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Crystal Structures, Crystal Chemistry, Symmetry and Space Groups

Solid state chemistry is concerned mainly with crystalline inorganic materials, their synthesis, structures, properties and applications. A good place to begin is with *crystal structures* and *crystal chemistry*. All necessary crystal structure information is contained in data on unit cells, their dimensions and the positions or atomic coordinates of atoms inside the unit cell. Crystal chemistry combines this basic structural information with information about the elements, their principal oxidation states, ionic radii, coordination requirements and preferences for ionic/covalent/metallic bonding. A working knowledge of the Periodic Table and the properties of elements is, of course, invaluable to be able appreciate crystal chemistry, but conversely, knowledge of crystal structures and especially crystal chemistry provides a very useful way to gain increased understanding of the elements and their compounds.

Many of the properties and applications of crystalline inorganic materials revolve around a surprisingly small number of structure types. In this chapter, the main families of inorganic structures are reviewed, especially those which have interesting properties; more details of the vast array of structures may be found in the encyclopaedic text by Wells and also in the Wyckoff *Crystal Structures* book series. First, however, we must consider some basic concepts of crystallography.

1.1 Unit Cells and Crystal Systems

Crystals are built up of regular arrangements of atoms in three dimensions; these arrangements can be represented by a repeat unit or motif called the *unit cell*. The unit cell is defined as *the smallest repeating unit which shows the full symmetry of the crystal structure*. Let us see exactly what this means, first in two dimensions. A section through the NaCl structure is shown in Fig. 1.1(a); possible repeat units are given in (b) to (e). In each, the repeat unit is a square and adjacent squares share edges and corners. Adjacent squares are identical, as they must be by definition; thus, all the squares in (b) have Cl^- ions at their corners and centres. The repeat units in (b), (c) and (d) are all of the same size and, in fact, differ only in their relative position. The choice of origin of the repeat unit is to some extent a matter of personal taste, even though its size, shape and orientation are fixed. The repeat unit of NaCl is usually chosen as (b) or (c) rather than (d) because it is easier to draw and visualise the structure as a whole if the repeat unit contains atoms or ions at special positions such as corners and edge centres. Another guideline is that usually the origin is chosen so that the symmetry of the structure is evident (Section 1.3).

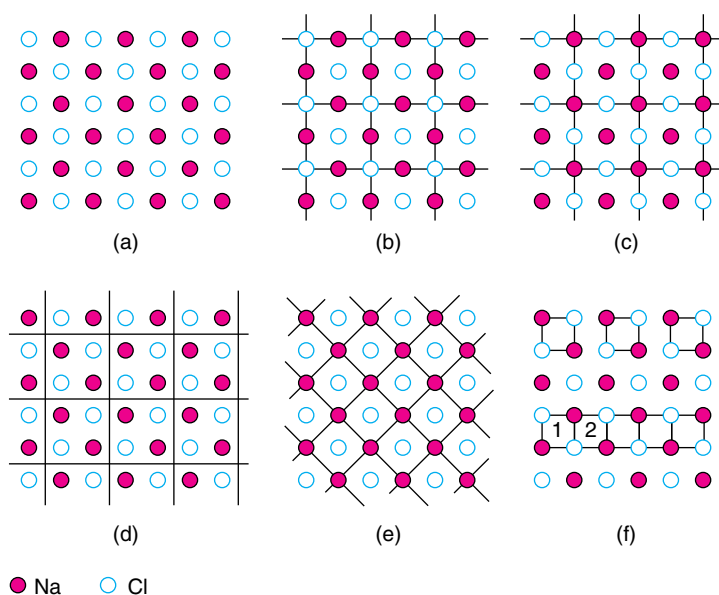


Figure 1.1 (a) Section through the NaCl structure, showing (b–e) possible repeat units and (f) incorrect units.

In the hypothetical case that two-dimensional (2D) crystals of NaCl could form, the repeat unit shown in (e), or its equivalent with Cl at the corners and Na in the middle, would be the correct unit. Comparing (e) and, for example, (c), both repeat units are square and show the 2D symmetry of the structure; as the units in (e) are half the size of those in (c), (e) would be preferred according to the above definition of the unit cell. In three dimensions, however, the unit cell of NaCl is based on (b) or (c), rather than (e) because only they show the cubic symmetry of the structure (see later).

In (f) are shown two examples of what is *not* a repeat unit. The top part of the diagram contains isolated squares whose area is one-quarter of the squares in (c). It is true that each square in (f) is identical but it is not permissible to isolate unit cells or areas from each other, as happens here. The bottom part of the diagram contains units that are not identical; thus square 1 has Na in its top right corner whereas 2 has Cl in this position.

The unit cell of NaCl in three dimensions is shown in Fig. 1.2; it contains Na at the corner and face centre positions with Cl at the edge centres and body centre. Each face of the unit cell looks like the unit

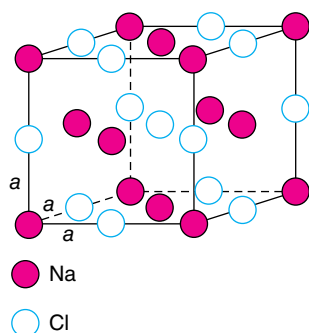


Figure 1.2 Cubic unit cell of NaCl, $a = b = c$.

Table 1.1 The seven crystal systems

Crystal system	Unit cell shape ^b	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	One threefold axis	R
Monoclinic ^a	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	None	P

^a Two settings of the monoclinic cell are used in the literature, the most commonly used one given here, with b as the unique axis and the other with c defined as the unique axis: $a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$.

