapour phase onto a substrate (Wittmann & Lotz, 1985) and *in situ* crystallization of monomers that have first been epitaxially oriented on a suitable substrate (Rickert *et al.*, 1979).

A number of other possibilities for crystal growth also exist. Langmuir troughs have been used to orient monomers that may have hydrophilic moieties. If the monomers contain triple bonds that can be cross-linked, then a polymer film can be formed, *e.g.*, if the condensed monomer film is exposed to ultraviolet light (Day & Lando, 1980). It may be possible to carry out the polymerization within a confined space (Rybníkar *et al.*, 1994) or in dilute solution (Liu & Geil, 1993) to form crystals suitable for electron diffraction data collection. In the latter case, whisker formation with the chain axis parallel to the lath plane has been observed. Films can be cast on a water surface by evaporation of an organic solvent from a polymer solution. The film can then be stretched to give a suitably oriented specimen for data collection (Vainshtein & Tatarinova, 1967). In addition, it may just be possible to obtain suitable data from drawn microfibrils to supplement the single-crystal diffraction information from other preparations.

Data collection from these thin microcrystals often employs the selected-area diffraction technique in the electron microscope that is described in detail elsewhere (Dorset, 1995b). Using an approximately eucentric goniometric tilting device in the electron microscope, the sampling of three-dimensional reciprocal space is tomographic, *i.e.* the tilts of a nearly planar Ewald sphere surface (owing to the very small electron wavelength) are always referred to a set of reciprocal axes that intersect (0, 0, 0). For any given crystal habit, there is always a missing set of data owing to the physical limitation to the tilt imposed by the finite thickness of the specimen holder within the pole-piece gap of the electron microscope

objective lens (Vainshtein, 1964). For this reason, it is desirable to crystallize two orthogonal orientations of the chain packing (using the above-mentioned approaches), if possible, so that all of the reciprocal lattice can be sampled. If electron micrographs are to be used as an additional source of crystallographic phases then 'low-dose' techniques for recording such images should be employed to reduce the deleterious effects of radiation damage caused by the inelastic interactions of the electron beam with the crystalline sample (Tsuji, 1989).

When the diffraction patterns are recorded on photographic film and these are then measured with a densitometer, relative reflection intensities can often be expressed simply as the integrated peak area without need for a Lorentz correction (Dorset, 1995b). Only if the diffraction maxima are extensively arced (*e.g.* in patterns from epitaxial films) is such a correction required. That is to say, $|\Phi_{\text{obs}}| \propto K I_{\text{obs}}^{1/2}$ where $|\Phi_{\text{obs}}|$ is the observed structure-factor magnitude. Assuming the kinematical approximation holds, the calculated value is

$$\Phi_h^{\text{calc}} = \sum_i f_i \exp 2\pi i(\mathbf{h} \cdot \mathbf{r}),$$

where f_i are the electron scattering factors (Doyle & Turner, 1968), *e.g.* as tabulated in Table 4.3.1.1 in *IT C*. By analogy with X-ray crystallography (see Chapter 2.2), normalized values can be found from

$$|E_h|^2 = I_h^{\text{obs}} / \varepsilon \sum_i f_i^2,$$

with the usual scaling condition that $\langle E_h^2 \rangle = 1.000$. [Note, however, that these intensities only describe the chain monomer packing in the 'stem' region of the lamellar microcrystal. Details owing to the surface chain folds are lost (even if they are strictly periodic), because of reasons similar to those described by Cowley (1961) for the electron scattering from elastically bent silicate crystals.]

4.5.3.3. Crystal structure analysis

Two approaches to crystal structure analysis are generally employed in polymer electron crystallography. As already mentioned, the procedure adapted from fibre X-ray crystallography relies on the construction of a model (Brisse, 1989; Perez & Chanzy, 1989). Conformational searches (Campbell Smith & Arnott, 1978) simultaneously minimize the fit of observed diffraction data to calculated values (the *R* factor based on structure factors computed *via* known atomic scattering factors) and a nonbonded atom-atom potential function (Tadokoro, 1979). Reviews of structures solved by this approach have been published (Dorset, 1989, 1995b).

Recently, direct phasing methods of the kind used in X-ray crystallography (Chapter 2.2 and, applied to electron diffraction, Section 2.5.7) have also been found to be particularly effective for electron crystallographic structure analyses (Dorset, 1995b). While the Fourier transform of an electron micrograph would be the most easily imagined direct method, yielding crystallographic phases after image analysis (see Section 2.5.5), this use of micrographs has been of less importance to polymer crystallography than it has been in the study of globular proteins, even though there is at least one notable example where it has been helpful (Isoda *et al.*, 1983a) for the determination of a structure from X-ray fibre data. On the other hand, high-resolution images of polymer crystals are of considerable use for the characterization of packing defects (Isoda *et al.*, 1983b).

In polymer electron crystallography, the sole reliance on the diffraction intensities for structure analysis has proven, in recent years, to be quite effective. Several direct-methods approaches have been pursued, including the use of probabilistic techniques, either in

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the symbolic addition procedure, or in more automated procedures involving the tangent formula (see Chapter 2.2). The Sayre (1952) equation has been found to be particularly effective, where the correct structure is identified *via* some figure of merit after algebraic phase values are used to generate multiple solutions (Stanley, 1986). More recently, maximum-entropy and likelihood methods (Gilmore *et al.*, 1993) have also been effective for solving such structures. After the initial atomic model is found, it can be improved by refinement, generally using Fourier techniques. Least-squares refinement can be carried out under most favourable circumstances (Dorset, 1995a), but requires the availability of a sufficient number of diffraction data. Even so, the refinement of thermal parameters must be uncoupled from that of the atomic positions. Also, positional shifts must be dampened (if X-ray crystallographic software is used) to prevent finding a false minimum, especially if the kinematical *R* factor is used as a figure of merit.

4.5.3.4. Examples of crystal structure analyses

At least four kinds of electron diffraction intensity data sets have been used as tests for direct phase determination *via* the approaches mentioned above.

Case 1: Zonal data sets – view down the chain axis. Such data are from the least optimal projection of the polymer packing, because of extensive atomic overlap along the chain axis. Initially, symbolic addition was used to find phase values for *hk0* data sets from six representative polymers, including three complicated saccharide structures (Dorset, 1992). Most of the determinations were strikingly successful. Later, an unknown data set from the polysaccharide chitosan was obtained from Grenoble (Mazeau *et al.*, 1994) and direct phase determination was able to find a correct model (Dorset, 1995b). More recently, other polymers have been tested [including one case where an electron micrograph provided many of the starting phase terms (Dorset, 1995b)] also comparing favourably with the solution found by energy minimization of a linkage model. For all examples considered so far, the projected symmetry was centrosymmetric.

Later, it was found that a partial phase set provided by symbolic addition could be expanded to the complete zone by the Sayre equation (Dorset *et al.*, 1995). In all of these tests (Dorset, 1995b), there were only one or two examples where there were serious deviations from the phase terms found by other methods. Even in these instances, the potential maps could still be used as envelopes for the actual projection of the chain structure (Dorset, 1992).

Case 2: Zonal data set – view onto the chain axes. Electron diffraction data from a projection onto the polymer chain axes would be more useful if individual atomic positions were to be resolved. An interesting example where such a view can be obtained is an *h0l* data set from the polypeptide poly- γ -methyl-L-glutamate. Electron diffraction data were collected from stretched films by Vainshtein & Tatarinova (1967). In projection, the cell constants are $a = 4.72$, $c = 6.83$ Å with plane-group symmetry *pg*. As shown in Table 4.5.3.1, there were 19 unique intensity data used for the analysis. After initial phase assignment by symbolic addition, a correct solution could be visualized which, after Fourier refinement (Dorset, 1995b), differed from the original one by a mean phase difference of only 6°.

The progress of this structure analysis can be reviewed to give a representative example. Since the *h00* reflections have centrosymmetric phases, the value $\varphi_{100} = 0$ was chosen as a single origin-defining point. From high-probability Σ_1 three-phase invariants (assessed after calculation of normalized structure factors $|E_h|$), one could assign $\varphi_{200} = \varphi_{400} = 0$. Symbolic values were then given to three other phases, *viz.* $\varphi_{106} = a$; $\varphi_{103} = b$; $\varphi_{101} = c$. From this entire basis, other values could be found from highly probable Σ_2

Table 4.5.3.1. *Structure analysis of poly- γ -methyl-L-glutamate in the β form*

<i>h0l</i>	$ E_h $	$ F_o $	$ F_c $	φ (°) (previous)	φ (°) (this study)
002	0.48	0.72	0.57	−63	−51
004	0.43	0.38	0.31	49	73
006	3.01	1.47	0.88	1	−3
100	1.48	2.12	2.37	0	0
200	1.03	1.04	1.06	0	0
300	0.30	0.65	0.89	0	0
400	0.35	0.15	0.46	0	0
500	0.23	0.07	0.04	180	180
101	0.75	1.02	0.67	−169	−178
201	0.32	0.31	0.42	90	108
102	0.42	0.48	0.56	17	14
202	0.40	0.33	0.64	41	43
103	0.95	0.85	0.77	88	90
203	0.51	0.36	0.42	91	88
303	0.12	0.06	0.31	92	87
403	0.13	0.04	0.54	90	90
104	0.66	0.45	0.27	−22	−13
105	0.55	0.28	0.29	−26	−7
106	1.75	0.69	0.58	5	−5

Fractional coordinates

	This study		Vainshtein & Tatarinova (1967)	
	<i>x</i>	<i>z</i>	<i>x</i>	<i>z</i>
$C\alpha, \beta$	0.048	0.000	0.042	0.000
C'	0.067	0.331	0.092	0.330
O	0.281	0.335	0.300	0.330
N	0.000	0.161	−0.025	0.175

three-phase invariants, as follows:

$$\begin{aligned}
 \varphi_{006} &= \varphi_{106} + \varphi_{\bar{1}00} \therefore \varphi_{006} = a \\
 \varphi_{105} &= \varphi_{006} + \varphi_{10\bar{1}} \therefore \varphi_{105} = a - c + \pi \\
 \varphi_{203} &= \varphi_{106} + \varphi_{10\bar{3}} \therefore \varphi_{203} = a - b + \pi \\
 \varphi_{300} &= \varphi_{100} + \varphi_{200} \therefore \varphi_{300} = 0 \\
 \varphi_{002} &= \varphi_{103} + \varphi_{\bar{1}0\bar{1}} \therefore \varphi_{002} = b - c \\
 \varphi_{004} &= \varphi_{006} + \varphi_{00\bar{2}} \therefore \varphi_{004} = a - b + c.
 \end{aligned}$$

(These invariant relationships include phase interactions among symmetry-related Miller indices characteristic of the plane group.) Additionally $c = \pi$ could be specified to complete origin definition for the zone. It was then possible to permute values of *a* and *b* to arrive at test phase values for this subset, *i.e.* to generate a multiple set of solutions. When $a = 0$, $b = \pi/2$, the map in Fig. 4.5.3.1 was observed. After finding trial atomic positions for Fourier refinement (assuming that two carbon-atom positions were eclipsed in this projection), the final phase set was found as shown in Table 4.5.3.1. Although the crystallographic residual to the observed data, calculated with the model coordinates, was rather large (0.32), there was a close agreement with the earlier determination.

More recently a similar data set, collected from oriented crystal ‘whiskers’ of poly(*p*-oxybenzoate) in plane group *pg* was analysed. Again the Sayre equation, *via* a multisolution approach, was used to produce a map that contained 13 of 18 possible atomic positions for

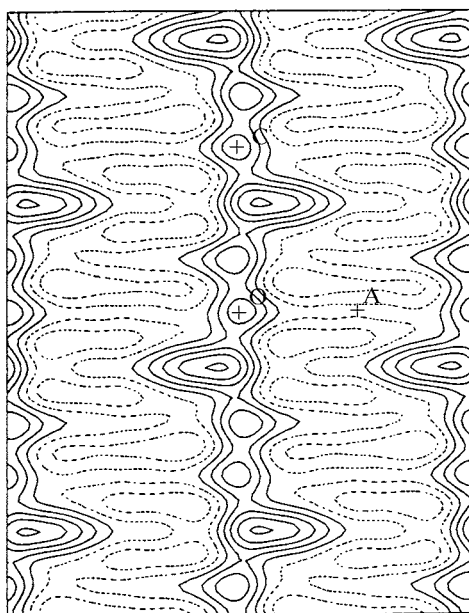


Fig. 4.5.3.1. Initial potential map for poly- γ -methyl-L-glutamate (plane group pg) found with phases generated by the Sayre equation.

the two subunits in the asymmetric unit. The complete structure was observed after the remaining five atom sites were identified in two subsequent cycles of Fourier refinement (Liu *et al.*, 1997) and the average atomic positions were found to be within 0.2 Å of the model derived from an energy minimization.

Case 3: Three-dimensional data – single crystal orientation. The first data set from a chain-folded lamella for a direct structure analysis was a centrosymmetric set (space group $P2_1/n$) from poly(1,4-*trans*-cyclohexanediyl dimethylene succinate), composed of 87 reflections (Brisse *et al.*, 1984). The phase determination was quite successful and atomic positions could be found as somewhat blurred density maxima in the three-dimensional maps (Dorset, 1991a). A model was constructed from these positions and the bonding parameters optimized to give the best fit to the data ($R = 0.29$).

Noncentrosymmetric three-dimensional intensity sets (orthorhombic space group $P2_12_12_1$) from the polysaccharides mannan (form I) (Chanzy *et al.*, 1987) and chitosan (Mazeau *et al.*, 1994) were also collected from tilted crystals. In both cases, direct phase determination by symbolic addition *via* an algebraic unknown was successful, even though the data were not sampled along the chain repeat. For the former polymer, a monomer model could be fitted to the blurred density profile, much as one would fit a polypeptide sequence to a continuous electron-density map (Dorset & McCourt, 1993; Dorset, 1995c). If the Sayre equation were used to predict phases and amplitudes within the ‘missing cone’ of unsampled data, then the fit of the monomer could be much more highly constrained.

Case 4: Three-dimensional data – two crystal orientations. The optimal case for collection of diffraction data is when two orthogonal projections of the same polymer polymorph can be obtained, respectively, by self-seeding and epitaxial orientation. While tilting these specimens, all of reciprocal space can be sampled for intensity data collection.

Polyethylene crystals were used to collect 50 unique maxima (Hu & Dorset, 1989) and, *via* symbolic addition, the centrosymmetric phases of 40 reflections (space group $Pnma$) could be readily determined (Dorset, 1991b). The structural features were readily observed in the three-dimensional potential maps (Fig. 4.5.3.2a), and atomic coordinates (with estimated values for hydrogen-atom positions) could be refined by least squares (Dorset, 1995b) to give a final R value of 0.19.

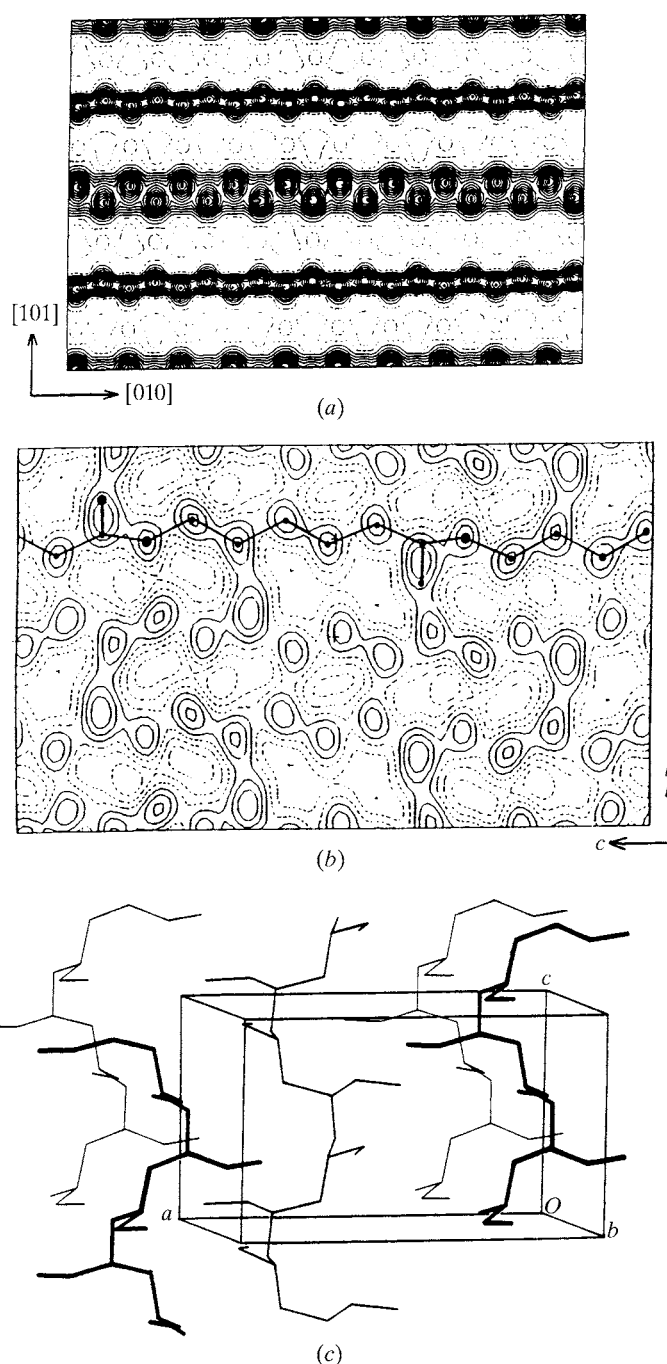


Fig. 4.5.3.2. Crystal structures of linear polymers determined from three-dimensional data. (a) Polyethylene; (b) poly(ϵ -caprolactone); (c) poly(1-butene), form (III).

Poly(ϵ -caprolactone) was epitaxially crystallized on benzoic acid and, with $hk0$ data from solution-crystallized samples, a unique set of 47 intensities was collected for the noncentrosymmetric orthorhombic unit cell (space group $P2_12_12_1$) (Hu & Dorset, 1990). Direct phase determination was achieved *via* symbolic addition, using one algebraic unknown to assign values to 30 reflections (Dorset, 1991c). Atomic positions along the chain repeat, including the carbonyl position, were clearly discerned in the $[100]$ projection (Fig. 4.5.3.2b) and the three-dimensional model was constructed to fit to the map calculated from all phased data, yielding a final crystallographic residual $R = 0.21$. This independent determination was able to distinguish between two rival fibre X-ray structures, in favour of the one that predicted a non-planar chain conformation.

4.5. POLYMER CRYSTALLOGRAPHY

Because of the methylene repeat, this is actually a difficult structure to solve by automated techniques. For example, the tangent formula and *SnB* (Miller *et al.*, 1993) could only find chain zigzag positions and not the position of the carbonyl oxygen atom (Dorset, 1995b).

The most complicated complete polymer crystal structure solved so far by direct methods using electron diffraction data (Dorset *et al.*, 1994) was based on 125 unique data (space group $P2_12_12_1$) from isotactic poly(1-butene), form (III), using orthogonal molecular orientations crystallized in Strasbourg (Kopp *et al.*, 1994). Initially, the standard NQUEST figure of merit (FOM) (De Titta *et al.*, 1975) was not suitable for identifying the correct solution among the multiple sets generated with the tangent formula. A solution could only be found when a separate phase determination was carried out with the $hk0$ data to compare with the multiple solutions generated. More recently, the minimal principle

(Hauptman, 1993), used as a FOM with the tangent formula or with a multiple random structure generator, *SnB*, correctly identified the structure on the first try (Dorset, 1995b). The maps clearly show individual carbon-atom positions in a 4_1 helix that parallels 2_1 helices of the space group (Fig. 4.5.3.2c). After Fourier refinement, the crystallographic residual was $R = 0.26$. The previous powder X-ray diffraction determination was based on only 21 diffraction maxima, some of which had as many as 15 individual contributors.

Acknowledgements

The work of both RPM and DLD was supported by the US National Science Foundation (grant DBI-9722862 for RPM).

4.6. Reciprocal-space images of aperiodic crystals

BY W. STEURER AND T. HAIBACH

4.6.1. Introduction

The discovery of materials with icosahedral diffraction symmetry (Shechtman *et al.*, 1984) was the main reason for the reassessment of the definition of *crystallinity* and for the introduction of the concept of *aperiodic crystals*. The first aperiodic crystal, *i.e.* a material with Bragg reflections not located only at reciprocal-lattice nodes, was identified long before (Dehlinger, 1927). In the following decades a wealth of incommensurately modulated phases and composite crystals were discovered. Nevertheless, only a few attempts have been made to develop a crystallography of aperiodic crystals; the most powerful of these was the higher-dimensional approach (see de Wolff, 1974, 1977; Janner & Janssen, 1979, 1980a,b; de Wolff *et al.*, 1981). In fact, incommensurate structures can be easily described using the higher-dimensional approach and also, fully equivalently, in a dual way: as a three-dimensional (3D) combination of one or more periodic basic structures and one or several modulation waves (de Wolff, 1984). However, with the discovery of quasicrystals and their noncrystalline symmetries, the latter approach failed and geometrical crystallography including the higher-dimensional approach received new attention. For more recent reviews of the crystallography of all three types of aperiodic crystals see van Smaalen (1995), of incommensurately modulated structures see Cummins (1990), of quasicrystals see Steurer (1990, 1996), of quasicrystals and their crystalline approximants see Goldman & Kelton (1993) and Kelton (1995). Textbooks on quasicrystals have been written by Janot (1994) and Senechal (1995).

According to the traditional crystallographic definition, an *ideal crystal* corresponds to an infinite 3D periodic arrangement of identical structure motifs. Its symmetry can be described by one of the 230 3D space groups. Mathematically, a periodic structure can be generated by the convolution of a function representing the structure motif with a lattice function. The structure motif can be given, for instance, by the electron-density distribution $\rho(\mathbf{r})$ of one primitive unit cell of the structure. The lattice function $g(\mathbf{r})$ is represented by a set of δ functions at the nodes $\mathbf{r} = \sum_{i=1}^3 k_i \mathbf{a}_i$ of a 3D lattice Λ with basis $\mathbf{a}_i$, $i = 1, \dots, 3$, and $k_i \in \mathbb{Z}$ ($\mathbb{Z}$ is the set of integer numbers). In reciprocal space, this convolution corresponds to the product of the Fourier transform $G(\mathbf{H})$ of the lattice function $g(\mathbf{r})$ and the Fourier transform $F(\mathbf{H}) = \int_V \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}$ of the structure motif $\rho(\mathbf{r})$. $G(\mathbf{H})$ is represented by the reciprocal lattice Λ^* decorated with δ functions on the reciprocal-lattice nodes $\mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^*$, with the reciprocal-basis vectors $\mathbf{a}_i^*$, $i = 1, \dots, 3$, defined by $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$ and $h_i \in \mathbb{Z}$. The product $G(\mathbf{H}) \times F(\mathbf{H})$ is called the weighted reciprocal lattice; the weights are given by the structure factors $F(\mathbf{H})$. Thus, the characteristic feature of an ideal crystal in direct and reciprocal space is the existence of a lattice. In direct space, this lattice is decorated with identical structure motifs preserving translational and point symmetry in the framework of *space-group symmetry*. In reciprocal space, only the point symmetry between structure factors is maintained. The *Fourier spectrum* (or *Fourier image*, *i.e.* the Fourier transform) of the electron-density distribution of an ideal crystal consists of a countably infinite set of discrete Bragg peaks with a strictly defined minimum distance.

This crystal definition can be generalized to $n > 3$ dimensions. A d -dimensional (d D) *ideal aperiodic crystal* can be defined as a d D irrational section of an n -dimensional (n D, $n > d$) crystal with n D lattice symmetry. The intersection of the n D *hypercrystal* with the d D physical space is equivalent to a projection of the weighted n D reciprocal lattice $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^n h_i \mathbf{d}_i^* | h_i \in \mathbb{Z}\}$ onto the d D physical space. The resulting set (Fourier module) $M^* =$

$\{\mathbf{H}^\parallel = \sum_{i=1}^n h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ is countably dense. *Countably dense* means that the dense set of Bragg peaks can be mapped one-to-one onto the set of natural numbers. Hence, the Bragg reflections can be indexed with integer indices on an appropriate basis. The Fourier module of the projected reciprocal-lattice vectors $\mathbf{H}^\parallel$ has the structure of a $\mathbb{Z}$ module of rank n . A $\mathbb{Z}$ module is a free Abelian group, its rank n is given by the number of free generators (rationally independent vectors). The dimension of a $\mathbb{Z}$ module is that of the vector space spanned by it. The vectors $\mathbf{a}_i^*$ are the images of the vectors $\mathbf{d}_i^*$ projected onto the physical space $\mathbb{V}^\parallel$. Thus, by definition, the 3D reciprocal space of an ideal *aperiodic crystal* consists of a countably dense set of Bragg reflections only. Contrary to an ideal *crystal*, a minimum distance between Bragg reflections does not exist in an aperiodic one. In summary, it may be stressed that the terms *aperiodic* and *periodic* refer to properties of crystal structures in d D space. In n D space, as considered here, lattice symmetry is always present and, therefore, the term *crystal* is used.

Besides the *aperiodic crystals* mentioned above, other classes of *aperiodic structures* with strictly defined construction rules exist (see Axel & Gratias, 1995). Contrary to the kind of aperiodic crystals dealt with in this chapter, the Fourier spectra of aperiodic structures considered in the latter reference are continuous and contain only in a few cases additional sharp Bragg reflections (δ peaks).

Experimentally, the borderline between aperiodic crystals and their periodic approximations (*crystalline approximants*) is not sharply defined. Finite crystal size, static and dynamic disorder, chemical impurities and defects broaden Bragg peaks and cause diffuse diffraction phenomena. Furthermore, the resolution function of the diffraction equipment is limited.

However, the concept of describing an aperiodic structure as a d D physical-space section of an n D crystal (see Section 4.6.2) is only useful if it significantly simplifies the description of its structural order. Thus, depending on the shape of the *atomic surfaces*, which gives information on the atomic ordering, incommensurately modulated structures (IMs, Sections 4.6.2.2 and 4.6.3.1), composite structures (CSs, Sections 4.6.2.3 and 4.6.3.2), or quasiperiodic structures (Qs, Sections 4.6.2.4 and 4.6.3.3) can be obtained from irrational cuts. The atomic surfaces are continuous $(n - d)$ -dimensional objects for IMs and CSs, and discrete $(n - d)$ -dimensional objects for Qs. A class of aperiodic crystals with discrete fractal atomic surfaces also exists (Section 4.6.2.5). In this case the Hausdorff dimension (Hausdorff, 1919) of the atomic surface is not an integer number and smaller than $n - d$. The most outstanding characteristic feature of a fractal is its scale invariance: the object appears similar to itself 'from near as from far, that is, whatever the scale' (Gouyet, 1996).

To overcome the problems connected with experimental resolution, the translational symmetry of periodic crystals is used as a hard constraint in the course of the determination of their structures. Hence, space-group symmetry is taken for granted and only the local atomic configuration in a unit cell (actually, asymmetric unit) remains to be determined. In reciprocal space, this assumption corresponds to a condensation of Bragg reflections with finite full width at half maximum (FWHM) to δ peaks accurately located at the reciprocal-lattice nodes. Diffuse diffraction phenomena are mostly neglected. This extrapolation to the existence of an ideal crystal is generally out of the question even if samples of very poor quality (high mosaicity, microdomain structure, defects, . . .) are investigated.

The same practice is convenient for the determination of real aperiodic structures once the type of idealized aperiodic ordering is 'known'. Again, the global ordering principle is taken as a hard

4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

constraint. For instance, the question of whether a structure is commensurately or incommensurately modulated can only be answered within a given experimental resolution. Experimentally, the ratio of the wavelength of a modulation to the period of the underlying lattice can always be determined as a rational number only. Saying that a structure is incommensurately modulated, with the above ratio being an irrational number, simply means that the experimental results can be better understood, modelled and interpreted assuming an incommensurate modulation. For example, an incommensurate charge-density wave can be moved through an ideal crystal without changing the energy of the crystal. This is not so for a commensurate modulation. In some cases, the modulation period changes with temperature in discrete steps ('devil's staircase'), generating a series of commensurate superstructures ('lock-in structures'); in other cases, a continuous variation can be observed within the experimental resolution. The latter case will be described best by an incommensurately modulated structure.

However, if only the local structure of an aperiodic crystal is of interest, a structure analysis does not take much more experimental effort than for a regular crystal. In contrast, for the analysis of the global structure, *i.e.* the characterization of the type of its 'aperiodicity', diffraction experiments with the highest possible resolution are essential. Some problems connected with the structure analysis of aperiodic crystals are dealt with in Section 4.6.4.

To determine the long-range order – whether a real 'quasicrystal' is perfectly quasiperiodic, on average quasiperiodic, a crystalline approximant or a nanodomain structure – requires information from experiments that are sensitive to changes of the global structure. Hence, one needs diffraction experiments that allow the accurate determination of the spatial intensity distribution. Consequently, the limiting factors for such experiments are the maximum spatial and intensity resolution of the diffraction and detection equipment, as well as the size and quality of the sample. Nevertheless, the resolution available on state-of-the-art standard synchrotron-beamline equipment is sufficient to test whether the ordering of atoms in an aperiodic crystal reaches the same degree of perfection as found in high-quality silicon. Of course, the higher the sample quality the more necessary it is to account for dynamical diffraction effects such as reflection broadening and displacement. Otherwise, a misinterpretation may bias the global structure modelling.

The following sections present an aid to the characterization of aperiodic crystals based on information from diffraction experiments and give a survey of aperiodic crystals from the viewpoint of the experimentally accessible reciprocal space. Characteristic features of the diffraction patterns of the different types of aperiodic crystals are shown. A standard way of determining the metrics and finding the optimum nD embedding is described. Structure-factor formulae for general and special cases are given.

4.6.2. The n -dimensional description of aperiodic crystals

4.6.2.1. Basic concepts

An incommensurate modulation of a lattice-periodic structure destroys its translational symmetry in direct and reciprocal space. In the early seventies, a method was suggested by de Wolff (1974) for restoring the lost lattice symmetry by considering the diffraction pattern of an *incommensurately modulated structure* (IMS) as a projection of an nD reciprocal lattice upon the physical space. n , the dimension of the superspace, is always larger than or equal to d , the dimension of the physical space. This leads to a simple method for the description and characterization of IMSs as well as a variety of new possibilities in their structure analysis. The nD embedding method is well established today and can be applied to all aperiodic crystals with reciprocal-space structure equivalent to a $\mathbb{Z}$ module

with finite rank n (Janssen, 1988). The dimension of the embedding space is determined by the rank of the $\mathbb{Z}$ module, *i.e.* by the number of reciprocal-basis vectors necessary to allow for indexing all Bragg reflections with integer numbers. The point symmetry of the 3D reciprocal space (Fourier spectrum) constrains the point symmetry of the nD reciprocal lattice and restricts the number of possible nD symmetry groups.

In the following sections, the nD descriptions of the four main classes of aperiodic crystals are demonstrated on simple 1D examples of incommensurately modulated phases, composite crystals, quasicrystals and structures with fractally shaped atomic surfaces. The main emphasis is placed on quasicrystals that show scaling symmetry, a new and unusual property in structural crystallography. A detailed discussion of the different types of 3D aperiodic crystals follows in Section 4.6.3.

4.6.2.2. 1D incommensurately modulated structures

A periodic deviation of atomic parameters from a reference structure (*basic structure*, BS) is called a *modulated structure* (MS). In the case of mutual incommensurability of the basic structure and the modulation period, the structure is called incommensurately modulated. Otherwise, it is called commensurately modulated. The modulated atomic parameters may be one or several of the following:

- (a) coordinates,
- (b) occupancy factors,
- (c) thermal displacement parameters,
- (d) orientation of the magnetic moment.

An incommensurately modulated structure can be described in a dual way by its *basic structure* $s(\mathbf{r})$ and a *modulation function* $f(t)$. This allows the structure-factor formula to be calculated and a full symmetry characterization employing representation theory to be performed (de Wolff, 1984). A more general method is the nD description: it relates the dD aperiodic incommensurately modulated structure to a periodic structure in nD space. This simplifies the symmetry analysis and structure-factor calculation, and allows more powerful structure-determination techniques.

The nD embedding method is demonstrated in the following 1D example of a displacively modulated structure. A basic structure $s(\mathbf{r}) = s(\mathbf{r} + n\mathbf{a})$, with period a and $n \in \mathbb{Z}$, is modulated by a function $f(t) = f(\mathbf{q} \cdot \mathbf{r}) = f(\alpha r) = f[\alpha r + (na/\alpha)]$, with the satellite vector $\mathbf{q} = \alpha \mathbf{a}^*$, period $\lambda = 1/q = a/\alpha$, and α a rational or irrational number yielding a commensurately or incommensurately modulated structure $s_m(\mathbf{r})$ (Fig. 4.6.2.1).

If the 1D IMS and its 1D modulation function are properly combined in a 2D parameter space $\mathbf{V} = (\mathbf{V}^{\parallel}, \mathbf{V}^{\perp})$, a 2D lattice-periodic structure results (Fig. 4.6.2.2). The actual atoms are generated by the intersection of the 1D physical (external, parallel) space $\mathbf{V}^{\parallel}$ with the continuous *hyperatoms*. The hyperatoms have the shape of the modulation function along the perpendicular (internal, complementary) space $\mathbf{V}^{\perp}$. They result from a convolution of the physical-space atoms with their modulation functions.

A basis $\mathbf{d}_1, \mathbf{d}_2$ (D basis) of the 2D hyperlattice $\Sigma = \{\mathbf{r} = \sum_{i=1}^2 n_i \mathbf{d}_i | n_i \in \mathbb{Z}\}$ is given by

$$\mathbf{d}_1 = \begin{pmatrix} a \\ -\alpha/c \end{pmatrix}_V, \mathbf{d}_2 = \begin{pmatrix} 0 \\ 1/c \end{pmatrix}_V,$$

where a is the translation period of the BS and c is an arbitrary constant. The components of the basis vectors are given on a 2D orthogonal coordinate system (V basis). The components of the basis vector $\mathbf{d}_1$ are simply the parallel-space period a of the BS and α times the perpendicular-space component of the basis vector $\mathbf{d}_2$. The vector $\mathbf{d}_2$ is always parallel to the perpendicular space and its length is one period of the modulation function in arbitrary units (this is expressed by the arbitrary factor $1/c$). An atom at position $\mathbf{r}$

4. DIFFUSE SCATTERING AND RELATED TOPICS

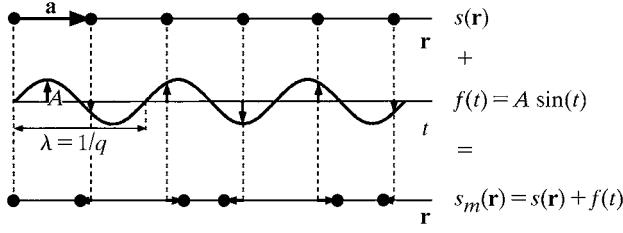


Fig. 4.6.2.1. The combination of a basic structure $s(\mathbf{r})$, with period a , and a sinusoidal modulation function $f(t)$, with amplitude A , period λ and $t = \mathbf{q} \cdot \mathbf{r}$, gives a modulated structure (MS) $s_m(\mathbf{r})$. The MS is aperiodic if a and λ are on incommensurate length scales. The filled circles represent atoms.

of the BS is displaced by an amount given by the modulation function $f(t)$, with $f(t) = f(\mathbf{q} \cdot \mathbf{r})$. Hence, the perpendicular-space variable t has to adopt the value $\mathbf{q} \cdot \mathbf{r} = \alpha \mathbf{a}^* \cdot \mathbf{r} = \alpha r$ for the physical-space variable $\mathbf{r}$. This can be achieved by assigning the slope α to the basis vector $\mathbf{d}_1$. The choice of the parameter c has no influence on the actual MS, *i.e.* the way in which the 2D structure is cut by the parallel space (Fig. 4.6.2.2c).

The basis of the lattice $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^2 h_i \mathbf{d}_i^* | h_i \in \mathbb{Z}\}$, reciprocal to Σ , can be obtained from the condition $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$:

$$\mathbf{d}_1^* = \begin{pmatrix} a^* \\ 0 \end{pmatrix}_V, \mathbf{d}_2^* = \begin{pmatrix} \alpha a^* \\ c \end{pmatrix}_V,$$

with $a^* = 1/a$. The metric tensors for the reciprocal and direct 2D lattices for $c = 1$ are

$$G^* = \begin{pmatrix} a^{*2} & \alpha a^{*2} \\ \alpha a^{*2} & 1 + \alpha^2 a^{*2} \end{pmatrix} \quad \text{and} \quad G = \begin{pmatrix} a^2 + \alpha^2 & -\alpha \\ -\alpha & 1 \end{pmatrix}.$$

The choice of an arbitrary number for c has no influence on the metrics of the physical-space components of the IMS in direct or reciprocal space.

The Fourier transform of the *hypercrystal* depicted in Fig. 4.6.2.2 gives the weighted reciprocal lattice shown in Fig. 4.6.2.3. The 1D diffraction pattern $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^2 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ in physical space is obtained by a projection of the weighted 2D reciprocal lattice Σ^* along $\mathbf{V}^\perp$ as the Fourier transform of a section in direct space corresponds to a projection in reciprocal space and *vice versa*:

$$M^* = \{\mathbf{H}^\parallel\} \xleftarrow{\text{projection } \pi^\parallel \text{ onto } \mathbf{V}^\parallel} \Sigma^* = \{\mathbf{H} = (\mathbf{H}^\parallel, \mathbf{H}^\perp)\}.$$

Reciprocal-lattice points lying in physical space are referred to as *main reflections*, all others as *satellite reflections*. All Bragg reflections can be indexed with integer numbers h_1, h_2 in the 2D description $\mathbf{H} = h_1 \mathbf{d}_1^* + h_2 \mathbf{d}_2^*$. In the physical-space description, the diffraction vector can be written as $\mathbf{H}^\parallel = h \mathbf{a}^* + m \mathbf{q} = \mathbf{a}^* (h_1 + \alpha h_2)$, with $\mathbf{q} = \alpha \mathbf{a}^*$ for the satellite vector and $m \in \mathbb{Z}$ the order of the satellite reflection. For a detailed discussion of the embedding and symmetry description of IMSs see, for example, Janssen *et al.* (1999).

A commensurately modulated structure with $\alpha' = m/n$ and $\lambda = (n/m)a$, $m, n \in \mathbb{Z}$, and with $c = 1$, can be generated by

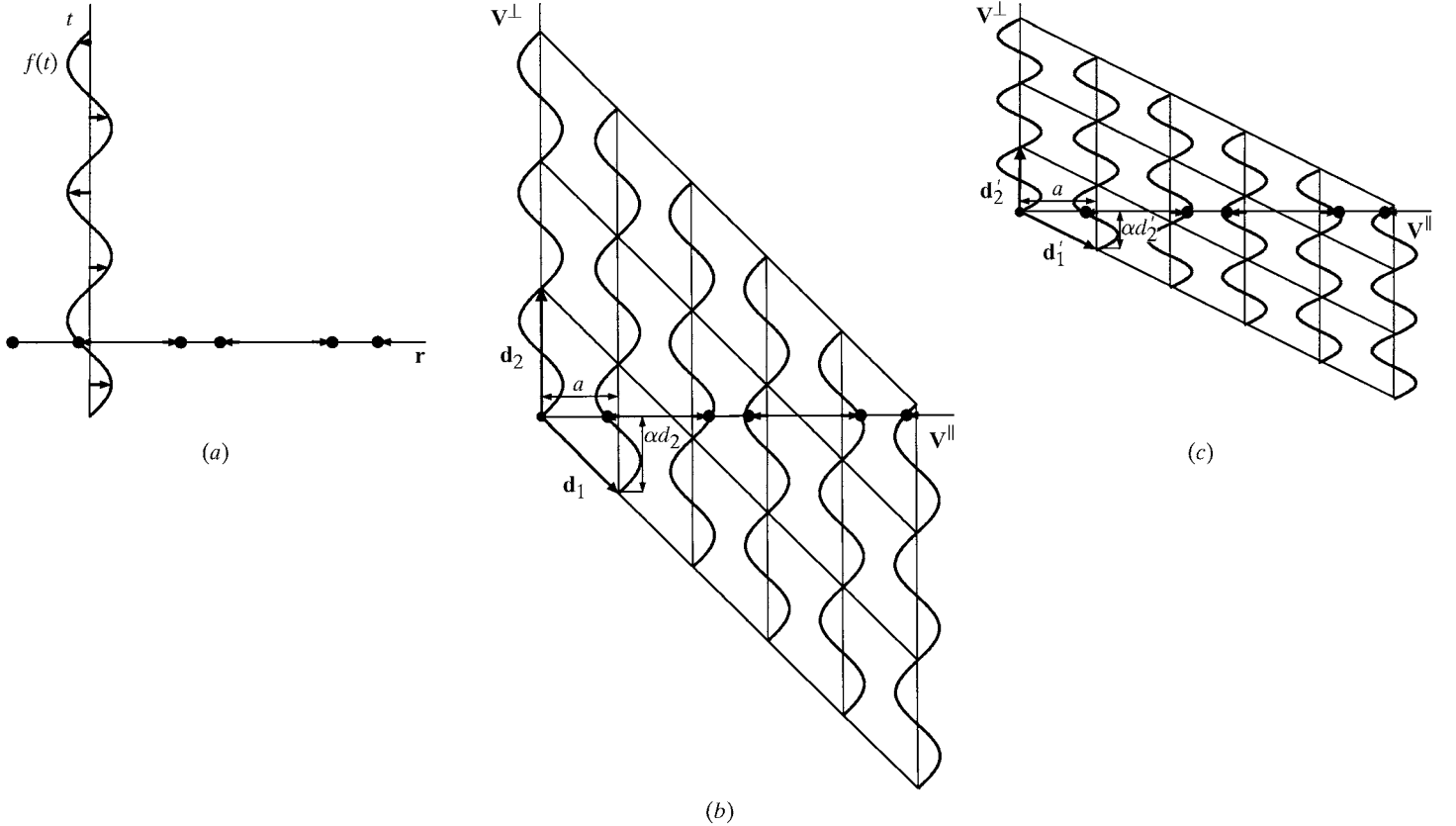


Fig. 4.6.2.2. 2D embedding of the sinusoidally modulated structure illustrated in Fig. 4.6.2.1. The correspondence between the actual displacement of an atom in the 1D structure and the modulation function defined in one additional dimension is illustrated in part (a). Adding to each atom its modulation function in this orthogonal dimension (perpendicular space $\mathbf{V}^\perp$) yields a periodic arrangement in 2D space $\mathbf{V}$, part (b). The MS results as a special section of the 2D periodic structure along the parallel space $\mathbf{V}^\parallel$. It is obvious from a comparison of (b) and (c) that the actual MS is independent of the perpendicular-space scale.

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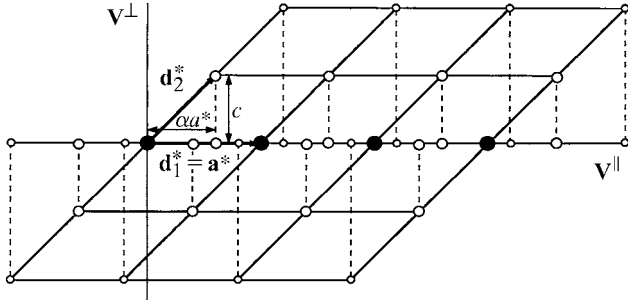


Fig. 4.6.2.3. Schematic representation of the 2D reciprocal-space embedding of the 1D sinusoidally modulated structure depicted in Figs. 4.6.2.1 and 4.6.2.2. Main reflections are marked by filled circles and satellite reflections by open circles. The sizes of the circles are roughly related to the reflection intensities. The actual 1D diffraction pattern of the 1D MS results from a projection of the 2D reciprocal space onto the parallel space. The correspondence between 2D reciprocal-lattice positions and their projected images is indicated by dashed lines.

shearing the 2D lattice Σ with a shear matrix S_m :

$$\mathbf{d}'_i = \sum_{j=1}^2 S_{mij} \mathbf{d}_j, \text{ with } S_m = \begin{pmatrix} 1 & -x \\ 0 & 1 \end{pmatrix}_D \text{ and } x = \alpha' - \alpha,$$

$$\mathbf{d}'_1 = \mathbf{d}_1 - x \mathbf{d}_2 = \begin{pmatrix} a \\ -\alpha \end{pmatrix}_V - (\alpha' - \alpha) \begin{pmatrix} 0 \\ 1 \end{pmatrix}_V = \begin{pmatrix} a \\ -\alpha' \end{pmatrix}_V, \\ \mathbf{d}'_2 = \mathbf{d}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_V.$$

The subscript D (V) following the shear matrix indicates that it is acting on the D (V) basis. The shear matrix does not change the distances between the atoms in the basic structure. In reciprocal space, using the inverted and transposed shear matrix, one obtains

$$\mathbf{d}'_i = \sum_{j=1}^2 (S_m^{-1})_{ij}^T \mathbf{d}_j^*, \text{ with } (S_m^{-1})^T = \begin{pmatrix} 1 & 0 \\ x & 1 \end{pmatrix}_D \text{ and } x = \alpha' - \alpha, \\ \mathbf{d}'_1 = \mathbf{d}_1^* = \begin{pmatrix} a^* \\ 0 \end{pmatrix}_V, \\ \mathbf{d}'_2 = x \mathbf{d}_1^* + \mathbf{d}_2^* = (\alpha' - \alpha) \begin{pmatrix} a^* \\ 0 \end{pmatrix}_V + \begin{pmatrix} \alpha a^* \\ 1 \end{pmatrix}_V = \begin{pmatrix} \alpha' a^* \\ 1 \end{pmatrix}_V.$$

4.6.2.3. 1D composite structures

In the simplest case, a *composite structure* (CS) consists of two intergrown periodic structures with mutually incommensurate lattices. Owing to mutual interactions, each subsystem may be modulated with the period of the other. Consequently, CSs can be considered as coherent intergrowths of two or more incommensurately modulated substructures. The substructures have at least the origin of their reciprocal lattices in common. However, in all known cases, at least one common reciprocal-lattice plane exists. This means that at least one particular projection of the composite structure exhibits full lattice periodicity.

The unmodulated (basic) 1D subsystems of a 1D incommensurate intergrowth structure can be related to each other in a 2D parameter space $\mathbf{V} = (\mathbf{V}^{\parallel}, \mathbf{V}^{\perp})$ (Fig. 4.6.2.4). The actual atoms result from the intersection of the physical space $\mathbf{V}^{\parallel}$ with the hypercrystal. The hyperatoms correspond to a convolution of the real atoms with infinite lines parallel to the basis vectors $\mathbf{d}_1$ and $\mathbf{d}_2$ of the 2D hyperlattice $\Sigma = \{\mathbf{r} = \sum_{i=1}^2 n_i \mathbf{d}_i | n_i \in \mathbb{Z}\}$.

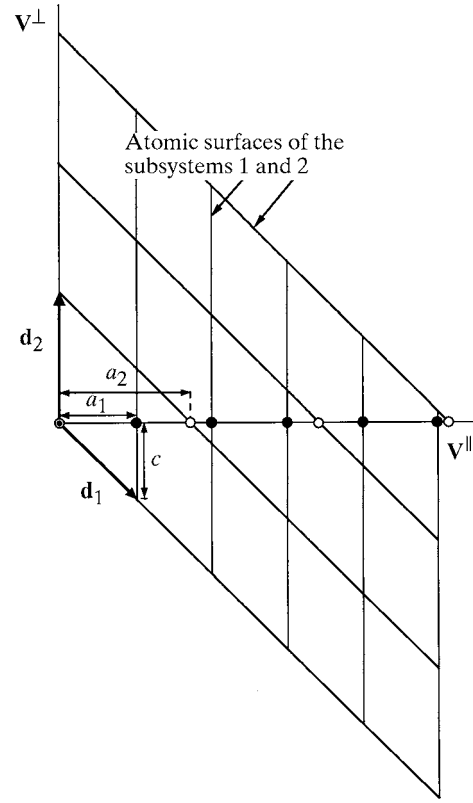


Fig. 4.6.2.4. 2D embedding of a 1D composite structure without mutual interaction of the subsystems. Filled and empty circles represent the atoms of the unmodulated substructures with periods a_1 and a_2 , respectively. The atoms result from the parallel-space cut of the linear atomic surfaces parallel to $\mathbf{d}_1$ and $\mathbf{d}_2$.

An appropriate basis is given by

$$\mathbf{d}_1 = \begin{pmatrix} a_1 \\ -c \end{pmatrix}_V, \mathbf{d}_2 = \begin{pmatrix} 0 \\ c(a_2/a_1) \end{pmatrix}_V,$$

where a_1 and a_2 are the lattice parameters of the two substructures and c is an arbitrary constant. Taking into account the interactions between the subsystems, each one becomes modulated with the period of the other. Consequently, in the 2D description, the shape of the hyperatoms is determined by their modulation functions (Fig. 4.6.2.5).

A basis of the reciprocal lattice $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^2 h_i \mathbf{d}_i^* | h_i \in \mathbb{Z}\}$ can be obtained from the condition $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$:

$$\mathbf{d}_1^* = \begin{pmatrix} a_1^* \\ 0 \end{pmatrix}_V, \mathbf{d}_2^* = \begin{pmatrix} a_2^* \\ (a_2^*/ca_1^*) \end{pmatrix}_V.$$

The metric tensors for the reciprocal and the direct 2D lattices for $c = 1$ are

$$G^* = \begin{pmatrix} a_1^{*2} & a_1^* a_2^* \\ a_1^* a_2^* & (1 + a_1^{*2})(a_2^*/a_1^*)^2 \end{pmatrix} \text{ and } G = \begin{pmatrix} 1 + a_1^2 & -a_2/a_1 \\ -a_2/a_1 & (a_2/a_1)^2 \end{pmatrix}.$$

The Fourier transforms of the hypercrystals depicted in Figs. 4.6.2.4 and 4.6.2.5 correspond to the weighted reciprocal lattices illustrated in Figs. 4.6.2.6 and 4.6.2.7. The 1D diffraction patterns $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^2 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ in physical space are obtained by a projection of the weighted 2D reciprocal lattices Σ^* upon $\mathbf{V}^{\parallel}$. All Bragg reflections can be indexed with integer numbers h_1, h_2 in both the 2D description $\mathbf{H} = h_1 \mathbf{d}_1^* + h_2 \mathbf{d}_2^*$ and in the 1D physical-space description with two parallel basis vectors $\mathbf{H}^{\parallel} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^*$.

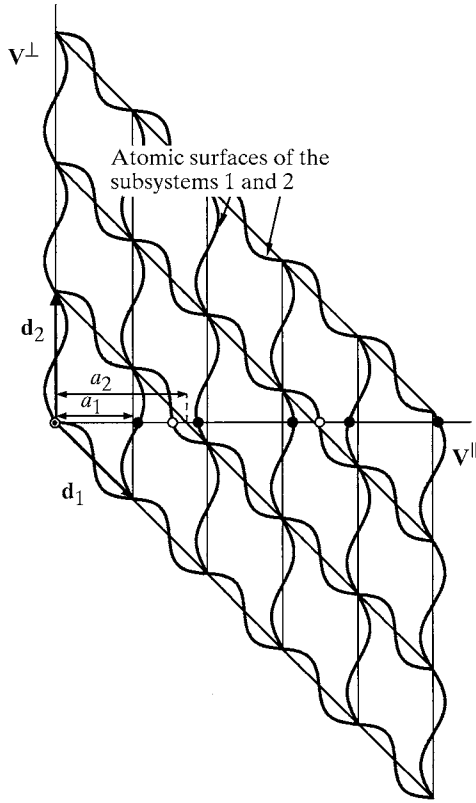


Fig. 4.6.2.5. 2D embedding of a 1D composite structure with mutual interaction of the subsystems causing modulations. Filled and empty circles represent the modulated substructures with periods a_1 and a_2 of the basic substructures, respectively. The atoms result from the parallel-space cut of the sinusoidal atomic surfaces running parallel to $\mathbf{d}_1$ and $\mathbf{d}_2$.

The reciprocal-lattice points $\mathbf{H} = h_1 \mathbf{d}_1^*$ and $\mathbf{H} = h_2 \mathbf{d}_2^*$, $h_1, h_2 \in \mathbb{Z}$, on the main axes $\mathbf{d}_1^*$ and $\mathbf{d}_2^*$ are the main reflections of the two substructures. All other reflections are referred to as satellite reflections. Their intensities differ from zero only in the case of modulated substructures. Each reflection of one subsystem coincides with exactly one reflection of the other subsystem.

4.6.2.4. 1D quasiperiodic structures

The Fibonacci sequence, the best investigated example of a 1D quasiperiodic structure, can be obtained from the substitution rule $\sigma: S \rightarrow L, L \rightarrow LS$, replacing the letter S by L and the letter L by the

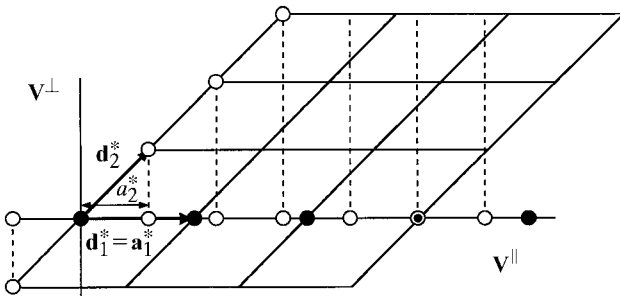


Fig. 4.6.2.6. Schematic representation of the reciprocal space of the embedded 1D composite structure depicted in Fig. 4.6.2.4. Filled and empty circles represent the reflections generated by the substructures with periods a_1 and a_2 , respectively. The actual 1D diffraction pattern of the 1D CS results from a projection of the 2D reciprocal space onto the parallel space. The correspondence between 2D reciprocal-lattice positions and their projected images is indicated by dashed lines.

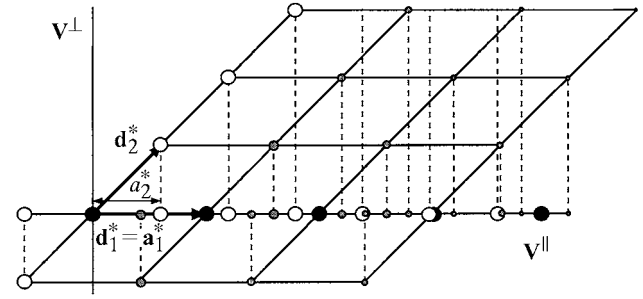


Fig. 4.6.2.7. Schematic representation of the reciprocal space of the embedded 1D composite structure depicted in Fig. 4.6.2.5. Filled and empty circles represent the main reflections of the two subsystems. The satellite reflections generated by the modulated substructures are shown as grey circles. The diameters of the circles are roughly proportional to the intensities of the reflections. The actual 1D diffraction pattern of the 1D CS results from a projection of the 2D reciprocal space onto the parallel space. The correspondence between 2D reciprocal-lattice positions and their projected images is indicated by dashed lines.

word LS (see *e.g.* Luck *et al.*, 1993). Applying the substitution matrix

$$S = \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}$$

associated with σ , this rule can be written in the form

$$\begin{pmatrix} S \\ L \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} S \\ L \end{pmatrix} = \begin{pmatrix} L \\ L + S \end{pmatrix}.$$

S gives the sum of letters, $L + S = S + L$, and not their order. Consequently, the same substitution matrix can also be applied, for instance, to the substitution $\sigma': S \rightarrow L, L \rightarrow SL$. The repeated action of S on the alphabet $A = \{S, L\}$ yields the words $A_n = \sigma^n(S)$ and $B_n = \sigma^n(L) = A_{n+1}$ as illustrated in Table 4.6.2.1. The frequencies of letters contained in the words A_n and B_n can be calculated by applying the n th power of the transposed substitution matrix on the unit vector. From

$$\begin{pmatrix} \nu_{n+1}^A \\ \nu_{n+1}^B \end{pmatrix} = S^T \begin{pmatrix} \nu_n^A \\ \nu_n^B \end{pmatrix}$$

it follows that

$$\begin{pmatrix} \nu_n^A \\ \nu_n^B \end{pmatrix} = (S^T)^n \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

In the case of the Fibonacci sequence, ν_n^B gives the total number of letters S and L, and ν_n^A the number of letters L.

An infinite Fibonacci sequence, *i.e.* a word B_n with $n \rightarrow \infty$, remains invariant under inflation (deflation). Inflation (deflation) means that the number of letters L, S increases (decreases) under the action of the (inverted) substitution matrix S . Inflation and deflation represent self-similarity (scaling) symmetry operations on the infinite Fibonacci sequence. A more detailed discussion of the scaling properties of the Fibonacci chain in direct and reciprocal space will be given later.

The Fibonacci numbers $F_n = F_{n-1} + F_{n-2}$ form a series with $\lim_{n \rightarrow \infty} (F_{n+1}/F_n) = \tau$ {the golden mean $\tau = [1 + (5)^{1/2}]/2 = 2 \cos(\pi/5) = 1.618 \dots$ }. The ratio of the frequencies of L and S in the Fibonacci sequence converges to τ if the sequence goes to infinity. The continued fraction expansion of the golden mean τ ,

4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

Table 4.6.2.1. *Expansion of the Fibonacci sequence $B_n = \sigma^n(L)$ by repeated action of the substitution rule $\sigma: S \rightarrow L, L \rightarrow LS$*

ν_L, ν_S are the frequencies of the letters L and S in word B_n .

B_n	ν_L	ν_S	n
L	1	0	0
LS	1	1	1
LSL	2	1	2
LSLLS	3	2	3
LSLLSLSL	5	3	4
LSLLSLSLLS	8	5	5
LSLLSLSLLSLSL	13	8	6
$\vdots$	$\vdots$	$\vdots$	$\vdots$
F_{n+1}	F_n	F_n	n

$$\tau = 1 + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \dots}}}$$

contains only the number 1. This means that τ is the ‘most irrational’ number, *i.e.* the irrational number with the worst truncated continued fraction approximation to it. This might be one of the reasons for the stability of quasiperiodic systems, where τ plays a role. The strong irrationality may impede the lock-in into commensurate systems (*rational approximants*).

