Symmetry in crystals

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CARMELO GIACOVAZZO

The crystalline state and isometric operations

Matter is usually classified into three states: gaseous, liquid, and solid. Gases are composed of almost isolated particles, except for occasional collisions; they tend to occupy all the available volume, which is subject to variation following changes in pressure. In liquids the attraction between nearest-neighbour particles is high enough to keep the particles almost in contact. As a consequence liquids can only be slightly compressed. The thermal motion has sufficient energy to move the molecules away from the attractive field of their neighbours; the particles are not linked together permanently, thus allowing liquids to flow.

If we reduce the thermal motion of a liquid, the links between molecules will become more stable. The molecules will then cluster together to form what is macroscopically observed as a rigid body. They can assume a random disposition, but an ordered pattern is more likely because it corresponds to a lower energy state. This ordered disposition of molecules is called the **crystalline state**. As a consequence of our increased understanding of the structure of matter, it has become more convenient to classify matter into the three states: gaseous, liquid, and crystalline.

Can we then conclude that all solid materials are crystalline? For instance, can common glass and calcite (calcium carbonate present in nature) both be considered as crystalline? Even though both materials have high hardness and are transparent to light, glass, but not calcite, breaks in a completely irregular way. This is due to the fact that glass is formed by long, randomly disposed macromolecules of silicon dioxide. When it is formed from the molten state (glass does not possess a definite melting point, but becomes progressively less fluid) the thermal energy which remains as the material is cooled does not allow the polymers to assume a regular pattern. This disordered disposition, characteristic of the liquid state, is therefore retained when the cooling is completed. Usually glasses are referred to as **overcooled liquids**, while non-fluid materials with a very high degree of disorder are known as **amorphous solids**.

A distinctive property of the crystalline state is a regular repetition in the three-dimensional space of an object (as postulated as early as the end of the eighteenth century by R. J. Haüy), made of molecules or groups of molecules, extending over a distance corresponding to thousands of molecular dimensions. However, a crystal necessarily has a number of defects at non-zero temperature and/or may contain impurities without losing its order. Furthermore:

1. Some crystals do not show three-dimensional periodicity because the

basic crystal periodicity is modulated by periodic distortions incommensurated with the basic periods (i.e. in incommensurately modulated structures, IMS). It has, however, been shown (p. 171 and Appendix 3.E) that IMSs are periodic in a suitable (3 + d)-dimensional space.

2. Some polymers only show a bi-dimensional order and most fibrous materials are ordered only along the fiber axis.

3. Some organic crystals, when conveniently heated, assume a state intermediate between solid and liquid, which is called the **mesomorphic** or **liquid crystal** state.

These examples indicate that periodicity can be observed to a lesser or greater extent in crystals, depending on their nature and on the thermodynamic conditions of their formation. It is therefore useful to introduce the concept of a **real crystal** to stress the differences from an ideal crystal with perfect periodicity. Although non-ideality may sometimes be a problem, more often it is the cause of favourable properties which are widely used in materials science and in solid state physics.

In this chapter the symmetry rules determining the formation of an ideal crystalline state are considered (the reader will find a deeper account in some papers devoted to the subject, or some exhaustive books,[1–5] or in the theoretical sections of the *International Tables for Crystallography*).[6]

In order to understand the periodic and ordered nature of crystals it is necessary to know the operations by which the repetition of the basic molecular motif is obtained. An important step is achieved by answering the following question: given two identical objects, placed in random positions and orientations, which operations should be performed to superpose one object onto the other?

The well known coexistence of **enantiomeric** molecules demands a second question: given two **enantiomorphous** (the term enantiomeric will only be used for molecules) objects, which are the operations required to superpose the two objects?

An exhaustive answer to the two questions is given by the theory of **isometric transformations**, the basic concepts of which are described in Appendix 1.A, while here only its most useful results will be considered.

Two objects are said to be **congruent** if to each point of one object corresponds a point of the other and if the distance between two points of one object is equal to the distance between the corresponding points of the other. As a consequence, the corresponding angles will also be equal in absolute value. In mathematics such a correspondence is called **isometric**.

The congruence may either be **direct** or **opposite**, according to whether the corresponding angles have the same or opposite signs. If the congruence is direct, one object can be brought to coincide with the other by a convenient **movement** during which it behaves as a rigid body. The movement may be:

(1) a **translation**, when all points of the object undergo an equal displacement in the same direction;

(2) a **rotation** around an axis; all points on the axis will not change their position;

(3) a **rototranslation** or **screw** movement, which may be considered as the combination (product) of a rotation around the axis and a translation along the axial direction (the order of the two operations may be exchanged).

If the congruence is opposite, then one object will be said to be enantiomorphous with respect to the other. The two objects may be brought to coincidence by the following operations:

(1) a symmetry operation with respect to a point, known as **inversion**;

(2) a symmetry operation with respect to a plane, known as **reflection**;

(3) the product of a rotation around an axis by an inversion with respect to a point on the axis; the operation is called **rotoinversion**;

(4) the product of a reflection by a translation parallel to the reflection plane; the plane is then called a **glide plane**.

(5) the product of a rotation by a reflection with respect to a plane perpendicular to the axis; the operation is called **rotoreflection**.

Symmetry elements

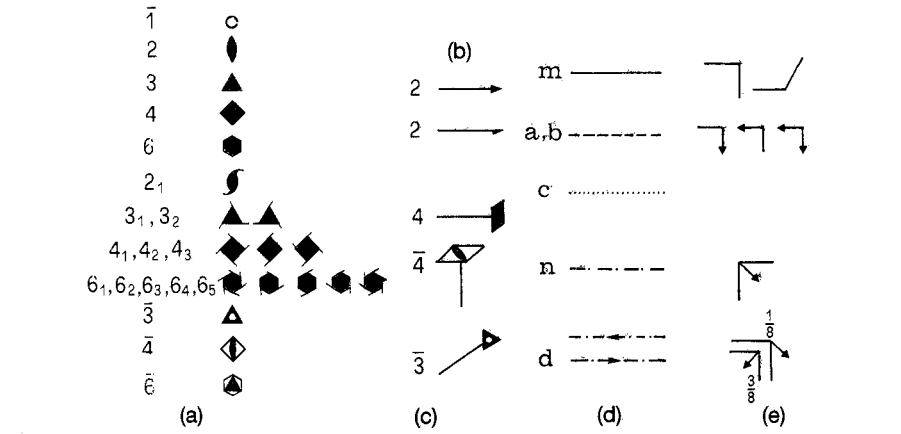
Suppose that the isometric operations described in the preceding section, not only bring to coincidence a couple of congruent objects, but act on the entire space. If all the properties of the space remain unchanged after a given operation has been carried out, the operation will be a **symmetry operation. Symmetry elements** are points, axes, or planes with respect to which symmetry operations are performed.

In the following these elements will be considered in more detail, while the description of translation operators will be treated in subsequent sections.

Axes of rotational symmetry

If all the properties of the space remain unchanged after a rotation of $2\pi/n$ around an axis, this will be called a symmetry axis of order n; its written symbol is n. We will be mainly interested (cf. p. 9) in the axes 1, 2, 3, 4, 6. Axis 1 is trivial, since, after a rotation of 360° around whatever direction the space properties will always remain the same. The graphic symbols for the 2, 3, 4, 6 axes (called two-, three-, four-, sixfold axes) are shown in Table 1.1. In the first column of Fig. 1.1 their effects on the space are illustrated. In keeping with international notation, an object is represented by a circle, with a + or − sign next to it indicating whether it is above or below the page plane. There is no graphic symbol for the 1 axis. Note that a 4 axis is at the same time a 2 axis, and a 6 axis is at the same time a 2 and a 3 axis.

Table 1.1. Graphical symbols for symmetry elements: (a) axes normal to the plane of projection; (b) axes 2 and 2_1 parallel to the plane of projection; (c) axes parallel or inclined to the plane of projection; (d) symmetry planes normal to the plane of projection; (e) symmetry planes parallel to the plane of projection



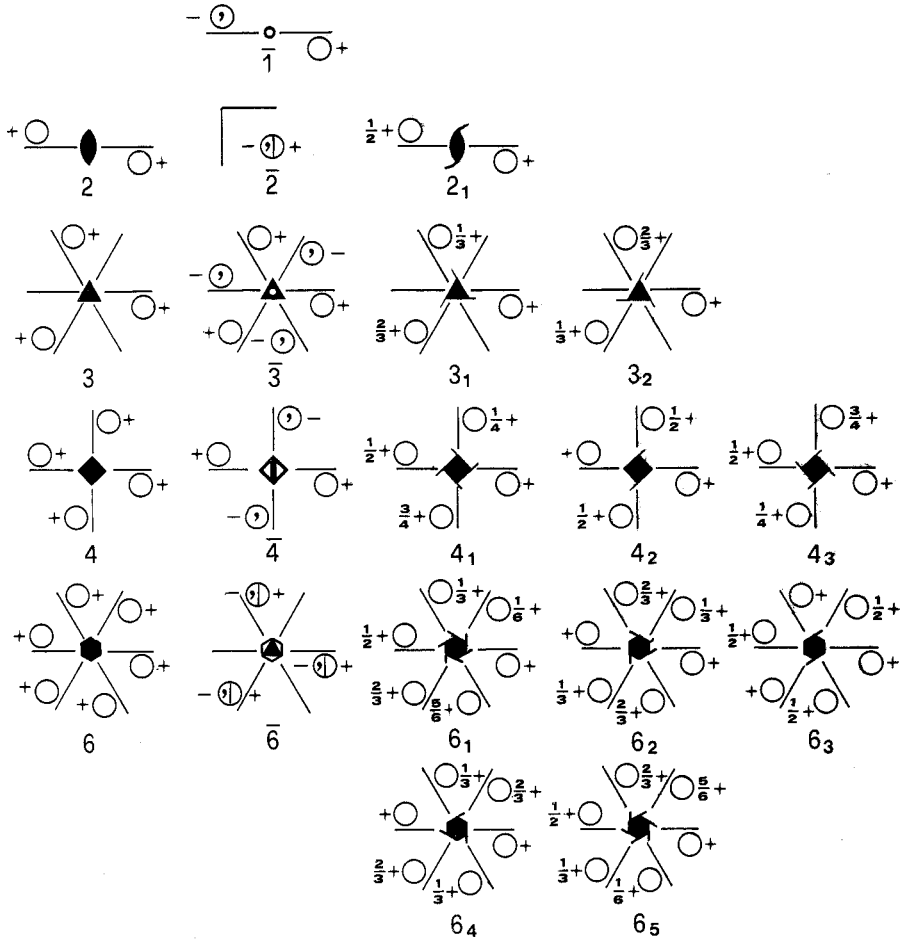


Fig. 1.1. Arrangements of symmetry-equivalent objects as an effect of rotation, inversion, and screw axes.

Axes of rototranslation or screw axes

A rototranslational symmetry axis will have an order n and a translational component t, if all the properties of the space remain unchanged after a $2\pi/n$ rotation around the axis and the translation by t along the axis. On p. 10 we will see that in crystals only screw axes of order 1, 2, 3, 4, 6 can exist with appropriate translational components.

Axes of inversion

An inversion axis of order n is present when all the properties of the space remain unchanged after performing the product of a $2\pi/n$ rotation around the axis by an inversion with respect to a point located on the same axis. The written symbol is $\bar{n}$ (read 'minus n' or 'bar n'). As we shall see on p. 9 we will be mainly interested in $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$ axes, and their graphic symbols are given in Table 1.1, while their effects on the space are represented in the second column of Fig. 1.1. According to international notation, if an object is represented by a circle, its enantiomorph is depicted by a circle with a comma inside. When the two enantiomorphous objects fall one on top of the other in the projection plane of the picture, they are represented by a single circle divided into two halves, one of which contains a comma. To each half the appropriate + or − sign is assigned.

We may note that:

(1) the direction of the $\bar{1}$ axis is irrelevant, since the operation coincides with an inversion with respect to a point;

(2) the $\bar{2}$ axis is equivalent to a reflection plane perpendicular to it; the properties of the half-space on one side of the plane are identical to those of the other half-space after the reflection operation. The written symbol of this plane is m;

(3) the $\bar{3}$ axis is equivalent to the product of a threefold rotation by an inversion: i.e. $\bar{3} = 3\bar{1}$;

(4) the $\bar{4}$ axis is also a 2 axis;

(5) the $\bar{6}$ axis is equivalent to the product of a threefold rotation by a reflection with respect to a plane normal to it; this will be indicated by $\bar{6} = 3/\mathrm{m}$.

Axes of rotoreflection

A rotoreflection axis of order n is present when all the properties of the space do not change after performing the product of a $2\pi/n$ rotation around an axis by a reflection with respect to a plane normal to it. The written symbol of this axis is $\tilde{n}$. The effects on the space of the $\tilde{1}$, $\tilde{2}$, $\tilde{3}$, $\tilde{4}$, $\tilde{6}$ axes coincide with those caused by an inversion axis (generally of a different order). In particular: $\tilde{1} = \mathrm{m}$, $\tilde{2} = \bar{1}$, $\tilde{3} = \bar{6}$, $\tilde{4} = \bar{4}$, $\tilde{6} = \bar{3}$. From now on we will no longer consider the $\tilde{n}$ axes but their equivalent inversion axes.

Reflection planes with translational component (glide planes)

A glide plane operator is present if the properties of the half-space on one side of the plane are identical to those of the other half-space after the product of a reflection with respect to the plane by a translation parallel to the plane. On p. 11 we shall see which are the glide planes found in crystals.

Symmetry operations relating objects referred by direct congruence are called **proper** (we will also refer to **proper symmetry axes**) while those relating objects referred by opposite congruence are called **improper** (we will also refer to **improper axes**).

Lattices

Translational periodicity in crystals can be conveniently studied by considering the geometry of the repetion rather than the properties of the motif which is repeated. If the motif is periodically repeated at intervals *a, b,* and *c* along three non-coplanar directions, the repetition geometry can be fully described by a periodic sequence of points, separated by intervals *a, b, c* along the same three directions. This collection of points will be called a **lattice**. We will speak of line, plane, and space lattices, depending on whether the periodicity is observed in one direction, in a plane, or in a three-dimensional space. An example is illustrated in Fig. 1.2(a), where HOCl is a geometrical motif repeated at intervals *a* and *b*. If we replace the molecule with a point positioned at its centre of gravity, we obtain the lattice of Fig. 1.2(b). Note that, if instead of placing the lattice point at the centre of gravity, we locate it on the oxygen atom or on any other point of the motif, the lattice does not change. Therefore the position of the lattice with respect to the motif is completely arbitrary.

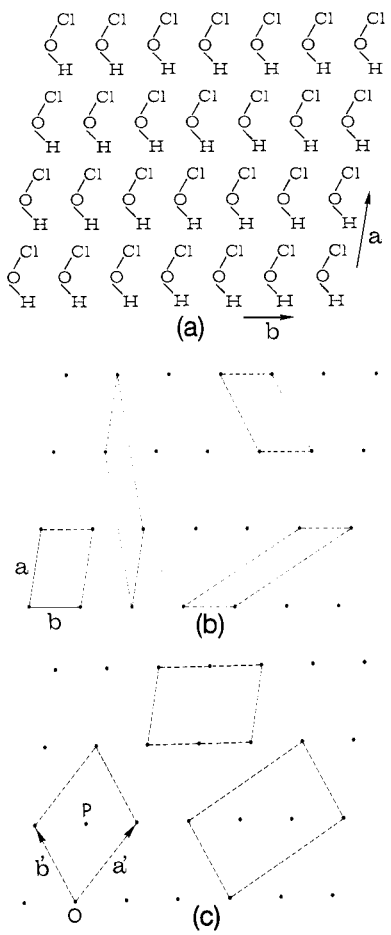


Fig. 1.2. (a) Repetition of a graphical motif as an example of a two-dimensional crystal; (b) corresponding lattice with some examples of primitive cells; (c) corresponding lattice with some examples of multiple cells.

If any lattice point is chosen as the origin of the lattice, the position of any other point in Fig. 1.2(b) is uniquely defined by the vector

$$\boldsymbol{Q}_{u,v} = u\boldsymbol{a} + v\boldsymbol{b} \tag{1.1}$$

where u and v are positive or negative integers. The vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ define a parallelogram which is called the *unit cell*: $\boldsymbol{a}$ and $\boldsymbol{b}$ are the basis vectors of the cell. The choice of the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is rather arbitrary. In Fig. 1.2(b) four possible choices are shown; they are all characterized by the property that each lattice point satisfies relation (1.1) with integer u and v.

Nevertheless we are allowed to choose different types of unit cells, such as those shown in Fig. 1.2(c), having double or triple area with respect to those selected in Fig. 1.2(b). In this case each lattice point will still satisfy (1.1) but u and v are no longer restricted to integer values. For instance, the point P is related to the origin O and to the basis vectors $\boldsymbol{a}'$ and $\boldsymbol{b}'$ through $(u, v) = (1/2, 1/2)$.

The different types of unit cells are better characterized by determining the number of lattice points belonging to them, taking into account that the points on sides and on corners are only partially shared by the given cell.

The cells shown in Fig. 1.2(b) contain only one lattice point, since the four points at the corners of each cell belong to it for only 1/4. These cells are called **primitive**. The cells in Fig. 1.2(c) contain either two or three

points and are called **multiple** or **centred cells**. Several kinds of multiple cells are possible: i.e. double cells, triple cells, etc., depending on whether they contain two, three, etc. lattice points.

The above considerations can be easily extended to linear and space lattices. For the latter in particular, given an origin O and three basis vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, each node is uniquely defined by the vector

$$\boldsymbol{Q}_{u,v,w} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}. \tag{1.2}$$

The three basis vectors define a parallelepiped, called again a **unit cell**. The directions specified by the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ are the X, Y, Z **crystallographic axes**, respectively, while the angles between them are indicated by α, β, and γ, with α opposing $\boldsymbol{a}$, β opposing $\boldsymbol{b}$, and γ opposing $\boldsymbol{c}$ (cf. Fig. 1.3). The volume of the unit cell is given by

$$V = \boldsymbol{a} \cdot \boldsymbol{b} \wedge \boldsymbol{c}$$

where the symbol '·' indicates the scalar product and the symbol '$\wedge$' the vector product. The orientation of the three crystallographic axes is usually chosen in such a way that an observer located along the positive direction of $\boldsymbol{c}$ sees $\boldsymbol{a}$ moving towards $\boldsymbol{b}$ by an anti-clockwise rotation. The faces of the unit cell facing $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ are indicated by A, B, C, respectively. If the chosen cell is primitive, then the values of u, v, w in (1.2) are bound to be integer for all the lattice points. If the cell is multiple then u, v, w will have rational values. To characterize the cell we must recall that a lattice point at vertex belongs to it only for 1/8th, a point on a edge for 1/4, and one on a face for 1/2.

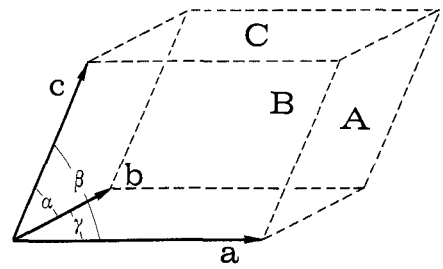


Fig. 1.3. Notation for a unit cell.

The rational properties of lattices

Since a lattice point can always be characterized by rational numbers, the lattice properties related to them are called **rational**. Directions defined by two lattice points will be called rational directions, and planes defined by three lattice points rational planes. Directions and planes of this type are also called **crystallographic directions** and **planes**.

Crystallographic directions

Since crystals are anisotropic, it is necessary to specify in a simple way directions (or planes) in which specific physical properties are observed.

Two lattice points define a **lattice row**. In a lattice there are an infinite number of parallel rows (see Fig. 1.4): they are identical under lattice translation and in particular they have the same translation period.

A lattice row defines a crystallographic direction. Suppose we have chosen a primitive unit cell. The two lattice vectors $\boldsymbol{Q}_{u,v,w}$ and $\boldsymbol{Q}_{nu,nv,nw}$, with u, v, w, and n integer, define two different lattice points, but only one direction. This property may be used to characterize a direction in a unique way. For instance, the direction associated with the vector $\boldsymbol{Q}_{9,3,6}$ can be uniquely defined by the vector $\boldsymbol{Q}_{3,1,2}$ with no common factor among the indices. This direction will be indicated by the symbol [3 1 2], to be read as 'three, one, two' and not 'three hundred and twelve'.

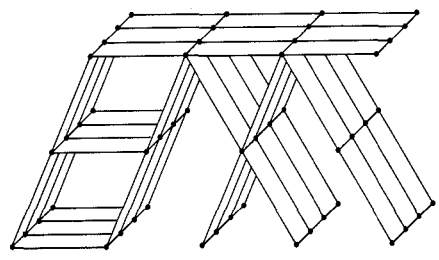


Fig. 1.4. Lattice rows and planes.

When the cell is not primitive u, v, w, and n will be rational numbers. Thus $\boldsymbol{Q}_{1/2,3/2,-1/3}$ and $\boldsymbol{Q}_{5/2,15/2,-5/3}$ define the same direction. The indices of the former may therefore be factorized to obtain a common denominator and no common factor among the numerators: $\boldsymbol{Q}_{1/2,3/2,-1/3} = \boldsymbol{Q}_{3/6,9/6,-2/6} \rightarrow$ [3 9 −2] to be read 'three', nine, minus two'.

Crystallographic planes

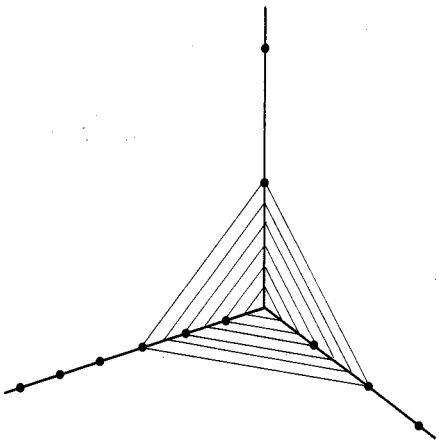


Fig. 1.5. Some lattice planes of the set (236).

Three lattice points define a crystallographic plane. Suppose it intersects the three crystallographic axes X, Y, and Z at the three lattice points $(p, 0, 0)$, $(0, q, 0)$ and $(0, 0, r)$ with integer p, q, r (see Fig. 1.5). Suppose that m is the least common multiple of p, q, r. Then the equation of the plane is

$$x'/pa + y'/qb + z'/rc = 1.$$

If we introduce the fractional coordinates $x = x'/a$, $y = y'/b$, $z = z'/c$, the equation of the plane becomes

$$x/p + y/q + z/r = 1. \tag{1.3}$$

Multiplying both sides by m we obtain

$$hx + ky + lz = m \tag{1.4}$$

where h, k, and l are suitable integers, the largest common integer factor of which will be 1.

We can therefore construct a family of planes parallel to the plane (1.4), by varying m over all integer numbers from $-\infty$ to $+\infty$. These will also be crystallographic planes since each of them is bound to pass through at least three lattice points.

The rational properties of all points being the same, there will be a plane of the family passing through each lattice point. For the same reason each lattice plane is identical to any other within the family through a lattice translation.

Let us now show that (1.4) represents a plane at a distance from the origin m times the distance of the plane

$$hx + ky + lz = 1. \tag{1.5}$$

The intercepts of the plane (1.5) on X, Y, Z will be $1/h$, $1/k$ and $1/l$ respectively and those of (1.4) m/h, m/k, m/l. It is then clear that the distance of plane (1.4) from the origin is m times that of plane (1.5). The first plane of the family intersecting the axes X, Y, and Z at three lattice points is that characterized by a m value equal to the least common mutiple of h, k, l. We can therefore conclude that eqn (1.4) defines, as m is varied, a family of identical and equally spaced crystallographic planes. The three indices h, k, and l define the family and are its **Miller indices**. To indicate that a family of lattice planes is defined by a sequence of three integers, these are included within braces: $(h\ k\ l)$. A simple interpretation of the three indices h, k, and l can be deduced from (1.4) and (1.5). In fact they

indicate that the planes of the family divide a in h parts, b in k parts, and c in l parts.

Crystallographic planes parallel to one of the three axes X, Y, or Z are defined by indices of type $(0kl)$, $(h0l)$, or $(hk0)$ respectively. Planes parallel to faces A, B, and C of the unit cell are of type $(h00)$, $(0k0)$, and $(00l)$ respectively. Some examples of crystallographic planes are illustrated in Fig. 1.6.

As a numerical example let us consider the plane

$$x/9 + y/6 + z/15 = 1 \tag{1.6}$$

which can be written as

$$10x + 15y + 6z = 90. \tag{1.7}$$

The first plane of the family with integer intersections on the three axes will be the 30th (30 being the least common multiple of 10, 15, and 6) and all the planes of the family can be obtained from the equation $10x + 15y + 6z = m$, by varying m over all integers from $-\infty$ to $+\infty$. We observe that if we divide p, q, and r in eqn (1.6) by their common integer factor we obtain $x/3 + y/2 + z/5 = 1$, from which

$$10x + 15y + 6z = 30. \tag{1.8}$$

Planes (1.7) and (1.8) belong to the same family. We conclude that a family of crystallographic planes is always uniquely defined by three indices h, k, and l having the largest common integer factor equal to unity.

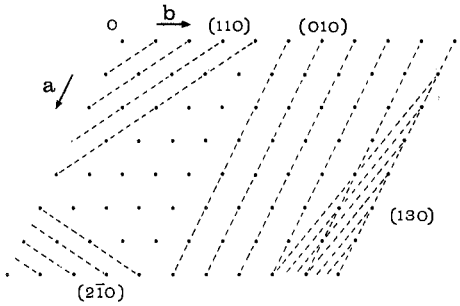


Fig. 1.6. Miller indices for some crystallographic planes parallel to Z (Z is supposed to be normal to the page).

Symmetry restrictions due to the lattice periodicity and vice versa

Suppose that the disposition of the molecules in a crystal is compatible with an n axis. As a consequence the disposition of lattice points must also be compatible with the same axis. Without losing generality, we will assume that n passes through the origin O of the lattice. Since each lattice point has identical rational properties, there will be an n axis passing through each and every lattice point, parallel to that passing through the origin. In particular each symmetry axis will lie along a row and will be perpendicular to a crystallographic plane.

