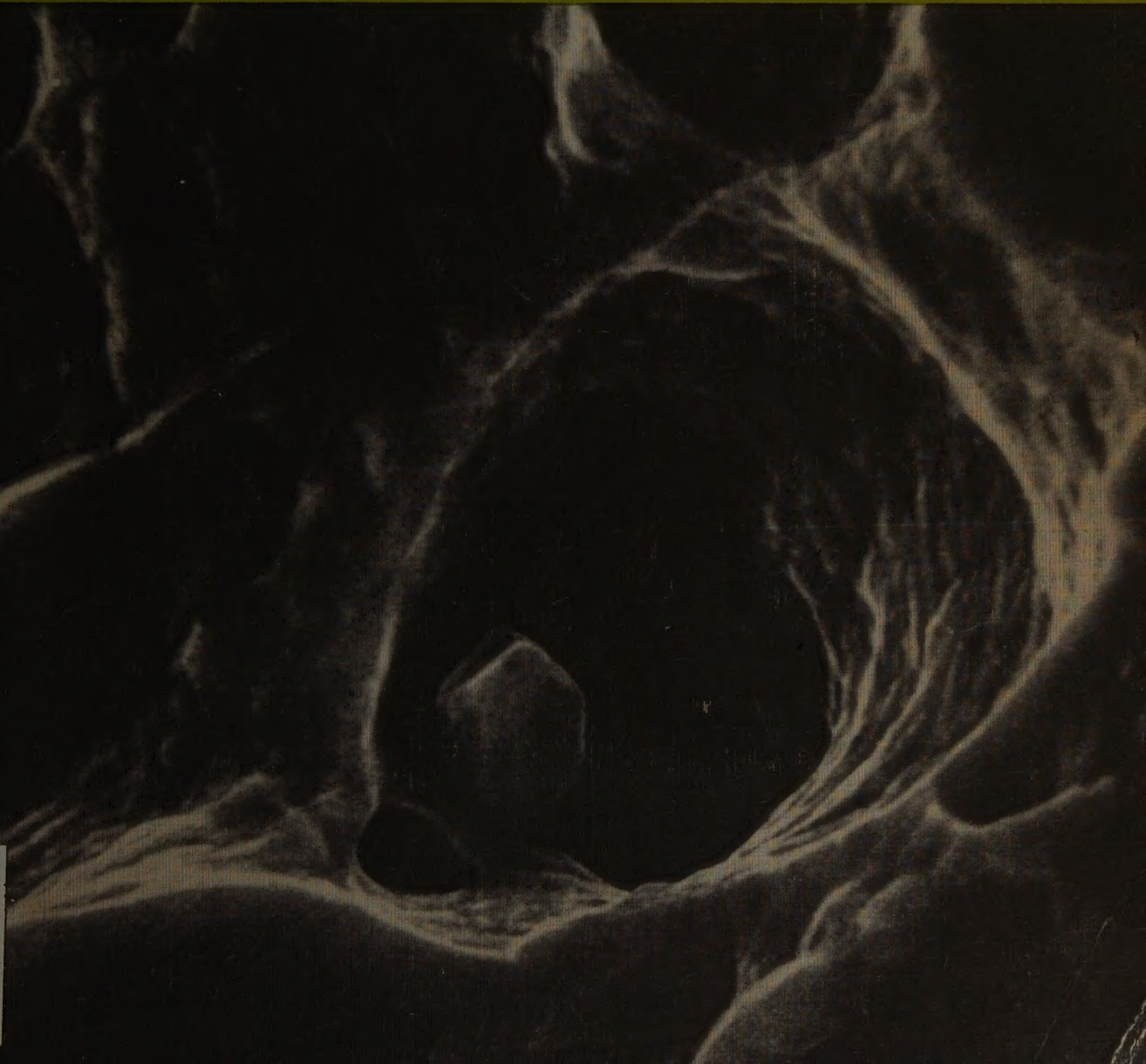
a first course in Crystallography

Alan Windle



A
FIRST COURSE
IN
CRYSTALLOGRAPHY

A
First Course
in
Crystallography

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Contents

Preface

Crystallography today must be one of the most widely used disciplines across the whole spectrum of natural and applied sciences. Rather than remaining confined to its historical context of geology, it has become an accepted part of chemistry, physics, metallurgy, materials science, molecular biology and electronic engineering; also mathematicians continue to play a significant rôle in the development of the subject in its own right.

The aim of this book is to provide a course of instruction in crystallography for anybody meeting the subject for the first time, whether this be at school, college or university, or as a part of any other type of further education. The book is designed as a direct teaching aid rather than a detailed exposition of the subject; the result is a concise text amplified by many diagrams, exercises and worked examples. The exercises are not all confined to the end of each chapter but also appear at strategic points within the text itself. Most of the exercises can be answered within the book, require minimal reference to other works and form a convenient basis for continuous assessment. Appendix 4 contains notes and answers relating to some of the questions.

The course is written within the context of existing crystallographic text books, and the author is indebted to the teaching and guidance he has obtained from these.

Particularly recommended to the reader for further reference are:

Crystallography and Crystal Defects	A. Kelly and G. W. Groves
Chemical Crystallography	C. W. Bunn
Crystals	C. W. Bunn
Elementary Crystallography	M. J. Buerger

The order and method in which the various crystallographic concepts are introduced has been largely influenced by the author's experience in teaching the subject to materials science and metallurgy students. It has become apparent that an immediate plunge into formal crystallographic theory along the admittedly elegant lines of translational symmetry, point group symmetry, and space group symmetry tends to discourage all but the highly motivated students. In addition the teaching of the subject is often 'hand in glove' with elementary instruction in diffraction methods for structure analysis, and in this context familiarity with lattices, indices and the stereographic projection is of more immediate practical use than an understanding of point and space groups.

The opening chapters deal with the analysis of repeating patterns and the description and classification of crystal lattices; this in turn leads to a first encounter with rotation, mirror and inversion symmetry elements. In Chapter 7 attention is turned to building up crystal structures from component atoms so as to give some insight as to why a given collection of atoms assumes a particular crystal structure and in Chapter 8 various real structures are analysed in terms of lattice and motif. The next three chapters explain the systems of directional and Miller indices and discuss the representation of lattice planes as a reciprocal lattice. Chapter 12 is devoted to teaching the use of the stereographic projection with particular emphasis being placed on practical exercises. A small but usable Wulff Net is printed on the back cover.

The final three chapters contain a fairly detailed treatment of point and space group symmetry. The derivation and representation of space groups is illustrated by particular examples; and a case study on the structure of calcium carbonate (aragonite) serves to relate the view of a crystal as the natural consequence of packing a group of atoms together to the analysis of its structure in terms of the various symmetry elements.

I am grateful to many for help and advice during the preparation of this work. In particular I should like to thank Professor Charles Newey of the Open University for his constructive and penetrating comments on the manuscript, and Dr George Parry of Imperial College for his suggestions in connection with the final three chapters.

The care with which Mrs T. Gillham typed the original student classwork notes greatly aided their development into the first manuscript draft, and I was especially fortunate to have many of the diagrams drawn by Mr Fred Huggins and Dr Stewart Murray whose draughtmanship was complemented by a knowledge of crystallography. Mr Hayward also helped with some of the photography; I thank him too.

In addition my thanks are due to Professor J. G. Ball who is Head of the Metallurgy and Materials Science Department at Imperial College and Mr S. L. Dennis of G. Bell & Sons who provided encouragement to initiate and sustain this project, and also to Janet, my wife, whose considerable contribution was altogether of a more homely nature.

1

Repeating Patterns and Lattices

1.1 The One-Dimensional Lattice

Figure 1.1 shows part of a long freight train. It is also an example of a pattern which repeats itself periodically in one dimension.

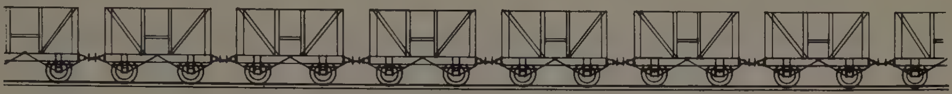


Fig. 1.1 A pattern which repeats itself in one dimension.

Each identical wagon can be taken as one unit of the pattern, and the way in which they are arranged to form the train is best described by means of a lattice.

A **lattice** is a geometric concept and can be defined as:

> 'An infinite, one-, two- or three-dimensional, regular arrangement of points, each of which has identical surroundings.'

In order to describe the arrangement of wagons, **lattice points** are placed at exactly equivalent positions within each unit of pattern, i.e. at the same point on each wagon. Let us choose, in this example, the centre of each left-hand wheel (Fig. 1.2).

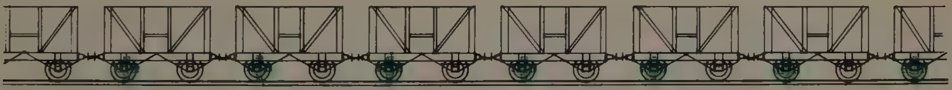


Fig. 1.2 A pattern with a lattice added.

The arrangement of the wagons is now fully described by the position of the lattice points alone, in fact by the one-dimensional **linear lattice** drawn below.

Fig. 1.3 The linear lattice.

1.2 Patterns in Two Dimensions

A pattern which is made up of identical units which repeat periodically in **two** dimensions can be described by a **planar lattice**.

Take for example a screen print on curtain material:

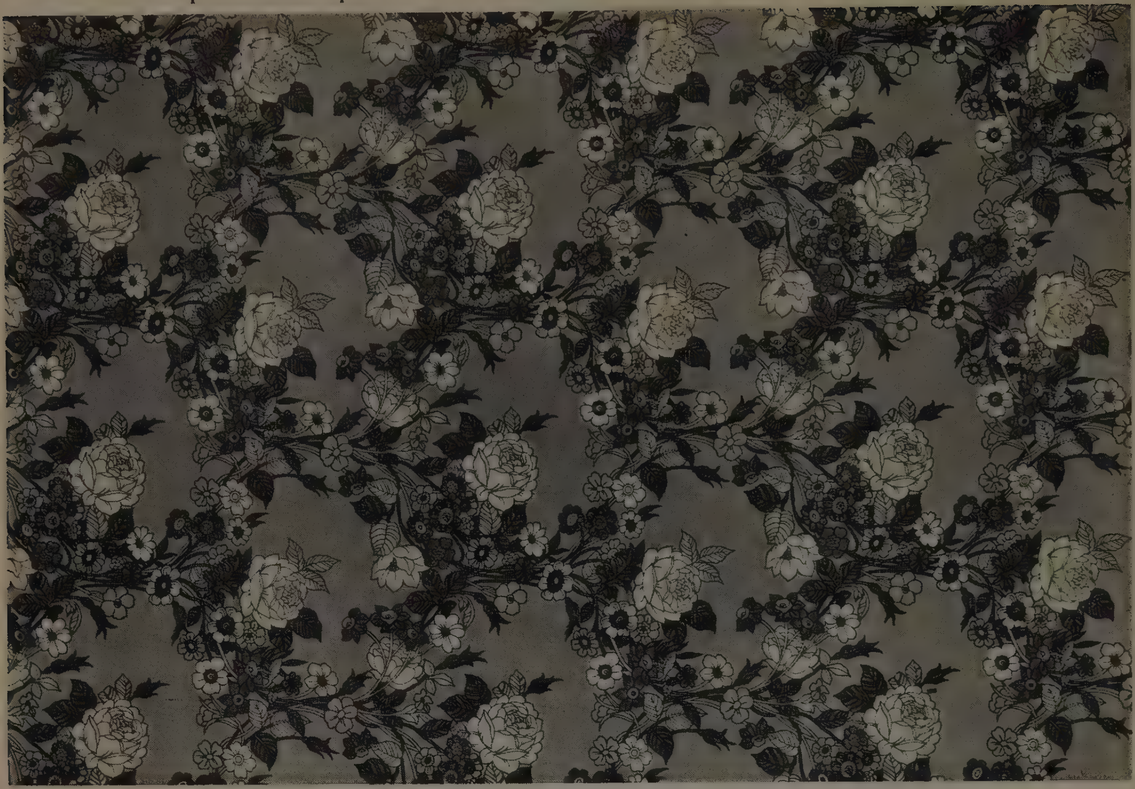


Fig. 1.4 A pattern repeating in two dimensions.

Lattice points can be placed at equivalent positions within each of the repeating units, choosing perhaps, for the sake of convenience, the centre of the rose (Fig. 1.5).

The resultant planar lattice (Fig. 1.6) fully describes the way the individual units are arranged to form the pattern.

1.3 A Crystal as a Repeating Pattern

A crystal is an excellent example of a pattern which repeats itself in three dimensions. The units of pattern from which the crystal is built up are either single atoms or groups of atoms. Each repeating unit is known as the **motif**. (The alternative term 'basis' is sometimes used.) The regular arrangement of the motifs in the crystal is described by assigning to each a lattice point and forming a three-dimensional or **space lattice**. A **crystal structure** is determined by the type, number and arrangement of atoms in the motif and by the relative positions of the motifs as defined by the space lattice.

This can be written as:

$$\text{Lattice} \quad + \quad \text{Motif} \quad \longrightarrow \quad \text{Crystal Structure}$$

Note: The + sign here is not used in the rigid arithmetic sense, for the motif is added to each and every lattice point. Strictly this is the process of convolution; so that one should say that a lattice convoluted with a motif generates a crystal structure.

However the + sign will do for now.

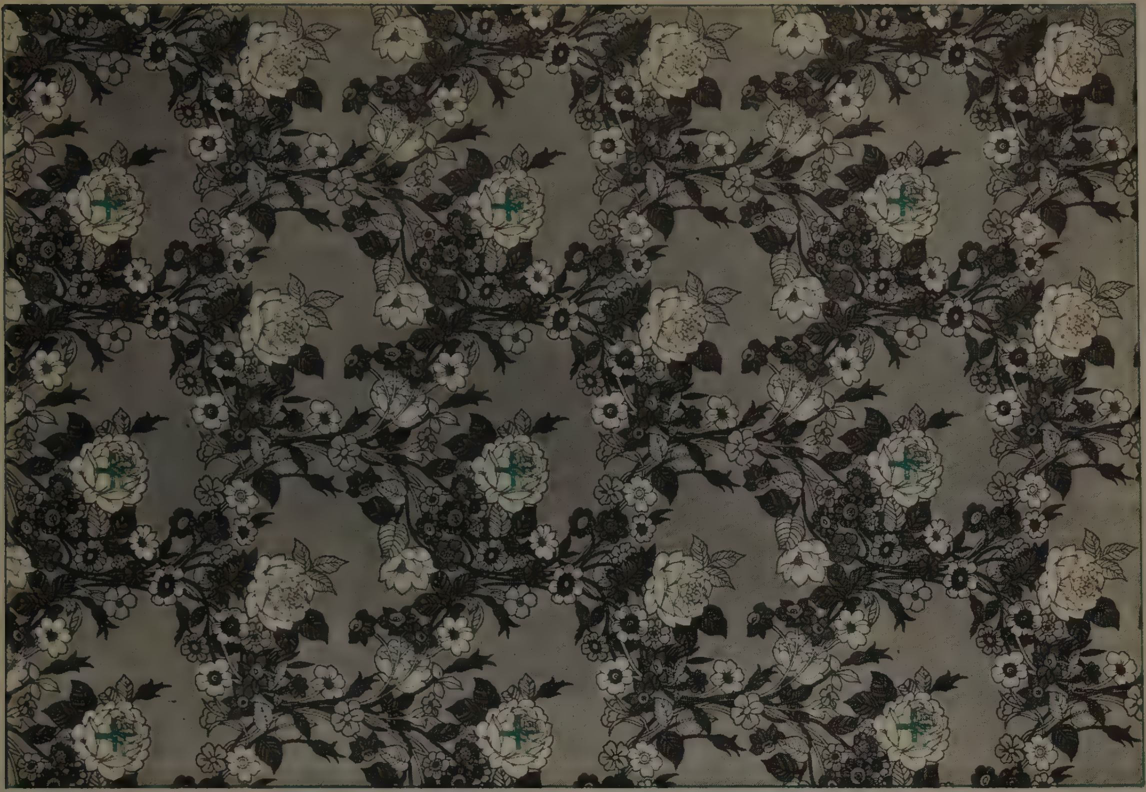


Fig. 1.5 As Fig. 1.4 but with a plane lattice added.

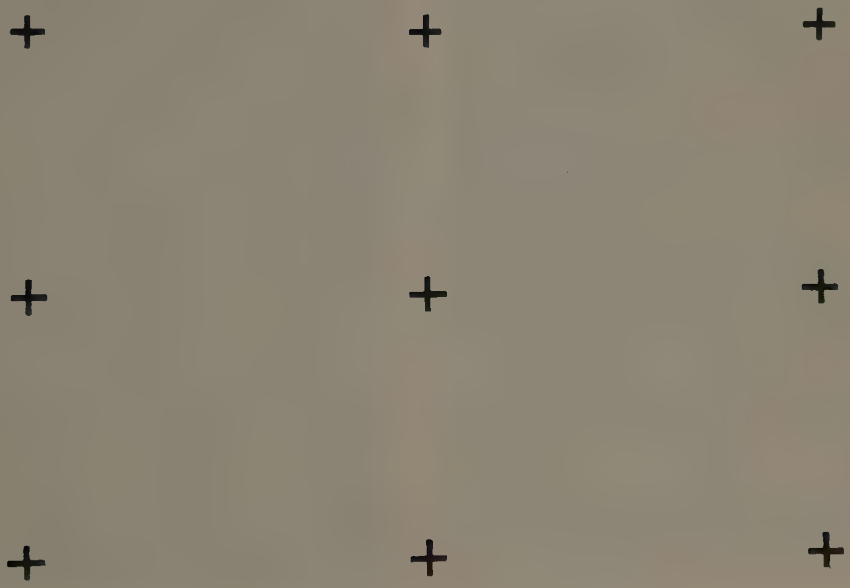


Fig. 1.6 The planar lattice.

TO DO

1. Draw lattices on the following planar patterns:

(*a*)

Fig. 1.7

(*b*)

Fig. 1.8

(*c*)

Fig. 1.9

(*d*)

Fig. 1.10

2. The diagram below represents a crystal structure which contains equal proportions of two types of atom.
Draw in some lattice points to form part of a space lattice and mark the atoms which belong to any **one** motif.

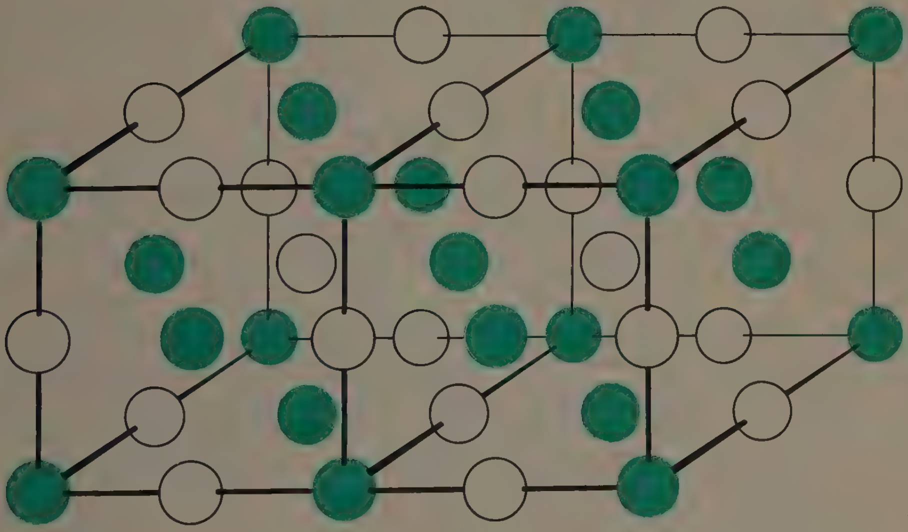


Fig. 1.11

TO BE ABLE TO DO

1. Define a lattice.
2. Explain the significance of the following terms in the context of crystallography:
   (*a*) Lattice Point.
   (*b*) Linear, Planar and Space Lattice.
   (*c*) Structure.
   (*d*) Motif.
3. Describe briefly the meaning of the statement:

$$\text{Lattice} + \text{Motif} \rightarrow \text{Crystal Structure.}$$

2

Describing the Lattice (Part 1) Translation Vectors

It would be most inconvenient if the only possible way of describing a lattice to another person was by drawing rows of dots on a piece of paper. Also the representation of a three-dimensional space lattice on a sheet of paper presents difficulties of its own.

A simpler method of communication is achieved if the **relative** positions of the lattice points are defined by **Primitive Translation Vectors** (also known as fundamental or conjugate translation vectors).

2.1 The Linear Lattice

A linear lattice can be described by just one Primitive Translation Vector **a**, drawn between two adjacent points.

Fig. 2.1

A vector drawn between any pair of points is called a **Lattice Translation Vector, r**. It is always an exact multiple of the primitive translation vector which is itself a special case of a lattice translation vector.

Therefore,

$$\mathbf{r} = u\mathbf{a}$$

where u = any integer, positive or negative.

2.2 The Planar Lattice

To describe a planar lattice a pair of primitive translation vectors are required.

They must be selected so that a suitable combination of them can define the relative positions of any two lattice points. A pair of such vectors are normally drawn from the same origin.

The operation of linear combinations of the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ (Fig. 2.2) of the form $u\mathbf{a}_1 + v\mathbf{a}_2$ (where u and v are positive or negative integers) can give translation from one lattice point to any other.

The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ therefore constitute a **primitive vector pair**. Similarly with $\mathbf{a}_3$ and $\mathbf{a}_4$.

These combinations are then equivalent to any lattice translation vector **r** as given by:

$$\mathbf{r} = u\mathbf{a}_1 + v\mathbf{a}_2$$

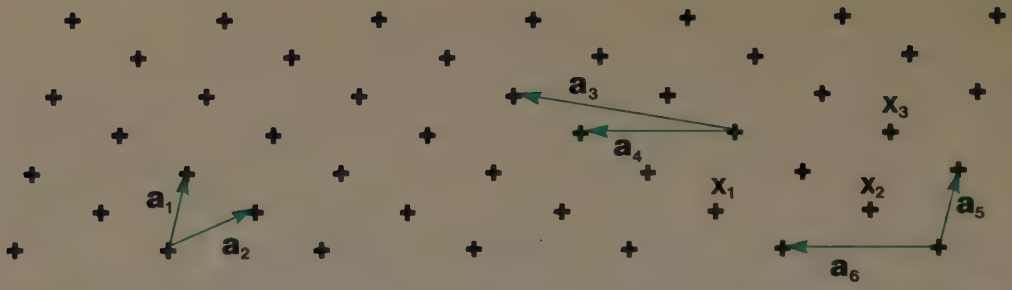


Fig. 2.2 Planar lattice showing two pairs of primitive translation vectors and one pair which are not primitive.

However, no combination of the pair of vectors $\mathbf{a}_5$ and $\mathbf{a}_6$, with u and v still integers, can give a translation from their origin to lattice points such as x_1, x_2, x_3, etc. They are therefore not a primitive vector pair being merely two lattice translation vectors.

2.3 The Space Lattice

A three-dimensional space lattice can be described by three vectors forming a **primitive vector group**. They are normally drawn from the same origin (Fig. 2.3).

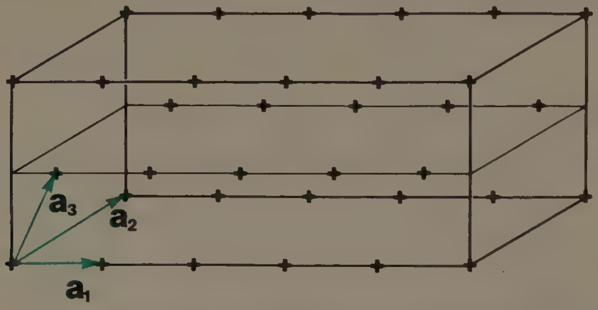


Fig. 2.3 Primitive translation vectors in three dimensions.

Any lattice translation vector, $\mathbf{r}$, can then be described by a suitable combination of the three vectors forming the primitive group, i.e.

$$\mathbf{r} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$$

TO DO

1. On the planar lattice below, indicate those pairs of vectors which are primitive.

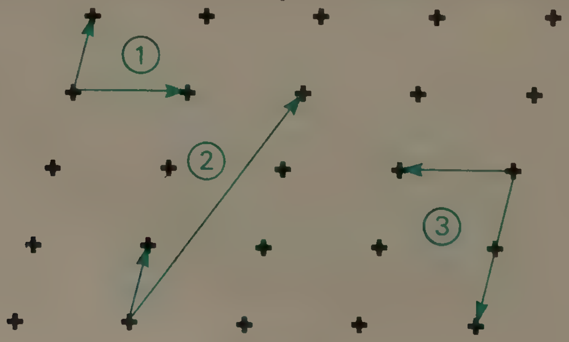


Fig. 2.4

2. On the planar lattice below draw in four different primitive vector pairs.

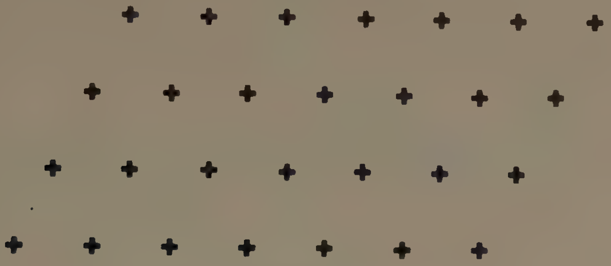


Fig. 2.5

3. Define the lattice translation vectors drawn below in terms of the primitive vector pair, $\mathbf{a}_1$ and $\mathbf{a}_2$.

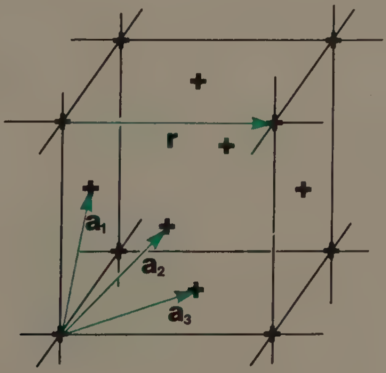
$\mathbf{r}_1$ =

$\mathbf{r}_2$ =

$\mathbf{r}_3$ =

$\mathbf{r}_4$ =

4. For the space lattice drawn below express $\mathbf{r}$ in terms of the primitive vector group, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$.



$\mathbf{r}$ =

TO BE ABLE TO DO

1. Define the difference between a lattice translation vector and a primitive translation vector.
2. Illustrate that a planar lattice can be fully defined by a primitive vector pair, and a space lattice by a primitive vector group.
3. Understand vector algebra (see Appendix 2).

3

Describing the Lattice (Part 2) The Lattice Unit Cell

The length and relative orientation of translation vectors constituting a primitive vector group is all the information needed to fully define a lattice. However, a sketch showing three primitive translation vectors drawn from one lattice point does not readily convey to the eye the shape of the lattice. If a parallelepiped is drawn with the three vectors as three of its edges, it illustrates much more clearly the general shape and form of the lattice. The parallelepiped is known as a **lattice unit cell**. The lattice unit cell also provides a framework within which atoms forming a representative part of the crystal structure can be drawn. A cell containing this additional information is known as a **structure cell**.

3.1 Primitive Cells

Primitive vector pairs drawn on a planar lattice can be viewed as outlining parallelograms (Fig. 3.1). These parallelograms are examples of what are called primitive unit cells (or strictly speaking primitive lattice unit cells).

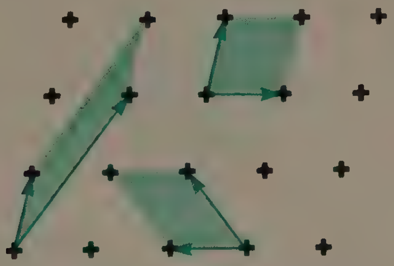


Fig. 3.1 Three primitive unit cells of a planar lattice.

The properties of such a **primitive unit cell** are:

(a) The cell will completely cover the lattice area when it is repeated with its origin at each lattice point in turn.

(b) The areas of different primitive cells are equal, irrespective of the choice of primitive translation vectors. (Verify this by measuring the three cells in Fig. 3.1. Parallelogram area = base × height.)

(c) Each cell contains the equivalent of **one** lattice point. Take for example one of the cells in Fig. 3.1. There is a lattice point at each of the four corners (total four lattice points), but each point is shared between a total of four cells and thus has an equivalent value of $\frac{1}{4}$.

For a space lattice any parallelepiped outlined by a primitive vector group is a primitive unit cell.

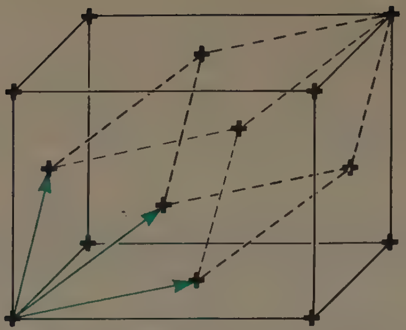


Fig. 3.2 A primitive cell and a non-primitive face centred cell drawn on the same space lattice.

Fig. 3.2 shows a primitive unit cell drawn within a part of a space lattice. As with a planar lattice, the primitive cell of a space lattice also contains just **one** lattice point. The reasoning goes as follows:

Maximum number of lattice points = 8 (one at each corner). But each point is shared between 8 primitive cells, thus the equivalent value of each to one cell is $\frac{1}{8}$. Therefore the total number of lattice points in the cell is $8 \times \frac{1}{8} = 1$.

The most convenient test to check whether a particular unit cell is primitive is to add up the equivalent number of lattice points it contains. Any cell with more than one is **non-primitive**.

3.2 Non-Primitive Cells

The cell in Fig. 3.3 is a **non-primitive unit cell** because it is outlined by a pair of lattice translation vectors which do not constitute a primitive vector pair.

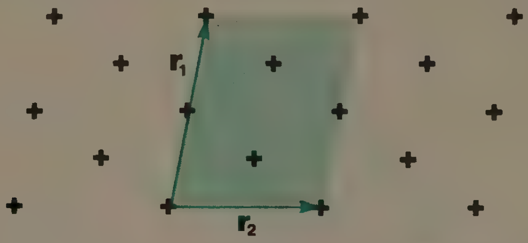


Fig. 3.3 A non-primitive unit cell on a planar lattice.

The number of lattice points it contains is worked out as follows:

Number of lattice points		*Equivalent value*	*Equivalent number*
Corners	4	$\frac{1}{4}$	1
Edges	2	$\frac{1}{2}$	1
Inside	2	1	2
		Total	4

Similarly the non-primitive cell of a space lattice drawn in Fig. 3.4 can be shown to contain 8 lattice points:

Number of lattice points		*Equivalent value*	*Equivalent number*
Corners	8	$\frac{1}{8}$	1
Edges	12	$\frac{1}{4}$	3
Faces	6	$\frac{1}{2}$	3
Inside	1	1	1
		Total	8

The volume of a non-primitive unit cell containing n lattice points is n times that of a primitive cell of the same space lattice.

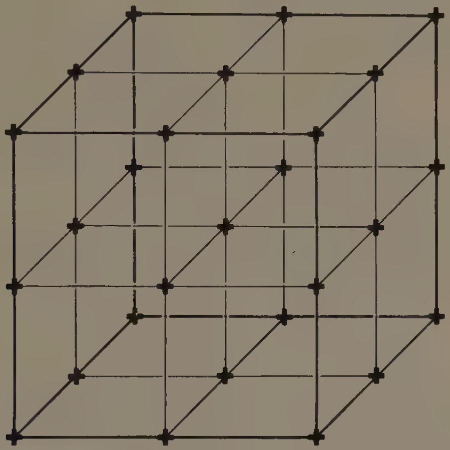


Fig. 3.4 A non-primitive unit cell built up from eight primitive ones.

When a non-primitive unit cell is made up of a number of adjacent primitive cells as in Fig. 3.4, it is alternatively known as a **multiple primitive unit cell**. A non-primitive cell consisting of a group of smaller non-primitive cells is sometimes referred to as a **multiple non-primitive unit cell**.

3.3 Areas and Volumes of Unit Cells

(N.B. see Appendix 2 for an outline of vector algebra.)

(*i*) *The area of a planar unit cell*

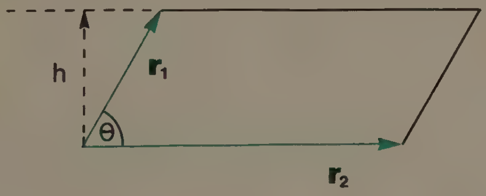


Fig. 3.5

The area of the parallelogram in Fig. 3.5 is given by base × height.

$$\text{The height} = |\mathbf{r}_1| \sin\theta$$

Therefore

$$\text{area} = |\mathbf{r}_2|\,|\mathbf{r}_1| \sin\theta$$

This can be written in vector notation as a vector product:

$$\text{Area} = \mathbf{r}_1 \times \mathbf{r}_2.$$

The vector product is itself a vector of magnitude equal to the area of the parallelogram and direction perpendicular to both $\mathbf{r}_1$ and $\mathbf{r}_2$.

(*ii*) *The volume of a three-dimensional unit cell*
The volume of a parallelepiped (Fig. 3.6) = base area × height

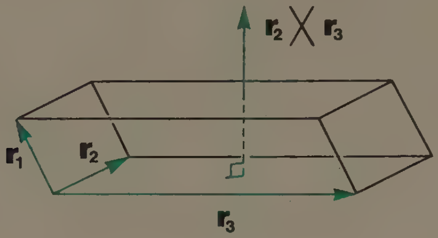


Fig. 3.6

The base area is the magnitude of the vector $\mathbf{r}_2 \times \mathbf{r}_3$. The height is the vector $\mathbf{r}_1$ resolved in the direction perpendicular to the base, i.e. parallel to the vector $\mathbf{r}_2 \times \mathbf{r}_3$.

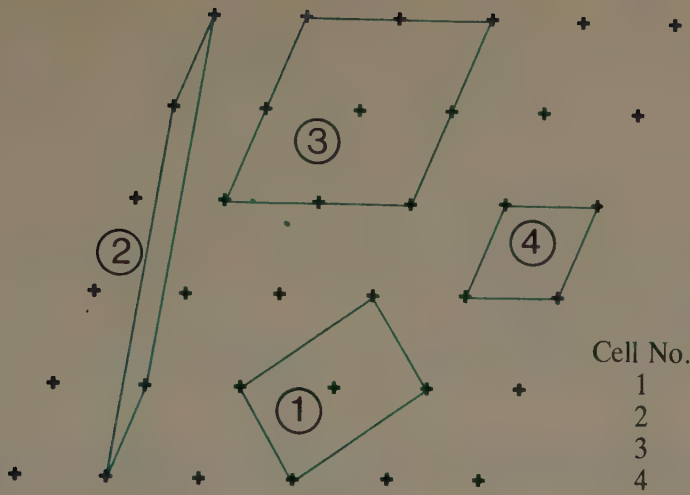
Therefore, $$\text{volume} = (\mathbf{r}_2 \times \mathbf{r}_3).\mathbf{r}_1.$$

TO DO

1. On the planar lattice construct four different primitive unit cells.

Fig. 3.7

2. Calculate the number of lattice points contained within each of the unit cells in Fig. 3.8, and tick those which are primitive.



Cell No.	No. of points
1	
2	
3	
4	

Fig. 3.8

3. What is the equivalent number of lattice points contained in the unit cell below? Is it primitive or non-primitive?

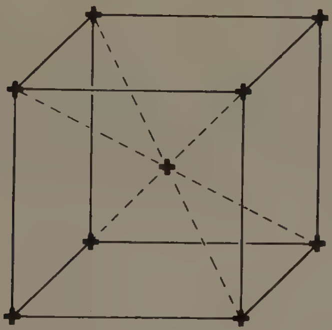


Fig. 3.9

Number of lattice points =

Note: All unit cells so far considered are known fully as **lattice** unit cells. They refer only to the lattice and should not depict any features of pattern or crystal structure.

TO BE ABLE TO DO

1. Write down:
   (*a*) The properties of a primitive unit cell.
   (*b*) The vector formulae for the area and volume of unit cells.
2. Explain the difference between primitive and non-primitive unit cells.

4

Elements of Symmetry — An Introduction

An understanding of the various forms of symmetry, their recognition and description, is of central importance in crystallography and symmetry theory will be discussed in some detail at a later stage. This chapter serves to introduce the topic and to provide the groundwork essential for the next two chapters which describe how symmetry is used as the basis for classifying the various forms of lattice.

4.1 Symmetry

If a lattice, or a shape, or an object can be moved in a certain way but still appear exactly the same, then it shows the property of **symmetry**. The movements which cause no change are known as **symmetry operations**, and the various different types of symmetry operation are classified as **symmetry elements**.

4.2 Translational Symmetry

The section of the freight train in Chapter 1 shows **translational symmetry** because any movement along the track by one or more truck lengths will leave the view of the train completely unchanged. Lattices illustrate the translational symmetry of the periodic patterns, and the translational symmetry operations are always lattice translation vectors. The translational symmetry element is defined for one dimension by a primitive translational vector and for two and three dimensions by primitive vector pairs and groups respectively.

4.3 Rotation Symmetry

We call shape A of Fig. 4.1 symmetrical, but shape B unsymmetrical. It is difficult to describe exactly the difference, but we can note some of the ways in which A **is** symmetrical.

If A is rotated about an axis perpendicular to the page and passing through its centre, it will appear exactly the same after every 60° of rotation. It will take six such operations to bring the hexagon back to its starting position; the symmetry element is thus a six-fold **rotation axis** or **hexad**.

It is impossible to find any such axis on shape B.

If we think of shape A as a piece of uniform cardboard, identical on each side, then in addition to the hexad there are six two-fold axes of **diads** lying in the plane of the shape (Fig. 4.2). A two-fold axis means that after a rotation of 180° the shape will appear unchanged.

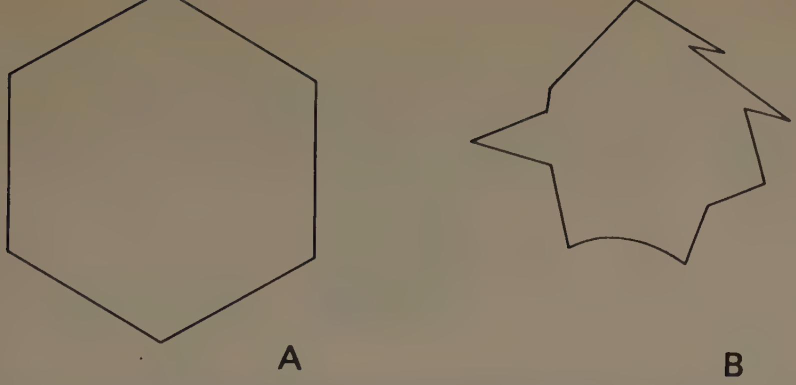


Fig. 4.1 Symmetrical and non-symmetrical shapes.

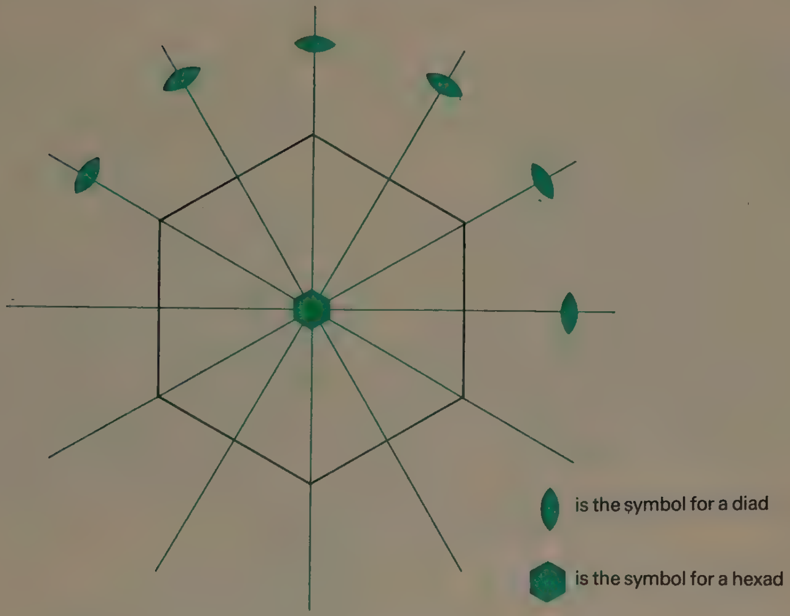


Fig. 4.2 A two-dimensional hexagon showing axes of rotational symmetry.

An equilateral triangle has a three-fold axis or **triad** perpendicular to it and passing through its centre, and three diads in its plane; Fig. 4.3(*a*).

A square has a four-fold axis or **tetrad** perpendicular to its centre, and four diads in its plane; Fig. 4.3(*b*).

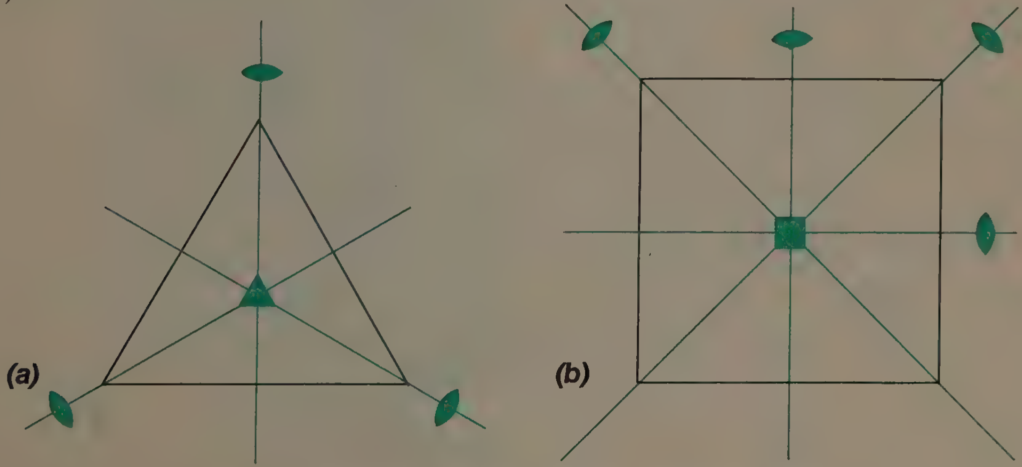


Fig. 4.3 The rotational symmetry axes of a triangle and a square.

If one is considering just geometric shapes then *n*-fold axes are possible. However, when the shapes are in fact unit cells of the lattice, they must fit together to fill all space. This places a restriction on the possible types of rotation axis. Those permissible in lattices are:

two-fold = diad
three-fold = triad
four-fold = tetrad
six-fold = hexad.

Figure 4.4 gives a two-dimensional illustration of this principle. It shows that attempts to completely cover an area with shapes containing other symmetry axes are doomed to failure.

e.g.

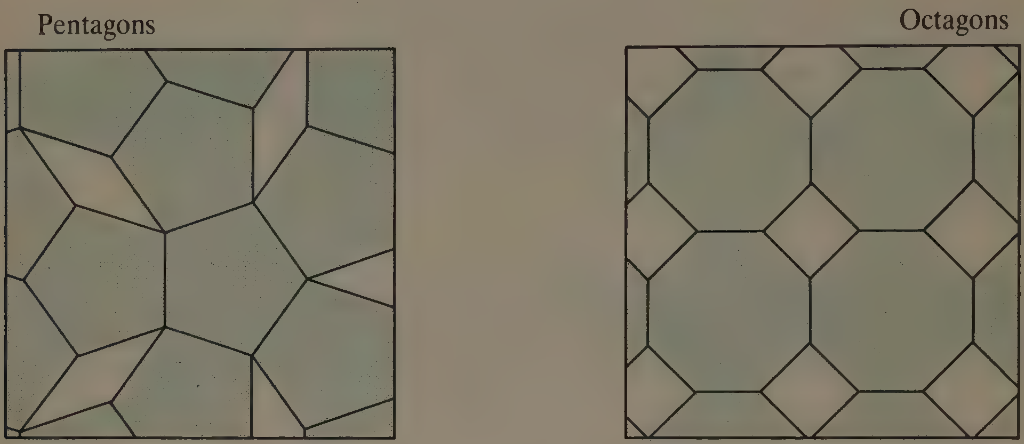


Fig. 4.4 Attempts to arrange pentagons and octagons so that they completely cover an area. It is not possible (N.B. shapes represent unit cells, not motifs).

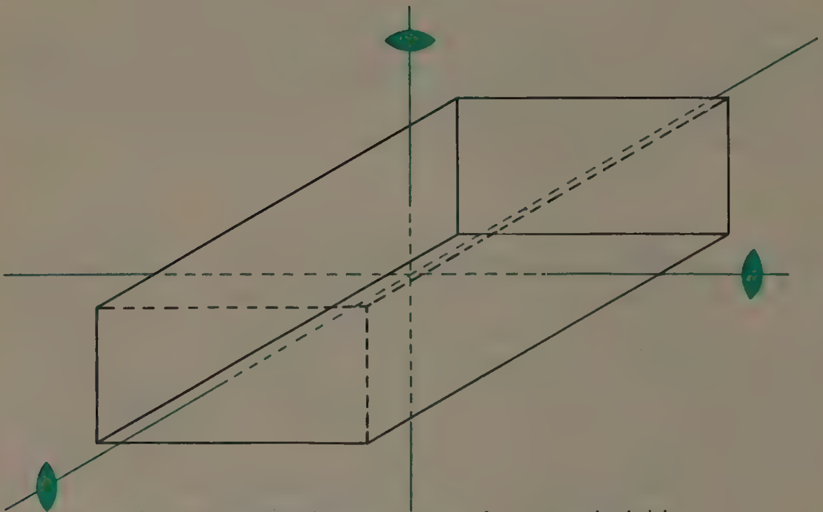


Fig. 4.5 Rotational symmetry axes of a rectangular brick.

Deciding upon the symmetry axes of three-dimensional shapes is a little more difficult. For example, a plain brick has three diad axes (Fig. 4.5).

A cube has higher symmetry and possesses many more axes. In addition to diads and tetrads, it also has four triads. The three-fold symmetry is readily appearent if a cube is viewed along one of its triads as in Fig. 4.6.

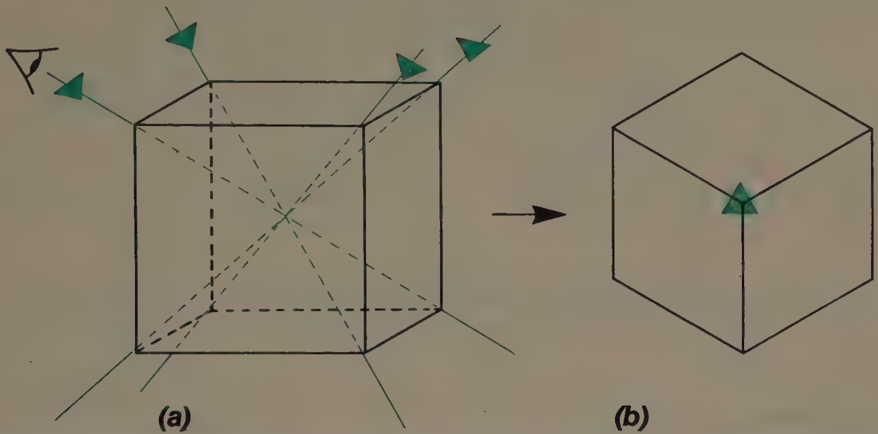


Fig. 4.6 Three-fold rotational symmetry axes of a cube. There are also two-fold and four-fold axes which are not shown.

4.4 Reflection Symmetry (Mirror Planes)

The model of the head in the photograph has just one symmetry element — a **mirror plane** dividing the left side from the right (Fig. 4.7). If the bust was cut in two along this plane and one half laid flat on a mirror, the effect would be similar to the original.

Mirror planes can be found in many geometric objects, and as with rotation axes, the higher the symmetry the greater their frequency of occurrence.

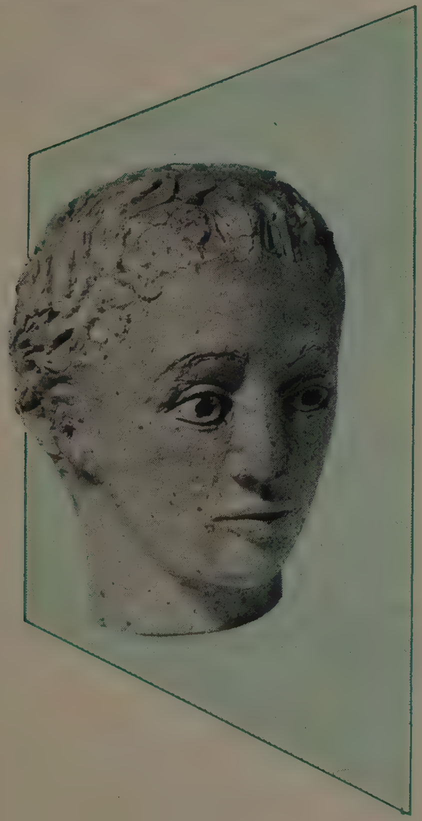


Fig. 4.7 An example of mirror symmetry.