By associating intervals (*e.g.* atomic distances) with length ratio τ to 1 to the letters L and S, a quasiperiodic structure $s(\mathbf{r})$ (*Fibonacci chain*) can be obtained. The invariance of the ratio of lengths $L/S = (L + S)/L = \tau$ is responsible for the invariance of the Fibonacci chain under scaling by a factor $\tau^n, n \in \mathbb{Z}$. Owing to a minimum atomic distance S in real crystal structures, the full set of inverse symmetry operators τ^{-n} does not exist. Consequently, the set of scaling operators $s = \{\tau^0 = 1, \tau^1, \dots\}$ forms only a semi-group, *i.e.* an associative groupoid. Groupoids are the most general algebraic sets satisfying only one of the group axioms: the associative law. The scaling properties of the Fibonacci sequence can be derived from the eigenvalues of the scaling matrix S . For this purpose the equation

$$\det |S - \lambda I| = 0$$

with eigenvalue λ and unit matrix I has to be solved. The evaluation of the determinant yields the characteristic polynomial

$$\lambda^2 - \lambda - 1 = 0,$$

yielding in turn the eigenvalues $\lambda_1 = [1 + (5)^{1/2}]/2 = \tau$, $\lambda_2 = [1 - (5)^{1/2}]/2 = -1/\tau$ and the eigenvectors $\mathbf{w}_1 = \begin{pmatrix} 1 \\ \tau \end{pmatrix}$, $\mathbf{w}_2 = \begin{pmatrix} 1 \\ -1/\tau \end{pmatrix}$. Rewriting the eigenvalue equation gives for the first (*i.e.* the largest) eigenvalue

$$\begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ \tau \end{pmatrix} = \begin{pmatrix} \tau \\ 1 + \tau \end{pmatrix} = \begin{pmatrix} \tau \\ \tau^2 \end{pmatrix} = \tau \begin{pmatrix} 1 \\ \tau \end{pmatrix}.$$

Identifying the eigenvector $\begin{pmatrix} 1 \\ \tau \end{pmatrix}$ with $\begin{pmatrix} S \\ L \end{pmatrix}$ shows that an infinite

Fibonacci sequence $s(\mathbf{r})$ remains invariant under scaling by a factor τ . This scaling operation maps each new lattice vector $\tau\mathbf{r}$ upon a vector $\mathbf{r}$ of the original lattice:

$$s(\tau\mathbf{r}) = s(\mathbf{r}).$$

Considering periodic lattices, these eigenvalues are integer numbers. For quasiperiodic ‘lattices’ (*quasilattices*) they always correspond to *algebraic numbers* (*Pisot numbers*). A Pisot number is the solution of a polynomial equation with integer coefficients. It is larger than one, whereas the modulus of its conjugate is smaller than unity: $\lambda_1 > 1$ and $|\lambda_2| < 1$ (Luck *et al.*, 1993). The total lengths l_n^A and l_n^B of the words A_n, B_n can be determined from the equations $l_n^A = \lambda_1^n l^A$ and $l_n^B = \lambda_1^n l^B$ with the eigenvalue λ_1 . The left Perron–Frobenius eigenvector $\mathbf{w}_1$ of S , *i.e.* the left eigenvector associated with λ_1 , determines the ratio S:L to 1: τ . The right Perron–Frobenius eigenvector $\mathbf{w}_1$ of S associated with λ_1 gives the relative frequencies, 1 and τ , for the letters S and L (for a definition of the Perron–Frobenius theorem see Luck *et al.*, 1993, and references therein).

The general case of an alphabet $A = \{L_1 \dots L_k\}$ with k letters (intervals) L_i , of which at least two are on incommensurate length scales and which transform with the substitution matrix S ,

$$L'_i \rightarrow \sum_{j=1}^k S_{ij} L_j,$$

can be treated analogously. S is a $k \times k$ matrix with non-negative integer coefficients. Its eigenvalues are solutions of a polynomial equation of rank k with integer coefficients (algebraic or Pisot numbers). The dimension n of the embedding space is generically equal to the number of letters (intervals) k involved by the substitution rule. From substitution rules, infinitely many different 1D quasiperiodic sequences can be generated. However, their atomic surfaces in the n D description are generically of fractal shape (see Section 4.6.2.5).

The quasiperiodic 1D density distribution $\rho(\mathbf{r})$ of the Fibonacci chain can be represented by the Fourier series

$$\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}^{\parallel}} F(\mathbf{H}^{\parallel}) \exp(-2\pi i \mathbf{H}^{\parallel} \cdot \mathbf{r}),$$

with $\mathbf{H}^{\parallel} \in \mathbb{R}$ (the set of real numbers). The Fourier coefficients $F(\mathbf{H}^{\parallel})$ form a Fourier module $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^2 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ equivalent to a $\mathbb{Z}$ module of rank 2. Thus a periodic function in 2D space can be defined by

$$\rho(\mathbf{r}^{\parallel}, \mathbf{r}^{\perp}) = (1/V) \sum_{\mathbf{H}} F(\mathbf{H}) \exp[-2\pi i (\mathbf{H}^{\parallel} \cdot \mathbf{r}^{\parallel} + \mathbf{H}^{\perp} \cdot \mathbf{r}^{\perp})],$$

where $\mathbf{r} = (\mathbf{r}^{\parallel}, \mathbf{r}^{\perp}) \in \Sigma$ and $\mathbf{H} = (\mathbf{H}^{\parallel}, \mathbf{H}^{\perp}) \in \Sigma^*$ are, by construction, direct and reciprocal lattice vectors (Figs. 4.6.2.8 and 4.6.2.9):

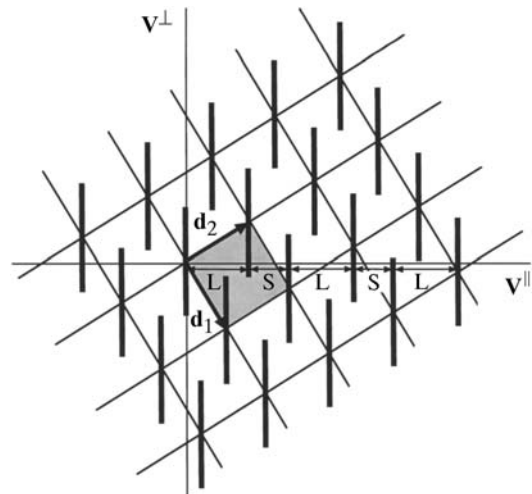


Fig. 4.6.2.8. 2D embedding of the Fibonacci chain. The short and long distances S and L, generated by the intersection of the atomic surfaces with the physical space $\mathbf{V}^{\parallel}$, are indicated. The atomic surfaces are represented by bars parallel to $\mathbf{V}^{\perp}$. Their lengths correspond to the projection of one unit cell (shaded) upon $\mathbf{V}^{\perp}$.

4. DIFFUSE SCATTERING AND RELATED TOPICS

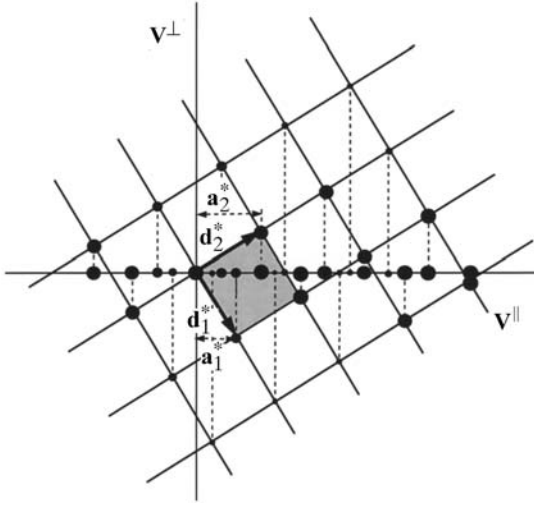


Fig. 4.6.2.9. Schematic representation of the reciprocal space of the embedded Fibonacci chain depicted in Fig. 4.6.2.8. The physical-space reciprocal basis $\mathbf{a}_1^*$ and $\mathbf{a}_2^*$ is marked. The diameters of the filled circles are roughly proportional to the reflection intensities. One 2D reciprocal-lattice unit cell is shadowed. The actual 1D diffraction pattern of the 1D Fibonacci chain results from a projection of the 2D reciprocal space onto the parallel space. The correspondence between 2D reciprocal-lattice positions and their projected images is indicated by dashed lines.

$$\mathbf{r} = n_1 \mathbf{d}_1 + n_2 \mathbf{d}_2, \text{ with } \mathbf{d}_1 = \frac{1}{a^*(2+\tau)} \begin{pmatrix} 1 \\ -\tau \end{pmatrix}_V,$$

$$\mathbf{d}_2 = \frac{1}{a^*(2+\tau)} \begin{pmatrix} \tau \\ 1 \end{pmatrix}_V;$$

$$\mathbf{H} = h_1 \mathbf{d}_1^* + h_2 \mathbf{d}_2^*, \text{ with } \mathbf{d}_1^* = a^* \begin{pmatrix} 1 \\ -\tau \end{pmatrix}_V, \mathbf{d}_2^* = a^* \begin{pmatrix} \tau \\ 1 \end{pmatrix}_V.$$

The 1D Fibonacci chain results from the cut of the parallel (physical) space with the 2D lattice Σ decorated with line elements for the *atomic surfaces* (acceptance domains). In this description, the atomic surfaces correspond simply to the projection of one 2D unit cell upon the perpendicular-space coordinate. This satisfies the condition that each unit cell contributes exactly to one point of the Fibonacci chain (*primitive unit cell*). The physical space $\mathbf{V}^{\parallel}$ is related to the eigenspace of the substitution matrix S associated with its eigenvalue $\lambda_1 = \tau$. The perpendicular space $\mathbf{V}^{\perp}$ corresponds to the eigenspace of the substitution matrix S associated with its eigenvalue $\lambda_2 = -1/\tau$. Thus, the physical space scales to powers of τ and the perpendicular space to powers of $-1/\tau$.

By block-diagonalization, the reducible substitution (scaling) matrix S can be decomposed into two non-equivalent irreducible representations. These can be assigned to the two 1D orthogonal subspaces $\mathbf{V}^{\parallel}$ and $\mathbf{V}^{\perp}$ forming the 2D embedding space $\mathbf{V} = \mathbf{V}^{\parallel} \oplus \mathbf{V}^{\perp}$. Thus, using $WSW^{-1} = S_V = S_V^{\parallel} \oplus S_V^{\perp}$, where

$$W = \begin{pmatrix} 1 & \tau \\ -\tau & 1 \end{pmatrix} = (\mathbf{d}_1^* \quad \mathbf{d}_2^*),$$

one obtains

$$\begin{pmatrix} 1 & \tau \\ -\tau & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}_D \begin{pmatrix} 1 & \tau \\ -\tau & 1 \end{pmatrix}^{-1} = \begin{pmatrix} \tau & 0 \\ 0 & -1/\tau \end{pmatrix}_V \\ = \begin{pmatrix} S^{\parallel} & 0 \\ 0 & S^{\perp} \end{pmatrix}_V,$$

the scaling operations $S^{\parallel}$ and $S^{\perp}$ in parallel and in perpendicular space as indicated by the partition lines.

The metric tensors for the reciprocal and the direct 2D square lattices read

$$G^* = |a^*|^2(2+\tau) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \text{ and } G = \frac{1}{|a^*|^2(2+\tau)} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The short distance S of the Fibonacci sequence is related to a^* by

$$S = 1/[a^*(2+\tau)] \\ = \min \left\{ \left| \pi^{\parallel}(\mathbf{d}_i - \mathbf{d}_j) \right| \left| \pi^{\perp}(\mathbf{d}_i - \mathbf{d}_j) \right| < \Omega_{AS} \wedge i, j \in \mathbb{Z} \right\},$$

with the projectors $\pi^{\parallel}$ and $\pi^{\perp}$ onto $\mathbf{V}^{\parallel}$ and $\mathbf{V}^{\perp}$. The *point density* ρ_p of the Fibonacci chain, i.e. the number of vertices per unit length, can be calculated using the formula

$$\rho_p = \frac{\Omega_{AS}}{\Omega_{UC}} = \frac{(1+\tau)/[a^*(2+\tau)]}{1/[|a^*|^2(2+\tau)]} = a^* \tau^2,$$

where Ω_{AS} and Ω_{UC} are the areas of the atomic surface and of the 2D unit cell, respectively.

For an infinite Fibonacci sequence generated from the intervals S and L an average distance d can be calculated:

$$d = \lim_{n \rightarrow \infty} \frac{F_n S + F_{n+1} L}{F_n + F_{n+1}} = \lim_{n \rightarrow \infty} \frac{F_n(S + \tau L)}{F_n(1 + \tau)} = \frac{S(1 + \tau^2)}{(1 + \tau)} = (3 - \tau)S.$$

Therefrom, the point density can also be calculated:

$$\rho_p = 1/d = 1/[(3 - \tau)S] = [a^*(2 + \tau)]/(3 - \tau) = a^* \tau^2.$$

An approximant structure of the Fibonacci sequence with a unit cell containing m intervals L and n intervals S can be generated by shearing the 2D lattice Σ by the shear matrix S_m ,

$$S_m = \frac{1}{2 + \tau} \begin{pmatrix} \tau^2 + x\tau + 1 & -x \\ x\tau^2 & \tau^2 - x\tau + 1 \end{pmatrix}_D,$$

where $x = (n\tau - m)/(m\tau + n)$:

$$\mathbf{d}'_i = \sum_{j=1}^2 S_{mij} \mathbf{d}_j;$$

$$\mathbf{d}'_1 = \frac{1}{2 + \tau} \left[(\tau^2 + x\tau + 1) \mathbf{d}_1 - x \mathbf{d}_2 \right]$$

$$= \frac{1}{(2 + \tau)a^*} \begin{pmatrix} 1 \\ -\tau - x \end{pmatrix}_V$$

$$= \frac{1}{(2 + \tau)a^*} \begin{pmatrix} 1 \\ -\frac{2n\tau + m\tau}{m\tau + n} \end{pmatrix}_V,$$

$$\mathbf{d}'_2 = \frac{1}{2 + \tau} \left[x\tau^2 \mathbf{d}_1 + (\tau^2 - x\tau + 1) \mathbf{d}_2 \right]$$

$$= \frac{1}{(2 + \tau)a^*} \begin{pmatrix} \tau \\ -x\tau + 1 \end{pmatrix}_V$$

$$= \frac{1}{(2 + \tau)a^*} \begin{pmatrix} \tau \\ \frac{2m\tau - n\tau}{m\tau + n} \end{pmatrix}_V.$$

This shear matrix does not change the magnitudes of the intervals L and S . In reciprocal space the inverted and transposed shear matrix is applied on the reciprocal basis,

4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

$$(S_m^{-1})^T = \frac{1}{2+\tau} \begin{pmatrix} \tau^2 - x\tau + 1 & -x\tau^2 \\ x & \tau^2 + x\tau + 1 \end{pmatrix}_D,$$

where $x = (n\tau - m)/(m\tau + n)$:

$$\begin{aligned} \mathbf{d}_i^* &= \sum_{j=1}^2 (S_m^{-1})_{ij}^T \mathbf{d}_j^*; \\ \mathbf{d}_1^* &= \frac{1}{2+\tau} \left[(\tau^2 - x\tau + 1) \mathbf{d}_1^* - x\tau^2 \mathbf{d}_2^* \right] \\ &= a^* \begin{pmatrix} 1 - x\tau \\ -\tau \end{pmatrix}_V \\ &= a^* \begin{pmatrix} \frac{2m\tau - n\tau}{m\tau + n} \\ -\tau \end{pmatrix}_V, \\ \mathbf{d}_2^* &= \frac{1}{2+\tau} \left[x\mathbf{d}_1^* + (\tau^2 + x\tau + 1) \mathbf{d}_2^* \right] \\ &= a^* \begin{pmatrix} \tau + x \\ 1 \end{pmatrix}_V \\ &= a^* \begin{pmatrix} \frac{2n\tau + m\tau}{m\tau + n} \\ 1 \end{pmatrix}_V. \end{aligned}$$

The point $x_n(t)$ of the n th interval L or S of an infinite Fibonacci sequence is given by

$$x_n(t) = \{x_0 + n(3 - \tau) - (\tau - 1)[\text{frac}(n\tau + t) - (1/2)]\}S,$$

where t is the phase of the modulation function $y(t) = (\tau - 1)[\text{frac}(n\tau + t) - (1/2)]$ (Janssen, 1986). Thus, the Fibonacci sequence can also be dealt with as an incommensurately modulated structure. This is a consequence of the fact that for 1D structures only the crystallographic point symmetries 1 and $\bar{1}$ allow the existence of a periodic average structure.

The embedding of the Fibonacci chain as an incommensurately modulated structure can be performed as follows:

(1) select a subset $\Lambda^* \subset M^*$ of strong reflections for main reflections $\mathbf{H} = h\mathbf{a}^*$, $h \in \mathbb{Z}$;

(2) define a satellite vector $\mathbf{q} = \alpha\mathbf{a}^*$ pointing from each main reflection to the next satellite reflection.

One possible way of indexing based on the same $\mathbf{a}^*$ as defined above is illustrated in Fig. 4.6.2.10. The scattering vector is given by $\mathbf{H}^\parallel = h(\tau + 1)\mathbf{a}^* + m\mathbf{q}$, where $\mathbf{q} = \tau\mathbf{a}^*$, or, in the 2D representation, $\mathbf{H} = h_1\mathbf{d}_1^* + h_2\mathbf{d}_2^*$, where $\mathbf{d}_1^* = a^* \begin{pmatrix} 1 + \tau \\ 0 \end{pmatrix}_V$ and $\mathbf{d}_2^* = a^* \begin{pmatrix} \tau \\ 1 \end{pmatrix}_V$, with the direct basis

$$\mathbf{d}_1 = \frac{1}{a^*(1 + \tau)} \begin{pmatrix} 1 \\ -\tau \end{pmatrix}_V, \quad \mathbf{d}_2 = \frac{1}{a^*} \begin{pmatrix} 0 \\ 1 \end{pmatrix}_V.$$

The modulation function is saw-tooth-like (Fig. 4.6.2.11).

4.6.2.5. 1D structures with fractal atomic surfaces

A 1D structure with a *fractal atomic surface* (Hausdorff dimension 0.9157...) can be derived from the Fibonacci sequence by squaring its substitution matrix S :

$$\begin{pmatrix} S \\ L \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} S \\ L \end{pmatrix} = \begin{pmatrix} S + L \\ S + 2L \end{pmatrix}$$

with $S^2 = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$,

corresponding to the substitution rule $S \rightarrow SL, L \rightarrow LLS$ as well

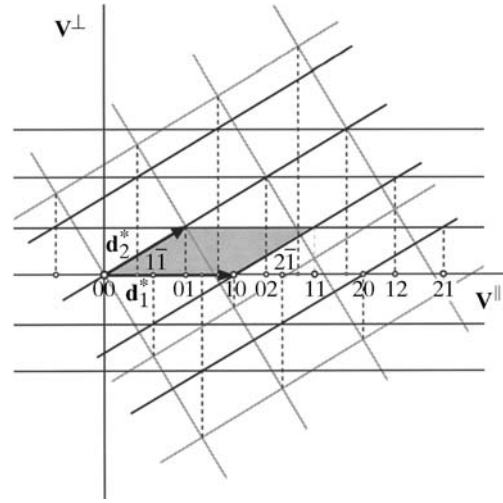


Fig. 4.6.2.10. Reciprocal space of the embedded Fibonacci chain as a modulated structure. Several main and satellite reflections are indexed. The square reciprocal lattice of the quasicrystal description illustrated in Fig. 4.6.2.9 is indicated by grey lines. The reflections located on $\mathbf{V}^\parallel$ can be considered to be projected either from the 2D square lattice of the embedding as for a QS or from the 2D oblique lattice of the embedding as for an IMS.

as two other non-equivalent ones (see Janssen, 1995). The eigenvalues λ_i are obtained by calculating

$$\det |S - \lambda I| = 0.$$

The evaluation of the determinant gives the characteristic polynomial

$$\lambda^2 - 3\lambda + 1 = 0,$$

with the solutions $\lambda_{1,2} = [3 \pm (5)^{1/2}]/2$, with $\lambda_1 = \tau^2$ and $\lambda_2 = 1/\tau^2 = 2 - \tau$, and the same eigenvectors $\mathbf{w}_1 = \begin{pmatrix} 1 \\ \tau \end{pmatrix}$, $\mathbf{w}_2 = \begin{pmatrix} 1 \\ -1/\tau \end{pmatrix}$ as for the Fibonacci sequence. Rewriting the eigenvalue equation gives

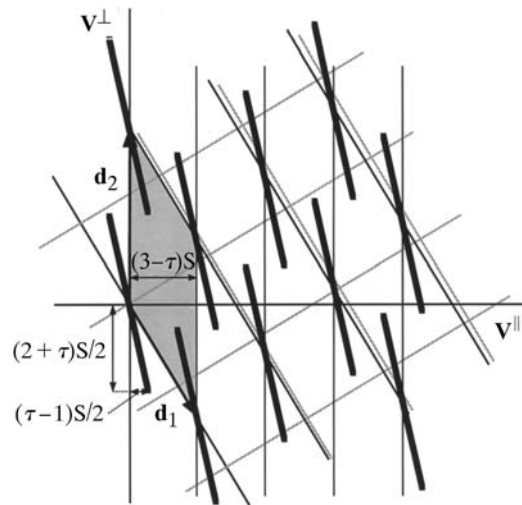


Fig. 4.6.2.11. 2D direct-space embedding of the Fibonacci chain as a modulated structure. The average period is $(3 - \tau)S$. The square lattice in the quasicrystal description shown in Fig. 4.6.2.8 is indicated by grey lines. The rod-like atomic surfaces are now inclined relative to $\mathbf{V}^\parallel$ and arranged so as to give a saw-tooth modulation wave.

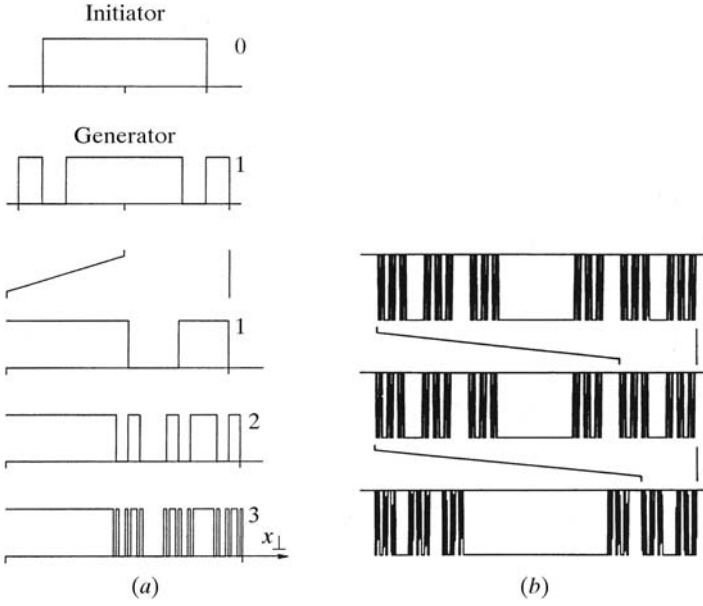


Fig. 4.6.2.12. (a) Three steps in the development of the fractal atomic surface of the squared Fibonacci sequence starting from an initiator and a generator. The action of the generator is to cut a piece from each side of the initiator and to add it where the initiator originally ended. This is repeated, cutting thinner and thinner pieces each time from the generated structures. (b) Magnification sequence of the fractal atomic surface illustrating its self-similarity. Each successive figure represents a magnification of a selected portion of the previous figure (from Zobetz, 1993).

$$\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} 1 \\ \tau \end{pmatrix} = \begin{pmatrix} \tau + 1 \\ 2\tau + 1 \end{pmatrix} = \begin{pmatrix} \tau^2 \\ \tau^3 \end{pmatrix} = \tau^2 \begin{pmatrix} 1 \\ \tau \end{pmatrix}.$$

Identifying the eigenvector $\begin{pmatrix} 1 \\ \tau \end{pmatrix}$ with $\begin{pmatrix} S \\ L \end{pmatrix}$ shows that the infinite 1D sequence $s(\mathbf{r})$ multiplied by powers of its eigenvalue τ^2 (scaling operation) remains invariant (each new lattice point coincides with one of the original lattice):

$$s(\tau^2 \mathbf{r}) = s(\mathbf{r}).$$

The fractal sequence can be described on the same reciprocal and direct bases as the Fibonacci sequence. The only difference in the 2D direct-space description is the fractal character of the perpendicular-space component of the hyperatoms (Fig. 4.6.2.12) (see Zobetz, 1993).

4.6.3. Reciprocal-space images

4.6.3.1. Incommensurately modulated structures (IMs)

One-dimensionally modulated structures are the simplest representatives of IMs. The vast majority of the one hundred or so IMs known so far belong to this class (Cummins, 1990). However, there is also an increasing number of IMs with 2D or 3D modulation. The dimension d of the modulation is defined by the number of rationally independent modulation wave vectors (satellite vectors) $\mathbf{q}_i$ (Fig. 4.6.3.1). The electron-density function of a dD modulated 3D crystal can be represented by the Fourier series

$$\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}).$$

The Fourier coefficients (structure factors) $F(\mathbf{H})$ differ from zero only for reciprocal-space vectors $\mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^* + \sum_{j=1}^d m_j \mathbf{q}_j =$

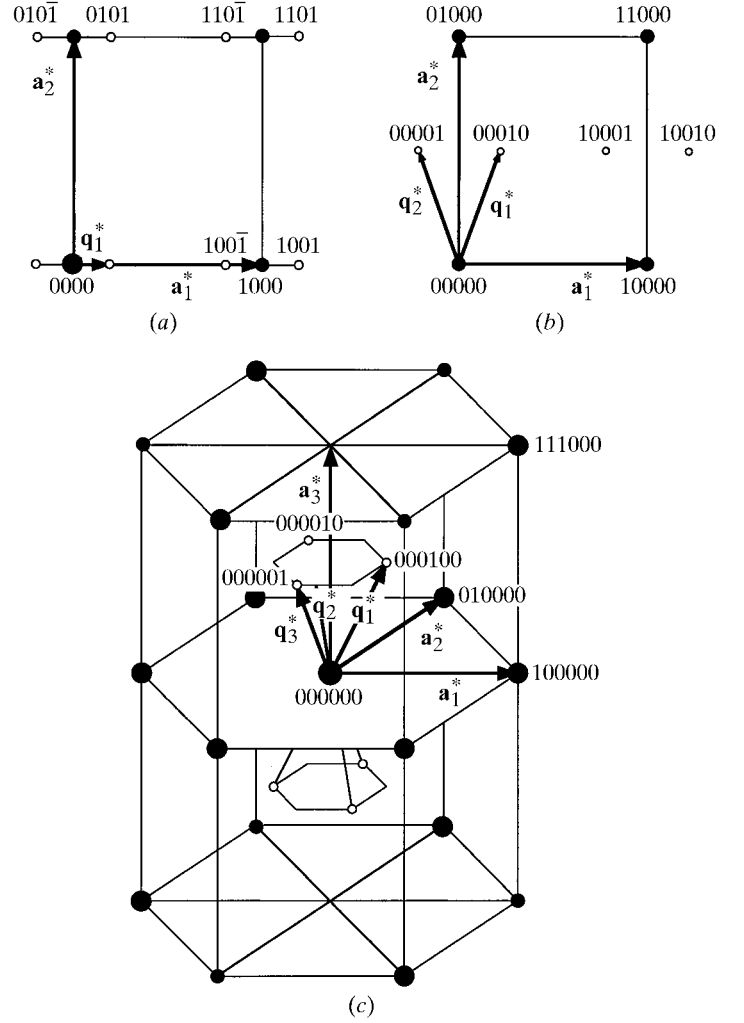


Fig. 4.6.3.1. Schematic diffraction patterns for IMs with (a) 1D, (b) 2D and (c) 3D modulation. The satellite vectors correspond to $\mathbf{q} = \alpha_1 \mathbf{a}_1^*$ in (a), $\mathbf{q}_1 = \alpha_{11} \mathbf{a}_1^* + (1/2) \mathbf{a}_2^*$ and $\mathbf{q}_2 = -\alpha_{12} \mathbf{a}_1^* + (1/2) \mathbf{a}_2^*$, where $\alpha_{11} = \alpha_{12}$, in (b), and $\mathbf{q}_1 = \alpha_{11} \mathbf{a}_1^* + \alpha_{31} \mathbf{a}_3^*$, $\mathbf{q}_2 = \alpha_{12} (-\mathbf{a}_1^* + \mathbf{a}_2^*) + \alpha_{32} \mathbf{a}_3^*$, $\mathbf{q}_3 = -\alpha_{13} \mathbf{a}_2^* + \alpha_{33} \mathbf{a}_3^*$, where $\alpha_{11} = \alpha_{12} = \alpha_{13}$ and $\alpha_{31} = \alpha_{32} = \alpha_{33}$, in (c). The areas of the circles are proportional to the reflection intensities. Main (filled circles) and satellite (open circles) reflections are indexed (after Janner *et al.*, 1983b).

$\sum_{i=1}^{3+d} h_i \mathbf{a}_i^*$ with $h_i, m_j \in \mathbb{Z}$. The d satellite vectors are given by $\mathbf{q}_j = \mathbf{a}_{3+j}^* = \sum_{i=1}^3 \alpha_{ij} \mathbf{a}_i^*$, with α_{ij} a $3 \times d$ matrix σ . In the case of an IM, at least one entry to σ has to be irrational. The wavelength of the modulation function is $\lambda_j = 1/q_j$. The set of vectors $\mathbf{H}$ forms a Fourier module $M^* = \{\mathbf{H} = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ of rank $n = 3 + d$, which can be decomposed into a rank 3 and a rank d submodule $M^* = M_1^* \oplus M_2^*$. $M_1^* = \{h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^*\}$ corresponds to a $\mathbb{Z}$ module of rank 3 in a 3D subspace (the physical space), $M_2^* = \{h_4 \mathbf{a}_4^* + \dots + h_{3+d} \mathbf{a}_{3+d}^*\}$ corresponds to a $\mathbb{Z}$ module of rank d in a dD subspace (perpendicular space). The submodule M_1 is identical to the 3D reciprocal lattice Λ^* of the average structure. M_2 results from the projection of the perpendicular-space component of the $(3 + d)D$ reciprocal lattice Σ^* upon the physical space. Owing to the coincidence of one subspace with the physical space, the dimension of the embedding space is given as $(3 + d)D$ and not as nD . This terminology points out the special role of the physical space.

Hence the reciprocal-basis vectors $\mathbf{a}_i^*, i = 1, \dots, 3 + d$, can be considered to be physical-space projections of reciprocal-basis

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vectors $\mathbf{d}_i^*, i = 1, \dots, 3 + d$, spanning a $(3 + d)$ D reciprocal lattice Σ^* :

$$\Sigma^* = \left\{ \mathbf{H} = \sum_{i=1}^{3+d} h_i \mathbf{d}_i^* \mid h_i \in \mathbb{Z} \right\},$$

$$\mathbf{d}_i^* = (\mathbf{a}_i^*, \mathbf{0}), i = 1, \dots, 3 \text{ and } \mathbf{d}_{3+j}^* = (\mathbf{a}_{3+j}^*, c\mathbf{e}_j^*), j = 1, \dots, d.$$

The first vector component of $\mathbf{d}_i^*$ refers to the physical space, the second to the perpendicular space spanned by the mutually orthogonal unit vectors $\mathbf{e}_j$. c is an arbitrary constant which can be set to 1 without loss of generality.

A direct lattice Σ with basis $\mathbf{d}_i, i = 1, \dots, 3 + d$ and $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$, can be constructed according to

$$\Sigma = \left\{ \mathbf{r} = \sum_{i=1}^{3+d} m_i \mathbf{d}_i \mid m_i \in \mathbb{Z} \right\},$$

$$\mathbf{d}_i = \left(\mathbf{a}_i, -\sum_{j=1}^d \alpha_{ij} (1/c) \mathbf{e}_j \right), i = 1, \dots, 3$$

$$\text{and } \mathbf{d}_{3+j} = \left(\mathbf{0}, (1/c) \mathbf{e}_j \right), j = 1, \dots, d.$$

Consequently, the aperiodic structure in physical space $\mathbf{V}^\parallel$ is equivalent to a 3D section of the $(3 + d)$ D hypercrystal.

4.6.3.1.1. Indexing

The 3D reciprocal space M^* of a $(3 + d)$ D IMS consists of two separable contributions,

$$M^* = \left\{ \mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^* + \sum_{j=1}^d m_j \mathbf{q}_j \right\},$$

the set of main reflections ($m_j = 0$) and the set of satellite reflections ($m_j \neq 0$) (Fig. 4.6.3.1). In most cases, the modulation is only a weak perturbation of the crystal structure. The main reflections are related to the average structure, the satellites to the difference between average and actual structure. Consequently, the satellite reflections are generally much weaker than the main reflections and can be easily identified. Once the set of main reflections has been separated, a conventional basis $\mathbf{a}_i^*, i = 1, \dots, 3$, for Λ^* is chosen.

The only ambiguity is in the assignment of rationally independent satellite vectors $\mathbf{q}_j$. They should be chosen inside the reciprocal-space unit cell (Brillouin zone) of Λ^* in such a way as to give a minimal number d of additional dimensions. If satellite vectors reach the Brillouin-zone boundary, centred $(3 + d)$ D Bravais lattices are obtained. The star of satellite vectors has to be invariant under the point-symmetry group of the diffraction pattern. There should be no contradiction to a reasonable physical modulation model concerning period or propagation direction of the modulation wave. More detailed information on how to find the optimum basis and the correct setting is given by Janssen *et al.* (1999) and Janner *et al.* (1983a,b).

4.6.3.1.2. Diffraction symmetry

The Laue symmetry group $K^L = \{R\}$ of the Fourier module M^* ,

$$M^* = \left\{ \mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^* + \sum_{j=1}^d m_j \mathbf{q}_j = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^* \right\}, \Lambda^* = \left\{ \mathbf{H} = \sum_{i=1}^3 h_i \mathbf{a}_i^* \right\},$$

is isomorphous to or a subgroup of one of the 11 3D crystallographic Laue groups leaving Λ^* invariant. The action of the point-group symmetry operators R on the reciprocal basis $\mathbf{a}_i^*, i = 1, \dots, 3 + d$, can be written as

$$R\mathbf{a}_i^* = \sum_{j=1}^{3+d} \Gamma_{ij}^T(R) \mathbf{a}_j^*, i = 1, \dots, 3 + d.$$

The $(3 + d) \times (3 + d)$ matrices $\Gamma^T(R)$ form a finite group of integral matrices which are reducible, since R is already an orthogonal transformation in 3D physical space. Consequently, R can be expressed as pair of orthogonal transformations ($R^\parallel, R^\perp$) in 3D physical and d D perpendicular space, respectively. Owing to their mutual orthogonality, no symmetry relationship exists between the set of main reflections and the set of satellite reflections. $\Gamma^T(R)$ is the transpose of $\Gamma(R)$ which acts on vector components in direct space.

For the $(3 + d)$ D direct-space (*superspace*) symmetry operator ($R_s, \mathbf{t}_s$) and its matrix representation $\Gamma(R_s, \mathbf{t}_s)$ on Σ , the following decomposition can be performed:

$$\Gamma(R_s) = \begin{pmatrix} \Gamma^\parallel(R) & 0 \\ \Gamma^M(R) & \Gamma^\perp(R) \end{pmatrix} \text{ and } \mathbf{t}_s = (\mathbf{t}_3, \mathbf{t}_d).$$

$\Gamma^\parallel(R)$ is a 3×3 matrix, $\Gamma^\perp(R)$ is a $d \times d$ matrix and $\Gamma^M(R)$ is a $d \times 3$ matrix. The translation operator $\mathbf{t}_s$ consists of a 3D vector $\mathbf{t}_3$ and a d D vector $\mathbf{t}_d$. According to Janner & Janssen (1979), $\Gamma^M(R)$ can be derived from $\Gamma^M(R) = \sigma \Gamma^\parallel(R) - \Gamma^\perp(R) \sigma$. $\Gamma^M(R)$ has integer elements only as it contains components of primitive-lattice vectors of Λ^* , whereas σ in general consists of a rational and an irrational part: $\sigma = \sigma^i + \sigma^r$. Thus, only the rational part gives rise to nonzero entries in $\Gamma^M(R)$. With the order of the Laue group denoted by N , one obtains $\sigma^i \equiv (1/N) \sum_R \Gamma^\perp(R) \sigma \Gamma^\parallel(R)^{-1}$, where $\Gamma^\perp(R) \sigma^i \Gamma^\parallel(R)^{-1} = \sigma^i$, implying that $\Gamma^M(R) = \sigma^r \Gamma^\parallel(R) - \Gamma^\perp(R) \sigma^r$ and $0 = \sigma^i \Gamma^\parallel(R) - \Gamma^\perp(R) \sigma^i$.

Example: In the case of a 3D IMS with 1D modulation ($d = 1$) the $3 \times d$ matrix

$$\sigma = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix}$$

has the components of the wavevector $\mathbf{q} = \sum_{i=1}^3 \alpha_i \mathbf{a}_i^* = \mathbf{q}^i + \mathbf{q}^r$. $\Gamma^\perp(R) = \varepsilon = \pm 1$ because for $d = 1$, $\mathbf{q}$ can only be transformed into $\pm \mathbf{q}$. Corresponding to $\mathbf{q}^i \equiv (1/N) \sum_R \varepsilon R \mathbf{q}$, one obtains $R^T \mathbf{q}^i \equiv \varepsilon \mathbf{q}^i$ (modulo Λ^*). The 3×1 row matrix $\Gamma^M(R)$ is equivalent to the difference vector between $R^T \mathbf{q}$ and $\varepsilon \mathbf{q}$ (Janssen *et al.*, 1999).

For a monoclinic modulated structure with point group $2/m$ for M^* (unique axis $\mathbf{a}_3$) and satellite vector $\mathbf{q} = (1/2)\mathbf{a}_1^* + \alpha_3 \mathbf{a}_3^*$, with α_3 an irrational number, one obtains

$$\begin{aligned} \mathbf{q}^i &\equiv (1/N) \sum_R \varepsilon R \mathbf{q} \\ &= \frac{1}{4} \left(+1 \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1/2 \\ 0 \\ \alpha_3 \end{pmatrix} \right. \\ &\quad + 1 \cdot \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1/2 \\ 0 \\ \alpha_3 \end{pmatrix} - 1 \cdot \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} 1/2 \\ 0 \\ \alpha_3 \end{pmatrix} \\ &\quad \left. - 1 \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} 1/2 \\ 0 \\ \alpha_3 \end{pmatrix} \right) \\ &= \begin{pmatrix} 0 \\ 0 \\ \alpha_3 \end{pmatrix}. \end{aligned}$$

From the relations $R^T \mathbf{q}^i \equiv \varepsilon \mathbf{q}^i$ (modulo Λ^*), it can be shown that

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the symmetry operations 1 and 2 are associated with the perpendicular-space transformations $\varepsilon = 1$, and m and $\bar{1}$ with $\varepsilon = -1$. The matrix $\Gamma^M(R)$ is given by

$$\Gamma^M(2) = \sigma^r \Gamma^\parallel(2) - \Gamma^\perp(2) \sigma^r$$

$$= \begin{pmatrix} 1/2 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} - (+1) \begin{pmatrix} 1/2 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \bar{1} \\ 0 \\ 0 \end{pmatrix}$$

for the operation 2, for instance.

The matrix representations $\Gamma^T(R_s)$ of the symmetry operators R in reciprocal $(3+d)$ D superspace decompose according to

$$\Gamma^T(R_s) = \begin{pmatrix} \Gamma^\parallel T(R) & \Gamma^{MT}(R) \\ 0 & \Gamma^\perp T(R) \end{pmatrix}.$$

Phase relationships between modulation functions of symmetry-equivalent atoms can give rise to systematic extinctions of different classes of satellite reflections. The extinction rules may include indices of both main and satellite reflections. A full list of systematic absences is given in the table of $(3+1)$ D superspace groups (Janssen *et al.*, 1999). Thus, once point symmetry and systematic absences are found, the superspace group can be obtained from the tables in a way analogous to that used for regular 3D crystals. A different approach for the symmetry description of IMSs from the 3D Fourier-space perspective has been given by Dräger & Mermin (1996).

4.6.3.1.3. Structure factor

The structure factor of a periodic structure is defined as the Fourier transform of the density distribution $\rho(\mathbf{r})$ of its unit cell (UC):

$$F(\mathbf{H}) = \int_{\text{UC}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}.$$

The same is valid in the case of the $(3+d)$ D description of IMSs. The parallel- and perpendicular-space components are orthogonal to each other and can be separated. The Fourier transform of the parallel-space component of the electron-density distribution of a single atom gives the usual atomic scattering factors $f_k(\mathbf{H}^\parallel)$. For the structure-factor calculation, one does not need to use $\rho(\mathbf{r})$ explicitly. The hyperatoms correspond to the convolution of the electron-density distribution in 3D physical space with the modulation function in d D perpendicular space. Therefore, the Fourier transform of the $(3+d)$ D hyperatoms is simply the product of the Fourier transform $f_k(\mathbf{H}^\parallel)$ of the physical-space component with the Fourier transform of the perpendicular-space component, the modulation function.

For a general *displacive modulation* one obtains for the i th coordinate x_{ik} of the k th atom in 3D physical space

$$x_{ik} = \bar{x}_{ik} + u_{ik}(\bar{x}_4, \dots, \bar{x}_{3+d}), \quad i = 1, \dots, 3,$$

where $\bar{x}_{ik}$ are the basic-structure coordinates and $u_{ik}(\bar{x}_4, \dots, \bar{x}_{3+d})$ are the modulation functions with unit periods in their arguments (Fig. 4.6.3.2). The arguments are $\bar{x}_{3+j} = \alpha_{ij} \bar{x}_{ik}^0 + t_j$, $j = 1, \dots, d$, where $\bar{x}_{ik}^0$ are the coordinates of the k th atom referred to the origin of its unit cell and t_j are the phases of the modulation functions. The modulation functions $u_{ik}(\bar{x}_4, \dots, \bar{x}_{3+d})$ themselves can be expressed in terms of a Fourier series as

$$u_{ik}(\bar{x}_4, \dots, \bar{x}_{3+d})$$

$$= \sum_{n_1=1}^{\infty} \dots \sum_{n_d=1}^{\infty} \left\{ {}^u C_{ik}^{n_1 \dots n_d} \cos[2\pi(n_1 \bar{x}_4 + \dots + n_d \bar{x}_{3+d})] \right.$$

$$\left. + {}^u S_{ik}^{n_1 \dots n_d} \sin[2\pi(n_1 \bar{x}_4 + \dots + n_d \bar{x}_{3+d})] \right\},$$

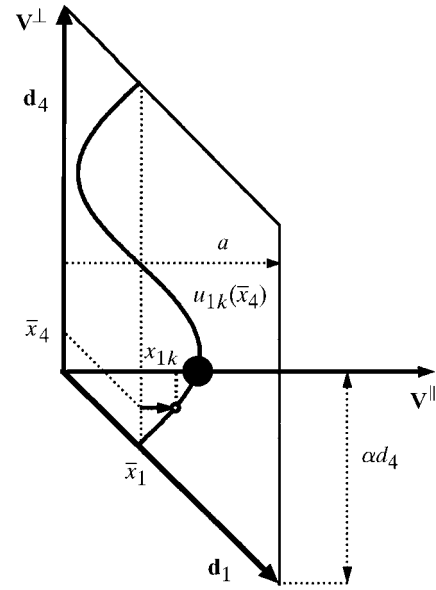


Fig. 4.6.3.2. The relationships between the coordinates $x_{1k}, x_{4k}, \bar{x}_1, \bar{x}_4$ and the modulation function u_{1k} in a special section of the $(3+d)$ D space.

where n_j are the orders of harmonics for the j th modulation wave of the i th component of the k th atom and their amplitudes are ${}^u C_{ik}^{n_1 \dots n_d}$ and ${}^u S_{ik}^{n_1 \dots n_d}$.

Analogous expressions can be derived for a *density modulation*, i.e., the modulation of the occupation probability $p_k(\bar{x}_4, \dots, \bar{x}_{3+d})$:

$$p_k(\bar{x}_4, \dots, \bar{x}_{3+d})$$

$$= \sum_{n_1=1}^{\infty} \dots \sum_{n_d=1}^{\infty} \left\{ {}^p C_k^{n_1 \dots n_d} \cos[2\pi(n_1 \bar{x}_4 + \dots + n_d \bar{x}_{3+d})] \right.$$

$$\left. + {}^p S_k^{n_1 \dots n_d} \sin[2\pi(n_1 \bar{x}_4 + \dots + n_d \bar{x}_{3+d})] \right\},$$

and for the modulation of the tensor of thermal parameters $B_{ijk}(\bar{x}_4, \dots, \bar{x}_{3+d})$:

$$B_{ijk}(\bar{x}_4, \dots, \bar{x}_{3+d})$$

$$= \sum_{n_1=1}^{\infty} \dots \sum_{n_d=1}^{\infty} \left\{ {}^B C_{ijk}^{n_1 \dots n_d} \cos[2\pi(n_1 \bar{x}_4 + \dots + n_d \bar{x}_{3+d})] \right.$$

$$\left. + {}^B S_{ijk}^{n_1 \dots n_d} \sin[2\pi(n_1 \bar{x}_4 + \dots + n_d \bar{x}_{3+d})] \right\}.$$

The resulting structure-factor formula is

$$F(\mathbf{H}) = \sum_{k=1}^{N'} \sum_{(R, t)} \int_0^1 d\bar{x}_4 \dots \int_0^1 d\bar{x}_{3+d} f_k(\mathbf{H}^\parallel) p_k$$

$$\times \exp \left(- \sum_{i,j=1}^{3+d} h_i [R B_{ijk} R^T] h_j + 2\pi i \sum_{j=1}^{3+d} h_j R x_{jk} + h_j t_j \right)$$

for summing over the set $(R, \mathbf{t})$ of superspace symmetry operations and the set of N' atoms in the asymmetric unit of the $(3+d)$ D unit cell (Yamamoto, 1982). Different approaches without numerical integration based on analytical expressions including Bessel functions have also been developed. For more information see Paciorek & Chapuis (1994), Petricek, Maly & Cisarova (1991), and references therein.

For illustration, some fundamental IMSs will be discussed briefly (see Korekawa, 1967; Böhm, 1977).

Harmonic density modulation. A harmonic density modulation can result on average from an ordered distribution of vacancies on atomic positions. For an IMS with N atoms per unit cell one obtains

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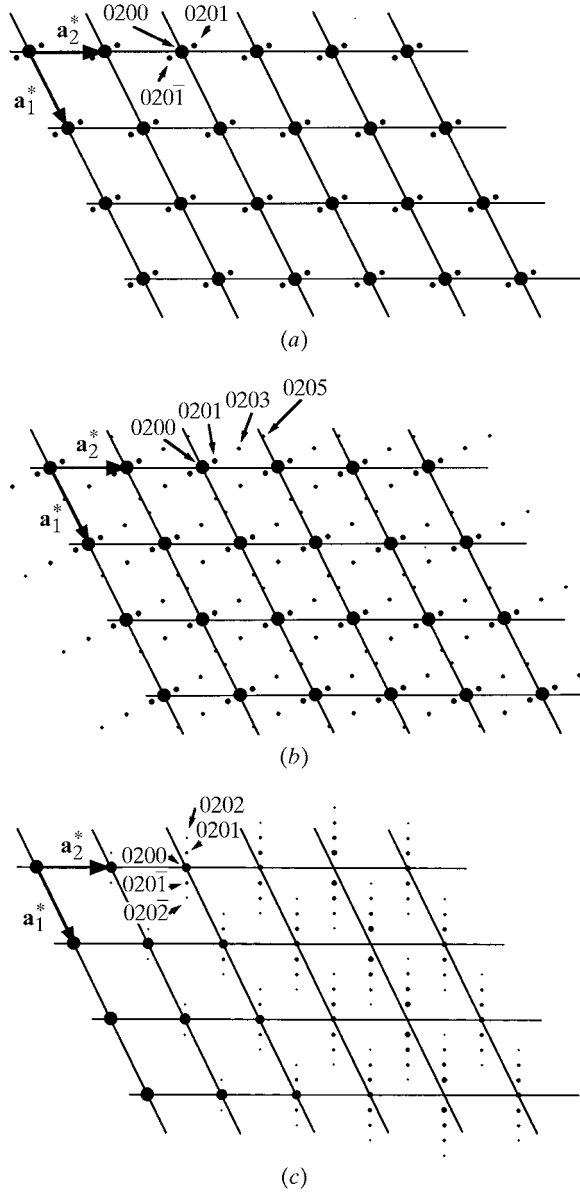


Fig. 4.6.3.3. Schematic diffraction patterns for 3D IMSs with (a) 1D harmonic and (b) rectangular density modulation. The modulation direction is parallel to $\mathbf{a}_2^*$. In (a) only first-order satellites exist; in (b), all odd-order satellites can be present. In (c), the diffraction pattern of a harmonic displacive modulation along $\mathbf{a}_1$ with amplitudes parallel to $\mathbf{a}_2^*$ is depicted. Several reflections are indexed. The areas of the circles are proportional to the reflection intensities.

for a harmonic modulation of the occupancy factor

$$p_k = (p_k^0/2) \{1 + \cos[2\pi(\bar{x}_{4,k} + \varphi_k)]\}, \quad 0 \leq p_k^0 \leq 1,$$

the structure-factor formula for the m th order satellite ($0 \leq m \leq 1$)

$$F_0(\mathbf{H}) = (1/2) \sum_{k=1}^N f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k),$$

$$F_m(\mathbf{H}) = (1/2) \sum_{k=1}^N f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) (p_k^0/2)^{|m|} \exp \left[2\pi i \left(\sum_{i=1}^3 h_i x_{ik} + m \varphi_k \right) \right].$$

Thus, a linear correspondence exists between the structure-factor magnitudes of the satellite reflections and the amplitude of the density modulation. Furthermore, only first-order satellites exist, since the modulation wave consists only of one term. An important criterion for the existence of a density modulation is that a pair of

satellites around the origin of the reciprocal lattice exists (Fig. 4.6.3.3).

Symmetric rectangular density modulation. The box-function-like modulated occupancy factor can be expanded into a Fourier series,

$$p_k = p_k^0 (4/\pi) \left\{ \sum_{n=1}^{\infty} [(-1)^{n+1}/(2n-1)] \cos[2\pi(2n-1)(\bar{x}_{4,k} + \varphi_k)] \right\},$$

$$0 \leq p_k^0 \leq 1,$$

and the resulting structure factor of the m th order satellite is

$$F_0(\mathbf{H}) = (1/2) \sum_{k=1}^N f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) \exp \left(2\pi i \sum_{i=1}^3 h_i x_{ik} \right),$$

$$F_m(\mathbf{H}) = (1/\pi m) \sin(m\pi/2) \sum_{k=1}^N f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) p_k^0$$

$$\times \exp \left[2\pi i \left(\sum_{i=1}^3 h_i x_{ik} + m \varphi_k \right) \right].$$

According to this formula, only odd-order satellites occur in the diffraction pattern. Their structure-factor magnitudes decrease linearly with the order $|m|$ (Fig. 4.6.3.3b)

Harmonic displacive modulation. The displacement of the atomic coordinates is given by the function

$$x_{ik} = x_{ik}^0 + A_{ik} \cos[2\pi(\bar{x}_{4,k} + \varphi_k)], \quad i = 1, \dots, 3,$$

and the structure factor by

$$F_0(\mathbf{H}) = \sum_{k=1}^N f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) J_0(2\pi \mathbf{H}^{\parallel} \cdot \mathbf{A}_k) \exp \left(2\pi i \sum_{i=1}^3 h_i x_{ik} \right),$$

$$F_m(\mathbf{H}) = \sum_{k=1}^N f_k(\mathbf{H}^{\parallel}) T_k(\mathbf{H}^{\parallel}) J_m(2\pi \mathbf{H}^{\parallel} \cdot \mathbf{A}_k)$$

$$\times \exp \left[2\pi i \left(\sum_{i=1}^3 h_i x_{ik} + m \varphi_k \right) \right].$$

The structure-factor magnitudes of the m th-order satellite reflections are a function of the m th-order Bessel functions. The arguments of the Bessel functions are proportional to the scalar products of the amplitude and the diffraction vector. Consequently, the intensity of the satellites will vary characteristically as a function of the length of the diffraction vector. Each main reflection is accompanied by an infinite number of satellite reflections (Figs. 4.6.3.3c and 4.6.3.4).

4.6.3.2. Composite structures (CSs)

Composite structures consist of N mutually incommensurate substructures with N basic sublattices $\Lambda_{\nu} = \{\mathbf{a}_{1\nu}, \mathbf{a}_{2\nu}, \mathbf{a}_{3\nu}\}$, with $\nu = 1, \dots, N$. The reciprocal sublattices $\Lambda_{\nu}^* = \{\mathbf{a}_{1\nu}^*, \mathbf{a}_{2\nu}^*, \mathbf{a}_{3\nu}^*\}$, with $\nu = 1, \dots, N$, have either only the origin of the reciprocal lattice or one or two reciprocal-lattice directions in common. Thus, one needs $(3+d) < 3N$ reciprocal-basis vectors for integer indexing of diffraction patterns that show Bragg reflections at positions given by the Fourier module M^* . The CSs discovered to date have at least one lattice direction in common and consist of a maximum number of $N = 3$ substructures. They can be divided in three main classes: channel structures, columnar packings and layer packings (see van Smaalen, 1992, 1995).

In the following, the approach of Janner & Janssen (1980b) and van Smaalen (1992, 1995, and references therein) for the description of CSs is used. The set of diffraction vectors of a CS, i.e. its Fourier module $M^* = \{\sum_{i=1}^{3+d} h_i \mathbf{a}_i^*\}$, can be split into the contributions of the ν subsystems by employing $3 \times (3+d)$ matrices $Z_{ik\nu}$ with integer coefficients $\mathbf{a}_{i\nu}^* = \sum_{k=1}^{3+d} Z_{ik\nu} \mathbf{a}_k^*$,

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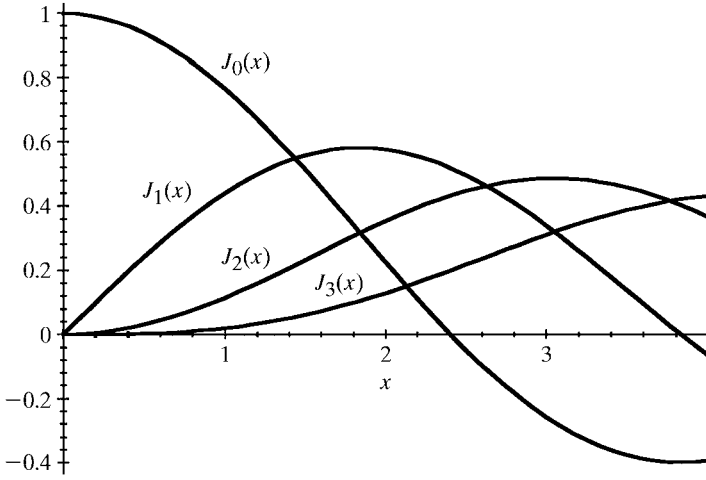


Fig. 4.6.3.4. The relative structure-factor magnitudes of m th-order satellite reflections for a harmonic displacive modulation are proportional to the values of the m th-order Bessel function $J_m(x)$.

$i = 1, \dots, 3$. In the general case, each subsystem will be modulated with the periods of the others due to their mutual interactions. Thus, in general, CSs consist of several intergrown incommensurately modulated substructures. The satellite vectors $\mathbf{q}_{j\nu}$, $j = 1, \dots, d$, referred to the ν th subsystem can be obtained from M^* by applying the $d \times (3 + d)$ integer matrices $V_{jk\nu}$: $\mathbf{q}_{j\nu} = \sum_{k=1}^{3+d} V_{jk\nu} \mathbf{a}_k^*$, $j = 1, \dots, d$. The matrices consisting of the components σ_ν of the satellite vectors $\mathbf{q}_{j\nu}$ with regard to the reciprocal sublattices Λ_ν^* can be calculated by $\sigma_\nu = (V_{3\nu} + V_{d\nu}\sigma)(Z_{3\nu} + Z_{d\nu}\sigma)^{-1}$, where the subscript 3 refers to the 3×3 submatrix of physical space and the subscript d to the $d \times d$ matrix of the internal space. The juxtaposition of the $3 \times (3 + d)$ matrix Z_ν and the $d \times (3 + d)$ matrix V_ν defines the non-singular $(3 + d) \times (3 + d)$ matrix W_ν ,

$$W_\nu = \begin{pmatrix} Z_\nu \\ V_\nu \end{pmatrix}.$$

This matrix allows the reinterpretation of the Fourier module M^* as the Fourier module $M_\nu^* = M^* W_\nu$ of a d -dimensionally modulated subsystem ν . It also describes the coordinate transformation between the superspace basis Σ and Σ_ν .

The superspace description is obtained analogously to that for IMSs (see Section 4.6.3.1) by considering the 3D Fourier module M^* of rank $3 + d$ as the projection of a $(3 + d)$ D reciprocal lattice Σ^* upon the physical space. Thus, one obtains for the definition of the direct and reciprocal $(3 + d)$ lattices (Janner & Janssen, 1980b)

$$\Sigma^* : \begin{cases} \mathbf{a}_i^* &= (\mathbf{a}_i^*, \mathbf{0}) & i = 1, \dots, 3 \\ \mathbf{a}_{3+j}^* &= (\mathbf{a}_{3+j}^*, \mathbf{e}_j^*) & j = 1, \dots, d \end{cases}$$

$$\Sigma : \begin{cases} \mathbf{a}_i &= (\mathbf{a}_i, -\sum_{j=1}^d \sigma_{ji} \mathbf{e}_j) & i = 1, \dots, 3 \\ \mathbf{a}_{3+j} &= (\mathbf{0}, \mathbf{e}_j) & j = 1, \dots, d. \end{cases}$$

4.6.3.2.1. Indexing

The indexing of diffraction patterns of composite structures can be performed in the following way:

- (1) find the minimum number of reciprocal lattices Λ_ν^* necessary to index the diffraction pattern;
- (2) find a basis for M^* , the union of sublattices Λ_ν^* ;
- (3) find the appropriate superspace embedding.

The $(3 + d)$ vectors $\mathbf{a}_i^*$ forming a basis for the 3D Fourier module $M^* = \{\sum_{i=1}^{3+d} h_i \mathbf{a}_i^*\}$ can be chosen such that $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ are

linearly independent. Then the remaining d vectors can be described as a linear combination of the first three, defining the $d \times 3$ matrix σ : $\mathbf{a}_{3+j}^* = \sum_{i=1}^{3+d} \sigma_{ji} \mathbf{a}_i^*$, $j = 1, \dots, d$. This is formally equivalent to the reciprocal basis obtained for an IMS (see Section 4.6.3.1) and one can proceed in an analogous way to that for IMSs.

4.6.3.2.2. Diffraction symmetry

The symmetry of CSs can be described with basically the same formalism as used for IMSs. This is a consequence of the formally equivalent applicability of the higher-dimensional approach, in particular of the superspace-group theory developed for IMSs [see Janner & Janssen (1980a,b); van Smaalen (1991, 1992); Yamamoto (1992a)].

4.6.3.2.3. Structure factor

The structure factor $F(\mathbf{H})$ of a composite structure consists of the weighted contributions of the subsystem structure factors $F_\nu(\mathbf{H}_\nu)$:

$$F(\mathbf{H}) = \sum_\nu |J_\nu| F_\nu(\mathbf{H}_\nu);$$

$$F_\nu(\mathbf{H}) = \sum_{(R^\nu, \mathbf{t}^\nu)} \sum_{k=1}^{N'} \int_0^1 d\bar{x}_{4,k}^\nu \dots \int_0^1 d\bar{x}_{3+d,k}^\nu f_k^\nu(\mathbf{H}^\parallel) p_k^\nu \times \exp \left(- \sum_{i,j=1}^{3+d} h_i^\nu [R^\nu B_{ijk}^\nu R^{\nu T}] h_j^\nu + 2\pi i \sum_{j=1}^{3+d} h_j^\nu R^\nu x_{jk}^\nu + h_j^\nu t_j^\nu \right),$$

with coefficients similar to those for IMSs.

