
2.1 Introduction

We continue our study of crystals by investigating the internal arrangements of crystalline materials. Crystals are characterized by periodicities in three dimensions.¹ An atomic grouping, or pattern motif which, itself, may or may not be symmetrical, is repeated again and again by a symmetry mechanism, namely the *space group* of the crystal. There are 230 space groups, and each crystal substance belongs to one or other of them. In its simplest form, a space group may be derived from the repetition of a pattern motif by the translations of a lattice, as discussed below. It can be developed further by incorporating additional symmetry elements, as demonstrated through the following text and Problem 2.1. We now enlarge on these ideas, starting with an examination of lattices.

2.2 Lattices

Every crystal has a lattice as its geometrical basis. A lattice may be described as a regular, infinite arrangement of points in space in which every point has exactly the same environment as any other point. This description is applicable, equally, in one-, two-, or three-dimensional space.

Lattice geometry in three-dimensional space is described in relation to three noncoplanar basic repeat (translation) vectors **a**, **b**, and **c**. Any lattice point may be chosen as an origin, whence a vector **r** to any other lattice point is given by

$$r = U\mathbf{a} + V\mathbf{b} + W\mathbf{c} \quad (2.1)$$

where U , V , and W are positive or negative integers or zero, and represent the coordinates of the given lattice point. The *direction* (directed line) joining the origin to the points U , V , W ; $2U$, $2V$, $2W$; . . . ; nU , nV , nW defines the row $[UVW]$. A set of such rows, or directions, related by the symmetry constitutes a form of directions $\langle UVW \rangle$; compare with zone symbols, Sect. 1.2.5. The magnitude r can be evaluated by (2.16) *mutatis mutandis*.²

¹ We shall not be concerned here with the aperiodic crystalline materials discussed in Sect. 1.4.3.

² "The necessary changes having been made."

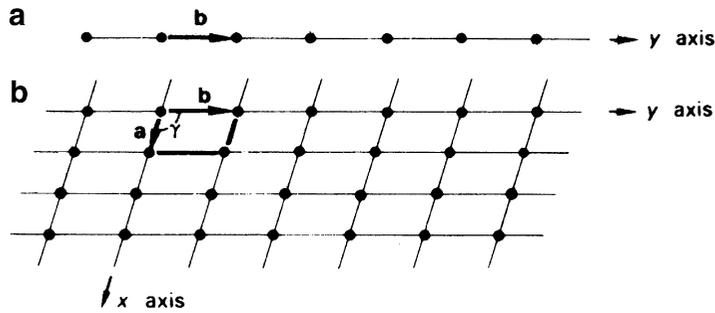


Fig. 2.1 Formation of a net. (a) Row (a one-dimensional lattice) of equally spaced points. (b) Regular stack of rows forming a net

We consider first lattices in two dimensions; the three-dimensional lattices then become an extension of the principles that evolve, rather like the symmetry operations discussed in the previous chapter.

2.2.1 Two-Dimensional Lattices

A two-dimensional lattice is called a *net*; it may be imagined as being formed by aligning, in a regular manner, one-dimensional *rows* of equally spaced points, Fig. 2.1a. The net (lattice) is the array of points; the connecting lines are a convenience, drawn to aid our appreciation of the lattice geometry.

Since nets exhibit symmetry, they can be allocated to the two-dimensional systems, Sect. 1.4.1, Table 1.1. The most general net is shown in Fig. 2.1b. A sufficient and representative portion of the lattice is the *unit cell*, outlined by the vectors **a** and **b**; an infinite number of such unit cells stacked side by side builds up the net.

The net under consideration exhibits twofold rotational symmetry about each lattice point; consequently, it is placed in the oblique system. The chosen unit cell is primitive, symbol *p*, which implies that one lattice point is associated with the area of the unit cell: each point is shared equally by four adjacent unit cells. In the oblique unit cell, $a \not\propto b$, and $\gamma \not\propto 90$ or 120° ; angles of 90 or 120° in a lattice imply symmetry higher than 2.

Consider next the stacking of unit cells in which $a \propto b$ but $\gamma = 90^\circ$, Fig. 2.2. The symmetry at every point is $2mm$, and this net belongs to the rectangular system. The net in Fig. 2.3 may be described by a unit cell in which $a' = b'$ and $\gamma' \not\propto 90$ or 120° . It may seem at first that such a net is oblique, but careful inspection shows that each point has $2mm$ symmetry, and so this net, too, is allocated to the rectangular system.

In order to display this fact clearly, a centered (symbol *c*) unit cell is chosen, shown in Fig. 2.3 by the vectors **a** and **b**. This cell has two lattice points per unit-cell area. It is left as an exercise to the reader to show that a centered, oblique unit cell does not represent a net with a fundamentally different arrangement of points from that in Fig. 2.1b.

³The symbol $\not\propto$ should be read as “not constrained by symmetry to equal.”

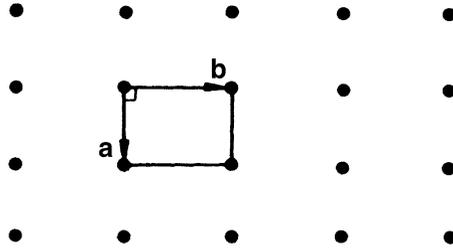


Fig. 2.2 Rectangular net with a p unit cell drawn in

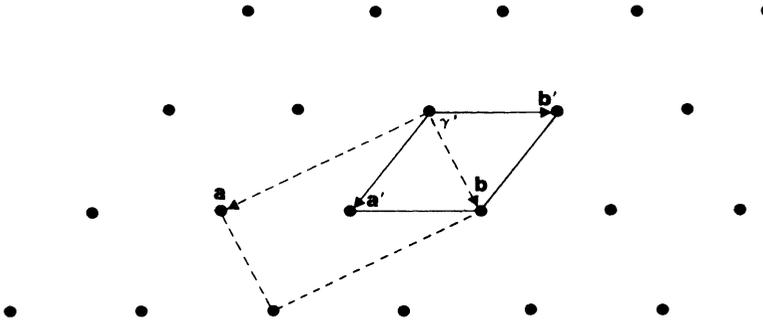


Fig. 2.3 Rectangular net with p and c unit cells drawn in; the c unit cell is the standard choice for this net

2.2.2 Choice of Unit Cell

From the foregoing discussion, it will be evident that there is an infinity of ways in which a unit cell might be chosen for a given lattice (and structure). However, we shall follow a universal crystallographic convention in choosing a unit cell: the unit cell is *the smallest repeat unit for which its delineating vectors are parallel to, or coincide with, important symmetry directions in the lattice*. Returning to Fig. 2.3, the centered cell is preferred because \mathbf{a} and \mathbf{b} coincide with the symmetry (m) lines in the net. The primitive unit cell (\mathbf{a}' , \mathbf{b}') is, of course, a possible unit cell, but it does not, in isolation, reveal the lattice symmetry clearly. The symmetry is still there; it is invariant under choice of unit cell. The following equations show the necessary equivalence of a' and b' :

$$a'^2 = a^2/4 + b^2/4 \quad (2.2)$$

$$b'^2 = a^2/4 + b^2/4 \quad (2.3)$$

the value of γ' depends only on the ratio a/b .

Two other nets exist, governed by the unit-cell relationships $a = b, \gamma = 90^\circ$ and $a = b, \gamma = 120^\circ$; their study constitutes the Problem 1.2 at the end of this chapter. The five two-dimensional lattices are summarized in Table 2.1. A lattice has the highest point-group symmetry of its system at each lattice point: compare Table 2.1 with Table 1.1 and Table 2.3 with Table 1.5.

Table 2.1 The five two-dimensional lattices

System	Unit-cell symbol(s)	Symmetry at lattice points	Unit-cell edges and angles
Oblique	p	2	$a \neq b; \gamma \neq 90^\circ, 120^\circ$
Rectangular	p, c	$2mm$	$a \neq b; \gamma = 90^\circ$
Square	p	$4mm$	$a = b; \gamma = 90^\circ$
Hexagonal	p	$6mm$	$a = b; \gamma = 120^\circ$

2.2.3 Three-Dimensional Lattices

The three-dimensional lattices, or Bravais lattices, may be imagined as being developed by the regular stacking of nets. There are 14 unique ways in which this can be done, and the corresponding Bravais lattices are distributed, unequally, among the seven crystal systems, as shown in Fig. 2.4. Each lattice is represented by a unit cell, outlined by three vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} . In accordance with convention, these vectors are chosen so that they both form a parallelepipedon of smallest volume in the lattice and are parallel to, or coincide with, important symmetry directions in the lattice; thus, not all conventional unit cells are primitive. In three dimensions, we encounter unit cells centered on a pair of opposite faces, body-centered, or centered on all faces. Table 2.2 lists the unit-cell types and their notation.

Fractional Coordinates

A fractional coordinate x is given by X/a , where X is that coordinate in absolute measure (\AA or nm) and a is the unit-cell repeat distance in the same direction and in the same units. Thus, a position x at 1.45 \AA along a unit cell of edge of length 12.34 \AA corresponds to a fractional coordinate of 0.1175.

Triclinic Lattice

If oblique nets are stacked in a general and regular manner, a triclinic lattice is obtained, Fig. 2.5. The unit cell is characterized by $\bar{1}$ symmetry at each lattice point, with the conditions $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90$ or 120° . This unit cell is primitive (symbol P), which means that one lattice point is associated with the unit-cell volume; each point is shared equally by eight adjacent unit cells in three dimensions; refer to Fig. 2.6 for this sharing principle. There is no symmetry direction to constrain the choice of the unit-cell vectors, and a parallelepipedon of smallest volume can always be chosen conventionally.

Monoclinic Lattices

The monoclinic system is characterized by one diad (rotation or inversion), with the y axis (and b) chosen along or parallel to it. The conventional unit cell is specified by the conditions $a \neq b \neq c$, $\alpha = \gamma = 90^\circ$, and $\beta \neq 90$ or 120° . Figure 2.6 illustrates a stereoscopic pair of drawings of a monoclinic lattice, showing eight P unit cells; according to convention, the β angle is chosen to be oblique.

Reference to Fig. 2.4 shows that there are two conventional monoclinic lattices, symbolized by the unit-cell types P and C .

A monoclinic unit cell centered on the A faces is equivalent to that described as C ; the choice of the b axis⁴ is governed by symmetry: a and c may be interchanged, but the direction of \mathbf{b} must then be reversed in order to preserve right-handed axes.

⁴ We often speak of the b axis (meaning the y axis) because our attention is usually confined to the unit cell.

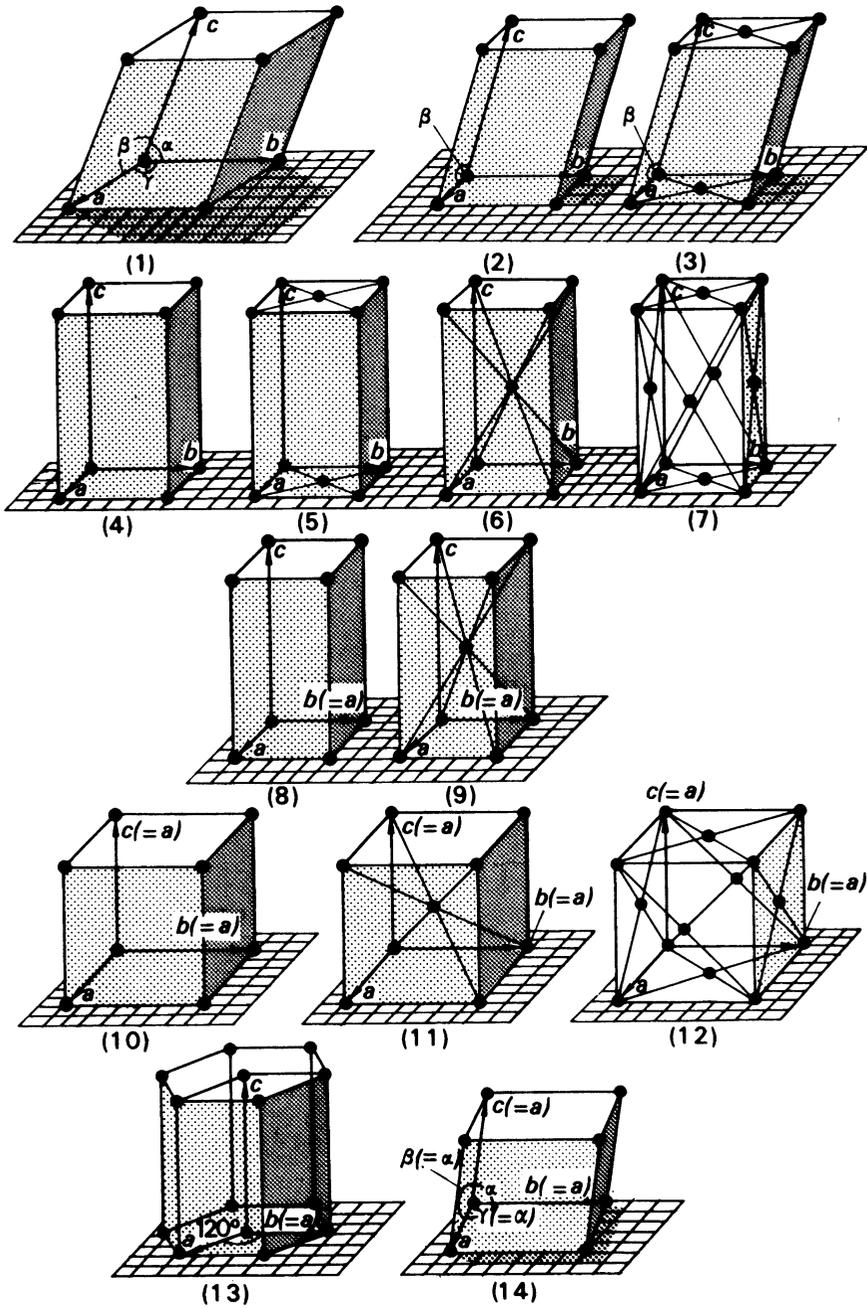
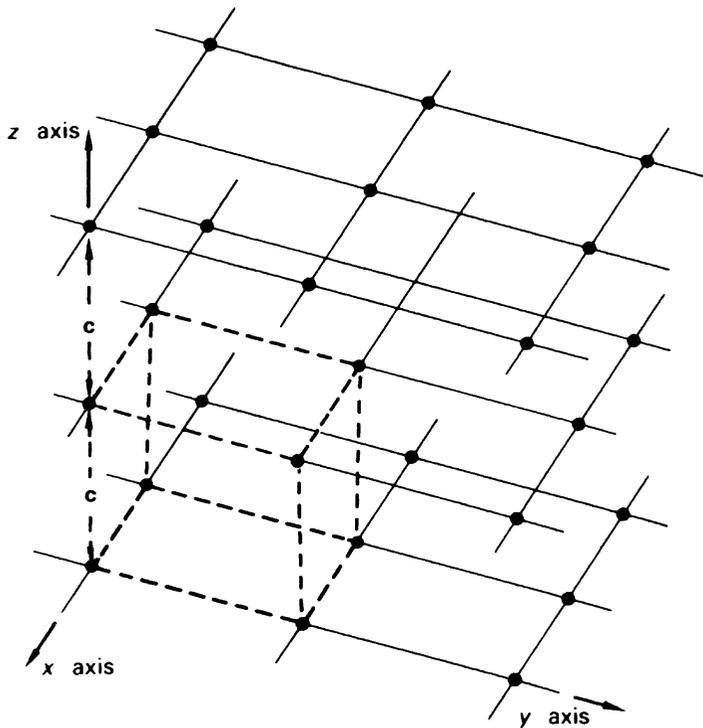


Fig. 2.4 Unit cells of the 14 Bravais lattices; interaxial angles are 90° unless indicated otherwise by a numerical value or symbol. (1) Triclinic *P*. (2) Monoclinic *P*. (3) Monoclinic *C*. (4) Orthorhombic *P*. (5) Orthorhombic *C*. (6) Orthorhombic *I*. (7) Orthorhombic *F*. (8) Tetragonal *P*. (9) Tetragonal *I*. (10) Cubic *P*. (11) Cubic *I*. (12) Cubic *F*. (13) Hexagonal *P*. (14) Trigonal *R*. Note that (13) shows three *P* hexagonal unit cells. A hexagon of lattice points without the central points in the basal planes shown does not lead to a lattice. Why?

Table 2.2 Notation for conventional crystallographic unit cells

Centering site(s)	Symbol	Miller indices of centred faces in the unit cell	Fractional coordinates of centered sites in the unit cell
None	<i>P</i>	–	–
<i>bc</i> faces	<i>A</i>	(100)	$0, \frac{1}{2}, \frac{1}{2}$
<i>ca</i> faces	<i>B</i>	(010)	$\frac{1}{2}, 0, \frac{1}{2}$
<i>ab</i> faces	<i>C</i>	(001)	$\frac{1}{2}, \frac{1}{2}, 0$
Body center	<i>I</i>	–	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
All faces	<i>F</i>	(100), (010), (001)	$\left\{ \begin{array}{l} 0, \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, 0, \frac{1}{2} \\ \frac{1}{2}, \frac{1}{2}, 0 \end{array} \right.$

**Fig. 2.5** Oblique nets stacked regularly at a vector spacing *c* to form a triclinic lattice

The centering of the *B* faces is illustrated in Fig. 2.7. In this situation a new unit cell, \mathbf{a}' , \mathbf{b}' , \mathbf{c}' , can be defined by the following equations:

$$\mathbf{a}' = \mathbf{a} \quad (2.4)$$

$$\mathbf{b}' = \mathbf{b} \quad (2.5)$$

$$\mathbf{c}' = \mathbf{a}/2 + \mathbf{c}/2 \quad (2.6)$$

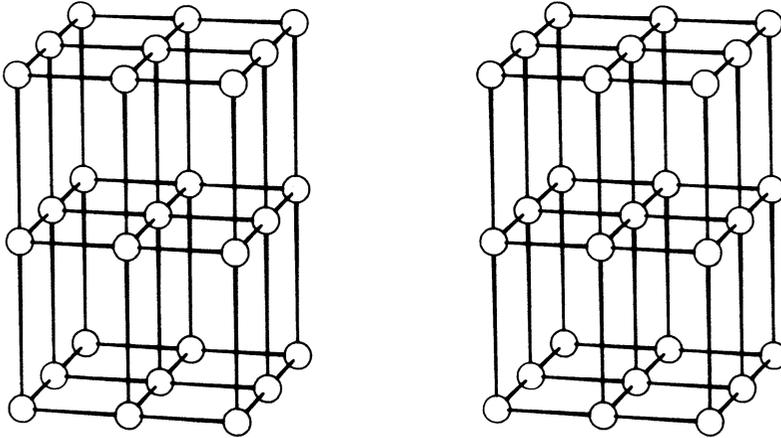


Fig. 2.6 Stereoview showing eight adjacent P unit cells in a monoclinic lattice. The sharing of lattice points among the unit cells can be seen readily by focusing attention on the central lattice point in the drawings. A similar sharing occurs with P unit cells of lattices in all systems

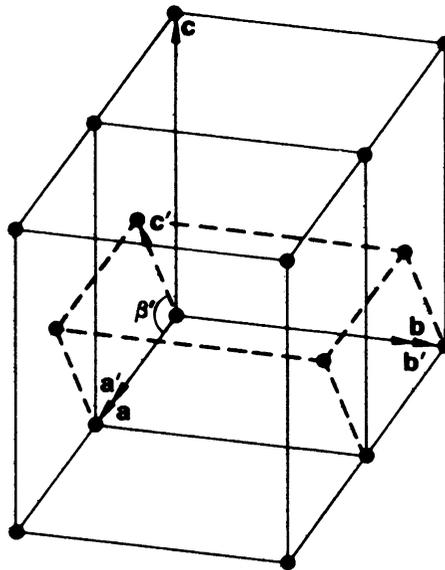


Fig. 2.7 Monoclinic lattice showing that $B \equiv P$; β is the angle between \mathbf{c} and \mathbf{a} , and β' the angle between \mathbf{c}' and \mathbf{a}'

If β is not very obtuse, an equivalent transformation $\mathbf{c}' = -\mathbf{a}/2 + \mathbf{c}/2$ can ensure that β' is obtuse (by convention). Since \mathbf{c}' lies in the ac plane, $\alpha' = \gamma' = 90^\circ$, but $\beta' \notin 90$ or 120° . The new monoclinic cell is primitive; symbolically we may write $B \equiv P$. Similarly, it may be shown that $I \equiv F \equiv C \equiv (A)$, Figs. 2.8 and 2.9.

If the C unit cell, Fig. 2.10, is reduced to primitive as shown, it no longer displays in isolation the characteristic monoclinic symmetry clearly (see Table 2.3); neither α' nor γ' is 90° . We may conclude that there are two distinct monoclinic lattices, described by the unit-cell types P and C .

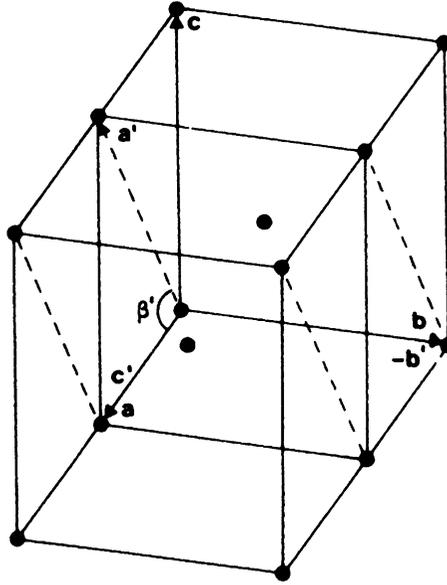


Fig. 2.8 Monoclinic lattice showing that $I \equiv C$

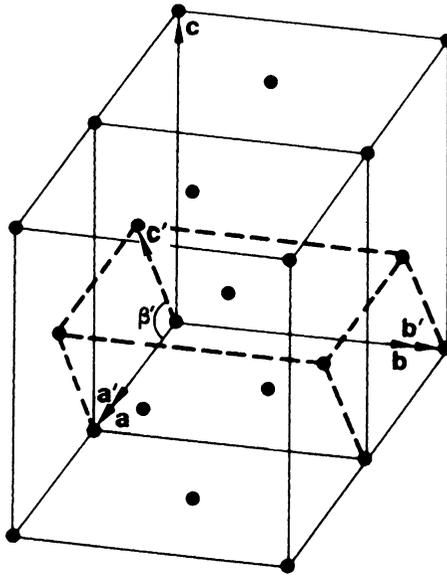


Fig. 2.9 Monoclinic lattice showing that $F \equiv C$

It may be necessary to calculate the new dimensions of a transformed unit cell. Consider the transformation $B \rightarrow P$, (2.4)–(2.6). Clearly, $a' = a$ and $b' = b$. Taking the scalar product⁵ of (2.6) with itself, we obtain

⁵The scalar (dot) product of two vectors \mathbf{p} and \mathbf{q} is denoted by $\mathbf{p} \cdot \mathbf{q}$, and is equal to $pq \cos \widehat{pq}$, where \widehat{pq} represents the angle between the (positive) directions of \mathbf{p} and \mathbf{q} .

