the $Fe^{3+}$ ions have on the powder pattern if it was present (a) as a separate iron hydroxide phase and (b) substituting for $Al^{3+}$ in the crystal structure of $Al(OH)_3$.

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# Chapter 6

# Point Groups, Space Groups and Crystal Structure

A working knowledge of space groups is valuable for anyone interested in crystal chemistry, even though one does not wish to become involved in the actual determination of crystal structures. Without such a knowledge, one is entirely dependent for information about crystal structures on the availability of three-dimensional crystal models and good quality drawings in the literature. Once the basic principles of space groups are grasped, however, it is possible to make drawings of a structure for oneself, from different orientations if required, or even to construct one's own three-dimensional models. All that is needed is a listing of the atomic coordinates in the structures and details of the relevant space group.

This chapter is written for the non-crystallographer; short-cuts are made and many of the complications and subtleties of space groups are avoided. The main objective is to show the relation between space groups and sets of atomic

coordinates, on the one hand, and three-dimensional crystal structures, on the other. As a background, it is assumed that the reader is familiar with unit cells, crystal systems, Bravais lattices and the elements of point and space symmetry. Summaries of these are given in Section 5.3 and Tables 5.2, 5.3. We begin with a discussion of point groups. Although point groups are not absolutely essential to the stated objective of this chapter it is well worth while to make their acquaintance. Point groups are much simpler than space groups because the elements of translational symmetry are absent from point groups. They therefore provide a relatively painless method of introduction to the subject while introducing the necessary concepts at an early stage.

## 6.1 Point groups

The elements of point symmetry which may be observed in crystals are the rotation axes 1, 2, 3, 4 and 6, the inversion axes $\bar{1}, \bar{2}, \bar{3}, \bar{4}$ and $\bar{6}$, and the mirror plane, $m$ (which is equivalent to $\bar{2}$). These symmetry elements may occur either alone or in various possible combinations with each other to give a total of thirty-two possible crystallographic point groups. The method of drawing and labelling point groups which is used here is the same as that recommended by *International*

Table 6.1 *Point symmetry elements*

| Symmetry element | Written symbol | Graphical symbol |
|---|---|---|
| | 1 | None |
| Rotation | 2 | ● |
| axes | 3 | ▲ |
| | 4 | ◆ |
| | 6 | ⬢ |
| | $\bar{1}$ | None* |
| Inversion | $\bar{2}(\equiv m)$ | ——† |
| | $\bar{3}(\equiv 3 + \bar{1})$ | △ |
| axes | $\bar{4}$ | ◈ |
| | $\bar{6}(= 3/m)$ | ⬡ |
| Mirror plane | $m$ | —— |

* The inversion axis, $\bar{1}$, equivalent to a centre of symmetry, is represented as ○ in space groups but does not have a formal graphical representation in point groups, even though it is present in many point groups.
† The inversion axis $\bar{2}$ does not have a separate graphical symbol other than that of the mirror plane equivalent to it.

Table 6.2 *The thirty-two point groups*

| Crystal system | Point groups |
|---|---|
| Triclinic | 1, $\bar{1}$ |
| Monoclinic | 2, $m$, 2/$m$ |
| Orthorhombic | 222, $mm2$, $mmm$ |
| Tetragonal | 4, $\bar{4}$, 4/$m$, 422, 4$mm$, $\bar{4}2m$, 4/$mmm$ |
| Trigonal | 3, $\bar{3}$, 32, 3$m$, $\bar{3}m$ |
| Hexagonal | 6, $\bar{6}$, 6/$m$, 622, 6$mm$, $\bar{6}m2$, 6/$mmm$ |
| Cubic | 23, $m3$, 432, $\bar{4}3m$, $m3m$ |

*Tables for X-ray Crystallography*, Vol. 1. The symbols for the different point symmetry elements are given in Table 6.1. The thirty-two point groups, classified according to their crystal system, are listed in Table 6.2 and Appendix 5.

### 6.1.1 Representation of point groups and selected examples

Point groups are represented graphically as *stereograms*. Stereograms are used a lot in, for example, geology to represent direction in crystals and to show the relative orientation of crystal faces. For present purposes, all we need to know is that point groups are represented by a circle (a sphere in projection), usually with one of the axes perpendicular to the plane of the circle and passing through its
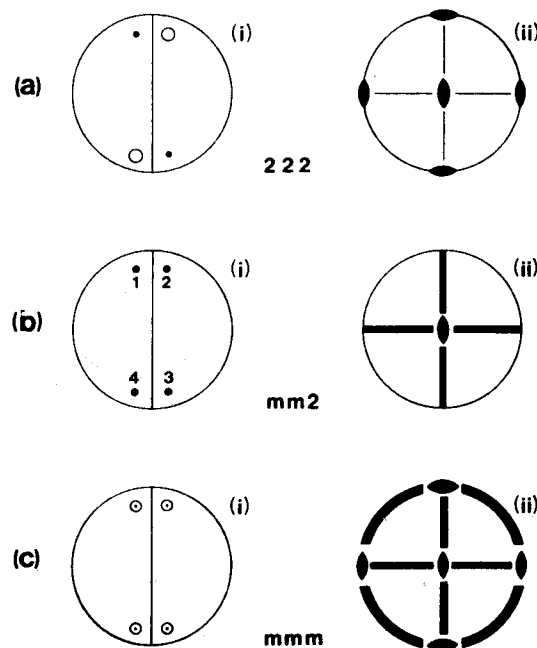


Fig. 6.1 The orthorhombic point groups

centre. The three orthorhombic point groups are drawn out in Fig. 6.1. For each, two diagrams are used. The right-hand one shows the symmetry elements that are present and the left-hand one shows the *equivalent positions* that are generated by the presence of these symmetry elements.

### 6.1.1.1 *222*

This orthorhombic point group has three mutually perpendicular twofold axes. That axis perpendicular to the plane of the paper is represented by the symbol in the centre of the circle (a, ii). The axes lying horizontally and vertically in the plane of the paper are represented by the two respective pairs of symbols lying on the circumference of the circle.

The presence of three mutually perpendicular twofold axes gives sets of four *equivalent positions* (a, i). An equivalent position is really the same as the 'identical orientation' used in defining symmetry elements. Thus the presence of a single twofold axis means that an object possessing such symmetry has two identical orientations (separated by rotation of 180°). In other words, a twofold axis has associated with it two equivalent positions. The dots and circles in the left-hand diagrams represent equivalent positions that are not in the plane of the paper; let us say that dots are above the plane and open circles are an equal distance below the plane.

The sequence of steps that is used in deriving the equivalent positions of point group 222 are set out in Fig. 6.2. Commencing with a single position in (i) (the thin vertical line that bisects the circle is merely a construction line), the effect of adding a twofold axis perpendicular to the plane of the paper is to generate a second position (ii). Both positions in (ii) must be at the same height, above the
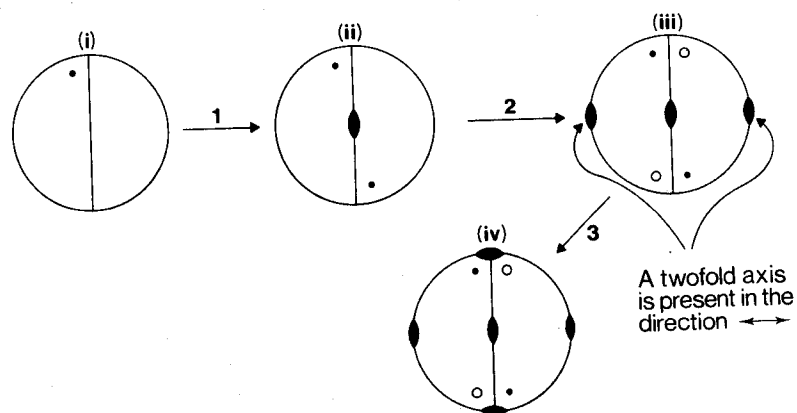


**Fig. 6.2** Equivalent positions in the point group 222. In step 1, a twofold axis perpendicular to the plane of the paper is added. In 2, a second twofold axis, in the plane of the paper and lying horizontal, is added. In 3, a third twofold axis, lying vertically in the plane of the paper has been automatically created by step 2

plane of the paper, since the twofold axis is perpendicular to this plane. On adding a second twofold axis, in the plane of the paper and, say, in the horizontal direction, each of the positions in (ii) generates another to give the four positions shown in (iii). Since this second rotation axis is in the plane of the paper, the two new positions generated by this axis must be below the plane of the paper and so are represented as open circles. Comparison of (iii) and (iv) shows that the addition of a third twofold axis, in the plane of the paper and lying vertical, does not lead to any extra equivalent positions in addition to the four already present. In fact, this third axis is also present in (iii) and is generated automatically by the other two axes. The point group 222 could therefore be represented in the shortest possible notation, as 22 because the third twofold axis is not independent. The longer notation is normally used in order to show consistency with the essential symmetry requirements (Table 5.2) for orthorhombic unit cells.

