

## CHAPTER 3

## THREE-DIMENSIONAL SPACE GROUPS

We now proceed to generate three-dimensional space symmetry groups by a procedure analogous to that followed in the case of two dimensions. Three-dimensional lattices are described and then the symmetry operations (glide and screw) that combine point operations with translation are discussed. Finally it is shown how the three-dimensional space groups arise. No effort is made to be systematic or complete (there are 230 three-dimensional space groups), however the ideas involved should be clear to the those who have read and understood Chapters 1 and 2.

## 3.1 Three-dimensional lattices

A unit cell of a three-dimensional lattice has edges that are three non-coplanar vectors  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  with magnitudes  $a$ ,  $b$  and  $c$ . The angle between  $\mathbf{a}$  and  $\mathbf{b}$  is  $\gamma$ ; that between  $\mathbf{b}$  and  $\mathbf{c}$  is  $\alpha$  and that between  $\mathbf{c}$  and  $\mathbf{a}$  is  $\beta$ . The unit cell of the lattice is specified by the parameters  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ . There are 14 three-dimensional Bravais lattices each having a different space group symmetry (compare five in two dimensions).

As in the two-dimensional case, centered cells are sometimes chosen for convenience<sup>1</sup> (see Fig. 3.1 below). Symbols are given to the lattices according to the kind of centering (recall the symbols  $p$  and  $c$  for two-dimensional lattices). These are given in Table 3.1.

Table 3.1. Symbols for three-dimensional lattices.  $n$  is the number of lattice points per unit cell

symbol	name	description	$n$
$P$	primitive	lattice points at corners only	1
$R$	rhombohedral	lattice points at corners only	1
$A$	A-centered	lattice points at corners and centers of $\mathbf{b}, \mathbf{c}$ faces	2
$B$	B-centered	lattice points at corners and centers of $\mathbf{a}, \mathbf{c}$ faces	2
$C$	C-centered	lattice points at corners and centers of $\mathbf{a}, \mathbf{b}$ faces	2
$I$	body-centered	lattice points at corners and body center	2
$F$	face-centered	lattice points at corners and all face centers	4

The symbol  $R$  is reserved for the lattice having a primitive cell of a particular shape ( $a = b = c$ ,  $\alpha = \beta = \gamma$ ) as explained below.

The 14 Bravais lattices are divided into seven crystal systems according to the

<sup>1</sup>We emphasize that a primitive cell can *always* be used for any lattice. The advantage of using centered cells is that it allows the use of orthogonal axes where they would not otherwise be possible.

constraints on the unit cell parameters imposed by symmetry. These are summarized in Table 3.2. The parameters are considered to be able to take any value within the constraints imposed. Note that there are 15 entries in the table. The reason is that the *lattice* for a crystal with trigonal symmetry and  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $a = b$  is the same as that for a hexagonal crystal. The other lattice ( $R$ ) listed as trigonal is often referred to a centered hexagonal unit cell.<sup>1</sup>

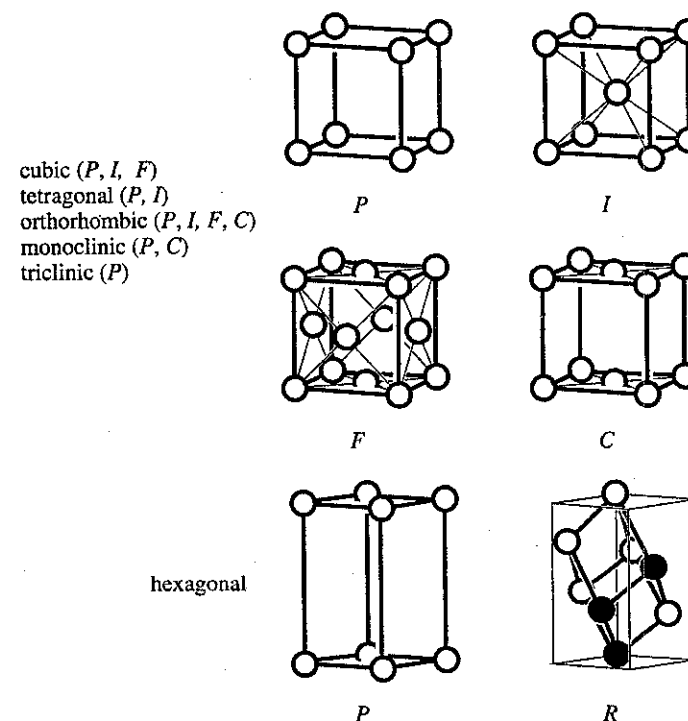


Fig. 3.1. Primitive and centered unit cells for lattices (see text).

Conventional unit cells for lattices are shown in Fig. 3.1 in which the *shape* of the unit

<sup>1</sup>Different definitions of crystal system are found. If the classification is by the symmetry of the lattice, then the hexagonal and trigonal symmetries with a primitive hexagonal lattice ( $P$ ) belong to the same system, but there is a separate system for symmetries with a rhombohedral lattice ( $R$ ). In the *International Tables* the classification (adopted here) is by space group symmetry. Trigonal symmetries (including rhombohedral) possess only 3-fold axes (all parallel)—hexagonal symmetries contain 6-fold axes.

cell is not necessarily cubic; for example a cell with just one face centered cannot have cubic symmetry. The data for the space groups in the *International Tables* refer to these cells.

Table 3.2. The three-dimensional Bravais lattices.

system	constraints	lattices
triclinic	none	<i>P</i>
monoclinic	$\alpha = \gamma = 90^\circ$	<i>P, C</i>
orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	<i>P, C, I, F</i>
tetragonal	$\alpha = \beta = \gamma = 90^\circ, a = b$	<i>P, I</i>
[trigonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ, a = b$	<i>P</i> ]
trigonal	$a = b = c, \alpha = \beta = \gamma$	<i>R</i>
hexagonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ, a = b$	<i>P</i>
cubic	$\alpha = \beta = \gamma = 90^\circ, a = b = c$	<i>P, I, F</i>

A monoclinic lattice has 2-fold axes in one direction only and the standard choice of axes for monoclinic cells is with *b* parallel to the 2-fold axes. However other choices are found in the literature. The conventional choice of axes for a centered monoclinic cell is such that the *a, b* face (i.e. the face containing *a* and *b*) is centered, so that the lattice symbol is *C*. However interchanging the names of *a* and *c* (and reversing the direction of *b* to maintain a right-handed coordinate system) will result in the *b, c* face being centered and the lattice symbol now becomes *A*. Yet another choice of axes will give a body-centered cell as shown in Fig. 3.2. This means that the *same* lattice can have *different* symbols (*A*, *C*, or *I*) according to the labeling of the axes and/or choice of unit cell vectors.

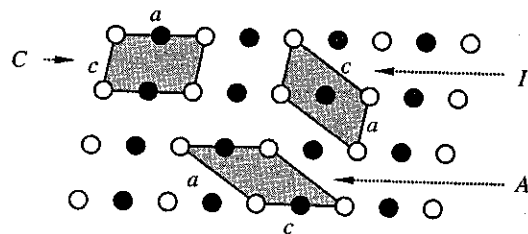


Fig 3.2. Three choices of unit cell for a centered monoclinic lattice. *b* is normal to the plane of the paper. Open circles are at  $y = 0$  and filled circles are at  $y = 1/2$ . On the top left is a *C*-centered cell, on the top right is a body-centered (*I*) cell and below is an *A*-centered cell.

The coordinate axes for conventional choices of cell for orthorhombic lattices are mutually perpendicular. The one-face-centered orthorhombic lattice is normally labeled *C*; this means that the *c* direction is normal to the centered face. It should be clear that

relabeling the axes can again result in the lattice being *B* or *A*.

Rhombohedral crystals are often described using a centered hexagonal cell (i.e. one with  $\alpha = \beta = 90^\circ, \gamma = 120^\circ, a = b$ ) with lattice points at 0,0,0 (the unit cell corners) and at  $1/3, 2/3, 2/3$  and at  $2/3, 1/3, 1/3$ . We will discuss this again, but note now that the *R* lattice does not have 6-fold symmetry (the symmetry at the points of the lattice is  $\bar{3}m$ ) even though the cell is referred to as "hexagonal." In the bottom of Fig. 3.1 we show on the left a primitive hexagonal cell and on the right we show (heavy lines) a primitive rhombohedral cell with a centered hexagonal cell lightly outlined (for more detail see Figs. 4.4 and 4.5); the hexagonal cell contains three lattice points (filled circles).

The cubic *F* lattice can be described using a primitive rhombohedral cell with  $\alpha = 60^\circ$ , and the cubic *I* lattice by a primitive rhombohedral cell with  $\alpha = \cos^{-1}(-1/3) = 109.47^\circ$ .

Table 3.3. Names and extended symbols for Bravais lattices.

symbol	point symmetry	name
1. <i>aP</i>	$\bar{1}$	primitive triclinic (anorthic)
2. <i>mP</i>	$2/m$	primitive monoclinic
3. <i>mC</i>	$2/m$	one-face-centered monoclinic
4. <i>oP</i>	$mmm$	primitive orthorhombic
5. <i>oC</i>	$mmm$	one-face-centered orthorhombic
6. <i>oI</i>	$mmm$	body-centered orthorhombic
7. <i>oF</i>	$mmm$	(all) face-centered orthorhombic
8. <i>tP</i>	$4/mmm$	primitive tetragonal
9. <i>tI</i>	$4/mmm$	body-centered tetragonal
10. <i>hP</i>	$6/mmm$	primitive hexagonal
11. <i>hR</i>	$\bar{3}m$	rhombohedral [using a hexagonal cell]
12. <i>cP</i>	$m\bar{3}m$	primitive cubic
13. <i>cI</i>	$m\bar{3}m$	body-centered cubic
14. <i>cF</i>	$m\bar{3}m$	(all) face-centered cubic

Lattices are sometimes given extended symbols that consist of first (in lower case) a letter that indicates the unit cell shape and then a symbol (upper case) that indicates the centering. Using this system<sup>1</sup> the symbols for lattices are given in Table 3.3 which also lists the point symmetry at a lattice point. The space group symmetry of the lattice (see Exercise 3) is simply found by combining the lattice symbol with the point group symbol (so that for example the face-centered cubic lattice has symmetry  $Fm\bar{3}m$ ). Note that every lattice is centrosymmetric.

<sup>1</sup>An example of the use of this system is in *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (see Book List). In this work structures are classified by a *Pearson symbol* which is one of the lattice symbols followed by the number of atoms in the unit cell. Thus the rutile structure (§ 3.4) is found under the heading *tP6*. The *Inorganic Crystal Structure Database* (Book List) can also be searched by *Pearson symbol*.

Note that in Table 3.3 above, trigonal is subsumed under hexagonal. In practice there is usually no problem with distinguishing trigonal and hexagonal symmetries, but when there is a wish to avoid ambiguity the following are useful:

hexagonal ( <i>sensu lato</i> )	includes trigonal symmetry
hexagonal ( <i>sensu stricto</i> )	only symmetry groups with a 6-fold axis

### 3.2 Glide and screw axes

Just as in two dimensions, before obtaining space groups by combining translational symmetry with point symmetry operations, we have to consider the possibility of compound symmetry operations that are combinations of point symmetry operations with translation. Two cases are recognized. These are: *glide*, which we met in two dimensions, and which is a combination of *reflection* and *translation*; and a new operation, that of *screw*, which is a combination of *rotation* and *translation*.

#### 3.2.1 Glide

Glide combines reflection in a plane (the *glide plane*) with translation. The translation must be parallel to the glide plane and in a direction parallel to a lattice vector. The magnitude of the glide translation must be one-half that of the corresponding lattice vector so that action of the glide operation twice will transform a point to an identical point related to the first by a lattice vector. Figure 3.3 illustrates the glide symmetry operation (compare Fig. 1.11, p. 14 and also Fig. 3.8, p. 67).

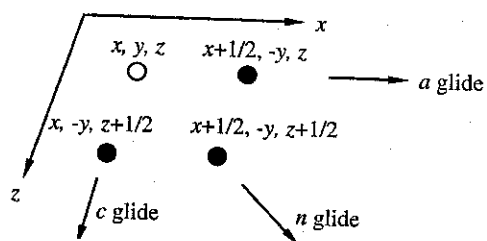


Fig. 3.3. Illustrating glide in the monoclinic system (*b* is normal to the page). The glide plane is in the plane of the paper and the coordinates of points produced by one operation of each of *a*, *c*, and *n* glide are shown (open circle to a filled circle). The origin has been chosen so that the glide plane is at  $y = 0$ .

If the glide is parallel to *a*, *b*, or *c* the symbol for the glide plane that appears in a space group symbol is *a*, *b* or *c* respectively. This case is called *axial glide*. A further possibility is that with (e.g.) a glide plane parallel to the *a,b* plane, the glide is along the direction  $\mathbf{a} \pm \mathbf{b}$  (also a lattice vector!). The glide translation is then  $(\mathbf{a} \pm \mathbf{b})/2$  and the symbol is *n*.

Likewise if the glide plane is parallel to the *a,c* plane, the glide translation may also be  $(\mathbf{a} \pm \mathbf{c})/2$  and if the glide plane is parallel to the *b,c* plane, the glide translation may be  $(\mathbf{b} \pm \mathbf{c})/2$ . The symbol is *n* in each of these cases also as the direction of the glide translation (now called *diagonal glide*) is clear from the orientation of the glide plane.

In lattices with centered cells there are primitive lattice vectors shorter than those defining the unit cell edges. The glide direction may be along a primitive cell vector such as  $(\mathbf{a} \pm \mathbf{b})/2$  etc. (face-centered cells) or  $(\mathbf{a} \pm \mathbf{b} \pm \mathbf{c})/2$  (body-centered cells). In these instances the magnitude of the glide vector is one-half that of the primitive-lattice vector and the symbol is *d*. Glide of this sort is called *diamond glide* as it is one of the symmetry elements of the diamond structure (which is face-centered cubic).

#### 3.2.2 Screw

Screw axes are a combination of proper rotations with translation. The translation must be along the rotation axis (why?). Let the axis be *c*; the combined operation is then a counterclockwise rotation about *c* followed by a translation *t* along the  $+\mathbf{c}$  direction.<sup>1</sup> Now consider an *N*-fold screw axis. Repeating the screw operation *N* times must result in the transformation of a point to an identical point separated from the original one by  $n\mathbf{c}$ , where *n* is an integer less than *N*.<sup>2</sup> Thus we have at once that  $Nt = nc$  or  $t = (n/N)\mathbf{c}$ . The symmetry element corresponding to these symmetry operations is called an  $N_n$  screw axis. Figure 3.4 illustrates the case of a  $3_1$  axis ( $N = 3$ ,  $n = 1$ ).

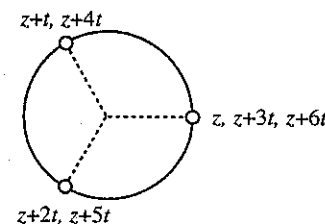


Fig. 3.4. Illustrating the effect of six applications of a  $3_1$  screw axis with translation *t* on a point originally with height *z*. The *z* axis is normal to the page with the  $+\mathbf{z}$  direction up.

In general then we have screw axes  $N_n$  with  $1 \leq n < N$  and  $N = 2, 3, 4, 6$ . The

<sup>1</sup>As in the case of glide, the order of carrying out the components of the combined operation is unimportant.

<sup>2</sup>This should be obvious from the definition of an *N*-fold axis. For a point symmetry element, carrying out the *N*-fold operation *N* times is equivalent to the identity operation. For the corresponding screw axis, carrying out the operation *N* times must be equivalent to a lattice translation, as we consider points separated by a lattice translation (which may be a multiple of a primitive translation) also to be *identical*. The case of  $n = N$  is the same as a pure rotation followed separately by a lattice translation.

possibilities are:

$$\begin{aligned} 2 &\rightarrow 2_1 \\ 3 &\rightarrow 3_1, 3_2 \\ 4 &\rightarrow 4_1, 4_2, 4_3 \\ 6 &\rightarrow 6_1, 6_2, 6_3, 6_4, 6_5 \end{aligned}$$

Recall that the translation is  $n/N$  of the lattice repeat vector along the axis.