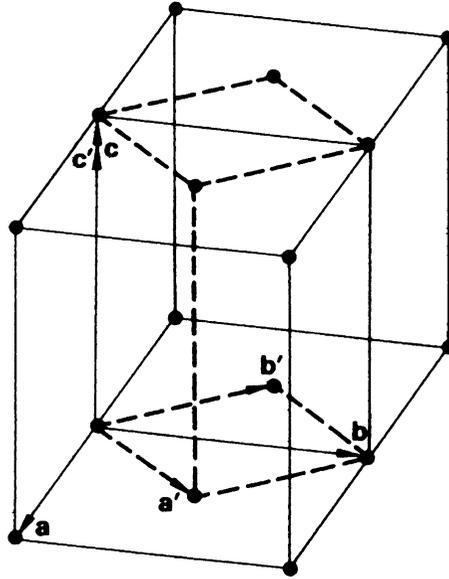


Fig. 2.10 Monoclinic lattice showing that $C \neq P$

Table 2.3 The 14 Bravais lattices and their notation

System	Unit cell(s)	Symmetry at lattice points	Axial relationships
Triclinic	P^a	$\bar{1}$	$a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ, 120^\circ$
Monoclinic	P, C	$2/m$	$a \neq b \neq c; \alpha = \gamma = 90^\circ; \beta \neq 90^\circ, 120^\circ$
Orthorhombic	P, C, I, F	mmm	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
Tetragonal	P, I	$\frac{4}{m}mm$	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$
Cubic	P, I, F	$m\bar{3}m$	$a = b = c; \alpha = \beta = \gamma = 90^\circ$
Hexagonal	P	$\frac{6}{m}mm$	$a = b \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ$
Trigonal ^b	R or P	$\bar{3}m$	$a = b = c; \alpha = \beta = \gamma \neq 90^\circ, <120^\circ$

^aCapital letters are used for unit cells in three-dimensional lattices

^bOn hexagonal axes, column 4 would be the same as for the hexagonal system, but the symmetry at each lattice point remains $\bar{3}m$. This table may be compared with Table 1.3

$$\mathbf{c}' \cdot \mathbf{c} = (\mathbf{a}/2 + \mathbf{c}/2) \cdot (\mathbf{a}/2 + \mathbf{c}/2) \tag{2.7}$$

Hence

$$c'^2 = a^2/4 + c^2/4 + ac(\cos \beta)/2 \tag{2.8}$$

The new angle β' is given by

$$\cos \beta' = \mathbf{a}' \cdot \mathbf{c}'/a'c' \tag{2.9}$$

In order to make β' obtuse, it may be necessary to begin with $-\mathbf{a}/2$ in (2.6).

Using (2.6) again and expanding, we obtain

$$\cos \beta' = [-a/2 + c(\cos \beta)/2]/c' = (-a + c \cos \beta)/(2c') \tag{2.10}$$

where c' is given by (2.8). This type of calculation can be carried out in any crystal system, giving due consideration to any nontrivial relationships between a , b , and c and between α , β , and γ (see, for example, Problem 2.3).

Orthorhombic Lattices

The monoclinic system was treated in some detail. It will not be necessary here to give such an extensive discussion for either the orthorhombic system or the remaining crystal systems. *Remember always to think of the unit cell as a representative portion of its lattice and not as a finite body.*

The orthorhombic system is characterized by three mutually perpendicular diad axes (rotation and/or inversion); the unit-cell vectors are chosen to be parallel to, or to coincide with, these axes. The orthorhombic unit cell is specified by the relationships $a \not\propto b \not\propto c$ and $\alpha = \beta = \gamma = 90^\circ$. It will not be difficult for the reader to verify that the descriptors P , C , I , and F are necessary and sufficient in this system. One way in which this exercise may be carried out is as follows. After centering the P unit cell, four questions must be considered, in the following order:

1. Does the centered unit cell represent a lattice?
2. If so, is its symmetry, in isolation, different from that of the P unit cell?
3. If the symmetry is unchanged, is the lattice different in type (arrangement of points) from the lattice or lattices already determined for the given system?
4. Has the unit cell been chosen correctly?

Notice that we answered these questions implicitly in discussing the monoclinic lattices.

The descriptors A , B , and C do not all remain equivalent for orthorhombic space groups in the class $mm2$; it is necessary to distinguish C from A (or B). The reader may like to consider now, or later, why this distinction is necessary.

Tetragonal Lattices

The tetragonal system is characterized by one tetrad (rotation or inversion) along z (c); the unit-cell conditions are $a = b \not\propto c$ and $\alpha = \beta = \gamma = 90^\circ$. There are two tetragonal lattices, specified by the unit-cell symbols P and I , Fig. 2.4; C and F tetragonal unit cells may be transformed to P and I , respectively, see also Problem 2.4.

Cubic Lattices

The symmetry of the cubic system is characterized by four triad axes at angles of $\cos^{-1}(1/3)$ to one another, or $\cos^{-1}(1/\sqrt{3})$ to x , y , and z ; they are the body diagonals $\langle 111 \rangle$ of a cube; the unit-cell conditions are $a = b = c$; $\alpha = \beta = \gamma = 90^\circ$. The four threefold axes, in this orientation, introduce twofold axes along $\langle 100 \rangle$; fourfold axes exist in three of the five cubic classes. There are three cubic Bravais lattices, Fig. 2.4, with conventional unit cells P , I , and F .

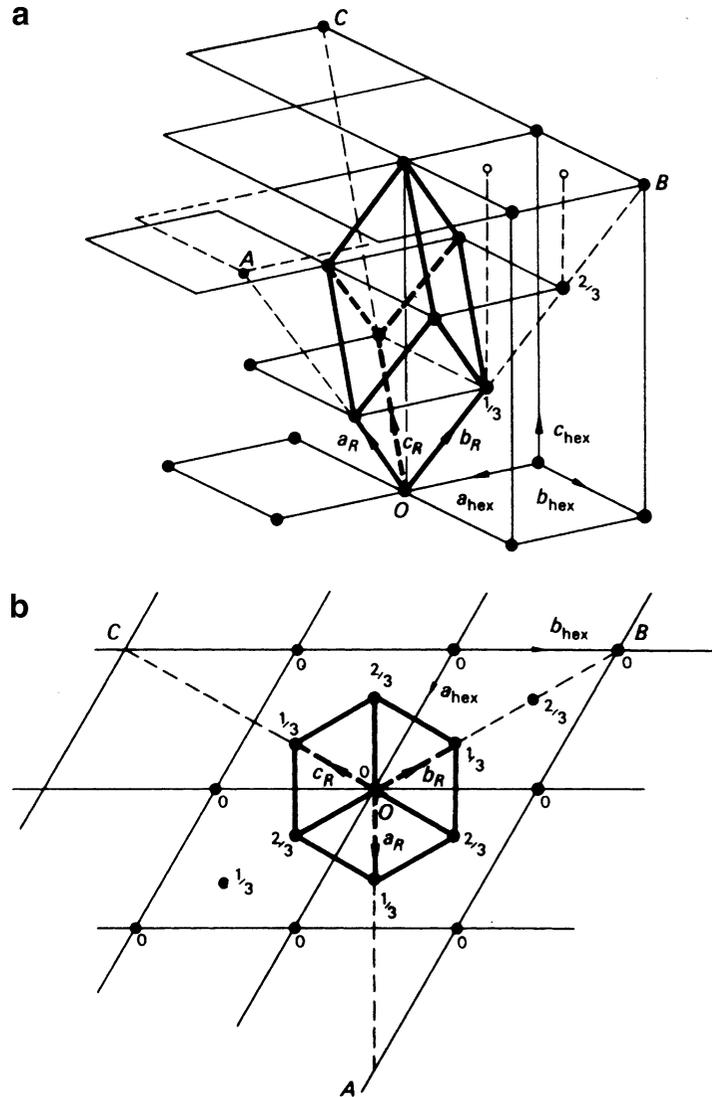
Hexagonal Lattice

The basic feature of a hexagonal lattice is that it should be able to accommodate a 6- or $\bar{6}$ -fold symmetry axis. This requirement is achieved by a lattice based on a P unit cell, with $a = b \not\propto c$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, the c direction being taken along the unique axis in the lattice.

Lattices in the Trigonal System

A two-dimensional unit cell in which $a = b$ and $\gamma = 120^\circ$ is compatible with either sixfold or threefold symmetry; see Fig. 2.22, plane groups $p6$ and $p3$. For this reason, the hexagonal lattice (P unit cell) may be used for certain crystals which belong to the trigonal system. However, as shown in Fig. 2.11, the presence of two threefold axes within a unit cell, with x , y coordinates of $\frac{2}{3}, \frac{1}{3}$ and $\frac{1}{3}, \frac{2}{3}$, and parallel to the z axis, introduces the possibility of a lattice which, although belonging to the trigonal system, has a triply primitive unit cell R_{hex} , with lattice points at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ (in addition to $0, 0, 0$) in the unit cell. Thus, for some trigonal crystals the unit cell will be P , and for others it will be R_{hex} , the

Fig. 2.11 Trigonal lattice; the fractions refer to values of c_{hex} . (a) Rhombohedral (R) unit cell in the obverse setting developed from a triply primitive hexagonal (R_{hex}) unit cell. In the *reverse* setting, the rhombohedral lattice and unit cell are rotated about $[111]$ 60° clockwise with respect to the R_{hex} axes. The ratio of the volumes of any two unit cells in one and the same lattice is equal to the ratio of the numbers of lattice points in the two unit-cell volumes. In the *reverse* setting, the lattice points in the unit cell lie at $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$. (b) Plan view of (a) as seen along c_{hex}



latter being distinguished by systematically absent X-ray reflections, Table 3.2. The R_{hex} cell can be transformed to a primitive rhombohedral unit cell R , with $a = b = c$ and $\alpha = \beta = \gamma \neq 90$ and $< 120^\circ$; the threefold axis is then along $[111]$. The R cell may be thought of as a cube extended (or squashed) along one of its threefold axes.

The lattice based on an R unit cell is the only truly exclusive trigonal lattice, the trigonal lattice based on a P unit cell being borrowed from the hexagonal system, Table 2.3.

We note in passing that the symbols P , R , A , B , C , I , and F cannot apply, strictly, to lattices [1]; they are unit-cell symbols, and refer to the *types* of unit cells already chosen to represent their lattices. However, terminology such as “ P lattice” is in general use and, as long as it is used with understanding, is perfectly acceptable.

2.3 Families of Planes and Interplanar Spacings

Figure 2.12 shows one unit cell of an orthorhombic lattice projected on to the a, b plane. The trace of the (110) plane nearest the origin O is indicated by a dashed line, and the perpendicular distance of this plane from O is $d(110)$. By repeating the operation of the translation $\pm\mathbf{d}(110)$ on the plane (110), a series, or *family*, of parallel, equidistant planes is generated, as shown in Fig. 2.13. Miller indices, Sect. 1.2.3, are by definition prime to one another: in discussing X-ray diffraction effects, however, it is necessary to consider planes for which the indices h, k , and l may contain a common factor while still making intercepts $a/h, b/k$, and c/l on the x, y , and z axes, respectively, as required by the definition of Miller indices. It follows that the plane with indices (nh, nk, nl) makes intercepts $a/nh, b/nk$, and c/nl along x, y , and z , respectively, and that this plane is nearer to the origin by a factor of $1/n$ than is the plane (hkl) . In other words, $d(nh, nk, nl) = d(hkl)/n$.

In general, we denote a family of planes as (hkl) where h, k , and l may contain a common factor. For example, the (220) family of planes is shown in Fig. 2.14 with interplanar spacing $d(220) = d(110)/2$; alternate (220) planes therefore coincide with (110) planes. Note, that an *external* crystal face normal to $d(hh0)$ would always be designated (110), since external observations reveal the shape but not the size for the unit cell.

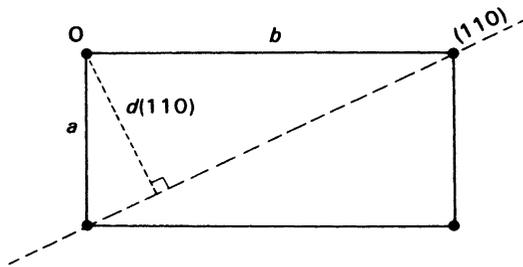


Fig. 2.12 One P unit cell in an orthorhombic lattice in projection on (001), showing the trace of the (110) plane

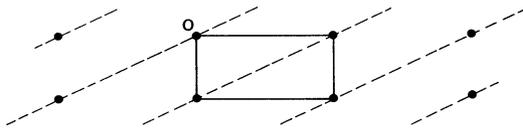


Fig. 2.13 Family of (110) planes in an orthorhombic lattice, as seen in projection along c

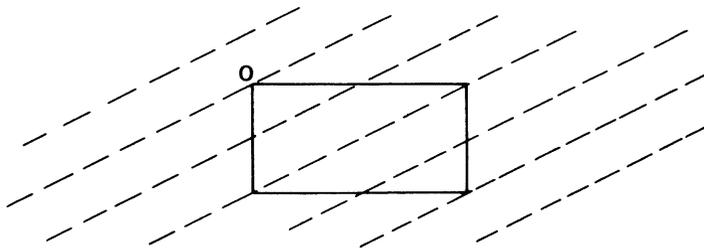


Fig. 2.14 Family of (220) planes in an orthorhombic lattice, as seen in projection along c

2.4 Reciprocal Lattice: Geometrical Treatment

Although we shall discuss the reciprocal lattice in detail in the next chapter, it is useful to introduce it here, because there exists a reciprocal lattice for each of the Bravais lattices. The reciprocal lattice, a lattice in reciprocal (diffraction) space, is derived here graphically from the Bravais lattice, a lattice in real (direct) space, and we choose the monoclinic system for an example.

Figure 2.15a represents a monoclinic lattice as seen in projection along the y axis, the normal to the (010) plane in this example. From the origin O of a P unit cell, lines are drawn normal to families of planes (hkl) in real space. We note in passing that the normal to a plane (hkl) does not, in general, coincide with the direction $[hkl]$: see Sect. 2.2. However, there are special cases, such as $[010]$ and the normal to (010) in the present example, in which the two directions do coincide.

Along each line, reciprocal lattice points hkl (no parentheses) are marked off such that the distance from the origin to the first point in any line is inversely proportional to the corresponding interplanar spacing $d(hkl)$.

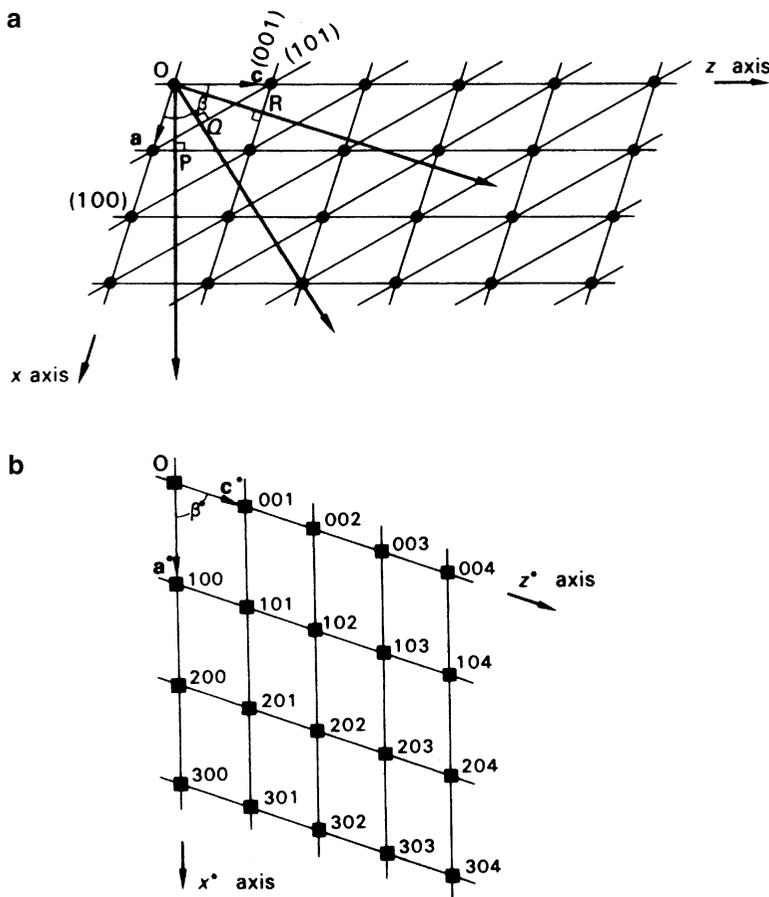


Fig. 2.15 Direct and reciprocal lattices. (a) Monoclinic P , as seen in projection along b , showing three families of planes. (b) Corresponding reciprocal lattice showing the points representing these three and other families of planes

In three dimensions, we refer to $d^*(100)$, $d^*(010)$, and $d^*(001)$ as a^* , b^* , and c^* , respectively, and so define a unit cell in the reciprocal lattice. In general,

$$d^*(hkl) = \kappa/d(hkl) \quad (2.11)$$

where κ is a constant. Hence, for the monoclinic system,

$$a^* = \kappa/d(100) = \kappa/(a \sin \beta) \quad (2.12)$$

From Fig. 2.15a, the scalar product $\mathbf{a} \cdot \mathbf{a}^*$ is given by

$$\mathbf{a} \cdot \mathbf{a}^* = aa^* \cos(\beta - 90) = a\kappa \frac{\cos(\beta - 90)}{a \sin \beta} = \kappa \quad (2.13)$$

The mixed scalar products, such as $\mathbf{a} \cdot \mathbf{c}^*$ are identically zero, because the angle between a and c^* is 90° .

The reciprocal lattice points form a true lattice with a representative unit cell outlined by \mathbf{a}^* , \mathbf{b}^* , and \mathbf{c}^* which, therefore, involves six reciprocal unit-cell parameters in the most general case, three sides a^* , b^* , and c^* , and three angles α^* , β^* , and γ^* . The size of the reciprocal unit cell is governed by the choice of the constant κ . In practice, κ may be taken as the wavelength λ of the X-radiation used in an experiment, in which case reciprocal lattice units are dimensionless. Alternatively, κ may be taken as unity, in which case reciprocal lattice units have the dimensions of length⁻¹. The different situations where one or other convention is used will become clear as we proceed.

A reciprocal lattice row hkl ; $2h, 2k, 2l$; ... may be considered to be derived from the families of planes (nh, nk, nl) with $n = 1, 2, \dots$, since $d(nh, nk, nl) = d(hkl)/n$. Hence,

$$d^*(nh, nk, nl) = nd^*(hkl) \quad (2.14)$$

where $d^*(hkl)$ is the distance of the reciprocal lattice point hkl from the origin, expressed in the appropriate reciprocal lattice units (RU). Since h , k , and l are the coordinates of reciprocal lattice points, the vector $\mathbf{d}^*(hkl)$ is given by

$$\mathbf{d}^*(hkl) = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (2.15)$$

Hence, taking the dot product of $\mathbf{d}^*(hkl)$ with itself, we have

$$\begin{aligned} \mathbf{d}^*(hkl) \cdot \mathbf{d}^*(hkl) &= d^{*2}(hkl) \\ &= h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} \\ &\quad + 2klb^*c^* \cos \alpha^* \\ &\quad + 2lhc^*a^* \cos \beta^* \\ &\quad + 2hka^*b^* \cos \gamma^* \end{aligned} \quad (2.16)$$

Now $d(hkl)$ may be obtained from (2.11) and (2.16). Simplifications of (2.16) arise through symmetry constraints on the unit-cell vectors in different crystal systems. The reader should check the entries in Table 2.4, starting with Table 2.3 and (2.16).

Table 2.4 Expressions for $d^{*2}(hkl)$, and $d^2(hkl)$ with $\kappa = 1$

System	$d^{*2}(hkl)$	$d^2(hkl)$
Triclinic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^* \cos \alpha^*$ $+ 2lhc^*a^* \cos \beta^* + 2hka^*b^* \cos \gamma^*$	$1/d^{*2}(hkl)$
Monoclinic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hla^*c^* \cos \beta^*$	$\left\{ \frac{1}{\sin^2 \beta} \left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right] + \frac{k^2}{b^2} \right\}^{-1}$
Orthorhombic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2}$	$\left\{ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right\}^{-1}$
Tetragonal	$(h^2 + k^2)a^{*2} + l^2c^{*2}$	$\left\{ \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right\}^{-1}$
Hexagonal and trigonal (P)	$(h^2 + k^2 + hk)a^{*2} + l^2c^{*2}$	$\left\{ \frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2} \right\}^{-1}$
Trigonal (R) (rhombohedral)	$[h^2 + k^2 + l^2 + 2(hk + kl + hl)(\cos \alpha^*)]a^{*2}$	$a^2(TR)^{-1}$, where $T = h^2 + k^2 + l^2 + 2(hk + kl + hl)$ $[(\cos^2 \alpha - \cos \alpha)/\sin^2 \alpha]$ and $R = (\sin^2 \alpha)/(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)$
Cubic	$(h^2 + k^2 + l^2)a^{*2}$	$\left\{ \frac{h^2 + k^2 + l^2}{a^2} \right\}^{-1} = \frac{a^2}{h^2 + k^2 + l^2}$

2.5 Unit-Cell Transformations

Here, we consider the transformations of unit-cell vectors, zone symbols and directions, Miller indices, reciprocal unit-cell vectors, and fractional coordinates of sites in the unit cell, all involving no change in the origin of the unit cell. Such transformations are necessary when a nonstandard unit cell needs to be re-cast in standard form.