The weights are the Jacobians of the transformations from $\mathbf{t}_\nu$ to $\mathbf{t}$, and $\mathbf{H}_\nu$ are the reflection indices with respect to the subsystem Fourier modules M_ν^* (van Smaalen, 1995, and references therein).

The relative values of $|J_\nu|$, where $J_\nu = \det [(V_{d\nu} - \sigma_\nu \cdot Z_{d\nu})^{-1}]$, are related to the volume ratios of the contributing subsystems. The subsystem structure factors correspond to those for IMSs (see Section 4.6.3.1). Besides this formula, based on the publications of Yamamoto (1982) and van Smaalen (1995), different structure-factor equations have been discussed (Kato, 1990; Petricek, Maly, Coppens *et al.*, 1991).

4.6.3.3. Quasiperiodic structures (QSs)

4.6.3.3.1. 3D structures with 1D quasiperiodic order

Structures with quasiperiodic order in one dimension and lattice symmetry in the other two dimensions are the simplest representatives of quasicrystals. A few phases of this structure type have been identified experimentally (see Steurer, 1990). Since the Fibonacci chain represents the most important model of a 1D quasiperiodic structure, it will be used in this section to represent the quasiperiodic direction of 3D structures with 1D quasiperiodic order. As discussed in Section 4.6.2.4, 1D quasiperiodic structures are on the borderline between quasiperiodic and incommensurately modulated structures. They can be described using either of the two approaches. In the following, the quasiperiodic description will be preferred to take account of the scaling symmetry.

The electron-density-distribution function $\rho(\mathbf{r})$ of a 1D quasiperiodically ordered 3D crystal can be represented by a Fourier series:

$$\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}).$$

The Fourier coefficients (structure factors) $F(\mathbf{H})$ differ from zero only for reciprocal-space vectors $\mathbf{H} = \sum_{i=1}^3 h_i^\parallel \mathbf{a}_i^*$ with $h_1^\parallel \in \mathbb{R}$, $h_2^\parallel, h_3^\parallel \in \mathbb{Z}$ or with integer indexing $\mathbf{H} = \sum_{i=1}^4 h_i \mathbf{a}_i^*$ with $h_i \in \mathbb{Z}$. The set of all vectors $\mathbf{H}$ forms a Fourier module $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^4 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ of rank 4 which can be decomposed into two rank 2 submodules $M^* = M_1^* \oplus M_2^*$. $M_1^* = \{h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^*\}$ corresponds

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to a $\mathbb{Z}$ module of rank 2 in a 1D subspace, $M_2^* = \{h_3 \mathbf{a}_3^* + h_4 \mathbf{a}_4^*\}$ corresponds to a $\mathbb{Z}$ module of rank 2 in a 2D subspace. Consequently, the first submodule can be considered as a projection from a 2D reciprocal lattice, $M_1^* = \pi^\parallel(\Sigma^*)$, while the second submodule is of the form of a reciprocal lattice, $M_2^* = \Lambda^*$.

Hence, the reciprocal-basis vectors $\mathbf{a}_i^*$, $i = 1, \dots, 4$, can be considered to be projections of reciprocal-basis vectors $\mathbf{d}_i^*$, $i = 1, \dots, 4$, spanning a 4D reciprocal lattice, onto the physical space $\Sigma^* = \{\mathbf{H} = \sum_{i=1}^4 h_i \mathbf{d}_i^* | h_i \in \mathbb{Z}\}$, with

$$\mathbf{d}_1^* = a_1^* \begin{pmatrix} 1 \\ -\tau \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{d}_2^* = a_1^* \begin{pmatrix} \tau \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{d}_3^* = a_3^* \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{d}_4^* = a_4^* \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

A direct lattice Σ with basis $\mathbf{d}_i$, $i = 1, \dots, 4$ and $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$, can be constructed according to (compare Fig. 4.6.2.8) $\Sigma = \{\mathbf{r} = \sum_{i=1}^4 m_i \mathbf{d}_i | m_i \in \mathbb{Z}\}$, with

$$\mathbf{d}_1 = \frac{1}{a_1^*(2+\tau)} \begin{pmatrix} 1 \\ -\tau \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{d}_2 = \frac{1}{a_1^*(2+\tau)} \begin{pmatrix} \tau \\ 1 \\ 0 \\ 0 \end{pmatrix},$$

$$\mathbf{d}_3 = \frac{1}{a_3^*} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{d}_4 = \frac{1}{a_4^*} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

Consequently, the structure in physical space $\mathbf{V}^\parallel$ is equivalent to a 3D section of the 4D hypercrystal.

4.6.3.3.1.1. Indexing

The reciprocal space of the Fibonacci chain is densely filled with Bragg reflections (Figs. 4.6.2.9 and 4.6.3.5). According to the n D embedding method, the shorter the parallel-space distance $\Delta \mathbf{H}^\parallel = \mathbf{H}_2^\parallel - \mathbf{H}_1^\parallel$ between two Bragg reflections, the larger the corresponding perpendicular-space distance $\Delta \mathbf{H}^\perp = \mathbf{H}_2^\perp - \mathbf{H}_1^\perp$ becomes. Since the structure factor $F(\mathbf{H})$ decreases rapidly as a function of $\mathbf{H}^\perp$ (Fig. 4.6.3.6), ‘neighbouring’ reflections of strong Bragg peaks are extremely weak and, consequently, the reciprocal space appears to be filled with *discrete* Bragg peaks even for low-resolution experiments.

This property allows an unambiguous identification of a correct set of reciprocal-basis vectors. However, infinitely many sets allowing a correct indexing of the diffraction pattern with integer indices exist. Nevertheless, an optimum basis (low indices are assigned to strong reflections) can be derived: the intensity distribution, not the metrics, characterizes the best choice of indexing. Once the minimum distance S in the structure is identified from chemical considerations, the reciprocal basis should be chosen as described in Section 4.6.2.4. It has to be kept in mind, however, that the identification of the metrics is not sufficient to distinguish in the 1D aperiodic case between an incommensurately modulated structure, a quasiperiodic structure or special kinds of structures with fractally shaped atomic surfaces.

A correct set of reciprocal-basis vectors can be identified in the following way:

- (1) Find pairs of strong reflections whose physical-space diffraction vectors are related to each other by the factor τ .
- (2) Index these reflections by assigning an appropriate value to a^* . This value should be derived from the shortest interatomic distance S expected in the structure.
- (3) The reciprocal basis is correct if all observable Bragg reflections can be indexed with integer numbers.

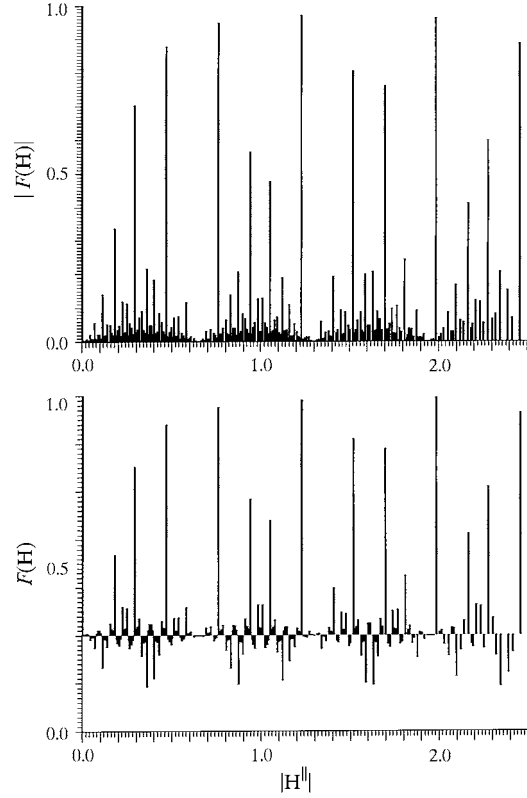


Fig. 4.6.3.5. The structure factors $F(\mathbf{H})$ (below) and their magnitudes $|F(\mathbf{H})|$ (above) of a Fibonacci chain decorated with equal point atoms are shown as a function of the parallel-space component $|\mathbf{H}^\parallel|$ of the diffraction vector. The short distance in the Fibonacci chain is $S = 2.5 \text{ \AA}$, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$ have been calculated and normalized to $F(00) = 1$.

4.6.3.3.1.2. Diffraction symmetry

The possible Laue symmetry group K^{3D} of the Fourier module $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^4 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ is any one of the direct product $K^{3D} = K^{2D} \otimes K^{1D} \otimes \bar{1}$. K^{2D} corresponds to one of the ten crystallographic 2D point groups, $K^{1D} = \{1\}$ in the general case of a quasiperiodic stacking of periodic layers. Consequently, the nine Laue groups $\bar{1}, 2/m, mmm, 4/m, 4/mmm, \bar{3}, \bar{3}m, 6/m$ and $6/mmm$ are possible. These are all 3D crystallographic Laue groups except for the two cubic ones.

The (unweighted) Fourier module shows only 2D lattice symmetry. In the third dimension, the submodule M_1^* remains invariant under the scaling symmetry operation $S^n M_1^* = \tau^n M_1^*$ with $n \in \mathbb{Z}$. The scaling symmetry operators S^n form an infinite group $s = \{\dots, S^{-1}, S^0, S^1, \dots\}$ of reciprocal-basis transformations S^n in superspace,

$$S^n = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D^n, \quad S^{-1} = \begin{pmatrix} \bar{1} & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D,$$

$$S^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}_D,$$

and act on the reciprocal basis $\mathbf{d}_i^*$ in superspace.

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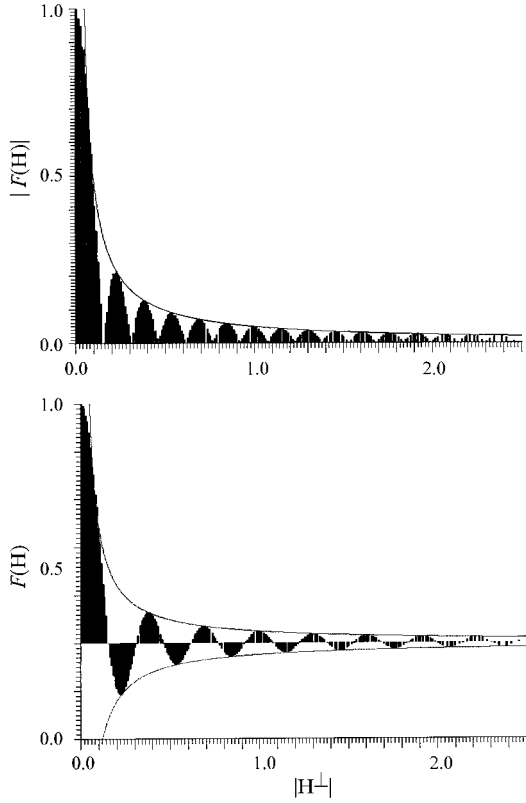


Fig. 4.6.3.6. The structure factors $F(\mathbf{H})$ (below) and their magnitudes $|F(\mathbf{H})|$ (above) of a Fibonacci chain decorated with equal point atoms are shown as a function of the perpendicular-space component $|\mathbf{H}^\perp|$ of the diffraction vector. The short distance in the Fibonacci chain is $S = 2.5 \text{ \AA}$, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$ have been calculated and normalized to $F(00) = 1$.

4.6.3.1.3. Structure factor

The structure factor of a periodic structure is defined as the Fourier transform of the density distribution $\rho(\mathbf{r})$ of its unit cell (UC):

$$F(\mathbf{H}) = \int_{\text{UC}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}.$$

The same is valid in the case of the nD description of a quasiperiodic structure. The parallel- and perpendicular-space components are orthogonal to each other and can be separated. In the case of the 1D Fibonacci sequence, the Fourier transform of the parallel-space component of the electron-density distribution of a single atom gives the usual atomic scattering factor $f(\mathbf{H}^\parallel)$. Parallel to $x^\perp$, $\rho(\mathbf{r})$ adopts values $\neq 0$ only within the interval $-(1+\tau)/[2a^*(2+\tau)] \leq x^\perp \leq (1+\tau)/[2a^*(2+\tau)]$ and one obtains

$$F(\mathbf{H}) = f(\mathbf{H}^\parallel) [a^*(2+\tau)/(1+\tau)] \times \int_{-(1+\tau)/[2a^*(2+\tau)]}^{+(1+\tau)/[2a^*(2+\tau)]} \exp(2\pi i \mathbf{H}^\perp \cdot x^\perp) dx^\perp.$$

The factor $[a^*(2+\tau)/(1+\tau)]$ results from the normalization of the structure factors to $F(\mathbf{0}) = f(0)$. With

$$\begin{aligned} \mathbf{H} &= h_1 \mathbf{d}_1^* + h_2 \mathbf{d}_2^* + h_3 \mathbf{d}_3^* + h_4 \mathbf{d}_4^* \\ &= h_1 a_1^* \begin{pmatrix} 1 \\ -\tau \\ 0 \\ 0 \end{pmatrix} + h_2 a_1^* \begin{pmatrix} \tau \\ 1 \\ 0 \\ 0 \end{pmatrix} + h_3 a_3^* \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} + h_4 a_4^* \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \end{aligned}$$

and $\mathbf{H}^\perp = a_1^*(-\tau h_1 + h_2)$ the integrand can be rewritten as

$$F(\mathbf{H}) = f(\mathbf{H}^\parallel) [a^*(2+\tau)/(1+\tau)] \times \int_{-(1+\tau)/[2a^*(2+\tau)]}^{+(1+\tau)/[2a^*(2+\tau)]} \exp[2\pi i(-\tau h_1 + h_2)x^\perp] dx^\perp,$$

yielding

$$F(\mathbf{H}) = f(\mathbf{H}^\parallel)(2+\tau)/[2\pi i(-\tau h_1 + h_2)(1+\tau)] \times \exp[2\pi i(-\tau h_1 + h_2)x^\perp] \Big|_{-(1+\tau)/[2a^*(2+\tau)]}^{+(1+\tau)/[2a^*(2+\tau)]}.$$

Using $\sin x = (e^{ix} - e^{-ix})/2i$ gives

$$F(\mathbf{H}) = f(\mathbf{H}^\parallel)(2+\tau)/[\pi(-\tau h_1 + h_2)(1+\tau)] \times \sin[\pi(1+\tau)(-\tau h_1 + h_2)]/(2+\tau).$$

Thus, the structure factor has the form of the function $\sin(x)/x$ with x a perpendicular reciprocal-space coordinate. The upper and lower limiting curves of this function are given by the hyperbolae $\pm 1/x$ (Fig. 4.6.3.6). The continuous shape of $F(\mathbf{H})$ as a function of $\mathbf{H}^\perp$ allows the estimation of an overall temperature factor and atomic scattering factor for reflection-data normalization (compare Figs. 4.6.3.6 and 4.6.3.7).

In the case of a 3D crystal structure which is quasiperiodic in one direction, the structure factor can be written in the form

$$F(\mathbf{H}) = \sum_{k=1}^n [T_k(\mathbf{H}) f_k(\mathbf{H}^\parallel) g_k(\mathbf{H}^\perp) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k)].$$

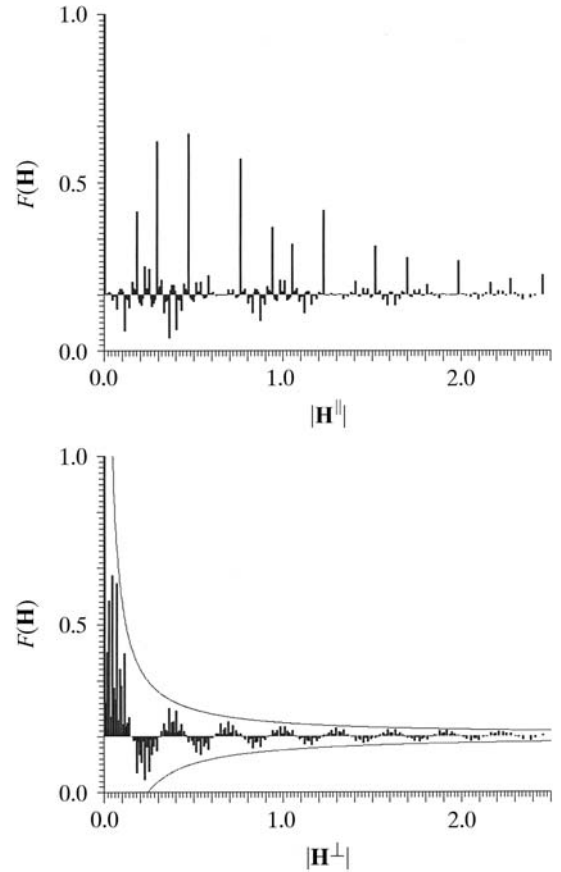


Fig. 4.6.3.7. The structure factors $F(\mathbf{H})$ of the Fibonacci chain decorated with aluminium atoms ($U_{\text{overall}} = 0.005 \text{ \AA}^2$) as a function of the parallel (above) and the perpendicular (below) component of the diffraction vector. The short distance is $S = 2.5 \text{ \AA}$, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$ have been calculated and normalized to $F(00) = 1$.

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The sum runs over all n averaged hyperatoms in the 4D unit cell of the structure. The *geometric form factor* $g_k(\mathbf{H}^\perp)$ corresponds to the Fourier transform of the k th atomic surface,

$$g_k(\mathbf{H}^\perp) = (1/A_{\text{UC}}^\perp) \int_{A_k} \exp(2\pi i \mathbf{H}^\perp \cdot \mathbf{r}^\perp) d\mathbf{r}^\perp,$$

normalized to $A_{\text{UC}}^\perp$, the area of the 2D unit cell projected upon $\mathbf{V}^\perp$, and A_k , the area of the k th atomic surface.

The atomic temperature factor $T_k(\mathbf{H})$ can also have perpendicular-space components. Assuming only harmonic (static or dynamic) displacements in parallel and perpendicular space one obtains, in analogy to the usual expression (Willis & Pryor, 1975),

$$T_k(\mathbf{H}) = T_k(\mathbf{H}^\parallel, \mathbf{H}^\perp) \\ = \exp(-2\pi^2 \mathbf{H}^\parallel T \langle \mathbf{u}_i^\parallel \mathbf{u}_j^{\parallel T} \rangle \mathbf{H}^\parallel) \exp(-2\pi^2 \mathbf{H}^\perp T \langle \mathbf{u}_i^\perp \mathbf{u}_j^{\perp T} \rangle \mathbf{H}^\perp),$$

with

$$\langle \mathbf{u}_i^\parallel \mathbf{u}_j^{\parallel T} \rangle = \begin{pmatrix} \langle \mathbf{u}_1^{\parallel 2} \rangle & \langle \mathbf{u}_1^\parallel \cdot \mathbf{u}_2^{\parallel T} \rangle & \langle \mathbf{u}_1^\parallel \cdot \mathbf{u}_3^{\parallel T} \rangle \\ \langle \mathbf{u}_2^\parallel \cdot \mathbf{u}_1^{\parallel T} \rangle & \langle \mathbf{u}_2^{\parallel 2} \rangle & \langle \mathbf{u}_2^\parallel \cdot \mathbf{u}_3^{\parallel T} \rangle \\ \langle \mathbf{u}_3^\parallel \cdot \mathbf{u}_1^{\parallel T} \rangle & \langle \mathbf{u}_3^\parallel \cdot \mathbf{u}_2^{\parallel T} \rangle & \langle \mathbf{u}_3^{\parallel 2} \rangle \end{pmatrix} \\ \text{and } \langle \mathbf{u}_i^\perp \mathbf{u}_j^{\perp T} \rangle = \langle \mathbf{u}_4^{\perp 2} \rangle.$$

The elements of the type $\langle \mathbf{u}_i \cdot \mathbf{u}_j^T \rangle$ represent the average values of the atomic displacements along the i th axis times the displacement along the j th axis on the V basis.

4.6.3.3.1.4. Intensity statistics

In the following, only the properties of the quasiperiodic component of the 3D structure, namely the Fourier module M_1^* , are discussed. The intensities $I(\mathbf{H})$ of the Fibonacci chain decorated with point atoms are only a function of the perpendicular-space component of the diffraction vector. $|F(\mathbf{H})|$ and $F(\mathbf{H})$ are illustrated in Figs. 4.6.3.5 and 4.6.3.6 as a function of $\mathbf{H}^\parallel$ and of $\mathbf{H}^\perp$. The distribution of $|F(\mathbf{H})|$ as a function of their frequencies clearly resembles a centric distribution, as can be expected from the centrosymmetric 2D sub-unit cell. The shape of the distribution function depends on the radius H_{max} of the limiting sphere in reciprocal space. The number of weak reflections increases with the square of H_{max} , that of strong reflections only linearly (strong reflections always have small $\mathbf{H}^\perp$ components).

The weighted reciprocal space of the Fibonacci sequence contains an infinite number of Bragg reflections within a limited region of the physical space. Contrary to the diffraction pattern of a periodic structure consisting of point atoms on the lattice nodes, the Bragg reflections show intensities depending on the perpendicular-space components of their diffraction vectors.

The reciprocal space of a sequence generated from hyperatoms with fractally shaped atomic surfaces (squared Fibonacci sequence) is very similar to that of the Fibonacci sequence (Figs. 4.6.3.8 and 4.6.3.9). However, there are significantly more weak reflections in the diffraction pattern of the ‘fractal’ sequence, caused by the geometric form factor.

4.6.3.3.1.5. Relationships between structure factors at symmetry-related points of the Fourier image

The two possible point-symmetry groups in the 1D quasiperiodic case, $K^{1D} = 1$ and $K^{1D} = \bar{1}$, relate the structure factors to

$$1 : F(\mathbf{H}) = -F(\bar{\mathbf{H}}), \\ \bar{1} : F(\mathbf{H}) = F(\bar{\mathbf{H}}).$$

A 3D structure with 1D quasiperiodicity results from the stacking of atomic layers with distances following a quasiperiodic sequence.

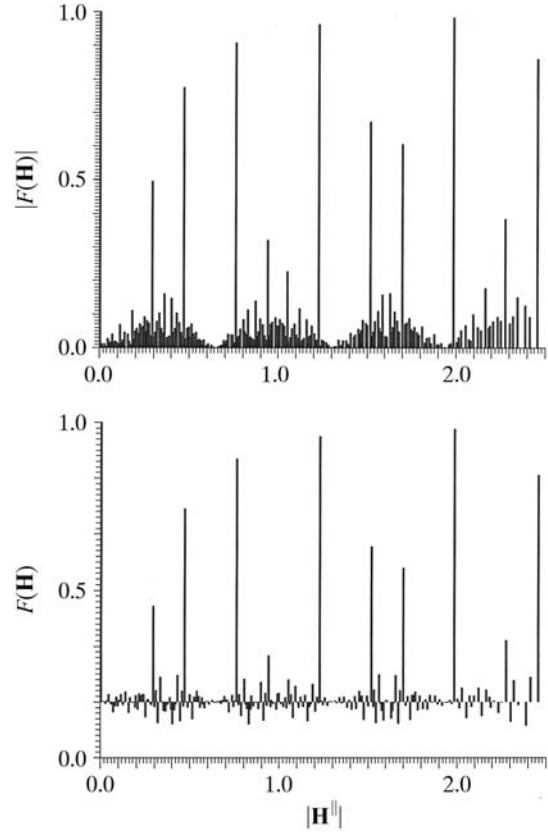


Fig. 4.6.3.8. The structure factors $F(\mathbf{H})$ (below) and their magnitudes $|F(\mathbf{H})|$ (above) of the squared Fibonacci chain decorated with equal point atoms are shown as a function of the parallel-space component $|\mathbf{H}^\parallel|$ of the diffraction vector. The short₁ distance is $S = 2.5 \text{ \AA}$, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$ have been calculated and normalized to $F(00) = 1$.

The point groups K^{3D} describing the symmetry of such structures result from the direct product $K^{3D} = K^{2D} \otimes K^{1D}$. K^{2D} corresponds to one of the ten crystallographic 2D point groups, K^{1D} can be $\{1\}$ or $\{1, m\}$. Consequently, 18 3D point groups are possible.

Since 1D quasiperiodic sequences can be described generically as incommensurately modulated structures, their possible point and space groups are equivalent to a subset of the $(3+1)$ D superspace groups for IMSs with satellite vectors of the type (00γ) , i.e. $\mathbf{q} = \gamma \mathbf{c}^*$, for the quasiperiodic direction $[001]$ (Janssen *et al.*, 1999).

From the scaling properties of the Fibonacci sequence, some relationships between structure factors can be derived. Scaling the physical-space structure by a factor τ^n , $n \in \mathbb{Z}$, corresponds to a scaling of the perpendicular space by the inverse factor $(-\tau)^{-n}$. For the scaling of the corresponding reciprocal subspaces, the inverse factors compared to the direct spaces have to be applied.

The set of vectors $\mathbf{r}$, defining the vertices of a Fibonacci sequence $s(\mathbf{r})$, multiplied by a factor τ coincides with a subset of the vectors defining the vertices of the original sequence (Fig. 4.6.3.10). The residual vertices correspond to a particular decoration of the scaled sequence, i.e. the sequence $\tau^2 s(\mathbf{r})$. The Fourier transform of the sequence $s(\mathbf{r})$ then can be written as the sum of the Fourier transforms of the sequences $\tau s(\mathbf{r})$ and $\tau^2 s(\mathbf{r})$;

$$\sum_k \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k) = \sum_k \exp(2\pi i \mathbf{H} \tau \mathbf{r}_k) + \sum_k \exp[2\pi i \mathbf{H} (\tau^2 \mathbf{r}_k + \tau)].$$

In terms of structure factors, this can be reformulated as

$$F(\mathbf{H}) = F(\tau \mathbf{H}) + \exp(2\pi i \tau \mathbf{H}) F(\tau^2 \mathbf{H}).$$

Hence, phases of structure factors that are related by scaling symmetry can be determined from each other.

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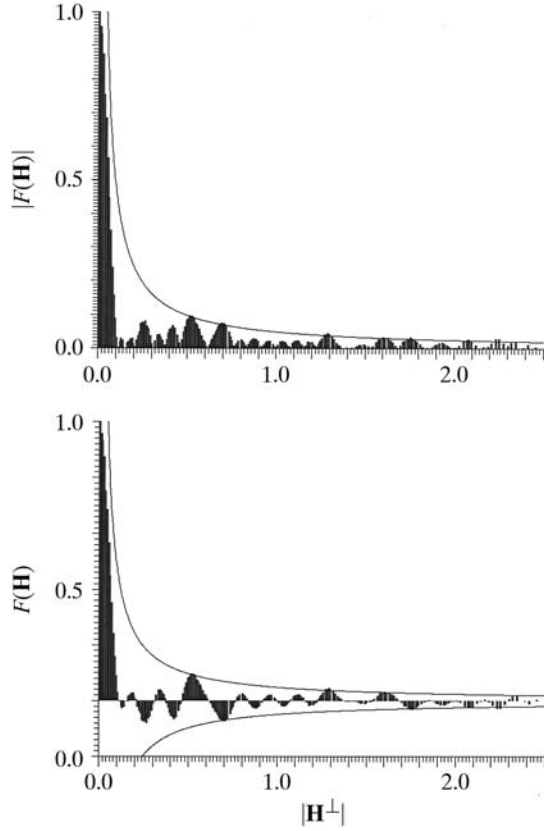


Fig. 4.6.3.9. The structure factors $F(\mathbf{H})$ (below) and their magnitudes $|F(\mathbf{H})|$ (above) of the squared Fibonacci chain decorated with equal point atoms are shown as a function of the perpendicular-space component $|\mathbf{H}^\perp|$ of the diffraction vector. The short a_1 distance is $S = 2.5 \text{ \AA}$, all structure factors within $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$ have been calculated and normalized to $F(00) = 1$.

Further scaling relationships in reciprocal space exist: scaling a diffraction vector $\mathbf{H} = h_1 \mathbf{d}_1^* + h_2 \mathbf{d}_2^* = h_1 a^* \begin{pmatrix} 1 \\ -\tau \end{pmatrix}_V + h_2 a^* \begin{pmatrix} \tau \\ 1 \end{pmatrix}_V$ with the matrix $S = \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}_D$,

$$\begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}_D \begin{pmatrix} h_1 \\ h_2 \end{pmatrix}_D = \begin{pmatrix} F_n & F_{n+1} \\ F_{n+1} & F_{n+2} \end{pmatrix}_D \begin{pmatrix} h_1 \\ h_2 \end{pmatrix}_D = \begin{pmatrix} F_n h_1 + F_{n+1} h_2 \\ F_{n+1} h_1 + F_{n+2} h_2 \end{pmatrix}_D,$$

increases the magnitudes of structure factors assigned to this particular diffraction vector $\mathbf{H}$,

$$|F(S^n \mathbf{H})| > |F(S^{n-1} \mathbf{H})| > \dots > |F(S \mathbf{H})| > |F(\mathbf{H})|.$$

This is due to the shrinking of the perpendicular-space component of the diffraction vector by powers of $(-\tau)^{-n}$ while expanding the parallel-space component by τ^n according to the eigenvalues τ and $-\tau^{-1}$ of S acting in the two eigenspaces $\mathbf{V}^\parallel$ and $\mathbf{V}^\perp$:

$$\begin{aligned} \pi^\parallel(S \mathbf{H}) &= (h_2 + \tau(h_1 + h_2))a^* = (\tau h_1 + h_2(\tau + 1))a^* \\ &= \tau(h_1 + \tau h_2)a^*, \end{aligned}$$

$$\begin{aligned} \pi^\perp(S \mathbf{H}) &= (-\tau h_2 + h_1 + h_2)a^* = (h_1 - h_2(\tau - 1))a^* \\ &= -(1/\tau)(-\tau h_1 + h_2)a^*, \end{aligned}$$

$$|F(\tau^n \mathbf{H}^\parallel)| > |F(\tau^{n-1} \mathbf{H}^\parallel)| > \dots > |F(\tau \mathbf{H}^\parallel)| > |F(\mathbf{H}^\parallel)|.$$

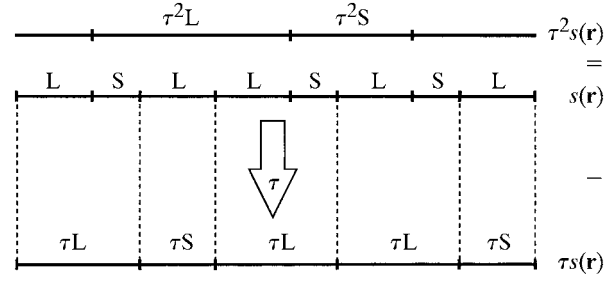


Fig. 4.6.3.10. Part $\dots \text{LSLLSLSL} \dots$ of a Fibonacci sequence $s(\mathbf{r})$ before and after scaling by the factor τ . L is mapped onto τL , S onto $\tau S = L$. The vertices of the new sequence are a subset of those of the original sequence (the correspondence is indicated by dashed lines). The residual vertices $\tau^2 s(\mathbf{r})$, which give when decorating $\tau s(\mathbf{r})$ the Fibonacci sequence $s(\mathbf{r})$, form a Fibonacci sequence scaled by a factor τ^2 .

Thus, for scaling n times we obtain

$$\begin{aligned} \pi^\perp(S^n \mathbf{H}) &= (-\tau(F_n h_1 + F_{n+1} h_2) + (F_{n+1} h_1 + F_{n+2} h_2))a^* \\ &= (h_1(-\tau F_n + F_{n+1}) + h_2(-\tau F_{n+1} + F_{n+2}))a^* \end{aligned}$$

with

$$\lim_{n \rightarrow \infty} (-\tau F_n + F_{n+1}) = 0 \text{ and } \lim_{n \rightarrow \infty} (-\tau F_{n+1} + F_{n+2}) = 0,$$

yielding eventually

$$\lim_{n \rightarrow \infty} (\pi^\perp(S^n \mathbf{H})) = 0 \text{ and } \lim_{n \rightarrow \infty} (F(S^n \mathbf{H})) = F(\mathbf{0}).$$

The scaling of the diffraction vectors $\mathbf{H}$ by S^n corresponds to a hyperbolic rotation (Janner, 1992) with angle $n\varphi$, where $\sinh \varphi = 1/2$ (Fig. 4.6.3.11):

$$\begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}^{2n} = \begin{pmatrix} \cosh 2n\varphi & \sinh 2n\varphi \\ \sinh 2n\varphi & \cosh 2n\varphi \end{pmatrix},$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}^{2n+1} = \begin{pmatrix} \sinh[(2n+1)\varphi] & \cosh[(2n+1)\varphi] \\ \cosh[(2n+1)\varphi] & \sinh[(2n+1)\varphi] \end{pmatrix}.$$

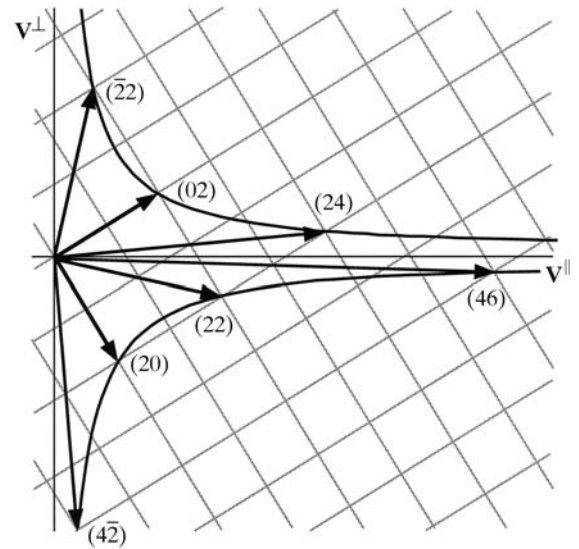


Fig. 4.6.3.11. Scaling operations of the Fibonacci sequence. The scaling operation S acts six times on the diffraction vector $\mathbf{H} = (4\bar{2})$ yielding the sequence $(4\bar{2}) \rightarrow (22) \rightarrow (20) \rightarrow (02) \rightarrow (22) \rightarrow (24) \rightarrow (46)$.

4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

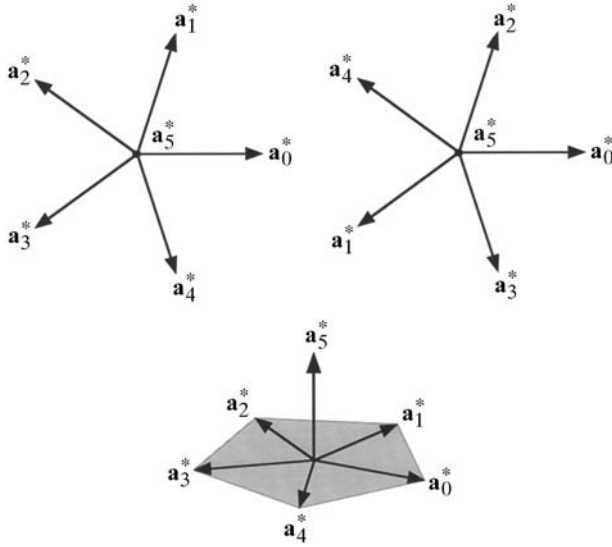


Fig. 4.6.3.12. Reciprocal basis of the decagonal phase in the 5D description projected upon $\mathbf{V}^{\parallel}$ (above left) and $\mathbf{V}^{\perp}$ (above right). Below, a perspective physical-space view is shown.

4.6.3.3.2. Decagonal phases

A structure quasiperiodic in two dimensions, periodic in the third dimension and with decagonal diffraction symmetry is called a decagonal phase. Its holohedral Laue symmetry group is $K = 10/mmm$. All reciprocal-space vectors $\mathbf{H} \in M^*$ can be represented on a basis (V basis) $\mathbf{a}_i^* = a_i^* (\cos 2\pi i/5, \sin 2\pi i/5, 0)$, $i = 1, \dots, 4$ and $\mathbf{a}_5^* = a_5^* (0, 0, 1)$ (Fig. 4.6.3.12) as $\mathbf{H} = \sum_{i=1}^5 h_i \mathbf{a}_i^*$. The vector components refer to a Cartesian coordinate system in physical (parallel) space. Thus, from the number of independent reciprocal-basis vectors necessary to index the Bragg reflections with integer numbers, the dimension of the embedding space has to be at least five. This can also be shown in a different way (Hermann, 1949).

The set M^* of all vectors $\mathbf{H}$ remains invariant under the action of the symmetry operators of the point group $10/mmm$. The symmetry-adapted matrix representations for the point-group generators, the tenfold rotation $\alpha = 10$, the reflection plane $\beta = m_2$ (normal of the reflection plane along the vectors $\mathbf{a}_i^* \mathbf{a}_{i+3}^*$ with $i = 1, \dots, 4$ modulo 5) and the inversion operation $\Gamma(\gamma) = \bar{1}$ may be written in the form

$$\Gamma(\alpha) = \begin{pmatrix} 0 & 1 & \bar{1} & 0 & 0 \\ 0 & 1 & 0 & \bar{1} & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \bar{1} & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}_D, \quad \Gamma(\beta) = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}_D$$

$$\Gamma(\gamma) = \begin{pmatrix} \bar{1} & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 0 & \bar{1} \end{pmatrix}_D.$$

By block-diagonalization, these reducible symmetry matrices can be decomposed into non-equivalent irreducible representations. These can be assigned to the two orthogonal subspaces forming the 5D embedding space $\mathbf{V} = \mathbf{V}^{\parallel} \oplus \mathbf{V}^{\perp}$, the 3D parallel (physical) subspace $\mathbf{V}^{\parallel}$ and the perpendicular 2D subspace $\mathbf{V}^{\perp}$. Thus, using $W\Gamma W^{-1} = \Gamma_V = \Gamma_V^{\parallel} \oplus \Gamma_V^{\perp}$, we obtain

$$\Gamma_V(\alpha) = \left(\begin{array}{ccc|cc} \cos(\pi/5) & -\sin(\pi/5) & 0 & 0 & 0 \\ \sin(\pi/5) & \cos(\pi/5) & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ \hline 0 & 0 & 0 & \cos(3\pi/5) & -\sin(3\pi/5) \\ 0 & 0 & 0 & \sin(3\pi/5) & \cos(3\pi/5) \end{array} \right)_V$$

$$= \left(\begin{array}{c|c} \Gamma^{\parallel}(\alpha) & 0 \\ \hline 0 & \Gamma^{\perp}(\alpha) \end{array} \right)_V,$$

$$\Gamma_V(\beta) = \left(\begin{array}{ccccc|cc} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{array} \right)_V, \quad \Gamma_V(\gamma) = \left(\begin{array}{ccccc|cc} \bar{1} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 & 0 \end{array} \right)_V,$$

where

$$W = \left(\begin{array}{ccccc|c} a_1^* \cos(2\pi/5) & a_2^* \cos(4\pi/5) & a_3^* \cos(6\pi/5) & a_4^* \cos(8\pi/5) & 0 & 0 \\ a_1^* \sin(2\pi/5) & a_2^* \sin(4\pi/5) & a_3^* \sin(6\pi/5) & a_4^* \sin(8\pi/5) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & a_5^* \\ \hline a_1^* \cos(6\pi/5) & a_2^* \cos(2\pi/5) & a_3^* \cos(8\pi/5) & a_4^* \cos(4\pi/5) & 0 & 0 \\ a_1^* \sin(6\pi/5) & a_2^* \sin(2\pi/5) & a_3^* \sin(8\pi/5) & a_4^* \sin(4\pi/5) & 0 & 0 \end{array} \right).$$

The column vectors of the matrix W give the parallel- (above the partition line) and perpendicular-space components (below the partition line) of a reciprocal basis in V space. Thus, W can be rewritten using the physical-space reciprocal basis defined above as

$$W = (\mathbf{d}_1^*, \mathbf{d}_2^*, \mathbf{d}_3^*, \mathbf{d}_4^*, \mathbf{d}_5^*),$$

yielding the reciprocal basis $\mathbf{d}_i^*, i = 1, \dots, 5$, in the 5D embedding space (D space):

$$\mathbf{d}_i^* = a_i^* \begin{pmatrix} \cos(2\pi i/5) \\ \sin(2\pi i/5) \\ 0 \\ \cos(6\pi i/5) \\ \sin(6\pi i/5) \end{pmatrix}_V, \quad i = 1, \dots, 4 \quad \text{and} \quad \mathbf{d}_5^* = a_5^* \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}_V.$$

The 5×5 symmetry matrices can each be decomposed into a 3×3 matrix and a 2×2 matrix. The first one, $\Gamma^{\parallel}$, acts on the parallel-space component, the second one, $\Gamma^{\perp}$, on the perpendicular-space component. In the case of $\Gamma(\alpha)$, the coupling factor between a rotation in parallel and perpendicular space is 3. Thus, a $\pi/5$ rotation in physical space is related to a $3\pi/5$ rotation in perpendicular space (Fig. 4.6.3.12).

With the condition $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$, a basis in direct 5D space is obtained:

$$\mathbf{d}_i = \frac{2}{5a_i^*} \begin{pmatrix} \cos(2\pi i/5) - 1 \\ \sin(2\pi i/5) \\ 0 \\ \cos(6\pi i/5) - 1 \\ \sin(6\pi i/5) \end{pmatrix}, \quad i = 1, \dots, 4, \quad \text{and} \quad \mathbf{d}_5 = \frac{1}{a_5^*} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}.$$

The metric tensors G, G^* are of the type

$$\begin{pmatrix} A & C & C & C & 0 \\ C & A & C & C & 0 \\ C & C & A & C & 0 \\ C & C & C & A & 0 \\ 0 & 0 & 0 & 0 & B \end{pmatrix}$$

with $A = 2a_1^{*2}, B = a_5^{*2}, C = -(1/2)a_1^{*2}$ for the reciprocal space and $A = 4/5a_1^{*2}, B = 1/a_5^{*2}, C = 2/5a_1^{*2}$ for the direct space. Thus, for the lattice parameters in reciprocal space we obtain

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$d_i^* = a_i^*(2)^{1/2}$, $i = 1, \dots, 4$; $d_5^* = a_5^*$; $\alpha_{ij}^* = 104.5^\circ$, $i, j = 1, \dots, 4$; $\alpha_{i5}^* = 90^\circ$, $i = 1, \dots, 4$, and for those in direct space $d_i = 2/[a_i^*(5)^{1/2}]$, $i = 1, \dots, 4$; $d_5 = 1/a_5^*$; $\alpha_{ij} = 60^\circ$, $i, j = 1, \dots, 4$; $\alpha_{i5} = 90^\circ$, $i = 1, \dots, 4$. The volume of the 5D unit cell can be calculated from the metric tensor G :

$$V = [\det(G)]^{1/2} = \frac{4}{5(5)^{1/2}(a_1^*)^4 a_5^*} = \frac{(5)^{1/2}}{4} (d_1)^4 d_5.$$

Since decagonal phases are only quasiperiodic in two dimensions, it is sufficient to demonstrate their characteristics on a 2D example, the canonical *Penrose tiling* (Penrose, 1974). It can be constructed from two unit tiles: a skinny (acute angle $\alpha_s = \pi/5$) and a fat (acute angle $\alpha_f = 2\pi/5$) rhomb with equal edge lengths a_r and areas $A_s = a_r^2 \sin(\pi/5)$, $A_f = a_r^2 \sin(2\pi/5)$ (Fig. 4.6.3.13). The areas and frequencies of these two unit tiles in the Penrose tiling are both in a ratio 1 to τ . By replacing each skinny and fat rhomb according to the inflation rule, a τ -inflated tiling is obtained. Inflation (deflation) means that the number of tiles is inflated (deflated), their edge lengths are decreased (increased) by a factor τ . By infinite repetition of this inflation operation, an infinite Penrose

tiling is generated. Consequently, this substitution operation leaves the tiling invariant.

From Fig. 4.6.3.13 it can be seen that the sets of vertices of the deflated tilings are subsets of the set of vertices of the original tiling. The τ -deflated tiling is dual to the original tiling; a further deflation by a factor τ gives the original tiling again. However, the edge lengths of the tiles are increased by a factor τ^2 , and the tiling is rotated around 36° . Only the fourth deflation of the original tiling yields the original tiling in its original orientation but with all lengths multiplied by a factor τ^4 .

Contrary to the reciprocal-space scaling behaviour of $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^4 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$, the set of vertices $M = \{\mathbf{r} = \sum_{i=1}^4 n_i \mathbf{a}_i | n_i \in \mathbb{Z}\}$ of the Penrose tiling is not invariant by scaling the length scale simply by a factor τ using the scaling matrix S :

$$S = \begin{pmatrix} 0 & 1 & 0 & \bar{1} \\ 0 & 1 & 1 & \bar{1} \\ \bar{1} & 1 & 1 & 0 \\ \bar{1} & 0 & 1 & 0 \end{pmatrix}_D \text{ acting on vectors } \mathbf{r} = \begin{pmatrix} n_1 \\ n_2 \\ n_3 \\ n_4 \end{pmatrix}_D.$$

The square of S , however, maps all vertices of the Penrose tiling upon other ones:

$$S^2 = \begin{pmatrix} 1 & 1 & 0 & \bar{1} \\ 0 & 2 & 1 & \bar{1} \\ \bar{1} & 1 & 2 & 0 \\ \bar{1} & 0 & 1 & 1 \end{pmatrix}_D, \quad \Gamma(\alpha)S^2 = \begin{pmatrix} 1 & 1 & \bar{1} & \bar{1} \\ 1 & 2 & 0 & \bar{2} \\ 0 & 2 & 1 & \bar{1} \\ \bar{1} & 1 & 1 & 0 \end{pmatrix}_D.$$

S^2 corresponds to a hyperbolic rotation with $\chi = \cosh^{-1}(3/2)$ in superspace (Janner, 1992). However, only operations of the type S^{4n} , $n = 0, 1, 2, \dots$, scale the Penrose tiling in a way which is equivalent to the $(4n)$ th substitutional operations discussed above. The rotoscaling operation $\Gamma(\alpha)S^2$, also a symmetry operation of the Penrose tiling, leaves a pentagram invariant as demonstrated in Fig. 4.6.3.14 (Janner, 1992). Block-diagonalization of the scaling matrix S decomposes it into two non-equivalent irreducible representations which give the scaling properties in the two orthogonal subspaces of the 4D embedding space, $\mathbf{V} = \mathbf{V}^\parallel \oplus \mathbf{V}^\perp$, the 2D parallel (physical) subspace $\mathbf{V}^\parallel$ and the perpendicular 2D subspace $\mathbf{V}^\perp$. Thus, using $WSW^{-1} = S_V \oplus S_V^\perp$, we obtain

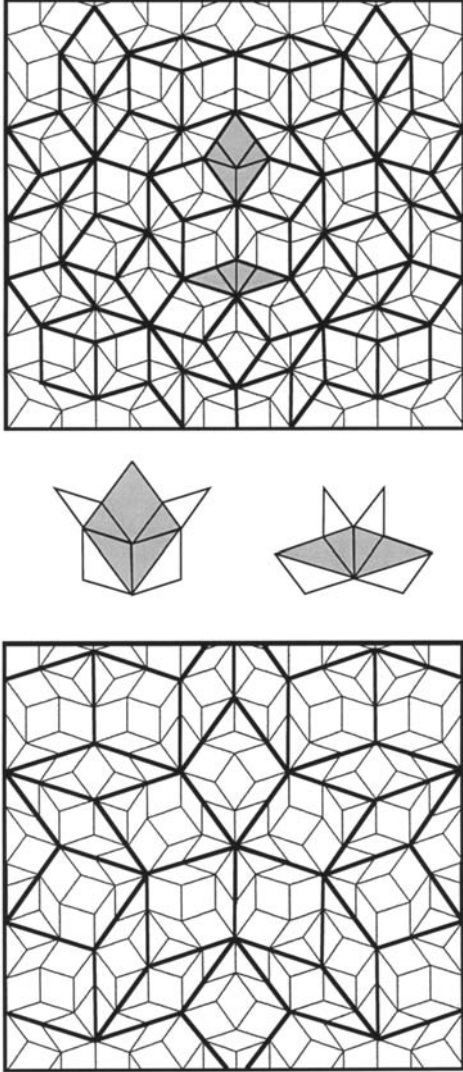


Fig. 4.6.3.13. A section of a Penrose tiling (thin lines) superposed by its τ -deflated tiling (above, thick lines) and by its τ^2 -deflated tiling (below, thick lines). In the middle, the inflation rule of the Penrose tiling is illustrated.

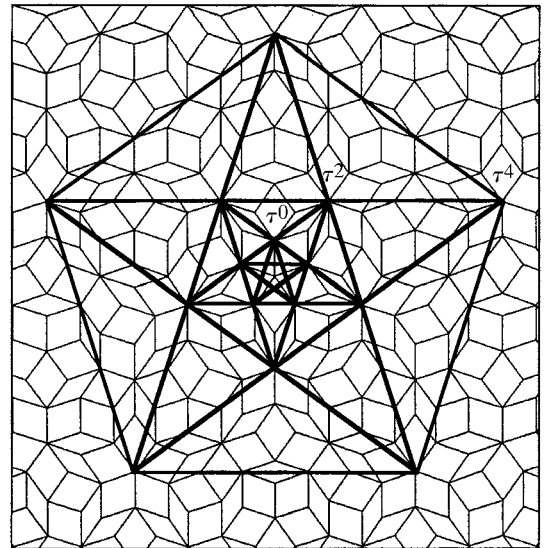


Fig. 4.6.3.14. Scaling symmetry of a pentagram superposed on the Penrose tiling. A vector pointing to a corner of a pentagon (star) is mapped by the rotoscaling operation (rotation around $\pi/5$ and dilatation by a factor τ^2) onto the next largest pentagon (star).

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$$S_V = \left(\begin{array}{cc|cc} \tau & 0 & 0 & 0 \\ 0 & \tau & 0 & 0 \\ 0 & 0 & -1/\tau & 0 \\ 0 & 0 & 0 & -1/\tau \end{array} \right)_V = \left(\begin{array}{c|c} S_V^{\parallel} & 0 \\ 0 & S_V^{\perp} \end{array} \right)_V,$$

where

$$W = \begin{pmatrix} a_1^* \cos(2\pi/5) & a_2^* \cos(4\pi/5) & a_3^* \cos(6\pi/5) & a_4^* \cos(8\pi/5) \\ a_1^* \sin(2\pi/5) & a_2^* \sin(4\pi/5) & a_3^* \sin(6\pi/5) & a_4^* \sin(8\pi/5) \\ a_1^* \cos(4\pi/5) & a_2^* \cos(8\pi/5) & a_3^* \cos(2\pi/5) & a_4^* \cos(6\pi/5) \\ a_1^* \sin(4\pi/5) & a_2^* \sin(8\pi/5) & a_3^* \sin(2\pi/5) & a_4^* \sin(6\pi/5) \end{pmatrix}.$$

The 2D Penrose tiling can also be embedded canonically in the 5D space. Canonically means that the 5D lattice is hypercubic and that the projection of one unit cell upon the 3D perpendicular space $V^{\perp}$, giving a rhomb-icosahedron, defines the atomic surface. However, the parallel-space image $\mathbf{a}_i^*$, $i = 1, \dots, 4$, with $\mathbf{a}_0^* = -(\mathbf{a}_1^* + \mathbf{a}_2^* + \mathbf{a}_3^* + \mathbf{a}_4^*)$, of the 5D basis $\mathbf{d}_i^*$, $i = 1, \dots, 4$ is not linearly independent. Consequently, the atomic surface consists of only a subset of the points contained in the rhomb-icosahedron: five equidistant pentagons (one with diameter zero) resulting as sections of the rhomb-icosahedron with five equidistant parallel planes (Fig. 4.6.3.15). The linear dependence of the 5D basis allows the embedding in the 4D space. The resulting hyper-rhombohedral hyperlattice is spanned by the basis $\mathbf{d}_i$, $i = 1, \dots, 4$, discussed above. The atomic surfaces occupy the positions $p/5(1111)$, $p = 1, \dots, 4$, on the body diagonal of the 4D unit cell. Neighbouring pentagons are in an *anti* position to each other (Fig. 4.6.3.16). Thus the 4D unit cell is decorated centrosymmetrically. The edge length a_r of a Penrose rhomb is related to the length of physical-space basis vectors a_i^* by $a_r = \tau S$, with the smallest distance $S = (2\tau/5a_i^*)$, $i = 1, \dots, 4$. The *point density* (number of vertices per unit area) of a Penrose tiling with Penrose rhombs of edge length a_r can be calculated from the ratio of the relative number of unit tiles in the tiling to their area:

$$\rho = \frac{1 + \tau}{a_r^2 [\sin(\pi/5) + \tau \sin(2\pi/5)]} = (5/2)a_i^{*2}(2 - \tau)^2 \tan(2\pi/5).$$

This is equivalent to the calculation from the 4D description,

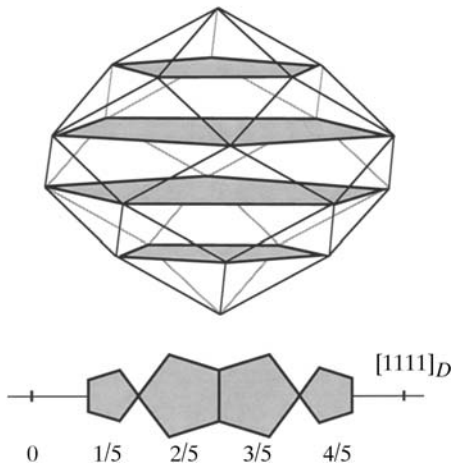


Fig. 4.6.3.15. Atomic surface of the Penrose tiling in the 5D hypercubic description. The projection of the 5D hypercubic unit cell upon $V^{\perp}$ gives a rhomb-icosahedron (above). The Penrose tiling is generated by four equidistant pentagons (shaded) inscribed in the rhomb-icosahedron. Below is a perpendicular-space projection of the same pentagons, which are located on the $[1111]_D$ diagonal of the 4D hyper-rhombohedral unit cell in the 4D description.

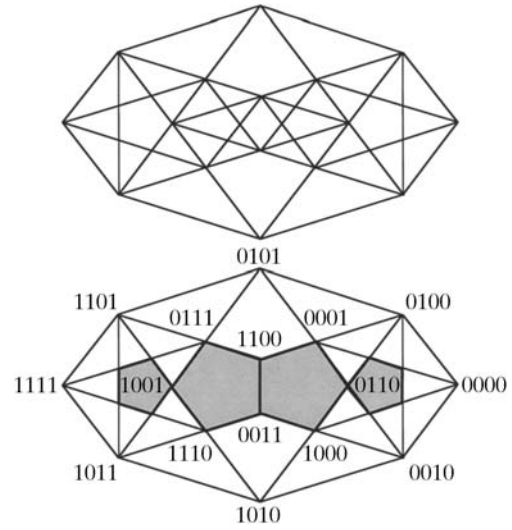


Fig. 4.6.3.16. Projection of the 4D hyper-rhombohedral unit cell of the Penrose tiling in the 4D description upon the perpendicular space. In the upper drawing all edges between the 16 corners are shown. In the lower drawing the corners are indexed and the four pentagonal atomic surfaces of the Penrose tiling are shaded.

$$\rho = \frac{\sum_{i=1}^4 \Omega_{AS}^i}{\Omega_{UC}} = \frac{\sum_{i=1}^4 (5/2)\lambda^2 \sin(2\pi/5)}{4/[5(5)^{1/2}|a_i^*|^4]} = (5/2)a_i^{*2}(2 - \tau)^2 \tan(2\pi/5),$$

where Ω_{AS} and Ω_{UC} are the area of the atomic surface and the volume of the 4D unit cell, respectively. The pentagon radii are $\lambda_{1,4} = 2(2 - \tau)/5a^*$ and $\lambda_{2,3} = 2(\tau - 1)/5a^*$ for the atomic surfaces in $(p/5)(1111)$ with $p = 1, 4$ and $p = 2, 3$. A detailed discussion of the properties of Penrose tiling is given in the papers of Penrose (1974, 1979), Jaric (1986) and Pavlovitch & Kleman (1987).

4.6.3.3.2.1. Indexing

The indexing of the submodule M_1^* of the diffraction pattern of a decagonal phase is not unique. Since M_1^* corresponds to a $\mathbb{Z}$ module of rank 4 with decagonal point symmetry, it is invariant under scaling by τ^n , $n \in \mathbb{Z}$: $S^n M^* = \tau^n M^*$. Nevertheless, an optimum basis (low indices are assigned to strong reflections) can be derived: not the metrics, as for regular periodic crystals, but the intensity distribution characterizes the best choice of indexing.

A correct set of reciprocal-basis vectors can be identified experimentally in the following way:

(1) Find directions of systematic absences or pseudo-absences determining the possible orientations of the reciprocal-basis vectors (see Rabson *et al.*, 1991).

(2) Find pairs of strong reflections whose physical-space diffraction vectors are related to each other by the factor τ .

(3) Index these reflections by assigning an appropriate value to a^* . This value should be derived from the shortest interatomic distance S and the edge length of the unit tiles expected in the structure.

(4) The reciprocal basis is correct if all observable Bragg reflections can be indexed with integer numbers.

4.6.3.3.2.2. Diffraction symmetry

The diffraction symmetry of decagonal phases can be described by the Laue groups $10/mmm$ or $10/m$. The set of all vectors $\mathbf{H}$ forms a Fourier module $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^5 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ of rank 5 in physical space which can be decomposed into two submodules

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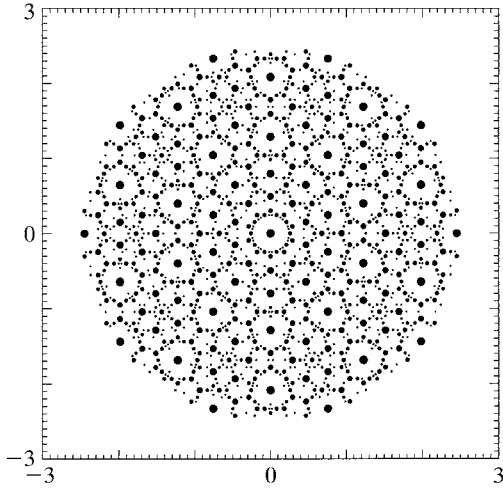


Fig. 4.6.3.17. Schematic diffraction pattern of the Penrose tiling (edge length of the Penrose unit rhombs $a_r = 4.04 \text{ \AA}$). All reflections are shown within $10^{-2}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$.