Let's examine  $3_1$  and  $3_2$  in more detail. Referred to axes with  $z$  along the screw direction and with  $x$  and  $y$  at right angles to  $z$ , and at  $120^\circ$  to each other (compare Fig. 1.5, p. 7), successive applications of  $3_1$  along the axis  $z=0$  will send a point at  $x, y, z$  to  $\bar{y}, x-y, z+1/3$ ;  $y-x, \bar{x}, z+2/3$ ;  $x, y, z+1$  (note that, as usual, we are measuring  $z$  in units of the repeat distance  $c$ ). The fourth point is identical to the first as it is just a lattice translation  $c$  away.

$3_2$  acting on  $x, y, z$  will give  $\bar{y}, x-y, z+2/3$ ;  $y-x, \bar{x}, z+4/3$ ;  $x, y, z+2$ . But note that we can always add or subtract an integer from the  $z$  coordinate so we could equally express the new coordinates as  $\bar{y}, x-y, z+2/3$ ;  $y-x, \bar{x}, z+1/3$ ;  $x, y, z+1$ .

Fig. 3.5 shows schematically a plot of these points. If the  $c$  axis were to be ascended by using successively higher points of  $3_1$  as steps, the path would be counterclockwise and a right-handed screw. Conversely, ascending  $3_2$  in the same way would result in clockwise motion along a left-handed screw.

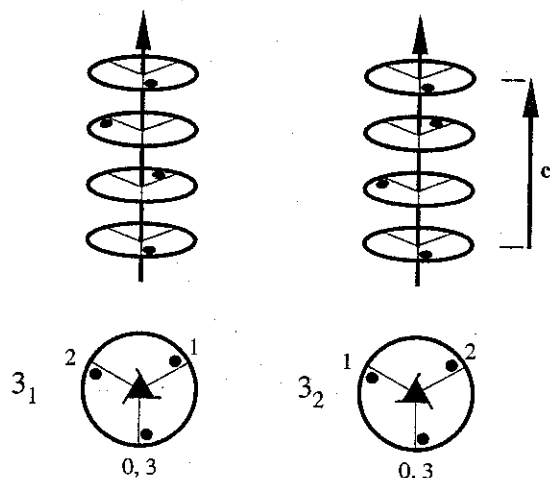


Fig. 3.5. Illustrating the operations of  $3_1$  (left) and  $3_2$  (right). The bottom portion is a projection down  $c$ . Numbers indicate heights in multiples of  $c/3$ . Notice the symbols for 3-fold screw axes.

The same discussion would hold for  $4_1$  and  $4_3$  (Fig. 3.6) except that now we use a

quarter turn and it takes four steps up the staircase to go up a height  $c$ .  $4_1$  is right-handed and  $4_3$  is left-handed. What about  $4_2$ ? Reference to the figure shows that at each point there are higher steps at the same height on the left and on the right so the ascent could be either clockwise or anticlockwise and  $4_2$  does not have a hand.

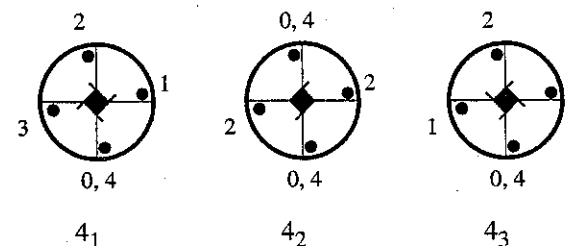


Fig. 3.6. Illustrating 4-fold screw axes. The numbers are elevations in multiples of  $c/4$ . Note that  $4_1$  and  $4_3$  include a  $2_1$  and that  $4_2$  includes a 2 axis. Notice also the symbols for 4-fold screw axes.

For 6-fold screws the possibilities are  $6_1, 6_2, 6_3, 6_4, 6_5$  (Fig. 3.7).  $6_1$  and  $6_5$  give right- and left-handed stairs related as mirror images (analogous to the pairs  $3_1, 3_2$  and  $4_1, 4_3$ ) but now there are six steps for each revolution.  $6_3$  is neutral (analogous to  $2_1$  and  $4_2$ ).  $6_2$  and  $6_4$  show a new feature: the points fall on two intertwined circular helices (*double helices*) as shown in Fig. 3.7.  $6_2$  is right-handed and  $6_4$  is left-handed.<sup>1</sup>

Some properties of screw axes (which also should be verified from the figures) are:

- $4_1, 4_3, 6_1, 6_3$  and  $6_5$  axes (only) include a  $2_1$  axis.
- $4_2, 6_2$  and  $6_4$  axes (only) include a 2 axis.
- $6_2$  and  $6_5$  axes include a  $3_2$  axis.
- $6_1$  and  $6_4$  axes include a  $3_1$  axis.
- A  $6_3$  axis includes a 3 axis.
- Points generated by  $6_2$  or  $6_4$  lie on a double helix.

Also to be noted is that there can be a mirror normal to  $2_1, 4_2$ , and  $6_3$  but not to  $3_1, 3_2, 4_1, 4_3, 6_1, 6_2, 6_4$ , and  $6_5$  as the latter group have a hand.

It is important to realize that our labels "left-handed" and "right-handed" are arbitrary, just as they are for right- and left-handed nuts and bolts and coordinate systems. We could have used terms such as "positive" and "negative" (as in electricity) or even "north" and "south" (as in magnetism). Indeed, when talking about pure rotations, we used the terms "positive" and "negative." Thus we saw that the "right-handed" screw  $6_2$  contains a "left-

<sup>1</sup>A "spiral" (better "helical") staircase is a familiar example of an object with a screw axis. If the staircase continued indefinitely the axis would be  $N_1$  (right-handed) or  $N_{N-1}$  (left-handed). The famous "miraculous" staircase in the Loretto Chapel in Santa Fe, New Mexico is  $161_5$ . There is a nice double helix stairway in King's Park, Perth (Western Australia) that is  $56_2$ .

handed" screw  $3_2$ . Our stair climber could have ascended the  $3_2$  screw in an anti-clockwise ("right handed") sense if he took not the next highest step (up  $c/3$ ) but the step in the other direction (up  $2c/3$ —see Fig. 3.19, p. 87).

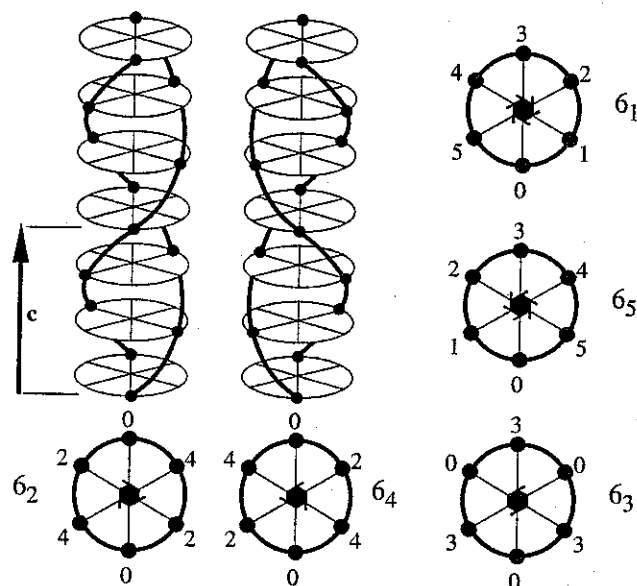


Fig. 3.7. Illustrating six-fold screw axes. The numbers are elevations in multiples of  $c/6$ . The double helices in  $6_2$  and  $6_4$  are suggested by heavy lines in the sketches in the top left (which correspond to the projections immediately below them).  $c$  is the repeat vector along the screw axis.

In this connection we quote from a famous lecture by Weyl<sup>1</sup>: "the inner structure of space does not permit us, except by arbitrary choice, to distinguish a left from a right screw...on [this fundamental concept] depends the entire theory of relativity...." If we were to pursue the subject here we would soon find ourselves in deep water.

Notice also that an asymmetric periodic object may well have screw axes of opposite hand as symmetry elements. An example is the cylinder packing labelled  $\beta$ -Mn in § 6.7.3 (p. 265).  $I4_1$  is discussed as an example of a space group with  $4_1$  and  $4_3$  axes in § 3.3.4 (p. 74). For more on screw axes and the "hand" (left or right) of crystals see § 3.6.

<sup>1</sup>Chapter 1 in *Symmetry* by H. Weyl [Princeton University Press (1952)]. This was written before the "non-conservation of parity" was discovered. On the latter topic in connection with hand, a readable account, that discusses Weyl's lecture, is Chapter 3 in *Elementary Particles* by C. N. Yang [Princeton University Press (1962)].

### 3.2.3 Comparison of screw and glide

In our illustrations of the effect of symmetry operations, for simplicity we show their effects on a point (a small circle). The reader should mentally replace the point with an asymmetric object. In Fig. 3.8 we contrast the effect of glide (arbitrarily labeled  $a$ ) with the effect of a  $2_1$  axis on an asymmetric object (a scalene triangle that is black on one side and white on the other).

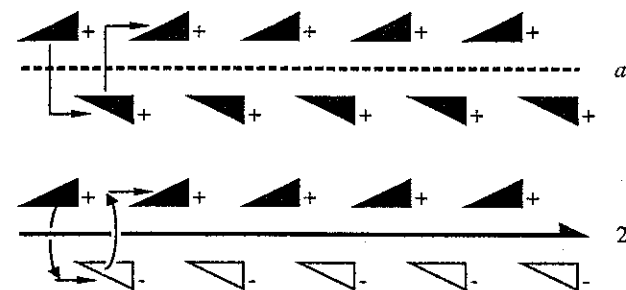


Fig. 3.8. Contrasting glide with  $2_1$ . Figures marked "+" are above the plane of the paper, and those marked "-" are below.

## 3.3 Three-dimensional space groups

We now consider how the space groups arise. We will consider just some of the simpler possibilities—our aim is to suggest how to proceed rather than to be rigorous. We emphasize that the immediate goal is that of being able to interpret (and use) space group symbols. The reader will find it helpful to work through the examples provided. It would also be very useful to have *International Tables A* at hand.

### 3.3.1 Triclinic space groups

In the triclinic system we have just a primitive lattice ( $P$ ) to combine with the point groups with 1-fold axes. The only possibilities are therefore  $P1$  and  $P\bar{1}$ .

### 3.3.2 Monoclinic space groups

In the monoclinic system we have to combine the  $P$  and  $C$  lattices with the point groups that have just one 2-fold axis ( $2$ ,  $m$  and  $2/m$ ). We then get the symmorphic groups  $P2$ ,  $Pm$ ,  $P2/m$ ,  $C2$ ,  $Cm$  and  $C2/m$ .

The next thing to do is to consider the possibilities that arise when 2 axes are changed to  $2_1$  axes and/or when mirrors are changed to glide. In the latter case we note that the mirror

planes are necessarily normal to **b** so that the glide planes are either *a*, *n* or *c*. However the labeling of the axes normal to **b** is arbitrary, so we adopt the convention (not universally adhered to) that the glide, if present, is *c* (see Fig. 3.12 below for the choice of axes that converts *Pc* to *Pn* or *Pa*). The distinct cases are listed in Table 3.4.

Table 3.4. The monoclinic space groups.

class	<i>P</i> lattice		<i>C</i> lattice	
2	<i>P2</i>	<i>P2<sub>1</sub></i>	<i>C2</i>	
<i>m</i>	<i>Pm</i>	<i>Pc</i>	<i>Cm</i>	<i>Cc</i>
<i>2/m</i>	<i>P2/m</i>	<i>P2<sub>1</sub>/m</i>	<i>P2/c</i>	<i>P2<sub>1</sub>/c</i>

The reader interested in confirming that this is indeed a full list might note that the combination of a *C* lattice with 2-fold rotation axes generates *2<sub>1</sub>* axes parallel to and interlaced with the 2 axes. Thus (see Fig. 3.9) *C2<sub>1</sub>* is the same as *C2*.

In Fig. 3.9, the two black triangles at the top left (at height *y* shown as “+”) are related by a 2-fold rotation axis. The pair to the right (at  $1/2+y$ ) are generated by *C* centering [ $(1/2, 1/2, 0)+$ ]. On the right the figure shows the symmetry elements generated by the combination of 2-fold rotations (symbolized by ellipses) and primitive unit cell translations [ $(a \pm b)/2$  and *c*]. Note the *2<sub>1</sub>* axes (symbolized by ellipses with two arms)—the reader should verify their existence in the pattern on the left in Fig. 3.9. The same pattern and symmetry elements would have been generated by starting with a *2<sub>1</sub>* axis and primitive unit cell translations.

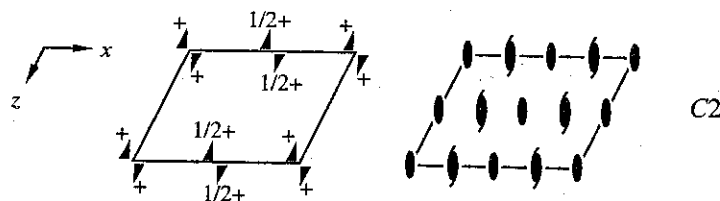


Fig. 3.9. Illustrating a unit cell of space group *C2*. **b** is the unique axis normal to the paper, **a** is horizontal and **c** runs down the page. Left: The pattern generated by 2-fold rotations, *C* centering and unit cell translations. Right: The generated symmetry elements.

We now consider space group *C2/m* (a rather common symmetry for crystals). Fig. 3.10 illustrates this space group in much the same way as Fig. 3.9 illustrated *C2*. A major difference is that a mirror plane at  $y = 0$  generates pairs of triangles above and below the plane and superimposed in the projection down **b** (and shown as gray triangles). This situation is symbolized by giving elevations as  $\pm$ . The *C* centering operation produces

corresponding triangles at elevations  $1/2 \pm$ . Note that there is also a mirror plane at  $y = 1/2$ . On the right the mirror plane is symbolized by a heavy bent line with arms parallel to the cell edges; by convention no elevation is shown for mirror planes at heights 0 and  $1/2$ . Also on the right the generated centers are shown as small open circles. Those with no elevations marked are at  $y = 0$  and  $y = 1/2$  and the site symmetry at these points is  $2/m$ . The other centers with elevations marked as “ $1/4$ ” are at  $y = 1/4$  and  $3/4$  and the symmetry at these points is  $\bar{1}$ . In a centrosymmetric crystal there are always eight centers per primitive cell (so in this case there are sixteen in the centered cell of twice the volume). It should be seen that *C2/m* also contains glide planes normal to **b**. These are symbolized in the same way as the mirror planes but with an arrow head pointing in the glide direction which can be seen to be **a**. These planes are at  $1/4$  and  $3/4$  (again by convention the elevation is just given as  $1/4$ ). The reader should verify the presence of the *a* glide operation noting that reflection in a plane at  $y = 1/4$  will transform an elevation “+” to “ $1/2-$ ” and so on. When we discuss subgroups of space groups, it will be seen that knowledge of the existence of the extra symmetry elements (*2<sub>1</sub>* axes and *a* glide in this example) is very useful.

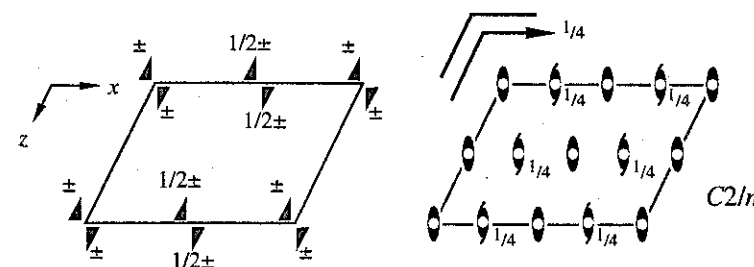


Fig. 3.10. Illustrating a unit cell of space group *C2/m*. **b** is the unique axis normal to the paper, **a** is horizontal and **c** runs down the page. Left: The pattern generated by the *2/m* axis, *C* centering and unit cell translations. Right: The generated symmetry elements.