### 6.1.1.2 *mm2*

This orthorhombic point group contains two mirror planes at right angles to each other with a twofold axis passing along the line of intersection of the mirror planes. In (b, ii) of Fig. 6.1, the twofold axis is perpendicular to the paper and the mirror planes are indicated in projection as the thick lines lying horizontally and vertically. This point group also has four equivalent positions and all are at the same height relative to the plane of the paper (b, i). Labelling the starting position as 1, the effect of adding the twofold axis is to generate position 3. The vertical mirror plane then generates position 2 from 1 and position 4 from 3. The horizontal mirror plane relates positions 1 and 4 and also 2 and 3; it does not create any new positions. As in the previous example, the third symmetry element is not independent but is generated by the combined operation of the other two elements. The choice of order of the symmetry elements is immaterial; any two out of the three, in combination, will generate the third element.

### 6.1.1.3 *mmm*

This orthorhombic point group contains, as essential symmetry elements, three mirror planes mutually perpendicular to each other and, as a consequence of the mirror planes, three mutually perpendicular twofold axes are generated. (Note that the reverse process does not occur. The three twofold axes in 222 do not lead to the generation of mirror planes.) These symmetry elements are shown in (c, ii) of Fig. 6.1. The symbols are the same as in the two previous examples, with the addition of the thick circle which indicates the presence of a mirror plane in the plane of the paper.

Eight equivalent positions occur in the point group *mmm*, four at the same height above the plane of the paper and four at the same height and below the plane (c, i). To see how these positions may be generated, the action of any two mirror planes generates four positions in a plane, as shown in (b, i) for the point group *mm2*. The action of the third mirror plane (the one lying in the plane of the paper) gives the eightfold set of positions in (c, i).
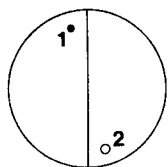
**Fig. 6.3** Triclinic point group, $\bar{1}$, with a centre of symmetry

Only three orthorhombic point groups are possible. If other combinations of symmetry elements are tried, many will turn out to be equivalent to one of the three allowed point groups. For instance, the combination $22m$ can readily be shown to yield the same set of positions and symmetries as $mmm$.

Of the three orthorhombic point groups, only $mmm$ possesses a centre of symmetry ($\bar{1}$). The appearance of a centre of symmetry is shown in Fig. 6.3 for the triclinic point group $\bar{1}$. Inversion through the centre of the circle converts position 1 to 2, and vice versa. Each position in $mmm$ has a centrosymmetrically related partner, but this is not the case for 222 and $mm2$. The relevance of centrosymmetry is discussed in Section 6.2.

### 6.1.1.4 *32*

Let us consider one example of trigonal symmetry which is characterized by a single threefold axis (Fig. 6.4). As the threefold axis is the unique axis it is arranged to be perpendicular to the plane of the paper (Fig. 6.4 (ii)). There are also three twofold axes lying in the plane of the paper and at 60° to each other. In fact, only one of these is independent and so only one appears in the symbol 32. To find the equivalent positions in this point group, start with position 1 and consider the effect of the threefold axis (rotation by 120°). Positions 3 and 5 result. Then consider the effect of one of the twofold axes, say XX' in (ii). This generates three new positions: $1 \rightarrow 4$, $3 \rightarrow 2$ and $5 \rightarrow 6$, and two more twofold axes YY' and ZZ' are also automatically generated, e.g. axis YY' relates positions 1 and 6, 2 and 5, 3 and 4.

Of the thirty two crystallographic point groups, twenty seven are non-cubic and we have looked at five of these. The remaining twenty two can be treated along similar lines and should cause no problem. The main difficulty likely to be encountered concerns the orientation of the different symmetry elements in a point group. Some guidelines are as follows. In monoclinic, hexagonal, trigonal and tetragonal point groups, the unique axis is arranged to be perpendicular to
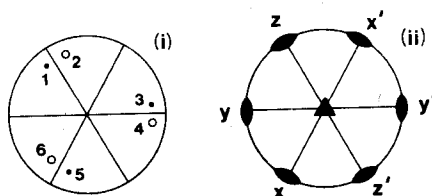


**Fig. 6.4** The trigonal point group 32

the plane of the paper (stereogram). A slashed line, as in 4/$mmm$, indicates that, in this case the fourfold axis has a mirror plane perpendicular to it; it would be clearer if the symbol were written as (4/$m$)$mm$. In tetragonal, trigonal and hexagonal point groups, the twofold axes, as in $\bar{4}2m$, are always in the plane perpendicular to the unique axis (in this case perpendicular to $\bar{4}$).

The five cubic point groups are rather more complicated to work with as they are difficult to represent by simple two-dimensional projections. This is because there are so many symmetry elements present and many are not perpendicular to each other, e.g. threefold and fourfold axes are at 45° to each other. Whereas non-cubic point groups may be drawn with their symmetry axes either in the plane or perpendicular to the plane of the stereograms, this is not generally possible for cubic point groups and oblique projections are needed to represent the threefold axes (see Appendix 5). No further discussion of cubic point groups will be given.

### 6.1.2 Examples of point symmetry of molecules: general and special positions

The relationships between point symmetry and structure are best seen by some examples taken from small molecules. Consider the methylene dichloride molecule, $CH_2Cl_2$ (Fig. 6.5). This possesses a single twofold axis which bisects the H—C—H and Cl—C—Cl bond angles (a) and two mirror planes (b and c). The twofold axis is parallel to the line of intersection of the mirror planes. These symmetry elements may be represented as in (d), in which the twofold axis is perpendicular to the plane of the paper and the mirror planes appear in projection as horizontal and vertical lines. From inspection of Fig. 6.1, it is seen that $CH_2Cl_2$ belongs to the point group $mm2$. However, the number of equivalent positions in $mm2$ (b, i) is four, and this does not appear to tally with the realities of the $CH_2Cl_2$ molecule. If we take a hydrogen atom as one equivalent position, there are only two hydrogens present and therefore only two possible equivalent
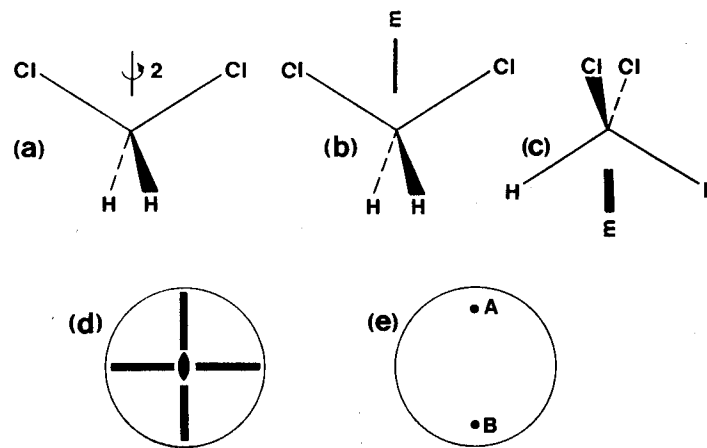


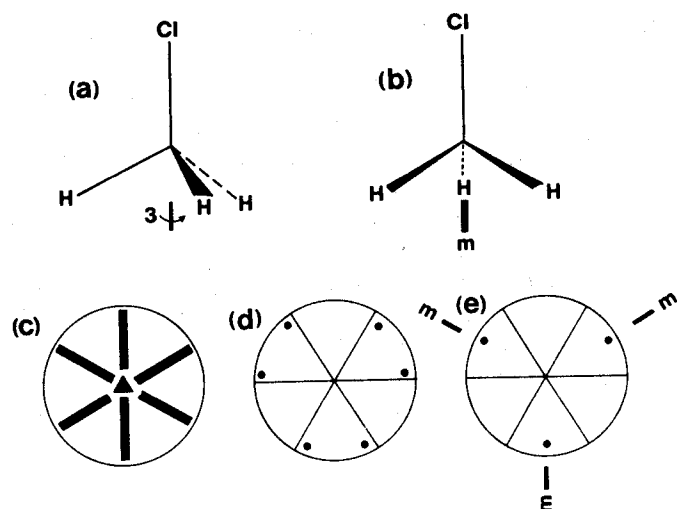**Fig. 6.5** The point group $mm2$ of the methylene dichloride molecule

Fig. 6.6 The point group 3m of the methyl chloride molecule

positions in the molecule. The anomaly is resolved by letting the equivalent positions in Fig. 6.1 (b, i) lie on the vertical mirror plane instead of to either side of the mirror. This yields the arrangement shown in Fig. 6.5(e), which has only two equivalent positions. Thus, positions 1 and 2 in Fig. 6.1 (b, i) become the single position A in Fig. 6.5(e). We can now distinguish between the *general equivalent positions* of a point group and the *special equivalent positions*; the latter arise when the general positions lie on a symmetry element such as a mirror plane or rotation axis. Thus A and B in Fig. 6.5(e) are special positions.