2.5.1 Bravais Unit-Cell Vectors

Let \mathbf{a} , \mathbf{b} , and \mathbf{c} be transformed to \mathbf{a}' , \mathbf{b}' , and \mathbf{c}' , such that

$$\begin{aligned} \mathbf{a}' &= s_{11}\mathbf{a} + s_{12}\mathbf{b} + s_{13}\mathbf{c} \\ \mathbf{b}' &= s_{21}\mathbf{a} + s_{22}\mathbf{b} + s_{23}\mathbf{c} \\ \mathbf{c}' &= s_{31}\mathbf{a} + s_{32}\mathbf{b} + s_{33}\mathbf{c} \end{aligned} \quad (2.17)$$

which may be written in matrix notation as

$$\begin{bmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{bmatrix} = \begin{bmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix} \quad (2.18)$$

or, more concisely, as

$$\mathbf{a}' = \mathbf{S} \cdot \mathbf{a} \quad (2.19)$$

where the dot \cdot here symbolizes matrix multiplication; \mathbf{a} and \mathbf{a}' represent the two sets of column vectors \mathbf{a} , \mathbf{b} , \mathbf{c} , and \mathbf{a}' , \mathbf{b}' , \mathbf{c}' , and \mathbf{S} is the 3×3 matrix of elements s_{ij} . The inverse transformation is obtained by multiplying both sides of (2.19) by \mathbf{S}^{-1} , since $\mathbf{S} \cdot \mathbf{S}^{-1} = \mathbf{I}$:

$$\mathbf{a} = \mathbf{S}^{-1} \cdot \mathbf{a}' \quad (2.20)$$

where \mathbf{S}^{-1} is the matrix

$$\mathbf{S}^{-1} = \begin{bmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{bmatrix} \quad (2.21)$$

The elements t_{ij} may be obtained by rearranging (2.17), or by the following equations:

$$t_{ij} = (-1)^{i+j} |\mathbf{M}_{ji}| / |\mathbf{S}|$$

$$|\mathbf{S}| = s_{11} \begin{vmatrix} s_{22}s_{23} \\ s_{32}s_{33} \end{vmatrix} + s_{21} \begin{vmatrix} s_{12}s_{13} \\ s_{22}s_{23} \end{vmatrix} + s_{31} \begin{vmatrix} s_{12}s_{13} \\ s_{22}s_{23} \end{vmatrix} \quad (2.22)$$

where $|\mathbf{M}_{ji}|$ is the minor determinant of \mathbf{S} obtained by striking out its j th row and i th column, and $|\mathbf{S}|$ is the determinant value of the matrix \mathbf{S} .

2.5.2 Directions (Zone Symbols)

From Sect. 2.2, we have

$$\mathbf{r} = U\mathbf{a} + V\mathbf{b} + W\mathbf{c} \quad (2.23)$$

and for the transformed cell

$$\mathbf{r} = U'\mathbf{a}' + V'\mathbf{b}' + W'\mathbf{c}' \quad (2.24)$$

Thus, from (2.23) and (2.24),

$$[U'V'W'] \begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix} = (UVW) \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} = (UVW)\mathbf{S}^{-1} \begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix} \quad (2.25)$$

or

$$(U'V'W') = (UVW)\mathbf{S}^{-1} \quad (2.26)$$

Hence, and concisely,

$$\mathbf{U}' = \mathbf{U}\mathbf{S}^{-1} = (\mathbf{S}^{-1})^T \mathbf{U} \quad (2.27)$$

where \mathbf{U} and \mathbf{U}' are now column vectors.

Since $(\mathbf{S}^{-1})^T = (\mathbf{S}^T)^{-1}$, pre-multiplication of (2.27) by \mathbf{S}^T leads to

$$\mathbf{S}^T \mathbf{U}' = \mathbf{S}^T (\mathbf{S}^T)^{-1} \mathbf{U} = \mathbf{U} \quad (2.28)$$

or

$$\mathbf{U} = \mathbf{S}^T \cdot \mathbf{U}' \quad (2.29)$$

2.5.3 Coordinates of Sites in the Unit Cell

For any point x, y, z in a unit cell, the vector \mathbf{r} from the origin to that point is given by

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \quad (2.30)$$

Comparison of this equation with (2.23), and by a procedure similar to (2.24)–(2.28), we see that coordinates transform as do zone symbols. Thus,

$$\mathbf{x}' = (\mathbf{S}^{-1})^T \cdot \mathbf{x} \quad (2.31)$$

2.5.4 Miller Indices

From (2.15) and (2.23), it follows that

$$\mathbf{d}^*(hkl) \cdot \mathbf{r} = hU + kV + lW \quad (2.32)$$

Thus, with (2.29),

$$\mathbf{d}^*(hkl) \cdot \mathbf{r} = [hkl] \cdot \begin{bmatrix} U \\ V \\ W \end{bmatrix} = [hkl] \cdot \mathbf{S}^T \cdot \begin{bmatrix} U' \\ V' \\ W' \end{bmatrix} \quad (2.33)$$

But also

$$\mathbf{d}^*(h'k'l') \cdot \mathbf{r} = [h'k'l'] \cdot \begin{bmatrix} U' \\ V' \\ W' \end{bmatrix} \quad (2.34)$$

because $\mathbf{d}^*(hkl)$ and $\mathbf{d}^*(h'k'l')$ are one and the same vector in the same plane but with different indices. Hence

$$[h'k'l'] = [hkl] \cdot \mathbf{S}^T \quad (2.35)$$

Transposing

$$\begin{bmatrix} h' \\ k' \\ l' \end{bmatrix} = \mathbf{S} \cdot \begin{bmatrix} h \\ k \\ l \end{bmatrix} \quad (2.36)$$

or

$$\mathbf{h}' = \mathbf{S} \cdot \mathbf{h} \quad (2.37)$$

where \mathbf{h} and \mathbf{h}' are column vectors with components h, k, l and h', k', l' , respectively. Thus, Miller indices transform in the same way as do unit-cell vectors in real space. If we operate on both sides of (2.37) by \mathbf{S}^{-1} , then

$$\mathbf{S}^{-1} \cdot \mathbf{h}' = \mathbf{S}^{-1} \cdot \mathbf{S} \cdot \mathbf{h}$$

or

$$\mathbf{h} = \mathbf{S}^{-1} \cdot \mathbf{h}' \quad (2.38)$$

We may note here that if a plane (hkl) lies in the $[UVW]$ zone and the normal to the plane is $d^*(hkl)$ then $\mathbf{d}^*(hkl) \cdot \mathbf{r} = 0$, then from (2.15) and (2.23), it follows that $hU + kV + lW = 0$, which is the Weiss Zone Law, since products such as $\mathbf{a} \cdot \mathbf{a}^*$ and $\mathbf{a} \cdot \mathbf{b}^*$ are unity and zero, respectively ($\kappa = 1$).

2.5.5 Reciprocal Unit-Cell Vectors

From (2.15), we develop

$$\begin{aligned} \mathbf{d}^*(hkl) &= [\mathbf{a}^* \mathbf{b}^* \mathbf{c}^*] \cdot \begin{bmatrix} h \\ k \\ l \end{bmatrix} \\ &= [\mathbf{a}^* \mathbf{b}^* \mathbf{c}^*] \cdot \mathbf{S}^{-1} \cdot \begin{bmatrix} h' \\ k' \\ l' \end{bmatrix} \end{aligned} \quad (2.39)$$

In the transformed reciprocal unit cell

$$\mathbf{d}^*(hkl) = [\mathbf{a}'^* \mathbf{b}'^* \mathbf{c}'^*] \cdot \begin{bmatrix} h' \\ k' \\ l' \end{bmatrix} \quad (2.40)$$

so that

$$[\mathbf{a}'^* \mathbf{b}'^* \mathbf{c}'^*] = [\mathbf{a}^* \mathbf{b}^* \mathbf{c}^*] \cdot \mathbf{S}^{-1} \quad (2.41)$$

Transposing

$$\begin{bmatrix} \mathbf{a}'^* \\ \mathbf{b}'^* \\ \mathbf{c}'^* \end{bmatrix} = (\mathbf{S}^{-1})^T \cdot \begin{bmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \end{bmatrix} \quad (2.42)$$

or

$$\mathbf{a}^* = (\mathbf{S}^{-1})^T \cdot \mathbf{a}'^* \quad (2.43)$$

so that reciprocal unit-cell vectors transform in the same way as do zone symbols.

As an example of the transformations that we have just derived, let a transformation matrix from unit cell 1 to unit cell 2 may be written as

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & \bar{2} \\ 1 & 2 & 1 \end{bmatrix}$$

Given the plane $(\bar{1}\bar{3}5)$ and the site $-0.10, 0.15, 0.25$ in unit cell 1, determine the corresponding values for unit cell 2.

$$\begin{aligned} \text{Miller indices: } h_2 &= h_1 + l_1 = 6 \\ k_2 &= k_1 - 2l_1 = \bar{1}\bar{3} \\ l_2 &= h_1 + 2k_1 + l_1 = 0 \end{aligned}$$

that is, the plane is $(6\bar{1}\bar{3}, 0)$ in unit cell 2.

For the coordinates we need the matrix $(\mathbf{S}^{-1})^T$. The determinant $|\mathbf{S}|$ is 4. Then, applying (2.22),

$$\mathbf{S}^{-1} = \begin{bmatrix} 5/4 & 1/2 & -1/4 \\ -1/2 & 0 & 1/2 \\ -1/4 & -1/2 & 1/4 \end{bmatrix}$$

whereupon the transpose becomes

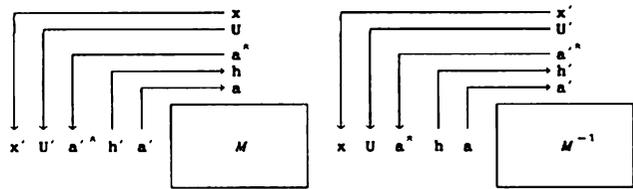
$$(\mathbf{S}^{-1})^T = \begin{bmatrix} 5/4 & -1/2 & -1/4 \\ 1/2 & 0 & -1/2 \\ -1/4 & 1/2 & 1/4 \end{bmatrix}$$

then the transformed coordinates are

$$\begin{aligned} x_2 &= 5x_1/4 - y_1/2 - z_1/4 = -0.2625 \\ y_2 &= x_1/2 - z_1/2 = -0.1750 \\ z_2 &= -x_1/4 + y_1/2 + z_1/4 = 0.1625 \end{aligned}$$

that is, the site $-0.2625, -0.1750, 0.1625$.

Fig. 2.16 Mnemonic scheme for operating on a matrix or its inverse and its inverse; two examples are shown



For example, if M is the matrix

$$\begin{array}{c} \text{a}' \rightarrow \\ \begin{array}{|c|} \hline \begin{array}{ccc} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & -\frac{2}{3} & \frac{1}{3} \end{array} \\ \hline \end{array} \end{array}$$

and \mathbf{a} represents the triplet a, b, c , then writing $\mathbf{a}' = M\mathbf{a}$, we have

$$\begin{aligned}
 \mathbf{a}' &= \frac{2}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{1}{3}\mathbf{c} \\
 \mathbf{b}' &= -\frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{1}{3}\mathbf{c} \\
 \mathbf{c}' &= -\frac{1}{3}\mathbf{a} - \frac{2}{3}\mathbf{b} + \frac{1}{3}\mathbf{c}
 \end{aligned}$$

and if the inverse matrix M^{-1} is

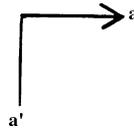
$$\begin{array}{c} \downarrow \mathbf{x}' \\ \begin{array}{|c|} \hline \begin{array}{ccc} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{array} \\ \hline \end{array} \end{array}$$

and \mathbf{x}' represents the triplet x', y', z' , then

$$\begin{aligned}
 x' &= x + z \\
 y' &= -x + y + z \\
 z' &= -y + z
 \end{aligned}$$

A reciprocal lattice has the same symmetry as the Bravais lattice from which it was deduced. This fact may be appreciated from a comparison of the constructions of the reciprocal lattice and the stereogram. Both of these constructions are built up from normals to planes, so that the symmetry expressed through the poles of a stereogram is the same as that at the reciprocal lattice points, but the reciprocal lattice adds dimensions to the representation; see also Sect. 3.4.1.

The transformations that we have discussed can be summarized by the mnemonic scheme in Fig. 2.16, for any matrix \mathbf{M} and its inverse \mathbf{M}^{-1} . The arrow symbols, such as



should be interpreted as \mathbf{a}' in terms of \mathbf{a} , and so on. The scheme for the inverse is equivalent to writing, $\mathbf{x}' = (\mathbf{M}^{-1})^T \cdot \mathbf{x}$ and then multiplying in the usual manner.

2.6 Rotational Symmetries of Lattices

We now discuss analytically the permissible rotational symmetries in the lattices of periodic crystals, already stated to be of degrees 1, 2, 3, 4, and 6. In Fig. 2.17, let A and B represent two adjacent lattice points, of repeat distance t , in any row. An R -fold rotation axis is imagined to act at each point and to lie normal to the plane of the diagram. An anticlockwise rotation of Φ about A maps B on to B' , and a clockwise rotation of the same value Φ about B maps A on to A' . It follows from the geometry of the figure that AB is parallel to $A'B'$ and, from the property of lattices, $A'B' = Jt$, where J is an integer. Lines $A'S$ and $B'T$ are drawn perpendicular to AB , as shown. Hence,

$$A'B' = TS = AB - (AT + BS) \tag{2.44}$$

or

$$Jt = t - 2t \cos \Phi \tag{2.45}$$

whence

$$\cos \Phi = (1 - J)/2 = M/2 \tag{2.46}$$

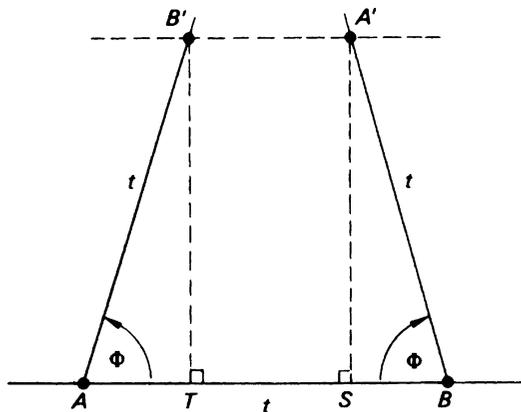


Fig. 2.17 Rotational symmetry in crystal lattices. Permissible values of Φ are $360(0)$, 180 , 120 , 90 , and 60° , corresponding to one-, two-, three-, four-, and sixfold rotations, respectively

where M is another integer. Since $-1 \leq \cos \Phi \leq 1$, it follows from (2.46) that the only admissible values for M are $0, \pm 1, \pm 2$, and these values give rise to the rotational symmetries already discussed. This treatment gives a quantitative aspect to the packing considerations mentioned previously, Sect. 1.4.2.

2.7 Space Groups

In order to extend our study of crystals further into the realm of atomic arrangements, we must consider now the symmetry of extended, ideally infinite, patterns in space. We recall that a point group describes the symmetry of a finite body, and that a lattice constitutes a mechanism for repetition, to an infinite extent, by translations parallel to three noncoplanar directions. We may ask, therefore, what is the result of repeating a point-group pattern by the translations of a Bravais lattice? It is a *space group*, and we shall see that it produces an arrangement like atoms in a crystal.

A space group can be described as *an infinite set of symmetry elements, the operation with respect to any of which brings the infinite array of points to which they refer into a state that is indistinguishable from that before the operation*. In practice, we may apply space-group rules to crystals because the dimensions of crystals used in experimental investigations are very large in comparison with the repeat distances of the pattern. For example, the dimension a of the face-centered cubic unit cell of sodium chloride is 0.564 nm. Thus, in a crystal of experimental size (ca. 0.2, 0.2, 0.2 mm), there are approximately 4.5×10^{16} unit cells.

A space group may be considered to be made up of two parts, a pattern motif and a repeat mechanism. An analogy can be drawn with a wallpaper-type pattern, a simple example of which is shown in Fig. 2.18a. We shall analyze this pattern.

The conventional unit cell for this pattern is indicated by the vectors \mathbf{a} and \mathbf{b} . If we choose a pattern motif consisting of two flowers, Fig. 2.18b, and continue it indefinitely by the repeat vectors \mathbf{a} and \mathbf{b} ,

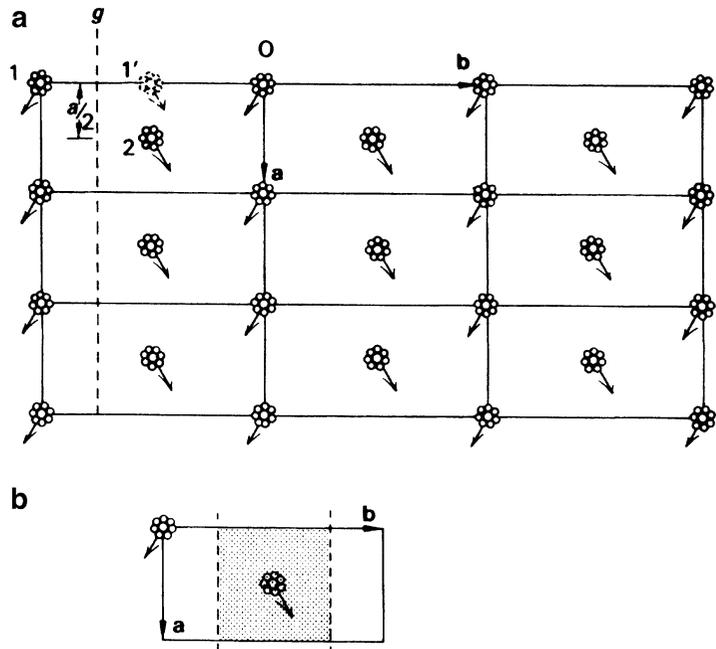
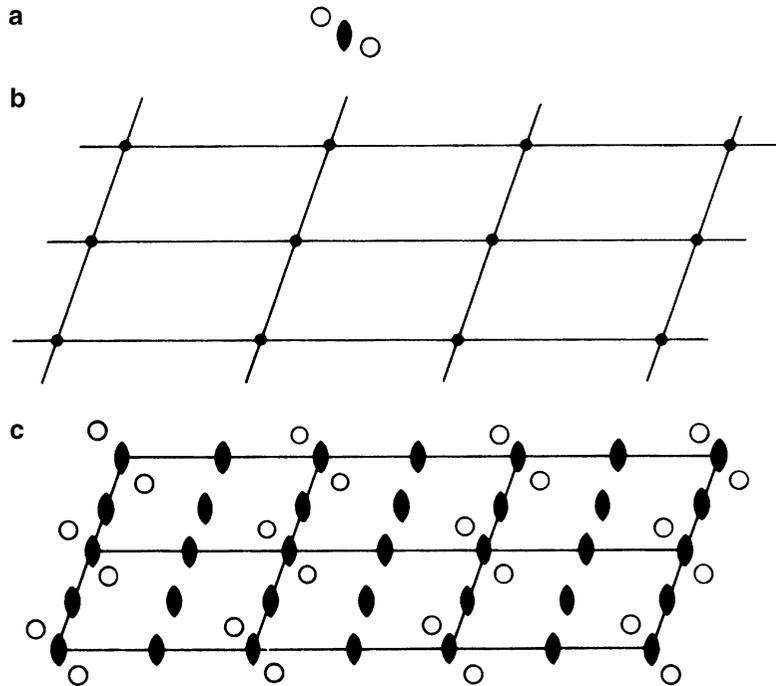


Fig. 2.18 Wallpaper-type pattern. (a) Extended pattern. (b) Asymmetric unit, or pattern motif; the space-group symmetry applied to the asymmetric unit generates the infinite pattern

Fig. 2.19 Plane group $p2$. (a) Twofold symmetry motif. (b) Oblique net with p unit cells outlined. (c) Extended pattern of plane group $p2$ obtained by a combination of (a) with (b)



the plane pattern is generated. However, we have ignored the symmetry between the two flowers in the pattern motif itself. If one flower (1) is reflected across the dashed line (g) to ($1'$) and then translated by $\mathbf{a}/2$, it then occupies the position of the second flower (2); thus, the pattern represented in Fig. 2.18a is brought from one state to another indistinguishable state by this symmetry operation. This operation takes place across a *glide line*, a symmetry element that occurs in some extended two-dimensional patterns. The two motions constitute a *single* symmetry operation.

The necessary and sufficient pattern motif for a whole, extended figure is a single flower, occupying the *asymmetric unit*—the unshaded (or shaded) portion of Fig. 2.18b. If the single flower is repeated by both the glide-line symmetry and the unit-cell translations, that is, overall by the space-group symmetry, then the infinitely extended pattern is generated. Thus, if we know the asymmetric unit of a crystal structure, which need not be the whole unit-cell contents, and the space-group symbol for the crystal, we can generate the whole structure.

2.7.1 Two-Dimensional Space Groups (Plane Groups)

Oblique System

Our discussion leads naturally into two-dimensional space groups, or *plane groups*. Consider the pattern motif showing twofold symmetry, illustrated in Fig. 2.19a; the symmetry symbols that we have used in point groups are continued into the realm of space groups. Next, consider a primitive oblique net, Fig. 2.19b; it is of infinite extent in the plane, and the framework of lines divides the field, conceptually, into a number of identical primitive (p) unit cells. An origin is chosen at a lattice point; it could be anywhere in the unit cell, but is desirably, and conventionally, linked to a symmetry element.

Now, let the motif be repeated around each point in the net, and in the same orientation, with the twofold rotation points of the motif and the net in coincidence, Fig. 2.19c. It will be seen that additional twofold rotation points are introduced at the unique fractional coordinates $0, \frac{1}{2}, \frac{1}{2}, 0$; and $\frac{1}{2}, \frac{1}{2}$ in each unit cell,

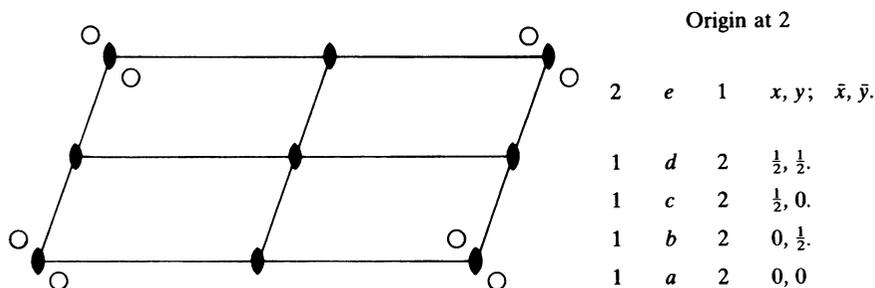


Fig. 2.20 Standard drawing and description of plane group $p2$. The lines which divide the unit cell into four quadrants are, as usual, drawn for convenience only

see Sect. 2.2.2. We must always look for such “extra” symmetry elements after the point-group motif has been operated on by the unit-cell translations. Ultimately, this will be found to be quite straightforward. Meanwhile, a simple check consists in ensuring that any point on the diagram can be reached from any other point by means of a *single* symmetry operation, including translations as necessary. This plane group is given the symbol $p2$.

In general, we shall not need to draw several unit cells; one cell will suffice provided that the pattern motif is completed around all lattice points intercepted by the given unit cell. Figure 2.20 illustrates the standard drawing of $p2$: the origin is taken on a twofold point, the x axis runs from top to bottom, and the y axis runs from left to right. Thus, the origin is considered to be in the top left-hand corner of the cell as drawn, but each twofold rotation point could be an equivalent origin; we must remember always that the drawing is a representative portion of an infinite array, whether in two or three dimensions.