^b The symbol $\neq$ means 'not necessarily equal to'. Sometimes, crystals possess *pseudo-symmetry*. For example, a unit cell may be geometrically cubic but not possess the essential symmetry elements for cubic symmetry; the true symmetry is then lower, perhaps tetragonal.

area shown in Fig. 1.1(c). As in the 2D case, the choice of origin is arbitrary; an equally valid unit cell could be chosen in which Na and Cl are interchanged. The unit cell of NaCl is *cubic*. The three edges: a , b and c are equal in length. The three angles: α (between b and c), β (between a and c) and γ (between a and b) are all 90° . A cubic unit cell also possesses certain symmetry elements and these, together with the shape define the cubic unit cell.

The seven *crystal systems* listed in Table 1.1 and shown in Fig. 1.3 are the seven independent unit cell shapes that are possible in three-dimensional (3D) crystal structures. Six of these unit cell shapes are closely inter-related and are either cubic or can be derived by distorting a cube in various ways, as shown in Fig. 1.3(b).

Thus, if one axis, c , is of different length to the others, the shape is *tetragonal*; if all three axes are different, the shape is *orthorhombic*. If, now, one of the angles, β , is not 90° , the shape is *monoclinic*, whereas if all three angles differ from 90° , the shape is *triclinic*. Finally, if the cube is stretched, or compressed, along a body diagonal so that all three angles remain equal, but different from 90° , the shape is *trigonal*.

The remaining unit cell shape is *hexagonal*. A hexagonal-shaped box is shown in Fig. 1.3(a) and discussed later with reference to Fig. 1.21, but the true unit cell is only one-third of this size, as shown.

Although it is common practice to describe unit cells by their shapes, it is more correct to describe them by the presence or absence of symmetry. Thus, for example, if a unit cell has four intersecting threefold axes, it must be cubic in shape; the reverse does not necessarily apply and the unit cell could be fortuitously cubic but not have the threefold symmetries in the atomic arrangements. The essential symmetry for each crystal system is given in the third column of Table 1.1. Let us deal next with symmetry.

1.2 Symmetry

1.2.1 Rotational symmetry; symmetry elements and operations

Symmetry is most easily defined using examples. Consider the silicate tetrahedron shown in Fig. 1.4 (a). If it is rotated about an axis passing along the vertical Si–O bond, then every 120° the tetrahedron finds itself in an identical position. Effectively, the three basal oxygens change position with each other

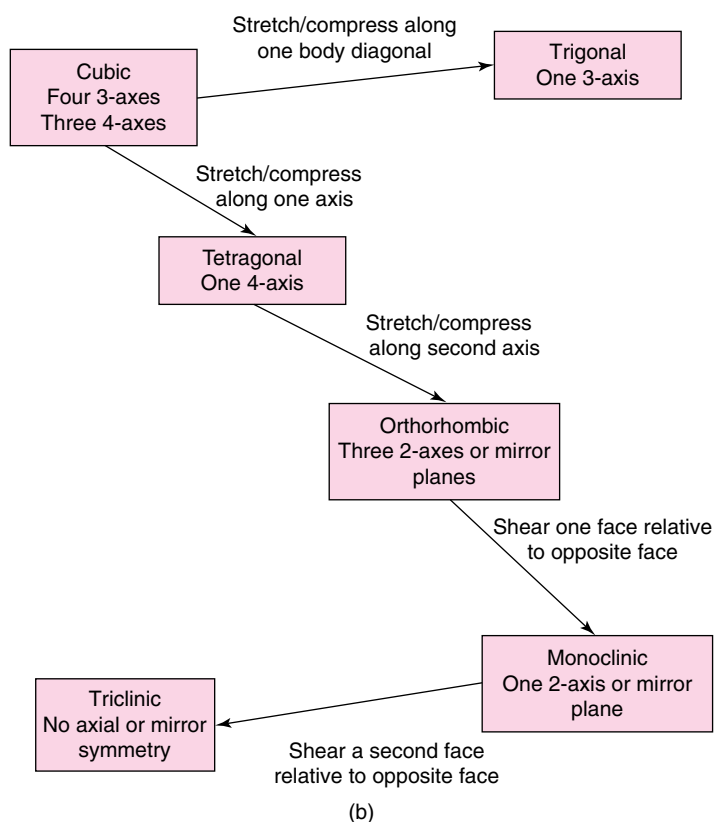
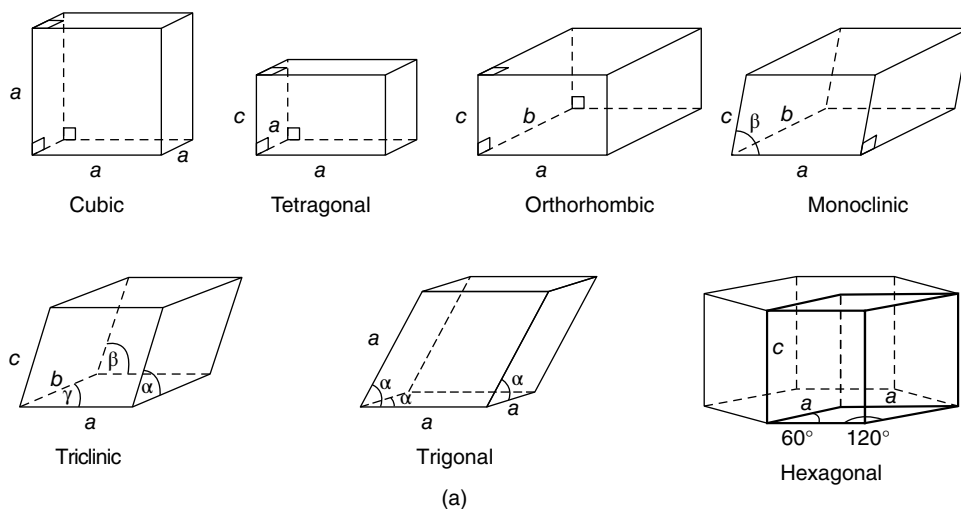


Figure 1.3 (a) The seven crystal systems and their unit cell shapes; (b) five of the seven crystal systems can be derived from cubic by structural distortions.