Although *C2/m* contains glide planes, they are *a* glide, and *C2/c* is a distinct space group. Fig. 3.11 illustrates *C2/c* in the same way that Fig. 3.10 illustrated *C2/m*. Now triangles do not superimpose in projection with their mirror images, which are generated by the *c* glide plane at  $y = 0$ . The mirror images of black triangles are shown as white triangles and vice versa. The reader should work through this example as for *C2/m* discussed in the previous paragraph. Note now the existence of *n* glide planes (as indicated by the direction of the arrow) at  $y = 1/4$  and  $y = 3/4$ . In contrast to *C2/m*, in *C2/c* the 2-fold axes do not intersect centers and there are no mirror planes (only glide planes).

Even with **b** unique the three possibilities of choosing **a** and **c** (see e.g. Fig. 3.2) result in a variety of possible symbols for monoclinic space groups that are centered and/or have glide planes. Thus *C* can become *A* or *I*. In a similar way a glide *c* can become *a* or *n* as illustrated in Fig. 3.12.

Because there can be ambiguity about which axis is chosen as the unique axis it is a

common practice to use extended symbols with 1's as place markers (cf. § 2.4, p. 45) and the symbol is to be interpreted the same way as that for an orthorhombic symmetry group. Thus with  $b$  unique  $P2$  becomes  $P121$  (2-fold axis parallel to  $y$ ) and with  $c$  unique it becomes  $P112$  (2-fold axis parallel to  $z$ ).  $Pc$  is written  $P1c1$  or  $P11a$  and so on. Fortunately the *International Tables* (vol. A) considers all these possibilities. The various symbols encountered for monoclinic space groups are listed in the tables at the end of this book. The different choices of axes are referred to as different *settings* of the space group.

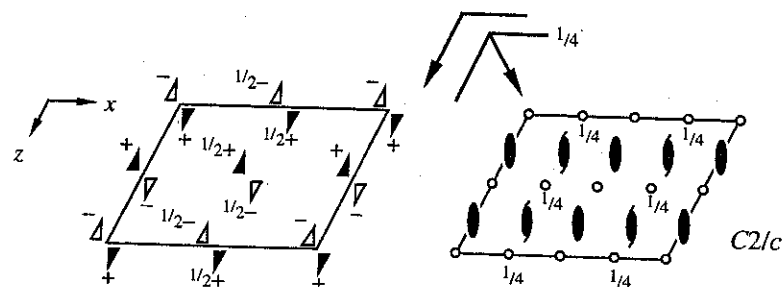


Fig. 3.11. Illustrating a unit cell of space group  $C2/c$ .  $b$  is the unique axis normal to the paper,  $a$  is horizontal and  $c$  runs down the page. Left: The pattern generated by the 2-axis,  $c$  glide,  $C$  centering and unit cell translations. Right: The generated symmetry elements.

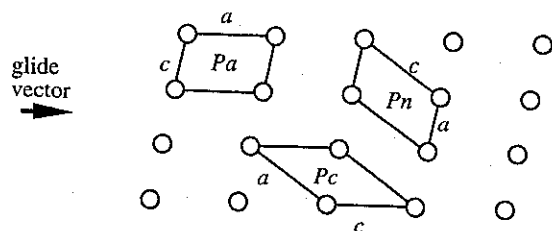


Fig. 3.12. Illustrating three choices of unit cell for  $Pc$ .  $b$  is the unique axis normal to the plane of the paper and the glide plane is in that plane. The glide vector is  $c/2$  ( $Pc$ ) =  $a/2$  ( $Pa$ ) =  $(a + c)/2$  ( $Pn$ ).

### 3.3.3 Orthorhombic space groups

In the orthorhombic system there are three axes at right angles with 2-fold symmetry elements along each axis. The point groups to consider are therefore  $222$ ,  $mm2$  and  $mmm$ . There are also four types of lattice ( $P$ ,  $C$ ,  $F$  and  $I$ ) to consider, so the number of possibilities becomes much greater (it turns out that there are 69 distinct orthorhombic

space groups). Thus in contrast to the monoclinic pair  $P2$  and  $P2_1$ , we have  $P222$ ,  $P222_1$ ,  $P2_12_12$  and  $P2_12_12_1$ .<sup>1</sup> Mirrors can become glide ( $a$ ,  $b$ ,  $c$ ,  $n$ , or  $d$ ). Because of this complexity it would take us much too long to systematically generate all the orthorhombic space groups in the manner suggested in the monoclinic case.

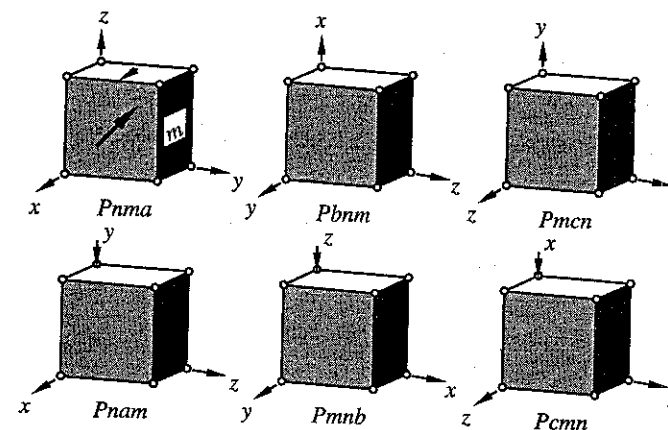


Fig. 3.13. Different settings of the space group  $Pnma$ . The diagrams show the orientations of the  $n$  glide plane (shaded, front face), the axial glide plane (unshaded, top face) and the mirror,  $m$  (black face) with respect to the axes. The arrows show the directions of the axes for a right-handed system.

Again we have to adopt some conventions for the labeling of axes. These are outlined in the *International Tables* and will not be given here. The conventions adopted there we call the standard setting; it is important to recognize that other settings are often chosen.<sup>2</sup> The significance of the order of symbols in a space group symbol is the same as that given in § 2.4 for point groups except that the first symbol represents the lattice type. Thus in the symbol  $Pnma$  the " $P$ " tells us that the lattice is primitive. The next three symbols indicate that there are respectively: an  $n$  glide plane normal to  $x$ , a mirror plane normal to  $y$  and then an  $a$  glide plane normal to  $z$ .<sup>3</sup> As there are six possible permutations of the  $x$ ,  $y$  and  $z$  axes, this space group can have six different symbols:  $Pnma$ ,  $Pbnm$ ,  $Pmcn$ ,  $Pnam$ ,  $Pmnb$  and  $Pcmn$ . Fortunately a concordance of symbols is given in the *International Tables* (see also the Tables at the end of the book). Figure 3.13 illustrates the arrangement of the

<sup>1</sup>Note that when there is an "odd man out" it is labeled the  $c$  axis in the standard setting. Thus  $P222_1$  not  $P2_122$  etc. similarly we have  $Pmm2$  and not  $Pm2m$  etc. as the standard setting.

<sup>2</sup>Mineralogists (and some others) often use the convention that  $c < a < b$ . Another recommendation, which we prefer, is to use standard settings, and to use  $a < b < c$  when there is flexibility of choice of all three axes (as in  $Pmmm$  etc.) and  $a < b$  in cases such as  $Pmm2$  where two axes can be chosen arbitrarily.

<sup>3</sup>The orientation of glide planes (as that of mirror planes) is given by the directions of their normals. Thus the direction of the normal to the  $n$  glide plane is parallel to the  $x$  direction (the  $n$  glide plane is normal to the  $x$  direction as stated).

symmetry elements with respect to the axes in this particular case.<sup>1</sup>

The full symbol for  $Pnma$  is  $P2_1/n2_1/m2_1/a$ . If the inversion center is removed one of the acentric space groups  $P2_12_12_1$ ,  $Pnm2_1$ ,  $Pn2_1a$  or  $P2_1ma$  (see § 3.5) is obtained. It is not uncommon for materials with closely related structures to have one or other of these symmetries. Note that the standard settings for the last three groups (which are polar) result in the symbols  $Pnm2_1$ ,  $Pna2_1$  and  $Pmc2_1$ .

Fig. 3.14 shows how the symmetry elements of  $Pnma$  are illustrated in the *International Tables* in the standard orientation of **a** down the page, **b** horizontally on the page and **c** normal to the page. Light lines outline a unit cell and small circles show the locations of  $\bar{1}$  points (centers) at  $z = 0$  and  $z = 1/2$ . The full heavy lines represent the traces of mirror planes normal to **b** and the dot-dash lines represent the traces of  $n$  glide planes normal to **a**. The bent arrow at the top right shows that there is a glide plane at  $z = 1/4$  (i.e. normal to **c**) with the glide direction along the arrow (i.e. **a**). As the spacing between mirror or glide planes is half the translation normal to them, there is also an *a* glide plane at  $z = 3/4$ . The ovals with two arms represent  $2_1$  axes parallel to **c**, and the arrows with half heads are  $2_1$  axes in the plane of the paper. Those parallel to **b** are at  $z = 0$  (and necessarily also at  $z = 1/2$ ), and those parallel to **a** are at  $z = 1/4$  (and at  $z = 3/4$ ).

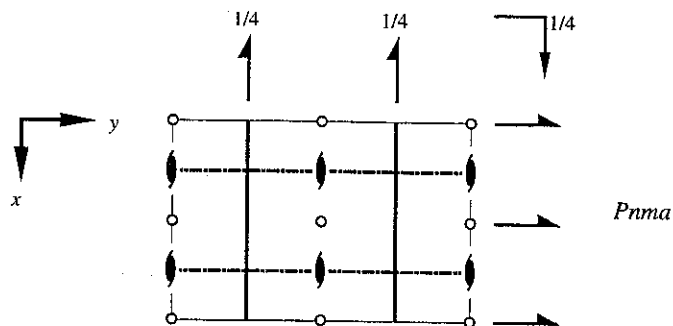


Fig. 3.14. The symmetry elements of  $Pnma$ . For an interpretation see text.

Recall that monoclinic space groups with centered cells have additional symmetry elements that do not appear in the space group symbol. Thus  $C2$  also has  $2_1$  axes, and  $C2/m$  also has  $2_1$  axes and *a* glide planes. Similarly orthorhombic space groups with centered cells have additional symmetry elements that do not appear in the space group symbol. In the *International Tables* a useful table (Table 4.3.1) lists these extra symmetry elements as in the following examples:

$$\begin{array}{ccc} C m c m & I m m m \\ b n n & n n n \end{array}$$

This means that in  $Cmcm$ , normal to **a** there are also *b* glide planes, and normal to **b** and

<sup>1</sup>Symmetry  $Pnma$  is particularly common, occurring for more than 8% of inorganic structures. For more on the occurrence of particular symmetry groups see § 3.7.7 (p. 94).

**c** there are also *n* glide planes. Likewise in  $Immm$  there are *n* glide planes normal to all three axes. We could write  $Cmcm$  as  $Cbnn$  or even  $Cmcn$ , etc. and write  $Immm$  as  $Innn$ . Fortunately practical, if arbitrary, rules were long ago decided on for preference of symbols (e.g. *m* has preference over glide). Fortunately also, in this instance, the rules are universally obeyed by crystallographers.<sup>1</sup> But note that with permutation of axes the symbols of the other symmetry elements may also change as in (for example) two different settings of  $Cmcm$ :

$$\begin{array}{ccc} C m c m & A m m a \\ b n n & n c n \end{array}$$

### 3.3.4 Tetragonal space groups

In the tetragonal system there is normally no ambiguity about the choice of axes. The *z* axis is always parallel to the 4-fold axis, and *x* and *y* are normal to *z* and to each other. The symbol for the space group is again a symbol for the lattice type followed by a three-position symbol derived from the point group symbol (see § 2.4). Thus with a body-centered lattice there are in the class  $4/mmm$  (among others) the space groups  $I4/mmm$  and  $I4_1/amd$ .

In the class  $\bar{4}2m$  there are two distinct space groups  $P\bar{4}2m$  and  $P\bar{4}2m$ . In the first of these the mirror planes are normal to *x* and *y*, and 2-fold axes at 45° to *x* and *y*; in the second the mirrors are normal to directions at 45° to *x* and *y*, and the 2-fold axes along *x* and *y*. (Compare the positions of “2” and “*m*” in the space group symbols.) Recall that the orientation of the axes is determined by the lattice translations.

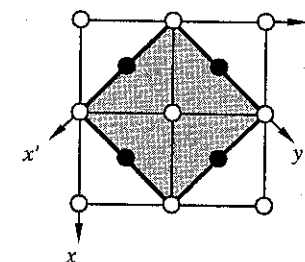


Fig. 3.15. A body-centered tetragonal lattice (projected down **c**) with four unit cells indicated with light lines and a face-centered cell (heavier lines, shaded). Open circles are lattice points at  $z = 0$  and filled circles are lattice points at  $z = 1/2$ .

Occasionally a body-centered tetragonal crystal is described in terms of a face-centered tetragonal cell of twice the volume. As shown in Fig. 3.15, the *x* and *y* axes are rotated by 45° when the cell changes. The last two symbols in the space group symbol have then to be interchanged. Thus  $I\bar{4}2m$  becomes  $F\bar{4}m2$  and  $I\bar{4}m2$  becomes  $F\bar{4}2m$ . Sometimes the

<sup>1</sup>But see P. M. de Wolff *et al.*, *Acta Crystallographica* A48, 727 (1992) for proposed changes to five orthorhombic space group symbols. Although logical, we hope these suggestions are not adopted.



change is more subtle:  $I4_1/amd$  becomes  $F4_1/ddm$ .<sup>1</sup>

There are primitive tetragonal space groups  $P4$ ,  $P4_1$ ,  $P4_2$  and  $P4_3$ , but only two corresponding body-centered tetragonal groups  $I4$  (which contains an equal density of  $4_2$  axes) and  $I4_1$  (which contains an equal density of  $4_3$  axes). This means that an acentric structure that has symmetry  $I4_1$  (and hence has distinct right- and left-handed forms) will have both  $4_1$  and  $4_3$  axes, but the arrangement around the two axes will not be related by mirror symmetry. Contrast the situation in the centrosymmetric space group  $I4_1/a$  where there are again  $4_1$  and  $4_3$  axes but they are now related by the  $a$  glide operation.

### 3.3.5 Trigonal and hexagonal space groups

In the trigonal and hexagonal systems one setting is usually adopted. Except as noted below for crystals with a rhombohedral lattice, the  $z$  axis is taken parallel to the 3- or 6-fold axis. The  $x$  and  $y$  axes are perpendicular to  $z$  and at  $120^\circ$  to each other. Again the significance of the last two positions of the space group symbol is the same as for point groups (§ 2.4). Thus in  $P31m$  the normals to the mirrors are at  $90^\circ$  to the  $x$  and  $y$  axes (i.e. the  $x$  and  $y$  axes are parallel to the mirrors) whereas in  $P3m1$  the normals to the mirrors are parallel to the  $x$  and  $y$  axes (compare  $p31m$  and  $p3m1$  in Fig. 1.13). Note also the two distinct space groups  $P6_3/mmc$  and  $P6_3/mcm$ .

In the case of rhombohedral crystals the 3-fold axis is along a body diagonal of the primitive unit cell—parallel to  $a + b + c$ . The lattice symbol is now always  $R$ . Thus we have the space groups  $R3$ ,  $R\bar{3}$ ,  $R32$ ,  $R3m$ ,  $R3c$ ,  $R\bar{3}m$  and  $R\bar{3}c$ . It is worth noting that the  $R$  lattice already contains both  $3_1$  and  $3_2$  axes.<sup>2</sup>

Rhombohedral crystals are very often described in terms of a hexagonal unit cell with three times the volume and with  $c$  parallel to the 3-fold axis as described in § 3.1 and in more detail later (§ 4.4.2, p. 104). In this case the space group symbol is unchanged. The nature of the cell chosen is always clear from the parameters given ( $a$  and  $\alpha$  for a primitive cell;  $a$  and  $c$  for a hexagonal cell). It never hurts to be explicit however.