Let $\boldsymbol{T}$ be the period vector of a row passing through O and normal to n. We will then have lattice points (see Fig. 1.7(a)) at $\boldsymbol{T}$, $-\boldsymbol{T}$, $\boldsymbol{T}'$, and $\boldsymbol{T}''$. The vector $\boldsymbol{T}' - \boldsymbol{T}''$ must also be a lattice vector and, being parallel to $\boldsymbol{T}$, we will have $\boldsymbol{T}' - \boldsymbol{T}'' = m\boldsymbol{T}$ where m is an integer value: in a scalar form

$$2\cos(2\pi/n) = m \qquad (m \text{ integer}). \tag{1.9}$$

Equation (1.9) is only verified for $n = 1, 2, 3, 4, 6$. It is noteworthy that a 5 axis is not allowed, this being the reason why it is impossible to pave a room only with pentagonal tiles (see Fig. 1.7(b).

A unit cell, and therefore a lattice, compatible with an n axis will also be compatible with an $\bar{n}$ axis and vice versa. Thus axes $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$ will also be allowed.

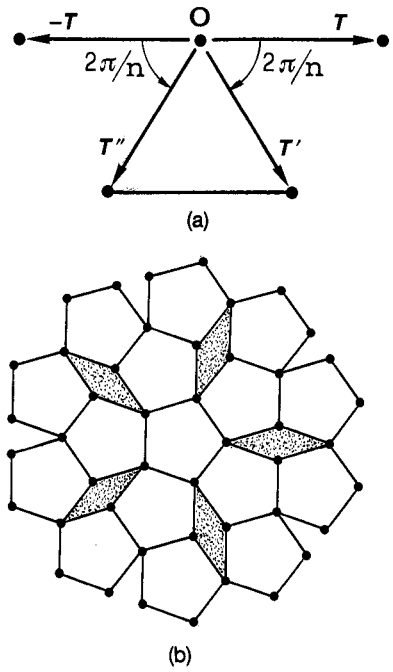


Fig. 1.7. (a) Lattice points in a plane normal to the symmetry axis n passing through O. (b) Regular pentagons cannot fill planar space.

Let us now consider the restrictions imposed by the periodic nature of crystals on the translational components $\boldsymbol{t}$ of a screw axis. Suppose that this lies along a row with period vector $\boldsymbol{T}$. Its rotational component must correspond to $n = 1, 2, 3, 4, 6$. If we apply the translational component n times the resulting displacement will be $n\boldsymbol{t}$. In order to maintain the periodicity of the crystal we must have $n\boldsymbol{t} = p\boldsymbol{T}$, with integer p, or

$$\boldsymbol{t} = (p/n)\boldsymbol{T}. \tag{1.10}$$

For instance, for a screw axis of order 4 the allowed translational components will be $(0/4)\boldsymbol{T}$, $(1/4)\boldsymbol{T}$, $(2/4)\boldsymbol{T}$, $(3/4)\boldsymbol{T}$, $(4/4)\boldsymbol{T}$, $(5/4)\boldsymbol{T}, \ldots$; of these only the first four will be distinct. It follows that:

(1) in (1.10) p can be restricted within $0 \leqslant p < n$;

(2) the n-fold axis may be thought as a special screw with $\boldsymbol{t} = \boldsymbol{0}$. The nature of a screw axis is completely defined by the symbol n_p. The graphic symbols are shown in Table 1.1: the effects of screw axes on the surrounding space are represented in Fig. 1.8. Note that:

1. If we draw a helicoidal trajectory joining the centres of all the objects related by a 3_1 and by a 3_2 axis, we will obtain, in the first case a right-handed helix and in the second a left-handed one (the two helices are enantiomorphous). The same applies to the pairs 4_1 and 4_3, 6_1 and 6_5, and 6_2 and 6_4.

2. 4_2 is also a 2 axis, 6_2 is also a 2 and a 3_2, 6_4 is also a 2 and a 3_1, and 6_3 is also a 3 and a 2_1.

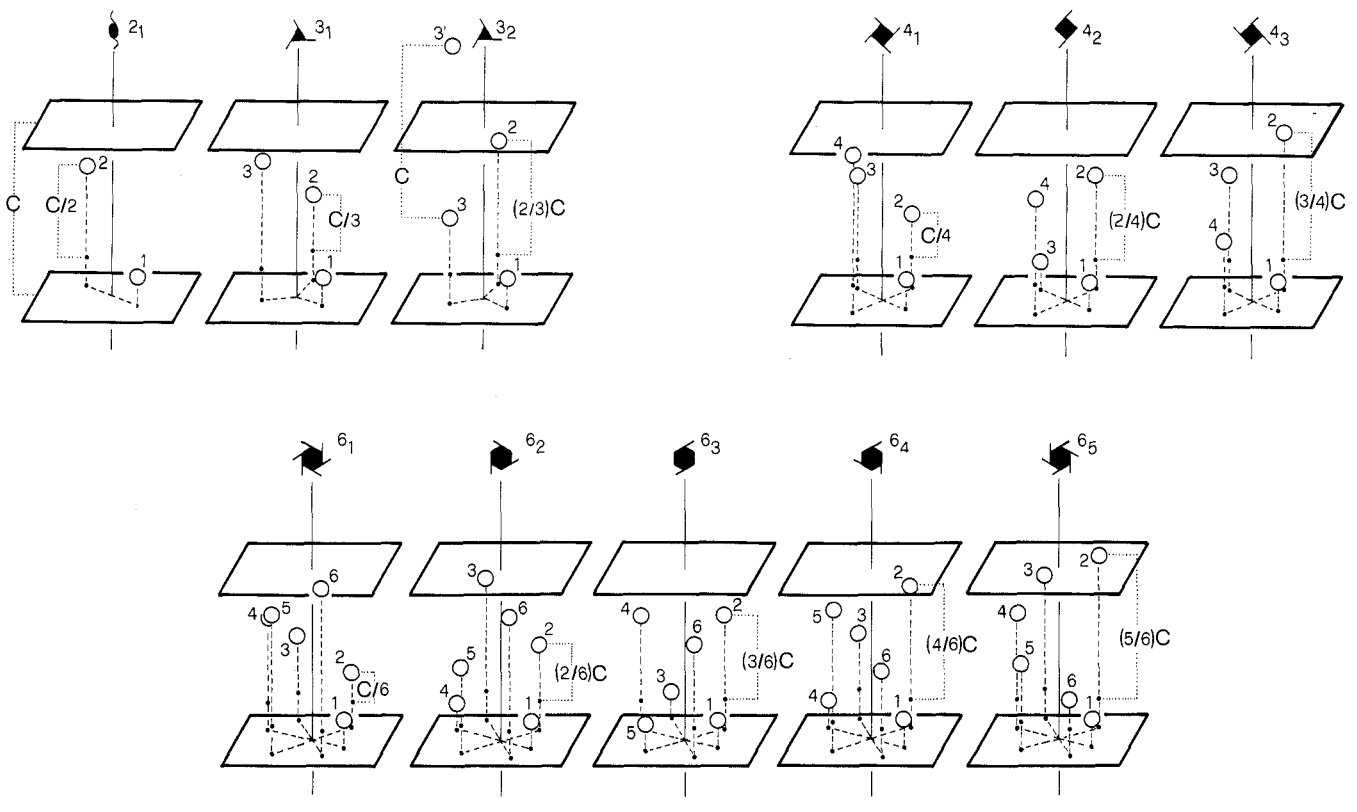


Fig. 1.8. Screw axes: arrangement of symmetry-equivalent objects.

We will now consider the restrictions imposed by the periodicity on the translation component $\boldsymbol{t}$ of a glide plane. If we apply this operation twice, the resulting movement must correspond to a translation equal to $p\boldsymbol{T}$, where p may be any integer and $\boldsymbol{T}$ any lattice vector on the crystallographic plane on which the glide lies. Therefore $2\boldsymbol{t} = p\boldsymbol{T}$, i.e. $\boldsymbol{t} = (p/2)\boldsymbol{T}$. As p varies over all integer values, the following translations are obtained $0\boldsymbol{T}$, $(1/2)\boldsymbol{T}$, $(2/2)\boldsymbol{T}$, $(3/2)\boldsymbol{T}, \ldots$ of which only the first two are distinct. For $p = 0$ the glide plane reduces to a mirror m. We will indicate by a, b, c axial glides with translational components equal to $\boldsymbol{a}/2$, $\boldsymbol{b}/2$, $\boldsymbol{c}/2$ respectively, by n the **diagonal** glides with translational components $(\boldsymbol{a} + \boldsymbol{b})/2$ or $(\boldsymbol{a} + \boldsymbol{c})/2$ or $(\boldsymbol{b} + \boldsymbol{c})/2$ or $(\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c})/2$.

In a non-primitive cell the condition $2\boldsymbol{t} = p\boldsymbol{T}$ still holds, but now $\boldsymbol{T}$ is a lattice vector with rational components indicated by the symbol d. The graphic symbols for glide planes are given in Table 1.1.

Point groups and symmetry classes

In crystals more symmetry axes, both proper and improper, with or without translational components, may coexist. We will consider here only those combinations of operators which do not imply translations, i.e. the combinations of proper and improper axes intersecting in a point. These are called **point groups**, since the operators form a mathematical **group** and leave one point fixed. The set of crystals having the same point group is called **crystal class** and its symbol is that of the point group. Often point group and crystal class are used as synonyms, even if that is not correct in principle. The total number of crystallographic point groups (for three-dimensional crystals) is 32, and they were first listed by Hessel in 1830.

The simplest combinations of symmetry operators are those characterized by the presence of only one axis, which can be a proper axis or an inversion one. Also, a proper and an inversion axis may be simultaneously present. The 13 independent combinations of this type are described in Table 1.2. When along the same axis a proper axis and an inversion axis are simultaneously present, the symbol $n/\bar{n}$ is used. Classes coinciding with other classes already quoted in the table are enclosed in brackets.

The problem of the coexistence of more than one axis all passing by a common point was first solved by Euler and is illustrated, with a different approach, in Appendix 1.B. Here we only give the essential results. Let us suppose that there are two proper axes l_1 and l_2 intersecting in O (see Fig. 1.9). The l_1 axis will repeat in Q an object originally in P, while l_2 will

Table 1.2. Single-axis crystallographic point groups

Proper axis		Improper axis		Proper and improper axis	
1		$\bar{1}$		$(1/\bar{1} = \bar{1})$	
2		$\bar{2} \equiv m$		$2/\bar{2} = 2/m$	
3		$\bar{3} \equiv 3\bar{1}$		$(3/\bar{3} = \bar{3})$	
4		$\bar{4}$		$4/\bar{4} = 4/m$	
6		$\bar{6} \equiv 3/m$		$6/\bar{6} = 6/m$	
5	+	5	+	3	= 13

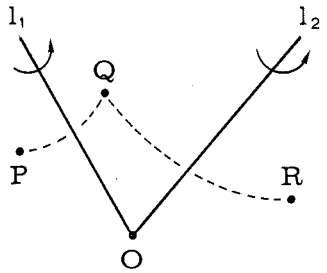


Fig. 1.9. Arrangement of equivalent objects around two intersecting symmetry axes.

Table 1.3. For each combination of symmetry axes the minimum angles between axes are given. For each angle the types of symmetry axes are quoted in parentheses

Combination of symmetry axes	α (deg)	β (deg)	γ (deg)
2 2 2	90 (2 2)	90 (2 2)	90 (2 2)
3 2 2	90 (2 3)	90 (2 3)	60 (2 2)
4 2 2	90 (2 4)	90 (2 4)	45 (2 2)
6 2 2	90 (2 6)	90 (2 6)	30 (2 2)
2 3 3	54 44′08″ (2 3)	54 44′08″ (2 3)	70 31′44″ (3 3)
4 3 2	35 15′52″ (2 3)	45 (2 4)	54 44′08″ (4 3)

repeat in R the object in Q. P and Q are therefore directly congruent and this implies the existence of another proper operator which repeats the object in P directly in R. The only allowed combinations are $n22$, 233, 432, 532 which in crystals reduce to 222, 322, 422, 622, 233, 432. For these combinations the smallest angles between the axes are listed in Table 1.3, while their disposition in the space is shown in Fig. 1.10. Note that the combination 233 is also consistent with a tetrahedral symmetry and 432 with a cubic and octahedral symmetry.

Suppose now that in Fig. 1.9 l_1 is a proper axis while l_2 is an inversion one. Then the objects in P and in Q will be directly congruent, while the object in R is enantiomorphic with respect to them. Therefore the third operator relating R to P will be an inversion axis. We may conclude that if one of the three symmetry operators is an inversion axis also another must be an inversion one. In Table 1.4 are listed all the point groups characterized by combinations of type PPP, PII, IPI, IIP (P = proper, I = improper), while in Table 1.5 the classes with axes at the same time proper and improper are given. In the two tables the combinations coinciding with previously considered ones are closed within brackets. The

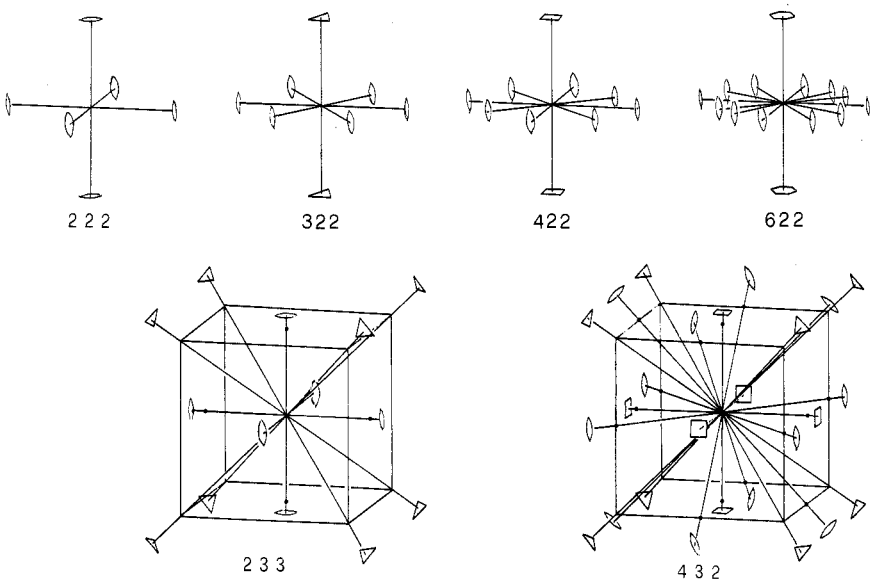


Fig. 1.10. Arrangement of proper symmetry axes for six point groups.

Table 1.4. Crystallographic point groups with more than one axis

P P P	P I I	I P I	I I P	
2 2 2	2 m m			
3 2 2	3 m m	$\bar{3}\ 2\ m$		
4 2 2	4 m m	$\bar{4}\ 2\ m$		
6 2 2	6 m m	$\bar{6}\ 2\ \bar{2} \rightarrow \bar{6}\,2\,m$		
2 3 3	$2\ \bar{3}\ \bar{3} \rightarrow \frac{2}{m}\bar{3}\ \bar{3}$			
4 3 2	$4\ \bar{3}\ \bar{2} \rightarrow \bar{4}\frac{3}{\bar{1}}\frac{1}{m}$ $\rightarrow \frac{4}{m}\bar{3}\frac{2}{m} \rightarrow m\ \bar{3}\ m$	$\bar{4}\ 3\ m$	$\left(\bar{4}\ \bar{3}\ 2 \rightarrow \frac{\bar{4}}{m}\frac{3}{\bar{1}}\frac{2}{m} \rightarrow \frac{4}{m}\bar{3}\frac{2}{m}\right)$	
6	+6	+4	+0	= 16

Table 1.5. Crystallographic point groups with more than one axis, each axis being proper and improper simultaneously

$\frac{2}{\bar{2}}\frac{2}{\bar{2}}\frac{2}{\bar{2}} = \frac{2}{m}\frac{2}{m}\frac{2}{m}$;	$\left(\frac{3}{\bar{3}}\frac{2}{\bar{2}}\frac{2}{\bar{2}} = \bar{3}\frac{2}{m}\frac{2}{m}\right)$;	$\frac{4}{\bar{4}}\frac{2}{\bar{2}}\frac{2}{\bar{2}} = \frac{4}{m}\frac{2}{m}\frac{2}{m}$;
$\frac{6}{\bar{6}}\frac{2}{\bar{2}}\frac{2}{\bar{2}} = \frac{6}{m}\frac{2}{m}\frac{2}{m}$;	$\left(\frac{2}{\bar{2}}\frac{3}{\bar{3}}\frac{3}{\bar{3}} = \frac{2}{m}\ \bar{3}\ \bar{3}\right)$;	$\left(\frac{4}{\bar{4}}\frac{3}{\bar{3}}\frac{2}{\bar{2}} = \frac{4}{m}\bar{3}\frac{2}{m}\right)$

results so far described can be easily derived by recalling that:

1. If two of the three axes are symmetry equivalent, they can not be one proper and one improper; for example, the threefold axes in 233 are symmetry referred by twofold axes, while binary axes in 422 differing by 45° are not symmetry equivalent.
2. If an even-order axis and a $\bar{1}$ axis (or an m plane) coexist, there will also be an m plane (or a $\bar{1}$ axis) normal to the axis and passing through the intersection point. Conversely, if m and $\bar{1}$ coexist, there will also be a 2 axis passing through $\bar{1}$ and normal to m.

In Tables 1.2, 1.4, and 1.5 the symbol of each point group does not reveal all the symmetry elements present: for instance, the complete list of symmetry elements in the class $2/m\bar{3}\bar{3}$ is 2/m 2/m $2/m\bar{1}3333$. On the other hand, the symbol $2/m\bar{3}\bar{3}$ is too extensive, since only two symmetry operators are independent. In Table 1.6 are listed the conventional symbols used for the 32 symmetry classes. It may be noted that crystals with inversion symmetry operators have an equal number of 'left' and 'right' moieties; these parts, when considered separately, are one the enantiomorph of the other.

The conclusions reached so far do not exclude the possibility of crystallizing molecules with a molecular symmetry different from that of the 32 point groups (for instance with a 5 axis). In any case the symmetry of the crystal will belong to one of them. To help the reader, some molecules and their point symmetry are shown in Fig. 1.11.

It is very important to understand how the symmetry of the physical properties of a crystal relates to its point group (this subject is more extensively described in Chapter 9). Of basic relevance to this is a postulate

Table 1.6. List of the 32 point groups

Crystal systems	Point groups			Laue classes	Lattice point groups
	Non-centro-symmetric		Centro-symmetric		
Triclinic	1		$\bar{1}$	$\bar{1}$	$\bar{1}$
Monoclinic	2	m	2/m	2/m	2/m
Orthorhombic	222	mm2	mmm	mmm	mmm
Tetragonal	4	$\bar{4}$	4/m	4/m	4/mmm
	422	4mm, $\bar{4}$2m	4/mmm	4/mmm	
Trigonal	3		$\bar{3}$	$\bar{3}$	$\bar{3}$m
	32	3m	$\bar{3}$m	$\bar{3}$m	
Hexagonal	6	$\bar{6}$	6/m	6/m	6/mmm
	622	6mm, $\bar{6}$2m	6/mmm	6/mmm	
Cubic	23		m$\bar{3}$	m$\bar{3}$	m$\bar{3}$m
	432	$\bar{4}$3m	m$\bar{3}$m	m$\bar{3}$m	

of crystal physics, known as the **Neumann principle**: 'the symmetry elements of any physical property must include the symmetry elements of the crystal point group'. In keeping with this principle, the physical properties may present a higher, but not a lower, symmetry than the point group. For instance:

1. **Cubic** crystals (see later for their definition) are optically isotropic: in this case the physical property has a symmetry higher than that of the point group.

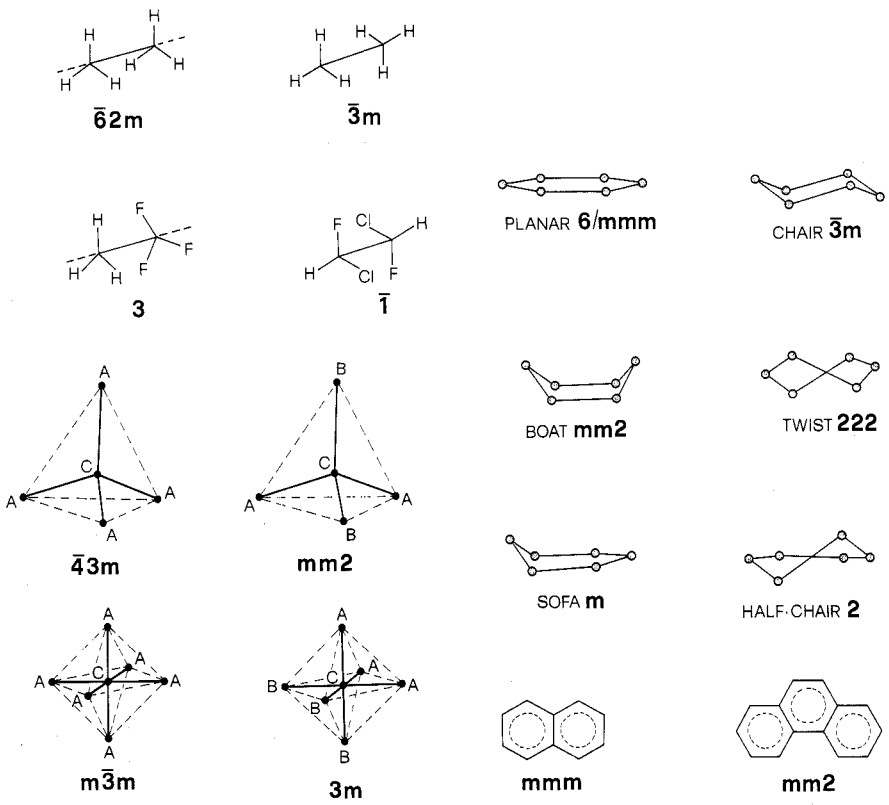


Fig. 1.11. Molecular examples of some point groups.

2. The variation of the refractive index of the crystal with the vibration direction of a plane-polarized light wave is represented by the **optical indicatrix** (see p. 607). This is in general a three-axis **ellipsoid**: thus the lowest symmetry of the property 'refraction' is 2/m 2/m 2/m, the point group of the ellipsoid. In crystal classes belonging to tetragonal, trigonal, or hexagonal systems (see Table 1.6) the shape of the indicatrix is a rotational ellipsoid (the axis is parallel to the main symmetry axis), and in symmetry classes belonging to the cubic system the shape of the indicatrix is a sphere. For example, in the case of tourmaline, with point group 3m, the ellipsoid is a revolution around the threefold axis, showing a symmetry higher than that of the point group.

We shall now see how it is possible to guess about the point group of a crystal through some of its physical properties:

1. The morphology of a crystal tends to conform to its point group symmetry. From a morphological point of view, a crystal is a solid body bounded by plane natural surfaces, the **faces**. The set of symmetry-equivalent faces constitutes a **form**: the form is *open* if it does not enclose space, otherwise it is *closed*. A crystal form is named according to the number of its faces and to their nature. Thus a **pedion** is a single face, a **pinacoid** is a pair of parallel faces, a **sphenoid** is a pair of faces related by a diad axis, a **prism** a set of equivalent faces parallel to a common axis, a **pyramid** is a set of planes with equal angles of inclination to a common axis, etc. The morphology of different samples of the same compound can show different types of face, with different extensions, and different numbers of edges, the external form depending not only on the structure but also on the chemical and physical properties of the environment. For instance, galena crystals (PbS, point group m$\bar{3}$m) tend to assume a cubic, cube-octahedral, or octahedral habit (Fig. 1.12(a)). Sodium chloride grows as cubic crystals from neutral aqueous solution and as octahedral from active solutions (in the latter case cations and anions play a different energetic role). But at the same temperature crystals will all have constant dihedral angles between corresponding faces (J. B. L. Rome' de l'Ile, 1736–1790). This property, the observation of which dates back to N. Steno (1669) and D. Guglielmini (1688), can be explained easily, following R. J. Haüy (1743–1822), by considering that faces coincide with lattice planes and edges with lattice rows. Accordingly, Miller indices can be used as form symbols, enclosed in braces: $\{hkl\}$. The indices of well-developed faces on natural crystals tend to have small values of h, k, l, (integers greater than six are rarely involved). Such faces correspond to lattice planes with a high density of lattice points per unit area, or equivalently, with large intercepts a/h, b/k, c/l on the reference axes (**Bravais' law**). An important extension of this law is obtained if space group symmetry (see p. 22) is taken into account: screw axes and glide planes normal to a given crystal face reduce its importance (Donnay–Harker principle).

The origin within the crystal is usually chosen so that faces (hkl) and $(\bar{h}\bar{k}\bar{l})$ are parallel faces an opposite sides of the crystal. In Fig. 1.13 some idealized crystal forms are shown.

The orientation of the faces is more important than their extension. The orientations can be represented by the set of unit vectors normal to them. This set will tend to assume the point-group symmetry of the given crystal

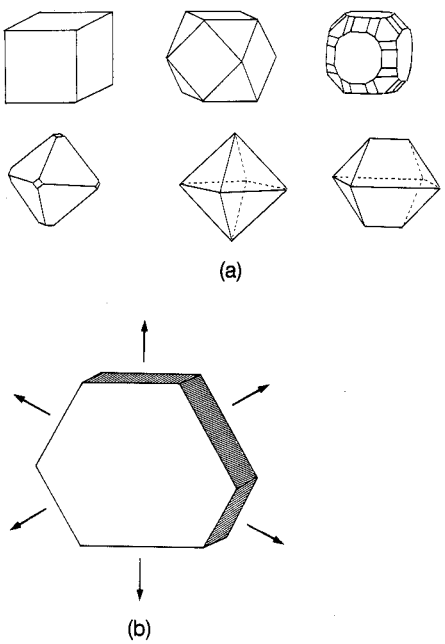


Fig. 1.12. (a) Crystals showing cubic or cube-octahedral or octahedral habitus, (b) crystal with a sixfold symmetry axis.