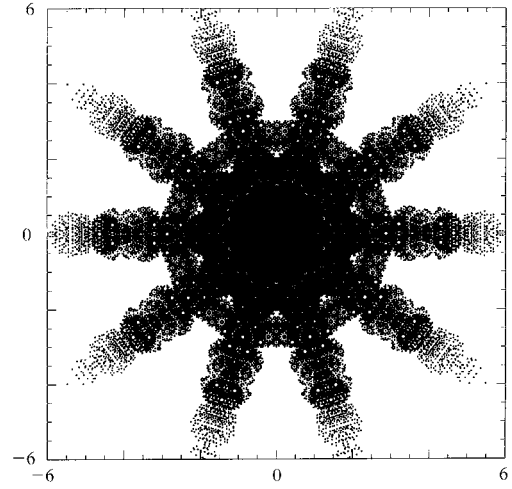


Fig. 4.6.3.19. The perpendicular-space diffraction pattern of the Penrose tiling (edge length of the Penrose unit rhombs $a_r = 4.04 \text{ \AA}$). All reflections are shown within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$.

$M^* = M_1^* \oplus M_2^*$. $M_1^* = \{h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* + h_4\mathbf{a}_4^*\}$ corresponds to a $\mathbb{Z}$ module of rank 4 in a 2D subspace, $M_2^* = \{h_5\mathbf{a}_5^*\}$ corresponds to a $\mathbb{Z}$ module of rank 1 in a 1D subspace. Consequently, the first submodule can be considered as a projection from a 4D reciprocal lattice, $M_1^* = \pi^\parallel(\Sigma^*)$, while the second submodule is of the form of a regular 1D reciprocal lattice, $M_2^* = \Lambda^*$. The diffraction pattern of the Penrose tiling decorated with equal point scatterers on its vertices is shown in Fig. 4.6.3.17. All Bragg reflections within $10^{-2}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ are depicted. Without intensity-truncation limit, the diffraction pattern would be densely filled with discrete Bragg reflections. To illustrate their spatial and intensity distribution, an enlarged section of Fig. 4.6.3.17 is shown in Fig. 4.6.3.18. This picture shows all Bragg reflections within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$. The projected 4D reciprocal-lattice unit cell is drawn and several reflections are indexed. All reflections are arranged along lines in five symmetry-equivalent orientations. The perpendicular-space diffraction patterns (Figs. 4.6.3.19 and 4.6.3.20) show a characteristic star-like

distribution of the Bragg reflections. This is a consequence of the pentagonal shape of the atomic surfaces: the Fourier transform of a pentagon has a star-like distribution of strong Fourier coefficients.

The 5D decagonal space groups that may be of relevance for the description of decagonal phases are listed in Table 4.6.3.1. These space groups are a subset of all 5D decagonal space groups fulfilling the condition that the 5D point groups they are associated with are isomorphous to the 3D point groups describing the diffraction symmetry. Their structures are comparable to 3D hexagonal groups. Hence, only primitive lattices exist. The orientation of the symmetry elements in the 5D space is defined by the isomorphism of the 3D and 5D point groups. However, the action of the tenfold rotation is different in the subspaces $\mathbf{V}^\parallel$ and $\mathbf{V}^\perp$: a rotation of $\pi/5$ in $\mathbf{V}^\parallel$ is correlated with a rotation of $3\pi/5$ in $\mathbf{V}^\perp$. The reflection and inversion operations are equivalent in both subspaces.

4.6.3.3.2.3. Structure factor

The structure factor for the decagonal phase corresponds to the Fourier transform of the 5D unit cell,

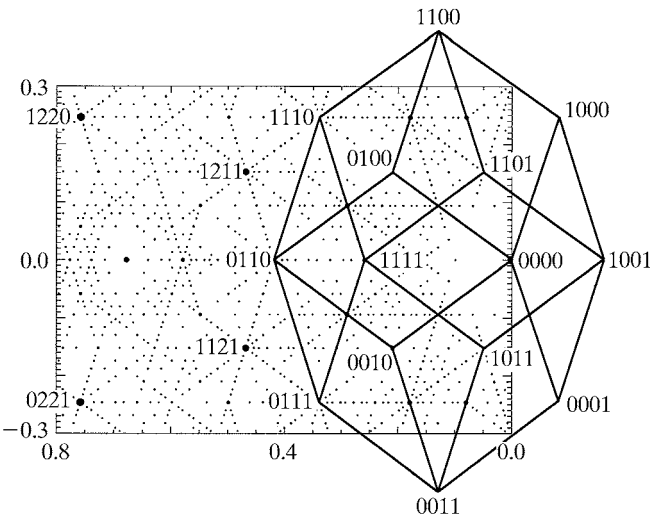


Fig. 4.6.3.18. Enlarged section of Fig. 4.6.3.17. All reflections shown are selected within the given limits from a data set within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $0 \leq |\mathbf{H}| \leq 2.5 \text{ \AA}^{-1}$. The projected 4D reciprocal-lattice unit cell is drawn and several reflections are indexed.

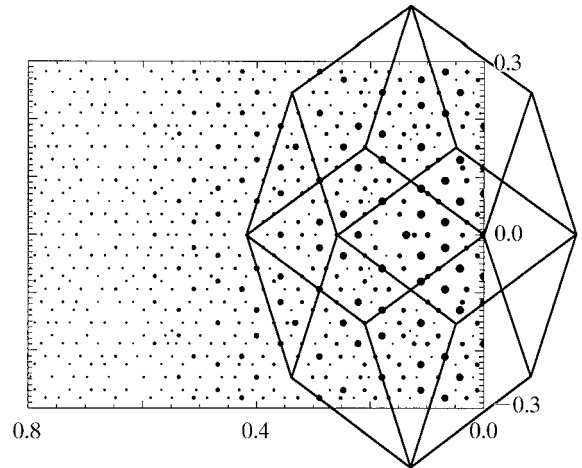


Fig. 4.6.3.20. Enlarged section of Fig. 4.6.3.19 showing the projected 4D reciprocal-lattice unit cell.

4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

Table 4.6.3.1. 3D point groups of order k describing the diffraction symmetry and corresponding 5D decagonal space groups with reflection conditions (see Rabson et al., 1991)

3D point group	k	5D space group	Reflection condition
$\frac{10}{m} \frac{2}{m} \frac{2}{m}$	40	$P \frac{10}{m} \frac{2}{m} \frac{2}{m}$	No condition
		$P \frac{10}{m} \frac{2}{c} \frac{2}{c}$	$h_1 h_2 h_3 h_4 h_5 : h_5 = 2n$ $h_1 h_2 \bar{h}_3 \bar{h}_4 h_5 : h_5 = 2n$
		$P \frac{10}{m} \frac{2}{m} \frac{2}{c}$	$h_1 h_2 \bar{h}_3 \bar{h}_4 h_5 : h_5 = 2n$
		$P \frac{10}{m} \frac{2}{c} \frac{2}{m}$	$h_1 h_2 h_3 h_4 h_5 : h_5 = 2n$
$\frac{10}{m}$	20	$P \frac{10}{m}$	No condition
		$P \frac{10}{m}$	$0000h_5 : h_5 = 2n$
1022	20	$P1022$	No condition
		$P10_222$	$0000h_5 : jh_5 = 10n$
10mm	20	$P10mm$	No condition
		$P10cc$	$h_1 h_2 h_3 h_4 h_5 : h_5 = 2n$ $h_1 h_2 \bar{h}_3 \bar{h}_4 h_5 : h_5 = 2n$
		$P10_5mc$	$h_1 h_2 \bar{h}_3 \bar{h}_4 h_5 : h_5 = 2n$
		$P10_5cm$	$h_1 h_2 h_3 h_4 h_5 : h_5 = 2n$
$\bar{1}0m2$	20	$P\bar{1}0m2$	No condition
		$P\bar{1}0c2$	$h_1 h_2 h_3 h_4 h_5 : h_5 = 2n$
		$P\bar{1}02m$	No condition
		$P\bar{1}02c$	$h_1 h_2 \bar{h}_3 \bar{h}_4 h_5 : h_5 = 2n$
10	10	$P10$	No condition
		$P10_j$	$0000h_5 : jh_5 = 10n$

where $A_{UC}^\perp$ is the area of the 5D unit cell projected upon $\mathbf{V}^\perp$ and A_k is the area of the k th atomic surface. The area $A_{UC}^\perp$ can be calculated using the formula

$$A_{UC}^\perp = (4/25a_i^{*2})[(7 + \tau) \sin(2\pi/5) + (2 + \tau) \sin(4\pi/5)].$$

Evaluating the integral by decomposing the pentagons into triangles, one obtains

$$g_k(\mathbf{H}^\perp) = \frac{1}{A_{UC}^\perp} \sin\left(\frac{2\pi}{5}\right) \times \sum_{j=0}^4 \frac{A_j [\exp(iA_{j+1}\lambda_k) - 1] - A_{j+1} [\exp(iA_j\lambda_k) - 1]}{A_j A_{j+1} (A_j - A_{j+1})}$$

with $j = 0, \dots, 4$ running over the five triangles, where the radii of the pentagons are λ_j , $A_j = 2\pi\mathbf{H}^\perp \cdot \mathbf{e}_j$,

$$\mathbf{H}^\perp = \pi^\perp(\mathbf{H}) = \sum_{j=0}^4 h_j a_j^* \begin{pmatrix} 0 \\ 0 \\ 0 \\ \cos(6\pi j/5) \\ \sin(6\pi j/5) \end{pmatrix}$$

and the vectors

$$\mathbf{e}_j = \frac{1}{a_j^*} \begin{pmatrix} 0 \\ 0 \\ 0 \\ \cos(2\pi j/5) \\ \sin(2\pi j/5) \end{pmatrix} \text{ with } j = 0, \dots, 4.$$

As shown by Ishihara & Yamamoto (1988), the Penrose tiling can be considered to be a superstructure of a pentagonal tiling with only one type of pentagonal atomic surface in the n D unit cell. Thus, for the Penrose tiling, three special reflection classes can be distinguished: for $|\sum_{i=1}^4 h_i| = m \bmod 5$ and $m = 0$ the class of strong main reflections is obtained, and for $m = \pm 1, \pm 2$ the classes of weaker first- and second-order satellite reflections are obtained (see Fig. 4.6.3.18).

4.6.3.3.2.4. Intensity statistics

This section deals with the reciprocal-space characteristics of the 2D quasiperiodic component of the 3D structure, namely the Fourier module M_1^* . The radial structure-factor distributions of the Penrose tiling decorated with point scatterers are plotted in Figs. 4.6.3.21 and 4.6.3.22 as a function of parallel and perpendicular space. The distribution of $|F(\mathbf{H})|$ as a function of their frequencies clearly resembles a centric distribution, as can be expected from the centrosymmetric 4D subunit cell. The shape of the distribution function depends on the radius of the limiting sphere in reciprocal space. The number of weak reflections increases to the power of four, that of strong reflections only quadratically (strong reflections always have small $\mathbf{H}^\perp$ components). The radial distribution of the structure-factor amplitudes as a function of perpendicular space clearly shows three branches, corresponding to the reflection classes $\sum_{i=1}^4 h_i = m \bmod 5$ with $|m| = 0$, $|m| = 1$ and $|m| = 2$ (Fig. 4.6.3.23).

The weighted reciprocal space of the Penrose tiling contains an infinite number of Bragg reflections within a limited region of the physical space. Contrary to the diffraction pattern of a periodic structure consisting of point atoms on the lattice nodes, the Bragg reflections show intensities depending on the perpendicular-space components of their diffraction vectors (Figs. 4.6.3.19, 4.6.3.20 and 4.6.3.22).

$$F(\mathbf{H}) = \sum_{k=1}^N f_k(\mathbf{H}^\parallel) T_k(\mathbf{H}^\parallel, \mathbf{H}^\perp) g_k(\mathbf{H}^\perp) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k),$$

with 5D diffraction vectors $\mathbf{H} = \sum_{i=1}^5 h_i \mathbf{d}_i^*$, N hyperatoms, parallel-space atomic scattering factor $f_k(\mathbf{H}^\parallel)$, temperature factor $T_k(\mathbf{H}^\parallel, \mathbf{H}^\perp)$ and perpendicular-space geometric form factor $g_k(\mathbf{H}^\perp)$. $T_k(\mathbf{H}^\parallel, \mathbf{0})$ is equivalent to the conventional Debye–Waller factor and $T_k(\mathbf{0}, \mathbf{H}^\perp)$ describes random fluctuations along the perpendicular-space coordinate. These fluctuations cause characteristic jumps of vertices in physical space (*phason flips*). Even random phason flips map the vertices onto positions which can still be described by physical-space vectors of the type $\mathbf{r} = \sum_{i=1}^5 n_i \mathbf{a}_i$. Consequently, the set $M = \{\mathbf{r} = \sum_{i=1}^5 n_i \mathbf{a}_i | n_i \in \mathbb{Z}\}$ of all possible vectors forms a $\mathbb{Z}$ module. The shape of the atomic surfaces corresponds to a selection rule for the positions actually occupied. The geometric form factor $g_k(\mathbf{H}^\perp)$ is equivalent to the Fourier transform of the atomic surface, i.e. the 2D perpendicular-space component of the 5D hyperatoms.

For example, the canonical Penrose tiling $g_k(\mathbf{H}^\perp)$ corresponds to the Fourier transform of pentagonal atomic surfaces:

$$g_k(\mathbf{H}^\perp) = (1/A_{UC}^\perp) \int_{A_k} \exp(2\pi i \mathbf{H}^\perp \cdot \mathbf{r}) \, d\mathbf{r},$$

4. DIFFUSE SCATTERING AND RELATED TOPICS

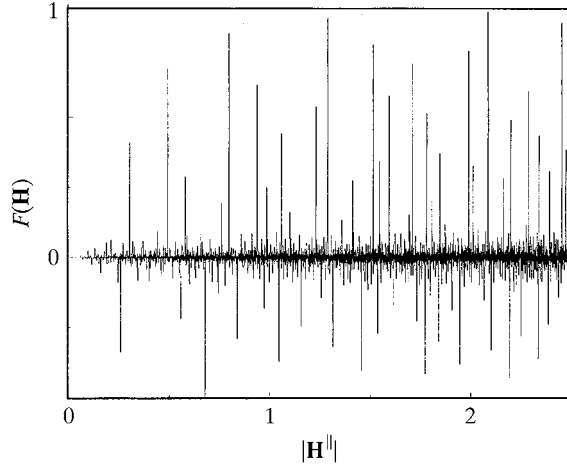


Fig. 4.6.3.21. Radial distribution function of the structure factors $F(\mathbf{H})$ of the Penrose tiling (edge length of the Penrose unit rhombs $a_r = 4.04 \text{ \AA}$) decorated with point atoms as a function of $\mathbf{H}^{\parallel}$. All structure factors within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $0 \leq |\mathbf{H}^{\parallel}| \leq 2.5 \text{ \AA}^{-1}$ have been used and normalized to $F(0000) = 1$.

4.6.3.3.2.5. Relationships between structure factors at symmetry-related points of the Fourier image

Scaling the Penrose tiling by a factor τ^{-n} by employing the matrix S^{-n} scales at the same time its reciprocal space by a factor τ^n :

$$S\mathbf{H} = \begin{pmatrix} 0 & 1 & 0 & \bar{1} & 0 \\ 0 & 1 & 1 & \bar{1} & 0 \\ \bar{1} & 1 & 1 & 0 & 0 \\ \bar{1} & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}_D \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \end{pmatrix} = \begin{pmatrix} h_2 - h_4 \\ h_2 + h_3 - h_4 \\ -h_1 + h_2 + h_3 \\ -h_1 + h_3 \\ h_5 \end{pmatrix}.$$

Since this operation increases the lengths of the diffraction vectors by the factor τ in parallel space and decreases them by the factor $1/\tau$ in perpendicular space, the following distribution of structure-

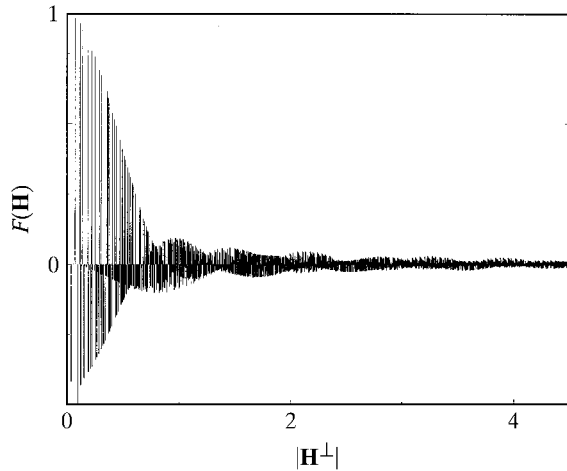


Fig. 4.6.3.22. Radial distribution function of the structure factors $F(\mathbf{H})$ of the Penrose tiling (edge length of the Penrose unit rhombs $a_r = 4.04 \text{ \AA}$) decorated with point atoms as a function of $\mathbf{H}^{\perp}$. All structure factors within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $0 \leq |\mathbf{H}^{\parallel}| \leq 2.5 \text{ \AA}^{-1}$ have been used and normalized to $F(0000) = 1$.

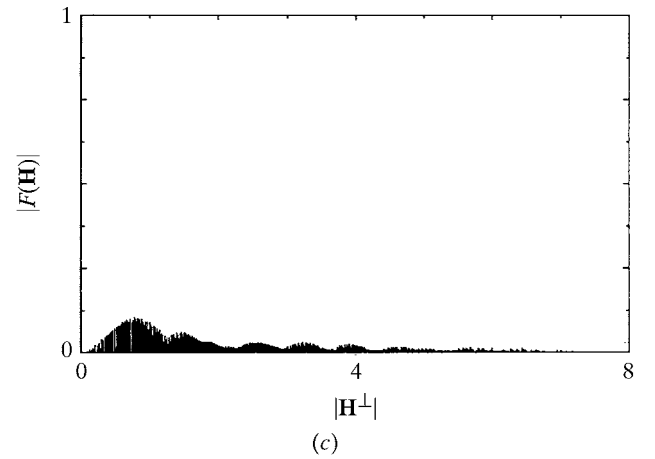
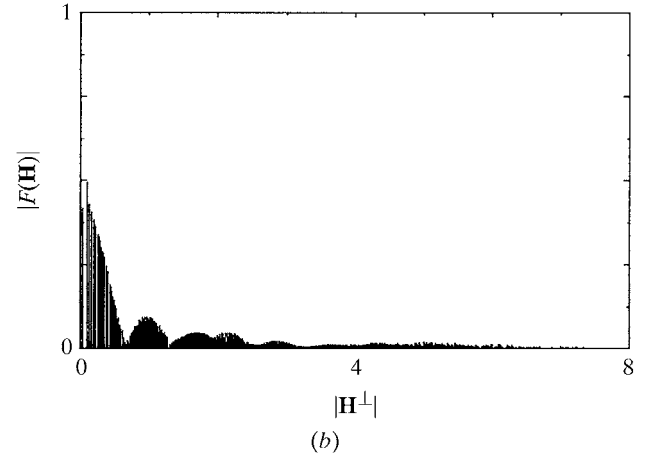
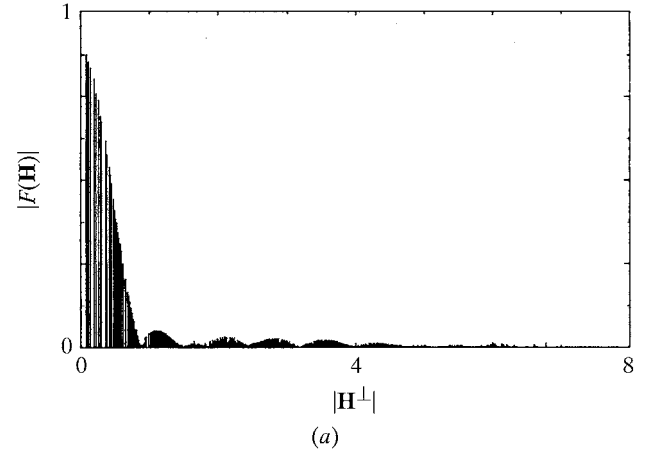


Fig. 4.6.3.23. Radial distribution function of the structure-factor magnitudes $|F(\mathbf{H})|$ of the Penrose tiling (edge length of the Penrose unit rhombs $a_r = 4.04 \text{ \AA}$) decorated with point atoms as a function of $\mathbf{H}^{\perp}$. All structure factors within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $0 \leq |\mathbf{H}^{\parallel}| \leq 2.5 \text{ \AA}^{-1}$ have been used and normalized to $F(0000) = 1$. The branches with (a) $|\sum_{i=1}^4 h_i| = 0 \bmod 5$, (b) $|\sum_{i=1}^4 h_i| = 1 \bmod 5$ and (c) $|\sum_{i=1}^4 h_i| = 2 \bmod 5$ are shown.

factor magnitudes (for point atoms at rest) is obtained:

$$|F(S^n \mathbf{H})| > |F(S^{n-1} \mathbf{H})| > \dots > |F(S^1 \mathbf{H})| > |F(\mathbf{H})|,$$

$$|F(\tau^n \mathbf{H}^{\parallel})| > |F(\tau^{n-1} \mathbf{H}^{\parallel})| > \dots > |F(\tau \mathbf{H}^{\parallel})| > |F(\mathbf{H})|.$$

The scaling operations S^n , $n \in \mathbb{Z}$, the roto-scaling operations $(\Gamma(\alpha)S^2)^n$ (Fig. 4.6.3.14) and the tenfold rotation $(\Gamma(\alpha))^n$, where

4.6. RECIPROCAL-SPACE IMAGES OF APERIODIC CRYSTALS

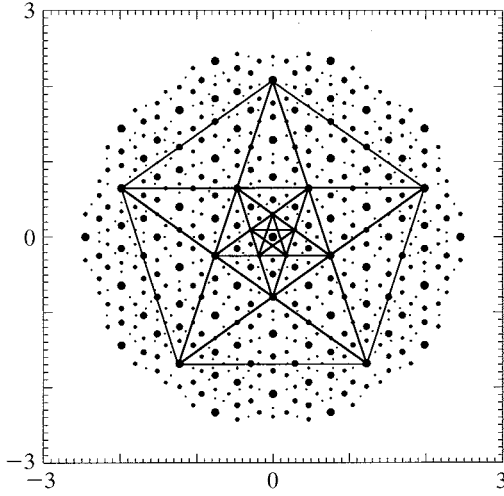


Fig. 4.6.3.24. Pentagrammatic relationships between scaling symmetry-related positive structure factors $F(\mathbf{H})$ of the Penrose tiling (edge length $a_r = 4.04 \text{ \AA}$) in parallel space. The magnitudes of the structure factors are indicated by the diameters of the filled circles.

$$(\Gamma(\alpha)S^2)^n = \begin{pmatrix} 1 & 1 & \bar{1} & \bar{1} & 0 \\ 1 & 2 & 0 & \bar{2} & 0 \\ 0 & 2 & 1 & \bar{1} & 0 \\ \bar{1} & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}_D^n,$$

connect all structure factors with diffraction vectors pointing to the nodes of an infinite series of pentagrams. The structure factors with positive signs are predominantly on the vertices of the pentagram while the ones with negative signs are arranged on circles around the vertices (Figs. 4.6.3.24 to 4.6.3.27).

4.6.3.3.3. Icosahedral phases

A structure that is quasiperiodic in three dimensions and exhibits icosahedral diffraction symmetry is called an icosahedral phase. Its holohedral Laue symmetry group is $K = m\bar{3}5$. All reciprocal-space vectors $\mathbf{H} = \sum_{i=1}^6 h_i \mathbf{a}_i^* \in M^*$ can be represented on a basis

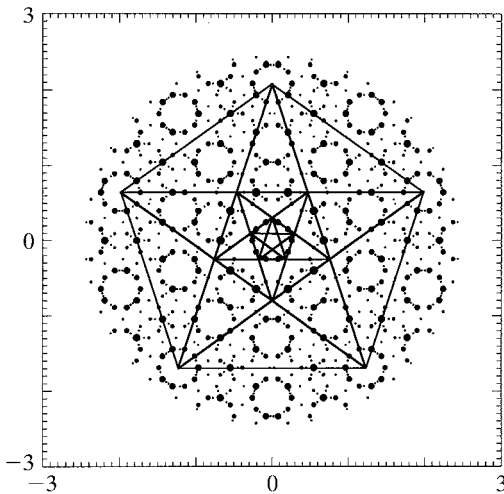


Fig. 4.6.3.25. Pentagrammatic relationships between scaling symmetry-related negative structure factors $F(\mathbf{H})$ of the Penrose tiling (edge length $a_r = 4.04 \text{ \AA}$) in parallel space. The magnitudes of the structure factors are indicated by the diameters of the filled circles.

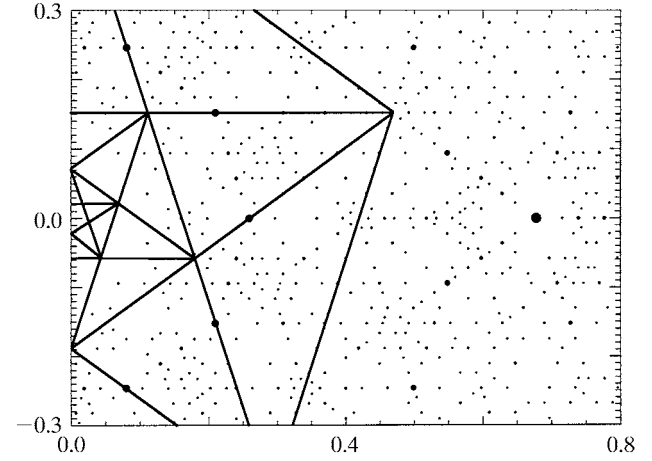
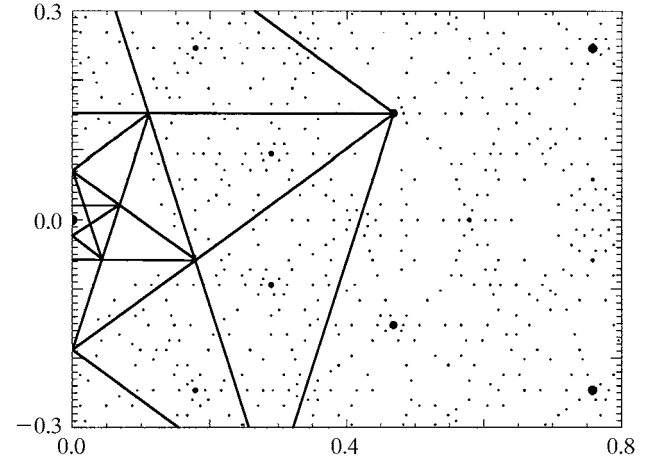


Fig. 4.6.3.26. Pentagrammatic relationships between scaling symmetry-related structure factors $F(\mathbf{H})$ of the Penrose tiling (edge length $a_r = 4.04 \text{ \AA}$) in parallel space. Enlarged sections of Figs. 4.6.3.24 (above) and 4.6.3.25 (below) are shown.

$\mathbf{a}_1^* = a^*(0, 0, 1)$, $\mathbf{a}_i^* = a^*[\sin \theta \cos(2\pi i/5), \sin \theta \sin(2\pi i/5), \cos \theta]$, $i = 2, \dots, 6$ where $\sin \theta = 2/(5)^{1/2}$, $\cos \theta = 1/(5)^{1/2}$ and $\theta \simeq 63.44^\circ$, the angle between two neighbouring fivefold axes (Fig. 4.6.3.28). This can be rewritten as

$$\begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \\ \mathbf{a}_5^* \\ \mathbf{a}_6^* \end{pmatrix} = a^* \begin{pmatrix} 0 & 0 & 1 \\ \sin \theta \cos(4\pi/5) & \sin \theta \sin(4\pi/5) & \cos \theta \\ \sin \theta \cos(6\pi/5) & \sin \theta \sin(6\pi/5) & \cos \theta \\ \sin \theta \cos(8\pi/5) & \sin \theta \sin(8\pi/5) & \cos \theta \\ \sin \theta & 0 & \cos \theta \\ \sin \theta \cos(2\pi/5) & \sin \theta \sin(2\pi/5) & \cos \theta \end{pmatrix} \begin{pmatrix} \mathbf{e}_1^V \\ \mathbf{e}_2^V \\ \mathbf{e}_3^V \end{pmatrix},$$

where $\mathbf{e}_i^V$ are Cartesian basis vectors. Thus, from the number of independent reciprocal-basis vectors needed to index the Bragg reflections with integer numbers, the dimension of the embedding space has to be six. The vector components refer to a Cartesian coordinate system (V basis) in the physical (parallel) space.

The set $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^6 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ of all diffraction vectors remains invariant under the action of the symmetry operators of the icosahedral point group $K = m\bar{3}5$. The symmetry-adapted matrix representations for the point-group generators, one fivefold rotation α , a threefold rotation β and the inversion operation γ , can be written in the form

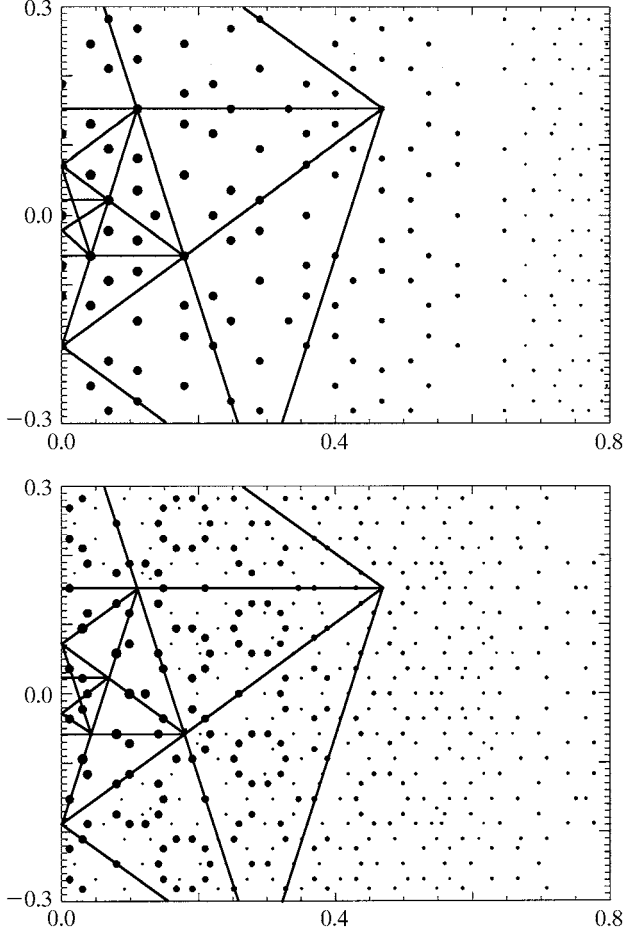


Fig. 4.6.3.27. Pentagrammatic relationships between scaling symmetry-related structure factors $F(\mathbf{H})$ of the Penrose tiling (edge length $a_r = 4.04 \text{ \AA}$) in perpendicular space. Enlarged sections of positive (above) and negative structure factors (below) are shown.

$$\Gamma(\alpha) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}_D, \Gamma(\beta) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}_D,$$

$$\Gamma(\gamma) = \begin{pmatrix} \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{1} \end{pmatrix}_D.$$

Block-diagonalization of these reducible symmetry matrices decomposes them into non-equivalent irreducible representations. These can be assigned to the two orthogonal subspaces forming the 6D embedding space $\mathbf{V} = \mathbf{V}^{\parallel} \oplus \mathbf{V}^{\perp}$, the 3D parallel (physical) subspace $\mathbf{V}^{\parallel}$ and the perpendicular 3D subspace $\mathbf{V}^{\perp}$. Thus, using $W\Gamma W^{-1} = \Gamma^{\text{red}} = \Gamma^{\parallel} \oplus \Gamma^{\perp}$, we obtain

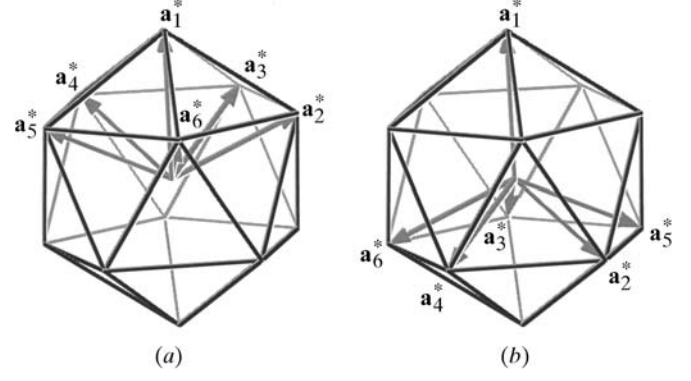


Fig. 4.6.3.28. Perspective (a) parallel- and (b) perpendicular-space views of the reciprocal basis of the 3D Penrose tiling. The six rationally independent vectors $\mathbf{a}_i^*$ point to the edges of an icosahedron.

$$\Gamma(\alpha) = \left(\begin{array}{cc|ccc} \cos(2\pi/5) & -\sin(2\pi/5) & 0 & 0 & 0 & 0 \\ \sin(2\pi/5) & \cos(2\pi/5) & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & \cos(4\pi/5) & -\sin(4\pi/5) & 0 \\ 0 & 0 & 0 & \sin(4\pi/5) & \cos(4\pi/5) & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right)_V$$

$$= \left(\begin{array}{c|c} \Gamma^{\parallel} & 0 \\ \hline 0 & \Gamma^{\perp} \end{array} \right)_V,$$

where

$$W = a^* \left(\begin{array}{ccccc} 0 & sc4 & sc6 & sc8 & s & sc2 \\ 0 & ss4 & ss6 & ss8 & 0 & ss2 \\ 1 & c & c & c & c & c \\ \hline 0 & -sc8 & -sc2 & -sc6 & -s & -sc4 \\ 0 & -ss8 & -ss2 & -ss6 & 0 & -ss4 \\ 1 & -c & -c & -c & -c & -c \end{array} \right)_V,$$

$c = \cos \theta$, $s = \sin \theta$, $scn = \sin \theta \cos(n\pi/5)$, $ssn = \sin \theta \sin(n\pi/5)$. The column vectors of the matrix W give the parallel- (above the partition line) and perpendicular-space components (below the partition line) of a reciprocal basis in $\mathbf{V}$. Thus, W can be rewritten using the physical-space reciprocal basis defined above and an arbitrary constant c ,

$$W = \begin{pmatrix} \mathbf{a}_1^* & \mathbf{a}_2^* & \mathbf{a}_3^* & \mathbf{a}_4^* & \mathbf{a}_5^* & \mathbf{a}_6^* \\ c\mathbf{a}_1^* & -c\mathbf{a}_4^* & -c\mathbf{a}_6^* & -c\mathbf{a}_3^* & -c\mathbf{a}_5^* & -c\mathbf{a}_2^* \end{pmatrix}$$

$$= (\mathbf{d}_1^* \ \mathbf{d}_2^* \ \mathbf{d}_3^* \ \mathbf{d}_4^* \ \mathbf{d}_5^* \ \mathbf{d}_6^*),$$

yielding the reciprocal basis $\mathbf{d}_i^*$, $i = 1, \dots, 6$, in the 6D embedding space (D space)

$$\mathbf{d}_1^* = a^* \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ c \end{pmatrix} \text{ and } \mathbf{d}_i^* = a^* \begin{pmatrix} \sin \theta \cos(2\pi i/5) \\ \sin \theta \sin(2\pi i/5) \\ \cos \theta \\ -c \sin \theta \cos(4\pi i/5) \\ -c \sin \theta \sin(4\pi i/5) \\ -c \cos \theta \end{pmatrix}, i = 2, \dots, 6.$$

The 6×6 symmetry matrices can each be decomposed into two 3×3 matrices. The first one, $\Gamma^{\parallel}$, acts on the parallel-space component, the second one, $\Gamma^{\perp}$, on the perpendicular-space component. In the case of $\Gamma(\alpha)$, the coupling factor between a rotation in parallel and perpendicular space is 2. Thus a $2\pi/5$

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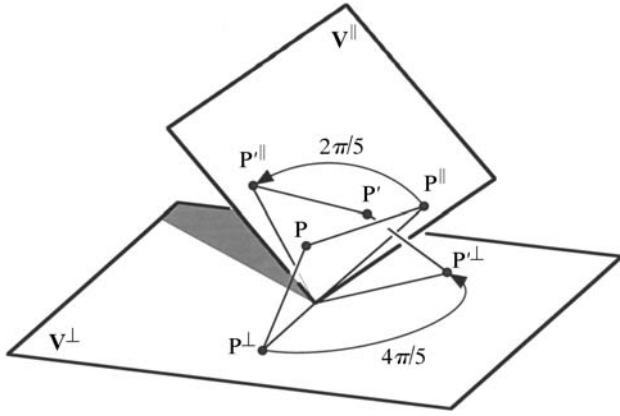


Fig. 4.6.3.29. Schematic representation of a rotation in 6D space. The point P is rotated to P' . The component rotations in parallel and perpendicular space are illustrated.

rotation in physical space is related to a $4\pi/5$ rotation in perpendicular space (Figs. 4.6.3.28 and 4.6.3.29).

With the condition $\mathbf{d}_i \cdot \mathbf{d}_j^* = \delta_{ij}$, the basis in direct 6D space is obtained:

$$\mathbf{d}_1 = \frac{1}{2a^*} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1/c \end{pmatrix} \text{ and } \mathbf{d}_i = \frac{1}{2a^*} \begin{pmatrix} \sin \theta \cos(2\pi i/5) \\ \sin \theta \sin(2\pi i/5) \\ \cos \theta \\ -(1/c) \sin \theta \cos(4\pi i/5) \\ -(1/c) \sin \theta \sin(4\pi i/5) \\ -(1/c) \cos \theta \end{pmatrix}, \quad i = 2, \dots, 6.$$

The metric tensors G , G^* are of the type

$$\begin{pmatrix} A & B & B & B & B & B \\ B & A & B & -B & -B & B \\ B & B & A & B & -B & -B \\ B & -B & B & A & B & -B \\ B & -B & -B & B & A & B \\ B & B & -B & -B & B & A \end{pmatrix},$$

with $A = (1 + c^2)a^{*2}$, $B = [(5)^{1/2}/5](1 - c^2)a^{*2}$ for the reciprocal space and $A = (1 + c^2)/[4(ca^*)^2]$, $B = [(5)^{1/2}(c^2 - 1)]/[20(ca^*)^2]$ for the direct space. For $c = 1$ we obtain hypercubic direct and reciprocal 6D lattices.

The lattice parameters in reciprocal and direct space are $d_i^* = a^*(2)^{1/2}$ and $d_i = 1/[(2)^{1/2}a^*]$ with $i = 1, \dots, 6$, respectively. The volume of the 6D unit cell can be calculated from the metric tensor G . For $c = 1$ it is simply $V = [\det(G)]^{1/2} = \{1/[(2)^{1/2}a^*]\}^6$.

The best known example of a 3D quasiperiodic structure is the canonical 3D *Penrose tiling* (see Janssen, 1986). It can be constructed from two unit tiles: a prolate and an oblate rhombohedron with equal edge lengths a_r (Fig. 4.6.3.30). Each face of the rhombohedra is a rhomb with acute angles $\alpha_r = \arccos[1/(5)^{1/2}] \simeq 63.44^\circ$. Their volumes are $V_p = (4/5)a_r^3 \sin(2\pi/5)$, $V_o = (4/5)a_r^3 \sin(\pi/5) = V_p/\tau$, and their frequencies $\nu_p:\nu_o = \tau:1$. The resulting point density (number of vertices per unit volume) is $\rho_p = (\tau + 1)/(\tau V_p + V_o) = (\tau/a_r^3) \sin(2\pi/5)$. Ten prolate and ten oblate rhombohedra can be packed to form a rhombic triacontahedron. The icosahedral symmetry of this zonohedron is broken by the many possible decompositions into the rhombohedra. Removing one zone of the

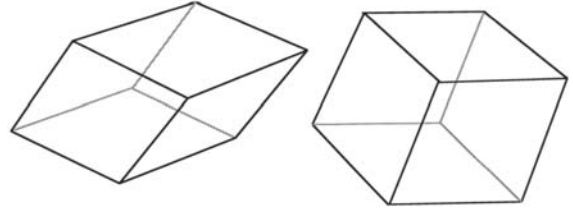


Fig. 4.6.3.30. The two unit tiles of the 3D Penrose tiling: a prolate [$\alpha_p = \arccos(5^{-1/2}) \simeq 63.44^\circ$] and an oblate ($\alpha_o = 180^\circ - \alpha_p$) rhombohedron with equal edge lengths a_r .

triacontahedron gives a rhomb-icosahedron consisting of five prolate and five oblate rhombohedra. Again, the singular fivefold axis of the rhomb-icosahedron is broken by the decomposition into rhombohedra. Removing one zone again gives a rhombic dodecahedron consisting of two prolate and two oblate rhombohedra. Removing the last remaining zone leads finally to a single prolate rhombohedron. Using these zonohedra as elementary clusters, a matching rule can be derived for the 3D construction of the 3D Penrose tiling (Levine & Steinhardt, 1986; Socolar & Steinhardt, 1986).

The 3D Penrose tiling can be embedded in the 6D space as shown above. The 6D hypercubic lattice is decorated on the lattice nodes with 3D triacontahedra obtained from the projection of a 6D unit cell upon the perpendicular space $V^\perp$ (Fig. 4.6.3.31). Thus the edge length of the rhombs covering the triacontahedron is equivalent to the length $\pi^\perp(\mathbf{d}_i) = 1/2a^*$ of the perpendicular-space component of the vectors spanning the 6D hypercubic lattice $\Sigma = \{\mathbf{r} = \sum_{i=1}^6 n_i \mathbf{d}_i | n_i \in \mathbb{Z}\}$.

4.6.3.3.3.1. Indexing

There are several indexing schemes in use. The generic one uses a set of six rationally independent reciprocal-basis vectors pointing to the corners of an icosahedron, $\mathbf{a}_1^* = a^*(0, 0, 1)$, $\mathbf{a}_i^* = a^*[\sin \theta \cos(2\pi i/5), \sin \theta \sin(2\pi i/5), \cos \theta]$, $i = 2, \dots, 6$, $\sin \theta = 2/(5)^{1/2}$, $\cos \theta = 1/(5)^{1/2}$, with $\theta \simeq 63.44^\circ$, the angle between two neighbouring fivefold axes (setting 1) (Fig. 4.6.3.28). In this case, the physical-space basis corresponds to a simple projection of the 6D reciprocal basis $\mathbf{d}_i^*$, $i = 1, \dots, 6$. Sometimes, the same set of six reciprocal-basis vectors is referred to a differently oriented Cartesian reference system (C basis, with

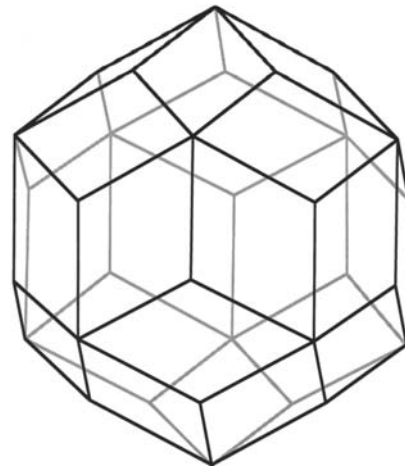


Fig. 4.6.3.31. Atomic surface of the 3D Penrose tiling in the 6D hypercubic description. The projection of the 6D hypercubic unit cell upon $V^\perp$ gives a rhombic triacontahedron.

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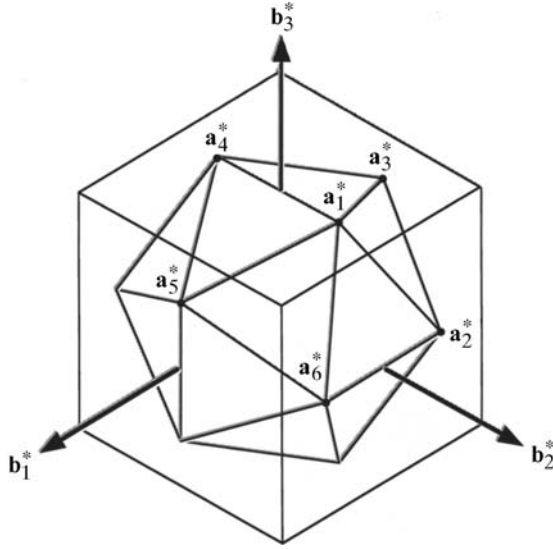


Fig. 4.6.3.32. Perspective parallel-space view of the two alternative reciprocal bases of the 3D Penrose tiling: the cubic and the icosahedral setting, represented by the bases $\mathbf{b}_i^*$, $i = 1, \dots, 3$, and $\mathbf{a}_i^*$, $i = 1, \dots, 6$, respectively.

basis vectors $\mathbf{e}_i$ along the twofold axes) (Bancel *et al.*, 1985). The reciprocal basis is

$$\begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \\ \mathbf{a}_5^* \\ \mathbf{a}_6^* \end{pmatrix} = \frac{a^*}{(1 + \tau^2)^{1/2}} \begin{pmatrix} 0 & 1 & \tau \\ -1 & \tau & 0 \\ -\tau & 0 & 1 \\ 0 & -1 & \tau \\ \tau & 0 & 1 \\ 1 & \tau & 0 \end{pmatrix} \begin{pmatrix} \mathbf{e}_1^C \\ \mathbf{e}_2^C \\ \mathbf{e}_3^C \end{pmatrix}.$$

An alternate way of indexing is based on a 3D set of cubic reciprocal-basis vectors $\mathbf{b}_i^*$, $i = 1, \dots, 3$ (setting 2) (Fig. 4.6.3.32):

$$\begin{pmatrix} \mathbf{b}_1^* \\ \mathbf{b}_2^* \\ \mathbf{b}_3^* \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 & \bar{1} & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \end{pmatrix}_D \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \\ \mathbf{a}_5^* \\ \mathbf{a}_6^* \end{pmatrix} \\ = \frac{a^*}{(1 + \tau^2)^{1/2}} \begin{pmatrix} \mathbf{e}_1^C \\ \mathbf{e}_2^C \\ \mathbf{e}_3^C \end{pmatrix}.$$

The Cartesian C basis is related to the V basis by a $\theta/2$ rotation around $[100]_C$, yielding $[001]_V$, followed by a $\pi/10$ rotation around $[001]_C$:

$$\begin{pmatrix} \mathbf{e}_1^C \\ \mathbf{e}_2^C \\ \mathbf{e}_3^C \end{pmatrix} = \begin{pmatrix} \cos(\pi/10) & \sin(\pi/10) & 0 \\ -\cos(\theta/2)\sin(\pi/10) & \cos(\theta/2)\cos(\pi/10) & \sin(\theta/2) \\ \sin(\theta/2)\sin(\pi/10) & -\sin(\theta/2)\cos(\pi/10) & \cos(\theta/2) \end{pmatrix}_V \begin{pmatrix} \mathbf{e}_1^V \\ \mathbf{e}_2^V \\ \mathbf{e}_3^V \end{pmatrix}.$$

Thus, indexing the diffraction pattern of an icosahedral phase with integer indices, one obtains for setting 1 $\mathbf{H} = \sum_{i=1}^6 h_i \mathbf{a}_i^*$, $h_i \in \mathbb{Z}$. These indices $(h_1 h_2 h_3 h_4 h_5 h_6)$ transform into the second setting to $(h/h' k/k' l/l')$ with the fractional cubic indices $h_1^c = h + h'\tau$, $h_2^c = k + k'\tau$, $h_3^c = l + l'\tau$. The transformation matrix is

$$\begin{pmatrix} h \\ h' \\ k \\ k' \\ l \\ l' \end{pmatrix}_C = \begin{pmatrix} 0 & \bar{1} & 0 & 0 & 0 & 1 \\ 0 & 0 & \bar{1} & 0 & 1 & 0 \\ 1 & 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}_D \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \\ h_6 \end{pmatrix}_D = \begin{pmatrix} h_6 - h_2 \\ h_5 - h_3 \\ h_1 - h_4 \\ h_6 + h_2 \\ h_5 + h_3 \\ h_1 + h_4 \end{pmatrix}_D.$$

4.6.3.3.3.2. Diffraction symmetry

The diffraction symmetry of icosahedral phases can be described by the Laue group $K = m\bar{3}5$. The set of all vectors $\mathbf{H}$ forms a Fourier module $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^6 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ of rank 6 in physical space. Consequently, it can be considered as a projection from a 6D reciprocal lattice, $M^* = \pi^\parallel(\Sigma^*)$. The parallel and perpendicular reciprocal-space sections of the 3D Penrose tiling decorated with equal point scatterers on its vertices are shown in Figs. 4.6.3.33 and 4.6.3.34. The diffraction pattern in perpendicular space is the Fourier transform of the triacontahedron. All Bragg reflections within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ are depicted. Without intensity-truncation limit, the diffraction pattern would be densely filled with discrete Bragg reflections.

The 6D icosahedral space groups that are relevant to the description of icosahedral phases (six symmorphic and five non-symmorphic groups) are listed in Table 4.6.3.2. These space groups are a subset of all 6D icosahedral space groups fulfilling the condition that the 6D point groups they are associated with are isomorphic to the 3D point groups $\frac{2}{m}\bar{3}5$ and 235 describing the diffraction symmetry. From 826 6D (analogues to) Bravais groups (Levitov & Rhyner, 1988), only three fulfil the condition that the projection of the 6D hypercubic lattice upon the 3D physical space is compatible with the icosahedral point groups $\frac{2}{m}\bar{3}5$, 235: the primitive hypercubic Bravais lattice P , the body-centred Bravais lattice I with translation $1/2(111111)$, and the face-centred Bravais lattice F with translations $1/2(110000) + 14$ further cyclic permutations. Hence, the I lattice is twofold primitive (*i.e.* it contains two vertices per unit cell) and the F lattice is 16-fold primitive. The orientation of the symmetry elements in the 6D space is defined by the isomorphism of the 3D and 6D point groups. The action of the fivefold rotation, however, is different in the subspaces $\mathbf{V}^\parallel$ and $\mathbf{V}^\perp$: a rotation of $2\pi/5$ in $\mathbf{V}^\parallel$ is correlated with a rotation of $4\pi/5$ in $\mathbf{V}^\perp$. The reflection and inversion operations are equivalent in both subspaces.

4.6.3.3.3.3. Structure factor

The structure factor of the icosahedral phase corresponds to the Fourier transform of the 6D unit cell,

$$F(\mathbf{H}) = \sum_{k=1}^N f_k(\mathbf{H}^\parallel) T_k(\mathbf{H}^\parallel, \mathbf{H}^\perp) g_k(\mathbf{H}^\perp) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_k),$$

with 6D diffraction vectors $\mathbf{H} = \sum_{i=1}^6 h_i \mathbf{a}_i^*$, parallel-space atomic scattering factor $f_k(H^\parallel)$, temperature factor $T_k(\mathbf{H}^\parallel, \mathbf{H}^\perp)$, and perpendicular-space geometric form factor $g_k(\mathbf{H}^\perp)$. $T_k(\mathbf{H}^\parallel, \mathbf{0})$ is equivalent to the conventional Debye–Waller factor and $T_k(\mathbf{0}, \mathbf{H}^\perp)$ describes random fluctuations in perpendicular space. These fluctuations cause characteristic jumps of vertices (*phason flips*) in the physical space. Even random phason flips map the vertices onto positions that can still be described by physical-space vectors of the type $\mathbf{r} = \sum_{i=1}^6 n_i \mathbf{a}_i$. Consequently, the set $M = \{\mathbf{r} = \sum_{i=1}^6 n_i \mathbf{a}_i | n_i \in \mathbb{Z}\}$ of all possible vectors forms a $\mathbb{Z}$ module. The shape of the atomic surfaces corresponds to a selection rule for the positions actually occupied. The geometric form factor $g_k(\mathbf{H}^\perp)$ is equivalent to the Fourier transform of the *atomic surface*, *i.e.* the 3D perpendicular-space component of the 6D *hyperatoms*.

For the example of the canonical 3D Penrose tiling, $g_k(\mathbf{H}^\perp)$ corresponds to the Fourier transform of a triacontahedron:

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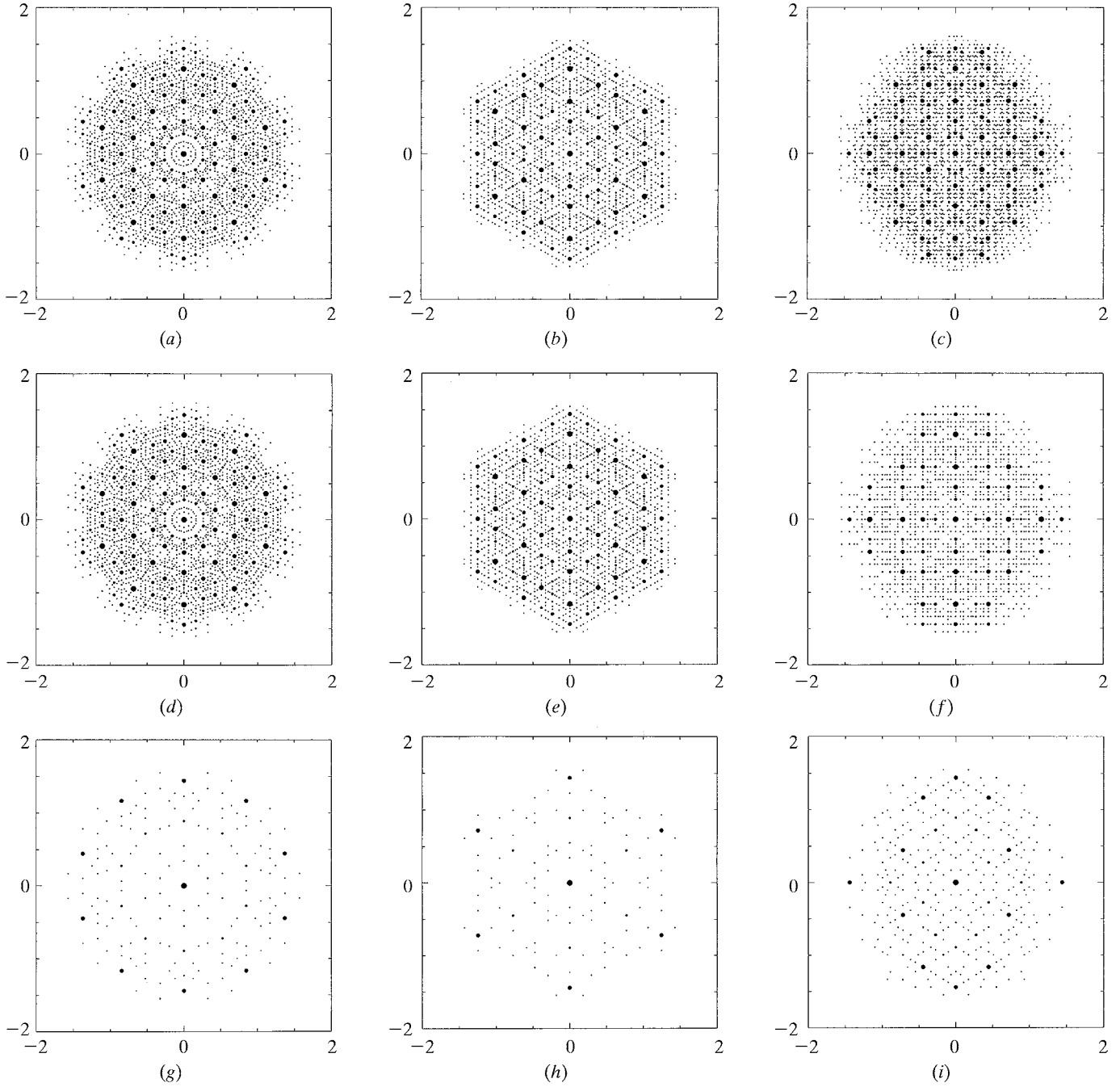


Fig. 4.6.3.33. Physical-space diffraction patterns of the 3D Penrose tiling decorated with point atoms (edge lengths of the Penrose unit rhombohedra $a_r = 5.0$ Å). Sections with five-, three- and twofold symmetry are shown for the primitive 6D analogue of Bravais type *P* in (a, b, c), the body-centred 6D analogue to Bravais type *I* in (d, e, f) and the face-centred 6D analogue to Bravais type *F* in (g, h, i). All reflections are shown within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $-6 \leq h_i \leq 6, i = 1, \dots, 6$.

$$g_k(\mathbf{H}^\perp) = (1/A_{\text{UC}}^\perp) \int_{A_k} \exp(2\pi i \mathbf{H}^\perp \cdot \mathbf{r}) d\mathbf{r},$$

where $A_{\text{UC}}^\perp$ is the volume of the 6D unit cell projected upon $\mathbf{V}^\perp$ and A_k is the volume of the triacontahedron. $A_{\text{UC}}^\perp$ and A_k are equal in the present case and amount to the volumes of ten prolate and ten oblate rhombohedra: $A_{\text{UC}}^\perp = 8a_r^3 [\sin(2\pi/5) + \sin(\pi/5)]$. Evaluating the integral by decomposing the triacontahedron into trigonal pyramids, each one directed from the centre of the triacontahedron to three of its corners given by the vectors $\mathbf{e}_i, i = 1, \dots, 3$, one obtains

$$g(\mathbf{H}^\perp) = (1/A_{\text{UC}}^\perp) \sum_R g_k(R^T \mathbf{H}^\perp),$$

with $k = 1, \dots, 60$ running over all site-symmetry operations R of the icosahedral group,

$$g_k(\mathbf{H}^\perp) = -iV_r [A_2 A_3 A_4 \exp(iA_1) + A_1 A_3 A_5 \exp(iA_2) + A_1 A_2 A_6 \exp(iA_3) + A_4 A_5 A_6] \times (A_1 A_2 A_3 A_4 A_5 A_6)^{-1},$$

$A_j = 2\pi \mathbf{H}^\perp \cdot \mathbf{e}_j, j = 1, \dots, 3, A_4 = A_2 - A_3, A_5 = A_3 - A_1, A_6 = A_1 - A_2$ and $V_r = \mathbf{e}_1 \cdot (\mathbf{e}_2 \times \mathbf{e}_3)$ the volume of the parallelepiped defined by the vectors $\mathbf{e}_i, i = 1, \dots, 3$ (Yamamoto, 1992b).

