5

Crystallography and crystal structures

- How does a lattice differ from a structure?
- What is a unit cell?
- What is meant by a (1 0 0) plane?

Crystallography describes the ways in which atoms and molecules are arranged in crystals. Many chemical and physical properties depend on crystal structure, and an understanding of crystallography is essential if the properties of materials are to be understood.

In earlier centuries, crystallography developed via two independent routes. The first of these was observational. It was long supposed that the regular and beautiful shapes of mineral crystals were an expression of internal order, and this order was described by the classification of external shapes, the *habit* of crystals. All crystals could be classified into one of 32 crystal classes, belonging to one of seven crystal systems. The regularity of crystals, together with the observation that many crystals could be cleaved into smaller and smaller units, gave rise to the idea that all crystals were built up from elementary volumes, that came to be called unit cells, with a shape defined by the crystal system. A second route, the mathematical description of the arrangement of arbitrary objects in space, was developed in the latter years of the 19th century. Both of these play a part in helping us to understand crystals and their properties. The two approaches were unified with the exploitation of X-ray and other diffraction methods, which are now used to determine crystal structures on a routine basis.

5.1 Crystallography

5.1.1 Crystal lattices

Crystal structures and crystal lattices are different, although these terms are frequently (and incorrectly) used as synonyms. A crystal structure is built of atoms. A crystal lattice is an infinite pattern of points, each of which must have the same surroundings in the same orientation. A lattice is a mathematical concept. If any lattice point is chosen as the origin, the position of any other lattice point is defined by

$$\boldsymbol{P}(u\,v\,w) = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are vectors, called basis vectors, and u, v and w are positive or negative integers. Clearly, there are any number of ways of choosing $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$, and crystallographic convention is to choose vectors that are small and reveal the underlying symmetry of the lattice. The parallelepiped

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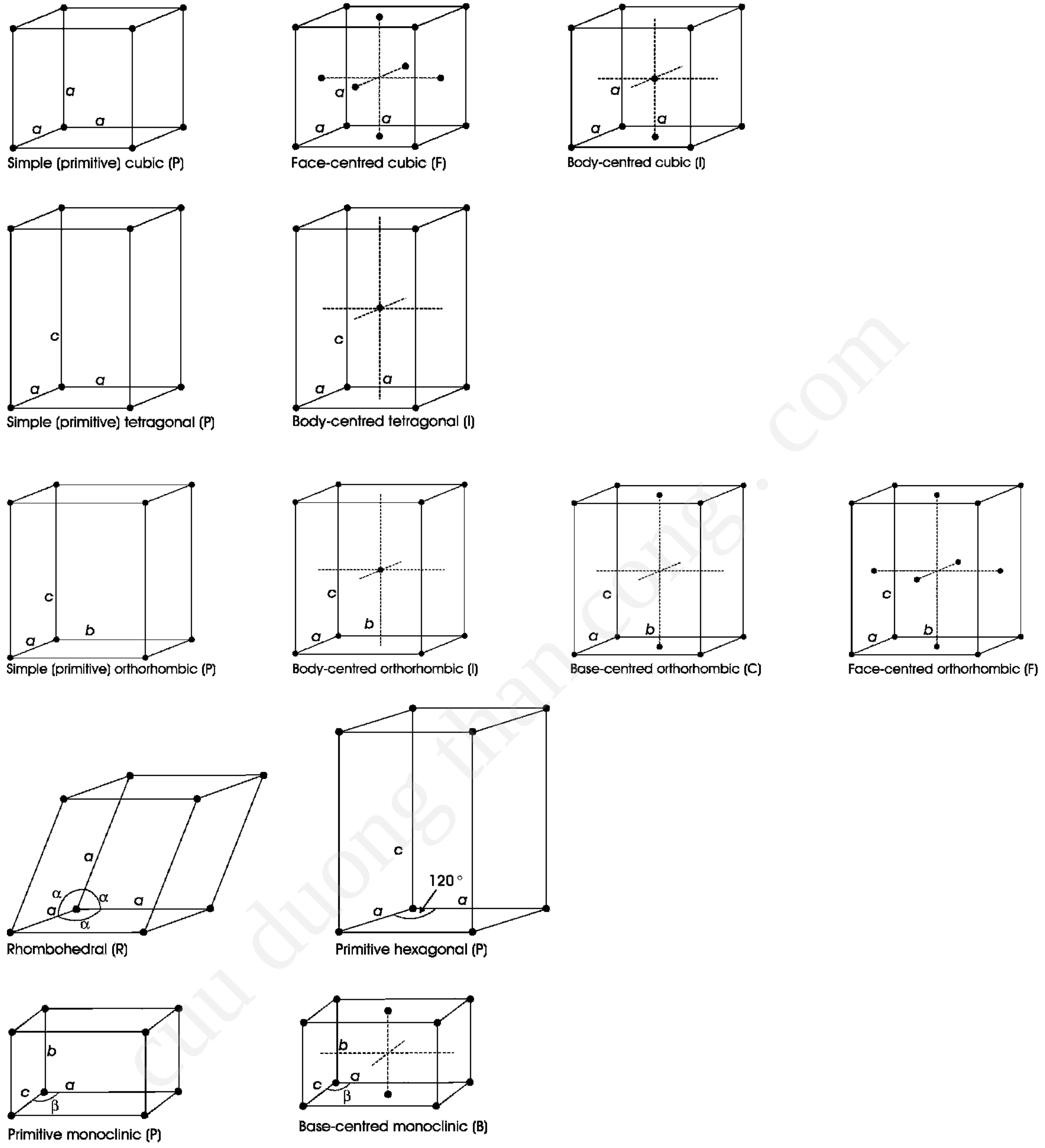


Simple (primitive) cubic (P)

Face-centred cubic (F)

Body-centred cubic (I)

Simple (primitive) tetragonal (P)

Body-centred tetragonal (I)

Simple (primitive) orthorhombic (P)

Body-centred orthorhombic (I)

Base-centred orthorhombic (C)

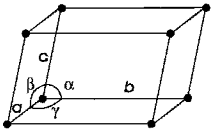
Face-centred orthorhombic (F)

Rhombohedral (R)

Primitive hexagonal (P)

Primitive monoclinic (P)

Base-centred monoclinic (B)



Triclinic (primitive) (P)

Figure 5.1 The 14 Bravais lattices. Note that the lattice points are *not* atoms. The axes associated with the lattices are shown, and are described in Table 5.1. The monoclinic lattices have been drawn with the *b* axis vertical, to emphasise that it is normal to the plane containing the *a* and *c* axes formed by the three basis vectors ***a***, ***b*** and ***c*** defines the unit cell of the lattice, with edges of length a_0, b_0, and c_0. The numerical values of the unit cell edges and the angles between them are collectively called the lattice parameters or unit cell parameters. The unit cell is not unique and is chosen for convenience and to reveal the underlying symmetry of the crystal.

There are only 14 possible three-dimensional lattices, called Bravais lattices (Figure 5.1). Bravais lattices are sometimes called direct lattices. The smallest unit cell possible for any of the lattices, the one that contains just one lattice point, is called the primitive unit cell. A primitive unit cell, usually drawn with a lattice point at each corner, is labelled P. All other lattice unit cells contain more than one lattice point. A unit cell with a lattice point at each corner and one at the centre of the unit cell (thus containing two lattice points in total) is called a body-centred unit cell, and labelled I. A unit cell with a lattice point in the middle of each face, thus containing four lattice points, is called a face-centred unit cell, and labelled F. A unit cell that has just one of the faces of the unit cell centred, thus containing two lattice points, is labelled A-face-centred if the faces cut the *a* axis, B-face-centred if the faces cut the *b* axis and C-face-centred if the faces cut the *c* axis.

The external form of crystals, the internal crystal structures and the three-dimensional Bravais lattices need to be defined unambiguously. For this purpose, a set of axes is used, defined by the vectors ***a***, ***b*** and ***c***, with lengths a_0, b_0, and c_0. These axes are chosen to form a right-handed set and, conventionally, the axes are drawn so that the *a* axis points out from the page, the *b* axis points to the right and the *c* axis is vertical (Figure 5.1). The angles between the axes are chosen to be equal to or greater than 90° whenever possible. These are labelled α, β and γ, where α lies between *b* and *c*, β lies between *a* and *c*, and γ lies between *a* and *b*. Just seven different arrangements of axes are needed in order to specify all three-dimensional structures and lattices (Table 5.1), these being identical to the crystal systems derived by studies of the morphology of crystals.

Table 5.1 The crystal systems

System	Unit cell parameters
Cubic (isometric)	$a = b = c$; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
Tetragonal	$a = b \neq c$; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
Orthorhombic	$a \neq b \neq c$; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
Monoclinic	$a \neq b \neq c$; $\alpha = 90°$, $\beta \neq 90°$, $\gamma = 90°$
Triclinic	$a \neq b \neq c$; $\alpha \neq 90°$, $\beta \neq 90°$, $\gamma \neq 90°$
Hexagonal	$a = b \neq c$; $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$
Rhombohedral	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$ $a' = b' \neq c'$; $\alpha' = 90°$, $\beta' = 90°$, $\gamma' = 120°$

The unique axis in the monoclinic unit cell is the *b* axis. It would be better to choose the *c* axis, as then the unique axis in tetragonal, hexagonal and orthorhombic crystals with a polar axis (see below) would all have the same designation. However, convention is now fixed and monoclinic unit cells are usually described with the *b* axis as unique. Rhombohedral unit cells are often specified in terms of a different (bigger) hexagonal unit cell.

5.1.2 *Crystal structures and crystal systems*

All crystal structures can be built up from the Bravais lattices by placing an atom or a group of atoms at each lattice point. The crystal structure of a simple metal and that of a complex protein may both be described in terms of the same lattice, but whereas the number of atoms allocated to each lattice point is often just one for a simple metallic crystal it may easily be thousands for a protein crystal. The number of atoms associated with each lattice point is called the *motif*, the *lattice complex* or the *basis*. The motif is a fragment of structure that is just sufficient, when repeated at each of the lattice points, to construct the whole of the crystal. A crystal structure is built up from a lattice plus a motif.

The axes used to describe the structure are the same as those used for the direct lattices, corresponding to the basis vectors lying along the unit cell edges. The position of an atom within the unit cell is given as *x*, *y*, *z*, where the units are a_0 in a direction along the *a* axis, b_0 along the *b* axis, and c_0 along the *c* axis. An atom with the coordinates

$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is at the body centre of the unit cell, that is $\frac{1}{2}\,a_0$ along the a axis, $\frac{1}{2}\,b_0$ along the b axis and $\frac{1}{2}\,c_0$ along the c axis.

Different compounds which crystallise with the same crystal structure, for example the two alums, $NaAl(SO_4)_2.12H_2O$ and $NaFe(SO_4)_2.12H_2O$, are said to be isomorphous(1) or isostructural. As noted in Section 3.1.3, sometimes the crystal structure of a compound will change with temperature and with applied pressure. This is called polymorphism. Polymorphs of elements are known as allotropes. Graphite and diamond are two allotropes of carbon, formed at different temperatures and pressures.

Because repetition of the unit cell must reproduce the crystal, the atomic contents of the unit cell must also be representative of the overall composition of the material. It is possible to determine the density of a compound by dividing the total mass of the atoms in the unit cell by the unit cell volume, described in more in Section 5.3.2.

5.1.3 Symmetry and crystal classes

The shape and symmetry of crystals attracted the attention of early crystallographers and, until the internal structure of crystals could be determined, was an important method of classification of minerals. The external shape, or habit, of a crystal is described as isometric (like a cube), prismatic (like a prism, often with six sides), tabular (like a rectangular tablet or thick plate), lathy (lath-like) or acicular (needle-like). An examination of the disposition of crystal faces, which reflected the symmetry of the crystal, led to an appreciation that all crystals could not only be allocated to one of the seven crystal systems but also to one of 32 crystal classes.

The crystal class mirrors the internal symmetry of the crystal. The internal symmetry of any isolated object, including a crystal, can be described by a combination of axes of rotation and mirror planes, all of which will be found to intersect in a point within the object. There are just 32 combinations of these symmetry elements, each of which is a *crystallographic point group*. The point group is equivalent to the crystal class of a crystal, and the terms are often used interchangeably.

Point groups are used extensively in crystal physics to relate external and internal symmetry to the physical properties that can be observed. For example, the piezoelectric effect (see Section 11.2.2) is found only in crystals that lack a centre of symmetry. A unit cell with a centre of symmetry at a position $(0, 0, 0)$ is such that any atom at a position (x, y, z) is accompanied by a similar atom at $(-x, -y, -z)$. Crystallographic notation writes negative signs above the symbol to which they apply, thus: $(\bar{x}, \bar{y}, \bar{z})$. Crystals that do not possess a centre of symmetry have one or more polar directions and polar axes. A polar axis is one that is not related by symmetry to any other direction in the crystal. That is, if an atom occurs at $+z$ on a polar c axis, there is no similar atom at $-z$. This can be illustrated with reference to an SiO_4 tetrahedron, a group that lacks a centre of symmetry (Figure 5.2). The oxygen atom at $+z$ on the c axis is not paired with a similar oxygen atom at $-z$.

The symmetry of the internal structure of a crystal is obtained by combining the point group symmetry with the symmetry of the lattice. It is found that 230 different patterns arise. These are called *space groups*. Every crystal structure can be assigned to

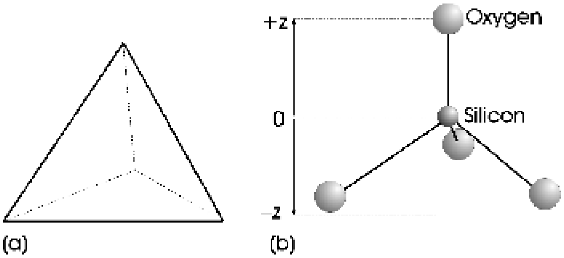


Figure 5.2 (a) An ideal tetrahedron. All faces are composed of equilateral triangles. (b) An ideal tetrahedral (SiO_4) unit. A silicon atom lies at the tetrahedron centre, and four equispaced oxygen atoms are arranged at the tetrahedral vertices. An oxygen atom at $+z$ does not have a counterpart at $-z$, and the unit is not centrosymmetric

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(1) This description originally applied to the same external form of the crystals rather than the internal arrangement of the atoms.

a space group. The space group, because it is concerned with the symmetry of the crystal structure, places severe restrictions on the placing of atoms within the unit cell. The determination of a crystal structure generally starts with the determination of the correct space group for the sample. Further information on the importance of symmetry in crystal structure analysis will be found in the Further Reading section at the end of this chapter.

5.1.4 Crystal planes and Miller indices

The facets of a well-formed crystal or internal planes through a crystal structure are specified in terms of Miller Indices. These indices, h, k and l, written in round brackets $(h\,k\,l)$, represent not just one plane but the set of all parallel planes $(h\,k\,l)$. The values of h, k and l are the fractions of a unit cell edge, a_0, b_0 and c_0, respectively, intersected by this set of planes. A plane that lies parallel to a cell edge, and so never cuts it, is given the index 0 (zero). Some examples of the Miller indices of important crystallographic planes follow.

A plane that passes across the end of the unit cell cutting the a axis and parallel to the b and c-axes of the unit cell has Miller indices $(1\,0\,0)$ (Figure 5.3a). The indices indicate that the plane cuts the cell edge running along the a axis at a position $1\,a_0$ and does not cut the cell edges parallel to the b or c axes at all. A plane parallel to this that cuts the a cell edge in half, at $a_0/2$, has indices $(2\,0\,0)$ (Figure 5.3b). Similarly, parallel planes cutting the a cell edge at $a_0/3$ would have Miller indices of $(3\,0\,0)$ (Figure 5.3c). Remember that $(1\,0\,0)$ represents all of the set of other identical planes as well. There is no need to specify a plane $(100, 0\,0)$, it is simply $(1\,0\,0)$. Any general plane parallel to $(1\,0\,0)$ is written $(h\,0\,0)$.