The asymmetric unit (which may be a chemical species) represented here by O, may be placed anywhere in the unit cell, but for convenience, near the origin. It is then repeated by the symmetry $p2$ to build up the complete picture, taking care to complete the arrangements around each corner of the unit cell. The additional twofold points can then be identified. The reader should now carry out this construction.

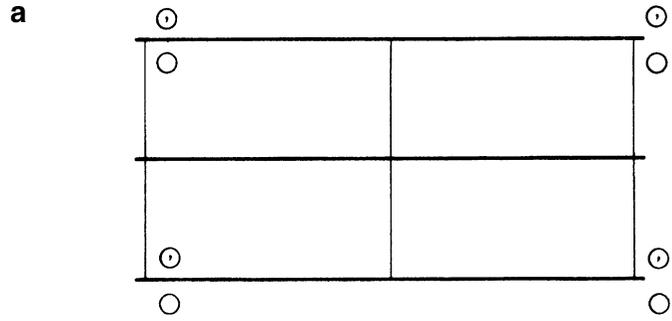
The list of fractional coordinates in Fig. 2.20 refers to the unique symmetry-related sites in the unit cell. The first row of these sites, related by the space-group symmetry, lists the *general equivalent positions*. In $p2$ they are given the coordinates x, y , and \bar{x}, \bar{y} . We could use $1 - x, 1 - y$ instead of \bar{x}, \bar{y} , but it is more usual to list the set of coordinates near one and the same origin.

Each coordinate line in the space-group description lists, in order from left to right, the number of positions in each set, the Wyckoff [2] notation, used for reference purposes, the symmetry at each site in the set, and the fractional coordinates of all sites in the set.

In a conceptual two-dimensional crystal, or projected real atomic arrangement, the asymmetric unit may contain either a single atom or a group of atoms. If it consists of part, half, in this plane group, of one molecule then the whole molecule, as seen in projection at least, must contain twofold rotational symmetry, or a symmetry of which 2 is a subgroup.

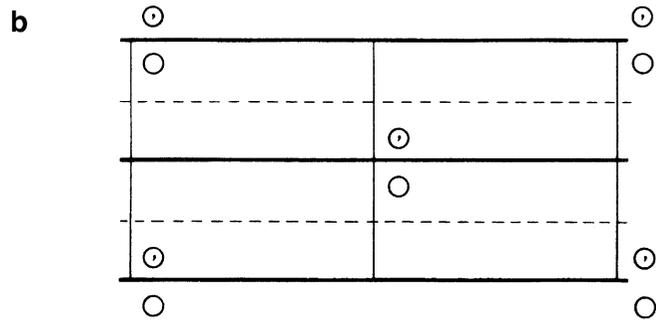
There are four unique twofold rotation points in the unit cell; in the Wyckoff notation they are the sets (a), (b), (c), and (d), and they constitute the sets of *special equivalent positions*, point symmetry 2 in this plane group. Notice that general positions always have symmetry 1, whereas special positions always have a higher crystallographic point-group symmetry. Where the unit cell contains fewer (an integral submultiple) of a species than the number of general equivalent positions in its space group, then it may be assumed that the species are occupying special equivalent positions and have the symmetry consistent with that of the special site. Exceptions to this rule may arise in disordered structures, Sect. 8.9.

Fig. 2.21 Plane groups in the rectangular system. (a) *pm*. (b) *cm*; glide lines (*g*) are indicated by the dashed lines



Origin on *m*

2	<i>c</i>	1	<i>x, y; x̄, y.</i>
1	<i>b</i>	<i>m</i>	$\frac{1}{2}, y.$
1	<i>a</i>	<i>m</i>	$0, y.$



Origin on *m*

				Limiting conditions
			$(0, 0; \frac{1}{2}, \frac{1}{2}) +$	
4	<i>b</i>	1	<i>x, y; x̄, y.</i>	<i>hk: h + k = 2n</i>
2	<i>a</i>	<i>m</i>	$0, y.$	As above

Rectangular System

We move next to the rectangular system, which includes point groups *m* and *2mm*, and both *p* and *c* unit cells. We shall consider first plane groups *pm* and *cm*.

The formation of these plane groups may be considered along the lines already described for *p2*, and we refer immediately to Fig. 2.21a. The origin is chosen on *m*, but its *y* coordinate is not defined by this symmetry element. In a structure of this symmetry, the origin is specified by fixing arbitrarily the *y* coordinate of one of the atoms in the unit cell. In *pm*, the general equivalent positions are two in number, and there are two sets of special equivalent positions on *m* lines.

Plane group *cm*, Fig. 2.21b, introduces several new features. The coordinate list is headed by the expression $(0, 0; \frac{1}{2}, \frac{1}{2}) +$; this means that the two translations $0, 0$ and $\frac{1}{2}, \frac{1}{2}$ are added to all the listed coordinates. Hence, the full list of general (equivalent) positions would read

$$x, y; \quad \bar{x}, y; \quad \frac{1}{2} + x, \frac{1}{2} + y; \quad \frac{1}{2} - x, \frac{1}{2} + y$$

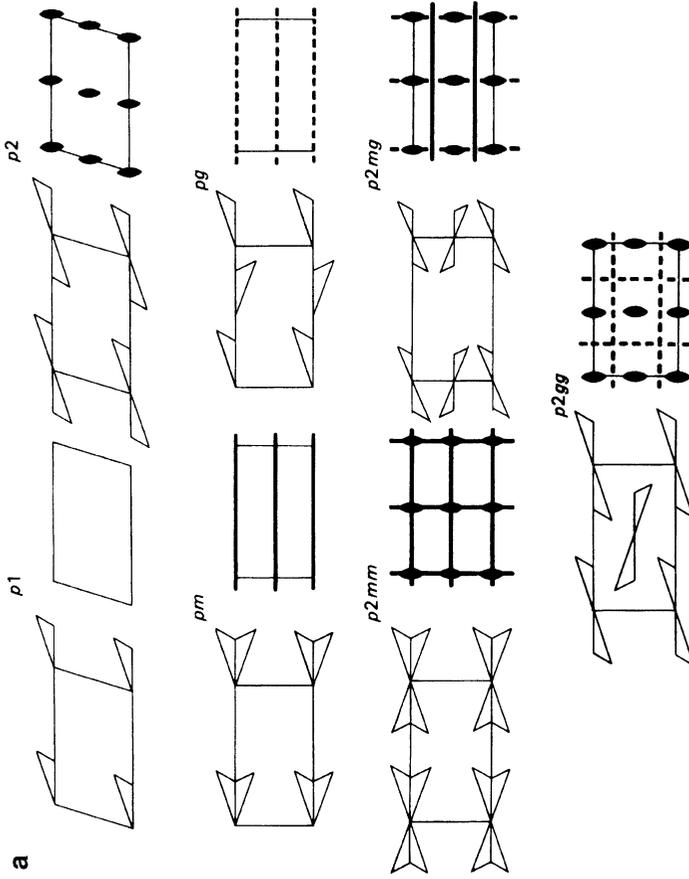


Fig. 2.22

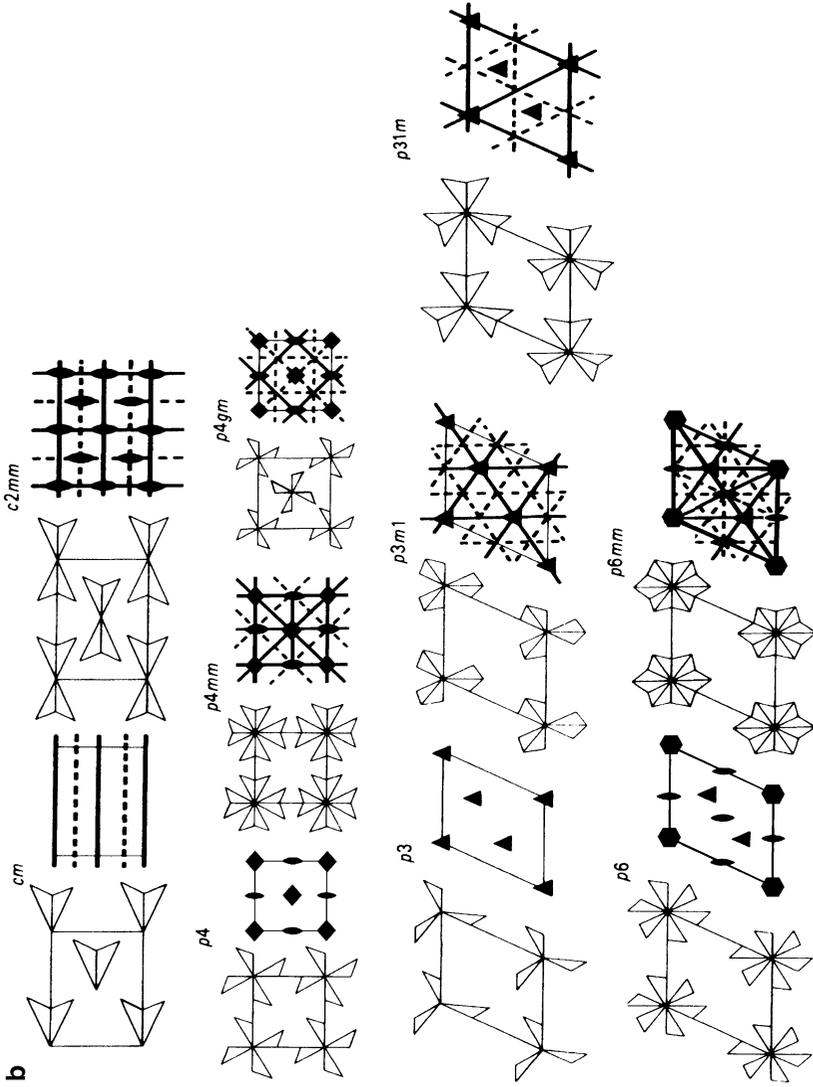


Fig. 2.22 (continued) Unit cells of the 17 plane groups. The general equivalent positions are represented here by scalene triangle motifs instead of the usual circle. It may be noted that the conventional unit-cell drawing shows the immediate environment of each cell

Given x , the distance $\frac{1}{2} - x$, for example, is found by first moving $\frac{1}{2}$ along the a axis from the origin and then moving back along the same line by the amount x .

The centering of the unit cell in conjunction with the m lines introduces the glide-line symmetry element, symbol g and graphic symbol $- - -$. The glide lines interleave the mirror lines, and their action is a combination of reflection and translation, the two movements comprising again a single symmetry operation. The translational component is one half of the repeat distance in the direction of the glide line. Thus, the pair of general positions x, y and $\frac{1}{2} - x, \frac{1}{2} + y$ are related by the g line at $x = \frac{1}{4}, y = 0$. We shall encounter glide lines in any centered plane group where m lines are present, and in certain other groups. For example, we may ask if there is any meaning to the symbol pg , a glide-symmetry motif repeated by the translations of a p unit-cell? The answer is that pg is a possible plane group; in fact, it is the symmetry of the pattern in Fig. 2.18. The differing orientations of the glide lines in Figs. 2.18 and 2.22 (standard) are expressed by the *full* symbols $p11g (g \perp y)$ and $p1g1 (g \perp x)$, respectively.

There is only one set of special positions in cm , in contrast to two sets in pm . This situation arises because the centering condition in cm requires that both mirror lines in the unit cell be included in one and the same set. If we try to postulate two sets, by analogy with pm , we obtain

$$0, y; \quad \frac{1}{2}, \frac{1}{2} + y \quad (2.47)$$

and

$$\frac{1}{2}, y; \quad 0(\text{or } 1), \frac{1}{2} + y \quad (2.48)$$

However, expressions (2.47) and (2.48) involve only a shift in the origin, and therefore do not constitute two different sets of special equivalent positions.

We could refer to plane group cm by the symbol cg . If we begin with the origin on g and mark in the general positions as before, we should find now the glide lines interleaved with m lines. Two patterns that differ only in the choice of origin or in the numerical values attached to the coordinates of the equivalent positions do not constitute different space groups. The reader can illustrate this statement by drawing cg , and by drawing pg also, can show that pm and pg are different. The glide line or, indeed, any translational symmetry element is not encountered in point groups; it is a property of infinite patterns.

The 17 Plane Groups

The 17 plane groups are illustrated in Fig. 2.22. The two diagrams for each plane group show the general equivalent positions and the symmetry elements. The asymmetric unit is represented therein by a scalene triangle instead of by the usual circle. Space groups that are derived by the repetition of a point-group motif by the lattice translations are termed *symmorphic* space groups, as with $p2$, pm , and $c2mm$, but otherwise as *non-symmorphic* space groups, as with pg , $p2mg$, and $p2gg$.

Conditions Governing X-Ray Reflection

Our main reason for studying space-group symmetry is that it provides information about the repeat patterns of atoms in crystal structures. X-ray diffraction spectra are characterized in position by the indices of the families of planes from which, in the Bragg treatment of diffraction which we consider in Sect. 3.3.2, the X-rays are considered to be reflected. The pattern of the indices of the reflecting planes reveals information about the space group of the crystal. Where a space group contains translational symmetry, certain sets of reflections will be systematically absent from the experimental diffraction data record. We meet this situation for the first time in cm , Fig. 2.21b; two-dimensional reflections $hk (l = 0)$ are limited to those for which the sum $h + k$ is an even number.

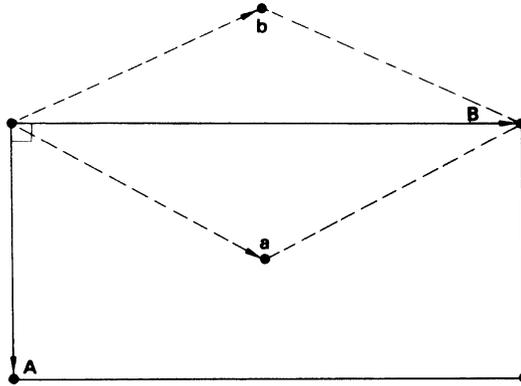


Fig. 2.23 Centered rectangular unit cell \mathbf{A} , \mathbf{B} and primitive unit cell \mathbf{a} , \mathbf{b} within the same lattice

Figure 2.23 illustrates a rectangular lattice. Two unit cells are depicted on this lattice, a centered cell with vectors \mathbf{A} and \mathbf{B} , and a primitive cell with vectors \mathbf{a} and \mathbf{b} . The relationship between them is summarized by the equations

$$\begin{aligned} \mathbf{A} &= \mathbf{a} - \mathbf{b} \\ \mathbf{B} &= \mathbf{a} + \mathbf{b} \end{aligned} \quad (2.49)$$

We have shown in Sect. 2.5.4 that Miller indices of planes transform in the same way as unit-cell vectors, so it follows that

$$\begin{aligned} H &= h - k \\ K &= h + k \end{aligned} \quad (2.50)$$

where H and K apply to the unit cell \mathbf{A} , \mathbf{B} and h and k to the unit cell \mathbf{a} , \mathbf{b} . Adding equations (2.50), we obtain

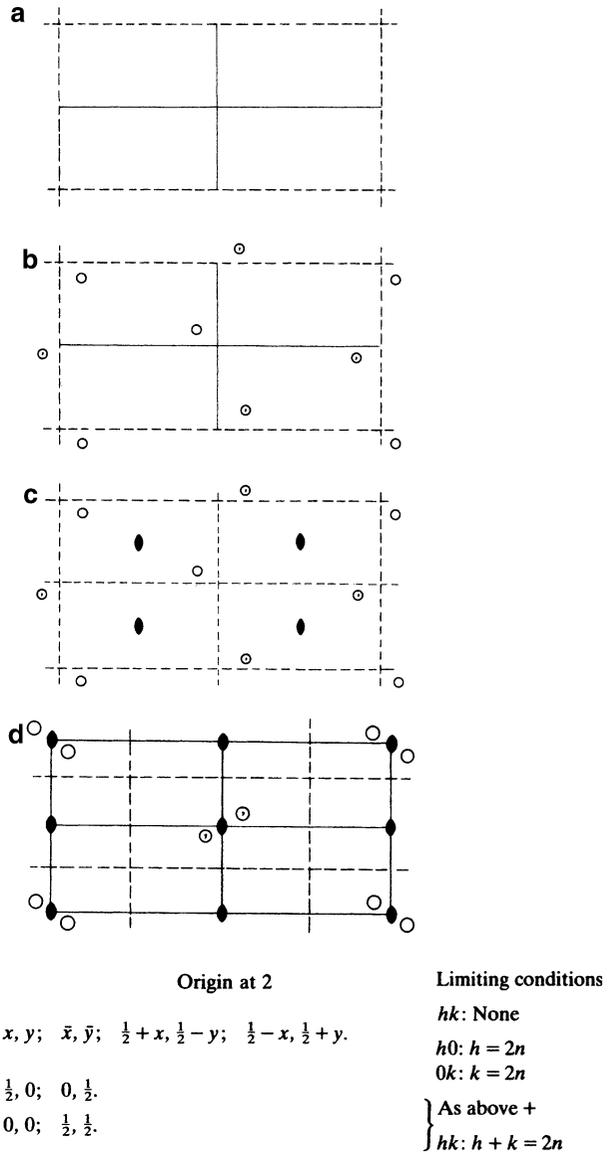
$$H + K = 2h \quad (2.51)$$

which is even for all values of h . Thus, in this centered unit cell, reflections can occur only when the sum of the indices, $H + K$, is an even integer. This topic is discussed more fully in Sect. 3.7ff, whereupon the significance of the extreme right-hand column of data in figures such as Figs. 2.21 and 2.24 will become clear.

2.7.2 Plane Groups Related to $2mm$

Point group $2mm$ belongs to the rectangular system and, as a final example in two dimensions, we shall study plane group $p2gg$. It is often helpful to recall the “parent” point group of any space group: we ignore the unit-cell symbol, and replace any translational symmetry elements by the

Fig. 2.24 Formation and description of plane group $p2gg$



corresponding nontranslational symmetry elements. Thus, pg is derived from point group m , and $p2gg$ from $2mm$.

In point group $2mm$, we know that the two m lines intersect in the twofold rotation point, and this remains true for plane group $p2mm$. In $p2gg$, however, we may not assume that the twofold rotation point lies at the intersection of the g lines. In our study of point groups, we saw that the symmetry elements in a given symbol have a definite relative orientation with respect to the crystallographic axes; this is preserved in the corresponding space groups. Thus, we know that the g lines are normal to the x and y axes, and we can take an origin, initially, at their intersection, Fig. 2.24a. In Fig. 2.24b, the general equivalent positions have been inserted; this diagram reveals the positions of the twofold points, inserted now in Fig. 2.24c, together with the additional g lines in the unit cell. The standard

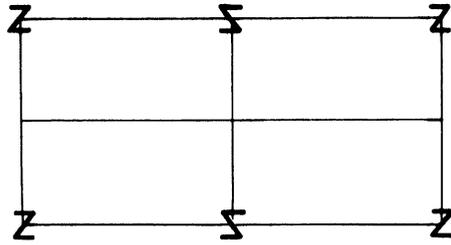


Fig. 2.25 Occupation of the special positions $0, 0$ and $0, \frac{1}{2}$ in $p2gg$ leads to pm ($p1m1$) symmetry, even though the occupying entity has itself symmetry 2

orientation of $p2gg$ places the twofold point at the origin; Fig. 2.24d shows this setting and the description of this plane group. We see again that two interacting symmetry elements have a combined action which is equivalent to that of a third symmetry element, but their positions must be chosen correctly. This question did not arise in point groups because, by definition, all symmetry elements pass through a point, the origin. What group would arise if we did place the twofold rotation point at the intersection of the glide lines?

There are two sets of special equivalent positions in $p2gg$, but the pairs of twofold rotation points that constitute each set must be selected correctly. One way of ensuring a proper selection is by inserting the coordinate values of the point-group symmetry element constituting a special position into the coordinates of the general positions. Thus, by taking $x = y = 0$, for one of the twofold points, we obtain a set of special positions with coordinates $0,0$ and $\frac{1}{2}, \frac{1}{2}$. If we had chosen $0,0$ and $0, \frac{1}{2}$ as a set, the resulting pattern would not have conformed to $p2gg$ symmetry, but to pm , as Fig. 2.25 shows. Special positions always form a subset of the general positions, under the same space-group symmetry.

The general equivalent positions give rise to two conditions limiting reflections, because the structure is “halved” with respect to a for the reflections $h0$, and with respect to b for the reflections $0k$. The special positions take both of these conditions, and the extra conditions shown, because occupancy of the special positions in this plane group gives rise to centered arrangements. The entities occupying special positions must, themselves, be consistent with the symmetry of the crystal structure.

After the development of the structure factor in Sects. 3.2.3ff and 3.5.1ff, limiting conditions will be derived analytically.

2.7.3 Three-Dimensional Space Groups

The principles that have emerged from the discussion on plane groups can be extended to three dimensions. Whereas the plane groups are limited to 17 in number, there are 230 space groups. We shall limit our discussion to a few space groups mainly in the monoclinic and orthorhombic systems. We believe this will prove a satisfactory working procedure because many of the important principles will evolve and, from a practical point of view, a large percentage of crystals belong to these two systems.

Monoclinic Space Groups

In the monoclinic system, the lattices are characterized by P and C unit-cell descriptors, and the point groups are 2 , m , and $2/m$. We consider first space groups $P2$ and $C2$.

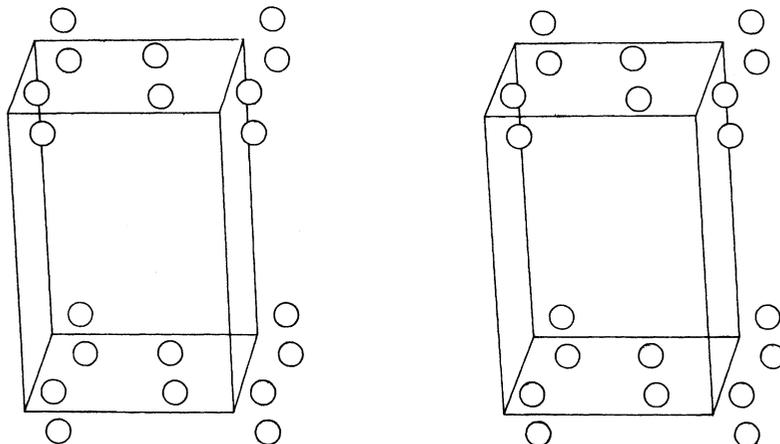


Fig. 2.26 Stereoscopic pair of illustrations of the environs of one unit cell of space group $C2$; the general equivalent positions are shown. The diagram reveals nine axes of symmetry 2 , and six axes of symmetry 2_1 . Can you identify their positions?

As with the plane groups, we may begin with a motif, which has twofold symmetry, but now about a line or axis, in three-dimensional space. This motif is arranged in a fixed orientation with respect to the points of a monoclinic lattice. Figure 2.26 shows a stereoscopic pair of illustrations for a unit cell of space group $C2$, drawn with respect to the conventional right-handed axes.