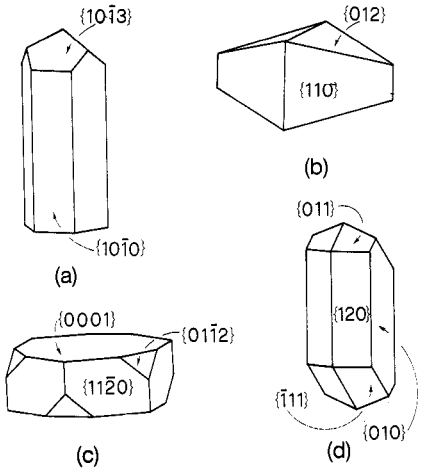


Fig. 1.13. Some simple crystal forms: (a) cinnabar, HgS, class 32; (b) arsenopyrite, FeAsS, class mmm; (c) ilmenite, $FeTiO_3$, class $\bar{3}$; (d) gypsum, $CaSO_4$, class 2/m.

independently of the morphological aspect of the samples. Thus, each sample of Fig. 1.12(a) shows an m$\bar{3}$m symmetry, and the sample in Fig. 1.12(b) shows a sixfold symmetry if the normals to the faces are considered instead of their extensions. The morphological analysis of a crystalline sample may be used to get some, although not conclusive, indication, of its point-group symmetry.

2. Electrical charges of opposite signs may appear at the two hands of a **polar axis** of a crystal subject to compression, because of the **piezoelectric** effect (see p. 619). A polar axis is a rational direction which is not symmetry equivalent to its opposite direction. It then follows that a polar direction can only exist in the 21 non-centrosymmetric point groups (the only exception is the 432 class, where piezoelectricity can not occur). In these groups not all directions are polar: in particular a direction normal to an even-order axis or to a mirror plane will never be polar. For instance, in quartz crystals (SiO_2, class 32), charges of opposite sign may appear at the opposite hands of the twofold axes, but not at those of the threefold axis.

3. A point group is said to be **polar** if a polar direction, with no other symmetry equivalent directions, is allowed. Along this direction a permanent electric dipole may be measured, which varies with temperature (**pyroelectric** effect, see p. 606). The ten polar classes are: 1, 2, m, mm2, 4, 4mm, 6, 6mm, 3, 3m. Piezo- and pyroelectricity tests are often used to exclude the presence of an inversion centre. Nevertheless when these effects are not detectable, no definitive conclusion may be drawn.

4. Ferroelectric crystals show a permanent dipole moment which can be changed by application of an electric field. Thus they can only belong to one of the ten polar classes.

5. The symmetry of a crystal containing only one enantiomer of an optically active molecule must belong to one of the 11 point groups which do not contain inversion axes.

6. Because of non-linear optical susceptibility, light waves passing through non-centrosymmetric crystals induce additional waves of frequency twice the incident frequency. This phenomenon is described by a third-rank tensor, as the piezoelectric tensor (see p. 608): it occurs in all non-centrosymmetric groups except 432, and is very efficient[7] for testing the absence of an inversion centre.

7. Etch figures produced on the crystal faces by chemical attack reveal the face symmetry (one of the following 10 two-dimensional point groups).

Point groups in one and two dimensions

The derivation of the crystallographic point groups in a two-dimensional space is much easier than in three dimensions. In fact the reflection with respect to a plane is substituted by a reflection with respect to a line (the same letter m will also indicate this operation); and $\bar{n}$ axes are not used. The total number of point groups in the plane is 10, and these are indicated by the symbols: 1, 2, 3, 4, 6, m, 2mm, 3m, 4mm, 6mm.

The number of crystallographic point groups in one dimension is 2: they are 1 and m $\equiv (\bar{1})$.

The Laue classes

In agreement with Neumann's principle, physical experiments do not normally reveal the true symmetry of the crystal: some of them, for example diffraction, show the symmetry one would obtain by adding an inversion centre to the symmetry elements actually present. In particular this happens when the measured quantities do not depend on the atomic positions, but rather on the interatomic vectors, which indeed form a centrosymmetric set. Point groups differing only by the presence of an inversion centre will not be differentiated by these experiments. When these groups are collected in classes they form the 11 **Laue classes** listed in Table 1.6.

The seven crystal systems

If the crystal periodicity is only compatible with rotation or inversion axes of order 1, 2, 3, 4, 6, the presence of one of these axes will impose some restrictions on the geometry of the lattice. It is therefore convenient to group together the symmetry classes with common features in such a way that crystals belonging to these classes can be described by unit cells of the same type. In turn, the cells will be chosen in the most suitable way to show the symmetry actually present.

Point groups 1 and $\bar{1}$ have no symmetry axes and therefore no constraint axes for the unit cell; the ratios $a:b:c$ and the angles α, β, γ can assume any value. Classes 1 and $\bar{1}$ are said to belong to the **triclinic** system.

Groups 2, m, and 2/m all present a 2 axis. If we assume that this axis coincides with the b axis of the unit cell, $\boldsymbol{a}$ and $\boldsymbol{c}$ can be chosen on the lattice plane normal to $\boldsymbol{b}$. We will then have $\alpha = \gamma = 90°$ and β unrestricted and the ratios $a:b:c$ also unrestricted. Crystals with symmetry 2, m, and 2/m belong to the **monoclinic** system.

Classes 222, mm2, mmm are characterized by the presence of three mutually orthogonal twofold rotation or inversion axes. If we assume these as reference axes, we will obtain a unit cell with angles $\alpha = \beta = \gamma = 90°$ and with unrestricted $a:b:c$ ratios. These classes belong to the **orthorhombic** system.

For the seven groups with only one fourfold axis [4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}$2m, 4/mmm] the $\boldsymbol{c}$ axis is chosen as the direction of the fourfold axis and the $\boldsymbol{a}$ and $\boldsymbol{b}$ axes will be symmetry equivalent, on the lattice plane normal to $\boldsymbol{c}$. The cell angles will be $\alpha = \beta = \gamma = 90°$ and the ratios $a:b:c = 1:1:c$. These crystals belong to the **tetragonal** system.

For the crystals with only one threefold or sixfold axis [3, $\bar{3}$, 32, 3m, $\bar{3}$m, 6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}$2m, 6/mm] the $\boldsymbol{c}$ axis is assumed along the three- or sixfold axis, while $\boldsymbol{a}$ and $\boldsymbol{b}$ are symmetry equivalent on the plane perpendicular to $\boldsymbol{c}$. These point groups are collected together in the **trigonal** and **hexagonal** systems, respectively, both characterized by a unit cell with angles $\alpha = \beta = 90°$ and $\gamma = 120°$, and ratios $a:b:c = 1:1:c$.

Crystals with four threefold axes [23, m$\bar{3}$, 432, $\bar{4}$3m, m$\bar{3}$m] distributed as the diagonals of a cube can be referred to orthogonal unit axes coinciding with the cube edges. The presence of the threefold axes ensures that these directions are symmetry equivalent. The chosen unit cell will have $\alpha = \beta = \gamma = 90°$ and ratios $a:b:c = 1:1:1$. This is called the **cubic** system.

The Bravais lattices

In the previous section to each crystal system we have associated a primitive cell compatible with the point groups belonging to the system. Each of these primitive cells defines a lattice type. There are also other types of lattices, based on non-primitive cells, which can not be related to the previous ones. In particular we will consider as different two lattice types which can not be described by the same unit-cell type.

In this section we shall describe the five possible plane lattices and fourteen possible space lattices based both on primitive and non-primitive cells. These are called Bravais lattices, after Auguste Bravais who first listed them in 1850.

Plane lattices

An oblique cell (see Fig. 1.14(a)) is compatible with the presence of axes 1 or 2 normal to the cell. This cell is primitive and has point group 2.

If the row indicated by m in Fig. 1.14(b) is a reflection line, the cell must be rectangular. Note that the unit cell is primitive and compatible with the point groups m and 2mm. Also the lattice illustrated in Fig. 1.14(c) with $a = b$ and $\gamma \neq 90°$ is compatible with m. This plane lattice has an oblique primitive cell. Nevertheless, each of the lattice points has a 2mm symmetry and therefore the lattice must be compatible with a rectangular system. This can be seen by choosing the rectangular centred cell defined by the unit vectors $\boldsymbol{a}'$ and $\boldsymbol{b}'$. This orthogonal cell is more convenient because a simpler coordinate system is allowed. It is worth noting that the two lattices shown in Figs. 1.14(b) and 1.14(c) are of different type even though they are compatible with the same point groups.

In Fig. 1.14(d) a plane lattice is represented compatible with the presence of a fourfold axis. The cell is primitive and compatible with the point groups 4 and 4mm.

In Fig. 1.14(e) a plane lattice compatible with the presence of a three- or a sixfold axis is shown. A unit cell with a rhombus shape and angles of 60° and 120° (also called hexagonal) may be chosen. A centred rectangular cell can also be selected, but such a cell is seldom chosen.

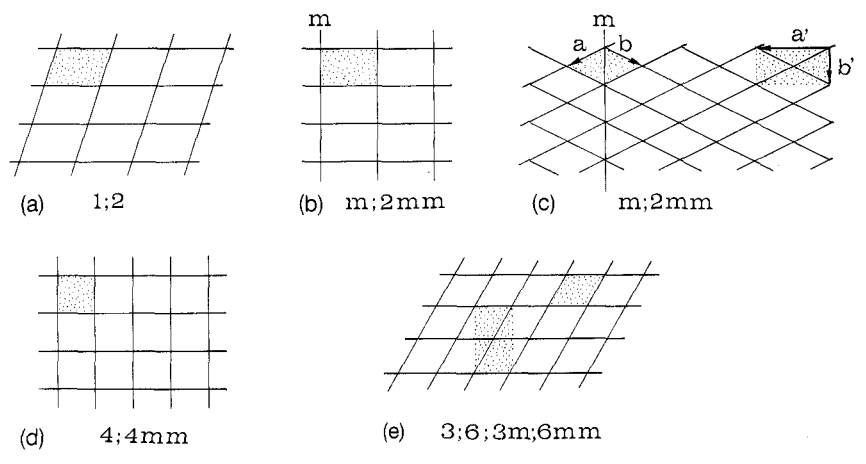


Fig. 1.14. The five plane lattices and the corresponding two-dimensional point groups.

Table 1.7. The five plane lattices

Cell	Type of cell	Point group of the net	Lattice parameters
Oblique	p	2	a, b, γ
Rectangular	p, c	2mm	$a, b, \gamma = 90°$
Square	p	4mm	$a = b, \gamma = 90°$
Hexagonal	p	6mm	$a = b, \gamma = 120°$

The basic features of the five lattices are listed in Table 1.7.

Space lattices

In Table 1.8 the most useful types of cells are described. Their fairly limited number can be explained by the following (or similar) observations:

1. A cell with two centred faces must be of type F. In fact a cell which is at the same time A and B, must have lattice points at $(0, 1/2, 1/2)$ and $(1/2, 0, 1/2)$. When these two lattice translations are applied one after the other they will generate a lattice point also at $(1/2, 1/2, 0)$;
2. A cell which is at the same time body and face centred can always be reduced to a conventional centred cell. For instance an I and A cell will have lattice points at positions $(1/2, 1/2, 1/2)$ and $(0, 1/2, 1/2)$: a lattice point at $(1/2, 0, 0)$ will then also be present. The lattice can then be described by a new A cell with axes $\boldsymbol{a}' = \boldsymbol{a}/2$, $\boldsymbol{b}' = \boldsymbol{b}$, and $\boldsymbol{c}' = \boldsymbol{c}$ (Fig. 1.15).

It is worth noting that the positions of the additional lattice points in Table 1.8 define the minimal translational components which will move an object into an equivalent one. For instance, in an A-type cell, an object at (x, y, z) is repeated by translation into $(x, y + m/2, z + n/2)$ with m and n integers: the shortest translation will be $(0, 1/2, 1/2)$.

Let us now examine the different types of three-dimensional lattices grouped in the appropriate crystal systems.

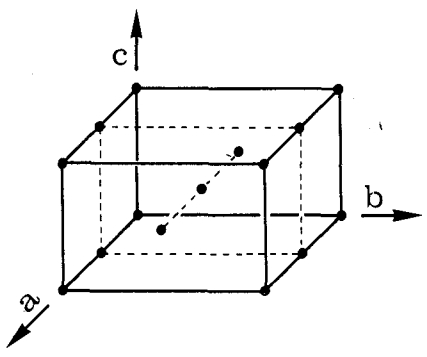


Fig. 1.15. Reduction of an I- and A-centred cell to an A-centred cell.

Table 1.8. The conventional types of unit cell

Symbol	Type	Positions of additional lattice points	Number of lattice points per cell
P	primitive	—	1
I	body centred	(1/2, 1/2, 1, 2)	2
A	A-face centred	(0, 1/2, 1/2)	2
B	B-face centred	(1/2, 0, 1/2)	2
C	C-face centred	(1/2, 1/2, 0)	2
F	All faces centred	(1/2, 1/2, 0), (1/2, 0, 1/2)	2
		(0, 1/2, 1/2)	4
R	Rhombohedrally centred (de scription with 'hexagonal axes')	(1/3, 2/3, 2/3), (2/3, 1/3, 1/3)	3

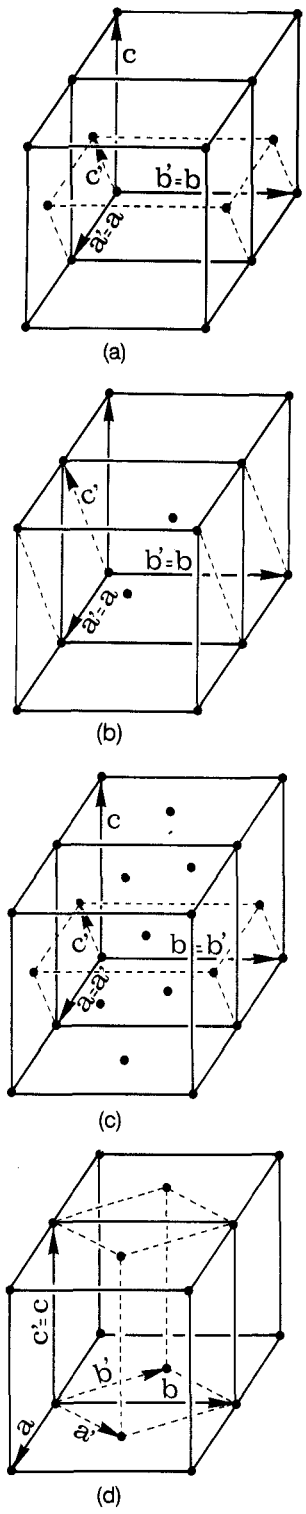


Fig. 1.16. Monoclinic lattices: (a) reduction of a B-centred cell to a P cell; (b) reduction of an I-centred to an A-centred cell; (c) reduction of an F-centred to a C-centred cell; (d) reduction of a C-centred to a P non-monoclinic cell.

Triclinic lattices

Even though non-primitive cells can always be chosen, the absence of axes with order greater than one suggests the choice of a conventional primitive cell with unrestricted α, β, γ angles and $a{:}b{:}c$ ratios. In fact, any triclinic lattice can always be referred to such a cell.

Monoclinic lattices

The conventional monoclinic cell has the twofold axis parallel to $\boldsymbol{b}$, angles $\alpha = \gamma = 90°$, unrestricted β and $a{:}b{:}c$ ratios. A B-centred monoclinic cell with unit vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ is shown in Fig. 1.16(a). If we choose $\boldsymbol{a}' = \boldsymbol{a}$, $\boldsymbol{b}' = \boldsymbol{b}$, $\boldsymbol{c}' = (\boldsymbol{a} + \boldsymbol{c})/2$ a primitive cell is obtained. Since $\boldsymbol{c}'$ lies on the $(\boldsymbol{a}, \boldsymbol{c})$ plane, the new cell will still be monoclinic. Therefore a lattice with a B-type monoclinic cell can always be reduced to a lattice with a P monoclinic cell.

An I cell with axes $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ is illustrated in Fig. 1.16(b). If we choose $\boldsymbol{a}' = \boldsymbol{a}$, $\boldsymbol{b}' = \boldsymbol{b}$, $\boldsymbol{c}' = \boldsymbol{a} + \boldsymbol{c}$, the corresponding cell becomes an A monoclinic cell. Therefore a lattice with an I monoclinic cell may always be described by an A monoclinic cell. Furthermore, since the $\boldsymbol{a}$ and $\boldsymbol{c}$ axes can always be interchanged, an A cell can be always reduced to a C cell.

An F cell with axes $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ is shown in Fig. 1.16(c). When choosing $\boldsymbol{a}' = \boldsymbol{a}$, $\boldsymbol{b}' = \boldsymbol{b}$, $\boldsymbol{c}' = (\boldsymbol{a} + \boldsymbol{c})/2$ a type-C monoclinic cell is obtained. Therefore, also, a lattice described by an F monoclinic cell can always be described by a C monoclinic cell.

We will now show that there is a lattice with a C monoclinic cell which is not amenable to a lattice having a P monoclinic cell. In Fig. 1.16(d) a C cell with axes $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ is illustrated. A primitive cell is obtained by assuming $\boldsymbol{a}' = (\boldsymbol{a} + \boldsymbol{b})/2$, $\boldsymbol{b}' = (-\boldsymbol{a} + \boldsymbol{b})/2$, $\boldsymbol{c}' = \boldsymbol{c}$, but this no longer shows the features of a monoclinic cell, since $\gamma' \neq 90°$, $\boldsymbol{a}' = \boldsymbol{b}' \neq \boldsymbol{c}'$, and the 2 axis lies along the diagonal of a face. It can then be concluded that there are two distinct monoclinic lattices, described by P and C cells, and not amenable one to the other.

Orthorhombic lattices

In the conventional orthorhombic cell the three proper or inversion axes are parallel to the unit vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, with angles $\alpha = \beta = \gamma = 90°$ and general $a{:}b{:}c$ ratios. With arguments similar to those used for monoclinic lattices, the reader can easily verify that there are four types of orthorhombic lattices, P, C, I, and F.

Tetragonal lattices

In the conventional tetragonal cell the fourfold axis is chosen along $\boldsymbol{c}$ with $\alpha = \beta = \gamma = 90°$, $a = b$, and unrestricted c value. It can be easily verified that because of the fourfold symmetry an A cell will always be at the same time a B cell and therefore an F cell. The latter is then amenable to a tetragonal I cell. A C cell is always amenable to another tetragonal P cell. Thus only two different tetragonal lattices, P and I, are found.

Cubic lattices

In the conventional cubic cell the four threefold axes are chosen to be parallel to the principal diagonals of a cube, while the unit vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ are parallel to the cube edges. Because of symmetry a type-A (or B or C)

cell is also an F cell. There are three cubic lattices, P, I, and F which are not amenable one to the other.

Hexagonal lattices

In the conventional hexagonal cell the sixfold axis is parallel to $\boldsymbol{c}$, with $\boldsymbol{a} = \boldsymbol{b}$, unrestricted $\boldsymbol{c}$, $\alpha = \beta = 90°$, and $\gamma = 120°$. P is the only type of hexagonal Bravais lattice.

Trigonal lattices

As for the hexagonal cell, in the conventional trigonal cell the threefold axis is chosen parallel to $\boldsymbol{c}$, with $\boldsymbol{a} = \boldsymbol{b}$, unrestricted $\boldsymbol{c}$, $\alpha = \beta = 90°$, and $\gamma = 120°$. Centred cells are easily amenable to the conventional P trigonal cell.

Because of the presence of a threefold axis some lattices can exist which may be described via a P cell of rhombohedral shape, with unit vectors $\boldsymbol{a}_R$, $\boldsymbol{b}_R$, $\boldsymbol{c}_R$ such that $a_R = b_R = c_R$, $\alpha_R = \beta_R = \gamma_R$, and the threefold axis along the $\boldsymbol{a}_R + \boldsymbol{b}_R + \boldsymbol{c}_R$ direction (see Fig. 1.17). Such lattices may also be described by three triple hexagonal cells with basis vectors $\boldsymbol{a}_H$, $\boldsymbol{b}_H$, $\boldsymbol{c}_H$ defined according to[6]

$$\boldsymbol{a}_H = \boldsymbol{a}_R - \boldsymbol{b}_R, \qquad \boldsymbol{b}_H = \boldsymbol{b}_R - \boldsymbol{c}_R, \qquad \boldsymbol{c}_H = \boldsymbol{a}_R + \boldsymbol{b}_R + \boldsymbol{c}_R$$

or

$$\boldsymbol{a}_H = \boldsymbol{b}_R - \boldsymbol{c}_R, \qquad \boldsymbol{b}_H = \boldsymbol{c}_R - \boldsymbol{a}_R, \qquad \boldsymbol{c}_H = \boldsymbol{a}_R + \boldsymbol{b}_R + \boldsymbol{c}_R$$

or

$$\boldsymbol{a}_H = \boldsymbol{c}_R - \boldsymbol{a}_R, \qquad \boldsymbol{b}_H = \boldsymbol{a}_R - \boldsymbol{b}_R, \qquad \boldsymbol{c}_H = \boldsymbol{a}_R + \boldsymbol{b}_R + \boldsymbol{c}_R.$$

These hexagonal cells are said to be in **obverse** setting. Three further triple hexagonal cells, said to be in **reverse** setting, can be obtained by changing $\boldsymbol{a}_H$ and $\boldsymbol{b}_H$ to $-\boldsymbol{a}_H$ and $-\boldsymbol{b}_H$. The hexagonal cells in obverse setting have centring points (see again Fig. 1.17)) at

$$(0, 0, 0), \qquad (2/3, 1/3, 1/3), \qquad (1/3, 2/3, 2/3)$$

while for reverse setting centring points are at

$$(0, 0, 0), \qquad (1/3, 2/3, 1/3),, \quad (2/3, 1/3, 2/3).$$

It is worth noting that a rhombohedral description of a hexagonal P lattice is always possible. Six triple rhombohedral cells with basis vectors $\boldsymbol{a}'_R$, $\boldsymbol{b}'_R$,

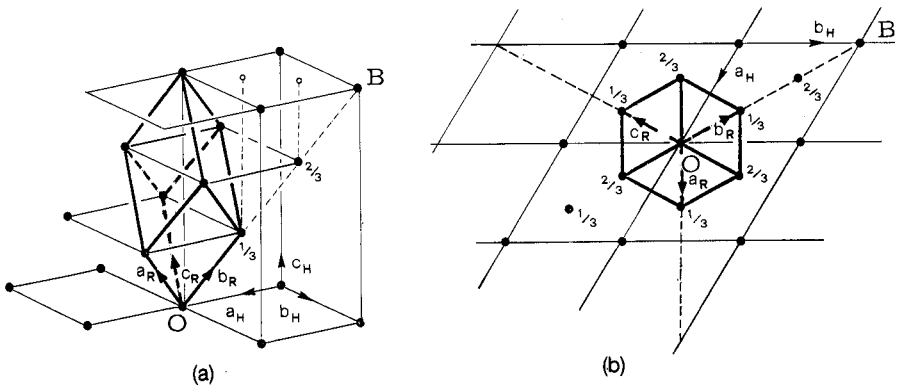


Fig. 1.17. Rhombohedral lattice. The basis of the rhombohedral cell is labelled $\boldsymbol{a}_R$, $\boldsymbol{b}_R$, $\boldsymbol{c}_R$, the basis of the hexagonal centred cell is labelled $\boldsymbol{a}_h$, $\boldsymbol{b}_h$, $\boldsymbol{c}_h$ (numerical fractions are calculated in terms of the $\boldsymbol{c}_h$ axis). (a) Obverse setting; (b) the same figure as in (a) projected along $\boldsymbol{c}_h$.

c'_R can be obtained from a_H, b_H, c_H by choosing:

$$a'_R = a_H + c_H, \qquad b'_R = b_H + c_H, \qquad c'_R = -(a_H + b_H) + c_H$$

$$a'_R = -a_H + c_H, \qquad b'_R = -b_H + c_H, \qquad c'_R = a_H + b_H + c_H$$

and cyclic permutations of a'_R, b'_R, c'_R. Each triple rhomobohedral cell will have centring points at (0, 0, 0), (1/3, 1/3, 1/3), (2/3, 2/3, 2/3).

In conclusion, some trigonal lattices may be described by a hexagonal P cell, others by a triple hexagonal cell. In the first case the nodes lying on the different planes normal to the threefold axis will lie exactly one on top of the other, in the second case lattice planes are translated one with respect to the other in such a way that the nth plane will superpose on the $(n+3)$th plane (this explains why a rhombohedral lattice is not compatible with a sixfold axis).

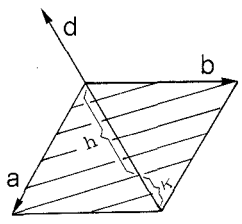


Fig. 1.18. Intersections of the set of crystallographic planes $(h\,k\,l)$ with the three symmetry-equivalent ***a, b, d*** axes in trigonal and hexagonal systems.

When, for crystals belonging to the hexagonal or trigonal systems, a hexagonal cell is chosen, then on the plane defined by $\boldsymbol{a}$ and $\boldsymbol{b}$ there will be a third axis equivalent to them. The family of planes (hkl) (see Fig. 1.18) divides the positive side of $\boldsymbol{a}$ in h parts and the positive side of $\boldsymbol{b}$ in k parts. If the third axis (say $\boldsymbol{d}$) on the $(\boldsymbol{a}, \boldsymbol{b})$ plane is divided in i parts we can introduce an extra index in the symbol of the family, i.e. $(hkil)$. From the same figure it can be seen that the negative side of $\boldsymbol{d}$ is divided in $h+k$ parts, and then $i = -(h+k)$. For instance (1 2 −3 5), (3 −5 2 1), (−2 0 2 3) represent three plane families in the new notation. The four-index symbol is useful to display the symmetry, since $(hkil)$, $(kihl)$, and $(ihkl)$ are symmetry equivalent planes.

Also, lattice directions can be indicated by the four-index notation. Following pp. 7–8, a direction in the $(\boldsymbol{a}, \boldsymbol{b})$ plane is defined by a vector $(\mathrm{P}-\mathrm{O}) = m\mathbf{a} + n\boldsymbol{b}$. If we introduce the third axis $\boldsymbol{d}$ in the plane, we can write $(\mathrm{P}-\mathrm{O}) = m\boldsymbol{a} + n\boldsymbol{b} + 0\boldsymbol{d}$. Since a decrease (or increase) of the three coordinates by the same amount j does not change the point P, this may be represented by the coordinates: $u = m - j$, $v = n - j$, $i = -j$.