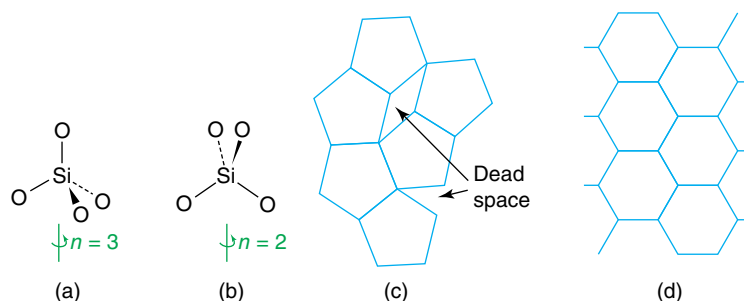


Figure 1.4 (a) Threefold and (b) twofold rotation axes; (c) the impossibility of forming a complete layer of pentagons; (d) a complete layer of hexagons.

every 120° . During a complete 360° rotation, the tetrahedron passes through three identical positions. The fact that different (i.e. >1) identical orientations are possible means that the SiO_4 tetrahedron possesses symmetry. The axis about which the tetrahedron may be rotated is called a *rotation axis*; it is an example of a *symmetry element*. The process of rotation is an example of a *symmetry operation*.

The symmetry elements that are important in crystallography are listed in Table 1.2. There are two nomenclatures for labelling them, the Hermann–Mauguin system used in crystallography and the Schönflies system used in spectroscopy. Ideally, there would be only one system which everybody uses, but this is unlikely to come about since (a) both systems are very well established, (b) crystallographers require elements of *space symmetry* that spectroscopists do not and vice versa, (c) spectroscopists use a more extensive range of *point symmetry* elements than crystallographers.

The symmetry element described above for the silicate tetrahedron is a rotation axis, with symbol n . Rotation about this axis by $360/n$ degrees gives an identical orientation and the operation is repeated n times before the original configuration is regained. In this case, $n = 3$ and the axis is a *threefold rotation axis*. The SiO_4 tetrahedron possesses four threefold rotation axes, one in the direction of each Si–O bond.

When viewed from another angle, SiO_4 tetrahedra possess *twofold rotation axes* [Fig. 1.4(b)] which pass through the central Si and bisect the O–Si–O bonds. Rotation by 180° leads to indistinguishable orientations of the tetrahedra. The SiO_4 tetrahedron possesses three of these twofold axes.

Crystals may display rotational symmetries 2, 3, 4 and 6. Others, such as $n = 5, 7$, are never observed in 3D crystal structures based on a regular periodic repetition of the unit cell and its contents. This is shown in Fig. 1.4(c), where a fruitless attempt has been made to pack pentagons to form a

Table 1.2 Symmetry elements

	Symmetry element	Hermann–Mauguin symbols (crystallography)	Schönflies symbols (spectroscopy)
Point symmetry	Mirror plane	m	σ_v, σ_h
	Rotation axis	$n = 2, 3, 4, 6$	C_n (C_2, C_3 , etc.)
	Inversion axis	$\bar{n}$ ($= \bar{1}, \bar{2}$, etc.)	—
	Alternating axis ^a	—	S_n (S_1, S_2 , etc.)
	Centre of symmetry	$\bar{1}$	i
Space symmetry	Glide plane	a, b, c, d, n	—
	Screw axis	$2_1, 3_1$, etc.	—

^a The *alternating axis* is a combination of rotation (n -fold) and reflection perpendicular to the rotation axis. It is little used in crystallography.

complete layer; thus, individual pentagons have fivefold symmetry but the array of pentagons does not. For hexagons with sixfold rotation axes (d), a complete layer is easily produced; both the individual hexagons and the overall array exhibit sixfold symmetry. This is not to say that molecules that have pentagonal symmetry, $n = 5$, cannot exist in the crystalline state. They can, of course, but their fivefold symmetry cannot be exhibited by the crystal as a whole.

1.2.2 Quasicrystals

The discovery of a new state of matter, the *quasicrystalline state*, by Schechtman and colleagues, published in 1984 (and which led to the Nobel Prize in Chemistry in 2011) appeared at first sight to violate the rules concerning allowable rotational symmetries in crystal lattices. From their single-crystal diffraction patterns, rotational symmetries such as $n = 5$ but also $n = 10$ and 12 were observed whereas, as shown in Fig. 1.4(c), a regular crystal lattice exhibiting fivefold rotational symmetry cannot exist. The answer to this conundrum is that quasicrystals do not have regularly repeating crystal structures based on a single unit cell motif. Instead, they have fully ordered but non-periodic arrays constructed from more than one motif or building block.

Elegant examples of quasisymmetry are found in so-called Penrose tiling, as shown in Fig. 1.5. In this example, space is filled completely by a combination of red and blue diamonds; such a tiling pattern has many local areas of fivefold symmetry but the structure as a whole is not periodic, does not