A general plane parallel to the a and c axes, perpendicular to the b axis, and so only cutting the b cell edge, has indices $(0\,k\,0)$ (Figure 5.3d), and a general plane parallel to the a and b axes and perpendicular to the c axis, and so cutting the c cell edge, has indices $(0\,0\,l)$ (Figure 5.3e).

Planes that cut two edges and parallel to a third are described by indices $(h\,k\,0)$, $(0\,k\,l)$ or $(h\,0\,l)$. Figures 5.4(a)–(c) show, respectively: (1 1 0), intersecting

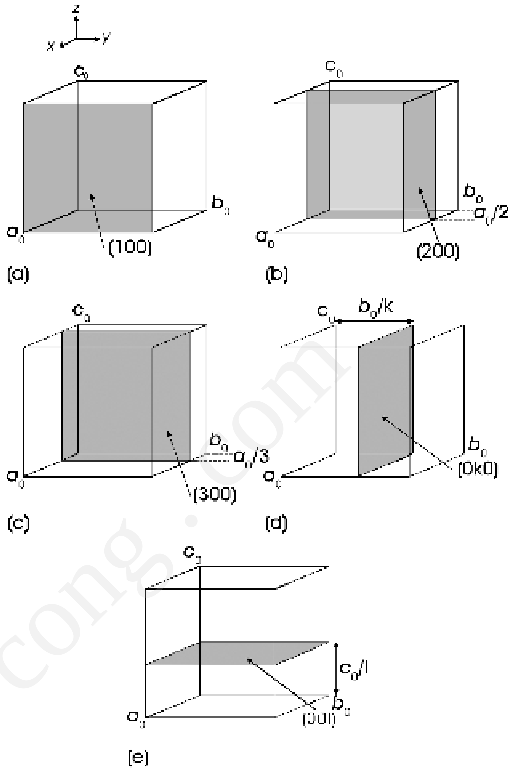

Figure 5.3 Miller indices of crystal planes. (a). (1 0 0); (b). (2 0 0); (c). (3 0 0); (d). (0 k 0); (e). (0 l 0)

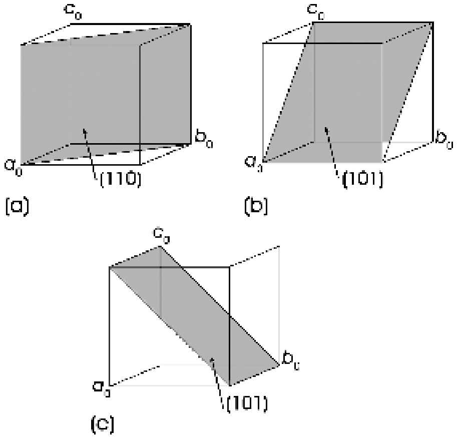

Figure 5.4 Miller indices of crystal planes in cubic crystals: (a) (1 1 0), (b) (1 0 1) and (c) (0 1 1)

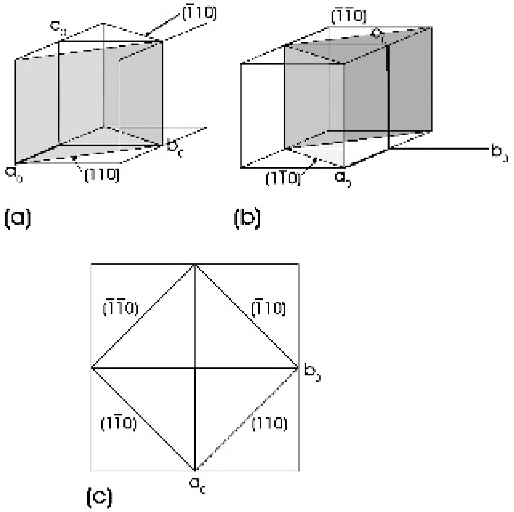

Figure 5.5 Miller indices of crystal planes in a cubic crystal: (a) (1 1 0) and ($\bar{1}$ 1 0), (b) (1 $\bar{1}$ 0) and ($\bar{1}$ $\bar{1}$ 0) and (c) projection down the c axis, showing all four equivalent {1 1 0} planes

the cell edges in 1 a_0 and 1 b_0 and parallel to c; (1 0 1), intersecting the cell edges in 1 a_0 and 1 c_0 and parallel to b; and (0 1 1), intersecting the cell edges in 1 b_0 and 1 c_0 and parallel to a.

Negative intersections are written with a negative sign over the index and are pronounced 'bar h', 'bar k' and 'bar l'. For example, there are four planes related to the (1 1 0) plane. As well as the (1 1 0) plane, a similar plane also cuts the b axis in 1 b_0, but the a axis is cut in a negative direction, at $-a_0$ (Figure 5.5a). Two other related planes, one of which cuts the b axis at $-b_0$, and so has Miller indices (1 $\bar{1}$ 0), pronounced '(one, bar one, zero)' and the other, with Miller indices ($\bar{1}$ $\bar{1}$ 0), are drawn in Figure 5.5(b). Because the Miller indices ($h\,k\,l$) refer to a set of planes, ($\bar{1}$ $\bar{1}$ 0) is equivalent to (1 1 0), as the position of the axes is arbitrary. Similarly, the plane with Miller indices (1 $\bar{1}$ 0) is equivalent to ($\bar{1}$ 1 0) (Figure 5.5c).

This notation is readily extended to cases where a plane cuts all three unit cell edges (Figure 5.6). An easy way to determine Miller indices is given in Section S1.6.

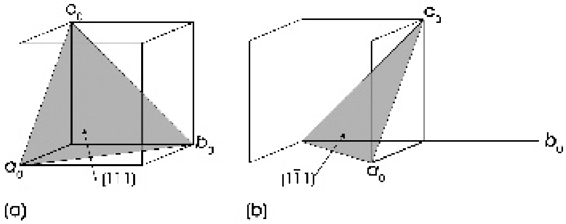

Figure 5.6 Miller indices in cubic crystals: (a) (1 1 1) and (b) (1 $\bar{1}$ 1)

In crystals of high symmetry there are often several sets of ($h\,k\,l$) planes that are identical, from the point of view of both symmetry and of the atoms lying in the plane. For example, in a cubic crystal, the (1 0 0), (0 1 0) and (0 0 1) planes are identical in every way. Similarly, in a tetragonal crystal, (1 1 0) and ($\bar{1}$ 1 0) planes are identical. Curly brackets, {$h\,k\,l$}, designate these related planes. Thus, in the cubic system, the symbol {1 0 0} represents the three sets of planes (1 0 0), (0 1 0) and (0 0 1). Similarly, in the cubic system, {1 1 0} represents the six sets of planes (1 1 0), (1 0 1), (0 1 1), ($\bar{1}$ 1 0), ($\bar{1}$ 0 1), and (0 $\bar{1}$ 1), and the symbol {1 1 1} represents the four sets (1 1 1), (1 1 $\bar{1}$), (1 $\bar{1}$ 1) and ($\bar{1}$ 1 1).

5.1.5 Hexagonal crystals and Miller–Bravais indices

The Miller indices of planes parallel to the c axis in crystals with a hexagonal unit cell, such as magnesium, can be ambiguous (Figure 5.7). In this representation, the c cell edge is normal to the plane of the page. Three sets of planes, imagined to be perpendicular to the plane of the figure, are shown. From the procedure just outlined, the sets have the following Miller indices: A, (1 1 0); B, (1 $\bar{2}$ 0); and C, ($\bar{2}$ 1 0). Although these seem to refer to different types of plane, clearly they are identical from the point of view of atomic constitution. In order to eliminate this confusion, four indices, ($h\,k\,i\,l$), are often used to specify planes in a hexagonal crystal. These are called Miller–Bravais indices and are

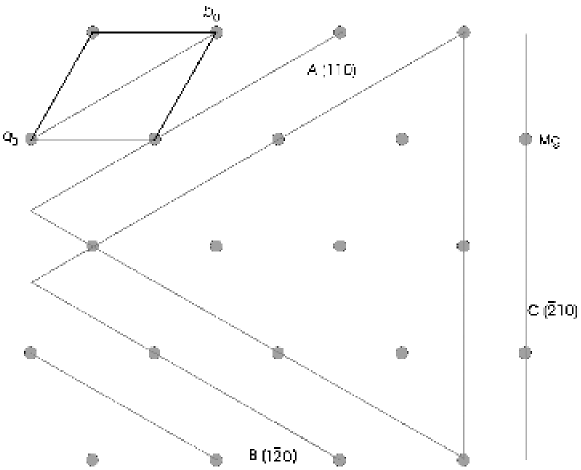

Figure 5.7 Miller indices in hexagonal crystals. Although the indices appear to represent different types of plane, in fact they all are identical

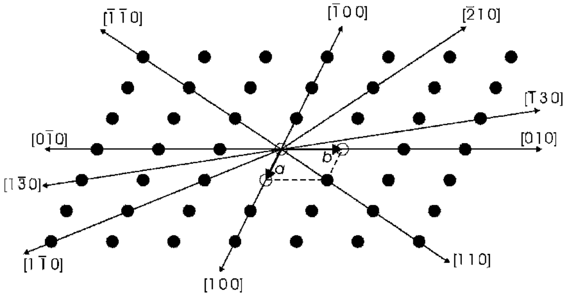

Figure 5.8 Directions in a lattice. The directions do not take into account the length of the vectors, and the indices are given by the smallest integers that lie along the vector direction

used only in the hexagonal system. The index i is given by:

$$h + k + i = 0,$$

or

$$i = -(h + k)$$

In reality this third index is not needed. However, it does help to bring out the relationship between the planes. Using four indices, the planes are: A, $(1\,1\,\bar{2}\,0)$; B, $(1\,\bar{2}\,1\,0)$; and C, $(\bar{2}\,1\,1\,0)$. Because it is a redundant index, the value of i is sometimes replaced by a dot, to give indices $(h\,k\,.\,l)$. This nomenclature emphasises that the hexagonal system is under discussion without actually including a value for i.

5.1.6 Directions

The response of a crystal to an external stimulus, such as a tensile stress, electric field and so on, is usually dependent on the direction of the applied stimulus. It is therefore important to be able to specify directions in crystals in an unambiguous fashion. Directions are written generally as $[u\,v\,w]$ and are enclosed in square brackets. Note that the symbol $[u\,v\,w]$ means all parallel directions or vectors.

The three indices u, v and w define the coordinates of a point with respect to the crystallographic a b and c axes. The index u gives the coordinates in terms of a_0 along the a axis, the index v gives the coordinates in terms of b_0 along the b axis and the index w gives the coordinates in terms of c_0 along the c axis. The direction $[u\,v\,w]$ is simply the vector pointing from the origin to the point with coordinates u, v, w (Figure 5.8). For example, the direction $[1\,0\,0]$ is parallel to the a unit cell edge, the direction $[0\,1\,0]$ is parallel to the b cell edge, and $[0\,0\,1]$ is parallel to the c cell edge. Because directions are vectors, $[u\,v\,w]$ is not identical to $[\bar{u}\,\bar{v}\,\bar{w}]$, in the same way that the direction 'north' is not the same as the direction 'south'. Remember, though, that, *any* parallel direction shares the symbol $[u\,v\,w]$, because the origin of the coordinate system is not fixed and can always be moved to the starting point of the vector (Figure 5.9). A north wind is always a north wind, regardless of where you stand.

As with Miller indices, it is sometimes convenient to group together all directions that are identical by virtue of the symmetry of the structure. These are represented by the notation $\langle u\,v\,w \rangle$. In a cubic crystal, $\langle 1\,0\,0 \rangle$ represents the six directions $[1\,0\,0]$, $[\bar{1}\,0\,0]$, $[0\,1\,0]$, $[0\,\bar{1}\,0]$, $[0\,0\,1]$, $[0\,0\,\bar{1}]$.

A zone is a set of planes, all of which are parallel to a single direction, called the zone axis. The

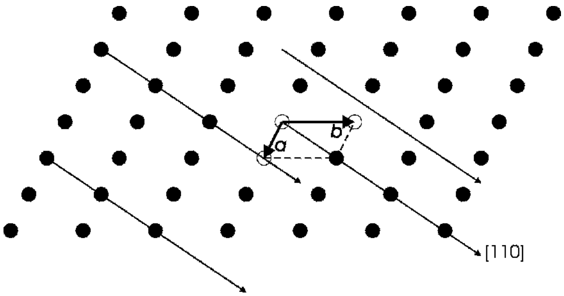

Figure 5.9 Parallel directions. These all have the same indices, [110]

zone axis $[u\,v\,w]$ is perpendicular to the plane $(u\,v\,w)$ in cubic crystals but *not* in crystals of other symmetry.

It is sometimes important to specify a vector with a definite length perhaps to indicate the displacement of one part of a crystal with respect to another part, as in an antiphase boundary or crystallographic shear plane. In such a case, the direction of the vector is written as above, and a prefix is added to give the length. The prefix is usually expressed in terms of the unit cell dimensions. For example, in a cubic crystal, a displacement of two unit cell lengths parallel to the b axis would be written $2\,a_0[0\,1\,0]$.

As with Miller indices, to specify directions in hexagonal crystals a four-index system, $[u'\,v'\,t\,w']$ is sometimes used. The conversion of a three-index set to a four-index set is given by the following rules:

$$
\begin{aligned}
[u\,v\,w] &\rightarrow [u'\,v'\,t\,w'] \\
u' &= \frac{n}{3}(2\,u - v) \\
v' &= \frac{n}{3}(2\,v - u) \\
t &= -(u' + v') \\
w' &= n\,w
\end{aligned}
$$

In these equations, n is a factor sometimes needed to make the new indices into smallest integers. Thus directions $[0\,0\,1]$ always transform to $[0\,0\,0\,1]$. The three equivalent directions in the basal $(0\,0\,0\,1)$ plane of a hexagonal crystal structure such as magnesium, Figure 5.10, are obtained by using the above transformations. The correspondence is:

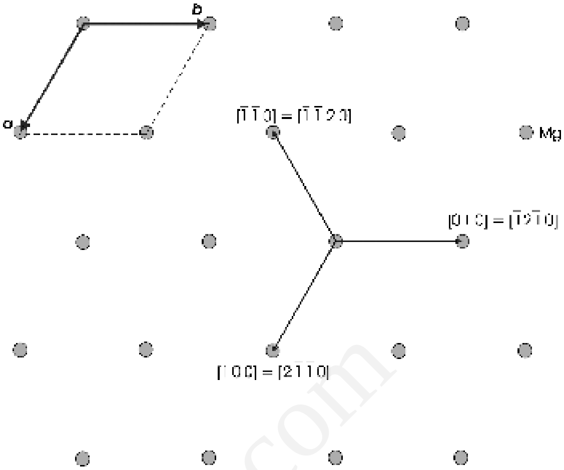

Figure 5.10 Directions in the basal $(0\,0\,1)$ plane of a hexagonal crystal structure, given in terms of three indices, $[u\,v\,w]$, and four indices, $[u'\,v'\,t\,w']$

$$
\begin{aligned}
[1\,0\,0] &= [2\,\bar{1}\,\bar{1}\,0] \\
[0\,1\,0] &= [\bar{1}\,2\,\bar{1}\,0] \\
[\bar{1}\,\bar{1}\,0] &= [\bar{1}\,\bar{1}\,2\,0]
\end{aligned}
$$

The relationship between directions and planes depends on the symmetry of the crystal. In cubic crystals (and *only* cubic crystals) the direction $[h\,k\,l]$ is normal to the plane $(h\,k\,l)$.