As a further example, consider the point symmetry of the methyl chloride molecule, $CH_3Cl$ (Fig. 6.6). The molecule possesses one threefold axis along the direction of the C—Cl bond (a). It does not have any twofold axes but has three mirror planes oriented at 60° to each other; one is shown in (b). The threefold axis coincides with the line of intersection of the mirror planes. The symmetry elements are shown as a stereogram in (c) and by comparison of this with Appendix 5 we see that the point group is 3m. The six general equivalent positions in 3m are given in (d). We again have the problem that there are more equivalent positions than possible atoms, and this is overcome by allowing the general positions to lie on the mirror planes (e); the number of positions is thereby reduced to three.

### 6.1.3 Centrosymmetric and non-centrosymmetric point groups

Of the thirty two point groups, twenty one do not possess a centre of symmetry. The absence of a centre of symmetry is an essential but not sufficient requirement for the presence in crystals of optical activity, pyroelectricity and piezoelectricity (Chapter 15). Optical activity is confined to fifteen of the twenty

one non-centrosymmetric point groups and piezoelectricity to twenty of these. This is of use in, for example, the search for new materials with piezoelectric activity; it is a waste of time trying to detect piezoelectricity in crystals whose point group is not among the twenty active groups! Crystallographers also make some use of the piezoelectric effect in structure determinations. It is a considerable help in solving an unknown structure to know the space group at the outset. If a test for piezoelectricity is carried out with positive results, this limits the choice of space group to the non-centrosymmetric ones. The absence of piezoelectricity does not necessarily mean, however, that the point group and space group are centrosymmetric.

### 6.2 Space groups

The combination of the thirty-two possible point groups and the fourteen Bravais lattices (which in turn are combinations of the seven crystal systems, or unit cell shapes, and the different possible lattice types) gives rise to 230 possible space groups. All crystalline materials have a structure which belongs to one of these space groups. This does not, of course, mean that only 230 different crystal structures are possible. For the same reason, the human body (from its external appearance) is not the only object to belong to point group $\bar{2}$—teapots also do.

Space groups are formed by adding elements of translation to the point groups. The space symmetry elements, screw axes and glide planes are derived from their respective point symmetry elements, rotation axes and mirror planes by adding a translation step in between each operation of rotation or reflection (see Section 5.3.4). A complete tabulation of all the possible screw axes and glide planes and their symbols is not given here. Instead, symbols are explained as they arise. Also, there is space to discuss only a few of the simpler space groups. The interested reader is recommended to acquire his own copy of *International Tables for X-ray Crystallography*, Vol. 1; once the basic rules have been learned, by working through the examples given here, there should be no difficulty in understanding and using any space group.

The written symbol of a space group is a list of between two and four characters. The first character is always a capital letter which corresponds to the lattice type—P, I, A, etc. The remaining characters correspond to some of the symmetry elements that are present. If the crystal system has a unique or principal axis (e.g. the fourfold axis in tetragonal crystals), the symbol for this axis appears immediately after the lattice symbol. For the remaining characters, there are no universal rules but, instead, different rules for different crystal systems. As these rules are not essential to an understanding of space groups and are not usually of interest to the non-specialist, they are not repeated here.

Space groups are usually drawn as parallelograms with the plane of the parallelogram corresponding to the xy plane of the unit cell. By convention (Fig. 6.7), the origin is taken as the top left-hand corner, with y horizontally, x vertically (downwards) and the positive z direction pointing up out of the plane of the paper. For each space group, two parallelograms are used, the left-hand one
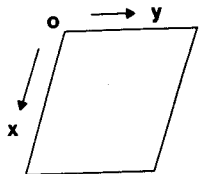
**Fig. 6.7** Convention used to label axes in a space group

to give the equivalent positions and the right-hand one the symmetry elements that are present. Let us see some examples. Each one will introduce at least one new feature.

### 6.2.1 Triclinic PĪ

This space group is primitive and centrosymmetric; it is shown in Fig. 6.8. The right-hand diagram shows the symmetry elements: there are centres of symmetry at the origin ($t$), midway along the $a$ and $b$ edges and in the middle of the C face (i.e. the face bounded by $a$ and $b$). Additional centres of symmetry, not shown, occur in the middle of the other faces, halfway along the $c$ edge and at the body centre of the unit cell.

The left-hand diagram gives the equivalent positions in the space group PĪ. To derive them, it is necessary to choose a starting position and operate on this position with the various symmetry elements that are present. The conventional starting position is at 1, close to the origin and with small positive values of $x$, $y$ and $z$ (the latter indicated by the + sign). This position must be present in all other unit cells (definition of the unit cell) and three of these are shown as 1', 1" and 1'''.

Consider now the effect of the centre of symmetry, $t$, at the origin of the unit cell. This acts upon position 1 to create position 2. The minus sign at 2 indicates a negative $z$ height and the comma shows that position 2 is enantiomorphous relative to position 1. The effect of any reflection or inversion operation is to
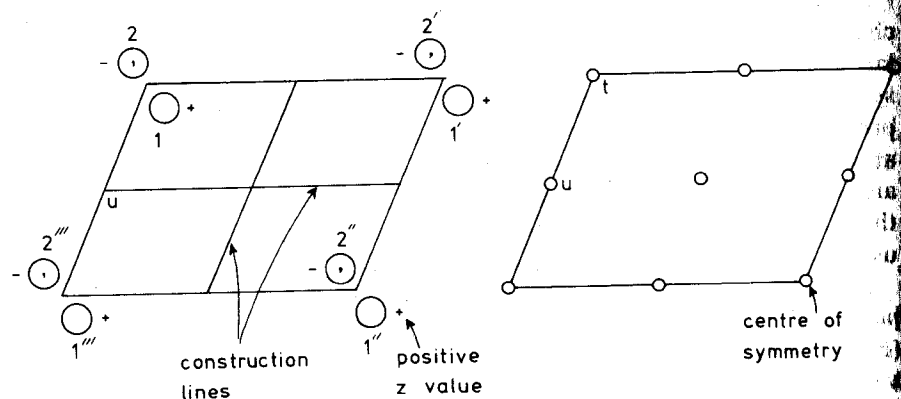


**Fig. 6.8** Space group PĪ. Coordinates of equivalent positions: $xyz$, $\bar{x}\bar{y}\bar{z}$
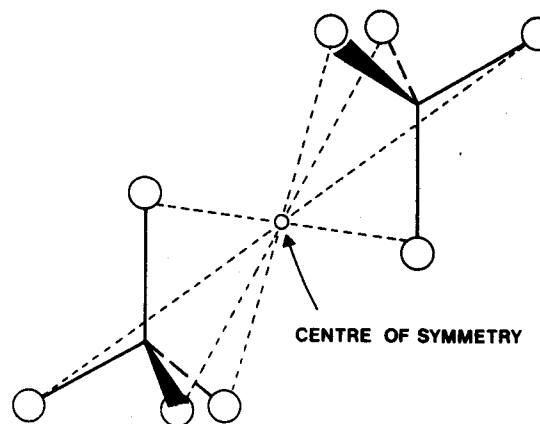
**Fig. 6.9** Two tetrahedra related by a centre of symmetry.

convert a left-handed object into a right-handed one. This is shown in Fig. 6.9 for two tetrahedra which are positioned so as to be related to each other by inversion through a centre of symmetry. Thus, although individual tetrahedra do not possess a centre of symmetry, groupings of tetrahedra may possess one. Positions 2', 2" and 2''' in Fig. 6.8 are automatically generated from position 2 because they are equivalent positions in neighbouring cells.

The next step is to write down the coordinates of the equivalent positions. This is done in the form $x$, $y$, $z$ where $x$, $y$ and $z$ are the fractional distances, relative to the unit cell edge dimensions, from the origin of the cell. Let position 1 have fractional coordinates $x$, $y$ and $z$. Position 2 is then $-x$, $-y$, $-z$. Position 2" is at $1-x$, $1-y$, $-z$, etc. If a position lies outside the unit cell under consideration, an equivalent position within the unit cell can be found, usually by adding or subtracting 1 from one or more of the fractional coordinates. Position 2" is outside the cell because it has a negative $z$ value; the equivalent position inside the cell is given by a displacement of one unit cell in the $z$ direction and has coordinates $1-x$, $1-y$, $1-z$. In shorthand, these coordinates are written as $\bar{x}$, $\bar{y}$, $z$. The unit cell in the space group PĪ has two equivalent positions, $x$, $y$, $z$ (position 1) and $\bar{x}$, $\bar{y}$, $\bar{z}$ (height $c$ above 2").

Although only one centre of symmetry is necessary to generate the equivalent positions in PĪ other centres of symmetry are automatically created. For example, the centre of symmetry at $u$ arises because pairs of positions such as 1 and 2''', 2 and 1''', etc., are centrosymmetrically related through $u$. This may be seen from the diagram or may be proven by comparing coordinates of the three positions. Positions 2''' and 1 are equidistant from $u$ and lie on a straight line that passes through $u$.