4.6.3.3.3.4. Intensity statistics

The radial structure-factor distributions of the 3D Penrose tiling decorated with point scatterers are plotted in Fig. 4.6.3.35 as a function of parallel and perpendicular space. The distribution of $|F(\mathbf{H})|$ as a function of their frequencies clearly resembles a centric

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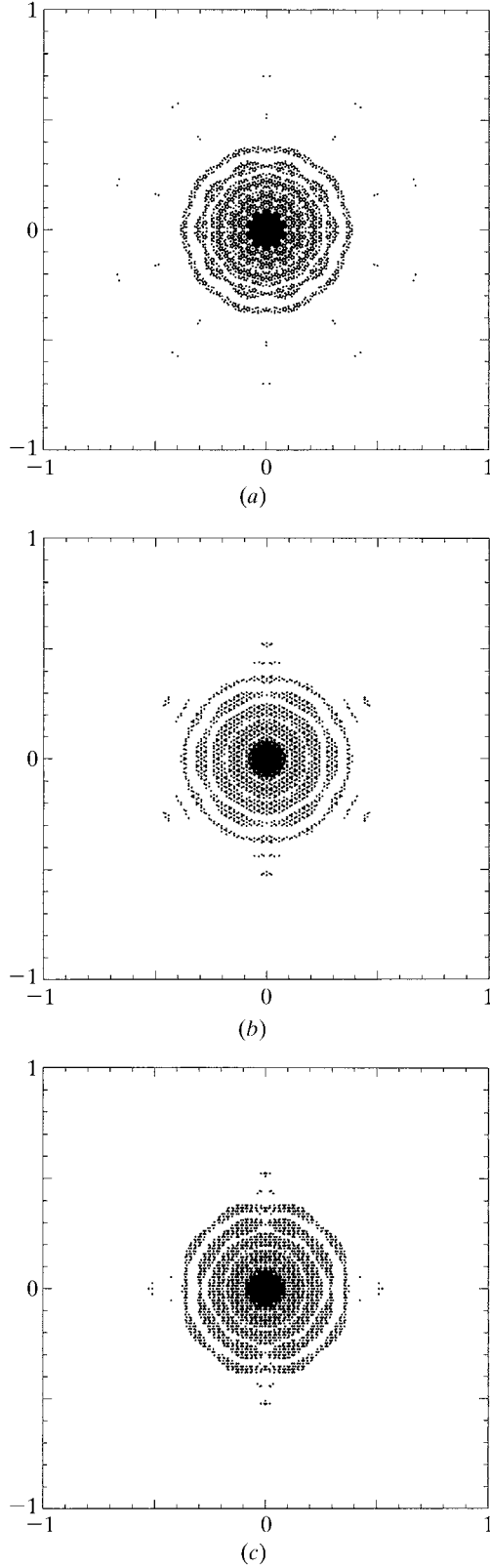


Fig. 4.6.3.34. Perpendicular-space diffraction patterns of the 3D Penrose tiling decorated with point atoms (edge lengths of the Penrose unit rhombohedra $a_r = 5.0$ Å). Sections with (a) five-, (b) three- and (c) twofold symmetry are shown for the primitive 6D analogue of Bravais type P . All reflections are shown within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $-6 \leq h_i \leq 6, i = 1, \dots, 6$.

distribution, as can be expected from the centrosymmetric unit cell. The shape of the distribution function depends on the radius of the limiting sphere in reciprocal space. The number of weak reflections

Table 4.6.3.2. 3D point groups of order k describing the diffraction symmetry and corresponding 6D decagonal space groups with reflection conditions (see Levitov & Rhyner, 1988; Rokhsar et al., 1988)

3D point group	k	5D space group	Reflection condition
$\frac{2}{m}\bar{3}5$	120	$P\frac{2}{m}\bar{3}5$	No condition
		$P\frac{2}{n}\bar{3}5$	$h_1h_2h_3h_4h_5h_6 : h_5 - h_6 = 2n$
		$I\frac{2}{m}\bar{3}5$	$h_1h_2h_3h_4h_5h_6 : \sum_{i=1}^6 h_i = 2n$
		$F\frac{2}{m}\bar{3}5$	$h_1h_2h_3h_4h_5h_6 : \sum_{i \neq j=1}^6 h_i + h_j = 2n$
		$F\frac{2}{n}\bar{3}5$	$h_1h_2h_3h_4h_5h_6 : \sum_{i \neq j=1}^6 h_i + h_j = 2n$ $h_1h_2h_3h_4h_5h_6 : h_5 - h_6 = 4n$
235	60	$P235$	No condition
		$P235_1$	$h_1h_2h_3h_4h_5h_6 : h_1 = 5n$
		$I235$	$h_1h_2h_3h_4h_5h_6 : \sum_{i=1}^6 h_i = 2n$
		$I235_1$	$h_1h_2h_3h_4h_5h_6 : \sum_{i=1}^6 h_i = 2n$ $h_1h_2h_3h_4h_5h_6 : h_1 + 5h_2 = 10n$
		$F235$	$h_1h_2h_3h_4h_5h_6 : \sum_{i \neq j=1}^6 h_i + h_j = 2n$
		$F235_1$	$h_1h_2h_3h_4h_5h_6 : \sum_{i \neq j=1}^6 h_i + h_j = 2n$ $h_1h_2h_3h_4h_5h_6 : h_1 + 5h_2 = 10n$

increases as the power 6, that of strong reflections only as the power 3 (strong reflections always have small $\mathbf{H}^\perp$ components).

The weighted reciprocal space of the 3D Penrose tiling contains an infinite number of Bragg reflections within a limited region of the physical space. Contrary to the diffraction pattern of a periodic structure consisting of point atoms on the lattice nodes, the Bragg reflections show intensities depending on the perpendicular-space components of their diffraction vectors.

4.6.3.3.5. Relationships between structure factors at symmetry-related points of the Fourier image

The weighted 3D reciprocal space $M^* = \{\mathbf{H}^\parallel = \sum_{i=1}^6 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ exhibits the icosahedral point symmetry $K = m\bar{3}5$. It is invariant under the action of the scaling matrix S^3 :

$$S = \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & 1 & -1 \\ 1 & -1 & -1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 \end{pmatrix}_D, S^3 = \begin{pmatrix} 2 & 1 & 1 & 1 & 1 & 1 \\ 1 & 2 & 1 & -1 & -1 & 1 \\ 1 & 1 & 2 & 1 & -1 & -1 \\ 1 & -1 & 1 & 2 & 1 & -1 \\ 1 & -1 & -1 & 1 & 2 & 1 \\ 1 & 1 & -1 & -1 & 1 & 2 \end{pmatrix}_D,$$

$$\begin{pmatrix} 2 & 1 & 1 & 1 & 1 & 1 \\ 1 & 2 & 1 & -1 & -1 & 1 \\ 1 & 1 & 2 & 1 & -1 & -1 \\ 1 & -1 & 1 & 2 & 1 & -1 \\ 1 & -1 & -1 & 1 & 2 & 1 \\ 1 & 1 & -1 & -1 & 1 & 2 \end{pmatrix}_D \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \\ \mathbf{a}_5^* \\ \mathbf{a}_6^* \end{pmatrix} = \tau^3 \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \\ \mathbf{a}_5^* \\ \mathbf{a}_6^* \end{pmatrix}.$$

The scaling transformation $(S^{-3})^T$ leaves a primitive 6D reciprocal lattice invariant as can easily be seen from its application on the indices:

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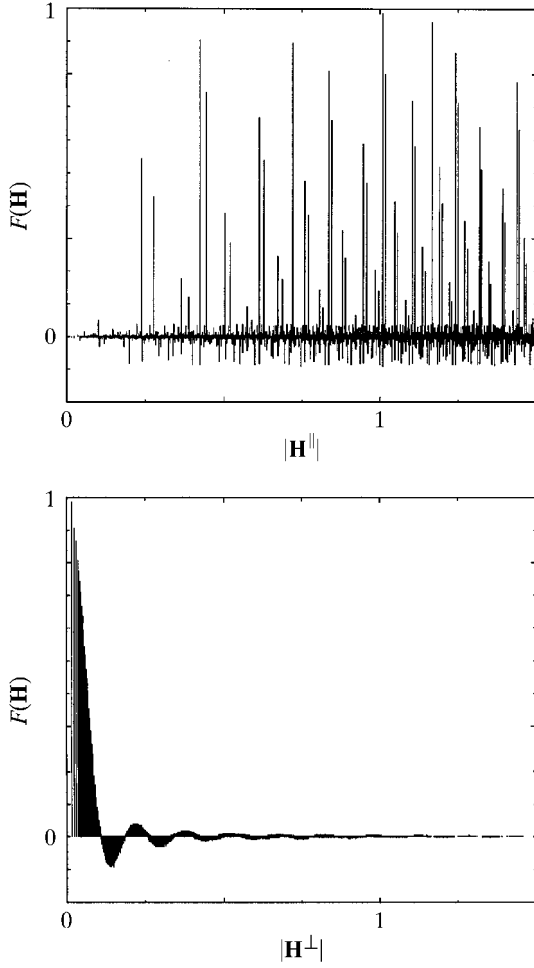


Fig. 4.6.3.35. Radial distribution function of the structure factors $F(\mathbf{H})$ of the 3D Penrose tiling (edge lengths of the Penrose unit rhombohedra $a_r = 5.0$ Å) decorated with point atoms as a function of $|\mathbf{H}^{\parallel}|$ (above) and $|\mathbf{H}^{\perp}|$ (below). All reflections are shown within $10^{-6}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $-6 \leq h_i \leq 6, i = 1, \dots, 6$.

$$\begin{pmatrix} h'_1 \\ h'_2 \\ h'_3 \\ h'_4 \\ h'_5 \\ h'_6 \end{pmatrix} = \begin{pmatrix} -2 & 1 & 1 & 1 & 1 & 1 \\ 1 & -2 & 1 & -1 & -1 & 1 \\ 1 & 1 & -2 & 1 & -1 & -1 \\ 1 & -1 & 1 & -2 & 1 & -1 \\ 1 & -1 & -1 & 1 & -2 & 1 \\ 1 & 1 & -1 & -1 & 1 & -2 \end{pmatrix}_D \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \\ h_6 \end{pmatrix}.$$

The matrix $(S^{-1})^T$ leaves $M^* = \{\mathbf{H}^{\parallel} = \sum_{i=1}^6 h_i \mathbf{a}_i^* | h_i \in \mathbb{Z}\}$ invariant,

$$\begin{pmatrix} h'_1 \\ h'_2 \\ h'_3 \\ h'_4 \\ h'_5 \\ h'_6 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -1 & 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 & -1 & 1 \\ 1 & 1 & -1 & -1 & 1 & -1 \end{pmatrix}_D \begin{pmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \\ h_6 \end{pmatrix},$$

for any $\mathbf{H} = \sum_{i=1}^6 h_i \mathbf{d}_i^*$ with h_i all even or all odd, corresponding to a 6D face-centred hypercubic lattice. In a second case the sum $\sum_{i=1}^6 h_i$ is even, corresponding to a 6D body-centred hypercubic lattice. Block-diagonalization of the matrix S decomposes it into two irreducible representations. With $WSW^{-1} = S_V = S_V^{\parallel} \oplus S_V^{\perp}$ we obtain

$$S_V = \left(\begin{array}{ccc|ccc} \tau & 0 & 0 & 0 & 0 & 0 \\ 0 & \tau & 0 & 0 & 0 & 0 \\ 0 & 0 & \tau & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & -1/\tau & 0 & 0 \\ 0 & 0 & 0 & 0 & -1/\tau & 0 \\ 0 & 0 & 0 & 0 & 0 & -1/\tau \end{array} \right)_V = \left(\begin{array}{c|c} S^{\parallel} & 0 \\ \hline 0 & S^{\perp} \end{array} \right)_V,$$

the scaling properties in the two 3D subspaces: scaling by a factor τ in parallel space corresponds to a scaling by a factor $(-\tau)^{-1}$ in perpendicular space. For the intensities of the scaled reflections analogous relationships are valid, as discussed for decagonal phases (Figs. 4.6.3.36 and 4.6.3.37, Section 4.6.3.3.2.5).

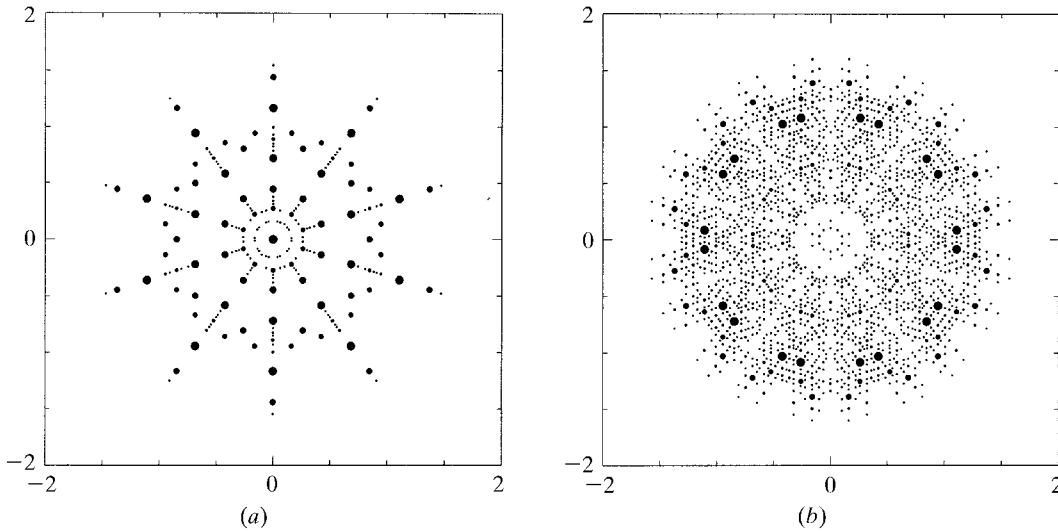


Fig. 4.6.3.36. Parallel-space distribution of (a) positive and (b) negative structure factors of the 3D Penrose tiling of the 6D P lattice type decorated with point atoms (edge lengths of the Penrose unit rhombohedra $a_r = 5.0$ Å). The magnitudes of the structure factors are indicated by the diameters of the filled circles. All reflections are shown within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $-6 \leq h_i \leq 6, i = 1, \dots, 6$.

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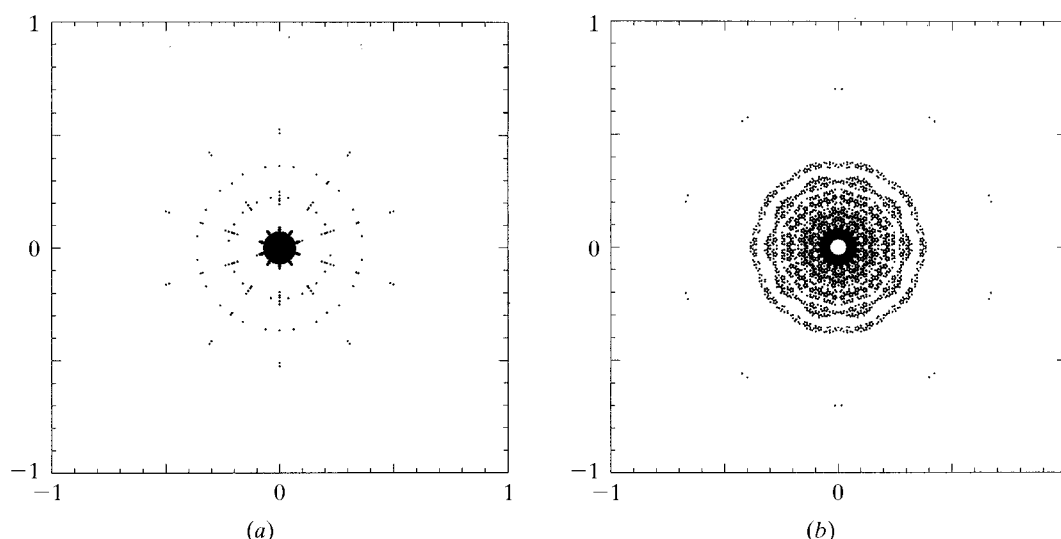


Fig. 4.6.3.37. Perpendicular-space distribution of (a) positive and (b) negative structure factors of the 3D Penrose tiling of the 6D P lattice type decorated with point atoms (edge lengths of the Penrose unit rhombohedra $a_r = 5.0 \text{ \AA}$). The magnitudes of the structure factors are indicated by the diameters of the filled circles. All reflections are shown within $10^{-4}|F(\mathbf{0})|^2 < |F(\mathbf{H})|^2 < |F(\mathbf{0})|^2$ and $-6 \leq h_i \leq 6, i = 1, \dots, 6$.

4.6.4. Experimental aspects of the reciprocal-space analysis of aperiodic crystals

4.6.4.1. Data-collection strategies

Theoretically, aperiodic crystals show an infinite number of reflections within a given diffraction angle, contrary to periodic crystals. The number of reflections to be included in a structure analysis of a *periodic* crystal may be very high (one million for virus crystals, for instance) but there is no ambiguity in the selection of reflections to be collected: all Bragg reflections within a limiting sphere in reciprocal space, usually given by $0 \leq \sin \theta / \lambda \leq 0.7 \text{ \AA}^{-1}$, are used. All reflections, observed and unobserved, are included to fit a reliable structure model.

However, for *aperiodic* crystals it is not possible to collect the infinite number of dense Bragg reflections within $0 \leq \sin \theta / \lambda \leq 0.7 \text{ \AA}^{-1}$. The number of observable reflections

within this limiting sphere depends only on the spatial and intensity resolution.

What happens if not all reflections are included in a structure analysis? How important is the contribution of reflections with large perpendicular-space components of the diffraction vector which are weak but densely distributed? These problems are illustrated using the example of the Fibonacci sequence. An infinite model structure consisting of Al atoms with isotropic thermal parameter $B = 1 \text{ \AA}^2$, and distances $S = 2.5 \text{ \AA}$ and $L = \tau S$, was used for the calculations (Table 4.6.4.1).

It turns out that 92.6% of the total diffracted intensity of 161 322 reflections is included in the 44 strongest reflections and 99.2% in the strongest 425 reflections. It is remarkable, however, that in all the experimental data for icosahedral and decagonal quasicrystals collected so far, rarely more than 20 to 50 reflections along reciprocal-lattice lines corresponding to net planes with Fibonacci-

Table 4.6.4.1. *Intensity statistics of the Fibonacci chain for a total of 161 322 reflections with $-1000 \leq h_i \leq 1000$ and $0 \leq \sin \theta / \lambda \leq 2 \text{ \AA}^{-1}$*

In the upper line, the number of reflections in the respective interval is given; in the lower line the partial sums $\sum I(\mathbf{H})$ of the intensities $I(\mathbf{H})$ are given as a percentage of the total diffracted intensity. The $F(00)$ reflection is not included in the sums.

	$F(\mathbf{H})/F(\mathbf{H})_{\max} \geq 0.1$	$0.1 > F(\mathbf{H})/F(\mathbf{H})_{\max} \geq 0.01$	$0.01 > F(\mathbf{H})/F(\mathbf{H})_{\max} \geq 0.001$	$F(\mathbf{H})/F(\mathbf{H})_{\max} < 0.001$
$0 \leq \sin \theta / \lambda \leq 0.2 \text{ \AA}^{-1}$ $\sum I(\mathbf{H})$	17 52.53%	148 2.56%	1505 0.27%	14 511 0.03%
$0.2 \leq \sin \theta / \lambda \leq 0.4 \text{ \AA}^{-1}$ $\sum I(\mathbf{H})$	11 27.03%	107 2.03%	1066 0.19%	14 998 0.02%
$0.4 \leq \sin \theta / \lambda \leq 0.6 \text{ \AA}^{-1}$ $\sum I(\mathbf{H})$	9 9.84%	64 0.96%	654 0.12%	15 456 0.01%
$0.6 \leq \sin \theta / \lambda \leq 0.8 \text{ \AA}^{-1}$ $\sum I(\mathbf{H})$	6 2.94%	27 0.34%	326 0.07%	15 823 0.01%
$0.8 \leq \sin \theta / \lambda \leq 2 \text{ \AA}^{-1}$ $\sum I(\mathbf{H})$	1 0.23%	35 0.79%	338 0.06%	96 720 0.01%
Total sum	44 92.57%	381 6.67%	3389 0.70%	157 508 0.06%

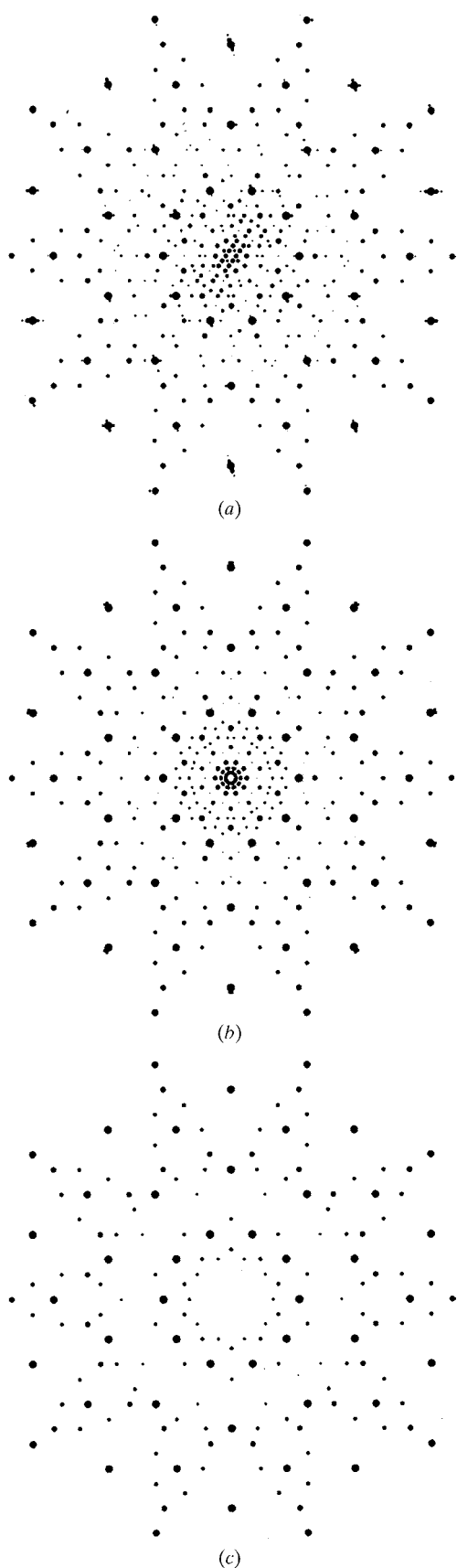


Fig. 4.6.4.1. Simulated diffraction patterns of (a) the ≈ 52 Å single-crystal approximant of decagonal Al-Co-Ni, (b) the fivefold twinned approximant, and (c) the decagonal phase itself (Estermann *et al.*, 1994).

sequence-like distances could be observed. The consequences for structure determinations with such truncated data sets are primarily a lower resolution in perpendicular space than in physical space. This corresponds to a smearing of the hyperatoms in the perpendicular space. For the derivation of the local structure-building elements (clusters) of aperiodic crystals this is only a minor problem: the smeared hyperatoms give rise to split atoms and a biased electron-density distribution. The information on the global aperiodic structure, however, which is contained in the detailed shape of the atomic surfaces, is severely reduced when using a low-resolution diffraction data set. A combination of high-resolution electron microscopy, lattice imaging and diffraction techniques allows a good characterization of the local and global order even in these cases. For a more detailed analysis of these problems see Steurer (1995).

4.6.4.2. Commensurability versus incommensurability

The question whether an aperiodic crystal is really aperiodic or rather a high-order approximant is of different importance depending on the point of view. As far as real finite crystals are considered, definitions of *periodic* and *aperiodic real crystals* and of *periodic* and *aperiodic perfect crystals* have to be given first. *Real crystals*, despite periodicity or aperiodicity, are the actual samples under investigation. Partial information about their actual structure can be obtained today by imaging methods (scanning tunnelling microscopy, atomic force microscopy, high-resolution transmission electron microscopy, . . .). Basically, the real crystal structure can be determined using full diffraction information from Bragg and diffuse scattering. In practice, however, only 'Bragg reflections' are included in a structure analysis. 'Bragg reflections' result from the integration of diffraction intensities from extended volumes around a limited number of Bragg-reflection positions ($\mathbb{Z}$ module). This process of intensity condensation at Bragg points corresponds in direct space to an averaging process. The real crystal structure is projected upon one unit cell in direct space defined by the $\mathbb{Z}$ module in reciprocal space. Generally, the identification of appropriate reciprocal-space metrics is not a problem in the case of crystals. It can be problematic, however, in the case of aperiodic crystals, in particular quasicrystals (see Lancon *et al.*, 1994). The metrics, and to some extent the global order in the case of quasicrystals, are fixed by assigning the reciprocal basis. The spatial resolution of a diffraction experiment defines the accuracy of the resulting metrics. The decision whether the rational number obtained for the relative length of a satellite vector indicates a commensurate or an incommensurate modulation can only be made considering temperature- and pressure-dependent chemical and physical properties of the material. The same is valid for other types of aperiodic crystals.

4.6.4.3. Twinning and nanodomain structures

High-order approximants of quasicrystals often occur in orientationally twinned form or, on a smaller scale, as oriented nanodomain structures. These structures can be identified by electron microscopy, and, in certain cases, also by high-resolution X-ray diffractometry (Kalning *et al.*, 1994). If the intensity and spatial resolution is sufficient, characteristic reflection splitting and diffuse diffraction phenomena can be observed. It has been demonstrated that for the determination of the local structure (structure-building elements) it does not matter greatly whether one uses a data set for a real quasicrystal or one for a twinned approximant (Estermann *et al.*, 1994). Examples of reciprocal-space images of an approximant, a twinned approximant and the related decagonal phase are shown schematically in Fig. 4.6.4.1 and for real samples in Fig. 4.6.4.2.

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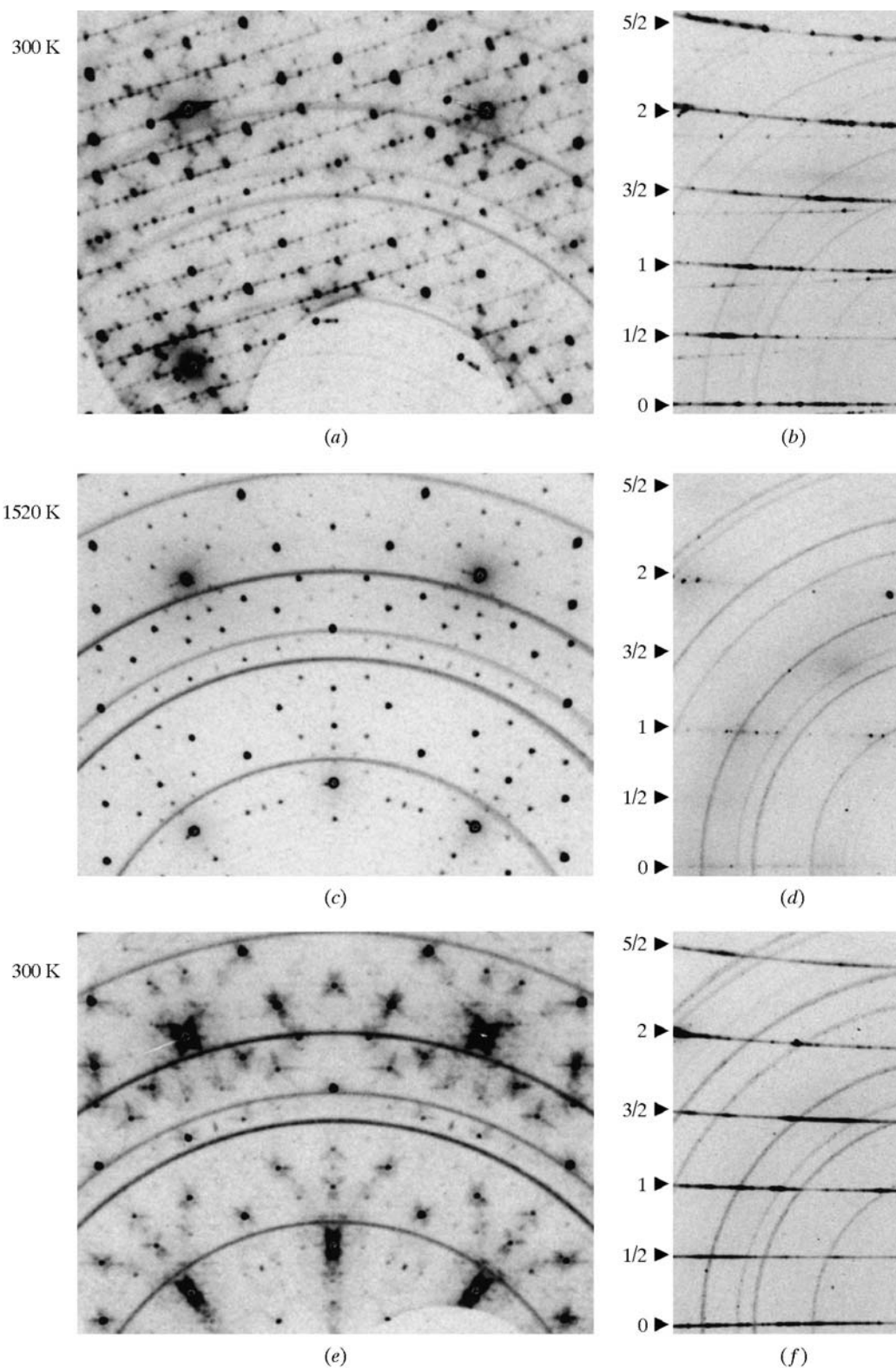


Fig. 4.6.4.2. Zero-layer X-ray diffraction patterns of decapristmatic $\text{Al}_{73.5}\text{Co}_{21.7}\text{Ni}_{4.8}$ crystals taken parallel and perpendicular to the crystal axis on an image-plate scanner (Mar Research) at different temperatures. In (a) and (b), room-temperature (RT) diffraction patterns from a sample quenched after annealing at 1073 K are shown. Reflections from both a crystalline approximant and a decagonal phase are visible. The period along the unique direction in the decagonal phase and the corresponding period in the approximant phase is $\simeq 8 \text{ \AA}$ (b). At 1520 K, a single-phase decagonal quasicrystal is present with $\simeq 4 \text{ \AA}$ fundamental structure (c, d). In (e, f), the RT diffraction patterns of the slowly cooled sample indicate a single-phase nanodomain structure with $\simeq 8 \text{ \AA}$ periodicity along the unique direction.

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4. DIFFUSE SCATTERING AND RELATED TOPICS

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5.1. Dynamical theory of X-ray diffraction

BY A. AUTHIER

5.1.1. Introduction

The first experiment on X-ray diffraction by a crystal was performed by W. Friedrich, P. Knipping and M. von Laue in 1912 and Bragg's law was derived in 1913 (Bragg, 1913). Geometrical and dynamical theories for the intensities of the diffracted X-rays were developed by Darwin (1914*a,b*). His dynamical theory took into account the interaction of X-rays with matter by solving recurrence equations that describe the balance of partially transmitted and partially reflected amplitudes at each lattice plane. This is the first form of the dynamical theory of X-ray diffraction. It gives correct expressions for the reflected intensities and was extended to the absorbing-crystal case by Prins (1930). A second form of dynamical theory was introduced by Ewald (1917) as a continuation of his previous work on the diffraction of optical waves by crystals. He took into account the interaction of X-rays with matter by considering the crystal to be a periodic distribution of dipoles which were excited by the incident wave. This theory also gives the correct expressions for the reflected and transmitted intensities, and it introduces the fundamental notion of a wavefield, which is necessary to understand the propagation of X-rays in perfect or deformed crystals. Ewald's theory was later modified by von Laue (1931), who showed that the interaction could be described by solving Maxwell's equations in a medium with a continuous, triply periodic distribution of dielectric susceptibility. It is this form which is most widely used today and which will be presented in this chapter.

The geometrical (or kinematical) theory, on the other hand, considers that each photon is scattered only once and that the interaction of X-rays with matter is so small it can be neglected. It can therefore be assumed that the amplitude incident on every diffraction centre inside the crystal is the same. The total diffracted amplitude is then simply obtained by adding the individual amplitudes diffracted by each diffracting centre, taking into account only the geometrical phase differences between them and neglecting the interaction of the radiation with matter. The result is that the distribution of diffracted amplitudes in reciprocal space is the Fourier transform of the distribution of diffracting centres in physical space. Following von Laue (1960), the expression *geometrical theory* will be used throughout this chapter when referring to these geometrical phase differences.

The first experimentally measured reflected intensities were not in agreement with the theoretical values obtained with the more rigorous dynamical theory, but rather with the simpler geometrical theory. The integrated reflected intensities calculated using geometrical theory are proportional to the square of the structure factor, while the corresponding expressions calculated using dynamical theory for an infinite perfect crystal are proportional to the modulus of the structure factor. The integrated intensity calculated by geometrical theory is also proportional to the volume of the crystal bathed in the incident beam. This is due to the fact that one neglects the decrease of the incident amplitude as it progresses through the crystal and a fraction of it is scattered away. According to geometrical theory, the diffracted intensity would therefore increase to infinity if the volume of the crystal was increased to infinity, which is of course absurd. The theory only works because the strength of the interaction is very weak and if it is applied to very small crystals. How small will be shown quantitatively in Sections 5.1.6.5 and 5.1.7.2. Darwin (1922) showed that it can also be applied to large imperfect crystals. This is done using the model of mosaic crystals (Bragg *et al.*, 1926). For perfect or nearly perfect crystals, dynamical theory should be used. Geometrical theory presents another drawback: it gives no indication as to the phase of

the reflected wave. This is due to the fact that it is based on the Fourier transform of the electron density limited by the external shape of the crystal. This is not important when one is only interested in measuring the reflected intensities. For any problem where the phase is important, as is the case for multiple reflections, interference between coherent blocks, standing waves *etc.*, dynamical theory should be used, even for thin or imperfect crystals.

Until the 1940s, the applications of dynamical theory were essentially intensity measurements. From the 1950s to the 1970s, applications were related to the properties (absorption, interference, propagation) of wavefields in perfect or nearly perfect crystals: anomalous transmission, diffraction of spherical waves, interpretation of images on X-ray topographs, accurate measurement of form factors, lattice-parameter mapping. In recent years, they have been concerned mainly with crystal optics, focusing and the design of monochromators for synchrotron radiation [see, for instance, Batterman & Bilderback (1991)], the location of atoms at crystal surfaces and interfaces using the standing-waves method [see, for instance, the reviews by Authier (1989) and Zegenhagen (1993)], attempts to determine phases using multiple reflections [see, for instance, Chang (1987) and Hümmel & Weckert (1995)], characterization of the crystal perfection of epilayers and superlattices by high-resolution diffractometry [see, for instance, Tanner (1990) and Fewster (1993)], *etc.*

For reviews of dynamical theory, see Zachariasen (1945), von Laue (1960), James (1963), Batterman & Cole (1964), Authier (1970), Kato (1974), Brümmer & Stephanik (1976), Pinsker (1978), Authier & Malgrange (1998), and Authier (2001). Topography is described in Chapter 2.7 of *IT C* (1999), in Tanner (1976) and in Tanner & Bowen (1992). For the use of Bragg-angle measurements for accurate lattice-parameter mapping, see Hart (1981).

A reminder of some basic concepts in electrodynamics is given in Section A5.1.1.1 of the Appendix.

5.1.2. Fundamentals of plane-wave dynamical theory

5.1.2.1. Propagation equation

The wavefunction Ψ associated with an electron or a neutron beam is *scalar* while an electromagnetic wave is a *vector* wave. When propagating in a medium, these waves are solutions of a *propagation equation*. For electrons and neutrons, this is Schrödinger's equation, which can be rewritten as

$$\Delta\Psi + 4\pi^2k^2(1 + \chi)\Psi = 0, \quad (5.1.2.1)$$

where $k = 1/\lambda$ is the wavenumber in a vacuum, $\chi = \varphi/W$ (φ is the potential in the crystal and W is the accelerating voltage) in the case of electron diffraction and $\chi = -2mV(\mathbf{r})/h^2k^2$ [$V(\mathbf{r})$ is the Fermi pseudo-potential and h is Planck's constant] in the case of neutron diffraction. The dynamical theory of electron diffraction is treated in Chapter 5.2 [note that a different convention is used in Chapter 5.2 for the scalar wavenumber: $k = 2\pi/\lambda$; compare, for example, equation (5.2.2.1) and its equivalent, equation (5.1.2.1)] and the dynamical theory of neutron diffraction is treated in Chapter 5.3.

In the case of X-rays, the propagation equation is deduced from Maxwell's equations after neglecting the interaction with protons. Following von Laue (1931, 1960), it is assumed that the positive charge of the nuclei is distributed in such a way that the medium is everywhere locally neutral and that there is no current. As a first approximation, magnetic interaction, which is very weak, is not taken into account in this review. The propagation equation is

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derived in Section A5.1.1.2 of the Appendix. Expressed in terms of the local electric displacement, $\mathbf{D}(\mathbf{r})$, it is given for monochromatic waves by

$$\Delta \mathbf{D}(\mathbf{r}) + \text{curl curl } \chi \mathbf{D}(\mathbf{r}) + 4\pi^2 k^2 \mathbf{D}(\mathbf{r}) = 0. \quad (5.1.2.2)$$

The interaction of X-rays with matter is characterized in equation (5.1.2.2) by the parameter χ , which is the dielectric susceptibility. It is classically related to the electron density $\rho(\mathbf{r})$ by

$$\chi(\mathbf{r}) = -R\lambda^2 \rho(\mathbf{r})/\pi, \quad (5.1.2.3)$$

where $R = 2.81794 \times 10^{-6}$ nm is the classical radius of the electron [see equation (A5.1.1.2) in Section A5.1.1.2 of the Appendix].

The dielectric susceptibility, being proportional to the electron density, is triply periodic in a crystal. It can therefore be expanded in Fourier series:

$$\chi = \sum_{\mathbf{h}} \chi_{\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (5.1.2.4)$$

where $\mathbf{h}$ is a reciprocal-lattice vector and the summation is extended over all reciprocal-lattice vectors. The sign convention adopted here for Fourier expansions of periodic functions is the *standard crystallographic* sign convention defined in Section 2.5.2.3. The relative orientations of wavevectors and reciprocal-lattice vectors are defined in Fig. 5.1.2.1, which represents schematically a Bragg reflection in direct and reciprocal space (Figs. 5.1.2.1a and 5.1.2.1b, respectively).

The coefficients $\chi_{\mathbf{h}}$ of the Fourier expansion of the dielectric susceptibility are related to the usual structure factor $F_{\mathbf{h}}$ by

$$\chi_{\mathbf{h}} = -R\lambda^2 F_{\mathbf{h}}/(\pi V), \quad (5.1.2.5)$$

where V is the volume of the unit cell and the structure factor is given by

$$\begin{aligned} F_{\mathbf{h}} &= \sum_j (f_j + f'_j + i f''_j) \exp(-M_j - 2\pi i \mathbf{h} \cdot \mathbf{r}_j) \\ &= |F_{\mathbf{h}}| \exp(i\varphi_{\mathbf{h}}). \end{aligned} \quad (5.1.2.6)$$

f_j is the form factor of atom j , f'_j and f''_j are the dispersion corrections [see, for instance, *IT C*, Section 4.2.6] and $\exp(-M_j)$ is the Debye-Waller factor. The summation is over all the atoms in the unit cell. The phase $\varphi_{\mathbf{h}}$ of the structure factor depends of course on the choice

of origin of the unit cell. The Fourier coefficients $\chi_{\mathbf{h}}$ are dimensionless. Their order of magnitude varies from 10^{-5} to 10^{-7} depending on the wavelength and the structure factor. For example, $\chi_{\mathbf{h}}$ is -9.24×10^{-6} for the 220 reflection of silicon for Cu $K\alpha$ radiation.

In an absorbing crystal, absorption is taken into account phenomenologically through the imaginary parts of the index of refraction and of the wavevectors. The dielectric susceptibility is written

$$\chi = \chi_r + i\chi_i. \quad (5.1.2.7)$$

The real and imaginary parts of the susceptibility are triply periodic in a crystalline medium and can be expanded in a Fourier series,

$$\begin{aligned} \chi_r &= \sum_{\mathbf{h}} \chi_{r\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) \\ \chi_i &= \sum_{\mathbf{h}} \chi_{i\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{r}), \end{aligned} \quad (5.1.2.8)$$

where

$$\begin{aligned} \chi_{r\mathbf{h}} &= -R\lambda^2 F_{r\mathbf{h}}/(\pi V), \\ \chi_{i\mathbf{h}} &= -R\lambda^2 F_{i\mathbf{h}}/(\pi V) \end{aligned} \quad (5.1.2.9)$$

and

$$\begin{aligned} F_{r\mathbf{h}} &= \sum_j (f_j + f'_j) \exp(-M_j - 2\pi i \mathbf{h} \cdot \mathbf{r}_j) \\ &= |F_{r\mathbf{h}}| \exp(i\varphi_{r\mathbf{h}}), \end{aligned} \quad (5.1.2.10a)$$

$$\begin{aligned} F_{i\mathbf{h}} &= \sum_j (f''_j) \exp(-M_j - 2\pi i \mathbf{h} \cdot \mathbf{r}_j) \\ &= |F_{i\mathbf{h}}| \exp(i\varphi_{i\mathbf{h}}). \end{aligned} \quad (5.1.2.10b)$$

It is important to note that

$$F_{r\mathbf{h}}^* = F_{r\bar{\mathbf{h}}} \text{ and } F_{i\mathbf{h}}^* = F_{i\bar{\mathbf{h}}} \text{ but that } F_{\mathbf{h}}^* \neq F_{\bar{\mathbf{h}}}, \quad (5.1.2.11)$$

where f^* is the imaginary conjugate of f .

The *index of refraction* of the medium for X-rays is

$$n = 1 + \chi_{ro}/2 = 1 - R\lambda^2 F_o/(2\pi V), \quad (5.1.2.12)$$

where F_o/V is the number of electrons per unit volume. This index is very slightly smaller than one. It is for this reason that specular reflection of X-rays takes place at grazing angles. From the value of the critical angle, $(-\chi_{ro})^{1/2}$, the electron density F_o/V of a material can be determined.

The linear absorption coefficient is

$$\mu_o = -2\pi k \chi_{io} = 2R\lambda F_{io}/V. \quad (5.1.2.13)$$

For example, it is 143.2 cm^{-1} for silicon and Cu $K\alpha$ radiation.

5.1.2.2. Wavefields

The notion of a wavefield, introduced by Ewald (1917), is one of the most fundamental concepts in dynamical theory. It results from the fact that since the propagation equation (5.1.2.2) is a second-order partial differential equation with a periodic interaction coefficient, its solution has the same periodicity,

$$\mathbf{D} = \exp(-2\pi i \mathbf{K}_o \cdot \mathbf{r}) \sum_{\mathbf{h}} \mathbf{D}_{\mathbf{h}} \exp(2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (5.1.2.14)$$

where the summation is over all reciprocal-lattice vectors $\mathbf{h}$. Equation (5.1.2.14) can also be written

$$\mathbf{D} = \sum_{\mathbf{h}} \mathbf{D}_{\mathbf{h}} \exp(-2\pi i \mathbf{K}_{\mathbf{h}} \cdot \mathbf{r}), \quad (5.1.2.15)$$

where

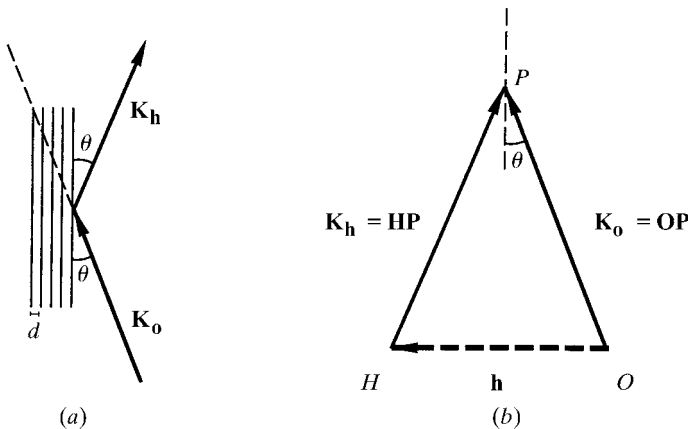


Fig. 5.1.2.1. Bragg reflection. (a) Direct space. Bragg reflection of a wave of wavevector $\mathbf{K}_o$ incident on a set of lattice planes of spacing d . The reflected wavevector is $\mathbf{K}_h$. Bragg's law $2d \sin \theta = n\lambda$ can also be written $2d_{hkl} \sin \theta = \lambda$, where $d_{hkl} = d/n = 1/OH = 1/h$ is the inverse of the length of the corresponding reciprocal-lattice vector $\mathbf{OH} = \mathbf{h}$ (see part b). (b) Reciprocal space. P is the tie point of the wavefield consisting of the incident wave $\mathbf{K}_o = \mathbf{OP}$ and the reflected wave $\mathbf{K}_h = \mathbf{HP}$. Note that the wavevectors are oriented *towards* the tie point.

5. DYNAMICAL THEORY AND ITS APPLICATIONS

$$\mathbf{K}_h = \mathbf{K}_o - \mathbf{h}. \quad (5.1.2.16) \quad \text{part,}$$

Expression (5.1.2.15) shows that the solution of the propagation equation can be interpreted as an infinite sum of plane waves with amplitudes $\mathbf{D}_h$ and wavevectors $\mathbf{K}_h$. This sum is a *wavefield*, or *Ewald wave*. The same expression is used to describe the propagation of any wave in a periodic medium, such as phonons or electrons in a solid. Expression (5.1.2.14) was later called a *Bloch wave* by solid-state physicists.

The wavevectors in a wavefield are deduced from one another by translations of the reciprocal lattice [expression (5.1.2.16)]. They can be represented geometrically as shown in Fig. 5.1.2.1(b). The wavevectors $\mathbf{K}_o = \mathbf{OP}$; $\mathbf{K}_h = \mathbf{HP}$ are drawn *away* from reciprocal-lattice points. Their common extremity, P , called the *tie point* by Ewald, characterizes the wavefield.

In an absorbing crystal, wavevectors have an imaginary part,

$$\mathbf{K}_o = \mathbf{K}_{or} + i\mathbf{K}_{oi}; \quad \mathbf{K}_h = \mathbf{K}_{hr} + i\mathbf{K}_{hi},$$

and (5.1.2.16) shows that all wavevectors have the same imaginary part,

$$\mathbf{K}_{oi} = \mathbf{K}_{hi}, \quad (5.1.2.17)$$

and therefore undergo the same absorption. This is one of the most important properties of wavefields.

5.1.2.3. Boundary conditions at the entrance surface

The choice of the 'o' component of expansion (5.1.2.15) is arbitrary in an infinite medium. In a semi-infinite medium where the waves are created at the interface with a vacuum or air by an incident plane wave with wavevector $\mathbf{K}_o^{(a)}$ (using von Laue's notation), the choice of $\mathbf{K}_o$ is determined by the boundary conditions.

This condition for wavevectors at an interface demands that their tangential components should be continuous across the boundary, in agreement with Descartes-Snell's law. This condition is satisfied when the difference between the wavevectors on each side of the interface is parallel to the normal to the interface. This is shown geometrically in Fig. 5.1.2.2 and formally in (5.1.2.18):

$$\mathbf{K}_o - \mathbf{K}_o^{(a)} = \mathbf{OP} - \mathbf{OM} = \overline{MP} \cdot \mathbf{n}, \quad (5.1.2.18)$$

where $\mathbf{n}$ is a unit vector normal to the crystal surface, oriented towards the inside of the crystal.

There is no absorption in a vacuum and the incident wavevector $\mathbf{K}_o^{(a)}$ is real. Equation (5.1.2.18) shows that it is the component normal to the interface of wavevector $\mathbf{K}_o$ which has an imaginary

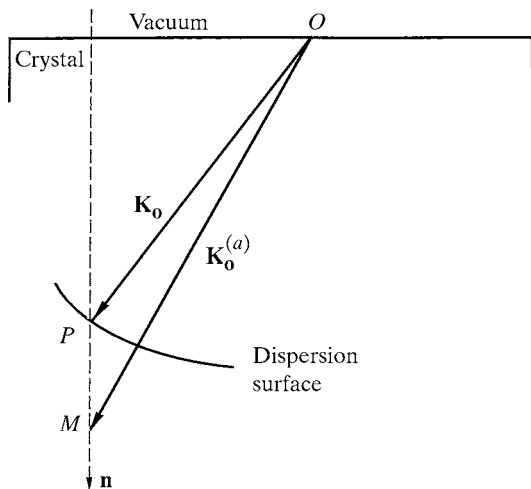


Fig. 5.1.2.2. Boundary condition for wavevectors at the entrance surface of the crystal.

$$\mathbf{K}_{oi} = \mathcal{I}(\overline{MP}) \cdot \mathbf{n} = -\mu \mathbf{n} / (4\pi\gamma_o), \quad (5.1.2.19)$$

where $\mathcal{I}(f)$ is the imaginary part of f , $\gamma_o = \cos(\mathbf{n} \cdot \mathbf{s}_o)$ and $\mathbf{s}_o$ is a unit vector in the incident direction. When there is more than one wave in the wavefield, the effective absorption coefficient μ can differ significantly from the normal value, μ_o , given by (5.1.2.13) – see Section 5.1.5.

5.1.2.4. Fundamental equations of dynamical theory

In order to obtain the solution of dynamical theory, one inserts expansions (5.1.2.15) and (5.1.2.4) into the propagation equation (5.1.2.2). This leads to an equation with an infinite sum of terms. It is shown to be equivalent to an infinite system of linear equations which are the *fundamental equations* of dynamical theory. Only those terms in (5.1.2.15) whose wavevector magnitudes K_h are very close to the vacuum value, k , have a non-negligible amplitude. These wavevectors are associated with reciprocal-lattice points that lie very close to the Ewald sphere. Far from any Bragg reflection, their number is equal to 1 and a single plane wave propagates through the medium. In general, for X-rays, there are only two reciprocal-lattice points on the Ewald sphere. This is the so-called *two-beam* case to which this treatment is limited. There are, however, many instances where several reciprocal-lattice points lie simultaneously on the Ewald sphere. This corresponds to the *many-beam* case which has interesting applications for the determination of phases of reflections [see, for instance, Chang (1987) and Hümmel & Weckert (1995)]. On the other hand, for electrons, there are in general many reciprocal-lattice points close to the Ewald sphere and many wavefields are excited simultaneously (see Chapter 5.2).

In the two-beam case, for reflections that are not highly asymmetric and for Bragg angles that are not close to $\pi/2$, the fundamental equations of dynamical theory reduce to

$$\begin{aligned} 2X_o D_o - kC\chi_h D_h &= 0 \\ -kC\chi_h D_o + 2X_h D_h &= 0, \end{aligned} \quad (5.1.2.20)$$

where $C = 1$ if $\mathbf{D}_h$ is normal to the $\mathbf{K}_o, \mathbf{K}_h$ plane and $C = \cos 2\theta$ if $\mathbf{D}_h$ lies in the plane; this is due to the fact that the amplitude with which electromagnetic radiation is scattered is proportional to the sine of the angle between the direction of the electric vector of the incident radiation and the direction of scattering (see, for instance, *ITC*, Section 6.2.2). The polarization of an electromagnetic wave is classically related to the orientation of the electric vector; in dynamical theory it is that of the electric displacement which is considered (see Section A5.1.1.3 of the Appendix).

The system (5.1.2.20) is therefore a system of four equations which admits four solutions, two for each direction of polarization. In the *non-absorbing* case, to a very good approximation,

$$\begin{aligned} X_o &= K_o - nk, \\ X_h &= K_h - nk. \end{aligned} \quad (5.1.2.21)$$

In the case of an *absorbing crystal*, X_o and K_h are complex. Equation (5.1.5.2) gives the full expression for X_o .

5.1.2.5. Dispersion surface

The fundamental equations (5.1.2.20) of dynamical theory are a set of linear homogeneous equations whose unknowns are the amplitudes of the various waves which make up a wavefield. For the solution to be non-trivial, the determinant of the set must be set equal to zero. This provides a secular equation relating the magnitudes of the wavevectors of a given wavefield. This equation is that of the locus of the tie points of all the wavefields that may

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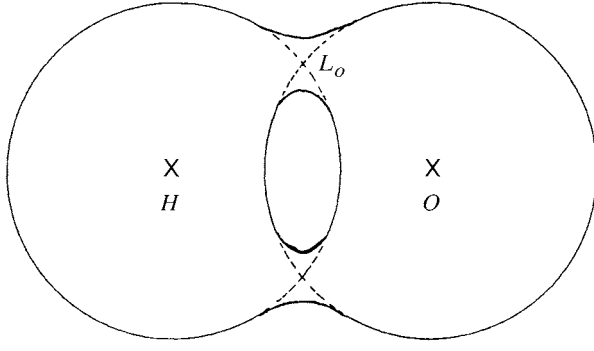


Fig. 5.1.2.3. Intersection of the dispersion surface with the plane of incidence. The dispersion surface is a connecting surface between the two spheres centred at reciprocal-lattice points O and H and with radius nk . L_o is the Lorentz point.

propagate in the crystal with a given frequency. This locus is called the *dispersion surface*. It is a constant-energy surface and is the equivalent of the index surface in optics. It is the X-ray analogue of the constant-energy surfaces known as Fermi surfaces in the electron band theory of solids.

In the two-beam case, the dispersion surface is a surface of revolution around the diffraction vector $\mathbf{OH}$. It is made from two spheres and a connecting surface between them. The two spheres are centred at O and H and have the same radius, nk . Fig. 5.1.2.3 shows the intersection of the dispersion surface with a plane passing through $\mathbf{OH}$. When the tie point lies on one of the two spheres, far from their intersection, only one wavefield propagates inside the crystal. When it lies on the connecting surface, two waves are excited simultaneously. The equation of this surface is obtained by equating to zero the determinant of system (5.1.2.20):

$$X_o X_h = k^2 C^2 \chi_h \chi_{\bar{h}} / 4. \quad (5.1.2.22)$$

Equations (5.1.2.21) show that, in the zero-absorption case, X_o and X_h are to be interpreted as the distances of the tie point P from the spheres centred at O and H , respectively. From (5.1.2.20) it can be seen that they are of the order of the vacuum wavenumber times the Fourier coefficient of the dielectric susceptibility, that is five or six orders of magnitude smaller than k . The two spheres can therefore be replaced by their tangential planes. Equation (5.1.2.22) shows that the product of the distances of the tie point from these planes is constant. The intersection of the dispersion surface with the plane passing through $\mathbf{OH}$ is therefore a hyperbola (Fig. 5.1.2.4) whose diameter [using (5.1.2.5) and (5.1.2.22)] is

$$\overline{A_{o2}A_{o1}} = |C|R\lambda(F_h F_{\bar{h}})^{1/2} / (\pi V \cos \theta). \quad (5.1.2.23)$$

It can be noted that the larger the diameter of the dispersion surface, the larger the structure factor, that is, the stronger the interaction of the waves with the matter. When the polarization is parallel to the plane of incidence ($C = \cos 2\theta$), the interaction is weaker.

The asymptotes T_o and T_h to the hyperbola are tangents to the circles centred at O and H , respectively. Their intersection, L_o , is called the *Lorentz point* (Fig. 5.1.2.4).

A wavefield propagating in the crystal is characterized by a tie point P on the dispersion surface and two waves with wavevectors $\mathbf{K}_o = \mathbf{OP}$ and $\mathbf{K}_h = \mathbf{HP}$, respectively. The ratio, ξ , of their amplitudes D_h and D_o is given by means of (5.1.2.20):

$$\xi = \frac{D_h}{D_o} = \frac{2X_o}{kC\chi_{\bar{h}}} = \frac{-2\pi V X_o}{R\lambda C F_{\bar{h}}}. \quad (5.1.2.24)$$

The hyperbola has two branches, 1 and 2, for each direction of polarization, that is, for $C = 1$ or $\cos 2\theta$ (Fig. 5.1.2.5). Branch 2 is

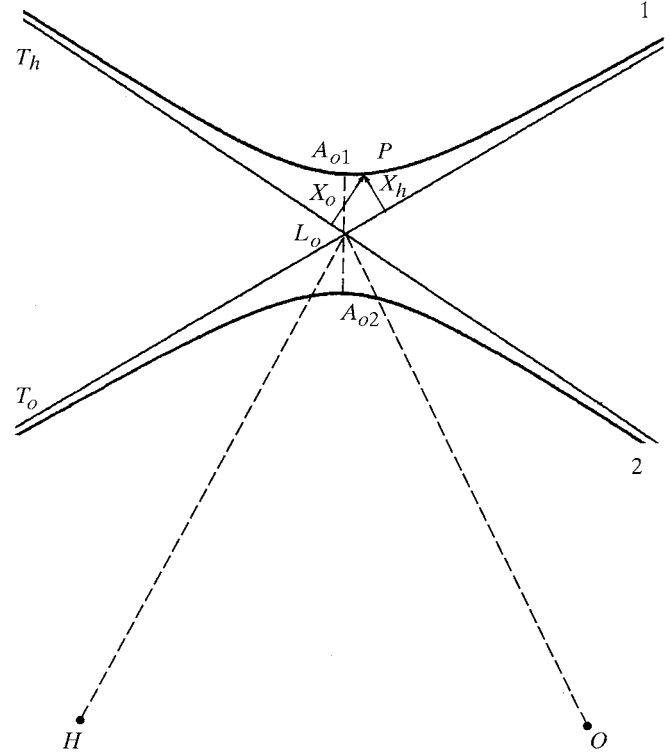


Fig. 5.1.2.4. Intersection of the dispersion surface with the plane of incidence shown in greater detail. The Lorentz point L_o is far away from the nodes O and H of the reciprocal lattice: $OL_o = HL_o = 1/\lambda$ is about 10^5 to 10^6 times larger than the diameter $A_{o1}A_{o2}$ of the dispersion surface.

the one situated on the same side of the asymptotes as the reciprocal-lattice points O and H . Given the orientation of the wavevectors, which has been chosen away from the reciprocal-lattice points (Fig. 5.1.2.1b), the coordinates of the tie point, X_o and X_h , are positive for branch 1 and negative for branch 2. The phase of ξ is therefore equal to $\pi + \varphi_h$ and to φ_h for the two branches, respectively, where φ_h is the phase of the structure factor [equation (5.1.2.6)]. This difference of π between the two branches has important consequences for the properties of the wavefields.

As mentioned above, owing to absorption, wavevectors are actually complex and so is the dispersion surface.

5.1.2.6. Propagation direction

The energy of all the waves in a given wavefield propagates in a common direction, which is obtained by calculating either the group velocity or the Poynting vector [see Section A5.1.1.4, equation (A5.1.1.8) of the Appendix]. It can be shown that, averaged over time and the unit cell, the Poynting vector of a wavefield is

$$\mathbf{S} = (c/\varepsilon_0) \exp(4\pi \mathbf{K}_{oi} \cdot \mathbf{r}) [|D_o|^2 \mathbf{s}_o + |D_h|^2 \mathbf{s}_h], \quad (5.1.2.25)$$

where $\mathbf{s}_o$ and $\mathbf{s}_h$ are unit vectors in the $\mathbf{K}_o$ and $\mathbf{K}_h$ directions, respectively, c is the velocity of light and ε_0 is the dielectric permittivity of a vacuum. This result was first shown by von Laue (1952) in the two-beam case and was generalized to the n -beam case by Kato (1958).