5.1.7 *The reciprocal lattice*

Many of the physical properties of crystals, as well as the geometry of the three-dimensional patterns of radiation diffracted by crystals, are most easily described by using the reciprocal lattice. Each reciprocal lattice point is associated with a set of crystal planes with Miller indices $(h\,k\,l)$ and has coordinates $h\,k\,l$. The position of the $h\,k\,l$ spot in the reciprocal lattice is closely related to the orientation of the $(h\,k\,l)$ planes and to the spacing between these planes, $d_{h\,k\,l}$, called the interplanar spacing. Crystal structures and Bravais lattices, sometimes called the direct lattice, are said to occupy real space, and the reciprocal lattice occupies reciprocal space. The reciprocal lattice is defined in terms of three basis vectors labelled ***a****, ***b**** and ***c****. The lengths of the basis vectors of the reciprocal lattice are:

$$a* = \frac{1}{d_{1\,0\,0}} \quad b* = \frac{1}{d_{0\,1\,0}} \quad c* = \frac{1}{d_{0\,0\,1}}$$

For cubic, tetragonal and orthorhombic crystals, these are:

$$a* = \frac{1}{a_0} \quad b* = \frac{1}{b_0} \quad c* = \frac{1}{c_0}$$

For crystals of other symmetries, the relationship between the direct and reciprocal lattice distances is more complex (see Section S1.7)

The reciprocal lattice of a crystal is easily derived from the unit cell. For cubic cells, the reciprocal lattice axes are parallel to the direct lattice axes, which themselves are parallel to the unit cell edges, and the spacing of the lattice points $h\,k\,l$, along the three reciprocal axes, is equal to the reciprocal of the unit cell dimensions, $1/a_0 = 1/b_0 = 1/c_0$ (Figure 5.11). For some purposes it is convenient to multiply the length of the reciprocal axes by a constant. Thus, physics texts usually multiply the axes given in Figure 5.11 by 2π, and crystallographers by λ, the wavelength of the radiation used to obtain a diffraction pattern. The derivation of the reciprocal lattice for symmetries other than cubic is given in Section S1.8.

5.2 The determination of crystal structures

Crystal structures are determined by using diffraction (see Section 14.7.3). The extent of diffraction is significant only when the wavelength of the radiation is very similar to the dimensions of the object that is irradiated. In the case of crystals, radiation with a wavelength similar to that of the spacing of the atoms in the crystal will be diffracted. X-ray diffraction is the most widespread technique used for structure determination, but diffraction of electrons and neutrons is also of great importance, as these reveal features that are not readily observed with X-rays.

The physics of diffraction by crystals has been worked out in detail. It is found that the incident radiation is diffracted in a characteristic way, called a diffraction pattern. If the positions of the

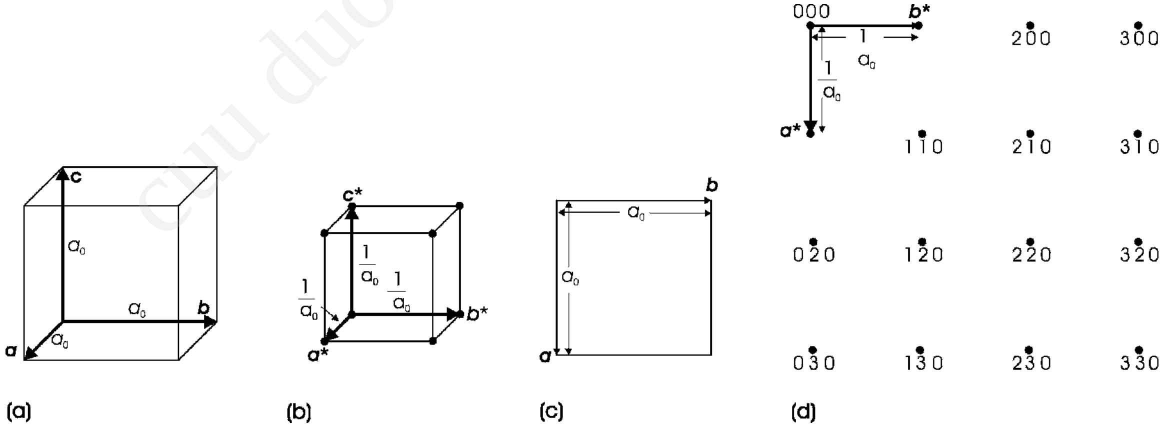

Figure 5.11 The direct lattice and reciprocal lattice of a cubic crystal: (a), (c) the direct lattice, specified by vectors ***a***, ***b*** and ***c***, with unit cell edges a_0 $(a_0 = b_0 = c_0)$; (b), (d) the reciprocal lattice, specified by vectors ***a****, ***b**** and ***c****, with unit cell edges $1/a_0$, $(1/a_0 = 1/b_0 = 1/c_0)$. The vector ***a**** is parallel to ***a***, ***b**** parallel to ***b*** and ***c**** parallel to ***c***. The vector from 0 0 0 to $h\,k\,l$ in the reciprocal lattice is perpendicular to the $(h\,k\,l)$ plane in a cubic crystal

diffracted beams are recorded, they map out the reciprocal lattice of the crystal. The intensities of the beams are a function of the arrangements of the atoms in space and of some other atomic properties, especially the atomic number of the atoms. Thus, if the positions and the intensities of the diffracted beams are recorded, it is possible to deduce the arrangement of the atoms in the crystal and their chemical nature.

5.2.1 *Single-crystal X-ray diffraction*

In this technique, which is the most important structure determination tool, a small single crystal of the material, of the order of a fraction of a millimetre in size, is mounted in a beam of X-rays. The diffraction pattern used to be recorded photographically, but now the task is carried out electronically. The technique has been used to solve enormously complex structures, such as that of huge proteins, or DNA.

Problems still remain, though, in this area of endeavour. Any destruction of the perfection in the crystal structure degrades the sharpness of the diffracted beams. This in itself can be used for crystallite size determination. Poorly crystalline material gives poor information, and truly amorphous samples give virtually no crystallographic information this way.

5.2.2 *Powder X-ray diffraction and crystal identification*

A common problem for many scientists is to determine which compounds are present in a polycrystalline sample. The diffraction pattern from a powder placed in the path of an X-ray beam gives rise to a series of cones rather than spots, because each plane in the crystallite can have any orientation (Figure 5.12a). The positions and intensities of the diffracted beams are recorded along a narrow strip (Figure 5.12b), and the diffracted beams are often

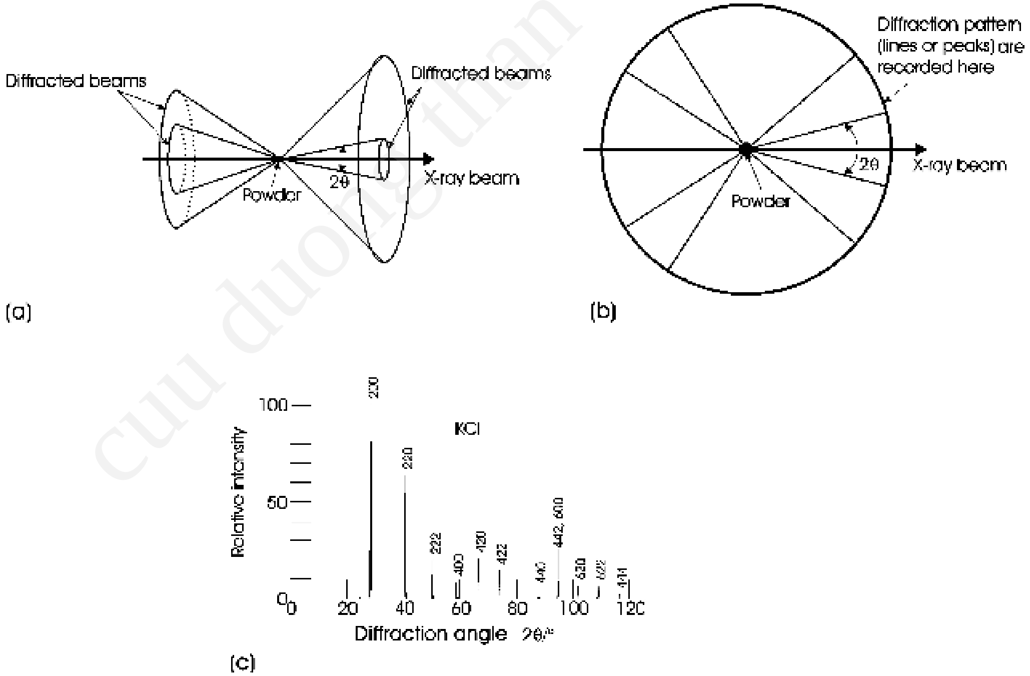

Figure 5.12 Powder X-ray diffraction: (a) a beam of X-rays incident on a powder is diffracted into a series of cones; (b) the intensities and positions of the diffracted beams are recorded along a circle, to give a diffraction pattern. (c) The diffraction pattern from powdered potassium chloride, KCl, a cubic crystal. The numbers above the ‘lines’ are the Miller indices of the diffracting planes

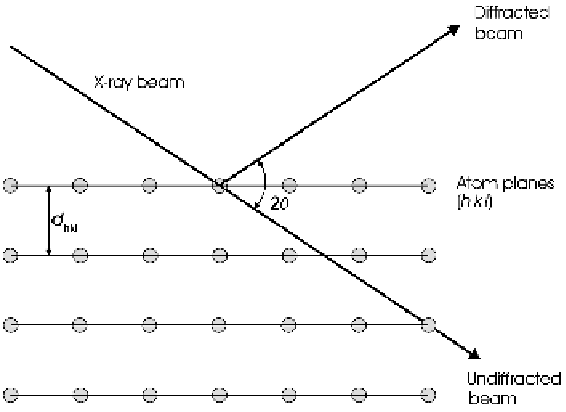

Figure 5.13 The geometry of Bragg reflection from a set of crystal planes, $(h\,k\,l)$, with interplanar spacing $d_{h\,k\,l}$

called lines (Figure 5.12c). The position of a difracted beam (not the intensity) is found to depend only on the interplanar spacing, $d_{h\,k\,l}$, and the wavelength of the X-rays used. Bragg's Law, Equation (5.1), gives the connection between these quantities:

$$\lambda = 2\,d_{h\,k\,l}\,\sin\,\theta \tag{5.1}$$

where λ is the wavelength of the X-radiation, $d_{h\,k\,l}$ is the interplanar spacing of the $(h\,k\,l)$ planes and θ is the diffraction angle (Figure 5.13). (Although the geometry of Figure 5.13 is identical to that of reflection, the physical process occurring is diffraction.) The relationship is simplest for cubic crystals. In this case, the interplanar spacing is givenby:

$$\frac{1}{d_{h\,k\,l}^2} = \frac{h^2 + k^2 + l^2}{a_0^2}$$

hence, $d_{h\,k\,l} = a_0, a_0/\sqrt{2}, a_0/\sqrt{3}, a_0/\sqrt{4}$, etc., where a_0 is the cubic unit cell lattice parameter.

The positions of the lines on the diffraction pattern of a single phase can be used to derive the unit cell dimensions of the material. The unit cell of a solid with a fixed composition is a constant. If the solid has a composition range, as in a solid solution or an alloy, the cell parameters will vary. Vegard's law, first propounded in 1921, states that the lattice parameter of a solid solution of two phases with similar structures will be a linear function of the lattice parameters of the two end members of the composition range (Figure 5.14a):

$$x = \frac{a_{\mathrm{ss}} - a_1}{a_2 - a_1}$$

where a_1 and a_2 are the lattice parameters of the parent phases, a_{ss} is the lattice parameter of the solid solution, and x is the mole fraction of the parent phase with lattice parameter a_2. This 'law' is simply an expression of the idea that the cell parameters are a direct consequence of the sizes of the component atoms in the solid solution. Vegard's law, in its ideal form (Figure 5.14a), is almost never obeyed exactly. A plot of cell parameters that lies below the ideal line (Figure 5.14b) is said to show a negative deviation from Vegard's law, and a plot that lies

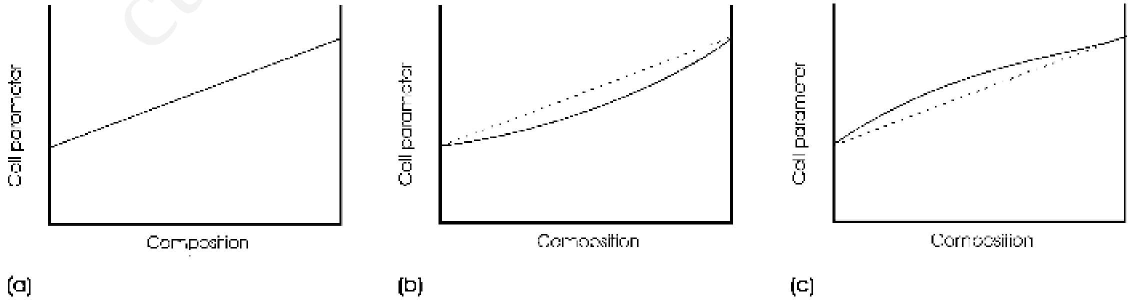

Figure 5.14 Vegard's law relating unit cell parameters to composition: (a) ideal Vegard's law behaviour; (b) a negative deviation from Vegard's law; and (c) a positive deviation from Vegard's law

above the ideal line (Figure 5.14c) is said to show a positive deviation form Vegard's law. In these cases, atomic interactions, which modify the size effects, are responsible for the deviations. In all cases, a plot of composition versus cell parameters can be used to determine the composition of intermediate compositions in a solid solution.

When the intensity and the positions of the diffraction pattern are taken into account, the pattern is unique for a single substance. The X-ray diffraction pattern of a substance can be likened to a fingerprint, and mixtures of different crystals can be analysed if a reference set of patterns is consulted. This technique is routine in metallurgical and mineralogical laboratories. The same technique is widely used in the determination of phase diagrams.

The experimental procedure can be illustrated with reference to the sodium fluoride–zinc fluoride ($NaF–ZnF_2$) system. Suppose that pure NaF is mixed with it a few percent of pure ZnF_2 and the mixture heated at 600 °C until reaction is complete. The X-ray powder diffraction pattern will show the presence of two phases: NaF, which will be the major component, and a small amount of a new compound (point A, Figure 5.15). A repetition of the experiment, with gradually increasing amounts of ZnF_2, will yield a similar result, but the amount of the new phase will increase relative to the amount of NaF until a mixture of 1NaF plus $1ZnF_2$ is heated. At this composition, only one phase will be indicated on the X-ray powder diagram. It has the composition $NaZnF_3$.