The positions $x$, $y$, $z$ and $\bar{x}$, $\bar{y}$, $\bar{z}$ are called *general positions* and apply to any value of $x$, $y$ and $z$ between 0 and 1. In certain circumstances, $x$, $y$, $z$ and $\bar{x}$, $\bar{y}$, $\bar{z}$ coincide, e.g. if $x = y = z = \frac{1}{2}$. In this case, there is only one position, called a *special position*. The special positions in PĪ arise when the general position lies on a centre of

symmetry. The coordinates of the onefold special positions are, therefore, $(0, 0, 0)$, $(\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and correspond to the corner, edge, face and body centres of the unit cell.

### 6.2.2 Monoclinic C2

The convention adopted here for labelling the unique twofold axis in monoclinic space groups is that which is in most common use, namely, with $b$ as the unique axis. It is a pity that this is different to the use of $c$ as the unique axis in tetragonal, trigonal and hexagonal cells but this usage for monoclinic cells is now so well established that it is unlikely to be altered. With $b$ as the unique axis the unit cell projects onto the $xy$ plane as a rectangle (because $\gamma = 90°$), as shown in Fig. 6.10. Since $\beta \neq 90°$, the $z$ axis is not perpendicular to the plane of the paper but is inclined to the vertical.

The C-centring in space group C2 means that the Bravais lattice has a lattice point at the origin (with coordinates $0, 0, 0$) and a lattice point in the middle of the side bounded by $a$ and $b$, at $\frac{1}{2}, \frac{1}{2}, 0$. For any position $x, y, z$ in this space group, there will, therefore, be an equivalent position at $x + \frac{1}{2}, y + \frac{1}{2}, z$ (i.e. $(x, y, z)$ $+ (\frac{1}{2}, \frac{1}{2}, 0)$). This C-centring has no representation in the right-hand diagram of Fig. 6.10 but can be seen in the left-hand diagram. The main symmetry element that is present is a twofold rotation axis (d), parallel to $b$ and coincident with $b$ (i.e. passing through $x = 0, z = 0$). A twofold rotation axis in the plane of the paper is indicated by an arrow. Other symmetry elements are generated by a combination of the twofold rotation axis and the C-centring, namely, a twofold rotation axis (e) parallel to $b$, cutting the $x$ axis at $\frac{1}{2}$ and the $z$ axis at 0, and two twofold screw axes (f and g), again parallel to $b$ and cutting the $x$ axis at
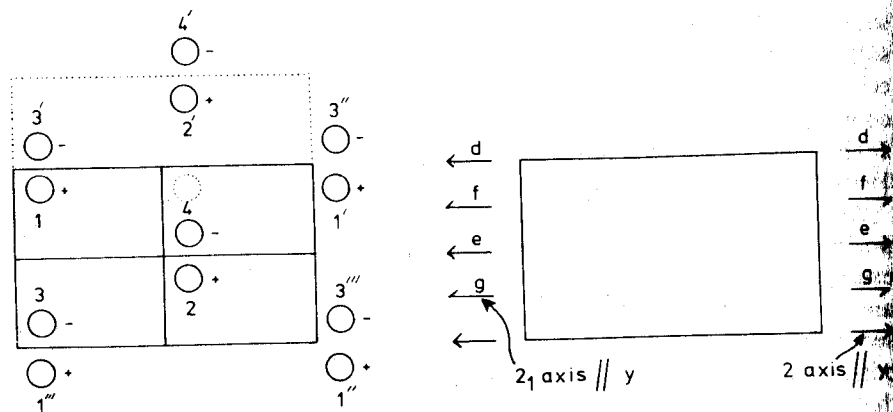


**Fig. 6.10** Monoclinic space group C2
Coordinates of equivalent positions
$000 : xyz, \bar{x}y\bar{z}$
$\frac{1}{2}\frac{1}{2}0 : x + \frac{1}{2} y + \frac{1}{2} z, \frac{1}{2} - x \frac{1}{2} + y \bar{z}$

$\frac{1}{4}$ and $\frac{3}{4}$ and $z$ at 0. Screw axes in the plane of the paper are represented as half arrows.

Space group C2 has four equivalent positions. To see how they arise, let us take position 1 as a general position; $1', 1''$ and $1'''$ are the equivalent positions in neighbouring unit cells. The effect of C-centring is to create position 2 which is displaced by $(\frac{1}{2}, \frac{1}{2}, 0)$ from position 1. The effect of the twofold rotation axis (d) is to rotate position 1 about the $b$ edge by 180° and create position 3'. As 1 has a positive $z$ coordinate, 3' must have a corresponding negative $z$ value. Similarly, positions 2 and 4' are related by this same twofold rotation axis; 4 and 4' are identical positions in adjacent cells. Alternatively, 4 may be regarded as generated by the action of the C-centring on 3'.

The new twofold rotation axis (e) that is created relates, for example, positions 1 and 3, 2 and 4, 1''' and 3', etc. The twofold screw axis (f) relates, for example, 1 and 4: in a combined operation, 1 is translated halfway along $y$, retaining its $x$ and $z$ values, to the position shown as the dotted circle and then rotated 180° about the axis parallel to $y$ and at $x = \frac{1}{4}, z = 0$, to arrive at 4. Repetition of the process takes position 4 to 1' which effectively takes us back to the starting position. Similarly, related sets of positions are 3', 2 and 3''; 3, 2' and 3'''; 1''', 4' and 1'', etc. By similar reasoning, screw axis (g) relates positions 3, 2 and 3''', and so on.

The coordinates of positions 1 to 4 are as follows: $x, y, z; x + \frac{1}{2}, y + \frac{1}{2}, z; \bar{x}, y,$ $- z; \frac{1}{2} - x, \frac{1}{2} + y, - z$. As positions 3 and 4 lie below the plane of the paper, they are outside the chosen unit cell. The positions equivalent to 3 and 4 that are inside the cell are displaced by one cell along $z$ and have coordinates $\bar{x}, y, \bar{z}$ and $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$. These four positions can be grouped into two sets: $x, y, z; \bar{x}, y, \bar{z}$ and $x + \frac{1}{2}, y + \frac{1}{2}, z; \frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$, such that the second set is related to the first by the lattice centring (i.e. by adding $\frac{1}{2}, \frac{1}{2}, 0$ to the coordinates). It is common practice (e.g. in *International Tables of X-ray crystallography*) to list only those positions that belong to the first set and at the same time specify that the other positions are created by the lattice centring. This leads to considerable shortening and simplification in labelling the equivalent positions of the more complex and higher symmetry space groups.

The general positions in space group C2 are fourfold, i.e. there are four of them per cell, but if they lie on the twofold rotation axes their number is reduced to two and they become special positions. Thus, if $x = z = 0$, the two positions have coordinates $0, y, 0$ and $\frac{1}{2}, y + \frac{1}{2}, 0$. A second set of special positions arises when $x = 0, z = \frac{1}{2}$ (the reader may like to check that there is a twofold axis parallel to $b$ and at $x = 0, z = \frac{1}{2}$ not indicated in Fig. 6.10: it is at height $c/2$ above axis d).

We have seen earlier how the presence of lattice centring or elements of space symmetry lead to systematically absent reflections from the X-ray patterns. For space group C2, the C-centring imposes the condition that only those reflections that satisfy the rule, for $hkl$: $h + k = 2n$, may be observed. The $2_1$ screw axes parallel to $b$ impose the condition for reflection that for $0k0$: $k = 2n$. However, this is also a consequence of the C-centring condition, for the special case that $h = l = 0$ and so does not lead to any extra absences.

### 6.2.3 Monoclinic C2/m

This space group, shown in Fig. 6.11, is also C-centred and has, as its principal symmetry elements, a mirror plane perpendicular (/) to a twofold axis. The twofold axis is parallel to $b$, by convention, and therefore the mirror plane is the $xz$ plane. Two mirror planes are present in the cell; they intersect $b$ at 0 and $\frac{1}{2}$ and are shown as thick vertical lines in Fig. 6.11. As in the space group C2, there are two twofold rotation axes, parallel to $b$ and intersecting $a$ at 0 and $\frac{1}{2}$, and two $2_1$ screw axes parallel to $b$ and intersecting $a$ at $\frac{1}{4}$ and $\frac{3}{4}$. All of these 2 and $2_1$ axes are at $c$ height equal to zero. An additional set of axes, not shown, occurs at $c = \frac{1}{2}$. Also present, as will be discussed later, are centres of symmetry and glide planes.

The space group C2/m contains eight general equivalent positions, all of which may be generated from position 1 by the combined action of the C-centring, twofold axis and mirror plane. Thus, the C-centring creates an equivalent position, 2, after translation by $\frac{1}{2}, \frac{1}{2}, 0$. Action of the twofold axis passing through the origin generates 6′ from 1. Position 3 is similarly related to 2 by the action of the twofold axis passing through $a = \frac{1}{2}$, $c = 0$. Alternatively, 3 may be generated from 6′ by the C-centring condition. The mirror plane at $b = 0$ generates positions 8″ from 1 and 7‴ from 6′. Note that 8″ and 1 are at the same positive $c$ value and that 8″ contains a comma to indicate its enantiomorphous relation to 1. Positions 4 and 5 are related to 3 and 2 by the mirror plane that cuts $b$ at $\frac{1}{2}$; alternatively, 4 and 5 are generated from 7‴ and 8″ by the centring.