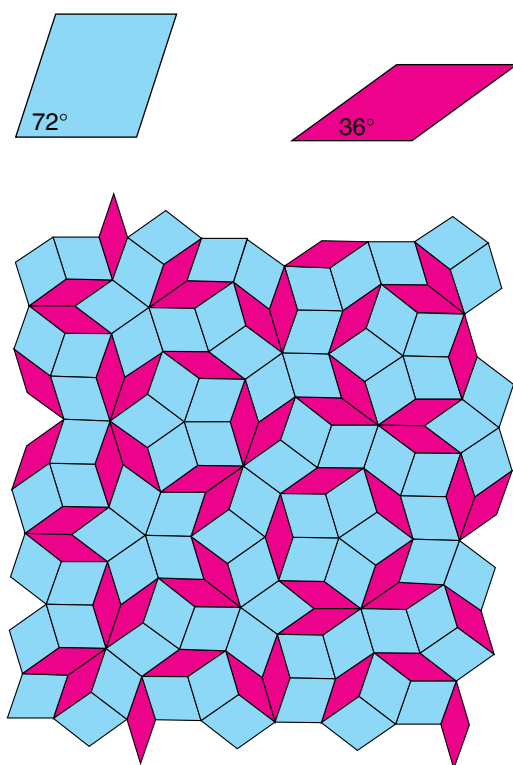


Figure 1.5 Two-dimensional Penrose tiling constructed by packing together two different sets of parallelograms. C. Janot, *Quasicrystals: A Primer*, Oxford University Press (1997). Penrose was co-recipient of the 2020 Nobel Prize in physics, in a totally different area to quasicrystals and Penrose tiling, for ‘discovery that black hole formation is a robust prediction of the general theory of relativity’.

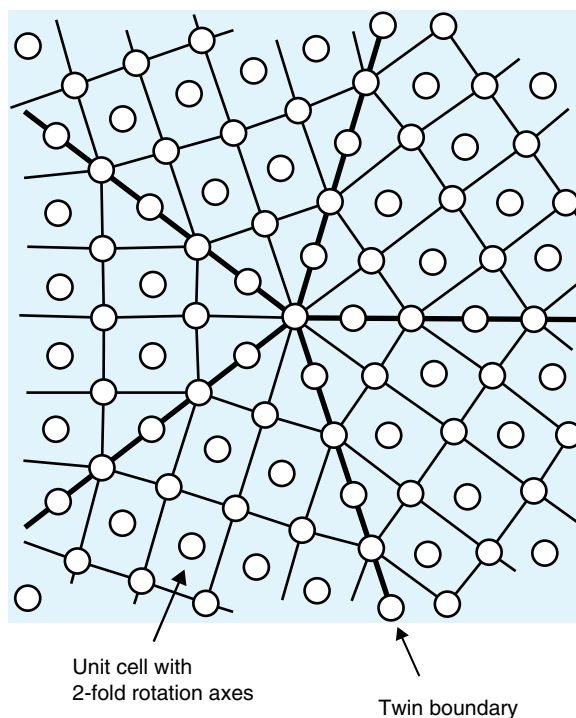


Figure 1.6 Hypothetical twinned structure showing fivefold symmetry. Adapted from J. M. Dubois, *Useful Quasicrystals*, World Scientific Publishing Company (2005).

exhibit fivefold symmetry and a regular repeat unit cannot be identified. Quasicrystals have since been discovered in a wide range of alloy systems and also in organic polymer and liquid crystal systems; they have been discovered in Nature in an Al–Cu–Fe alloy named icosahedrite that was believed to have been part of a meteorite and had existed on Earth for billions of years. It is probably just a matter of time before they are discovered also in inorganic oxide materials, natural or synthetic.

In the early days of work on quasicrystals, an alternative explanation for possible fivefold symmetry was based on *twinning*, as shown schematically in Fig. 1.6. Five identical crystalline segments are shown, each of which has twofold rotational symmetry in projection. Pairs of crystal segments meet at a coherent interface or *twin plane* in which the structures on either side of the twin plane are mirror images of each other. The five crystal segments meet at a central point which exhibits fivefold symmetry as a macroscopic element of point symmetry but the individual crystal segments clearly do not exhibit any fivefold symmetry. Schechtman showed conclusively that twinning such as shown in Fig. 1.6 could not explain the quasicrystalline state.

The discovery of quasicrystals without long range periodicity and an identifiable unit cell, has forced the International Union of Crystallography to reconsider what is meant by a ‘crystal’. Since well-prepared quasicrystals have highly ordered structures, many of which are thermodynamically stable and give sharp single crystal diffraction patterns, quasicrystals need to have a home in a wider definition of crystallinity. The requirement for crystallinity to be associated with long range periodicity has served the scientific community well for nearly a century; however, it is now necessary to include quasicrystals that are highly ordered but lack long range periodicity. The terms ‘classical crystal’ and ‘aperiodic crystal’ have been suggested to distinguish between crystals that do, and do not, exhibit long range periodicity.

The consequences that aperiodicity within ordered structures has for the electronic structure and optoelectronic properties of quasicrystals are still being evaluated. Periodicity has provided an important starting point in the development of theoretical concepts such as Brillouin zones and the band theory of solids. It has also underpinned theories of dislocations and explanations about the mechanical properties of crystalline materials, especially metals and alloys. However, it is probably fair to say that, at present, although quasicrystals are much more than a scientific curiosity, they do not, as yet, fit into the general panorama of mainstream solid state sciences, perhaps because of the challenges and difficulties associated with evaluating and presenting aperiodic crystallography in terms of higher dimensional space.

1.2.3 Mirror symmetry

A *mirror plane*, m , exists when two halves of, for instance, a molecule can be interconverted by carrying out the imaginary process of reflection across the mirror plane. The silicate tetrahedron possesses six mirror planes, one of which, running vertically and perpendicular to the plane of the paper, is shown in Fig. 1.7(a). The silicon and two oxygens, 1 and 2, lie on the mirror plane and are unaffected by reflection. The other two oxygens, 3 and 4, are interchanged on reflection. A second mirror plane lies in the plane of the paper; for this, Si and oxygens 3, 4 lie on the mirror but oxygen 2, in front of the mirror, is the image of oxygen 1, behind the mirror.

The photograph in Fig. 1.7(d) shows the British comedian Harry Worth creating a mirror image of half of his body by posing at the end of a high street shop window. Half of the picture is of his body and half is its mirror image. It therefore exhibits perfect mirror symmetry which is never achieved by human bodies in reality!