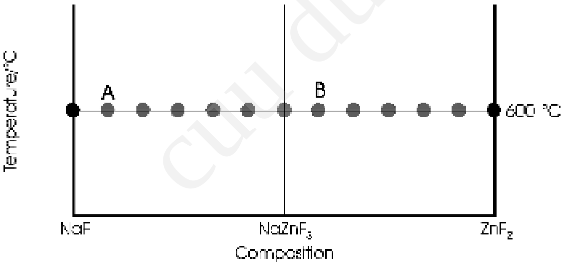

Figure 5.15 The determination of phase relations using X-ray diffraction. The X-ray powder patterns will show a single material to be present only at the exact compositions NaF, $NaZnF_3$ and ZnF_2. At points such as A, the solid will consist of NaF and $NaZnF_3$. At points such as B, the solid will consist of $NaZnF_3$ and ZnF_2. The proportions of components in the mixtures will vary across the composition range

A slight increase in the amount of ZnF_2 in the reaction mixture again yields an X-ray pattern that shows two phases to be present. Now, however, the compounds are $NaZnF_3$ and ZnF_2 (point B, Figure 5.15). This state of affairs continues as more ZnF_2 is added to the initial mixture, with the amount of $NaZnF_3$ decreasing and the amount of ZnF_2 increasing until pure NaF_2 is reached. Careful preparations reveal the fact that NaF or ZnF_2 appear alone on the X-ray films only when they are pure, and $NaZnF_3$ appears alone only at the exact composition of one mole NaF plus one mole ZnF_2. In addition, over all the composition range studied, the unit cell dimensions of each of these three phases will be unaltered.

An extension of the experiments to higher temperatures will allow the whole of the solid part of the phase diagram to be mapped.

5.2.3 Neutron diffraction

Neutron diffraction is very similar to X-ray diffraction in principle but is quite different in practice, because neutrons need to be generated in a nuclear reactor. One advantage of using neutron diffraction is that it is often able to distinguish between atoms that are difficult to distinguish with X-rays. This is because the scattering of X-rays depends on the atomic number of the elements, but this is not true for neutrons and, in some instances, neighbouring atoms have quite different neutron-scattering capabilities, making them easily distinguished. Another advantage is that neutrons have a spin and so interact with unpaired electrons in the structure. Thus neutron diffraction gives rise to information about the magnetic properties of the material. The antiferromagnetic arrangement of the Ni^{2+} ions in nickel oxide, for example, was determined by neutron diffraction (see Section 12.3.3).

5.2.4 Electron diffraction

Electrons are charged particles and interact very strongly with matter. This has two consequences for structure determination. First, electrons will pass only through a gas or very thin solids. Second, each electron will be diffracted many times in traversing the sample, making the theory of electron diffraction more complex than the theory of X-ray diffraction. The relationship between the position and intensity of a diffracted beam is not easily related to the atomic positions in the unit cell. Moreover, delicate molecules are easily damaged by the intense electron beams needed for a successful diffraction experiment. Electron diffraction, therefore, is not used in the same routine way as X-ray diffraction for structure determination.

Electrons, however, do have one advantage. Because they are charged they can be focused by magnetic lenses to form an image. The mechanism of diffraction as an electron beam passes through a thin flake of solid allows defects such as dislocations to be imaged with a resolution close to atomic dimensions. Similarly, diffraction (reflection) of electrons from surfaces of thick solids allows surface details to be recorded, also with a resolution close to atomic scales. Thus although electron diffraction is not widely used in structure determination it is used as an important tool in the exploration of the microstructures and nanostructures of solids.

5.3 Crystal structures

5.3.1 Unit cells, atomic coordinates and nomenclature

Irrespective of the complexity of a crystal structure, it can be constructed by the packing together of unit cells. This means that the positions of all of the atoms in the crystal do not need to be given, only those in a unit cell. The minimum amount of information needed to specify a crystal structure is thus the unit cell type, the cell parameters and the positions of the atoms in the unit cell. For example, the unit cell of the rutile form of titanium dioxide has a tetragonal unit cell, with cell parameters, $a_0 = b_0 = 0.459\,\text{nm}$, $c_0 = 0.296\,\text{nm}$.(2)

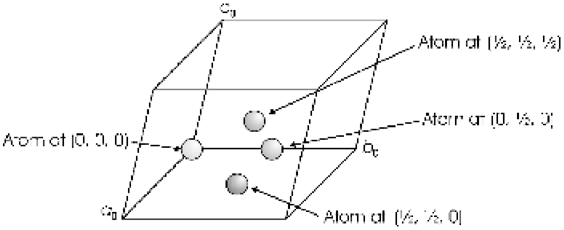

Figure 5.16 The positions of atoms in a unit cell. Atom positions are specified as fractions of the cell edges, not with respect to Cartesian axes

The (x, y, z) coordinates of the atoms in each unit cell are expressed as fractions of a_0, b_0 and c_0, the cell sides. Thus, an atom at the centre of a unit cell would have a position specified as $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, irrespective of the type of unit cell. Similarly, an atom at each corner of a unit cell is specified by $(0, 0, 0)$. The normal procedure of stacking the unit cells together means that this atom will be duplicated at every other corner. For an atom to occupy the centre of a face of the unit cell, the coordinates will be $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, for C-face-centred, A-face-centred and B-face-centred cells, respectively. Atoms on cell edges are specified at positions $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$ or $(0, 0, \frac{1}{2})$, for atoms on the *a b* and *c* axes, respectively. Stacking of the unit cells to build a structure will ensure that atoms appear on all of the cell edges and faces. These positions are illustrated in Figure 5.16.

A unit cell reflects the symmetry of the crystal structure. Thus, an atom at a position (x, y, z) in a unit cell may require the presence of atoms at other positions in order to satisfy the symmetry of the structure. For example, a unit cell with a centre of symmetry will, of necessity, require that an atom at (x, y, z) be paired with an atom at $(-x, -y, -z)$. To avoid long repetitive lists of atom positions in complex structures, crystallographic descriptions usually list only the minimum number of atomic positions which, when combined with the symmetry of the structure, given as the space group, generate all the atom positions in the unit cell. Additionally, the Bravais lattice type and the motif are often specified as well as the number of formula units in the unit cell, written as Z. Thus, in the unit cell of rutile, given above, $Z = 2$. This means that there are

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(2) The unit cell dimensions are often specified in terms of the Ångström unit, Å, where 10 Å = 1 nm.

two TiO_2 units in the unit cell; that is, two titanium atoms and four oxygen atoms. In the following sections, these features of nomenclature will be developed in the descriptions of some widely encountered crystal structures.

A vast number of structures have been determined, and it is very convenient to group those with topologically identical structures together. On going from one member of the group to another the atoms in the unit cell differ, reflecting a change in chemical compound, and the atomic coordinates and unit cell dimensions change slightly, reflecting the difference in atomic size. Frequently, the group name is taken from the name of a mineral, as mineral crystals were the first solids used for structure determination. Thus all solids with the *halite* structure have a unit cell similar to that of sodium chloride, NaCl. This group includes the oxides NiO, MgO and CaO (see Section 5.3.9). Metallurgical texts often refer to the structures of metals using a symbol for the structure. These symbols were employed by the journal *Zeitschrift für Kristallographie*, in the catalogue of crystal structures Strukturberichte Volume 1, published in 1920, and are called Strukturberichte symbols. For example, all solids with the same crystal structure as copper are grouped into the A1 structure type. These labels remain a useful shorthand for simple structures but become cumbersome when applied to complex materials, when the mineral name is often more convenient (e.g. see the *spinel* structure, Section 5.3.10).

5.3.2 The density of a crystal

The atomic contents of the unit cell give the composition of the material. The theoretical density of a crystal can be found by calculating the mass of all the atoms in the unit cell. (The mass of an atom is its molar mass divided by the Avogadro constant; see Section S1.1). The mass is divided by the unit cell volume. To count the number of atoms in a unit cell, we use the following information:

- an atom within the cell counts as 1;
- an atom in a face counts as 1/2;
- an atom on an edge counts as 1/4;
- an atom on a corner counts as 1/8.

A quick method to count the number of atoms in a unit cell is to displace the unit cell outline to remove all atoms from corners, edges and faces. The atoms remaining, which represent the unit cell contents, are all within the boundary of the unit cell and count as 1.

The measured density of a material gives the average amount of matter in a large volume. For a solid that has a variable composition, such as an alloy or a nonstoichiometric phase, the density will vary across the phase range. Similarly, an X-ray powder photograph yields a measurement of the average unit cell dimensions of a material and, for a solid that has a variable composition, the unit cell dimensions are found to change in a regular way across the phase range. These two techniques can be used in conjunction with each other to determine the most likely point defect model to apply to a material. As both techniques are averaging techniques they say nothing about the real organisation of the defects, but they do suggest first approximations.

The general procedure is to determine the unit cell dimensions, the crystal structure type and the real composition of the material. The ideal composition of the unit cell will be known from the structure type. The ideal composition is adjusted by the addition of extra atoms (interstitials or substituted atoms) or removal of atoms (vacancies) to agree with the real composition. A calculation of the density of the sample assuming either that interstitials or vacancies are present is then made. This is compared with the measured density to discriminate between the two alternatives.

5.3.2.1 Example: iron monoxide

The method can be illustrated by reference to iron monoxide. Iron monoxide, often known by its mineral name of wüstite, has the *halite* (NaCl) structure. In the normal *halite* structure, there are four metal and four nonmetal atoms in the unit cell, and compounds with this structure have an ideal composition $MX_{1.0}$ (see Section 5.3.9 for further information on the *halite* structure). Wüstite has a composition that is always oxygen-rich compared with the ideal formula of $FeO_{1.0}$. Data for an actual sample found an oxygen:iron ratio of 1.058, a density of 5728 kg m^{-3} and a cubic lattice parameter, a_0, of 0.4301 nm[3]. The real composition can be obtained by assuming either that there are extra oxygen atoms in the unit cell, as interstitials (Model A), or that there are iron vacancies present (Model B).

Model A Assume that the iron atoms in the crystal are in a perfect array, identical to the metal atoms in *halite*, and that an excess of oxygen is due to interstitial oxygen atoms present in addition to those on the normal anion positions. The *ideal* unit cell of the structure contains four iron atoms and four oxygen atoms and so, in this model, the unit cell must contain four atoms of iron and $4(1+x)$ atoms of oxygen. The unit cell contents are Fe_4O_{4+4x} and the composition is $FeO_{1.058}$.

- The mass of 1 unit cell in model A, m_A, is

$$\begin{aligned} m_A &= \frac{1}{N_A}\{(4 \times 55.85) + [4 \times 16 \times (1+x)]\} \\ &= \frac{1}{N_A}[(4 \times 55.85) + (4 \times 16 \times 1.058)]\ \mathrm{g} \\ &= 4.834 \times 10^{-25}\ \mathrm{kg}. \end{aligned}$$

- The volume, v, of the cubic unit cell is given by a_0^3, thus:

$$v = (0.4301 \times 10^{-9})^3\ \mathrm{m}^3 = 7.9562 \times 10^{-29}\ \mathrm{m}^3.$$

- The density, ρ, is given by the mass, m_A, divided by the volume, v:

$$\begin{aligned} \rho &= \frac{4.834 \times 10^{-25}\ \mathrm{kg}}{7.9562 \times 10^{-29}\ \mathrm{m}^3} \\ &= 6076\ \mathrm{kg\ m}^{-3}. \end{aligned}$$

Model B Assume that the oxygen array is perfect and identical to the nonmetal atom array in the *halite* structure. As there are more oxygen atoms than iron atoms, the unit cell must contain some vacancies on the iron positions. In this case, one unit cell will contain four atoms of oxygen and $(4-4x)$ atoms of iron. The unit cell contents are $Fe_{4-4x}O_4$, and the composition is $Fe_{1/1.058}O_{1.0}$ or $Fe_{0.945}O$.

- The mass of one unit cell in model B, m_B, is

$$\begin{aligned} m_B &= \frac{1}{N_A}\{[4 \times (1-x) \times 55.85] + (4 \times 16)\} \\ &= \frac{1}{N_A}[(4 \times 0.945 \times 55.85) + (4 \times 16)]\ \mathrm{g} \\ &= 4.568 \times 10^{-25}\ \mathrm{kg}. \end{aligned}$$

- The density, ρ, is given by m_B divided by the volume, v, to yield

$$\begin{aligned} \rho &= \frac{4.568 \times 10^{-25}\ \mathrm{kg}}{7.9562 \times 10^{-29}\ \mathrm{m}^3} \\ &= 5741\ \mathrm{kg\ m}^{-3} \end{aligned}$$

Conclusion The difference in the two values is surprisingly large. The experimental value of the density, 5728 kg m^{-3}, is in good accord with that for model B, in which vacancies on the iron positions are assumed. This indicates that the formula should be written $Fe_{0.945}O$.

5.3.3 The cubic close-packed (A1) structure

- General formula: M; example: Cu.
- Lattice: cubic face-centred, $a_0 = 0.360$ nm.
- $Z = 4$ Cu.
- Atom positions: $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$; $(0, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, 0, \frac{1}{2})$.

There are four lattice points in the face-centred unit cell, and the motif is one atom at $(0, 0, 0)$. The structure is typified by copper (Figure 5.17). The cubic close-packed structure is adopted by many metals (see Figure 6.1, page 152) and by the noble

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[3] The data are from the classical paper by E.R. Jette and F. Foote; *Journal of Chemical Physics*, volume 1, page 29, 1933.

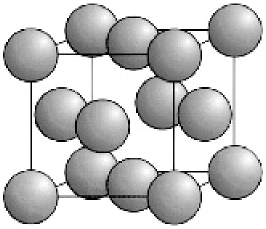

Figure 5.17 The A1 structure of copper

gases, Ne(s), Ar(s), Kr(s), Xe(s). This structure is often called the face-centred cubic (fcc) structure but, from a crystallographic point of view, this name is not ideal(4) and it is convenient to use the Strukturbericht symbol, A1. Each atom has 12 nearest neighbours and, if the atoms are supposed to be hard touching spheres, the fraction of the volume occupied is 0.7405. More information on this structure is given in Section 6.1.1

5.3.4 The body-centred cubic (A2) structure

- General formula: *M*; example: W.
- Lattice: cubic body-centred, $a_0 = 0.316\,\text{nm}$.
- $Z = 2\,\text{W}$.
- Atom positions: $(0, 0, 0)$; $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$.

There are two lattice points in the body-centred unit cell, and the motif is one atom at $(0, 0, 0)$. The structure is adopted by tungsten, W (Figure 5.18) and by many other metallic elements (see Figure 6.1, page 152). This structure is often called the body-centred cubic (bcc) structure. As with the A1 structure, this is not a good name (see Footnote 4) and it is better to refer to the Strukturbericht symbol, A2. In this structure, each atom has eight nearest neighbours and six next-nearest neighbours at only 15 % greater distance. If the atoms are supposed to be hard touching spheres, the fraction of the volume occupied is 0.6802. This is less than that for either the A1 structure (Section 5.3.3) or the A3 structure (Section 5.3.5), both of which have a volume fraction of occupied space of 0.7405. The bcc structure is often the high-temperature structure of a metal that has a close-packed structure at lower temperature. More information on this structure is given in Section 6.1.1.

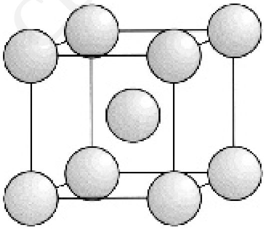

Figure 5.18 The A2 structure of tungsten

5.3.5 The hexagonal (A3) structure

- General formula: *M*; example: Mg.
- Lattice: primitive hexagonal, $a_0 = 0.321\,\text{nm}$, $c_0 = 0.521\,\text{nm}$.
- $Z = 2\,\text{Mg}$.
- Atom positions: $(0, 0, 0)$; $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$.

The lattice is primitive, and so there is only one lattice point in each unit cell. The motif is two atoms, one atom at $(0, 0, 0)$ and one atom at $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$. The structure is represented by magnesium, Mg (Figure 5.19). If the atoms are supposed to be hard touching spheres, the fraction of the volume occupied is 0.7405 and the ratio *c*/*a* is

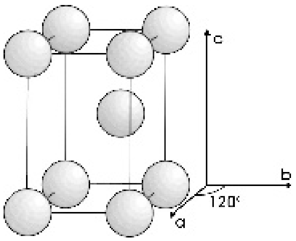

Figure 5.19 The A3 structure of magnesium

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(4) See H.D. Megaw, *Crystal Structures*, Saunders, London, 1973.

equal to $\sqrt{8}/\sqrt{3}, = 1.633$. Many metals adopt the A3 structure, some over a limited temperature range (see Figure 6.1, page 152). More information on this structure is given in Section 6.1.1.