The coordinates of the eight equivalent positions within the cell, together with their number, if shown, are $x, y, z$ (1); $x + \frac{1}{2}, y + \frac{1}{2}, z$ (2); $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$; $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, z$ (5); $\bar{x}, y, \bar{z}$; $\bar{x}, \bar{y}, \bar{z}$; $x, \bar{y}, z$ (8). These eight positions may be grouped into two sets of four positions that are related by the C-centring. The coordinates of both sets are given in Fig. 6.11. Several sets of special positions are possible in this space group, e.g. if $y = 0$, a fourfold set occurs which contains $x, 0,$
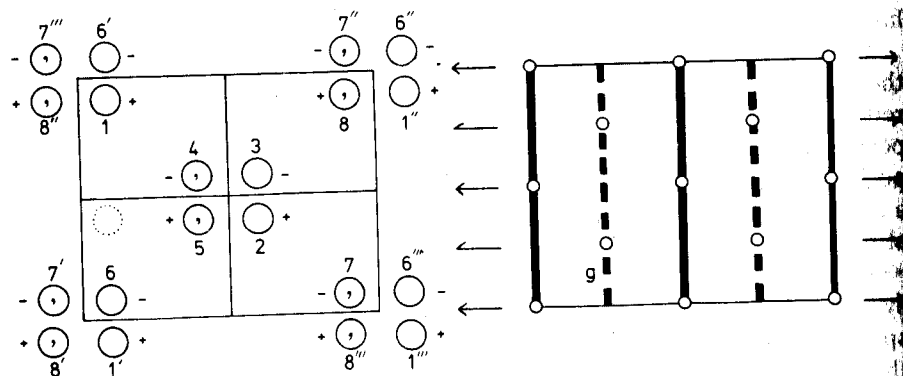


Fig. 6.11 Monoclinic space group C2/m. Coordinates of equivalent positions
$$000: xyz, \ x\bar{y}z, \ \bar{x}y\bar{z}, \ \bar{x}\bar{y}\bar{z}$$
$$\tfrac{1}{2}\tfrac{1}{2}0: \tfrac{1}{2} + x \ \tfrac{1}{2} + y \ z, \ \tfrac{1}{2} + x \ \tfrac{1}{2} - y \ z, \ \tfrac{1}{2} - x \ \tfrac{1}{2} + y \ \bar{z}, \ \tfrac{1}{2} - x \ \tfrac{1}{2} - y \ \bar{z}$$

$z$; $\bar{x}, 0, \bar{z}$; $x + \frac{1}{2}, \frac{1}{2}, z$; $\frac{1}{2} - x, \frac{1}{2}, \bar{z}$. If both $x$ and $y = 0$ and $z = \frac{1}{2}$, a twofold set arises which contains $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

The combination of a mirror plane perpendicular to a twofold axis, together with the C-centring, leads to the generation of several other symmetry elements. These include $2_1$ screw axes parallel to $b$, centres of symmetry and glide planes. For example, the centre of symmetry created at the origin relates positions 1 and 7‴, 6′ and 8″. The thick dashed line $g$ in the right-hand diagram indicates a glide plane for which the translation component is $a/2$ and reflection is across a plane lying perpendicular to $b$. Such a glide plane is called 'an $a$ glide perpendicular to $b$'. Thus, position 1 is translated by $a/2$ to the position shown as the dotted circle; reflection across the plane, $g$, which cuts $b$ at $\frac{1}{4}$ leads to position 5. Repetition of the process converts 5 into 1′, which is equivalent to the starting position, 1. Similarly, positions 8, 2 and 8‴ are related by the glide plane which cuts $b$ at $\frac{3}{4}$.

The presence of glide planes in a crystal may sometimes by detected by the absence of a set of X-ray reflections. For an $a$ glide perpendicular to $b$, the condition limiting the $h0l$ reflections is that $h = 2n$ (i.e. only even $h$ values may be observed). In the space group C2/m, this condition is part of the more general condition for C-centring, namely, that for $hkl$, $h + k = 2n$. Independent evidence for the existence of the glide plane is therefore not immediately available from the X-ray patterns.

### 6.2.4 Orthorhombic P222₁

This primitive orthorhombic space group has twofold rotation axes parallel to $x$ and $y$ and a twofold screw axis parallel to $z$. The feature of this space group, shown in Fig. 6.12, which makes the generation of the equivalent positions a little difficult to visualize, is that the twofold rotation axes parallel to $y$ occur at a $c$ height of $\frac{1}{4}$. Consider first the effect of the axis parallel to $y$ at $a = 0$ and $c = \frac{1}{4}$. The starting position 1 has a small positive $z$ coordinate of $+ z$. The twofold axis is at $z = \frac{1}{4}$; therefore, position 1 is at $(\frac{1}{4} - z)$ *below* the twofold axis. The new position, 2′,
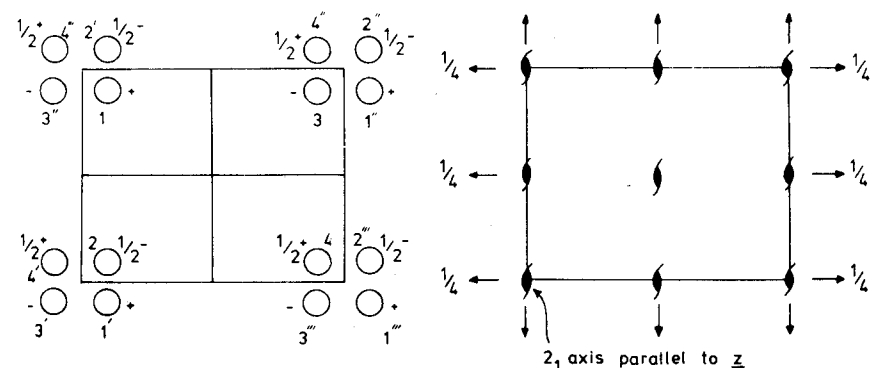


2₁ axis parallel to $\underline{z}$

Fig. 6.12 Orthorhombic space group P222₁. Coordinates of equivalent positions $xyz$,
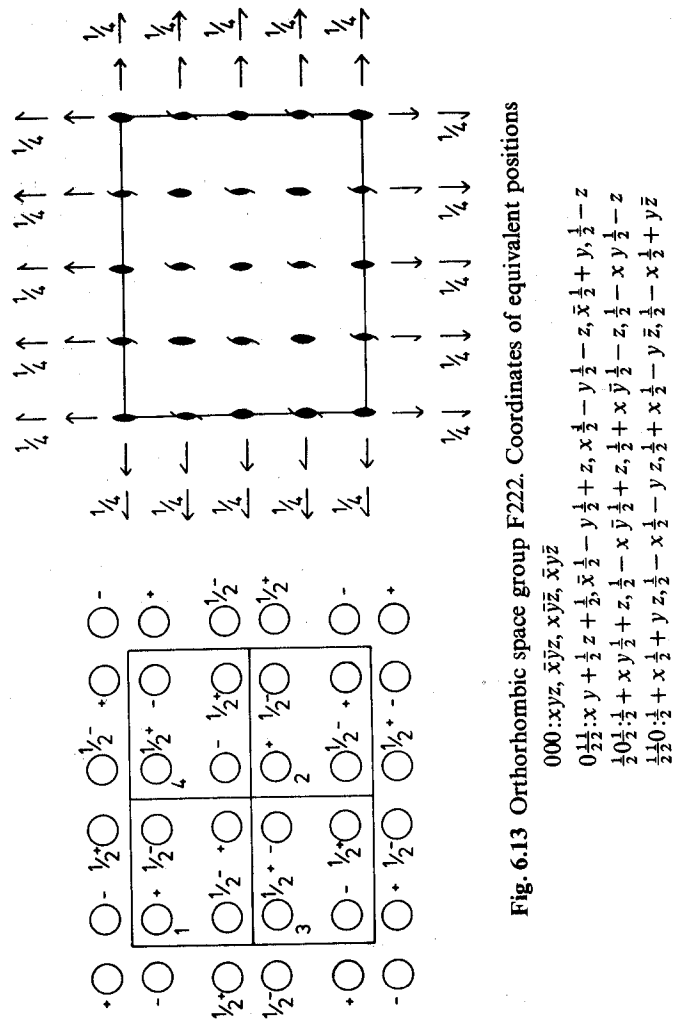$$\bar{x}y\tfrac{1}{2} - z, \ x\bar{y}\bar{z}, \ \bar{x}\bar{y}\tfrac{1}{2} + z$$