If we choose $j = (m+n)/3$, then $u = (2m-n)/3$, $v = (2n-m)/3$, $i = -(m+n)/3$. In conclusion the direction $[mnw]$ may be represented in the new notation as $[uviw]$, with $i = -(u+v)$. On the contrary, if a direction is already represented in the four-index notation $[uviw]$, to pass to the three-index one, $-i$ should be added to the first three indices in order to bring to zero the third index, i.e. $[u-i\ \ v-i\ \ w]$.

A last remark concerns the point symmetry of a lattice. There are seven three-dimensional lattice point groups, they are called **holohedries** and are listed in Table 1.6 (note that $\bar{3}$m is the point symmetry of the rhombohedral lattice). In two dmensions four holohedries exist: 2, 2mm, 4mm, 6mm.

The 14 Bravais lattices are illustrated in Fig. 1.19 by means of their conventional unit cells (see Appendix 1.C for a different type of cell). A detailed description of the metric properties of crystal lattices will be given in Chapter 2.

The space groups

A crystallographic space group is the set of geometrical symmetry operations that take a three-dimensional periodic object (say a crystal) into itself.

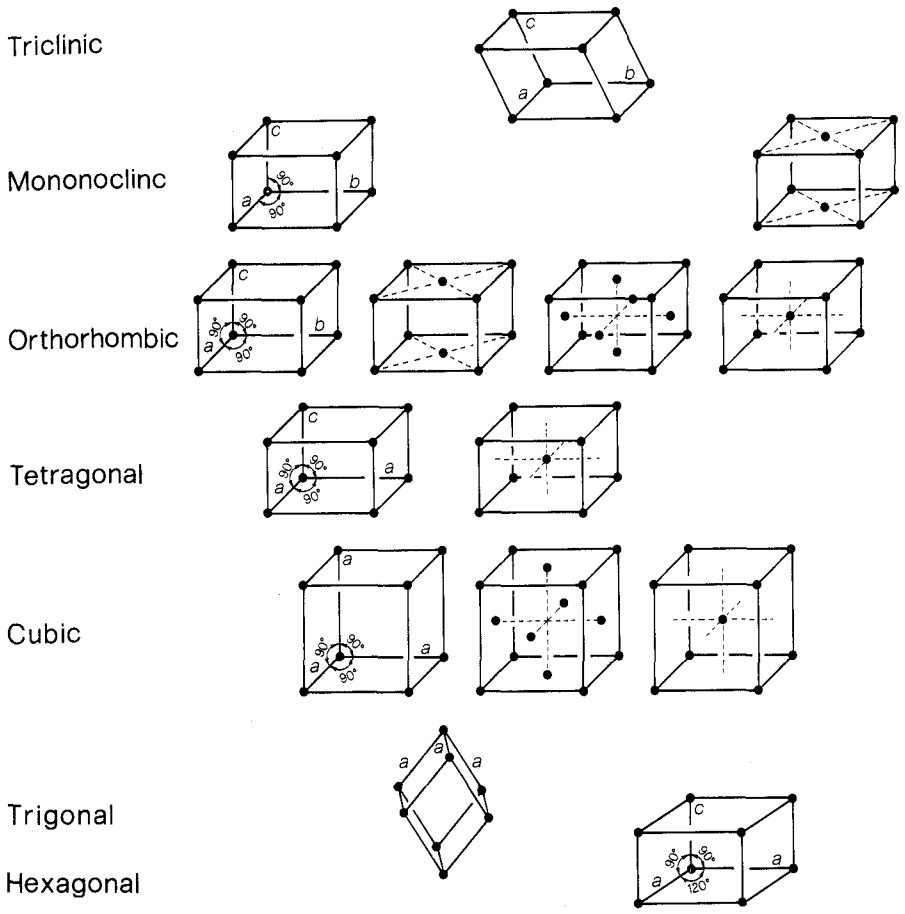


Fig. 1.19. The 14 three-dimensional Bravais lattices.

The total number of crystallographic space groups is 230. They were first derived at the end of the last century by the mathematicians Fedorov (1890) and Schoenflies (1891) and are listed in Table 1.9.

In Fedorov's mathematical treatment each space group is represented by a set of three equations: such an approach enabled Fedorov to list all the space groups (he rejected, however, five space groups as impossible: *Fdd*2, *Fddd*, I$\bar{4}$3*d*, P4$_3$32, P4$_1$32). The Schoenflies approach was most practical and is described briefly in the following.

On pp. 11–16 we saw that 32 combinations of either simple rotation or inversion axes are compatible with the periodic nature of crystals. By combining the 32 point groups with the 14 Bravais lattices (i.e. P, I, F, . . .) one obtains only 73 (symmorphic) space groups. The others may be obtained by introducing a further variation: the proper or improper symmetry axes are replaced by screw axes of the same order and mirror planes by glide planes. Note, however, that when such combinations have more than one axis, the restriction that all symmetry elements must intersect in a point no longer applies (cf. Appendix 1.B). As a consequence of the presence of symmetry elements, several symmetry-equivalent objects will coexist within the unit cell. We will call the smallest part of the unit cell which will generate the whole cell when applying to it the symmetry

Table 1.9. The 230 three-dimensional space groups arranged by crystal systems and point groups. Space groups (and enantiomorphous pairs) that are uniquely determinable from the symmetry of the diffraction pattern and from systematic absences (see p. 159) are shown in bold-type. Point groups without inversion centres or mirror planes are emphasized by boxes

Crystal system	Point group	Space groups
Triclinic	$\boxed{1}$	P1
	$\bar{1}$	P$\bar{1}$
Monoclinic	$\boxed{2}$	P2, P2_1, C2
	m	Pm, P*c*, Cm, C*c*
	2/m	P2/m, P2_1/m, C2/m, P2/*c*, **P2_1/*c***, C2/*c*
Orthorhombic	$\boxed{222}$	P222, **P222_1**, **P2_12_12**, **P$2_12_12_1$**, **C222_1**, C222, F222, I222, I$2_12_12_1$
	mm2	Pmm2, Pm*c*2_1, P*cc*2, Pm*a*2_1, P*ca*2_1, P*nc*2_1, P*mn*2_1, P*ba*2, P*na*2_1, P*nn*2, Cmm2, Cm*c*2_1, C*cc*2, Amm2, A*b*m2, Am*a*2, A*ba*2, Fmm2, ***Fdd*2**, Imm2, I*ba*2, Ima2
	mmm	Pmmm, ***Pnnn***, P*ccm*, ***Pban***, Pmm*a*, ***Pnna***, Pm*na*, **P*cca***, P*bam*, **P*ccn***, P*bcm*, P*nnm*, Pmm*n*, **P*bcn***, **P*bca***, P*nma*, Cm*cm*, Cm*ca*, Cmmm, C*ccm*, Cmm*a*, **C*cca***, Fmmm, **F*ddd***, Immm, I*bam*, **I*bca***, Imm*a*
Tetragonal	●	P4, **P4_1**, P4_2, **P4_3**, I4, **I4_1**
	$\bar{4}$	P$\bar{4}$, I$\bar{4}$
	4/m	P4/m, P4_2/m, **P4/*n***, **P4_2/*n***, I4/m, **I4_1/*a***
	$\boxed{422}$	P422, **P42_12**, P4_122, **P4_12_12**, **P4_222**, **P4_22_12**, **P4_322**, **P4_32_12**, I422, **I4_122**
	4mm	P4mm, P4*b*m, P4_2*cm*, P4_2*nm*, P4*cc*, P4*nc*, P4_2*mc*, P4_2*bc*, I4mm, I4*cm*, I4_1*md*, **I4_1*cd***
	$\bar{4}$m	P$\bar{4}$2m, P$\bar{4}$2*c*, P$\bar{4}2_1$m, **P$\bar{4}2_1$*c***, P$\bar{4}$m2, P$\bar{4}$*c*2, P$\bar{4}$*b*2, P$\bar{4}$*n*2, I$\bar{4}$m2, I$\bar{4}$*c*2, I$\bar{4}$2m, I$\bar{4}$2*d*
	4/mmm	P4/mmm, P4/m*cc*, **P4/*nbm***, **P4/*nnc***, P4/m*bm*, P4/m*nc*, **P4/*nmm***, **P4/*ncc***, P4_2/mm*c*, P4_2/m*cm*, **P4_2/*nbc***, **P4_2/*nnm***, P4_2/m*bc*, P4_2m*nm*, **P4_2/*nmc***, **P4_2/*ncm***, I4/mmm, I4/m*cm*, **I4_1/*amd***, **I4_1/*acd***
Trigonal–hexagonal	$\boxed{3}$	P3, P3_1, P3_2, R3
	$\bar{3}$	P$\bar{3}$, R$\bar{3}$
	$\boxed{32}$	P312, P321, **P3_112**, **P3_121**, **P3_212**, **P3_221**, R32
	3m	P3m1, P31m, P3*c*1, P31*c*, R3m, R3*c*
	$\bar{3}$m	P$\bar{3}$1m, P$\bar{3}$1*c*, P$\bar{3}$m1, P$\bar{3}$*c*1, R$\bar{3}$m, R$\bar{3}$*c*
	$\boxed{6}$	P6, **P6_1**, **P6_5**, P6_3, **P6_2**, **P6_4**,
	$\bar{6}$	P$\bar{6}$
	6/m	P6/m, P6_3/m
	$\boxed{622}$	P622, **P6_122**, **P6_522**, **P6_222**, **P6_422**, **P6_322**
	6mm	P6mm, P6*cc*, P6_3*cm*, P6_3*mc*
	$\bar{6}$m	P$\bar{6}$m2, P$\bar{6}$*c*2, P$\bar{6}$2m, P$\bar{6}$2*c*
	6/mmm	P6/mmm, P6/m*cc*, P6_3/m*cm*, P6_3/m*mc*
Cubic	$\boxed{23}$	P23, F23, I23, **P2_13**, I2_13
	m$\bar{3}$	Pm$\bar{3}$, **P*n*$\bar{3}$**, Fm$\bar{3}$, **F*d*$\bar{3}$**, Im$\bar{3}$, **P*a*$\bar{3}$**, **I*a*$\bar{3}$**
	$\boxed{432}$	P432, **P4_232**, F432, **F4_132**, I432, **P4_332**, **P4_132**, I4_132
	$\bar{4}$3m	P$\bar{4}$3m, F$\bar{4}$3m, I$\bar{4}$3m, P$\bar{4}$3*n*, F$\bar{4}$3*c*, **I$\bar{4}$3*d***
	m$\bar{3}$m	Pm$\bar{3}$m, **P*n*$\bar{3}$*n***, Pm$\bar{3}$n, P*n*$\bar{3}$**m**, Fm$\bar{3}$m, Fm$\bar{3}$*c*, **F*d*$\bar{3}$m**, **F*d*$\bar{3}$*c***, Im$\bar{3}$m, **I*a*$\bar{3}$*d***

operations an **asymmetric unit**. The asymmetric unit is not usually uniquely defined and can be chosen with some degree of freedom. It is nevertheless obvious that when rotation or inversion axes are present, they must lie at the borders of the asymmetric unit.

According to the international (Hermann–Mauguin) notation, the space-group symbol consists of a letter indicating the centring type of the conventional cell, followed by a set of characters indicating the symmetry elements. Such a set is organized according to the following rules:

1. For triclinic groups: no symmetry directions are needed. Only two space groups exist: P1 and P$\bar{1}$.
2. For monoclinic groups: only one symbol is needed, giving the nature of the unique dyad axis (proper and/or inversion). Two settings are used: y-axis unique, z-axis unique.
3. For orthorhombic groups: dyads (proper and/or of inversion) are given along x, y, and z axis in the order. Thus P$ca2_1$ means: primitive cell, glide plane of type c normal to x-axis, glide plane of type a normal to the y-axis, twofold screw axis along z.
4. For tetragonal groups: first the tetrad (proper and/or of inversion) axis along z is specified, then the dyad (proper and/or of inversion) along x is given, and after that the dyad along [110] is specified. For example, $P4_2/nbc$ denotes a space group with primitive cell, a 4 sub 2 screw axis along z to which a diagonal glide plane is perpendicular, an axial glide plane b normal to the x axis, an axial glide plane c normal to [110]. Because of the tetragonal symmetry, there is no need to specify symmetry along the y-axis.
5. For trigonal and hexagonal groups: the triad or hexad (proper and/or of inversion) along the z-axis is first given, then the dyad (proper and/or of inversion) along x and after that the dyad (proper and/or of inversion) along [1$\bar{1}$0] is specified. For example, $P6_3mc$ has primitive cell, a sixfold screw axis 6 sub 3 along z, a reflection plane normal to x and an axial glide plane c normal to [1$\bar{1}$0].
6. For cubic groups: dyads or tetrads (proper and/or of inversion) along x, followed by triads (proper and/or of inversion) along [111] and dyads (proper and/or of inversion) along [110].

We note that:

1. The combination of the Bravais lattices with symmetry elements with no translational components yields the 73 so-called **symmorphic** space groups. Examples are: P222, Cmm2, F23, etc.
2. The 230 space groups include 11 enantiomorphous pairs: $P3_1$ ($P3_2$), $P3_112$ ($P3_212$), $P3_121$ ($P3_221$), $P4_1$ ($P4_3$), $P4_122$ ($P4_322$), $P4_12_12$ ($P4_32_12$), $P6_1$ ($P6_5$), $P6_2$ ($P6_4$), $P6_122$ ($P6_522$), $P6_222$ ($P6_422$), $P4_132$ ($P4_332$). The (+) isomer of an optically active molecule crystallizes in one of the two enantiomorphous space groups, the (−) isomer will crystallize in the other.
3. Biological molecules are enantiomorphous and will then crystallize in space groups with no inversion centres or mirror planes; there are 65 groups of this type (see Table 1.9).
4. The point group to which the space group belongs is easily obtained from the space-group symbol by omitting the lattice symbol and by replacing

the screw axes and the glide planes with their corresponding symmorphic symmetry elements. For instance, the space groups $P4_2/mmc$, $P4/ncc$, $I4_1/acd$, all belong to the point group 4/mmm.

5. The frequency of the different space groups is not uniform. Organic compounds tend to crystallize in the space groups that permit close packing of triaxial ellipsoids.[8] According to this view, rotation axes and reflection planes can be considered as rigid scaffolding which make more difficult the comfortable accommodation of molecules, while screw axes and glide planes, when present, make it easier because they shift the molecules away from each other.

Mighell and Rodgers [9] examined 21 051 organic compounds of known crystal structure; 95% of them had a symmetry not higher than orthorhombic. In particular 35% belonged to the space group $P2_1/c$, 13.3% to $P\bar{1}$, 12.4% to $P2_12_12_1$, 7.6% to $P2_1$ and 6.9% to $C2/c$. A more recent study by Wilson,[10] based on a survey of the 54 599 substances stored in the Cambridge Structural Database (in January 1987), confirmed Mighell and Rodgers' results and suggested a possible model to estimate the number N_{sg} of structures in each space group of a given crystal class:

$$N_{sg} = A_{cc} \exp\{-B_{cc}[2]_{sg} - C_{cc}[m]_{sg})$$

where A_{cc} is the total number of structures in the crystal class, $[2]_{sg}$ is the number of twofold axes, $[m]_{sg}$ the number of reflexion planes in the cell, B_{cc} and C_{cc} are parameters characteristic of the crystal class in question. The same results cannot be applied to inorganic compounds, where ionic bonds are usually present. Indeed most of the 11 641 inorganic compounds considered by Mighell and Rodgers crystallize in space groups with orthorhombic or higher symmetry. In order of decreasing frequency we have: Fm3m, $Fd3m$, $P6_3/mmc$, $P2_1/c$, $Pm\bar{3}m$, $R\bar{3}m$, C2/m, $C2/c$, ...

The standard compilation of the plane and of the three-dimensional space groups is contained in volume A of the *International Tables for Crystallography*. For each space groups the *Tables* include (see Figs 1.20 and 1.21).

1. At the first line: the short international (Hermann–Mauguin) and the Schoenflies symbols for the space groups, the point group symbol, the crystal system.

2. At the second line: the sequential number of the plane or space group, the full international (Hermann–Mauguin) symbol, the Patterson symmetry (see Chapter 5, p. 327). Short and full symbols differ only for the monoclinic space groups and for space groups with point group mmm, 4/mmm, $\bar{3}m$, 6/mmm, $m\bar{3}$, $m\bar{3}m$. While in the short symbols symmetry planes are suppressed as much as possible, in the full symbols axes and planes are listed for each direction.

3. Two types of space group diagrams (as orthogonal projections along a cell axis) are given: one shows the position of a set of symmetrically equivalent points, the other illustrates the arrangement of the symmetry elements. Close to the graphical symbols of a symmetry plane or axis parallel to the projection plane the 'height' h (as a fraction of the shortest lattice translation normal to the projection plane) is printed. If $h = 0$ the height is omitted. Symmetry elements at h also occur at height $h + 1/2$.

4. Information is given about: setting (if necessary), origin, asymmetric unit, symmetry operations, symmetry generators (see Appendix 1.E) selected to generate all symmetrical equivalent points described in block 'Positions'. The origin of the cell for centrosymmetric space groups is usually chosen on an inversion centre. A second description is given if points of high site symmetry not coincident with the inversion centre occur. For example, for $Pn\bar{3}n$ two descriptions are available, the first with origin at 432, and the second with origin at $\bar{3}$. For non-centrosymmetric space groups the origin is chosen at a point of highest symmetry (e.g. the origin for $P\bar{4}2c$ is chosen at $\bar{4}1c$) or at a point which is conveniently placed with respect to the symmetry elements. For example, on the screw axis in $P2_1$, on the glide plane in Pc, at $1a2_1$ in $Pca2_1$, at a point which is surrounded symmetrically by the three 2_1 axis in $P2_12_12_1$.

5. The block **positions** (called also Wyckoff positions) contains the **general position** (a set of symmetrically equivalent points, each point of which is left invariant only by application of an identity operation) and a list of **special positions** (a set of symmetrically equivalent points is in special position if each point is left invariant by at least two symmetry operations of the space group). The first three block columns give information about **multiplicity** (number of equivalent points per unit cell), **Wyckoff letter** (a code scheme starting with *a* at the bottom position and continuing upwards in alphabetical order), **site symmetry** (the group of symmetry operations which leaves invariant the site). The symbol adopted[9] for describing the site symmetry displays the same sequence of symmetry directions as the space group symbol. A dot marks those directions which do not contribute any element to the site symmetry. To each Wyckoff position a **reflection condition**, limiting possible reflections, may be associated. The condition may be general (it is obeyed irrespective of which Wyckoff positions are occupied by atoms (see Chapter 3, p. 159) or special (it limits the contribution to the structure factor of the atoms located at that Wyckoff position).

6. Symmetry of special projections. Three orthogonal projections for each space group are listed: for each of them the projection direction, the Hermann–Mauguin symbol of the resulting plane group, and the relation between the basis vectors of the plane group and the basis vectors of the space group, are given, together with the location of the plane group with respect to the unit cell of the space group.

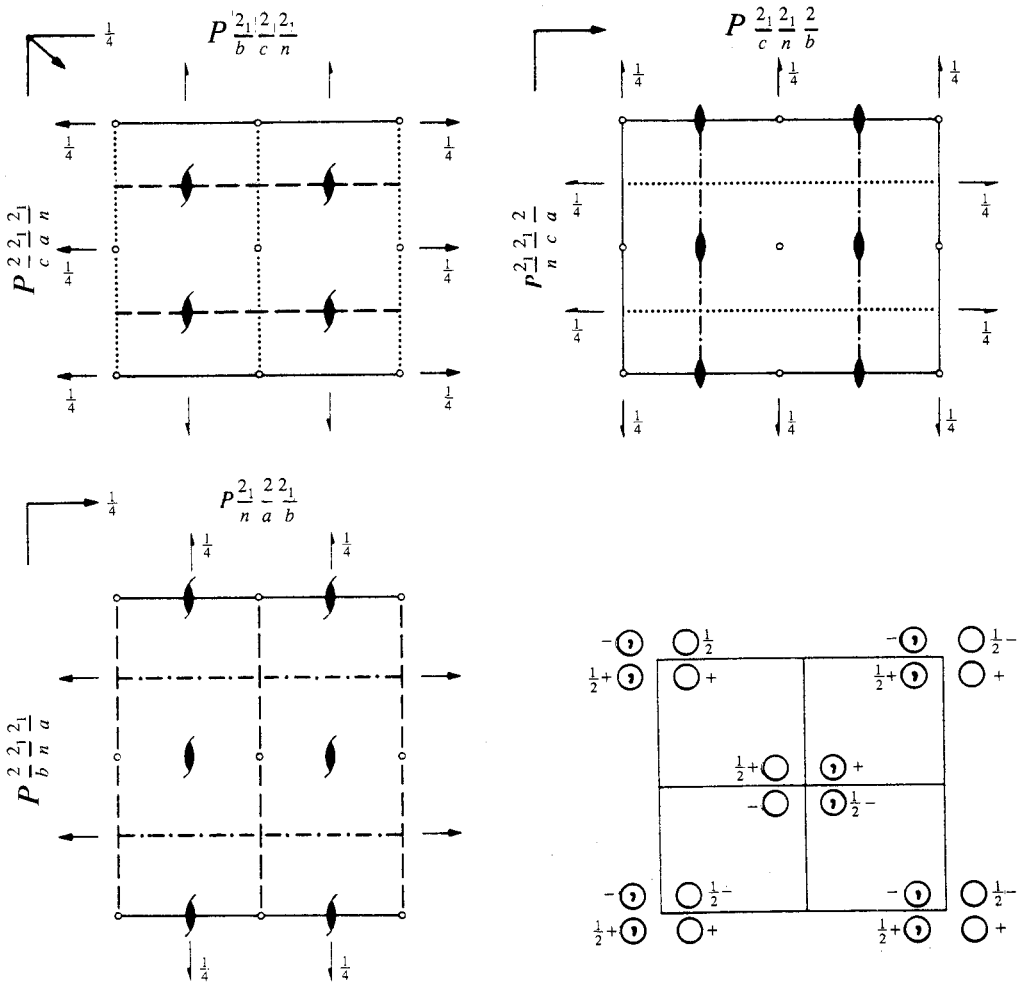
7. Information about maximal subgroups and minimal supergroups (see Appendix 1.E) is given.

In Figs. 1.20 and 1.21 descriptions of the space groups $Pbcn$ and $P4_222$ are respectively given as compiled in the *International Tables for Crystallography*. In order to obtain space group diagrams the reader should perform the following operations:

1. Some or all the symmetry elements are traced as indicated in the space-group symbol. This is often a trivial task, but in certain cases special care must be taken. For example, the three twofold screw axes do not intersect each other in $P2_12_12_1$, but two of them do in $P2_12_12$ (see Appendix 1.B).

$Pbcn$ $\quad D_{2h}^{14}$ $\quad mmm$ $\quad$ Orthorhombic

No. 60 $\quad P\,2_1/b\,2/c\,2_1/n$ $\quad$ Patterson symmetry $Pmmm$



Origin at $\bar{1}$ on $1\,c\,1$

Asymmetric unit $\quad 0 \le x \le \frac{1}{2};\quad 0 \le y \le \frac{1}{2};\quad 0 \le z \le \frac{1}{2}$

Symmetry operations

(1) 1	(2) $2(0,0,\frac{1}{2})\ \ \frac{1}{4},\frac{1}{4},z$	(3) $2\ \ 0,y,\frac{1}{4}$	(4) $2(\frac{1}{2},0,0)\ \ x,\frac{1}{4},0$
(5) $\bar{1}\ \ 0,0,0$	(6) $n(\frac{1}{2},\frac{1}{2},0)\ \ x,y,\frac{1}{4}$	(7) $c\ \ x,0,z$	(8) $b\ \ \frac{1}{4},y,z$

Fig. 1.20. Representation of the group $Pbcn$ (as in *International Tables for Crystallography*).

CONTINUED

No. 60 *Pbcn*

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	d	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(3) $\bar{x},y,\bar{z}+\frac{1}{2}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	$0kl$: $k=2n$
			(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(7) $x,\bar{y},z+\frac{1}{2}$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$	$h0l$: $l=2n$
							$hk0$: $h+k=2n$
							$h00$: $h=2n$
							$0k0$: $k=2n$
							$00l$: $l=2n$
							Special: as above, plus
4	c	.2.	$0,y,\frac{1}{4}$	$\frac{1}{2},\bar{y}+\frac{1}{2},\frac{3}{4}$	$0,\bar{y},\frac{3}{4}$	$\frac{1}{2},y+\frac{1}{2},\frac{1}{4}$	hkl : $h+k=2n$
4	b	$\bar{1}$	$0,\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$	hkl : $h+k,l=2n$
4	a	$\bar{1}$	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	hkl : $h+k,l=2n$

Symmetry of special projections

Along [001] $c2mm$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p2gm$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

Along [010] $p2gm$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{c}$ $\boldsymbol{b}'=\boldsymbol{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2]$P2_12_12_1(P2_12_12)$ 1; 2; 3; 4
[2]$P112_1/n(P2_1/c)$ 1; 2; 5; 6
[2]$P12/c1(P2/c)$ 1; 3; 5; 7
[2]$P2_1/b11(P2_1/c)$ 1; 4; 5; 8
[2]$Pbc2_1(Pca2_1)$ 1; 2; 7; 8
[2]$Pb2n(Pnc2)$ 1; 3; 6; 8
[2]$P2_1cn(Pna2_1)$ 1; 4; 6; 7

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3]$Pbcn(\boldsymbol{a}'=3\boldsymbol{a})$; [3]$Pbcn(\boldsymbol{b}'=3\boldsymbol{b})$; [3]$Pbcn(\boldsymbol{c}'=3\boldsymbol{c})$

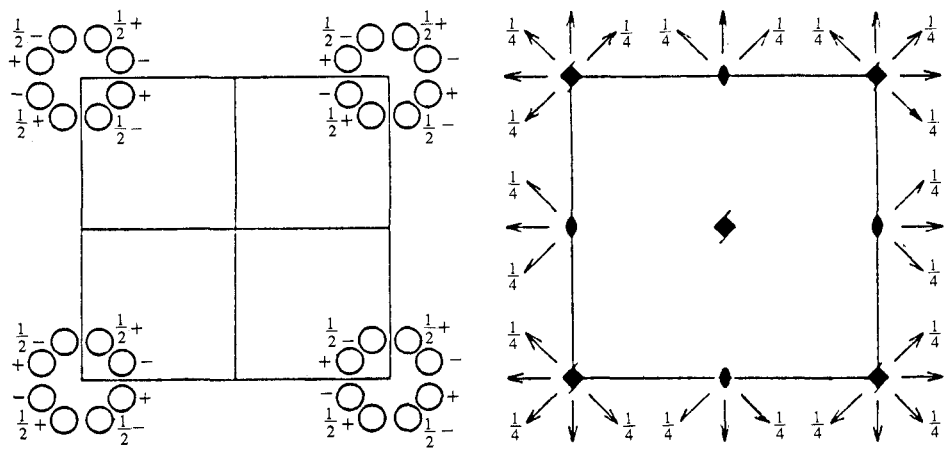
Minimal non-isomorphic supergroups

I none

II [2]$Abma(Cmca)$; [2]$Bbab(Ccca)$; [2]$Cmcm$; [2]$Ibam$; [2]$Pbcb(2\boldsymbol{a}'=\boldsymbol{a})(Pcca)$; [2]$Pmca(2\boldsymbol{b}'=\boldsymbol{b})(Pbcm)$; [2]$Pbmn(2\boldsymbol{c}'=\boldsymbol{c})(Pmna)$

$P4_222$ D_4^5 422 Tetragonal

No. 93 $P4_222$ Patterson symmetry $P4/mmm$



Origin at 222 at 4_221

Asymmetric unit $0 \leq x \leq \frac{1}{2}$; $0 \leq y \leq 1$; $0 \leq z \leq \frac{1}{4}$

Symmetry operations

(1) 1	(2) 2 0,0,z	(3) $4^+(0,0,\frac{1}{2})$ 0,0,z	(4) $4^-(0,0,\frac{1}{2})$ 0,0,z
(5) 2 0,y,0	(6) 2 x,0,0	(7) 2 $x,x,\frac{1}{4}$	(8) 2 $x,\bar{x},\frac{1}{4}$

Fig. 1.21. Representation of the group $P4_222$ (as in *International Tables for Crystallography*).