From (5.1.2.25) and equation (5.1.2.22) of the dispersion surface, it can be shown that the propagation direction of the wavefield lies along the normal to the dispersion surface at the tie point (Fig. 5.1.2.5). This result is also obtained by considering the group velocity of the wavefield (Ewald, 1958; Wagner, 1959). The angle α

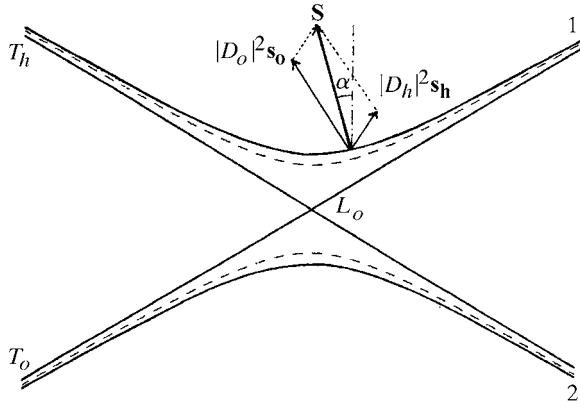


Fig. 5.1.2.5. Dispersion surface for the two states of polarization. Solid curve: polarization normal to the plane of incidence ($C = 1$); broken curve: polarization parallel to the plane of incidence ($C = \cos 2\theta$). The direction of propagation of the energy of the wavefields is along the Poynting vector, $\mathbf{S}$, normal to the dispersion surface.

between the propagation direction and the lattice planes is given by

$$\tan \alpha = \left[(1 - |\xi|^2) / (1 + |\xi|^2) \right] \tan \theta. \quad (5.1.2.26)$$

It should be noted that the propagation direction varies between $\mathbf{K}_o$ and $\mathbf{K}_h$ for both branches of the dispersion surface.

5.1.3. Solutions of plane-wave dynamical theory

5.1.3.1. Departure from Bragg's law of the incident wave

The wavefields excited in the crystal by the incident wave are determined by applying the boundary condition mentioned above for the continuity of the tangential component of the wavevectors (Section 5.1.2.3). Waves propagating in a vacuum have wavenumber $k = 1/\lambda$. Depending on whether they propagate in the incident or in the reflected direction, the common extremity, M , of their wavevectors

$$\mathbf{OM} = \mathbf{K}_o^{(a)} \text{ and } \mathbf{HM} = \mathbf{K}_h^{(a)}$$

lies on spheres of radius k and centred at O and H , respectively. The intersections of these spheres with the plane of incidence are two circles which can be approximated by their tangents T'_o and T'_h at their intersection point, L_a , or *Laue point* (Fig. 5.1.3.1).

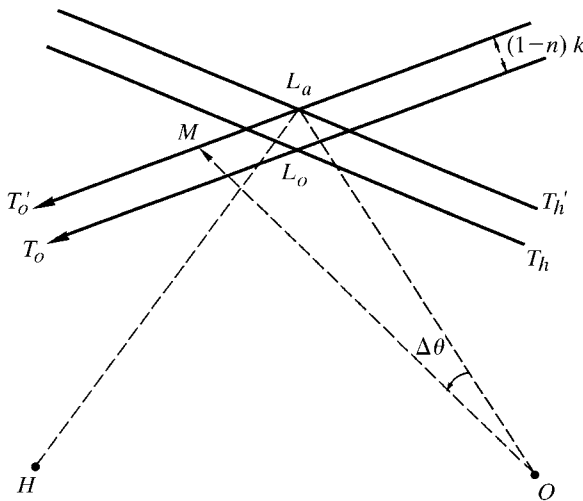


Fig. 5.1.3.1. Departure from Bragg's law of an incident wave.

Bragg's condition is exactly satisfied according to the geometrical theory of diffraction when M lies at L_a . The departure $\Delta\theta$ from Bragg's incidence of an incident wave is defined as the angle between the corresponding wavevectors $\mathbf{OM}$ and $\mathbf{OL}_a$. As $\Delta\theta$ is very small compared to the Bragg angle in the general case of X-rays or neutrons, one may write

$$\mathbf{K}_o^{(a)} = \mathbf{OM} = \mathbf{OL}_a + \mathbf{L}_a\mathbf{M}, \quad (5.1.3.1)$$

$$\Delta\theta = \overline{L_a M} / k.$$

The tangent T'_o is oriented in such a way that $\Delta\theta$ is negative when the angle of incidence is smaller than the Bragg angle.

5.1.3.2. Transmission and reflection geometries

The boundary condition for the continuity of the tangential component of the wavevectors is applied by drawing from M a line, $\mathbf{Mz}$, parallel to the normal $\mathbf{n}$ to the crystal surface. The tie points of the wavefields excited in the crystal by the incident wave are at the intersections of this line with the dispersion surface. Two different situations may occur:

(a) *Transmission, or Laue case* (Fig. 5.1.3.2). The normal to the crystal surface drawn from M intersects *both* branches of the dispersion surface (Fig. 5.1.3.2a). The reflected wave is then directed towards the *inside* of the crystal (Fig. 5.1.3.2b). Let γ_o and γ_h be the cosines of the angles between the normal to the crystal surface, $\mathbf{n}$, and the incident and reflected directions, respectively:

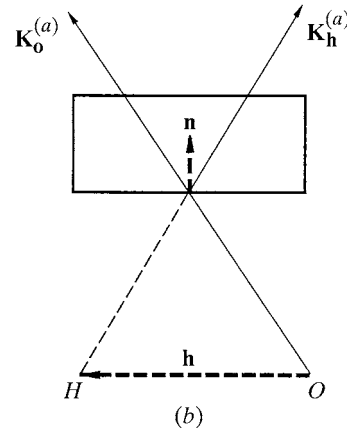
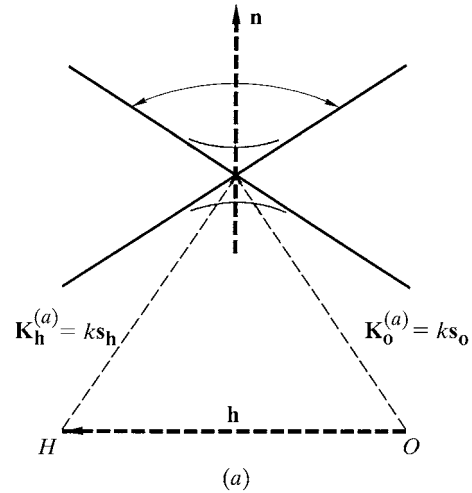


Fig. 5.1.3.2. Transmission, or Laue, geometry. (a) Reciprocal space; (b) direct space.

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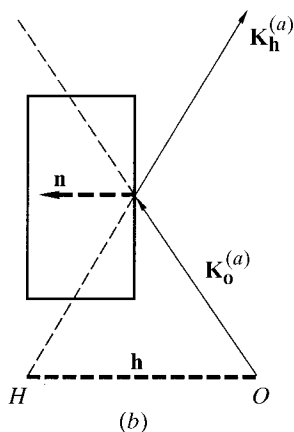
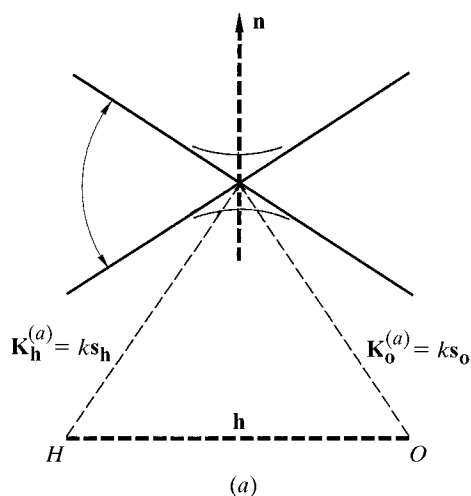


Fig. 5.1.3.3. Reflection, or Bragg, geometry. (a) Reciprocal space; (b) direct space.

$$\gamma_\varrho = \cos(\mathbf{n}, \mathbf{s}_\varrho); \quad \gamma_h = \cos(\mathbf{n}, \mathbf{s}_h). \quad (5.1.3.2)$$

It will be noted that they are both positive, as is their ratio,

$$\gamma \equiv \gamma_h/\gamma_\rho. \quad (5.1.3.3)$$

This is the *asymmetry ratio*, which is very important since the width of the rocking curve is proportional to its square root [equation (5.1.3.6)].

(b) *Reflection, or Bragg case* (Fig. 5.1.3.3). In this case there are three possible situations: the normal to the crystal surface drawn from M intersects either branch 1 or branch 2 of the dispersion surface, or the intersection points are imaginary (Fig. 5.1.3.3a). The reflected wave is directed towards the *outside* of the crystal (Fig. 5.1.3.3b). The cosines defined by (5.1.3.2) are now positive for γ_o and negative for γ_h . The asymmetry factor is therefore also negative.

5.1.3.3. Middle of the reflection domain

It will be apparent from the equations given later that the incident wavevector corresponding to the middle of the reflection domain is, in both cases, $\mathbf{OI}$, where I is the intersection of the normal to the crystal surface drawn from the Lorentz point, L_o , with T'_o (Figs. 5.1.3.4 and 5.1.3.5), while, according to Bragg's law, it should be $\mathbf{OL}_a$. The angle $\Delta\theta$ between the incident wavevectors $\mathbf{OL}_a$ and $\mathbf{OI}$, corresponding to the middle of the reflecting domain according to the geometrical and dynamical theories, respectively, is

$$\Delta\theta_\rho = \overline{L_a I}/k = R\lambda^2 F_\rho(1 - \gamma)/(2\pi V \sin 2\theta). \quad (5.1.3.4)$$

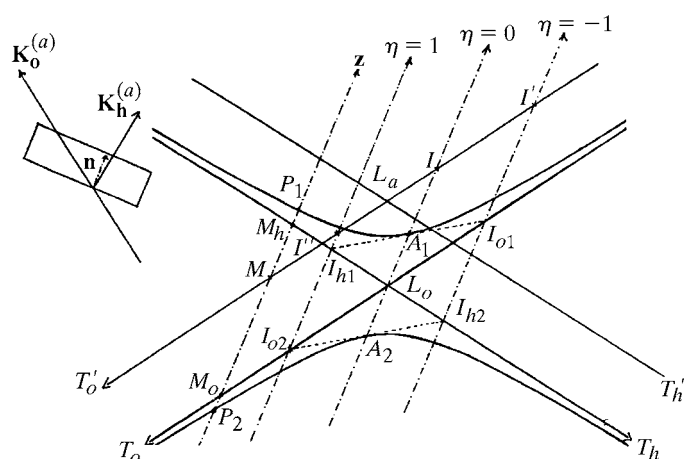


Fig. 5.1.3.4. Boundary conditions at the entrance surface for transmission geometry.

In the Bragg case, the asymmetry ratio γ is negative and $\Delta\theta_o$ is never equal to zero. This difference in Bragg angle between the two theories is due to the refraction effect, which is neglected in geometrical theory. In the Laue case, $\Delta\theta_o$ is equal to zero for symmetric reflections ($\gamma = 1$).

5.1.3.4. Deviation parameter

The solutions of dynamical theory are best described by introducing a reduced parameter called the *deviation parameter*,

$$\eta = (\Delta\theta - \Delta\theta_o)/\delta, \quad (5.1.3.5)$$

where

$$\delta = R\lambda^2|C|(|\gamma|F_hF_{\bar{h}})^{1/2}/(\pi V \sin 2\theta), \quad (5.1.3.6)$$

whose real part is equal to the half width of the rocking curve (Sections 5.1.6 and 5.1.7). The width 2δ of the rocking curve is sometimes called the *Darwin width*.

The definition (5.1.3.5) of the deviation parameter is independent of the geometrical situation (reflection or transmission case); this is not followed by some authors. The present convention has the advantage of being quite general.

In an absorbing crystal, η , $\Delta\theta_o$ and δ are complex, and it is the real part, $\Delta\theta_{or}$, of $\Delta\theta_o$ which has the geometrical interpretation given in Section 5.1.3.3. One obtains

$$\begin{aligned} \eta &= \eta_r + i\eta_i \\ \eta_r &= (\Delta\theta - \Delta\theta_{or})/\delta_r; \eta_i = A\eta_r + B \\ A &= -\tan\beta \end{aligned} \quad (5.1.3.7)$$

$$B = \left\{ \chi_{io} / \left[|C| (|\chi_h \chi_{\bar{h}}|)^{1/2} \cos \beta \right] \right\} (1 - \gamma) / 2 (|\gamma|)^{1/2},$$

where β is the phase angle of $(\chi_h \chi_{\bar{h}})^{1/2}$ [or that of $(F_h F_{\bar{h}})^{1/2}$].

5.1.3.5. Pendellösung and extinction distances

Let

$$\Lambda_o = \pi V(\gamma_o|\gamma_h|)^{1/2}/[R\lambda|C|(F_h F_{\bar{h}})^{1/2}]. \quad (5.1.3.8)$$

This length plays a very important role in the dynamical theory of diffraction by both perfect and deformed crystals. For example, it is 15.3 μm for the 220 reflection of silicon, with Mo $K\alpha$ radiation and a symmetric reflection.

In *transmission* geometry, it gives the period of the interference between the two excited wavefields which constitutes the *Pendellösung* effect first described by Ewald (1917) (see Section

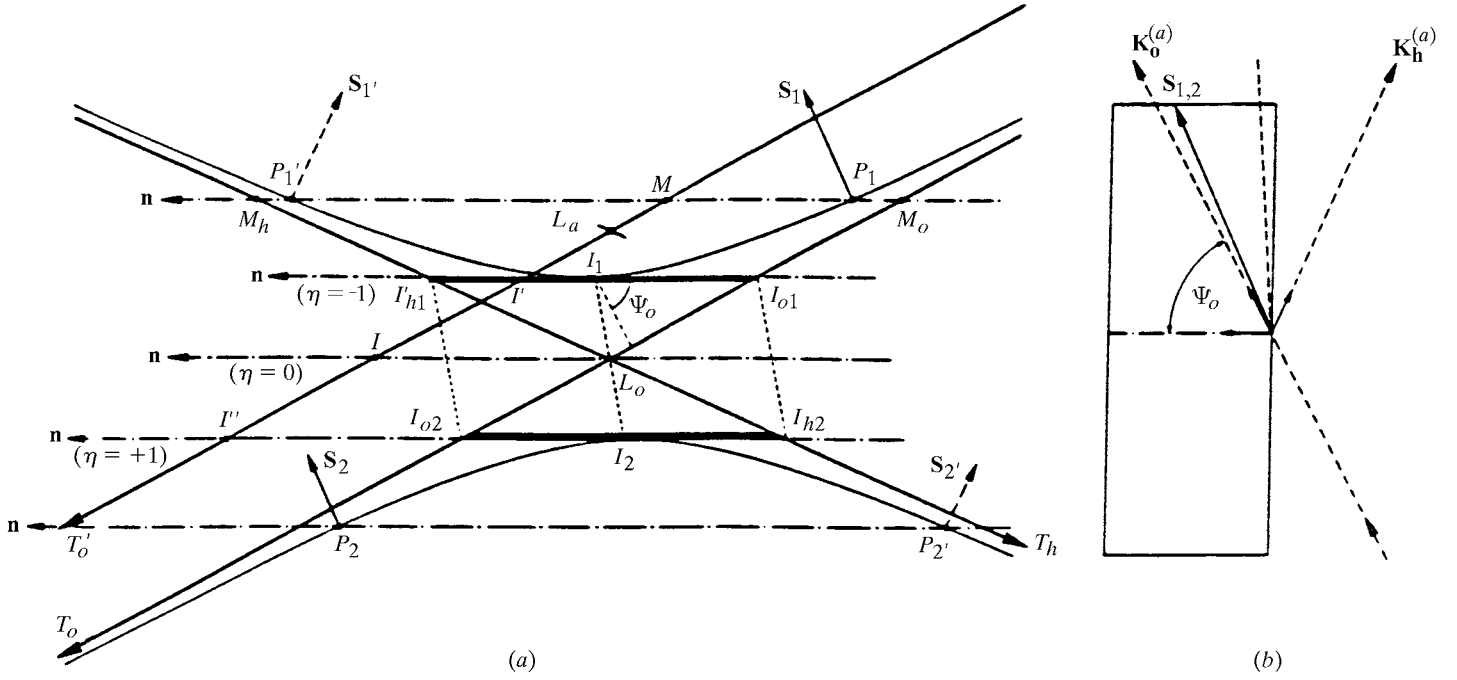


Fig. 5.1.3.5. Boundary conditions at the entrance surface for reflection geometry. (a) Reciprocal space; (b) direct space.

5.1.6.3); Λ_o in this case is called the *Pendellösung distance*, denoted Λ_L hereafter. Its geometrical interpretation, in the zero-absorption case, is the inverse of the diameter A_2A_1 of the dispersion surface in a direction defined by the cosines γ_h and γ_o with respect to the reflected and incident directions, respectively (Fig. 5.1.3.4). It reduces to the inverse of $A_{o2}A_{o1}$ (5.1.2.23) in the symmetric case.

In *reflection geometry*, it gives the absorption distance in the total-reflection domain and is called the *extinction distance*, denoted Λ_B (see Section 5.1.7.1). Its geometrical interpretation in the zero-absorption case is the inverse of the length $I_{o1}I_{h1} = I_{h2}I_{o2}$, Fig. 5.1.3.5.

In a *deformed crystal*, if distortions are of the order of the width of the rocking curve over a distance Λ_o , the crystal is considered to be slightly deformed, and ray theory (Penning & Polder, 1961; Kato, 1963, 1964a,b) can be used to describe the propagation of wavefields. If the distortions are larger, new wavefields may be generated by interbranch scattering (Authier & Balibar, 1970) and generalized dynamical diffraction theory such as that developed by Takagi (1962, 1969) should be used.

Using (5.1.3.8), expressions (5.1.3.5) and (5.1.3.6) can be rewritten in the very useful form:

$$\begin{aligned} \eta &= (\Delta\theta - \Delta\theta_o)\Lambda_o \sin 2\theta / (\lambda|\gamma_h|), \\ \delta &= \lambda|\gamma_h| / (\Lambda_o \sin 2\theta). \end{aligned} \quad (5.1.3.9)$$

The order of magnitude of the Darwin width 2δ ranges from a fraction of a second of an arc to ten or more seconds, and increases with increasing wavelength and increasing structure factor. For example, for the 220 reflection of silicon and Cu $K\alpha$ radiation, it is 5.2 seconds.

5.1.3.6. Solution of the dynamical theory

The coordinates of the tie points excited by the incident wave are obtained by looking for the intersection of the dispersion surface, (5.1.2.22), with the normal $\mathbf{Mz}$ to the crystal surface (Figs. 5.1.3.4 and 5.1.3.5). The ratio ξ of the amplitudes of the waves of the

corresponding wavefields is related to these coordinates by (5.1.2.24) and is found to be

$$\begin{aligned} \xi_j &= D_{hj}/D_{oj} \\ &= -S(C)S(\gamma_h)[(F_h F_{\bar{h}})^{1/2}/F_{\bar{h}}] \\ &\quad \times \left\{ \eta \pm [\eta^2 + S(\gamma_h)]^{1/2} \right\} / (|\gamma|)^{1/2}, \end{aligned} \quad (5.1.3.10)$$

where the plus sign corresponds to a tie point on branch 1 ($j = 1$) and the minus sign to a tie point on branch 2 ($j = 2$), and $S(\gamma_h)$ is the sign of γ_h (+1 in transmission geometry, -1 in reflection geometry).

5.1.3.7. Geometrical interpretation of the solution in the zero-absorption case

5.1.3.7.1. Transmission geometry

In this case (Fig. 5.1.3.4) $S(\gamma_h)$ is +1 and (5.1.3.10) may be written

$$\xi_j = -S(C) \left[\eta \pm (\eta^2 + 1)^{1/2} \right] / \gamma^{1/2}. \quad (5.1.3.11)$$

Let A_1 and A_2 be the intersections of the normal to the crystal surface drawn from the Lorentz point L_o with the two branches of the dispersion surface (Fig. 5.1.3.4). From Sections 5.1.3.3 and 5.1.3.4, they are the tie points excited for $\eta = 0$ and correspond to the middle of the reflection domain. Let us further consider the tangents to the dispersion surface at A_1 and A_2 and let I_{o1} , I_{o2} and I_{h1} , I_{h2} be their intersections with T_o and T_h , respectively. It can be shown that $I_{o1}I_{h2}$ and $I_{o2}I_{h1}$ intersect the dispersion surface at the tie points excited for $\eta = -1$ and $\eta = +1$, respectively, and that the *Pendellösung distance* $\Lambda_L = 1/A_2A_1$, the width of the rocking curve $2\delta = I_{o1}I_{o2}/k$ and the deviation parameter $\eta = M_o M_h / A_2 A_1$, where M_o and M_h are the intersections of the normal to the crystal surface drawn from the extremity of any incident wavevector $\mathbf{OM}$ with T_o and T_h , respectively.

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5.1.3.7.2. Reflection geometry

In this case (Fig. 5.1.3.5) $S(\gamma_h)$ is now -1 and (5.1.3.10) may be written

$$\xi_j = S(C) \left[\eta \pm (\eta^2 - 1)^{1/2} \right] / |\gamma|^{1/2}. \quad (5.1.3.12)$$

Now, let I_1 and I_2 be the points of the dispersion surface where the tangent is parallel to the normal to the crystal surface, and further let I_{o1}, I_{h1}, I' and I_{o2}, I_{h2}, I'' be the intersections of these two tangents with T_o, T_h and T'_o , respectively. For an incident wave of wavevector $\mathbf{OM}$ where M lies between I' and I'' , the normal to the crystal surface drawn from M has no real intersection with the dispersion surface and $I'I''$ defines the total-reflection domain. The tie points I_1 and I_2 correspond to $\eta = -1$ and $\eta = +1$, respectively, the extinction distance $\Lambda_L = 1/I_{o1}I_{h1}$, the width of the total-reflection domain $2\delta = I_{o1}I_{o2}/k = I'I''/k$ and the deviation parameter $\eta = -M_o M_h / I_{o1} I_{h1}$, where M_o and M_h are the intersections with T_o and T_h of the normal to the crystal surface drawn from the extremity of any incident wavevector $\mathbf{OM}$.

5.1.4. Standing waves

The various waves in a wavefield are coherent and interfere. In the two-beam case, the intensity of the wavefield, using (5.1.2.14) and (5.1.2.24), is

$$|D|^2 = |D_o|^2 \exp(4\pi \mathbf{K}_{oi} \cdot \mathbf{r}) \times [1 + |\xi|^2 + 2C|\xi| \cos 2\pi(\mathbf{h} \cdot \mathbf{r} + \Psi)], \quad (5.1.4.1)$$

where Ψ is the phase of ξ ,

$$\xi = |\xi| \exp(i\Psi). \quad (5.1.4.2)$$

Equation (5.1.4.1) shows that the interference between the two waves is the origin of *standing waves*. The corresponding nodes lie on planes such that $\mathbf{h} \cdot \mathbf{r}$ is a constant. These planes are therefore parallel to the diffraction planes and their periodicity is equal to d_{hkl} (defined in the caption for Fig. 5.1.2.1a). Their position within the unit cell is given by the value of the phase Ψ .

In the Laue case, Ψ is equal to $\pi + \varphi_h$ for branch 1 and to φ_h for branch 2, where φ_h is the phase of the structure factor, (5.1.2.6). This means that the *nodes* of standing waves lie on the maxima of the hkl Fourier component of the electron density for branch 1 while the *anti-nodes* lie on the maxima for branch 2.

In the Bragg case, Ψ varies continuously from $\pi + \varphi_h$ to φ_h as the angle of incidence is varied from the low-angle side to the high-angle side of the reflection domain by rocking the crystal. The nodes lie on the maxima of the hkl Fourier components of the electron density on the low-angle side of the rocking curve. As the crystal is rocked, they are progressively shifted by half a lattice spacing until the anti-nodes lie on the maxima of the electron density on the high-angle side of the rocking curve.

Standing waves are the origin of the phenomenon of anomalous absorption, which is one of the specific properties of wavefields (Section 5.1.5). Anomalous scattering is also used for the location of atoms in the unit cell at the vicinity of the crystal surface: when X-rays are absorbed, fluorescent radiation and photoelectrons are emitted. Detection of this emission for a known angular position of the crystal with respect to the rocking curve and therefore for a known value of the phase Ψ enables the emitting atom within the unit cell to be located. The principle of this method is due to Batterman (1964, 1969). For reviews, see Golovchenko *et al.* (1982), Materlik & Zegenhagen (1984), Kovalchuk & Kohn (1986), Bedzyk (1988), Authier (1989), and Zegenhagen (1993).

5.1.5. Anomalous absorption

It was shown in Section 5.1.2.2 that the wavevectors of a given wavefield all have the same imaginary part (5.1.2.17) and therefore the same absorption coefficient μ (5.1.2.19). Borrmann (1950, 1954) showed that this coefficient is much smaller than the normal one (μ_o) for wavefields whose tie points lie on branch 1 of the dispersion surface and much larger for wavefields whose tie points lie on branch 2. The former case corresponds to the *anomalous transmission effect*, or *Borrmann effect*. As in favourable cases the minimum absorption coefficient may be as low as a few per cent of μ_o , this effect is very important from both a fundamental and a practical point of view.

The physical interpretation of the Borrmann effect is to be found in the standing waves described in Section 5.1.4. When the nodes of the electric field lie on the planes corresponding to the maxima of the hkl component of the electron density, the wavefields are absorbed anomalously less than when there is no diffraction. Just the opposite occurs for branch 2 wavefields, whose anti-nodes lie on the maxima of the electron density and which are absorbed more than normal.

The effective absorption coefficient μ is related to the imaginary part of the wavevectors through (5.1.2.19),

$$\mu = -4\pi\gamma_o K_{oi},$$

and to the imaginary part of the ratio of the amplitude of the reflected to the incident wave through

$$\mu = \mu_o - 4\pi X_{oi}, \quad (5.1.5.1)$$

where X_{oi} is the imaginary part of X_o , which, using (5.1.2.24) and (5.1.3.10), is given by

$$X_o = R\lambda|C|S(\gamma_h)(F_h F_h^*)^{1/2} \times \{ \eta \pm [\eta^2 + S(\gamma_h)]^{1/2} \} / [2\pi V(|\gamma|)^{1/2}]. \quad (5.1.5.2)$$

Taking the upper sign (+) for the $\pm$ term corresponds to tie points on branch 1 and taking the lower sign (−) corresponds to tie points on branch 2.

The calculation of the imaginary part X_{oi} is different in the Laue and in the Bragg cases. In the former case, the imaginary part of $(\eta^2 + 1)^{1/2}$ is small and can be approximated while in the latter, the imaginary part of $(\eta^2 - 1)^{1/2}$ is large when the real part of the deviation parameter, η_r , lies between 1 and -1 , and cannot be calculated using the same approximation.

5.1.6. Intensities of plane waves in transmission geometry

5.1.6.1. Absorption coefficient

In transmission geometry, the imaginary part of X_o is small and, using a first-order approximation for the expansion of $(\eta^2 + 1)^{1/2}$, (5.1.5.1) and (5.1.5.2), the effective absorption coefficient in the absorption case is

$$\mu_j = \mu_o \left[\frac{1}{2}(1 + \gamma^{-1}) \mp \frac{(\eta_r/2)(1 - \gamma^{-1}) + |C|(\gamma^{-1})^{1/2}|F_{ih}/F_{io}|\cos\varphi}{(\eta_r^2 + 1)^{1/2}} \right], \quad (5.1.6.1)$$

where $\varphi = \varphi_{rh} - \varphi_{ih}$ is the phase difference between F_{rh} and F_{ih} [equation (5.1.2.10)], the upper sign (−) for the $\mp$ term corresponds to branch 1 and the lower sign (+) corresponds to branch 2 of the dispersion surface. In the symmetric Laue case ($\gamma = 1$, reflecting planes normal to the crystal surface), equation (5.1.6.1) reduces to

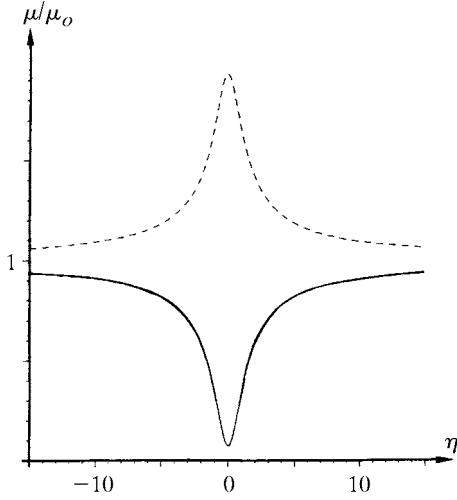


Fig. 5.1.6.1. Variation of the effective absorption with the deviation parameter in the transmission case for the 400 reflection of GaAs using Cu $K\alpha$ radiation. Solid curve: branch 1; broken curve: branch 2.

$$\mu_j = \mu_o \left[1 \mp \frac{|C||F_{ih}/F_{io}|\cos\varphi}{(\eta_r^2 + 1)^{1/2}} \right].$$

Fig. 5.1.6.1 shows the variations of the effective absorption coefficient μ_j with η_r for wavefields belonging to branches 1 and 2 in the case of the 400 reflection of GaAs with Cu $K\alpha$ radiation. It can be seen that for $\eta_r = 0$ the absorption coefficient for branch 1 becomes significantly smaller than the normal absorption coefficient, μ_o . The minimum absorption coefficient, $\mu_o(1 - |CF_{ih}/F_{io}|\cos\varphi)$, depends on the nature of the reflection through the structure factor and on the temperature through the Debye–Waller factor included in F_{ih} [equation (5.1.2.10b)] (Ohtsuki, 1964, 1965). For instance, in diamond-type structures, it is smaller for reflections with even indices than for reflections with odd indices. The influence of temperature is very important when $|F_{ih}/F_{io}|$ is close to one; for example, for germanium 220 and Mo $K\alpha$ radiation, the minimum absorption coefficient at 5 K is reduced to about 1% of its normal value, μ_o (Ludewig, 1969).

5.1.6.2. Boundary conditions for the amplitudes at the entrance surface – intensities of the reflected and refracted waves

Let us consider an infinite plane wave incident on a crystal plane surface of infinite lateral extension. As has been shown in Section 5.1.3, two wavefields are excited in the crystal, with tie points P_1 and P_2 , and amplitudes D_{o1}, D_{h1} and D_{o2}, D_{h2} , respectively. Maxwell's boundary conditions (see Section A5.1.1.2 of the Appendix) imply continuity of the tangential component of the electric field and of the normal component of the electric displacement across the boundary. Because the index of refraction is so close to unity, one can assume to a very good approximation that there is continuity of the three components of both the electric field and the electric displacement. As a consequence, it can easily be shown that, *along the entrance surface*, for all components of the electric displacement

$$\begin{aligned} D_o^{(a)} &= D_{o1} + D_{o2} \\ 0 &= D_{h1} + D_{h2}, \end{aligned} \quad (5.1.6.2)$$

where $D_o^{(a)}$ is the amplitude of the incident wave.

Using (5.1.3.11), (5.1.5.2) and (5.1.6.2), it can be shown that the *intensities* of the four waves are

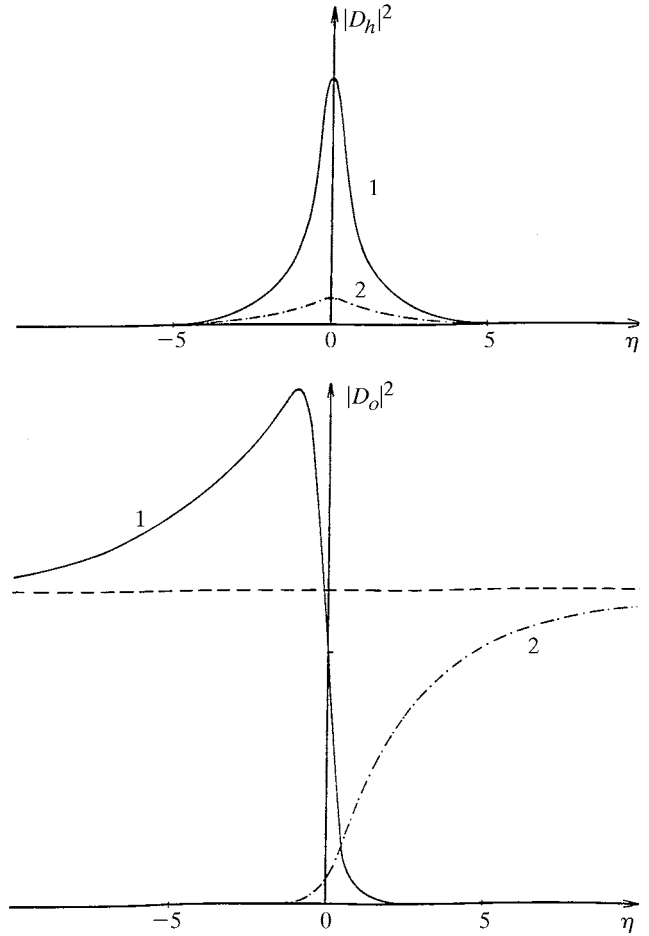


Fig. 5.1.6.2. Variation of the intensities of the reflected and refracted waves in an absorbing crystal for the 220 reflection of Si using Mo $K\alpha$ radiation, $t = 1$ mm ($\mu t = 1.42$). Solid curve: branch 1; dashed curve: branch 2.

$$\begin{aligned} |D_{oj}|^2 &= |D_o^{(a)}|^2 \exp(-\mu_j z / \gamma_o) \left[(1 + \eta_r^2)^{1/2} \mp \eta_r \right]^2 \\ &\quad \times [4(1 + \eta_r^2)]^{-1}, \\ |D_{hj}|^2 &= |D_o^{(a)}|^2 \exp(-\mu_j z / \gamma_o) |F_h/F_h| [4\gamma(1 + \eta_r^2)]^{-1}; \end{aligned} \quad (5.1.6.3)$$

top sign: $j = 1$; bottom sign: $j = 2$.

Fig. 5.1.6.2 represents the variations of these four intensities with the deviation parameter. Far from the reflection domain, $|D_{h1}|^2$ and $|D_{h2}|^2$ tend toward zero, as is normal, while

$$\begin{aligned} |D_{o1}|^2 &\gg |D_{o2}|^2 \text{ for } \eta_r \Rightarrow -\infty, \\ |D_{o1}|^2 &\ll |D_{o2}|^2 \text{ for } \eta_r \Rightarrow +\infty. \end{aligned}$$

This result shows that the wavefield of highest intensity ‘jumps’ from one branch of the dispersion surface to the other across the reflection domain. This is an important property of dynamical theory which also holds in the Bragg case and when a wavefield crosses a highly distorted region in a deformed crystal [the so-called *interbranch scattering*: see, for instance, Authier & Balibar (1970) and Authier & Malgrange (1998)].

5.1.6.3. Boundary conditions at the exit surface

5.1.6.3.1. Wavevectors

When a wavefield reaches the exit surface, it breaks up into its two constituent waves. Their wavevectors are obtained by applying

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again the condition of the continuity of their tangential components along the crystal surface. The extremities, M_j and N_j , of these wavevectors

$$\mathbf{OM}_j = \mathbf{K}_{oj}^{(d)} \quad \mathbf{HN}_j = \mathbf{K}_{hj}^{(d)}$$

lie at the intersections of the spheres of radius k centred at O and H , respectively, with the normal $\mathbf{n}'$ to the crystal exit surface drawn from P_j ($j = 1$ and 2) (Fig. 5.1.6.3).

If the crystal is wedge-shaped and the normals $\mathbf{n}$ and $\mathbf{n}'$ to the entrance and exit surfaces are not parallel, the wavevectors of the waves generated by the two wavefields are not parallel. This effect is due to the refraction properties associated with the dispersion surface.

5.1.6.3.2. Amplitudes – Pendellösung

We shall assume from now on that the crystal is plane parallel. Two wavefields arrive at any point of the exit surface. Their constituent waves interfere and generate emerging waves in the refracted and reflected directions (Fig. 5.1.6.4). Their respective

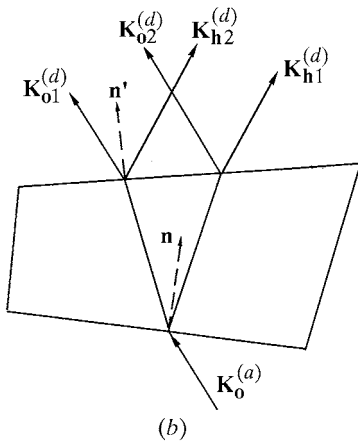
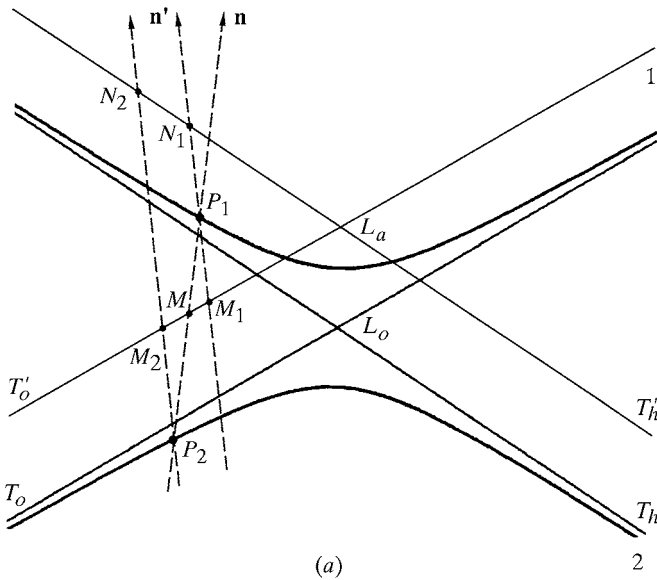


Fig. 5.1.6.3. Boundary condition for the wavevectors at the exit surface. (a) Reciprocal space. The wavevectors of the emerging waves are determined by the intersections M_1 , M_2 , N_1 and N_2 of the normals $\mathbf{n}'$ to the exit surface, drawn from the tie points P_1 and P_2 of the wavefields, with the tangents T'_o and T'_h to the spheres centred at O and H and of radius k , respectively. (b) Direct space.

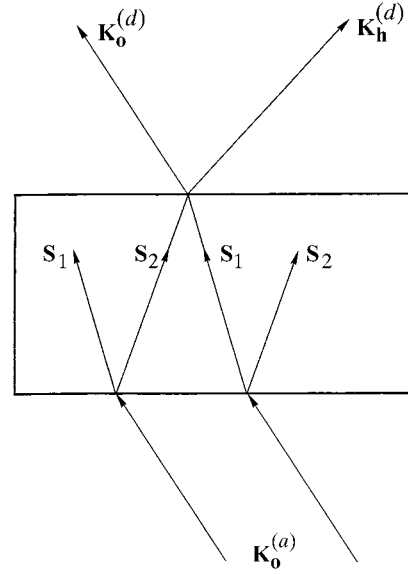


Fig. 5.1.6.4. Decomposition of a wavefield into its two components when it reaches the exit surface. $\mathbf{S}_1$ and $\mathbf{S}_2$ are the Poynting vectors of the two wavefields propagating in the crystal belonging to branches 1 and 2 of the dispersion surface, respectively, and interfering at the exit surface.

amplitudes are given by the boundary conditions

$$\begin{aligned} D_o^{(d)} \exp(-2\pi i \mathbf{K}_o^{(d)} \cdot \mathbf{r}) &= D_{o1} \exp(-2\pi i \mathbf{K}_{o1} \cdot \mathbf{r}) \\ &\quad + D_{o2} \exp(-2\pi i \mathbf{K}_{o2} \cdot \mathbf{r}) \\ D_h^{(d)} \exp(-2\pi i \mathbf{K}_h^{(d)} \cdot \mathbf{r}) &= D_{h1} \exp(-2\pi i \mathbf{K}_{h1} \cdot \mathbf{r}) \\ &\quad + D_{h2} \exp(-2\pi i \mathbf{K}_{h2} \cdot \mathbf{r}), \end{aligned} \quad (5.1.6.4)$$

where $\mathbf{r}$ is the position vector of a point on the exit surface, the origin of phases being taken at the entrance surface.

In a plane-parallel crystal, (5.1.6.4) reduces to

$$\begin{aligned} D_o^{(d)} &= D_{o1} \exp(-2\pi i \overline{MP_1} \cdot t) + D_{o2} \exp(-2\pi i \overline{MP_2} \cdot t) \\ D_h^{(d)} &= D_{h1} \exp(-2\pi i \overline{MP_1} \cdot t) + D_{h2} \exp(-2\pi i \overline{MP_2} \cdot t), \end{aligned}$$

where t is the crystal thickness.

In a *non-absorbing* crystal, the amplitudes squared are of the form

$$|D_o^{(d)}|^2 = |D_{o1}|^2 + |D_{o2}|^2 + 2D_{o1}D_{o2} \cos 2\pi \overline{P_2P_1} t.$$

This expression shows that the intensities of the refracted and reflected beams are oscillating functions of crystal thickness. The period of the oscillations is called the *Pendellösung* distance and is

$$\Lambda = 1/\overline{P_2P_1} = \Lambda_L/(1 + \eta_r^2)^{1/2}.$$

5.1.6.4. Reflecting power

For an *absorbing* crystal, the intensities of the reflected and refracted waves are

$$\begin{aligned} |D_o^{(d)}|^2 &= |D_o^{(a)}|^2 A_\eta \left\{ \cosh(2v + \mu_a t) \right. \\ &\quad \left. + \cos \left[2\pi t \Lambda^{-1} - 2\eta_i(1 + \eta_r^2)^{-1/2} \right] \right\} \\ |D_h^{(d)}|^2 &= |D_o^{(a)}|^2 |F_h/F_h| \gamma^{-1} A_\eta [\cosh(\mu_a t) - \cos(2\pi t \Lambda^{-1})], \end{aligned} \quad (5.1.6.5)$$

where

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$$A_\eta = [\exp -\mu_o t(\gamma_o^{-1} + \gamma_h^{-1})]/2(1 + \eta_r^2),$$

$$\mu_a = \mu_j \left[1/2(\gamma_o^{-1} - \gamma_h^{-1})\eta_r \right. \\ \left. + |C||F_{ih}/F_{io}| \cos \varphi / (\gamma_o \gamma_h)^{1/2} \right] (1 + \eta_r^2)^{-1/2},$$

$$v = \arg \sinh \eta_r$$

and μ_j is given by equation (5.1.6.1).

Depending on the absorption coefficient, the cosine terms are more or less important relative to the hyperbolic cosine term and the oscillations due to *Pendellösung* have more or less contrast.

For a non-absorbing crystal, these expressions reduce to

$$|D_o^{(d)}|^2 = |D_o^{(a)}|^2 \left[\frac{1 + 2\eta^2 + \cos(2\pi t \Lambda^{-1})}{2(1 + \eta_r^2)} \right],$$

$$|D_h^{(d)}|^2 = |D_o^{(a)}|^2 \left[\frac{1 - \cos(2\pi t \Lambda^{-1})}{2\gamma(1 + \eta_r^2)} \right]. \quad (5.1.6.6)$$

What is actually measured in a counter receiving the reflected or the refracted beam is the *reflecting power*, namely the ratio of the energy of the reflected or refracted beam on the one hand and the energy of the incident beam on the other. The energy of a beam is obtained by multiplying its intensity by its cross section. If l is the width of the trace of the beam on the crystal surface, the cross sections of the incident (or refracted) and reflected beams are proportional to (Fig. 5.1.6.5) $l_o = l\gamma_o$ and $l_h = l\gamma_h$, respectively.

The reflecting powers are therefore:

$$\text{Refracted beam: } I_o = l_o |D_o^{(d)}|^2 / l_o |D_o^{(a)}|^2 = |D_o^{(d)}|^2 / |D_o^{(a)}|^2,$$

$$\text{Reflected beam: } I_h = l_h |D_h^{(d)}|^2 / l_o |D_o^{(a)}|^2 = \gamma |D_h^{(d)}|^2 / |D_o^{(a)}|^2. \quad (5.1.6.7)$$

Using (5.1.6.6), it is easy to check that $I_o + I_h = 1$ in the non-absorbing case; that is, that conservation of energy is satisfied. Equations (5.1.6.6) show that there is a periodic exchange of energy between the refracted and the reflected waves as the beam penetrates the crystal; this is why Ewald introduced the expression *Pendellösung*.

The oscillations in the rocking curve were first observed by Lefeld-Sosnowska & Malgrange (1968, 1969). Their periodicity can be used for accurate measurements of the form factor [see, for

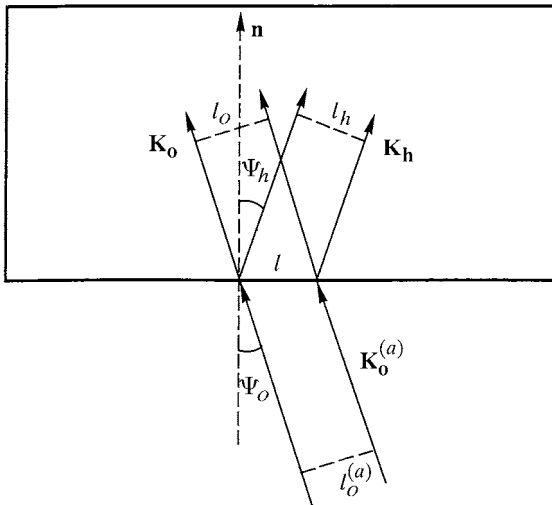


Fig. 5.1.6.5. Cross sections of the incident, $K_o^{(a)}$, refracted, K_h , and reflected, K_h , waves.

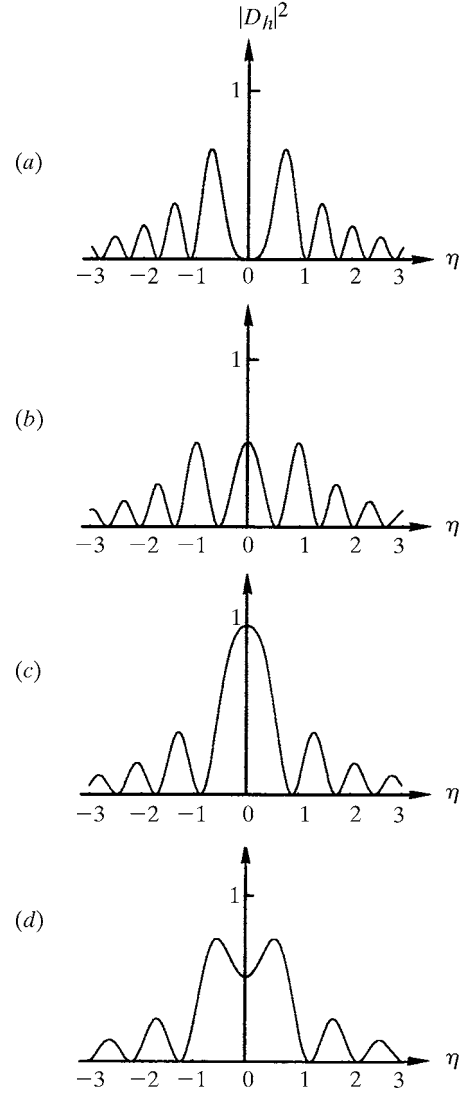


Fig. 5.1.6.6. Theoretical rocking curves in the transmission case for non-absorbing crystals and for various values of t/Λ_L : (a) $t/\Lambda_L = 1.25$; (b) $t/\Lambda_L = 1.5$; (c) $t/\Lambda_L = 1.75$; (d) $t/\Lambda_L = 2.0$.

instance, Bonse & Teworte (1980)]. Fig. 5.1.6.6 shows the shape of the rocking curve for various values of t/Λ_L .

The width at half-height of the rocking curve, averaged over the *Pendellösung* oscillations, corresponds in the non-absorbing case to $\Delta\eta = 2$, that is, to $\Delta\theta = 2\delta$, where δ is given by (5.1.3.6).

5.1.6.5. Integrated intensity

5.1.6.5.1. Non-absorbing crystals

The integrated intensity is the ratio of the total energy recorded in the counter when the crystal is rocked to the intensity of the incident beam. It is proportional to the area under the line profile:

$$I_{hi} = \int_{-\infty}^{+\infty} I_h d(\Delta\theta). \quad (5.1.6.8)$$

The integration was performed by von Laue (1960). Using (5.1.3.5), (5.1.6.6) and (5.1.6.7) gives

$$I_{hi} = A \int_0^{2\pi t \Lambda_L^{-1}} J_0(z) dz,$$

where $J_0(z)$ is the zeroth-order Bessel function and

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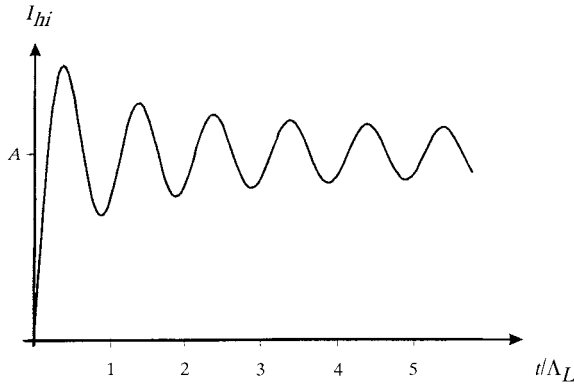


Fig. 5.1.6.7. Variations with crystal thickness of the integrated intensity in the transmission case (no absorption) (arbitrary units). The expression for A is given in the text.

$$A = \frac{R\lambda^2 |CF_h|(\gamma)^{1/2}}{2V \sin 2\theta}.$$

Fig. 5.1.6.7 shows the variations of the integrated intensity with t/Λ_L .

5.1.6.5.2. Absorbing crystals

The integration was performed for absorbing crystals by Kato (1955). The integrated intensity in this case is given by

$$I_{hi} = A |F_h/F_{\bar{h}}| \exp[-1/2\mu_o t(\gamma_o^{-1} + \gamma_h^{-1})] \times \left[\int_0^{2\pi t \Lambda_L^{-1}} J_0(z) dz - 1 + I_0(\zeta) \right],$$

where

$$\zeta = \mu_o t \left\{ \left[|C|^2 |F_{ih}/F_{io}|^2 \cos^2 \varphi + (\gamma_h - \gamma_o)/(4\gamma_o \gamma_h) \right] / (\gamma_o \gamma_h) \right\}^{1/2}$$

and $I_0(\zeta)$ is a modified Bessel function of zeroth order.

5.1.6.6. Thin crystals – comparison with geometrical theory

Using (5.1.6.6) and (5.1.6.7), the reflecting power of the reflected beam may also be written

$$I_h = \pi^2 t^2 \Lambda_o^{-2} f(\eta),$$

where

$$f(\eta) = \left[\frac{\sin U(1 + \eta^2)^{1/2}}{U(1 + \eta^2)^{1/2}} \right]^2$$

and

$$U = \pi t \Lambda_o^{-1}.$$

When $t \Lambda_o^{-1}$ is very small, $f(\eta)$ tends asymptotically towards the function

$$f_1(\eta) = \left[\frac{\sin U\eta}{U\eta} \right]^2$$

and I_h towards the value given by geometrical theory. The condition for geometrical theory to apply is, therefore, that the crystal thickness be much smaller than the *Pendellösung* distance. In practice, the two theories agree to within a few per cent for a crystal

thickness smaller than or equal to a third of the *Pendellösung* distance [see Authier & Malgrange (1998)].

5.1.7. Intensity of plane waves in reflection geometry

5.1.7.1. Thick crystals

5.1.7.1.1. Non-absorbing crystals

Rocking curve. The geometrical construction in Fig. 5.1.3.5 shows that, in the Bragg case, the normal to the crystal surface drawn from the extremity of the incident wavevector intersects the dispersion surface either at two points of the same branch, P_1, P'_1 , for branch 1, P_2, P'_2 for branch 2, or at imaginary points. It was shown in Section 5.1.2.6 that the propagation of the wavefields inside the crystal is along the normal to the dispersion surface at the corresponding tie points. Fig. 5.1.3.5 shows that this direction is oriented towards the outside of the crystal for tie points P'_1 and P'_2 . In a very thick crystal, these wavefields cannot exist because there is always a small amount of absorption. One concludes that in the thick-crystal case and in reflection geometry, only one wavefield is excited inside the crystal. It corresponds to branch 1 on the low-angle side of the rocking curve and to branch 2 on the high-angle side. Using the same approximations as in Section 5.1.6.2, the amplitude $\mathbf{D}_h^{(a)}$ of the wave reflected at the crystal surface is obtained by applying the boundary conditions, which are particularly simple in this case:

$$\mathbf{D}_o = \mathbf{D}_o^{(a)}, \quad \mathbf{D}_h^{(a)} = \mathbf{D}_h.$$

The reflecting power is given by an expression similar to (5.1.6.7):

$$I_h = |\gamma| |\xi_j|^2,$$

where the expression for ξ_j is given by (5.1.3.12), and $j = 1$ or 2 depending on which wavefield propagates towards the inside of the crystal. When the normal to the entrance surface intersects the dispersion surface at imaginary points, *i.e.* when $-1 < \eta < +1$,

$$|\xi|^2 = |\gamma|^{-1}, \quad I_h = 1, \quad (5.1.7.1)$$

and there is *total reflection*. Outside the total-reflection domain, the reflecting power is given by

$$I_h = \left[|\eta| - (\eta^2 - 1)^{1/2} \right]^2. \quad (5.1.7.2)$$

The rocking curve has the well known top-hat shape (Fig. 5.1.7.1). Far from the total-reflection domain, the curve can be

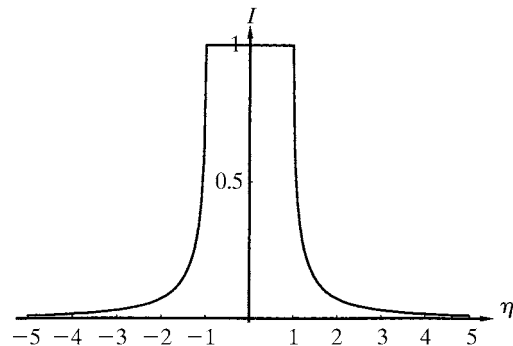


Fig. 5.1.7.1. Theoretical rocking curve in the reflection case for a non-absorbing thick crystal in terms of the deviation parameter.

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approximated by the function

$$I_h \approx 1/(4\eta^2).$$

Width of the total-reflection domain. The width of the total-reflection domain is equal to $\Delta\eta = 2$ and its angular width is therefore equal, using (5.1.3.5), to 2δ , where δ is given by (5.1.3.6). It is proportional to the structure factor, the polarization factor C and the square root of the asymmetry factor $|\gamma|$. Using an asymmetric reflection, it is therefore possible to decrease the width at wish. This is used in monochromators to produce a pseudo plane wave [see, for instance, Kikuta & Kohra (1970)]. It is possible to deduce the value of the form factor from very accurate measurements of the rocking curve; see, for instance, Kikuta (1971).

Integrated intensity. The integrated intensity is defined by (5.1.6.8):

$$I_{hi} = 8\delta/3. \quad (5.1.7.3)$$

Penetration depth. Within the domain of total reflection, there are two wavefields propagating inside the crystal with imaginary wavevectors, one towards the inside of the crystal and the other one in the opposite direction, so that they cancel out and, globally, no energy penetrates the crystal. The absorption coefficient of the waves penetrating the crystal is

$$\mu = -4\pi K_{oi}\gamma_o = 2\pi\gamma_o(1 - \eta^2)^{1/2}/\Lambda_B, \quad (5.1.7.4)$$

where Λ_B is the value taken by Λ_o [equation (5.1.3.8)] in the Bragg case.

The penetration depth is a minimum at the middle of the reflection domain and at this point it is equal to $\Lambda_B/2\pi$. This attenuation effect is called *extinction*, and Λ_B is called the *extinction length*. It is a specific property owing to the existence of wavefields. The resulting propagation direction of energy is parallel to the crystal surface, but with a cross section equal to zero: it is an *evanescent wave* [see, for instance, Cowan *et al.* (1986)].

5.1.7.1.2. Absorbing crystals

Rocking curve. Since the sign of γ is negative, $[\eta^2 + S(\gamma h)]^{1/2}$ in (5.1.3.10) has a very large imaginary part when $|\eta_r| \leq 1$. It cannot be calculated using the same approximations as in the Laue case. Let us set

$$Z \exp(i\Psi') = \eta \mp (\eta^2 - 1)^{1/2}. \quad (5.1.7.5)$$

The reflecting power is

$$I_h = (F_h/F_{\bar{h}})^{1/2} Z^2, \quad (5.1.7.6)$$

where $Z = [L - (L^2 - 1)^{1/2}]^{1/2}$, $L = |\eta|^2 + \rho^2$ and $\rho = |\eta^2 - 1|$ is the modulus of expression (5.1.7.5) where the sign is chosen in such a way that Z is smaller than 1.

The expression for the reflected intensity in the absorbing Bragg case was first given by Prins (1930). The way of representing it given here was first used by Hirsch & Ramachandran (1950). The properties of the rocking curve have been described by Fingerland (1971).

There is no longer a total-reflection domain and energy penetrates the crystal at all incidence angles, although with a very high absorption coefficient within the domain $|\eta_r| \leq 1$. Fig. 5.1.7.2 gives an example of a rocking curve for a thick absorbing crystal. It was first observed by Renninger (1955). The shape is asymmetric and is due to the anomalous-absorption effect: it is lower than normal on the low-angle side, which is associated with wavefields belonging to branch 1 of the dispersion surface, and larger than normal on the high-angle side, which is associated with branch 2 wavefields. The amount of asymmetry depends on the value of the ratio A/B of the coefficients in the expression for the imaginary part

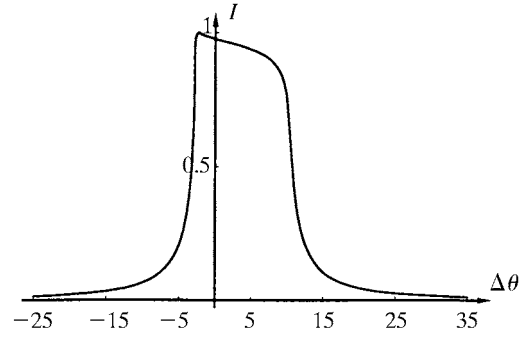


Fig. 5.1.7.2. Theoretical rocking curve in the reflection case for a thick absorbing crystal. The 400 reflection of GaAs using Cu $K\alpha$ radiation is shown.

of the deviation parameter in (5.1.3.7): the smaller this ratio, the more important the asymmetry.

Absorption coefficient. The effective absorption coefficient, taking into account both the Borrmann effect and extinction, is given by (Authier, 1986)

$$\mu = \mu_o + 2(|F_h F_{\bar{h}}|)^{1/2} \frac{R\lambda}{V(|\gamma|)^{1/2}} Z \sin(\beta + \Psi'),$$

where β is defined in equation (5.1.3.7) and Ψ' in equation (5.1.7.5), and where the sign is chosen in such a way that Z converges. Fig. 5.1.7.3 shows the variation of the penetration depth $z_o = \gamma_o/\mu$ with the deviation parameter.