**Fig. 6.13** Orthorhombic space group F222. Coordinates of equivalent positions

$000: xyz, \bar{x}\bar{y}z, x\bar{y}\bar{z}, \bar{x}y\bar{z}$

$0\frac{1}{2}\frac{1}{2}: x y+\frac{1}{2} z+\frac{1}{2}, \bar{x}\frac{1}{2}-y\frac{1}{2}+z, x\frac{1}{2}-y\frac{1}{2}-z, \bar{x}\frac{1}{2}+y\frac{1}{2}-z$

$\frac{1}{2}0\frac{1}{2}: \frac{1}{2}+x y \frac{1}{2}+z, \frac{1}{2}-x\bar{y}\frac{1}{2}+z, \frac{1}{2}+x\bar{y}\frac{1}{2}-z, \frac{1}{2}-x y\frac{1}{2}-z$

$\frac{1}{2}\frac{1}{2}0: \frac{1}{2}+x\frac{1}{2}+y z, \frac{1}{2}-x\frac{1}{2}-y z, \frac{1}{2}+x\frac{1}{2}-y\bar{z}, \frac{1}{2}-x\frac{1}{2}+y\bar{z}$

formed by rotation about this axis is, therefore, at $(\frac{1}{4} - z)$ *above* the twofold axis, i.e. it has $z$ coordinate $\frac{1}{4} + (\frac{1}{4} - z) = \frac{1}{2} - z$. This is shortened to $\frac{1}{2} -$ in Fig. 6.12. Consider now the twofold axis parallel to $x$ and at $b = c = 0$ (i.e. passing through the origin). This axis generates positions 3″ from 1 and 4‴ (its equivalent in the cell below) from 2′. With these two axes we have generated all four equivalent positions in this space group. The third axes, the $2_1$ axis parallel to $z$, is automatically generated by the combined action of the other two axes and is not independent of them. This $2_1$ axis relates, for example, positions 1 and 4‴ (i.e. translation of position 1 by $c/2$ followed by 180° rotation about $c$ gives 4‴). Positions 2′ and 3″ are similarly related. The coordinates of the equivalent positions are given in Fig. 6.12. The only symmetry element which causes systematically absent reflections in P222₁ is the $2_1$ axis parallel to $z$, i.e. only $00l$ reflections for which $l = 2n$ may be observed. Several sets of twofold special positions arise, e.g. if $y = z = 0$ (i.e. $x,0,0; \bar{x},0,\frac{1}{2}$).

### 6.2.5 Orthorhombic F222

The new feature of this space group is that it has a face centred lattice which, as can be seen from Fig. 6.13, leads to a considerable increase in the number of symmetry elements and equivalent positions. The basic symmetry elements are three intersecting twofold axes, parallel to $x, y$ and $z$ and passing through the origin. Many other twofold axes occur automatically, e.g. one intersecting the cell at $a = \frac{1}{4}, c = \frac{1}{4}$ and parallel to $b$ and another at $a = \frac{1}{4}, b = \frac{1}{4}$ and parallel to $c$. Also many $2_1$ axes are created, e.g. one at $a = 0, b = \frac{1}{4}$ parallel to $c$ and another at $b = \frac{1}{4}$, $c = 0$ and parallel to $a$.

There are sixteen general equivalent positions which fall into four groups related by the face centring condition. The four sets are related as $(0,0,0); (\frac{1}{2},\frac{1}{2},0); (\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$. Thus, position 1, $(x, y, z)$, is related to positions 2 to 4: $(x + \frac{1}{2}, y + \frac{1}{2}, z); (x + \frac{1}{2}, y, z + \frac{1}{2})$ and $(x, y + \frac{1}{2}, z + \frac{1}{2})$. Generation of the remaining equivalent positions by the action of the twofold axes should be a straightforward matter. Coordinates of the equivalent positions are given in Fig. 6.13.

### 6.2.6 Tetragonal I4₁

The principal axis in the space group I4₁ (Fig. 6.14) is a $4_1$ screw axis parallel to $z$. There are four such axes which intersect the unit cell at $x = \frac{1}{4}, y = \frac{1}{4}; x = \frac{3}{4}, y = \frac{1}{4}; x = \frac{1}{4}, y = \frac{3}{4}$ and $x = \frac{3}{4}, y = \frac{3}{4}$. The operation of a $4_1$ screw axis involves translation of $\frac{1}{4}$ combined with rotation by 90° about the axis. The positions 1 to 4 are related to each other by the $4_1$ axis at $s$, and it can be seen that these positions lie on a spiral about $s$. The symbols of screw axes $s$ and $t$ are reversed because their direction of rotation is different; $s$ involves a clockwise rotation and $t$ an anticlockwise rotation (e.g. the sequence of positions 7′, 2, 5, 4′).

The body centring relates positions 1–4 to 5–8 and the cell contains eight general equivalent positions. These are listed in Fig. 6.14. Several twofold axes parallel to $z$ are also generated. Two conditions are imposed on the reflections which are possible for this space group. For the body centring, only the reflec-
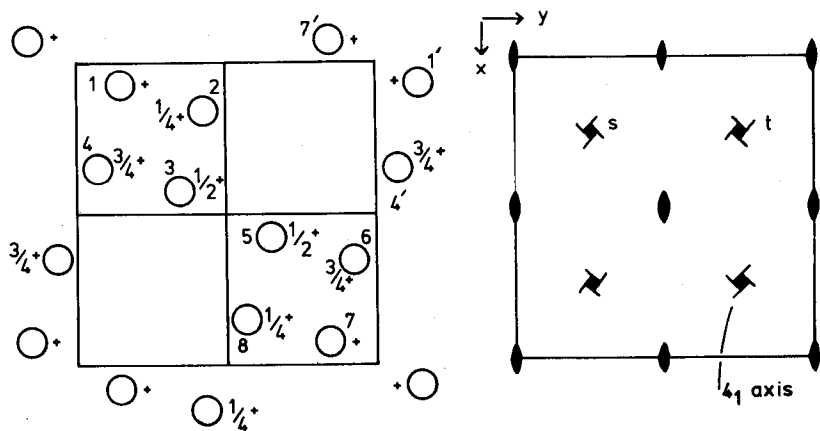
**Fig. 6.14** Tetragonal space group I4₁. Coordinates of equivalent positions

$000: xyz, \bar{x}\bar{y}z, \bar{y}\frac{1}{2}+x\frac{1}{4}+z, y\frac{1}{2}-x\frac{1}{4}+z$

$\frac{1}{2}\frac{1}{2}\frac{1}{2}: x+\frac{1}{2}\,y+\frac{1}{2}\,z+\frac{1}{2}, \frac{1}{2}-x\frac{1}{2}-y\frac{1}{2}+z, \frac{1}{2}-y\,x\frac{3}{4}+z, \frac{1}{2}+y\,\bar{x}\frac{3}{4}+z$

tions $hkl: h+k+l=2n$ may be observed. The $4_1$ screw axis places on the $00l$ reflections the condition that $l=4n$.

## 6.3 Space groups and crystal structures

The purpose of this section is to show how drawings or models of crystal structures may be made if one knows the space group and essential atomic coordinates of the structure. As examples, two simple structures are considered in some detail. This is then followed by a more systematic approach to crystal chemistry in Chapter 7.

### 6.3.1 The perovskite structure, SrTiO₃

The basic information that we need to know is the following:

Unit cell: cubic, $a = 3.905\,\text{Å}$

Space group: P$m3m$ (number 221 in *International Tables for X-ray crystallography*, Vol. 1)

Atomic coordinates: Ti in 1(a) at $0, 0, 0$

Sr in 1(b) at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

O in 3(d) at $0, 0, \frac{1}{2}$

This is, in fact, a very simple example since although the space group P$m3m$ is complicated, as are all cubic space groups, all the atoms in perovskite lie on special positions. There are forty-eight general equivalent positions in the space group P$m3m$ but a large number of special positions arise when atoms lie on symmetry elements. Titanium occupies a onefold special position at the origin of

the unit cell; the symbol 1(a) indicates that there is only one position in this set and (a) is a label, the Wyckoff lablel, for this (set of) position(s). Strontium also occupies a onefold special position, 1(b), at the body centre of the cell. Oxygen occupies a threefold special position 3(d); the coordinates of one of these positions are given—$0, 0, \frac{1}{2}$—and the only remaining information that is needed from the space group is the coordinates of the other two oxygen positions. From *International Tables*, these are $0, \frac{1}{2}, 0$ and $\frac{1}{2}, 0, 0$.