1.2.4 Centre of symmetry and inversion axes

A *centre of symmetry*, $\bar{1}$, exists when any part of a structure can be reflected through this centre of symmetry, which is a point and an identical arrangement found on the other side. An AlO_6 octahedron has a centre of symmetry, Fig. 1.7(b), located on the Al atom. If a line is drawn from any oxygen, e.g. 1, through the centre and extended an equal distance on the other side, it terminates at another oxygen, 2. A tetrahedron, e.g. SiO_4 , does not have a centre of symmetry (a).

The *inversion axis*, $\bar{n}$, is a combined symmetry operation involving rotation (according to n) and inversion through the centre. A $\bar{4}$ (*fourfold inversion*) axis is shown in (c). The first stage involves rotation by $360/4 = 90^\circ$ and takes, for example, oxygen 2 to position 2'. This is followed by inversion

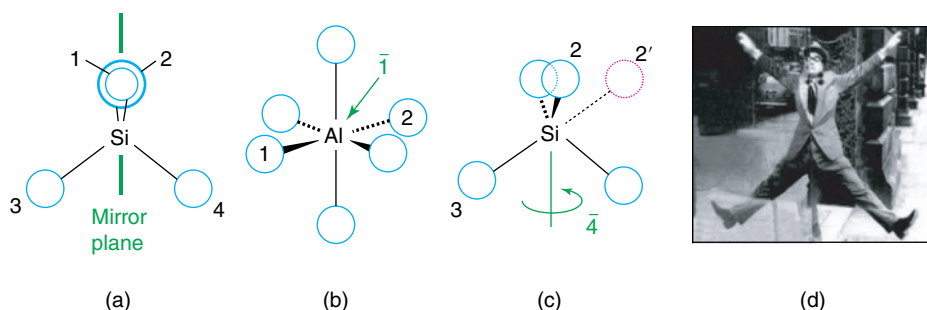


Figure 1.7 Symmetry elements: (a) mirror plane; (b) centre of symmetry; (c) fourfold inversion axis. (d) The British comedian Harry Worth creating a mirror image of half of his body by reflection in a shop window.

through the centre, at Si, and leads to position 3. Oxygens 2 and 3 are therefore related by a $\bar{4}$ axis. Possible inversion axes in crystals are limited to $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$ for the same reason that only certain pure rotation axes are allowed. The onefold inversion axis is not a separate symmetry element, but is simply equivalent to the centre of symmetry; also, the twofold inversion axis is the same as a mirror plane perpendicular to that axis.

1.2.5 Point symmetry and space symmetry

The symmetry elements discussed so far are elements of *point symmetry*. For each, at least one point stays unchanged during the symmetry operation, i.e. an atom lying on a centre of symmetry, rotation axis or mirror plane does not move during the respective symmetry operations. Finite-sized molecules can only possess point symmetry elements, whereas crystals may have extra symmetries that include translation steps as part of the symmetry operation. These are elements of *space symmetry*, of which there are two types.

The *screw axis* combines translation and rotation; the atoms or ions in a crystal which possesses screw axes appear to lie on spirals about these axes. A schematic example is shown in Fig. 1.8(a). All you need to demonstrate a screw axis is a handful of coins which can be arranged on a flat surface with either their heads (H) or tails (T) facing upwards. The symbol for a screw axis, X_Y , indicates translation by the fraction Y/X of the unit cell edge in the direction of the screw axis together with

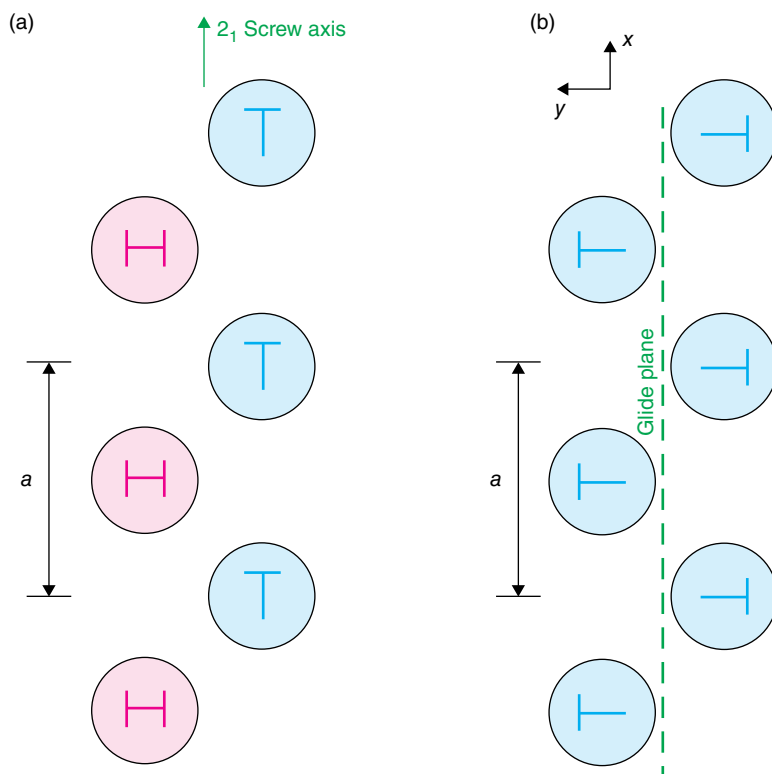


Figure 1.8 Arrangement of coins with heads (H) and tails (T) illustrating (a) a 2_1 screw axis parallel to a and (b) an a glide plane perpendicular to b ; in each case, translation between symmetry-related objects is by $a/2$.

simultaneous rotation by $360/X^\circ$ about the screw axis. Thus, a 4_2 axis parallel to a involves translation by $a/2$ and rotation by 90° ; this process takes place twice along a for every unit cell.