Example:

The cardboard equilateral triangle in Fig. 4.8 has three mirror planes perpendicular to its plane and parallel to the three diads. But, unlike the axes, the mirror planes would remain if one side of the cardboard was painted a different colour from the other; this action however would destroy the fourth mirror plane (Fig. 4.8(*b*)) which lies parallel to and bisects the triangle.

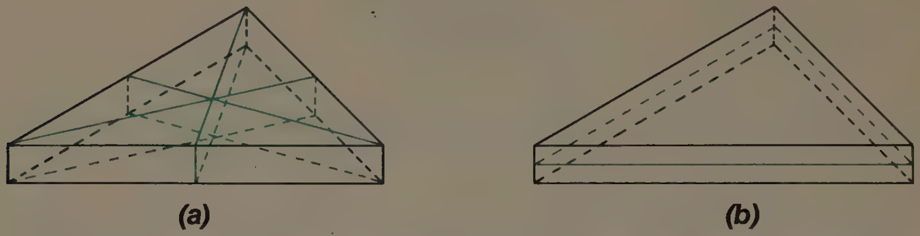


Fig. 4.8 Mirror plane symmetry possessed by an equilateral triangle cut out of cardboard.

4.5 Inversion Symmetry

This symmetry element involves reflection through a point called the **centre of symmetry**.

A three-dimensional structure possesses inversion symmetry if it remains unchanged when every small element of the structure with general coordinates (x, y, z) is reflected through the centre of symmetry (at 0, 0, 0) to an equivalent point at $(-x, -y, -z)$.

Another way of looking at inversion symmetry is to think of building a large structure from very many small but identical bricks. One can ensure that the structure has inversion symmetry if for every brick laid at coordinates (x, y, z) another is put down at $(-x, -y, -z)$. E.g. for one brick at $(-10, 5, -3)$ another should be put at $(10, -5, 3)$ etc. Again the origin of the coordinates will be the centre of symmetry (Fig. 4.9(*a*) and (*b*)).

All infinite lattices have centres of symmetry at each lattice point and at other special positions. Crystal structures however do not necessarily show inversion symmetry. For those that do it can be said that for every atom at (x, y, z) an identical atom will be found at $(-x, -y, -z)$ when $(0, 0, 0)$ is positioned at the centre of symmetry—which is of course just a further statement of the definition of the inversion element.

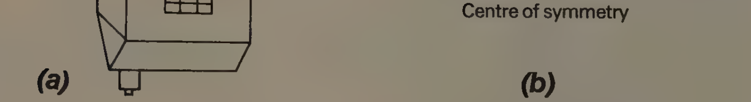


Fig. 4.9 Two examples of inversion symmetry. In each case every small unit of the structure can be reflected through the centre of symmetry without causing any change in the shape, orientation or position of the overall structure.

4.6 Symmetry Theory

This chapter serves as only an introduction to some of the basic ideas of symmetry theory, a full treatment of the subject being a scientific discipline in its own right. It is worth noting at this stage, however, that inversion and reflection symmetry elements can combine with rotation axes to produce new elements which play an essential rôle in the formulation of what is known as point group symmetry (Chapter 15). A further development of symmetry theory involves all possible combinations of point group elements with the lattice translation operation to generate collections of self-consistent elements known as space groups (Chapter 16).

TO DO

1. Cut out and make up various geometric models using the outlines drawn in Appendix 1.
2. On the hexagonal prism and the tetrahedron mark the points of emergence of the various symmetry axes as follows:

diad ⬮ triad ▲ tetrad ■ hexad ⬢

Alternatively draw in the symmetry axes on the diagrams below.

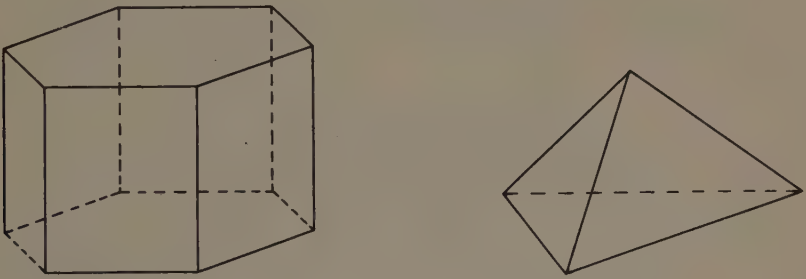


Fig. 4.10

3. Repeat the previous exercise using the cube and the regular octahedron. Alternatively draw in the axes on the diagrams. How many square base pyramids can you find in the octahedron?

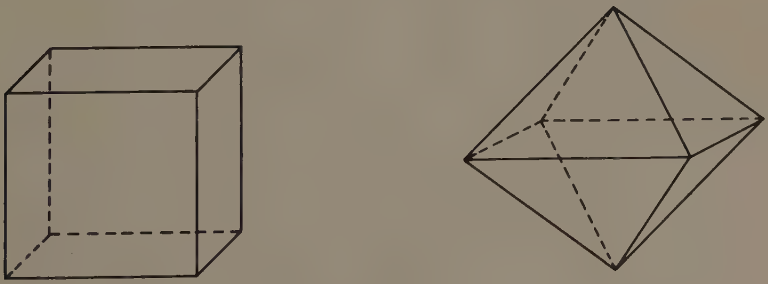


Fig. 4.11

4. Mark in, either on the cube and hexagonal prism models or on the diagrams below, the traces of all mirror planes.

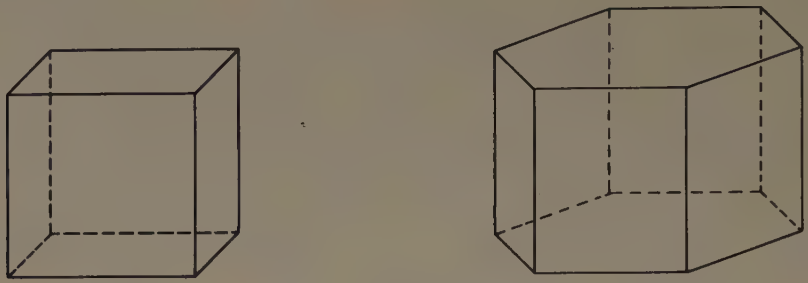


Fig. 4.12

5. List those of the above shapes which show inversion symmetry.

TO BE ABLE TO DO

1. Describe the four simple types of symmetry element: translation, rotation, reflection and inversion.

5

The Planar Lattices Their Symmetry and Classification into Systems

5.1 Planar Crystal Systems

The symmetry groupings called '**systems**' do not apply to lattices alone; they are a fundamental part of all symmetry theory. There are **four** planar **crystal systems** (the qualification 'crystal' here means that only systems based on diads, triads, tetrads and hexads are being considered — c.f. Section 4.3) and each has minimum symmetry entry requirements listed in Table 5.1.

TABLE 5.1

Planar crystal system	*Minimum symmetry requirements*
Oblique	None
Rectangular	One mirror plane
Square	One tetrad
Hexagonal	One triad **or** one hexad

There are **five** distinct planar lattices. In the following sections they are analysed in terms of their symmetry elements and allocated to the appropriate crystal systems.

5.2 Parallelogram Lattice

Note: The lattices tend to be named after the shape of their unit cells.

$$|\mathbf{a}_1| \neq |\mathbf{a}_2| \qquad \alpha \neq 90°$$

Fig. 5.1

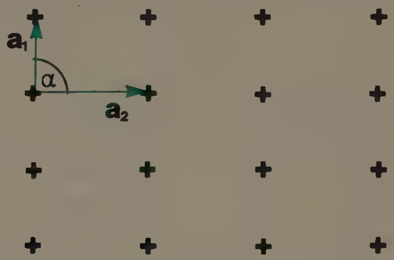
The operation of a rotation axis perpendicular to the lattice plane and through a lattice point will bring all the lattice points into co-incidence every 180° of rotation. It is thus a diad and is also the highest order of rotation symmetry present. This rotation element, together with the absence of reflection symmetry characterises the parallelogram lattice.

There is, of course, a diad through every lattice point, but in addition similar axes appear midway between every adjacent pair of lattice points (Fig. 5.2).

Fig. 5.2 A slightly enlarged unit cell of the parallelogram lattice (Fig. 5.1) showing the positions of the diad axes.

In accord with Table 5.1 the parallelogram lattice belongs to the oblique system.

5.3 Rectangular Lattice



$$|\mathbf{a}_1| \neq |\mathbf{a}_2| \qquad \alpha = 90°.$$

Fig. 5.3

A rectangular lattice is also characterised by two-fold rotational symmetry, but in addition it possesses mirror planes which distinguish it from the parallelogram lattice. There are two sets of mirror planes, each lying parallel to one of the rows of lattice points; they intersect at the diads (Fig. 5.4).

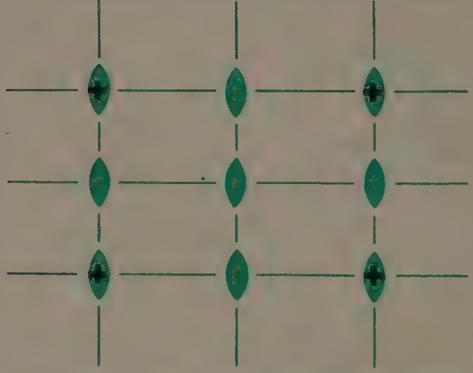


Fig. 5.4 The positions of the diad axes and mirror planes on the primitive rectangular lattice.

The presence of mirror symmetry means that the rectangular lattice belongs to the rectangular system (as one would expect!).

5.4 Diamond or Centred Rectangular Lattice

$$|\mathbf{a}_1| = |\mathbf{a}_2| \qquad \alpha \neq 90°.$$

Fig. 5.5

At first sight a diamond lattice differs significantly from a rectangular one, but it shares the same symmetry elements, i.e. diads and two sets of mirror planes (Fig. 5.6), and therefore also belongs to the rectangular system. In fact a rectangular unit cell can be drawn, but it has a lattice point at its centre as well as each corner and is therefore non-primitive (Fig. 5.5).

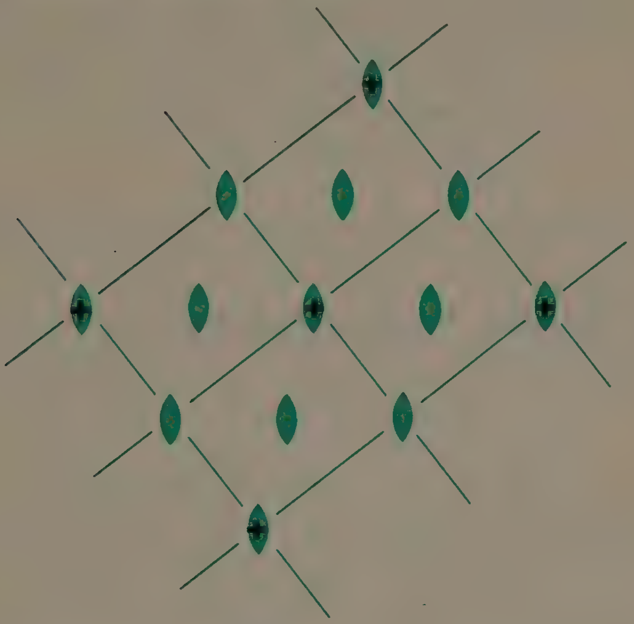


Fig. 5.6 The positions of the diad axes and mirror planes on a centred rectangular lattice.

The advantage of using a centred rectangular unit cell is that it immediately suggests the presence of reflection symmetry. Correspondingly, the lattice is more usually referred to as centred rectangular than as diamond.

5.5 Square Lattice

$$|\mathbf{a}_1| = |\mathbf{a}_2| \qquad \alpha = 90°$$

Fig. 5.7

The presence of four-fold rotation symmetry classifies a planar lattice as square and allocates it to the square system.

In addition to a tetrad at each lattice point, there is one in the centre of every square cell. There are also diads at the midpoints of the square edges and both ‘square’ and diagonal mirror planes (Fig. 5.8).

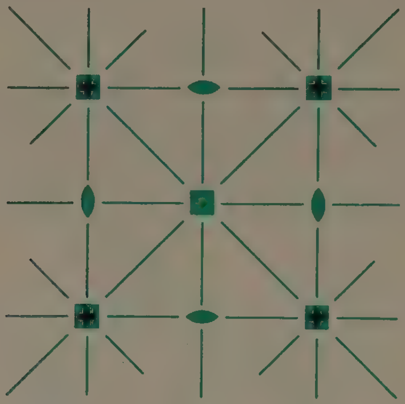


Fig. 5.8 The positions of the diad and tetrad axes and the mirror planes on a square lattice.

5.6 Triequiangular (or Hexagonal or Rhombohedral) Lattice

$$|\mathbf{a}_1| = |\mathbf{a}_2| \qquad \alpha = 120°.$$

Fig. 5.9

This lattice has six-fold rotational symmetry and also six sets of mirror planes.

The combination of three differently orientated unit cells of the triequiangular lattice forms a multiple primitive unit cell with a hexagonal outline (Fig. 5.9). This cell is useful in that it shows at a glance the six-fold symmetry of the lattice.

The six-fold rotation axes only occur at the lattice points, but there are further three-fold and two-fold axes as shown in Fig. 5.10.

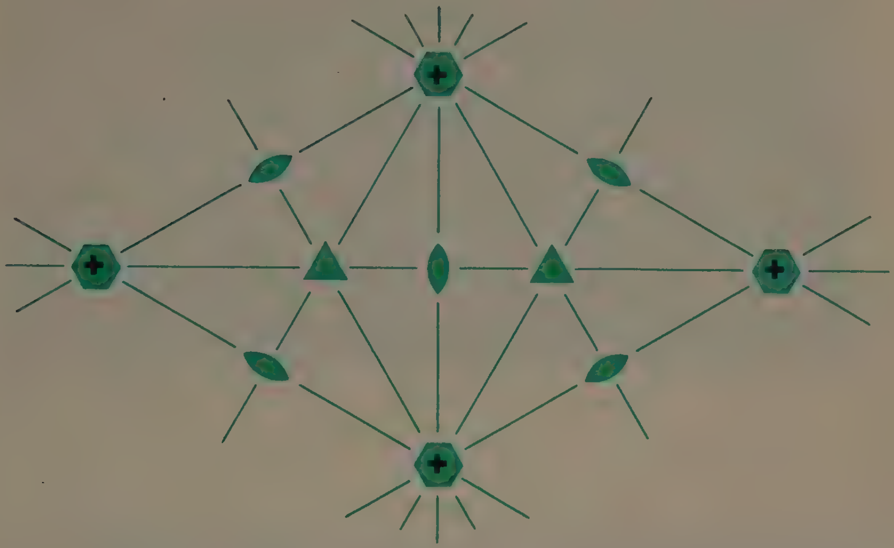


Fig. 5.10 The positions of diads, triads, hexads and mirror planes on the triequiangular lattice.

The presence of hexads puts this lattice in the hexagonal system.

5.7 Summary

TABLE 5.2. THE PLANAR LATTICES

Lattice	*Primitive unit cell*	*Rotation and reflection elements present*	*System*
Parallelogram	$\lvert \mathbf{a}_1 \rvert \neq \lvert \mathbf{a}_2 \rvert \; \alpha \neq 90^\circ$	diads	Oblique
Rectangular	$\lvert \mathbf{a}_1 \rvert \neq \lvert \mathbf{a}_2 \rvert \; \alpha = 90^\circ$	diads, mirrors	Rectangular
Diamond or centred rectangular	$\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert \; \alpha \neq 90^\circ$	diads, mirrors	Rectangular
Square	$\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert \; \alpha = 90^\circ$	tetrads, diads, mirrors	Square
Triequiangular	$\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert \; \alpha = 120^\circ$	hexads, triads, diads, mirrors	Hexagonal

TO DO

1. On the planar pattern below draw in the lattice which illustrates its translational symmetry. Name the lattice, and the system to which it belongs.

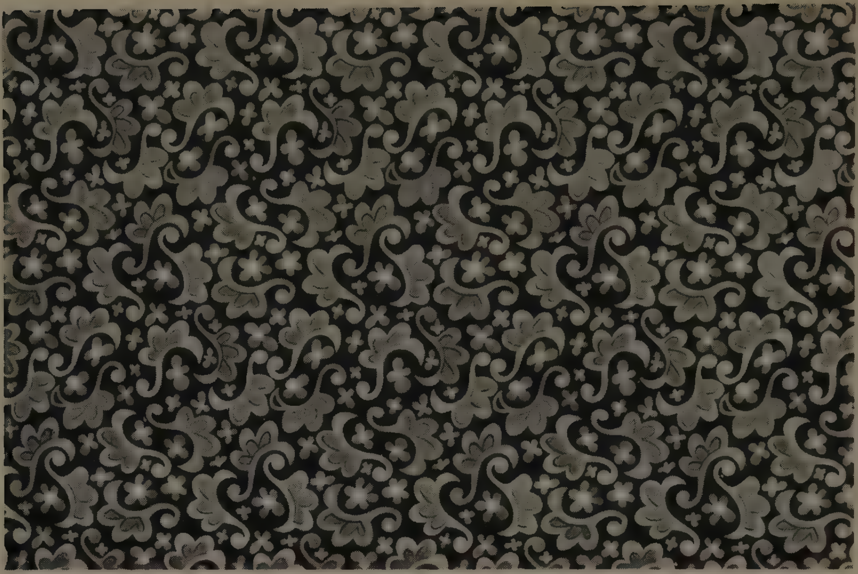


Fig. 5.11

Lattice is .... ·

Lattice system is ....

2. Draw in on the pattern in question 1 (above) all mirror planes and rotation axes (perpendicular to the page) possessed by the infinite *lattice.*
   Note that the symmetry elements do not apply to the pattern which has only translational symmetry.
   What system does the repeating pattern belong to?
   (This apparent paradox is discussed in Chapter 14)

YOU SHOULD BE ABLE TO

1. List five different planar lattices, and their characterising symmetry elements.
2. Explain the advantage of describing a diamond lattice with a non-primitive, centred rectangular unit cell.
3. Explain the difference between 'planar system' and 'planar crystal system'.

6

The Space Lattices Their Symmetry and Classification into Systems

In this chapter the three-dimensional crystal systems are listed, and the distinct space lattices which represent the different possible ways of arranging points in space are built up by regularly stacking planar lattices.

6.1 Crystal Systems

Each of the three-dimensional crystal systems (normally referred to simply as 'crystal systems') corresponds to a permitted combination of rotation axes. The systems are listed in Table 6.1, together with in each case the minimum symmetry required by a crystal or lattice before it is eligible.

TABLE 6.1

Crystal system	*Minimum symmetry requirements*
Triclinic	None
Monoclinic	One diad **or** one mirror plane
Orthorhombic	Three diads at right angles to each other (i.e. orthogonal)
Tetragonal	One tetrad
Cubic	Four triads orientated as the body diagonals of a cube
Hexagonal	One triad **or** one hexad

The crystal system classification chosen for this text includes the trigonal (or rhombohedral) system with the hexagonal system. (See Section 15.1 for further comment.)

6.2 Stacking of Parallelogram Lattices

If parallelogram lattices are stacked with constant stagger, but with neither the lattice points nor the diads in vertical register, the two-fold symmetry is lost (Fig. 6.2(a)). A space lattice built up in this way is known as **triclinic** and belongs to the triclinic system.

Space Lattice	Triclinic
Rotational Symmetry	None
Unit Cell	$\lvert \mathbf{a}_1 \rvert \neq \lvert \mathbf{a}_2 \rvert \neq \lvert \mathbf{a}_3 \rvert$ $\alpha_1 \neq \alpha_2 \neq \alpha_3 \neq 90°$
System	Triclinic

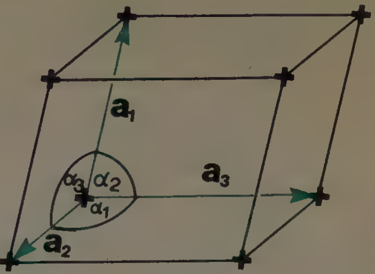


Fig. 6.1

If the parallelogram lattices are uniformly stacked with their lattice points directly above each other, the two-fold rotational symmetry is preserved, and a **monoclinic** space lattice is formed (Fig. 6.2(*b*)).

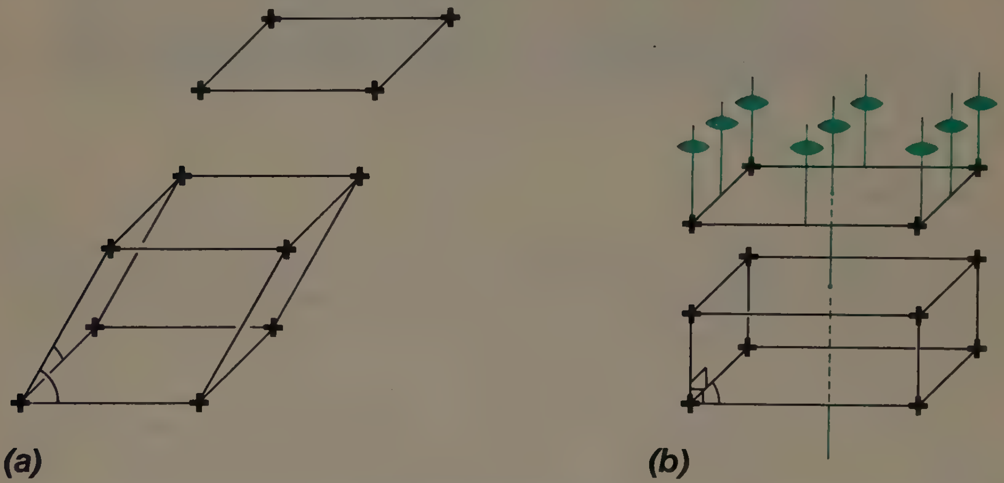


Fig. 6.2 Regular stacking of parallelograms to make either (*a*) a triclinic space lattice or (*b*) a monoclinic space lattice in which the diad axes are preserved.

The existence of two-fold axes which do not pass through the parallelogram lattice points, provides the opportunity of stacking the lattices with the two-fold axes in register but with the lattice points staggered. Such a construction gives rise to a space lattice that is monoclinic as far as symmetry is concerned, but which possesses a primitive unit cell typical of the triclinic system with $\alpha_1 \neq \alpha_2 \neq \alpha_3 \neq 90°$. It is always possible however to select non-primitive unit cells which are obviously monoclinic having $\alpha_1 = \alpha_2 = 90°$, $\alpha_3 \neq 90°$. These cells can be either **base centred** with an extra lattice point in the centre of one pair of opposing rectangular faces, or **body centred** with the extra lattice point in the middle of the cell. In Fig. 6.3(*a*), the diad in the centre of the parallelogram of each alternate layer is in register with the lattice point diad, whereas in Fig 6.3(*b*) it is the diad in the middle of the parallelogram edge that is arranged in this way. In each case the base centred unit cell is outlined. It is standard practice to use the non-primitive unit cell as its shape immediately indicates that the lattice belongs to the monoclinic system. The lattice is also named after the cell chosen, for example, base centred monoclinic.

As an exercise locate the body centred monoclinic cells for the arrangements in Figs. 6.3(*a*) and 6.3(*b*).

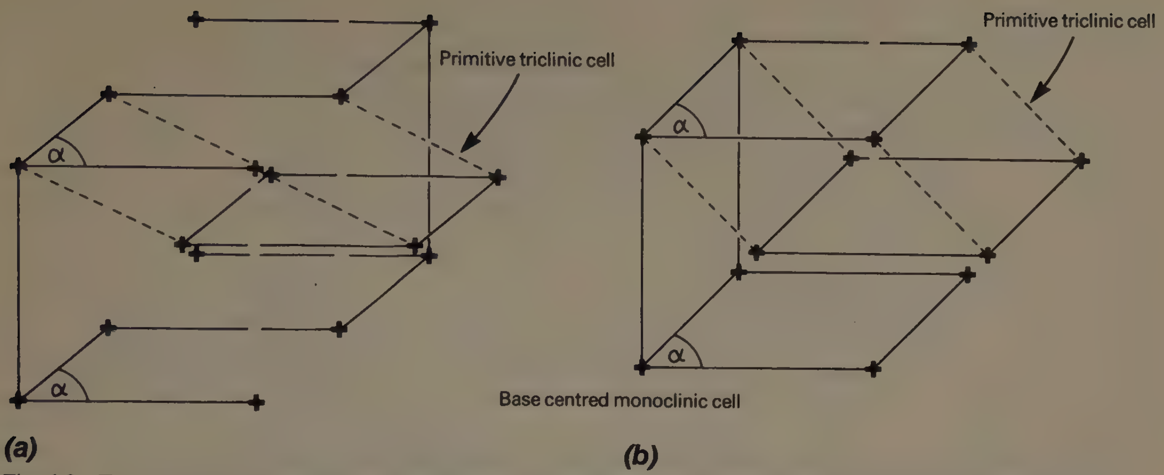


Fig. 6.3 Two methods of stacking parallelograms which give a monoclinic space lattice with the characteristic diads but no primitive monoclinic unit cell. In each case the monoclinic cell is non-primitive base (side) centred.

Space Lattices	Primitive Monoclinic Base Centred Monoclinic (A or B)
Rotational Symmetry	Parallel Diads
Unit Cell	$\lvert \mathbf{a}_1 \rvert \neq \lvert \mathbf{a}_2 \rvert \neq \lvert \mathbf{a}_3 \rvert$ $\alpha_1 = \alpha_2 = 90°$ $\alpha_3 \neq 90°$
System	Monoclinic

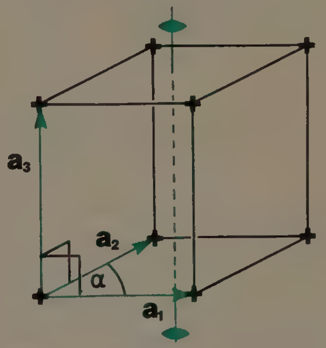


Fig. 6.4

6.3 Stacking of Rectangular Lattices

If primitive rectangular planar lattices are stacked so that the two-fold rotation symmetry is preserved, it is possible to construct orthorhombic space lattices of the primitive, body centred, and base centred types (Fig. 6.4). (The base centred orthorhombic cell has additional lattice points positioned in the centre of any one pair of opposing faces.)

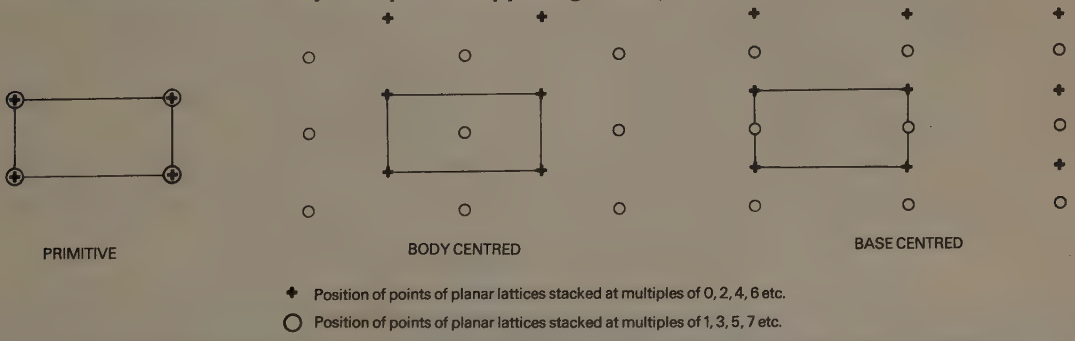


Fig. 6.5 Plans of rectangular lattices illustrating how they can be stacked to make either primitive, body centred or base centred orthorhombic space lattices.

The stacking of rectangular planar lattices so as to preserve the two-fold rotational symmetry generates two additional two-fold axes at right angles to the first and to each other. Three orthogonal two-fold axes are the basic symmetry elements of the **orthorhombic** space lattice.

A **face centred** orthorhombic cell can be built up by stacking centred rectangular lattices. It has an additional lattice point in the centre of each face (see Ex. 6.3).

Space Lattices	Primitive Orthorhombic Body Centred Orthorhombic Base (A, B or C) Centred Orthorhombic Face Centred Orthorhombic
Rotational Symmetry	Orthogonal diads
Unit Cell	$\lvert \mathbf{a}_1 \rvert \neq \lvert \mathbf{a}_2 \rvert \neq \lvert \mathbf{a}_3 \rvert$ $\underline{\alpha}_1 = \alpha_2 = \underline{\alpha}_3 = 90°$
System	Orthorhombic

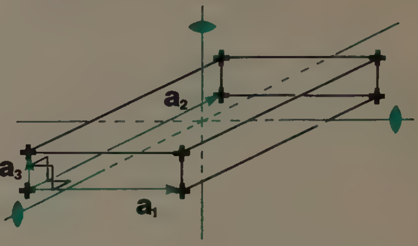


Fig. 6.6

6.4 Stacking of Square Lattices

It is possible, by judicious selection of interplanar spacing, to stack the primitive rectangular lattices so as to produce a *tetragonal* space lattice with $\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert \neq \lvert \mathbf{a}_3 \rvert$, but it is more convenient to think of the tetragonal lattice being built up by stacking square lattices so as to preserve the tetrad, but with a spacing not equal to the square edge length.

Space Lattices	Primitive Tetragonal Body Centred Tetragonal
Rotational Symmetry	Orthogonal tetrad and two diads
Unit Cell	$\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert \neq \lvert \mathbf{a}_3 \rvert$ $\underline{\alpha}_1 = \underline{\alpha}_2 = \underline{\alpha}_3 = 90°$
System	Tetragonal

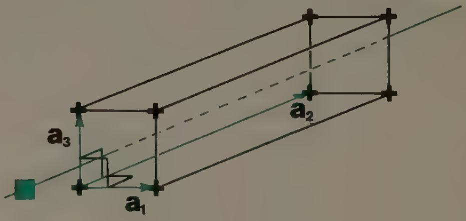


Fig. 6.7

If square lattices are stacked with the appropriate spacings, it is possible to generate the three different types of *cubic* space lattice (see Ex. 6.1).

Space Lattices	Primitive Cubic Body Centred Cubic Face Centred Cubic
Rotational Symmetry	Four orthogonal tetrads, four triads along the cube body diagonals and diads parallel to the cube face diagonals
Unit Cell	$\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert = \lvert \mathbf{a}_3 \rvert$ $\alpha_1 = \alpha_2 = \alpha_3 = 90°$
System	Cubic

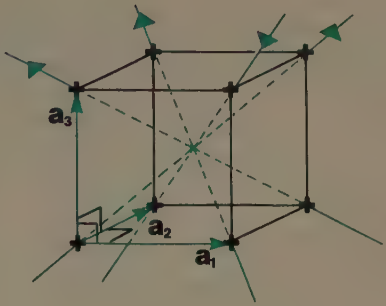


Fig. 6.8

6.5 Stacking of Triequiangular Lattices

Hexagonal space lattices can be built up by stacking planar triequiangular lattices directly above each other so as to preserve the hexads.

If, however, the triequiangular lattices are stacked with the hexads in vertical register with the triads as shown in Fig. 6.9 (cf. also Fig. 5.10), a lattice is created which contains only two- and three-fold rotational symmetry, the hexads having been destroyed. By stacking in this way every fourth layer is exactly above the first, and it is therefore possible for the first and fourth layers to form the top and bottom of a non-primitive hexagonal lattice cell (Fig. 6.9). The cell contains the equivalent of three lattice points, one distributed at the eight corners and the other two evenly spaced along a long body diagonal. It is referred to as **rhombohedral** non-primitive and the lattice is correspondingly known as **rhombohedral hexagonal.** It is possible to choose a primitive unit cell for this lattice which is a rhombohedron with $\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert = \lvert \mathbf{a}_3 \rvert$ and $\alpha_1 = \alpha_2 = \alpha_3 \neq 90°$ (see Ex. 6.2), but the convenience of sharing the same unit cell as the hexagonal lattice tends to outweigh the advantages of the primitive cell.

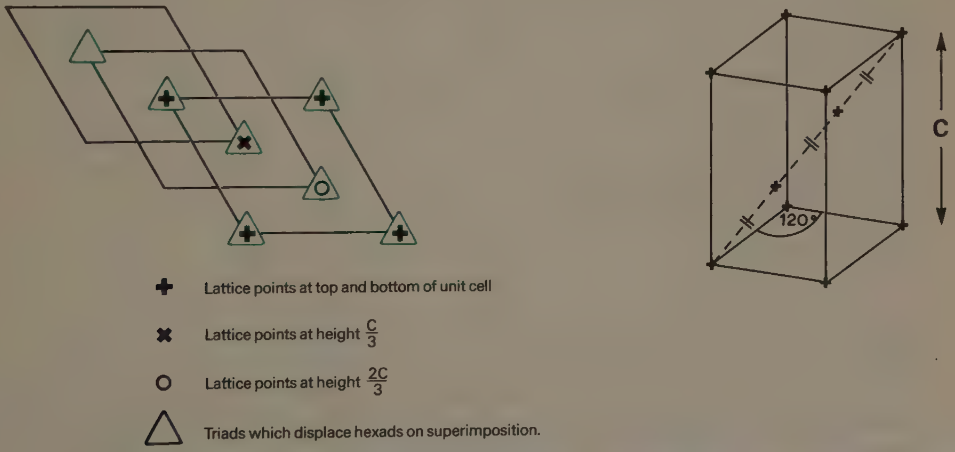


Fig. 6.9 The stacking of triequiangular planar lattices which produces a rhombohedrally non-primitive (R. type) hexagonal space lattice.

Space Lattices	Primitive Hexagonal Rhombohedral Hexagonal
Rotational Symmetry	Hexads, triads and diads in the primitive case but only triads and diads for the rhombohedral lattice.
Unit Cell	$\lvert \mathbf{a}_1 \rvert = \lvert \mathbf{a}_2 \rvert \neq \lvert \mathbf{a}_3 \rvert$ $\alpha_1 = \alpha_2 = 90°$ $\alpha_3 = 120°$
System	Hexagonal

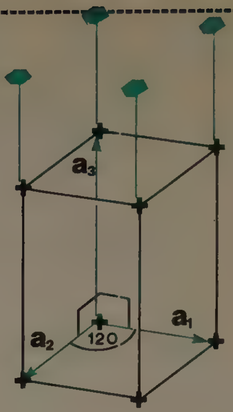


Fig. 6.10

6.6 Summary of Space Lattices

The 14 possible types of space lattice are known as **Bravais lattices**. They are distributed between 6 (7) crystal systems and each has a name which includes that of the system to which it belongs (unlike planar lattices). The Bravais lattices are listed in Table 6.2.

The various lattice types which may belong to the same system are distinguished with the help of the following abbreviations:

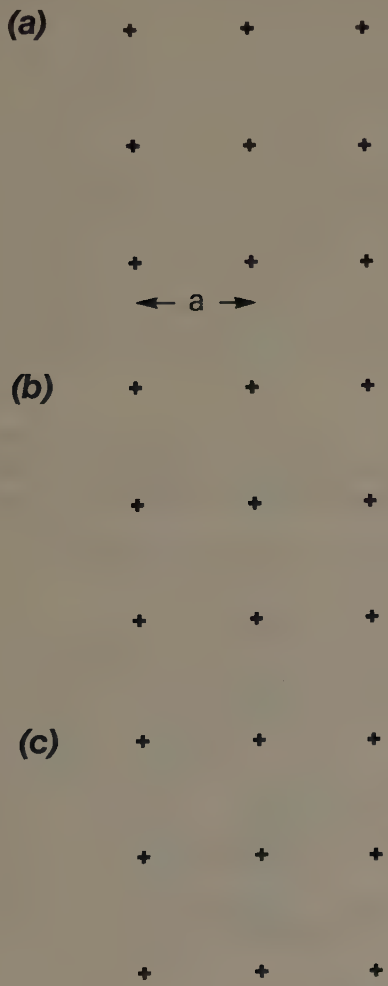
Primitive	P
Body Centred	I
Face Centred	F
Base Centred	A, B or C depending on whether centred face is parallel to $\mathbf{a}_2$ and $\mathbf{a}_3$, $\mathbf{a}_3$ and $\mathbf{a}_1$, or $\mathbf{a}_1$ and $\mathbf{a}_2$
Rhombohedral	R

TABLE 6.2. THE BRAVAIS LATTICES

Bravais lattice	*Abbreviation*	*Crystal system*
Triclinic	—	Triclinic
Primitive Monoclinic	—	Monoclinic
Base (A or B) Centred Monoclinic	—	
Primitive Orthorhombic	—	Orthorhombic
Body Centred Orthorhombic	—	
Face Centred Orthorhombic	—	
Base (A, B or C) Centred Orthorhombic	—	
Primitive Tetragonal	—	Tetragonal
Body Centred Tetragonal	B.C.T.	
Primitive Cubic	—	Cubic
Body Centred Cubic	B.C.C.	
Face Centred Cubic	F.C.C.	
Primitive Hexagonal	Hex.	Hexagonal
Rhombohedral Hexagonal	R. Hex.	

TO DO

1. Drawn below are three square planar lattices.
   Mark on the first the position of the points of a planar lattice immediately above in a stacking sequence that will give a primitive cubic space lattice. Also record the spacing between the adjacent planes in terms of ‘a’.
   On the second, repeat the procedure but to give a body centred cubic lattice.
   On the third, repeat the procedure but to give a face centred cubic lattice.
   In each case draw in a plan of the unit cell on the lattice.



P Planar spacing =

I Planar spacing =

F Planar spacing =

Fig. 6.11

2. Drawn below is a lattice cell based on the full hexagonal prism. Its complete title is ‘multiple non-primitive rhombohedral hexagonal lattice cell’ and it contains the equivalent of nine lattice points.
   Construct within it a primitive rhombohedral lattice cell.
   $(\alpha_1 = \alpha_2 = \alpha_3 \neq 90°; \ |\mathbf{a}_1| = |\mathbf{a}_2| = |\mathbf{a}_3|)$.

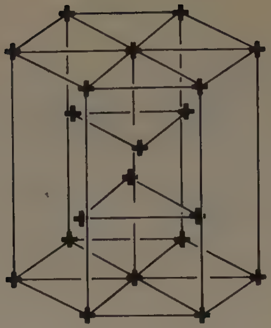


Fig. 6.12

3. Show by sketches how centred rectangular lattices may be stacked to give:
   (*a*) A face centred orthorhombic lattice.
   (*b*) A base centred orthorhombic lattice.

4. Below is the non-primitive unit cell of the face centred cubic lattice. Draw within it the primitive unit cell of that lattice. The primitive cell is outlined by the vectors, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{a}_1$.

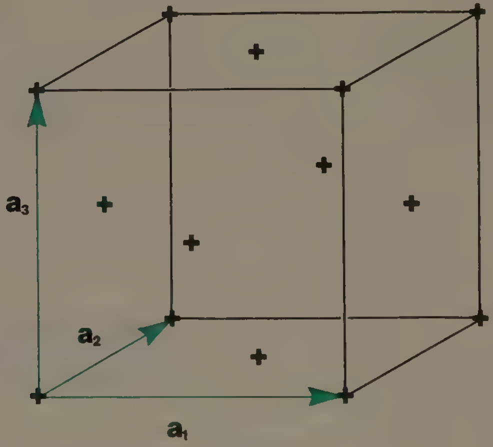


Fig. 6.13

YOU SHOULD BE ABLE TO

1. List the 14 Bravais lattices and their distribution between the six crystal systems.
2. Sketch the unit cells characteristic of each system.

7

Atomic Bonding, Packing and Crystal Structures

7.1 Atomic Bonding

The way in which atoms pack together to form crystals depends only on the electrostatic forces, both attractive and repulsive, that exist between them. The repulsive forces are strong but short range, so that it is possible to think of an atom as a ball of finite size. The so-called **rigid ball model** is not too drastic a simplification and is a considerable help in the understanding of atomic packing.

The packing of atoms of the same type to form a crystal is influenced solely by the directional nature of the bonding forces; but in the case where more than one type of atom is present several other factors must also be considered. These are:

(*a*) the relative sizes of the atoms,
(*b*) the direction and strength of the bonding forces associated with each atom type, and
(*c*) the requirement of electrical neutrality of the crystal.

Atomic bonding is the result of the redistribution of outer electrons when atoms are brought near to each other.

An isolated atom is electrically neutral as the electrons completely screen the positive charge of the nucleus. Interaction between adjacent atoms will distort the electron clouds so that the centre of gravity of the negative charge does not coincide with that of the positive charge. An **electric dipole** of some form is thus created and electrostatic attraction between oppositely charged ends of nearby dipoles binds the atoms into a crystal.

The various distributions of electron charge which occur as a result of interaction between adjacent atoms can only be fully understood in terms of wave mechanics, but they serve as a convenient basis for classifying the different types of bonding.

There are five discernible types of bonding, three strong and two comparatively weak:

(*i*) *Metallic*

Properties: Strong, non-directional and can occur between both like and dissimilar atoms.

Structure: The outer electrons are redistributed to form a fairly uniform cloud between the positive ions. They can be thought of as forming a kind of 'glue', in that the ions are bound together by virtue of their common attraction to the negatively charged cloud between them.

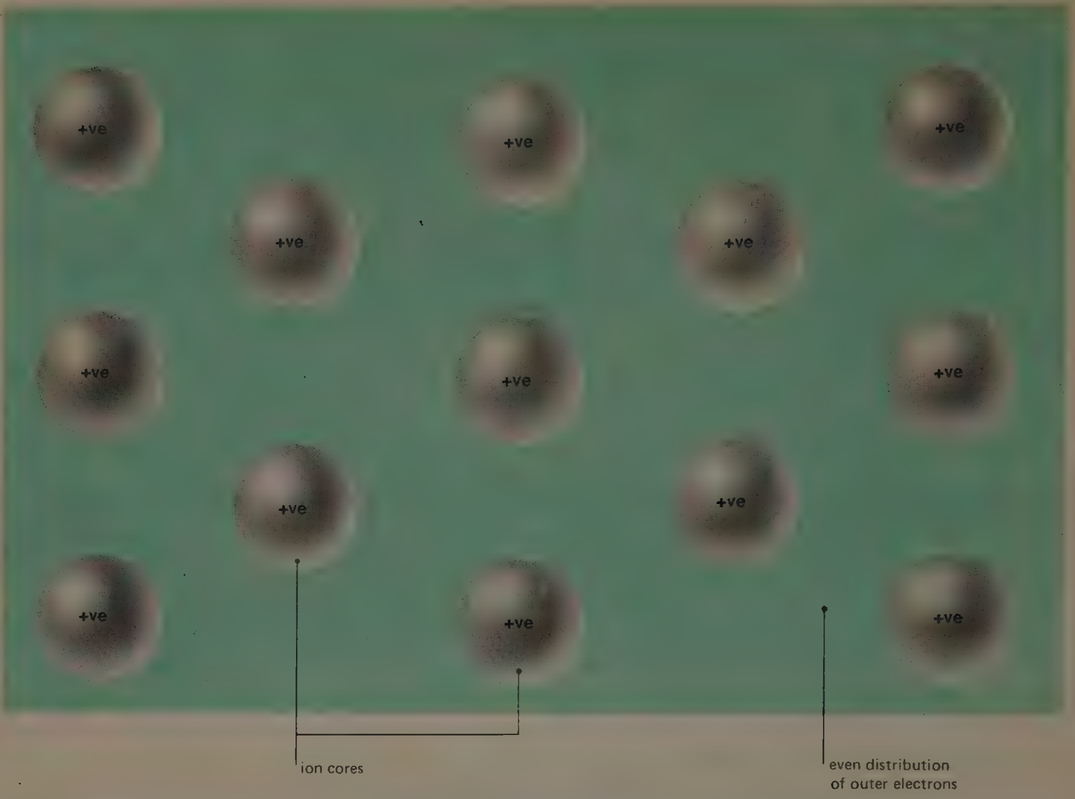


Fig. 7.1 The metallic bond.

(*ii*) *Covalent*

Properties: Strong, very directional and normally occurs between like atoms, but there is often a substantial covalent contribution to bonds with ionic character between dissimilar atoms.

Structure: One outer electron from each of two adjacent atoms is concentrated into the region midway between the two atoms. The electrostatic attraction of the positive ions to the negative electron cloud exceeds the mutual repulsion between the ions. There is therefore a net bonding force.

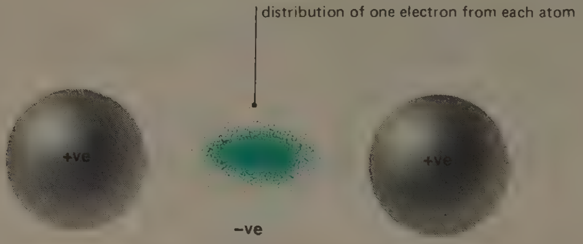
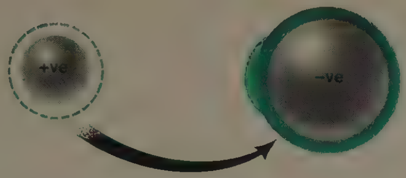


Fig. 7.2 The covalent bond.

(*iii*) *Ionic*

Properties: Strong, non-directional and can only occur between dissimilar atoms.

Structure: If two types of atom are present, electron transfer occurs from the outer shells of the electropositive atoms to the outer shells of the electronegative ones, thus creating both positive and negative ions. The electrostatic attraction between the dissimilar ions is the source of the bonding. There is invariably some covalent character to an ionic bond.



electron transferred into outer state of electronegative atom to give two oppositely charged atoms.

Fig. 7.3 The ionic bond.

(*iv*) *Van de Waals*

Properties: Weak, non-directional and occurs between all atoms in solids, but only makes a significant contribution to total bonding where no other strong bond type is present (e.g. solid argon which melts at −189°C).

Structure: Although, on average, the centres of gravity of the positive and negative charge within an atom coincide, at any instant there are likely to be statistical departures from this state, and hence momentary dipoles. A dipole on one atom will tend to encourage a similar orientated dipole on an adjacent atom, and therefore bonding results.

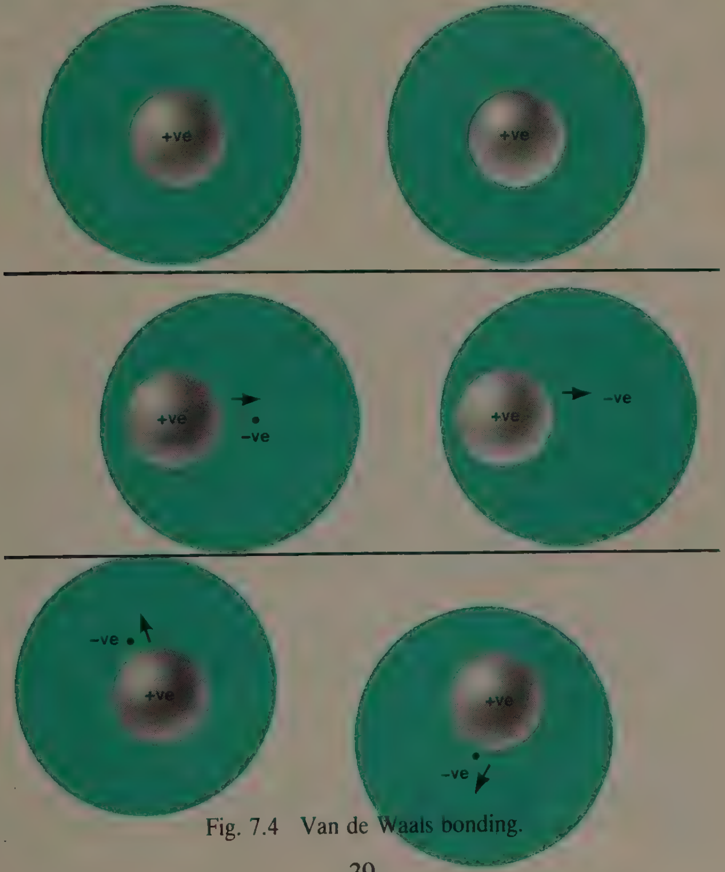


Fig. 7.4 Van de Waals bonding.

(*v*) *Permanent dipole*

Properties: Weak, directional and occurs between dissimilar atoms, one frequently being hydrogen,

Structure: When a covalent bond between two different atoms has a significant amount of ionic character, there will be some distortion of the electron cloud forming the bond towards the more electronegative atom. The pair of atoms therefore constitute a permanent electric dipole and will bond to neighbouring dipoles of suitable orientation.

This type of bonding frequently occurs between dipoles in which the electropositive atom is hydrogen. In this case the bond is known specifically as a **hydrogen bond**.

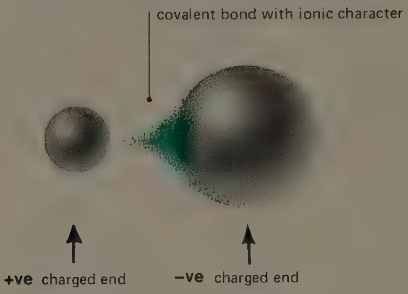


Fig. 7.5 Permanent dipole bond.

Two points:

(*a*) These explanations are as detailed as is possible without recourse to the concepts of wave mechanics.
(*b*) It must always be remembered that crystals in which there is only one form of bonding are the exception rather than the rule, although a predominant bond type can usually be identified.