2. Once conveniently located, the symmetry operators are applied to a point P in order to obtain the **symmetry equivalent** points P′, P″, ... If P′, P″, . . . , fall outside the unit cell, they should be moved inside by means of appropriate lattice translations. The first type of diagram is so obtained.

3. New symmetry elements are then placed in the unit cell so producing the second type of diagram.

Some space group diagrams are collected in Fig. 1.22. Two simple crystal structures are shown in Figs 1.23 and 1.24: symmetry elements are also located for convenience.

The plane and line groups

There are 17 plane groups, which are listed in Table 1.10. In the symbol g stays for a glide plane. Any space group in projection will conform to one of these plane groups. There are two line groups: p1 and pm.

A periodic decoration of the plane according to the 17 plane groups is shown in Fig. 1.25.

CONTINUED

No. 93 $P4_222$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	p	1	(1) x,y,z (5) $\bar{x},y,\bar{z}$	(2) $\bar{x},\bar{y},z$ (6) $x,\bar{y},\bar{z}$	(3) $\bar{y},x,z+\frac{1}{2}$ (7) $y,x,\bar{z}+\frac{1}{2}$	(4) $y,\bar{x},z+\frac{1}{2}$ (8) $\bar{y},\bar{x},\bar{z}+\frac{1}{2}$	$00l$: $l=2n$
							Special: as above, plus
4	o	..2	$x,x,\frac{3}{4}$	$\bar{x},\bar{x},\frac{3}{4}$	$\bar{x},x,\frac{1}{4}$	$x,\bar{x},\frac{1}{4}$	$0kl$: $l=2n$
4	n	..2	$x,x,\frac{1}{4}$	$\bar{x},\bar{x},\frac{1}{4}$	$\bar{x},x,\frac{3}{4}$	$x,\bar{x},\frac{3}{4}$	$0kl$: $l=2n$
4	m	.2.	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	hhl : $l=2n$
4	l	.2.	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,0$	$0,\bar{x},0$	hhl : $l=2n$
4	k	.2.	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	hhl : $l=2n$
4	j	.2.	$x,0,0$	$\bar{x},0,0$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	hhl : $l=2n$
4	i	2..	$0,\frac{1}{2},z$	$\frac{1}{2},0,z+\frac{1}{2}$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}+\frac{1}{2}$	hkl : $h+k+l=2n$
4	h	2..	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},z+\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\bar{z}$	$\frac{1}{2},\frac{1}{2},\bar{z}+\frac{1}{2}$	hkl : $l=2n$
4	g	2..	$0,0,z$	$0,0,z+\frac{1}{2}$	$0,0,\bar{z}$	$0,0,\bar{z}+\frac{1}{2}$	hkl : $l=2n$
2	f	2.22	$\frac{1}{2},\frac{1}{2},\frac{1}{4}$	$\frac{1}{2},\frac{1}{2},\frac{3}{4}$			hkl : $l=2n$
2	e	2.22	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$			hkl : $l=2n$
2	d	222.	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$			hkl : $h+k+l=2n$
2	c	222.	$0,\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$			hkl : $h+k+l=2n$
2	b	222.	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $l=2n$
2	a	222.	$0,0,0$	$0,0,\frac{1}{2}$			hkl : $l=2n$

Symmetry of special projections

Along [001] $p4mm$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p2mm$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

Along [110] $p2mm$
$\boldsymbol{a}'=\frac{1}{2}(-\boldsymbol{a}+\boldsymbol{b})$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,x,\frac{1}{4}$

Maximal non-isomorphic subgroups

I [2]$P4_211$ ($P4_2$) 1; 2; 3; 4
[2]$P221$ ($P222$) 1; 2; 5; 6
[2]$P212$ ($C222$) 1; 2; 7; 8

IIa none

IIb [2]$P4_122$ ($\boldsymbol{c}'=2\boldsymbol{c}$); [2]$P4_322$ ($\boldsymbol{c}'=2\boldsymbol{c}$); [2]$C4_222_1$ ($\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{b}'=2\boldsymbol{b}$) ($P4_22_12$);
[2]$F4_122$ ($\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{b}'=2\boldsymbol{b}, \boldsymbol{c}'=2\boldsymbol{c}$) ($I4_122$)

Maximal isomorphic subgroups of lowest index

IIc [3]$P4_222$ ($\boldsymbol{c}'=3\boldsymbol{c}$); [2]$C4_222$ ($\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{b}'=2\boldsymbol{b}$) ($P4_222$)

Minimal non-isomorphic supergroups

I [2]$P4_2/mmc$; [2]$P4_2/mcm$; [2]$P4_2/nbc$; [2]$P4_2/nnm$; [3]$P4_232$

II [2]$I422$; [2]$P422$ ($2\boldsymbol{c}'=\boldsymbol{c}$)

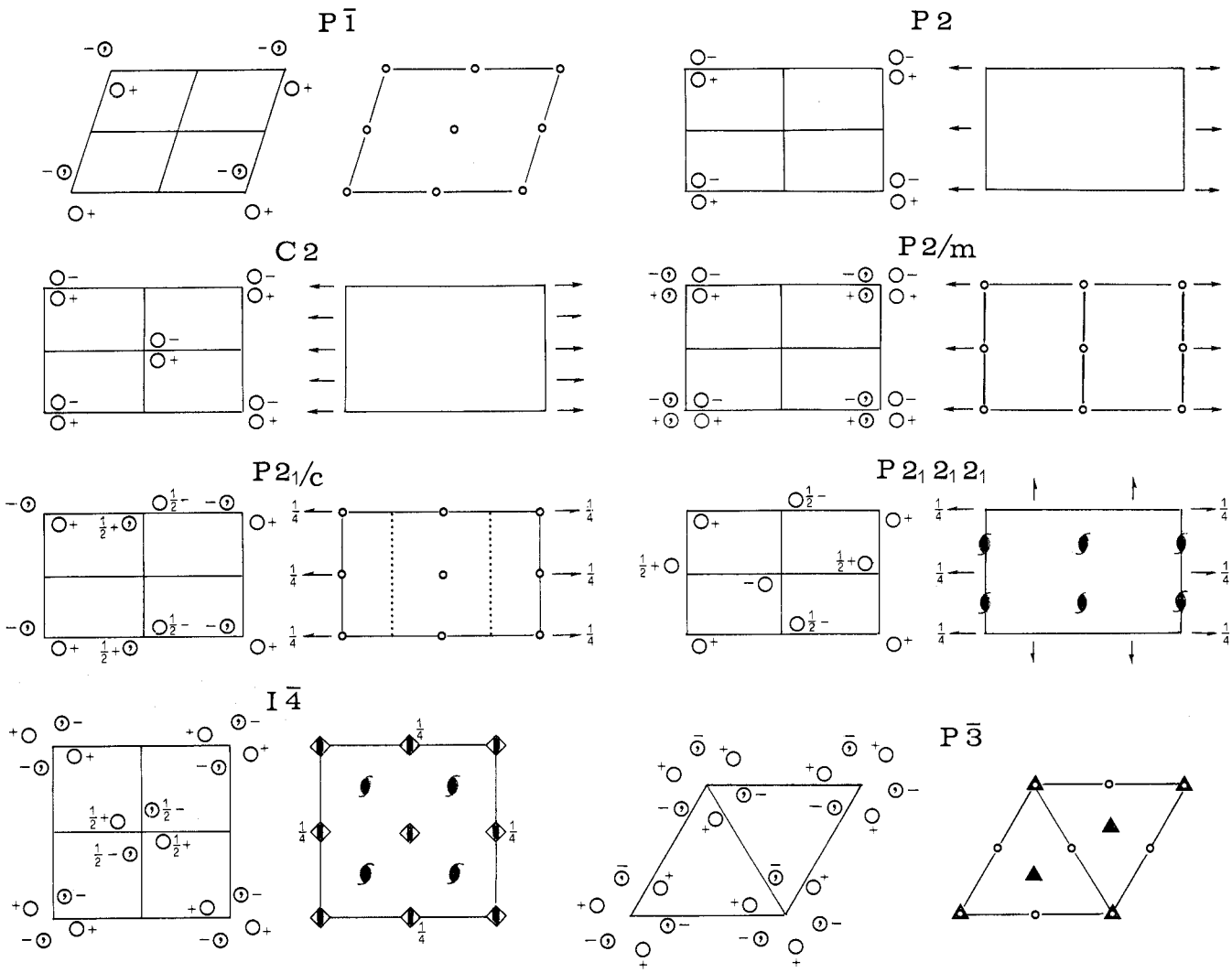


Fig. 1.22. Some space group diagrams.

On the matrix representation of symmetry operators

A symmetry operation acts on the fractional coordinates x, y, z of a point P to obtain the coordinates (x', y', z') of a symmetry-equivalent point P′:

$$\mathbf{X}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} T_1 \\ T_2 \\ T_3 \end{pmatrix} = \mathbf{CX} = \mathbf{RX} + \mathbf{T}. \quad (1.11)$$

The **R** matrix is the **rotational component** (proper or improper) of the symmetry operation. As we shall see in Chapter 2 its elements may be 0, +1, −1 and its determinant is ±1. **T** is the matrix of the translational component of the operation. A list of all the rotation matrices needed to conventionally describe the 230 space groups are given in Appendix 1.D.

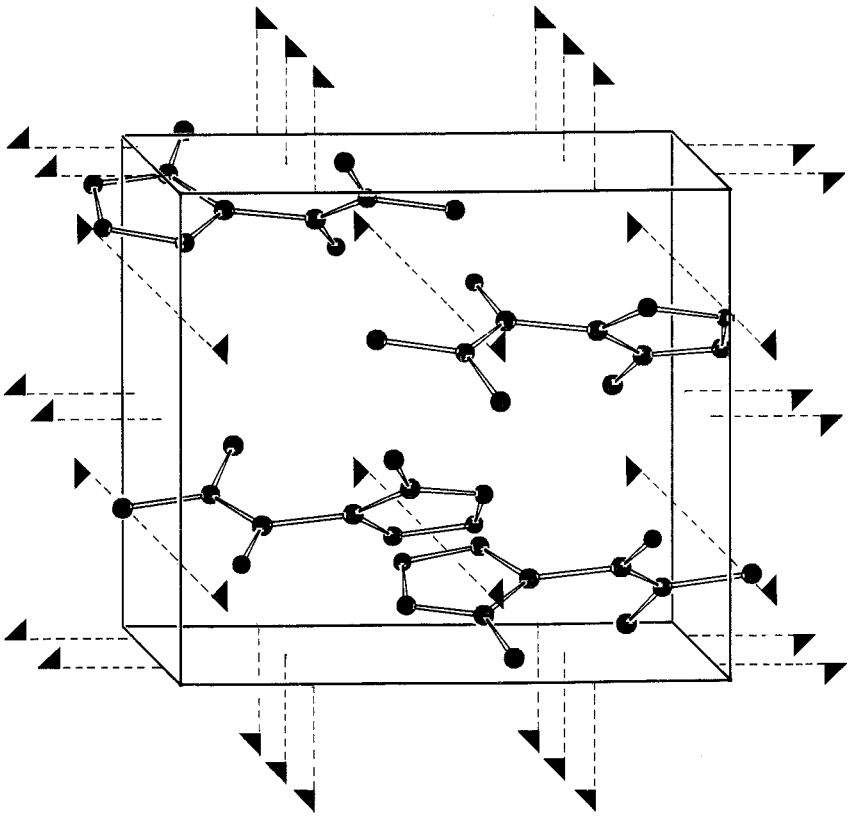


Fig. 1.23. A $P2_12_12_1$ crystal structure (G. Chiari, D. Viterbo, A. Gaetani Manfredotti, and C. Guastini (1975). *Cryst. Struct. Commun.*, 4,561) and its symmetry elements (hydrogen atoms are not drawn).

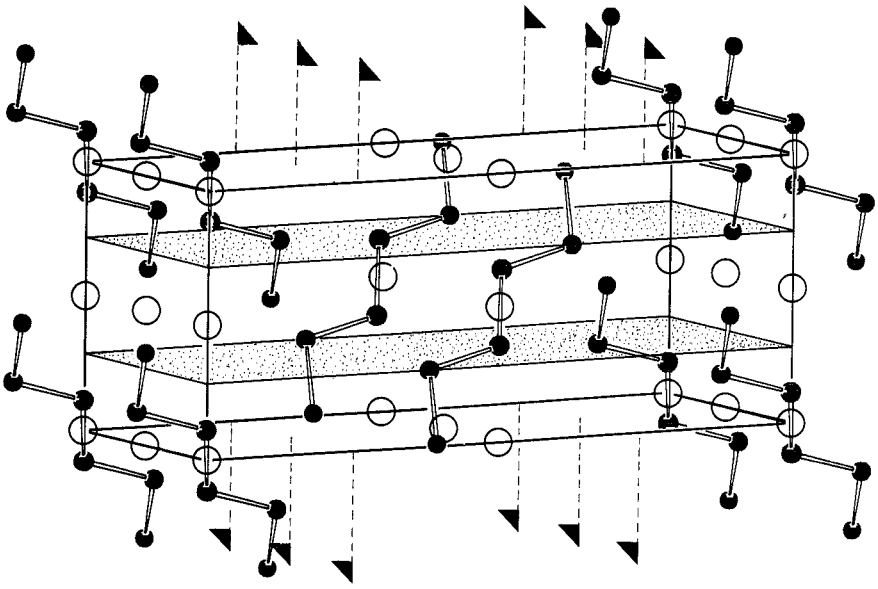


Fig. 1.24. A $P2_1/c$ crystal structure (M. Calleri, G. Ferraris, and D. Viterbo (1966). *Acta Cryst.*, **20**, 73) and its symmetry elements (hydrogen atoms are not drawn). Glide planes are emphasized by the shading.

Table 1.10. The 17 plane groups

Oblique cell	p1, p2
Rectangular cell	pm, pg, cm, p2mm, p2mg, p2gg, c2mm
Square cell	p4, p4mm, p4gm
Hexagonal cell	p3, p3m1, p31m, p6, p6mm

When applying the symmetry operator $\mathbf{C}_1 \equiv (\mathbf{R}_1, \mathbf{T}_1)$ to a point at the end of a vector $\boldsymbol{r}$, we obtain $\mathbf{X}' = \mathbf{C}_1\mathbf{X} = \mathbf{R}_1\mathbf{X} + \mathbf{T}_1$. If we then apply to $\boldsymbol{r}'$ the symmetry operator $\mathbf{C}_2$, we obtain

$$\mathbf{X}'' = \mathbf{C}_2\mathbf{X}' = \mathbf{R}_2(\mathbf{R}_1\mathbf{X} + \mathbf{T}_1) + \mathbf{T}_2 = \mathbf{R}_2\mathbf{R}_1\mathbf{X} + \mathbf{R}_2\mathbf{T}_1 + \mathbf{T}_2.$$

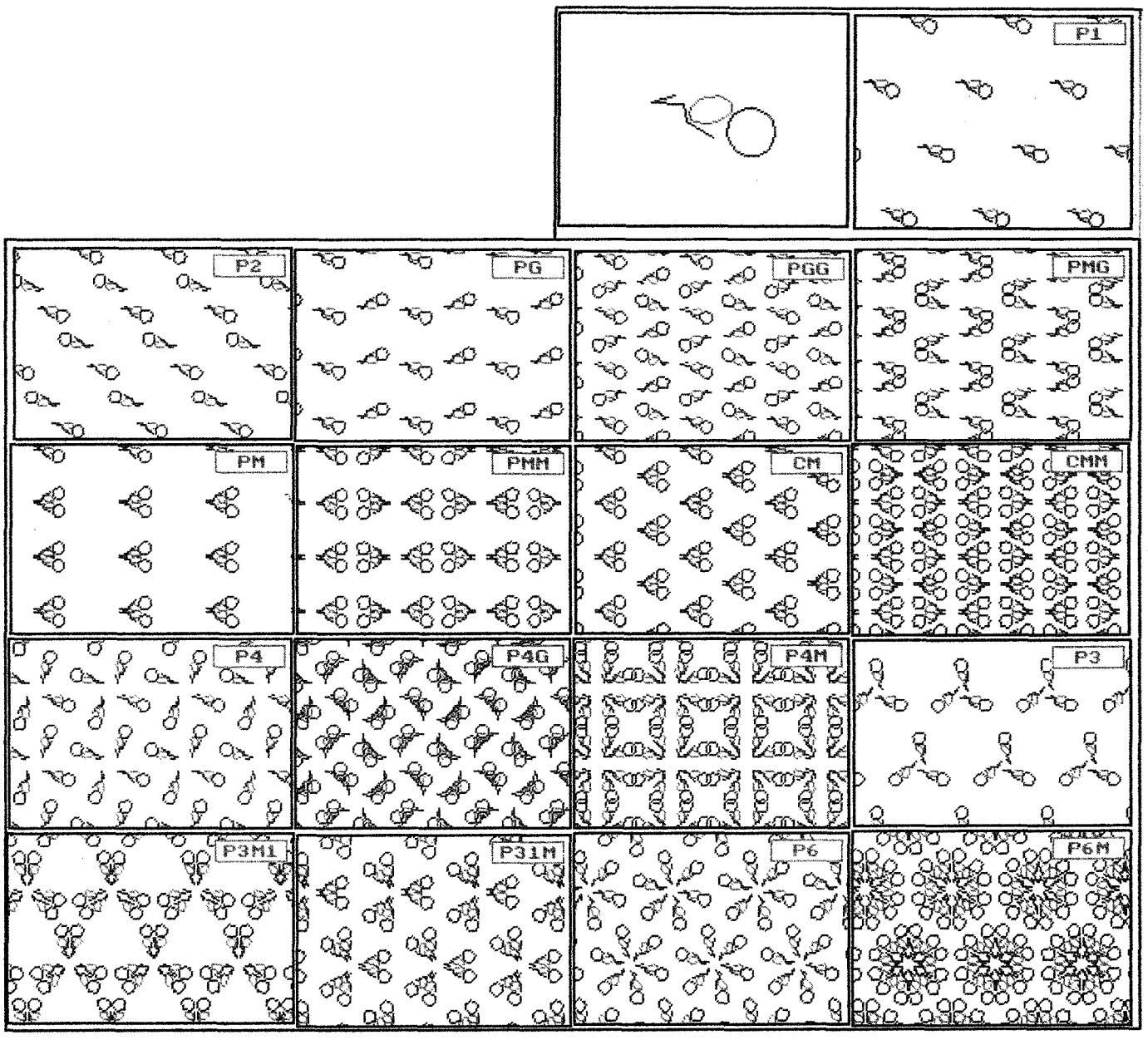


Fig. 1.25. A periodic decoration of the plane according to the 17 crystallographic plane groups (drawing by SYMPATI, a computer program by L. Loreto and M. Tonetti, *Pixel*, **9**, 9–20; Nov 1990).

Since the symmetry operators form a mathematical group, a third symmetry operator must be present (see also pp. 11–12),

$$\mathbf{C}_3 = \mathbf{C}_2\mathbf{C}_1 = (\mathbf{R}_2\mathbf{R}_1, \mathbf{R}_2\mathbf{T}_1 + \mathbf{T}_2), \tag{1.12}$$

where $\mathbf{R}_2\mathbf{R}_1$ is the rotational component of $\mathbf{C}_3$ and $(\mathbf{R}_2\mathbf{T}_1 + \mathbf{T}_2)$ is its translational component. In particular the operator $\mathbf{C}^2 = \mathbf{CC}$ will be present and in general also the $\mathbf{C}^j$ operator. Because of (1.12)

$$\mathbf{C}^j = [\mathbf{R}^j, (\mathbf{R}^{j-1} + \ldots + \mathbf{R} + \mathbf{I})\mathbf{T}]. \tag{1.13}$$

Let us now apply this result to the space group $P6_1$. Once we have defined the $\mathbf{R}$ and $\mathbf{T}$ matrices corresponding to an anti-clockwise rototranslation of 60° around z, we obtain all the six points equivalent to a point $\boldsymbol{r}$ by applying to it the operators $\mathbf{C}^j$ with j going from 1 to 6. Obviously $\mathbf{C}^6 = \mathbf{I}$ and $\mathbf{C}^{6+j} = \mathbf{C}^j$. For this reason we will say that the 6_1 operator is of **order** six (similarly 2 and m are of order two).

If $\boldsymbol{r}$ is transferred to $\boldsymbol{r}'$ by $\mathbf{C} = (\mathbf{R}, \mathbf{T})$ there will also be an inverse operator $\mathbf{C}^{-1} = (\mathbf{R}', \mathbf{T}')$ which will bring $\boldsymbol{r}'$ back to $\boldsymbol{r}$. Since we must have $\mathbf{C}^{-1}\mathbf{C} = \mathbf{I}$, because of (1.12) we will also have $\mathbf{R}'\mathbf{R} = \mathbf{I}$ and $\mathbf{R}'\mathbf{T} + \mathbf{T}' = \mathbf{0}$, and therefore

$$\mathbf{C}^{-1} = (\mathbf{R}^{-1}, -\mathbf{R}^{-1}\mathbf{T}) \tag{1.14}$$

where $\mathbf{R}^{-1}$ is the inverse matrix of $\mathbf{R}$. In the $P6_1$ example, $\mathbf{C}^{-1} = \mathbf{C}^5$. When all the operators of the group can be generated from only one operator (indicated as the **generator of the group**) we will say that the group is **cyclic**.

All symmetry operators of a group can be generated from at most three generators. For instance, the generators of the space group $P6_122$ are 6_1 and one twofold axis. Each of the 12 different operators of the group may be obtained as $\mathbf{C}_1^j$, $j = 1, 2, \ldots, 6$, say the powers of 6_1, or as $\mathbf{C}_2$, the twofold axis operator, or as their product. We can then represent the symmetry operators of $P6_122$ as the product $\{\mathbf{C}_1\}\{\mathbf{C}_2\}$, where $\{\mathbf{C}\}$ indicates the set of distinct operators obtained as powers of $\mathbf{C}$. Similarly there are two generators of the group P222 but three of the group $P\bar{4}3m$. In general all the operations of a space group may be represented by the product $\{\mathbf{C}_1\}\{\mathbf{C}_2\}\{\mathbf{C}_3\}$. If only two generators are sufficient, we will set $\mathbf{C}_3 = \mathbf{I}$, and if only one is sufficient, then $\mathbf{C}_2 = \mathbf{C}_3 = \mathbf{I}$. The list of the generators of all point groups is given in Appendix 1.E.

So far we have deliberately excluded from our considerations the translation operations defined by the Bravais lattice type. When we take them into account, all the space-group operations may be written in a very simple way. In fact the set of operations which will transfer a point $\boldsymbol{r}$ in a given cell into its equivalent points in any cell are:

$$\{\mathbf{T}\}\{\mathbf{C}_1\}\{\mathbf{C}_2\}\{\mathbf{C}_3\} \tag{1.15}$$

where $\mathbf{T} = m_1\boldsymbol{a} + m_2\boldsymbol{b} + m_3\boldsymbol{c}$ is the set of lattice translations.

The theory of symmetry groups will be outlined in Appendix 1.E.

Appendices

1.A The isometric transformations

It is convenient to consider a Cartesian basis $(\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)$. Any transformation which will keep the distances unchanged will be called an isometry or

an isometric mapping or a **movement C**. It will be a linear transformation, in the sense that a point P defined by the positional vector $\boldsymbol{r} = x\boldsymbol{e}_1 + y\boldsymbol{e}_2 + z\boldsymbol{e}_3$ is related to a point P′, with positional vector $\boldsymbol{r}' = x'\boldsymbol{e}_1 + y'\boldsymbol{e}_2 + z'\boldsymbol{e}_3$ by the relation

$$\mathbf{X}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} T_1 \\ T_2 \\ T_3 \end{pmatrix} = \mathbf{CX} = \mathbf{RX} + \mathbf{T} \quad (1.A.1)$$

with the extra condition

$$\bar{\mathbf{R}}\mathbf{R} = \mathbf{I} \qquad \text{or} \qquad \mathbf{R} = \bar{\mathbf{R}}^{-1}. \quad (1.A.2)$$

$\bar{\mathbf{R}}$ indicates the transpose of the matrix $\mathbf{R}$ and $\mathbf{I}$ is the identity matrix.

We note that $\mathbf{X}$ and $\mathbf{X}'$ are the matrices of the components of the vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$ respectively, while $\mathbf{T}$ is the matrix of the components of the translation vector $\boldsymbol{t} = T_1\boldsymbol{e}_1 + T_2\boldsymbol{e}_2 + T_3\boldsymbol{e}_3$.