The *glide plane* combines translation and reflection, as shown schematically in Fig. 1.8(b). Translation may be parallel to any of the unit cell axes (a , b , c), to a face diagonal (n) or to a body diagonal (d). The a , b , c and n glide planes all have a translation step of half the unit cell in that direction; by definition, the d glide has a translation step which is $1/4$ of the body diagonal. For the *axial glide planes* a , b and c , it is important to know both the direction of the translation and the reflection plane, e.g. an a glide may be perpendicular to b (i.e. reflection across the ac plane), Fig 1.8(b), or perpendicular to c .

Most crystal structures contain examples of space symmetry elements which are often difficult to visualise unless one has 3D models available. An example of both a screw axis and a glide plane in the same structure is shown in Fig 1.21 and discussed in Section 1.12. It is always amusing to look for symmetries in everyday objects. Next time you are in a car park, look at the arrangement of parking lots, especially if they are arranged diagonally, and see if they are displaced relative to each other in the form of a glide plane!

One difference between *crystals* and *quasicrystals* concerns space symmetry. Crystals, as a bare minimum, exhibit a periodic translation from one unit cell to the next. In many cases, translational symmetry elements, i.e. screw axes and glide planes, are also present. By contrast, quasicrystals do not exhibit space symmetry: they do not have a regular repeat unit, nor can translational symmetry elements be identified.

1.3 Symmetry and Choice of Unit Cell

The geometric shapes of the various crystal systems (unit cells) are listed in Table 1.1 and are shown in Fig. 1.3. These shapes do not *define* the unit cell; they are merely a consequence of the presence of certain symmetry elements.

A *cubic* unit cell is defined as one having four threefold symmetry axes. These run parallel to the cube body diagonals, one of which is shown in Fig. 1.9(a); an automatic consequence of this condition is that $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. The *essential* symmetry elements by which each crystal system is defined are listed in Table 1.1. In most crystal systems, additional symmetry elements are also present. For instance, cubic crystals may have many others, including three fourfold axes passing through the centres of each pair of opposite cube faces (a) and mirror planes in two sets of orientations (b, c).

The *tetragonal* unit cell, Table 1.1, has a single fourfold axis and may be regarded as a cube that is either squashed or elongated along one axis. Consequently, all threefold rotation axes and two of the fourfold axes are lost. An example is given by the structure of CaC_2 . This is related to the NaCl

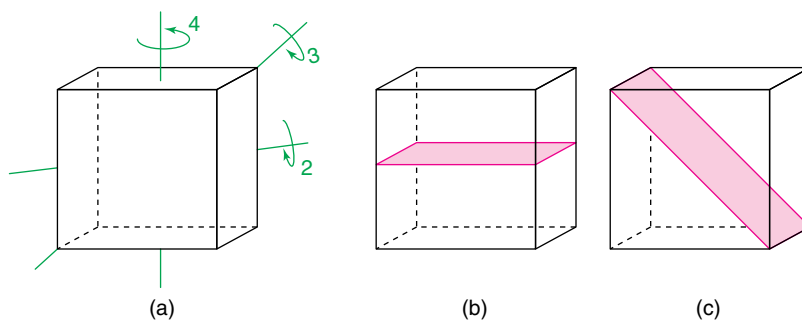


Figure 1.9 (a) Two-, three- and fourfold axes and (b, c) mirror planes of a cube.

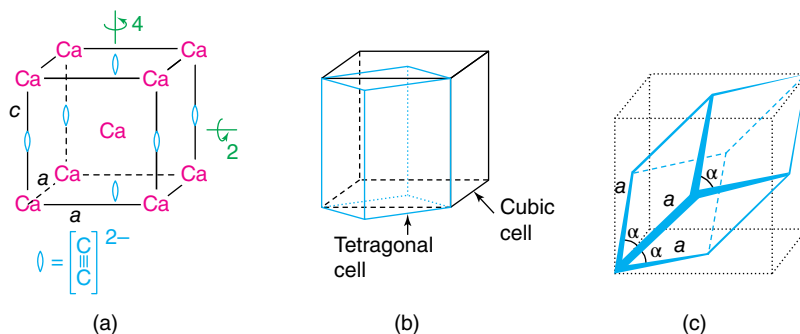


Figure 1.10 (a) Tetragonal unit cell of CaC_2 : note the cigar-shaped carbide ions are aligned parallel to c ; (b) relation between ‘tetragonal’ and cubic cells for NaCl; (c) derivation of a primitive trigonal unit cell for NaCl from the cubic cell.

structure but, because the carbide ion is cigar-shaped rather than spherical, one of the cell axes becomes longer than the other two, Fig. 1.10(a). A similar tetragonal cell may be drawn for NaCl; it occupies half the volume of the true, cubic unit cell, Fig. 1.10(b). The choice of a tetragonal unit cell for NaCl is rejected, however, because it does not show the full cubic symmetry, i.e. it does not show the threefold axes. A tetragonal unit cell has one axis, the *unique axis*, which is of a different length to the other two. By convention, this is chosen as the c axis, Table 1.1.

The *trigonal* system is characterised by a single threefold axis. Its shape is derived from a cube by stretching or compressing the cube along one of its body diagonals, Fig. 1.10(c). The threefold axis parallel to this direction is retained but those along the other body diagonals are destroyed. All three cell edges remain the same length; all three angles stay the same but are not equal to 90° . It is possible to describe such a trigonal cell for NaCl with $\alpha = \beta = \gamma = 60^\circ$ with Na at the corners and Cl in the body centre (or vice versa), but this is again unacceptable because NaCl has symmetry higher than trigonal.