7.2 Packing of Identical Spheres

The structure of a crystal in which the atoms are held together by non-directional bonding forces will be the same as that shown by spheres packed carefully together so as to occupy minimum volume. In the case of just one layer, spheres are packed most densely if each is centred on a point of a planar hexagonal lattice (Fig. 7.6). Such a plane is called a **close packed plane**.

A close packed plane contains three **close packed directions**, these being the lines along which the spheres touch (Fig. 7.6). It is not surprising that the most densely packed three-dimensional structure will be obtained by stacking close packed planes. The stacking sequence can follow either of two regimes and produces a regular three-dimensional crystal with a **close packed structure**. Such structures are often found in crystals of metals and other solids which are built up from identical atoms with non-directional bonds.

Figure 7.7 shows a close packed layer of atoms. The position of each atom centre is marked by a letter 'A'. A subsequent layer will fit snugly on the first if it is displaced sideways to put its atom centres either in positions 'B' or in positions 'C'.

There are two possible regular stacking sequences which produce close packed crystal structures. The positional sequence ABABABAB . . . (or ACACACAC . . . or BCBCBCBC . . .) gives rise to the **hexagonal close packed structure** (h.c.p.), whereas the **face centred cubic structure** (f.c.c.) corresponds to the sequence ABCABCABCABC. . . . The stacking of the close packed layers to give

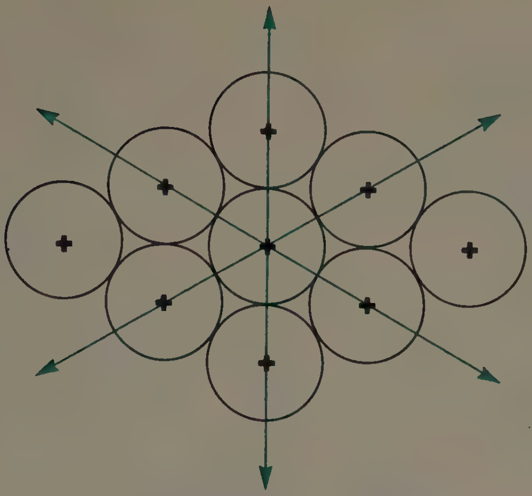


Fig. 7.6 A part of one close packed plane with the three close packed directions indicated.

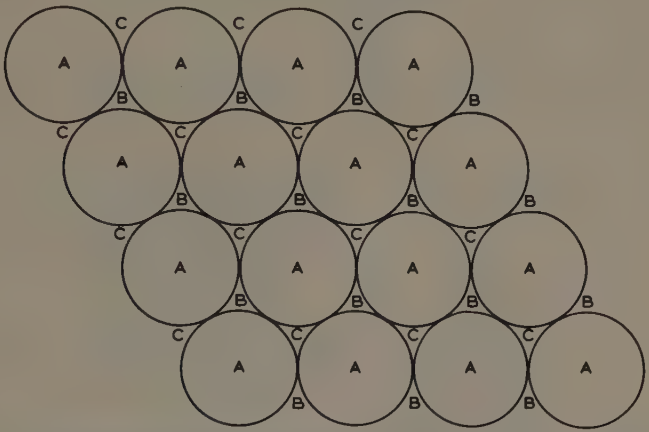


Fig. 7.7 The two possible ways of stacking a second close packed layer snugly on the first. The atom centres of the second layer are either at BBBB . . . or CCCC. . . .

these structures is illustrated in Figs. 7.8 and 7.9, and in sections (*i*) and (*ii*) below the two structures are described with the aid of structure cells. Section (*iii*) introduces another important crystal structure known as **body centred cubic** (b.c.c.) which although not close packed does contain some close packed directions. In each case the structure cell is drawn in two different ways. In the left-hand diagram (Figs. 7.10, 7.11 and 7.13) the atom positions are marked by spheres, much smaller than the actual atom sizes which are drawn to scale in the right-hand diagram. The type of presentation on the left is generally considered clearer and is much more widely used.

(*i*) *Hexagonal close packed structure* (*h.c.p.*)

The relationship between the h.c.p. structure cell and the ABABABAB . . . type stacking of the close packed planes is shown in Fig. 7.10. The h.c.p. structure cell is based on the primitive hexagonal

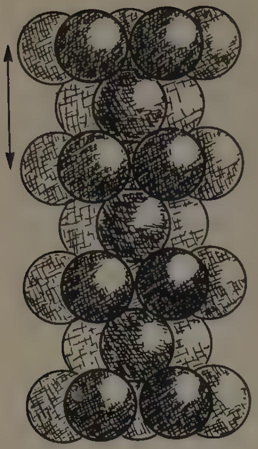


Fig. 7.8 The ARABA . . . stacking sequence of close packed layers which gives the b.c.p. structure. (Reproduced by permission from Pauling: *The Nature of the Chemical Bond.* Cornell University Press.)

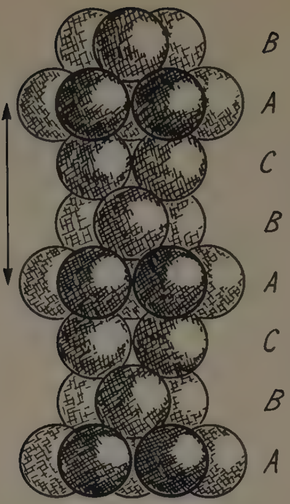


Fig. 7.9 The ABCABCAB stacking sequence of close packed planes which leads to the f.c.c. structure. (Reproduced by permission from Pauling: *The Nature of the Chemical Bond*, Cornell University Press.)

lattice unit cell (or rather the multiple primitive hexagonal lattice cell). The motif is of two atoms. It follows that there are two atoms/lattice point, the equivalent of two atoms/primitive unit cell, and six atoms/multiple hexagonal cell.

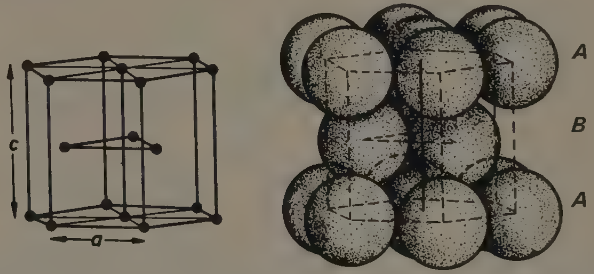


Fig. 7.10 (Reproduced by permission from Smallman: *Modern Physical Metallurgy*, Butterworth.)

(*ii*) *Face centred cubic structure* (*f.c.c.*)

The f.c.c. structure, corresponding to the ABCABCABC . . . stacking sequence, contains three further sets of close packed planes each at about 70° to the stacked layers. The total of four sets of close packed planes are orientated as the faces of a tetrahedron and the structure has cubic symmetry. For this reason the hexagonal structure cell with four layers apparent in Fig. 7.9 is abandoned in favour of a face centred cubic cell in which the close packed planes are the major triangular sections of the cube (Fig. 7.11). One of the close packed planes in the cubic structure is clearly illustrated in Fig. 7.12. The f.c.c. structure is built up by adding a motif of one atom to each lattice point of an f.c.c. lattice.

(*iii*) *Body centred cubic structure* (*b.c.c.*)

Another commonly occurring structure in metal crystals is body centred cubic, in which the atoms lie on the points of a body centred cube lattice.

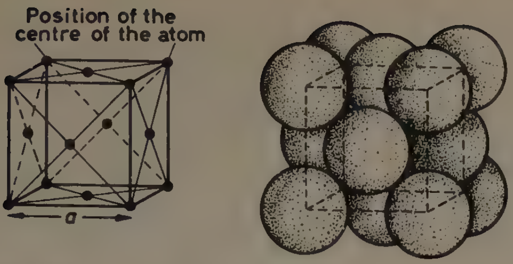


Fig. 7.11 (Reproduced by permission from Smallman: *Modern Physical Metallurgy*, Butterworth.)

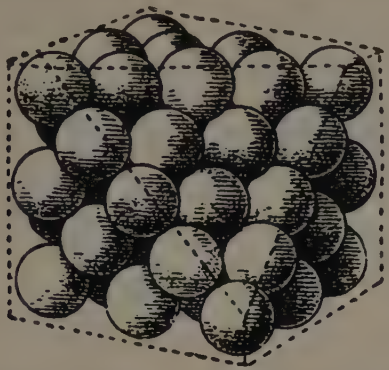


Fig. 7.12 Part of an f.c.c. structure sectioned to show one of the close packed planes {111}. (Reproduced by permission from Pauling: *The Nature of the Chemical Bond*, Cornell University Press.)

It is not a close packed structure and contains no close packed planes, however the planes lying on the diagonal sections (one of which is shaded on Fig. 7.13) each contain two close packed directions. These directions are along the body diagonals of the cube.

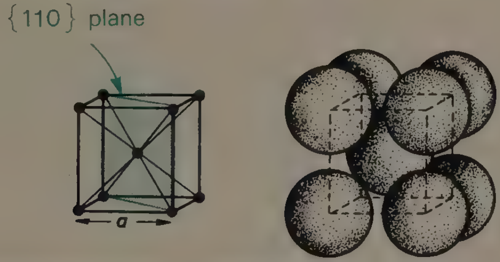


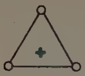
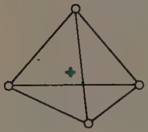
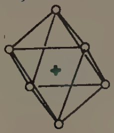
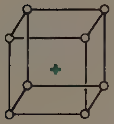
Fig. 7.13 Unit cell of the b.c.c. structure with the ⟨111⟩ close packed directions drawn in. (Reproduced by permission from Smallman: *Modern Physical Metallurgy*, Butterworth.)

7.3 Packing of Non-Identical Spheres

The holes in between the atoms of a crystal, called **interstices** can house smaller atoms without appreciable distortion of the host lattice. Just how much smaller the **interstitial atom** has to be depends, of course, on the size of the hole and this is directly related to the particular arrangement of atoms immediately surrounding it.

If one again thinks in terms of the rigid ball model, it is fairly easy to estimate the maximum size of an atom that can be accommodated in an interstice without forcing the surrounding atoms apart. This information is summarised in Table 7.1

TABLE 7.1

TYPE OF INTERSTICE *i.e. arrangement of closely packed atoms immediately surrounding the interstice*	*RADIUS RATIO FOR PERFECT FIT* $\frac{\textit{interstitial atom radius}}{\textit{host atom radius}}$	*COORDINATION NUMBER* *number of host atoms touching interstitial atom*
Triangular 	0·16	3
Tetrahedral 	0·22	4
Octahedral 	0·41	6
Cubic 	0·73	8

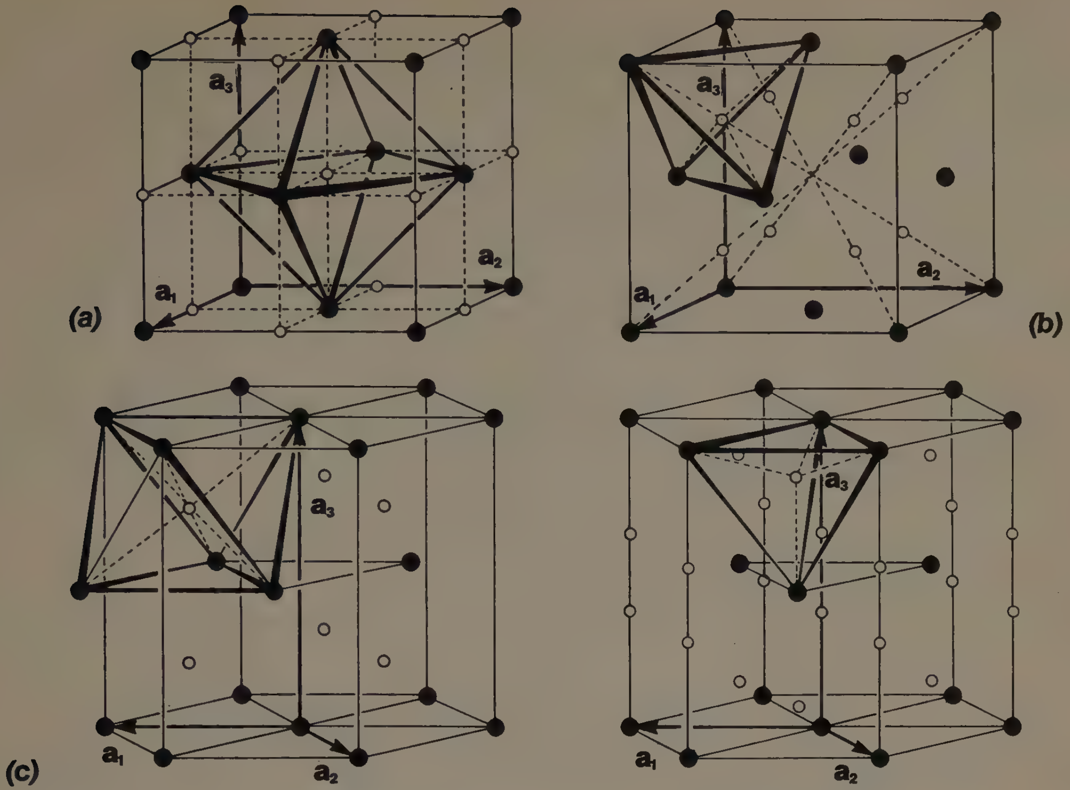
o Centre of surrounding atoms.
\+ Centre of interstice.

Close packed structures contain both tetrahedral and octahedral interstices, whereas in b.c.c., although both types of interstice can be recognised, they are distorted. If an interstitial atom is small enough to fit into either the octahedral or tetrahedral interstice of a close packed structure, it is most likely to be found in the tetrahedral one which is the smaller; for, in general, an interstitial atom will prefer an interstice in which it is smaller than a perfect fit, but smaller by as small degree as possible. (This however does not apply to ionic crystals.)

Figure 7.14 shows the positions of the octahedral and tetrahedral interstices in the f.c.c. and h.c.p. structure cells. The coordinates of all the interstices found in both cells given in Table 7.2 (page 46) are expressed in terms of the lattice translation vectors marked in Fig. 7.14 (*a*) and (*b*) and the primitive translation vectors in Fig. 7.14 (*c*) and (*d*). It is a very valuable exercise to identify these interstices on ball models of the two structures.

If an alloying element of similar atomic size is added to a close packed metal, there will not be room for the new atoms in either the octahedral or tetrahedral interstices. Instead they will substitute randomly for the host atoms producing what is known as a **substitutional solid solution** (Fig. 7.15).

In some instances the bonding forces between two different types of atoms forming a metal alloy are significantly larger than those between like atoms. As a result a particular atom will tend to be located so that it is completely surrounded by atoms of the other type. If there is a fairly simple ratio between the numbers of the two atoms present, it is possible that the alloy will become **ordered**, which means that the positioning of the atoms of different types will be related crystallographically. β-brass (an alloy of 50% Cu and 50% Zn) at room temperature is an example of an ordered alloy (Fig. 7.16).



Tetrahedral interstices
\+ Octahedral interstices

Tetrahedral interstices
\+ Octahedral interstices

Fig. 7.14 The tetrahedral and octahedral interstices in the f.c.c. and h.c.p. structure cells. The open circles represent the positions of the interstices, and the full circles mark the centres of the atoms.

(*a*) f.c.c. structure cell showing the octahedral interstices.
(*b*) f.c.c. structure cell showing the tetrahedral interstices.
(*c*) h.c.p. structure cell with octahedral interstices.
(*d*) h.c.p. structure cell with tetrahedral interstices.
(Based on Barrett and Massalski: *Structure of Metals*, McGraw-Hill, Figs. 10.8 and 10.10.)

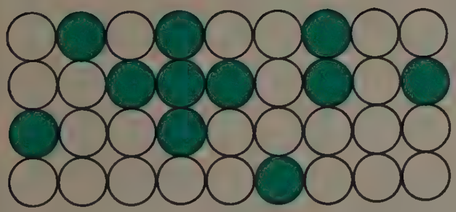


Fig. 7.15 A substitutional solid solution.

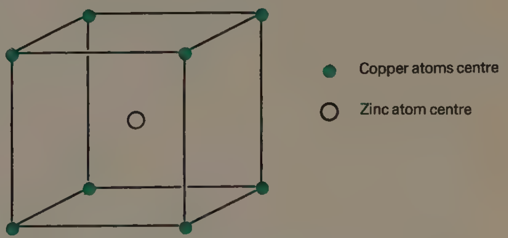


Fig. 7.16 The structure cell of ordered β-brass.

TABLE 7.2

STRUCTURE	*INTERSTICE*	*COORDINATES*		*EQUIVALENT NUMBER*	
				per structure cell	*per atom*
f.c.c.	octahedral	$0\tfrac{1}{2}0$ $\tfrac{1}{2}00$ $00\tfrac{1}{2}$ $1\tfrac{1}{2}0$ $\tfrac{1}{2}10$ $10\tfrac{1}{2}$ $0\tfrac{1}{2}1$ $\tfrac{1}{2}01$ $01\tfrac{1}{2}$ $1\tfrac{1}{2}1$ $\tfrac{1}{2}11$ $11\tfrac{1}{2}$	Middle of cube edges	4	1
		$\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$	Cube centre		
	tetrahedral	$\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}$ $\tfrac{1}{4}\tfrac{3}{4}\tfrac{1}{4}$ $\tfrac{3}{4}\tfrac{1}{4}\tfrac{1}{4}$ $\tfrac{3}{4}\tfrac{3}{4}\tfrac{1}{4}$ $\tfrac{1}{4}\tfrac{1}{4}\tfrac{3}{4}$ $\tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4}$ $\tfrac{3}{4}\tfrac{1}{4}\tfrac{3}{4}$ $\tfrac{3}{3}\tfrac{3}{4}\tfrac{3}{4}$		8	2
h.c.p.	octahedral	$\tfrac{2}{3}\tfrac{1}{3}\tfrac{1}{4}$ $\tfrac{\bar{1}}{3}\tfrac{1}{3}\tfrac{1}{4}$ $\tfrac{\bar{1}}{3}\tfrac{\bar{2}}{3}\tfrac{1}{4}$ $\tfrac{2}{3}\tfrac{1}{3}\tfrac{3}{4}$ $\tfrac{\bar{1}}{3}\tfrac{1}{3}\tfrac{3}{4}$ $\tfrac{\bar{1}}{3}\tfrac{\bar{2}}{3}\tfrac{3}{4}$		6	1
	tetrahedral	$\tfrac{1}{3}\tfrac{2}{3}\tfrac{1}{8}$ $\tfrac{\bar{2}}{3}\tfrac{\bar{1}}{3}\tfrac{1}{8}$ $\tfrac{1}{3}\tfrac{\bar{1}}{3}\tfrac{1}{8}$ $\tfrac{1}{3}\tfrac{2}{3}\tfrac{7}{8}$ $\tfrac{\bar{2}}{3}\tfrac{\bar{1}}{3}\tfrac{7}{8}$ $\tfrac{1}{3}\tfrac{\bar{1}}{3}\tfrac{7}{8}$ $00\tfrac{3}{8}$ $00\tfrac{5}{8}$		12	2
		$10\tfrac{3}{8}$ $11\tfrac{3}{8}$ $01\tfrac{3}{8}$ $\bar{1}0\tfrac{3}{8}$ $\bar{1}\bar{1}\tfrac{3}{8}$ $0\bar{1}\tfrac{3}{8}$ $10\tfrac{5}{8}$ $11\tfrac{5}{8}$ $01\tfrac{5}{8}$ $\bar{1}0\tfrac{5}{8}$ $\bar{1}\bar{1}\tfrac{5}{8}$ $0\bar{1}\tfrac{5}{8}$	on the vertical edges of the multiple structure cell		

7.4 Ionic Crystals

Ionic crystals are built up from both positive and negative ions which must be present in exact proportions if electrical neutrality is to be maintained. For example, a crystal of calcium fluoride (CaF_2) will contain two monovalent fluorine ions for each divalent calcium one.

The strongest bonding in an ionic crystal is obtained if each ion of one type is completely surrounded by dissimilar neighbours. It is therefore realistic to think of an ionic crystal as consisting of the larger ions (normally the negatively charged anions) arranged in a particular crystal structure, with the smaller ions (positively charged cations) sitting in the interstices. In this context the figures used to illustrate the different types of insterstice in Table 7.1 are **anion polyhedra**.

We must now consider the question: What will be the most probable ionic structure? Given that the ratio of cation radius to anion radius is fixed and also that the proportion of cations to anions is correct for electrical neutrality. To start with there are two ground rules. First, because of the strong attraction between anion and cation, the cation will select an anion interstice in which it can touch all of the anions at once, so that if anything the radius ratio will tend to exceed that for a perfect fit. Also for the same reason the distorted interstices between anions in a b.c.c. arrangement will not be good hosts for cations and accordingly this structural arrangement is not common. The second ground rule is that the crystal structure will be that which maximises the coordination number.

When the cation has a charge of 1, 2 or 3, the anion polyhedra usually pack as closely together as possible. So that for tetrahedral and octahedral packing the final anion arrangement will be either h.c.p. or f.c.c., and for cubic packing, primitive cubic. The choice between the h.c.p. and f.c.c. structures will be determined by more subtle aspects of the bonding such as the presence of some directional covalent contribution to the predominantly ionic bonds. Cation charges higher than 3 usually lead to more open packing of the polyhedra. These structures are discussed in Section 7.6.

As an example we will look at an imaginary ionic crystal A_2B which has a cation/anion radius ratio of 0·3. Bearing in mind the necessity of trying to maximise the coordination number, it is best to consider first the possibility of cubic anion polyhedra which have the high coordination number of 8. This arrangement is ruled out because its critical radius ratio exceeds 0·3 (see Table 7.1). The same applies to the octahedral anion polyhedra which have a critical radius ratio of 0·41. The most stable anion polyhedra will be tetrahedral, and these occur in both h.c.p. and f.c.c. anion arrangements. In each case it can be seen from Table 7.2 that there are two polyhedra per anion (each anion is of course shared by several polyhedra). So for crystal A_2B, 'A' cations will fill all the tetrahedral interstices of the 'B' anion polyhedra.

If the chemical formula had been AB with the same radius ratio then only half of the tetrahedral interstices would contain cations, and these would be regularly distributed throughout the crystal.

Some general criteria for stable packing are given in Table 7.3.

TABLE 7.3

Radius ratio $\frac{r_c}{r_a}$	*Stable packing*	*Maximum cation/anion ratio in common anion arrangements*
0·16 to 0·22	Triangular	—
0·22 to 0·41	Tetrahedral	2::1 in f.c.c. and h.c.p.
0·41 to 0·73	Octahedral	1::1 in f.c.c. and h.c.p.
0·73 to 1·0	Cubic	1::1 in primitive cubic

These predictions are obeyed fairly closely by ionic crystals, and some well-behaved examples are listed in Table 7.4.

TABLE 7.4

	$\frac{r_c}{r_a}$	*Predicted packing*	*Observed packing*
SiO_2	0·29	Tetrahedral	Tetrahedral
NaCl	0·54	Octahedral	Octahedral
CsCl	0·93	Cubic	Cubic

7.5 Examples of Ionic Structures based on Close Packed Anion Polyhedra

In this section the deductions which can be made about the structure of a selection of five simple ionic crystals on the basis of the observed proportion of anions to cations and the corresponding ionic radius ratio, are outlined in note form. Also given in each case is a brief description of the actual structure.

As each structure is considered it is strongly recommended that a sketch be made of the appropriate structure cell.

(*i*) *Sodium Chloride* NaCl

$$\frac{r_c}{r_a} = 0{\cdot}54$$

Therefore sodium in octahedral interstices. Anion arrangement either f.c.c. or h.c.p.

Cation/anion ratio = 1::1, therefore all octahedral interstices filled.

Actual Structure: Chlorine ions in an f.c.c. arrangement with sodium atoms in all the octahedral interstices.

(*ii*) *Caesium Chloride* CsCl

$\frac{r_c}{r_a} = 0{\cdot}93$

Therefore caesium in cubic interstices. Anion arrangement primitive cubic.

Cation/anion ratio 1::1, therefore all cubic interstices filled.

Actual Structure: Chlorine ions in a simple cubic arrangement with caesium ions in all the cubic interstices.

(*iii*) *Aluminium Oxide* Al_2O_3

$\frac{r_c}{r_a} = 0{\cdot}43$

Therefore aluminium in octahedral interstices. Anion arrangement either f.c.c. or h.c.p.

Cation/anion ratio 2::3, therefore $\frac{2}{3}$ of octahedral interstices filled.

Actual Structure: Oxygen ions in an h.c.p. arrangement with aluminium ions filling $\frac{2}{3}$ of the octahedral interstices of each layer.

(*iv*) *Lithium Sulphide* Li_2S

$\frac{r_c}{r_a} = 0{\cdot}33$

Therefore lithium in the tetrahedral interstices. Anion arrangement either f.c.c. or h.c.p.

Cation/anion ratio 2::1, therefore all the tetrahedral interstices filled.

Actual Structure: Sulphur ions in an f.c.c. arrangement with lithium ions in all the tetrahedral interstices.

(*v*) *Calcium Fluoride* CaF_2

$\frac{r_c}{r_a} = 0{\cdot}75$

Therefore calcium in cubic interstices. Anion arrangement primitive cubic.

Cation/anion ratio 1::2, therefore $\frac{1}{2}$ of the cubic interstices filled.

Actual Structure: Fluorine ions on a primitive cubic lattice with calcium ions in half of the cubic interstices. This structure however is usually depicted with the calcium cations in an f.c.c. arrangement and the fluorine anions filling all the tetrahedral interstices. Extend your diagram to show that both structure cells are representative of the same structure.

7.6 More Open Packing of Anion Polyhedra

In cases where the cation charge is greater than 3, the anion polyhedra do not fit together to form either close packed or primitive cubic structures, but are arranged so as to maximise the distance between the highly charged cations which strongly repel each other.

This behaviour is well illustrated by two particular crystal structures: silica (SiO_2) in which four oxygen ions form a tetrahedron around each silicon ion, and rutile (TiO_2) in which six oxygen ions form an octahedron around each titanium ion.

The Si-O_4 tetrahedra of a form of silica called cristobalite are arranged in a cubic structure. Each unit is surrounded tetrahedrally by four other units, the oxygen ions at the corners being shared (Fig. 7.17). The lattice of this structure is f.c.c. with a motif of a pair of SiO_4 tetrahedra. If one tetrahedron of the pair is centred on the origin, 0, 0, 0, then the other will be at $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$.

Check this for yourself by inspection of Fig. 7.17.

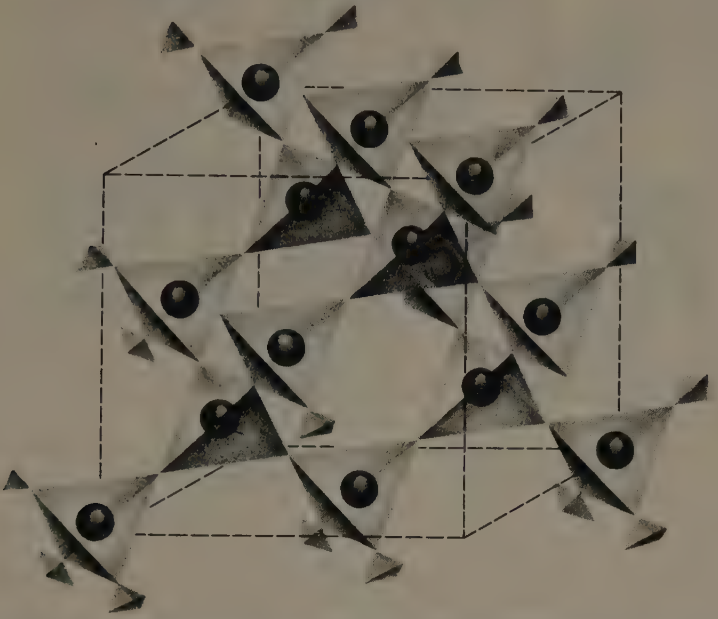


Fig. 7.17 The structure unit cell of the cristobalite form of silica. The Si–O_4 tetrahedra are formed at the corners so that each oxygen ion is shared between two silicon ions. (Reproduced by permission from Moffatt *et al.*: *Structure and Properties of Materials*, Wiley.)

It is worth noting that under some conditions silica may not crystallise at all but form a glass in which the tetrahedra are joined corner to corner to make a random network.

The structure of rutile has a primitive tetragonal lattice with a motif of two TiO_6 octahedra, one at 0, 0, 0, and the other in the body centred position at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ (Fig. 7.18). The octahedra are arranged so that they share corners and some edges. Note that the lattice is not b.c.t. because the octahedron at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ is orientated differently from those at the corners of the structure cell.

In the case when the charge on a cation within an anion polyhedron equals the total anion charge, the unit is electrically neutral and hence a molecule. Such molecules can be bound together by either Van de Waals or permanent dipole bonds to form crystals; for example water molecules in an ice crystal are bound together by hydrogen bonds with the oxygen atoms arranged in an h.c.p. structure, whereas the tetrahedral molecules of silicon tetrafluoride (SiF_4) which crystallise on a b.c.c. lattice below −90°C are held together by Van de Waals bonds.

7.7 Covalent Crystals

Some of the best examples of directional covalent bonds are those associated with the carbon atom. In the crystal called diamond each carbon atom has four tetrahedrally orientated covalent bonds. These hold the atoms together in a regular three-dimensional array and create a crystal that is in fact one giant molecule. The strength and well defined directionality of the bonds gives diamond its high

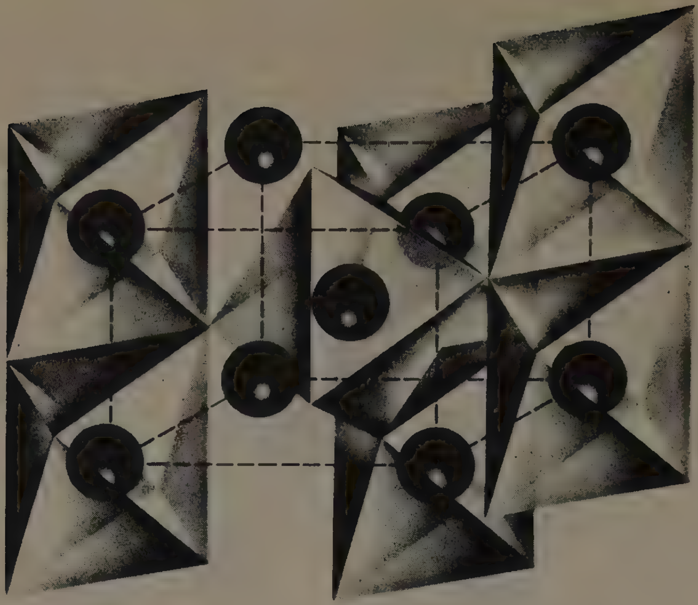


Fig. 7.18 The structure cell of TiO_2 (rutile). The octahedron around two of the titanium ions at the front of the cell have been omitted for clarity. (Reproduced by permission from Moffatt *et al.*: *Structure and Properties of Materials*, Wiley.)

rigidity and hardness. The arrangement of the carbon atoms is the same as that of the SiO_4 tetrahedra in a quartz crystal (Fig. 7.17). The lattice is f.c.c. with a motif of two carbon atoms, one at 0, 0, 0, the other at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, within the structure cell (Fig. 7.19(*a*)). The structure is known as **diamond cubic**.

Silicon and germanium also crystallise in a diamond cubic structure. Compounds such as boron nitride and one form of zinc sulphide (Fig. 7.19(*b*)) have a similar crystal structure but with a motif of two unlike atoms; in addition in the case of the compounds there is a significant ionic contribution to the essentially covalent bonds.

The long covalently bonded chain molecules of regular organic polymers repeatedly fold back on themselves and are held together to form a crystal by fairly weak Van de Waals bonds. The chain

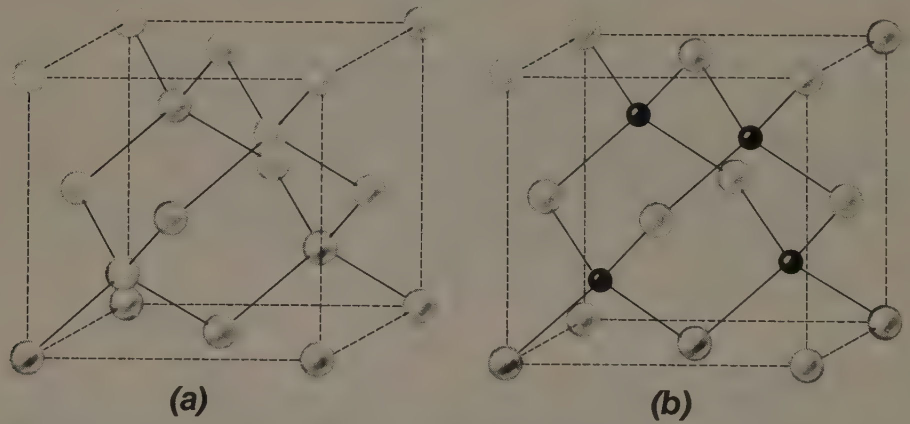


Fig. 7.19 (*a*) The atomic arrangement in diamond, compared with (*b*) that for zincblende (sphalerite). In both structures, the translational symmetry is face centred cubic with a basis of two atoms, one at 000 and the other at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. Thus each atom has only four nearest neighbours, placed at tetrahedral angles. In zincblende, the four neighbours are all of the opposite chemical species.

structure is governed by the directional nature of the four carbon bonds, whereas the crystal structure depends on the packing of the chains. Fig. 7.20 shows the crystal structure of polyethylene.

The lattice is primitive orthorhombic, and the motif consists of the repeating units of two chains, one at 0, 0, 0, and the second which is rotated about the chain axis by about 110° with respect to the first, at $\frac{1}{2}$, $\frac{1}{2}$, 0.

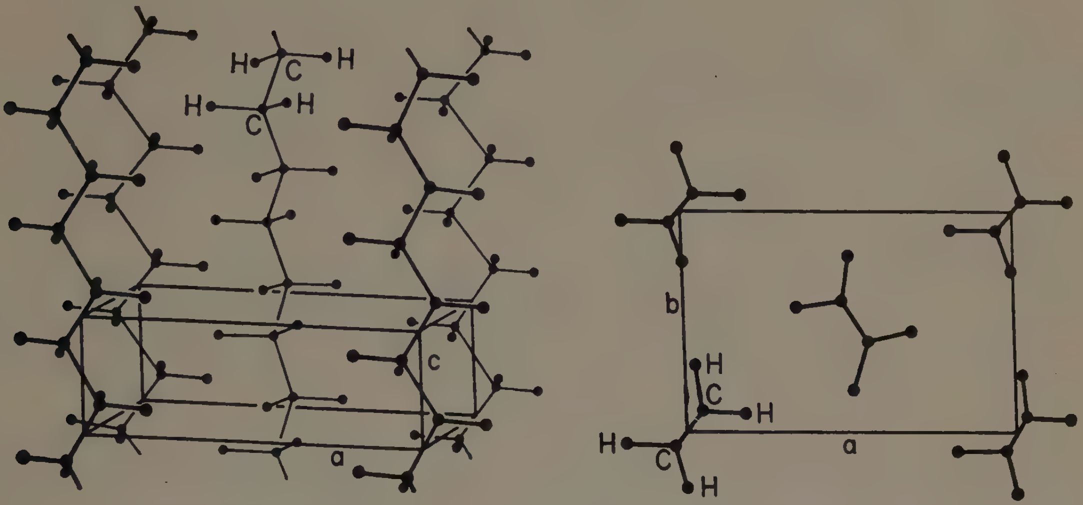


Fig. 7.20 (*a*) The arrangement of the molecular chains of polyethylene showing their zig-zag structure and the way they pack to give an orthorhombic structure cell.
(*b*) A plan view of the structure cell.
(Reproduced by permission from R. Hill (Ed.): *Synthetic Polymers*, Elsevier.)

8
Conventions for Describing Actual Crystal Structures

8.1 Types of Motif (or Basis)

(*a*) One single atom.
(*b*) A group of like atoms. Such groups are usually small but by no means necessarily so. For example, the structure of α Manganese has a body centred cubic lattice, but each motif contains 29 Mn atoms.
(*c*) A group consisting of atoms of more than one type.

A motif may also include or consist of one or more statistical atoms. For example, in the case of a disordered alloy containing 25% atoms A and 75% atoms B distributed at random, it is convenient to consider each atom as identical and having 25% A character and 75% B character.

8.2 Classification of Crystal Structure

The only really definitive way of describing a crystal structure is the method used in the previous chapter. That is in terms of its lattice (Bravais lattice type and unit cell dimensions) and its motif (atom coordinates expressed as fractions of unit cell dimensions). However a general classification of structure types known as the **Strukturbericht System** has been widely acknowledged.

Each recognisable structure type is assigned a letter and a figure.
The letter *A* signifies an element.

For example:

*A*1	f.c.c. structure	e.g. Copper
*A*2	b.c.c. structure	e.g. Iron
*A*3	h.c.p. structure	e.g. Cadmium
*A*4	Diamond cubic	e.g. Silicon
*A*7	R. Hex.	e.g. Bismuth
*A*12	(complicated)	e.g. α Manganese

The letter *B* signifies two types of atom in equal proportion.

For example:

*B*1	e.g. NaCl
*B*2	e.g. CsCl

*B*3	e.g. ZnS cubic
*B*4	e.g. ZnS hex.
*B*5	e.g. NiAs

The letter *C* implies a chemical formula of the type AB_2 containing three atoms. For example:

*C*1	e.g. CaF_2

The system becomes rather less explicit, however, on moving to the *D* series, which includes all structures with the general formula A_nB_m. More complicated compounds are grouped in the series *E* to *K* while *L* type structures are alloys, *S* type: silicates and *O* type organic compounds.

An alternative method of classification relies on three parameters:

(*a*) Lattice system.
(*b*) Lattice type (i.e. whether primitive, body centred, etc.).
(*c*) Number of atoms/structure cell.

The lattice system is described by a lower case letter and the lattice type by a capital, as follows:

Triclinic	*a*	Primitive	*P*
Monoclinic	*m*	Body centred	*I*
Orthorhombic	*o*	Face centred	*F*
Tetragonal	*t*	Base centred	*A*, *B* or *C*
Hexagonal	*h*	Rhombohedral	*R*
Cubic	*c*		

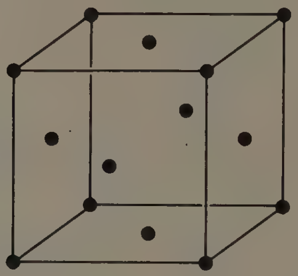
So that, for example, the structure of ordered Cu_3Au would be designated as *cP*4, and that of close packed hexagonal zinc as *hP*2; with in each case the figures indicating the number of atoms per structure cell.

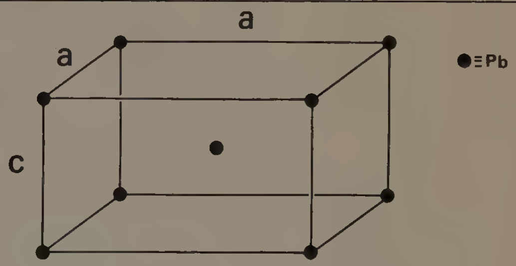
To describe the structure further, the point group symmetry of the motif can be listed using the standard symbolic notation. We will not look at this further at this stage.

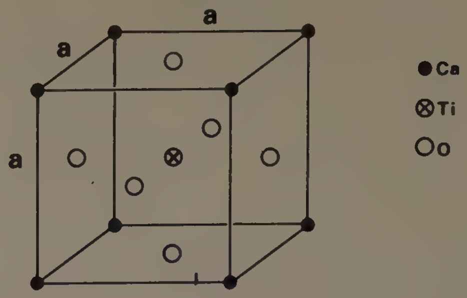
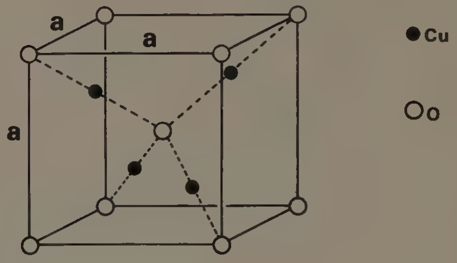
8.3 Examples

Complete the following table by inserting lattice type, motif (atom positions in the unit cell), and/or a sketch of the structure cell as required.

Material	*Lattice*	*Motif*	*Structure cell*
β Zr	b.c.c.		

Material	*Lattice*	*Motif*	*Structure cell*
Ni		Ni atom at 0, 0, 0,	
Ge	f.c.c.	Ge at 0, 0, 0 & $\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{4}$	
Alloy of Au+10% Cu (no atomic order present)			
-α Zr		Zr at 0, 0, 0, & $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$	

Material	*Lattice*	*Motif*	*Structure cell*
Ordered Cu_3Au	Primitive cubic		
BaF_2	f.c.c.	Ba at 0, 0, 0 F at $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$ $-\frac{1}{4}-\frac{1}{4}-\frac{1}{4}$	
PbO_2		Pb Pb O 0·31, 0·31, 0 O (1−0·31), (1−0·31), 0 O ($\frac{1}{2}$+0·31), ($\frac{1}{2}$−0·31), $\frac{1}{2}$ O ($\frac{1}{2}$−0·31), ($\frac{1}{2}$+0·31), $\frac{1}{2}$	 Mark in the oxygen positions
Poly-ethylene		(describe in words)	Refer to Fig. 7.20 and the figure in question 3, Chapter 15 $a = 7{\cdot}40$ $b = 4{\cdot}93$ $c = 2{\cdot}53$ C–C distance = 1·54 Å C–H distance = 1·10 Å

Material	*Lattice*	*Motif*	*Structure cell*
Perovskite $CaTiO_3$			
FeS	Primitive Hexagonal	Fe 0, 0, 0 Fe 0, 0, $\frac{1}{2}$ S $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$ S $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$	
Cu_2O			

9

Directional Indices

9.1 Definition of Directional Indices

In Chapter 2, a lattice translation vector $\mathbf{r}$ was defined for a space lattice as:

$$\mathbf{r} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3.$$

Where u, v, w are integers and $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ constitute a non-coplanar primitive vector group such as may be selected to outline a primitive unit cell. The direction of the vector $\mathbf{r}$ relative to the lattice is defined by the ratio of $u :: v :: w$.

u, v and w divided by their highest common factor (H.C.F.) are the **indices** describing the direction of r. They are enclosed in **square brackets** to signify the fact, i.e.

$$\left[\frac{u,\ v,\ w}{\text{their H.C.F.}}\right]$$

9.2 Directional Indices in Two Dimensions

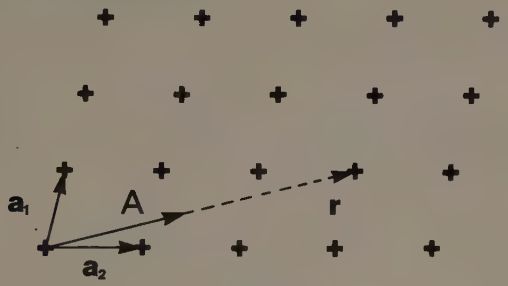


Fig. 9.1

Consider the direction of the arrow A in Fig. 9.1. This is not a lattice translation vector because it does not end at a lattice point. If it is extended until it meets a lattice point, it becomes the translation vector $\mathbf{r}$, where $\mathbf{r} = \mathbf{a}_1 + 3\mathbf{a}_2$.

The indices of the direction are then [1 3].

If one were to consider the exactly opposite direction to arrow A, then:

$$\mathbf{r} = -1\mathbf{a}_1 - 3\mathbf{a}_2.$$

The indices are **not** written [−1 −3] but [$\bar{1}$ $\bar{3}$] and pronounced bar one, bar three.

Another example, based on Fig. 9.2:

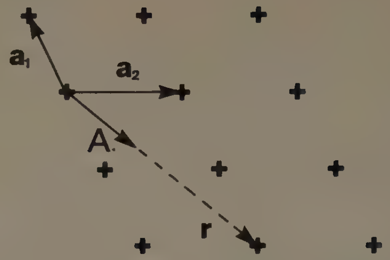


Fig. 9.2 The indices of the direction A are $[\bar{2}1]$ (pronounced bar two, one).

Three points to note:

(*a*) If an alternative primitive vector pair to that in Fig. 9.2 is chosen, the indices describing the same direction will be different. It can be seen from Fig. 9.3 that the indices of direction A are now $[5\ \bar{2}]$.

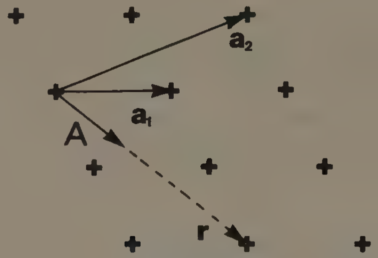


Fig. 9.3 Same lattice and direction as Fig. 9.2, but different unit translation vectors.

(*b*) If A is an arbitrary direction it may have to be extended a very great amount before meeting a lattice point. Its indices would then be very high, e.g. [47 196]. Directions leading to high indices are known as **irrational**, but fortunately are seldom important in a crystallographic context.

(*c*) If vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are not a primitive pair, and outline a non-primitive unit cell there is a possibility that u and v may not be integers. This, however, has no effect on the final form of the indices because they express the ratio of u to v.

In Fig. 9.4 direction A is extended to **r**.

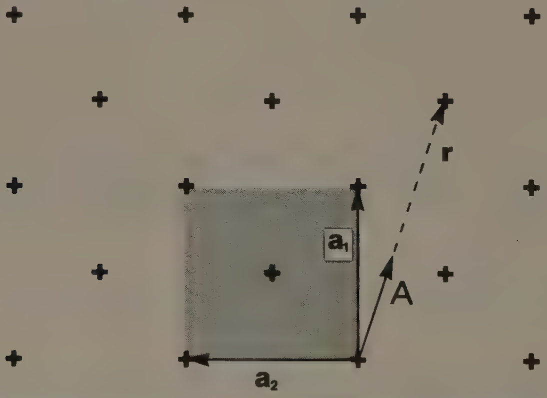


Fig. 9.4 A planar lattice described by a non-primitive unit cell.

$$\mathbf{r} = \tfrac{3}{2}\mathbf{a}_1 - \tfrac{1}{2}\mathbf{a}_2.$$

The H.C.F. of u and v is $\frac{1}{2}$, therefore indices of direction A are given by:

$$\left[\frac{\frac{3}{2}}{\frac{1}{2}} \quad -\frac{\frac{1}{2}}{\frac{1}{2}}\right] = [3 \quad \bar{1}].$$

9.3 Determination of Directional Indices in Three Dimensions

Three-dimensional lattices are most usually represented by a sketch of a primitive, or non-primitive unit cell. So it is sensible to formulate a method for the determination of indices of a direction drawn **within** a unit cell.

Recipe to determine the indices of a particular direction (referring to Fig. 9.5).

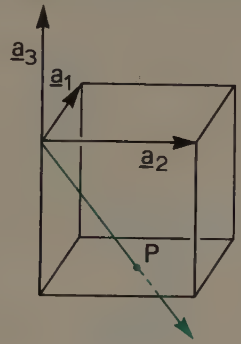


Fig. 9.5

(1) Draw the direction as a line so that it intersects the unit cell twice, once at a lattice point.

(2) Take the intersected lattice point as the origin of the translation vectors, $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ on which the cell is based.

(3) Read off the coordinates of the point P as fractions of the translation vectors (in example: $\frac{1}{2}, \frac{1}{2}, -1$).

(4) Divide these by their H.C.F. and express as indices.

H.C.F. $= \frac{1}{2}$
Directional indices $= [1 \quad 1 \quad \bar{2}]$.

With experience it is often possible to mentally extend the line until it intersects a lattice point, the coordinates of which give the indices directly.

9.4 Symmetry and Directional Indices in Planar Lattices

The possession of symmetry elements by a lattice renders particular sets of directions **equivalent**. We will again illustrate the principles by first considering planar lattices.

(*i*) *Parallelogram lattice*

All lattices possess centres of inversion symmetry at each lattice point; hence on the parallelogram lattice drawn in Fig 9.6 direction A is equivalent to direction B,

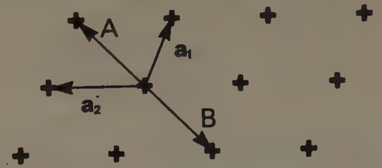


Fig. 9.6 Parallelogram lattice illustrating the general rule of the equivalence of opposite lattice directions.

i.e. direction A $[11]$ = direction B $[\bar{1}\bar{1}]$ or in general $[uv] = [\bar{u}\bar{v}]$.

The operation of the diad rotation axis perpendicular to the plane would also render $[uv] = [\bar{u}\bar{v}]$.

(*ii*) *Rectangular lattice*

A rectangular lattice (primitive or non-primitive) possesses two orthogonal sets of mirror planes (Fig. 9.7).