A movement, leaving the distances unchanged, will also maintain the angles fixed in absolute value. Since the determinant of the product of two matrices is equal to the product of the two determinants, from (1.A.2) we have $(\det \mathbf{R})^2 = 1$, and then $\det \mathbf{R} = \pm 1$. We will refer to **direct** or **opposite movements** and to **direct** or **opposite congruence** relating an object and its transform, depending on whether $\det \mathbf{R}$ is $+1$ or -1.

Direct movements

Let us separate (1.A.1) into two movements:

$$\mathbf{X}' = \mathbf{X}_\mathrm{O} + \mathbf{T} \quad (1.A.3)$$

$$\mathbf{X}_\mathrm{O} = \mathbf{RX}. \quad (1.A.4)$$

(1.A.3) adds to each position vector a fixed vector and corresponds therefore to a translation movement. (1.A.4) leaves the origin point invariant. In order to find the other points left invariant we have to set $\mathbf{X}_\mathrm{O} = \mathbf{X}$ and obtain

$$(\mathbf{R} - \mathbf{I})\mathbf{X} = \mathrm{O} \quad (1.A.5a)$$

(1.A.5a) will have solutions for $\mathbf{X} \neq 0$ only if $\det(\mathbf{R} - \mathbf{I}) = 0$. Since $\det(\mathbf{R} - \mathbf{I}) = \det(\mathbf{R} - \bar{\mathbf{R}}\mathbf{R}) = \det[(\mathbf{I} - \bar{\mathbf{R}})\mathbf{R}] = \det(\mathbf{I} - \bar{\mathbf{R}}) \det \mathbf{R} = \det(\mathbf{I} - \bar{\mathbf{R}}) = -\det(\mathbf{R} - \mathbf{I})$, then this condition is satisfied. Therefore one of the three equations represented by (1.A.4) must be a linear combination of the other two. The two independent equations will define a line, which is the locus of the invariants points; the movement described by (1.A.4) is therefore a rotation. In conclusion, a direct movement can be considered as the combination (or, more properly, the product) of a translation with a rotation around an axis.

If in eqn (1.A.1) is $\mathbf{R} \equiv \mathbf{I}$ then the movement is a pure translation, if $\mathbf{T} = \mathrm{O}$ the movement is a pure rotation. When the translation is parallel to the rotation axis the movement will be indicated as **rototranslation**. An example of direct movement is the transformation undergone by the points of a rigid body when it is moved. Another example is the anti-clockwise rotation around the z axis of an angle θ; this will move $\boldsymbol{r}(x, y, z)$ into

$\boldsymbol{r}'(x', y', z')$ through the transformation

$$x' = x\cos\theta - y\sin\theta$$
$$y' = x\sin\theta + y\cos\theta$$
$$z' = z$$

which in matrix notation becomes $\mathbf{X}' = \mathbf{RX}$, with

$$\mathbf{R} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (1.A.5b)$$

$\mathbf{R}^{-1}$ can be obtained by substituting θ with $-\theta$ and it can be immediately seen that, in agreement with (1.A.2), $\mathbf{R} = \bar{\mathbf{R}}^{-1}$.

We will now show that any direct movement can be carried out by means of a translation or a rotation or a rototranslation. Let us suppose that an isometric transformation relates the three non-collinear points A, B, C with the points A′, B′, C′ respectively. If $\boldsymbol{a}$ is the translation bringing A on A′, then, if also B and C superpose on B′ and C′, the movement is a translation; if not, then the complete superposition can be achieved by a rotation $\mathbf{R}$ around an axis $\boldsymbol{l}$ passing through A′. If $\boldsymbol{l}$ is perpendicular to $\boldsymbol{a}$, the movement resulting from the combination of the rotation and translation operations is still a pure rotation around an axis parallel to $\boldsymbol{l}$ (see Appendix 1.B). If $\boldsymbol{a}$ is not perpendicular to $\boldsymbol{l}$, then it can be decomposed into two translational components $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$, one perpendicular and the other parallel to $\boldsymbol{l}$. The product of $\mathbf{R}$ times $\boldsymbol{a}_1$ is a pure rotation around an axis parallel to $\boldsymbol{l}$, which, when composed with $\boldsymbol{a}_2$, results in a rototranslation movement.

Opposite movements

An opposite movement can be obtained from a direct one by changing the sign to one or three rows of the $\mathbf{R}$ matrix. For instance, when changing the sign of the third row, we substitute the vector (x', y', z') with $(x', y', -z')$, i.e. the point P′ with its symmetry related with respect to a plane at $z = 0$. This operation is called a **reflection** with respect to the plane at $z = 0$. Changing the signs of all three rows of the $\mathbf{R}$ matrix implies the substitution of the vector (x', y', z') with $(-x', -y', -z')$, i.e. of the point P with its symmetry related with respect to the origin of the coordinate system. This operation is called **inversion** with respect to a point.

We may conclude that each direct movement, followed by a reflection with respect to a plane or by an inversion with respect to a point yields an opposite movement. On the other hand an opposite movement may be obtained as the product of a direct movement by a reflection with respect to a plane or by an inversion with respect to a point.

1.B. Some combinations of movements

Only those combinations of movements explicitly mentioned in this book will be considered (for further insight, the reader is referred to the splendid book by Lockwood and MacMillan[4]). The stated laws may be interpreted

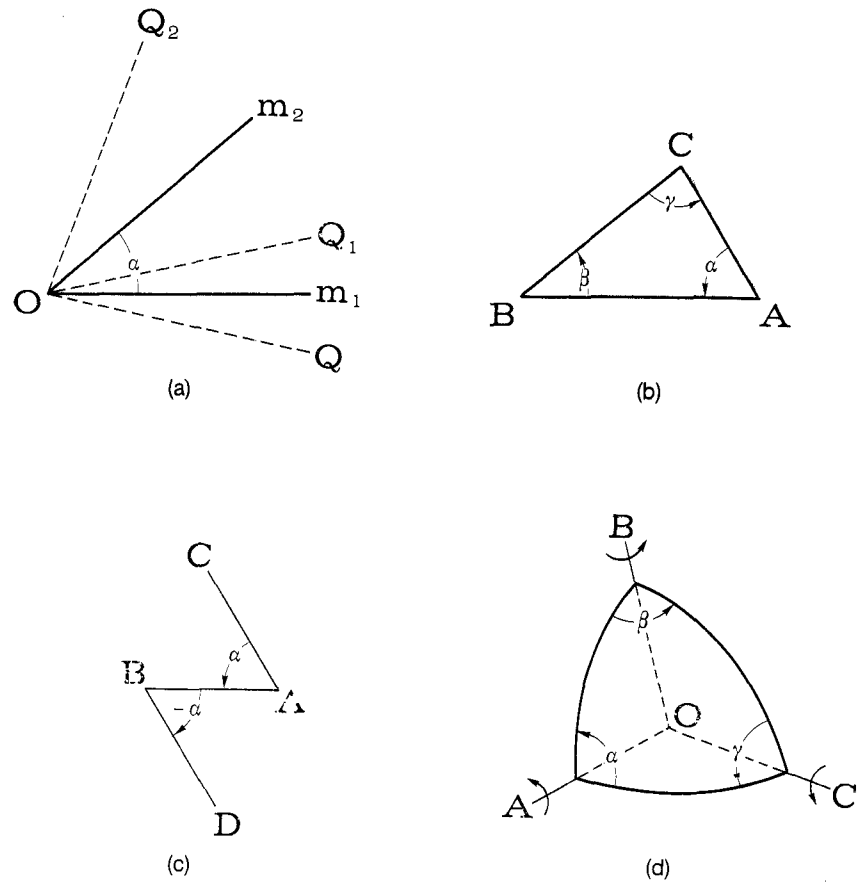


Fig. 1.B.1. (a) Composition of two reflections; (b) composition of two rotations about parallel axes; (c) composition of two rotations, the first through α and the second through $-\alpha$, about parallel axes; (d) composition of two rotations about axes passing through a point.

in terms of combinations of symmetry operations if all the space is invariant with respect to the movements.

1. *Composition of two reflections.* In Fig. 1.B.1(a) the two reflection planes m_1 and m_2 are at a dihedral angle α and intersect along a line, the trace of which is in O. The image of OQ with respect to m_1 is OQ_1 and the image of OQ_1 with respect to m_2 is OQ_2. It is possible to superpose OQ to OQ_2 by a rotation of 2α around the axis through O. We may conclude that the product of the two reflections is a rotation of 2α around O; in symbols $m_1m_2 = R$. The product is not commutative ($m_1m_2 \neq m_2m_1$): in fact by first reflecting OQ with respect to m_2 and then reflecting the image with respect to m_1 we obtain a 2α rotation in the opposite direction.

2. *The Silvester theorem relative to three parallel rotation axes.* The traces of the three axes on the plane of Fig. 1.B.1(b) are A, B, C. The Silvester theorem states that consecutive anti-clockwise rotations of 2α, 2β, 2γ around A, B, C respectively produce the identity. In fact, because of point 1, the rotations are equivalent to reflection operations with respect to the three pairs of planes AC–AB, BA–BC, CB–CA respectively and all these reflections cancel each other out. Since $\alpha + \beta + \gamma = \pi$, two successive rotations of 2α and 2β around A and B respectively, will be equivalent to a rotation of $+(2\alpha + 2\beta)$ around C. When $\alpha = -\beta$, the third axis goes to infinity and the resulting movement is a translation.

In Fig. 1.B.1(c) AC moves to AB by a rotation of α around A; by a $-\alpha$ rotation around B BA goes to BD. The resulting movement brings AC to BD and can be achieved by a translation of DA = 2AB sin $(\alpha/2)$ perpendicular to the direction of the rotation axes and at an angle of $(\pi - \alpha)/2$ with respect to AB. In symbols: $\mathbf{R}_\alpha \mathbf{R}'_{-\alpha} = \mathbf{T}$. We can then deduce the following point 3.

3. A rotation and a translation perpendicular to the rotation axis combine in a resulting rotation movement around an axis parallel to the original axis.

4. *The Silvester theorem relative to three rotation axes passing through a point.* In Fig. 1.B.1(d) ABC is a spherical triangle with angles α, β, γ in A, B, C respectively. If A, B, C are in a clockwise order, rotations of 2α, 2β, 2γ around A, B, C leave the figure unchanged. In fact, because of point 1, the three rotations correspond to the products of the reflections with respect to the pairs of planes AOC–AOB, AOB–BOC, BOC–COA respectively, and these reflections cancel each other out. Since $\alpha + \beta + \gamma > \pi$, then consecutive rotations of 2α around A and of 2β around B are equivalent to a rotation of 2γ around C, with $2\gamma \neq (2\alpha + 2\beta)$.

5. *Coexistence of rotation axes passing through a point*: the *Euler theorem.* We will study this problem using the Silvester theorem treated in point 4. In Fig. 1.B.1(d) let OA and OB be two symmetry rotation axes of order m and n respectively. The angles α and β are chosen in such a way that $2\alpha = 2\pi/m$ and $2\beta = 2\pi/n$. Because of the Silvester theorem, anti-clockwise rotations of 2α and 2β around OA and OB are equivalent to a 2γ anti-clockwise rotation around OC. C is therefore a symmetry axis of order $p = 2\pi/2\gamma = \pi/\gamma$. The angles of the spherical triangle are then π/m, π/n and π/p. Since the sum of the angles must be greater than π, the inequality $1/m + 1/n + 1/p > 1$ follows. The possible solutions of this inequality are: l, 2, 2 with l integer >1; 2, 3, 3; 4, 3, 2; 5, 3, 2. We can now consider the different solutions, keeping in mind that the surface of a sphere of radius r is $4\pi r^2$ and that of a spherical triangle is $(\alpha + \beta + \gamma - \pi)r^2$:

(a) Solution l, 2, 2. α, β, and γ are equal to $\pi/2$, $\pi/2$, π/l respectively and A and B may be chosen on an equatorial circle with C as a pole. The binary axes are therefore always at 90° with respect to the l axis. Values of l different from 2, 3, 4, 6 correspond to non-crystallographic groups which occur as possible symmetries of molecules or as approximate local site symmetries in crystals.

(b) Solution 2, 3, 3. α, β, and γ are equal to $\pi/2$, $\pi/3$, $\pi/3$ respectively and the area of the spherical triangle is $\pi r^2/6$. On the sphere there will be 24 such triangles. The 24 $\pi/2$ angles meet four at a time at six vertices and the 48 $\pi/3$ angles meet six at a time at eight vertices. This implies the presence of three twofold axes and of four threefold axes. The three twofold axes will be perpendicular one to the other and can be assumed as the axes of a reference system. The four threefold axes run from the centre to the points $(1, 1, 1)$, $(1, -1, -1)$, $(-1, 1, -1)$, $(-1, -1, 1)$. The group of rotations is consistent with the symmetry of a tetrahedron.

(c) Solution 4, 3, 2. α, β, and γ are equal to $\pi/2$, $\pi/3$, $\pi/4$ respectively and the area of the spherical triangle is $\pi r^2/12$. On the sphere there will

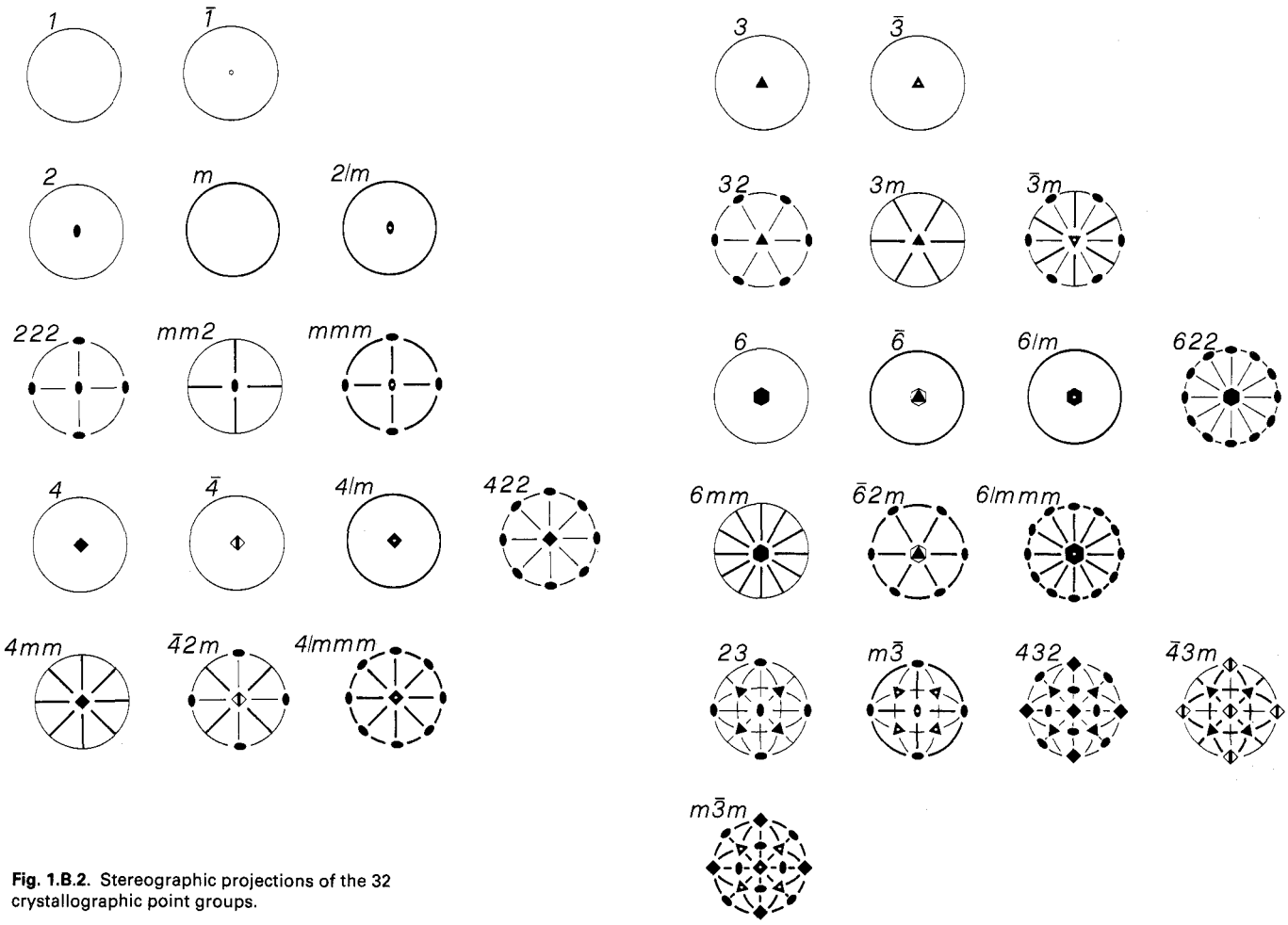


Fig. 1.B.2. Stereographic projections of the 32 crystallographic point groups.

be 48 such triangles. The 48 $\pi/2$ angles meet four at a time at twelve vertices, the 48 $\pi/3$ angles meet six at a time at eight vertices and the 48 $\pi/4$ angles meet eight at a time at six vertices. A total of six twofold axes, of four threefold axes, and of three fourfold axes will be present. The three fourfold axes will be perpendicular one to the other and can be assumed as the axes of a reference system. The threefold axes are located along the [1, 1,1], [1, −1, −1], [−1, 1, −1], [−1, −1, 1] directions, while the twofold axes are on the bisecting lines of the angles between the fourfold axes. The group of rotations is consistent with the symmetry of a cube and of an octahedron (see Fig. 1.10).

The mutual disposition of the symmetry elements in the 32 crystallographic point groups is illustrated in Fig. 1.B.2, where the so called 'stereographic projections' are shown. The c axis is normal to the plane, the a axis points down the page, and the b axis runs horizontally in the page from left ro right. A stereographic projection is defined as follows (see Fig. 1.B.3(a)). A unit sphere is described around the crystal in C. A point P (terminal of some symmetry axis) in the $+z$ hemisphere is defined in the (x, y) plane as intersection P′ of that plane with the line

connecting the point with the south pole of the unit sphere. If the point to be projected is in the $-z$ hemisphere then the north pole is used.

In Fig. 1.B.3(b) parts of the stereographic projections for m$\bar{3}$m are magnified in order to make clearer the statements made in the text.

(d) Solution 5, 3, 2. This solution, which is compatible with the symmetry of the regular icosahedron (20 faces, 12 vertices) and its dual, the regular pentagon–dodecahedron, (12 faces, 20 vertices), but not with the periodicity property of crystals, will not be examined.

It is however of particular importance in Crystallography as symmetry of viruses molecules and in quasi-crystals.

6. *Composition of two glide planes.* In Fig. 1.B.4 let S and S′ be the traces of two glide planes forming an angle α and O be the trace of their intersection line. The translational components OA and OB are chosen to lie on the plane of the drawing and Q is the meeting point of the axes of the OA and OB segments. X, Y, and Q′ are the reflection images of Q with respect to S, S′, and to the point O, respectively. The product S′S moves Q to Q′ and then back to Q. Since S′S is a direct movement it leaves Q unchanged and corresponds to a rotation around an axis normal to the plane of the figure and passing through Q. Since S′S moves first A to O and then to B, the rotation angle AQB $= 2\alpha$. Note that the two glides are equivalent to a rotation around an axis not passing along the intersection line of S and S′.

7. *Composition of two twofold axes, with and without translational component.* From point 5 we know that the coexistence of two orthogonal twofold axes passing by O, implies a third binary axis perpendicular to them and also passing through O (see Fig. 1.B.5(a)). The reader can easily verify the following conclusions:

(a) if one of the two axes is 2_1 (Fig. 1.B.5(b)), then another 2 axis, at 1/4 from O and intersecting orthogonally the screw axis, will exist;

(b) if two 2_1 intersect in O (Fig. 1.B.5(c)), then another 2 axis perpendicular to them and passing at (1/4, 1/4) from O will be present;

(c) if a pair of mutually perpendicular 2 axes is separated by 1/4 of a period (Fig. 1.B.5(d)), then a 2_1 axis orthogonally intersecting both axes will exist;

(d) if a 2 and a 2_1 axis are separated by 1/4 of a period (Fig. 1.B.5(e)) there will then be a new 2_1 axis normal to both of them and intersecting the first 2_1 axis at 1/4 from the 2 axis;

(e) if two orthogonal screws are separated by 1/4 of a period (Fig. 1.B.5(f)), then a third screw axis normal to them and passing at (1/4, 1/4) from them will be present.

1.C. Wigner–Seitz cells

The 14 Bravais lattices are compatible with cells which are different from those conventionally associated to them. A conventional cell is a parallelepiped: as such it may be considered as a particular type of polyhedron. There are several families of polyhedra with which we can fill up the space

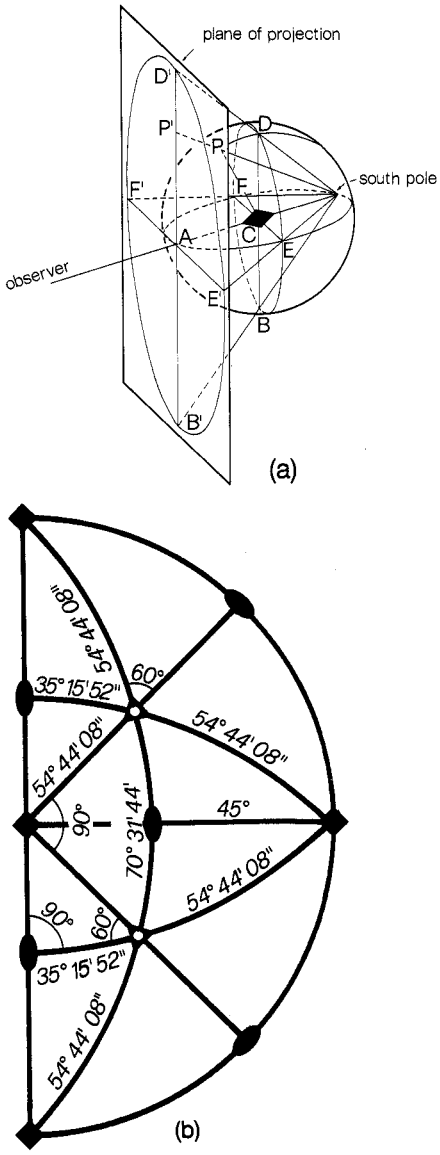


Fig. 1.B.3. (a) Geometry of the stereographic projection. (b) Angular values occurring in m$\bar{3}$m stereographic projection.

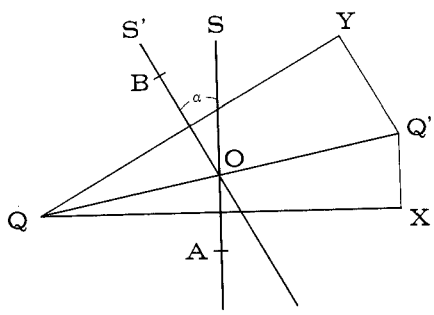


Fig. 1.B.4. Composition of two glide planes.

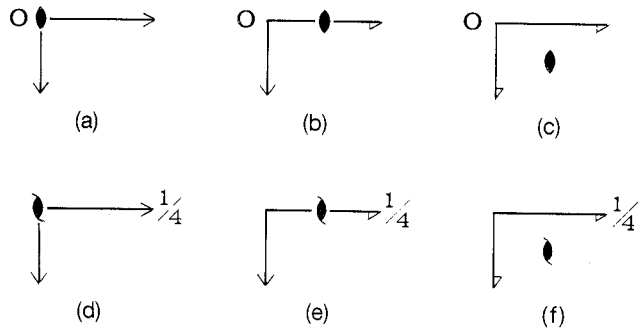


Fig. 1.B.5. Various arrangements of three orthogonal binary axes. The length of the graphical symbol for screw axes in the plane of the page corresponds to half repetition period.

by translation. A very important type is the one obtained through the **Dirichlet construction**. Each lattice point is connected with a line to its nearest neighbours. We then trace through the mid-points of the segments the planes perpendicular to them. These intersecting planes will delimit a region of the space which is called called the **Dirichlet region** or **Wigner–Seitz cell**. An example in two dimensions is given in Fig. 1.C.1(a) and two three-dimensional examples are illustrated in Fig. 1.C.1(b, c). The Wigner–Seitz cell is always primitive and coincides with the Bravais cell if this is rectangular and primitive. A construction identical to the Wigner–Seitz cell delimits in the reciprocal space (cf. Chapters 2 and 3) a cell conventionally known as the **first Brillouin zone**. There will be 14 first Brillouin zones corresponding to the 14 Bravais lattices. We recall here that to a lattice I in direct space corresponds an F lattice in reciprocal space and vice versa (see Appendix 2.D); then, the first Brillouin zone of an I lattice will look like a Wigner–Seitz cell of an F lattice and vice versa. The Brillouin zones are very important in the study of lattice dynamics and in electronic band theory.

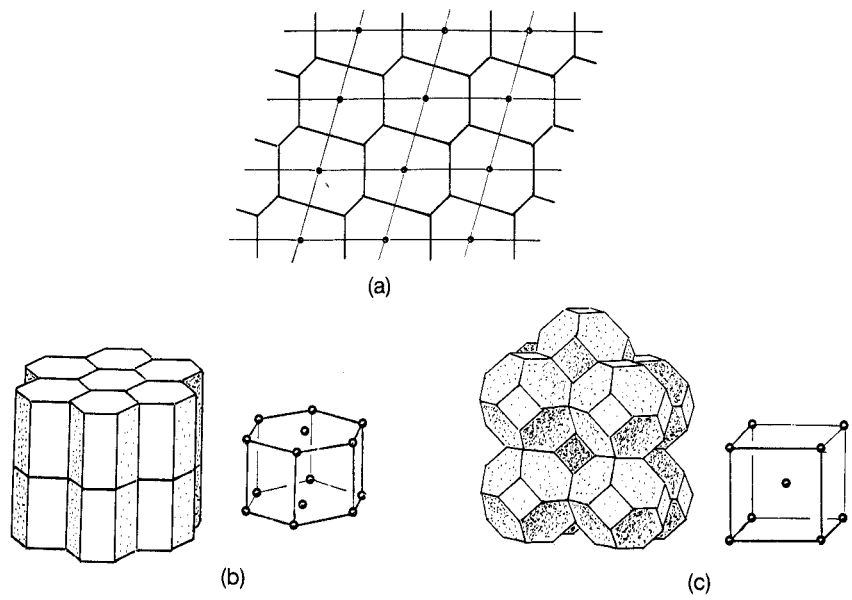


Fig. 1.C.1. Examples of Wigner–Seitz cells.