5.1.7.2. Thin crystals

5.1.7.2.1. Non-absorbing crystals

Boundary conditions. If the crystal is thin, the wavefield created at the reflecting surface at A and penetrating inside can reach the back surface at B (Fig. 5.1.7.4a). The *incident* direction there points towards the *outside* of the crystal, while the *reflected* direction

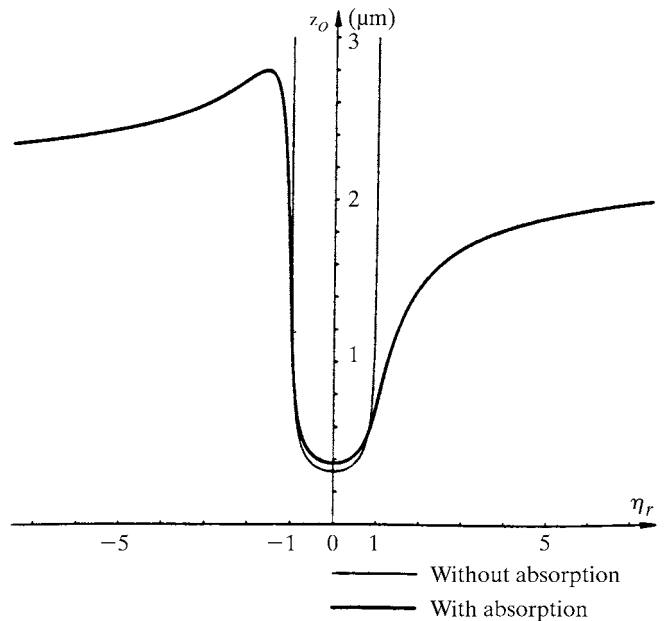


Fig. 5.1.7.3. Bragg case: thick crystals. Variation of the penetration depth with incidence angle (represented here by the dimensionless deviation parameter η_r). Thin curve: without absorption; thick curve: with absorption for the 400 reflection of GaAs using Cu $K\alpha$ radiation.

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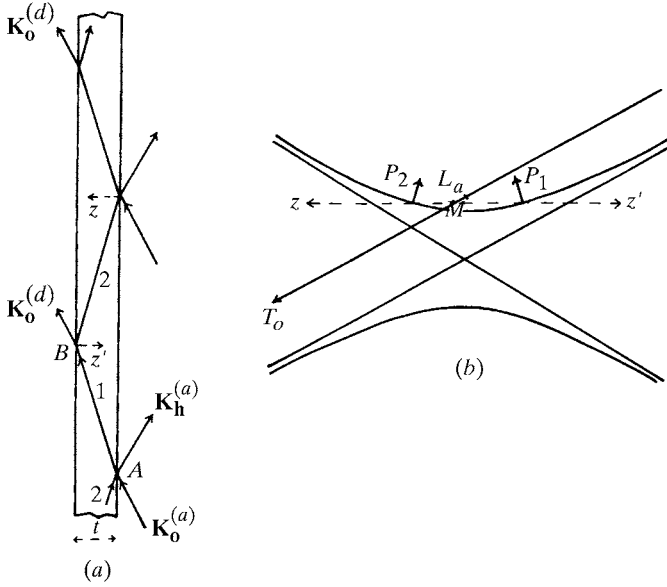


Fig. 5.1.7.4. Bragg case: thin crystals. Two wavefields propagate in the crystal. (a) Direct space; (b) reciprocal space.

points towards the inside. The wavefield propagating along AB will therefore generate at B :

(i) a partially transmitted wave outside the crystal, $D_o^{(d)} \exp(-2\pi i \mathbf{K}_o^{(d)} \cdot \mathbf{r})$;

(ii) a partially reflected wavefield inside the crystal.

The corresponding tiepoints are obtained by applying the usual condition of the continuity of the tangential components of wavevectors (Fig. 5.1.7.4b). If the crystal is a plane-parallel slab, these points are M and P_2 , respectively, and $\mathbf{K}_o^{(d)} = \mathbf{K}_o^{(a)}$.

The boundary conditions are then written:

(i) entrance surface:

$$D_{o1} + D_{o2} = D_o^{(a)}, \quad D_{h1} + D_{h2} = D_h^{(a)};$$

(ii) back surface:

$$D_{o1} \exp(-2\pi i \mathbf{K}_{o1} \cdot \mathbf{r}) + D_{o2} \exp(-2\pi i \mathbf{K}_{o2} \cdot \mathbf{r}) = D_o^{(a)} \exp(-2\pi i \mathbf{K}_o^{(d)} \cdot \mathbf{r}),$$

$$D_{h1} \exp(-2\pi i \mathbf{K}_{h1} \cdot \mathbf{r}) + D_{h2} \exp(-2\pi i \mathbf{K}_{h2} \cdot \mathbf{r}) = 0.$$

Rocking curve. Using (5.1.3.10), it can be shown that the expressions for the intensities reflected at the entrance surface and transmitted at the back surface, I_h and I_o , respectively, are given by different expressions within total reflection and outside it:

(i) $|\eta| < 1$:

$$I_h = |\gamma| \frac{|D_h^{(a)}|^2}{|D_o^{(a)}|^2} = \frac{\cosh^2[\pi(t/\Lambda_B)(1 - \eta^2)^{1/2}] - 1}{\cosh^2[\pi(t/\Lambda_B)(1 - \eta^2)^{1/2}] - \eta^2} \quad (5.1.7.7a)$$

$$I_o = \frac{|D_o^{(d)}|^2}{|D_o^{(a)}|^2} = \frac{1 - \eta^2}{\cosh^2[\pi(t/\Lambda_B)(1 - \eta^2)^{1/2}] - \eta^2},$$

where Λ_B is the value taken by Λ_o [equation (5.1.3.8)] in the Bragg case.

There is no longer a total-reflection domain but the extinction effect still exists, as is shown by the hyperbolic cosine term. The maximum height of the rocking curve decreases as the thickness of the crystal decreases.

(ii) $|\eta| > 1$:

$$I_h = \frac{1 - \cos^2[\pi(t/\Lambda_B)(\eta^2 - 1)^{1/2}]}{\eta^2 - \cos^2[\pi(t/\Lambda_B)(\eta^2 - 1)^{1/2}]}, \quad (5.1.7.7b)$$

$$I_o = \frac{\eta^2 - 1}{\eta^2 - \cos^2[\pi(t/\Lambda_B)(\eta^2 - 1)^{1/2}]}.$$

The cosine terms show that the two wavefields propagating within the crystal interfere, giving rise to *Pendellösung* fringes in the rocking curve. These fringes were observed for the first time by Batterman & Hildebrandt (1967, 1968). The angular positions of the minima of the reflected beam are given by

$$\eta = \mp (K^2 \Lambda_B^2 t^{-2} + 1)^{1/2},$$

where K is an integer.

Integrated intensity. The integrated intensity is

$$I_{hi} = \pi \delta \tanh[\pi t / \Lambda_B], \quad (5.1.7.8)$$

where t is the crystal thickness. When this thickness becomes very large, the integrated intensity tends towards

$$I_{hi} = \pi \delta. \quad (5.1.7.9)$$

This expression differs from (5.1.7.3) by the factor π , which appears here in place of $8/3$. von Laue (1960) pointed out that because of the differences between the two expressions for the reflecting power, (5.1.7.2) and (5.1.7.7b), perfect agreement could not be expected. Since some absorption is always present, expression (5.1.7.3), which includes the factor $8/3$, should be used for very thick crystals. In the presence of absorption, however, expression (5.1.7.8) for the reflected intensity for thin crystals does tend towards that for thick crystals as the crystal thickness increases.

Comparison with geometrical theory. When t/Λ_B is very small (thin crystals or weak reflections), (5.1.7.8) tends towards

$$I_{hi} = R^2 \lambda^2 t |F_h|^2 / (V^2 \gamma_o \sin 2\theta), \quad (5.1.7.10)$$

which is the expression given by geometrical theory. If we call this intensity $I_{hi}(\text{geom.})$, comparison of expressions (5.1.7.8) and (5.1.7.10) shows that the integrated intensity for crystals of intermediate thickness can be written

$$I_{hi} = I_{hi}(\text{geom.}) \frac{\tanh(\pi t / \Lambda_B)}{(\pi t / \Lambda_B)}, \quad (5.1.7.11)$$

which is the expression given by Darwin (1922) for primary extinction.

5.1.7.2.2. Absorbing crystals

Reflected intensity. The intensity of the reflected wave for a thin absorbing crystal is

$$I_h = |\gamma| \left| \frac{D_h^{(a)}}{D_o^{(a)}} \right|^2$$

$$= \left| \frac{F_h}{F_o} \right| \frac{\cosh 2b - \cos 2a}{L \cosh 2b + (L^2 - 1)^{1/2} \sinh 2b - \cos(2a + 2\Psi')}, \quad (5.1.7.12)$$

where

$$2a = [\pi t / \Lambda_B] \rho \cos(\beta + \omega),$$

$$2b = [\pi t / \Lambda_B] \rho \sin(\beta + \omega).$$

L , ρ and ψ' are defined in (5.1.7.5), β is defined in (5.1.3.7) and ω is the phase angle of $(\eta^2 - 1)^{1/2}$.

Comparison with geometrical theory. When t/Λ_B decreases towards zero, expression (5.1.7.12) tends towards $[\sin(\pi t \eta / \Lambda_B) / \eta]^2$; using (5.1.3.5) and (5.1.3.8), it can be shown that expression (5.1.7.12) can be written, in the non-absorbing symmetric case, as

$$I_h = \frac{R^2 \lambda^2 C^2 |F_h|^2 t^2}{V^2 \sin^2 \theta} \left\{ \frac{\sin[2\pi k \cos(\theta) t \Delta\theta]}{[2\pi k \cos(\theta) t \Delta\theta]} \right\}^2, \quad (5.1.7.13)$$

where d is the lattice spacing and $\Delta\theta$ is the difference between the angle of incidence and the middle of the reflection domain. This expression is the classical expression given by geometrical theory [see, for instance, James (1950)].

5.1.8. Real waves

5.1.8.1. Introduction

The preceding sections have dealt with the diffraction of a plane wave by a semi-infinite perfect crystal. This situation is actually never encountered in practice, although with various devices, in particular using synchrotron radiation, it is possible to produce highly collimated monochromated waves which behave like pseudo plane waves. The wave from an X-ray tube is best represented by a spherical wave. The first experimental proof of this fact is due to Kato & Lang (1959) in the transmission case. Kato extended the dynamical theory to spherical waves for non-absorbing (1961a,b) and absorbing crystals (1968a,b). He expanded the incident spherical wave into plane waves by a Fourier transform, applied plane-wave dynamical theory to each of these components and took the Fourier transform of the result again in order to obtain the final solution. Another method for treating the problem was used by Takagi (1962, 1969), who solved the propagation equation in a medium where the lateral extension of the incident wave is limited and where the wave amplitudes depend on the lateral coordinates. He showed that in this case the set of fundamental linear equations (5.1.2.20) should be replaced by a set of partial differential equations. This treatment can be applied equally well to a perfect or to an imperfect crystal. In the case of a perfect crystal, Takagi showed that these equations have an analytical solution that is identical with Kato's result. Urugami (1969, 1970) observed the spherical wave in the Bragg (reflection) case, interpreting the observed intensity distribution using Takagi's theory. Saka *et al.* (1973) subsequently extended Kato's theory to the Bragg case.

Without using any mathematical treatment, it is possible to make some elementary remarks by considering the fact that the divergence of the incident beam falling on the crystal from the source is much larger than the angular width of the reflection domain. Fig. 5.1.8.1(a) shows a spatially collimated beam falling on a crystal in the transmission case and Fig. 5.1.8.1(b) represents the corresponding situation in reciprocal space. Since the divergence of the incident beam is larger than the angular width of the dispersion surface, the plane waves of its Fourier expansion will excite every point of both branches of the dispersion surface. The propagation directions of the corresponding wavefields will cover the angular range between those of the incident and reflected beams (Fig. 5.1.8.1a) and fill what is called the *Borrmann triangle*. The intensity distribution within this triangle has interesting properties, as described in the next two sections.

5.1.8.2. Borrmann triangle

The first property of the Borrmann triangle is that the angular density of the wavefield paths is inversely proportional to the

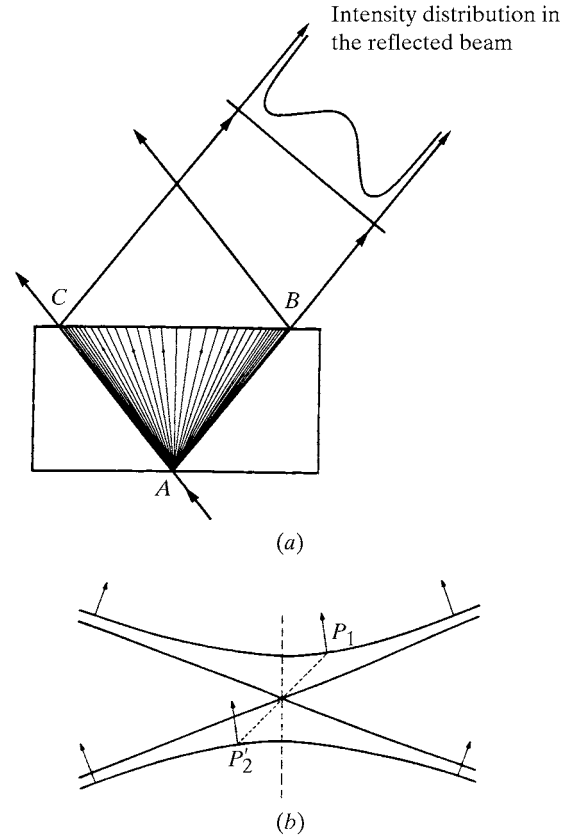


Fig. 5.1.8.1. Borrmann triangle. When the incident beam is divergent, the whole dispersion surface is excited and the wavefields excited inside the crystal propagate within a triangle filling all the space between the incident direction, AC, and the reflected direction, AB. Along any direction Ap within this triangle two wavefields propagate, having as tie points two conjugate points, P and P' , at the extremities of a diameter of the dispersion surface. (a) Direct space; (b) reciprocal space.

curvature of the dispersion surface around their tie points. Let us consider an incident wavepacket of angular width $\delta(\Delta\theta)$. It will generate a packet of wavefields propagating within the Borrmann triangle. The angular width $\Delta\alpha$ (Fig. 5.1.8.2) between the paths of the corresponding wavefields is related to the radius of curvature $\mathcal{R}$ of the dispersion surface by

$$\mathcal{A} = \Delta\alpha / \delta(\Delta\theta) = k \cos \theta (\mathcal{R} \cos \alpha), \quad (5.1.8.1)$$

where α is the angle between the wavefield path and the lattice planes [equation (5.1.2.26)] and $\mathcal{A}$ is called the amplification ratio. In the middle of the reflecting domain, the radius of curvature of the dispersion surface is very much shorter than its value, k , far from it (about 10^4 times shorter) and the amplification ratio is therefore very large. As a consequence, the energy of a wavepacket of width $\delta(\Delta\theta)$ in reciprocal space is spread in direct space over an angle $\Delta\alpha$ given by (5.1.8.1). The intensity distribution on the exit surface BC (Fig. 5.1.8.1a) is therefore proportional to $I_h / \mathcal{A}$. It is represented in Fig. 5.1.8.3 for several values of the absorption coefficient:

(i) Small values of $\mu_0 t$ (less than 2 or 3) (Fig. 5.1.8.3a). The intensity distribution presents a wide minimum in the centre where the density of wavefields is small and increases very sharply at the edges where the density of wavefields is large, although it is the reverse for the reflecting power I_{hj} . This effect, called the *margin effect*, was predicted qualitatively by Borrmann (1959) and von Laue (1960), demonstrated experimentally by Kato & Lang (1959), and calculated by Kato (1960).

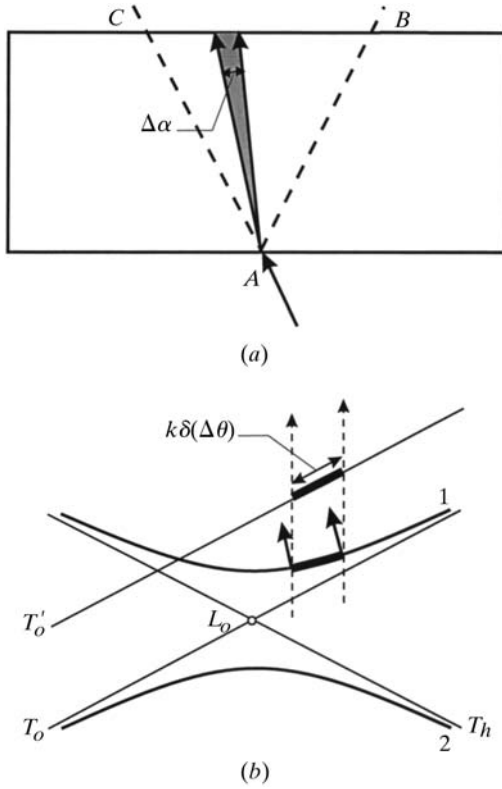


Fig. 5.1.8.2. Packet of wavefields of divergence $\Delta\alpha$ excited in the crystal by an incident wavepacket of angular width $\delta(\Delta\theta)$. (a) Direct space; (b) reciprocal space.

(ii) Large values of $\mu_0 t$ (of the order of 6 or more) (Fig. 5.1.8.3b). The predominant factor is now anomalous absorption. The wavefields propagating along the edges of the Borrmann triangle undergo normal absorption, while those propagating parallel to the lattice planes (or nearly parallel) correspond to tie points in the centre of the dispersion surface and undergo anomalously low absorption. The intensity distribution now has a maximum in the centre. For values of μt larger than 10 or so, practically only the wavefields propagating parallel to the lattice planes go through the crystal, which acts as a wave guide: this is the Borrmann effect.

5.1.8.3. Spherical-wave Pendellösung

Fig. 5.1.8.4 shows that along any path Ap inside the Borrmann triangle two wavefields propagate, one with tie point P_1 , on branch 1, the other with the point P'_2 , on branch 2. These two points lie on the extremities of a diameter of the dispersion surface. The two wavefields interfere, giving rise to *Pendellösung* fringes, which were first observed by Kato & Lang (1959), and calculated by Kato (1961b). These fringes are of course quite different from the plane-wave *Pendellösung* fringes predicted by Ewald (Section 5.1.6.3) because the tie points of the interfering wavefields are different and their period is also different, but they have in common the fact that they result from interference between wavefields belonging to different branches of the dispersion surface.

Kato has shown that the intensity distribution at any point at the base of the Borrmann triangle is proportional to

$$\left\{ J_0 \left[A(x_o x_h)^{1/2} \right] \right\}^2,$$

where $A = 2\pi(\gamma_o \gamma_h)^{1/2} / (\Lambda_L \sin \theta)$ and x_o and x_h are the distances of p from the sides AB and AC of the Borrmann triangle (Fig. 5.1.8.4). The equal-intensity fringes are therefore located along the locus of the points in the triangle for which the product of the distances to the

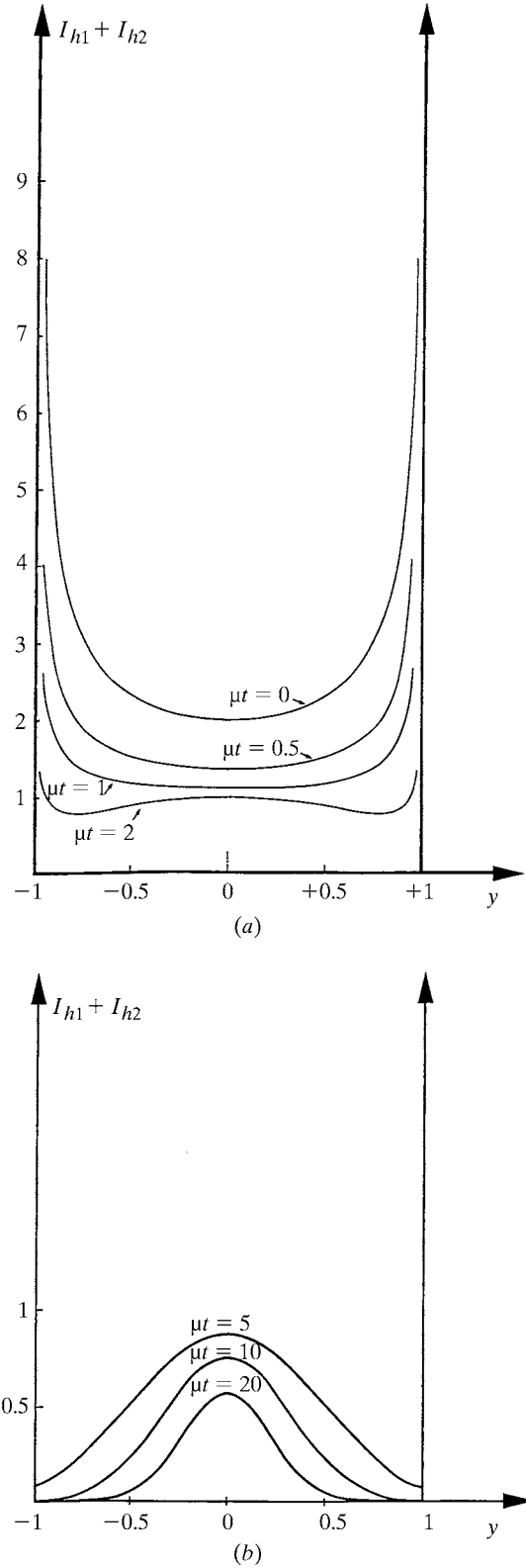


Fig. 5.1.8.3. Intensity distribution along the base of the Borrmann triangle. y is a normalized coordinate along BC . (a) Small values of μt . The interference (spherical-wave *Pendellösung*) between branch 1 and branch 2 is neglected. (b) Large values of μt .

sides is constant, that is hyperbolas having AB and AC as asymptotes (Fig. 5.1.8.4b). These fringes can be observed on a section topograph of a wedge-shaped crystal (Fig. 5.1.8.5). The technique of section topography is described in *IT C*, Section 2.7.2.2. The *Pendellösung* distance Λ_L depends on the polarization

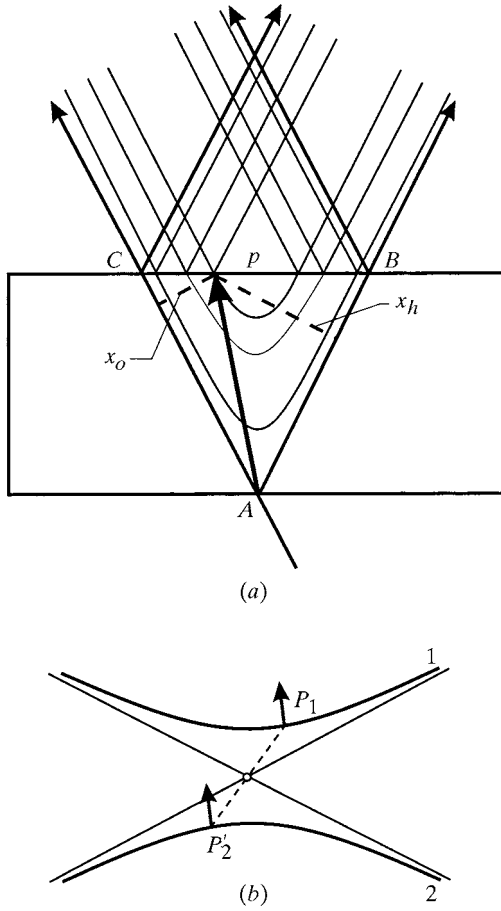


Fig. 5.1.8.4. Interference at the origin of the *Pendellösung* fringes in the case of an incident spherical wave. (a) Direct space; (b) reciprocal space.

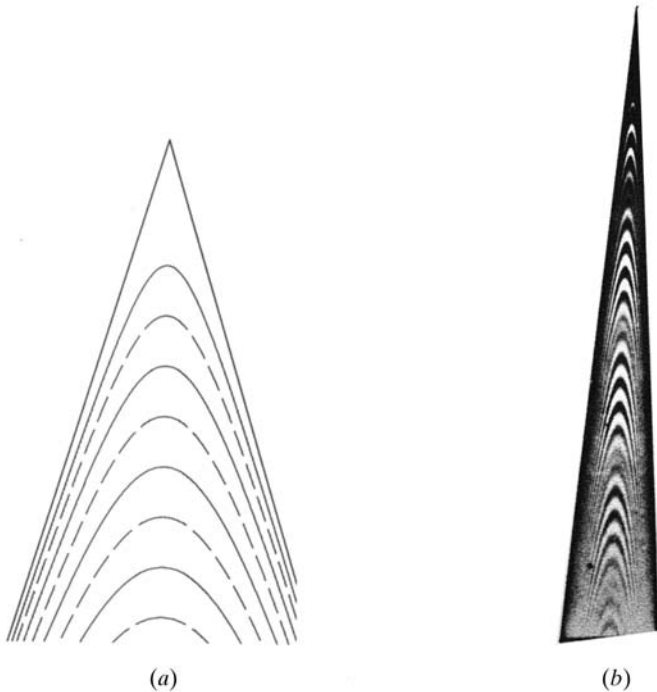


Fig. 5.1.8.5. Spherical-wave *Pendellösung* fringes observed on a wedge-shaped crystal. (a) Computer simulation (solid lines: maxima; dashed lines: minima). (b) X-ray section topograph of a wedge-shaped silicon crystal (444 reflection, Mo $K\alpha$ radiation).

state [see equation (5.1.3.8)]. If the incident wave is unpolarized, one observes the superposition of the *Pendellösung* fringes corresponding to the two states of polarization, parallel and perpendicular to the plane of incidence. This results in a beat effect, which is clearly visible in Fig. 5.1.8.5.

Appendix 5.1.1.

A5.1.1.1. Dielectric susceptibility – classical derivation

Under the influence of the incident electromagnetic radiation, the medium becomes polarized. The dielectric susceptibility, which relates this polarization to the electric field, thus characterizes the interaction of the medium and the electromagnetic wave. The classical derivation of the dielectric susceptibility, χ , which is summarized here is only valid for a very high frequency which is also far from an absorption edge. Let us consider an electromagnetic wave,

$$\mathbf{E} = \mathbf{E}_0 \exp 2\pi i(\nu t - \mathbf{k} \cdot \mathbf{r}),$$

incident on a bound electron. The electron behaves as if it were held by a spring with a linear restoring force and is an oscillator with a resonant frequency ν_0 . The equation of its motion is written in the following way:

$$m \, d^2 \mathbf{a} / dt^2 = -4\pi^2 \nu_0 m \mathbf{a} = \mathbf{F},$$

where the driving force $\mathbf{F}$ is due to the electric field of the wave and is equal to $-e\mathbf{E}$. The magnetic interaction is neglected here.

The solution of the equation of motion is

$$\mathbf{a} = -e\mathbf{E} / [4\pi^2 m(\nu_0 - \nu^2)].$$

The resonant frequencies of the electrons in atoms are of the order of the ultraviolet frequencies and are therefore much smaller than X-ray frequencies. They can be neglected and the expression of the amplitude of the electron reduces to

$$\mathbf{a} = e\mathbf{E} / (4\pi^2 \nu^2).$$

The dipolar moment is therefore

$$\mathcal{M} = -e\mathbf{a} = -e^2 \mathbf{E} / (4\pi^2 \nu^2 m).$$

von Laue assumes that the negative charge is distributed continuously all over space and that the charge of a volume element $d\tau$ is $-e\rho \, d\tau$, where ρ is the electronic density. The electric moment of the volume element is

$$d\mathcal{M} = -e^2 \rho \mathbf{E} \, d\tau / (4\pi^2 \nu^2 m).$$

The polarization is equal to the moment per unit volume:

$$\mathbf{P} = d\mathcal{M} / d\tau = -e^2 \rho \mathbf{E} / (4\pi^2 \nu^2 m).$$

It is related to the electric field and electric displacement through

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 (1 + \chi) \mathbf{E}. \quad (\text{A5.1.1.1})$$

We finally obtain the expression of the dielectric susceptibility,

$$\chi = -e^2 \rho / (4\pi^2 \epsilon_0 \nu^2 m) = -R \lambda^2 \rho / \pi, \quad (\text{A5.1.1.2})$$

where $R = e^2 / (4\pi \epsilon_0 m c^2)$ ($= 2.81794 \times 10^{-15} \text{ m}$) is the classical radius of the electron.

A5.1.1.2. Maxwell's equations

The electromagnetic field is represented by two vectors, $\mathbf{E}$ and $\mathbf{B}$, which are the electric field and the magnetic induction, respectively. To describe the interaction of the field with matter, three other vectors must be taken into account, the electrical current density, $\mathbf{j}$, the electric displacement, $\mathbf{D}$, and the magnetic field, $\mathbf{H}$. The space and time derivatives of these vectors are related in a continuous

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medium by Maxwell's equations:

$$\begin{aligned}\text{curl } \mathbf{E} &= -\partial \mathbf{B} / \partial t \\ \text{curl } \mathbf{H} &= \partial \mathbf{D} / \partial t + \mathbf{j} \\ \text{div } \mathbf{D} &= \rho \\ \text{div } \mathbf{B} &= 0,\end{aligned}\quad (\text{A5.1.1.3})$$

where ρ is the electric charge density.

The electric field and the electric displacement on the one hand, and the magnetic field and the magnetic induction on the other hand, are related by the so-called *material relations*, which describe the reaction of the medium to the electromagnetic field:

$$\begin{aligned}\mathbf{D} &= \varepsilon \mathbf{E} \\ \mathbf{B} &= \mu \mathbf{H},\end{aligned}$$

where ε and μ are the dielectric constant and the magnetic permeability, respectively.

These equations are complemented by the following boundary conditions at the surface between two neighbouring media:

$$\begin{aligned}\mathbf{E}_{T1} - \mathbf{E}_{T2} &= 0 & \mathbf{D}_{N1} - \mathbf{D}_{N2} &= 0 \\ \mathbf{H}_{T1} - \mathbf{H}_{T2} &= 0 & \mathbf{B}_{N1} - \mathbf{B}_{N2} &= 0.\end{aligned}\quad (\text{A5.1.1.4})$$

From the second and the third equations of (A5.1.1.3), and using the identity

$$\text{div} (\text{curl } \mathbf{y}) = 0,$$

it follows that

$$\text{div } \mathbf{j} + \partial \rho / \partial t = 0. \quad (\text{A5.1.1.5})$$

A5.1.1.3. Propagation equation

In a vacuum, ρ and $\mathbf{j}$ are equal to zero, and the first two equations of (A5.1.1.3) can be written

$$\begin{aligned}\text{curl } \mathbf{E} &= -\mu_0 \partial \mathbf{H} / \partial t \\ \text{curl } \mathbf{H} &= \varepsilon_0 \partial \mathbf{E} / \partial t,\end{aligned}$$

where ε_0 and μ_0 are the dielectric constant and the magnetic permeability of a vacuum, respectively.

By taking the curl of both sides of the second equation, it follows that

$$\text{curl curl } \mathbf{E} = -\varepsilon_0 \mu_0 \partial^2 \mathbf{E} / \partial t^2.$$

Using the identity $\text{curl curl } \mathbf{E} = \text{grad div } \mathbf{E} - \Delta \mathbf{E}$, the relation $\varepsilon_0 \mu_0 = 1/c^2$, where c is the velocity of light, and noting that $\text{div } \mathbf{E} = \text{div } \mathbf{D} = 0$, one finally obtains the equation of propagation of an electromagnetic wave in a vacuum:

$$\Delta \mathbf{E} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}. \quad (\text{A5.1.1.6})$$

Its simplest solution is a plane wave:

$$\mathbf{E} = \mathbf{E}_0 \exp 2\pi i(\nu t - \mathbf{k} \cdot \mathbf{r}),$$

of which the wavenumber $k = 1/\lambda$ and the frequency ν are related by

$$k = \nu/c.$$

The basic properties of the electromagnetic field are described, for instance, in Born & Wolf (1983).

The propagation equation of X-rays in a crystalline medium is derived following von Laue (1960). The interaction of X-rays with charged particles is inversely proportional to the mass of the particle and the interaction with the nuclei can be neglected. As a first approximation, it is also assumed that the magnetic interaction of X-rays with matter is neglected, and that the magnetic permeability μ can be taken as equal to the magnetic permeability of a vacuum, μ_0 . It is further assumed that the negative and positive charges are both continuously distributed and compensate each other in such a way that there is neutrality and no current everywhere: ρ and $\mathbf{j}$ are equal to zero and $\text{div } \mathbf{D}$ is therefore also equal to zero. The electric displacement is related to the electric field by (A5.1.1.1) and the electric part of the interaction of X-rays with matter is expressed through the dielectric susceptibility χ , which is given by (A5.1.1.2). This quantity is proportional to the electron density and varies with the space coordinates. It is therefore concluded that $\text{div } \mathbf{E}$ is different from zero, as opposed to what happens in a vacuum. For this reason, the propagation equation of X-rays in a crystalline medium is expressed in terms of the electric displacement rather than in terms of the electric field. It is obtained by eliminating $\mathbf{H}$, $\mathbf{B}$ and $\mathbf{E}$ in Maxwell's equations and taking into account the above assumptions:

$$\Delta \mathbf{D} + \text{curl curl } \chi \mathbf{D} = \frac{1}{c^2} \frac{\partial^2 \mathbf{D}}{\partial t^2}. \quad (\text{A5.1.1.7})$$

Only coherent scattering is taken into account here, that is, scattering without frequency change. The solution is therefore a wave of the form

$$\mathbf{D}(\mathbf{r}) \exp 2\pi i \nu t.$$

By replacing $\mathbf{D}$ with this expression in equation (A5.1.1.7), one finally obtains the propagation equation (5.1.2.2) (Section 5.1.2.1).

In a crystalline medium, χ is a triply periodic function of the space coordinates and the solutions of this equation are given in terms of Fourier series which can be interpreted as sums of electromagnetic plane waves. Each of these waves is characterized by its wavevector, $\mathbf{K}_h$, its electric displacement, $\mathbf{D}_h$, its electric field, $\mathbf{E}_h$, and its magnetic field, $\mathbf{H}_h$. It can be shown that, as a consequence of the fact that $\text{div } \mathbf{D} = 0$ and $\text{div } \mathbf{E} \neq 0$, $\mathbf{D}_h$ is a transverse wave ($\mathbf{D}_h$, $\mathbf{H}_h$ and $\mathbf{K}_h$ are mutually orthogonal) while $\mathbf{E}_h$ is not. The electric displacement is therefore a more suitable vector for describing the state of the field inside the crystal than the electric field.

A5.1.1.4. Poynting vector

The propagation direction of the energy of an electromagnetic wave is given by that of the Poynting vector defined by (see Born & Wolf, 1983)

$$\mathbf{S} = \mathcal{R}(\mathbf{E} \wedge \mathbf{H}^*), \quad (\text{A5.1.1.8})$$

where $\mathcal{R}()$ means real part of $()$.

The intensity I of the radiation is equal to the energy crossing unit area per second in the direction normal to that area. It is given by the value of the Poynting vector averaged over a period of time long compared with $1/\nu$:

$$\mathbf{I} = |\mathbf{S}| = c\varepsilon |\mathbf{E}|^2 = c|\mathbf{D}|^2/\varepsilon.$$

5.2. Dynamical theory of electron diffraction

BY A. F. MOODIE, J. M. COWLEY AND P. GOODMAN

5.2.1. Introduction

Since electrons are charged, they interact strongly with matter, so that the single scattering approximation has a validity restricted to thin crystals composed of atoms of low atomic number. Further, at energies of above a few tens of keV, the wavelength of the electron is so short that the geometry of two-beam diffraction can be approximated in only small unit cells.

It is therefore necessary to develop a scattering theory specific to electrons and, preferably, applicable to imaging as well as to diffraction. The development, started by Born (1926) and Bethe (1928), and continuing into the present time, is the subject of an extensive literature, which includes reviews [for instance: Howie (1978), Humphreys (1979)] and historical accounts (Goodman, 1981), and is incorporated in Chapter 5.1. Here, an attempt will be made to present only that outline of the main formulations which, it is hoped, will help the nonspecialist in the use of the tables. No attempt will be made to follow the historical development, which has been tortuous and not always logical, but rather to seek the simplest and most transparent approach that is consistent with brevity. Only key points in proofs will be sketched in an attempt to display the nature, rather than the rigorous foundations of the arguments.

5.2.2. The defining equations

No many-body effects have yet been detected in the diffraction of fast electrons, but the velocities lie well within the relativistic region. The one-body Dirac equation would therefore appear to be the appropriate starting point. Fujiwara (1962), using the scattering matrix, carried through the analysis for forward scattering, and found that, to a very good approximation, the effects of spin are negligible, and that the solution is the same as that obtained from the Schrödinger equation provided that the relativistic values for wavelength and mass are used. In effect a Klein–Gordon equation (Messiah, 1965) can be used in electron diffraction (Buxton, 1978) in the form

$$\nabla^2 \psi_b + \frac{8\pi^2 m |e| \varphi}{h^2} \psi_b + \frac{8\pi^2 m_0 |e| W}{h^2} \left(1 + \frac{|e| W}{2m_0 c^2}\right) \psi_b = 0.$$

Here, W is the accelerating voltage and φ , the potential in the crystal, is defined as being positive. The relativistic values for mass and wavelength are given by $m = m_0(1 - v^2/c^2)^{-1/2}$, and taking ‘ e ’ now to represent the modulus of the electronic charge, $|e|$,

$$\lambda = h[2m_0 e W (1 + e W / 2m_0 c^2)]^{-1/2},$$

and the wavefunction is labelled with the subscript b in order to indicate that it still includes back scattering, of central importance to LEED (low-energy electron diffraction).

In more compact notation,

$$[\nabla^2 + k^2(1 + \varphi/W)]\psi_b = (\nabla^2 + k^2 + 2k\sigma\varphi)\psi_b = 0. \quad (5.2.2.1)$$

Here $k = |\mathbf{k}|$ is the scalar wavenumber of magnitude $2\pi/\lambda$, and the interaction constant $\sigma = 2\pi m e \lambda / h^2$. This constant is approximately 10^{-3} for 100 kV electrons.

For fast electrons, φ/W is a slowly varying function on a scale of wavelength, and is small compared with unity. The scattering will therefore be peaked about the direction defined by the incident beam, and further simplification is possible, leading to a forward-scattering solution appropriate to HEED (high-energy electron diffraction).

5.2.3. Forward scattering

A great deal of geometric detail can arise at this point and, further, there is no generally accepted method for approximation, the various procedures leading to numerically negligible differences and to expressions of precisely the same form. Detailed descriptions of the geometry are given in the references.

The entrance surface of the specimen, in the form of a plate, is chosen as the x, y plane, and the direction of the incident beam is taken to be close to the z axis. Components of the wavevector are labelled with suffixes in the conventional way; $\mathbf{K}_0 = \mathbf{k}_x + \mathbf{k}_y$ is the transverse wavevector, which will be very small compared to $\mathbf{k}_z$. In this notation, the excitation error for the reflection is given by

$$\zeta_h = \frac{K_0^2 - |\mathbf{K}_0 + 2\pi\mathbf{h}|^2}{4\pi|\mathbf{k}_z|}.$$

An intuitive method argues that, since $\varphi/W \ll 1$, then the component of the motion along z is little changed by scattering. Hence, making the substitution $\psi_b = \psi \exp\{ik_z z\}$ and neglecting $\partial^2 \psi / \partial z^2$, equation (5.2.2.1) becomes

$$\frac{\partial \psi}{\partial z} = i \left[\frac{1}{2k_z} (\nabla_{x,y}^2 + K_0^2) + \sigma \varphi \right] \psi, \quad (5.2.3.1)$$

where

$$\nabla_{x,y}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2},$$

and $\psi(x, y, 0) = \exp\{i(k_x x + k_y y)\}$.

Equation (5.2.3.1) is of the form of a two-dimensional time-dependent Schrödinger equation, with the z coordinate replacing time. This form has been extensively discussed. For instance, Howie (1966) derived what is essentially this equation using an expansion in Bloch waves, Berry (1971) used a Green function in a detailed and rigorous derivation, and Goodman & Moodie (1974), using methods due to Feynman, derived the equation as the limit of the multislice recurrence relation. A method due to Coronas *et al.* (1982) brings out the relationship between the HEED and LEED equations. Equation (5.2.2.1) is cast in the form of a first-order system,

$$\frac{\partial}{\partial z} \begin{pmatrix} \psi_b \\ \frac{\partial \psi_b}{\partial z} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -(\nabla_{x,y}^2 + k^2 + 2k\sigma\varphi) & 0 \end{pmatrix} \begin{pmatrix} \psi_b \\ \frac{\partial \psi_b}{\partial z} \end{pmatrix}.$$

A splitting matrix is introduced to separate the wavefunction into the forward and backward components, $\psi_b^\pm$, and the fast part of the phase is factored out, so that $\psi_b^\pm = \psi^\pm \exp\{\pm ik_z z\}$. In the resulting matrix differential equation, the off-diagonal terms are seen to be small for fast electrons, and equation (5.2.2.1) reduces to the pair of equations

$$\frac{\partial \psi^\pm}{\partial z} = \pm i \left[\frac{1}{2k_z} (\nabla_{x,y}^2 + K_0^2) + \sigma \varphi \right] \psi^\pm. \quad (5.2.3.2)$$

The equation for $\psi^\pm$ is the Lontovich & Fock (1946) parabolic equation.

5.2.4. Evolution operator

Equation (5.2.3.1) is a standard and much studied form, so that many techniques are available for the construction of solutions. One of the most direct utilizes the causal evolution operator. A recent account is given by Gratiis & Portier (1983).

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In terms of the ‘Hamiltonian’ of the two-dimensional system,

$$-\mathbf{H}(z) \equiv \frac{1}{2k_z} (\nabla_{x,y}^2 + K_0^2) + \sigma\varphi,$$

the evolution operator $\mathbf{U}(z, z_0)$, defined by $\psi(z) = \mathbf{U}(z, z_0)\psi_0$, satisfies

$$i \frac{\partial}{\partial z} \mathbf{U}(z, z_0) = \mathbf{H}(z) \mathbf{U}(z, z_0), \quad (5.2.4.1a)$$

or

$$\mathbf{U}(z, z_0) = 1 - i \int_{z_0}^z \mathbf{U}(z, z_1) \mathbf{H}(z_1) dz_1. \quad (5.2.4.1b)$$

5.2.5. Projection approximation – real-space solution

Many of the features of the more general solutions are retained in the practically important projection approximation in which $\varphi(x, y, z)$ is replaced by its projected mean value $\varphi_p(x, y)$, so that the corresponding Hamiltonian $\mathbf{H}_p$ does not depend on z . Equation (5.2.4.1b) can then be solved directly by iteration to give

$$\mathbf{U}_p(z, z_0) = \exp\{-i\mathbf{H}_p(z - z_0)\}, \quad (5.2.5.1)$$

and the solution may be verified by substitution into equation (5.2.4.1a).

Many of the results of dynamical theory can be obtained by expansion of equation (5.2.5.1) as

$$\mathbf{U}_p \equiv \mathbf{1} - i\mathbf{H}_p(z - z_0) + \frac{i^2}{2!} \mathbf{H}_p^2(z - z_0) - \dots,$$

followed by the direct evaluation of the differentials. Such expressions can be used, for instance, to explore symmetries in image space.

5.2.6. Semi-reciprocal space

In the derivation of electron-diffraction equations, it is more usual to work in semi-reciprocal space (Tournarie, 1962). This can be achieved by transforming equation (5.2.2.1) with respect to x and y but not with respect to z , to obtain Tournarie’s equation

$$\frac{d^2|U\rangle}{dz^2} = -\mathbf{M}_b(z)|U\rangle. \quad (5.2.6.1a)$$

Here $|U\rangle$ is the column vector of scattering amplitudes and $\mathbf{M}_b(z)$ is a matrix, appropriate to LEED, with $\mathbf{k}$ vectors as diagonal elements and Fourier coefficients of the potential as nondiagonal elements.

This equation is factorized in a manner parallel to that used on the real-space equation [equation (5.2.3.1)] (Lynch & Moodie, 1972) to obtain Tournarie’s forward-scattering equation

$$\frac{d|U^\pm\rangle}{dz} = \pm i\mathbf{M}^\pm(z)|U^\pm\rangle, \quad (5.2.6.1b)$$

where

$$\mathbf{M}^\pm(z) = \pm[\mathbf{K} + (1/2)\mathbf{K}^{-1}V(z)],$$

$$[K_{ij}] = \delta_{ij}K_i,$$

and

$$[V_{ij}] = 2k_z \sum_l V_{i-j} \exp\{-2\pi ilz\},$$

where $V_i \equiv \sigma v_i$ are the scattering coefficients and v_i are the structure amplitudes in volts. In order to simplify the electron-diffraction expression, the third crystallographic index ‘ l ’ is taken to represent the periodicity along the z direction.

The double solution involving $\mathbf{M}$ of equation (5.2.6.1b) is of interest in displaying the symmetry of reciprocity, and may be compared with the double solution obtained for the real-space equation [equation (5.2.3.2)]. Normally the $\mathbf{M}^+$ solution will be followed through to give the fast-electron forward-scattering equations appropriate in HEED. $\mathbf{M}^-$, however, represents the equivalent set of equations corresponding to the z reversed reciprocity configuration. Reciprocity solutions will yield diffraction symmetries in the forward direction when coupled with crystal-inverting symmetries (Section 2.5.3).

Once again we set out to solve the forward-scattering equation (5.2.6.1a,b) now in semi-reciprocal space, and define an operator $\mathbf{Q}(z)$ [compare with equation (5.2.4.1a)] such that

$$|U_z\rangle = \mathbf{Q}_z|U_0\rangle \quad \text{with} \quad U_0 = |0\rangle;$$

i.e., $\mathbf{Q}_z$ is an operator that, when acting on the incident wavevector, generates the wavefunction in semi-reciprocal space.

Again, the differential equation can be transformed into an integral equation, and once again this can be iterated. In the projection approximation, with $\mathbf{M}$ independent of z , the solution can be written as

$$\mathbf{Q}_p = \exp\{i\mathbf{M}_p(z - z_0)\}.$$

A typical off-diagonal element is given by $V_{i-j}/\cos\theta_i$, where θ_i is the angle through which the beam is scattered. It is usual in the literature to find that $\cos\theta_i$ has been approximated as unity, since even the most accurate measurements are, so far, in error by much more than this amount.

This expression for $\mathbf{Q}_p$ is Sturkey’s (1957) solution, a most useful relation, written explicitly as

$$|U\rangle = \exp\{i\mathbf{M}_p T\}|0\rangle \quad (5.2.6.2)$$

with T the thickness of the crystal, and $|0\rangle$, the incident state, a column vector with the first entry unity and the rest zero.

$$\mathbf{S} = \exp\{i\mathbf{M}_p T\}$$

is a unitary matrix, so that in this formulation scattering is described as rotation in Hilbert space.

5.2.7. Two-beam approximation

In the two-beam approximation, as an elementary example, equation (5.2.6.2) takes the form

$$\begin{pmatrix} u_0 \\ u_h \end{pmatrix} = \exp\left\{i \begin{pmatrix} 0 & V^*(\mathbf{h}) \\ V(\mathbf{h}) & K_h \end{pmatrix} T\right\} \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (5.2.7.1)$$

If this expression is expanded directly as a Taylor series, it proves surprisingly difficult to sum. However, the symmetries of Clifford algebra can be exploited by summing in a Pauli basis thus,

$$\begin{aligned} & \exp\left\{i \begin{pmatrix} 0 & V^*(\mathbf{h}) \\ V(\mathbf{h}) & K_h \end{pmatrix} T\right\} \\ &= \exp\left\{i \frac{K_h T}{2}\right\} \mathbf{E} \exp\left\{i \left(\frac{K_h}{2} \boldsymbol{\sigma}_3 + V^R \boldsymbol{\sigma}_1 - V^I \boldsymbol{\sigma}_2\right) T\right\}. \end{aligned}$$

Here, the $\boldsymbol{\sigma}_i$ are the Pauli matrices

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_3 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix},$$

$$\mathbf{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

and V^R, V^I are the real and imaginary parts of the complex scattering coefficients appropriate to a noncentrosymmetric crystal,

5. DYNAMICAL THEORY AND ITS APPLICATIONS

i.e. $V_h = V^R + iV^I$. Expanding,

$$\begin{aligned} & \exp\left\{i\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right)T\right\} \\ &= \mathbf{E} + i\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right)T \\ & \quad - \frac{1}{2}\left(\frac{K_h}{2}\sigma_3 + V^R\sigma_1 - V^I\sigma_2\right)^2 T^2 + \dots, \end{aligned}$$

using the anti-commuting properties of σ_i :

$$\begin{cases} \sigma_i\sigma_j + \sigma_j\sigma_i = 0 \\ \sigma_i\sigma_i = 1 \end{cases}$$

and putting $[(K_h/2)^2 + V(\mathbf{h})V^*(\mathbf{h})] = \Omega$, $\mathbf{M}_2 = [(K_h/2)\sigma_3 + V^R\sigma_1 - V^I\sigma_2]$, so that $\mathbf{M}_2^2 = \Omega\mathbf{E}$ and $\mathbf{M}_2^3 = \Omega\mathbf{M}_2$, the powers of the matrix can easily be evaluated. They fall into odd and even series, corresponding to sine and cosine, and the classical two-beam approximation is obtained in the form

$$\mathbf{Q}_2 = \exp\{i(K_h/2)T\}\mathbf{E}\left[(\cos\Omega^{1/2}T)\mathbf{E} + i\left(\frac{\sin\Omega^{1/2}T}{\Omega^{1/2}}\right)\mathbf{M}_2\right]. \quad (5.2.7.2)$$

This result was first obtained by Blackman (1939), using Bethe's dispersion formulation. Ewald and, independently, Darwin, each with different techniques, had, in establishing the theoretical foundations for X-ray diffraction, obtained analogous results (see Section 5.1.3).

The two-beam approximation, despite its simplicity, exemplifies some of the characteristics of the full dynamical theory, for instance in the coupling between beams. As Ewald pointed out, a formal analogy can be found in classical mechanics with the motion of coupled pendulums. In addition, the functional form $(\sin ax)/x$, deriving from the shape function of the crystal emerges, as it does, albeit less obviously, in the N -beam theory.

This derivation of equation (5.2.7.2) exhibits two-beam diffraction as a typical two-level system having analogies with, for instance, lasers and nuclear magnetic resonance and exhibiting the symmetries of the special unitary group $SU(2)$ (Gilmire, 1974).

5.2.8. Eigenvalue approach

In terms of the eigenvalues and eigenvectors, defined by

$$\mathbf{H}_p|j\rangle = \gamma_j|j\rangle,$$

the evolution operator can be written as

$$\mathbf{U}(z, z_0) = \int |j\rangle \exp\{\gamma_j(z - z_0)\} \langle j| dj.$$

This integration becomes a summation over discrete eigen states when an infinitely periodic potential is considered.

Despite the early developments by Bethe (1928), an N -beam expression for a transmitted wavefunction in terms of the eigenvalues and eigenvectors of the problem was not obtained until Fujimoto (1959) derived the expression

$$U_h = \sum_j \psi_0^{j*} \psi_h^j \exp\{-i2\pi\gamma_j T\}, \quad (5.2.8.1)$$

where ψ_h^j is the h component of the j eigenvector with eigenvalue γ_j .

This expression can now be related to those obtained in the other formulations. For example, Sylvester's theorem (Frazer *et al.*, 1963) in the form

$$f(\mathbf{M}) = \sum_j \mathbf{A}_j f(\gamma_j)$$

when applied to Sturkey's solution yields

$$\Phi_h = \exp(i\mathbf{M}_p z) = \sum \mathbf{P}_j \exp\{i2\pi\gamma_j z\}$$

(Kainuma, 1968; Hurley *et al.*, 1978). Here, the $\mathbf{P}_j$ are projection operators, typically of the form

$$\mathbf{P}_j = \prod_{n \neq j} \frac{(\mathbf{M}_p - \mathbf{E}\gamma_n)}{\gamma_j - \gamma_n}.$$

On changing to a lattice basis, these transform to $\psi_0^{j*} \psi_h^j$.

Alternatively, the semi-reciprocal differential equation can be uncoupled by diagonalizing $\mathbf{M}_p$ (Goodman & Moodie, 1974), a process which involves the solution of the characteristic equation

$$|\mathbf{M}_p - \gamma_j \mathbf{E}| = 0. \quad (5.2.8.2)$$

5.2.9. Translational invariance

An important result deriving from Bethe's initial analysis, and not made explicit in the preceding formulations, is that the fundamental symmetry of a crystal, namely translational invariance, by itself imposes a specific form on wavefunctions satisfying Schrödinger's equation.

Suppose that, in a one-dimensional description, the potential in a Hamiltonian $\mathbf{H}_t(x)$ is periodic, with period t . Then,

$$\varphi(x+t) = \varphi(x)$$

and

$$\mathbf{H}_t \psi(x) = \mathbf{E} \psi(x).$$

Now define a translation operator

$$\mathbf{\Gamma} f(x) = f(x+t),$$

for arbitrary $f(x)$. Then, since $\mathbf{\Gamma} \varphi(x) = \varphi(x)$, and ∇^2 is invariant under translation,

$$\mathbf{\Gamma} \mathbf{H}_t(x) = \mathbf{H}_t(x)$$

and

$$\mathbf{\Gamma} \mathbf{H}_t(x) \psi(x) = \mathbf{H}_t(x+t) \psi(x+t) = \mathbf{H}_t(x) \mathbf{\Gamma} \psi(x).$$

Thus, the translation operator and the Hamiltonian commute, and therefore have the same eigenfunctions (but not of course the same eigenvalues), *i.e.*

$$\mathbf{\Gamma} \psi(x) = \alpha \psi(x).$$

This is a simpler equation to deal with than that involving the Hamiltonian, since raising the operator to an arbitrary power simply increments the argument

$$\mathbf{\Gamma}^m \psi(x) = \psi(x+mt) = \alpha^m \psi(x).$$

But $\psi(x)$ is bounded over the entire range of its argument, positive and negative, so that $|\alpha| = 1$, and α must be of the form $\exp\{i2\pi kt\}$.

Thus, $\psi(x+t) = \mathbf{\Gamma} \psi(x) = \exp\{i2\pi kt\} \psi(x)$, for which the solution is

$$\psi(x) = \exp\{i2\pi kt\} q(x)$$

with $q(x+t) = q(x)$.

This is the result derived independently by Bethe and Bloch. Functions of this form constitute bases for the translation group, and are generally known as Bloch functions. When extended in a direct fashion into three dimensions, functions of this form ultimately embody the symmetries of the Bravais lattice; *i.e.* Bloch functions are the irreducible representations of the translational component of the space group.

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5.2.10. Bloch-wave formulations

In developing the theory from the beginning by eigenvalue techniques, it is usual to invoke the periodicity of the crystal in order to show that the solutions to the wave equation for a given wavevector $\mathbf{k}$ are Bloch waves of the form

$$\psi = C(\mathbf{r}) \exp\{i\mathbf{k} \cdot \mathbf{r}\},$$

where $C(\mathbf{r})$ has the periodicity of the lattice, and hence may be expanded in a Fourier series to give

$$\psi = \sum_{\mathbf{h}} C_{\mathbf{h}}(\mathbf{k}) \exp\{i(\mathbf{k} + 2\pi\mathbf{h}) \cdot \mathbf{r}\}. \quad (5.2.10.1)$$

The $C_{\mathbf{h}}(\mathbf{k})$ are determined by equations of consistency obtained by substitution of equation (5.2.10.1) into the wave equation.

If N terms are selected in equation (5.2.10.1) there will be N Bloch waves where wavevectors differ only in their components normal to the crystal surface, and the total wavefunction will consist of a linear combination of these Bloch waves. The problem is now reduced to the problem of equation (5.2.8.2).

The development of solutions for particular geometries follows that for the X-ray case, Chapter 5.1, with the notable differences that:

(1) The two-beam solution is not adequate except as a first approximation for particular orientations of crystals having small unit cells and for accelerating voltages not greater than about 100 keV. In general, many-beam solutions must be sought.

(2) For transmission HEED, the scattering angles are sufficiently small to allow the use of a small-angle forward-scattering approximation.

(3) Polarization effects are negligible except for very low energy electrons.

Humphreys (1979) compares the action of the crystal, in the Bloch-wave formalism, with that of an interferometer, the incident beam being partitioned into a set of Bloch waves of different wavevectors. 'As each Bloch wave propagates it becomes out of phase with its neighbours (due to its different wavevector). Hence interference occurs. For example, if the crystal thickness varies, interference fringes known as thickness fringes are formed.' For the two-beam case, these are the fringes of the pendulum solution referred to previously.

5.2.11. Dispersion surfaces

One of the important constructs of the Bloch-wave formalism is the dispersion surface, a plot of the permitted values of the z component of a Bloch wavevector against the component of the incident wavevector parallel to the crystal surface. The curve for a particular Bloch wave is called a branch. Thus, for fast electrons, the two-beam approximation has two branches, one for each eigenvalue, and the N -beam approximation has N .

A detailed treatment of the extensive and powerful theory that has grown from Bethe's initial paper is to be found, for example, in Hirsch *et al.* (1965). Apart from its fundamental importance as a theoretical tool, this formulation provides the basis for one of the most commonly used numerical techniques, the essential step being the estimation of the eigenvalues from equation (5.2.8.2) [see *IT C* (1999, Section 4.3.6.2)].

5.2.12. Multislice

Multislice derives from a formulation that generates a solution in the form of a Born series (Cowley & Moodie, 1962). The crystal is treated as a series of scattering planes on to which the potential from the slice between z and $z + \Delta z$ is projected, separated by vacuum gaps Δz , not necessarily corresponding to any planes or spacings of the material structure. The phase change in the electron beam

produced by passage through a slice is given by

$$q = \exp\left\{-i\sigma \int_{z_1}^{z_1+\Delta z} \varphi(x, y, z) dz\right\},$$

and the phase distribution in the x, y plane resulting from propagation between slices is given by

$$p = \exp\left\{\frac{ik(x^2 + y^2)}{2\Delta z}\right\},$$

where the wavefront has been approximated by a paraboloid. Thus, the wavefunction for the $(n + 1)$ th slice is given by

$$\begin{aligned} \psi_{n+1} &= \left[\psi_n * \exp\left\{\frac{ik(x^2 + y^2)}{2\Delta z}\right\} \right] \exp\{-i\sigma\varphi_{n+1}\} \\ &= [\psi_n * p]q, \end{aligned} \quad (5.2.12.1)$$

where $*$ is the convolution operator (Cowley, 1981).

This equation can be regarded as the finite difference form of the Schrödinger equation derived by Feynman's (1948) method. The calculation need be correct only to first order in Δz . Writing the convolution in equation (5.2.12.1) explicitly, and expanding in a Taylor series, the integrals can be evaluated to yield equation (5.2.3.1) (Goodman & Moodie, 1974).

If equation (5.2.12.1) is Fourier transformed with respect to x and y , the resulting recurrence relation is of the form

$$U_{n+1} = [U_n P] * Q_n, \quad (5.2.12.2)$$

where P and Q are obtained by Fourier transforming p and q above. This form is convenient for numerical work since, for a perfect crystal, it is: discrete, as distinct from equation (5.2.12.1) which is continuous in the variables [see *IT C* (1999, Section 4.3.6.1)]; numerically stable at least up to 5000 beams; fast; and only requires a computer memory proportional to the number of beams (Goodman & Moodie, 1974).