5.3.6 The diamond (A4) structure

- General formula: M; example: C.
- Lattice: cubic face-centred, $a_0 = 0.356\,\text{nm}$.
- $Z = 8$ C.
- Atom positions: $(0,0,0)$; $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$; (repeat in the face-centred pattern).

There are four lattice points in the face-centred unit cell, and the motif is two atoms, one atom at $(0,0,0)$ and one at $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$. The structure is adopted by diamond and, in it, each carbon atom is bonded to four other carbon atoms that are arranged tetrahedrally around it (Figure 5.20). The bonds, of length 0.154 nm, are extremely strong sp^3 hybrids. The crystal can be regarded as a giant molecule.

The elements silicon ($a_0 = 0.542\,\text{nm}$) and germanium ($a_0 = 0.564\,\text{nm}$) also have the same structure as diamond. Grey tin has the same structure ($a_0 = 0.649\,\text{nm}$) below a temperature of 13.2 °C.

5.3.7 The hexagonal (graphite), A9 structure

- General formula: C; graphite.
- Lattice: primitive hexagonal, $a_0 = 0.246\,\text{nm}$, $c_0 = 0.671\,\text{nm}$.
- $Z = 4$ C.
- Atom positions: $(0,0,0)$; $\left(0,0,\frac{1}{2}\right)$; $\left(\frac{1}{3},\frac{2}{3},0\right)$; $\left(\frac{2}{3},\frac{1}{3},\frac{1}{2}\right)$.

The lattice is primitive, and so there is only one lattice point in each unit cell. The motif is four atoms, at the positions specified above.

Graphite is a form of elemental carbon. The bonding in this material is closely related to that in benzene. The structure is made up of planar layers of carbon atoms bonded via sp^2 hybrid orbitals to give a strong framework with a hexagonal geometry (Figure 5.21). Because the bonding electrons are held in place, this skeleton is insulating. Above and below the layers, delocalised π bonds form a cloud of delocalised electrons which, because the layers are stacked directly on top of each other, repel each other strongly. This results in a large interlayer distance (0.335 nm) compared with the C–C distance in the plane

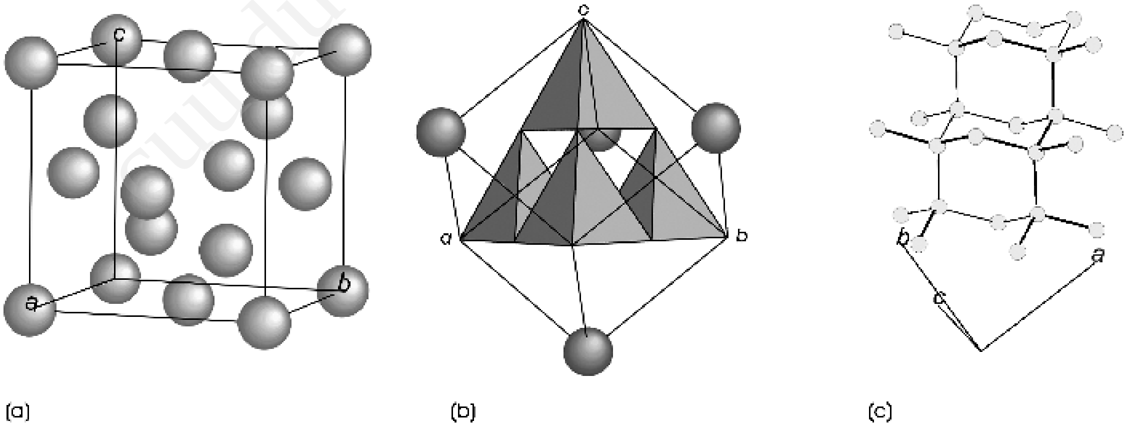

Figure 5.20 The A4 structure of diamond: (a) atoms in the unit cell, (b) projection approximately down the [1 1 1] direction to show the structure as carbon-centred tetrahedra; and (c) a similar projection to (b), to reveal the tetrahedral bond geometry

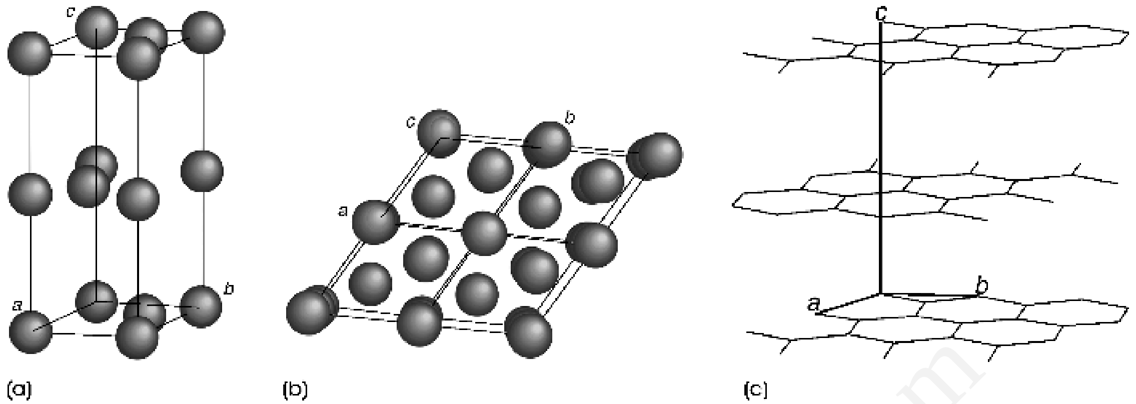

Figure 5.21 The A9 structure of graphite: (a) perspective view of the structure; (b) Projection approximately down the [0 0 1] direction; (c) the structure drawn as hexagonal sheets, in which a carbon atom lies at each hexagonal vertex

(0.141 nm). The bonding between layers is very weak, made up of a van der Waals interaction between the delocalised electrons. Hence, although each layer of graphite is strong, the layers slide over one another easily. Graphite is easily cleaved in this direction and is a good dry lubricant. The delocalised electrons between the layers are similar to electrons in a metal, and these make graphite an electronic conductor parallel to the layers.

5.3.8 The structure of boron nitride

Boron nitride, BN, has a very similar structure to graphite but the hexagonal sheets are composed of boron and nitrogen atoms. It is white, chemically inert and a good insulator. The electronic structure of boron is $1s^2 2s^2 2p^1$ and that of nitrogen is $1s^2 2s^2 2p^3$. In order to generate the BN structure, the boron and the nitrogen atoms must form sp^2 hybrid bonds in the B–N sheets. In the case of boron, sp^2 hybridisation uses all of the outer electrons. In the case of nitrogen, sp^2 hybrid orbitals are formed by promoting one of the $2s^2$ electrons to give the configuration $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^2$. After formation of the sp^2 orbitals, the remaining two p electrons are located in the (filled) p_z orbital.

The σ bonding in the BN sheets that results is strong and similar to the bonding in the graphite sheets. However, π bonding between the full $2p_z$ orbitals of nitrogen and the empty $2p_z$ orbitals of boron is not possible. This is because the orbital energies of boron and nitrogen are too dissimilar for a large energy gain, and hence bonding, to take place. Thus, no delocalised electrons are present in the structure, and BN is an insulator. Because of this, the boron and nitrogen atoms in alternate layers 'avoid' each other. This allows for the more efficient packing of the filled p_z orbitals, and the layers are closer than they are in graphite. Nevertheless, the lack of bonding between the layers still means that BN retains the easy cleavage of graphite and is still a good dry lubricant.

5.3.9 The halite (rock salt, sodium chloride, B1) structure

- General formula: *MX*; example: NaCl.
- Lattice: cubic face-centred, $a_0 = 0.563\,\text{nm}$.
- $Z = 4$ NaCl.
- Atom positions: Na at $(0, 0, 0)$; Cl at $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$; (repeat in the face-centred pattern).

There are four lattice points in the face-centred unit cell, and the motif is one sodium atom at $(0, 0, 0)$ and one chlorine atom at $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$. In this structure, called the *halite*, *rock salt* or sodium chloride

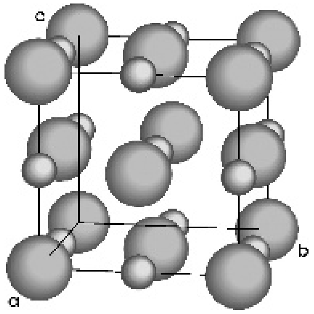

Figure 5.22 The B1 *halite* structure of NaCl

structure, each ion is surrounded by six ions of the opposite type at the corners of a regular octahedron (Figure 5.22).

This structure is extremely common and is adopted by many oxides, sulphides, halides and nitrides, with a formula *MX*.

5.3.10 The spinel ($H1_1$) structure

- General formula: AB_2X_4; example: $MgAl_2O_4$.
- Lattice: face-centred cubic, $a_0 = 0.809\,\text{nm}$.
- $Z = 8$ $MgAl_2O_4$.
- Atom positions: there are 56 atoms in the unit cell, the positions of which will not be listed here.

There are four lattice points in the face-centred unit cell, and the motif is two $MgAl_2O_4$ complexes. This structure is named after the mineral spinel, $MgAl_2O_4$. The oxygen atoms in the crystal structure are in the same relative positions as the chlorine atoms in eight unit cells of halite, stacked together to form a 2 × 2 × 2 cube (Figure 5.23). Thus in the cubic unit cell of spinel there are 32 oxygen atoms, to give a unit cell content of $Mg_8Al_{16}O_{32}$. The magnesium and aluminium atoms are inserted into this array in an ordered fashion. To a good approximation, all of the magnesium atoms are surrounded by four oxygen atoms in the form of a tetrahedron and are said to occupy tetrahedral positions, or sites, in the structure. Similarly, to a good approximation, the aluminium atoms are surrounded by six oxygen atoms and are said to occupy octahedral positions or sites (see below). When the structure is viewed down the [1 1 1] direction the oxygen atoms can be seen to form cubic close-packed layers, emphasising the relationship with the *halite* (NaCl) structure (see below).

The mineral spinel, $MgAl_2O_4$, has given its name to an important group of compounds with the same

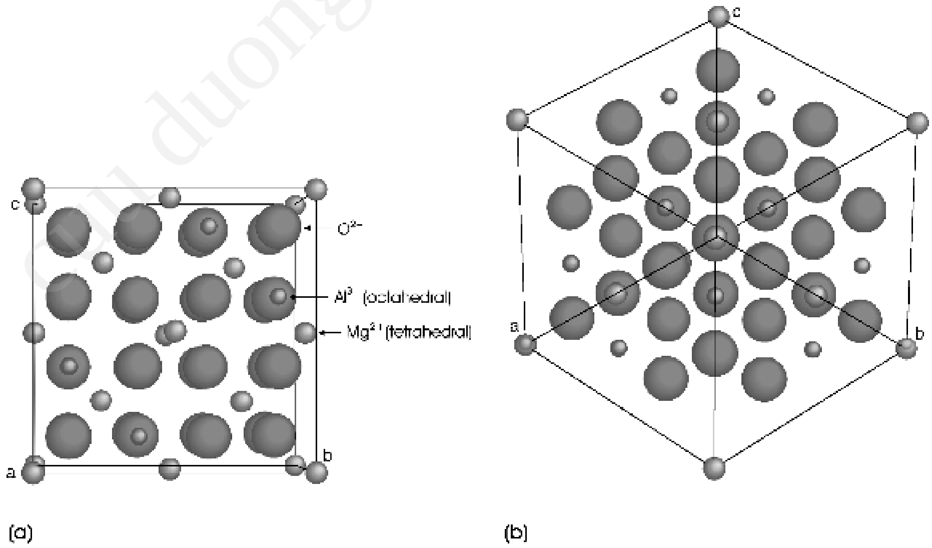

Figure 5.23 The $H1_1$ normal spinel structure of $MgAl_2O_4$: (a) projected down the [1 0 0] direction; (b) projected down the [1 1 1] direction (projected)

structure, collectively known as *spinels*, which includes halides, sulphides and nitrides as well as oxides. Only oxide spinels are considered here. These are often regarded as ionic compounds. The formula of the oxide spinels, AB_2O_4, is satisfied by a number of combinations of cations, the commonest of which is A^{2+} and B^{3+}, typified by Mg^{2+} and Al^{3+} in spinel itself.

In each unit cell there are the same number of octahedral sites as there are oxygen ions, that is, 32, and twice as many tetrahedral sites as oxygen ions, that is 64. However, not all of these can be occupied. The A^{2+} and B^{3+} cations are inserted into this array in an ordered fashion, filling half of the available octahedral positions and an eighth of the available tetrahedral positions. This means that there are 8 occupied tetrahedral sites and 16 occupied octahedral sites in a unit cell.

There are two principle arrangements of cations found. If the 8 A^{2+} ions per unit cell are confined to the available tetrahedral sites, these are filled completely. The 16 B^{3+} ions are then confined to the octahedral sites. This cation distribution is often depicted as $(A)[B_2]O_4$, with the tetrahedral cations in round brackets and the octahedral cations in square brackets. This is called the *normal spinel* structure, and *spinels* with this arrangement of cations are said to be normal spinels. If the 8 A^{2+} ions are placed in half of the available 16 octahedral sites, half of the B^{3+} ions must be placed in the remaining octahedral sites and the other half in the tetrahedral sites. This can be written as $(B)[AB]O_4$. This arrangement is called the *inverse spinel* structure and compounds with this cation arrangement are said to be inverse spinels.

In reality, very few *spinels* have exactly the normal or inverse structure, and these are sometimes called mixed *spinels*. The cation distribution between the two sites is a function of a number of parameters, including temperature. This variability is described by an occupation factor, λ, which gives the fraction of B^{3+} cations in tetrahedral positions. A normal *spinel* is characterised by a value of λ of 0, and an inverse *spinel* by a value of λ of 0.5. The spinel $MgAl_2O_4$ has a value of λ of 0.05, and so is quite a good approximation to a normal *spinel*.

Cubic $A^{2+}Fe^{3+}O_4$ ferrites form an important group of magnetic oxides that have an inverse *spinel* structure, $(Fe^{3+})[A^{2+}Fe^{3+}]O_4$. Lodestone, or magnetite, Fe_3O_4, is an inverse *spinel* with a more correct formula of $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$. The tetrahedral and octahedral sites in cubic ferrites provide two magnetic substructures, which give these oxides very flexible magnetic properties that can be tailored by varying the cations and the distribution between the octahedral and tetrahedral sites (see Section 12.3.5). In reality, the distribution of the cations in cubic ferrites is rarely perfectly normal or inverse, and the distribution tends to vary with temperature. Thus processing conditions are important if the desired magnetic properties are to be obtained.

5.4 Structural relationships

A list of atomic positions is often not very helpful when a variety of structures have to be compared. In this section two ways of looking at structures that facilitate comparisons are described. In the first of these, structures are described in terms of being built up by packing together spheres, and, in the other, in terms of polyhedra linked by corners and edges.

5.4.1 Sphere packing

The structure of many crystals can conveniently be described in terms of an ordered packing of spheres, representing spherical atoms or ions. Although there are an infinite number of ways of doing this, only two main arrangements, called closest (or close) packing, are sufficient to describe many crystal structures. These structures are made up of close-packed layers of spheres. Each close-packed layer consists of a hexagonal arrangement of spheres just touching each other to fill the space as much as possible (Figure 5.24).