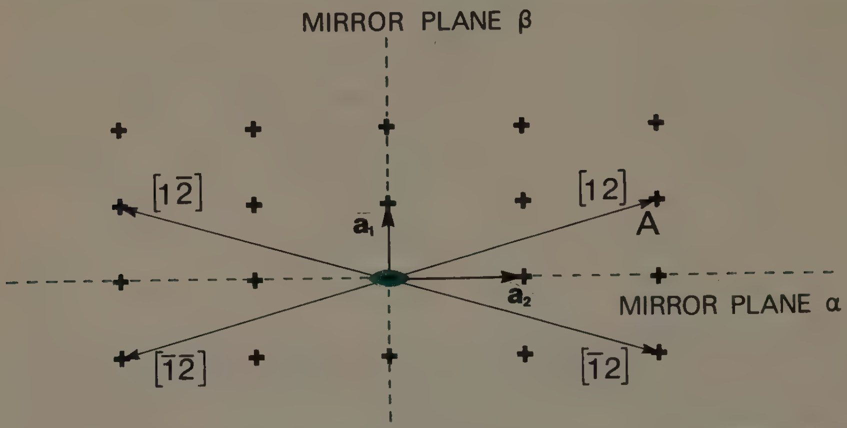


Fig. 9.7 A primitive rectangular lattice showing two orthogonal mirror planes and the four equivalent directions ⟨12⟩. The lattice also possesses diad symmetry elements (cf. Fig. 5.4).

Starting with the direction A $[12]$, the operation of centre of symmetry and/or diad leads to the equivalent direction $[\bar{1}\bar{2}]$.

The operation of mirror plane α and/or β generates $[\bar{1}2]$ and $[1\bar{2}]$. In general terms $[uv] = [\bar{u}\bar{v}] = [\bar{u}v] = [u\bar{v}]$. All the directions of the '*uv* type' are equivalent and are written in **diamond brackets** as $\langle uv \rangle_{\text{rectangular}}$.

(*iii*) *Square lattice*

The existence of the tetrad and additional mirror planes in a square lattice lead to additional equivalent directions (Fig. 9.8).

Again starting with direction $[12]$, the operation of the tetrad generates $[2\bar{1}]$, $[\bar{1}\bar{2}]$ and $[\bar{2}1]$. Operation of any of the mirror planes α_1, β_1, α_2 and β_2 will generate the four further equivalent directions $[21]$, $[1\bar{2}]$, $[\bar{2}\bar{1}]$ and $[\bar{1}2]$. Follow these through on the diagram.

So, in general terms,

$$\begin{aligned} &[uv] = [\bar{u}\bar{v}] = [\bar{u}v] = [u\bar{v}] \\ &= [vu] = [\bar{v}\bar{u}] = [\bar{v}u] = [v\bar{u}] = \langle uv \rangle_{\text{square}}. \end{aligned}$$

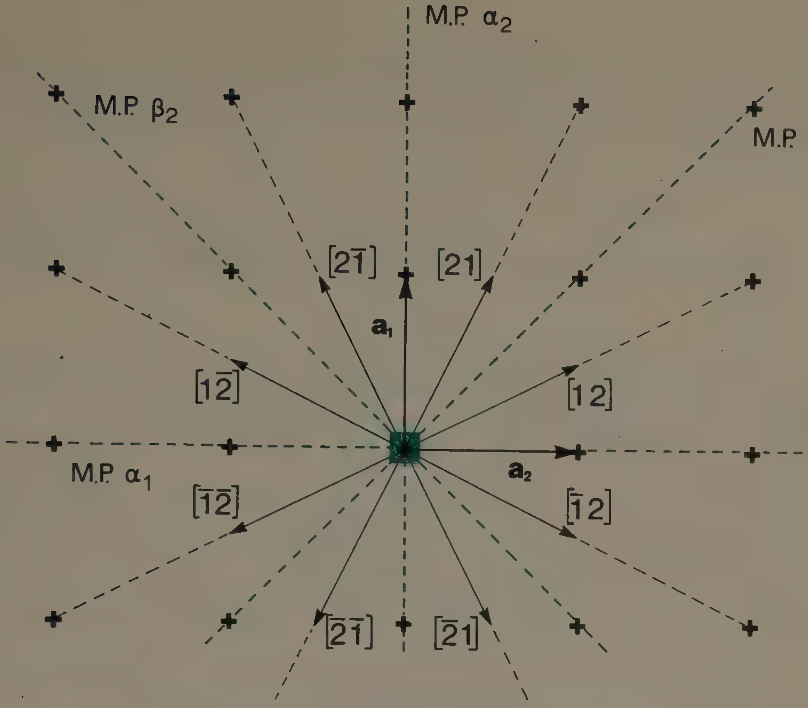


Fig. 9.8 A square lattice with the eight equivalent directions ⟨12⟩.

(*iv*) *Hexagonal lattice* (Fig. 9.9)

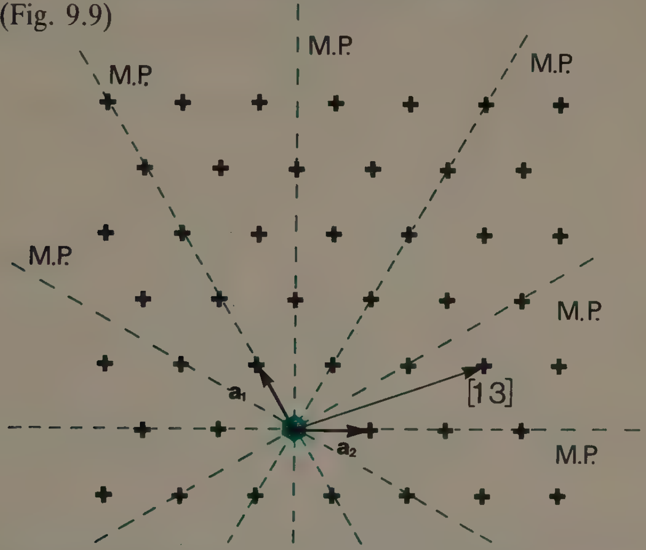


Fig. 9.9 A hexagonal lattice showing the symmetry elements which are responsible for generating eleven directions equivalent to [13].

The operation of the hexad and mirror planes on the direction [13] generates the following equivalent directions:

$$\begin{array}{cccccc} & [23] & [32] & [31] & [2\bar{1}] & [1\bar{2}] \\ [\bar{1}\bar{3}] & [\bar{2}\bar{3}] & [\bar{3}\bar{2}] & [\bar{3}\bar{1}] & [\bar{2}1] & [\bar{1}2] \end{array}$$

(Check these for yourself.)

The indices however give no indication of their equivalence.

(*v*) *Hexagonal lattice (alternative indexing system)*

The generally accepted way round the difficulty that symmetrically equivalent directions have mathematically non-equivalent indices is to index the directions using **three** translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ as axes which define a multiple planar unit cell as drawn in Fig. 9.10. So

$$\mathbf{r} = U\mathbf{a}_1 + V\mathbf{a}_2 + I\mathbf{a}_3.$$

(I is used rather than W which is reserved for the additional index required to define a direction in three dimensions.)

Now, there are a tremendous number of possible combinations of U, V and I which will give $\mathbf{r}$. For example the direction B, drawn in Fig. 9.10, which has 'conventional' directional coordinates in terms of $\mathbf{a}_1$ and $\mathbf{a}_2$ of $[uv] = [41]$, could be defined in the three-index system as:

$$\begin{aligned} [UVI] &= [2\bar{1}\bar{2}] \\ &\text{or } [521] \\ &\text{or } [410] \\ &\text{or } [1\bar{2}\bar{3}] \end{aligned}$$

and many others . . . .

The system only becomes sensible when the additional condition is imposed that $U + V + I = 0$. Equivalent directions then have mathematically equivalent indices.

In the case of directions which are perpendicular to one of the three axes, the determination of indices is straightforward. For example direction A (Fig. 9.10) which is perpendicular to $\mathbf{a}_2$ will have indices: $[UVI] = [10\bar{1}]$ (i.e. $\mathbf{r}_A = 1\mathbf{a}_1 + 0\mathbf{a}_2 - 1\mathbf{a}_3$ and $U + V + I = 0$).

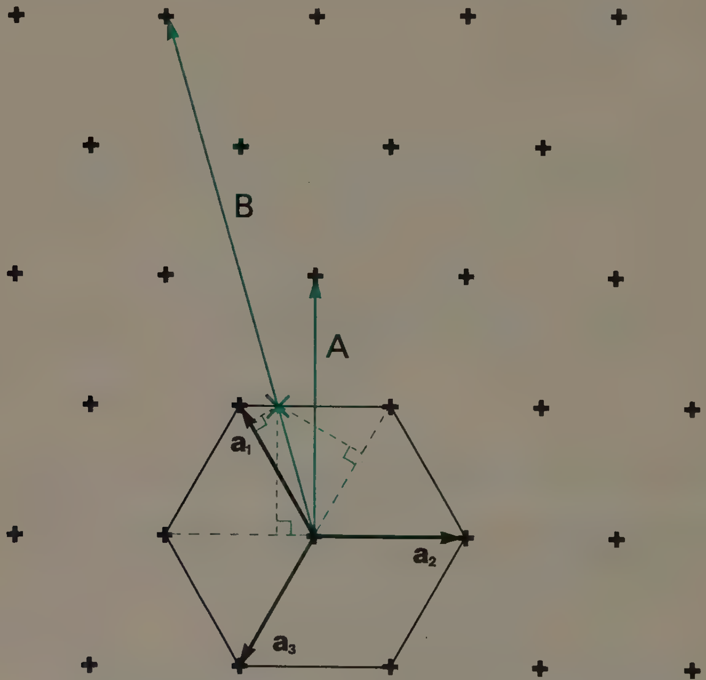


Fig. 9.10 A planar non-primitive hexagonal cell defined by the three vectors: $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$.

For a more general direction such as B (Fig. 9.10) the determination by inspection of the indices $[UVI]$ which define the direction and also satisfy the condition $U+V+I=0$ can be a little tedious — to say the least.

It is possible, however, to find the indices in a systematic way by the procedure outlined below.

Referring again to direction B in Fig. 9.10 the first stage is to project either point X or the end of the vector as a perpendicular on to the three axes in turn.

For point X this gives intercepts at:

$$\begin{aligned} \tfrac{7}{8}\mathbf{a}_1 &\quad \text{along } \mathbf{a}_1 \\ -\tfrac{1}{4}\mathbf{a}_2 &\quad \text{along } \mathbf{a}_2 \\ -\tfrac{5}{8}\mathbf{a}_3 &\quad \text{along } \mathbf{a}_3. \end{aligned}$$

If the coefficients are divided through by their highest common factor, i.e. $\frac{1}{8}$, we obtain the indices of the direction as $[7\bar{2}\bar{5}]$.

If $7\mathbf{a}_1$'s, $-2\mathbf{a}_2$'s and $-5\mathbf{a}_3$'s are laid off on Fig. 9.10 (or rather an extension of it!), they add up to a vector in direction B but exactly three times the length of B. This factor of three is not too important as far as planar indices are concerned, but it must be kept in mind when determining three-dimensional hexagonal indices; it is also accounted for by the appearance of the fraction $\frac{1}{3}$ in the equations below.

The directional indices $[uv]$ and $[UVI]$ are related as follows:

$$\begin{aligned} u &= U-I & \qquad U &= \tfrac{1}{3}(2u-v) \\ v &= V-I & \qquad V &= \tfrac{1}{3}(2v-u) \\ & & I &= -\tfrac{1}{3}(u+v) = -(U+V). \end{aligned}$$

These equations also apply for the three-dimensional systems $[uvw]$ and $[UVIW]$ with the additional relation:

$$w=W.$$

To summarise for two dimensions:

(1) The existence of a centre of inversion symmetry puts $[\bar{u}\bar{v}]=[uv]$. A two-fold rotation axis perpendicular to the plane has the same effect.
Example: parallelogram lattice.

(2) Two orthogonal sets of mirror planes as found in a rectangular lattice put $[uv]$ and $[\bar{u}\bar{v}]=[\bar{u}v]$ and $[u\bar{v}]$; i.e. all permutations of sign (positive or negative) possible, but u and v are not interchanged.

(3) Both the four-fold rotation axis and the four sets of mirror planes possessed by the square lattice render directions equivalent which have all permutations of sign and order.

(4) Equivalent directions in a hexagonal lattice have indices which do not always bear a numerical relationship to each other.

(5) The reference of directions on a planar hexagonal lattice to three axes (translation vectors) gives indices $[UVI]$ which, in the case of equivalent directions, appear equivalent, U, V and I being interchanged as regards sign and position. In this indice system the condition $U+V+I=0$ must always be upheld.

9.5 Symmetry Related Indices in Three Dimensions

Let us build up a **monoclinic lattice** by stacking parallelogram lattices directly above each other (see Chapter 6). Now, $[uv]$ is only $\equiv [\bar{u}\bar{v}]$ but because a vertical plane through this lattice is planar rectangular we have:

$$vw \equiv \bar{v}\bar{w} \equiv \bar{v}w \equiv v\bar{w}$$
$$uw \equiv \bar{u}\bar{w} \equiv \bar{u}w \equiv u\bar{w}$$

Therefore, $$[u\ v\ w] \equiv [\bar{u}\bar{v}\bar{w}] \equiv [uv\bar{w}] \equiv [\bar{u}\bar{v}w]$$

So that $\langle uvw \rangle_{\text{monoclinic}}$ represents four equivalent directions.

For a tetragonal lattice built up by stacking square lattices on top of each other

$$[uv] \equiv [\bar{u}\bar{v}] \equiv [u\bar{v}] \equiv [\bar{u}v] \equiv [vu] \equiv [\bar{v}\bar{u}] \equiv [\bar{v}u] \equiv [v\bar{u}]$$

i.e. signs and positions variable (square lattice condition). But in planes perpendicular to the square lattices the rectangular condition holds in which only the signs of v and w are variable

Hence, $$[vw] \equiv [\bar{v}\bar{w}] \equiv [v\bar{w}] \equiv [\bar{v}w]$$

and $$[uw] \equiv [\bar{u}\bar{w}] \equiv [u\bar{w}] \equiv [\bar{u}w]$$

It follows from these combinations that, for equivalence, the only restrictions on the signs and positions of the three indices for the tetragonal lattice is that the w index must appear in the third position.

Hence $$[uvw] \equiv [\bar{u}\bar{v}w] \equiv [\bar{u}vw] \equiv [u\bar{v}w]$$

and repeated with $\bar{w}$

$$[vuw] \equiv [\bar{v}\bar{u}w] \equiv [\bar{v}uw] \equiv [v\bar{u}w]$$

and repeated with $\bar{w}$

Therefore $\langle uvw \rangle_{\text{TETRAGONAL}}$ represents 16 equivalent directions.

The number of equivalent directions can be reduced if either a pair or all of the indices uvw are equal, or if one or two of them are zero.

E.g. for the tetragonal case, for direction type $\langle 100 \rangle_{\text{TET}}$

$$[100] \equiv [\bar{1}00] \equiv [010] \equiv [0\bar{1}0]$$ i.e. four equivalent.

For type $\langle 111 \rangle_{\text{TET}}$

$$[111] \equiv [\bar{1}\bar{1}\bar{1}] \equiv [\bar{1}\bar{1}1] \equiv [11\bar{1}] \equiv [\bar{1}11] \equiv [1\bar{1}\bar{1}] \equiv [\bar{1}1\bar{1}] \equiv [1\bar{1}1]$$ i.e. eight equivalent.

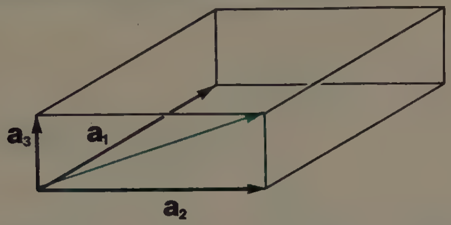
But for $\langle 121 \rangle_{\mathrm{TET}}$ there are the full 16 different but equivalent directions.

Verify these for yourself. (See notes on question 4.)

> **Remember:** Equivalent directions in a lattice do not necessarily apply to a crystal structure where the motif symmetry may be less than that of the lattice.

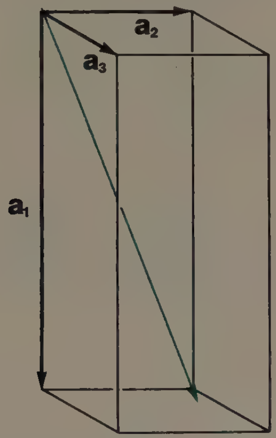
9.6 Examples of the Determination of Directional Indices

1.



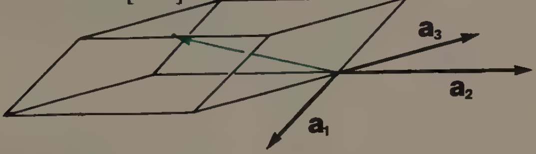
Intercept with unit cell at origin and $0\mathbf{a}_1$, $1\mathbf{a}_2$, $1\mathbf{a}_3$, therefore direction = [011].

2.



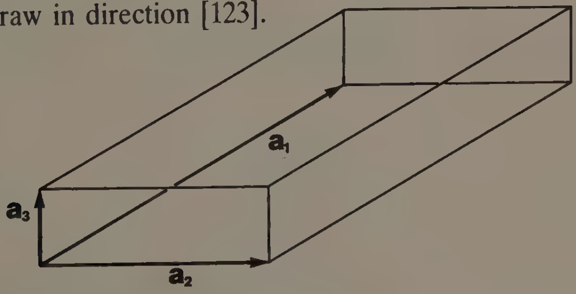
Intercept at $1\mathbf{a}_1$, $\frac{3}{4}\mathbf{a}_2$, $\frac{1}{2}\mathbf{a}_3$, direction = [432].

3.



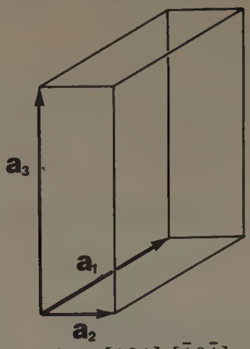
Intercept at $-\mathbf{a}_1$, $-\frac{1}{2}\mathbf{a}_2$, $-\mathbf{a}_3$, direction = $[\bar{2}\bar{1}\bar{2}]$.

4. On the cell below draw in direction [123].



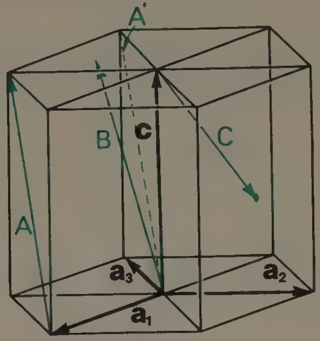
Draw in [123]. Intercepts at $\frac{1}{3}\mathbf{a}_1$, $\frac{1}{2}\mathbf{a}_2$, $1\mathbf{a}_3$ and 0, 0, 0.

5. On the orthorhombic cell below draw in $\langle 101 \rangle$.



First determine equivalent combinations, i.e. $[101]$ $[\bar{1}0\bar{1}]$, $[10\bar{1}]$ $[\bar{1}01]$.

6. To determine indices of directions A, B and C in its hexagonal cell (Fig. 9.16) using both the three- and four-index systems. (Equivalent to two- and three-index systems of a planar hexagonal lattice.)



(*i*) Three-index system. Using $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{c}$.

Direction A:

Mentally translate so it passes through origin (dotted line). Intercept at $-\mathbf{a}_1$, $-\mathbf{a}_2$, $\mathbf{c}$, therefore $[uvw] = [\bar{1}\bar{1}1]$.

Direction B:

Intercept at $-\frac{1}{3}\mathbf{a}_1$, $-\frac{2}{3}\mathbf{a}_2$, $\mathbf{c}$ $\qquad [uvw] = [\bar{1}\ \bar{2}\ 3]$.

Direction C:

Intercept at $\frac{1}{2}\mathbf{a}_1$, $\mathbf{a}_2$, $-\frac{1}{2}\mathbf{c}$ (mentally transposing origin to middle of top hexagon) $[uvw] = [1\ \ 2\ \ 1]$.

(*ii*) Four-index system. Using $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ and $\mathbf{c}$.

Direction A:

Transpose as before and apply the system outlined in Section 9.4(*v*). Coordinates of projections of direction on to $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are $-\frac{1}{2}$ $-\frac{1}{2}$ 1.

therefore
$$UVI = \bar{1}\bar{1}2$$
$$(U+V+I=0).$$

But the length of the vector $-\mathbf{a}_1$, $-\mathbf{a}_2$, $+2\mathbf{a}_3$ is three times the component of vector **A** in the basal plane. Therefore the intercept on the c axis will be at $3\mathbf{c}$. Hence

$$[UVIW] = [\bar{1}\bar{1}23].$$

Checking back by calculation using relations from section 9.4:

$$u = U - I = \bar{3}$$
$$v = V - I = \bar{3}$$
$$w = W \quad = 3.$$

Therefore $[uvw] = [\bar{3}\bar{3}3]$ or $[\bar{1}\bar{1}1]$.

Direction B:

Because this direction is perpendicular to $\mathbf{a}_1$ it is fairly easy to obtain its vector components as $-\frac{1}{3}\mathbf{a}_2$, $\frac{1}{3}\mathbf{a}_3$ and $\mathbf{c}$. So the indices are $[0\bar{1}13]$.

Alternatively one can draw perpendicular projections of the basal plane components on to $\mathbf{a}_2$ and $\mathbf{a}_3$. This gives $0\mathbf{a}_1$, $-\frac{1}{2}\mathbf{a}_2$, $\frac{1}{2}\mathbf{a}_3$ and hence $0\bar{1}1$ which represents a basal plane component three times the drawn length. The c intercept is therefore $3\mathbf{c}$ and the indices $[0\bar{1}13]$ as before.

Checking back by calculation:

$$u = U - I = \bar{1}$$
$$v = V - I = \bar{2}$$
$$w = W \quad = 3.$$

Therefore $[uvw] = [\bar{1}\bar{2}3]$.

Direction C:

The direction is perpendicular to $\mathbf{a}_1$. Therefore by inspection
$$UVIW = 0,\ \tfrac{1}{2},\ -\tfrac{1}{2},\ -\tfrac{1}{2}$$
$$= [01\bar{1}\bar{1}].$$

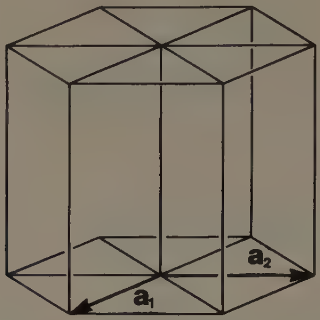
Checking:

$$u = U - I = 1$$
$$v = V - I = 2$$
$$w = W \quad = \bar{1}.$$

Therefore $[uvw] = [12\bar{1}]$.

TO DO

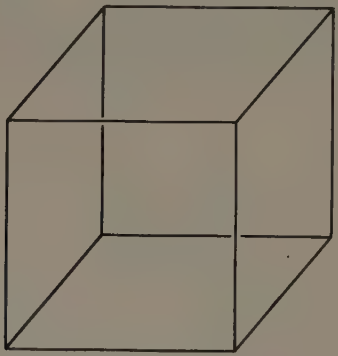
1. Referring to the hexagonal cell below:
   - (*i*) Insert directions of the type $\langle 121 \rangle$.
   - (*ii*) Write out the directional indices of these directions $[uvw]$.
   - (*iii*) Read off their indices in the four-index system.
   - (*iv*) Check the relationship by calculation.



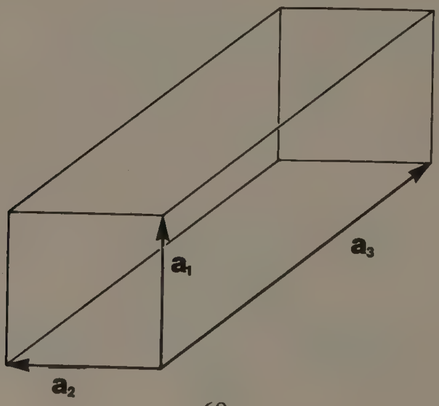
2. In an orthorhombic lattice four of these directions are equivalent. Ring them.

$$\begin{array}{ccc} [\bar{1}12] & [1\bar{1}2] & [12\bar{1}] \\ [1\bar{1}\bar{2}] & [\bar{1}1\bar{2}] & [\bar{1}\bar{2}1]. \end{array}$$

3. Draw on the cubic unit cell below examples of all directions of the types $\langle 111 \rangle$ and $\langle 110 \rangle$.



4. On the unit cell below draw in all directions of the type $\langle 121 \rangle_{\mathrm{TET}}$.



Remember: These symmetry groupings do not necessarily apply to a crystal structure based on the lattice.

YOU SHOULD BE ABLE TO

Write down the recipe for determining directional indices in three-dimensional structures, and also describe the four-index system for hexagonal lattices together with its advantage.

10

Crystal Planes and Miller Indices

10.1 Historical

The prominent school of crystallography which grew up at Cambridge during the last century under the leadership of Professor W. H. Miller, developed a system of describing the relative orientation of naturally occurring crystal faces. The system was based, not on angles, but on three-figure groups known subsequently as **Miller indices**.

Each face was assigned a set of indices as follows:

(*i*) The lines of intersection of three of the most prominent faces were taken as axes (x, y, z).

(*ii*) Another prominent face was selected which intersected the three axes. It was known as the **reference face**.

(*iii*) The distances between the origin of the axes and their points of intersection with the reference face were measured (A_1, A_2 and A_3 on Fig. 10.1).

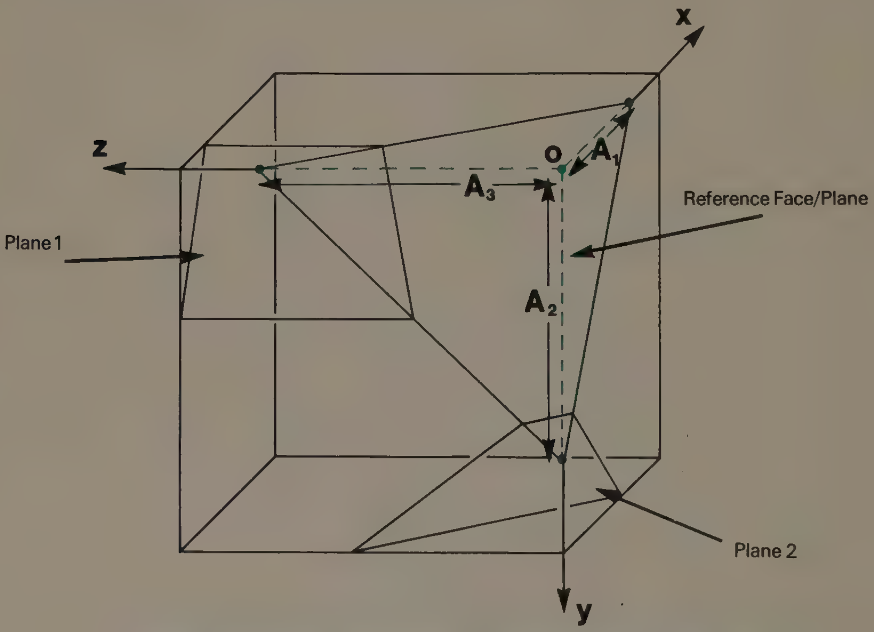


Fig. 10.1 A sketch representing crystal facets to illustrate Miller's method of indexing.

(*iv*) Similar distances were measured for other faces (B_1, B_2 and B_3, etc.) and the indices of these faces taken as the ratio:

$\frac{A_1}{B_1} :: \frac{A_2}{B_2} :: \frac{A_3}{B_3}$ expressed as whole numbers, *hkl.*

Example:

The following intersection distances were measured for the planes in Fig. 10.1:

	Reference plane	*Plane 1*	*Plane 2*
x	0·82	0·21	By projection −0·60
y	0·82	0·42	0·80
z	0·82	∞	By projection −0·60

Therefore indices of plane 1

$$\frac{0{\cdot}82}{0{\cdot}21} :: \frac{0{\cdot}82}{0{\cdot}42} :: \frac{0{\cdot}82}{\infty} = h :: k :: l = (210).$$

Indices of plane 2

$$\frac{0.82}{-0{\cdot}60} :: \frac{0{\cdot}82}{0{\cdot}80} :: \frac{0{\cdot}82}{-0{\cdot}60} = h :: k :: l = (\bar{4}3\bar{4}).$$

By the same token the indices of the reference plane are (111).

Two points to note:

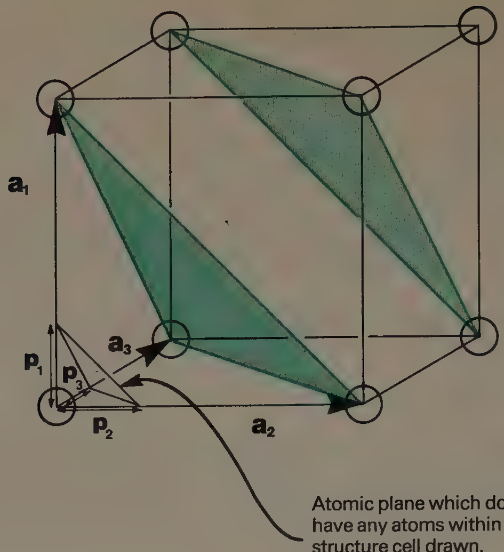
(1) As with directional indices, negative indices are written using the bar notation.

(2) Unlike directional indices, Miller indices are written in **curved brackets**.

Examination of many crystals, showed that the indices *hkl* of both natural and cleavage faces, were invariably small numbers. Another crystallographer, A. R. J. Haüy, summed up these observations as **'the Law of Rational Indices'**. He also proposed that the law was a natural consequence of some periodic internal structure of the crystal. Or, in other words, that the crystal was built up from many identical units.

10.2 Indices of Atom Planes

The classic X-ray diffraction experiments of Laue, Bragg and others confirmed that a crystal was a periodic array of atoms in three dimensions. It was found that both natural faces and cleavage planes corresponded to the more prominent atomic planes (i.e. those most densely populated by atoms).



Atomic plane which does not have any atoms within the structure cell drawn.

Fig. 10.2

Miller therefore, in ascribing indices to crystal faces, was in fact indexing prominent planes of atoms.

Consider now a primitive cubic structure cell (Fig. 10.2).

It is likely that a crystal with this structure would, in the bulk, show facets which correspond to the cube faces, and intersect to generate suitable axes, *x*, *y* and *z* (Fig. 10.1). A typical reference face might have corresponded to those atomic planes drawn within the cell (Fig. 10.2). In Miller terminology, the reference face would define the three distances A_1, A_2 and A_3 along the *x*, *y* and *z* axes. Scaled down about 100,000,000 times, these distances from the primitive vector group $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ which defines the unit cell.

The points of intersection of any other atom plane with the three vectors of the primitive group can be determined, and their distances from the origin ($\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$), expressed as fractions of the vector lengths, i.e.

$$\frac{\mathbf{p}_1}{\mathbf{a}_1} :: \frac{\mathbf{p}_2}{\mathbf{a}_2} :: \frac{\mathbf{p}_3}{\mathbf{a}_3} \text{ (Fig. 10.2)}$$

But, Miller had chosen to express his ratios in terms of

$$\frac{\mathbf{A}_1}{\mathbf{P}_1} :: \frac{\mathbf{A}_2}{\mathbf{P}_2} :: \frac{\mathbf{A}_3}{\mathbf{P}_3}$$

so that the fractional intercept distances from the unit cell have to be inverted (reciprocals taken) before they can be expressed as a ratio to give Miller indices.

Miller may have decided on his particular system so as to avoid the appearance of infinities in his indices. Somehow a zero is cleaner looking. In the context of modern crystallography his choice has proved more than just convenient. This is because diffraction effects which are utilised for crystal structure analysis are described best in terms of the Fourier transform of the crystal lattice (the reciprocal lattice), and Miller's indices of a plane turn out to be virtually the coordinates of the corresponding reciprocal lattice point. (See Chapter 11 and Appendix 3 for explanation of these concepts.)

If a different plane had been chosen as the reference face, the indices derived for other faces would be different. This would be equivalent to choosing a different group of translation vectors and hence a different unit cell.

10.3 Recipe for the Determination of Miller Indices

(*i*) Consider a plane drawn in a unit cell.

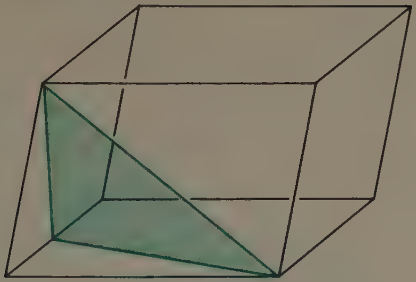


Fig. 10.3

(*ii*) Choose three axes with an origin not lying on the plane, which, ideally, all intersect the plane.

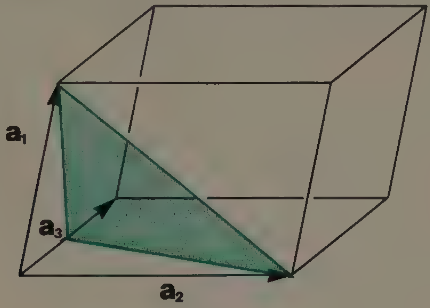


Fig. 10.4

(*iii*) Measure the distance along each axis from the origin to the point of intersection with the plane and express as a fraction (or multiple) of the corresponding translation vector. In some cases the axes may have to be projected in a negative direction before the intercept is located.

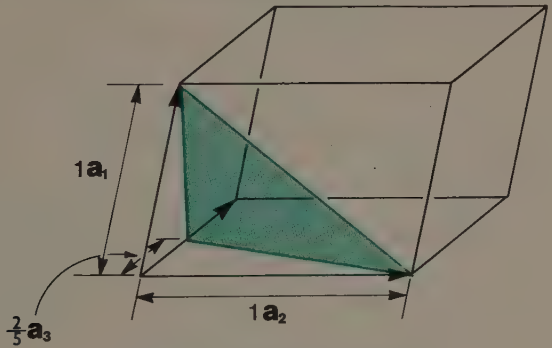


Fig. 10.5 Intercepts of $\frac{2}{5}\mathbf{a}$, $\mathbf{a}_2$, $\mathbf{a}_3$.

(*iv*) Take reciprocals of each of the fractions (multiples) and multiply through by a suitable factor to convert to the three smallest possible integers, i.e.

$$\left(\frac{5}{2}\ \ \frac{1}{1}\ \ \frac{1}{1}\right)\times 2 \rightarrow (522)$$

which are the Miller indices of the plane.

10.4 Zones of Planes

A **zone** of planes is a series of non-parallel planes which are all parallel to (or contain) one particular direction known as the **zone axis**.

A zone of planes is drawn within the unit cell in Fig. 10.6. The determination of the indices of these planes is summarised in Table 10.1.

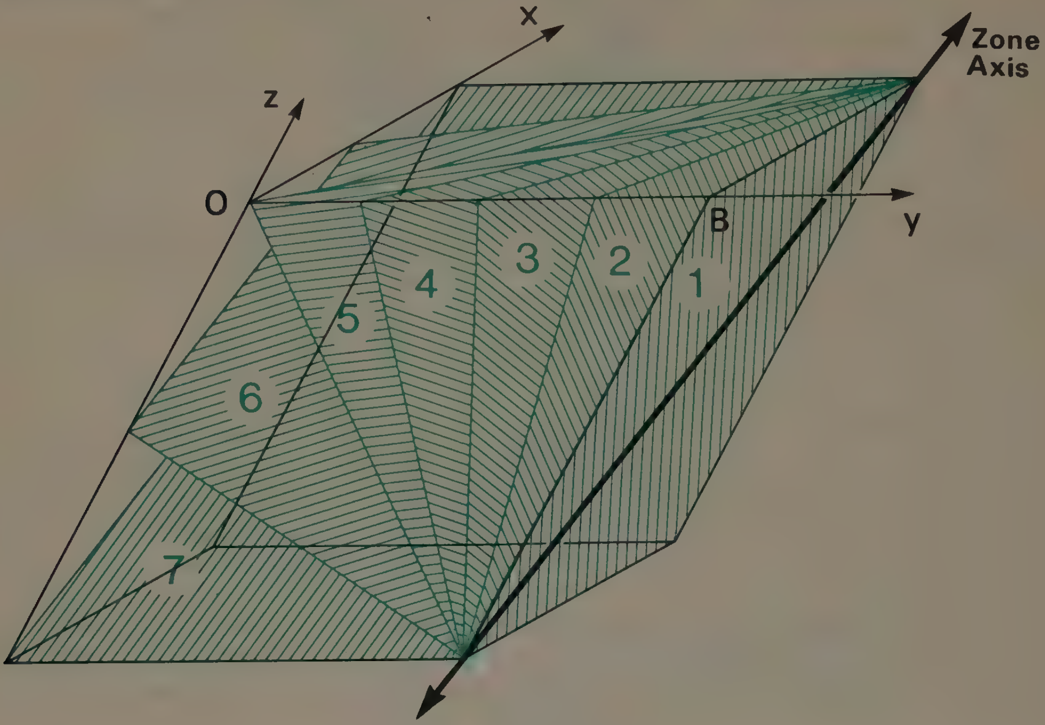


Fig. 10.6 A zone of planes.

TABLE 10.1

Plane	*Axes transfer to give non-zero intercepts*	*Intercepts*	*Reciprocals*	*Indices*
1	None	$\infty 1 \infty$	010	010
2	None	$-3\ \frac{3}{4}\ 3$	$\frac{1}{3}\frac{4}{3}\frac{1}{3}$	$\bar{1}41$
3	None	$-1\ \frac{1}{2}\ 1$	$\bar{1}21$	$\bar{1}21$
4	None	$-\frac{1}{3}\ \frac{1}{4}\ \frac{1}{3}$	$\bar{3}43$	$\bar{3}43$
5	Transfer origin to B	$1-1-1$	$1\bar{1}\bar{1}$	$\bar{1}11$
6	None	$\frac{1}{2}-1-\frac{1}{2}$	$2\bar{1}\bar{2}$	$\bar{2}12$
7	None	$1\infty-1$	$10\bar{1}$	$\bar{1}01$

A degree of numerical symmetry can usually be detected in the indices of planes belonging to the same zone. In the example above $h+l=0$.

The Miller indices of planes of one zone (hkl) are related to the directional indices of the zone axis $[uvw]$ as follows:

$$hu + kv + lw = 0.$$

Hence in the example above the zone axis is [101].

Formally one can determine the directional indices of the intersection between two planes $h_1\ k_1\ l_1$ and $h_2\ k_2\ l_2$ as follows:

$$u = k_1 l_2 - k_2 l_1$$
$$v = l_1\ h_2 - l_2\ h_1$$
$$w = h_1 k_2 - h_2 k_1.$$

Apply these equations to any two planes in the example, and check that the zone axis is [101].

The grouping of planes into zones is completely independent of the crystal system.

10.5 Forms of Planes

A **form of planes** is a series of non-parallel planes related by a particular symmetry element. As in the case of equivalent directions, the number of planes of one **form** depends on the symmetry of the lattice or crystal structure, and increases as the symmetry increases.

The various permutations of Miller indices, which describe lattice planes of the same form, depend on the lattice system in much the same way as directional indices. The rules are summarised in Table 10.2.

TABLE 10.2

e.g. system	*Permutations of Miller indices for planes of the same form*	*Number of planes of type (hkl)* in form*
Triclinic	All indices positive, or all negative	2
Monoclinic	Two particular indices (e.g. h and k) with the same sign	4
Orthorhombic	All possible permutations of sign	8
Tetragonal	All possible permutations of sign and two indices may be interchanged (those derived from the two equal axes)	16
Cubic	All possible permutations of sign and indices	48
Hexagonal	Indices of the same form may bear no numerical relationship to each other (see below) (For the R. Hexagonal lattice the number of planes in a form is reduced to 12)	24

* i.e. three, non-zero different indices.

Planes (hkl) and $(\bar{h}\bar{k}\bar{l})$ are parallel, and in the case of lattice (rather than atomic) planes. They are identical. They are counted separately though in the totals in the third column of Table 10.2.

If the symmetry of a crystal structure is less than that of the lattice, then the number of planes in any form is likely to be reduced.

A form of planes is designated by the indices hkl enclosed in **curly brackets**, e.g. $\{hkl\}$. Double curved brackets are sometimes used, e.g. $((hkl))$.

Example:

Draw in planes of the form {123} on the tetragonal lattice cell ($\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3$).

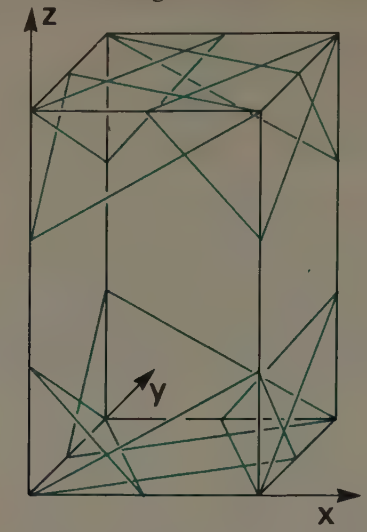


Fig. 10.7 Planes of the form {123} in a tetragonal lattice.

Planes belonging to this form are:

(a) $(123)\ (\bar{1}\bar{2}\bar{3})$
(b) $(\bar{1}23)\ (1\bar{2}\bar{3})$
(c) $(1\bar{2}3)\ (\bar{1}2\bar{3})$
(d) $(12\bar{3})\ (\bar{1}\bar{2}3)$
(e) $(213)\ (\bar{2}\bar{1}\bar{3})$
(f) $(\bar{2}13)\ (2\bar{1}\bar{3})$
(g) $(2\bar{1}3)\ (\bar{2}1\bar{3})$
(h) $(21\bar{3})\ (\bar{2}\bar{1}3)$.

Therefore there are eight distinguishable equivalent planes which are drawn in on Fig. 10.7.

Label the planes on the figure (a), (b), (c), etc.

10.6 Miller-Bravais Indices

The Miller–Bravais system is a four-index system ($hkil$) based on a non-primitive hexagonal cell (hexagonal prism). It has the same advantages as the four-index system used for directions and endows planes belonging to the same form with indices which are numerically related to each other.

For example, consider the form of planes parallel to the c axis in Fig. 10.8.

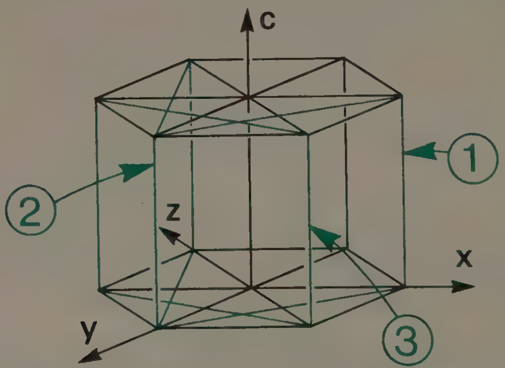


Fig. 10.8 A hexagonal cell depicting three distinct planes of one form.

	Plane 1	*Plane 2*	*Plane 3*
In the three-index system:			
Indices based on axes *x*, *y* and *c*	(110)	($\bar{2}$10)	($\bar{1}$20)
In the Miller-Bravais system:			
Coordinates of points of intersection with axes *x*, *y*, *z* and *c*	$1\ 1\ -\frac{1}{2}\ \infty$	$-\frac{1}{2}\ 1\ 1\ \infty$	$-1\ \frac{1}{2}\ -1\ \infty$
Reciprocals to give indices (*hkil*)	(11$\bar{2}$0)	($\bar{2}$110)	($\bar{1}$2$\bar{1}$0)

Unlike the four-index system for directional indices in hexagonal lattices considered in the previous Chapter, the method for finding Miller-Bravais indices does not vary in principle from that used for three-index Miller indices. In effect one simply adds in a fourth index *i* which is the negative of the sum of *h* and *k*. The result is numerical symmetry between indices for planes of the same form, which is not always obtained when just three indices are used.

TO DO

1. Insert on the monoclinic cell below the {121} form of planes.

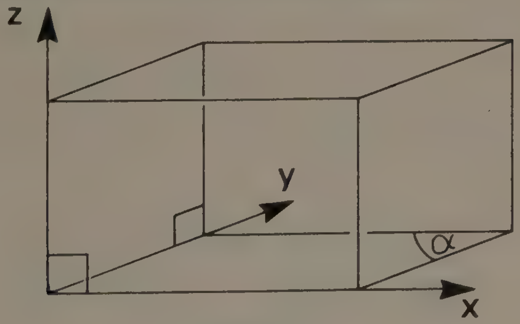


Fig. 10.9

2. Four of the following planes belong to the same zone. Determine the direction of the zone axis.

(234) (20$\bar{1}$) (1$\bar{1}\bar{1}$) (241) ($\bar{2}\bar{2}$1) (43$\bar{2}$) (101) (010) (4$\bar{3}$2).

Zone axis is ....

3. Draw in on the tetragonal cell below the following:
(111), [111], (130), [130], {100}.

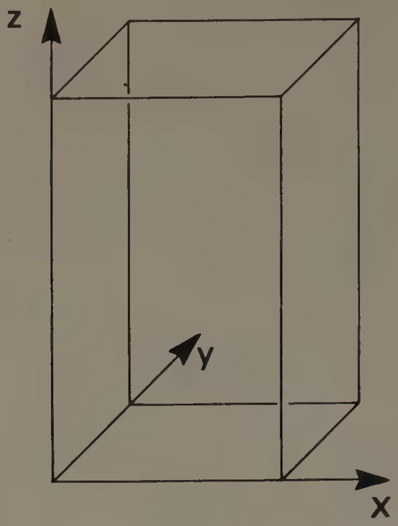
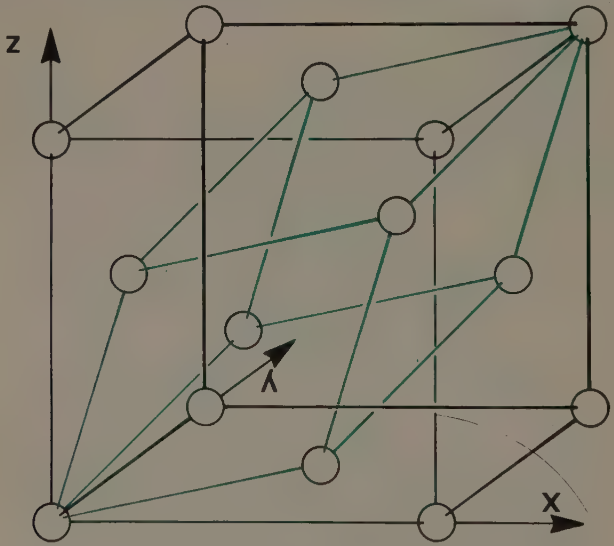


Fig. 10.10

4. The f.c.c. cell below contains a primitive unit cell of the lattice.
Determine the Miller indices referred to the non-primitive cell axes, of $\{100\}_{\text{primitive}}$.
Determine $(hkl)_{\text{primitive}}$ of another plane which belongs to the same form as $\{100\}_{\text{primitive}}$



$(hkl)_{\text{primitive}} =$ ....

Fig. 10.11

5. On the hexagonal non-primitive cell below insert the form of planes $\{10\bar{1}2\}$. Determine their indices in the Miller system.

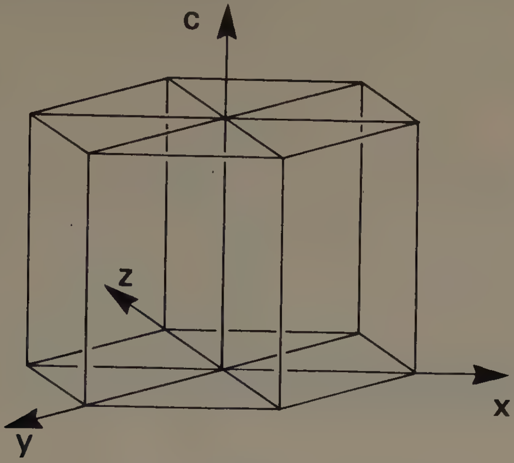


Fig. 10.12

TO BE ABLE TO DO

1. Write down:

   (*a*) The recipes for determining Miller and Miller–Bravais indices.
   (*b*) The definitions of a zone and form of planes.

2. Explain the meaning of the four different types of brackets used to identify crystallographic indices.

11

Spacing of Lattice Planes, the Reciprocal Lattice

This chapter sets out to introduce the reader to the geometry and construction of the reciprocal lattice. Additional background material is grouped in Appendix 3.

11.1 The Interplanar Spacing, '*d*'

The spacing of a particular **set of planes** (*hkl*) is the perpendicular distance between adjacent planes of the set (Fig. 11.1).

Fig. 11.1 A set of planes.

The spacing is a function of (*hkl*), and the size and shape of the lattice unit cell. In general, the higher the indices, the smaller the spacing.

Geometric formulae relate the interplanar spacing, written d_{hkl}, to the indices and unit cell parameters. For example, for a cubic lattice:

$$d_{hkl} = \frac{a}{\sqrt{(h^2+k^2+l^2)}}.$$

For a hexagonal lattice:

$$d^2_{hkl} = \frac{3a_1^2}{4(h^2+hk+k^2)} \cdot \frac{a_3^2}{l^2}$$

For the triclinic lattice however:

$$\frac{1}{d^2_{hkl}} = [h^2 a_2^2 a_1^2 \sin^2\alpha + k^2 a_1^2 a_3^2 \sin^2\beta + l^2 a_1^2 a_2^2 \sin^2\gamma + 2hka_1 a_2 a_3^2(\cos\alpha\cos\beta - \cos\gamma) + 2kla_1^2 a_2 a_3(\cos\beta\cos\gamma - \cos\alpha) + 2hla_1 a_2^2 a_3(\cos\gamma\cos\alpha - \cos\beta)] / [a_1^2 a_2^2 a_3^2(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)]$$

where a_1, a_2 and a_3 are the side lengths of the unit cell, and the angles between a_1a_2, a_2a_3, and a_3a_1, are γ, α and β respectively.