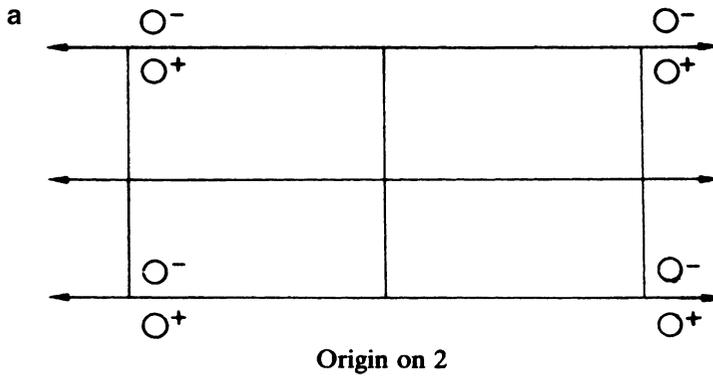
In Fig. 2.27, space groups $P2$ and $C2$ are shown in projection. The standard drawing of space-group diagrams is on the a, b plane of the unit cell, with $+x$ running from top to bottom, $+y$ from left to right, both in the plane of the paper, and $+z$ directed upwards from the paper. The positive or negative signs attached to the representative points indicate the z coordinates, that is, in the symbolism O^+ and O^- , the signs stand for z and \bar{z} , respectively. The relationship with the preferred stereogram notation Sect. 1.3, will be evident here.

In both $P2$ and $C2$, the origin is chosen on 2 , and is, thus, defined with respect to the x and z axes, but not with respect to y ; compare pm and cm . How is the origin fixed in Pm ? The graphic symbol for a diad axis in the plane of the diagram is \rightarrow ; if the axis lies at, say, $z = \frac{1}{4}$, the symbol $\rightarrow \frac{1}{4}$ is used.

In space group $P2$, the general and special equivalent positions may be derived quite readily. The special sets (b) and (d) should be noted carefully; they are sometimes forgotten by the beginner because symmetry elements distant $c/2$ from those drawn in the a, b plane are not indicated on the conventional diagrams. The diad axis at $x = 0, \frac{1}{2}$, for example, relates x, y, z to a point at $\bar{x}, y, 1 - z$; its presence, and that of the diad at $x = z = \frac{1}{2}$, may be illustrated by drawing the space group in projection on the ac plane of the unit cell. The reader should make this drawing and compare it with Fig. 2.27a.

It is often useful to consider a structure in projection on to one of the principal planes (100), (010), or (001). The symmetry of a projected space group corresponds to that of a plane group, and the symmetries of the principal projections are included with the space-group description, Fig. 2.27. The full plane-group symbols, given in parentheses, indicate the orientations of all symmetry elements, including identity, in the space group, Table 1.5. In $C2$, certain projections produce more than one repeat in some directions; the projected cell dimensions, represented by a' and b' are then halved with respect to their original values. The Miller indices transform with the change of unit cell: thus, for example, with b halved, 220 becomes 210, and 210 becomes 410 (which is equivalent to halving the k index in each case).

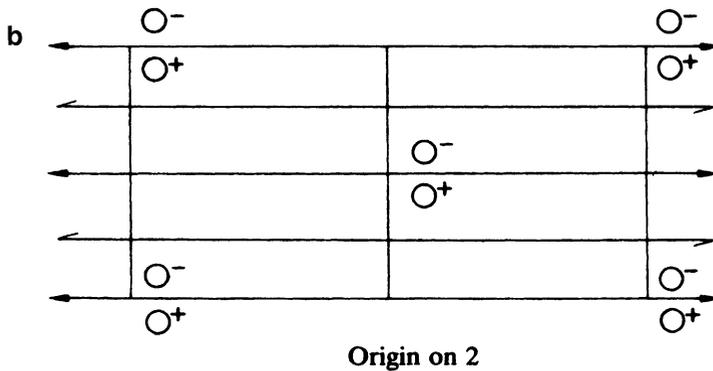
The projection of $C2$ on to (100) is shown by Fig. 2.28 in three stages, starting from the y and z coordinates of the set of general equivalent positions. The symmetry of the projection is determined by the arrangements of points, now in two dimensions, and the relation between them is clearly that of



2	<i>e</i>	1	$x, y, z;$	$\bar{x}, y, \bar{z}.$	Limiting conditions $hkl:$ } $h0l:$ } None $0k0:$ }
1	<i>d</i>	2	$\frac{1}{2}, y, \frac{1}{2}.$		
1	<i>c</i>	2	$\frac{1}{2}, y, 0.$		
1	<i>b</i>	2	$0, y, \frac{1}{2}.$		
1	<i>a</i>	2	$0, y, 0.$		

Symmetry of special projections

(001) *pm1* (*p1m1*) (100) *p1m* (*p11m*) (010) *p2* (*p211*)



				$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) +$	Limiting conditions $hkl: h + k = 2n$ $h0l: (h = 2n)$ $0k0: (k = 2n)$ } As above
4	<i>c</i>	1	$x, y, z;$	$\bar{x}, y, \bar{z}.$	
2	<i>b</i>	2	$0, y, \frac{1}{2}.$		
2	<i>a</i>	2	$0, y, 0.$		

Symmetry of special projections

(001) *cm1* (*c1m1*) (100) *p1m* (*p11m*) $b' = b/2$ (010) *p2* (*p211*) $a' = a/2$

Fig. 2.27 Monoclinic space groups in the standard setting. (a) *P2*. (b) *C2*

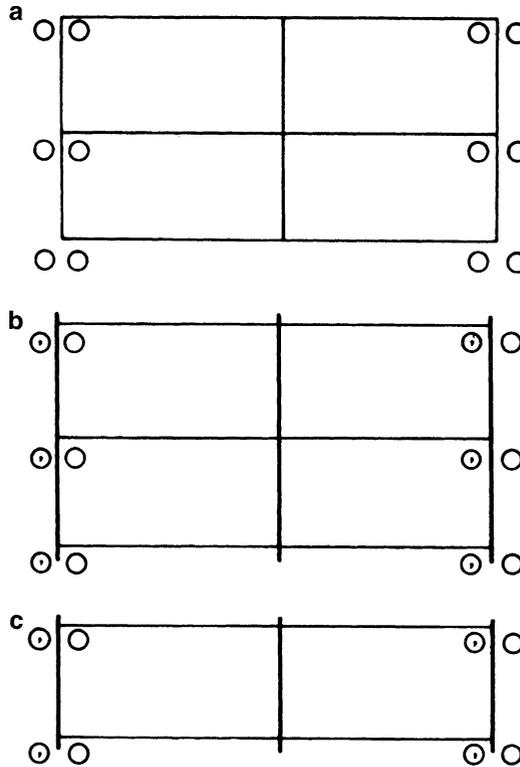


Fig. 2.28 Projection of $C2$ on to (100) . (a) y, z Positions from $C2$ (z axis *left to right*). (b) Two-dimensional symmetry elements, m lines, added. (c) One unit cell: $p1m$ ($p11m$), $b' = b/2$, $c' = c$. Plane groups $p11m$ and $p1m1$ are equivalent because they correspond only to an interchange of the x and y axes; 1 is the trivial symmetry element

m symmetry. A correct and sufficient projected unit cell is determined by **a** and **b/2**. It is important to remember that, in the plane groups, as in the two-dimensional point groups, all symmetry operations take place wholly within the plane of the figure.

The general equivalent positions in $C2$ may be obtained by adding the translations $\frac{1}{2}, \frac{1}{2}, 0$, namely, those associated with a C unit cell (Table 2.2), to the equivalent positions of $P2$. This operation is equivalent to repeating the original twofold motif at the lattice points of the C monoclinic unit cell. This simple relationship between P and C cells is indicated by the heading $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) +$ of the coordinate list in $C2$; it may be compared with that for cm , Fig. 2.21b.

There are four sets of special positions in $P2$, but only two sets in $C2$; the reason for this has been discussed in relation to plane groups pm and cm , Sect. 2.7.1.

2.7.4 Screw Axes

Screw axes are symmetry elements that can relate points in an infinite, three-dimensional, regular array; they are not a feature of point groups. A screw-axis operation may be thought of as a combination of rotation and translation, although it is a *single* symmetry operation: an infinitely long spiral staircase gives an indication of the nature of the symmetry operation.

Imagine that the bottom step, Fig. 2.29, is rotated, anticlockwise, looking in a direction down the stairs, by 60° about the vertical support, or axis, and then translated upward by one sixth of the repeat

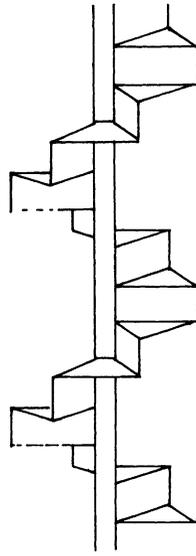


Fig. 2.29 Spiral staircase: an illustration of 6_1 screw-axis symmetry

distance between steps in similar orientations; it then takes the place of the second step, which itself moves upward in a similar manner. Clearly, if this procedure were repeated six times, the bottom step would reach the position and orientation of the sixth step up; we symbolize this screw axis as 6_1 . Infinite length is, theoretically, a requirement because as the bottom step is rotated and translated upward, so another step, below the figure, comes up into its position in order that indistinguishability is maintained. The spiral staircases of the Monument in London and of the Statue of Liberty in New York seem to be of infinite length, and might be considered as macroscopic near-examples of screw axes. Examine them carefully on your next visit and determine their symmetry nature.

The centering of the unit cell in $C2$ introduces screw axes which interleave the diad axes, Fig. 2.27. A screw axis may be designated R_p ($p < R$) and a screw-axis operation consists of an R -fold rotation coupled with a translation parallel to the screw axis of p/R times the repeat in the direction of the axis. For $p = R$, the translation parallel to the screw axis is unity, and result of the operation corresponds effectively to simple rotation: $P2_2 \equiv P2$. In $C2$, the screw axis is of the type 2_1 and has a translational component of $\frac{1}{2}$ parallel to b . The general equivalent positions x, y, z and $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$ are related by a 2_1 axis along $[\frac{1}{4}, y, 0]$.⁶ Screw axes are present in the positions shown by their graphic symbol \rightarrow (see also Table 2.5).

Limiting Conditions in $C2$

We referred briefly to limiting conditions in Sect. 2.7.1. The limiting conditions for $C2$ are listed in Fig. 2.27. Two of them are placed in parentheses; this notation is used to indicate that they are dependent upon a more general condition. Thus, since we know that the hkl reflections are limited by the condition $h + k = 2n$ (even), because the cell is C -centered, it follows that the $h0l$ reflections are limited by $h = 2n$ (0 is effectively an even number). There are several other nonindependent conditions that could have been listed. For example, $0kl$: $k = 2n$ and $h00$: $h = 2n$. However, in the monoclinic system, in addition to the

⁶ We use this notation to describe lines, in this example, the line parallel to the y axis through $x = \frac{1}{4}, z = 0$.

Table 2.5 Notation for symmetry axes in space groups, and limiting conditions for screw axes

Symbol	Graphic symbol	Screw-axis orientation and translation	Limiting condition
1	None		
$\bar{1}$	o		
2	 (normal to paper) (parallel to paper)		
2 ₁	 (normal to paper) (parallel to paper)	[100] $a/2$ [010] $b/2$ [001] $c/2$	$h00: h = 2n$ $0k0: k = 2n$ $00l: l = 2n$
3			
$\bar{3}$			
3 ₁		[0001] $c/3$	$000l: l = 3n$
3 ₂		[0001] $2c/3$	$000l: l = 3n$
4			
$\bar{4}$			
4 ₁ , 4 ₃		[100] $a/4, 3a/4$ [010] $b/4, 3b/4$ [001] $c/4, 3c/4$	$h00: h = 4n$ $0k0: k = 4n$ $00l: l = 4n$
4 ₂			
6			
$\bar{6}$			
6 ₁ , 6 ₅		[0001] $c/6, 5c/6$	$000l: l = 6n$
6 ₂ , 6 ₄		[0001] $2c/6, 4c/6$	$000l: l = 3n$
6 ₃		[0001] $3c/6$	$000l: l = 2n$

Notes: (1) The 3₁ and 3₂ axes are referred to the hexagonal setting of the trigonal system. (2) Compare the 2₁, 4₂, and 6₃ axes, the 4₁ and 4₃ axes, and 3₁, 3₂, 6₂, 6₄ axes

hkl reflections, we are concerned particularly only with $h0l$ and $0k0$, because the symmetry plane is parallel to (010) and the symmetry axis is parallel to [010]. This feature is discussed more fully in Sect. 3.7ff.

Space Group $P2_1$

Space groups $C2$ and $C2_1$ are equivalent and may be compared with the pair cm and cg . On the other hand, $P2$ contains no translational symmetry, so $P2_1$ is a new space group, Fig. 2.30; it occurs with a frequency of 6% among recorded structures. There are no special positions in $P2_1$. Special positions cannot exist on a translational symmetry element, since it would mean that the entity placed on such an element consisted of a pattern of infinite repeat.

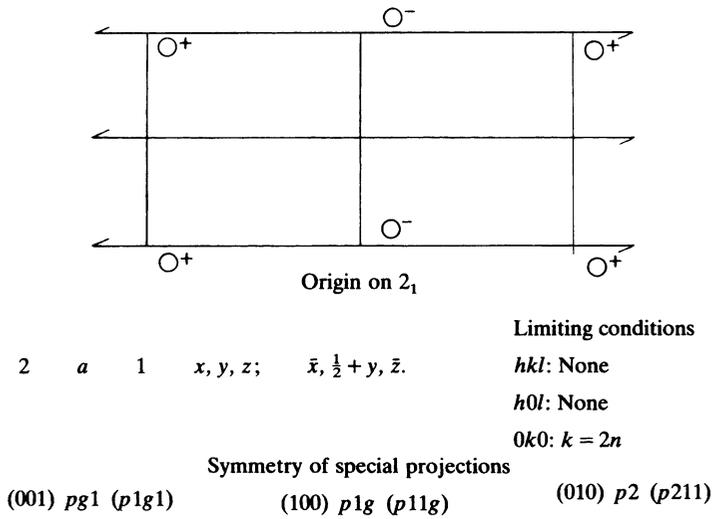


Fig. 2.30 General equivalent positions and symmetry elements in space group $P2_1$

2.7.5 Glide Planes

Consider again Fig. 2.18, but let each dashed line be now the trace of a glide plane normal to b . Whereas in two dimensions, the direction of translation, after the reflection part of the operation, is unequivocal, in three dimensions there are several possibilities, although each of them will not necessarily give rise to a different space group.

In the case of the glide plane normal to b , the reflection is across the mirror plane normal to b , and the direction of translation could be along a of amount $a/2$, along c of amount $c/2$, along a diagonal direction n of amount $(a + c)/2$, or, in certain groups, along a diagonal direction d of amount such as $(a \pm c)/4$. The d -glide plane is not often encountered in practice, and will not be discussed in detail here [3].

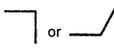
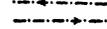
The graphic symbols for glide planes carry information about the glide planes. Thus, in Fig. 2.36, an a -glide plane at $c/4$ is shown by the arrow with $\frac{1}{4}$ adjacent to it. The symbol n may refer to more than one orientation (Table 2.6), but the space-group symbol here, which relates back to the corresponding point-group symbol in Table 1.5, provides the necessary information. Thus, if the n -glide plane is normal to a , the translation component of the n -glide-symmetry operation must be $(b + c)/2$. This is why it is so important to understand fully the Hermann–Mauguin point-group notation [4], Table 1.5, because that for space groups follows in a parallel manner. The translational components for screw axes and for glide planes are always integer fractions of the repeat distances.

If a space group is formed from the combination of a point group with m planes and a lattice of centered unit cells, glide planes are always introduced into the space group. The nature and direction of the translations in screw-axis and glide-plane symmetries are implicit in their symbolism (see Tables 2.5 and 2.6).

Space Group $P2_1/c$

As an example of a space group with glide planes, we shall study $P2_1/c$, a space group encountered frequently (36%) in practice. This space group is derived from point group $2/m$, and must, therefore, be centrosymmetric. However, the center of symmetry does not lie at the intersection of 2_1 and c .

Table 2.6 Notation for symmetry planes in space groups, and limiting conditions for glide planes

Symbol	Graphic symbol		Glide plane orientation and translation	Limiting condition
m		\perp paper	–	–
		\parallel paper	–	–
a		\perp paper	$(h0l) a/2$	$h0l: h = 2n$
		\parallel paper	$(hk0) a/2$	$hk0: h = 2n$
b		\perp paper	$(0kl) b/2$	$0kl: k = 2n$
		\parallel paper	$(hk0) b/2$	$hk0: k = 2n$
c		\perp paper	$(0kl) c/2$	$0kl: l = 2n$
		\perp paper	$(h0l) c/2$	$h0l: l = 2n$
n		\perp paper	$(0kl) (b + c)/2$	$0kl: k + l = 2n$
		\perp paper	$(h0l) (c + a)/2$	$h0l: l + h = 2n$
		\parallel paper	$(hk0) (a + b)/2$	$hk0: h + k = 2n$
d		\perp paper	$(0kl) (b \pm c)/4$	$0kl: k + l = 4n$
		\perp paper	$(h0l) (c \pm a)/4$	$h0l: l + h = 4n$
		\parallel paper	$(hk0) (a \pm b)/4$	$hk0: h + k = 4n$

Notes: (1) The trigonal system is here referred to hexagonal axes. (2) An arrow shows the direction of the glide translation. A fraction indicates the z height of the plane. (3) The condition $(a + b + c)/4$ exists for d -glide planes parallel to $\{1\bar{1}0\}$ in the tetragonal and cubic systems

It is normally desirable to place the origin on a center of symmetry in centrosymmetric space groups and, in this example, we must determine the appropriate positions of the symmetry elements in the unit cell. We note here that sometimes an origin will have a point symmetry greater than $\bar{1}$, for example, $2/m$ or mmm , but $\bar{1}$ is a subgroup of such symmetries. We shall approach the solution of this problem in two ways, the first of which is similar to our treatment of plane group $p2gg$.

Since the screw axis must intersect the glide plane normally, according to the space-group symbol, the point of intersection will be taken as an origin and the space group drawn, Fig. 2.31. We see now that the centers of symmetry lie at points such as $0, \frac{1}{4}, \frac{1}{4}$. This point may be taken as a new origin, and the space group redrawn, Fig. 2.32; the fraction $\frac{1}{4}$ placed next to the center of symmetry symbol indicates its fractional position above (and below) the ab plane.

It is desirable, however, to be able to draw the standard space-group illustration at the outset. From a choice of origin, and using the full meaning of the space-group symbol, we can obtain the positions of the symmetry elements by means of a simple scheme:

Let the symmetry elements be placed as follows:

$\bar{1}$ at $0, 0, 0$ (choice of origin)

2_1 along $[p, y, r]$, parallel to the y axis

c the plane (x, q, z) , normal to the y axis

It is important to note that we have employed only the standard choice of origin and the information contained in the space-group symbol. Next, we carry out the symmetry operations as shown in the scheme of Fig. 2.33.

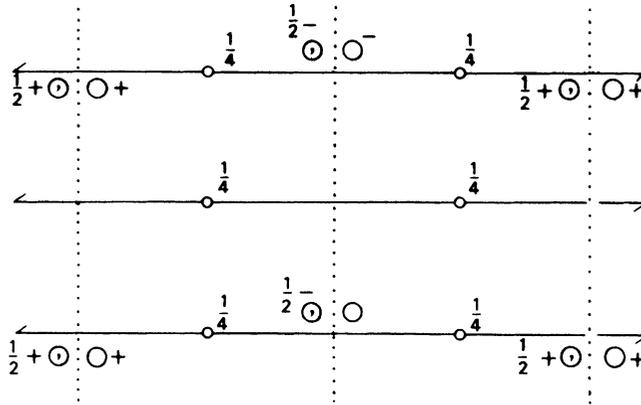


Fig. 2.31 Space group $P2_1/c$ with the origin at an intersection of 2_1 and c

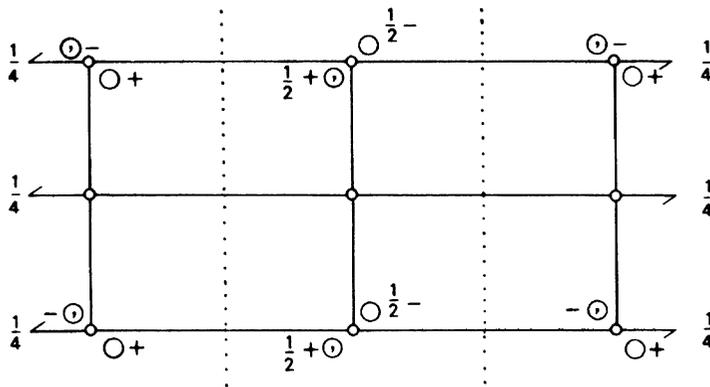


Fig. 2.32 Space group $P2_1/c$ with the origin on $\bar{1}$ (standard setting)

$$\begin{aligned}
 (1) \quad x, y, z &\xrightarrow{2_1} 2p - x, \frac{1}{2} + y, 2r - z \quad (2) \\
 &\quad \quad \quad \downarrow -c \\
 &\quad \quad \quad 2p - x, 2q - \frac{1}{2} - y, -\frac{1}{2} + 2r - z \quad (3) \\
 &\quad \quad \quad \downarrow \bar{1} \\
 &\quad \quad \quad -x, -y, -z \quad (4)
 \end{aligned}$$

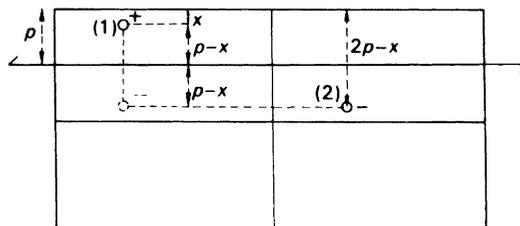


Fig. 2.33 Operation about a 2_1 axis along the line $[p, y, 0]$: The x coordinate of point 2 relative to that of point 1 is $2p - x$. A similar construction may be used for the y coordinate in the c -glide operation

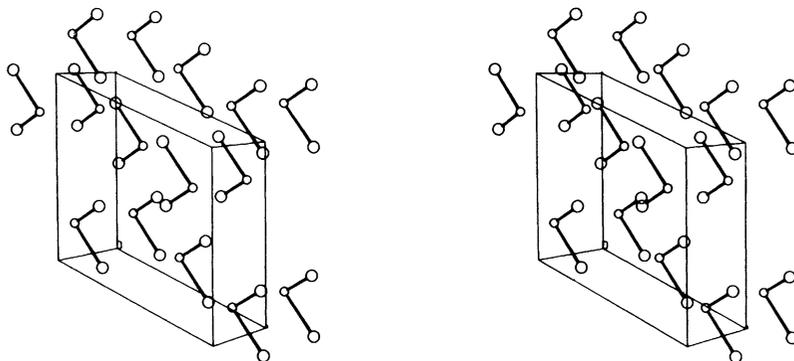


Fig. 2.34 Stereoview of the unit cell for the structure of diiodo- $(N, N, N', N'$ -tetramethylethylenediamine)zinc(II), showing the zinc and iodine (larger circles) atoms

The symbol $-c$ is used to indicate that the c -glide translation of $\frac{1}{2}$ is subtracted, which is crystallographically equivalent to being added.⁷

We use the fact that the combined effect of two operations is equivalent to a third operation, starting from the original point (1). Symbolically, in operator notation, $\mathbf{c} 2_1 = \bar{1}$, that is, 2_1 followed by c is equivalent to $\bar{1}$. Thus, points (3) and (4) are one and the same, whence, by comparing coordinates, $p = 0$ and $q = r = \frac{1}{4}$. Comparison with Fig. 2.32 shows that these conditions lead to the desired positions of the symmetry elements in $P2_1/c$.