1.D. The space-group matrices

All the rotation matrices **R** needed to conventionally describe all 230 space groups will be listed. They operate according to the relation $\mathbf{X}' = \mathbf{RX}$. The matrices are grouped following the directions along which they operate, and for the hexagonal and trigonal systems they are preceded by the letter H. They may be constructed using the following practical criterion: in the first, second, and third columns are the coordinates of the points symmetry related to points (1, 0, 0), (0, 1, 0), and (0, 0, 1) respectively.

The determinant of a matrix will have a +1 or a −1 value depending on whether the represented operation is of rotation or of inversion type. This number, together with the trace (sum of the diagonal elements) of a matrix, are characteristic of the symmetry element:

element	1	2	3	4	6	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{6}$,
trace	3	$\bar{1}$	0	1	2	$\bar{3}$	1	0	$\bar{1}$	$\bar{2}$,
determinant	1	1	1	1	1	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$.

The matrix of the $\bar{n}$ operator may be simply obtained from that of the n operator by multiplying by the matrix corresponding to the $\bar{1}$ operator:

$$\bar{1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

This corresponds to changing the sign of all the elements of the original matrix. Therefore in the following list we will not give all the 64 matrices necessary to describe the space groups, but only the 32 matrices corresponding to proper symmetry elements.

Direction [0 0 0]

$$1 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Direction [1 0 0]

$$2 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}; \quad \mathrm{H2} \equiv \begin{pmatrix} 1 & \bar{1} & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}; \quad 4 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & \bar{1} & 0 \end{pmatrix}; \quad 4^3 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & 1 & 0 \end{pmatrix}.$$

Direction [0 1 0]

$$2 \equiv \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}; \quad \mathrm{H2} \equiv \begin{pmatrix} \bar{1} & 0 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}; \quad 3 \equiv \begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \quad 4^3 \equiv \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}.$$

Direction [0 0 1]

$$2 \equiv \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \mathrm{H3} \equiv \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \mathrm{H3}^2 \equiv \begin{pmatrix} \bar{1} & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad 4 \equiv \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$4^3 \equiv \begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \mathrm{H6} \equiv \begin{pmatrix} 1 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \mathrm{H6}^5 \equiv \begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Direction [1 1 0]

$$2 \equiv \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

Direction [1 0 1]

$$2 \equiv \begin{pmatrix} 0 & 0 & 1 \\ 0 & \bar{1} & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

Direction [0 1 1]

$$2 \equiv \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

Direction [1 $\bar{1}$ 0]

$$2 \equiv \begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

Direction [$\bar{1}$ 0 1]

$$2 \equiv \begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}.$$

Direction [0 1 $\bar{1}$]

$$2 \equiv \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \end{pmatrix}.$$

Direction [1 1 1]

$$3 \equiv \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}; \; 3^2 \equiv \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}.$$

Direction [$\bar{1}$ 1 1]

$$3 \equiv \begin{pmatrix} 0 & \bar{1} & 0 \\ 0 & 0 & 1 \\ \bar{1} & 0 & 0 \end{pmatrix}; \; 3^2 \equiv \begin{pmatrix} 0 & 0 & \bar{1} \\ \bar{1} & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

Direction [1 $\bar{1}$ 1]

$$3 \equiv \begin{pmatrix} 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \\ 1 & 0 & 0 \end{pmatrix}; \; 3^2 \equiv \begin{pmatrix} 0 & 0 & 1 \\ \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \end{pmatrix}.$$

Direction [1 1 $\bar{1}$]

$$3 \equiv \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & \bar{1} \\ \bar{1} & 0 & 0 \end{pmatrix}; \; 3^2 \equiv \begin{pmatrix} 0 & 0 & \bar{1} \\ 1 & 0 & 0 \\ 0 & \bar{1} & 0 \end{pmatrix}.$$

Direction [2 1 0]

$$\mathrm{H2} \equiv \begin{pmatrix} 1 & 0 & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

Direction [1 2 0].

$$\mathrm{H2} \equiv \begin{pmatrix} \bar{1} & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

1.E. Symmetry groups

A **group** G is a set of elements $g_1, g_2, \ldots g_j, \ldots$ for which a combination law is defined, with the following four properties: **closure**, the combination of two elements of the group is an element of the group $g_i g_j = g_k$; **associativity**, the associative law $(g_i g_j) g_k = g_i (g_j g_k)$ is valid; **identity**, there is only one element e in the group such that $eg = ge = g$; **inversion**, each element g in the group has one and only one inverse element g^{-1} such that $g^{-1}g = gg^{-1} = e$.

Examples of groups are:

(1) the set of all integer numbers (positive, negative, and zero), when the combination law is the sum. In this case $e = 0$, $g^{-1} = -g$;

(2) the rational numbers, excluding zero, when the law is the product: $e = 1$, $g^{-1} = 1/g$;

(3) the set of all $n \times n$ son-singular matrices under the product law: e is the diagonal matrix with $a_{ii} = 1$;

(4) the set of all lattice vectors $\boldsymbol{r}_{u,v,w} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$ with u, v, w positive, negative, or null integers, when the combination law is the vector sum: then $e = \boldsymbol{r}_{0,0,0}$, $g^{-1} = -g$.

The number of different elements of a group is called the order of the group and can be finite or infinite. If a group also possesses the commutative property $g_i g_j = g_j g_i$ for any i and j, then G is said to be **Abelian**. With reference to the examples given above, (1), (2), (4) are infinite and Abelian groups, (3) is infinite and non-Abelian.

If g is an element of G, all powers of g must be contained in G. An integer n may exist for which

$$g^n = e; \tag{1.E.1}$$

then $g^{n+1} = g$, $g^{n+2} = g^2, \ldots$ If n is the smallest integer for which (1.E.1) is satisfied, there will only be n distinct powers of g. Since $g^j g^{n-j} = g^{n-j} g^j = e$, then g^{n-j} is the inverse of g^j. The element g is then said to be of order n and

Table 1.E.1. List of generators for non-cyclic point groups. There are 21 proper generators in all

Point group	Generators	Point group	Generators
2/m	$2_{[010]}$, $\bar{2}_{[010]}$	$\bar{3}$m	$\bar{3}_{[001]}$, $\bar{2}_{[100]}$
222	$2_{[100]}$, $2_{[010]}$	$\bar{6}$2m	$\bar{2}_{[100]}$, $2_{[1\bar{1}0]}$
mm2	$\bar{2}_{[100]}$, $2_{[001]}$	622	$2_{[100]}$, $2_{[1\bar{1}0]}$
mmm	$\bar{2}_{[100]}$, $\bar{2}_{[010]}$, $\bar{2}_{[001]}$	6/m	$6_{[001]}$, $\bar{2}_{[001]}$
422	$2_{[100]}$, $2_{[1\bar{1}0]}$	6mm	$\bar{2}_{[100]}$, $\bar{2}_{[1\bar{1}0]}$
4/m	$4_{[001]}$, $\bar{2}_{[001]}$	6/mmm	$\bar{2}_{[100]}$, $\bar{2}_{[1\bar{1}0]}$, $\bar{2}_{[001]}$
4mm	$\bar{2}_{[100]}$, $\bar{2}_{[1\bar{1}0]}$	23	$3_{[111]}$, $2_{[001]}$
$\bar{4}$2m	$2_{[100]}$, $\bar{2}_{[1\bar{1}0]}$	432	$3_{[111]}$, $2_{[110]}$
4/mmm	$\bar{2}_{[100]}$, $\bar{2}_{[1\bar{1}0]}$ $\bar{2}_{[001]}$	m$\bar{3}$	$3_{[111]}$, $\bar{2}_{[001]}$
32	$3_{[001]}$, $2_{[100]}$	$\bar{4}$3m	$3_{[111]}$, $\bar{2}_{[110]}$
3m	$3_{[001]}$, $\bar{2}_{[100]}$	m$\bar{3}$m	$3_{[111]}$, $\bar{2}_{[1\bar{1}0]}$, $\bar{2}_{[001]}$

the set of all powers of g is a group of order n:

$$G_1 = (g, g^2, \ldots, g^{n-1}, g^n = e). \tag{1.E.2}$$

A group, such as (1.E.2), in which all the elements are powers of a single generating element, is called **cyclic**. All cyclic groups are Abelian, but the converse is not true. An example of cyclic group of order n is the set of rotations around a given axis, which are multiple of an angle $\alpha = 2\pi/n$.

Any point group can be represented as the product of powers of at most three elements, which are the **generators** of the group. In Table 1.E.1 the list of the generators of the non-cyclic groups is reported. We also note that the definition of the generators is not unique. For instance in the class 222 we may chose the generators $2_{[100]}$ and $2_{[010]}$, or $2_{[100]}$ and $2_{[001]}$, or $2_{[010]}$ and $2_{[001]}$.

When the physical properties of the group elements are not specified the group is said to be **abstract**. From a mathematical point of view all its properties are determined by its **multiplication table**. For a group of n elements this table has the form:

$$\begin{array}{c|cccc} & g_1 & g_2 & g_n & \cdots \\ \hline g_1 & g_1^2 & g_1g_2 & g_1g_n & \cdots \\ g_2 & g_2g_1 & g_2^2 & g_2g_n & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_n & g_ng_1 & g_ng_2 & g_n^2 & \cdots \end{array} \tag{1.E.3}$$

We note that

1. Each element appears once and only once in a given row (or column) of the table. In order to demonstrate this statement let us consider the ith row of the table and suppose that there are two different elements g_j and g_k, for which $g_ig_j = g_ig_k = g_p$. Then g_p would appear twice in the row, but by multiplying the two equations by g_i^{-1} we obtain $g_j = g_k$, in contrast with the hypothesis.

2. Each row (column) is different from any other row (column); this property follows immediately from property 1.

3. For abelian groups the table is symmetric with respect to the diagonal.

Table 1.E.2. The 18 abstract groups corresponding to the 32 crystallographic point groups

Point group	Order of the group	Characteristic relations
1	1	$g = e$
$\bar{1}$, 2, m	2	$g^2 = e$
3	3	$g^3 = e$
4, $\bar{4}$	4	$g^4 = e$
2/m, mm2, 222	4	$g_1^2 = g_2^2 = (g_1g_2)^2 = e$
6, $\bar{6}$, $\bar{3}$	6	$g^6 = e$
32, 3m	6	$g_1^3 = g_2^2 = (g_1g_2)^2 = e$
mmm	8	$g_1^2 = g_2^2 = g_3^2 = (g_1g_2)^2 = (g_1g_3)^2 = (g_2g_3)^2 = e$
4/m	8	$g_1^4 = g_2^2 = g_1g_2g_1^3g_2 = e$
4mm, 422, $\bar{4}$2m	8	$g_1^4 = g_2^2 = (g_1g_2)^2 = e$
6/m	12	$g_1^6 = g_2^2 = g_1g_2g_1^5g_2 = e$
$\bar{3}$m, $\bar{6}$2m, 6mm, 622	12	$g_1^6 = g_2^2 = (g_1g_2)^2 = e$
23	12	$g_1^3 = g_2^2 = (g_1g_2)^3 = e$
4/mmm	16	$g_1^2 = g_2^2 = g_3^2 = (g_1g_2)^2 = (g_1g_3)^2 = (g_2g_3)^4 = e$
432, $\bar{4}$3m	24	$g_1^4 = g_2^2 = (g_1g_2)^3 = e$
m$\bar{3}$	24	$g_1^3 = g_2^3 = (g_1^2g_2g_1g_2)^2 = e$
6/mmm	24	$g_1^2 = g_2^2 = g_3^2 = (g_1g_2)^2 = (g_1g_3)^2 = (g_2g_3)^6 = e$
m$\bar{3}$m	48	$g_1^4 = g_2^6 = (g_1g_2)^2 = e$

Groups having the same multiplication table, even though their elements might have different physical meaning, are called **isomorphous**. They must have the same order and may be considered as generated from the same abstract group. For instance the three point groups 222, 2/m and mm2 are isomorphous. To show this let us choose g_1, g_2, g_3, g_4 in the following way.

group 222: 1, 2, 2, 2;
group 2/m; 1, 2, m, $\bar{1}$;
group mm2; 1, m, m, 2.

The multiplication table of the abstract group is

	1	2	3	4
1	1	2	3	4
2	2	1	4	3
3	3	4	1	2
4	4	3	2	1

In Table 1.E.2 the 32 crystallographic point groups are grouped into 18 abstract groups and for each of them the defining relationships are listed. We note that all cyclic groups of the same order are isomorphous.

Subgroups

A set H of elements of the group G satisfying the group conditions is called a **subgroup** of G. The subgroup H is **proper** if there are symmetry operations of G not contained in H. Examples of subgroups are:

(1) the set of even integers (including zero) under the sum law is a subgroup of the group of all integers;

(2) the point group 32 has elements $g_1 = 1$, $g_2 = 3_{[001]}$, $g_3 = 3^2 = 3^{-1}$, $g_4 = 2_{[100]}$, $g_5 = 2_{[010]}$, $g_6 = 2_{[\bar{1}\bar{1}0]}$; $H = (g_1, g_2, g_3)$ is a subgroup of G;

(3) the point groups 1, 2, $\bar{1}$, m are subgroups of the point group 2/m;

(4) 222 is a subgroup of 422;

(5) the set T of all primitive lattice translations is a subgroup of the space group G.

Conversely G may be considered a **supergroup** of H.

Subgroup–group–supergroup relationships are very important in the study of phase transitions and of order–disorder problems.

Cosets

Let $H = (h_1, h_2, \ldots)$ be a subgroup of G and g_i an element of G not contained in H. Then the products

$$g_iH = (g_ih_1, g_ih_2, \ldots) \text{ and } Hg_i = (h_1g_i, h_2g_i, \ldots)$$

form a left and a right coset of H respectively. In general they will not be identical.

Furthermore H can not have any common element with g_iH or Hg_i. In fact, if for instance, we had $g_ih_j = h_k$, it would follow that $g_i = h_kh_j^{-1}$, i.e. contradicting the hypothesis, g_i would belong to H.

It can be shown that two right (or left) cosets, either have no common element or are identical one to the other. This allows us to decompose G with respect to H in the following way:

$$G = H \cup g_iH \cup g_qH \cup \ldots \tag{1.E.4a}$$

or

$$G = H \cup Hg_i \cup Hg_q \cup \ldots . \tag{1.E.4b}$$

It follows that the order of a subgroup is a divisor of the order of the group and if this is a prime number, the only subgroup of G is e and G must also be cyclic.

The decomposition of the group 2/m into separate left cosets with respect to the subgroup 2 is:

$$2/m = 1(1,2) \cup \bar{1}(1,2) = (1,2) \cup (\bar{1}, m)$$

The number of distinct cosets obtained from the decomposition of a group with respect to a subgroup is called **index of the subgroup**. In the previous example, the index of the subgroup 2 of the group 2/m is two.

A coset is never a group because it does not contain the element e.

Conjugate classes

An element g_i is said to be conjugate to an element g_j of G if G contains an element g_k such that

$$g_i = g_k^{-1}g_jg_k. \tag{1.E.5}$$

If g_j is fixed and g_k varies within G, then the set of elements g_i forms a **class of conjugate elements**.

In agreement with relation (1.E.5) the element e forms a class on its own. Since each element of G can not belong to two different classes, it is possible to decompose G into the factorized set $G = e \cup T_1 \cup T_2 \cup \ldots$.

A physical or geometrical meaning may be attributed to the classes. In

the transformation (1.E.5), let the element g_k be a coordinate transformation due to a symmetry operator and the element g_j a matrix operator related to another symmetry operation. Since g_j is transformed by (1.E.5) (see eqn (2.E.7)), the operators belonging to the same class are changed one onto the other by coordinate transformations represented by the elements of the group. For instance, for the point group 32 three classes may be set up:

$$(e),\ (3, 3^{-1}),\ (2_{[100]}, 2_{[010]}, 2_{[\bar{1}\bar{1}0]}.)$$

As we will see later, the character is identical for the matrix representation of all the elements of the same class.

The following rules may be useful to set up the point-group classes:

(1) the classes are formed by one element only for the point groups up to orthorhombic; this means that each symmetry operator commutes with all the others;

(2) in an Abelian group the classes are formed by only one element;

(3) the operators identity, inversion, and reflection with respect to a mirror plane perpendicular to the principal symmetry axis (the axis with the highest order), are each in a separate class.

Conjugate subgroups

Let H be a subgroup of G and g an element of G not in H. Then all the elements $g^{-1}\mathrm{H}g$, form a group. H and $g^{-1}\mathrm{H}g$ are conjugate subgroups.

Normal subgroups and factor groups

If the right and left cosets of the subgroup H are the same, i.e. $\mathrm{H}g_i = g_i\mathrm{H}$ for every i, then $g_i^{-1}\mathrm{H}g_i = \mathrm{H}$. This relation is still valid when g_i is in H since both $g_i\mathrm{H}$ and g_i belong to H. Conversely, if a subgroup is transformed into itself when applying all the elements of the group, the corresponding left and right cosets must be equal.

Subgroups which are transformed into themselves by applying all the elements of the group, are called **invariant** or **normal**. They must contain complete classes.

For instance the subgroup 2 of the point group 2/m is normal since $\bar{1}(1, 2) = (1, 2)\bar{1}$, $m(1, 2) = (1, 2)m$. Furthermore, in the group 32, the subgroup $(1, 3, 3^{-1})$ is normal, while $(1, 2_{[100]})$ is not; the subgroup T of all the primitive lattice translations is an invariant subgroup of the space group G.

Let H be a normal subgroup of G with index p, while n is the order of G. Because of (1.E.4) the order of H is n/p. We observe that for H and all its distinct cosets, the following multiplication law may be established:

$$(g_i\mathrm{H}g_j\mathrm{H}) = g_i\mathrm{H}\mathrm{H}g_j = g_i\mathrm{H}g_j = g_ig_j\mathrm{H}$$

Besides, it is:

$$(g_i\mathrm{H})^{-1}(g_i\mathrm{H}) = \mathrm{H}^{-1}g_i^{-1}g_i\mathrm{H} = e,$$

$$\mathrm{H}(g_i\mathrm{H}) = g_i\mathrm{H}\mathrm{H} = g_i\mathrm{H}.$$

We can now define a new type of group of order p, called a **factor group** or **quotient group**, indicated by the symbol G/H: its elements are cosets of

H. The following multiplication table is for the quotient group (we assume $g_1 = e$).

$$\begin{array}{c|cccc} & g_1\mathrm{H} & g_2\mathrm{H} & & g_p\mathrm{H} \\ \hline g_1\mathrm{H} & g_1\mathrm{H} & g_2\mathrm{H} & \ldots\ldots & g_p\mathrm{H} \\ g_2\mathrm{H} & g_2\mathrm{H} & g_2^2\mathrm{H} & \ldots\ldots & g_2g_p\mathrm{H} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ g_p\mathrm{H} & g_p\mathrm{H} & g_pg_2\mathrm{H} & & g_p^2\mathrm{H}. \end{array} \qquad (1.\mathrm{E}.6)$$

For instance, for the quotient group (2/m)/2, (1.E.6) becomes

$$\begin{array}{c|cc} & (1,2) & (\bar{1},\mathrm{m}) \\ \hline (1,2) & (1,2) & (\bar{1},\mathrm{m}) \\ (\bar{1},\mathrm{m}) & (\bar{1},\mathrm{m}) & (1,2) \end{array}$$

As a further example let us consider the elements of the point group 4mm: e, 4, 4^3, $4^2 = 2$, $\bar{2}_{[100]}$, $\bar{2}_{[010]}$, $\bar{2}_{[110]}$, $\bar{2}_{[1\bar{1}0]}$. Five classes may be formed: (e), (2), $(4, 4^3)$, $(\bar{2}_{[100]}, \bar{2}_{[010]})$, $(\bar{2}_{[110]}, \bar{2}_{[1\bar{1}0]})$. The subgroup $\mathrm{H} = (e, 2)$ is invariant and the factor group with respect to H may be written as: H, 4H, $\bar{2}_{[100]}\mathrm{H}$, $\bar{2}_{[110]}\mathrm{H}$.

The relation between G and G/H is a $n/p \to 1$ correspondence, i.e. $\mathrm{G} \to \mathrm{H}$. In detail $g_1\mathrm{H} = \mathrm{H} \to e$, $g_2\mathrm{H} \to f_2, \ldots, g_p\mathrm{H} \to f_p$. A correspondence of this type (many $\to$ one) is called **homomorphism** and G/H is said to be homomorphic with G.

Isomorphism is then a special case of homomorphism for which there is a one to one correspondence. A homomorphic correspondence allows us to reduce the study of the multiplication laws of the group G to that of the multiplication laws of the smaller G/H group.

To display many of the abstract definitions given so far, we consider as major example, the point group $\mathrm{G} \equiv 23$: say

$$\mathrm{G} \equiv \{1, 3_{[111]}, 3^2_{[111]}, 3_{[\bar{1}11]}, 3^2_{[\bar{1}11]}, 3_{[1\bar{1}1]}, 3^2_{[1\bar{1}1]},$$
$$3_{[11\bar{1}]}, 3^2_{[11\bar{1}]}, 2_{[100]}, 2_{[010]}, 2_{[001]}\}$$

Readers will find the four classes:

$$(1),\ (3_{[111]}, 3_{[\bar{1},1,1]}, 3_{[1\bar{1}1]}, 3_{[11\bar{1}]}),$$
$$(3^2_{[111]}, 3^2_{[\bar{1}11]}, 3^2_{[1\bar{1}1]}, 3^2_{[11\bar{1}]}),$$
$$(2_{[100]}, 2_{[010]}, 2_{[001]}),$$

and the ten subgroups

$$\{1\},\ \{1, 2_{[100]}\},\ \{1, 2_{[010]}\},\ \{1, 2_{[001]}\}$$
$$\{1, 3_{[111]}, 3^2_{[111]}\},\ \{1, 3_{[\bar{1}11]}, 3^2_{[\bar{1}11]}\},\ \{1, 3_{[1\bar{1}1]}, 3^2_{[1\bar{1}1]}\}$$
$$\{1, 3_{[11\bar{1}]}, 3^2_{[11\bar{1}]}\},\ \{1, 2_{[100]}, 2_{[010]}, 2_{[001]}\},\ \mathrm{G},$$

of which only $\{1\}$, $\{1, 2_{[100]}, 2_{[010]}, 2_{[001]}\}$, and G are invariant subgroups.

Calculate now the factored group of $\mathrm{H} \equiv \{1, 2_{[100]}, 2_{[010]}, 2_{[001]}\}$: we multiply it by an element not in H, say $3_{[111]}$, and obtain

$$3_{[111]}\mathrm{H} = \{3_{[111]}, 3_{[\bar{1}11]}, 3_{[1\bar{1}1]}, 3_{[11\bar{1}]}\}.$$

We take now an element not in H or in $3_{[111]}\mathrm{H}$, say $3^2_{[111]}$, and we get

$$3^2_{[111]}\mathrm{H} = \{3^2_{[111]}, 3^2_{[\bar{1}11]}, 3^2_{[1\bar{1}1]}, 3^2_{[11\bar{1}]}\}.$$

The group is now exhausted and we may write

$$G = H \cup (3_{[111]}H) \cup \{3^2_{[111]}H\}.$$

On assuming $g_1 = e$, then $\{e, 3_{[111]}H, 3^2_{[111]}H\}$ form a group under the following multiplication table

	e	$3_{[111]}H$	$3^2_{[111]}H$
e	e	$3_{[111]}H$	$3^2_{[111]}H$
$3_{[111]}H$	$3_{[111]H}$	$3^2_{[111]}H$	e
$3^2_{[111]}H$	$3^2_{[111]}H$	e	$3_{[111]}H$.

This group is homomorphic with G itself if we associate the elements in H to e, the elements in 3[111]H with the 'element' $3_{[111]}H$, the elements in $3^2_{[111]}H$ with the 'element' $3^2_{[111]}H$.

Maximal subgroups and minimal supergroups

The number of subgroups of a space group is always infinite. They may be the site-symmetry groups (groups without a lattice), or line groups, ribbon groups, rod groups, plane groups, or space groups. For example, the set T of all the primitive lattice translations is a subgroup (invariant) of the space group. Further subgroups may be found by considering the set of all the translations defined by a superlattice. We are here interested only in subgroups which are space groups themselves.

Let us first recall the concept of **proper subgroup**. A subgroup H is called proper subgroup of a group G if there are symmetry operations of G not contained in H. Now we define maximal subgroups: a subgroup H of a space group G is called a maximal subgroup of G if there is no proper subgroup M of G such that H is a proper subgroup of M. For example, $P112_1$, $P12_11$, $P2_111$ are maximal subgroups of $P2_12_12_1$, while P1 is not maximal.

For every H, according to (1.E.4), a right coset decomposition of G relative to H may be made. The index of the decomposition determines the degree of 'dilution' of the symmetry in H with respect to that in G. Such a dilution may be obtained in three different ways:

1. By eliminating some symmetry operators (e.g., from $G = P2_12_12_1$ to $H = P2_111$). Subgroups of this kind, are called **Translationengleiche** or **t subgroups**. Since the point group β of G is finite, the number of subgroups, and therefore, of maximal subgroups, is finite. All the maximal subgroups of type t for any given G are listed in the *International Tables* as **type *I* maximal non-isomorphous subgroups** (see Figs 1.20 and 1.21).

2. By loss of translational symmetry, i.e. by thinning out the lattice. Such subgroups are called **Klassengleiche** or ***k* subgroups** and are classified as **type *II***. A subset of k subgroups are those belonging to the same space group G or to its enantiomorphic: their number is infinite and they are called **maximal isomorphous subgroups**. Those of lowest index are listed as *IIc* in the *International Tables*. For example, if G = C222, maximal isomorphous subgroups of lowest index are C222 with $\boldsymbol{a}' = 3\boldsymbol{a}$ or $\boldsymbol{b}' = 3\boldsymbol{b}$ and C222 with $\boldsymbol{c}' = 2\boldsymbol{c}$.