This relation represents crystallographic trigonometry at its most complex. It serves its best purpose as a background against which one aspect of the usefulness of the reciprocal lattice concept can be clearly seen.

11.2 Introduction to the Reciprocal Lattice

Mathematically the reciprocal lattice is the **Fourier transform** of the real lattice. An amplification of this statement together with a more detailed explanation of the reciprocal lattice concept forms the basis of Appendix 3. Here, we will confine ourselves to the practical aspects of the reciprocal lattice and its usefulness in the field of crystallography.

The orientation and spacing of a set of planes can be fully defined by just one vector which we will call **d**. The vector is perpendicular to the set of planes and of length proportional to the interplanar spacing, *d*.

Now, **if**:

(*a*) a vector **g** is defined which is parallel to **d** but with a length proportional to the **reciprocal** of the interplanar spacing *d*,

and

(*b*) **g** vectors corresponding to all the sets of planes in the lattice are drawn from the same origin.

then

Points at the tips of all the **g** vectors will themselves form a lattice, the 'reciprocal lattice'.

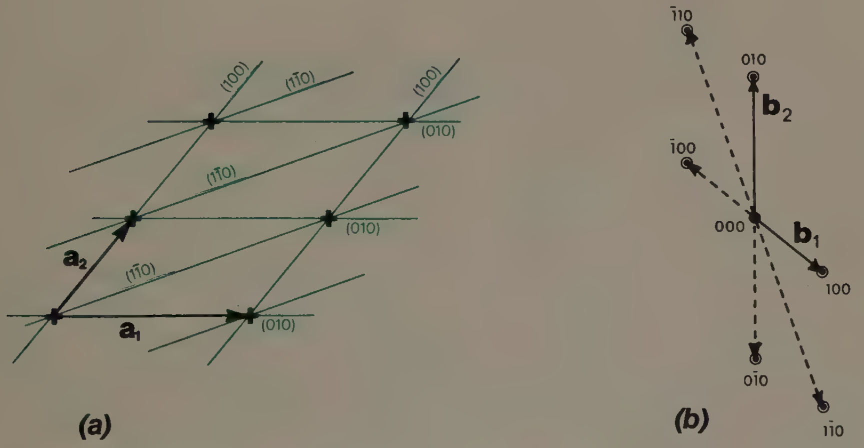


Fig. 11.2 (*a*) Section of a space lattice showing edge-on views of the planes (100) (010) and (1̄10). (*b*) Part of the reciprocal lattice with the points corresponding to these planes.

As it happens it is not possible to build up the complete reciprocal lattice in this way, for one has to include also all possible multiples of the **g** vectors. Another way of looking at this is to say that additional hypothetical lattice planes with '*d*' spacings which are simple fractions, i.e. $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, etc. of the spacing of the actual lattice planes must be included. Also for each reciprocal lattice vector **g** there is an equivalent vector $-\mathbf{g}$. Therefore $\mathbf{g} = n/\mathbf{d}$ where n is a positive or negative integer.

Figure 11.2*a* shows three sets of lattice planes which are perpendicular to the page drawn on a section of a space lattice and in Fig. 11.2*b* the reciprocal lattice points corresponding to these planes.

The **g** vectors are the lattice translation vectors of the reciprocal lattice and can therefore be defined in terms of the reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ which form a primitive vector group so that

$$\mathbf{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

The reason for choosing the letters *h*, *k*, *l* for the three integers rather than, say, *u*, *v*, *w*, as in Chapter 2, will become obvious in the next section.

11.3 Miller Indices and the Reciprocal Lattice

Look at Fig. 11.2 again. The reciprocal lattice point labelled $1\bar{1}0$ because it corresponds to the $(1\bar{1}0)$ set of planes also has coordinates in terms of $\mathbf{b}_1$, $\mathbf{b}_2$ (and $\mathbf{b}_3$) of 1, −1, 0!

So we can say that: $\mathbf{g}_{(1\bar{1}0)} = 1\mathbf{b}_1 - 1\mathbf{b}_2 + 0\mathbf{b}_3$.

Or in general that: $\mathbf{g}_{(hkl)} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$,

where *hkl* are the Miller indices of the lattice plane.

Also, $\mathbf{d}_{(hkl)} = n/\mathbf{g}_{(hkl)} = n/(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)$.

Figure 11.3 shows a section of a real lattice, and the traces of some of lattice planes perpendicular to the section. On the right is a part of the corresponding reciprocal lattice in the same orientation.

As an exercise index each reciprocal lattice point in two ways:

(*a*) with the Miller indices of the corresponding lattice planes,

(*b*) with its coordinates in terms of $\mathbf{b}_1$ and $\mathbf{b}_2$.

If the real lattice parameter in the x direction is 3Å, calculate the scale of the reciprocal lattice as drawn in Å^{-1}/cm. (Assume the real lattice to be triequiangular.)

Scale factor = ...

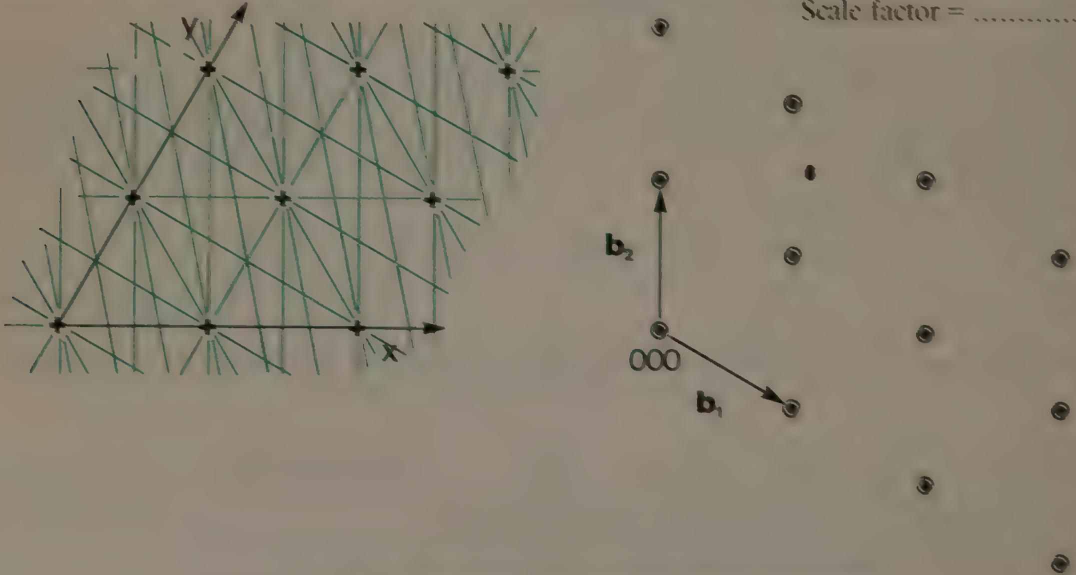


Fig. 11.3 Some lattice planes and the corresponding reciprocal lattice.

Once the unit cell of the reciprocal lattice has been determined — and this must be based on a primitive vector group corresponding to the (100), (010) and (001) planes of the real lattice or the direct relationship between the Miller indices and the reciprocal lattice coordinates will not hold — it is then a straightforward matter to calculate **g** and hence the interplanar spacing of any set of planes.

If the above equation for $\mathbf{d}_{hkl}$ is written without vectors being used we get, for the most complex case of the triclinic lattice, the relation:

$$\frac{1}{d^2_{(hkl)}} = h^2b_1{}^2 + k^2b_2{}^2 + l^2b_3{}^2 + 2hkb_1b_2 \cos\gamma + 2klb_2b_3 \cos\alpha + 2hlb_1b_3 \cos\beta \, .$$

Compare this equation with that near the end of Section 11.1 which was derived without recourse to the reciprocal lattice concept and see also Appendix 2*f*.

11.4 Non-Primitive Unit Cells

Consider the (110) set of planes of a lattice indexed according to a non-primitive body centred cubic unit cell. The spacing of these planes is the same as for a primitive cubic cell with

$$d_{110} = \frac{a}{\sqrt{2}}$$

where a = cube edge length.

Therefore

$$|\,\mathbf{g}\,|_{110} = n\left(\frac{\sqrt{2}}{a}\right) \qquad (|\,\mathbf{g}\,| \text{ means magnitude of vector } \mathbf{g}).$$

However because of the extra lattice point at the centre of the b.c.c. cell, the spacing of the (100) planes is $a/2$ (compared with 'a' for a primitive cubic cell). So

$$|\,\mathbf{g}\,|_{110} = n\left(\frac{2}{a}\right) .$$

Representing these **g** vectors as a part of a reciprocal lattice, we obtain points with coordinates which are multiples of 2, 0, 0 only (Fig. 11.4).

The completed reciprocal lattice is similar to that corresponding to a primitive cubic real lattice, but with certain points **systematically absent**.

The missing points relate to lattice planes of a spacing that is halved by the presence of the body centred lattice point. The indices of such planes can be determined either by inspection or by algebra.

A lattice point having coordinates x, y, z (referred to the unit cell axes) will lie on the plane hkl if:

$$hx + ky + lz = \textbf{zero} \text{ or an } \textbf{integer}.$$

Therefore, by substituting the fractional coordinates of the lattice points which render the cell non-primitive, it is possible to detect combinations of hkl which do not satisfy the above relation and are therefore coordinates of the **missing** reciprocal lattice points.

The body centred cubic cell is rendered non-primitive by the lattice point at $x = \frac{1}{2}$, $y = \frac{1}{2}$, $z = \frac{1}{2}$. The reciprocal lattice points are missing if the **sum** of their coordinates is an **odd integer**. Verify this statement for yourself.

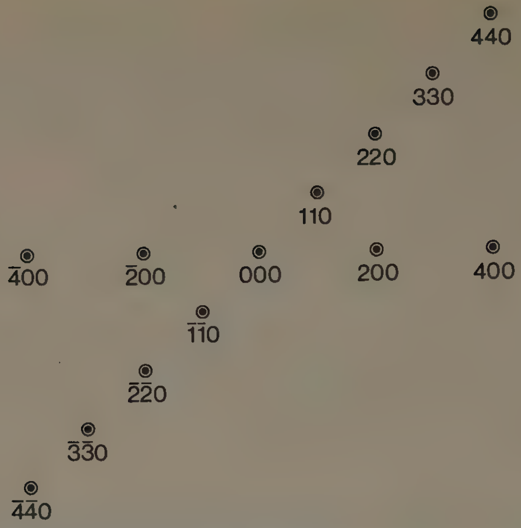


Fig. 11.4 Two rows of a reciprocal lattice derived from a b.c.c. real lattice.

Hence for b.c.c.:

(*hkl*)	
100	Reciprocal lattice points with coordinates 100, 300, 500, etc. **missing**.
110	No points missing.
111	Points with coordinates, 111, 333, 555, etc. **missing**.

If this procedure is continued and the *hkn* layers of the reciprocal lattice drawn, it can be seen from Fig. 11.5 that the reciprocal lattice is face centred cubic.

Fig. 11.5 A projected plan view of the f.c.c. reciprocal lattice derived from the b.c.c. real lattice.

It is important to appreciate that if the b.c.c. lattice had been indexed according to a primitive unit cell, the reciprocal lattice would be exactly the same; only the primitive vector group and hence point coordinates would be different, all combinations of *hkl* being present.

11.5 The Use of the Reciprocal Lattice

The reciprocal lattice leads to simplified geometric expressions for the spacing of crystal planes. This in itself is useful in studies of crystals using the techniques of X-ray, electron or neutron diffraction. There is, however, a much more direct relationship between diffraction and the reciprocal lattice; for a recorded diffraction pattern is simply a projection of part of the Fourier Transform of the crystal which is much the same thing as the reciprocal lattice. The positions of the diffraction spots and hence reciprocal lattice points define the crystal lattice, whereas the crystal motif determines the relative intensity of the spots.

Diffraction is the pre-eminent tool of crystallographers; and it cannot be fully employed without a sound grasp of the reciprocal lattice concept. Correspondingly it is impossible to demonstrate the full elegance and usefulness of the concept in a book which tacitly avoids description of diffraction techniques.

TO DO

1. Draw and index the $h0l$ section of the reciprocal lattice of a primitive tetragonal lattice with $a = 2{\cdot}4$Å and $c = 7{\cdot}2$Å. Restrict your diagram to values of h and $l < \pm 4$, and state the scale chosen.

Fig. 11.6

2.

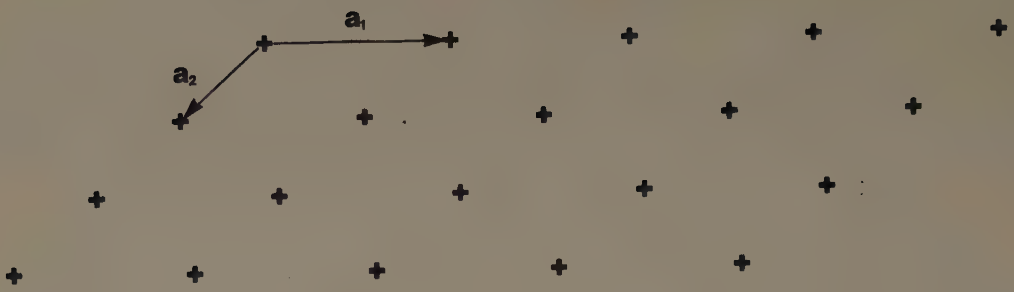
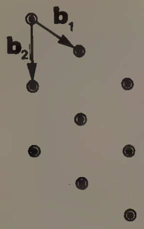


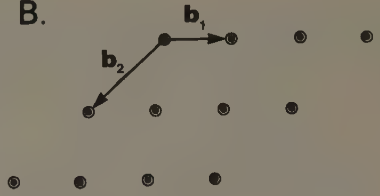
Fig. 11.7

Indicate which, if any, of the three reciprocal lattices below is equivalent to the real lattice above.

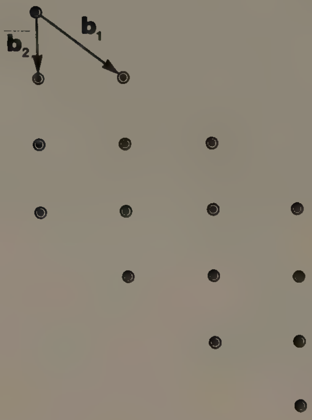
A.



B.



C.



(Scales are arbitrary)

Tick: A
B
C
None of these.

3. Draw the *hk*0 and *hk*1 sections of the reciprocal lattice corresponding to the face centred cubic space lattice. Determine the missing indices by drawing planes in the f.c.c. unit cell below; but if in doubt use the algebraic relation as a check. Of what type is the reciprocal lattice?

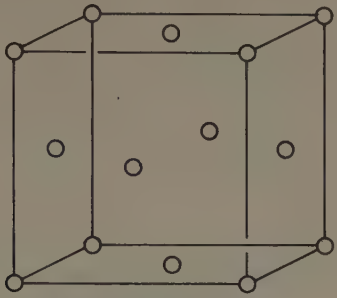


Fig. 11.8

Lattice type: ....

Fig. 11.9

TO BE ABLE TO DO

1. Construct any of the important sections of the reciprocal lattice from each of the 14 Bravais lattices.
2. Obtain, by geometric construction, an approximate value for the interplanar spacing and orientation of any set of planes in any space lattice.
3. Determine which points of a reciprocal lattice appear to be missing, when the corresponding real lattice is indexed according to a non-primitive unit cell.

12

Stereographic Projection

12.1 The Problem

We have seen that crystallographic directions and orientations of lattice planes can be described using systems of indices. Indices, by definition, require reference axes which can either be taken as the intersection of crystal faces or, more normally, from the unit cell of the crystal structure.

Situations frequently arise in which the measurement and recording of the orientations of directions and planes is necessary **before** they can be identified and indexed. An example is the determination of the orientation of a single crystal and the identification of its symmetry elements by the Laue technique of X-ray diffraction.

Crystallographers have developed a method of **graphic representation** which enables the spatial orientation of crystal planes and directions to be drawn on a piece of paper. The method uses **stereographic projection** and it is possible to measure stereo angles directly from the drawing.

12.2 Reference Sphere

We are only concerned with the relative spatial orientations of crystal directions and planes. For this reason the directions and planes can be translated in space, as long as their orientations are not changed, until they all pass through one point: the **origin**.

The next step is to draw a reference sphere of unit radius, centred on the origin, and focus attention on the intersections of the directions and planes with the surface of the sphere.

The directions, represented of course by lines, will each intersect the sphere surface at two antipodal points. These points are usually referred to as **poles**.

The planes will intersect the sphere surface to give circles known as **great circles**. (Circles on the surface of a sphere whose planes do not pass through the centre are **small circles**.)

In practice it is often neater to represent the orientation of a plane by its normal, i.e. by a pole rather than a great circle.

12.3 Reference Grid

At this stage the information about the relative orientations of directions and planes is displayed as a series of poles and great circles on the surface of the reference sphere. Now, the distance between two of the poles is directly proportional to the angle between the directions they represent, **as long as** this distance is measured along a great circle.

It would be ideal if there was also drawn on the surface of the sphere a great circle, calibrated in degrees, which passed through the two poles. The angle between the two directions could then be read off directly.

Unfortunately, in order to cater for all possible positions of the poles, the sphere surface would have to be smothered in calibrated great circles. Instead, a limited number of great circles is drawn so that they all pass through two antipodal points and are spaced, say, every degree around the axis joining the points. These great circles are exactly analogous to lines of longitude drawn on models or maps of the earth, and the two antipodal points correspond to the North and South Poles.

The calibration marks on the great circles can be joined together to form a series of small circles (lines of latitude). The calibration marks at 90° from the North and South Poles join up to give another great circle (equator).

How can this grid of great and small circles be used for measuring the angle between the directions represented by poles A and B (Fig. 12.1) which do not lie on the same great circle? It is possible to bring one calibrated great circle into register with both poles (to within a degree anyway) by suitable rotation of the whole grid, but not the reference sphere, about the axis shown.

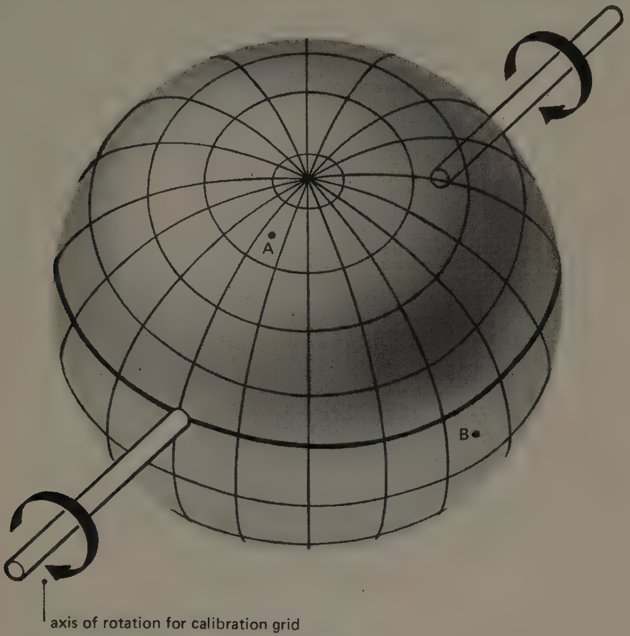


Fig. 12.1 Calibration grid of great and small circles marked on a reference sphere.

At this point the analogy with lines of longitude and latitude is lost, for the axis joining the North and South Poles is the axis of the earth's rotation and cannot be rotated at will.

12.4 Stereographic Projection

So far we have had to think of directions and planes passing through an origin and intersecting a sphere centred on that origin. In practical terms we would have to construct a sphere and mark the poles, etc. on its surface. It would also be necessary to make a calibrated wire grid which would fit on the sphere and be slid over it to bring a particular great circle into line with both poles. Such operations using a model sphere are obviously far from convenient and are only likely to be performed for teaching purposes.

Geographers have been faced with this problem for centuries and they have developed various systems of projecting information such as maps, lines of longitude, etc. from the surface of a sphere on to paper.

Crystallographers have appropriated one of these systems known as **stereographic projection**, and use it to project the information on the surface of the reference sphere together with the calibrated reference grid onto flat paper. The general choice of the stereographic projection for crystallographic purposes derives from two of its properties:

(*a*) All circles, great and small, on the reference sphere or forming the reference grid are projected as circles or as arcs of circles.

(*b*) Angles of intersection on the surface of the reference sphere are projected without distortion.

The geometry of the stereographic projection is as follows:

All information on the north half of the reference sphere is projected in the direction of the South Pole on to the equatorial plane.

Information on the southern hemisphere can also be projected on to the equatorial plane in the direction of the North Pole, but it must then be suitably annotated to prevent confusion with that from the northern hemisphere.

Except in the case of the representation of the operation of symmetry elements, information from one hemisphere is often sufficient.

The two poles A and B in the northern hemisphere of Fig. 12.2(*a*) when projected towards the South Pole on to the equatorial plane give the stereographic projection in Fig. 12.2(*b*).

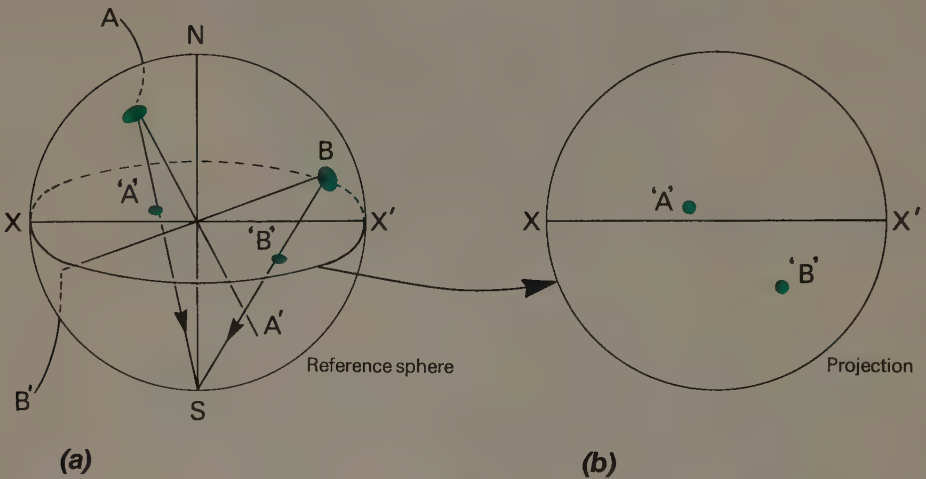


Fig. 12.2 Two directions AA′ and BB′ intersect the northern hemisphere of the reference sphere at *A* and *B*. The stereographic projection of these poles is drawn on the right.

In order to measure angles between the projected poles it is necessary also to project the calibrated grid. It must be possible, however, to rotate the grid about an axis parallel to the plane of its equator (Fig. 12.1) to bring any two poles on to the same great circle. For this reason the grid is projected with its North and South Poles positioned on the equator of the reference sphere.

A grid projected in this way is shown in Fig. 12.3 and is called a stereographic net or **Wulff net** after a Russian who helped popularise its use in crystallography early this century — although such nets had been prepared for naval navigation purposes many years earlier.

To facilitate the use of the stereographic projection in conjunction with a Wulff net, the projection is normally drawn on tracing paper and has the same diameter as a Wulff net printed on card. A pin or peg in the centre of the net locates the projection and enables both to be rotated relative to each other.

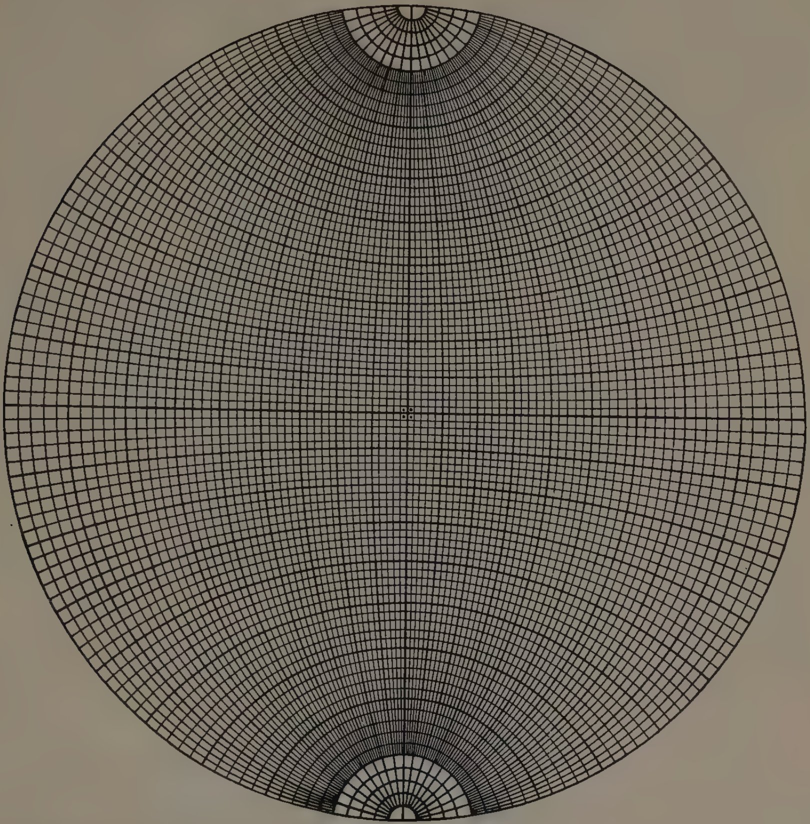


Fig. 12.3 Stereographic projection of the calibrated grid of great and small circles known as a Wulff net.

12.5 Projection of Important Directions and Planes of a Cubic Crystal

Consider three important groups of directions:

$\langle 100\rangle$	Parallel to the cube edge.
$\langle 110\rangle$	Parallel to the face diagonal.
$\langle 111\rangle$	Parallel to the body diagonal.

Imagine the crystal at the centre of the reference sphere with [001] coincident with the N–S axis of the sphere. The [100] and [010] directions will lie in the equatorial plane (Fig. 12.4(a)).

The stereographic projection of the poles on the northern hemisphere and on the equator (this being a special case in which each direction gives rise to two poles $[hkO]$ and $[\bar{h}\bar{k}O]$ on the circumference) is shown in Fig. 12.4(b) and (c). This forms the basis of what is known as the 001 **standard projection** of a cubic crystal.

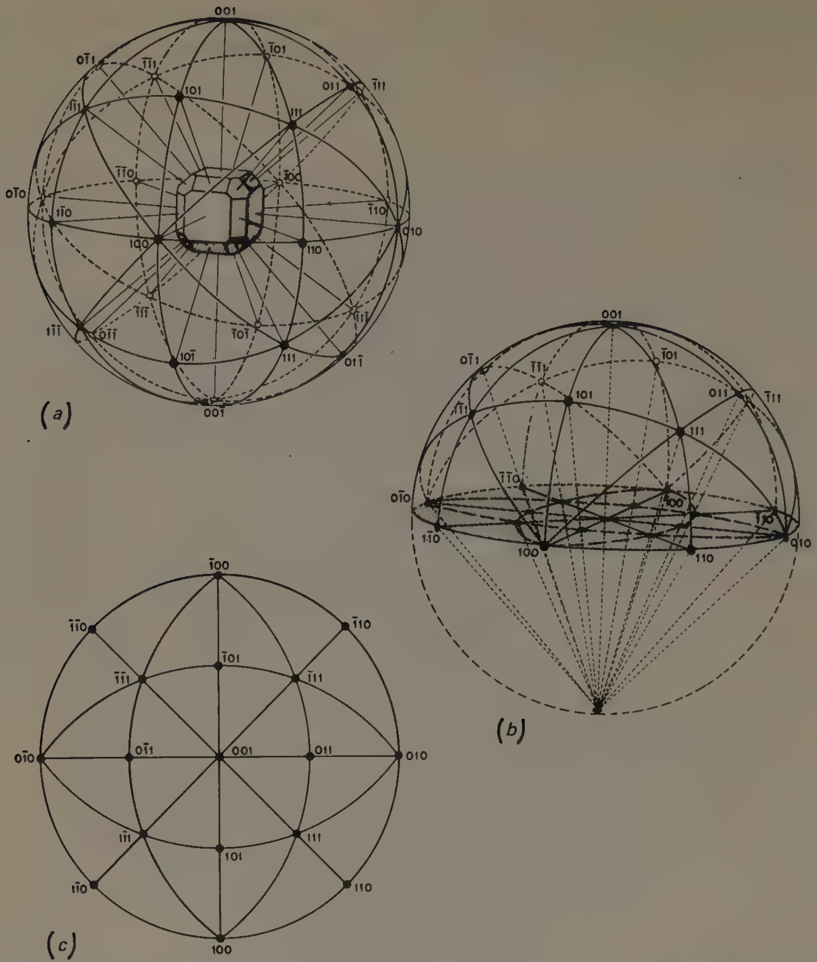


Fig. 12.4 The stereographic projection of the important directions and planes in a cubic crystal oriented with [001] parallel to the N–S axis of the reference sphere. (Reproduced by permission from Wood: *Crystal Orientation Manual*, Columbia University Press.)

12.6 Important Manipulations of the Stereographic Projection

A. To measure the angle between two poles:

(*i*) Rotate the stereographic projection (stereogram) over the Wulff net until both poles lie on the same **great** circle. (There may not be a great circle drawn at exactly the correct angle, but it is easy to align the poles so that they are exactly the same distance from the nearest great circle on the Wulff net.)

(*ii*) The angle can then be read off using the calibrations on the great circle (n.b. in some smaller Wulff nets the calibrations are every 2°).

B. To plot the trace of a plane when a pole representing its normal has already been plotted.

(In the special case of a crystal with cubic symmetry the normal to the plane (*hkl*) is the direction [*hkl*].)

(*i*) Rotate the projection until the pole lies on the equator of the Wulff net.

(*ii*) Count 90° along the equator passing through the centre of the net, and mark a second point.

(*iii*) Trace the great circle that passes through this point.

C. Given a stereographic projection of a crystal in a particular orientation; to draw another projection of the crystal after it has been rotated in space to a new orientation. (This procedure can be used to change a general projection into a standard one, or a standard of one type (e.g. 001) into one of another (e.g. 111).)

(*i*) Decide which pole will be in the centre of the projection after the crystal has been rotated. If it does not already appear on the projection, draw it in.

(*ii*) Rotate the projection until this pole lies over the equator of the Wulff net and count the number of degrees along the equator between the pole and the centre.

(*iii*) Move all other poles by that number of degrees in the same direction (i.e. all to the left or all to the right) along their own small circles.

(*iv*) Poles that move off the net are dropped.

(*v*) Strictly, one should determine the poles which are moved into the active (northern) hemisphere and hence on to the stereogram by the rotation, and plot them. In practice it is usually easy to fill in these poles on the basis of symmetry criteria.

12.7 Exercises in the Use of Stereographic Projection

Equipment:

(*i*) Wulff net with central pin or peg, preferably mounted on a board. The net on the back cover is calibrated in 2° intervals and is too small for precise work. It is adequate, however, for these exercises.

(*ii*) Squares of tracing paper large enough to cover the Wulff net.

(*iii*) Some means of reinforcing tracing paper around central pin, e.g. Sellotape or Scotch tape.

Exercise 1. Drawing a Cubic 001 Standard Projection

Only plot information from one half of reference sphere and index all poles and traces of planes; try to have a cube in front of you as you proceed.

(*a*) Draw in [001], [010] and [100] poles (see Fig. 12.4).

(*b*) Draw in traces of (100), (010) and (001).

(*c*) Draw in poles corresponding to ⟨110⟩ directions and traces of the {110} planes.

(*d*) Measure the angle between [101] and any direction in the plane (101). Angle = ...

(*e*) Draw in ⟨111⟩ and measure $[111]\frown[1\bar{1}1]$. Angle = ...
(Relevant angular data appears below.)

(*f*) Draw in the trace of the plane (111) and count the number of ⟨110⟩ directions which are parallel to the plane. Number = ...

(*g*) Measure the following angles

$$(001)\frown(011) = \ldots\ldots\ldots\ldots\ldots\ldots$$
$$(001)\frown(111) = \ldots\ldots\ldots\ldots\ldots\ldots$$
$$(011)\frown(111) = \ldots\ldots\ldots\ldots\ldots\ldots$$

Note that the angle between two planes is the angle between the normals to these planes.

Cubic data:

$$\left(\begin{array}{ll} \{100\}\frown\{100\} = 0^\circ, 90^\circ & \{100\}\frown\{110\} = 0^\circ, 60^\circ, 90^\circ \\ \{100\}\frown\{110\} = 45^\circ, 90^\circ & \{110\}\frown\{111\} = 35{\cdot}3^\circ, 90^\circ \\ \{100\}\frown\{111\} = 54{\cdot}7^\circ & \{111\}\frown\{111\} = 0^\circ, 70{\cdot}5^\circ \end{array}\right)$$

Exercise 2. Rotation of Cubic 001 Standard Projection to make a 111 Standard Projection

(*a*) Trace the poles (only) from the 001 standard projection on to another stereogram.

(*b*) Rotate the stereogram until [111] is on the equator of the Wulff net and replot and re-index all points as described in Section 12.6*C*. Angle of rotation of the crystal to bring [111] to the centre of the stereogram = ...

(*c*) What type of crystal rotation symmetry axis is [111]? ....

(*d*) Measure the angle $[111]\frown[11\bar{1}]$ ....

Exercise 3. Plotting Orientation Data previously derived from a Laue X-ray Photograph of a Cubic Single Crystal

The Laue X-ray diffraction method is used for determining the orientation of single crystals. It is possible to obtain the orientation of zone axes by measuring the recorded diffraction pattern. Before exposure three orthogonal reference axes are marked on the crystal:

z = parallel to beam (positive direction towards X-ray tube),

x = horizontal (positive to the right when viewed from tube),

y = vertical (positive upwards).

By measuring the film (not shown) the orientations of three prominent zone axes (low index crystal directions) were determined as:

		α	γ
direction	1	124°	10°
	2	215°	9°
	3	358°	16°

α is the angle between the positive y direction and the crystal direction projected onto the xy plane and it is positive clockwise when viewed from the tube. γ is the angle between the crystal direction and the xy plane and is positive when the 'end' of the direction used to define α is rotated towards the tube.

The geometry of the back reflection X-ray method means that γ is always positive and that α can have values within the complete angular range 0–360°.

(*a*) Consider the z (beam) direction to be perpendicular to the stereogram which is viewed as from the X-ray tube. Mark in the poles $xx'yy'$ and z on the stereogram.

(*b*) To plot the first direction count α degrees around the perimeter of the stereogram from y and mark a small point. Next rotate the stereogram so that this point lies on either end of the meridian or equator, count γ degrees towards the centre and plot the pole.

(*c*) Repeat the procedure for the other two poles.

(*d*) Measure the angles between all the poles. If the angle is greater than 90° express as 180°$-\theta$.

θ_{12} θ_{13} = ...

θ_{23} ......

(*e*) By comparing these angles with those tabulated in *Exercise 1*, index the poles:

Pole	Indices
1	....
2	....
3	....

Exercise 4. Plotting Zone Circles and Rotation to form Standard Projection. The Unit Triangle. (Using data and stereogram from Exercise 3.)

An addition to the plotting procedure in the previous exercise can generate a few more poles from the existing data. It involves plotting zone circles and can only apply to cubic crystals.

The directions plotted so far are those of prominent zone axes. The normals to all the planes in the zone (i.e. parallel to the zone axis), will, in a cubic crystal, lie in one low index plane which has the zone axis as its normal.

The low index planes associated with several zone axes will intersect along low index directions. These can be plotted to give the additional poles.

(*a*) On your stereogram from Exercise 3, draw in the traces of the planes of which the plotted poles are normals. These traces are also known as zone circles.

(*b*) Measure the angles between the poles at the intersection of these traces and hence index.

(*c*) Measure one or two angles between the poles generated by the intersecting zone circles and the poles originally plotted. Check they are compatible with the indexing.

The poles plotted represent a projection of a cubic crystal but not in standard form.

(*d*) Rotate one of the $\langle 100 \rangle$ poles into the centre and also move all other poles to give a rudimentary 001 standard projection (see Manipulation *c* above).

(*e*) Rotate the poles corresponding to x, y and z axes also.

(*f*) Match up the rotated crystal directions with the poles on the previously prepared 001 cubic projection, and trace the x, y and z poles on to this standard projection.

In a cubic crystal all directions belonging to either $\langle 100\rangle$, $\langle 110\rangle$ or $\langle 111\rangle$ are equivalent. Therefore the triangle joining the poles [001], [011] and [111], often called the **unit triangle**, is typical of all other angularly similar triangles on the stereogram. It follows that the orientation relationship between the crystal and any random direction can be expressed by plotting the pole of the direction within the unit triangle.

(*g*) By making one or more 90° rotations of the stereogram about the $\langle 100\rangle$ tetrad axes move the pole defining the y axis into one of the eight triangles in the centre of the stereogram. The poles at the corners of this triangle can then be taken as: [001],[011] and [111].

(*h*) Measure the following angles:

$$y \text{ axis}\,\widehat{\;}\,\langle 001\rangle = \ldots\ldots\ldots$$

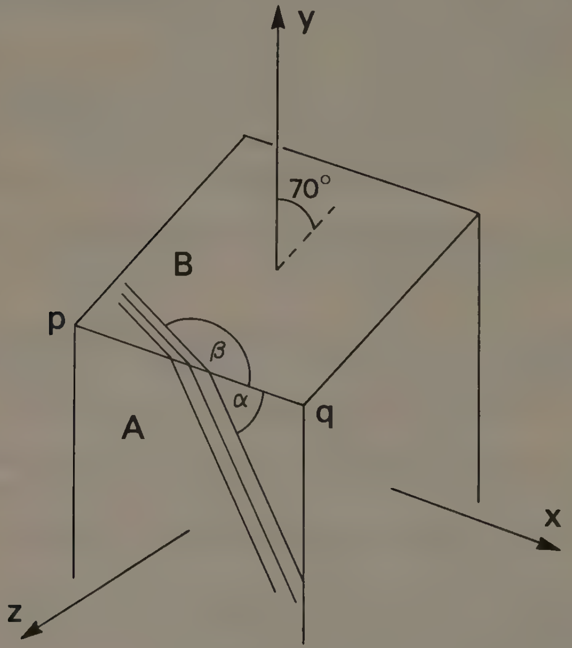
$$y \text{ axis}\,\widehat{\;}\,\langle 011\rangle = \ldots\ldots\ldots$$

$$Y \text{ axis}\,\widehat{\;}\,\langle 111\rangle = \ldots\ldots\ldots$$

Exercise 5. Two Surface Analysis

The crystal which was the subject of Exercises 3 and 4 possesses two flat faces which intersect along a line *p q*. (Fig. 12.5). Face A is perpendicular to the X-ray beam (z axis), Face B is at an angle of 70° to the y axis and the line of intersection between the two faces is parallel to the x axis.

Mechanical deformation of the crystal has led to slip on one well defined set of crystal planes, called **slip planes**. The intersection of these planes with faces A and B gives rise to dark lines known as **slip lines**. The slip lines on faces A and B make angles α and β respectively with the edge *pq*.



$\alpha = 55°$
$\beta = 157{\cdot}5°$

Fig. 12.5

It is required to determine the indices of the slip plane.

The first stage is to plot the trace of the slip plane on the stereogram.

(*a*) Prepare a stereogram looking along the z direction. The Face A will be represented by the perimeter, draw in the trace of Face B as well as the poles yy' and xx' which represent the y and x axes.

(*b*) Plot the poles representing the directions of the slip lines; these will lie on the traces of the corresponding faces.

(*c*) The slip plane will be parallel to both sets of slip lines so its trace will pass through both poles. Draw in this trace.

If Exercise 3 has already been completed, i.e. the crystallographic orientation of the crystal determined, it is possible to find the indices $\{hkl\}$ of the slip plane.

(*d*) Superimpose the trace of the slip plane on to the crystal stereogram before it was rotated to give an 001 projection, and align xx', yy' and z.

(*e*) What are the indices of the slip plane?

slip plane {..................}

Exercise 6. Standard Projection of a Hexagonal Crystal

(*a*) Calculate the angles $\widehat{(0001)\,\{10\bar{1}1\}}$ and $\widehat{(0001)\,\{11\bar{2}1\}}$ titanium which has a c/a ratio of 1·48. (A sketch of a hexagonal unit cell will help here.)

(*b*) Plot the normals to the planes of the forms: $\{10\bar{1}0\}$, $\{10\bar{1}1\}$, $\{11\bar{2}0\}$, $\{11\bar{2}1\}$ on an 0001 standard projection.

(*c*) Calculate the angle $\widehat{[11\bar{2}1]\,[0001]}$ and plot the $[11\bar{2}1]$ pole.

$\widehat{[11\bar{2}1]\,(11\bar{2}1)}_{\text{normal}} =$ ....

(*d*) Re-index the poles of the planes belonging to the same form as $\{11\bar{2}1\}$ in the three-index (hkl) system.

These planes are:

13

A Précis of Chapters 1–12 and a Look Forward to 14, 15 and 16

13.1 Chapters 1–12

A crystal is a crystal for two reasons: first it is made up of myriads of identical units which are either individual atoms or small groups of atoms. Secondly, the units are arranged regularly and periodically in three dimensions.

The units are referred to as motifs and their periodic arrangement is best described by using a lattice, so that in effect the crystal structure is broken down into two components; the lattice and the motif. The lattice can be thought of as the imaginary scaffolding which positions in space each and every motif unit and displays what is known as the translational symmetry of the crystal.

One of the basic achievements of the science of crystallography is the classification of the different observed crystal types into recognised groups. The first steps in the classification sequence can be made in terms of the crystal lattice (although this was not the historical approach), while the nature of the motif can be used as a basis for determining further groupings and subgroupings.

Before the classification of space lattices is considered in detail, however, it is sensible to find the most convenient methods by which they can be described. A description can be made either algebraically in terms of translation vectors which make up a primitive vector group, or by drawing a lattice unit cell bounded by eight lattice points. The lattice unit cell is particularly useful in that its shape can indicate at a glance the type of lattice, and it is an easy matter to mark in on it the appropriate dimensions and angles. It also provides a convenient framework within which atoms can be drawn to depict the crystal structure, such a cell is then known as a structure cell.

Symmetry operations are essentially operations on a three-dimensional shape, a crystal, a lattice, or whatever, which leave it unchanged in appearance. All space lattices (which we take as being of infinite extent) have translational symmetry and inversion symmetry with the centres of symmetry at, and midway between, the lattice points. Lattices are classified on the basis of the rotational and mirror symmetry elements which they possess. It is possible to build the different types of space lattice by regularly stacking planar (two-dimensional) lattices and in this way the development of the various characteristic rotational and mirror symmetry elements can be clearly followed. There are 14 different ways of arranging points in space and these give rise to the 14 Bravais lattices. The symmetry criteria group these lattices into seven Crystal Systems each with a characteristic unit cell. It is however convenient for both the system based on one triad and that based on the hexad to be described in terms of a hexagonal unit cell, and for this reason they are often (as in this text) grouped together into one system. The total of seven systems is then reduced to six.

For the analysis and description of crystal structure, the space lattice is an invaluable aid. However, as far as the actual physical process of crystal growth is concerned it is no more than a figment of the imagination. The individual atoms do not crystallise by 'looking round' for their allocated lattice point and moving smartly on to it, rather they simply pack together as closely as possible under the influence of the interatomic bonding forces. The final crystal structure is therefore determined solely by the packing behaviour of the individual atoms. Several factors can be identified which control packing and ultimately the crystal structure. In markedly covalent crystals such as diamond the directionality of the bonds plays a large part in determining the final structure. In cases where directional bonding is not strong, the atomic packing is similar to that of hard spheres. For crystals with only one type of atom the two most closely packed structures are face centred cubic and hexagonal close packed. The body centred cubic structure is a little more open, but is preferred in some circumstances. The presence of atoms of different sizes in ionic crystals makes the packing possibilities more varied. The cations are usually smaller than the anions, and will surround themselves with as many oppositely charged anions as they can touch at the same time. The packing will therefore depend on the ratio of the anion and cation radii; and the arrangement of anions which will provide the appropriate number of suitably sized interstices will dictate the final crystal structure. However, in cases where the cation charge is greater than three the overall anion arrangement will also be influenced by the repulsion between the cations, and will tend as a result to be somewhat less close packed.

There are two particular crystallographic conventions which are widely used. They are based on groups of three indices and relate the orientations of crystallographic planes and directions to the orientation of the crystal lattice. The indices are referred to the set of translation vectors which outlines the chosen unit cell.

Directional indices represent the ratios in which the three translation vectors must be combined to give a resultant vector parallel to the direction in question. They are identified as such by enclosing within square brackets. Directions which are related by symmetry elements within either a lattice or a crystal are known as equivalent directions and are represented *en bloc* by one set of positive indices within diamond brackets.

The orientations of crystal or lattice planes are described by Miller indices; they are derived by expressing the intersections of a plane with the three translation vectors in terms of the vector lengths, and writing the indices as three whole numbers which give the ratio of the reciprocals of the three lengths. Miller indices are written in curved brackets while equivalent, symmetry related planes are distinguished by curly brackets.

The spacing between different parallel planes can be calculated using appropriate geometric formulae which although simple in the cases of cubic and hexagonal lattices, become more cumbersome as the symmetry of the lattice is reduced. The interplanar spacing is a very important crystal parameter, especially as far as diffraction effects are concerned, and its calculation is greatly aided if the lattice is expressed as its own Fourier transform which turns out to be another lattice when plotted as a function of $(\text{length})^{-1}$. It is correspondingly called the reciprocal lattice and has a designated origin. The reciprocal lattice vectors are perpendicular to sets of planes in the real lattice and their length is proportional to the reciprocal of the interplanar spacing. An important property of the reciprocal lattice is realised if its points are given coordinates based on a set of primitive translation vectors which correspond to the faces of the unit cell of the real lattice. The coordinates of the reciprocal lattice points are then equal to, or multiples of, the Miller indices of the corresponding real lattice planes.

Systems of indices refer orientations of directions and planes to the crystal lattice. The nature and orientation of the lattice however is not always known in advance and it is often necessary to consider the relative orientations of directions and planes in direct angular terms. The intersection of directions and planes with the surface of a reference sphere serves as a good basis for angular measurements, but it is more convenient still if the information on the sphere surface is put into a planar format using the stereographic projection. An identical projection of the angular calibration marks on the sphere surface (similar to lines of latitude and longitude) forms what is known as a Wulff net. It is used to make angular measurements from the stereographic projection in addition to acting as a guide for plotting projected directions and planes.

13.2 Chapters 14, 15 and 16: An Introduction

The symmetry shown by a crystal is a complex combination of translation, rotation, reflection and inversion elements. There are 230 possible combinations and the rather informal approach to symmetry used in the previous chapters is not the best way of deriving them. A systematic listing is necessary of the different symmetry elements and their interactions one with another. This constitutes the formal core of crystallography and has been left to the end of this book for reasons outlined in the preface.

Chapter 14 is a two-dimensional treatment of both point and space group symmetry. It serves as an introduction to the concepts and ideas which form the basis of Chapters 15 and 16.

Chapter 15 is devoted to the description and derivation of the 32 point groups of symmetry elements found in crystals. Space group symmetry, which is described in Chapter 16, is built up as the result of the repetition of the point groups by lattices of the same crystal system. The interactions of rotation axes and mirror planes with the translational symmetry produces screw and glide plane elements. These new elements are also incorporated into the overall pattern of space group symmetry.

The rate at which new ideas are introduced in these final chapters is somewhat higher than in the previous twelve. It is therefore likely that progress through this part of the course will be a little slower, and it will be helpful to refer to one or two of the other texts listed.

For the symmetry theory, *Elementary Crystallography* by M. J. Buerger has been chosen as the definitive source in matters of terminology and logic.

14

An Introduction to Point Groups and Space Groups in Two Dimensions

14.1 Preamble

As the symmetry of lattices has been discussed in Chapters 5 and 6, we are now in a position to consider the symmetry exhibited by the complete crystal structure; and for this purpose it is still convenient to think of a crystal in terms of its motif and lattice. The symmetry of the motif is looked at in much the same way as that of the various shapes in Chapter 4; it can be described in the first instance using elements passing through one point and known collectively as a point group. The natural combination of the point group symmetry of the motif with the symmetry of the lattice generates what are known as space groups. A space group fully defines the symmetry of a crystal. The principles of point group and space group symmetry are best introduced by first considering two-dimensional patterns: and that is the purpose of this chapter.

14.2 Two-Dimensional Point Groups

A **point group** is a collection of symmetry elements possessed by a shape or form which all pass through one point in space.