### 3.3.6 Cubic space groups

In the cubic system there is a universal choice of axes. In the space group symbol, after the symbol for the lattice, the significance of the positions is the same as given for the point groups (§ 2.4, p. 47). Thus in the class  $m\bar{3}m$  there are (for example)  $Fd\bar{3}m$  and  $Ia\bar{3}d$ . It might be noted that in the older literature these symbols are  $Fd3m$  and  $Ia3d$  respectively (i.e. the bar over the 3 is dropped just as in the short symbols for the point groups). The full symbols for these space groups are  $F4_1/d\bar{3}2/m$  and  $I4_1/a\bar{3}2/d$ . Other points to notice include the fact that there are four separate groups  $P432$ ,  $P4_132$ ,  $P4_232$  and  $P4_332$  but only groups  $I432$  and  $F432$  (both of which already contain  $4_2$  axes) and  $I4_132$  and  $F4_132$

<sup>1</sup>The  $a$  glide planes normal to the 4-fold axis have translations alternately  $a/2$  and  $b/2$  in the  $I$  cell. These directions become  $(a \pm b)/4$  in the  $F$  cell so now the glide is  $d$  instead of  $a$ .

<sup>2</sup>Thus there are not separate space groups  $R3_1$  or  $R3_2$ . Contrast the three separate space groups  $P3$ ,  $P3_1$  and  $P3_2$ .

(both of which already contain  $4_3$  axes)—cf. the discussion of tetragonal groups above.

The group  $I23$  also contains  $2_1$  axes but there is nevertheless a separate group  $I2_13$  which also contains 2 axes. The difference between them (as discussed below) is that in  $I23$  the 2 axes all intersect (as do the  $2_1$  axes) in  $I2_13$  they do not. In this case the symbols for the two space groups have to be assigned arbitrarily.

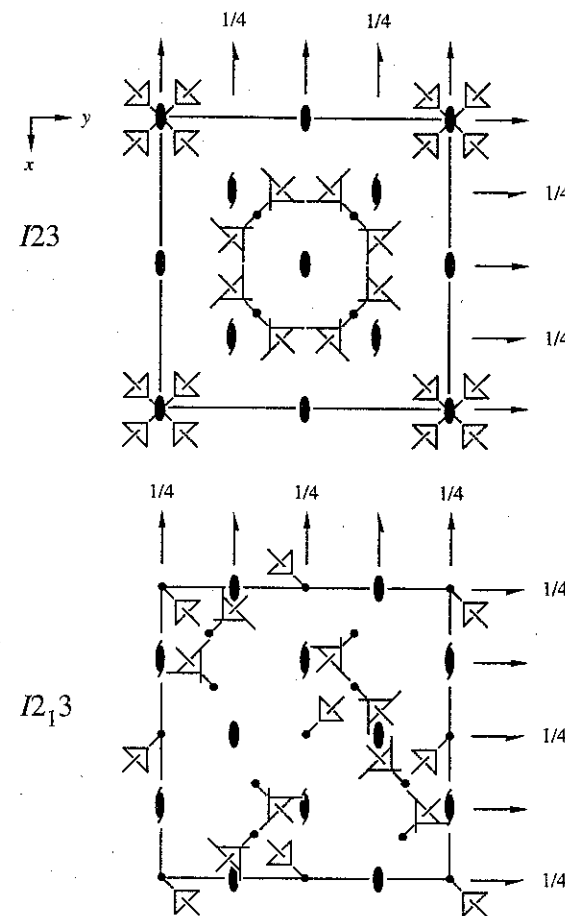


Fig 3.16. The symmetry elements of  $I23$  and  $I2_13$ . The meaning of the symbols is explained in the text (§ 3.3.6).

In addition to the 3 or  $\bar{3}$  axes in four different directions, the cubic space groups have 3<sub>1</sub> and 3<sub>2</sub> axes each in four different directions. Their location will depend on the space group. There are two different cases to consider. In the first case the 3 or  $\bar{3}$  axes intersect (at the origin) and the 3<sub>1</sub> and 3<sub>2</sub> axes intersect in pairs. In the second case the 3 or  $\bar{3}$  axes do not intersect, and in fact there is no intersection of any of the three-fold axes.

Figure 3.16 illustrates this point for  $I23$  (first case) and  $I2_13$  (second case). To interpret the figure, note that  $x$  is down the page,  $y$  is horizontal (left to right) and  $z$  extends up out of the plane. 3-fold axes (shown as short lines through triangles) intersect the plane  $z = 0$  at the points shown as small filled circles and go upwards from there parallel to body diagonals. Triangles represent 3 axes and triangles with arms represent screw (3<sub>1</sub> or 3<sub>2</sub>) axes. Thus in  $I2_13$ , 3<sub>1</sub> axes along <sup>1</sup>[111] intersect the plane  $z = 0$  at  $1/3, 2/3, 0$  and 3<sub>2</sub> axes along  $[\bar{1}\bar{1}\bar{1}]$  intersect the plane  $z = 0$  at  $2/3, 1/3, 0$ . 2-fold axes are symbolized as described above (§ 3.3.3, p. 70 and Fig. 3.14); those parallel to the plane of the paper are either at  $z = 0$  and  $1/2$  (no height shown) or at  $z = 1/4$  and  $3/4$  (height shown as  $1/4$ ).

Note also that in  $I2_13$ , the 2 axes do not intersect with themselves or with any of the 3-fold axes. The same is true of the 2<sub>1</sub> axes, but the 2 and 2<sub>1</sub> axes do intersect. Cubic crystal structures with space groups that have non-intersecting symmetry axes are often rather hard to understand and depict, but can sometimes be described as based on packings of cylinders whose axes are along non-intersecting symmetry axes (§ 6.7). In space groups with non-intersecting 3-fold axes there is no site of cubic point symmetry (which can only be at a point where four 3-fold axes intersect).

The locations of the symmetry elements in cubic groups are shown in a similar way in the *International Tables*. It is rewarding to learn the symbolism and to practice reading the diagrams.

Two choices of origin are made for centrosymmetric space groups in which the intersection of 3 or  $\bar{3}$  axes is not at an inversion center. The first choice is at the intersection of the 3-fold axes and is therefore at a site of cubic symmetry ( $\bar{4}3m$ , 432 or 23). The second choice is at a site of inversion symmetry; see § 3.7.4 (p. 91) for details.

### 3.3.7. Space group and crystal class

It should be obvious that to obtain the crystal class (the point group from which the space group was derived) from the space group symbol, one should (a) drop the lattice symbol, (b) drop all subscripts, and (c) change all glide symbols to "m." Thus  $I4_1/amd \rightarrow 4/mmm$ ,  $P2_1/c \rightarrow 2/m$  etc. If the point group is centrosymmetric then the space group is also (do Exercise 4).

## 3.4 Using the *International Tables*

The *International Tables* provide a wealth of information about the space groups including the nature and location of all symmetry elements in the unit cell. The tables

should also be consulted for the symbols for symmetry elements. All that are needed for our immediate purposes are the coordinates of equivalent points in a unit cell. Our first example is for  $P2_1/c$ ; the special and general positions are given with Wyckoff notation ( $a$ ,  $b$ , etc.) in Table 3.4. Note that the origin of coordinates is taken on a center of symmetry:

Table 3.4. Special and general positions of  $P2_1/c$ .

general:	4 $e$	$x, y, z$ ; $\bar{x}, \bar{y}, \bar{z}$ ; $\bar{x}, 1/2+y, 1/2-z$ ; $x, 1/2-y, 1/2+z$
special	2 $d$	$1/2, 0, 1/2$ ; $1/2, 1/2, 0$
	2 $c$	$0, 0, 1/2$ ; $0, 1/2, 0$
	2 $b$	$1/2, 0, 0$ ; $1/2, 1/2, 1/2$
	2 $a$	$0, 0, 0$ ; $0, 1/2, 1/2$

It is important to recognize that in order to derive the general positions (4  $e$  in this example) the location of the symmetry elements in the unit cell must be known. Fortunately this has been done for every space group in the *International Tables*. The symmetry operations are in the present case:

inversion through the origin	$x, y, z \rightarrow \bar{x}, \bar{y}, \bar{z}$
$c$ glide about plane at $y = 1/4$ <sup>1</sup>	$x, y, z \rightarrow x, 1/2-y, 1/2+z$
rotation about 2 <sub>1</sub> along $x = 0, z = 1/4$	$x, y, z \rightarrow \bar{x}, 1/2+y, 1/2-z$

The structure of AgO has symmetry  $P2_1/c$  and a crystallographic description of AgO is:

AgO	$P2_1/c$ , $a = 5.859$ , $b = 3.484$ , $c = 5.500$ Å, $\beta = 107.51^\circ$
	Ag(1) in 2 $a$ ; Ag(2) in 2 $d$ ; O in 4 $e$ , $x = 0.296$ , $y = 0.345$ , $z = 0.222$

It may be seen that there are two kinds of Ag atom in the structure. When atoms of a given element appear on sites that are not related by symmetry, we say that they are *crystallographically* distinct and distinguish them by numbering. We translate the above description as follows: There is one kind of Ag atom at positions  $0, 0, 0$  and  $0, 1/2, 1/2$  in the unit cell and a second kind of Ag which is at  $1/2, 0, 1/2$  and  $1/2, 1/2, 0$ . In AgO it turns out that the compound is really Ag(I)Ag(III)O<sub>2</sub> and that Ag(1) is Ag(I) and Ag(2) is Ag(III).<sup>2</sup>

The O positions in the unit cell are obtained as:

0.296, 0.345, 0.222	=	0.296, 0.345, 0.222
-0.296, -0.345, -0.222	=	0.704, 0.655, 0.778
-0.296, 0.845, 0.278	=	0.704, 0.845, 0.278
0.296, 0.155, 0.722	=	0.296, 0.155, 0.722

<sup>1</sup>Compare this case with Fig. 3.3 where the glide plane is at  $y = 0$ .

<sup>2</sup>Be sure to note that Arabic numerals (1 and 2 in this instance) are used as arbitrary identification numbers, but Roman numerals (I and III in this case) refer to oxidation states which are *inferred* from structural details (see Exercise 4.7.3).

<sup>1</sup>We explain notation such as  $[111]$  in the next chapter.  $[111]$  refers to the direction from  $0, 0, 0$  to  $1, 1, 1$ .

In the first column the values of  $x$ ,  $y$  and  $z$  have been substituted into the expressions for the 4  $e$  positions; in the second column 1.0 has been added to any negative coordinates to bring the atoms all into the same unit cell (i.e. so that  $0 \leq x < 1$ ,  $0 \leq y < 1$ ,  $0 \leq z < 1$ ).

As a second example we take a crystallographic description of the rutile form of  $\text{TiO}_2$ .

$\text{TiO}_2$   $P4_2/mnm$ ,  $a = 4.594$ ,  $c = 2.958$  Å  
Ti in 2  $a$ ; O in 4  $f$ ,  $x = 0.305$

We recognize the symmetry to be tetragonal. Turning to the *International Tables* we find for this space group that 2  $a$  correspond to 0,0,0 and 1/2,1/2,1/2, so this is where the Ti atoms are located in the unit cell. The 4  $f$  positions are given as  $x,x,0$ ;  $\bar{x},\bar{x},0$ ;  $1/2+x,1/2-x,1/2$ ;  $1/2-x,1/2+x,1/2$ . Proceeding as for the O atoms in AgO we determine the coordinates of the four O atoms in the unit cell of rutile are:

0.305, 0.305, 0; 0.695, 0.695, 0; 0.805, 0.195, 0.5; 0.195, 0.805, 0.5

Sometimes there is a remarkable economy in this type of description. For example the structure of spinel,  $\text{MgAl}_2\text{O}_4$  has 56 atoms in the unit cell, yet it is completely specified by symmetry information and just two numbers ( $a$  and  $x$ ):

$\text{MgAl}_2\text{O}_4$   $Fd\bar{3}m$ ,  $a = 8.080$  Å  
Mg in 8  $a$ , Al in 16  $d$ , O in 32  $e$ ,  $x = 0.262$

From the *International Tables* we find that the coordinates of 32  $e$  are:

(0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0) +  
 $x,x,x$ ;  $x,1/4-x,1/4-x$ ;  $1/4-x,x,1/4-x$ ;  $1/4-x,1/4-x,x$   
 $\bar{x},\bar{x},\bar{x}$ ;  $\bar{x},3/4+x,3/4+x$ ;  $3/4+x,\bar{x},3/4+x$ ;  $3/4+x,3/4+x,\bar{x}$

The interpretation of this is that to the coordinates in the second and third lines above, we must add in turn 0,0,0; 0,1/2,1/2; 1/2,0,1/2 and 1/2,1/2,0. The last three quantities are in fact primitive lattice translations for a face-centered cell ( $Fd\bar{3}m$  is face-centered cubic). The coordinates of O in the unit cell are then (please verify, noting that  $\bar{x} = 1-x = 0.738$ ;  $1/4-x = -0.012 \equiv 0.988$ ;  $3/4+x = 1.012 \equiv 0.012$ ; etc.):

0.262, 0.262, 0.262	0.262, 0.762, 0.762	0.762, 0.262, 0.762	0.762, 0.762, 0.262
0.262, 0.988, 0.988	0.262, 0.488, 0.488	0.762, 0.988, 0.488	0.762, 0.488, 0.988
0.988, 0.262, 0.988	0.988, 0.762, 0.488	0.488, 0.262, 0.488	0.488, 0.762, 0.988
0.988, 0.988, 0.262	0.988, 0.488, 0.762	0.488, 0.988, 0.762	0.488, 0.488, 0.262
0.738, 0.738, 0.738	0.738, 0.238, 0.238	0.238, 0.738, 0.238	0.238, 0.238, 0.738
0.738, 0.012, 0.012	0.738, 0.512, 0.512	0.238, 0.012, 0.512	0.238, 0.512, 0.012
0.012, 0.738, 0.012	0.012, 0.238, 0.512	0.512, 0.738, 0.512	0.512, 0.238, 0.012
0.012, 0.012, 0.738	0.012, 0.512, 0.238	0.512, 0.012, 0.238	0.512, 0.512, 0.738

The metal atom positions are found from the *International Tables* by obtaining the coordinates for positions 8  $a$  and 16  $d$ . These are:

(0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0) +  
8  $a$  1/8,1/8,1/8; 7/8,7/8,7/8  
16  $d$  1/2,1/2,1/2; 1/2,1/4,1/4; 1/4,1/2,1/4; 1/4,1/4,1/2

We now know where all the atoms are, but are not really much wiser about the structure. In fact the situation of the would-be crystal chemist at this point may be likened to that of a student of architecture who is given coordinates of bricks, rather than an architectural drawing. Accordingly, the next steps are to draw the structure (or make a model), to find nearest neighbors and coordination numbers and to calculate bond lengths and angles.

Because we realize that it would be tedious for the reader to have to reach for the *International Tables* every time that he/she wants to draw or do calculations on a structure (which we hope is often), we usually give explicitly the coordinates of special and general positions of a space group when reporting a structure. Especially for cubic groups it is desirable to have some concise way of doing this. We use the following conventions.

1. The origin is always taken at a center of symmetry if present.
2.  $\pm$  means plus and minus  
 $\pm(x,y,z)$  means  $x,y,z$  and  $\bar{x},\bar{y},\bar{z}$   
 $\pm x,y,z$  means  $x,y,z$  and  $\bar{x},y,z$   
 $\pm(\pm x,y,z)$  means  $x,y,z$ ;  $\bar{x},y,z$ ;  $\bar{x},\bar{y},\bar{z}$ ;  $x,\bar{y},\bar{z}$
3. Centering is expressed as a letter followed by + or  $\pm$   
 $I$  refers to (0,0,0; 1/2,1/2,1/2)  
 $F$  refers to (0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0)  
 $A$  refers to (0,0,0; 0,1/2,1/2)  
 $B$  refers to (0,0,0; 1/2,0,1/2)  
 $C$  refers to (0,0,0; 1/2,1/2,0)  
 $R$  refers to (0,0,0; 1/3,2/3,2/3; 2/3,1/3,1/3)
4. Cyclic permutation is expressed as  $(...)\kappa$   
 $(x,y,z)\kappa$  means  $x,y,z$ ;  $z,x,y$ ;  $y,z,x$   
(This corresponds to the operation of a threefold axis through the origin and along [111].)