The change in the x coordinate in the operation (1) \rightarrow (2) is illustrated in Fig. 2.33; the argument can be applied to any similar situation in other space groups, and we consider one coordinate at a time. The completion of the details of this space group forms the basis of a problem at the end of this chapter.

We shall not discuss centered monoclinic space groups, but they do not present difficulty once the primitive space groups have been mastered. Figure 2.34 shows a stereoscopic pair of illustrations of the zinc and iodine atoms in the structure of diiodo- $(N, N, N', N'$ -tetramethylethylenediamine)zinc(II) [5]. It crystallizes in space group $C2/c$ with four molecules per unit cell; the zinc atoms lie on twofold axes. The reader should make a drawing of $C2/c$, putting in all the symmetry elements and a set of general equivalent positions, for comparison with Fig. 2.34.

2.7.6 Analysis of the Space-Group Symbol

In this section we consider the general relationship between space-group symbols and point-group symbols. On encountering a space-group symbol, the first problem is to determine the parent point group. This process has been discussed, Sect. 2.7.2; here are a few more examples. It is not necessary to have explored all space groups in order to carry out this exercise:

$$P2_1/c \rightarrow (2_1/c) \rightarrow (2/c) \rightarrow 2/m$$

$$Ibca \rightarrow mmm$$

$$P4_12_12 \rightarrow 422$$

$$F\bar{4}3c \rightarrow \bar{4}3m$$

⁷ ± 1 may always be added to a coordinate to give a crystallographically equivalent position.

Next we must identify a crystal system for each point group:

$2/m \rightarrow$ monoclinic

$mmm \rightarrow$ orthorhombic

$422 \rightarrow$ tetragonal

$\bar{4}3m \rightarrow$ cubic

Now, from Table 1.5, we can associate certain crystallographic directions with each symmetry element in the space group symbol:

$P2_1/c$: Primitive, monoclinic unit cell; c -glide plane $\perp b$; 2_1 axis $\parallel b$; centrosymmetric.

$Ibca$: Body-centered, orthorhombic unit cell; b -glide plane $\perp a$; c -glide plane $\perp b$; a -glide plane $\perp c$; centrosymmetric.

$P4_12_12$: Primitive, tetragonal unit cell; 4_1 axis $\parallel c$; 2_1 axes $\parallel a$ and b ; twofold axes at 45° to a and b , in the ab plane; non-centrosymmetric.

$F\bar{4}3c$: Face-centered, cubic unit cell; $\bar{4}$ axes $\parallel a$, b , and c ; threefold axes $\parallel \langle 111 \rangle$; c -glide planes $\perp \langle 110 \rangle$; non-centrosymmetric.

It should be noted carefully that the symmetry elements, where there are more than two present, in a given space-group symbol may not intersect in the third, equivalent symmetry element, and the origin must always be selected with care. Appropriate procedures for the monoclinic and orthorhombic systems have been discussed; in working with higher symmetry space groups, similar rules can be drawn up, as we shall see.

Because of the similarities between space groups and their parent point groups, a reflection symmetry, for example, in a given orientation with respect to the crystallographic axes always produces similar changes in the *signs* of the coordinates. Thus, an m plane perpendicular to z in point group mmm changes x, y, z to x, y, \bar{z} . The a -glide plane in $Pnma$, which is at $c/4$, changes x, y, z to $\frac{1}{2} + x, y, \frac{1}{2} - z$; the translational components of $\frac{1}{2}$ are a feature of the space group, but the signs of x, y , and z are still $+$, $+$, and $-$ after the operation, as with mmm .

2.7.7 Orthorhombic Space Groups

We shall consider two orthorhombic space groups, $P2_12_12_1$ and $Pnma$. The first is illustrated in Fig. 2.35; it should be noted that the three mutually perpendicular 2_1 axes do *not* intersect one another in this space group. Although $P2_12_12_1$, which occurs to the extent of ca. 10%, is a non-centrosymmetric space group, the three principal projections are centrosymmetric; each corresponds to the two-dimensional space group $p2gg$.

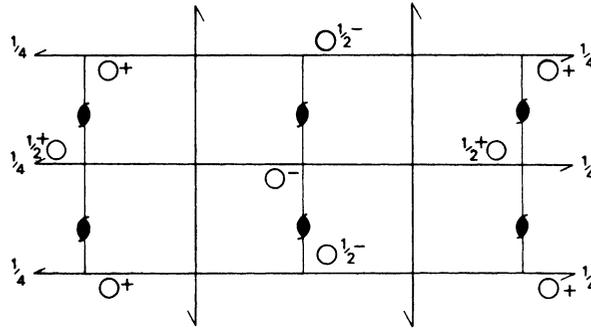
Change of Origin

Consider the projection of $P2_12_12_1$ on to (001). From the general equivalent positions we obtain the two-dimensional set of coordinates:

$$x, y; \quad \frac{1}{2} - x, \bar{y}; \quad \frac{1}{2} + x, \frac{1}{2} - y; \quad \bar{x}, \frac{1}{2} + y$$

It is convenient to change the origin to a twofold rotation point, currently at $\frac{1}{4}, 0$. To carry out this transformation, the coordinates of the new origin are subtracted from the original coordinates:

$$x - \frac{1}{4}, y; \quad \frac{1}{4} - x, \bar{y}; \quad \frac{1}{4} + x, \frac{1}{2} - y; \quad -x - \frac{1}{4}, \frac{1}{2} + y$$



Origin halfway between three pairs of nonintersecting screw axes

$$4 \quad a \quad 1 \quad x, y, z; \quad \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z; \quad \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \quad \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z.$$

Limiting conditions

- $hkl:$
 - $0kl:$
 - $h0l:$
 - $hk0:$
- } None
- $h00: h = 2n$
 - $0k0: k = 2n$
 - $00l: l = 2n$

Symmetry of special projections

(001) $p2gg$

(100) $p2gg$

(010) $p2gg$

Fig. 2.35 Space group $P2_12_12_1$. In space-group diagrams, \bullet represents a 2_1 axis normal to the plane of projection (Lonsdale K, Henry NFM (1965) International tables for X-ray crystallography, vol I. Kynoch Press. Reproduced by courtesy of I. U. Cr.)

Next, new variables x_0 and y_0 are chosen such that $x_0 = x - \frac{1}{4}$ and $y_0 = y$. Then, by substitution, we obtain:

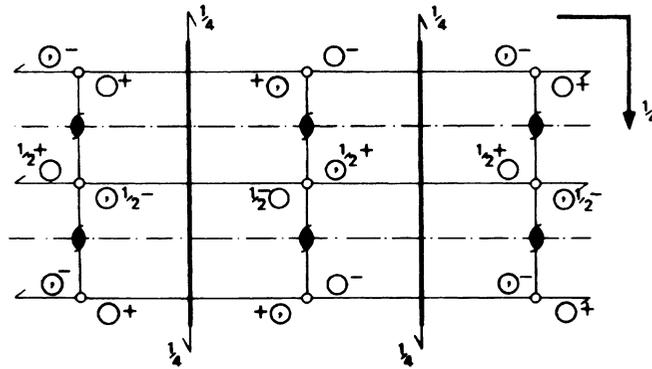
$$x_0, y_0; \quad \bar{x}_0, \bar{y}_0; \quad \frac{1}{2} + x_0, \frac{1}{2} - y_0; \quad \frac{1}{2} - x_0, \frac{1}{2} + y_0$$

If the subscript is dropped, these coordinates are exactly those given already for $p2gg$, Fig. 2.24d, which is the plane group of the projection of $P2_12_12_1$ on (001), and also on (100) and (010). This type of change of origin is useful when studying projections.

The orthorhombic space group $Pnma$ is shown with the origin on $\bar{1}$ in Fig. 2.36. The symbol tells us that the unit cell is primitive, with an n -glide plane normal to the x axis (see Table 2.6), an m plane normal to y , and an a -glide plane normal to z . Although this space group is derived from point group mmm , we have a problem similar to that discussed with $P2_1/c$. The solution of this type of problem depends upon the fact that, in the standard orientation, $\mathbf{m m m} = \bar{1}$, and is illustrated fully in Problem 2.10 at the end of this chapter. It may be noted that a double application of Euler's theorem is used here:

$$\mathbf{m m} = \mathbf{mm2} \quad \text{and} \quad \mathbf{m (mm2)} \equiv \bar{1}$$

The coordinates of the general and the special equivalent positions can be derived easily from the diagram. The translational symmetry elements n and a give rise to the limiting conditions shown on the diagram. Nonindependent conditions are shown in parentheses; in the orthorhombic system, all of the classes of reflection listed should be considered, as will be discussed in Sect. 3.7ff.



Origin at $\bar{1}$

8 *d* $\bar{1}$ $x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z; \bar{x}, \frac{1}{2} + y, \bar{z}; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z;$ Limiting conditions
 $\bar{x}, \bar{y}, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; x, \frac{1}{2} - y, z; \frac{1}{2} + x, y, \frac{1}{2} - z.$ *hkl*: None

*Ok**l*: $k + l = 2n$

*h**0**l*: None

*hk**0*: $h = 2n$

*h**0**0*: ($h = 2n$)

*0**k**0*: ($k = 2n$)

*0**0**l*: ($l = 2n$)

4 *c* *m* $x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z}; \frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z.$

As above

4 *b* $\bar{1}$ $0, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; \frac{1}{2}, \frac{1}{2}, 0.$

} As above +

4 *a* $\bar{1}$ $0, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$

} *hkl*: $h + l = 2n; k = 2n$

Symmetry of special projections

(011) *p*2*gm*

(100) *c*2*mm*

(010) *p*2*gg*

Fig. 2.36 Space group *Pnma*; the full space-group symbol is $P\frac{2_1}{n}\frac{2_1}{m}\frac{2_1}{a}$ (Lonsdale K, Henry NFM (1965) International tables for X-ray crystallography, vol I. Kynoch Press. Reproduced by courtesy of I. U. Cr.)

It is useful to remember that among the triclinic, monoclinic, and orthorhombic space groups, at least, pairs of coordinates which have one *sign* change of *x*, *y*, or *z* indicate a symmetry plane normal to the axis of the coordinate with the changed sign. If two sign changes exist, a symmetry axis lies parallel to the axis of the coordinate that has *not* changed sign. Three sign changes indicate a center of symmetry. In these three systems, where any coordinate, say *x*, is related by symmetry to another at $t - x$, that symmetry element intersects the *x* axis at $t/2$, by virtue of Fig. 2.33 *mutatis mutandis*.

2.7.8 Relative Orientations of Symmetry Elements in Space Groups

Earlier in this chapter, we looked briefly at the problem of choosing the relative positions of the symmetry elements in space groups while keeping a particular symmetry element at a given site, such as a center of symmetry at the origin in space groups of class $2/m$. We now discuss some simple rules whereby this task can be accomplished readily, with due regard to the relative orientations of the symmetry elements given by the space-group symbol itself, Tables 1.5 and 2.5. We shall consider here the symmetry planes and symmetry axes in space groups derived from point groups *mmm* and $2/m$, although the rules can be applied more widely.

Half-Translation Rule

Location of Symmetry Planes

Consider space group $Pnna$: the translations associated with the three symmetry planes are $(b + c)/2$, $(c + a)/2$ and $a/2$, respectively. If they are summed, the result T is $(a + b/2 + c)$. We disregard the whole translations a and c because they refer to unit-cell repetitions. Thus, the center of symmetry is found displaced by $T/2$, or $b/4$, from the point of intersection of the three symmetry planes n , n , and a . This means that, with $\bar{1}$ at the origin, we have $n|| (0, y, z)$, $n|| (x, \frac{1}{4}, z)$ and $a|| (x, y, 0)$. As a second example, consider $Pmma$. The only translation is $a/2$; thus, $T = a/2$, and the center of symmetry is displaced by $a/4$ from the intersection of m , m and a .

Space group $Imma$ may be formed from $Pmma$ by introducing the body-centering translation $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, Fig. 6.18b. Alternatively, the half-translation rule may be applied to the complete space-group symbol. In all, $Imma$ contains the translations $(a + b + c)/2$ and $a/2$, so that $T = a + (b + c)/2$, or $(b + c)/2$; hence, the center of symmetry is displaced by $(b + c)/4$ from the intersection of m , m and a . This center of symmetry lies in one of the four sets, Wyckoff (a)–(d), that are introduced by the body-centering translation at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, half the I translation, from a $Pmma$ center of symmetry. This alternative setting is given in the *International Tables for X-Ray Crystallography* [3]; it corresponds to that in Fig. 6.18b with the origin shifted to the center of symmetry at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. Space groups in class mmm based on A , B , C , and F unit cells similarly introduce additional sets of centers of symmetry. The reader may care to apply these rules to space group $Pnma$ and then check the result with Fig. 2.36. Note that there are two sets of special equivalent positions on $\bar{1}$, which is why an origin on either center of symmetry can be chosen.

Type and Location of Symmetry Axes

The quantity T also shows the types of twofold axes parallel to a , b , and c . Thus, if T contains an $a/2$ component, then if a twofold axis parallel to a exists in the space group, it is a 2_1 axis. Similarly for twofold axes parallel to y and z . Thus, in $Pnna$, $T = b/2$, and so $2_x \equiv 2$, $2_y \equiv 2_1$, and $2_z \equiv 2$. In $Pbca$, $T = (b + c + a)/2$; hence, all axes are 2_1 and the full space-group symbol is $P \frac{2_1}{b} \frac{2_1}{c} \frac{2_1}{a}$.

The location of each twofold axis may be obtained from the orientation of the symmetry plane perpendicular to it, being displaced by half the corresponding glide translation, where appropriate. Thus, in $Pnna$, we find 2 along $[x\frac{1}{4}, \frac{1}{4}]$, 2_1 along $[\frac{1}{4}, y, \frac{1}{4}]$ and 2 along $[\frac{1}{4}, 0, z]$. In $Pmma$, 2_1 is along $[x, 0, 0]$, 2 is along $[0, y, 0]$ and 2 is along $[\frac{1}{4}, 0, z]$. The reader may care to continue the study with space group $Pnma$, and then check the results against Fig. 2.36.

In the monoclinic space groups of class $2/m$, a 2_1 axis with a translational component of $b/2$ shifts the center of symmetry by $b/4$ with respect to the point of intersection of 2_1 with m ; carry out Problem 7.3 and check your result in Tutorial Solution 7.3. In $P2/c$, the center of symmetry is shifted by $c/4$ with respect to $2/c$, and in $P2_1/c$ the corresponding shift is $(b + c)/4$, see Fig. 2.32.

General Equivalent Positions

Once we know the positions of the symmetry elements in a space-group pattern, the coordinates of the general equivalent positions in the unit cell follow readily.

Consider $Pmma$. Following out the above analysis, we may write the orientation of the symmetry elements:

$\bar{1}$ at 0,0,0; choice of origin

m_x , the plane $(\frac{1}{4}, y, z)$

m_y , the plane $(x, 0, z)$

a , the plane $(x, y, 0)$

Taking a point x, y, z across each of the three symmetry planes, we have, from Fig. 2.33:

$$\begin{aligned} x, y, z &\xrightarrow{m_x} \frac{1}{2} - x, y, z \\ &\xrightarrow{m_y} x, \bar{y}, z \\ &\xrightarrow{a} \frac{1}{2} + x, y, \bar{z} \end{aligned}$$

If these four points are now operated on by $\bar{1}$ the total of eight equivalent positions for $Pmma$ are obtained: $\pm \{x, y, z; \frac{1}{2} - x, y, z; x, \bar{y}, z; \frac{1}{2} + x, y, \bar{z}\}$.

A similar analysis may be carried out for the space groups in the $mm2$ class, with respect to origins on 2 or 2₁, although we have not discussed these space groups in this book. For example, work through the space group Pma^* , and check your result with Sect. 3.7.2 and Fig. 3.25, or with the *International Tables for X-ray Crystallography* [3].

2.7.9 Tetragonal and Hexagonal Space Groups

We shall examine one space group from each of the tetragonal and hexagonal systems because new features arise on account of the higher rotational symmetry in these two systems.

Tetragonal Space Group $P4nc$

It is evident that this space group is based on the point group $4mm$. Reference to Table 1.5 shows that the symbol has the following interpretation: a fourfold axis along z ; n -glide planes normal to x (and to y , because of the fourfold symmetry); c -glide planes normal to $[110]$ and its fourfold symmetry-related direction $[1\bar{1}0]$. The orientation of the n glides can be handled in the manner already discussed.

In the case of the c glide, it is straightforward to show, from Problem 2.21, that if the glide plane intercepts the x and y axes at the value q , then a point x, y, z is reflected across the glide plane and translated to the position $q - y, q - x, \frac{1}{2} + z$. Thus, as in Sect. 2.7.5, we can set up the interpretation of the symbol $P4nc$, again using Euler's theorem, that the combination of any two operations is equivalent to a third operation. Thus, $\mathbf{n} \mathbf{4} = \mathbf{c}$, but, in contradistinction to the point group $4mm$, the three operators do not all pass through the origin point.

Let the symmetry elements be placed as follows:

4 along the z axis, that is, the line $[0, 0, z]$

n normal to x , being the plane (x, β, z)

c normal to $[110]$, the plane (q, q, z)

A point x, y, z (1) rotated about the 4-axis becomes \bar{y}, x, z (2); this point is taken across the n glide to $\frac{1}{2} - y, 2\beta - x, \frac{1}{2} + z$ (3). If we now operate on the original point (1) by the c glide, then x, y, z is reflected to $q - y, q - x, \frac{1}{2} + z$ (4). Now, points (3) and (4) are one and the same, so that $q = \frac{1}{2}$ and $\alpha = \frac{1}{4}$. This setting of the symmetry elements gives rise to the standard diagram for $P4nc$, shown in Fig. 2.37. A similar result may be obtained by an initial *clockwise* rotation and the equivalent n glide parallel to (α, y, z) . The positions of the additional symmetry elements, not apparent from the symbol, should again be noted. The diagram of the unit cell and its environs is complete, because any point shown can be reached from any other point on the diagram by a single symmetry operation, plus unit-cell translations as necessary.

Hexagonal Space Group $P6_3/m$

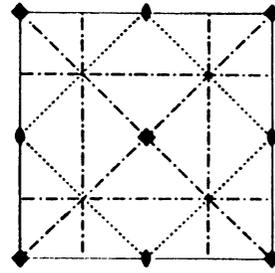
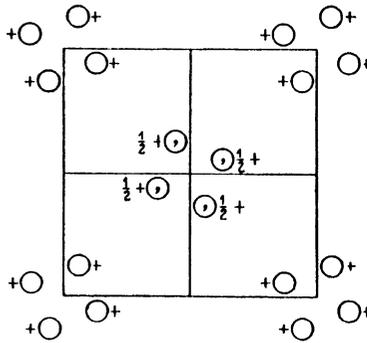
In this space group we encounter sixfold and threefold rotation operations. From Web Appendix WA4, we show that a point x, y, z on hexagonal axes rotated anticlockwise about a 6_3 screw axis along

$P4nc$
 C_{4v}^6

No. 104

$P4nc$

$4mm$ Tetragonal



Origin on 4

Conditions limiting possible reflections

Number of positions, Wyckoff notation, and point symmetry

Coordinates of equivalent positions

General:

8	<i>c</i>	1	$x, y, z;$	$\bar{x}, \bar{y}, z;$	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z;$	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z;$
			$\bar{y}, x, z;$	$y, \bar{x}, z;$	$\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} + z;$	$\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} + z.$

$hkl:$ No conditions
 $Ok:$ $k + l = 2n$
 $hhl:$ $l = 2n$

4	<i>b</i>	2	$0, \frac{1}{2}, z;$	$\frac{1}{2}, 0, z;$	$0, \frac{1}{2}, \frac{1}{2} + z;$	$\frac{1}{2}, 0, \frac{1}{2} + z.$
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Special:
 $hkl:$ $h + k = 2n; l = 2n$

2	<i>a</i>	4	$0, 0, z;$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z.$
---	----------	---	------------	----------------------------------------------

$hkl:$ $h + k + l = 2n$

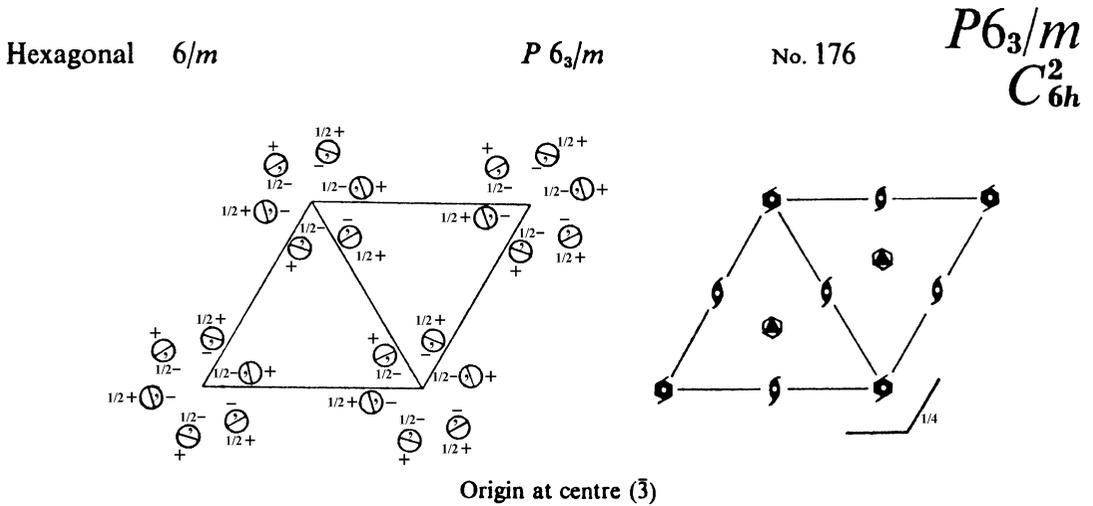
Fig. 2.37 Diagrams to show the general equivalent positions and symmetry elements for the tetragonal space group $P4nc$ (Lonsdale K, Henry NFM (1965) International tables for X-ray crystallography, vol I. Kynoch Press. Reproduced by courtesy of I. U. Cr.)

z would be moved to the position $x - y, x, \frac{1}{2} + z$. The translation of $\frac{1}{2}$ accompanying the z coordinate arises from the translation associated with the 6_3 axis, namely, a translation of $3/6$, or $\frac{1}{2}$ along z . The sequence of points obtained by the successive operations of 6_3 about $[0001]$ are:

$$\begin{array}{cccc}
 x, y, z; & x - y, x, \frac{1}{2} + z; & \bar{y}, x - y, z; & \bar{x}, \bar{y}, \frac{1}{2} + z; \\
 (1) & (2) & (3) & (4) \\
 y - x, \bar{x}, z; & y, y - x, \frac{1}{2} + z & & \\
 (5) & (6) & &
 \end{array}$$

Points (1) and (3) are related by a threefold rotation: note that $3 \equiv 6_3^2$, that is, two successive operations of 6_3 , whereas points (1) and (4) are related by 2_1 symmetry. The space group is completed by introducing the m plane at $z = \frac{1}{4}$; this position ensures that the center of symmetry is at the origin; actually the symmetry at the origin is $\bar{3}$: $\bar{1}$ is a subgroup of $\bar{3}$. Other important symmetry elements now in evidence include $\bar{6}$, 3 , and $\bar{1}$.