In the case of two-dimensional shapes the symmetry elements making up the point group are rotation axes and mirror planes, both of which are perpendicular to the plane of the shape. Also, for two dimensions the operation of the inversion element cannot be distinguished from that of a diad, and it is in fact automatically included with tetrads and hexads as well.

Let us consider a shape which has as low a symmetry as possible. The letter P will do fine as the only symmetry element it possesses is a one-fold rotation axis — which is trivial (Fig. 14.1).

Fig. 14.1

If we wanted to illustrate a mirror plane we could choose the letter B, or if a diad axis the letter S (Fig. 14.2). Instead, we will produce patterns to illustrate point group symmetry which are multiples of the letter P, by operating on this symbol with the appropriate point group elements. An example of the operation of a tetrad on P to make a pattern with four-fold symmetry is shown in Fig. 14.3.

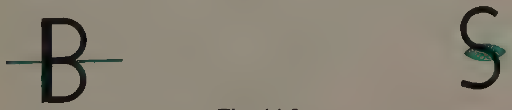


Fig. 14.2

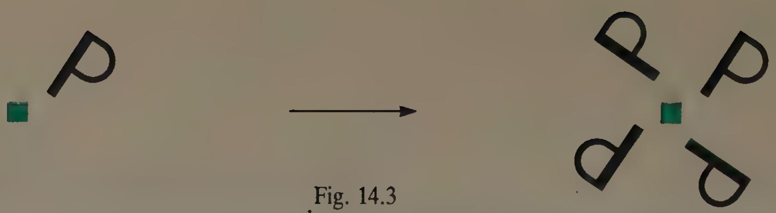
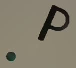
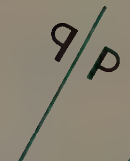
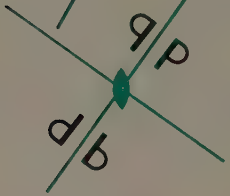
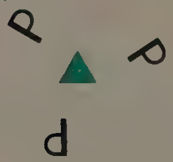
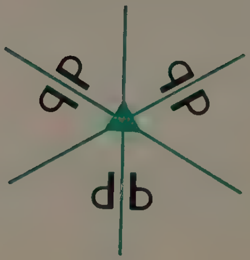


Fig. 14.3

The ten possible two-dimensional point groups based on permissible combinations of rotation axes and mirror planes are tabulated in Fig. 14.4. They are assigned to systems using the same symmetry criteria as for lattices (see Table 5.1). Rotation axes of order 5 and 7 upwards have been omitted because they cannot exist in a repeating structure such as a crystal (see Section 4.3). For this reason the point groups based on one-, two-, three-, four- and six-fold axes are known specifically as **crystallographic point groups**.

Operation	*Point group*	*International symbol*	*Two-dimensional system*
One one-fold axis		1	Oblique
One two-fold axis		2	Oblique
One mirror plane		m	Rectangular
One two-fold axis, two mirror planes		2 mm	Rectangular
One three-fold axis		3	Hexagonal
One three-fold axis, one mirror plane which is operated on by the axis to produce two others		3 m	Hexagonal

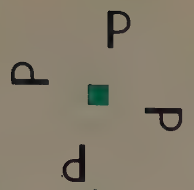
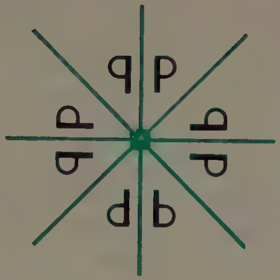
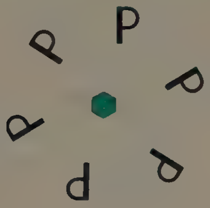
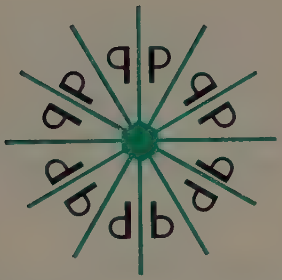
One four-fold axis		4	Square
One four-fold axis, two mirror planes at 45° to each other, the tetrad generates the other mirrors		4 *mm*	Square
One six-fold axis		6	Hexagonal
One six-fold axis, two mirror planes at 30° to each other, the hexad generates the other mirrors		6 *mm*	Hexagonal

Fig. 14.4 The ten two-dimensional point groups.

It is important to note however that there is nothing to prevent the packing of shapes based on 'forbidden' rotation axes into a repeating pattern. For example octagons fit nicely on to a square lattice and regular polygons with many sides would pack in a similar way to circles. But in each case there is no way in which the 'forbidden' symmetry axis of the motif can be transmitted to the final repeating structure.

14.3 Packing of Two-dimensional Motifs

Motifs with a one-fold rotation axis will, on symmetry grounds, pack together to give a repeating pattern based on a parallelogram lattice (*cf.* Section 5.1). It is perhaps conceivable that motifs with this symmetry might pack on a rectangular lattice with $\alpha = 90.0000°$ — but this would be most unlikely. Motifs with the point group symmetry 2 will also pack to give a parallelogram lattice, whereas a rectangular lattice requires motifs having the point groups *m* or 2 *mm* which contain one or more mirror planes.

One can now begin to formulate a general rule that a particular motif will pack regularly to give a lattice which displays its point group symmetry elements.

It follows that motifs with point groups 4 and 4 *mm* will pack on a square lattice and those with 6 and 6 *mm* on to a triequiangular one. In some cases, however, the lowest symmetry lattice which displays the symmetry elements of the motif point group will also contain some elements of higher order. Motifs with point group 1 pack on a parallelogram lattice which contains diads, and motifs with point groups 3 and 3 *m* will pack to give a triequiangular lattice which contains hexads.

In short, the lattice will tend to belong to the same two-dimensional system as the motif. (This statement, though, is a little too general and not strictly true in the case of the glide reflection groups discussed in the next section.)

At this point we must question why the planar repeating patterns in Chapter 1 have very much lower symmetries than their lattices (see also Exercise 5.1), with the motifs most certainly not belonging to the same systems as the lattices. The anomoly is nothing to do with glide-reflection groups and can be best understood by thinking about a bathroom finished in square tiles, each with an identical but asymmetric flower painted on it. The lattice describing the repeating pattern would also be square and have the corresponding symmetry elements of tetrads, diads, mirrors, etc.; however, the complete pattern would not have any of these elements because of the asymmetry of the motif. The reason why the lattice in this case has a much higher symmetry than the pattern as a whole, is that the important symmetry as far as packing is concerned is the square shape of the tile, the painted flowers having no influence on the lattice type — as long as they are the same way up. Similarly with the patterns of Chapter 1; the lattice is in no way a direct consequence of the design forming each motif, and would have been chosen before the motifs were added.

In three dimensions the symmetry elements possessed by a group of atoms forming a motif are usually directly related to the external shape of the motif and hence influence the packing and resultant lattice symmetry. One does not have to consider the implications of designs drawn on the surfaces of atoms! In creating two-dimensional analogues to help understand crystal symmetry it is important however that the patterns chosen for motifs are plain and as simple as possible so as to avoid any features which might affect the motif symmetry but have no influence on the packing.

14.4 Two-Dimensional Space Groups (Plane Groups)

Thinking about the packing of motifs can give a good idea of the relationships between point group and lattice symmetry. But it is necessary to formalise in symmetry terms the addition of motifs to a lattice. The combination of a point group with the symmetry of a lattice gives rise to what is known as a **space group**, or more correctly for two dimensions, a **plane group**. The straightforward combination of the ten two-dimensional point groups with the planar lattices of the corresponding systems generates 13 of the 17 possible plane groups. These 13 groups are listed in the third column of Table 14.1 and are designated by the combination of a lower case letter which indicates whether the lattice is primitive or centred (*p* for primitive, *c* for centred) and the point group symbol.

Before discussion of the four glide reflection groups it is worth noting the occurrence of the pair of plane groups *p*3*m*1 and *p*31*m* based on the point group 3*m*. The two groups arise because the point group mirror planes can be aligned parallel to either the sides or the medians of the triangles which make up the triangular lattice. Fig. 14.5 shows these two groups and incidentally serves as an introduction to the graphic method of representing space groups by superimposing the symmetry elements on the planar unit cell.

TABLE 14.1. PLANE GROUPS

System (Lattice type)	*Point group*	*Plane group*		
		Based directly on point groups	*Glide-reflection groups*	
Oblique (*p* Parallelogram)	1	*p*1		
	2	*p*2		
Rectangular (*p* Rectangular)	*m*	*pm*	*pg*	
(*c* Rectangular)		*cm*		
	2*mm*	*p*2*mm*	*p*2*mg*	Sometimes abbreviated by omitting the '2'.
		*c*2*mm*	*p*2*gg*	
Square (*p* Square)	4	*p*4		
	4*mm*	*p*4*mm*	*p*4*gm*	
Hexagonal (*p* Triequiangular)	3	*p*3		
	3*m*	*p*3*m*1 *p*31*m*		
	6	*p*6		
	6*mm*	*p*6*mm*		

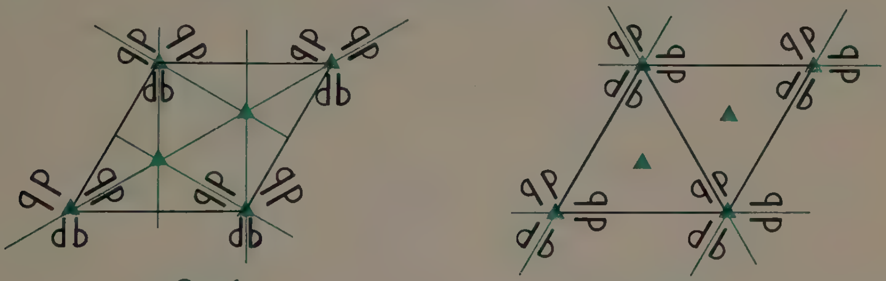


Fig. 14.5 The plane groups *p*3*m*1 and *p*31*m*.

Now for the **glide-reflection groups:**

Mention has already been made that different symmetry elements can interact to produce new elements (Section 4.6). In the realm of plane groups it is possible for a mirror plane to combine with the translational symmetry of the lattice to produce what is called a glide-reflection element. It involves reflection across a mirror plane and subsequent translation of the reflection parallel to the plane by half of the lattice repeat distance in that direction.

Figure 14.6 shows the simplest glide reflections group designated *pg*. The glide planes, like the mirror planes, are perpendicular to the planar cell but are distinguished by drawing their traces as dashed lines.

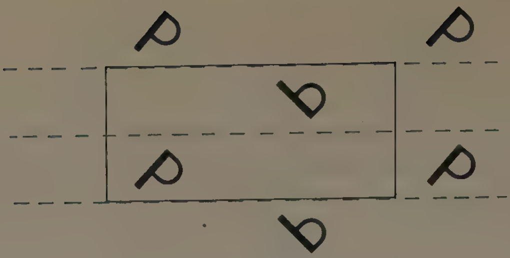


Fig. 14.6 The plane group *pg*.

A more complex plane group, *p4gm*, which includes a glide-reflection element is shown in Fig. 14.7.

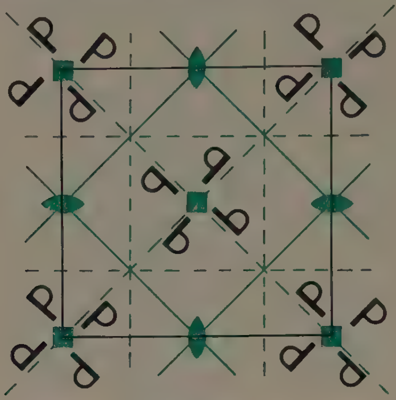


Fig. 14.7 The plane group *p4gm*.

Follow through the operation of the glide-reflection elements on the symbol **P** in Fig. 14.7 and note that there are both mirror planes and glide planes at 45° to the cell edge. In writing the plane group designation, mirror planes take precedence over glide planes parallel to them, so the group is *p4gm* rather than *p4gg*. Similarly the group *cm* contains a set of glide planes which do not appear in the designation (Fig. 14.8).

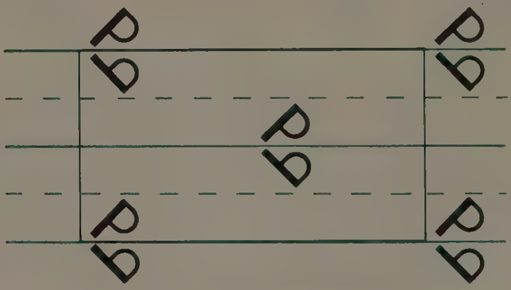


Fig. 14.8 The plane group *cm*.

The 17 plane groups are all illustrated in the *International Tables of X-ray Crystallography* and are also reproduced in *Crystallography and Crystal Defects* by Kelly and Groves. Instead of showing the operation of the symmetry elements on a symbol such as **P** , International Tables use a simple circle, and in cases where its mirror image occurs a comma is added as a distinguishing mark. The circles which are related by the symmetry elements mark what are called equivalent positions or equipoints: they are discussed in greater detail in Chapter 16. Because the symmetry elements are drawn in black, they are depicted on a separate unit cell plan from the symbols on which they operate; the plane group *p*4*gm* (abbreviated to *p*4*g* in International Tables) represented in this way is drawn in Fig. 14.9.

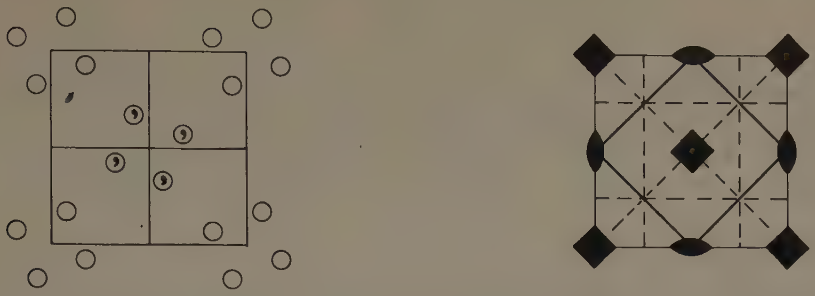


Fig. 14.9 The plane group *p*4*gm* as illustrated in *International Tables of X-ray Crystallography.*

14.5 The ‘P’ Shaped Molecule

As a postscript it is worth considering that if the symbol **P** represented a two-dimensional molecule; what would be the most likely plane group for the packing of the molecules?

It appears that there are two arrangements which give compact motifs that can pack closely on a lattice (Fig. 14.10).

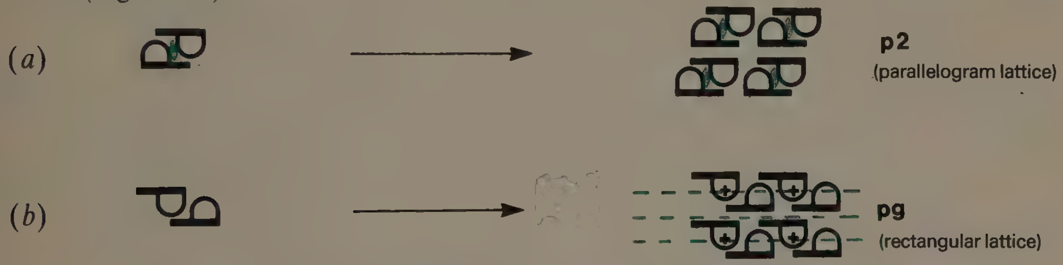


Fig. 14.10 Two probable packing arrangements for the planar ‘*P* shaped molecules’.

Obviously the arrangement (*b*) would only be a contender if the two-dimensional molecules are available in left- and right-handed versions.

TO DO

1. Write down the point groups which describe the symmetry of the following letters:

Point group

P

O

I

N

T

2. Group together several letter T's to give a design which has the point group symmetry 3.

3. Drawn below are several motifs. Write down their point group symmetry and the two-dimensional crystal system to which they are likely to belong.

Point group *System*

(a) 

(b) 

(c) 

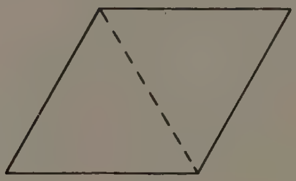
(d) SOS

(e) 

(f) 

(g) 

4. The plane group $p31m$ drawn in Fig. 14.5 also contains some glide reflection planes which are not shown on the diagram. Draw in **all** the $p31m$ symmetry elements on the cell outline below.

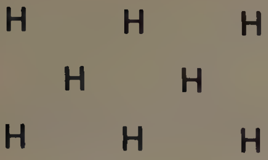


5. Identify the plane groups and symmetry elements of the following patterns.

Symmetry elements (draw within unit cell)

Plane group

(a)

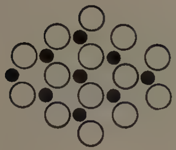


– – – – – –

(b)

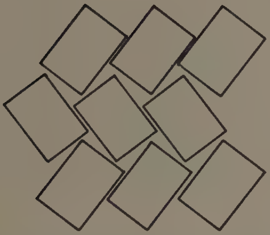
– – – – – –

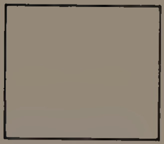
(c)



– – – – – –

(d)





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6. Using a motif based on a collection of the symbols '§' (and mirror image of same) draw patterns having the following plane groups:

(*a*) pmg

(*b*) p1

(*c*) p6

(*d*) pgg

7. When you next take afternoon tea determine the two-dimensional point group symmetry of the cake doily.

TO UNDERSTAND

For two dimensions:

1. The way in which point group symmetry elements can be illustrated by considering their operation on the symbol **P**.
2. The method of representing plane group symmetry elements on a planar unit cell.
3. The interaction between the mirror and translation symmetry operation to produce a glide-reflection element.

15

Point Groups (in three dimensions)

15.1 Crystal Classes

The shape of a faceted crystal and its measured physical properties such as elastic modulus, thermal expansion, electrical resistance, etc. show symmetry characteristic of the crystal type. The symmetry elements observed in this way show no translational component. They all pass through one point in space and hence constitute a point group.

Translational aspects of symmetry can only be revealed when the atomic arrangement within the crystal is examined using techniques such as X-ray diffraction.

Crystals are grouped into 32 **classes** on the basis of their point group symmetry alone and the classes are further grouped into 6- or 7-Crystal Systems (see Fig. 15.9).

The 7-System grouping is probably the neater as far as point group symmetry is concerned, for each System corresponds to a particular order of principal rotation axis. In the 6-System notation, the Crystal Classes based on a triad axis are grouped into the Hexagonal System along with the hexad-based Classes. The logic of this approach is that each system is linked to the most convenient lattice unit cell, and the structures of both triad and hexad-based Crystal Classes are best displayed on a hexagonal unit cell.

In this book lattice unit cells and crystal structures are considered in detail before point group symmetry theory is introduced. For this reason the 6-System notation has been chosen.

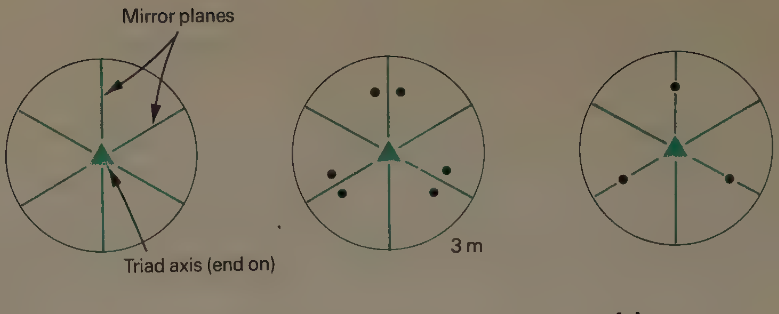
15.2 Stereographic Representation of Point Groups

The arrangement of the symmetry elements forming a point group is best illustrated on a stereographic projection. It is also possible by this means to show the results of the operation of the point group on a symbol of general orientation.

Take for example the point group called $3m$. The triad is taken as parallel to the N–S axis of the reference sphere and the mirror planes which are parallel to the triad are therefore projected as straight lines (Fig. 15.1(*a*)). As far as the stereographic projection is concerned the most convenient symbol for demonstrating the operation of the point group elements is a line with one end at the centre of the reference sphere (i.e. at the 'point' of the point group). The pole where this line intersects the northern hemisphere of the reference sphere is plotted as a single point on the projection, or in cases where the intersection is on the southern hemisphere, as a small ring.

The full stereographic representation of the point group $3m$ is shown in Fig. 15.1(*b*). Note how the poles have been multiplied by the operation of the symmetry elements.

As the symbol represented by the poles or rings is simply a line it is important that it is in a general orientation compared with the symmetry elements. If, for instance, it was sited on one of the mirror planes of the point group $3m$, the final arrangement of the poles would not in any way reveal the operation of the mirror symmetry elements (Fig. 15.1(*c*)).



(a) **(b)** **(c)**

Fig. 15.1 (*a*) The stereographic representation of the symmetry elements of the point group $3m$.
(*b*) The result of the operation of the symmetry elements on line symbol in general orientation.
(*c*) The effect of placing the symbol in a special position on one of the mirror planes.

Another point group known as $\frac{2}{m}$ has a mirror plane perpendicular to the diad axis. The projection of the mirror plane is therefore coincident with the circumference of the stereographic projection itself and is drawn more heavily (Fig. 15.2). Note how the mirror plane has generated pairs of poles immediately above each other.

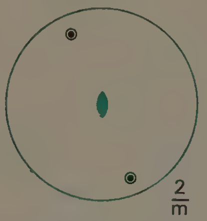


Fig. 15.2 Stereographic projection of the point group $\frac{2}{m}$ showing the mirror plane perpendicular to the diad.

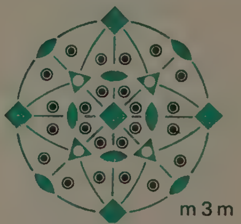
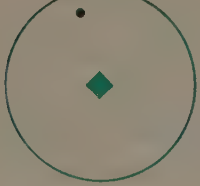


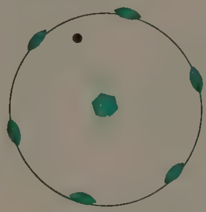
Fig. 15.3 Stereographic projection of the point group $m3m$. Note the triad axes at 55° to the tetrads.

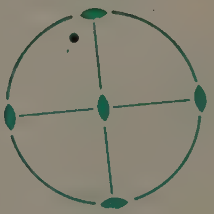
In the cubic system symmetry axes and mirror planes occur at acute angles to the projection plane. This can be seen clearly in the projection of the cubic point group $m3m$ (Fig. 15.3).

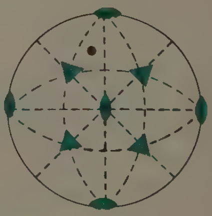
The logic behind the symbols which are used to name the point groups will become apparent later in the chapter. It will suffice at this stage to note that a number describing a rotation axis followed by the letter 'm', implies a mirror plane either parallel, or at a predefined angle, to the axis. On the other hand the axis number apparently divided by 'm', as in $\frac{2}{m}$, represents a mirror plane perpendicular to the axis. Many accepted point group symbols are in fact simplified versions, $m3m$ is one such, and do not in themselves fully communicate the symmetry elements present, fulfilling instead more the role of labels.

Exercise A. Complete the following stereograms of point groups by operating with the elements shown on the single pole.









15.3 Proper and Improper Rotation Axes

There are two types of symmetry element which are really basic to the derivation of the three-dimensional point groups: rotation symmetry and inversion symmetry. These two elements can also operate together in a compound fashion to generate another element known as a **roto-inversion**, or simply, **improper axis**.

An *n*th order roto-inversion symmetry element executes normal (or 'proper') rotations of $\frac{2\pi}{n}$ **each** of which is followed by an inversion. The element is designated by writing the order of the rotation axis with a 'bar' over it. Improper axes are represented on a projection by modifications of the proper axis symbols (Fig. 15.4).

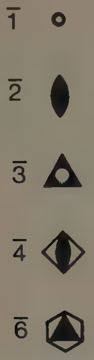


Fig. 15.4 The symbols used to identify the different types of roto-inversion axis.

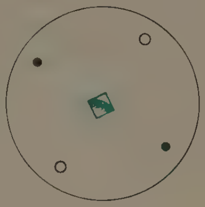


Fig. 15.5 The stereographic representation of the point group based on the roto-inversion axis $\bar{4}$. Note that the group does not have a centre of symmetry.

A stereographic representation of the operation of a four-fold roto-inversion axis is shown in Fig. 15.5. Follow through the sequence of operations and note that this element, as with $\bar{2}$ and $\bar{6}$ axes does not itself contain a centre of symmetry. However the $\bar{1}$ and $\bar{3}$ axes are equivalent to the operation of the inversion element subsequent to the complete operation of their proper counterparts (Fig. 15.6).

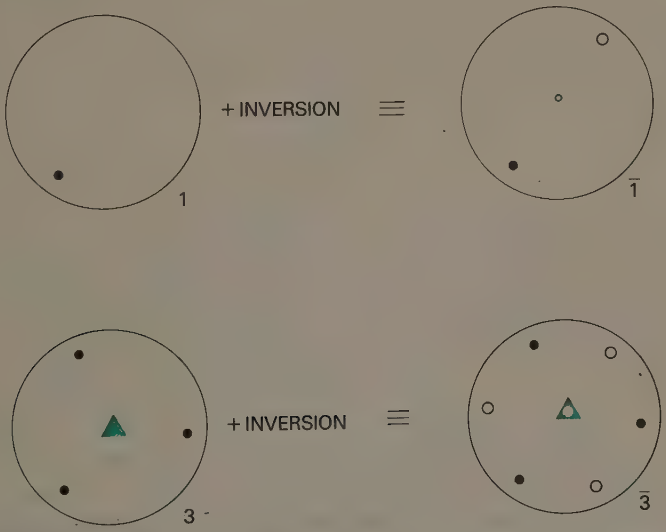
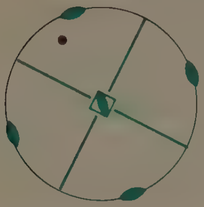
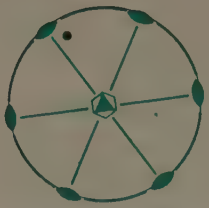
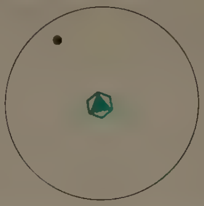


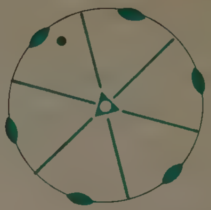
Fig. 15.6 Diagrams to illustrate that $\bar{1}$ and $\bar{3}$ point groups can also be generated by the addition of the inversion symmetry element to the point groups 1 and 3.

Exercise B. Complete the following stereograms of point groups by operating with the elements shown on the single pole and decide which have a centre of symmetry.









The various permissible combinations of the two basic and one composite element (rotation, inversion and roto-inversion) can generate all 32 possible point groups. Mirror planes are not required to generate any of the groups, but both a two-fold roto-inversion axis on one hand, and any even-fold proper or improper axis with the subsequent operation of an inversion element on the other, are equivalent to a mirror plane perpendicular to the axis. Examples of these relations are shown in Fig. 15.7. It is crystallographic convention to refer to such elements in terms of the mirror plane rather than the various combinations of rotation and inversion symmetry.

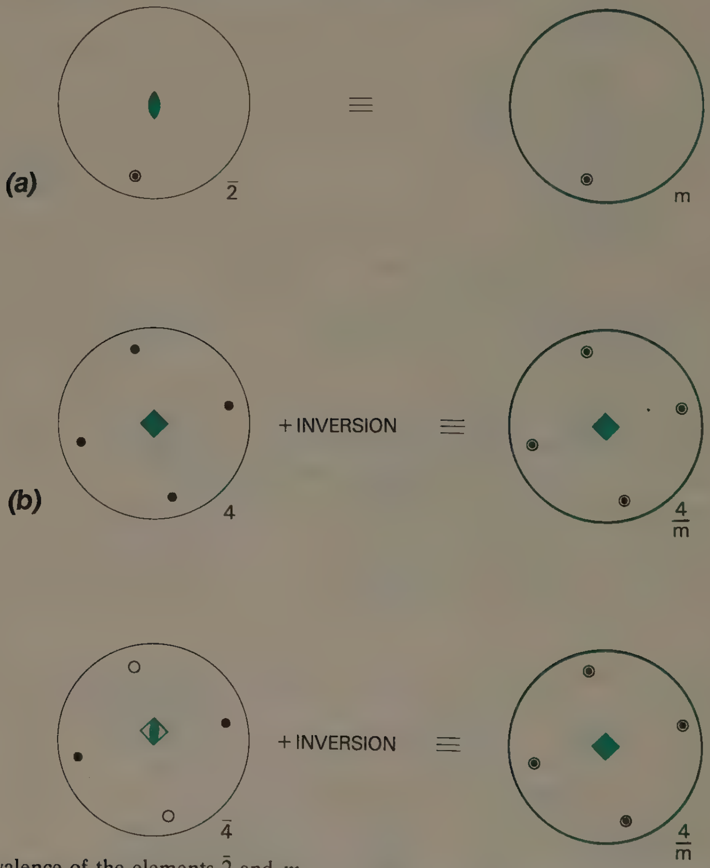


Fig. 15.7 (*a*) The equivalence of the elements $\bar{2}$ and *m*.
(*b*) Stereograms showing that the addition of the inversion element to the point groups 4 and $\bar{4}$ generates in each case the point group $\frac{4}{m}$. The positioning of *m* in $\frac{4}{m}$ indicates that the mirror plane is perpendicular to the tetrad. The addition of the inversion element to 2, $\bar{2}$, 6 and $\bar{6}$ also generates similar perpendicular mirror planes.

We are now in a position to summarise some of the more important relationships between point group symmetry elements (Table 15.1).

TABLE 15.1. RELATIONSHIP BETWEEN SOME SYMMETRY ELEMENTS

1 or 3	+	Inversion	$\longrightarrow$	$\bar{1}$ or $\bar{3}$
2, 4 or 6	+	Inversion	$\longrightarrow$	$\frac{2}{m}, \frac{4}{m}$ or $\frac{6}{m}$
$\bar{2}, \bar{4}$ or $\bar{6}$	+	Inversion	$\longrightarrow$	$\frac{2}{m}, \frac{4}{m}$ or $\frac{6}{m}$
		$\bar{2} = m$		

If any of the elements or element combinations in the right-hand column of Table 15.1 occur as a part of a point group symbol; then that point group has a centre of symmetry.

It should be noted that the alternate operation of a rotation axis and a perpendicular mirror plane produces another type of improper rotation element known as a **roto-reflection axis** and written $\tilde{n}$. This element, however, does not lead to any symmetry operations which cannot also be generated by roto-inversion axes (see Exercise 15.1), and in this text the term 'improper axis' refers to the roto-inversion type.

The 13 point groups which can be generated by suitable combinations of *one* rotation axis and the inversion element are listed in Table 15.2.

TABLE 15.2. POINT GROUPS BASED ON ONE ROTATION AXIS

One Proper Axis	1	2	3	4	6
One Improper Axis	$\bar{1}$	$\bar{2} = m$	$\bar{3}$	$\bar{4}$	$\bar{6}$
Either Proper or Improper Axis + Inversion	$(\bar{1})$	$\frac{2}{m}$	$(\bar{3})$	$\frac{4}{m}$	$\frac{6}{m}$

15.4 Combination of Non-Parallel Rotation Axes

So far we have only discussed three-dimensional point groups based on one rotation axis. The next stage is to ask if it is possible to combine, at a point in space, two or more non-parallel crystallographic rotation axes so that they are self-consistent. The answer is 'yes', but only for a few specific configurations. The permissible combinations can be determined by using a geometric construction due to Euler and the subsequent solution of a spherical triangle. For a description of this analysis see Chapter 5 of Buerger's *Elementary Crystallography.*

The permissible combinations, omitting the trivial situation with two one-fold axes, are shown in Fig. 15.8.

The axial combinations illustrated are those which define the resulting point groups; with the exception of 222, it can be seen that operation of the rotation axes on each other will generate additional axes not shown in the diagrams.

Further point groups can be produced by combining proper and improper versions of the above

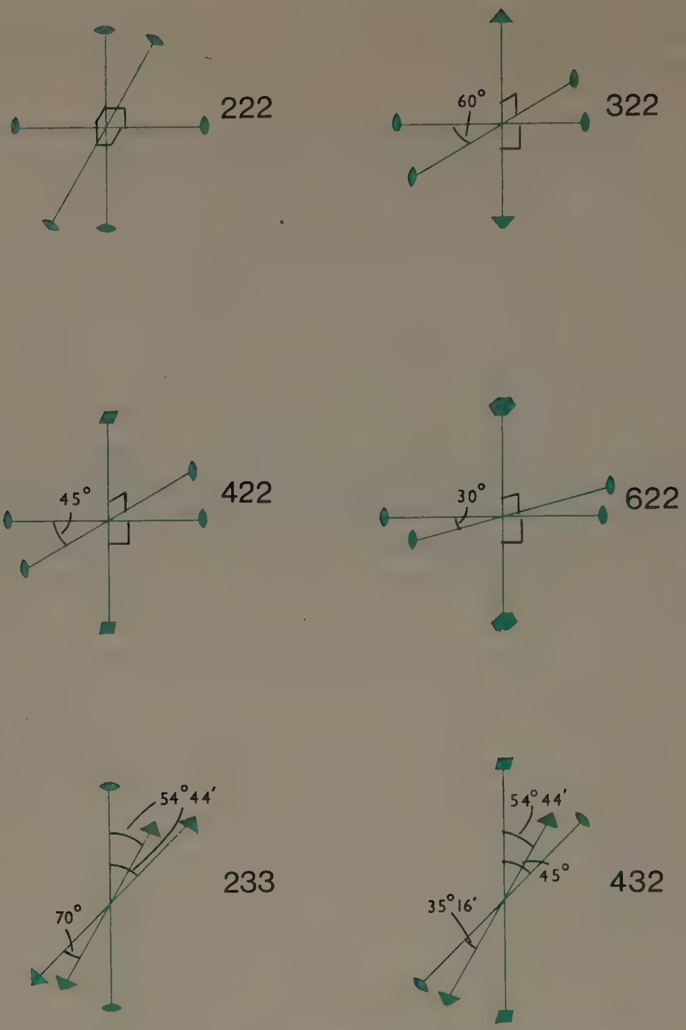


Fig. 15.8 The permissible combinations of proper symmetry axes at a point.

axes, but with the restriction that two of the axes must always be improper. Point groups of this type in which the three symbols are interchanged in order are equivalent. The permissible distinct combinations are listed in Table 15.3.

The first stage in sorting out these particular combinations of elements is to look for those which have a centre of symmetry; they can be recognised by the presence of a $\bar{3}$ axis. The combinations in Table 15.3 which have a centre of symmetry are boxed and re-grouped on the right with their other axes modified as a result of the operation of this element upon them and in accordance with the relations in Table 15.1.

We must also consider the creation of new point groups by the operation of the inversion element on the axial combinations which do not already have a centre of symmetry. Point groups produced in this way are listed in Table 15.4.

Table 15.5 summarises the point groups which can be derived from the permissible axial combinations. In accordance with standard practice the substitution of m for $\bar{2}$ has been made (e.g. $2\bar{2}\bar{2}$ becomes $2mm$).

TABLE 15.3. PERMISSIBLE AXIAL COMBINATIONS

222	$2\bar{2}\bar{2}$			
322	$3\bar{2}\bar{2}$	$\boxed{\bar{3}2\bar{2}}$		$\bar{3}\,\frac{2}{m}\,\frac{2}{m}$
422	$4\bar{2}\bar{2}$	$\bar{4}2\bar{2}$		
622	$6\bar{2}\bar{2}$	$\bar{6}\bar{2}2$		
233	$\boxed{2\bar{3}\bar{3}}$	$\boxed{\bar{2}\bar{3}3}$		$\frac{2}{m}\,\bar{3}\,\bar{3}$ (both)
432	$\boxed{4\bar{3}\bar{2}}$	$\bar{4}3\bar{2}$	$\boxed{\bar{4}\bar{3}2}$	$\frac{4}{m}\,\bar{3}\,\frac{2}{m}$ (both)

TABLE 15.4. ADDITION OF CENTRE OF SYMMETRY TO AXIAL COMBINATIONS

(222 or $2\bar{2}\bar{2}$)	+	Inversion	=	$\frac{2}{m}\,\frac{2}{m}\,\frac{2}{m}$
(322 or $3\bar{2}\bar{2}$)	+	Inversion	=	$\bar{3}\,\frac{2}{m}\,\frac{2}{m}$*
(422, $4\bar{2}\bar{2}$ or $\bar{4}2\bar{2}$)	+	Inversion	=	$\frac{4}{m}\,\frac{2}{m}\,\frac{2}{m}$
(622, $6\bar{2}\bar{2}$ or $\bar{6}\bar{2}2$)	+	Inversion	=	$\frac{6}{m}\,\frac{2}{m}\,\frac{2}{m}$
233	+	Inversion	=	$\frac{2}{m}\,\bar{3}\,\bar{3}$*
(432 or $\bar{4}3\bar{2}$)	+	Inversion	=	$\frac{4}{m}\,\bar{3}\,\frac{2}{m}$*

* These point groups have already been generated by simple proper/improper combinations of the same axes (see Table 15.3).

TABLE 15.5 POINT GROUPS BASED ON NON-PARALLEL AXES

No centre of symmetry			*Inherent centre of symmetry*	*New groups produced by addition of centre of symmetry*
222	2*mm*			$\frac{2}{m}\,\frac{2}{m}\,\frac{2}{m}$
322	3*mm*			
422	4*mm*	$\bar{4}2m$	$\bar{3}\,\frac{2}{m}\,\frac{2}{m}$	$\frac{4}{m}\,\frac{2}{m}\,\frac{2}{m}$
622	6*mm*	$\bar{6}m2$		$\frac{6}{m}\,\frac{2}{m}\,\frac{2}{m}$
233			$\frac{2}{m}\,\bar{3}\,\bar{3}$	
432		$\bar{4}3m$	$\frac{4}{m}\,\bar{3}\,\frac{2}{m}$	

The 19 point groups listed in Table 15.5 together with the 13 groups based on one rotation axis listed in Table 15.2 make up the 32 crystallographic point groups. These are displayed in detail in Fig. 15.9.

15.5 Tour of the Crystallographic Point Groups

We have already mentioned that the various crystal classes or point groups can be grouped into systems on the basis of the order of the principal rotation axis. This scheme works fine as long as any

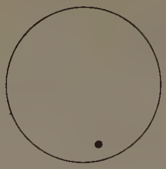
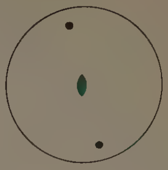
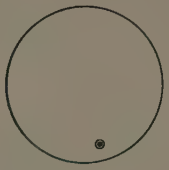
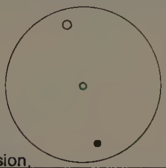
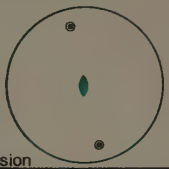
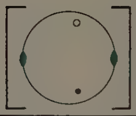
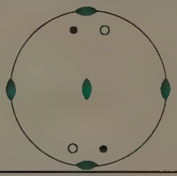
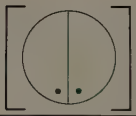
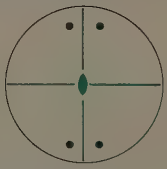
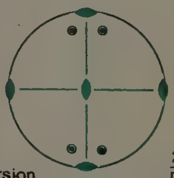
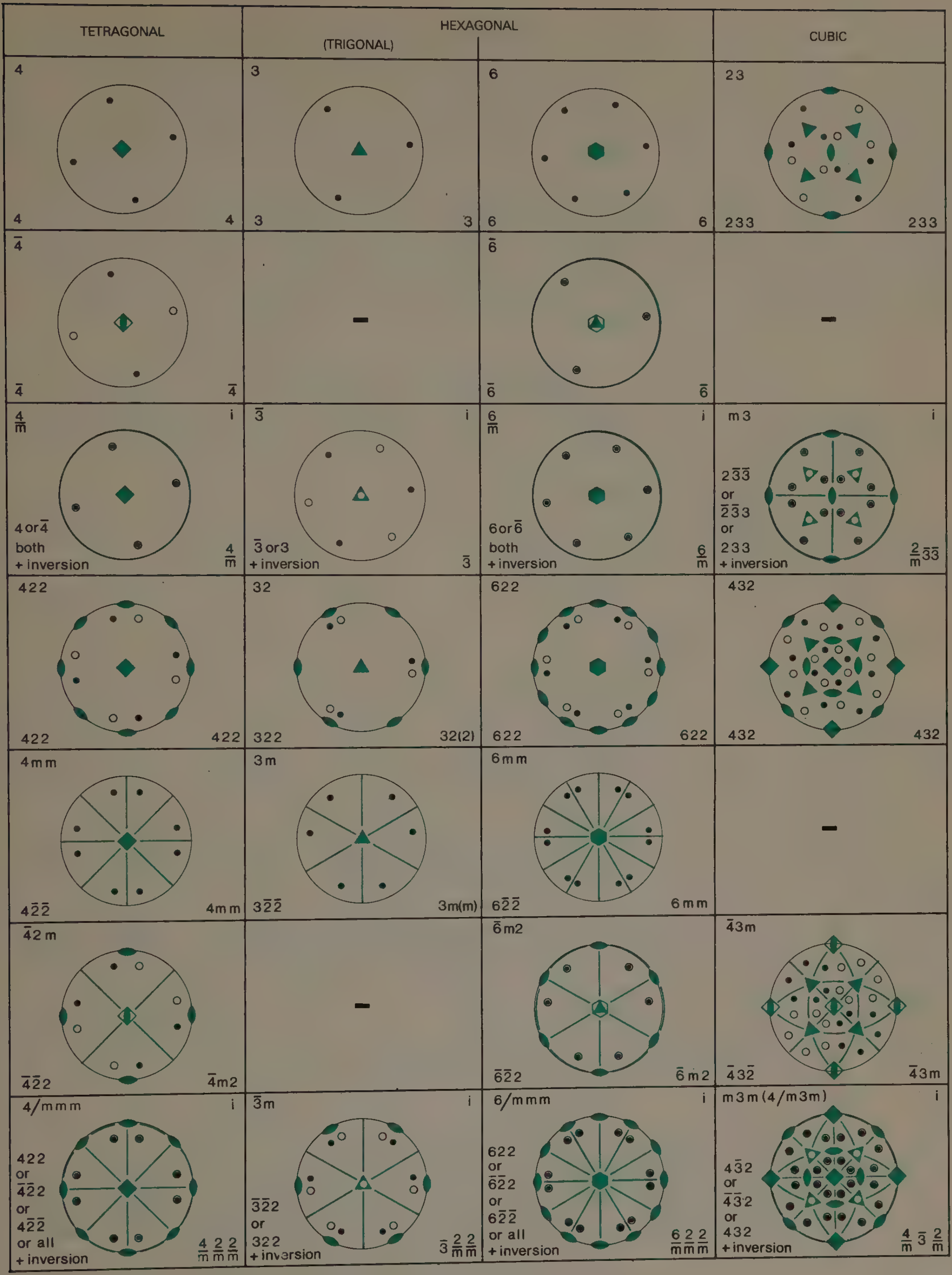
SYMMETRY OPERATIONS	TRICLINIC	MONOCLINIC (1st setting)
One Proper Rotation Axis.	1  1 1	2  2 2
One Roto-Inversion (improper) Axis.	—	m  $\bar{2}$ m
One Proper Axis combined with Centre of Symmetry or improper axis with inherent centre of symmetry.	$\bar{1}$ i  $\bar{1}$ or inversion. $\bar{1}$	$\frac{2}{m}$ i  2 or $\bar{2}$ both + inversion $\frac{2}{m}$
	MONOCLINIC (2nd setting)	ORTHORHOMBIC
Permissible combinations of the non parallel proper axes.	(1 2 = 2) 	222  222 222
Combinations of two improper axes and one proper axis which do not contain a centre of symmetry.	(1 $\bar{2}$ = m) 	2mm  2$\bar{2}\bar{2}$ 2mm
Same operations as the row above.	—	—
Permissible combinations of these non parallel axes which either have an inherent centre of symmetry or have had one added.	(1 2 + inv. = $\frac{2}{m}$) 	m m m i  222 or 2$\bar{2}\bar{2}$ both +inversion $\frac{2}{m}\frac{2}{m}\frac{2}{m}$

Fig. 15.9 The 32 three-dimensional point groups.


TETRAGONAL
HEXAGONAL
(TRIGONAL)
CUBIC
4
4
4
3
3
3
6
6
6
23
233
233
4̄
4̄
4̄
–
6̄
6̄
6̄
–
4/m
i
4 or 4̄
both
+ inversion
4/m
3̄
i
3̄ or 3
+ inversion
3̄
6/m
i
6 or 6̄
both
+ inversion
6/m
m3
i
23̄3̄
or
2̄3̄3
or
233
+ inversion
2/m 3̄3̄
422
422
422
32
322
32(2)
622
622
622
432
432
432
4mm
42̄2̄
4mm
3m
32̄2̄
3m(m)
6mm
62̄2̄
6mm
–
4̄2m
4̄2̄2
4̄m2
–
6̄m2
6̄2̄2
6̄m2
4̄3m
4̄32̄
4̄3m
4/mmm
i
422
or
4̄2̄2
or
42̄2̄
or all
+ inversion
4/m 2/m 2/m
3̄m
i
3̄2̄2
or
322
+ inversion
3̄ 2/m 2/m
6/mmm
i
622
or
6̄2̄2
or
62̄2̄
or all
+ inversion
6/m 2/m 2/m
m3m (4/m3m)
i
43̄2
or
4̄3̄2
or
432
+ inversion
4/m 3̄ 2/m

other symmetry elements are either perpendicular or parallel to the principal axis, but in the case of the point groups based on the axial combinations 233 and 432, the triads are at 54°44′ to the first named axis. These groups do not fit logically into any of the systems based on a principal axis and are therefore collected into a system of their own, the **cubic** or **isometric** system.

Figure 15.9 is a schematic arrangement of all 32 three-dimensional point groups. The crystal systems more or less correspond to the columns; and the development of various point groups as additional symmetry elements are brought to bear, can be followed by moving down each column. Each point group or crystal class is represented by a stereogram showing the important symmetry elements (in colour) and the repetitions of a symbol, plotted as a pole, as a result of the operation of these elements. The key to the arrangement of the information grouped around each stereogram is given in Fig. 15.10.

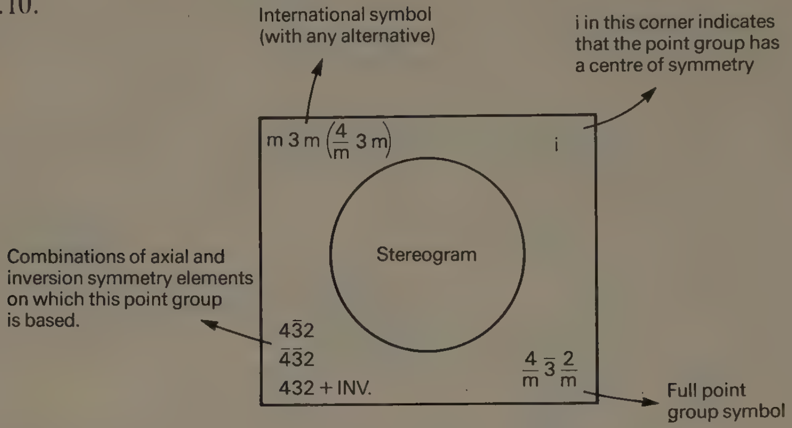


Fig. 15.10 Key to the arrangement of information around the stereograms in Fig. 15.9.

The simplest point groups are those containing one rotation axis of order 1, 2, 3, 4 or 6 which can be either pure rotation (proper) or roto-inversion (improper) axes. These are represented by stereograms in the first two rows of Fig. 15.9, with the exception of $\bar{1}$ and $\bar{3}$ which, because they have a centre of symmetry, are put in row three. Also, the cubic groups are put on one side for the moment. $\bar{2}$ is conventionally described in terms of a mirror plane, *m*, but the two elements are synonymous.

The third row down shows the result of the operation of an inversion element on the point groups in either of the first two rows.

The fourth row contains the point groups based on combinations of three non-parallel rotation axes. In the first column one diad lying in the plane of the stereogram is identical to the same axis perpendicular to the page, i.e. the point group is 2. This, however, has appeared before and belongs to the monoclinic system — which now takes over column 1. Similarly the point group 222, along with further groups of higher symmetry based on a two-fold axis, is in the orthorhombic rather than monoclinic system, and the column heading is changed accordingly. The point group 322 is generally known as 32 because the second diad can also be generated by the operation of the triad on the first diad.

The point groups in the fifth and sixth rows are based on the permissible combinations of rotation axes which include two improper axes but do not have a centre of symmetry. In row 5, the combination of a proper principal axis with two improper axes at 90° to it produces point groups which can also be derived in terms of adding mirror planes parallel to the principal axis, and this approach is found in some texts.