Maximal non-isomorphous subgroups of C222 are also P222, $P2_12_12$, $P2_122$, $P22_12$, $P222_1$, which have the same conventional cell: for practical

reasons they are labelled as subgroups of type *IIa*. Space groups with primitive cells have no entry in the block *IIa*. Some further subgroups of C222 are $C222_1$ (with $\boldsymbol{c}' = 2\boldsymbol{c}$), I222 (with $\boldsymbol{c}' = 2\boldsymbol{c}$) and $I2_12_12_1$ (with $\boldsymbol{c}' = 2\boldsymbol{c}$). These subgroups have conventional cells larger than that of C222 and are denoted as subgroups of type *IIb*. For *k* subgroups the point group β of G is unchanged.

3. By combination of 1 and 2. In this case both the translation group T and the point group β of G are changed.

A theorem by Hermann states that a maximal subgroup of G is either a *t* subgroup or a *k* subgroup. Thus in the *International Tables* only *I, IIa, IIb,* and *IIc* subgroups are listed.

Sometimes we are interested to the possible space groups G′ of which a given space group G is a subgroup. G′ is called a minimal supergroup of the group G if G is a maximal subgroup of G′. Of course we will have a minimal *t*, or a minimal non-isomorphous *k*, or a minimal isomorphous *k* supergroup G′ of G according to whether G is a maximal *t*, or a maximal non-isomorphous *k*, or a maximal isomorphous *k* subgroup of G′. The minimal non-isomorphous supergroups of C222 are:

of type *t*: *C*mmm, C*cc*m, Cmm*a*, C*cca*, P422, $P42_12$, $P4_222$, $P42_12$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, P622, $P6_222$, $P6_422$,
of type *k*: F222, P222 (with $\boldsymbol{a}' = \boldsymbol{a}/2$, $\boldsymbol{b}' = \boldsymbol{b}/2$).

Maximal subgroups and minimal supergroups for three-dimensional crystallographic point groups

With trivial changes the definitions of maximal subgroup and minimal supergroup given above for space groups may be applied to three-dimensional crystallographic point groups. For example, it will be easily seen that Laue symmetry is always a minimal supergroup of index 2 of a non-centrosymmetric point group.

A scheme showing the subgroup and supergroup relationships for point groups is illustrated in Fig. 1.E.1. Maximal invariant subgroups are indicated by full lines: if two or three maximal invariant subgroups exist with the same symbol then double or triple full lines are used.

A set of maximal conjugate subgroups is referred to by a broken line. For example, from 3m three conjugate subgroups of type m can be formed. Thus a dashed line refers 3m to m. Furthermore, from 422 two invariant subgroups of type 222 with index 2 can be formed (no symmetry operation of 422 refers one subgroup to the other). Thus in Fig. 1.E.1 a double solid line refers 422 to 222.

Limiting groups in two and three dimensions

In two dimensions there are two types of point groups:

1, 2, 3, 4, 5, 6, . . .
m, 2mm, 3m, 4mm, 5m, 6mm, ...

For very large values of the order of the rotation axis the two types approach ∞ and ∞*m* respectively. From the geometrical point of view ∞ and ∞m are identical, and our standard notation will be ∞m (the situation

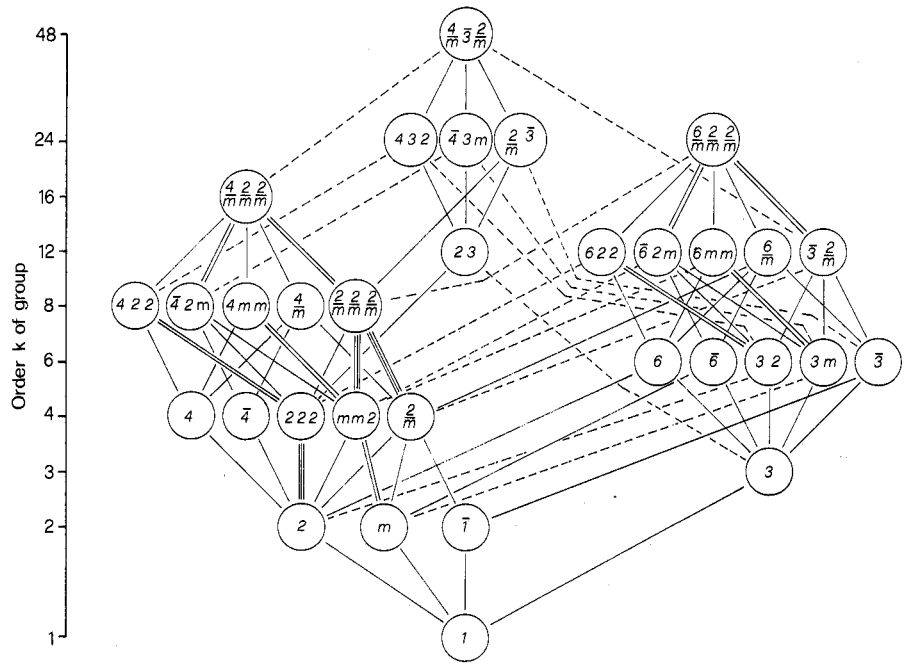


Fig. 1.E.1. Group, subgroup, supergroup relationships for point groups (from *International Tables for Crystallography*).

$\infty \neq \infty$m occurs when the rotation direction is taken into account: i.e. for a magnetic field round a disc).

In three dimensions a point group can include continuous rotations about one or about all axes (this is a consequence of the Euler theorem applied to such a limiting case). In the first case two groups can be identified, ∞m and $\frac{\infty}{\mathrm{m}}\frac{2}{\mathrm{m}}$, according to whether there is or not a mirror perpendicular to ∞ axis (the symmetry of the two groups can be represented by a circular cone and by a circular cylinder respectively). The symbol $\frac{\infty}{\mathrm{m}}\frac{\infty}{\mathrm{m}}$ represents the case in which continuous rotation about any axis is allowed (the symmetry is represented by a sphere).

Representation of a group

If a square matrix **d** can be associated to each $g \in \mathrm{G}$, in such a way that when $g_i g_j = g_k$ also $\mathbf{d}_i \mathbf{d}_j = \mathbf{d}_k$, then the matrices form a group D isomorphous with G. These matrices form an **isomorphous or exact representation** of the group: the order n of the matrices is the **dimension** of the representation. In accordance with this point of view, in Chapter 1 we have represented the symmetry groups through square matrices of order 3. Different representations of G may be obtained through a transformation of the type

$$\mathbf{d}'_j = \mathbf{q}^{-1}\mathbf{d}_j\mathbf{q}. \tag{1.E.7}$$

When condition (1.E.7) is verified for the two representations $\Gamma^1(\mathbf{d}_1, \mathbf{d}_2, \ldots)$ and $\Gamma^2(\mathbf{d}'_1, \mathbf{d}'_2, \ldots)$ then the two representations are said to be equivalent, since **q** can be interpreted as a change of coordinate system. It is often possible to find a new coordinate system for which each matrix **d**

is transformed into

$$\left(\begin{array}{c|c} \mathbf{d}^1 & 0 \\ \hline 0 & \mathbf{d}^2 \end{array}\right) \tag{1.A.13}$$

with $\mathbf{d}^1$ of order $m < n$ and $\mathbf{d}^2$ of order $(n - m)$. If this can not be obtained by any transformation, then the representation is called **irreducible**; otherwise it is called **reducible**. Sometimes $\mathbf{d}^1$ and $\mathbf{d}^2$ can be further reduced, and at the end of the process each matrix $\mathbf{d}_j$ will be transformed into

$$\mathbf{q}^{-1}\mathbf{d}_j\mathbf{q} = \text{diag}\,[\mathbf{d}_j^{(1)}, \mathbf{d}_j^{(2)}, \ldots, \mathbf{d}_j^{(s)}] = \mathbf{d}_j'$$

where $\mathbf{d}_j^{(i)}$ are themselves matrices.

The matrices $\mathbf{d}_1^{(1)}, \mathbf{d}_2^{(1)}, \mathbf{d}_3^{(1)}, \ldots$ all have the same dimension. Similarly $\mathbf{d}_1^{(2)}, \mathbf{d}_2^{(2)}, \mathbf{d}_3^{(2)}, \ldots$ have the same dimension. From the rule of the product of blocked matrices it follows that $(\mathbf{d}_1^{(1)}, \mathbf{d}_2^{(1)}, \mathbf{d}_3^{(1)}, \ldots)$ form a representation of the group, as well as $(\mathbf{d}_1^{(2)}, \mathbf{d}_2^{(2)}, \mathbf{d}_3^{(2)}, \ldots)$, etc.

It can be shown that for finite groups the number of irreducible representations is equal to the number of classes. For instance an isomorphous (reducible) representation of the point group 32 is

$$g_1 = 1 \Leftrightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \; g_2 = 3_{[001]} \Leftrightarrow \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix};$$

$$g_3 = 3^2_{[001]} \Leftrightarrow \begin{pmatrix} \bar{1} & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \; g_4 = 2_{[100]} \Leftrightarrow \begin{pmatrix} 1 & \bar{1} & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix};$$

$$g_5 = 2_{[010]} \Leftrightarrow \begin{pmatrix} \bar{1} & 0 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}; \; g_6 = 2_{[110]} \Leftrightarrow \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

Also the two-dimensional irreducible representation

$$g_1 \Leftrightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \; g_2 \Leftrightarrow \begin{pmatrix} 0 & 1 \\ \bar{1} & \bar{1} \end{pmatrix}; \; g_3 \Leftrightarrow \begin{pmatrix} \bar{1} & \bar{1} \\ 1 & 0 \end{pmatrix};$$

$$g_4 \Leftrightarrow \begin{pmatrix} 1 & 0 \\ \bar{1} & \bar{1} \end{pmatrix}; \; g_5 \Leftrightarrow \begin{pmatrix} \bar{1} & \bar{1} \\ 0 & 1 \end{pmatrix}; \; g_6 \Leftrightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

and the one-dimensional non-exact (homomorphic) representations exist:

$$g_1 \to 1; \; g_2 \to 1; \; g_3 \to 1; \; g_4 \to \bar{1}; \; g_5 \to \bar{1}; \; g_6 \to \bar{1}$$

$$g_1 \to 1; \; g_2 \to 1; \; g_3 \to 1; \; g_4 \to 1; \; g_5 \to 1; \; g_6 \to 1.$$

Character tables

The sum of the diagonal elements of a matrix, elsewhere called **trace**, in group theory is called character and is indicated by $\chi(g)$. It is obvious that $\chi(g_1)$ defines the dimensionality of the representation. The complete set of characters for a given representation is called the **character of the**

representation. Since the traces of two matrices related by a coordinate transformation are identical, the characters of two equivalent representations will be identical (the converse is also true). Several properties of a point group may be deduced from the characters of its irreducible representations alone. It is therefore convenient to set them up in tables called **character tables**. Each row of the table refers to a particular irreducible representation and each column to a given class.

1.F. Symmetry generalization

Only a few intuitive elements of this subject are given, since a full treatment would exceed the limits of the present book. The reader is referred to specific texts or papers.[1–3]

The symmetry groups G_n^m

A space may or may not be periodic in all its m dimensions. The corresponding symmetry groups are indicated by G_n^m, with $m \geqslant n$, where n is the number of dimensions of the subspace in which the group is periodic. In this space only symmetry operations transforming the space into itself will be allowed. For instance in the G_1^3 groups, describing objects periodic in one direction and finite in the other two, at least one line will remain invariant with respect to all symmetry operations.

The G^1 groups

1. G_0^1 groups. In a one-dimensional space (a line), which is non-periodic, only two symmetry operators are conceivable: 1 and $\bar{1}$ (which is the reflection operator m). The only two (point) groups are therefore 1 and $\bar{1}$.
2. G_1^1 groups. Besides the 1 and $\bar{1}$ operators, they contain the translation operator. Only two groups of type G_1^1 are then possible.

The G^2 groups

1. G_0^2 groups. In a two-dimensional space (a plane), which is non-periodic, the only conceivable operators are those of rotation around an axis perpendicular to the plane and of reflection with respect to a line on the plane. The number of (point) groups is infinite, but there are only ten crystallographic groups (see p. 16).
2. G_1^2 (**border**) groups. In a two-dimensional space, periodic in one dimension, only the symmetry operators (and their combinations), which transform that direction into itself, are allowed. We may therefore consider reflection planes parallel or perpendicular to the invariant direction, glides with translational component parallel to it and two-fold axes. There are seven G_1^2 groups (the symmetries of **linear decorations**) which are represented in Fig. 1.F.1.
3. G_2^2 groups. There are the 17 plane groups described on the pages 30 and 34.

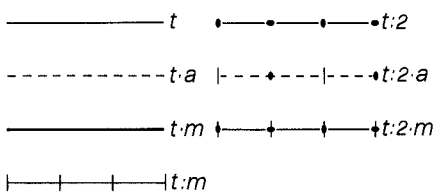


Fig. 1.F.1. The seven border groups.

The G^3 groups

1. G_0^3 groups. There describe non-periodic spaces in three dimensions. The number of (point) groups is infinite (see Appendix 1.B), but there are only 32 crystallographic point groups (see pp. 11–16).

2. G_1^3 (**rod**) groups. Rod groups may be considered as arising from the combination of one-dimensional translation groups with point groups G_0^3. They describe three-dimensional objects which are periodic in only one direction (say z). This must remain invariant with respect to all symmetry operations. The only allowed operations are therefore n and $\bar{n}$ axes coinciding with z, 2 and $\bar{2}$ axes perpendicular to it, screw axes and glide planes with a translational component parallel to the invariant direction.

There are 75 G_1^3 crystallographic groups. In Table 1.F.1 the rod group symbols are shown alongside the point groups from which they are derived. The first position in the symbol indicates the axis (n or $\bar{n}$) along z, the

Table 1.F.1. The 75 rod groups

Point group	Rod groups					
1	1					
2	2	2_1				
3	3	3_1	3_2			
4	4	4_1	4_3	4_2		
6	6	6_1	6_5	6_2	6_4	6_3
1m	1m	1c				
2mm	2mm	2_1mc	2cc			
3m	3m	3c				
4mm	4mm	4_2mc	4cc			
6mm	6mm	6_3mc	6cc			
m	m					
2/m	2/m	2_1/m				
4/m	4/m	4_2/m				
6/m	6/m	6_3/m				
m2m	m2m	m2c				
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	$\frac{2_1}{m}\frac{2}{m}\frac{2}{c}$	$\frac{2}{m}\frac{2}{c}\frac{2}{c}$			
$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$\frac{4_2}{m}\frac{2}{m}\frac{2}{c}$	$\frac{4}{m}\frac{2}{c}\frac{2}{c}$			
$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$	$\frac{6}{m}\frac{2}{c}\frac{2}{c}$			
12	12					
222	222	2_122				
32	32	3_12	3_22			
422	422	4_122	4_322	4_222		
622	622	6_122	6_522	6_222	6_422	6_322
$\bar{1}$	$\bar{1}$					
$\bar{3}$	$\bar{3}$					
$\bar{4}$	$\bar{4}$					
$\bar{6}$	$\bar{6}$					
$\bar{1}\frac{2}{m}$	$\bar{1}\frac{2}{m}$	$\bar{1}\frac{2}{c}$				
$\bar{3}\frac{2}{m}$	$\bar{3}\frac{2}{m}$	$\bar{3}\frac{2}{c}$				
$\bar{4}$m2	$\bar{4}$m2	$\bar{4}c2$				
$\bar{6}$m2	$\bar{6}$m2	$\bar{6}c2$				

second position refers to axes (n or $\bar{n}$) in the plane (x, y) normal to the invariant direction, the third position for axes in the (x, y) plane bisecting the previous ones. Glides in the z direction are denoted by c.

3. G_2^3 groups. There are called **layer** groups and describe[4,5,12,13] the symmetries of doubly periodic three-dimensional objects. They are useful in describing the patterns of walls, panels, and, at an atomic level, in describing structures with layer molecular units.

Let us denote by z the direction perpendicular to the layer plane. It will be the vertical axis from now on: directions in the plane will be called horizontal. Rotations can only occur about a vertical axis, and if twofold, also about a horizontal one. No more than one horizontal reflection plane can exist, otherwise translational symmetry should also occur along the z axis. The layer groups can be enumerated according to the five nets quoted in Table 1.7 for the plane lattices. In Table 1.F.2 the 80 layer groups are divided in blocks, each block divided by the subsequent by a double line: each block refers to a specific net (in sequence, parallelogram, rectangular, centred rectangular, square, hexagonal) and contains the point groups compatible with the net and the corresponding layer groups.

The number of point groups which can be used is 31: the 32 three-dimensional point groups minus the five incompatible groups 23, $m\bar{3}$, 432, $\bar{4}3m$, $m\bar{3}m$ plus four second settings (this time the z axis is distinguishable from x and y: so 2 is different from 12, or 2/m from $\bar{1}2/m$, . . .).

The first position in the layer group symbol gives the type of cell, the second refers to the z direction. The third and fourth positions refer:

(a) for rectangular nets, to x and y respectively;

(b) for a square net, to x (and therefore to y) and to a diagonal direction;

(c) for a hexagonal net, to x (and therefore symmetry related axes) and to diagonals directions.

As subgroups of the G_2^3 groups we may consider the G_2^2 groups, which are obtained by projecting the G_2^3 groups along the axis normal to the singular plane.

4. G_3^3 groups. These are the 230 space groups (see pp. 22–30).

The G_n^4 groups

The three-dimensional Euclidean space may be insufficient to describe the symmetries of some physical objects. We can therefore introduce one or more additional continuous variables (e.g. the time, the phase of a wave function, etc.), thus passing from a three-dimensional space into a space with dimensions $m > 3$. In a four-dimensional Euclidean space the symmetry groups G_n^4 may be constructed from their three-dimensional projections G_n^3, which are all well known. Thus there are 227 point groups G_0^4 and 4895 groups G_4^4.

The groups of colour symmetry

Groups in which three variables have a geometrical meaning while the fourth has a different physical meaning and is not continuous, are

Table 1.F.2. The layer groups

Point group	Plane groups			
1	p1			
2	p2			
m	pm	p*b*		
2/m	p2/m	p2/*b*		
$\bar{1}$	p$\bar{1}$			
1m	p1m	p1*b*		
2mm	p2mm	p2*b*m	p2*ba*	
m2m	pm2m	pm2_1*a*	p*a*2_1m	p*a*2*a*
	p*n*2_1m	p*n*2*a*	p*b*2m	p*b*2_1*a*
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	p$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	p$\frac{2}{m}\frac{2}{b}\frac{2_1}{m}$	p$\frac{2}{m}\frac{2_1}{b}\frac{2_1}{a}$	
	p$\frac{2}{b}\frac{2}{m}\frac{2_1}{m}$	p$\frac{2}{b}\frac{2_1}{m}\frac{2_1}{a}$	p$\frac{2}{b}\frac{2}{b}\frac{2}{m}$	p$\frac{2}{b}\frac{2_1}{b}\frac{2}{a}$
	p$\frac{2}{n}\frac{2_1}{m}\frac{2_1}{m}$	p$\frac{2}{n}\frac{2_1}{b}\frac{2}{m}$	p$\frac{2}{n}\frac{2}{b}\frac{2}{a}$	
12	p12	p12_1		
222	p222	p222_1	p22_12_1	
$\bar{1}\frac{2}{m}$	p$\bar{1}\frac{2}{m}$	p$\bar{1}\frac{2}{b}$	p$\bar{1}\frac{2_1}{m}$	p$\bar{1}\frac{2_1}{b}$
1m	*c*1m			
2mm	$c_2$mm			
m2m	*c*m2m	*cg*2m		
$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	c$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	*c*$\frac{2}{g}\frac{2}{m}\frac{2}{m}$		
12	c12			
222	*c*222			
$\bar{1}\frac{2}{m}$	*c*$\bar{1}\frac{2}{m}$			
4	p4			
4mm	p4mm	p4*g*m		
4/m	p4m/m	p4/*n*		
$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	p$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	p$\frac{4}{m}\frac{2_1}{g}\frac{2}{m}$	p$\frac{4}{m}\frac{2_1}{g}\frac{2}{m}$	p$\frac{4}{n}\frac{2}{g}\frac{2}{m}$
$\bar{4}$	p$\bar{4}$			
422	p22	p42_12		
$\bar{4}$m2	p$\bar{4}$m2	p$\bar{4}$g2	p$\bar{4}$2m	p$\bar{4}2_1$m
3	p3			
3m	p3m1	p31m		
$\bar{3}$*m*	p$\bar{3}$			
32	p321	p312		
$\bar{3}\frac{2}{m}$	p$\bar{3}\frac{2}{m}$1	p$\bar{3}1\frac{2}{m}$		
6	p6			
6mmm	p6mm			
6/m	p6/m			
$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	*p*$\frac{6}{m}\frac{2}{m}\frac{2}{m}$			
$\bar{6}$	p$\bar{6}$			
622	p622			
$\bar{6}$m2	p$\bar{6}$m2	p$\bar{6}$2m		

particularly important in crystallography. For instance:

1. The position and orientation of the magnetic moments of the cobalt atoms in the $CoAl_2O_4$ structure (space group $Fd\bar{3}m$) may be described by means of a two-colour group (see Fig. 1.F.2(a)) in which each colour corresponds to a given polarity of the magnetic moment. Groups of this type are also called 'groups with antisymmetry' or 'black-white' symmetry. More complicated cases require more colours, and the term **colour symmetry** is used. Classical groups involve only neutral points.

   As a further example let us consider the case of NiO, a material used in the ceramic and electronic industries. At room temperature, NiO is rhombohedral with edge length $a_R \simeq 2.952$ Å and $\alpha_R \simeq 60°4'$: α_R approaches 60° with increasing temperature, and, above 250°C, NiO is cubic with $a_C \simeq 4.177$ Å. The relation between the two cells is shown in Fig. 1.F.2(b): the same set of lattice points is described by the primitive rhombohedral unit cell and by the face-centred cubic cell provided that $\alpha_R = 60°$ exactly and $a_R = a/\sqrt{2}$. If the cube is compressed (or extended) along one of the four threefold axes of the cubic unit cell then symmetry reduces from cubic to rhombohedral (the only threefold axis is the compression axis). The polymorphism of NiO is due to its magnetic properties. Each Ni^{2+} ion has two unpaired spins (the $[Ar]3d^8$ electronic configuration). At room temperature the spins in NiO form an ordered antiferromagnetic array: layers of Ni^{2+} with net spin magnetic moments all in the same direction alternate with layers of Ni^{2+} with magnetic moments all in the opposite direction, as in Fig. 1.F.2(c). In these conditions the threefold axis is unique and the structure is rhombohedral. Above 250 °C the antiferromagnetic ordering is lost: the rhombohedral → cubic transition occurs and NiO displays ordinary paramagnetism.

2. If we project a G_3^3 group, in which a 6_1 axis is present, on a plane perpendicular to the axis, we obtain a G_2^2 group. But, if we assign a different colour to each of the six atoms related by the 6_1 axis, we will obtain a colour group $G_2^{2\cdot(6)}$ with a clear meaning of the symbols.

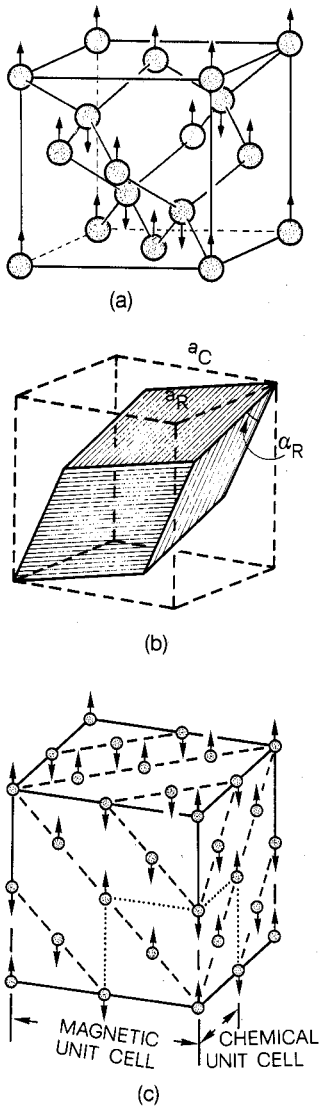


Fig. 1.F.2. Examples of structure described by an antisymmetry group: (a) $CoAl_2O_4$ magnetic structure; (b) geometrical relation between a face-centered cubic unit cell and a primitive rhombohedral unit cell; (c) antiferromagnetic superstructure of NiO (only Ni^{2+} ions are shown).

In the groups with antisymmetry there will be four types of equivalence between geometrically related objects: identity, identity after an inversion operation, anti-identity (the two objects differ only in the colour), identity after both an inversion operation and a change in colour. A general rotation matrix may be written in the form

$$\mathbf{R} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & 0 \\ R_{21} & R_{22} & R_{23} & 0 \\ R_{31} & R_{32} & R_{33} & 0 \\ 0 & 0 & 0 & R_{44} \end{pmatrix}$$

where $R_{44} = -1$ or $+1$ depending on whether or not the operation changes the colour.

For the three-dimensional groups with antisymmetry we observe that, because of the existence of the anti-identity operation $1'$ (only the colour is changed), the anti-translation operation $t' = t1'$ will also exist. New types of Bravais lattices, such as those given in Fig. 1.F.3, will come out. As an example, in Fig. 1.F.2(c) the quasi-cubic magnetic unit cell of NiO has an

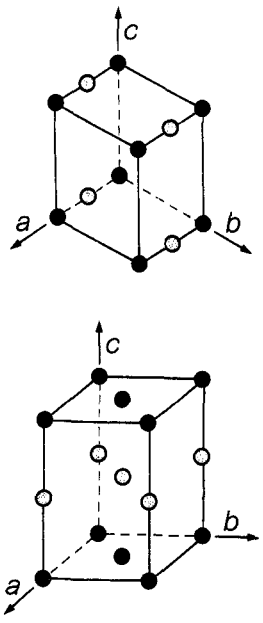


Fig. 1.F.3. Two antisymmetrical Bravais lattices.

edge length twice that of the chemical unit cell. It may be seen[14] that if the five Bravais lattices are centred by black and white lattice points (in equal percentage) then five new plane lattices are obtained. In three dimensions there are 36 black and white Bravais lattices, including the traditional uncoloured lattices.

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