Figure 2.38 illustrates space group $P6_3/m$. The 12 general equivalent positions comprise the six listed above and another six obtained by their inversion across the center of symmetry at the origin; all coordinates change sign. Consider point (2) reflected across the m plane to $x - y, x, \frac{1}{2} - z$. How may this point be reached from x, y, z in a single operation? Either a clockwise $\bar{3}$ operation, or an



Number of positions, Wyckoff notation, and point symmetry			Coordinates of equivalent positions			Conditions limiting possible reflections
12	<i>i</i>	1	$x, y, z;$ $\bar{x}, \bar{y}, \bar{z};$ $\bar{x}, \bar{y}, \frac{1}{2} + z;$ $x, y, \frac{1}{2} - z;$	$\bar{y}, x - y, z;$ $y, y - x, \bar{z};$ $y, y - x, \frac{1}{2} + z;$ $\bar{y}, x - y, \frac{1}{2} - z;$	$y - x, \bar{x}, z;$ $x - y, x, \bar{z};$ $x - y, x, \frac{1}{2} + z;$ $y - x, \bar{x}, \frac{1}{2} - z.$	General: <i>hkil</i> : No conditions 000: $l = 2n$
6	<i>h</i>	<i>m</i>	$x, y, \frac{1}{2};$ $\bar{x}, \bar{y}, \frac{1}{2};$	$\bar{y}, x - y, \frac{1}{2};$ $y, y - x, \frac{1}{2};$ $x - y, x, \frac{1}{2}.$		Special: as above, plus no extra conditions
6	<i>g</i>	$\bar{1}$	$\frac{1}{2}, 0, 0;$ $0, \frac{1}{2}, 0;$ $\frac{1}{2}, \frac{1}{2}, 0;$ $\frac{1}{2}, 0, \frac{1}{2};$ $0, \frac{1}{2}, \frac{1}{2};$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$			<i>hkil</i> : $l = 2n$
4	<i>f</i>	3	$\frac{1}{2}, \frac{2}{3}, z;$ $\frac{1}{2}, \frac{1}{3}, \bar{z};$ $\frac{1}{2}, \frac{1}{3}, \frac{1}{2} + z;$ $\frac{1}{2}, \frac{1}{3}, \frac{1}{2} - z.$			<i>hkil</i> : If $h - k = 3n$, then $l = 2n$
4	<i>e</i>	3	$0, 0, z;$ $0, 0, \bar{z};$ $0, 0, \frac{1}{2} + z;$ $0, 0, \frac{1}{2} - z.$			<i>hkil</i> : $l = 2n$
2	<i>d</i>	$\bar{6}$	$\frac{1}{2}, \frac{1}{3}, \frac{1}{2};$ $\frac{1}{2}, \frac{1}{3}, \frac{1}{2}.$			} <i>hkil</i> : If $h - k = 3n$, then $l = 2n$
2	<i>c</i>	$\bar{6}$	$\frac{1}{2}, \frac{1}{3}, \frac{1}{2};$ $\frac{1}{2}, \frac{1}{3}, \frac{1}{2}.$			
2	<i>b</i>	$\bar{3}$	$0, 0, 0;$ $0, 0, \frac{1}{2}.$			} <i>hkil</i> : $l = 2n$
2	<i>a</i>	$\bar{6}$	$0, 0, \frac{1}{2};$ $0, 0, \frac{1}{2}.$			

Fig. 2.38 Diagrams to show the general equivalent positions and symmetry elements for the hexagonal space group $P6_3/m$ (Lonsdale K, Henry NFM (1965) International tables for X-ray crystallography, vol I. Kynoch Press. Reproduced by courtesy of I. U. Cr.)

anticlockwise $\bar{3}^2$ operation, which is equivalent to two successive anticlockwise $\bar{3}$ operations, relates these two points; we note in passing that both $\bar{3}$ and 3^2 are symmetry operations in this group, related to the single symmetry element $\bar{3}$.

A scheme for handling hexagonal space groups, similar to those used for the lower-symmetry systems, could be devised, but it will be more straightforward to use matrix operations, as we shall now demonstrate.

2.8 Matrix Representation of Symmetry Operations

The representation of symmetry operations by matrices has a certain inherent elegance, and is useful for displaying the close relationship between point groups and space groups. In this discussion, we shall use the triplet x, y, z to represent a point in three-dimensional space. It could lie on the normal to the face of a crystal or be an atom in a crystal structure, and we can indicate it concisely by the vector \mathbf{x} .

A symmetry operation may be written as

$$\mathbf{R} \mathbf{x} + \mathbf{t} = \mathbf{x}' \tag{2.52}$$

where \mathbf{x} and \mathbf{x}' are column vector triplets before and after the operation, \mathbf{R} is a matrix representing the symmetry operation, and \mathbf{t} is a translation vector with components parallel to $x, y,$ and z .

2.8.1 Matrices in Point-Group Symmetry

From the definition of point group, Sect. 1.4, it follows that \mathbf{t} is identically zero in a point group. All symmetry elements pass through a single point, the origin: if it were not the case, then parallel symmetry axes, for example, could be generated. The consequence of this arrangement for a twofold axis is shown in Fig. 2.39.

Thus, for point groups, (2.52) reduces to

$$\mathbf{R} \mathbf{x} = \mathbf{x}' \tag{2.53}$$

Let \mathbf{R}_1 represent an m plane perpendicular to the x axis, as in the orthorhombic system, for example. Then, we have

$$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}_{\mathbf{R}_1} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix}_{\mathbf{x}} = \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix}_{\mathbf{x}'} \tag{2.54}$$

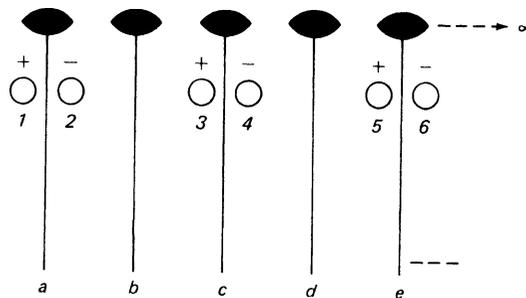


Fig. 2.39 Points 1 and 2, related by the diad (twofold axis) a , when rotated about the axis b produce points 4 and 3. But 3 and 4 are now related by another diad, c . The effect of diad c on points 1 and 2 is to produce points 6 and 5. But these points are related to 3 and 4 by diad d and to each other by diad e . Now 3 and 4, for example, can be rotated about e , and so on. Clearly, this process would lead to an infinite number of parallel, equidistant diad axes, together with the symmetry-related points, a situation that is totally incompatible with a point group

The multiplication is carried out, as usual, *along the row and down the column*, with the result at the intersection marked; that is,

$$\begin{bmatrix} \text{---} \rightarrow \\ \text{---} \downarrow \end{bmatrix} \cdot \begin{bmatrix} \text{---} \downarrow \\ \text{---} \rightarrow \end{bmatrix} = \begin{bmatrix} * \\ * \\ * \end{bmatrix} \quad (2.55)$$

$\mathbf{R}_1 \quad \mathbf{x} \quad \mathbf{x}'$

$$\bar{x} = -1 \times x + 0 \times y + 0 \times z \quad (2.56)$$

and similarly for y and z .

Let the triplet \mathbf{x}' now suffer reflection across a mirror plane normal to y , using matrix \mathbf{R}_2 :

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} \quad (2.57)$$

$\mathbf{R}_2 \quad \mathbf{x} \quad \mathbf{x}''$

It should be clear that the relationship between \mathbf{x} and \mathbf{x}'' is that of a twofold rotation about the z axis. Thus, for the two m planes,

$$\mathbf{m} \mathbf{m} = 2 \quad (2.58)$$

as we have seen already, Sect. 1.4.2.

Another way of reaching the same final result is first to combine the two matrices \mathbf{R}_1 and \mathbf{R}_2 ,

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (2.59)$$

$\mathbf{R}_2 \quad \mathbf{R}_1 \quad \mathbf{R}_3$

and then to use the right-hand side of (2.59) in (2.53):

$$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ \bar{y} \\ z \end{bmatrix} \quad (2.60)$$

$\mathbf{R}_3 \quad \mathbf{x} \quad \mathbf{x}''$

Equation (2.59) corresponds to operation $\mathbf{R}_2 \mathbf{R}_1$ (\mathbf{R}_1 followed by \mathbf{R}_2), the order of multiplication following (2.55). If a rotational symmetry axis forming an operator \mathbf{R} is less than or equal to degree 2 or to m , the order of multiplication need not be followed, but it is good practice to multiply the matrices in the standard manner; we can highlight this feature by considering point group $4mm$.

The matrices for a fourfold rotation along the z axis and an m plane perpendicular to x are, in order,

$$\begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (2.61)$$

$\mathbf{R}_2 \quad \mathbf{R}_3 \quad \mathbf{R}_3$

Hence, $\mathbf{R}_2 \mathbf{R}_1 = \mathbf{R}_3$, and $\mathbf{R}_3 \mathbf{x}(x, y, z) = \mathbf{x}'(y, x, z)$; \mathbf{R}_3 represents an m plane symmetry operator normal to $[1\bar{1}0]$. Multiplying in the reverse order, that is,

$$(\mathbf{R}_1 \mathbf{R}_2)\mathbf{x} = \mathbf{x}'' \quad (2.62)$$

gives

$$\mathbf{R}_1 \mathbf{R}_2 = \mathbf{R}_4 \quad (2.63)$$

where \mathbf{x}'' is now \bar{y}, \bar{x}, z , and \mathbf{R}_4 is a matrix operator representing an m plane normal to $[110]$. Write out this matrix. The m planes represented by \mathbf{R}_3 and \mathbf{R}_4 are equivalent under symmetry \mathbf{R}_1 or \mathbf{R}_2 , but lead to physically different sites. Thus, if we are expecting \mathbf{x}' from \mathbf{x} and obtain \mathbf{x}'' instead, it may be confusing and, in considering some physical properties, could be significantly different. All other point groups may be treated in the standard manner just described.

2.8.2 Matrices in Space-Group Symmetry

In space-group symmetry, \mathbf{t} in (2.52) is not necessarily equal to zero. Such a situation will exist whenever the space group under consideration contains translational symmetry. We will consider first space group $P2_1/c$, Sect. 2.7.5. As before, we set the origin on $\bar{1}$ (\mathbf{R}_3), 2_1 (\mathbf{R}_1) along $[p, y, r]$, and c (\mathbf{R}_2) the plane (x, q, z) . The operation \mathbf{R}_1 followed by \mathbf{R}_2 , from our previous discussion, may be formulated as

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}_{\mathbf{R}_2} + \begin{bmatrix} 0 \\ 2q \\ \frac{1}{2} \end{bmatrix}_{\mathbf{t}_2} \cdot \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}_{\mathbf{R}_1} + \begin{bmatrix} 2p \\ \frac{1}{2} \\ 2r \end{bmatrix}_{\mathbf{t}_1} = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}_{\mathbf{R}_3} + \begin{bmatrix} 0 \\ 0 \\ \mathbf{t}_3 \end{bmatrix} \quad (2.64)$$

Matrix \mathbf{R}_1 is just that for twofold rotation about a line parallel to the y axis, as represented above, and \mathbf{R}_2 is the matrix for an m plane normal to y , as given above. The translation vectors \mathbf{t}_1 and \mathbf{t}_2 may be obtained from the setting, following the argument relating to Fig. 2.33. Matrix \mathbf{R}_3 is the multiplication $\mathbf{R}_2 \mathbf{R}_1$ and, clearly, is equivalent to a center of symmetry ($\bar{1}$) at the origin. Since, by definition of the standard origin, \mathbf{t}_3 must be zero, we have the translation vectors

$$\mathbf{t}_2 + \mathbf{t}_1 = \mathbf{t}_3 = 0 \quad (2.65)$$

It follows that $p = 0$, $q = \frac{1}{4}$ and $r = \frac{1}{4}$, as before. These results may be regarded as a matrix justification of the scheme used in Sect. 2.7.5, and expressed in the half-translation rule, Sect. 2.7.8.

As a final example, we shall consider space group $Pnma$, see Sect. 2.7.7. From the symbol, we can write

\mathbf{R}_1 : n is the plane (p, y, z) with n -translation $0, \frac{1}{2}, \frac{1}{2}$

\mathbf{R}_2 : m is the plane (x, q, z) with no translation

\mathbf{R}_3 : a is the plane (x, y, r) with a -translation $\frac{1}{2}, 0, 0$

\mathbf{R}_4 : $\bar{1}$ is the center of symmetry at $0,0,0$ (no translation)

We know that, for space groups in the mmm class, we have

$$\mathbf{R}_3 \mathbf{R}_2 \mathbf{R}_1 = \mathbf{R}_4 \quad (2.66)$$

Hence,

$$\begin{aligned}
 & \left[\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{array} \right]_{\mathbf{R}_3} + \left[\begin{array}{c} \frac{1}{2} \\ 0 \\ 2r \end{array} \right]_{\mathbf{t}_3} \left\{ \left[\begin{array}{ccc} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{array} \right]_{\mathbf{R}_2} + \left[\begin{array}{c} 0 \\ 2q \\ 0 \end{array} \right]_{\mathbf{t}_2} \left[\begin{array}{ccc} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right]_{\mathbf{R}_1} + \left[\begin{array}{c} 2p \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right]_{\mathbf{t}_1} \right\} \\
 & = \left[\begin{array}{ccc} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{array} \right]_{\mathbf{R}_4} + \left[\begin{array}{c} 0 \\ 0 \\ 0 \end{array} \right]_{\mathbf{t}_4}
 \end{aligned} \tag{2.67}$$

And we have

$$\mathbf{t}_3 + \mathbf{t}_2 + \mathbf{t}_1 = \mathbf{t}_4 = 0 \tag{2.68}$$

Multiplying the matrices and adding the translation vectors we obtain $p = \frac{1}{4}$, $q = \frac{1}{4}$, and $r = \frac{1}{4}$ as given in Fig. 2.36. The full symbol of point group mmm is $\frac{2}{m} \frac{2}{m} \frac{2}{m}$, so that in $Pnma$ there are 2 or 2_1 axes normal to the symmetry planes. We can obtain the results readily from (2.67), inserting the values of p , q , and r into the translation vectors; if the fraction $\frac{1}{2}$ appears in line with the x coordinate in a plane normal to x , then the axis is 2_1 , and similarly for the y and z positions. Hence, the full symbol for this space group is $P \frac{2_1}{n} \frac{2_1}{m} \frac{2_1}{a}$. The same result could be achieved with the scheme used for solving Problem 2.10, perhaps with less elegance.

The essential difference between point groups and space groups rests in the translation vectors, and the infinite space to which the space groups refer. Symmorphic space groups such as Pm , $C2/m$, and $Imm2$, some of which contain translational symmetry elements, do not need any special treatment to determine the orientation of the symmetry elements with respect to the origin, since the symmorphic space groups contain the point-group symbol, the origin is given immediately, for example, on m in Pm , at $2/m$ ($\bar{1}$) in $C2/m$, and along $mm2$ in $Imm2$; all translation vectors in equations such as (2.64) are zero in these space groups. The half-translation rule, once understood, is the simplest method of locating the origin, certainly for the non-symmorphic space groups in the monoclinic and orthorhombic systems, which represent the majority of known crystals.

2.9 Diffraction Symbols

We look ahead briefly to some results in later chapters, and note that after a crystal has been examined to the extent that indices can be assigned to the X-ray diffraction spectra, the totality of the diffraction information can be assembled into a *diffraction symbol*. This parameter includes the Laue group and the symmetry determined through the systematic absences.

Table 2.7 Orthorhombic space group diffraction symbols

Diffraction symbol				Point group		
				222	<i>mm2</i>	<i>mmm</i>
<i>mmmP</i>	.	.	.	<i>P222</i>	<i>Pmn2</i>	<i>Pmmm</i>
<i>mmmP</i>	.	.	2_1	<i>P222₁</i>		
<i>mmmP</i>	2_1	2_1	.	<i>P2₁2₁2</i>		
<i>mmmP</i>	2_1	2_1	2_1	<i>P2₁2₁2₁</i>		
<i>mmmP</i>	<i>c</i>	.	.		$Pc2m = \begin{pmatrix} Pma2 \\ Pmc2_1 \end{pmatrix}$	<i>Pcmm = Pmma</i>
<i>mmmP</i>	<i>n</i>	.	.		<i>Pnm2₁ = Pmn2₁</i>	<i>Pnmm = Pmmm</i>
<i>mmmP</i>	<i>c</i>	<i>c</i>	.		<i>Pcc2</i>	<i>Pccm</i>
<i>mmmP</i>	<i>c</i>	<i>a</i>	.		<i>Pca2₁</i>	<i>Pcam = Pbcm</i>
<i>mmmP</i>	<i>b</i>	<i>a</i>	.		<i>Pba2</i>	<i>Pbam</i>
<i>mmmP</i>	<i>n</i>	<i>c</i>	.		<i>Pnc2</i>	<i>Pncm = Pmna</i>
<i>mmmP</i>	<i>n</i>	<i>a</i>	.		<i>Pna2₁</i>	<i>Pnam = Pnma</i>
<i>mmmP</i>	<i>n</i>	<i>n</i>	.		<i>Pnn2</i>	<i>Pnnm</i>
<i>mmmP</i>	<i>c</i>	<i>c</i>	<i>a</i>			<i>Pcca</i>
<i>mmmP</i>	<i>b</i>	<i>c</i>	<i>a</i>			<i>Pbca</i>
<i>mmmP</i>	<i>c</i>	<i>c</i>	<i>n</i>			<i>Pccn</i>
<i>mmmP</i>	<i>b</i>	<i>a</i>	<i>n</i>			<i>Pban</i>
<i>mmmP</i>	<i>b</i>	<i>c</i>	<i>n</i>			<i>Pbcn</i>
<i>mmmP</i>	<i>n</i>	<i>n</i>	<i>a</i>			<i>Pnna</i>
<i>mmmP</i>	<i>n</i>	<i>n</i>	<i>n</i>			<i>Pnnn</i>
<i>mmmC</i>	.	.	.	<i>C222</i>	$Cmm2 = \begin{pmatrix} Cmm2 \\ Cm2m \end{pmatrix}$	<i>Cmmm</i>
<i>mmmC</i>	.	.	2_1	<i>C222₁</i>		
<i>mmmC</i>	.	<i>c</i>	.		$Cmc2_1 = \begin{pmatrix} Cmc2_1 \\ Ama2 \end{pmatrix}$	<i>Cmcm</i>
<i>mmmC</i>	.	.	<i>a</i>		<i>C2ma = Abm2</i>	<i>Cmma</i>
<i>mmmC</i>	.	<i>c</i>	<i>a</i>		<i>C2ca = Aba2</i>	<i>Cmca</i>
<i>mmmC</i>	<i>c</i>	<i>c</i>	.		<i>Ccc2</i>	<i>Cccm</i>
<i>mmmC</i>	<i>c</i>	<i>c</i>	<i>a</i>			<i>Ccca</i>
<i>mmmI</i>	.	.	.	$\left[\begin{matrix} I222 \\ I2_12_12_1 \end{matrix} \right]$	<i>Imm2</i>	<i>Immm</i>
<i>mmmI</i>	.	<i>a</i>	.		<i>Ima2</i>	<i>Imam = Imma</i>
<i>mmmI</i>	<i>b</i>	<i>a</i>	.		<i>Iba2</i>	<i>Ibam</i>
<i>mmmI</i>	<i>b</i>	<i>c</i>	<i>a</i>			<i>Ibca</i>
<i>mmmF</i>	.	.	.	<i>F222</i>	<i>Fmm2</i>	<i>Fmmm</i>
<i>mmmF</i>	<i>d</i>	<i>d</i>	.		<i>Fdd2</i>	
<i>mmmF</i>	<i>d</i>	<i>d</i>	<i>d</i>			<i>Fddd</i>

Notes: (1) Space groups shown in bold type, e.g. ***P2₁2₁2₁***, are uniquely determinable when the Laue group is known. (2) Space groups shown in italic type, e.g. *Pccm*, are not uniquely determinable even when the Laue group is known. (3) Special pairs of space groups are enclosed in brackets, e.g. [*I222*, *I2₁2₁2₁*]. (4) Space groups enclosed in parentheses, e.g. *Pma2*, *Pc2m*, are determinable if the point group and its orientation are known. (5) In rows containing two symbols, e.g. *Pc2m* and *Pma2*, the symbol on the right is the standard setting, whether or not it is in parentheses

In Table 2.7, we list the diffraction symbols for the orthorhombic space groups. A full discussion of diffraction symbols for the 230 space groups may be found in the *International Tables for X-Ray Crystallography* (2002, Volume A) or (1965, Volume I).

2.10 Some Other Types of Symmetry

The symmetry concepts dealt with so far have referred to the classical “non-color” groups. Consideration of other patterns, such as those of wallpapers, tiled walls and floors of the Alhambra, reveal the existence of *color symmetry*, the simplest example of which is black-white symmetry.