The structure of NaNO_3 is a trigonal distortion of the NaCl structure: instead of spherical Cl^- ions, it has triangular nitrate groups. These lie on planes perpendicular to one of the unit cell body diagonals. This causes a compression along one body diagonal (or rather an expansion in the plane perpendicular to the diagonal). All fourfold symmetry axes and all but one of the threefold axes are destroyed.

The *hexagonal* crystal system is discussed later (Fig. 1.21).

The *orthorhombic* unit cell may be regarded as a shoebox in which the angles are 90° but the sides are of unequal length. It usually possesses several mirror planes and twofold axes; the minimum requirement for orthorhombic symmetry is the presence of three mutually perpendicular mirror planes or twofold axes.

The *monoclinic* unit cell may be derived from our orthorhombic shoebox by partially shearing the top face relative to the bottom face and in a direction parallel to one of the box edges. As a consequence, one angle departs from 90° and most of the symmetry is lost, apart from a mirror plane and/or a single twofold axis. One of the monoclinic unit cell axes is unique since it is perpendicular to the other two. The unique axis is usually defined as b , with $\alpha = \gamma = 90^\circ$ (but see Table 1.1, footnote).

The *triclinic* system possesses no essential symmetry. Its unit cell has sides of unequal length and the angles are unequal and differ from 90° .

We have specified the essential symmetry elements for each crystal system. Consequently, the unit cell shapes follow automatically. The converse does not apply, however, in crystals which exhibit *pseudo-symmetry*. For example, the unit cell of a particular structure may be geometrically cubic but the atomic arrangement may not exhibit the requisite symmetry elements and, instead, the true crystal system may have symmetry lower than cubic.

1.4 Lattice, Bravais Lattice

It is very useful to be able to represent the manner of repetition of atoms, ions or molecules in a crystal by an array of points; the array is called a *lattice* and the points *lattice points*; each lattice point has exactly the same environment and the same arrangement of surrounding atoms. The section of the NaCl structure shown in Fig. 1.11(a) may be represented by an array of points (b); each point represents one Na and one Cl but whether the point is located at Na, at Cl, or in between is irrelevant. The unit cell is constructed by linking the lattice points; two ways of doing this, A and B, are shown in (b). A cell such as B which has lattice points only at the corners is *primitive*, P, whereas a cell such as A which has additional lattice points is *centred*. Several types of centred lattice are possible.

The *face centred lattice*, F, contains additional lattice points in the centre of each face (c). An example of a face centred cubic, *fcc*, structure is Cu metal. A *side centred lattice* contains extra lattice points on only one pair of opposite faces. It is labelled a C-centred lattice if the extra lattice points are on the *ab* face of the unit cell, as in (d). Similarly, an A-centred lattice has lattice points on the *bc* face.

A *body centred lattice*, I, has an extra lattice point at the body centre (e). α -Iron is *body centred cubic*, *bcc*, because it has a cubic unit cell with Fe atoms at the corner and body centre positions.

CsCl is also cubic with Cs at corners and Cl at the body centre (or vice versa), but it is *primitive*, P. This is because, for a lattice to be body centred, the atom or group of atoms located at or near the corner must be identical with those at or near the body centre.

In the simplest cases of monatomic metals such as Cu and α -Fe, mentioned above, the arrangement of metal atoms in the structure is simply the same as the arrangement of lattice points. In more complex structures such as NaCl, the lattice point represents an ion pair. This is still a very simple example, however, and in most inorganic structures the lattice point represents a considerable number of atoms. In crystals of organic molecules such as proteins, the lattice point represents an entire protein molecule. Obviously the lattice point gives no information whatsoever as to the atoms and their arrangements which it represents; what the lattice does show is how these species are packed together in 3D.

The combination of crystal system and lattice type gives the *Bravais lattice* of a structure. There are 14 possible Bravais lattices. They are given in Table 1.1, and shown in Fig. 1.12, by combining crystal

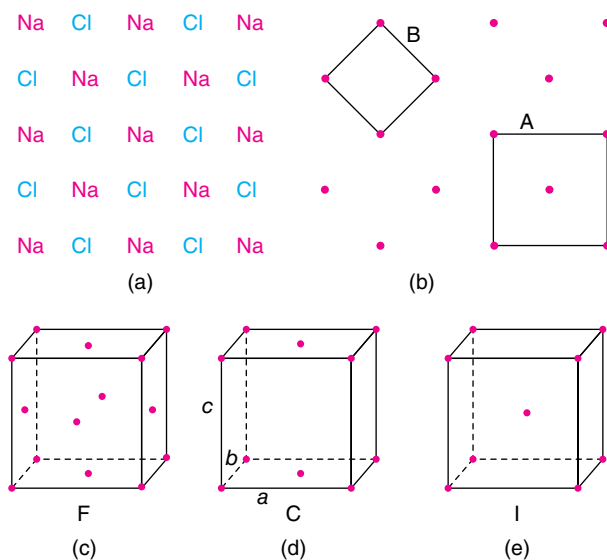


Figure 1.11 Representation of (a) the NaCl structure in two dimensions by (b) an array of lattice points; (c) face centred, (d) side centred and (e) body centred lattices.