From this information, the unit cell and atomic positions may be drawn, first as a projection down one of the cubic cell axes (Fig. 6.15a) and then as an oblique projection to show the atomic positions more clearly (Fig. 6.15b). The coordination environment of each atom may be seen in (b) and interatomic distances calculated by simple geometry. The octahedral coordination by oxygen of one of
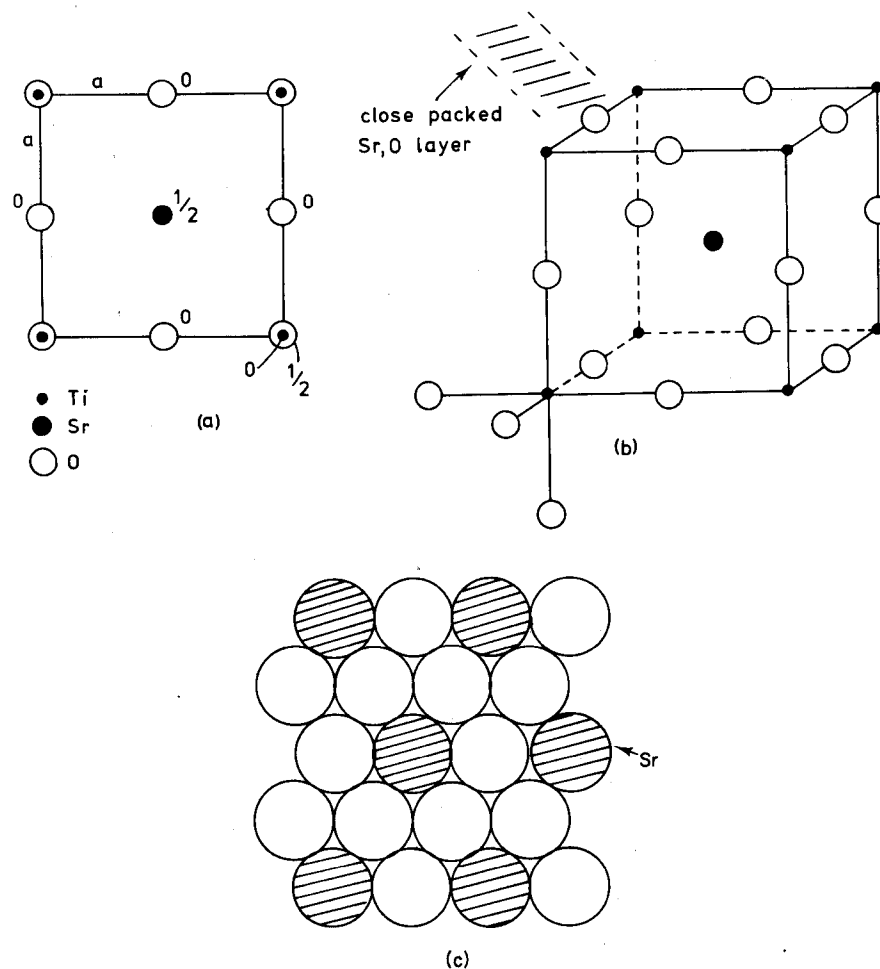


**Fig. 6.15** The perovskite structure of SrTiO₃

the corner titaniums is shown. The Ti—O bond length $= a/2 = 1.953$ Å. The strontium in the cube centre is equidistant from all twelve oxygens at the centres of the edges of the unit cell. The strontium–oxygen distance is equal to half the diagonal of any cell face, i.e. $a/\sqrt{2}$ or 2.76 Å (from the geometry of triangles, the length of a cell face diagonal is equal to $\sqrt{a^2 + a^2}$).

Each oxygen has two titaniums as its nearest cationic neighbours, at a distance of 1.953 Å, and four strontium atoms, coplanar with the oxygen at a distance of 2.76 Å. However, eight other oxygens are at the same distance, 2.76 Å, as the four strontiums. It is debatable whether the oxygen coordination number is best regarded as two (linear) or as six (a grossly squashed octahedron with two short and four long distances) or as fourteen (six cations and eight oxygens). No firm recommendation is made!

Having arrived at the unit cell of $SrTiO_3$, the atomic coordinates, coordination numbers and bond distances, we now wish to view the structure on a rather larger scale. There are several questions which may be asked. Does the structure have a close packed anion arrangement? The close packing approach provides a good way of classifying many crystal structures, Chapter 7. Can the structure be regarded as some kind of framework with atoms in the interstices? Many silicate structures may be thought of in this way. Can smaller polymeric units in the structure be identified? Orthosilicates have, for example, discrete $SiO_4^{4-}$ tetrahedra. Some answers to these questions are as follows.

Perovskite does not contain close packed oxide ions as such but the oxygens and strontiums, considered together, do form a cubic close packed array with the layers parallel to the (111) planes (Fig. 6.15b and c). To see this, compare the perovskite structure with that of NaCl(Fig. 5.9). The latter contains $Cl^-$ ions at the edge centre and body centre positions of the cell and is cubic close packed. By comparison, perovskite contains $O^{2-}$ ions at the edge centres and $Sr^{2+}$ at the body centre. The structure of the mixed Sr, O close packed layers in perovskite is such that one quarter of the atoms are strontium, arranged in a regular fashion (Fig. 6.15c).

It is quite common for fairly large cations, such as $Sr^{2+}$ ($r = 1.13$ Å) to play apparently different roles in different structures, i.e. as twelve coordinate packing ions in perovskite or as octahedrally coordinated cations within a close packed oxide array, as in SrO (rock salt structure).

The formal relation between rock salt and perovskite also includes the $Na^+$ and $Ti^{4+}$ cations as both are in octahedral sites. Whereas in NaCl all octahedral sites are occupied (corners and face centres), in perovskite only one quarter (the corner sites) are occupied.

Perovskite may also be regarded as a framework structure constructed from corner-sharing ($TiO_6$) octahedra and with $Sr^{2+}$ ions placed in twelve-coordinate interstices. The octahedral coordination of one titanium is shown in Fig. 6.15b; each oxygen of this octahedron is shared with one other octahedron, such that the Ti–O–Ti arrangement is linear. In this way, octahedra are linked at their corners to form sheets, Appendix 2, Fig. A2.4c, and neighbouring sheets are linked similarly to form a three-dimensional framework.

A further discussion of crystal structures, including close packing and linked polyhedra, is given in Chapter 7, while perovskites and their use as ferroelectric and dielectric materials are discussed in Chapter 15.

### 6.3.2 The rutile structure, $TiO_2$

We need to know the following information:

Unit cell: tetragonal, $a = 4.594$, $c = 2.958$ Å

Space group: $P4_2/mnm$ (number 136)

Atomic coordinates: Ti in 2(a) at $(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

O in 4(f) at $(x, x, 0), (\bar{x}, \bar{x}, 0),$

$(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}), (\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2})$

As in the perovskite structure, only special positions are used to accommodate atoms and the general positions (sixteenfold) are unoccupied. The titanium positions are fixed at the corner and body centre but the oxygen has a variable parameter, $x$, whose value must be determined experimentally. Crystal structure determination and refinement gives $x = 0.30$ for $TiO_2$. The unit cell of rutile is shown projected onto the $xy$ plane in Fig. 6.16(a).

We next need to determine the coordination environment of the atoms. The body centre titanium at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is coordinated octahedrally to six oxygens. Four of these—two at 0 and two at 1 directly above the two at 0—are coplanar with titanium. Two oxygens at $z = \frac{1}{2}$ are collinear with titanium and form the axes of the octahedron. The corner titaniums are also octahedrally coordinated but the orientation of their octahedra is different (Fig. 6.16b). The oxygens are coordinated trigonally to three titaniums: e.g. oxygen at 0 in (a) is coordinated to titanium atoms at the corner, at the body centre and at the body centre of the cell below.

Since the oxygen atoms form the corners of $TiO_6$ octahedra this means that each corner oxygen is shared between three octahedra. The octahedra are linked by sharing edges and corners to form a three-dimensional framework. Consider the $TiO_6$ octahedron in the centre of the cell in (b); a similar octahedron in identical orientation occurs in the cells above and below such that octahedra in adjacent cells share edges to form infinite chains parallel to $c$ (see Appendix 2, Fig. A2.4a). For example, titanium atoms at $z = +\frac{1}{2}$ and $-\frac{1}{2}$ in adjacent cells are both coordinated to two oxygens at $z = 0$. Chains of octahedra are similarly formed by the octahedra centred at the corners of the unit cell. The two types of chains, which differ in orientation about $z$ by 90° and which are $c/2$ out of step with each other, are linked by their corners to form a three-dimensional framework (Fig. 6.16c).

The rutile structure is also commonly described as a distorted hexagonal close packed oxide array with half the octahedral sites occupied by titanium. A $3 \times 3$ block of unit cells is shown in Fig. 6.16(d) with only the oxygen positions marked.