These layers of spheres can be stacked in two principal ways to generate the structures. In the first of these, a second layer fits into the dimples in the first layer, and the third layer is stacked in dimples

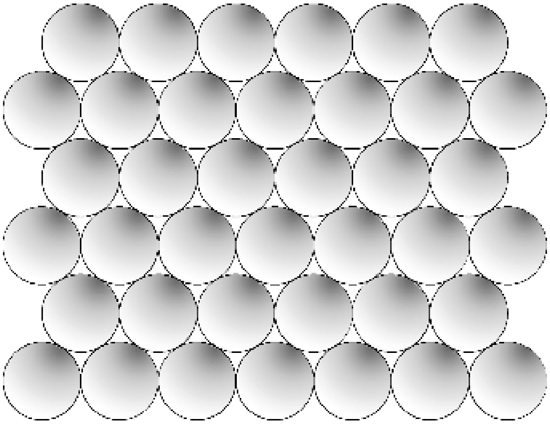

Figure 5.24 A single close-packed layer of spheres

on top of the second layer to lie over the first layer (Figure 5.25). This sequence is repeated indefinitely. If the position of the spheres in the first layer is labelled A, and the positions of the spheres in the second, B, the complete stacking is described by the sequence ABABAB.... The structure has a hexagonal symmetry and unit cell. The *a* and *b* axes lay in the close-packed A sheet, and the hexagonal *c* axis is perpendicular to the stacking and runs from one A sheet to the next. There are two spheres (two atoms) in a unit cell, at positions $(0, 0, 0)$ and $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$. If the spheres just touch, the relationship between the sphere radius, *r*, and the lattice parameter a_0, is:

$$2\,r = a_0$$

The ratio of c_0/a_0 in this ideal sphere packing is 1.633. The structure is identical to the A3 structure, described in Section 5.3.5. In most real structures the c_0/a_0 ratio departs from this ideal value of 1.633.

The second structure of importance is also formed by two layers of spheres, A and B, as before. The difference lies in the position of the third layer, which is not above either A or B, and is given the position label C (Figure 5.26). This three-layer stacking is repeated indefinitely, thus: ABCABC....

Although this structure can be described in terms of a hexagonal unit cell, the structure turns out to be cubic, and this description is always chosen. In terms of the cubic unit cell, there are atoms at the corners of the cell and in the centre of each of the faces. The close-packed layers lie along the [1 1 1] direction (Figure 5.27). The spacing of the close-packed planes for an ideal packing, d_{cp}, is a third of the body diagonal of the cubic unit cell (i.e. $a_0/\sqrt{3}$). If the spheres just touch, the relationship between

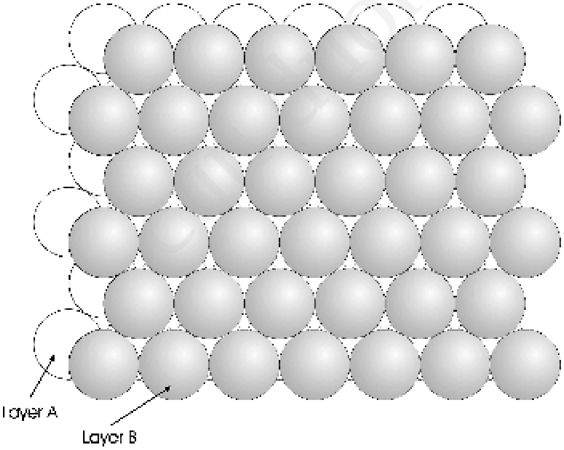

Figure 5.25 Hexagonal closest packing of spheres. All layers are identical to those in Figure 5.24. The first layer is labelled A, the second, B. Subsequent layers follow the sequence ... ABAB ...

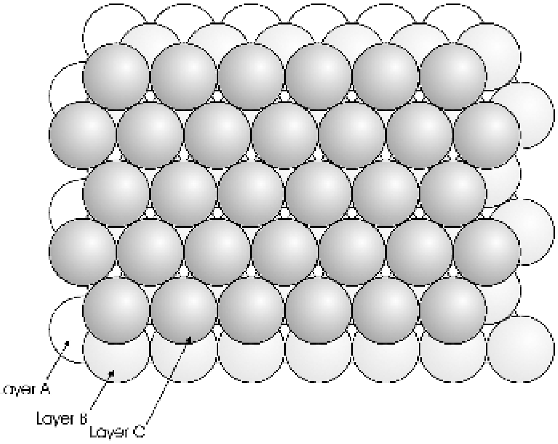

Figure 5.26 Cubic closest packing of spheres. All layers are identical to those in Figure 5.24. The first layer is labelled A, the second B and the third C. Subsequent layers follow the sequence ... ABCABC ...

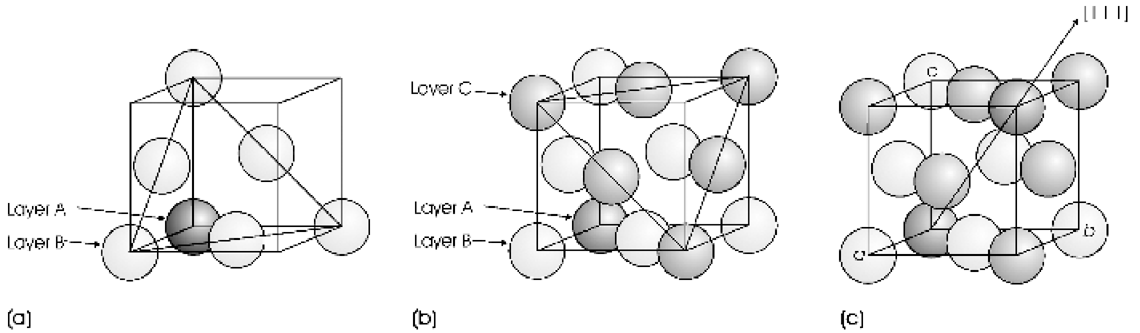

Figure 5.27 The cubic A1 structure in terms of cubic closest packing. The layers in Figure 5.26 lie perpendicular to the [1 1 1] direction and form $(1\,1\,1)$ planes. (a) The first two layers, A and B; (b) the first three layers, A, B and, C; and (c) the fourth layer, completed by an atom at the top corner; this is identical to the position $(0, 0, 0)$ in the unit cell and so is part of an A layer

the sphere radius, r, and the lattice parameter a_0, is:

$$r = \frac{a_0}{\sqrt{8}}$$

The relationship between the spacing of the close-packed planes of spheres, d_{cp}, the cell parameter a_0, and r, is therefore:

$$d_{\text{cp}} = \frac{a_0}{\sqrt{3}} = \frac{r\sqrt{8}}{\sqrt{3}} = 1.63299\,r$$

The cubic close-packed structure is identical to the A1 structure described in Section 5.3.3.

Both the hexagonal closest packing of spheres and the cubic closest packing of spheres result in the (equally) densest packing of spheres. The fraction of the total volume occupied by the spheres, when they touch, is 0.7405.

The sphere arrangements described are only two of an infinite number of ways for spheres to be stacked. It is surprising, for example, that the sequence ABAC is not commonly encountered in metal structures, although this is the structure of the metal lanthanum (La). In addition, a number of more complex arrangements have been found, especially in the compounds silicon carbide (SiC) and zinc sulphide (ZnS).

5.4.2 Ionic structures in terms of anion packing

The ionic model suggests that because many ions have a closed shell of outer electrons they can be regarded as spherical. Moreover, because anions have gained electrons whereas cations have lost electrons it seems reasonable to regard anions as larger than cations. Packing the large anions together and inserting small cations into the gaps in the anion array so formed can reveal relationships between structures that are otherwise difficult to recognise.

The problem of packing spherical anions, (neglecting charges), is the same as the geometric problem as packing spheres. In such structures, the spheres do not fill all the available volume. There are small holes between the spheres that occur in layers between the sheets of spheres. These holes, which are called interstices, interstitial sites or interstitial positions, are of two types (Figure 5.28). In one type of position, three spheres in the lower layer are surmounted by one sphere in the layer above, or vice versa. The geometry of this site is that of a tetrahedron. The other position is made up of a lower layer of three spheres and an upper layer of three spheres. The shape of the enclosed space is not so easy to see but is found to have an octahedral geometry.

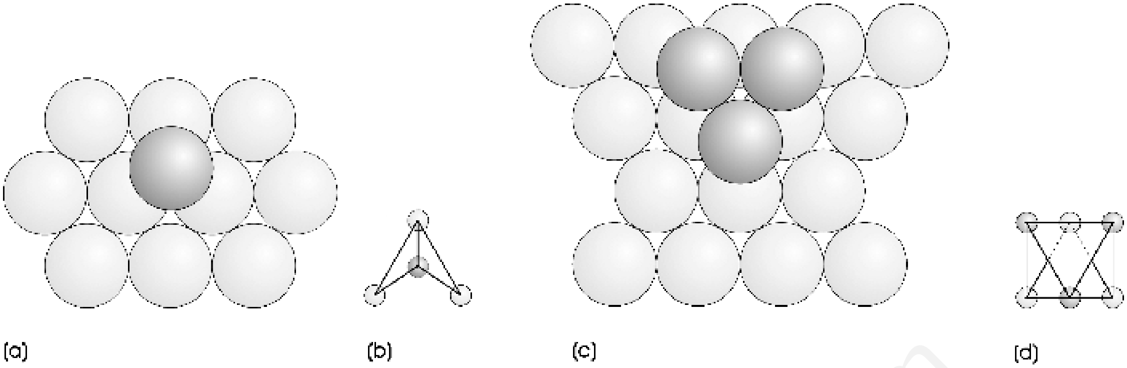

Figure 5.28 Tetrahedral and octahedral sites in cubic closest packed arrays of spheres: (a) a tetrahedral site between two layers and (b) the same site drawn as a polyhedron; (c) an octahedral site between two layers and (d) the same site drawn as a polyhedron

In the two closest packed sequences, . . . ABCABC . . . and . . . ABAB . . ., there are 2 *N* tetrahedral interstices and *N* octahedral interstices for every *N* anions. Structures are derived by placing cations into the interstices, making sure that the total positive charge on the cations is equal to the total negative charge on the anions. The formula of the structure can be found by counting up the numbers of ions of each sort present.

Consider the structures that arise from a cubic close-packed array of *X* anions. If every octahedral position contains an *M* cation there are equal numbers of cations and anions in the structure. The formula of the compounds with this structure is *MX*, and the structure corresponds to the *halite* (NaCl, B1) structure. In the case of halide anions, X^-, to maintain charge balance, each cation must have a charge of +1, and the alkali halide, *MX*, structure results. Should oxygen anions, O^{2-}, form the anion array, the cations must necessarily have a charge of 2+, to ensure that the charges balance, and the oxides will have a formula *M*O, but still retain the *halite* structure. This structure is possessed by a number of oxides, including MgO, CaO, SrO, BaO, MnO, FeO, CoO, NiO and CoO.

Should the anions adopt hexagonal close packing and all of the octahedral sites contain a cation, the hexagonal analogue of the *halite* structure is produced. In this case, the formula of the crystal is again *MX*. The structure is the *nicolite* (NiAs) structure and is adopted by a number of alloys and metallic sulphides, including NiAs, CoS, VS, FeS and TiS.

If only a fraction of the octahedral positions in the hexagonal packed array of anions is filled, a variety of structures results. The *corundum* structure is adopted by the oxides α-Al_2O_3, V_2O_3, Ti_2O_3 and Fe_2O_3. In this structure two-thirds of the octahedral sites are filled in an ordered way. Of the structures that form when only half of the octahedral sites are occupied, those of rutile (TiO_2) and α-PbO_2 are best known. The difference between the two structures lies in the way in which the cations are ordered. In the rutile form of TiO_2 the cations occupy straight rows of sites whereas in α-PbO_2 the rows are staggered.

A large number of structures can be generated by the various patterns of filling the octahedral or tetrahedral interstices. The number can be extended if both types of position are occupied. One important structure of this type is the *spinel* structure, discussed in Section 5.3.10. The oxide lattice can be equated to a cubic close-packed array of oxygen ions, and the cubic unit cell contains 32 oxygen atoms. There are, therefore, 32 octahedral sites and 64 tetrahedral sites for cations. The unit contains only 16 octahedral (*B* cations) and 8 tetrahedral (*A* cations), which are distributed in an ordered way over these positions to give the formula AB_2O_4, where $A = M^{2+}$, and $B = M^{3+}$. The formula of the

Table 5.2 Some structures in terms of anion packing

Fraction of sites occupied		Sequence of anion layers	
tetrahedral	octahedral	. . . ABAB . . .	. . . ABCABC . . .
0	1	NiAs (nicolite)	NaCl (halite)
$\frac{1}{2}$	0	ZnO, ZnS (wurtzite)	ZnS (sphalerite or zinc blende)
0	$\frac{2}{3}$	Al_2O_3 (corundum)	–
0	$\frac{1}{2}$	TiO_2 (rutile), α-PbO_2	TiO_2 (anatase)
$\frac{1}{8}$	$\frac{1}{2}$	Mg_2SiO_4 (olivine)	$MgAl_2O_4$ (spinel)

cubic spinels is therefore $A_8B_{16}O_{32}$ or, as usually written, AB_2O_4. If all the A cations are tetrahedral sites we have a normal *spinel*, $(A)[B_2]O_4$. If they are in octahedral sites we have an inverse *spinel*, $(B)[AB]O_4$.

Structures containing cations in tetrahedral sites can be described in exactly the same way. In this case, there are twice as many tetrahedral sites as anions and so, if all sites are filled, the formula of the solid will be M_2X. When half are filled this becomes MX, and so on.

A survey of some of the structures that can be linked in this way is given in Table 5.2.

5.4.3 Polyhedral representations

It is often necessary to focus on the surroundings of a particular atom or ion in a solid and, for this purpose, structures drawn in terms of polyhedra are helpful. The polyhedra selected are generally metal–nonmetal coordination polyhedra. These are composed of a central metal atom surrounded by nonmetal atoms. By reducing the nonmetal atoms to points and then joining the points by lines one is able to construct the polyhedral shape. These polyhedra are then linked together to build up the complete structure. This representation has already been used as a way of describing the structure of diamond (Figure 5.20).

The advantage of using polyhedral representations of solids is that family relationships can be illustrated clearly. The disadvantage is that important structural details are often ignored, especially when polyhedra are idealised.

The complex families of silicates are best compared if the structures are described in terms of linked tetrahedra. The tetrahedral shape used is the idealised coordination polyhedron of the $[SiO_4]$ unit (Figure 5.29). Each silicon atom is linked to four oxygen atoms by tetrahedrally directed sp^3 hybrid bonds. For example, Figure 5.30 shows the way in which the $[SiO_4]$ tetrahedra are linked in the commonest form of silica (SiO_2), quartz. The $[SiO_4]$ units are very strong and persist during physical and chemical reactions, so that structural transformations are also often easily visualised in terms of the rearrangement of the $[SiO_4]$ tetrahedra.