The bottom row contains point groups generated by the operation of the inversion element on the permissible combinations of non-parallel axes. A point group produced in this way is the same irrespective of whether the original axes were a mixture of proper and improper, or all proper. If one or more of the non-parallel rotation axes is $\bar{1}$ or $\bar{3}$ then the point group already has a centre of symmetry and will be grouped in the final row without further symmetry operation. For example, the point group $\bar{3}$m can be produced by the operation of a centre of symmetry on 32, but it is also the symmetry resulting from the combination of the axes $\bar{3}\bar{2}\bar{2}$.

The basic symmetry elements of the cubic system are four triads directed towards the corners of a cube, along with a diad perpendicular to each cube face. If the triads are improper axes the group has a centre of symmetry and three orthogonal mirror planes (row 3).

The combination of rotation axes 432 also belongs to the cubic system (row 4). If two of these axes are improper, the resulting point group will be either $\bar{4}3m$ or if the triad is improper, $m3m$ in which case a centre of symmetry will also be present.

15.6 Summary of Point Groups and Their Derivation

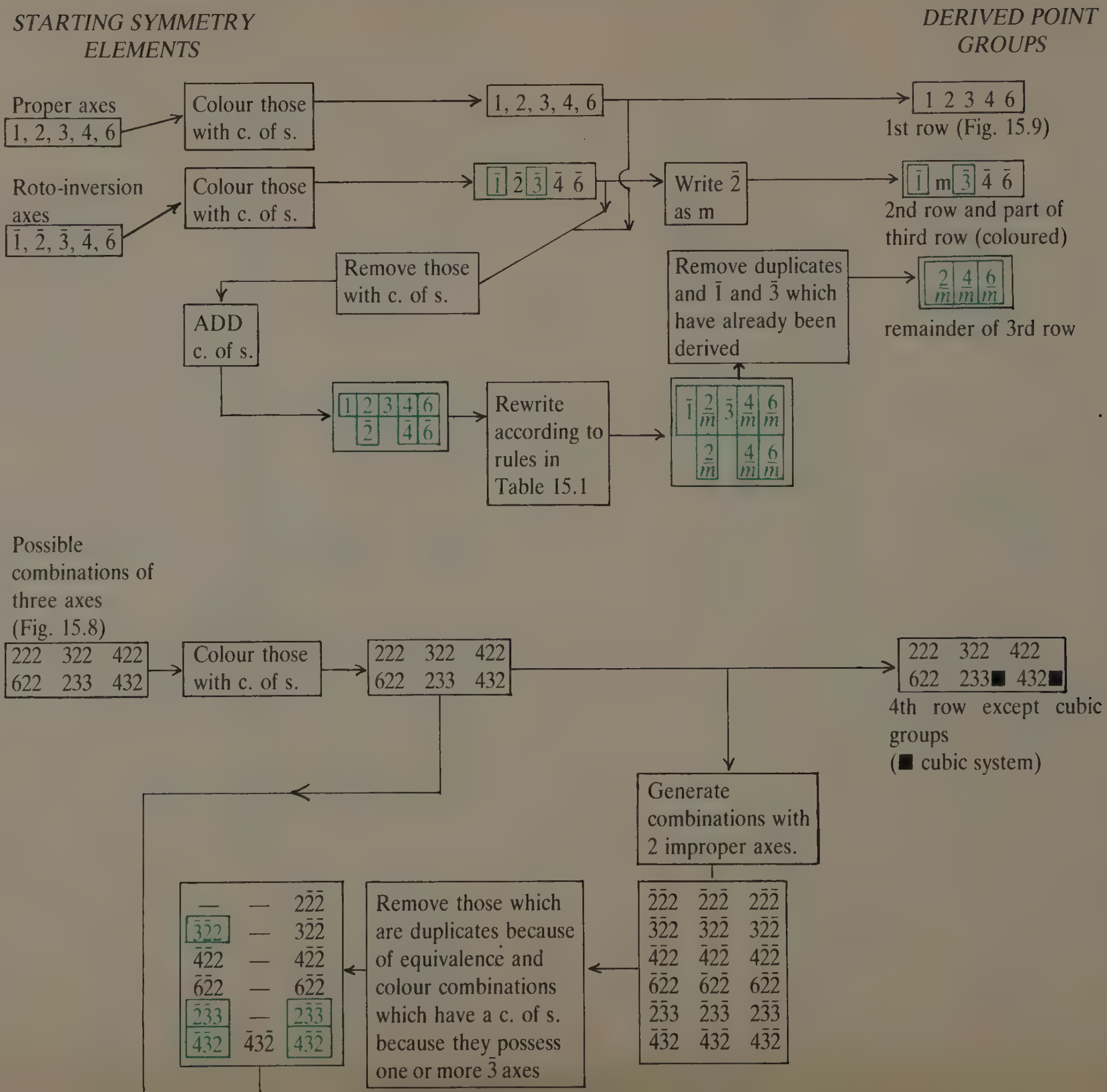
A schematic summary of the 32 crystallographic point groups, using the full derived notation, is given in Table 15.6, and Table 15.7 is a chart laying out the logic processes involved in their derivation.

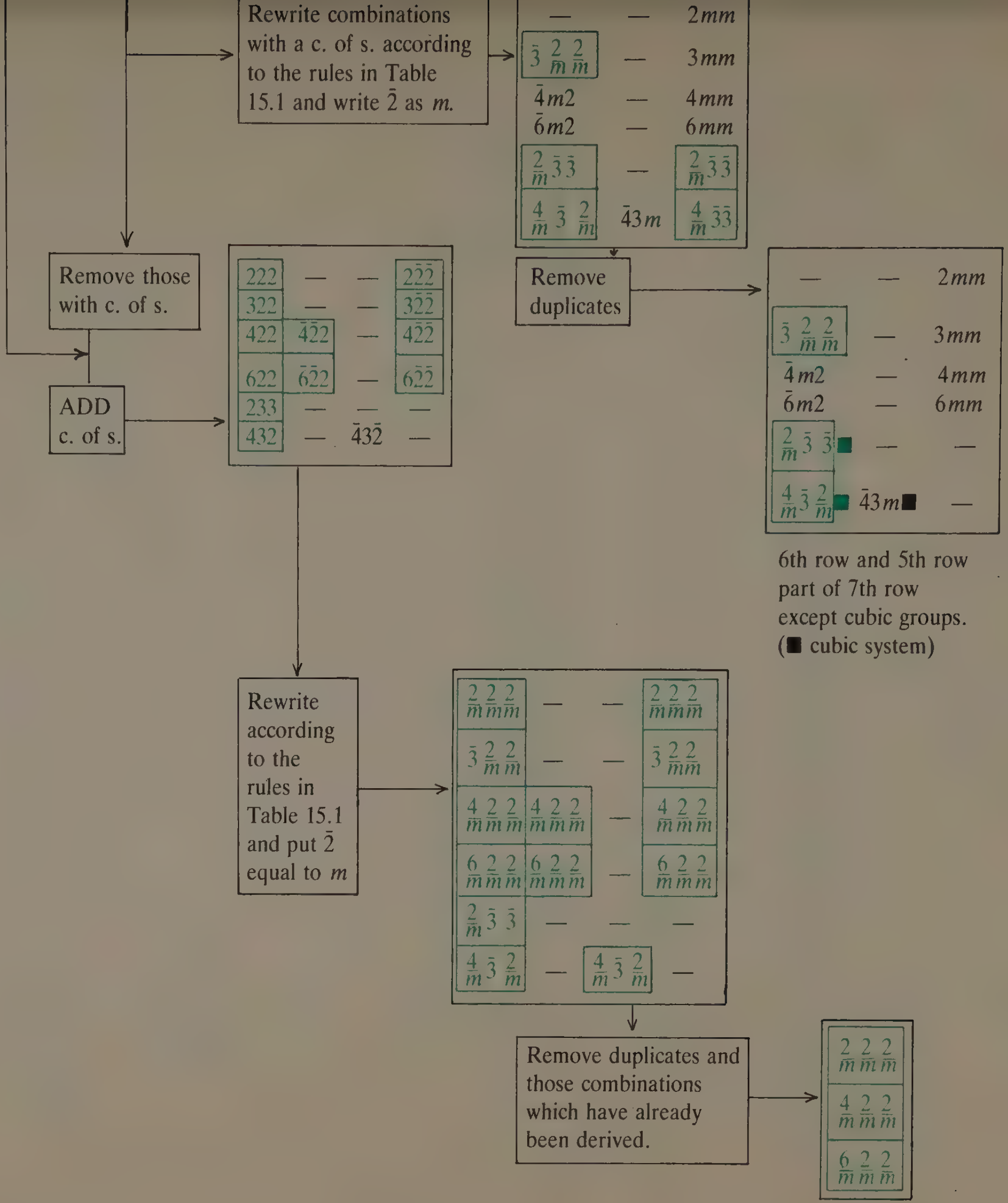
TABLE 15.6. THE CRYSTALLOGRAPHIC POINT GROUPS

Proper axis	1	2	3	4	6	— Enantiomorphous		
Roto-inversion (improper)		m		$\bar{4}$	$\bar{6}$			
	$\bar{1}$		$\bar{3}$					
Added centre of symmetry		$\frac{2}{m}$		$\frac{4}{m}$	$\frac{6}{m}$	Centre of symmetry		
3 proper axes		222	322	422	622	223	432	— Enantimorphous
3 axes with 2 improper		$2mm$	$3mm$ $\bar{3}\frac{2}{m}\frac{2}{m}$	$4mm$ $\bar{4}2m$	$6mm$ $\bar{6}m2$	$\frac{2}{m}\bar{3}\bar{3}$	$\bar{4}3m$	
Added centre of symmetry		$\frac{2}{m}\frac{2}{m}\frac{2}{m}$		$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$		$\frac{4}{m}\bar{3}\frac{2}{m}$	Centre of symmetry

The classification of 11 point groups as **'enantiomorphous'** (opposite-shape) derives from the observation of left- and right-handed editions of some crystals. This phenomenon is only observed when the crystal point group contains neither a centre of symmetry nor any roto-inversion axis (and by implication no mirror planes).

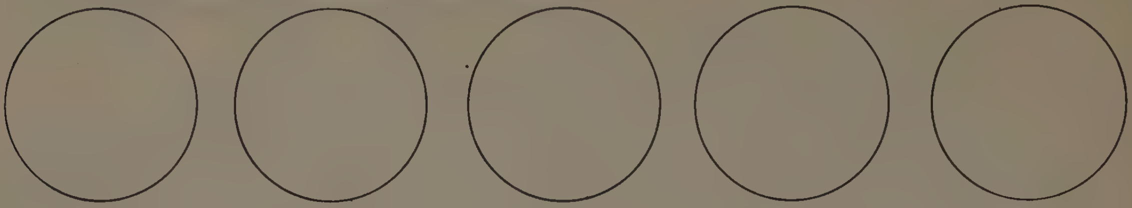
TABLE 15.7. CHART SUMMARISING THE DERIVATION OF THE 32 POINT GROUPS




Rewrite combinations with a c. of s. according to the rules in Table 15.1 and write $\bar{2}$ as m.
Remove those with c. of s.
ADD c. of s.
Remove duplicates
Rewrite according to the rules in Table 15.1 and put $\bar{2}$ equal to m
Remove duplicates and those combinations which have already been derived.
6th row and 5th row part of 7th row except cubic groups. (■ cubic system)
222, 322, 422, 622, 233, 432
$4\bar{2}2$, $6\bar{2}2$, $\bar{4}3\bar{2}$
$2\bar{2}\bar{2}$, $3\bar{2}\bar{2}$, $4\bar{2}\bar{2}$, $6\bar{2}\bar{2}$
$\bar{3}\frac{2}{m}\frac{2}{m}$, $\bar{4}m2$, $\bar{6}m2$, $\frac{2}{m}\bar{3}\bar{3}$, $\frac{4}{m}\bar{3}\frac{2}{m}$, $\bar{4}3m$
2mm, 3mm, 4mm, 6mm, $\frac{2}{m}\bar{3}\bar{3}$, $\frac{4}{m}\bar{3}\bar{3}$
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$, $\bar{3}\frac{2}{m}\frac{2}{m}$, $\frac{4}{m}\frac{2}{m}\frac{2}{m}$, $\frac{6}{m}\frac{2}{m}\frac{2}{m}$, $\frac{2}{m}\bar{3}\bar{3}$, $\frac{4}{m}\bar{3}\frac{2}{m}$

TO DO

1. By drawing stereograms in the circles below show that each of the roto-reflection axes $\tilde{1}, \tilde{2}, \tilde{3}, \tilde{4}$ and $\tilde{6}$ is equivalent to a roto-inversion axes.



$\tilde{1} =$ $\tilde{2} =$ $\tilde{3} =$ $\tilde{4} =$ $\tilde{6} =$

2. Determine the point group symmetry of the following:

Point group symmetry

(*a*) a plain cube

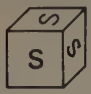
(*b*) a regular octahedron

(*c*) a regular tetrahedron

3. A cube has a series of letters printed on its surfaces as shown in the diagrams below. (Letters on opposing faces are the same way up.)
In each case determine the point group symmetry (n.b. it need not belong to the cubic system).

Point group

(*a*)

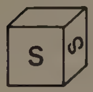


(*b*)

(*c*)

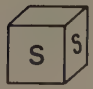
top and bottom faces blank

(*d*)



top and bottom faces blank

(*e*)

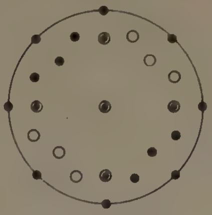


top and bottom faces blank, all 'S's the same way up

(*f*)

all faces blank but with one corner cut off to give a small equilateral face

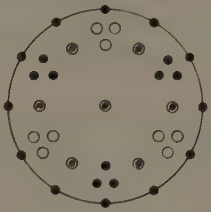
4. The normals to the facets of a crystal are plotted on the stereogram below: determine the point group symmetry, and mark in all the elements you can find.



Point group =

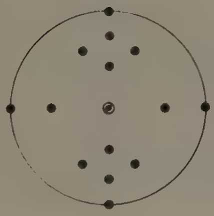
Note that many of these poles will be in special positions and hence lie on the symmetry elements, try not to be confused by them. It may help to point out that poles immediately above a horizontal diad will appear double (i.e. ⊙) while those above or below a $\bar{2}$ axis will remain single.

Repeat the exercise using the stereogram below:



Point group =

And again with this stereogram:



Point group =

5. What are the point groups (at a lattice point) of the 14 Bravais lattices?

Lattice	*Point group symmetry*
Triclinic (P)	
Monoclinic (P)	
Monoclinic (I)	
Orthorhombic (P)	
Orthorhombic (A, B or C)	
Orthorhombic (I)	
Orthorhombic (F)	

Lattice	*Point group symmetry*
Tetragonal (P)	
Tetragonal (I)	
Hexagonal (P)	
Hexagonal (R)	
Cubic (P)	
Cubic (I)	
Cubic (F)	

TO LEARN AND UNDERSTAND

1. The way in which rotation and inversion symmetry elements can interact to form a roto-inversion axis.
2. The distinction between a roto-inversion element, and the successive operation of both proper rotation and inversion elements in their own right.
3. The representation of the various point group symmetry elements and operations on a stereographic projection.
4. The relationships between symmetry elements as summarised in Table 15.1.
5. The way in which the permissible combinations of three non-parallel rotation axes can form the basis for the derivation of 19 of the 32 point groups.

TO PONDER AND DISCUSS

When one views the image of oneself in a mirror left and right are reversed but not head and feet. Why?

16
Space Groups

16.1 Introduction

The concepts behind the derivation of space groups have already been introduced in Chapter 14 for the two-dimensional situation. In three dimensions the combination of the 32 point groups with the 14 Bravais lattices leads to the formation of 230 different space groups. The systematic derivation of these groups is a protracted procedure, and is most 'at home' in crystallographic reference texts. For example in M. J. Buerger's *Elementary Crystallography* the theory and derivation of space groups occupies 325 out of the 525 pages.

Just as the addition of the motif to each and every lattice point forms the crystal structure, so the combination of point group symmetry and translational symmetry creates a 'space group' of elements which fully defines the symmetry of a crystal. However in the derivation of space groups one must take into account the fact that mirror planes and rotation axes interact with the translation elements to make two new types of element. These are known as **glide planes** and **screw axes** respectively and are described in Sections 16.2 and 16.3.

Space groups therefore are built up by distributing a particular type of point group on a lattice of the same system; but with additional variations made possible by the fact that the point groups can be compounded by the operation of screw axes and glide planes.

This chapter provides an outline of the methods of space group derivation, and concentrates in some detail on the representation of space group symmetry and its application to real crystal structures.

16.2 Glide Planes

A glide plane is the three-dimensional equivalent of the glide-reflection element discussed in Chapter 14. It involves 'reflection' across the plane, as if it were a mirror plane, followed by translation in a direction parallel to the plane by $\frac{1}{2}$ of a lattice translation vector (Fig. 16.1).

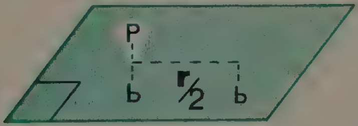


Fig. 16.1 The glide-reflection space group symmetry element.

The possible three-dimensional glide-reflection elements are summarised in Table 16.1. It can be seen that in addition to glide in the direction of the unit cell axis, it is also possible along the face diagonals, and in the case of a body centred cell, along body diagonals.

TABLE 16.1. THE GLIDE PLANE ELEMENTS

Glide plane element	*Translation component*		*Symbol*
	Direction	*Magnitude*	
Axial glide	|| to **a** axis	$\frac{\mathbf{a}}{2}$	*a*
Axial glide	|| to **b** axis	$\frac{\mathbf{b}}{2}$	*b*
Axial glide	|| to **c** axis	$\frac{\mathbf{c}}{2}$	*c*
Diagonal glide	|| to face diagonal	$\frac{\mathbf{a}+\mathbf{b}}{2}$, $\frac{\mathbf{b}+\mathbf{c}}{2}$, $\frac{\mathbf{c}+\mathbf{a}}{2}$	*n*
Diamond glide	|| to face diagonal for face centred cell	$\frac{\mathbf{a}+\mathbf{b}}{4}$, $\frac{\mathbf{b}+\mathbf{c}}{4}$, $\frac{\mathbf{c}+\mathbf{a}}{4}$	*d*
	|| to body diagonal for body centred cell	$\frac{\mathbf{a}+\mathbf{b}+\mathbf{c}}{4}$	

16.3 Screw Axes

In three dimensions we must also consider the interaction between rotation axes and parallel translations. The combination of one unit of rotation of $\frac{2\pi}{n}$ radians due to an n-fold axis followed by a translation of $\mathbf{a}\frac{m}{n}$ along the axis, where **a** is a lattice repeat vector and m an integer, give rise to a new symmetry element known as a screw axis. All possible variants of screw axes can be described using m values from 1 to $n-1$ because the lattice itself produces translations which are multiples of n, so in practice the general symbol of a screw axes n_m always has $m<n$.

The permitted screw axes together with the motifs used to identify them are shown in Fig. 16.2.

The operation of the 3_1 axis is straightforward and by convention the rotation is clockwise looking along the direction of translation and produces a right-handed thread. Now look at the 3_2 axis. The first symmetry operation translates the figure '7' two-thirds of the way down the unit cell and rotates it 120°, the second operation translates it out of the unit cell and one-third of the way down the next, also rotating it a further 120°. However, the operation of lattice translation repeats the figure, which has now been rotated 240°, at a position one-third of the way down the first cell. The net result is that the screw axis 3_2 is equivalent to 3_1 but with its sense of rotation reversed, i.e. a left-handed thread. Such pairs of axes are known as enantiomorphous and are analogous to the enantiomorphous pairs of axial point groups. They are of particular significance when considering the crystallography of helical polymers where especially close packing can be obtained between enantiomorphic pairs of molecules.

16.4 The Possible Space Groups

The simplest approach to the derivation of space groups is to take a particular point group symmetry, e.g. $m3m$, and add it to one of the Bravais lattices of the same system, say face centred cubic, to form the space group $Fm3m$. Note that the letter designating the type of unit cell (P, F, I, etc.) is written as a capital. The lattice type chosen must of course be compatible with the system in question (cf. Table 6.2). It remains to examine all possible combinations based on the substitution of the different types of

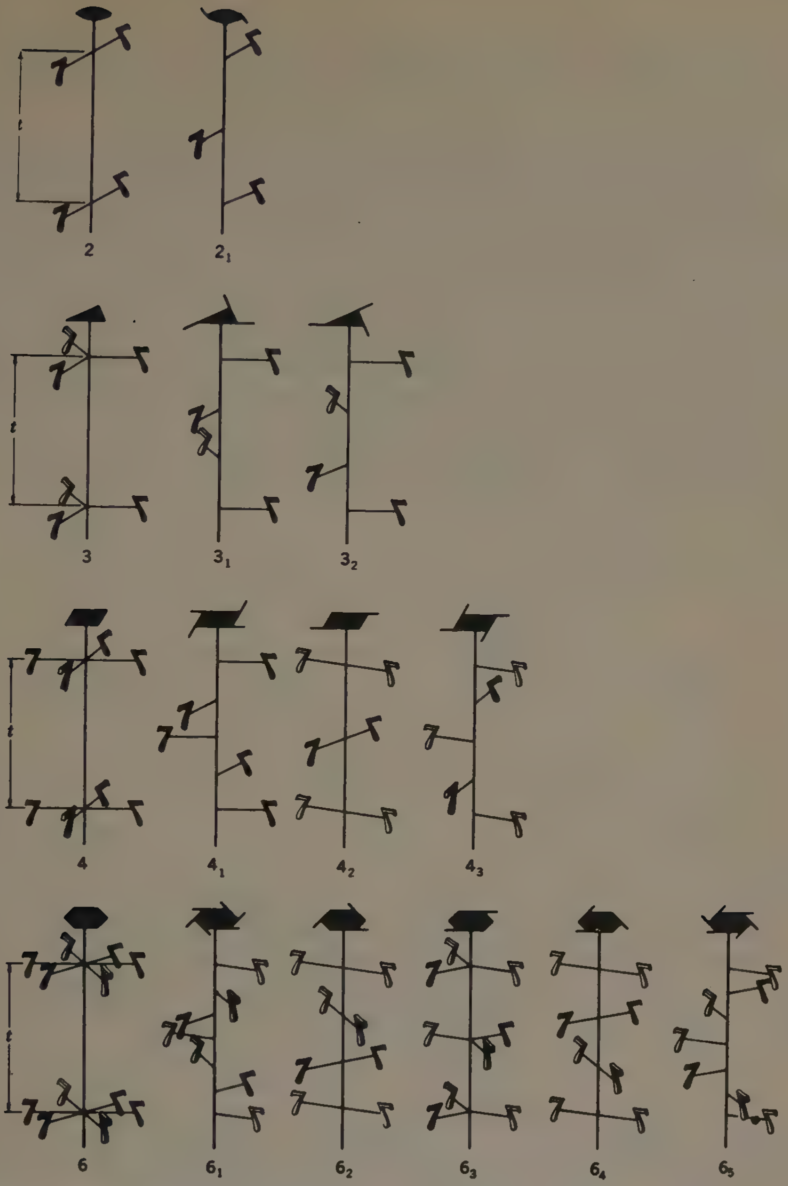


Fig. 16.2 The different types of screw axes. (Reproduced by permission from Azaroff: *Elements of X-Ray Crystallography*, McGraw-Hill.)

three-fold screw axis for the triads (in this example) and the various glide elements for the mirror planes. The resultant groups of symmetry elements must be self-consistent (i.e. one component must not invalidate another) and those which are equivalent to each other in spite of having apparently different arrangements of elements must be identified. When one considers the number of combinations of elements that must be reviewed and that groups of non-parallel screw axes may not necessarily intersect, the complexity of the task becomes apparent.

A branch of mathematics known as group theory can conveniently be applied to space group derivation and provides the most elegant solution to the problem. However, the manipulation of symmetry operations by means of group theory represents one of the more advanced aspects of crystallography and is beyond the scope of this text. We will, however, illustrate some of the first principles of space group derivation by generating the space groups based on the simple monoclinic point group, 2.

For this case the Bravais lattice types which are relevant are those compatible with the monoclinic system, that is, primitive (*P*) and base centred (*A* or *B*). Four possible combinations of lattice and point group elements which must be considered are shown in Fig. 16.3. The *B* centred cells, which for the monoclinic system are equivalent to the *A* centred ones, are not treated separately. The monoclinic cell is viewed, by convention, along the diads which are parallel to the *c* axis (i.e. in the 'first setting' cf. Fig. 15.9).

The circles on the cell plan represent symmetry related positions, called equivalent positions or **equipoints**, which are created by the operation of all the space group symmetry elements on one point in a general position at x, y, z. The symbol + by some of the circles and $\frac{1}{2}+$ by others indicates that the equipoints are displaced in the c direction by a positive fraction of the unit cell height in the first case, and by the same positive fraction plus $\frac{1}{2}$ of the unit cell height in the other. Note how the equipoints demonstrate the operation of the 2 and 2_1 axes.

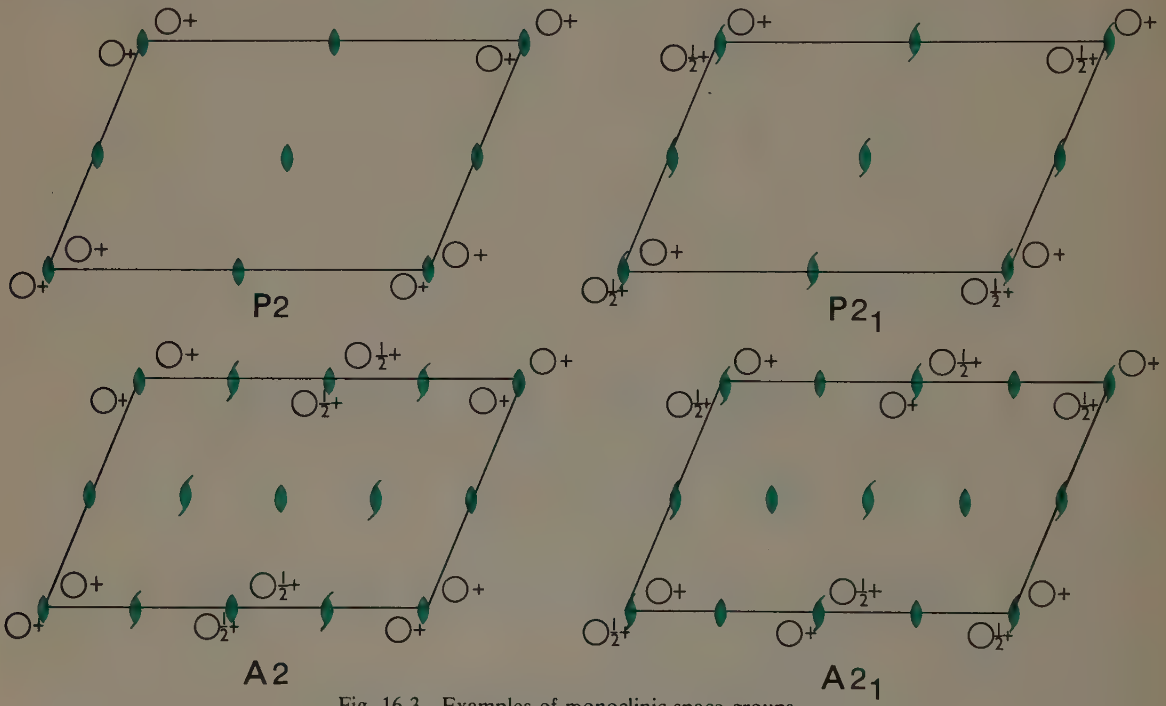


Fig. 16.3 Examples of monoclinic space groups.

Out of the four space groups $P2$, $P2_1$, $A2$ and $A2_1$; $A2$ and $A2_1$ can be seen to be equivalent with only the unit cell origins different. There are therefore three unique space groups based on the point group 2, and the symbol $A2_1$ is not used.

16.5 The Representation of Space Group Symmetry

In the previous section it was a comparatively simple matter to display the unidirectional 2 and 2_1 axes perpendicular to a plan of the unit cell. We will now consider how the symmetry elements of a more complicated space group can be represented, by looking at, as an example, the space group *Pnma* which is one of 28 such groups based on the point group *mmm* in the orthorhombic system.

Pnma is more fully written as $P\frac{2_1}{n}\frac{2_1}{m}\frac{2_1}{a}$, and consists of three orthogonal 2_1 screw axes perpendicular to: a diagonal glide plane, a mirror plane and an *a* glide plane respectively. By convention the first named axis is parallel to the *a* axis of the unit cell, the second parallel to the *b* axis, and the third parallel to *c*. It may happen however that, say, the *b* axis of a conventionally labelled structure cell is perpendicular to the axial glide plane instead of the mirror plane. This situation can be best handled by shuffling the space group symbols into the appropriate order to give one of the equivalent combinations listed in Table 16.2. Note that axial glide direction is always perpendicular to the diagonal glide plane, so that it is a '*b*' glide plane when the diagonal glide plane is perpendicular to the *b* axis of the unit cell, etc.

TABLE 16.2. EQUIVALENT COMBINATIONS OF *Pnma*

$P\frac{2_1}{n}\frac{2_1}{m}\frac{2_1}{a}$	$P\frac{2_1}{m}\frac{2_1}{n}\frac{2_1}{b}$
	$P\frac{2_1}{b}\frac{2_1}{n}\frac{2_1}{m}$
	$P\frac{2_1}{c}\frac{2_1}{m}\frac{2_1}{n}$
	$P\frac{2_1}{m}\frac{2_1}{c}\frac{2_1}{n}$
	$P\frac{2_1}{n}\frac{2_1}{a}\frac{2_1}{m}$

The conventional way of displaying the symmetry elements forming *Pnma*, is illustrated by Fig. 16.4 which is the reproduction of the appropriate page from the *International Tables of X-Ray Crystallography.* In the top left-hand corner the crystal system and class to which *Pnma* belongs are named; at centre top there is the full space group symbol; while at top right is the accepted abbreviated symbol together with a symbol belonging to another notation due to Schoenflies — in this case D_{2h}^{16} — which will not be considered further here.

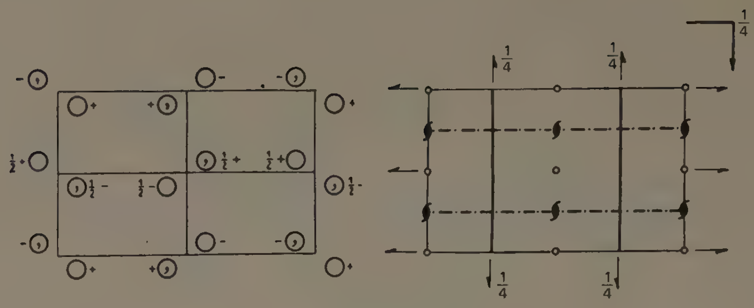
The left-hand of the two unit cell plans shows the equipoints generated by the operation of the space group symmetry on a point at the general position *x, y, z*. Equipoints marked with a ' , ' are mirror images of those with no ' , ' and the meaning of the $\frac{1}{2}+$ type symbols are the same as for the $P2_1$ and $A2$ space groups discussed in the previous section. The significance of equipoints together with the information below the two unit cell plans will be discussed further in the next section. The symmetry elements included in the full space group symbol are drawn on the right-hand plan, and both plans are drawn perpendicular tc the *c* axis with the *a* axis vertical down the page.

Focusing attention on the plan bearing the symmetry elements we will consider in turn each element of the full space group symbol, $P\frac{2_1}{n}\frac{2_1}{m}\frac{2_1}{a}$.

The 2_1 axes in the *a* direction (down the page) are drawn as split arrows just outside the cell plan. The values, $\frac{1}{4}$, by each arrow indicate that these 2_1 axes are displaced in the *c* direction by $\frac{1}{4}c$. The diagonal glide planes perpendicular to these axes are drawn as chain-dotted lines.

The 2_1 axes in the *b* direction are also represented by split arrows, but they are not displaced in the *c* direction. The mirror planes perpendicular to them are drawn as bold solid lines.

Orthorhombic $m\,m\,m$ $P\,2_1/n\,2_1/m\,2_1/a$ No. 62 $Pnma$ D_{2h}^{16}



Origin at $\bar{1}$

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
8	d	1	$x,y,z;\ \tfrac12+x,\tfrac12-y,\tfrac12-z;\ \bar{x},\tfrac12+y,\bar{z};\ \tfrac12-x,\bar{y},\tfrac12+z;$ $\bar{x},\bar{y},\bar{z};\ \tfrac12-x,\tfrac12+y,\tfrac12+z;\ x,\tfrac12-y,z;\ \tfrac12+x,y,\tfrac12-z.$	hkl: No conditions $0kl$: $k+l=2n$ $h0l$: No conditions $hk0$: $h=2n$ $h00$: $(h=2n)$ $0k0$: $(k=2n)$ $00l$: $(l=2n)$
				Special: as above, plus
4	c	m	$x,\tfrac14,z;\ \bar{x},\tfrac34,\bar{z};\ \tfrac12-x,\tfrac34,\tfrac12+z;\ \tfrac12+x,\tfrac14,\tfrac12-z.$	no extra conditions
4	b	$\bar{1}$	$0,0,\tfrac12;\ 0,\tfrac12,\tfrac12;\ \tfrac12,0,0;\ \tfrac12,\tfrac12,0.$	$\left.\right\}$ hkl: $h+l=2n$; $k=2n$
4	a	$\bar{1}$	$0,0,0;\ 0,\tfrac12,0;\ \tfrac12,0,\tfrac12;\ \tfrac12,\tfrac12,\tfrac12.$	

Symmetry of special projections

(001) pgm; $a'=a/2$, $b'=b$ (100) cmm; $b'=b$, $c'=c$ (010) pgg; $c'=c$, $a'=a$

Fig. 16.4 Representation of the space group *Pnma* reproduced from *International Tables of X-Ray Crystallography*.

The 2_1 axes perpendicular to the page are represented by the standard symbol introduced in Fig. 16.2 while the presence of an axial glide parallel to the page is shown by a right-angled arrow at the top right of the plan. The arrow points in the a direction (the direction of axial glide), and the figure $\tfrac14$ by the side of it indicates that the glide plane is displaced by $\tfrac14 c$ out of the page.

The positions of centres of symmetry are shown by small circles, and the fact that the origin of the unit cell is taken at one of these centres is confirmed by the statement 'Origin at $\bar{1}$' below the plans.

A summary of the various graphic symbols used to plot space group symmetry elements on a unit cell plan is given in Table 16.3.

Higher order screw and rotation axes are shown with the conventional symbols which may be drawn in perspective for axes parallel to the page.

TABLE 16.3. SYMBOLS FOR SPACE GROUP SYMMETRY ELEMENTS
(Based on *International Tables of X-Ray Crystallography*)

Element	*Symbol* *Normal to page*	*Parallel to page*
m		
a, b		
c		
n		
d		
2		
2_1		
Centre of symmetry		

When a centre of symmetry is coincident with an axis perpendicular to the page the symbol is modified (e.g. a 3_2 axis appears as ).

16.6 Equipoints

The equipoints shown in Figs 16.3 and 16.4 represent symmetry related positions within the unit cell. If one could visit all such positions in an actual crystal structure, the similarity between each site would be readily apparent. The differences, beyond those of spatial orientation, would be confined to variations associated with mirror images and inversions.

The equipoints illustrated are generated by the operation of the various symmetry elements on a point in a general position. In the case of space group *P*2 (Fig. 16.3), there are two such equipoints per unit cell. The **rank** of the equipoints is therefore 2, and the possible coordinates $x, y, z; \bar{x}, \bar{y}, z$. The operation of *P*2 on a point in a special position, which in this case means intersecting a diad, will generate only one equipoint in each unit cell. A summary of the positions of equipoints for the space group *P*2 are given in Table 16.4.

TABLE 16.4. EQUIPOINTS FOR SPACE GROUP *P*2

Rank	*Point group symmetry*	*Coordinates of equipoints*	
2	1	$x, y, z; \bar{x}, \bar{y}, z$	
1	2	$0, 0, z$	Special positions
1	2	$0, \frac{1}{2}, z$	
1	2	$\frac{1}{2}, 0, z$	
1	2	$\frac{1}{2}, \frac{1}{2}, z$	

Equipoint information can be a valuable asset to crystal structure determination. Let us say we have a compound AB_2 which crystallises in the monoclinic system with one molecule per unit cell and we know its space group is *P*2. The number of molecules per unit cell can be calculated from a knowledge of the molecular formula, unit cell volume and crystal density. The single atom of *A* in each unit cell must be in a special position of rank 1, for any attempt to put it in a general position will require a second atom in the same unit cell. The *B* atoms however will either both be in special positions or in a pair of equivalent general positions. Obviously the coordinates of the atoms will still have to be determined, but in a case as simple as this the combination of equipoint information with stereochemical data such as ionic size will provide a good estimate of the structure.

The equipoint information for the more complex space group *Pnma* is listed beneath the two unit cell plans in Fig. 16.4. The lay-out is much the same as that for *P*2 in Table 16.4, except that each of the equipoints is additionally distinguished by a letter of the alphabet. The letter *a* is assigned to what might be called the most specific special position, in this case the equipoints at centres of symmetry at 000, $0\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; the letter *b* is assigned to the next most specific special position and so on up to (in this case) the letter *d* for the general position. This notation is due to Wyckoff. Also in Fig. 16.4, there is information describing which X-ray 'reflections' can be expected to be missing as a result of this particular space group symmetry. It is expressed in terms of the conditions necessary for a reflection to be present.

16.7 A Case Study: The Crystal Structure of Aragonite

Aragonite is a crystalline form of calcium carbonate ($CaCO_3$) which is stable at room temperature. It belongs to the orthorhombic system, the *mmm* crystal class, and possesses the space group symmetry *Pnma* which we have already described in some detail.

(*a*) *Synthesis of structure from component atoms*

It is convenient, as a starting point, to consider the CO_3^{--} group as one of the building blocks of the aragonite structure. The C^{4+} ion has a radius of only 0·16 Å while the three O^{2-} ions each have a radius of 1·4 Å. The ratio of these two ionic radii is 0·11 which is not far removed from the ratio 0·16 which will allow the small ion to fit exactly in the middle of a triangle of three large ones (cf. Table 7.1). It is not surprising therefore that the CO_3^{--} group assumes triangular form, and the problem is reduced to one of describing the packing of Ca^{2+} ions of radius 1·0 Å together with the CO_3^{--} triangles. There is however a significant covalent contribution to the bonding between the carbon and oxygen atoms which also encourages the triangular arrangement of the oxygens. So that it is possible that the triangular format would be observed even if the radius ratio had a value very different from 0·16.

It has been determined that the calcium ions are in a hexagonal close packed arrangement (but not actually 'closepacked' in that the ions do not touch). The CO_3^{--} triangles which have an overall edge length of 5·6 Å are sited in the octahedral interstices between the calcium ions with the planes of the

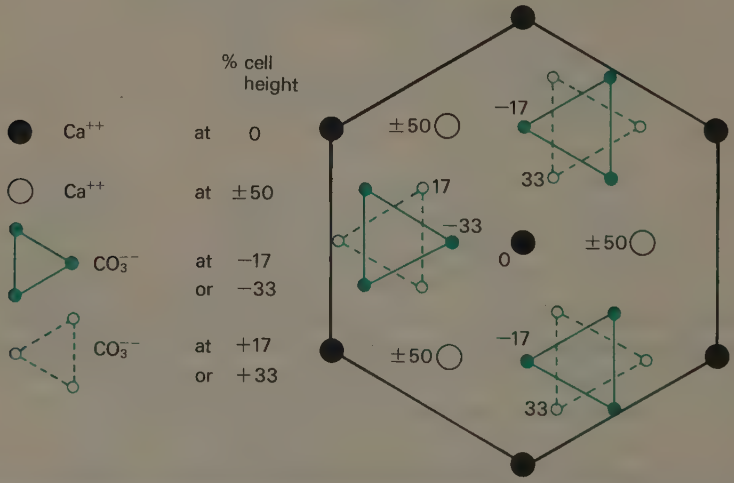


Fig. 16.5 Plan of the aragonite structure showing the positions of the oxygen ions in relation to an h.c.p. cell of calcium ions.

triangles parallel to the basal plane of the hexagon. The triangles fit in the rather open calcium octahedra either at $\frac{1}{6}$ cell height ($\frac{1}{3}$ of the octahedron height in a direction parallel to the *c* axis of the h.c.p. cell) or, after rotation by 180°, at $\frac{1}{3}$ height. Steric hindrance between oxygens in adjacent triangles means that out of the three octahedral interstices in the bottom half of the h.c.p. cell, two have CO_3^{2-} triangles at $\frac{1}{6}$ cell height and the third, one at $\frac{1}{3}$ height. The crystal structure, as a result of this arrangement, is relegated from the hexagonal to the orthorhombic system. A plan of the structure looking along the *c* axis showing the pseudo h.c.p. cell and the atom centre positions is drawn in Fig. 16.5.

The fact that there are three oxygen ions to every calcium and that both ionic radii are similar, means that in packing terms the calcium ions will be within coordination polyhedra of oxygens. It can be seen from Fig. 16.5 that each calcium ion has nine oxygen nearest neighbours. (Check this for yourself.)

(*b*) *Identification of space group symmetry elements*

Fig. 16.6 shows two projections of the aragonite unit cell looking along the *b* and *c* axes respectively. Space group symmetry elements are drawn in, and it can be seen that the three orthogonal 2_1 axes are, in turn, perpendicular to a mirror plane, an axial glide plane and a diagonal glide plane.

With reference to the two projections of the atom positions, personally verify that each of the **six** symmetry elements is marked in at the correct location, and draw in the 2_1 axes on the *c* projection.

The symmetry elements are those of the space group *Pnma* drawn in Fig. 16.4 and previously described at length. The mirror plane is perpendicular to the *a* unit cell axis, the axial glide is in the *c* direction with the glide plane perpendicular to the *b* axis and the diagonal glide plane is perpendicular to the *c* axis.

The full space group designation is therefore:

$$P\frac{2_1}{m}\frac{2_1}{c}\frac{2_1}{n} \quad \text{or} \quad Pmcn \text{ for short.}$$

(*c*) *X-ray diffraction and the aragonite structure*

Let us suppose that an X-ray diffraction photograph of aragonite has been prepared and each reflection indexed (i.e. assigned the indices of the diffracting planes which were responsible for it). The shape and dimension of the unit cell could then be determined from the photograph to be:

$$\text{orthorhombic}, \quad a = 4{\cdot}94\ \text{Å} \quad b = 7{\cdot}94\ \text{Å}, \quad c = 5{\cdot}72\ \text{Å}.$$

Because the translations associated with space group symmetry occur in increments of a few Ångstroms, the symmetry elements do not influence the external crystal form and for this reason space group symmetry is sometimes called **internal symmetry**. Space group symmetry however, has a marked effect on X-ray diffraction with glide and screw elements causing certain 'reflections' to be absent.

Examination of the indexed diffraction pattern of aragonite will reveal that no reflections having general indices *hkl* are absent. The lattice type is therefore confirmed as primitive.

Reflections of the type *h*00, 0*k*0 and 00*l* will be missing where *h*, *k* or *l* are odd numbers. This

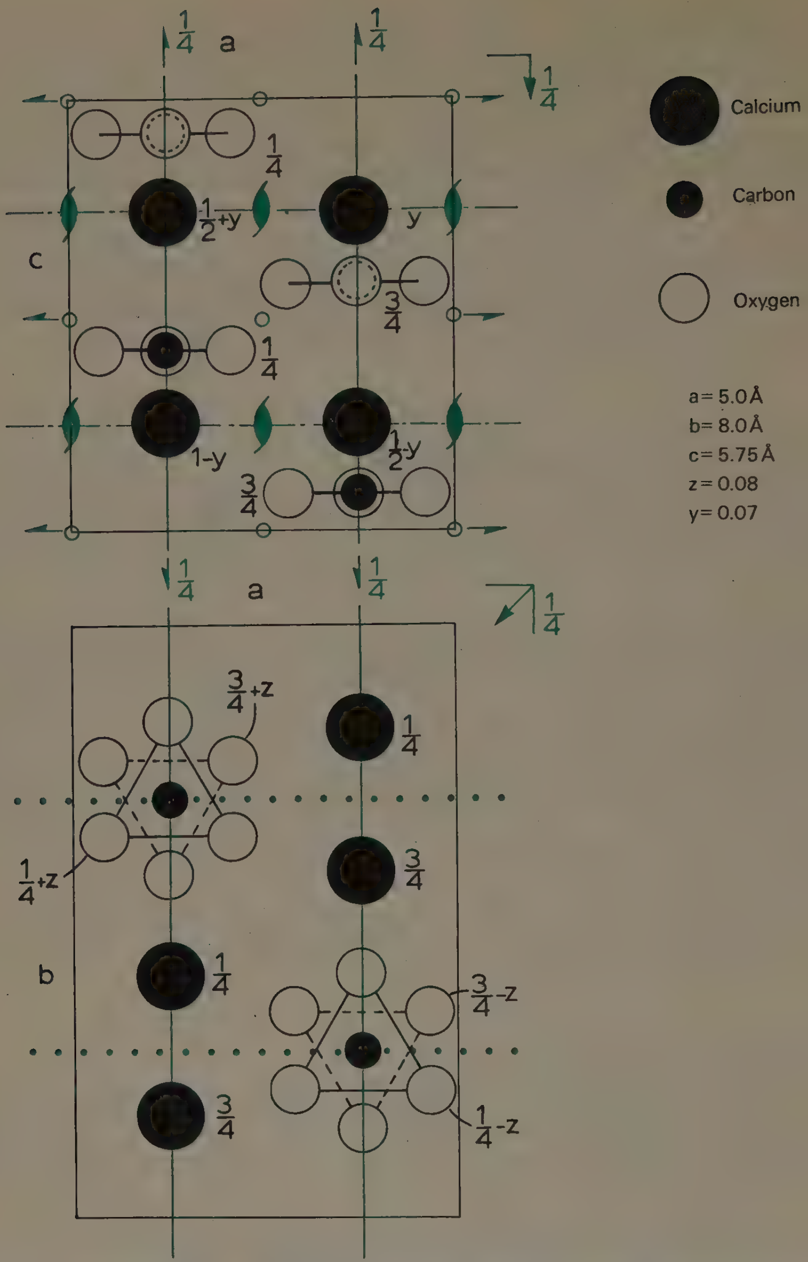


Fig. 16.6 Two projections of the structure cell of $CaCO_3$ (aragonite) showing the space group symmetry elements. The circles represent the atom centre positions and are smaller than the scale atomic size.

indicates that there is a 2_1 screw axis parallel to each of the principal axes. Reflections $h0l$ will be absent where l is odd revealing an axial glide plane perpendicular to the *b* axis with a glide direction *c*. Also *hk*0 reflections are missing when $h+k$ is odd, this is evidence for a diagonal glide plane perpendicular to the *c* axis. The presence of the mirror plane leads to no systematic absences, but the elements so far recognised are sufficient to fix the space group as *Pmcn*. The conditions for reflections to be **present** are listed in the right-hand column of Fig. 16.4.

Working on the assumption that the oxygen ions form a triangle around the carbon ions, we can make the next move in the structure determination by considering the equipoint information in Fig. 16.4. There are four $CaCO_3$ molecules in each unit cell. The Ca and C ions will therefore be distributed amongst the special positions listed. Because the carbon ion is surrounded by a triangle of O^- ions it cannot be at a centre of symmetry and the four carbons are therefore sited on the mirror planes. The CO_3^- triangles will have to be either parallel to these planes or at right angles, with their medians lying in the plane. In the first case the 12 oxygen ions will occupy three sets of special equipoints on the mirror planes, in the second only four oxygens will lie on the mirror planes, the remaining eight lying on one set of general equipoints. The calciums may lie either on the mirror planes or at either of the two sets of equivalent centres of symmetry. In the latter case *hkl* reflections in which both $k+l$ and h are odd integers, may be recognisably less intense than other *hkl* reflections because calcium ions at centres of symmetry will make no contribution to them. An absence of this effect on the diffraction pattern will suggest that the calciums are also on the mirror planes.

Now, if all oxygens are on the mirror planes, it will be necessary to fit six oxygen atoms (radius 1·40 Å) and two calcium atoms (radius 1·06 Å) (+ two carbons) into an area of 5·72×7·94 Å. The area of each mirror plane intersected by ions will then be 43 $Å^2$ whereas the total area of the plane is only 45·4 $Å^2$. Such packing is impossible, it would also be impossible if the calciums were at the centres of symmetry after all, so it must be concluded that the CO_3^- triangles are perpendicular to, and bisected by, the mirror planes.

Armed with this positional data, which is in accordance with the known structure, an approximate structure can be determined on the basis of most probable packing. The structure must be commensurate with the symmetry elements, and in particular with the centres of symmetry and mirror planes which cannot intersect an ion unless they are at its exact centre. The trial structure can be checked and refined by the use of more advanced X-ray methods involving calculations based on the measurement of the intensity of individual diffraction spots.