We now give examples (crystal structure information is usually given in this format subsequently):<sup>1</sup>

$\text{MgAl}_2\text{O}_4$   $Fd\bar{3}m$ ,  $a = 8.080$  Å  
Mg in 8  $a$ :  $F \pm (1/8,1/8,1/8)$   
Al in 16  $d$ :  $F + (1/2,1/2,1/2; (1/2,1/4,1/4)\kappa)$   
O in 32  $e$ :  $F \pm (x,x,x; (x,1/4-x,1/4-x)\kappa)$ ,  $x = 0.262$

<sup>1</sup>The first line always has the space group and lattice parameter(s).

$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$   $la\bar{3}d$ ,  $a = 11.846 \text{ \AA}$   
 Ca in 24 c:  $I \pm (1/8, 0, 1/4; 5/8, 0, 1/4)\kappa$   
 Al in 16 a:  $I + (0, 0, 0; 1/4, 1/4, 1/4; (0, 1/2, 1/2; 1/4, 3/4, 3/4)\kappa)$   
 Si in 24 d:  $I \pm (3/8, 0, 1/4; 7/8, 0, 1/4)\kappa$   
 O in 96 h:  $I \pm (x, y, z; 1/2 - x, 1/2 + y, z; x, 1/2 - y, 1/2 + z; 1/2 + x, y, 1/2 - z; 1/4 + x, 1/4 + z, 1/4 + y; 3/4 + x, 1/4 - z, 3/4 - y; 3/4 - x, 3/4 + z, 1/4 - y; 1/4 - x, 3/4 - z, 3/4 + y)\kappa$ ,  $x = -0.0381$ ,  $y = 0.0449$ ,  $z = 0.1514$

$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  is one of a large group of natural and synthetic materials known as *garnets*. Note that although this is a complex structure with 160 atoms in the unit cell, most of the structural information is contained in the symmetry and only four *numbers* ( $a$ ,  $x$ ,  $y$ ,  $z$ ) are necessary to specify the structure. For the O atoms in the structure we get 96 coordinate triplets. Any one of these could be given as the coordinates of the typical atom. Which to choose? Often the choice is that which corresponds to a minimum of  $x^2 + y^2 + z^2$ . In a cubic crystal this is an atom closest to the origin. In the case of  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  all six O atoms closest to an Al atom at the origin (Al has six equidistant O neighbors) have at least one negative coordinate, and the coordinates given above for O are the coordinates of one of them. It might be verified that  $x$ ,  $y$ ,  $z = 0.0381$ ,  $0.0449$ ,  $0.6514$  are also coordinates of one of the O atoms obtained from the first by  $I + (1/2 - x, 1/2 + y, z)$  and could equally have been given (and often are: some authors avoid negative coordinates and use the smallest set of positive coordinates) as the O coordinates to generate the other 95. Remember that you can always add an integer to, or subtract an integer from, any coordinate.

### 3.5 Sub- and super-groups of space groups

A *subgroup*  $H$  of a group  $G$  is one that contains some, but not all, of the elements of  $G$ . Conversely  $G$  is a *super-group* of  $H$ . The number of elements in the supergroup is always an integer ( $n$ ) times that of the subgroup. In the jargon,  $n$  is the index of  $H$  in  $G$ . If  $n$  is prime then  $H$  is a *maximal* subgroup of  $G$ .

The *International Tables* give information on subgroups and supergroups of the space groups that is of interest in many contexts. For example a small distortion of a symmetrical crystal structure may result in a lower symmetry which is a subgroup of the parent structure. Knowing the possible symmetries can be an invaluable aid to determining the structure.

The full symbol for  $Pnma$  is  $P2_1/n2_1/m2_1/a$  and the point group is  $2/m2/m2/m$  with order 8. Systematically removing half of the symmetry elements will result in a space group with point group of order 4 that is a subgroup of  $2/m2/m2/m$  (i.e.  $mm2$ ,  $222$  or  $2/m$ ). There are eight possibilities which are given in the *Tables*. We give first the symbol for the axes labeled as for  $Pnma$  and in parentheses the symbol in the standard setting.

These are the maximal subgroups of  $Pnma$ . In this instance each point group has an order (4) half that of the parent so the index is 2. Lower order subgroups are subgroups of the maximal subgroups and so on until finally  $P1$ , which is a subgroup of every space group, is reached.

$Pnm2_1$	$(Pmn2_1)$
$Pn2_1a$	$(Pna2_1)$
$P2_1ma$	$(Pmc2_1)$
$P2_12_12_1$	$(P2_12_12_1)$
$P112_1/a$	$(P2_1/c)$
$P12_1/m1$	$(P2_1/m)$
$P2_1/n11$	$(P2_1/c)$

In the above example, the subgroups retain the same lattice translation symmetry; such subgroups are called *translationengleiche* ("translationally equivalent"—*gleich* means "equal" or "same" in German) or *t* subgroups.  $t_n$  is used to denote a translationengleiche subgroup of index  $n$ .

Another kind of subgroup is possible for space groups with centered lattices in which the centering is lost but the point group (crystal class) remains the same—these subgroups are called *klassengleiche* ("same class") or *k* subgroups. Thus for  $Cmcm$  we find listed as maximal subgroups, eight *t* subgroups with a  $C$  lattice and eight *k* subgroups with a  $P$  lattice. An example of the latter is  $Pbnm$  (standard setting  $Pnma$ ). That  $Pbnm$  is a subgroup of  $Cmcm$  is by no means obvious unless it is known that  $Cmcm$  has  $b$  glide planes normal to  $a$ , and  $n$  glide planes normal to  $b$  (and so could also be written  $Cbnm$  as explained in § 3.3.3, p. 72). Providing such information is yet another invaluable service provided by the *International Tables*.  $k_n$  is used to denote a *klassengleiche* subgroup of index  $n$ .

The reader is urged to use Fig. 3.10 (p. 69) to see that the  $t_2$  subgroups of  $C2/m$  are  $C2$ ,  $Cm$  and  $C\bar{1}$ . In the last case the symmetry is triclinic and with the conventional (primitive) cell the symbol is  $P\bar{1}$ .

Similarly it should be apparent that the  $k_2$  subgroups of  $C2/m$  are  $P2/m$ ,  $P2_1/m$  ( $C2/m$  contains  $2_1$  axes),  $P2/a$  ( $C2/m$  contains  $a$  glide), and  $P2_1/a$ . In the last two cases interchanging the labels of the  $a$  and  $c$  axes gives the "standard" symbols  $P2/c$  and  $P2_1/c$  respectively.<sup>1</sup>

A special kind of *k* subgroup is an *isomorphic* subgroup (or *i* subgroup for short). This is one that has the same space group as its parent, but because some of the translational symmetry has been lost, the unit cell is enlarged. An example is given below.

In Chapter 6 we discuss how symmetrical, low-density sphere packings can be smoothly distorted into denser, lower-symmetry forms. The space group of the latter will be a subgroup of that of the low-density parent. An example is the distortion of an 11-coordinated sphere packing (described in § 6.3.1) with symmetry  $P4_2/mnm$  (full symbol  $P4_2/m2_1/n2/m$ ) to a denser version with symmetry  $Pnmm$ . The *International Tables* lists as a *t* subgroup of  $P4_2/m2_1/n2/m$  the non-standard space group  $P2/m2_1/n1$ . This symbol is to be interpreted as if it referred to tetragonal symmetry (the symbol is called the "tetragonal version"): thus parallel to  $z$  we have  $2/m$ , and parallel to  $x$  and  $y$  we have  $2_1/n$ . We see that in fact there are 2-fold axes along  $x$ ,  $y$  and  $z$  and the symmetry is

<sup>1</sup>For a detailed discussion of the subgroups of  $C2/m$  (including isomorphic subgroups with a doubled  $c$  axis) see § 7.13 of *Geometrical and Structural Crystallography* by J. V. Smith (Book List).

actually orthorhombic. The "orthorhombic version" of this space group symbol is  $P2_1/n2_1/n2/m$  (short symbol  $Pnmm$ ). The symmetry of the distorted structure is thus shown to be indeed a subgroup of the parent structure.

The symmetries of the structures of rutile ( $\text{TiO}_2$ ) and  $\text{CaCl}_2$  are the same as in the above example, and indeed the anion arrangements are related in much the same way as the two sphere packings.

Another structure related to that of rutile is the *trirutile* structure such as that of tapiolite,  $\text{Ta}_2\text{FeO}_6$ . In this compound the Ta and Fe atoms order in layers along  $c$  in a sequence  $\text{FeTaTa}...$ , compared with  $\text{TiTiTi}...$  in rutile, thus tripling  $c$ . The space group remains the same so this is an example of ordering producing an isomorphic subgroup. The space group of trirutile is a subgroup of that of rutile because  $2/3$  of the translations (along  $c$ ) have been lost; accordingly the index of the subgroup is 3 (it is an  $i_3$  subgroup).

Another example of a parent structure being reduced in symmetry is provided by the structure of sodalite,  $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ . We consider just the  $(\text{Al},\text{Si})\text{O}_2$  part of the structure which consists of a framework of  $\{\text{Al},\text{Si}\}\text{O}_4$  tetrahedra sharing corners, and for the moment we consider the  $(\text{Al},\text{Si})$  atoms to be disordered in a random manner. In its most symmetrical arrangement the O packing is as described in § 6.8.5 with symmetry  $Im\bar{3}m$ , but as discussed in that section, can distort to a denser arrangement with symmetry  $I\bar{4}3m$  which is a  $t_2$  subgroup of  $Im\bar{3}m$ . In both cases the tetrahedron centers (disordered  $\text{Si},\text{Al}$ ) are at the same positions:  $I \pm (1/4, 0, 1/2)\kappa$ . Ordering of the Si and Al atoms into two sets  $\pm(1/4, 0, 1/2)\kappa$  for one atom and  $\pm(1/4, 1/2, 0)\kappa$  for the other removes the body centering and reduces the symmetry further to  $P\bar{4}3n$ : a  $k_2$  subgroup of  $I\bar{4}3m$ .

A phase transition in  $\text{KH}_2\text{PO}_4$  has been intensively studied.<sup>1</sup> The room temperature phase (with disordered H atoms) has symmetry  $I\bar{4}2d$  and the low-temperature phase (in which the H atoms are ordered) has symmetry  $Fdd2$ . If the high temperature phase is described by a doubled cell as shown in Fig. 3.15, the space group symbol becomes  $F\bar{4}d2$  and the unit cells of both phases have very nearly equal dimensions.<sup>2</sup> The H ordering reduces the  $\bar{4}$  axis to a 2 axis and removes the 2 axes normal to  $c$ . The space group symbol written as if the system were still tetragonal (it is actually orthorhombic) is now  $F2d1$  ("tetragonal version") which becomes  $Fdd2$  ("orthorhombic version"). Note that both the last two symbols imply that the 2-fold axis is parallel to  $c$ . Note also that the translations of  $I\bar{4}2d$  are retained in  $Fdd2$  so the latter is a translationengleiche subgroup of the former. For comments on coordinates in these structures see § 3.7.4.

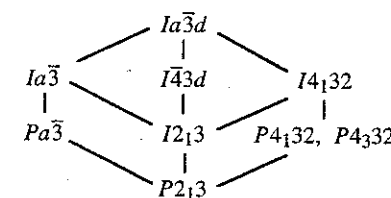
There is something apparently paradoxical in the observation that ordering reduces symmetry and disordering increases it. One's intuitive idea is surely that high symmetry is associated with "orderly" patterns. The solution to the paradox lies in recognizing that the

<sup>1</sup>The interest in this material stems in part from the fact that at low temperatures it has a spontaneous polarization which can be reversed by an electric field (i.e. it is *ferroelectric*). The elucidation of the role of ordering of H atoms in producing the ferroelectric phase was one of the early big successes of neutron crystallography [G. E. Bacon & R. S. Pease, *Proc. Roy. Soc. (London)*, Ser A 220, 397 (1953) and 230, 359 (1955)].

<sup>2</sup>For the room temperature phase with the  $F\bar{4}d2$  cell  $a = 10.54$ ,  $c = 6.98$  Å. At 77 K the  $Fdd2$  structure has  $a = 10.54$ ,  $b = 10.46$ ,  $c = 6.92$  Å.

symmetry we talk about in crystals is the *average* symmetry as revealed, for example, by diffraction of radiation from a large volume (many unit cells) of the crystal. Thus in disordered sodalite the tetrahedral sites are occupied *on average* by one half Al and one half Si and thus are considered equivalent and related by symmetry.<sup>1</sup> In the ordered version there are two sets of sites, one occupied by Al and the other by Si, and there cannot be a symmetry operation relating the two sets.

There is some interest in knowing which cubic groups have non-intersecting 3-fold axes. These will be the symmetry groups of cubic structures constructed of non-intersecting rods of atoms aligned parallel to the cube body diagonals (§ 6.7.3). In the table below the groups in each column are subgroups of the ones above them. In addition the groups in the center column are subgroups of the ones in the left and right columns of the row above.



### 3.6 Symmetry and the quartz structure—a case study

The  $\alpha$ -quartz form of  $\text{SiO}_2$  is an important mineral (comprising about 15% of the continental crust of the earth), it also has valuable physical properties (for example it is piezoelectric) that are a consequence of its symmetry. The structure is based on a framework of corner-sharing  $\{\text{Si}\}\text{O}_4$  tetrahedra and has occasioned a great deal of discussion, here we just focus on the symmetry aspects. The discussion illustrates several topics: the use of non-standard origins, subgroup-supergroup relationships, twinning, and the relationship between the hand of enantiomorphs and symmetry.

We start with a description of the structure of the high-temperature or  $\beta$ -quartz form.

$\beta$ -quartz	$P6_322$ , $a = 5.01$ , $c = 5.52$ Å
	Si in 3 $c$ : $(1/2, 0, 0)$ ; $0, 1/2, 2/3$ ; $1/2, 1/2, 1/3$
	O in 6 $f$ : $(x, 2x, 1/2)$ ; $2\bar{x}, \bar{x}, 1/6$ ; $x, \bar{x}, 5/6$ ; $\bar{x}, 2\bar{x}, 1/2$ ; $2x, x, 1/6$ ; $\bar{x}, x, 5/6$ , $x = 0.208$

We recognize the symmetry to be hexagonal and the crystal class (622) to be one of the enantiomorphous classes so that quartz exists as left- and right-handed forms (in essentially

<sup>1</sup>Only crystallographers really believe in fractional atoms. In a disordered crystal there may be no symmetry at all on an atomic level (i.e. on a *specific* as opposed to *average* site). In particular the microscopic translational symmetry is lost (if a translation is from a Si atom to an Al atom it is not a symmetry operation).

equal amounts as the  $\alpha$ -form in nature). As discussed below, the form we have described is called right-handed.<sup>1</sup> The left-handed enantiomorph has symmetry  $P6_422$ . The description of that structure is:

$\beta$ -quartz  $P6_422$ ,  $a = 5.01$ ,  $c = 5.52$  Å  
 Si in 3 c:  $(1/2, 0, 0; 0, 1/2, 1/3; 1/2, 1/2, 2/3)$   
 O in 6 j:  $(x, 2x, 1/2; 2\bar{x}, \bar{x}, 5/6; x, \bar{x}, 1/6; \bar{x}, 2\bar{x}, 1/2; 2x, x, 5/6; \bar{x}, x, 1/6)$ ,  $x = 0.208$

The only difference from the right-handed form is that we have replaced all the  $z$  coordinates by  $1-z$ . This corresponds to reflection in an imaginary mirror plane at  $z = 1/2$ , so that the two enantiomorphs are related as mirror images as expected.