Octahedral coordination is frequently adopted by the important 3d transition metal ions. In this coordination polyhedron, each cation is surrounded by six anions, to form an octahedral $[MO_6]$ group (Figure 5.31). The structure of rhenium trioxide, ReO_3, in terms of linked $[ReO_6]$ octahedra, has the appearance of a three-dimensional chessboard (Figure 5.32a). This structure is similar to that of tungsten trioxide, WO_3, but in the latter compound the octahedra are distorted slightly, so that the symmetry is reduced from cubic in ReO_3 to monoclinic in WO_3. The idealised ABO_3 *perovskite* structure is similar, but has the large A cation in the centre of the cage of octahedra (Figure 5.32b). Most real *perovskites*, such as barium titanate, $BaTiO_3$, are built of slightly distorted $[MO_6]$

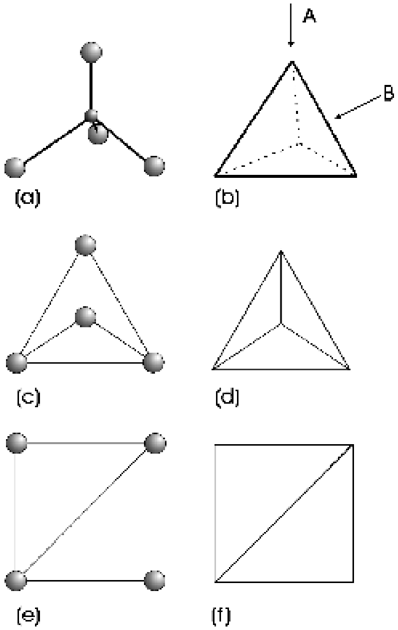

Figure 5.29 Representations of tetrahedra found in crystal structure diagrams: (a) a 'ball-and-stick' diagram of a tetrahedron, with a central silicon atom surrounded by four oxygen atoms and (b) its representation as a polyhedron. The views in parts (c), and (d) are the equivalent to those in parts (a) and (b), along the direction A in part (b), in which one tetrahedral vertex is uppermost. The views in parts (e) and (f) are the equivalent to those in parts (a) and (b), along the direction B in part (b), in which one tetrahedral edge is towards the observer

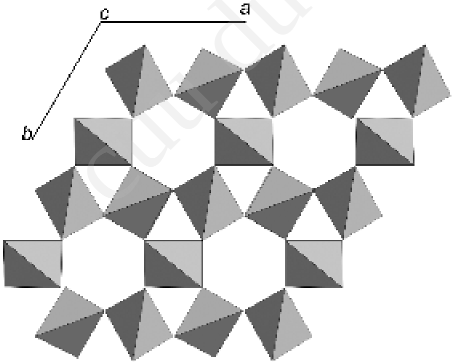

Figure 5.30 The structure of the high-temperature form of SiO_2, β-quartz, drawn as corner-shared tetrahedra projected down the hexagonal c axis (normal to the plane of the page). This projection obscures the fact that the tetrahedra form three-dimensional spirals, not rings

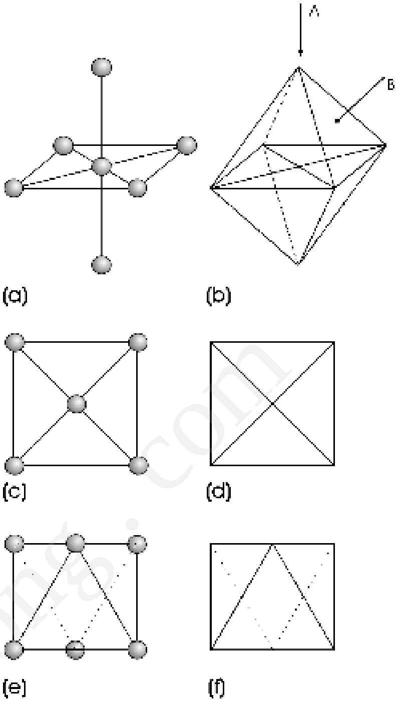

Figure 5.31 Representations of octahedra found in crystal structure diagrams: (a) a 'ball-and-stick' diagram of an octahedron, with a central metal atom surrounded by six oxygen atoms and (b) its representation as a polyhedron. The views in parts (c) and (d) are equivalent to those in parts (a) and (b), along the direction A in part (b), in which one octahedral vertex is uppermost. The views in parts (e) and (f) are the equivalent to those in parts (a) and (b), along the direction B in part (b), in which one octahedral face is towards the observer

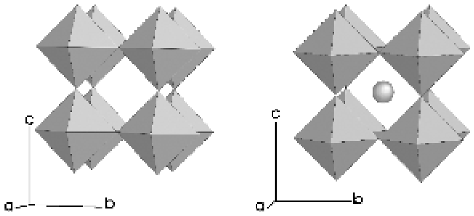

Figure 5.32 (a) The cubic ReO_3 structure represented as corner-shared ReO_6 octahedra; (b) the idealised cubic *perovskite* ABO_3 structure. The framework is identical to that in part (a) and consists of corner-shared BO_6 octahedra, containing an A cation in the central cage site (note $B \neq$ boron)

octahedra, which reduces the symmetry from cubic to orthorhombic or monoclinic.

Answers to introductory questions

How does a lattice differ from a structure?

Crystal structures and crystal lattices are different, although these terms are frequently (and incorrectly) used as synonyms. A crystal structure is built of atoms. A crystal lattice is an infinite pattern of points, each of which must have the same surroundings in the same orientation. A lattice is a mathematical concept. If any lattice point is chosen as the origin, the position of any other lattice point is defined by

$$\boldsymbol{P}(u\,v\,w) = u\,\boldsymbol{a} + v\,\boldsymbol{b} + w\,\boldsymbol{c}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are vectors, called basis vectors, and u, v and w are positive or negative integers. Clearly there are any number of ways of choosing $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$, and crystallographic convention is to choose vectors that are small and reveal the underlying symmetry of the lattice. There are only 14 possible three-dimensional lattices, called Bravais lattices.

All crystal structures can be built up from the Bravais lattices by placing an atom or a group of atoms at each lattice point. The crystal structure of a simple metal and that of a complex protein may be described in terms of the same lattice, but whereas the number of atoms allocated to each lattice point is often just one for a simple metallic crystal it may easily be thousands for a protein crystal. The number of atoms associated with each lattice point is called the motif, the lattice complex or the basis. The motif is a fragment of structure that is just sufficient, when repeated at each of the lattice points, to construct the whole of the structure. A crystal structure is built up from a lattice plus a motif.

What is a unit cell?

In a lattice, if any lattice point is chosen as the origin, the position of any other lattice point is defined by

$$\boldsymbol{P}(u\,v\,w) = u\,\boldsymbol{a} + v\,\boldsymbol{b} + w\,\boldsymbol{c}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are vectors, called basis vectors, and u, v and w are positive or negative integers. Clearly, there are any number of ways of choosing $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$, and crystallographic convention is to choose vectors that are small and reveal the underlying symmetry of the lattice. The parallelepiped formed by the three basis vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ defines the unit cell of the lattice, with edges of length a_0, b_0 and c_0. The numerical values of the unit cell edges and the angles between them are collectively called the lattice parameters or unit cell parameters. The unit cell is not unique and is chosen for convenience and to reveal the underlying symmetry of the crystal.

As a crystal structure can be derived from the addition of atoms to each lattice point, a crystal structure can also be described in terms of a unit cell. The complete crystal is built up by a regular stacking of unit cells to fill space. The axes used to describe the crystal structure are the same as those used for the lattices, corresponding to the basis vectors lying along the unit cell edges. The position of an atom within the unit cell is given as (x, y, z), where the units are a_0 in a direction along the a axis, b_0 along the b axis, and c_0 along the c axis.

What is meant by a (1 0 0) plane?

The facets of a well-formed crystal or internal planes through a crystal structure are specified in terms of Miller Indices. These indices, h, k and l, written in round brackets, $(h\,k\,l)$, represent not just one plane but the set of all parallel planes, $(h\,k\,l)$. The values of h, k and l are the fractions of a unit cell edge, a_0, b_0 and c_0, respectively, intersected by this family of planes. A plane that lies parallel to a cell edge, and so never cuts it, is given the index 0 (zero). A plane that passes across the end of the unit cell cutting the a axis and parallel to the b and c axes of the unit cell has Miller indices $(1\,0\,0)$. The indices indicate that the plane cuts the cell edge running along the a axis at a position $1\,a_0$, and does not cut the cell edges parallel to the *b* or *c* axes at all. Because the unit cell may be chosen anywhere in the structure, $(1\,0\,0)$ means all planes that intersect all the unit cells in the structure in the way specified. There is no need to specify a plane $(100, 0\,0)$, it is simply $(1\,0\,0)$.

Further reading

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Problems and exercises

Quick quiz

1 A crystal structure is:
  (a) A three-dimensional ordered array of points
  (b) A three-dimensional ordered array of atoms
  (c) A three-dimensional unit cell

2 A lattice is:
  (a) A three-dimensional ordered array of points
  (b) A three-dimensional ordered array of atoms
  (c) A three-dimensional unit cell

3 The basis vectors in a lattice define:
  (a) The unit cell
  (b) The crystal structure
  (c) The atom positions

4 The number of Bravais lattices is:
  (a) 12
  (b) 13
  (c) 14

5 A face-centred (F) unit cell contains:
  (a) One lattice point
  (b) Two lattice points
  (c) Four lattice points

6 A single face-centred unit cell with a lattice point in the plane cutting the *b* axis is:
  (a) A face-centred
  (b) B face-centred
  (c) C face-centred

7 A crystal system is:
  (a) A set of axes
  (b) A lattice
  (c) A unit cell

8 A tetragonal unit cell is defined by:
  (a) $a = b = c$
  (b) $a = b \neq c$
  (c) $a \neq b \neq c$

9 A crystal class summarises:
  (a) The internal symmetry of an object
  (b) The unit cell of the crystal
  (c) The type of crystal

10 A point group is identical to:
  (a) A crystal structure
  (b) A crystal lattice
  (c) A crystal class

11 The Miller indices $(h\,k\,l)$ represent:
  (a) A single plane in a crystal structure
  (b) A set of parallel planes in a crystal structure
  (c) A family of planes related by symmetry in a crystal structure

12 An $(h\,0\,0)$ plane in a crystal structure is:
  (a) Parallel to the *a* and *b* axes
  (b) Parallel to the *b* and *c* axes
  (c) Parallel to the *a* and *c* axes

13 A (1 1 0) plane in a crystal cuts:
  (a) The *a* and *b* axes

(b) The b and c axes

(c) The a and c axes

14 $\{h\,k\,l\}$ represents:
(a) A set of parallel planes
(b) A group of nonequivalent planes
(c) A family of symmetry-related planes

15 Miller–Bravais indices $(h\,k\,i\,l)$ are used with:
(a) All noncubic crystals
(b) Hexagonal crystals
(c) Primitive crystals

16 A direction in a crystal structure is represented by:
(a) $\{u\,v\,w\}$
(b) $[u\,v\,w]$
(c) $\langle u\,v\,w\rangle$

17 A family of directions related by symmetry is represented by:
(a) $\{u\,v\,w\}$
(b) $[u\,v\,w]$
(c) $\langle u\,v\,w\rangle$

18 Bragg's Law for X-ray diffraction is:
(a) $\lambda = 2\,d_{h\,k\,l}\,\sin\theta$
(b) $\lambda = d_{h\,k\,l}\,\sin\theta$
(c) $\lambda = 2\,d_{h\,k\,l}\,\cos\,\theta$

19 The atom coordinates $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ represent an atom at:
(a) The centre of a unit cell
(b) The face centres of a unit cell
(c) A position $\frac{1}{2}$ nm from the unit cell origin

20 In a cubic close-packed (A1) unit cell there:
(a) Is one atom
(b) Are two atoms
(c) Are four atoms

21 In a body-centred cubic (A2) unit cell there:
(a) Is one atom
(b) Are two atoms
(c) Are four atoms

22 In a hexagonal (A3) unit cell there:
(a) Is one atom
(b) Are two atoms
(c) Are four atoms

23 The symbol Z gives the number of:
(a) Formula units in a unit cell
(b) Atoms in a unit cell
(c) Positions in a unit cell

24 The lattice parameters give:
(a) The crystal symmetry
(c) The lattice symmetry
(c) The dimensions of the unit cell edges

25 The *halite* (sodium chloride, B1) structure has:
(a) Four atoms in a unit cell
(b) Four MX units in a unit cell
(c) Four NaCl units in a unit cell

26 The sphere packing giving rise to a hexagonal structure is:
(a) . . . ABABAB . . .
(b) . . . ABCABC . . .
(c) . . . ABACABAC . . .

27 In a cubic close-packed array of N spheres there are:
(a) N tetrahedral interstices
(b) $2\,N$ tetrahedral interstices
(c) $4\,N$ tetrahedral interstices

28 In a hexagonal close-packed array of N spheres there are:
(a) N octahedral interstices
(b) $2\,N$ octahedral interstices
(c) $4\,N$ octahedral interstices

29 A tetrahedron is a polyhedron with:
(a) Four triangular faces
(b) Six triangular faces
(c) Eight triangular faces

30 An octahedron is a polyhedron with:
(a) Four triangular faces

(b) Six triangular faces

(c) Eight triangular faces

31 The structure of lithium oxide can be thought of as having anions in a cubic close-packed array with lithium ions in all of the tetrahedral positions; the formula of the oxide is:
(a) Li_2O
(b) LiO
(c) LiO_2

32 The alloy nickel arsenide has a structure in which all of the arsenic atoms are in a hexagonal close-packed array and the nickel atoms occupy all of the octahedral positions; the formula of nickel arsenide is:
(a) Ni_3As
(b) Ni_2As
(c) NiAs

33 The wurtizite structure of zinc sulphide has the sulphur atoms in a hexagonal close-packed array and the zinc atoms occupying half the tetrahedral positions; the formula of the sulphide is:
(a) Zn_2S
(b) ZnS
(c) ZnS_2

Calculations and questions

5.1 Sketch and define cubic, tetragonal and orthorhombic unit cells. [Note: answer is not provided at the end of this book.]

5.2 The lines on Figure 5.33(A) represent planes in a cubic crystal parallel to the *c* axis, which is normal to the plane of the page. The circles mark the corners of the cubic unit cell. Index planes (a)–(d).

5.3 The lines on Figure 5.33(B) represent planes in a cubic crystal parallel to the *c* axis, which is normal to the plane of the page. The circles mark the corners of the cubic unit cell. Index planes (a)–(d).

5.4 The lines on Figure 5.33(C) represent planes in a cubic crystal parallel to the *c* axis, which is normal to the plane of the page. The circles mark the corners of the cubic unit cell. Index planes (a)–(d).

5.5 The lines on Figure 5.33(D) represent planes in a cubic crystal parallel to the *c* axis, which is normal to the plane of the page. The circles mark the corners of the cubic unit cell. Index planes (a)–(d).

5.6 Sketch the $(1\,1\,1)$ and $(1\,\bar{1}\,1)$ planes in a cubic crystal. [Note: answer is not provided at the end of this book.]

5.7 How many planes belong to $\{1\,1\,0\}$ in a cubic crystal? List them.

5.8 How many planes belong to $\{1\,1\,1\}$ in a cubic crystal? List them.

5.9 How many planes belong to $\{h\,h\,0\}$ in a cubic crystal? List them.

5.10 How many planes belong to $\{h\,k\,0\}$ in a cubic crystal? List them.

5.11 The lines on Figure 5.34(A) represent directions in a cubic crystal in the plane of the page. The circles mark the corners of the cubic unit cell. Index directions (a)–(e).

5.12 The lines on Figure 5.34(B) represent directions in a cubic crystal in the plane of the page. The circles mark the corners of the cubic unit cell. Index directions (a)–(e).

5.13 The lines on Figure 5.34(C) represent directions in a cubic crystal in the plane of the page. The circles mark the corners of the cubic unit cell. Index directions (a)–(e).

5.14 The lines on Figure 5.34(D) represent directions in a cubic crystal in the plane of the page. The circles mark the corners of the cubic unit cell. Index directions (a)–(e).