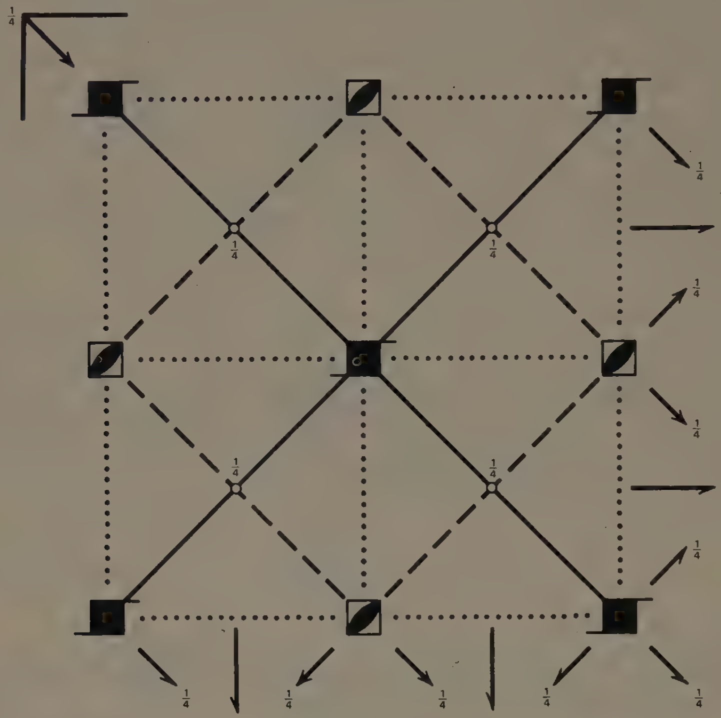
TO APPRECIATE

1. The combination of lattice translational symmetry with rotation axes and mirror planes to produce elements which are unique to space group symmetry.
2. The motifs used to indicate the various symmetry elements on a unit cell plan.
   (*a*) Rotation axes.
   (*b*) Roto-inversion axes.
   (*c*) Centres of symmetry.
   (*d*) Mirror planes.
   (*e*) Screw axes.
   (*f*) *a*, *b* and *c* glide planes.
   (*g*) Diagonal and diamond glide planes.
3. The presentation of space group information in the *International Tables of X-Ray Crystallography.*
4. The means of representing equipoint information on a unit cell plan and its usefulness in crystal structure determination.
5. The relationship between space group symmetry elements and X-ray reflections.

TO DO

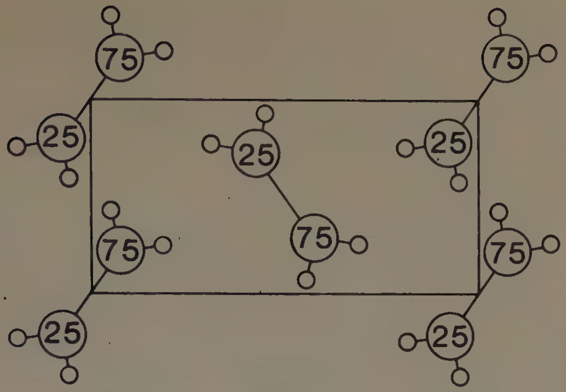
1. By referring to Fig. 16.2, list below the possible pairs of enantiomorphous screw axes.

2. Drawn below is a representation of a space group



What is the full space group symbol? ....
(Note that the third axial element of the symbol will be at 45° to be second, and that where different types of symmetry element are parallel, the space group symbol lists only the most basic element; i.e. rotation axis rather than screw axis, or mirror plane rather than axial glide plane rather than diagonal glide plane, and screw axis rather than rotoinversion axis).
What symmetry element does the symbol ◪ signify? ....
Draw in on the above diagram the equipoints derived from the general position *x*, *y*, *z* and check that they are consistent with all the symmetry elements.

3. The polyethylene molecule crystallises in the form of a planar zig-zag. The molecule itself has a 2_1 screw along its axis and perpendicular mirror planes bisecting each CH_2 group, see Fig. 7.20.
   The polyethylene unit cell is orthorhombic with the molecules aligned along the *c* axis. Looking along this direction at a unit cell plan, there is a molecule at each corner and one in the centre which has been rotated 110° about its axis. The unit cell is conventionally chosen so that the carbon atoms are at 25% *c* and 75% *c*.



(*a*) Draw in all the space group symmetry elements you can find on the above diagram.
(*b*) Determine the space group ....
(*c*) Mark in the positions of the centre of symmetry.
(*d*) What is the rank and point group symmetry of the equipoints corresponding to the carbon atom and hydrogen atom positions?

	Rank	*Point group symmetry*
Carbon	....	....
Hydrogen	....	....

4. The structure unit cell of diamond is face centred cubic with additional carbon atoms at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ and $\frac{3}{4}\frac{1}{4}\frac{3}{4}$. The structure of α Z*n*S is derived from diamond cubic, with the zinc atoms forming the f.c.c. cell and the sulphur atoms at the positions listed above. Diamond has a centre of symmetry, α Z*n*S does not.

Select the space groups of each of these two structures from the following list:

$$\begin{array}{ccc} F\bar{4}3m & F\frac{4}{m}\bar{3}\frac{2}{m} & F\frac{4_1}{d}\bar{3}\frac{2}{m} \\ \\ F\bar{4}3c & F\frac{4}{m}\bar{3}\frac{2}{c} & F\frac{4_1}{d}\bar{3}\frac{2}{c} \end{array}$$

Space group of diamond =

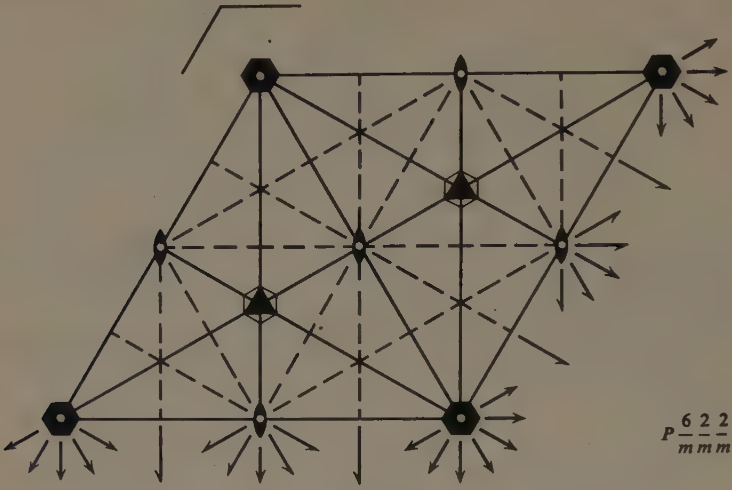
Space group of α Z*n*S =

Where, in unit cell coordinates, is the diamond centre of symmetry?

(It will be helpful to draw a plan of the unit cell remembering that the triad axes point to the cell corners; but do not necessarily expect to find the four-fold axes at the centre of the unit cell. A ball model of the unit cell would also be useful.)

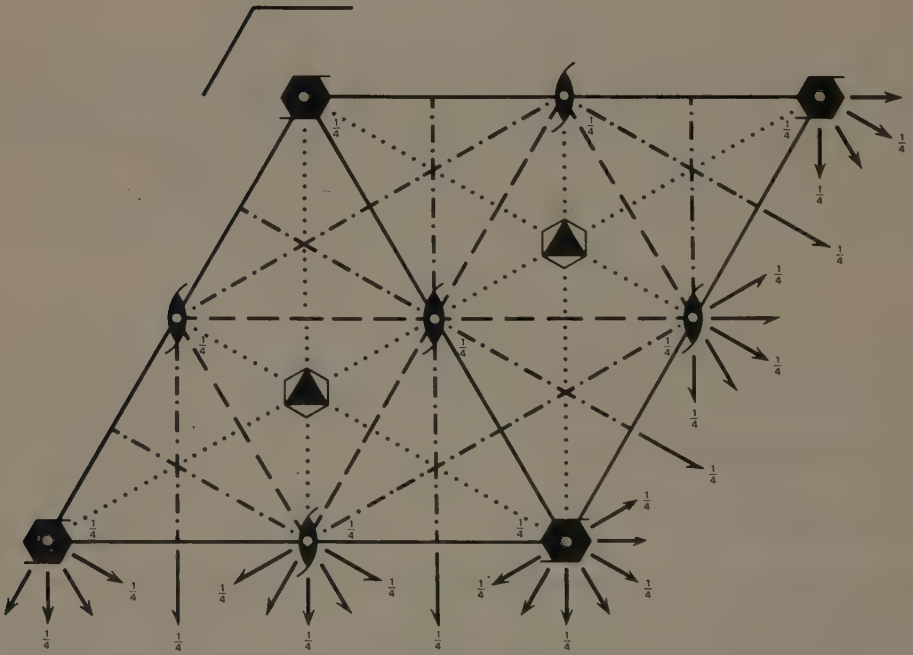
5. The four diagrams below and overleaf, show some space groups of the hexagonal system. Determine which one of the four describes the symmetry of the hexagonal close packed structure.

h.c.p. space group =



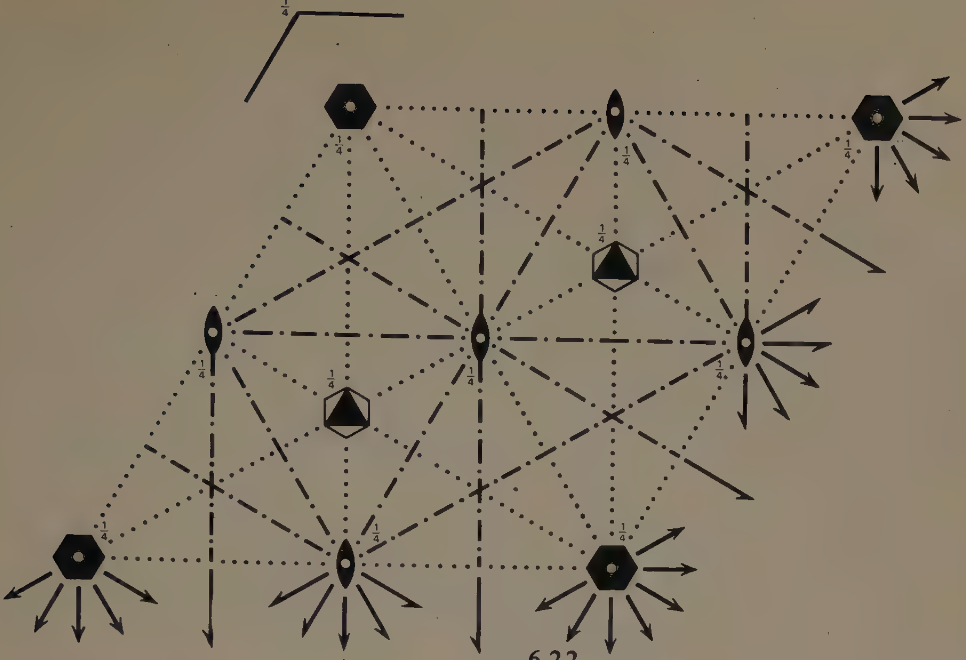
$P\frac{6}{m}\frac{2}{m}\frac{2}{m}$.

Fig. 16.9



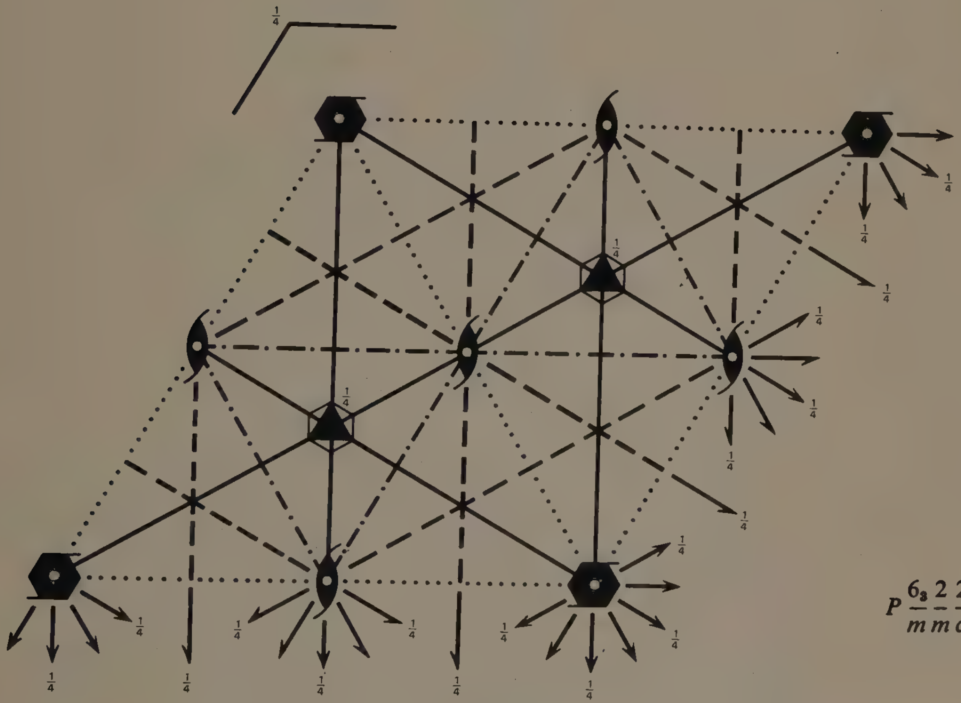
$P\frac{6_3}{m}\frac{2}{c}\frac{2}{m}$.

Fig. 16.10



$P\frac{6}{m}\frac{2}{c}\frac{2}{c}$.

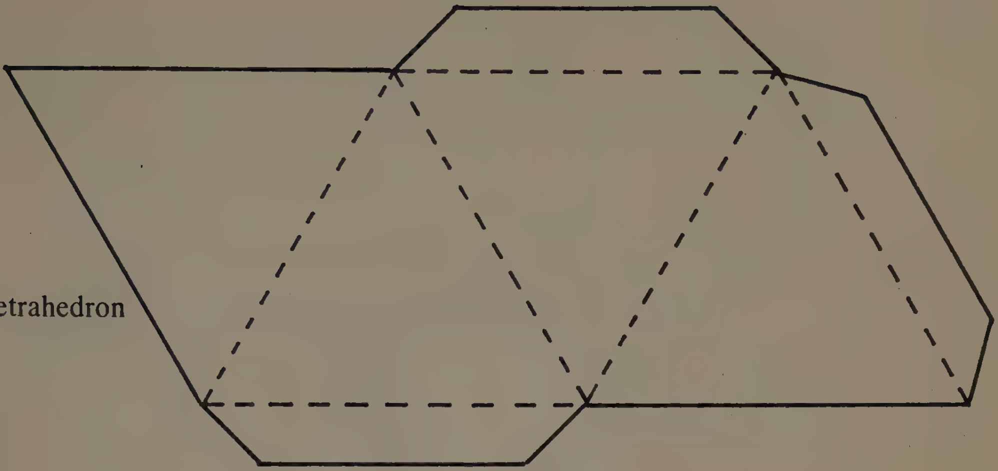
Fig. 16.11



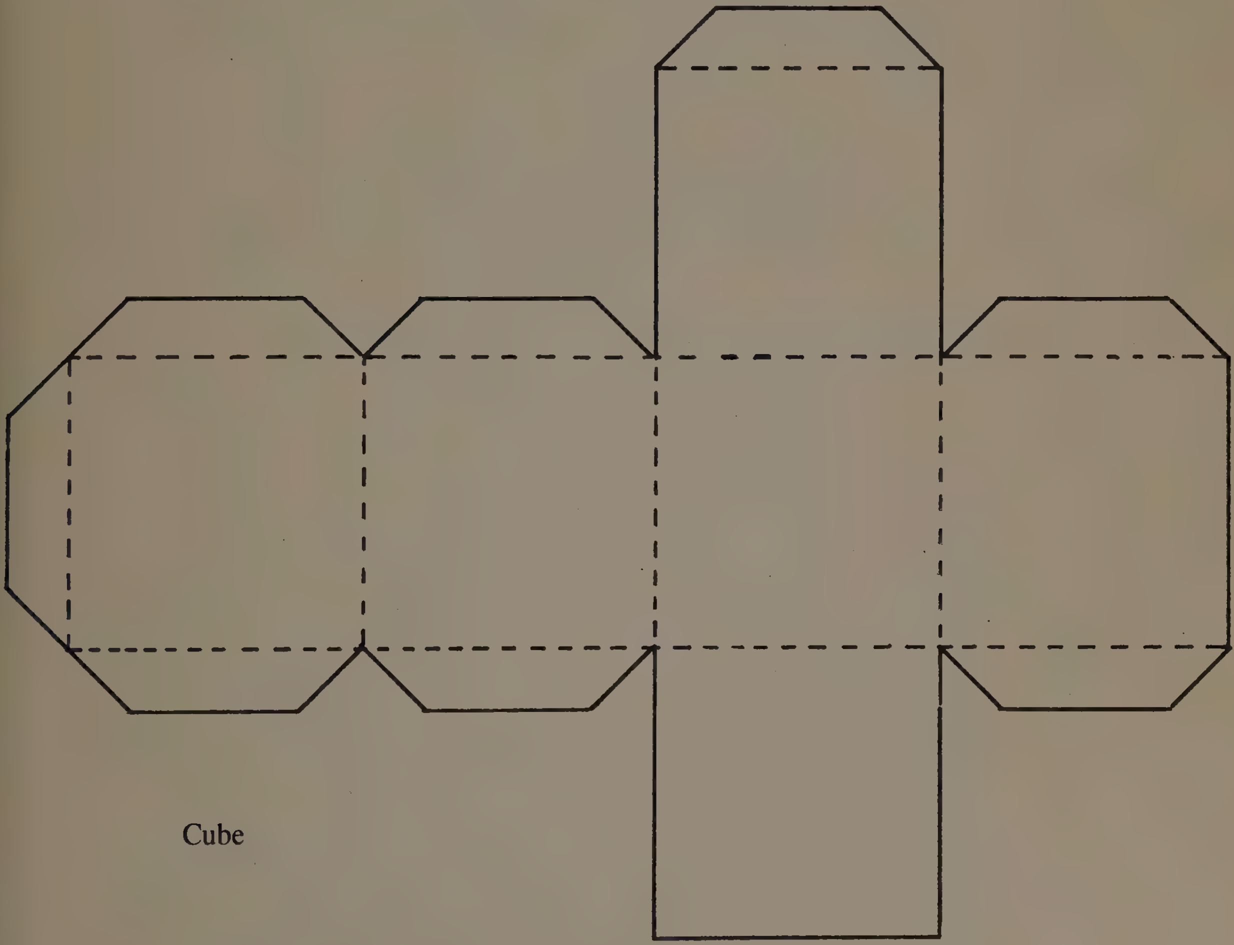
$P\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$.

Fig. 16.12

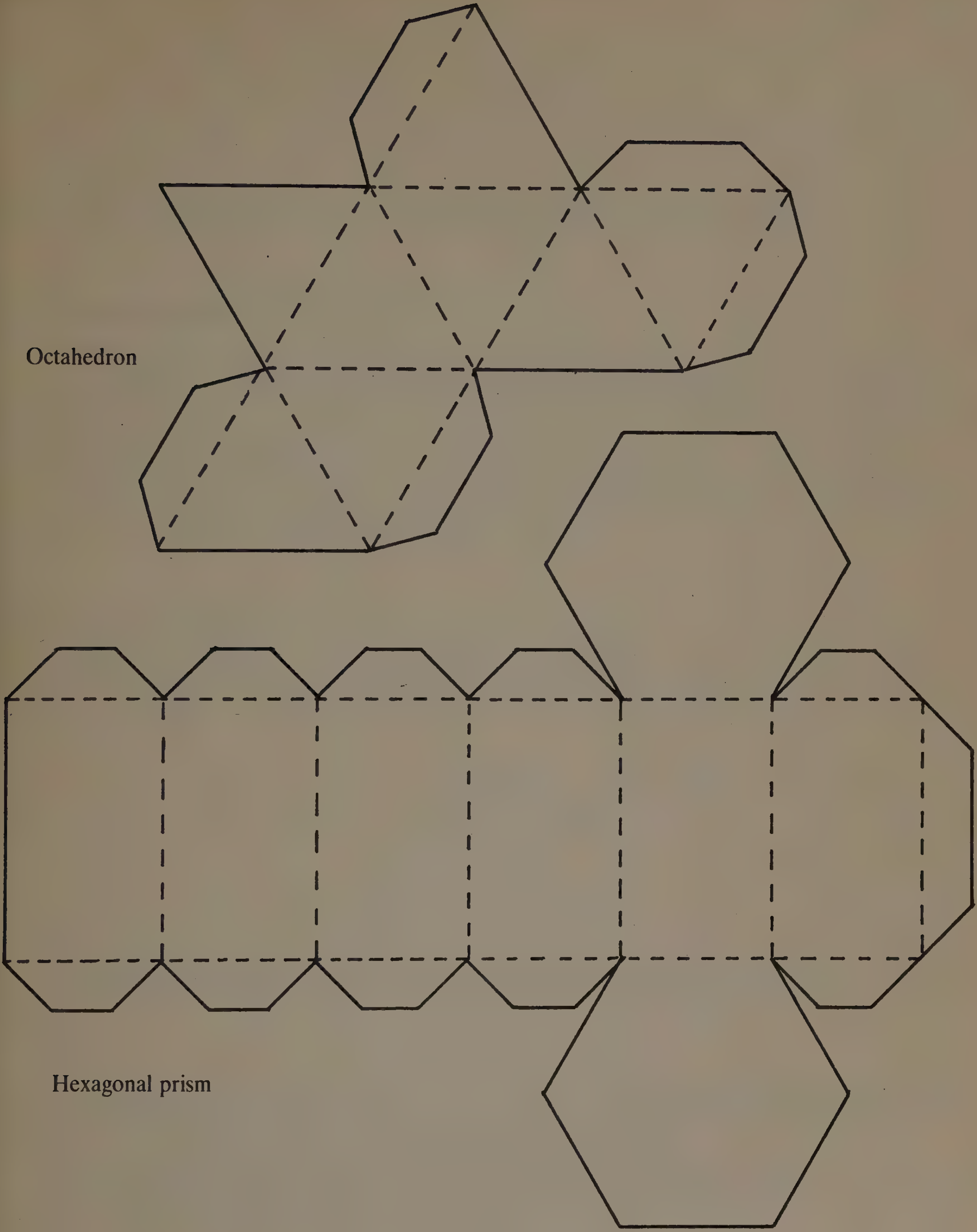
Appendix 1



Tetrahedron



Cube



Octahedron

Hexagonal prism

Appendix 2 Vectors from Scratch

(a) Representation of a Vector

The wind has both direction and magnitude. It is therefore a vector quantity and can be represented as an arrow which points in the direction it is blowing with a length proportional to its speed. Another use of a vector is to describe the relative positions of two points, say on a map or in a crystal structure. The length of the vector is proportional to the distance between the two points and its orientation is the relative orientation of the points.

A vector is indicated algebraically by either underlining the symbol or printing it in bold type, i.e. the vector 'a' is written $\underline{a}$ or **a**. In contrast to a vector, a quantity which has only magnitude but not direction (e.g. density, temperature, etc.) is called a scalar.

(b) Vector Addition and Coordinates

Consider moving from lattice point A to lattice point C on the planar lattice in Fig. A2.1. It is possible to go either directly there as described by vector **r** or via (say) point B along **a** and **b**.

In this case the vector **r** is the same thing as the sum of vectors **a** and **b**, and this is indicated by the relation $\mathbf{r}=\mathbf{a}+\mathbf{b}$.

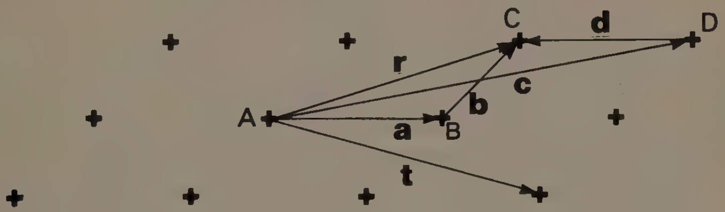


Fig. A2.1

Alternatively it is possible to go from A to C via point D along the vectors **c** and **d**. The vector **d** is of the same length and orientation as **a** but points in the opposite direction. It can therefore be written as $-\mathbf{a}$.

$$\text{So } \mathbf{r}=\mathbf{c}+\mathbf{d}=\mathbf{c}-\mathbf{a}.$$

Any vector in the above lattice can be described in terms of the addition of multiples of one pair of primitive vectors (cf. Chapter 2). In Fig. A2.1 for example we could take **a** and **b** as the primitive vectors in which case $\mathbf{r}=1\mathbf{a}+1\mathbf{b}$ (as above), $\mathbf{c}=2\mathbf{a}+\mathbf{b}$ and $\mathbf{t}=2\mathbf{a}-\mathbf{b}$.

The vectors **a** and **b** could also be drawn from the same origin, say 'A', in which case they will form the basis of coordinate axes. In terms of such axes the point 'C' will have the coordinates 1,1 the point 'D' 2,1 point 'B' 1,0 and point 'A' 0,0.

(c) Unit Vector and the Resolving of Vectors

A vector **a** can be split algebraically into its component parts. Its magnitude, a scalar quantity, can be written as | **a** | or simply '*a*' and its direction represented by a unit vector **A** which has the direction of **a** but unit magnitude. It follows that **a** = | **a** | **A**.

Frequently one wishes to know the component of a vector **a** in a particular direction which we will designate by a unit vector **B** (see Fig. A2.2).

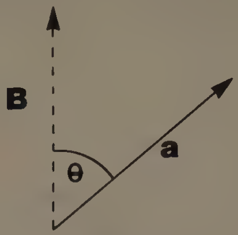


Fig. A2.2

By simple trigonometry the component of the vector **a** in the direction of **B** is | **a** | cos θ. The magnitude of this component can be considered as the product of the magnitudes of **B** (= 1) and **a** multiplied by cos θ.

(d) Scalar Product

In the previous section the magnitude of the resolved vector **a** was given by | **a** | | **B** | cos θ. This is in fact a particular example of what is know as a Scalar Product . of two vectors. In general the scalar product of the vectors **a** and **b** is a scalar of magnitude | **a** | . | **b** | cos θ and is written **a** . **b** (it is also known sometimes as a 'dot product').

(e) Vector Product

The magnitude of the vector product of the two vectors **a** and **b** is given by | **a** | | **b** | sin θ where θ is the angle between them. The product is written **aXb** and sometimes referred to as a 'cross product'. However unlike the scalar product, the vector product is itself a vector. The direction of this vector is perpendicular to both **a** and **b**, and its direction is such that a clockwise screw in this direction would produce a rotation which would pass through **a** before **b** when the angle between **a** and **b** is less than 180° (Fig. A2.3).

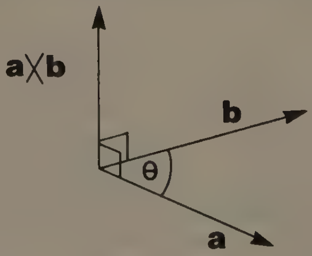


Fig. A2.3

(f) An Example of Vector Algebra

In Section 11.3 the expression for the spacing of lattice planes is written as:

$$\mathbf{d}_{(hkl)} = \frac{n}{(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)}$$

This can be expressed in non-vector terms by multiplying the expression by itself to give the scalar product. It is also convenient to work in terms of 1/**d**.

Therefore:

$$\frac{1}{\mathbf{d}_{(hkl)}} \cdot \frac{1}{\mathbf{d}_{(hkl)}} = \frac{1}{d^2_{(hkl)}}$$

$$= \frac{1}{n^2}\ (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)$$

Enumerating the scalar products between the vectors term by term, we have

$$\begin{aligned}
h\mathbf{b}_1 \cdot h\mathbf{b}_1 &= h^2 b_1^2 \\
k\mathbf{b}_2 \cdot k\mathbf{b}_2 &= k^2 b_2^2 \\
l\mathbf{b}_3 \cdot l\mathbf{b}_3 &= l^2 b_3^2 \\
h\mathbf{b}_1 \cdot k\mathbf{b}_2 &= hkb_1b_2 \cos\gamma \text{ (twice)} \\
k\mathbf{b}_2 \cdot l\mathbf{b}_3 &= klb_2b_3 \cos\alpha \text{ (twice)} \\
l\mathbf{b}_3 \cdot h\mathbf{b}_1 &= lhb_3b_1 \cos\beta \text{ (twice)}
\end{aligned}$$

therefore

$$\frac{1}{d^2_{(hkl)}} = \frac{1}{n^2}\ (h^2b_1^2 + k^2b_2^2 + l^2b_3^2 + 2hkb_1b_2\cos\gamma + 2klb_2b_3\cos\alpha + 2lhb_3b_1\cos\beta)$$

Appendix 3 Understanding the Reciprocal Lattice

'The Reciprocal Lattice is the Fourier Transform of the Real Lattice'

(a) What is a Fourier Transform?

A violin playing 'B^b' makes a very different sound from a French Horn playing the same note.

There are two ways of explaining this difference. It is possible in one case to speak in terms of the sound waveforms produced and say that the violin makes a 'saw tooth' wave whereas the horn's note has a more rounded waveform (Fig. A3.1).

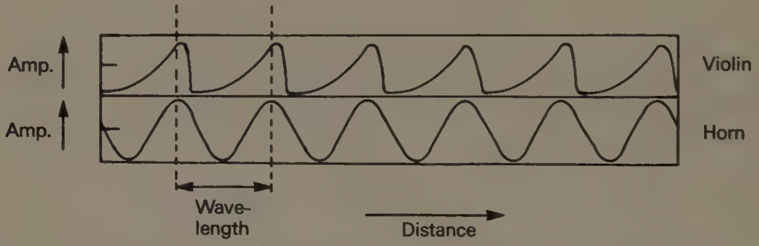


Fig. A3.1 The recorded sound waveforms of two musical instruments (schematic only).

One can, on the other hand, explain the difference between the two sounds in completely different terms. It can be said that the overtones or harmonics of the two instruments have different relative amplitudes. Here one is talking in terms of pure sine waves and saying in effect that any waveform can be viewed as a series of sine waves; a fundamental with the same wavelength as the waveform and overtones with wavelengths which are simple fractions of the fundamental, i.e. $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, $\frac{1}{5}$, etc.

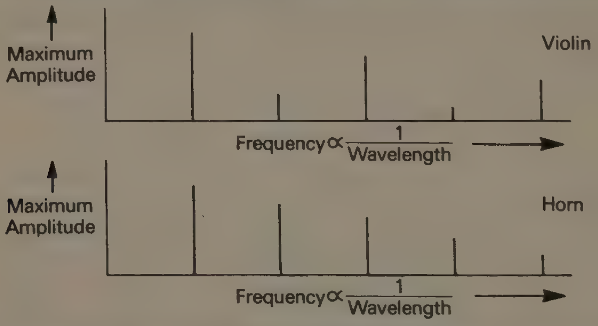


Fig. A3.2 Frequency–amplitude diagram for the sinusoidal components of the waveforms in Fig. A3.1.

Now, for conditions of constant sound velocity, the wavelength is proportional to the reciprocal of the frequency, so it is possible to represent any waveform by plotting the frequencies of the fundamental and overtones against the maximum amplitude of the sine wave in each case (Fig. A3.2).

We have said nothing about the relative phases of the fundamentals and overtones; these are best taken care of by using two maximum amplitude–frequency plots, one for sine and the other for cosine components. The necessity for both sines and cosines can be avoided however, if the peaks of the original waveform are symmetrical as in the case of the horn.

J. B. J. Fourier who was a scientific adviser to Napoleon was the first to appreciate that any waveform could be broken down into component sine waves, and the mathematical relationship between Fig. A3.1 and Fig. A3.2 is known as a Fourier transform.

The transform is fully defined as:

$$F_{(\mathbf{s})} = \int_{-\infty}^{\infty} f_{(\mathbf{r})}\, e^{2\pi\, i(\mathbf{s}\cdot\mathbf{r})}\, d\mathbf{r}$$

where **r** is a vector with units of length and **s** is a vector with units of reciprocal length.

A waveform is really, by definition, a periodic function and the transform of such a function will be periodic too. Correspondingly the transform of a non-periodic function will itself be non-periodic.

(b) Lattice Planes and Reciprocal Lattice Points

Imagine moving through a crystal structure in a direction perpendicular to a particular set of planes, say (100). One would observe a periodic variation in electron density which can be represented as a waveform. In the case of a lattice, rather than a structure, the planes are infinitely thin and the waveform will appear as in Fig. A3.3.

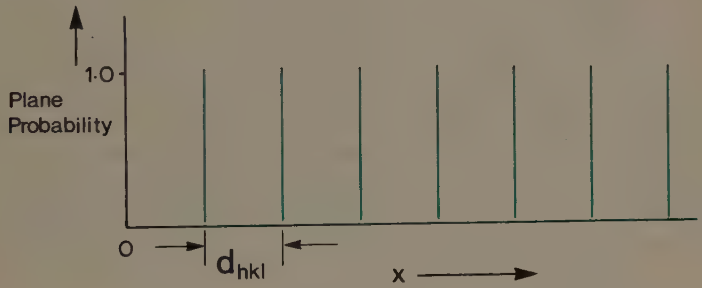


Fig. A3.3

This waveform differs in two ways from those considered in the previous section:

(*i*) Its amplitude is always positive.
(*ii*) It is discontinuous, the peaks being infinitely sharp.

In terms of the Fourier analysis (*i*) is taken into account by including a further ‘d.c.’ type component which has effectively infinite wavelength. The transform of this component gives an infinitely sharp peak at the origin on the 1/*wavelength* axis. The fact that the waveform is infinitely sharp means that the amplitude of the sine components remains constant right up to very high values of *n*.

The Fourier transform of one set of lattice planes is shown in Fig. A3.4. Because of the equal amplitude of the components the diagram can be simplified to a row of points at intervals of 1/*d*, in fact a one-dimensional **reciprocal lattice**, stretching on either side of the origin to plus and minus infinity (Fig. A3.5).

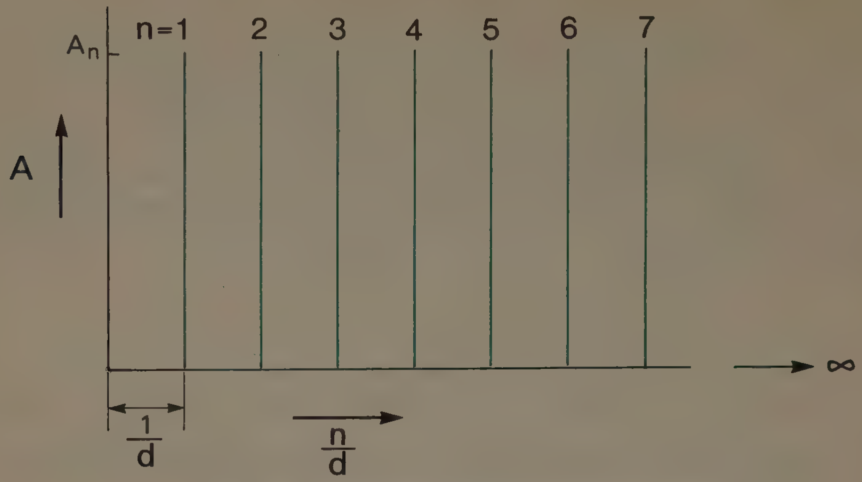


Fig. A3.4 The Fourier transform of one set of planes.

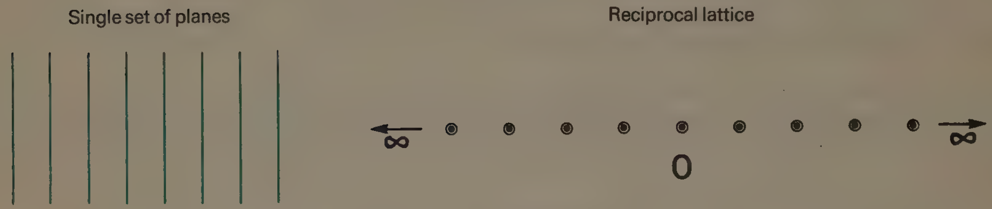


Fig. A3.5 A single set of planes and their Fourier transform drawn as a one-dimensional reciprocal lattice.

If one considers various sets of planes all perpendicular to the page, then their Fourier transforms will build up an infinite two-dimensional reciprocal lattice (Fig. A3.6).

In both two and three dimensions the Fourier transform of a lattice is another lattice in reciprocal space. The translation from the origin of the reciprocal lattice to any lattice point is described by a vector which has a magnitude equal to the reciprocal of the wavelength of one of the Fourier components of the real lattice. It is called the reciprocal lattice vector and is frequently designated **g**. This should be distinguished from the wave vector used by physicists which is defined with a magnitude $\frac{2\pi}{nh}$

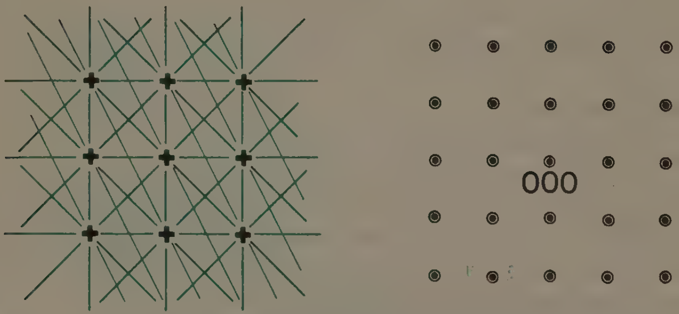


Fig. A3.6 A section of a real lattice showing a series of planes perpendicular to the page and the planar reciprocal lattice corresponding to these planes.

Each row of reciprocal lattice points passing through the origin is derived from a particular set of lattice planes. The (100) set of planes will therefore give a row of reciprocal lattice points with coordinates ±000, 100, 200, 300 . . . expressed in terms of the reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$. Similarly the set of planes (124) will give a row of reciprocal lattice points with coordinates ±000, 124, 248, . . ., etc.

There is a general pattern then that the coordinates of the reciprocal lattice points are equal to, or exact multiples of, the Miller indices of the lattice planes from which they are derived. However for this statement to be always true, the coordinates must be based on a pair of translation vectors (primitive or lattice) of the reciprocal lattice which correspond to the planes of the real lattice forming the faces of the lattice unit cell.

(c) Fourier Transform of a Crystal Structure

A crystal structure can be built up by positioning a motif unit on every lattice point. Mathematically this is the process of convolution of two functions one of which happens to be the lattice. Now, there is a theorem which states that the Fourier transform of the convolution of two functions (in this case the crystal structure) is equal to the product of the Fourier transforms of the individual functions.

The implications of this theorem are far reaching. The transform of a crystal structure is simply the transform of the crystal lattice, i.e. the reciprocal lattice, multiplied by the transform of the motif. It still looks like a reciprocal lattice but the amplitude at each of the points is variable as it is modulated by the transform of the motif.

Appendix 4 Notes and Answers for the Exercises

Chapter 1

2. The sodium chloride lattice is face centred cubic. There are two atoms, one sodium one chlorine, in each repeating unit, any adjacent pair will do.

Chapter 2

1. Vector pairs $\boxed{1}$ and $\boxed{2}$ are primitive. Combinations of vectors $\boxed{3}$ will not give translations to all the lattice points.

3. $\mathbf{r}_1 = \mathbf{a}_1 + 2\mathbf{a}_2$
   $\mathbf{r}_2 = -2\mathbf{a}_2$
   $\mathbf{r}_3 = -5\mathbf{a}_1 - 2\mathbf{a}_2$
   $\mathbf{r}_4 = 2\mathbf{a}_1 - \mathbf{a}_2.$

4. $\mathbf{r} = -\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3.$

Chapter 3

1. A primitive cell can only have lattice points at its corners. There must be none within it or cutting its sides.

2. Cell no. 1 2 lattice points.
   Cell no. 2 1 lattice point, therefore primitive.
   Cell no. 3 4 lattice points.
   Cell no. 4 1 lattice point, therefore primitive.

3. Two lattice points.

Chapter 4

2. Hexagonal prism 1 hexad, 6 diads.
   Tetrahedron 4 triads, 3 diads.

3. Cube 4 triads, 3 tetrads, 6 diads.
   Octahedron 4 triads, 3 tetrads, 6 diads.

4. Cube — 9 Mirror planes.
   Hexagonal prism — 7 Mirror planes.

5. Tetrahedron does not.

Chapter 5

1. The lattice is centred rectangular.

Chapter 6

1. (*a*) Planar spacing $= a$.
   (*b*) Planar spacing $= a/2$.
   (*c*) Planar spacing $= a/\sqrt{2}$.

2. Take the central lattice points of the top and bottom hexagons as two opposing corners of the primitive cell.

Chapter 8 Section 8.3

The following clues may help:
β Zr has two atoms per unit cell while nickel has four. The structure cell of Ge is f.c.c. with the Ge atoms at lattice points and in half of the tetrahedral interstices. Both Au and Cu are f.c.c. and the structure cell of α Zr is h.c.p.

It might be true to say that the structure cell of ordered Cu_3Au is f.c.c.

FeS can be thought of as two non-primitive h.c.p. cells on top of each other with one rotated 60° around the *c* axis with respect to the other.

Chapter 9

1. The directions of the type $\langle 121 \rangle$ in both index systems are:

$$\begin{array}{llcll}
[121] & [01\bar{1}1] & \qquad & [\bar{2}\bar{1}1] & [\bar{1}011] \\
[211] & [10\bar{1}1] & & [1\bar{1}1] & [1\bar{1}01] \\
[\bar{1}\bar{2}1] & [0\bar{1}11] & & [\bar{1}11] & [\bar{1}101].
\end{array}$$

In addition to these six there are also a further six equivalent and exactly opposite directions in which the indices are as above but with all the signs changed, i.e. $[\bar{1}\bar{2}\bar{1}]$ $[0\bar{1}1\bar{1}]$, etc.

2. $[\bar{1}12] = [1\bar{1}2] = [1\bar{1}\bar{2}] = [\bar{1}1\bar{2}]$.

3. $\langle 111 \rangle$ — body diagonals.
   $\langle 110 \rangle$ — face diagonals.

4. $[121]$ $[211]$ $[\bar{1}21]$ $[\bar{2}11]$ $[1\bar{2}1]$ $[2\bar{1}1]$ $[\bar{1}\bar{2}1]$ $[\bar{2}\bar{1}1]$.
   And opposite directions ($[\bar{1}\bar{2}\bar{1}]$, etc.) in each case.

Chapter 10

1. (121), $(\bar{1}\bar{2}1)$ and the opposite equivalents, $(\bar{1}\bar{2}\bar{1})$, $(12\bar{1})$.
2. The planes in the zone are: (010) $(20\bar{1})$ $(\bar{2}\bar{2}1)$ $(43\bar{2})$.
4. $(1\bar{1}1)$ $(\bar{1}11)$ $(11\bar{1})$.
   The plane $(111)_{\text{non primitive}}$ does not correspond to any plane of the type $\{100\}_{\text{primitive}}$ but because of the cubic symmetry it must belong to the same form. In fact $(111)_{\text{non primitive}} = (111)_{\text{primitive}}$.
   The primitive unit cell therefore contains four equivalent planes with the indices (100) (010) (001) (111).
5. Miller indices: (102) (012) $(\bar{1}12)$ $(\bar{1}02)$ $(0\bar{1}2)$ $(1\bar{1}2)$ — and their opposite equivalents.

Chapter 11

Section 11.3 0·193Å^{-1}/cm.

2. A.
3. b.c.c.

Chapter 12

2. (*b*) Angle of rotation 54·7°.
   (*c*) Triad.
   (*d*) $[11\bar{1}]$ could well not have been plotted on the 111 standard projection as it does not appear on the 100 standard. Observe however the behaviour of $[\bar{1}\bar{1}1]$ during rotation from the 100 to the 111 standard. After 35° rotation it reaches the perimeter of the stereogram and as it disappears $[11\bar{1}]$ appears at the diametrically opposed point and moves into the stereogram during the remaining 20° of rotation.
3. (*e*) Direction 1 $\langle 110\rangle$.
   Direction 2 $\langle 100\rangle$.
   Direction 3 $\langle 110\rangle$.
4. (*h*) Angle between y axis and $[001] = 36°$.
   Angle between y axis and $[011] = 16°$.
   Angle between y axis and $[111] = 25°$.
5. Slip plane $= \{111\}$.
6. (*a*) $(0001)\widehat{\ }\{10\bar{1}1\} = 59{\cdot}66^\circ$.
   $(0001)\widehat{\ }\{11\bar{2}1\} = 71{\cdot}33^\circ$.
   (*c*) $[11\bar{2}1]\widehat{\ }[0001] = 63{\cdot}74^\circ$.
   $[11\bar{2}1]\widehat{\ }(11\bar{2}1)_{\text{normal}}$ $7{\cdot}6^\circ$.

Chapter 14

1. 1, 2*mm*, 2*mm*, 2, *m*.

3. The likely systems are:

(*a*) Parallelogram
(*b*) Hexagonal
(*c*) Rectangular
(*d*) Parallelogram
(*e*) Rectangular
(*f*) Square
(*g*) Hexagonal.

4. The glide-reflection planes in $p31m$ are parallel to the mirror planes.

5. Plane groups:

(*a*) $c2mm$
(*b*) $p6mm$
(*c*) $p3m1$
(*d*) $p2gg$.

6. (*a*) Start by first opposing reflected pairs of symbols commensurate with the point group $2m$. These can be arranged at the corners of a rectangular cell with another inverted pair at the cell centre to give *pmg*.
   (*b*) In order to create the plane group $p1$ the two fold symmetry inherent in the symbol must be suppressed. This can be done by combining two of the symbols with different orientation. They can either be superimposed or adjacent. The multiple symbol can then be placed on a parallelogram lattice.
   (*c*) In this case the neatest approach is to superimpose three symbols to form a composite one with point group symmetry 6. These can then be placed at the corners of a hexagonal cell.
   (*d*) One symbol at each corner and one reversed at the centre of a rectangular unit cell will form this plane group.

Chapter 15

1. $\tilde{1}=\bar{2};\ \tilde{2}=\bar{1};\ \tilde{3}=\bar{6};\ \tilde{4}=\bar{4};\ \tilde{6}=\bar{3}.$

2. (*a*) $\frac{4}{m}\bar{3}\frac{2}{m}$; (*b*) $\frac{4}{m}\bar{3}\frac{2}{m}$; (*c*) $\bar{4}3m$.

3. (*a*) 233; (*b*) $\frac{2}{m}\bar{3}\bar{3}$; (*c*) $\frac{2}{m}\frac{2}{m}\frac{2}{m}$; (*d*) 222; (*e*) 422; (*f*) $3m$.

4. $\bar{4}2m$ $\bar{3}\frac{2}{m}\frac{2}{m}$ $2mm$.

5.
$\bar{1}$
$\frac{2}{m}$
$\frac{2}{m}$
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$

$\frac{4}{m}\frac{2}{m}\frac{2}{m}$
$\frac{4}{m}\frac{2}{m}\frac{2}{m}$
$\frac{6}{m}\frac{2}{m}\frac{2}{m}$
$\bar{3}\frac{2}{m}\frac{2}{m}$
$\frac{4}{m}\bar{3}\frac{2}{m}$
$\frac{4}{m}\bar{3}\frac{2}{m}$
$\frac{4}{m}\bar{3}\frac{2}{m}$

Note that all the lattice point groups are centrosymmetric.

Chapter 16

2. Because of the absence of triads at 35° to the unit cell plan, the space group is not cubic but tetragonal. The main axis is 4_2 perpendicular to a diagonal glide plane (n), there is a 2_1 axis horizontal on the page perpendicular to a c glide plane, and 2 and 2_1 axes diagonal on the page which are perpendicular to both mirror and glide planes.

   The insertion of equipoints will confirm the lattice as primitive.

3. (*b*) $P\frac{2_1}{n}\frac{2_1}{a}\frac{2_1}{m}$.

4. In diamond one of the four-fold axes is positioned (in cell plan coordinates) at $\frac{1}{2}$, $\frac{1}{4}$.

   The centre of symmetry in diamond is at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ and lattice related positions.

5. First consider one close packed layer of atoms. A hexad will pass through each atom centre and a triad through each of the small triangular holes between the atoms.

   If these layers are now stacked according to the ABAB . . . type regime (Fig. 7.8) to give an h.c.p. structure, the hexads will be converted to triads which, because they are perpendicular to mirror planes, are in effect $\bar{6}$ axes.

   Therefore, in the unit cell plans drawn, the atom centres of both the A and B layers are positioned on the $\bar{6}$ axes.

   At the points where the triads (i.e. triangular holes) of both the A and B layers coincide, the symmetry is that of 6_3 axes. (cf. Fig. 16.2).

   Only $P\frac{6_3}{m}\frac{2}{c}\frac{2}{m}$ and $P\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$ contain 6_3 axes — which narrows the choice of space groups down to two.

   Focusing attention on $P\frac{6_3}{m}\frac{2}{c}\frac{2}{m}$, the two atoms positioned on the $\bar{6}$ axes within the space group plan are not in the same layer; this is not consistent with the mirror plane which bisects the line joining both $\bar{6}$ axes.

   By elimination the space group of h.c.p. is therefore $P\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$ (or $P6_3/mmc$ for short).

Index