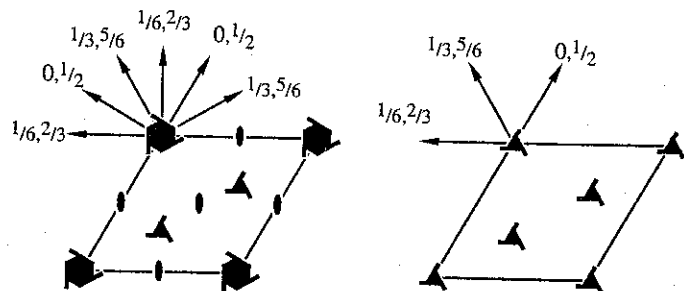


Fig. 3.17. The location of some of the symmetry elements of  $P6_422$  and  $P3_221$ .  $c$  is vertical out of the plane of the paper, and numbers represent elevations in fractions of  $c$ . The locations of  $2_1$  axes perpendicular to  $c$  are not shown. Note that the origin chosen for  $P3_221$  is not the same as that in the *International Tables*.

As well as the  $6_2$  axis (represented by a hexagon with three arms) at  $0, 0, z$ ,  $P6_422$  contains  $3_2$  axes (represented by triangles with three arms) at  $1/3, 2/3, z$  and  $2/3, 1/3, z$  as shown in Fig. 3.17. In the structure of right-handed quartz the  $\{\text{Si}\}\text{O}_4$  tetrahedra spiral around the  $3_2$  axes as shown in Fig. 3.18. We earlier described a  $3_2$  axis as “left-handed” and indeed the  $P6_422$  (right-handed) enantiomorph of quartz is sometimes described as “structurally left-handed.” On the other hand, the  $6_2$  axis was described as “right-handed” and if we focus instead on the helix of tetrahedra around that axis we would say that we have a right-handed structural unit; so it is not appropriate to refer to a structural “hand.” Why then do we call the  $P6_422$  form of  $\beta$ -quartz “right-handed”? The answer lies in the fact that the hand of a crystal is determined from its optical activity (rotation of the plane of polarization of light); clockwise rotation (when viewed looking towards the light source, i.e. light coming to the viewer) being called right handed (this is the Biot convention) or

<sup>1</sup>It is sometimes said that X-ray diffraction cannot distinguish between enantiomorphs of a crystal. This is not true when anomalous dispersion (absorption) is taken into account, and the absolute configuration of a number of enantiomorphous crystals has been determined by this technique. For an evaluation of the literature see A. M. Glazer & K. Stadnicka, *J. Appl. Crystallogr.* 19, 108 (1986).

dextrorotatory (+). This is the sense of the rotation of the plane of polarization of light when passing through a slice of  $P6_422$  quartz in a direction parallel to  $c$ . (Recall though that in a right-handed screw the rotation is anticlockwise when the translation is in a direction towards the viewer.) The opposite of “dextrorotatory” is “levorotatory” (–).<sup>1</sup>

Below about 573 °C, the  $\beta$  form transforms to  $\alpha$ -quartz, the main difference in the low-temperature structure (Fig. 3.18) being that the Si-O-Si angle is decreased by rotating the  $\{\text{Si}\}\text{O}_4$  tetrahedra in a concerted way about 2-fold axes perpendicular to  $c$ . In the  $P6_422$  enantiomorph this destroys the 2-fold rotation axis contained in the  $6_2$ -axis at  $0, 0, z$  and the latter is degraded to a  $3_2$  axis. The symmetry of the crystal becomes  $P3_221$ . Reference to Fig. 3.17 shows that the  $3_2$  axes at  $1/3, 2/3, z$  and  $2/3, 1/3, z$  remain.  $P3_221$  is a  $t_2$  subgroup of  $P6_422$ . A description of right-handed  $\alpha$ -quartz often seen is (note that we do not give the Wyckoff symbols for the positions for reasons to become apparent later):

$\alpha$ -quartz  $P3_221$ ,  $a = 4.92$ ,  $c = 5.41$  Å  
 Si at  $(x, 0, 0; 0, x, 2/3; \bar{x}, \bar{x}, 1/3)$ ,  $x = 0.470$   
 O at  $(x, y, z; y - x, \bar{x}, 1/3 + z; \bar{y}, x - y, 2/3 + z; x - y, \bar{y}, \bar{z}; y, x, 2/3 - z; \bar{x}, y - x, 1/3 - z)$   
 $x = 0.415$ ,  $y = 0.266$ ,  $z = 0.119$

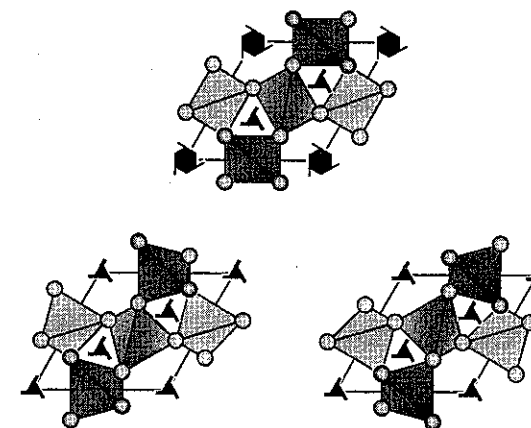


Fig. 3.18. Top: the oxygen atom positions in  $\beta$ -quartz ( $P6_422$ ). Bottom: on the left oxygen atom positions in  $\alpha_1$  and on the right  $\alpha_2$  twins of  $\alpha$ -quartz ( $P3_221$ ). The projection is along  $c$  and  $\text{O}_4$  tetrahedra are outlined. Silicon atoms (not shown) center the tetrahedra. In order of increasing depth of shading the tetrahedron centers are at  $z = 0, 1/3$  and  $2/3$ .

<sup>1</sup>See the discussion by Glazer & Stadnicka (*op. cit.* previous footnote). The sign of the optical activity associated with a helix of polarizable atoms depends on the orientation of the axis of maximum polarizability with respect to the helix. If the polarizability of the atoms were to be isotropic there would be no optical activity. For an account of the confusing history of the description of the quartz structure see P. J. Heaney in *Silica [Reviews in Mineralogy 29 (1994), p. 1-40]*. According to Heaney dextrorotatory quartz is morphologically right-handed (i.e. a macroscopic crystal of dextrorotatory quartz is right handed).

It should be apparent that if  $x_{Si} = 0.5$  in  $\alpha$ -quartz, the silicon atoms in the  $\alpha$ - and  $\beta$ -forms would then be in the same positions. In Table 3.5 below, the oxygen atom positions (rounded off for simplicity) in  $\beta$ -quartz are listed in the first column, and those given above for  $\alpha$ -quartz are listed in the second column. These differ only slightly. The oxygen positions in the two structures would be exactly the same if  $x, y, z$  in the  $P3_221$  form were 0.416, 0.208, 0.167.

Rotating the  $\alpha$  structure (by  $180^\circ$ ) around a 2-fold axis (now nonexistent in the crystal) along  $0,0,z$  will change the sign of the  $x$  and  $y$  coordinates to give the coordinates in the third column of the table. They correspond to substituting  $x = 0.585$ ,  $y = 0.784$ ,  $z = 0.119$  for the oxygen positions given above for  $P3_221$ . We have of course exactly the same structure, but in a different orientation.

As  $\beta$ -quartz is cooled to transform it to the  $\alpha$  form, these two orientations (which we call  $\alpha_1$  and  $\alpha_2$ ) nucleate at random points in the crystal. In the region of the interface where domains of  $\alpha_1$  and  $\alpha_2$  eventually meet, presumably there is an average structure, which is just a stranded element of  $\beta$ . When a crystal is composed of two parts related by a symmetry operation that is not a part of the structure (in this case a 2-fold rotation axis along  $0,0,z$ ), we say that it is composed of *twins* and the phenomenon is known as *twinning*. Quartz can be twinned in a number of different ways, the example we have just discussed is known as Dauphiné twinning. The situation where left- and right-handed forms are intergrown is known as Brazil twinning—here the twins are related by reflection (which again is not a symmetry element of the structure).

Table 3.5. Oxygen atom positions ( $x, y, z$ ) in right-handed quartz.  
Replacing all the  $z$  coordinates by  $1-z$  will give coordinates for left-handed quartz.

$\beta$	$\alpha_1$	$\alpha_2$
0.21, 0.42, 0.50	0.27, 0.42, 0.55	0.15, 0.42, 0.45
0.58, 0.79, 0.17	0.58, 0.85, 0.21	0.58, 0.73, 0.12
0.21, 0.79, 0.83	0.15, 0.73, 0.88	0.27, 0.85, 0.79
0.79, 0.58, 0.50	0.85, 0.58, 0.45	0.73, 0.58, 0.55
0.42, 0.21, 0.17	0.42, 0.27, 0.12	0.42, 0.15, 0.21
0.79, 0.21, 0.83	0.73, 0.15, 0.79	0.85, 0.27, 0.88

We haven't finished our story. For inscrutable reasons the origin of coordinates in  $P3_221$  is chosen differently in the *International Tables*—it is displaced by  $0,0,1/3$  from the position used above to describe  $\alpha$ -quartz. Thus the 2-fold axis in the  $x$  direction runs along  $x,0,0$  in  $P6_222$  but, with the origin chosen for  $P3_221$  in the *International Tables* the same axis runs along  $x,0,-1/3$ . The "non-standard" origin is almost invariably chosen by quartz aficionados (who are legion) as it makes the relation between the  $\alpha$ - and  $\beta$ -forms transparent. Unfortunately they do not always make this clear to outsiders.

In the *International Tables* the relevant positions in  $P3_221$  are given as:

Si in 3  $a$ : ( $x,0,2/3$ ;  $0,x,1/3$ ;  $\bar{x},\bar{x},0$ )  
O in 6  $c$ : ( $x,y,z$ ;  $\bar{y},x-y,z+2/3$ ;  $y-x,\bar{x},z+1/3$ ;  $y,x,\bar{z}$ ;  $x-y,\bar{y},1/3-z$ ;  $\bar{x},y-x,2/3-z$ )

To describe right-handed  $\alpha$ -quartz using this origin we can use the same values of  $x$  and  $y$  and subtract  $1/3$  from (or add  $2/3$  to) the value of  $z$  given above (0.119). Specifically for  $\alpha_1$  we have for Si:  $x = 0.470$  and for O:  $x = 0.415$ ,  $y = 0.266$ ,  $z = 0.786$ . For  $\alpha_2$  we have for Si:  $x = 0.530$  and for O:  $x = 0.585$ ,  $y = 0.734$ ,  $z = 0.786$ .

To describe left-handed  $\alpha$ -quartz using the origin given in the *International Tables* for  $P3_121$  use the coordinates in the previous paragraph but with  $z$  replaced by  $1-z$ .

Many framework silicates have analogs in which 2Si are replaced, in an ordered fashion, by Al and P. The analog of quartz is the berlinite form of  $AlPO_4$  in which Al and P alternate along the three-fold helices of the quartz structure. If the helices in the parent structure were  $3_2$  the symmetry along the helix of ordered atoms becomes  $3_1$  (with a doubled  $c$ ) as illustrated in Fig. 3.19.

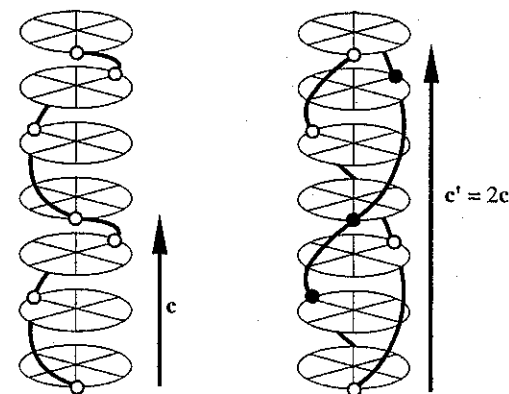


Fig. 3.19. Ordering on a  $3_2$  helix (shown on the left) produces a structure with a  $3_1$  axis (on the right) and with doubled repeat distances.

In right-handed  $\alpha$ -quartz the silicon atoms are in positions 3  $a$  of  $P3_221$ :  $\bar{x},\bar{x},0$ ;  $0,x,1/3$ ;  $x,0,2/3$  with  $x = 0.47$ . If the  $c$  axis repeat is doubled these positions become:

$\bar{x},\bar{x},0$	$0,x,1/6$	$x,0,1/3$	$\bar{x},\bar{x},1/2$	$0,x,2/3$	$x,0,5/6$
Si	Si	Si	Si	Si	Si
Al	P	Al	P	Al	P

The Al positions are in fact 3  $a$  of  $P3_121$  and the P positions are 3  $b$  of  $P3_121$ . In  $AlPO_4$   $x_{Al} \approx x_P \approx 0.46$ .

$P3_121$  is seen to be an isomorphic subgroup of index 2 of  $P3_221$  (and *vice versa*). Note that as  $P3_221$  quartz is optically right handed,  $P3_121$  berlinite is also right handed.

One of the major uses of quartz is as a piezoelectric oscillator in watches and other timing devices. It would be ironic if digital clocks using quartz oscillators entirely replaced

traditional clocks with their analog display of time, so that future generations lost sight of the meaning of the term "clockwise."<sup>1</sup>

### 3.7 Notes

#### 3.7.1 Additional symmetry elements in the unit cell

Let there be an inversion center at  $x_0, y_0, z_0$ . A point at  $x, y, z$  will be transformed to  $2x_0 - x, 2y_0 - y, 2z_0 - z$  by the inversion operation. Inversion centers with coordinates obtained by adding  $1/2$  to  $x_0$  and/or  $y_0$  and/or  $z_0$  will produce points with the same coordinates with 1 added on to the new values of  $x$  and/or  $y$  and/or  $z$  (i.e. in adjacent unit cells). In particular if there is an inversion center at  $0, 0, 0$  there will also be centers at  $1/2, 0, 0$ ;  $0, 1/2, 0$ ;  $0, 0, 1/2$ ;  $0, 1/2, 1/2$ ;  $1/2, 0, 1/2$ ;  $1/2, 1/2, 0$ ;  $1/2, 1/2, 1/2$ . These operating on a given point will always produce points identical with respect to a lattice translation. Thus the spacing of inversion centers is always one-half that of the *primitive* lattice translations and there are always exactly 8 per *primitive* cell.

Similar reasoning shows that mirror and glide planes are always spaced at intervals of one half the shortest lattice translation normal to the mirror and that the spacing between 2-fold axes is one-half of a lattice translation vector.

When elevations are given for centers, 2-fold axes, and symmetry planes in the *International Tables*,  $1/2$  should always be added to these elevations. Note that when no elevation is given it is implied to be zero and  $1/2$ .

Trigonal and hexagonal space groups will always have a 3- or 6-fold axis along  $1/3, 2/3, z$  and  $2/3, 1/3, z$  in addition to the one at  $0, 0, z$ .

In tetragonal space groups there are always 4-fold axes of the same kind ( $4, 4_1, \bar{4}$  etc.) with axes displaced by  $1/2, 1/2, 0$ . Be aware that the origin is not always chosen on a 4-fold axis in tetragonal space groups.

#### 3.7.2 General and special positions and lattice complexes

General positions are points at which there is no symmetry. The coordinates of general positions completely specify the space group. If  $\Gamma$  is a point group then the general positions of the space group  $P\Gamma$  also provide the coordinate symbols for the point group operations. The number of general positions in the primitive cell is the order of the point group. The maximum number of general positions will therefore be  $4 \times 48 = 192$  for a

<sup>1</sup>Piezoelectricity is the production of electric polarization by an applied mechanical stress. It can occur for all non-centrosymmetric crystal classes other than 432. In class 321 (that of  $\alpha$ -quartz) the  $a$  and  $b$  directions are polar and reversing their directions reverses the sign of the piezoelectric coefficients. Recall that the forms that we have called  $\alpha_1$  and  $\alpha_2$  are related in just this way (replacing  $x$  and  $y$  in one by  $\bar{x}$  and  $\bar{y}$  in the other) so that a crystal composed of equal amounts of each form would not be piezoelectric. To exploit the piezoelectric properties of quartz one must therefore avoid having both forms present (i.e. Dauphiné twinning—often called electrical twinning in this context). By convention the piezoelectric coefficients are referred to the  $\alpha_1$  form.

face-centered cubic cell in class  $m\bar{3}m$ .