An example of the classical symmetry that we have been studying is shown in Fig. 2.40. At the bottom of the illustration there are three fourfold rotation points, assuming a two-dimensional pattern. If we choose the center point as an origin, then another three points in identical orientation form the corners of a plane unit cell, set at 45° to the borders of the figure. It may be found convenient to make a copy of the figure for this study. Not surprisingly, twofold rotation points exist at the mid-points of the unit-cell edges, but the fourfold point at the center of the unit cell is in a different orientation from those at the corners. There are also *m* lines and *g* lines in the pattern: the plane group is $p4mg$: see also Fig. 2.22; $p4mg \equiv p4gm$ by interchange of axes.

2.10.1 Black-White Symmetry

The simplest nonclassical symmetry is *black-white* symmetry, of which Fig. 2.41 is an example. The elements of this pattern are black beetles and white beetles, and the same symmetry elements as in Fig. 2.40 are present in this illustration. The *m* lines in the figure are classical, but the *g* lines involve a color change from white to black and vice versa as do the fourfold rotation points. The plane group may be designated $p4'gm$.

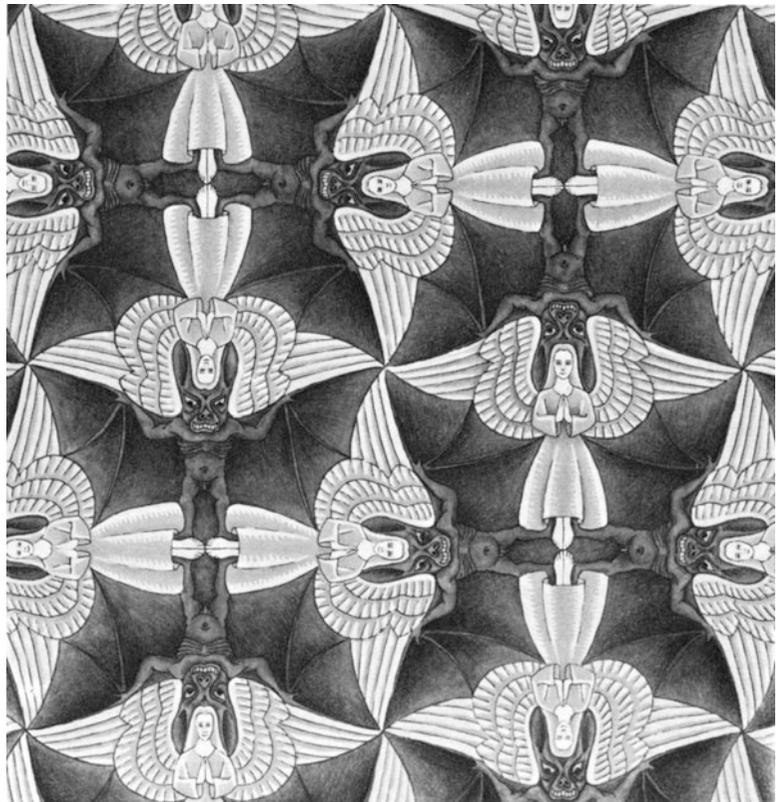
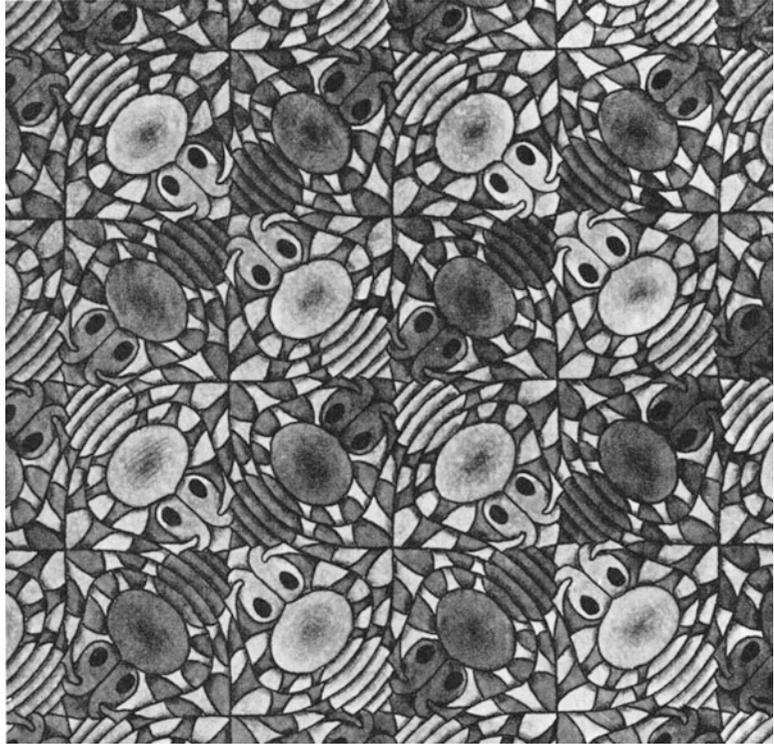


Fig. 2.40 Classical plane group of symmetry $p4mg$ (see also Fig. 2.22) (Macgillavry CH (1965) Symmetry aspects of M. C. Escher's periodic drawings. Reproduced by courtesy of I. U. Cr.). Scheltema and Holkema, Bohn (for I. U. Cr., 1976)

Fig. 2.41 Black/white plane group of symmetry $p4'gm$ (Macgillavry CH (1965) Symmetry aspects of M. C. Escher's periodic drawings. Reproduced by courtesy of I. U. Cr.)



Potassium Chloride

A practical example of very closely black-white symmetry is found in the structure of potassium chloride, which consists of the isoelectronic K^+ and Cl^- ions, Fig. 2.42. Because X-rays are scattered by electrons in a crystal structure, each of these species appears identical in an X-ray beam. Thus, the structure appeared on first examination to be based on a cubic P unit cell,⁸ since the resolution of the X-ray pattern at that time was not high.

After other alkali halides, notably sodium chloride, had been examined and their structures found to be cubic F , a more detailed examination showed that potassium chloride, too, was cubic F , and the true repeat distance was revealed. The X-ray reflections that would have been indicated the F cubic structure of potassium chloride were too weak to be revealed by the first experiments with the X-ray ionization spectrometer. The correct repeat period is found also by neutron scattering, since the scattering powers of the K^+ and Cl^- species differ significantly for neutron radiation, Sect. 12.5.

2.10.2 Color Symmetry

As an example of *color symmetry*, we examine Fig. 2.43. It comprises fish in four different colors and orientations, but all fish of any given color have identical orientations. The 90° difference in orientation between the pairs white-green, green-red, red-blue, and blue-white fish indicate the presence of fourfold color-rotation points. The almost square elements of fins, of sequence white,

⁸ See Bibliography (Bragg 1949).

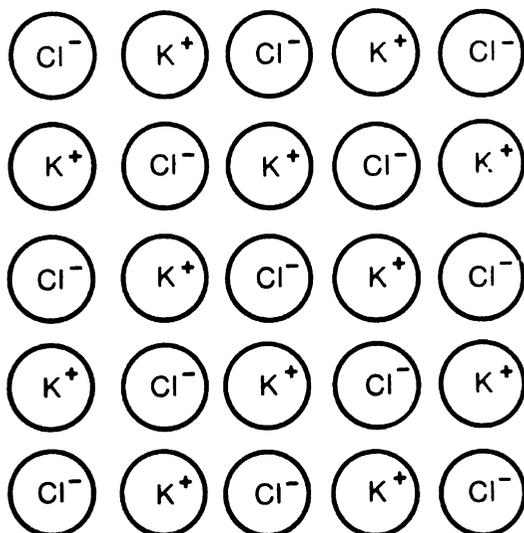


Fig. 2.42 The structure of potassium chloride, KCl, as seen in projection on to a cube face. Since K^+ and Cl^- are isoelectronic (18 electrons each), their scattering of X-rays (q.v.) is closely similar

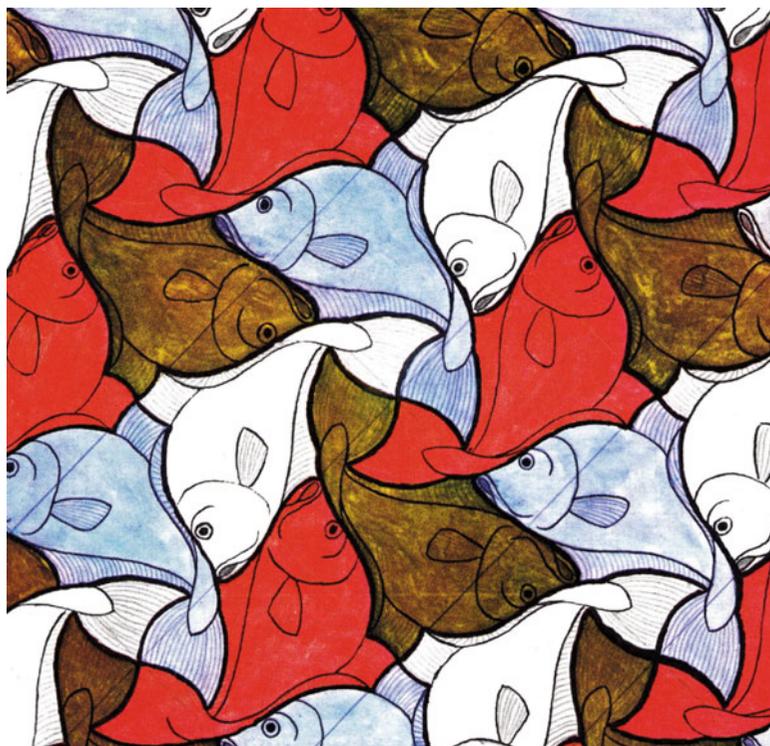


Fig. 2.43 An example of a color symmetry plane group (Macgillavry CH (1965) Symmetry aspects of M. C. Escher's periodic drawings. Reproduced by courtesy of I. U. Cr.)

green, red, blue, at the bottom center of the figure and three others in similar orientation form the corners of a square unit cell.

The fourfold color-rotation point at the center of the unit cell, consisting of areas of fish tails, shows the same color sequence but in a different orientation. The twofold rotation points are again evident at the mid-points of the cell edges. In this pattern, however, the twofold rotations involve a change of color, as indicated by the motifs at the fourfold rotation points: they are twofold *color-rotation* points.

For further discussions on black-white and color symmetry, the reader is referred to the works of Macgillavry and Shubnikov listed in the Bibliography at the end of the chapter.

2.11 Problems

- 2.1. Figure P2.1a shows the molecule of cyclosporin H repeated by translations in two dimensions. In Fig. P2.1b, the molecules are related also by twofold rotation operations, while still subjected to the same translations as in Fig. P2.1a. Four parallelogram-shaped, adjacent repeat units of pattern from an ideally infinite array are shown in each diagram. Convince yourself that

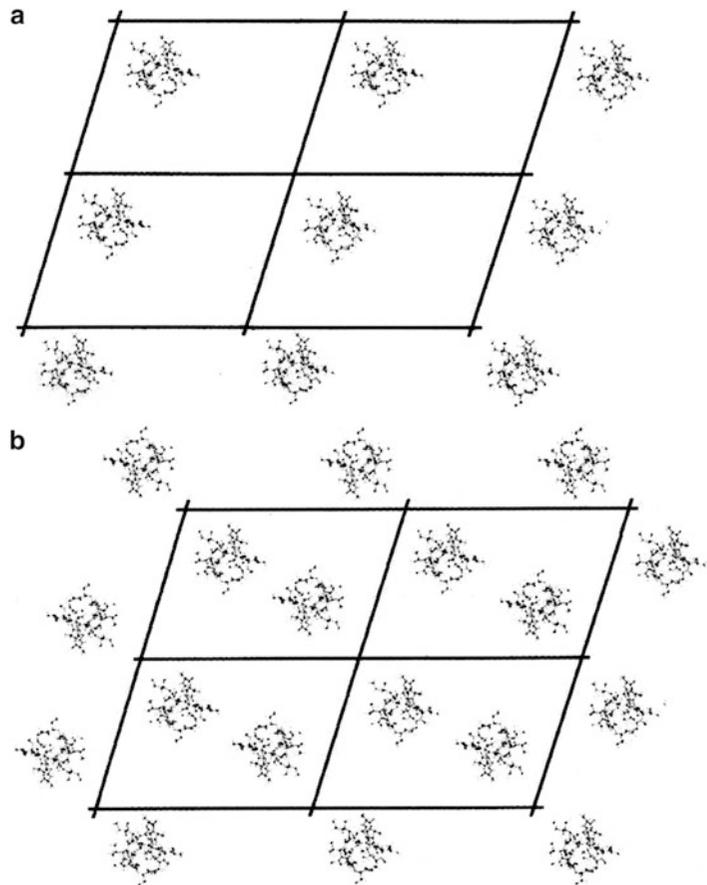


Fig. P2.1 (a) The molecule of cyclosporin H repeated by translations in two dimensions. (b) The molecules are related also by twofold rotation operations

Fig. P2.1a is formed by repeating a single molecule by the unit-cell translations shown, and that Fig. P2.1b follows from it by the addition of a single twofold operation acting at any parallelogram corner. Furthermore, for Fig. P2.1b state in words:

- (a) The locations of all twofold symmetry operators belonging to a single parallelogram unit.
 (b) How many of these twofold operators are unique to a single parallelogram unit?
- 2.2. Two nets are described by the unit cells (1) $a = b$, $\gamma = 90^\circ$ and (2) $a = b$, $\gamma = 120^\circ$. In each case: (a) What is the symmetry at each net point? (b) To which two-dimensional system does the net belong? (c) What are the results of centering the unit cell?
- 2.3. A monoclinic F unit cell has the dimensions $a = 6.000 \text{ \AA}$, $b = 7.000 \text{ \AA}$, $c = 8.000 \text{ \AA}$, and $\beta = 110.0^\circ$. Show that an equivalent monoclinic C unit cell, with an *obtuse* β angle, can represent the same lattice, and calculate its dimensions. What is the ratio of the volume of the C cell to that of the F cell?
- 2.4. Carry out the following exercises with drawings of a tetragonal P unit cell:
 (a) Center the B faces. Comment on the result.
 (b) Center the A and B faces. Comment on the result.
 (c) Center all faces. What conclusions can you draw now?
- 2.5. Calculate the length of $[31\bar{2}]$ for both unit cells in Problem 2.3.
- 2.6. The relationships $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$ or 90° or 120° , and $\gamma = 90^\circ$ may be said to define a triclinic system. Is this an eighth system? Give reasons for your answer.
- 2.7. (a) Draw a diagram to show the symmetry elements and general equivalent positions in $c2mm$, origin on $2mm$. Write the coordinates and point symmetry of the general and special positions, in their correct sets, and give the conditions limiting X-ray reflections in this plane group. (b) Draw a diagram of the symmetry elements in plane group $p2mg$, origin on 2 ; take care not to put the twofold point at the intersection of m and g . Why? On the diagram, insert each of the motifs P, V, and Z in turn, each letter drawn in its most symmetrical manner, using the *minimum* number of motifs consistent with the space-group symmetry.
- 2.8. (a) Continue the study of space group $P2_1/c$, Sect. 2.7.5. Write the coordinates of the general and special positions, in their correct sets. Give the limiting conditions for all sets of positions, and write the plane-group symbols for the three principal projections. Draw a diagram of the space group as seen along the b axis. (b) Biphenyl, , crystallizes in space group $P2_1/c$ with two molecules per unit cell. What can be deduced about both the positions of the molecules in the unit cell and the molecular conformation? The benzene rings in the molecule may be assumed to be planar.
- 2.9. Write the coordinates of the vectors between all pairs of general equivalent positions in $P2_1/c$ with respect to the origin, and note that they are of two types. What is the "weight," or multiplicity, of each vector set? Remember that $-\frac{1}{2}$ and $+\frac{1}{2}$ in a coordinate are crystallographically equivalent, because we can always add or subtract 1 from a fractional coordinate without altering its crystallographic implication.
- 2.10. The orientation of the symmetry elements in the orthorhombic space group $Pban$ may be written as follows⁹:

$$\begin{array}{l} \bar{1} \text{ at } 0, 0, 0 \text{ (choice of origin)} \\ \left. \begin{array}{l} b \text{ - glide } \parallel (p, y, z) \\ a \text{ - glide } \parallel (x, q, z) \\ n \text{ - glide } \parallel (x, y, r) \end{array} \right\} \text{(from the space - group symbol)} \end{array}$$

⁹In general, the symbol \parallel in this context indicates the plane (or line) specified; for example, the b -glide plane will be the plane (p, y, z) .

Determine p , q , and r from the following scheme, using the fact that $\mathbf{n} \mathbf{a} \mathbf{b} \equiv \mathbf{1}$:

$$\begin{array}{ccc}
 x, y, z & \xrightarrow{-b} & 2p - x, -\frac{1}{2} + y, z \\
 \downarrow i & & \downarrow a \\
 \{ \dots, \dots, \dots & \xleftarrow{-n} & \dots, \dots, \dots
 \end{array}$$

- 2.11. Construct a space-group diagram for $Pbam$, with the origin at the intersection of the three symmetry planes. List the coordinates of both the general equivalent positions and the centers of symmetry. Derive the standard coordinates for the general positions by transforming the origin to a center of symmetry.
- 2.12. Show that space groups Pa , Pc , and Pn represent the same pattern, but that Ca is different from Cc . What is the more usual symbol for space group Ca ? What would be the space group for Cc after an interchange of the x and z axes? Is Cn another monoclinic space group?
- 2.13. For each of the space groups $P2/c$, $Pca2_1$, $Cmcm$, $P4_21c$, $P6_122$, and $Pa3$:
- Write down the parent point group and crystal system.
 - List the full meaning conveyed by the symbol.
 - State the independent conditions limiting X-ray reflections.
 - List the Buerger diffraction symbols for these space groups.
- 2.14. Consider Fig. 2.25. What would be the result of constructing this diagram with Z alone, and not using its mirror image?
- 2.15. (a) Draw a P unit cell of a cubic lattice in the standard orientation.
 (b) Center the A faces. What system and standard unit-cell type now exist?
 (c) From the position at the end of (b), let c and all other lines parallel to it be angled backward a few degrees in the ac plane. What system and standard unit-cell type now exist?
 From the position at the end of (c), let c and all other lines parallel to it be angled sideways a few degrees in the bc plane. What system and standard unit-cell type now exist? For (b) to (d), write the transformation equations that take the unit cell as drawn into its standard orientation.
- 2.16. Set up matrices for the following symmetry operations: $\bar{4}$ along the z axis, m normal to the y axis. Hence, determine the Miller indices of a plane obtained by operating on (hkl) by $\bar{4}$, and on the resulting plane by the operation m . What are the nature and orientation of the symmetry element represented by the given combination of $\bar{4}$ followed by m ?
- 2.17. The matrices for an n -glide plane normal to a and an a -glide plane normal to b in an orthorhombic space group are as follows:

$$\begin{array}{ccc}
 \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} & + & \begin{bmatrix} \frac{1}{2} \\ 0 \\ 0 \end{bmatrix} \\
 \mathbf{a} & & \mathbf{t}
 \end{array}
 \quad
 \begin{array}{ccc}
 \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & + & \begin{bmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} \\
 \mathbf{n} & & \mathbf{t}
 \end{array}$$

What are the nature and orientation of the symmetry element arising from the combination of n followed by a ? What is the space-group symbol and its class?

- 2.18. (a) Determine the matrices for both a 6_3 rotation about $[0, 0, z]$ and a c -glide plane normal to the y axis and passing through the origin in space group $P6_3c*$. Use the fact that a threefold right-handed rotation converts the point x, y, z to $\bar{y}, x - y, z$, and that $2 \mathbf{3}^2 = \mathbf{6}$. (b) What is symmetry represented by the symbol $*$ in the space group symbol and what are the point-group and

- space-group symbols? (c) What is the matrix for the symmetry operation found in (b)? (d) Draw a diagram for the space group. List the number of general equivalent positions, their Wyckoff notation, point symmetry, coordinates, and conditions limiting reflections for the space group. (d) Are there any special equivalent positions? If so, list them as under (c).
- 2.19. A unit cell is determined as $a = b = 3 \text{ \AA}$, $c = 9 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. Later, it proves to be a triply primitive hexagonal unit cell. With reference to Fig. 2.11, determine the equations for the unit-cell transformation $R_{\text{hex}} \rightarrow R_{\text{obv}}$, and calculate the parameters of the rhombohedral unit cell.
- 2.20. In relation to Problem 2.19, given the plane $(13\bar{4})$ and zone symbol $[\bar{1}\bar{2} * 3]$ in the hexagonal unit cell, determine these parameters in the obverse rhombohedral unit cell. The symbol $*$ here indicates that the three integers given relate to the x , y , and z axes, respectively.
- 2.21. By means of a diagram, or otherwise, show that a site x, y, z reflected across the plane (qqz) in the tetragonal system has the coordinates $q - y, q - x, z$ after reflection.
- 2.22. Deduce a diffraction symbol table for the monoclinic space groups.
- 2.23. Draw the projection of an orthorhombic unit cell on (001) , and insert the trace of the (210) plane and the parallel plane through the origin.
- (a) Consider the transformation $\mathbf{a}' = \mathbf{a}/2$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$. Using the appropriate transformation matrix, write the indices of the (210) plane with respect to the new unit cell. Draw the new unit cell and insert the planes at the same perpendicular spacing, starting with the plane through the origin. Does the geometry of the diagram confirm the indices obtained from the matrix?
- (b) Make a new drawing, like the first, but now consider the transformation $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}/2$, $\mathbf{c}' = \mathbf{c}$. What does (210) become under this transformation? Draw the new unit cell and insert the planes as before. Does the geometry confirm the result from the matrix?
- 2.24. Why are space groups $Cmm2$ and $Amm2$ distinct, yet $Cmmm$ and $Ammm$ are equivalent?
- 2.25. An orthorhombic P unit cell has the dimensions $a = 5.50 \text{ \AA}$, $b = 6.75 \text{ \AA}$, $c = 12.20 \text{ \AA}$, and their reciprocals ($\kappa = 1$) are $a^* = 0.1818 \text{ \AA}^{-1}$, $b^* = 0.1481 \text{ \AA}^{-1}$, $c^* = 0.08197 \text{ \AA}^{-1}$. Use the matrix \mathbf{M} to transform: (a) The unit cell. (b) The Miller indices (312) . (c) The zone symbol $[102]$. (d) The reciprocal unit cell dimensions. (e) The point $x = 0.3142$, $y = 0.4703$, $z = -0.5174$.

$$\mathbf{M} = \begin{bmatrix} 1 & \bar{1} & \frac{1}{2} \\ 1 & 1 & -\frac{1}{2} \\ \frac{1}{4} & \frac{3}{4} & \frac{1}{8} \end{bmatrix}$$

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