5.2.13. Born series

In the impulse limit of equation (5.2.12.2), the integrals can be evaluated to give the Born series (Cowley & Moodie, 1957)

$$U(h, k) = \sum_n U_n(h, k),$$

where

$$\begin{aligned} U_n(h, k) &= \sum_l \sum_{h_1 k_1 l_1} \dots \sum_{h_{n-1} k_{n-1} l_{n-1}} i^n V(h_1, k_1, l_1) \\ &\quad \dots V\left(h - \sum_{r=1}^{n-1} h_r, k - \sum_{r=1}^{n-1} k_r, l - \sum_{r=1}^{n-1} l_r\right) \\ &\quad \times [\exp\{-2\pi i \zeta T\} / (2\pi i)^n] \\ &\quad \times \left(\exp\{i\pi \zeta T\} (\sin \pi \zeta T / \zeta) [(\zeta - \zeta_1) \dots (\zeta - \zeta_{n-1})]^{-1} \right. \\ &\quad \left. + \sum_{m=1}^{n-1} \exp\{i\pi \zeta_m T\} (\sin \pi \zeta_m T / \zeta_m) [(\zeta_m - \zeta_1) \right. \\ &\quad \left. \dots (\zeta_m - \zeta_{m-1})(\zeta_m - \zeta_{m+1}) \dots (\zeta_m - \zeta)]^{-1} \right) \end{aligned} \quad (5.2.13.1a)$$

and where n is the order of interaction. Here ζ is the excitation error of the reflection with index h, k , and ζ_i are the excitation errors for the reflections with indices h_i, k_i, l_i . Thus each constituent process may be represented by a diagram, starting on the origin of reciprocal

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space, possibly looped, and ending on the point with coordinates (h, k) .

This solution can also be obtained by iteration of the Green-function integral equation, the integrals being evaluated by means of suitably chosen contours on the complex k_z plane (Fujiwara, 1959), as well as by expansion of the scattering matrix (Fujimoto, 1959).

Clearly, two or more of the ζ_i will, in general, be equal in nearly all of the terms in equation (5.2.13.1a). Confluence is, however, readily described, the divided differences of arbitrary order transforming into differentials of the same order (Moodie, 1972).

The physical picture that emerges from equation (5.2.13.1a) is that of n -fold scattering, the initial wave being turned through $n - 1$ intermediate states, processes that can be presented by scattering diagrams in reciprocal space (Gjønnes & Moodie, 1965).

For a given scattering vector, constituent functions are evaluated for all possible paths in three dimensions, and those functions are then summed over l . There are therefore two distinct processes by which upper-layer lines can perturb wavefunctions in the zone, namely: by scattering out of the zone and then back in; and by intrusion of the effective shape function from another zone, the latter process being already operative in the first Born, or kinematical approximation.

The constituent functions to be evaluated can be transformed into many forms. One of the more readily described is that which assigns to each diagram an effective dynamical shape function. If there are no loops in the diagram of order n , this effective shape function is the $(n + 1)$ th divided difference of the constituent phase-shifted kinematical shape transforms. For general diagrams, divided differences in loops are replaced by the corresponding differentials. The resulting function is multiplied by the convolution of the contributing structure amplitudes and diagrams of all orders summed (Moodie, 1972).

While scattering diagrams have no utility in numerical work, they find application in the analysis of symmetries, for instance in the determination of the presence or absence of a centre of inversion [for a recent treatment, see Moodie & Whitfield (1995)] and in the detection of screw axes and glide planes (Gjønnes & Moodie, 1965). Methods for the direct determination of all space groups are described by Goodman (1975) and by Tanaka *et al.* (1983) (see Section 2.5.3).

Equation (5.2.13.1a) can be rewritten in a form particularly suited to the classification of approximations, and to describing the underlying symmetry of the formulation. The equation is written for compactness as

$$U_n(h) = E_n(h)Z_n(\zeta),$$

so that $E_n(h)$ depends only on crystal structure and $Z_n(\zeta)$ only on diffraction geometry. A transformation (Cowley & Moodie, 1962) involving bialternants leads to

$$U_n = \sum_{r=0}^{\infty} E_n(h) [(2\pi iT)^{n+r}/(n+r)!] h_r(\zeta, \zeta_1 \dots \zeta_{n-1}), \quad (5.2.13.1b)$$

where h_r is the complete homogeneous symmetric polynomial function of n variables of order r .

Upper-layer-line effects can, of course, be calculated in any of the formulations.

5.2.14. Approximations

So far, only the familiar first Born and two-beam approximations and the projection approximation have been mentioned. Several others, however, have a considerable utility.

A high-voltage limit can be calculated in standard fashion to give

$$U_{HVL}(h, k) = \mathcal{F} \exp \left\{ -i\sigma_c \int_0^T \varphi(x, y, z) dz \right\}, \quad (5.2.14.1)$$

where $\mathcal{F}$ is the Fourier transform operator, and $\sigma_c = 2\pi m_0 e \lambda_c / h^2$ with $\lambda_c = (h/m_0 c)$, the Compton wavelength. The phase-grating approximation, which finds application in electron microscopy, involves the assumption that equation (5.2.14.1) has some range of validity when σ_c is replaced by σ . This is equivalent to ignoring the curvature of the Ewald sphere and can therefore apply to thin crystals [see Section 2.5.2 and *IT C* (1999, Section 4.3.8)].

Approximations that involve curtailing the number of beams evidently have a range of validity that depends on the size of the unit cell. The most explored case is that of three-beam interactions. Kambe (1957) has demonstrated that phase information can be obtained from the diffraction data; Gjønnes & Høier (1971) analysed the confluent case, and Hurley & Moodie (1980) have given an explicit inversion for the centrosymmetric case. Analyses of the symmetry of the defining differential equation, and of the geometry of the noncentrosymmetric case, have been given by Moodie *et al.* (1996, 1998).

Niehrs and his co-workers (*e.g.* Blume, 1966) have shown that, at or near zones, effective two-beam conditions can sometimes obtain, in that, for instance, the central beam and six equidistant beams of equal structure amplitude can exhibit two-beam behaviour when the excitation errors are equal. Group-theoretical treatments have been given by Fukuhara (1966) and by Kogiso & Takahashi (1977). Explicit reductions for all admissible noncentrosymmetric space groups have been obtained by Moodie & Whitfield (1994). Extensions of such results have application in the interpretation of lattice images and convergent-beam patterns.

The approximations near the classical limit have been extensively explored [for instance, see Berry (1971)] but channelling has effectively become a separate subject and cannot be discussed here.

5.3. Dynamical theory of neutron diffraction

BY M. SCHLENKER AND J.-P. GUIGAY

5.3.1. Introduction

Neutron and X-ray scattering are quite similar both in the geometry of scattering and in the orders of magnitude of the basic quantities. When the neutron spin is neglected, *i.e.* when dealing with scattering by perfect non-magnetic crystals, the formalism and the results of the dynamical theory of X-ray scattering can be very simply transferred to the case of neutrons (Section 5.3.2). Additional features of the neutron case are related to the neutron spin and appear in diffraction by magnetic crystals (Section 5.3.3). The low intensities available, coupled with the low absorption of neutrons by most materials, make it both necessary and possible to use large samples in standard diffraction work. The effect of extinction in crystals that are neither small nor bad enough to be amenable to the kinematical approximation is therefore very important in the neutron case, and will be discussed in Section 5.3.4 together with the effect of crystal distortion. Additional possibilities arise in the neutron case because the neutrons can be manipulated from outside through applied fields (Section 5.3.5). Reasonably extensive tests of the predictions of the dynamical theory of neutron diffraction have been performed, with the handicap of the very low intensities of neutron beams as compared with X-rays: these are described in Section 5.3.6. Finally, the applications of the dynamical theory in the neutron case, and in particular neutron interferometry, are reviewed in Section 5.3.7.

5.3.2. Comparison between X-rays and neutrons with spin neglected

5.3.2.1. The neutron and its interactions

An excellent introductory presentation of the production, properties and scattering properties of neutrons is available (Scherer & Fåk, 1993, and other papers in the same book). A stimulating review on neutron optics, including diffraction by perfect crystals, has been written by Klein & Werner (1983). X-rays and neutrons are compared in terms of the basic quantities in Table 4.1.3.1 of *IT C* (1999), where Chapter 4.4 is devoted to neutron techniques.

The neutron is a massive particle for which the values relevant to diffraction are: no electric charge, rest mass $m = 1.675 \times 10^{-27}$ kg, angular momentum eigenvalues along a given direction $\pm \hbar/2$ (spin $\frac{1}{2}$) and a magnetic moment of -1.913 nuclear magneton, meaning that its component along a quantization direction z can take eigenvalues $\mu_z = \mp 0.996 \times 10^{-26}$ A m². The de Broglie wavelength is $\lambda = h/p$ where h is Planck's constant ($h = 2\pi\hbar = 6.625 \times 10^{-34}$ J s) and p is the linear momentum; $p = mv$ in the non-relativistic approximation, which always applies in the context of this chapter, v being the neutron's velocity. The neutron's wavelength, λ , and kinetic energy, E_c , are thus related by $\lambda = h/(2mE_c)^{1/2}$, or, in practical units, $\lambda [\text{\AA}] = 9.05/(E_c [\text{meV}])^{1/2}$. Thus, to be of interest for diffraction by materials, neutrons should have kinetic energies in the range 10^0 to 10^2 meV. In terms of the velocity, $\lambda [\text{\AA}] = 3.956/(v [\text{km s}^{-1}])$.

Neutron beams are produced by nuclear reactors or by spallation sources, usually pulsed. In either case they initially have an energy in the MeV range, and have to lose most of it before they can be used. The moderation process involves inelastic interactions with materials. It results in statistical distributions of energy, hence of velocity, close to the Maxwell distribution characteristic of the temperature T of the moderator. Frequently used moderators are liquid deuterium (D_2 , *i.e.* $^2\text{H}_2$) at 25 K, heavy water (D_2O) at room temperature and graphite allowed to heat up to 2400 K; the

corresponding neutron distributions are termed cold, thermal and hot, respectively.

The interaction of a neutron with an atom is usually described in terms of scattering lengths or of scattering cross sections. The main contribution corresponding to the nuclear interaction is related to the strong force. The interaction with the magnetic field created by atoms with electronic magnetic moments is comparable in magnitude to the nuclear term.

5.3.2.2. Scattering lengths and refractive index

The elastic scattering amplitude for scattering vector $\mathbf{s}$, $f(\mathbf{s})$, is defined by the wave scattered by an object placed at the origin when the incident plane wave is $\Psi_i = A \exp[i(\mathbf{k}_0 \cdot \mathbf{r} - \omega t)]$, written as $\Psi_s = A[f(\mathbf{s})/r] \exp[i(kr - \omega t)]$ with $k = |\mathbf{k}_0| = |\mathbf{k}_0 + \mathbf{s}| = 2\pi/\lambda$. In the case of the strong-force interaction with nuclei, the latter can be considered as point scatterers because the interaction range is very small, hence the scattering amplitude is isotropic (independent of the direction of $\mathbf{s}$). It is also independent of λ except in the vicinity of resonances. It is conventionally written as $-b$ so that most values of b , called the scattering length, are positive. A table of experimentally measured values of the scattering lengths b is given in *IT C* for the elements in their natural form as well as for many individual isotopes. It is apparent that the typical order of magnitude is the fm (femtometer, *i.e.* 10^{-15} m, or fermi), that there is no systematic variation with atomic number and that different isotopes have very different scattering lengths, including different signs. The first remark implies that scattering amplitudes of X-rays and of neutrons have comparable magnitudes, because the characteristic length for X-ray scattering (the scattering amplitude for forward scattering by one free electron) is $R = 2.8$ fm, the classical electron radius. The second and third points explain the importance of neutrons in structural crystallography, in diffuse scattering and in small-angle scattering. Scattering of neutrons by condensed matter implies the use of the bound scattering lengths, as tabulated in *IT C*. The 'free' scattering length, used in some presentations, is obtained by multiplying the bound scattering lengths by $A/(A+1)$, where A is the mass of the nucleus in atomic units.

A description in terms of an interaction potential is possible using the Fermi pseudo-potential, which in the case of the nuclear interaction with a nucleus at $\mathbf{r}_0$ can be written as $V(\mathbf{r}) = (h^2/2\pi m)b\delta(\mathbf{r} - \mathbf{r}_0)$, where δ denotes the three-dimensional Dirac distribution.

Refraction of neutrons at an interface can be conveniently described by assigning a refractive index to the material, such that the wavenumber in the material, k , is related to that in a vacuum, k_0 , by $k = nk_0$. Here

$$n = \left(1 - \frac{\lambda^2}{\pi V} \sum_i b_i\right)^{1/2},$$

where the sum is over the nuclei contained in volume V . With typical values, n is very close to 1 and $1 - n = (\lambda^2/2\pi V) \sum_i b_i$ is typically of the order of 10^{-5} . This small value, in the same range as for X-rays, gives a feeling for the order of magnitude of key quantities of the dynamical theory, in particular the Darwin width 2δ as discussed in Chapter 5.1. It also makes total external reflection possible on materials for which $\sum_i b_i > 0$: this is the basis for the neutron guide tubes now installed in most research reactors, as well as for reflectometry.

The notations prevailing in X-ray and in neutron crystallography are slightly different, and the correspondence is very simple: X-ray atomic scattering factors and structure factors are numbers. When

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multiplied by R , the classical electron radius, they become entirely equivalent to the corresponding quantities in neutron usage, which are lengths. It should be noted that the presence of different isotopes and the effect of nuclear spin (disordered except under very special conditions) give rise to incoherent elastic neutron scattering, which has no equivalent in the X-ray case. The scattering length corresponding to R times the atomic scattering factor for X-rays is therefore the coherent scattering length, b_{coh} , obtained by averaging the scattering length over the nuclear spin state and isotope distribution.

5.3.2.3. Absorption

Neutron absorption is related to a nuclear reaction in which the neutron combines with the absorbing nucleus to form a compound nucleus, usually in a metastable state which then decays. The scattering length describing this resonance scattering process depends on the neutron energy and contains an imaginary part associated with absorption in complete analogy with the imaginary part of the dispersion correction for the X-ray atomic scattering factors. The energies of the resonances are usually far above those of interest for crystallography, and the linear absorption coefficient varies approximately as $1/\nu$ or λ . It is important to note that, except for a very few cases (notably ^3He , ^6Li , ^{10}B , In, Cd, Gd), the absorption of neutrons is very small compared with that of X-rays, and even more so compared with that of electrons, and can be neglected to a first approximation.

5.3.2.4. Differences between neutron and X-ray scattering

There are major differences in the experimental aspects of neutron and X-ray scattering. Neutrons are only available in large facilities, where allocation of beam time to users is made on the basis of applications, and where admittance is restricted because of the hazards which nuclear technology can present in the hands of ill-intentioned users. Because of the radiation shielding necessary, as well as the large size of neutron detectors, neutron-scattering instrumentation is much bulkier than that for X-rays. Neutron beams are in some aspects similar to synchrotron radiation, in particular because in both cases the beams are initially 'white' and for most applications have to be monochromated. There is, however, a huge difference in the order of magnitudes of the intensities. Neutron beams are weak in comparison with laboratory X-ray sources, and weaker by many orders of magnitude than synchrotron radiation. Also, the beam sources are large in the case of neutrons, since they are essentially the moderators, whereas the source is very small in the case of synchrotron radiation, and this difference again increases the ratio of the brilliances in favour of X-rays. This encourages the use of large specimens in all neutron-scattering work, and makes the extinction problem more important than for X-rays. Furthermore, many experiments that are quick using X-rays become very slow, and give rise to impaired resolution, in the neutron case.

There are also at least two additional aspects of neutron scattering in comparison with X-ray scattering, apart from the effect of the magnetic moment associated with the intrinsic (spin) angular momentum of the neutron. On the one hand, the small velocity of neutrons, compared with the velocity of light, makes time-of-flight measurements possible, both in standard neutron diffraction and in investigations of perfect crystals. Because this velocity is of the same order of magnitude as that of ultrasound, the effect of ultrasonic excitation on neutron diffraction is slightly different from that in the X-ray case. On the other hand, the fact that neutrons have mass and a magnetic moment implies that they can be affected by external fields, such as gravity and magnetic fields, both during their propagation in air or in a vacuum and while being diffracted within crystals (Werner, 1980) (see Section 5.3.5).

Experiments completely different from the X-ray case can thus be performed with perfect crystals and with neutron interferometers (see Sections 5.3.6 and 5.3.7.3).

5.3.2.5. Translating X-ray dynamical theory into the neutron case

As shown in Chapter 5.1, the basic equations of dynamical theory, *viz* Maxwell's equations for the X-ray case and the time-independent Schrödinger equation in the neutron case, have exactly the same form when the effect of the neutron spin can be neglected, *i.e.* in situations that do not involve magnetism and when no externally applied potential is taken into account. The translation scheme for the scattering factors and structure factors is described above. The one formal difference is that the wavefunction is scalar in the neutron case, hence there is no equivalent to the parallel and perpendicular polarizations of the X-ray situation: C in equation (5.1.2.20) of Chapter 5.1 should therefore be set to 1.

The physics of neutron diffraction by perfect crystals is therefore expected to be very similar to that of X-ray diffraction, with the existence of wavefields, *Pendellösung* effects, anomalous transmission, intrinsic rocking-curve shapes and reflectivity *versus* thickness behaviour in direct correspondence. All experimental tests of these predictions confirm this view (Section 5.3.6).

Basic discussions of dynamical neutron scattering are given by Stassis & Oberteuffer (1974), Sears (1978), Rauch & Petrascheck (1978), and Squires (1978).

5.3.3. Neutron spin, and diffraction by perfect magnetic crystals

5.3.3.1. Polarization of a neutron beam and the Larmor precession in a uniform magnetic field

A polarized neutron beam is represented by a two-component spinor,

$$|\varphi\rangle = \begin{pmatrix} c \\ d \end{pmatrix} = c \begin{pmatrix} 1 \\ 0 \end{pmatrix} + d \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

which is the coherent superposition of two states, of different amplitudes c and d , polarized in opposite directions along the spin-quantization axis. The spinor components c and d are generally space- and time-dependent. We suppose that $\langle\varphi|\varphi\rangle = cc^* + dd^* = 1$. The polarization vector $\mathbf{P}$ is defined as

$$\mathbf{P} = \langle\varphi|\boldsymbol{\sigma}|\varphi\rangle,$$

where the vector $\boldsymbol{\sigma}$ represents the set of Pauli matrices σ_x , σ_y and σ_z . The components of $\mathbf{P}$ are

$$\begin{aligned} P_x &= (c^* \ d^*) \sigma_x \begin{pmatrix} c \\ d \end{pmatrix} = (c^* \ d^*) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \\ &= c^*d + cd^* \\ P_y &= (c^* \ d^*) \sigma_y \begin{pmatrix} c \\ d \end{pmatrix} = (c^* \ d^*) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \\ &= i(cd^* - c^*d) \\ P_z &= (c^* \ d^*) \sigma_z \begin{pmatrix} c \\ d \end{pmatrix} = (c^* \ d^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c \\ d \end{pmatrix} \\ &= cc^* - dd^*, \end{aligned} \quad (5.3.3.1)$$

from which it is clearly seen that, unlike P_z , the polarization components P_x and P_y depend on the phase difference between the spinor components c and d .

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In a region of a vacuum in which a uniform magnetic field $\mathbf{B}$ is present, a neutron beam experiences a magnetic potential energy represented by the matrix

$$-\mu_n \boldsymbol{\sigma} \cdot \mathbf{B} = \begin{pmatrix} -\mu_n B & 0 \\ 0 & \mu_n B \end{pmatrix},$$

μ_n being the neutron magnetic moment, if the directions of $\mathbf{B}$ and of the spin-quantization axis coincide. Consequently, different indices of refraction $n = 1 \pm (\mu_n B / 2E)$, where E is the neutron energy, should be associated with the spinor components c and d ; this induces between these spinor components a phase difference which is a linear function of the time (or, equivalently, of the distance travelled by the neutrons), hence, according to (5.3.3.1), a rotation around the magnetic field of the component of the neutron polarization perpendicular to this magnetic field. The time frequency of this so-called Larmor precession is $2\mu_n B / h$, where h is Planck's constant.

A neutron beam may be partially polarized; such a beam is conveniently represented by a spin-density matrix ρ , which is the statistical average of the spin-density matrices associated to the polarized beams which are mixed incoherently, the density matrix associated to the spinor

$$|\varphi\rangle = \begin{pmatrix} c \\ d \end{pmatrix}$$

being

$$|\varphi\rangle\langle\varphi| = \begin{pmatrix} c \\ d \end{pmatrix} \begin{pmatrix} c^* & d^* \end{pmatrix} = \begin{pmatrix} cc^* & cd^* \\ c^*d & dd^* \end{pmatrix}.$$

The polarization vector $\mathbf{P}$ is then obtained as

$$\mathbf{P} = \text{Tr}(\boldsymbol{\sigma}\rho). \quad (5.3.3.2)$$

In the common case of a non-polarized beam, the spin-density matrix is

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

It is easily seen that all components of $\mathbf{P}$ are then equal to 0.

Equation (5.3.3.2) is therefore applicable to the general case (polarized, partially polarized or non-polarized beam). The inverse relation giving the density matrix ρ as function of $\mathbf{P}$ is

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} \mathbf{P} \cdot \boldsymbol{\sigma}. \quad (5.3.3.3)$$

5.3.3.2. Magnetic scattering by a single ion having unpaired electrons

The spin and orbital motion of unpaired electrons in an atom or ion give rise to a surrounding magnetic field $\mathbf{B}(\mathbf{r})$ which acts on the neutron via the magnetic potential energy $-\boldsymbol{\mu}_n \cdot \mathbf{B}(\mathbf{r})$, where $\boldsymbol{\mu}_n$ is the neutron magnetic moment. Since this is a long-range interaction, in contrast to the nuclear interaction, the magnetic scattering length p , which is proportional to the Fourier transform of the magnetic potential energy distribution $-\boldsymbol{\mu}_n \cdot \mathbf{B}(\mathbf{r})$, depends on the angle of scattering.

The classical relation $\text{div } \mathbf{B}(\mathbf{r}) = 0$ shows clearly that the vector $\mathbf{B}(\mathbf{s})$, which is the Fourier transform of $\mathbf{B}(\mathbf{r})$, is perpendicular to the reciprocal-space vector $\mathbf{s}$. If we consider the magnetic field $\mathbf{B}(\mathbf{r})$ as resulting from a point-like magnetic moment $\boldsymbol{\mu}$ at position $\mathbf{r} = 0$, we get

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \text{curl} \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3},$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$ is the permittivity of a vacuum and

$\times$ denotes the cross product. $\mathbf{B}(\mathbf{r})$ can be Fourier-transformed into

$$\mathbf{B}(\mathbf{s}) = \mu_0 \mathbf{s} \times \frac{\boldsymbol{\mu} \times \mathbf{s}}{s^2} = \mu_0 \boldsymbol{\mu}_{\perp}(\mathbf{s}), \quad (5.3.3.4)$$

where $\boldsymbol{\mu}_{\perp}(\mathbf{s})$ is the projection of $\boldsymbol{\mu}$ on the plane perpendicular to $\mathbf{s}$ (reflecting plane).

This result can be applied by volume integration to the more general case of a spatially extended magnetization distribution, which for a single magnetic ion corresponds to the atomic shell of the unpaired electrons. It is thus shown that the magnetic scattering length is proportional to $\boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_{i\perp}$, where $\boldsymbol{\mu}_{i\perp}$ is the projection of the magnetic moment of the ion on the reflecting plane.

For a complete description of magnetic scattering, which involves the spin-polarization properties of the scattered beam, it is necessary to represent the neutron wavefunction in the form of a two-component spinor and the ion's magnetic moment as a spin operator which is a matrix expressed in terms of the Pauli matrices $\boldsymbol{\sigma}$ ($\sigma_x, \sigma_y, \sigma_z$). The magnetic scattering length is therefore itself a (2×2) matrix:

$$(p) = -(2\pi m / h^2) \mu_n \boldsymbol{\sigma} \cdot \mathbf{B}(\mathbf{s}) = -\mu_0 (2\pi m / h^2) \mu_n \boldsymbol{\sigma} \cdot \boldsymbol{\mu}_{i\perp}(\mathbf{s}) f_i(\sin \theta / \lambda), \quad (5.3.3.5)$$

where $f_i(\sin \theta / \lambda)$ is the dimensionless magnetic form factor of the ion considered and tends towards a maximum value of 1 when the scattering angle θ tends towards 0 (forward scattering). The value of $\mu_0 (2\pi m / h^2) \mu_n \mu_i$ is $p_1 = 2.70 \times 10^{-15} \text{ m}$ for $\mu_i = 1$ Bohr magneton.

According to (5.3.3.4) or (5.3.3.5), there is no magnetic scattering in directions such that the scattering vector $\mathbf{s}$ is in the same direction as the ion magnetic moment $\boldsymbol{\mu}_i$. Magnetic scattering effects are maximum when $\mathbf{s}$ and $\boldsymbol{\mu}_i$ are perpendicular.

The matrix (p) is diagonal if the direction of $\boldsymbol{\mu}_{i\perp}(\mathbf{s})$ is chosen as the spin-quantization axis. Therefore, there is no spin-flip scattering if the incident beam is polarized parallel or antiparallel to the direction of $\boldsymbol{\mu}_{i\perp}(\mathbf{s})$.

It is more usual to choose the spin-quantization axis (Oz) along $\boldsymbol{\mu}_i$. Let β be the angle between the vectors $\boldsymbol{\mu}_i$ and $\mathbf{s}$; the (x, y, z) components of $\boldsymbol{\mu}_{i\perp}(\mathbf{s})$ are then $(-\mu_i \sin \beta \cos \beta, 0, \mu_i \sin^2 \beta)$ if the y axis is chosen along $\boldsymbol{\mu}_i \times \mathbf{s}$. The total scattering length, which is the sum of the nuclear and the magnetic scattering lengths, is then represented by the matrix

$$(q) = \begin{pmatrix} b + p \sin^2 \beta & -p \sin \beta \cos \beta \\ -p \sin \beta \cos \beta & b - p \sin^2 \beta \end{pmatrix}, \quad (5.3.3.6)$$

where b is the nuclear scattering length and

$$p = -\mu_0 \frac{2\pi m}{h^2} \mu_n \mu_i f_i \left(\frac{\sin \theta}{\lambda} \right) = -p_1 \mu_i f_i \left(\frac{\sin \theta}{\lambda} \right),$$

with μ_i expressed in Bohr magnetons. The relations

$$(q) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} b + p \sin^2 \beta \\ -p \sin \beta \cos \beta \end{pmatrix} \text{ and } (q) \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -p \sin \beta \cos \beta \\ b - p \sin^2 \beta \end{pmatrix}$$

show clearly that the diagonal and the non-diagonal elements of the matrix (q) are, respectively, the spin-flip and the non-spin-flip scattering lengths. It is usual to consider the scattering cross sections, which are the measurable quantities. The cross sections for neutrons polarized parallel or antiparallel to the ion magnetic moment are

$$(d\sigma/d\Omega)_{\pm} = b^2 \pm 2bp \sin^2 \beta + (p \sin \beta)^2. \quad (5.3.3.7)$$

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These expressions are the sum of the spin-flip and non-spin-flip cross sections, which are equal to $(b \pm p \sin^2 \beta)^2$ and $(p \sin \beta \cos \beta)^2$, respectively. In the case of non-polarized neutrons, the interference term $(\pm 2bp \sin^2 \beta)$ between the nuclear and the magnetic scattering disappears; the cross section is then

$$(d\sigma/d\Omega) = b^2 + (p \sin \beta)^2. \quad (5.3.3.8)$$

In the general case of a partially polarized beam we can use the density-matrix representation. Let ρ_{inc} be the density matrix of the incident beam; it can be shown that the density matrix of the diffracted beam is equal to the following product of matrices: $(q)\rho_{\text{inc}}(q^*)$. Using the relations between the density matrix and polarization vector presented in the preceding section, we can obtain a general description of the diffracted beam as a function of the polarization properties of the incident beam. Such a formalism is of interest for dealing with new experimental arrangements, in which a three-dimensional polarization analysis of the diffracted beam is possible, as shown by Tasset (1989).

5.3.3.3. Dynamical theory in the case of perfect ferro-magnetic or collinear ferrimagnetic crystals

The most direct way to develop this dynamical theory in the two-beam case, which involves a single Bragg-diffracted beam of diffraction vector $\mathbf{h}$, is to consider spinor wavefunctions of the following form:

$$\varphi(\mathbf{r}) = \exp(i\mathbf{K}_0 \cdot \mathbf{r}) \begin{pmatrix} D_0 \\ E_0 \end{pmatrix} + \exp[i(\mathbf{K}_0 + \mathbf{h}) \cdot \mathbf{r}] \begin{pmatrix} D_h \\ E_h \end{pmatrix} \quad (5.3.3.9)$$

as approximate solutions of the wave equation inside the crystal,

$$\Delta\varphi(\mathbf{r}) + k^2\varphi(\mathbf{r}) = [u(\mathbf{r}) - \boldsymbol{\sigma} \cdot \mathbf{Q}(\mathbf{r})]\varphi(\mathbf{r}), \quad (5.3.3.10)$$

where $u(\mathbf{r})$ and $-\boldsymbol{\sigma} \cdot \mathbf{Q}(\mathbf{r})$ are, respectively, equal to the nuclear and the magnetic potential energies multiplied by $2m/\hbar^2$. In the calculation of $\varphi(\mathbf{r})$ in the two-beam case, we need only three terms in the expansions of the functions $u(\mathbf{r})$ and $\mathbf{Q}(\mathbf{r})$ into Fourier series:

$$\begin{aligned} u(\mathbf{r}) &= u_0 + u_{\mathbf{h}} \exp(i\mathbf{h} \cdot \mathbf{r}) + u_{-\mathbf{h}} \exp(-i\mathbf{h} \cdot \mathbf{r}) + \dots, \\ \mathbf{Q}(\mathbf{r}) &= \mathbf{Q}_0 + \mathbf{Q}_{\mathbf{h}} \exp(i\mathbf{h} \cdot \mathbf{r}) + \mathbf{Q}_{-\mathbf{h}} \exp(-i\mathbf{h} \cdot \mathbf{r}) + \dots \end{aligned}$$

We suppose that the crystal is magnetically saturated by an externally applied magnetic field $\mathbf{H}_a$. $\mathbf{Q}_0$ is then proportional to the macroscopic mean magnetic field $\mathbf{B} = \mu_0(\mathbf{M} + \mathbf{H}_a + \mathbf{H}_d)$, where $\mathbf{M}$ is the magnetization vector and $\mathbf{H}_d$ is the demagnetizing field. The results of Section 5.3.3.2 show that $\mathbf{Q}_{\mathbf{h}}$ and $\mathbf{Q}_{-\mathbf{h}}$ are proportional to the projection of $\mathbf{M}$ on the reflecting plane.

The four coefficients D_0 , D_h , E_0 and E_h of (5.3.3.9) are found to satisfy a system of four homogeneous linear equations. The condition that the associated determinant has to be equal to 0 defines the dispersion surface, which is of order 4 and has four branches. An incident plane wave thus excites a system of four wavefields of the form of (5.3.3.9), generally polarized in various directions. A particular example of a dispersion surface, having an unusual shape, is shown in Fig. 5.3.3.1.

This is a much more complicated situation than in the case of non-magnetic crystals, in which one only needs to consider scalar wavefunctions which depend on two coefficients, such as D_0 and D_h , and which are related to hyperbolic dispersion surfaces of order 2, as fully described in Chapter 5.1 on X-ray diffraction.

In fact, all neutron experiments related to dynamical effects in diffraction by magnetic crystals have been performed under such conditions that the magnetization vector in the crystal is perpendicular to the diffraction vector $\mathbf{h}$. In this case, the vectors $\mathbf{Q}_{\mathbf{h}}$ and $\mathbf{Q}_{-\mathbf{h}}$ are parallel or antiparallel to the vector $\mathbf{Q}_0$ which is chosen as the spin-quantization axis. The matrices $\boldsymbol{\sigma} \cdot \mathbf{Q}_0$, $\boldsymbol{\sigma} \cdot \mathbf{Q}_{\mathbf{h}}$ and $\boldsymbol{\sigma} \cdot \mathbf{Q}_{-\mathbf{h}}$ are then all diagonal matrices, and we obtain for the

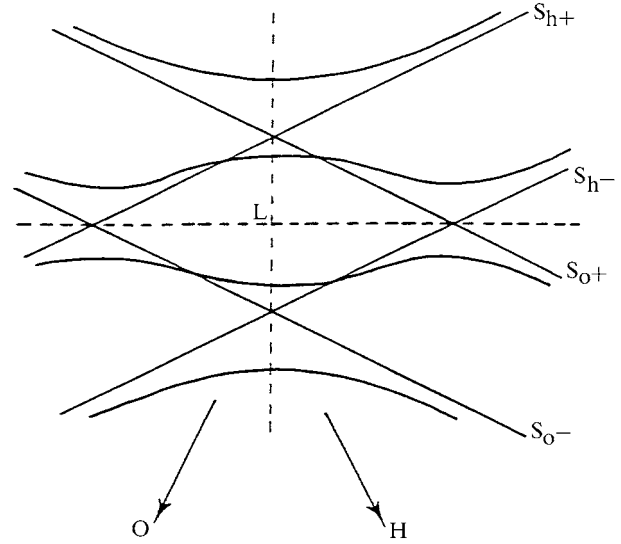


Fig. 5.3.3.1. Schematic plot of the two-beam dispersion surface in the case of a purely magnetic reflection such that $\mathbf{Q}_{\mathbf{h}} = \mathbf{Q}_{-\mathbf{h}} = \mathbf{Q}_0$ and that the angle between $\mathbf{Q}_0$ and $\mathbf{Q}_{\mathbf{h}}$ is equal to $\pi/4$.

two spin states ($\pm$) separate dynamical equations which are similar to the dynamical equations for the scalar case, but with different structure factors, which are either the sum or the difference of the nuclear structure factor F_N and of the magnetic structure factor F_M :

$$F_+ = F_N + F_M \text{ and } F_- = F_N - F_M. \quad (5.3.3.11)$$

F_N and F_M are related to the scattering lengths of the ions in the unit cell of volume V_c :

$$\begin{aligned} F_N &= V_c u_{\mathbf{h}} = \sum_i b_i \exp(-i\mathbf{h} \cdot \mathbf{r}_i); \\ F_M &= V_c |\mathbf{Q}_{\mathbf{h}}| = -\frac{\mu_0 m}{2\hbar^2} \mu_n \boldsymbol{\sigma} \cdot \sum_i \boldsymbol{\mu}_{i\perp}(\mathbf{h}) f_i \left(\frac{\sin \theta}{\lambda} \right) \exp(-i\mathbf{h} \cdot \mathbf{r}_i). \end{aligned}$$

The dispersion surface of order 4 degenerates into two hyperbolic dispersion surfaces, each of them corresponding to one of the polarization states ($\pm$). The asymptotes are different; this is related to different values of the refractive indices for neutron polarization parallel or antiparallel to $\mathbf{Q}_0$.

In some special cases the magnitudes of F_N and F_M happen to be equal. Only one polarization state is then reflected. Magnetic crystals with such a property (reflections 111 of the Heusler alloy Cu_2MnAl , or 200 of the alloy $\text{Co-8\% Fe}$) are very useful as polarizing monochromators and as analysers of polarization.

If the scattering vector $\mathbf{h}$ is in the same direction as the magnetization, this reflection is a purely nuclear one (with no magnetic contribution), since F_M is then equal to 0. Purely magnetic reflections (without nuclear contribution) also exist if the magnetic structure involves several sublattices.

If $\mathbf{h}$ is neither perpendicular to the average magnetization nor in the same direction, the presence of non-diagonal matrices in the dynamical equations cannot be avoided. The dynamical theory of diffraction by perfect magnetic crystals then takes the complicated form already mentioned.

Theoretical discussions of this complicated case of dynamical diffraction have been given by Stassis & Oberteuffer (1974), Mendiratta & Blume (1976), Sivardi re (1975), Belyakov & Bokun (1975, 1976), Schmidt *et al.* (1975), Bokun (1979), Guigay & Schlenker (1979a,b), and Schmidt (1983). However, to our knowledge, only limited experimental work has been carried out

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on this subject. Successful experiments could only be performed for the simpler cases mentioned above.

5.3.3.4. The dynamical theory in the case of perfect collinear antiferromagnetic crystals

In this case, there is no average magnetization ($\mathbf{Q}_0 = 0$). It is then convenient to choose the quantization axis in the direction of $\mathbf{Q}_h$ and $\mathbf{Q}_{-h}$. The dispersion surface degenerates into two hyperbolic surfaces corresponding to each polarization state along this direction for any orientation of the diffraction vector relative to the direction of the magnetic moments of the sublattices. These two hyperbolic dispersion surfaces have the same asymptotes. Furthermore, in the case of a purely magnetic reflection, they are identical.

The possibility of observing a precession of the neutron polarization in the presence of diffraction, in spite of the fact that there is no average magnetization, has been pointed out by Baryshevskii (1976).

5.3.3.5. The flipping ratio

In polarized neutron diffraction by a magnetically saturated magnetic sample, it is usual to measure the ratio of the reflected intensities I_+ and I_- measured when the incident beam is polarized parallel or antiparallel to the magnetization in the sample. This ratio is called the flipping ratio,

$$R = I_+/I_-, \quad (5.3.3.12)$$

because its measurement involves flipping the incident-beam polarization to the opposite direction. This is an experimentally well defined quantity, because it is independent of a number of parameters such as the intensity of the incident beam, the temperature factor or the coefficient of absorption. In the case of an ideally imperfect crystal, we obtain from the kinematical expressions of the integrated reflectivities

$$R_{\text{kin}}(\mathbf{h}) = (I_+/I_-)_{\text{kin}} = \left(\frac{|F_N + F_M|}{|F_N - F_M|} \right)^2. \quad (5.3.3.13)$$

In the case of an ideally perfect thick crystal, we obtain from the dynamical expressions of the integrated reflectivities

$$R_{\text{dyn}}(\mathbf{h}) = (I_+/I_-)_{\text{dyn}} = \frac{|F_N + F_M|}{|F_N - F_M|}. \quad (5.3.3.14)$$

In general, R_{dyn} depends on the wavelength and on the crystal thickness; these dependences disappear, as seen from (5.3.3.14), if the path length in the crystal is much larger than the extinction distances for the two polarization states. It is clear that the determination of R_{kin} or R_{dyn} allows the determination of the ratio F_M/F_N , hence of F_M if F_N is known. In fact, because real crystals are neither ideally imperfect nor ideally perfect, one usually introduces an extinction factor y (extinction is discussed below, in Section 5.3.4) in order to distinguish the real crystal reflectivity from the reflectivity of the ideally imperfect crystal. Different extinction coefficients y_+ and y_- are actually expected for the two polarization states. This obviously complicates the task of the determination of F_M/F_N .

In the kinematical approximation, the flipping ratio does not depend on the wavelength, in contrast to dynamical calculations for hypothetically perfect crystals (especially for the Laue case of diffraction). Therefore, an experimental investigation of the wavelength dependence of the flipping ratio is a convenient test for the presence of extinction. Measurements of the flipping ratio have been used by Bonnet *et al.* (1976) and by Kulda *et al.* (1991) in order to test extinction models. Baruchel *et al.* (1986) have compared nuclear and magnetic extinction in a crystal of MnP.

Instead of considering only the ratio of the integrated reflectivities, it is also possible to record the flipping ratio as a function of the angular position of the crystal as it is rotated across the Bragg position. Extinction is expected to be maximum at the peak and the ratio measured on the tails of the rocking curve may approach the kinematical value. It has been found experimentally that this expectation is not of general validity, as discussed by Chakravarthy & Madhav Rao (1980). It would be valid in the case of a perfect crystal, hence in the case of pure primary extinction. It would also be valid in the case of secondary extinction of type I, but not in the case of secondary extinction of type II [following Zachariasen (1967), type II corresponds to mosaic crystals such that the diffraction pattern from each block is wider than the mosaic statistical distribution].

5.3.4. Extinction in neutron diffraction (non-magnetic case)

The kinematical approximation, which corresponds to the first Born approximation in scattering theory, supposes that each incident neutron can be scattered only once and therefore neglects the possibility that the neutrons may be scattered several times. Because this is a simple approximation which overestimates the crystal reflectivity, the actual reduction of reflectivity, as compared to its kinematical value, is termed *extinction*. This is actually a typical dynamical effect, since it is a multiple-scattering effect.

Extinction effects can be safely neglected in the case of scattering by very small crystals; more precisely, this is possible when the path length of the neutron beam in the crystal is much smaller than $\Delta = V_c/\lambda F$, where λ is the neutron wavelength and F/V_c is the scattering length per unit volume for the reflection considered. Δ is sometimes called the 'extinction distance'.

A very important fact is that extinction effects also vanish if the crystal is imperfect enough, because each plane-wave component of the incident beam can then be Bragg-reflected in only a small volume of the sample. This is the extinction-free case of 'ideally imperfect crystals'. Conversely, extinction is maximum (smallest value of y) in the case of ideally perfect non-absorbing crystals.

Clearly, no significant extinction effects are expected if the crystal is thick but strongly absorbing, more precisely if the linear absorption coefficient μ is such that $\mu\Delta \gg 1$. Neutron diffraction usually corresponds to the opposite case ($\mu\Delta \ll 1$), in which extinction effects in nearly perfect crystals dominate absorption effects.

Extinction effects are usually described in the frame of the mosaic model, in which the crystal is considered as a juxtaposition of perfect blocks with different orientations. The relevance of this model to the case of neutron diffraction was first considered by Bacon & Lowde (1948). If the mosaic blocks are big enough there is extinction within each block; this is called *primary extinction*. Multiple scattering can also occur in different blocks if their misorientation is small enough. In this case, which is called *secondary extinction*, there is no phase coherence between the scattering events in the different blocks. The fact that empirical intensity-coupling equations are used in this case is based on this phase incoherence.

In the general case, primary and secondary extinction effects coexist. Pure secondary extinction occurs in the case of a mosaic crystal made of very small blocks. Pure primary extinction is observed in diffraction by perfect crystals.

The parameters of the mosaic model are the average size of the perfect blocks and the angular width of their misorientation distribution. The extinction theory of the mosaic model provides a relation between these parameters and the extinction coefficient,

defined as the ratio of the observed reflectivity to the ideal one, which is the kinematical reflectivity in this context.

In conventional work, the crystal structure factors of different reflections and the parameters of the mosaic model are fitted together to the experimental data, which are the integrated reflectivities and the angular widths of the rocking curves. In many cases, only the weakest reflections will be free, or nearly free, from extinction. The extinction corrections thus obtained can be considered as satisfactory in cases of moderate extinction. Nevertheless, extinction remains a real problem in cases of strong extinction and in any case if a very precise determination of the crystal structure factors is required.

There exist several forms of the mosaic model of extinction. For instance, in the model developed by Kulda (1988*a,b*, 1991), the mosaic blocks are not considered just as simple perfect blocks but may be deformed perfect blocks. This has the advantage of including the case of macroscopically deformed crystals, such as bent crystals.

A basically different approach, free from the distinction between primary and secondary extinction, has been proposed by Kato (1980*a,b*). This is a wave-optical approach starting from the dynamical equations for diffraction by deformed crystals. These so-called Takagi-Taupin equations (Takagi, 1962; Taupin, 1964) contain a position-dependent phase factor related to the displacement field of the deformed crystal lattice. Kato proposed considering this phase factor as a random function with suitably defined statistical characteristics. The wave amplitudes are then also random functions, the average of which represent the coherent wavefields while their statistical fluctuations represent the incoherent intensity fields.

Modifications to the Kato formulation have been introduced by Al Haddad & Becker (1988), by Becker & Al Haddad (1990, 1992), by Guigay (1989) and by Guigay & Chukhovskii (1992, 1995). Presently, it is not easy to apply this 'statistical dynamical theory' to real experiments. The widely used methods for extinction corrections are still based on the former mosaic model, according to the formulation of Zachariasen (1967), later improved by Becker & Coppens (1974*a,b*, 1975).

As in the X-ray case, acoustic waves produced by ultrasonic excitation can artificially induce a transition from perfect to ideally imperfect crystal behaviour. The effect of ultrasound on the scattering behaviour of distorted crystals is quite complex. A good discussion with reference to neutron-scattering experiments is given by Zolotoyabko & Sander (1995).

The situation of crystals with a simple distortion field is less difficult than the statistical problem of extinction. Klar & Rustichelli (1973) confirmed that the Takagi-Taupin equations, originally devised for X-rays, can be used for neutron diffraction with due account of the very small absorption, and used them for computing the effect of crystal curvature.

5.3.5. Effect of external fields on neutron scattering by perfect crystals

The possibility of acting on neutrons through externally applied fields during their propagation in perfect crystals provides possibilities that are totally unknown in the X-ray case. The theory has been given by Werner (1980) using the approaches (migration of tie points, and Takagi-Taupin equations) that are customary in the treatment of imperfect crystals (see above). Zeilinger *et al.* (1986) pointed out that the effective-mass concept, familiar in describing electrons in solid-state physics, can shed new light on this behaviour: because of the curvature of the dispersion surface at a near-exact Bragg setting, effective masses five orders of

magnitude smaller than the rest mass of the neutron in a vacuum can be obtained. Related experiments are discussed below.

An interesting proposal was put forward by Horne *et al.* (1988) on the coupling between the Larmor precession in a homogeneous magnetic field and the spin-orbit interaction of the neutron with non-magnetic atoms, a term which was dismissed in Section 5.3.2 because its contribution to the scattering length is two orders of magnitude smaller than that of the nuclear term. A resonance is expected to show up as highly enhanced diffracted intensity when a perfect sample is set for Bragg scattering and the magnetic field is adjusted so that the Larmor precession period is equal to the *Pendellösung* period.

5.3.6. Experimental tests of the dynamical theory of neutron scattering

These experiments are less extensive for neutron scattering than for X-rays. The two most striking effects of dynamical theory for non-magnetic nearly perfect crystals, *Pendellösung* behaviour and anomalous absorption, have been demonstrated in the neutron case too. *Pendellösung* measurement is described below (Section 5.3.7.2) because it is useful in the determination of scattering lengths. The anomalous transmission effect occurring when a perfect absorbing crystal is exactly at Bragg setting, *i.e.* the Borrmann effect, is often referred to in the neutron case as the suppression of the inelastic channel in resonance scattering, after Kagan & Afanas'ev (1966), who worked out the theory. A small decrease in absorption was detected in pioneering experiments on calcite by Knowles (1956) using the corresponding decrease in the emission of γ -rays and by Sippel *et al.* (1962), Shil'shtein *et al.* (1971), and Hastings *et al.* (1990) directly. Rocking curves of perfect crystals were measured by Sippel *et al.* (1964) in transmission, and by Kikuta *et al.* (1975). Integrated intensities were measured by Lambert & Malgrange (1982). The large angular amplification associated with the curvature of the dispersion surfaces near the exact Bragg setting was demonstrated by Kikuta *et al.* (1975) and by Zeilinger & Shull (1979).

In magnetic crystals, the investigations have been restricted to the simpler geometry where the scattering vector is perpendicular to the magnetization, and to few materials. *Pendellösung* behaviour was evidenced through the variation with wavelength of the flipping ratio for polarized neutrons by Baruchel *et al.* (1982) on an yttrium iron garnet sample, with the geometry selected so that the defects would not affect the Bragg reflection used. The inclination method was used successfully by Zelepukhin *et al.* (1989), Kvardakov & Somenkov (1990), and Kvardakov *et al.* (1990*a*) for the weak ferromagnet FeBO₃, and in the room-temperature weak-ferromagnetic phase of hematite, α -Fe₂O₃, by Kvardakov *et al.* (1990*b*), and Kvardakov & Somenkov (1992).

Experiments on the influence of defects in nearly perfect crystals have been performed by several groups. The effect on the rocking curve was investigated by Eichhorn *et al.* (1967), the intensities were measured by Lambert & Malgrange (1982) and by Albertini, Boeuf, Cesini *et al.* (1976), and the influence on the *Pendellösung* behaviour was discussed by Kvardakov & Somenkov (1992). Boeuf & Rustichelli (1974) and Albertini *et al.* (1977) investigated silicon crystals curved by a thin surface silicon nitride layer.

Many experiments have been performed on vibrating crystals; reviews are given by Michalec *et al.* (1988) and by Kulda *et al.* (1988). Because the velocity of neutrons is of the same order of magnitude as the velocity of acoustic phonons in crystals, the effect of ultrasonic excitation on dynamical diffraction takes on some original features compared to the X-ray case (Iolin & Entin, 1983); they could to some extent be evidenced experimentally (Iolin *et al.*, 1986; Chalupa *et al.*, 1986). References to experimental work on

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neutron scattering by imperfect crystals under ultrasonic excitation are included in Zolotoyabko & Sander (1995).

Some experiments with no equivalent in the X-ray case could be performed. The very strong incoherent scattering of neutrons by protons, very different physically but similar in its effect to absorption, was also shown to lead to anomalous transmission effects by Sippel & Eichhorn (1968). Because the velocity of thermal neutrons in a vacuum is five orders of magnitude smaller than the velocity of light, the flight time for neutrons undergoing Bragg scattering in Laue geometry in a perfect crystal could be measured directly (Shull *et al.*, 1980). The effect of externally applied fields was measured experimentally for magnetic fields by Zeilinger & Shull (1979) and Zeilinger *et al.* (1986). Slight rotation of the crystal, introducing a Coriolis force, was used by Raum *et al.* (1995), and gravity was tested recently, with the spectacular result that some states are accelerated upwards (Zeilinger, 1995).

5.3.7. Applications of the dynamical theory of neutron scattering

5.3.7.1. Neutron optics

Most experiments in neutron scattering require an intensity-effective use of the available beam at the cost of relatively high divergence and wavelength spread. The monochromators must then be imperfect ('mosaic') crystals. In some cases, however, it is important to have a small divergence and wavelength band. One example is the search for small variations in neutron energy in inelastic scattering without the use of the neutron spin-echo principle. Perfect crystals must then be used as monochromators or analysers, and dynamical diffraction is directly involved. As in the X-ray case, special designs can lead to strong decrease in the intensity of harmonics, *i.e.* of contributions of $\lambda/2$ or $\lambda/3$ (Hart & Rodrigues, 1978). The possibility of focusing neutron beams by the use of perfect crystals with the incident beam spatially modulated in amplitude through an absorber, or in phase through an appropriate patterning of the surface, in analogy with the Bragg-Fresnel lenses developed for X-rays, was suggested by Indenbom (1979).

The use of two identical perfect crystals in non-dispersive (+, −, ||) setting provides a way of measuring the very narrow intrinsic rocking curves expected from the dynamical theory. Any divergence added between the two crystals can be sensitively measured. Thus perfect crystals provide interesting possibilities for measuring very-small-angle neutron scattering. This was performed by Takahashi *et al.* (1981, 1983) and Tomimitsu *et al.* (1986) on amorphous materials, and by Kvardakov *et al.* (1987) for the investigation of ferromagnetic domains in bulk silicon-iron specimens under stress, both through the variations in transmission associated with refraction on the domain walls and through small-angle scattering. Imaging applications are described in Section 5.3.7.4. Badurek *et al.* (1979) used the different deflection of the two polarization states provided by a magnetic prism placed between two perfect silicon crystals to produce polarized beams.

Curved almost-perfect crystals or crystals with a gradient in the lattice spacing can provide focusing (Albertini, Boeuf, Lagomarsino *et al.*, 1976) and vibrating crystals can give the possibility of tailoring the reflectivity of crystals, as well as of modulating beams in time (Michalec *et al.*, 1988). A double-crystal arrangement with bent crystals was shown by Eichhorn (1988) to be a flexible small-angle-neutron-scattering device.

5.3.7.2. Measurement of scattering lengths by Pendellösung effects

As in X-ray diffraction, *Pendellösung* oscillations provide an accurate way of measuring structure factors, hence coherent neutron

scattering lengths. The equal-thickness fringes expected from a wedge-shaped crystal were observed by Kikuta *et al.* (1971). Three kinds of measurements were made. Sippel *et al.* (1965) measured as a function of thickness the integrated reflectivity from a perfect crystal of silicon, the thickness of which they varied by polishing after each measurement, obtaining a curve similar to Fig. 5.1.6.7, corresponding to equation 5.1.6.8. Shull (1968) restricted the measurement to wavefields that propagated along the reflecting planes, hence at exact Bragg incidence, by setting fine slits on the entrance and exit faces of 3 to 10 mm-thick silicon crystals, and measured the oscillation in diffracted intensity as he varied the wavelength of the neutrons used by rotating the crystal. Shull & Oberteuffer (1972) showed that a better interpretation of the data, when the beam is restricted to a fine slit, corresponds to the spherical wave approach (actually cylindrical wave), and the boundary conditions were discussed more generally by Arthur & Horne (1985). Somenkov *et al.* (1978) developed the inclination method, in which the integrated reflectivity is measured as the effective crystal thickness is varied non-destructively, by rotating the crystal around the diffraction vector, and used it for germanium. Belova *et al.* (1983) discuss this method in detail. The results obtained by this group for magnetic crystals are mentioned in Section 5.3.6. Structure-factor values for magnetic reflections were obtained by Kvardakov *et al.* (1995) for the weak ferromagnet FeBO₃.

5.3.7.3. Neutron interferometry

Because diffraction by perfect crystals provides a well defined distribution of the intensity and phase of the beam, interferometry with X-rays or neutrons is possible using ingeniously designed and carefully manufactured monolithic devices carved out of single crystals of silicon. The technical and scientific features of this family of techniques are well summarized by Bonse (1979, 1988), as well as other papers in the same volumes, and by Shull (1986).

X-ray interferometry started with the Bonse-Hart interferometer (Bonse & Hart, 1965). A typical device is the LLL skew-symmetric interferometer, where the L's stand for Laue, indicating transmission geometry in all crystal slabs. In these slabs, which can be called the splitter, the mirrors and the recombiner, the same pair of opposite reflections, in symmetrical Laue geometry, is used three times. In the first slab, the incident beam is coherently split into a transmitted and a diffracted beam. Each of these is then diffracted in the two mirrors, and the resulting beams interfere in the recombiner, again yielding a forward-diffracted and a diffracted beam, the intensities of both of which are measured. This version, the analogue of the Mach-Zehnder interferometer in optics, offers a sizeable space (several cm of path length) where two coherent parallel beams can be submitted to various external actions. Shifting the relative phase of these beams (*e.g.* by π , introducing an optical path-length difference of $\lambda/2$) results in the intensities of the outgoing beams changing from a maximum to a minimum.

Applications of neutron interferometry range from the very useful to the very exotic. The most useful one is probably the measurement of coherent neutron scattering lengths. Unlike the *Pendellösung* method described in Section 5.3.7.2, this method does not require the measured samples to be perfect single crystals, nor indeed crystals. Placing a slab of material across one of the beams and rotating it will induce an optical path-length difference of $(1 - n)t$ if t is the effective thickness along the beam, hence a phase shift of $2\pi(1 - n)t/\lambda$. With the expression of the refractive index n as given in Section 5.3.2.2, it is clear that for an isotopically pure material the scattering length b_{coh} can be deduced from the measurement of intensity *versus* the rotation angle of the phase shifter. This is a very versatile and much used method. The decrease in oscillation contrast can be used to obtain information of

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relevance to materials science, such as statistical properties of magnetic domain distributions (Korpiun, 1966) or precipitates (Rauch & Seidl, 1987); Rauch (1995) analyses the effect in terms of the neutron coherence function.

Many elegant experiments have been performed with neutron interferometers in efforts to set an upper limit to effects than can be considered as nonexistent, or to test expectations of basic quantum physics. Many papers are found in the same volumes as Bonse (1979) and Bonse (1988); excellent reviews have been given by Klein & Werner (1983), Klein (1988), and Werner (1995). Among the topics investigated are the effect of gravity (Colella *et al.*, 1975), the Sagnac effect, *i.e.* the influence of the Earth's rotation (Werner *et al.*, 1979), the Fizeau effect, *i.e.* the effect of the movement of the material through which the neutrons are transmitted (Arif *et al.*, 1988) and the Aharonov–Casher effect, *i.e.* the dual of the Aharonov–Bohm effect for neutral particles having a magnetic moment (Cimmino *et al.*, 1989).

5.3.7.4. Neutron diffraction topography and other imaging methods

These are the neutron form of the 'topographic' or diffraction imaging techniques, in which an image of a single crystal is obtained through the local variations in Bragg-diffracted intensity due to inhomogeneities in the sample. It is briefly described in Chapter 2.8 of *IT C*. It was pioneered by Doi *et al.* (1971) and by Ando & Hosoya (1972). Like its X-ray counterpart, neutron topography can reveal isolated defects, such as dislocations (Schlenker *et al.*, 1974; Malgrange *et al.*, 1976). Because of the small neutron fluxes available, it is not very convenient for this purpose, since the resolution is poor or the exposure times are very long. On the other hand, the very low absorption of neutrons in most materials makes it quite convenient for observing the gross defect structure in samples that would be too absorbing for X-rays (Tomimitsu & Doi, 1974; Baruchel *et al.*, 1978; Tomimitsu *et al.*, 1983; Kvardakov *et al.*, 1992), or the spatial modulation of distortion due to vibration, for example in quartz (Michalec *et al.*, 1975), and resonant magnetoelastic effects (Kvardakov & Some-

nkov, 1991). In particular, virtual slices of bulky as-grown samples can be investigated without cutting them using neutron section topography or neutron tomography (Schlenker *et al.*, 1975; Davidson & Case, 1976).

Neutron topography also shows the salient dynamical interference effect, *viz* *Pendellösung*, visually, in the form of fringes (Kikuta *et al.*, 1971; Malgrange *et al.*, 1976; Tomimitsu & Zeyen, 1978). Its unique feature, however, is the possibility of observing and directly characterizing inhomogeneities in the magnetic structure, *i.e.* magnetic domains of all kinds [ferromagnetic domains (Schlenker & Shull, 1973) and antiferromagnetic domains of various sorts (Schlenker & Baruchel, 1978), including spin-density wave domains (Ando & Hosoya, 1972, 1978; Davidson *et al.*, 1974), 180° or time-reversed domains in some materials and helimagnetic or chirality domains (Baruchel *et al.*, 1990)], or coexisting phases at a first-order phase transition (Baruchel, 1989). In such cases, the contrast is primarily due to local variations in the structure factor, a situation very unusual in X-ray topography, and good crystal quality, leading to dynamical scattering behaviour, is essential in the observation process only in a few cases (Schlenker *et al.*, 1978). It is often crucial, however, for making the domain structure simple enough to be resolved, in particular in the case of antiferromagnetic domains.

Imaging can also be performed for samples that need be neither crystals nor perfect. Phase-contrast imaging of a specimen through which the neutrons are transmitted can be performed in a neutron interferometer. It has been shown to reveal thickness variations by Bauspiess *et al.* (1978) and ferromagnetic domains by Schlenker *et al.* (1980). The same papers showed that phase edges show up as contrast when one of the interferometer paths is blocked, *i.e.* when the sample is placed effectively between perfect, identical crystals set for diffraction in a non-dispersive setting. Under the name of neutron radiography with refraction contrast, this technique, essentially a form of Schlieren imaging, was further developed by Podurets, Somenkov & Shil'shtein (1989), Podurets, Somenkov, Chistyakov & Shil'shtein (1989), and Podurets *et al.* (1991), who were able to image internal ferromagnetic domain walls in samples 10 mm thick.

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