Points lying on mirror planes, but otherwise unrestricted, will have two degrees of freedom (will be *bivariant*) and will thus have coordinates of the sort  $x, y, z_0$ , where  $z_0$  is 0 or a simple fraction (the mirror plane is  $z = z_0$ ), or  $x, x, z$  (the mirror plane is  $x = y$ ), etc. The site symmetry at such a point will be  $m$  and there will be only one-half as many such points as general positions.

Points lying on rotation axes will have only one degree of freedom (*univariant*) and will thus have coordinates such as  $x, 0, 0$  or  $x, x, x$ , etc. There will be at most one-half as many as there are general positions, but there may be less if the axis also coincides with the intersections of mirror planes and/or the order of the rotation axis is greater than 2. The site symmetry will now be  $N$  or  $Nm(m)$ . As univariant points lie on a rotation axis the coordinates can be construed as specifying the line of intersection of two planes. Thus  $x, 0, 0$  is the line of intersection of the planes  $y = 0$  and  $z = 0$ ; likewise  $x, x, x$  represents the intersection of the planes  $x = y$  and  $y = z$ .

Points lying on centers, or at the intersections of rotation axes, or the intersection of a rotation axis and a mirror, will have no free parameters (*invariant*). The site symmetry at such points will be one of the crystallographic point groups (it must of course be the same as, or a subgroup of, the crystal point group).

The fact that a point lies on a glide plane or a screw axis does not on the other hand reduce the number of points as the translational component will always take a given point to a new position. Thus (to take a random example) there are no special positions for  $Pca2_1$  because it contains no point operations (those that leave at least one point invariant).

Sets of symmetry-related points are sometimes called lattice complexes (but the term is sometimes used differently, so beware).

There is special interest in the cubic invariant lattice complexes which crop up in many different contexts, and they have been given symbols in the *International Tables* although these have not yet achieved wide currency (they are given in § 6.8.7). As an example, the positions  $8a$  of  $Fd\bar{3}m$  (symbol  $D$ ) are the positions of the atoms in the **diamond** form of carbon, silicon etc. as well as in a large number of compounds (Mg in  $MgAl_2O_4$  cited above). The positions  $16d$  of the same space group (symbol  $T$ ), which are the Al positions in  $MgAl_2O_4$ , are also the Cu positions in the important structure type  $MgCu_2$  (§ 6.6.3). Many other examples of the recurrence of common motifs will be adduced in later chapters.

#### 3.7.3 Matrix representations of symmetry operations<sup>1</sup>

A symmetry operation acting on a point  $x, y, z$  produces another point at  $x', y', z'$ . Using the conventional coordinate systems, the set of new points in a unit cell resulting from all the symmetry operations in a space group are given as the general positions in the *International Tables*. Let  $\mathbf{x}$  be the column vector ( $x / y / z$ ) and  $\mathbf{x}'$  be the column vector ( $x' / y' / z'$ ), then  $\mathbf{x}' = \mathbf{A}\mathbf{x} + \mathbf{t}$  where  $\mathbf{A}$  is the matrix corresponding to a point symmetry operation about the origin and  $\mathbf{t}$  is another column vector ( $t_x / t_y / t_z$ ). i.e.:

<sup>1</sup>This note is not for those who are uneasy with matrix manipulation; as we do not use the results later it may be omitted. See § 4.6.5 for some help with matrices.



$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} t_x \\ t_y \\ t_z \end{pmatrix}$$

This equation is sometimes expressed in terms of a four-dimensional matrix:

$$\begin{pmatrix} x' \\ y' \\ z' \\ 1 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & t_x \\ a_{21} & a_{22} & a_{23} & t_y \\ a_{31} & a_{32} & a_{33} & t_z \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix}$$

A compact symbol for the above matrix is  $\{\text{Alt}\}$  such that  $\mathbf{x}' = \{\text{Alt}\}\mathbf{x}$ .  $\{\text{Alt}\}$  is known as the *Seitz Operator*.

With conventional choices of bases all the elements of  $\mathbf{A}$  are  $\pm 1$  or 0. The nature of the symmetry operation can be found as follows [H. Wondratschek & J. Neubüser, *Acta Crystallogr.* 23, 349-352 (1967)]: Let  $\tau$  be the trace (sum of the diagonal elements) of  $\mathbf{A}$  and  $\Delta$  the determinant of  $\mathbf{A}$ , then the point symmetry element is determined as shown below:

$\tau\Delta =$	3	-1	0	1	2
$\Delta = 1$	1	2	3	4	6
$\Delta = -1$	1	$m$	$\bar{3}$	$\bar{4}$	$\bar{6}$

The space group operation is identified as follows:

If  $\Delta = 1$  there is an  $N$ -fold rotation or screw axis along axis  $\mathbf{q}$  given by the solutions of

$$(\mathbf{A} - \mathbf{E})\mathbf{q} = 0 \quad (\mathbf{E} \text{ is the identity matrix})$$

with translation  $\mathbf{d}$  (parallel to  $\mathbf{q}$ ) given by

$$\mathbf{d} = (1/N)\mathbf{B}\mathbf{t} \quad (\mathbf{B} = \mathbf{A}^{N-1} + \mathbf{A}^{N-2} + \dots + \mathbf{E})$$

points  $\mathbf{x}$  on the axis are the solutions of

$$(\mathbf{A} - \mathbf{E})\mathbf{x} = (\mathbf{B}/N - \mathbf{E})\mathbf{t}$$

If  $\Delta = -1$  then there is:

(a)  $\tau\Delta = 3$  an inversion center.

(b)  $\tau\Delta = -1$  a mirror or glide with translation  $\mathbf{d}$  given by

$$\mathbf{d} = (1/2)(\mathbf{A} - \mathbf{E})\mathbf{t}$$

and the points  $\mathbf{x}$  on the plane are the solutions of

$$(\mathbf{A} - \mathbf{E})\mathbf{x} = (1/2)(\mathbf{A} - \mathbf{E})\mathbf{t}$$

(c)  $\tau\Delta = 0, 1$  or 2 there is a  $\bar{3}, \bar{4}$  or  $\bar{6}$  axis along  $\mathbf{q}$  given by

$$(\mathbf{A} + \mathbf{E})\mathbf{q} = 0$$

and the inversion point  $\mathbf{x}$  is given by the solution of:

$$(\mathbf{A} - \mathbf{E})\mathbf{x} = -\mathbf{t}$$

It will be found that working through one or two examples (see e.g. Exercise 2) will make the above clear.

The inverse problem of finding the matrix corresponding to a given space group operation is easily solved from the above equations. For a clear and thorough exposition see M. B. Boisen & G. V. Gibbs, *Canadian Mineralogist*, 16, 293 (1978).

### 3.7.4 Alternative origins and unit cells

There are advantages to taking the origin at a center of symmetry in space groups that have them. Computer programs that generate space group coordinates often do it for a centric space group by adding a center to an acentric space group by also reversing the sign of all the coordinates (in getting  $Pnmm$  from  $P222$  for example). They then require that you use such an origin. Properties such as the electron density distribution  $[\rho(x,y,z)]$  of a centrosymmetric crystal become an even function  $[\rho(x,y,z) = \rho(-x,-y,-z)]$  if the origin is taken at a center. Expression of  $\rho(x,y,z)$  as a Fourier series requires only cosine terms in this case.

Why then ever take an alternative origin? Consider the diamond structure. The symmetry is  $Fd\bar{3}m$  and with origin at the center (half way between two neighboring C atoms, site symmetry  $\bar{3}m$ ) the C atom positions are 8  $a$ :  $F \pm (1/8, 1/8, 1/8)$ ; however if the origin is taken on an atom (with site symmetry  $\bar{4}3m$ ) the coordinates are (again 8  $a$ )  $F + (0,0,0; 1/4, 1/4, 1/4)$ . Now consider the cubic form of SiC. The structure is derived from that of diamond by replacing half the C atoms by Si destroying the inversion center and the symmetry is now  $F\bar{4}3m$  (an acentric subgroup of  $Fd\bar{3}m$ ). The point that was the old inversion center now has symmetry  $3m$  and the natural origin is the site of  $\bar{4}3m$  symmetry where the atoms are located, and which is chosen as the standard origin for  $F\bar{4}3m$ . The description of the structure is: Si in 4  $a$ :  $F + (0,0,0)$  and C in 4  $c$ :  $F + (1/4, 1/4, 1/4)$ . The relationships between the two structures are more readily apparent if the origin is chosen at the site with  $\bar{4}3m$  symmetry in both cases.

When alternative origins are given, the first choice used in the *International Tables* is at  $x_0, y_0, z_0$  from an inversion center (the second choice is on the center). To convert coordinates appropriate for the first choice to those appropriate for the second choice,

$x_0, y_0, z_0$  must be added to the first set. Values of  $x_0, y_0, z_0$  are given in Table 3.6 below. See § 3.6 (p. 86) for choice of origin in  $P3_121$  and  $P3_221$ .

Table 3.6. Coordinates  $x_0, y_0, z_0$  to add to convert from origin "choice 1" to "choice 2" in the *International Tables*

$Pnnn$	1/4, 1/4, 1/4
$Pban, Pmnn$	1/4, 1/4, 0
$Ccca$	0, 1/4, 1/4
$Fddd, Fd\bar{3}, Fd\bar{3}m$	-1/8, -1/8, -1/8
$P4/n, P4/nmm, P4/ncc$	-1/4, 1/4, 0
$P4_2/n, P4/nnc, Pn\bar{3}, Pn\bar{3}n, Pn\bar{3}m$	-1/4, -1/4, -1/4
$I4_1/a$	0, -1/4, -1/8
$I4_1/amd, I4_1/acd$	0, 1/4, -1/8
$P4/nbm$	-1/4, -1/4, 0
$P4_2/nbc, P4_2/nnm, P4_2/nmc, P4_2/ncm$	-1/4, 1/4, -1/4
$Fd\bar{3}c$	-3/8, -3/8, -3/8

A more subtle (and maddening) cause of confusion can arise in some polar space groups (i.e. those belonging to one of the polar crystal classes—see § 2.5.4). The general positions of  $Fdd2$  (class  $mm2$ ) are given in the *International Tables* as:

$$F + (x, y, z; \bar{x}, \bar{y}, z; 1/4+x, 1/4-y, 1/4+z; 1/4-x, 1/4+y, 1/4+z)$$

The second position is generated from the first by rotation about the 2-fold axis parallel to  $c$  and passing through the origin. The next two positions are generated from the first two by diamond glide: reflection in the plane  $y = 1/8$  followed by translation by  $a/4+c/4$ .

One of the most studied of all crystals with this symmetry is the low-temperature phase of  $KH_2PO_4$ . For reasons of their own, people who work with this material reverse the  $c$  component of the glide (so that it is  $a/4 - c/4$ ) and the general positions become (with  $-1/4$  replaced by  $3/4$ ):

$$F + (x, y, z; \bar{x}, \bar{y}, z; 1/4+x, 1/4-y, 3/4+z; 1/4-x, 1/4+y, 3/4+z)$$

To use their coordinates with the positions given in the *International Tables* the sign of all values of  $z$  must be reversed. This is simple enough to do if you are told, but compilations of structural data often neglect to make clear the choice of direction of  $z$ . The same problem can arise in  $I4_1md$  and  $I4_1cd$  which are polar supergroups of  $Fdd2$ .

The high-temperature phase of  $KH_2PO_4$  is often described as having space group  $F\bar{4}d2$  which is  $I\bar{4}2d$  using with a doubled cell (see Fig. 3.15).<sup>1</sup> Your computer program quite possibly does not recognize  $F\bar{4}d2$  either! We explain in Chapter 4 how to transform coordinates when a unit cell is transformed. To transform coordinates  $x, y, z$  for a face-centered tetragonal cell to  $x', y', z'$  for a body-centered tetragonal cell use  $x' = x - y, y' =$

<sup>1</sup>The reason for this is that the unit cells and coordinates of both phases are then very nearly the same. See § 3.5.

$x + y, z' = z$ . You may still have to be careful about choice of origin!

Occasionally a primitive tetragonal crystal is described by a similar doubled cell which is now  $C$  centered. The same rule applies.

### 3.7.5 Standardized description of crystal structures

Frequently crystal structures are determined and not recognized as the same as one previously determined for a different compound (for an example see Exercise 11). Among the reasons for this are choices of different settings of axes and choice of different origins as described in § 3.7.4, or (less frequently) assignment of a wrong space group.

Even if the "standard" settings of the *International Tables* are chosen there can still be freedom of choice of axes; for example space group  $Pmmm$  has the same symbol for any permutation of the axes. There can also be freedom of choice in assigning atoms to Wyckoff positions: for example in the structure of PtS with symmetry  $P4_2/mmc$ , the Pt atoms occupy the positions  $2c$ . The S atoms can be placed in either  $2e$  or  $2f$  resulting in identical structures but described with different origins (in both cases on a center).

With an increasing number of structures being published and entered into computer databases, it is important that they be reported in as "standard" as possible a way. Sensible proposals for this and a computer program to implement them have been described [E. Parthé & L. M. Gelato, *Acta Crystallogr.* A40, 169, (1984); L. M. Gelato & E. Parthé, *J. Appl. Crystallogr.* 20, 139 (1987)]. Unfortunately relationships between structures of different symmetries are sometimes obscured if standard descriptions are used. In those cases it would seem appropriate to use two descriptions.

To illustrate that this is not a trivial problem for non-crystallographers we recount an anecdote about the crystal structure of zircon ( $ZrSiO_4$ ). Two structure determinations in essential agreement were reported, but with different choices of origin (see Exercise 10). A structure simulation was subsequently carried out (by a third party) to determine which was correct! The reader is urged to do Exercise 11 (taken from Parthé & Gelato) which provides a more subtle example.

### 3.7.6 Other symmetry groups with translations

The enumeration of the classical space groups was performed 100 years ago. Most of the credit goes to E. S. Fedorov (Russia) and A. M. Schoenflies (Germany) who worked independently, but it should be noted that the final correct tally was only achieved by cross-checking each other's work. We should also mention in this connection the remarkable work at the same time of W. Barlow (England) who a (possibly apocryphal) tale has arranging hundreds of gloves (asymmetric objects!) on racks to simulate the space groups.<sup>1</sup>

The symmetry groups of three-dimensional objects with only two-dimensional

<sup>1</sup>Barlow (who has been called "one of the last great amateurs of science") also contributed greatly to our knowledge of sphere packings and invented some simple crystal structures, such as those of NaCl and CsCl. This last work was just what W. H. & W. L. Bragg needed for their early investigations of crystal structures (that of NaCl was the first determined). The proof in § 1.4 is attributed to Barlow.

periodicity (*layers*) or one-dimensional periodicity (*rods*) are sometimes of interest. The restriction to 1-, 2-, 3-, 4- or 6-fold rotations does not apply with one-dimensional periodicity, so the rod groups subject to that restriction are called *crystallographic* (as for the point groups). As the crystallographic one-dimensional and two-dimensional groups are also subgroups of space groups, information about them is implicit in the *International Tables*. Appendix 1 lists these groups and gives some hints for using the *Tables* to obtain the general and special positions for these groups and to locate their symmetry elements. Layer groups are of special interest to electron microscopy and we use the rod groups in the discussion of cylinder packings in Chapter 6.

### 3.7.7 The occurrence of symmetry groups

Experienced crystallographers often have a knack of knowing what kind of structure to expect once they know the symmetry and unit cell parameters. It is useful therefore to have some ideas about the factors determining the occurrence of symmetry groups.

Organic and many inorganic *molecules* are often assembled with great skill piecewise and are generally of low symmetry (and metastable). The crystals they form have symmetries suitable for efficient packing of such molecules; generally this requires the absence of pure rotation axes and mirror planes, but allows a low density of screw axes and glide planes. Thus in a survey<sup>1</sup> of about 40,000 organic crystal structures it was observed that about one third have symmetry  $P2_1/c$  but there was not a single example of a structure with symmetry  $P2/m$ . Only 64 examples of cubic symmetry were found and almost a third of these had symmetry  $Pa\bar{3}$  which is a favorable symmetry for packing of molecules [like  $\text{CO}_2$  and "congressane" (§ 5.1.10)] with large quadrupole moments. The same symmetry is found for pyrite,  $\text{FeS}_2$ , which contains  $\text{S}_2$  groups.