(a)

(b)
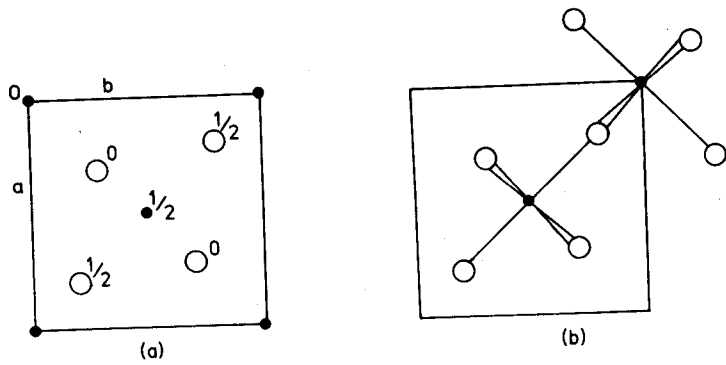
● Ti at 000; 0.5, 0.5, 0.5

○ O at 0.3, 0.3, 0; 0.7, 0.7, 0; 0.8, 0.2, 0.5; 0.2, 0.8, 0.5

(c)

○ O at z = 0

⊖ O at z = ½

(d)

(e)

¼ ↑     ¼ ↑

¼ ↙     ¼ →

¼ ↙     ¼ →

¼ ↓     ¼ ↓     (f)

◈ = ◆ + ○  4₂ screw axis + centre of symmetry

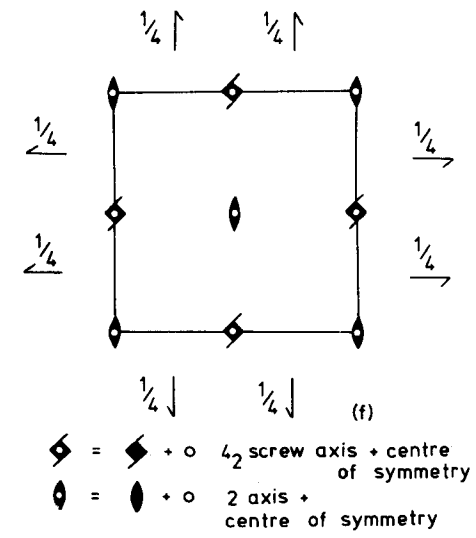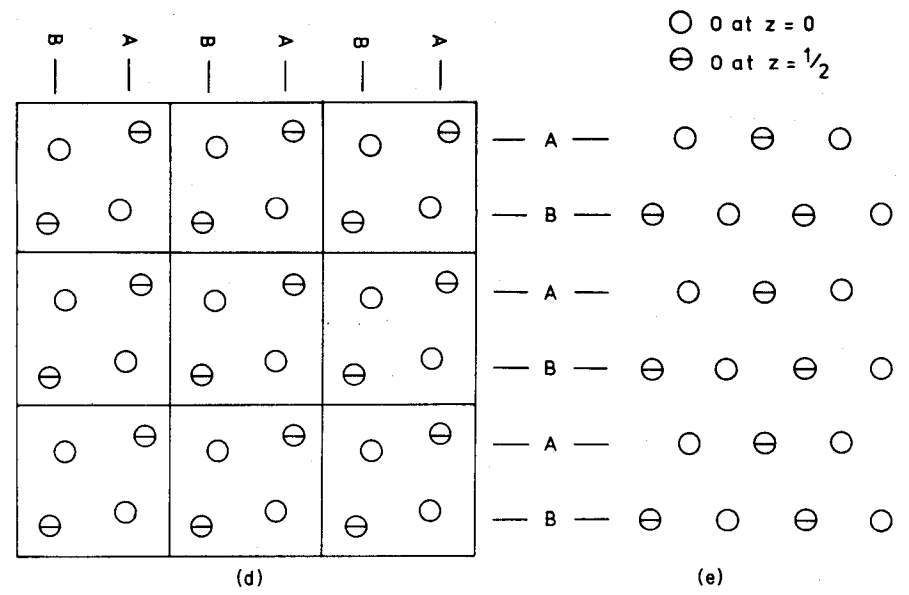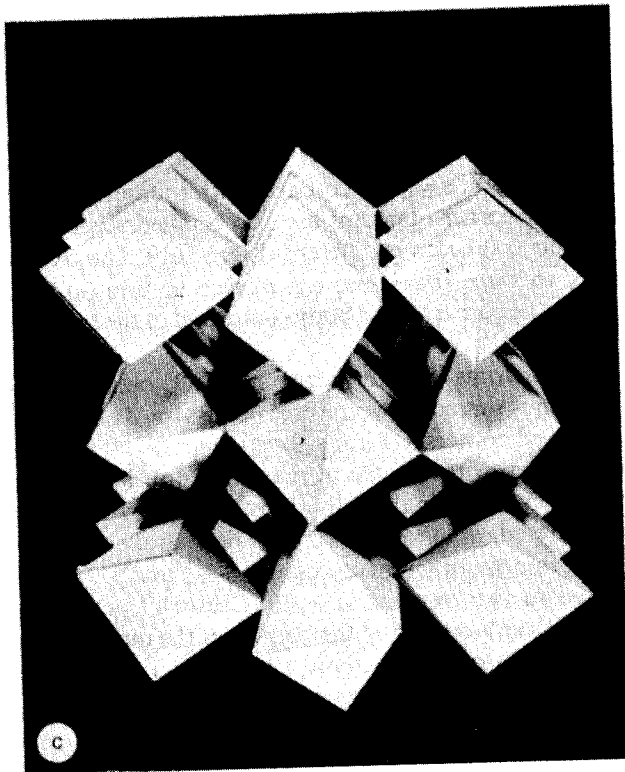◐ = ● + ○  2 axis + centre of symmetry

**Fig. 6.16** The rutile structure, $TiO_2$

Corrugated close packed layers occur, both horizontally and vertically. This contrasts with the undistorted hexagonal close packed arrangement (Fig. 6.16e), in which the layers occur in one orientation only (horizontally).

Very recently, an alternative way of describing the packing arrangement of oxide ions in rutile has been proposed. The oxide ion arrangement is a slightly distorted version of a new type of packing called *primitive tetragonal packing* (p.t.p.), which is characterized by fourfold symmetry and a sphere coordination number of *eleven*. This contrasts with hexagonal and cubic close packing which have a packing sphere coordination number of twelve and body centred tetragonal packing which has a coordination number of ten. More details are given in Chapter 7.

The bond lengths in $TiO_2$ may be calculated either graphically if (a) is drawn to scale or by geometry; e.g. for the Ti—O bond length between titanium at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and oxygen at $(0.3, 0.3, 0)$ the difference in $a$ and $b$ parameters of titanium and oxygen is $(\frac{1}{2} - 0.3)a = 0.92\,\text{Å}$. From a right-angled triangle calculation, the titanium–oxygen distance in projection down $c$ (Fig. 6.16a) is $\sqrt{0.92^2 + 0.92^2}$. However, titanium and oxygen have a difference in $c$ height of $(\frac{1}{2} - 0)c = 1.48\,\text{Å}$ and the Ti—O bond length is therefore equal to $\sqrt{0.92^2 + 0.92^2 + 1.48^2} = 1.97\,\text{Å}$. The axial Ti—O bond length between, for example, $Ti(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $O(0.8, 0.2, 0.5)$ is easier to calculate because both atoms are at the same $c$ height. It is equal to $\sqrt{2(0.3 \times 4.594)^2} = 1.95\,\text{Å}$.

Some of the symmetry elements in the space group $P4_2/mnm$ are shown in (Fig. 6.16f); most of them should be readily apparent on inspection of (a). Thus, the $4_2$ axes are located halfway along the cell edges although no atoms lie on these $4_2$ axes. The oxygen atoms are arranged on spirals around the $4_2$ axes such that translation by $c/2$ and rotation by $90°$ converts one oxygen position to another. Centres of symmetry are present, for example, at the cell corners and also 2 and $2_1$ axes and (not shown) mirror planes and glide planes.

## Questions

6.1 What point groups result on adding a centre of symmetry to point groups (a) 1, (b) 2, (c) 3, (d) $\bar{4}$, (e) 4, (f) 222, (g) $mm2$, (h) $4mm$, (i) 6, (j) $\bar{6}$, (k) $6m2$?

6.2 What point groups result from the combination of two mirror planes at (a) $90°$ to each other, (b) $60°$, (c) $45°$, (d) $30°$?

6.3 What point groups result from the combination of two intersecting twofold axes at (a) $90°$ to each other, (b) $60°$, (c) $45°$, (d) $30°$?

6.4 An atom in an orthorhombic unit cell has fractional coordinates 0.1, 0.15 and 0.2. Give the coordinates of a second atom in the unit cell that is related to the first by each of the following, separately: (a) body centring, (b) a centre of symmetry at the origin, (c) a 2 axis parallel to $z$ and passing through the origin, (d) a $2_1$ axis parallel to $z$ and passing through the origin, (e) A-centring.

6.5 $Li_2PdO_2$ has an orthorhombic unit cell, $a = 3.74$, $b = 2.98$, $c = 9.35\,\text{Å}$, $Z = 2$, space group $Immm$. Atomic coordinates are: Pd:2(a) 000; Li:4(i) $00z : z = 0.265$; O:4 (j) $0\frac{1}{2}z : z = 0.143$. Draw projections of the unit cell, determine

coordination numbers and bond lengths and describe the structure. (*J. Solid State Chem.*, **6**, 329, 1973.)

6.6 Repeat the above question but for the structures of (a) ilmenite (Table 16.8), (b) garnet (Table 16.7) and (c) spinel (Table 16.5).

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