5.15 How many directions does $\langle 1\,0\,0\rangle$ represent? List them.

5.16 How many directions does $\langle 1\,1\,0\rangle$ represent? List them.

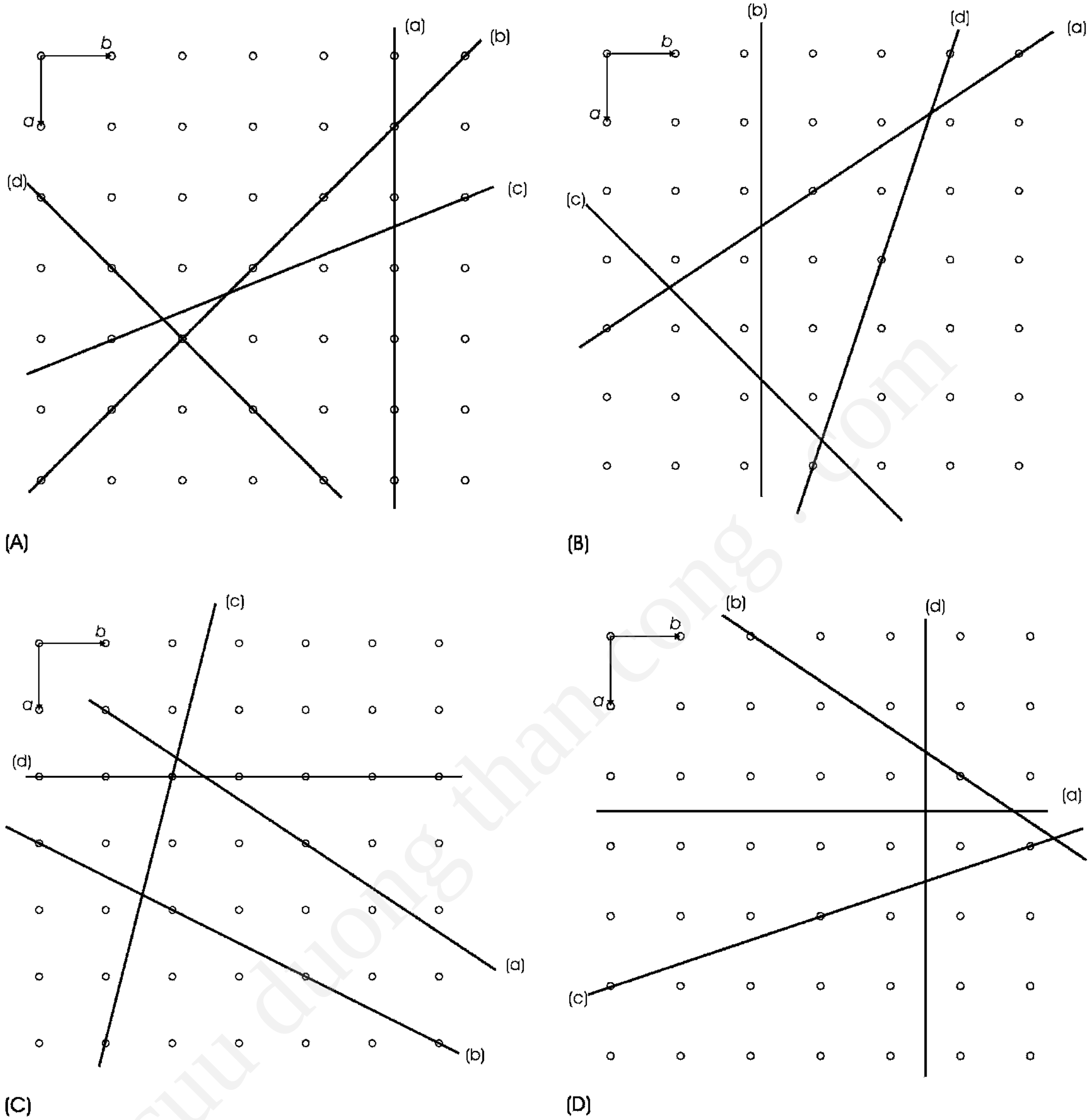

Figure 5.33 Planes in a cubic crystal, parallel to the *c* axis (normal to the plane of the page); circles mark the corners of the cubic unit cell: (A) for Question 5.2, (B) for Question 5.3, (C) for Question 5.4 and (D) for Question 5.5

5.17 What is the angle between (1 1 0) and [1 1 0] in a cubic crystal?

5.18 What is the angle between (1 3 2) and [1 3 2] in a cubic crystal?

5.19 Sketch the reciprocal lattice of a cubic crystal with $a_0 = 5\,\text{nm}$. [Note: answer is not provided at the end of this book.]

5.20 Nickel has an A1 (face-centred cubic) structure, with $a_0 = 0.352\,\text{nm}$. A powder sample

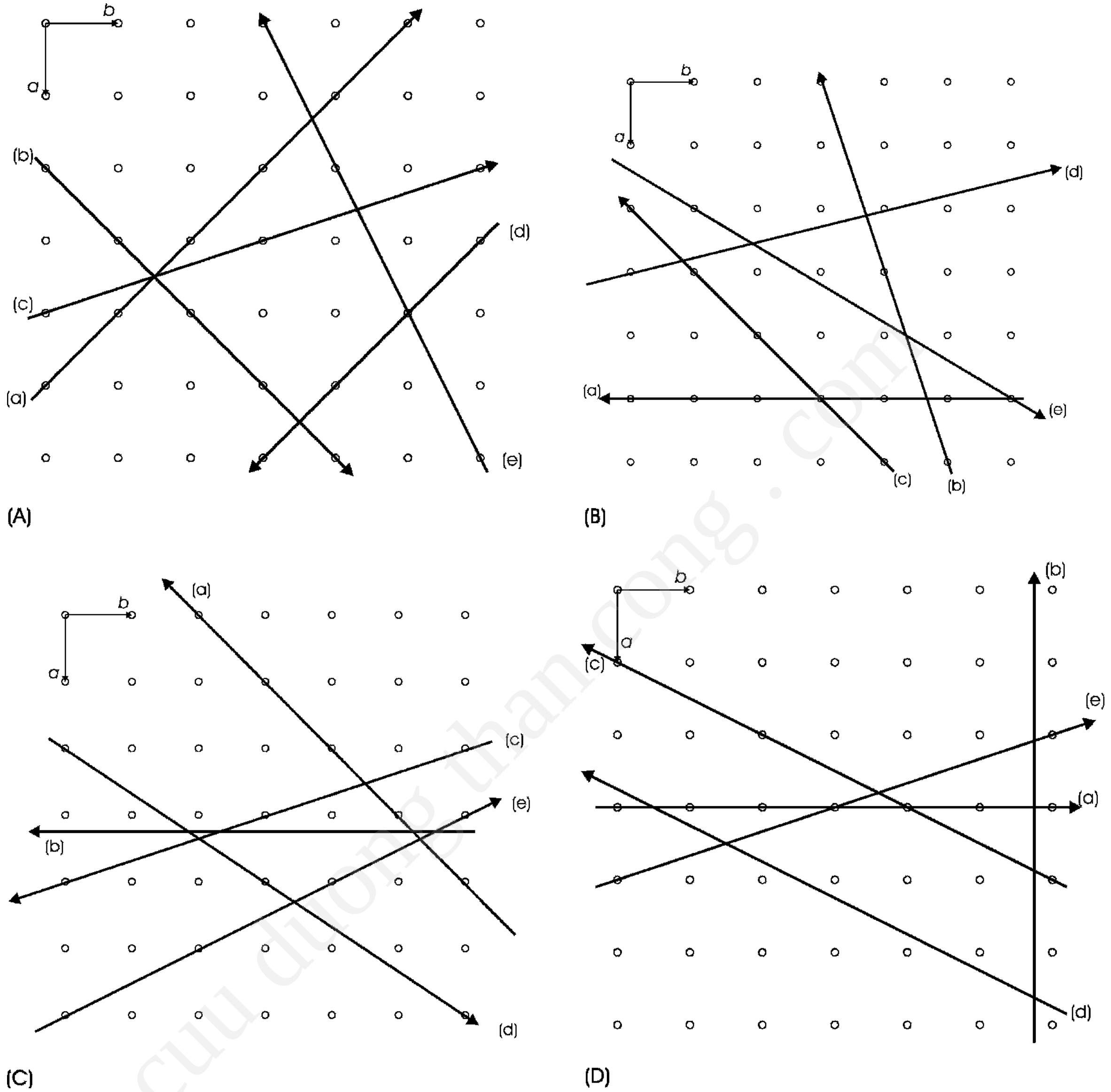

Figure 5.34 Directions in a cubic crystal, in the plane of the page; circles mark the corners of the cubic cell: (A) for Question 5.11, (B) for Question 5.12, (C) for Question 5.13 and (D) for Question 5.14

is irradiated with X-rays with a wavelength of 0.1542 nm. What angles would the diffracted beams from the (1 1 1), (2 2 0) and (4 0 0) planes make with the incident beam direction?

5.21 Tantalum has an A2 (body-centred cubic) structure, with $a_0 = 0.3303$ nm. A powder sample is irradiated with X-rays with a wavelength of 0.1542 nm. What angles would the diffracted beams from the (1 1 0), (2 1 1) and

(3 1 0) planes make with the incident beam direction?

5.22 A sample of the cubic alloy β-brass (an alloy of copper and zinc) gives an X-ray powder pattern in which, when the X-ray wavelength is 0.229 nm, the first three reflections are: (1 0 0), $\theta = 22.9°$; (1 1 0), $\theta = 33.35°$; (1 1 1), $\theta = 42.35°$. Calculate the lattice parameter of the brass.

5.23. A sample of the cubic *spinel* $CuAl_2O_4$ gives an X-ray powder pattern in which, when the X-ray wavelength is 0.1541 nm, the first three reflections are: (1 1 1), $\theta = 9.51°$; (2 0 0), $\theta = 11.00°$; (2 2 0), $\theta = 15.65°$. Calculate the lattice parameter of the spinel.

5.24 A mineral sample contains a crystalline oxide with a formula $NiAl_2O_x$, where x is uncertain. The crystals gave an X-ray powder pattern with reflections characteristic of a cubic material. The first reflection, (1 1 1), was at $\theta = 9.55°$ when the X-ray wavelength was 0.1541 nm. Confirm that the sample is the *spinel* nickel aluminate, $NiAl_2O_4$, which has $a_0 = 0.8048$ nm.

5.25 The unit cell size of CaO is 0.48105 nm, and that of SrO is 0.51602 nm. Both adopt the *halite* structure type. Estimate the composition of a crystal of formula $Ca_xSr_{1-x}O$, which was found to have a unit cell of 0.5003 nm.

5.26 A mixed cubic *spinel* $ZnAl_{2-x}Ga_xO_4$ is made up by heating together $ZnAl_2O_4$ ($a_0 =$ 0.8086 nm) and $ZnGa_2O_4$ ($a_0 = 0.8328$ nm). The X-ray powder pattern, taken using radiation of wavelength 0.1541 nm, gave the first reflection, (1 1 1), at a position $\theta = 9.435°$. Estimate the value of x and give the composition.

5.27 The cubic unit cell of iridium is drawn in Figure 5.35(a). What are the atomic coordinates? What is the unit cell type?

5.28 The cubic unit cell of CsCl is drawn in Figure 5.35(b). What are the atomic coordinates of each ion?

5.29 The cubic unit cell of perovskite, $CaTiO_3$, is drawn in Figure 5.35(c). What are the atomic coordinates of the atoms?

5.30 The coordinates of cubic nickel oxide are

$$\text{Ni}: (0,0,0),\ \left(\tfrac{1}{2},\tfrac{1}{2},0\right),\ \left(0,\tfrac{1}{2},\tfrac{1}{2}\right),\ \left(\tfrac{1}{2},0,\tfrac{1}{2}\right);$$

$$\text{O}: \left(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}\right),\ \left(0,0,\tfrac{1}{2}\right),\ \left(\tfrac{1}{2},0,0\right),\ \left(0,\tfrac{1}{2},0\right).$$

Sketch the unit cell [Note: not shown in answers at the end of this book.]. What is the formula of the oxide? What is the structure type?

5.31 A copper–gold alloy has a cubic structure. The atom positions are:

$$\text{Au}: (0,0,0);$$

$$\text{Cu}: \left(0,\tfrac{1}{2},\tfrac{1}{2}\right),\ \left(\tfrac{1}{2},0,\tfrac{1}{2}\right),\ \left(\tfrac{1}{2},\tfrac{1}{2},0\right).$$

Sketch the unit cell [Note: not shown in answers at the end of this book] and determine the formula of the alloy.

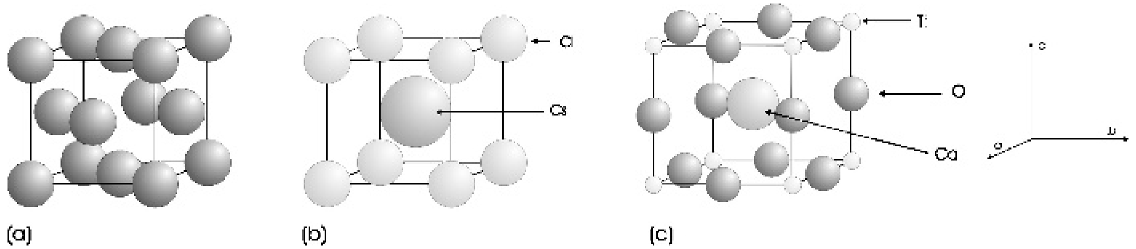

Figure 5.35 The cubic unit cells of (a) iridium, (b) CsCl and (c) perovskite ($CaTiO_3$)

5.32 Aluminium has a cubic A1 structure, with a lattice parameter of 0.361 nm. Estimate the density of the metal.

5.33 Tungsten has a cubic A2 structure, with a lattice parameter of 0.31651 nm. Estimate the density of the metal.

5.34 Magnesium has an A3 structure, with hexagonal lattice parameters of $a_0 = 0.320\,\text{nm}$, $c_0 = 0.520\,\text{nm}$. Estimate the density of the metal.

5.35 Copper has a cubic A1 structure and a density of $8.96 \times 10^3\,\text{kg}\,\text{m}^{-3}$. What is the length of the unit cell edge?

5.36 A sample of calcia-stabilised zirconia was prepared by heating 85 mol% ZrO_2 with 15 mol% CaO at 1600 °C. The material had a cubic unit cell with a lattice parameter, a_0, of 0.5144 nm and a measured density of $5485\,\text{kg}\,\text{m}^{-3}$. Calculate the theoretical density of the sample assuming that it contains either anion vacancies or cation interstitials and hence determine whether interstitials or vacancies are more likely to be present in the structure. [The parent structure is cubic *fluorite*, in which each unit cell contains four metal positions and eight nonmetal positions, to give an overall composition of MX_2.]

5.37 The unit cell of a zirconium sulphide, with a measured composition of 77 Zr:100 S, is of the *halite* (B1) type, with $a_0 = 0.514\,\text{nm}$. The measured density is $4.80 \times 10^3\,\text{kg}\,\text{m}^{-3}$. Calculate the theoretical density of ideal ZrS with the B1 structure assuming that it contains either zirconium vacancies or sulphur interstitials, and give an opinion on the defect structure of the real material.

5.38 Will the density of a crystal go up or down if it contains: (a) Schottky defects; (b) Frenkel defects; (c) vacancies; (d) interstitials?

5.39 An iron titanium oxide has the anions in a hexagonal close-packed array. The iron and titanium atoms each occupy a third of the octahedral sites available in an ordered array. What is the formula of the oxide? What is the likely parent structure of the oxide?