The inorganic crystals with which we are largely concerned in this book are very often the stable configurations (at a given temperature and pressure) of combinations of atoms in predetermined ratios and generally have higher symmetries. *Pearson's Handbook* (see Book List) contains about 50,000 inorganic structures and about 2500 structure *types*. The distribution of symmetries among the latter and the more common space groups (in percent) are:

triclinic	2.8				
monoclinic	20.1	$C2/m$	6.1	$P2_1/c$	5.5
orthorhombic	29.7	$Pnma$	6.1	$Cmcm$	3.1
tetragonal	15.1				
trigonal	10.7	$R\bar{3}m$	3.7		
hexagonal	12.1	$P6_3/mmc$	4.3		
cubic	9.5				

About three-quarters of the structure types are centrosymmetric. Of course some structure types have hundreds of representatives (they are usually of high symmetry) and many others have just one. With reference to the above table, note that  $Cmcm$  is a maximal

subgroup of index 3 of  $P6_3/mmc$  and that  $Pnma$  and  $C2/m$  are maximal subgroups of order 2 of  $Cmcm$ . Likewise  $P2_1/c$  is a maximal subgroup of index 2 of  $Pnma$  and  $C2/m$  is a maximal subgroup of index 3 of  $R\bar{3}m$ . The most common cubic symmetries are  $Fm\bar{3}m$  and  $Fd\bar{3}m$  (both supergroups of  $R\bar{3}m$ ).

The presence of high symmetry means that apparently complex structures (such as *spinel* and *garnet*; see § 3.4) can often be described by just a few parameters and appreciation of possible reasons for adoption of a particular symmetry can be a great aid to understanding such structures. For this reason we spend some time on the symmetries of sphere and cylinder packings in Chapter 6 (see especially § 6.8.1 and 6.8.10). For the symmetries of certain types of layer structure see § 5.6.14.

### 3.7.8 Incommensurate (modulated) crystals, quasicrystals and non-classical symmetries<sup>1</sup>

We should mention that in this book we are only concerned with structures that have symmetries described by one of the classical symmetry groups, in particular for "infinite" solids the symmetry is one of the 230 space groups. Corresponding to the lattice of these structures there is a reciprocal lattice (§ 4.5.1) in the space (*reciprocal space* or *Fourier space*) of the diffraction pattern of the structure. The diffraction pattern is conveniently indexed in terms of three non-coplanar reciprocal lattice vectors. The reader should know however, that the diffraction patterns of many solid materials (incommensurate crystals and quasicrystals) cannot be so indexed, but require more than three (sometimes as many as six) vectors to be indexed.

A simple kind of incommensurate crystal structure can arise as in the following example. Consider a structure of  $\text{Na}_2\text{CO}_3$  composed of Na atoms and  $\text{CO}_3$  groups in well-defined positions in a unit cell and described by a conventional space symmetry group. Now imagine the structure to be modulated by rotations of the  $\text{CO}_3$  groups by an angle whose magnitude depends on distance along an axis and with a periodicity different from, and incommensurate with, the basic lattice periodicity. In addition to the basic unit cell and its contents, we have also to specify the modulation function to describe the structure.<sup>2</sup> The diffraction pattern will have main diffraction spots at positions specified in terms of three reciprocal lattice vectors corresponding to the underlying lattice and satellite reflections whose positions relative to the main reflections are specified in terms of a fourth vector, and four numbers will be required to index the spots of the diffraction pattern. In *this* sense it may be considered "four-dimensional."

We mention quasicrystals briefly in § 5.5. The diffraction patterns of these have "non-crystallographic" symmetries. The first to be discovered (and many others subsequently) have icosahedral diffraction patterns that require six digits for indexing.

For crystallographic purposes it is sometimes convenient to consider such structures as projections onto three dimensions of higher dimensional structures with symmetries of

<sup>1</sup>Some acquaintance with X-ray diffraction is required to fully appreciate the content of this Note.

<sup>2</sup> $\text{Na}_2\text{CO}_3$  was one of the first incommensurately-modulated crystals discovered. The situation in the real crystal is a little more complicated than we have described.

<sup>1</sup>See the article by A. J. C. Wilson in *International Tables C*, p. 792.

higher dimensional space groups (see Appendix 2).

A recent interesting development is the recognition that the symmetries of diffraction patterns are not restricted to "crystallographic" symmetries (1-, 2-, 3-, 4- and 6-fold) axes. That restriction in real space came about (§ 1.4) because we restricted ourselves to lattices in which lattice points could not come arbitrarily close to each other—this is an eminently sensible restriction in real space, as atoms (which must be related to identical atoms by a lattice translation) can not approach arbitrarily close to each other. In reciprocal space, however, there is no physical reason for such a restriction and if it is lifted, axial symmetry groups with an  $N$ -fold axis with arbitrary  $N$ , and icosahedral groups are allowed. It turns out that the derivation of symmetry groups starting from reciprocal space is in many ways much more simple and elegant than the traditional way hinted at in this chapter, and it is quite possible that future texts will adopt the reciprocal space approach when the details are fully worked out. Key references are D. A. Rabson *et al.*, *Rev. Mod. Phys.* **63**, 699 (1991) and N. D. Mermin, *Rev. Mod. Phys.* **64**, 3 (1992). In these papers the 230 space groups are derived very elegantly, as are the 11 icosahedral space groups of reciprocal space. Note that there are no real space lattices corresponding to the icosahedral cases, so the term "reciprocal" lattice is unfortunate.

Despite the above remarks, we emphasize that in this book we are interested primarily in real space *structures* (arrangements of atoms in space) and that we use the language of space groups simply for a convenient, and succinct, method of describing such structures; and for this purpose a real space description is most intuitive. We also recognize that, unless one is completely familiar with Fourier transforms and their properties, working in reciprocal space can be somewhat daunting. Finally we observe that although the occurrence of incommensurate and quasi-crystals is being found to be quite common, at present structural details, on the level available for conventional crystals, are available in only a few cases.

### 3.8 Exercises

1. By choosing new axes  $P2_1/c$  (§ 3.4, p. 77) becomes  $P2_1/n$ . The coordinates of general positions now are (verify from the *International Tables*):

$$x, y, z; \bar{x}, \bar{y}, \bar{z}; 1/2+x, 1/2-y, 1/2+z; 1/2-x, 1/2+y, 1/2-z$$

2. The general positions of  $Pnma$  (full symbol  $P2_1/n2_1/m2_1/a$ ) are

$$\pm(x, y, z; 1/2+x, 1/2-y, 1/2-z; \bar{x}, 1/2+y, \bar{z}; 1/2-x, \bar{y}, 1/2+z)$$

From these the locations of the  $2_1$  axes parallel to  $x, y$  and  $z$  and the locations of the mirror and glide planes can be found. For example,  $x, y, z \rightarrow \bar{x}, 1/2+y, \bar{z}$  corresponds to operation of a  $2_1$  axis passing through the origin and parallel to  $y$ .

The special positions can be generated by appropriate substitutions for the general

positions. Thus  $y = 1/4$  (or  $y = 3/4$ ) will generate positions  $4c$  on the mirror planes. There are eight inversion centers in the cell (see Fig. 3.14, p. 72); substitute their coordinates for the general positions to generate  $4a$  and  $4b$ .

3. The symmetries of the Bravais lattices are (identify each lattice):

$$P\bar{1}, P2/m, C2/m, Pmmm, Cmmm, Immm, Fmmm, P4/mmm, I4/mmm, R\bar{3}m, P6/mmm, Pm\bar{3}m, Im\bar{3}m, Fm\bar{3}m.$$

4. For the following space groups determine (a) the Bravais lattice, (b) the crystal system, (c) the crystal class, (d) whether there is a center of symmetry. (Use the *International Tables* to check your answers).

$$Ia, Ccca, Amm2, I4_1/a, P4nc, I4_1/acd, R3c, P31c, P6_3mc, Ia\bar{3}, Fd\bar{3}c$$

5. Draw a projection down  $c$  of the rutile structure (§ 3.4, p. 78). Show that Ti has six near O atoms and O has three near Ti atoms. Shade in the  $\{Ti\}O_6$  polyhedra to see how they are connected. You should draw *at least* 4 unit cells. [Hint: see Chapter 4 for advice on drawing structures.]

6. Show that the following sets of points in a cubic unit cell all describe a face-centered lattice with a different choice of origin:

- (a)  $0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0$
- (b)  $0,0,1/2; 0,1/2,0; 1/2,0,0; 1/2,1/2,1/2$
- (c)  $1/4,1/4,1/4; 1/4,3/4,3/4; 3/4,1/4,3/4; 3/4,3/4,1/4$
- (d)  $3/4,3/4,3/4; 3/4,1/4,1/4; 1/4,3/4,1/4; 1/4,1/4,3/4$

7. Show that the Al atoms in the structure of  $Ca_3Al_2Si_3O_{12}$  structure (§ 3.4, p. 80) lie on points of a body-centered lattice described by a cell with doubled edge (so the cell contains 16 lattice points rather than 2).

8. The crystal structure of  $Cu_2O$  (cuprite) is cubic with:

$$\begin{array}{ll} \text{Cu at} & 0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0 \\ \text{O at} & 1/4,1/4,1/4; 3/4,3/4,3/4 \end{array}$$

The Cu atoms fall on the points of a face-centered lattice, and the O atoms fall on the points of a body-centered lattice. The lattice of the structure is primitive (in fact the space group is  $Pn\bar{3}m$ ). What is the coordination of Cu by O and of O by Cu (i.e. how many nearest neighbors and how are they arranged)?

9. The crystal structure of cuprite was one of the first determined. From the unit cell

parameter ( $a = 4.26 \text{ \AA}$ ) and the density ( $\rho = 6.1 \text{ g cm}^{-3}$ ) show that there must be 4 Cu and 2 O atoms in the unit cell. Now get a copy of the *International Tables* and show, by elimination, that the only possible cubic symmetry is  $Pn\bar{3}m$  (in which case the structure must be that given in Exercise 8) or  $P\bar{4}3m$ .<sup>1</sup> (Why can  $P23$ ,  $P4_232$  and  $Pn\bar{3}$  be ruled out?). [Hint: begin by eliminating all space groups in which positions  $a$  (which have the lowest multiplicity) consist of more than 2 points].

10. The structure of zircon,  $\text{ZrSiO}_4$ , has been described as:

$I4_1/amd$ ,  $a = 6.607$ ,  $c = 5.982 \text{ \AA}$ . Origin at  $\bar{4}2m$

Zr in 4  $a$ :  $I + (0,0,0; 0,1/2,1/4)$ . Si in 4  $b$ :  $I + (0,0,1/2; 0,1/2,3/4)$

O in 16  $h$ :  $I + (0,\pm x,z; \pm x,0,\bar{z} \ 0,1/2\pm x,1/4-\bar{z}; \pm x,1/2,1/4+z)$ ,  $x = 0.1839$ ,  $z = 0.3203$

Transforming to an origin at a center (see § 3.7.4, p.91):

Zr in 4  $a$ :  $I \pm (0,3/4,1/8)$ . Si in 4  $b$ :  $I \pm (0,1/4,3/8)$

O in 16  $h$ :  $I \pm (0,x,z; 0,1/2-x,z; 1/4+x, 1/4,3/4+z; 3/4-x,1/4,3/4+z)$ ,  $x = 0.0661$ ,  $z = 0.1953$

11. An important structure type is that of  $\text{CeCu}_2$ ;  $\text{KHg}_2$  has been described as having the same symmetry:

$\text{CeCu}_2$   $Imma$ ,  $a = 4.43$ ,  $b = 7.06$ ,  $c = 7.48 \text{ \AA}$

Ce in 4  $c$ :  $I \pm (0,1/4,z)$ ,  $z = 0.538$

Cu in 8  $h$ :  $I \pm (0,y,z; 0,1/2-y,z)$ ,  $y = 0.051$ ,  $z = 0.165$

$\text{KHg}_2$   $Imma$ ,  $a = 8.10$ ,  $b = 5.16$ ,  $c = 8.77 \text{ \AA}$

K in 4  $c$ :  $I \pm (0,1/4,z)$ ,  $z = 0.703$

Hg in 8  $h$ :  $I \pm (\pm x,1/4,z)$ ,  $x = 0.190$ ,  $z = 0.087$

Plot both structures in projection down the *shortest* axis and thus show that they are essentially the same (except for a change of scale).<sup>2</sup> An exactly equivalent description of the structure of  $\text{KHg}_2$  is (compare with that given for  $\text{CeCu}_2$ ):  $a = 5.16$ ,  $b = 8.10$ ,  $c = 8.77 \text{ \AA}$ . K in 4  $a$ ,  $z = 0.457$ ; Hg in 8  $h$ ,  $y = 0.060$ ,  $z = 0.163$ . [Hints: for some help with drawing structures see Chapter 4. These structures are nicely illustrated if the four shortest Cu-Cu or Hg-Hg bonds are drawn in (two of these superimpose in projection)—see § 7.3.5]

12. Use the *International Tables A* to find the maximal *non-polar*  $t$  subgroups ( $H$ ) of  $G = Pm\bar{3}m$ . [Hint: they will be found as maximal subgroups of maximal subgroups; the two highest symmetries have index 6 and 8 in  $G$  respectively. For the polar crystal classes, see p. 50.] These are the possible symmetries of the polar structures formed when a cubic perovskite (such as  $\text{BaTiO}_3$  or  $\text{SrTiO}_3$ ) deforms to polar structures at low temperature.

<sup>1</sup>Systematic absences in the powder pattern immediately point to  $Pn\bar{3}m$ . Specifically, reflections with indices  $hk0$  are absent for  $h+k$  odd (100, 210 etc.).

<sup>2</sup>This example is taken from *Elements of Inorganic Structural Chemistry* by E. Parthé (available from K. Sutter Parthé, 49 Chemin du Gué, CH-1213 Petit-Lancy, Switzerland).

## CHAPTER 4

### LATTICE GEOMETRY

In this chapter we explain how the directions of lines and the orientations of planes in a crystal are specified. The description necessarily involves reference to the coordinate system and if alternative unit cell descriptions are used the description of directions and so on. will change, so we next discuss unit cell transformations. Next we give a compendium of formulas useful for crystallographic calculations. Finally we present some comments and hints on drawing crystal structures.

#### 4.1 Directions in a crystal

##### 4.1.1 General

A direction in a crystal is specified by three integers  $u, v, w$  and is written  $[uvw]$ . The direction is then that of the vector  $ua + vb + wc$  where  $a, b$  and  $c$  are the unit cell (lattice) vectors. Normally  $u, v$  and  $w$  are integers that have no common factors other than 1 (i.e. they are *coprime*). Thus the direction of the  $x$ -axis is  $[100]$ , that of the  $y$ -axis is  $[010]$  and that of the  $z$ -axis is  $[001]$ . Note that  $[\bar{1}00]$  refers to the  $-x$  direction. Fig. 4.1 illustrates these and some other principal directions. In the figure the shape of the unit cell is to be considered quite general (i.e. not necessarily a cube) and the heavy lines meet at the origin; the filled circle is a point at  $0,1/2,1$ . In crystallography the symbol  $[uvw]$  is often said to represent a *zone axis* and all planes parallel to  $[uvw]$  are said to fall in that zone.

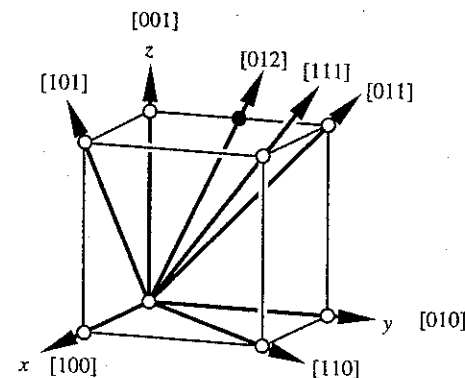


Fig. 4.1 Directions in a crystal.