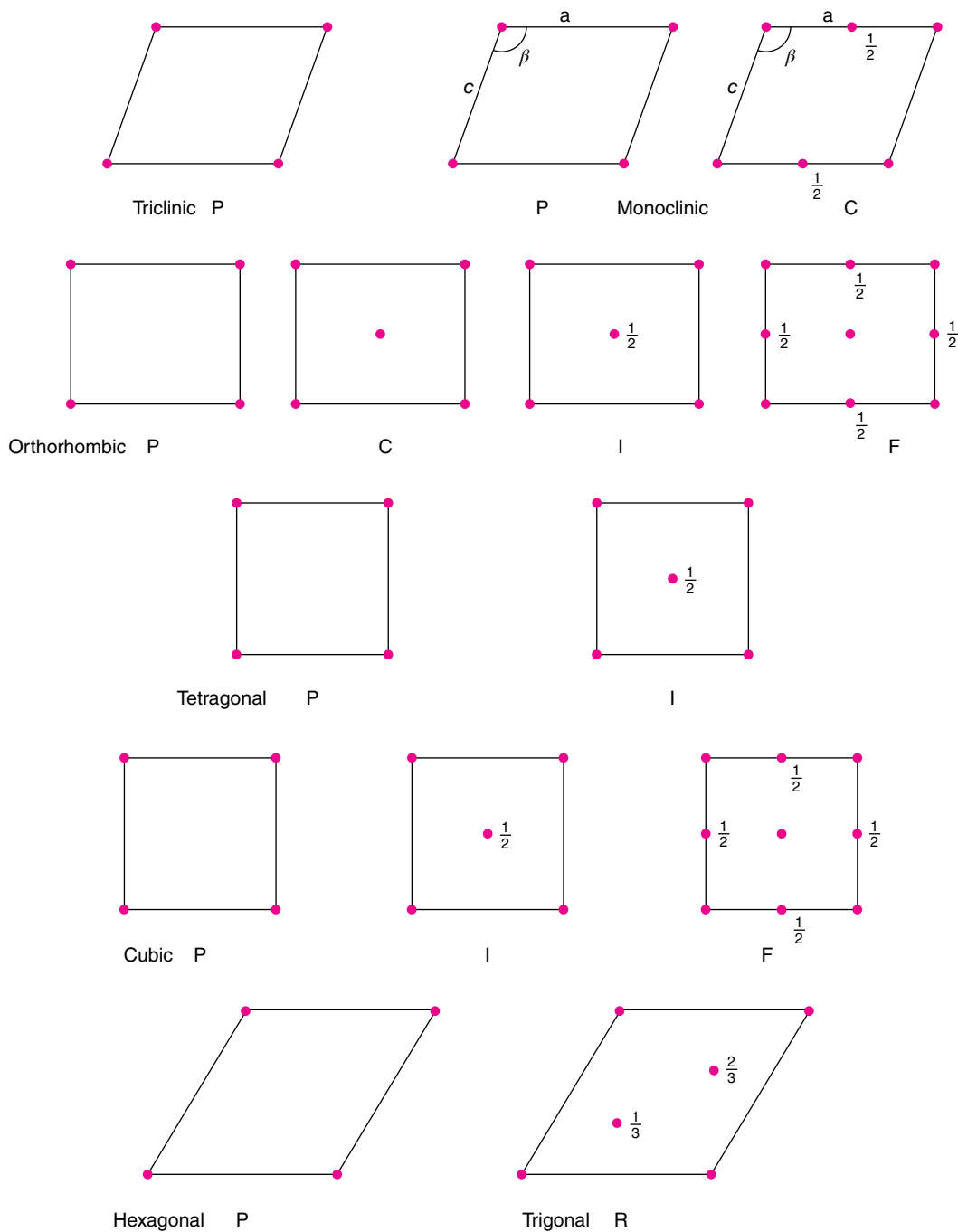


Figure 1.12 The unit cells of the 14 Bravais lattices: axes refer to the ab plane, unless specified. Heights of lattice points are 0, 1, unless specified. D. McKie and C. McKie, *Essentials of Crystallography*, John Wiley & Sons (1986).

system, column 1 and lattice type, column 4. For example, P-monoclinic, C-centred monoclinic and P-triclinic are three of the 14 possible Bravais lattices. The lattice type plus unit cell combinations which are absent either (a) would violate symmetry requirements, e.g. a C-centred lattice cannot be cubic because it would not have the necessary threefold axes or (b) may be represented by a smaller, alternative cell, e.g. a face centred tetragonal cell can be redrawn as a body centred tetragonal cell; the symmetry is still tetragonal but the volume is halved, Fig. 1.10(b).

1.5 Lattice Planes and Miller Indices

The concept of lattice planes causes considerable confusion because there are two separate ideas which can easily become mixed. Any simple structure, such as a metal or an ionic structure, may, in certain orientations, be regarded as built of layers or planes of atoms stacked to form a 3D structure. These layers are often related in a simple manner to the unit cell; for example, a unit cell face may coincide with a layer of atoms. The reverse is not necessarily true, however, especially in more complex structures and unit cell faces or simple sections through the unit cell often do not coincide with layers of atoms in the crystal. *Lattice planes*, a concept introduced with Bragg's law of diffraction (Chapter 5), are defined purely from the shape and dimensions of the unit cell. Lattice planes are entirely imaginary and simply provide a reference grid to which the atoms in the crystal structure may be referred. Sometimes, a given set of lattice planes coincides with layers of atoms, but not usually.

Consider the 2D array of lattice points shown in Fig. 1.13(a). This array may be divided into many different sets of rows and for each set there is a characteristic perpendicular distance, d , between pairs of adjacent rows. In three dimensions, these rows become *lattice planes* and adjacent planes are separated by the *interplanar d -spacing*, d . (Bragg's law treats X-rays as being diffracted from these various sets of lattice planes and the Bragg diffraction angle, θ , for each set is related to the d -spacing by Bragg's law.)

Lattice planes are labelled by assigning three numbers known as *Miller indices* to each set. The derivation of Miller indices is illustrated in Fig. 1.13(b) (and those for a hexagonal lattice are shown in Fig. 1.14). The origin of the unit cell is at point 0. Two planes are shown which are parallel and pass obliquely through the unit cell. A third plane in this set must, by definition, pass through the origin. Each of these planes continues out to the surface of the crystal and in so doing cuts through many more unit cells; also, there are many more planes in this set parallel to the two shown, but which do not pass through this particular unit cell.

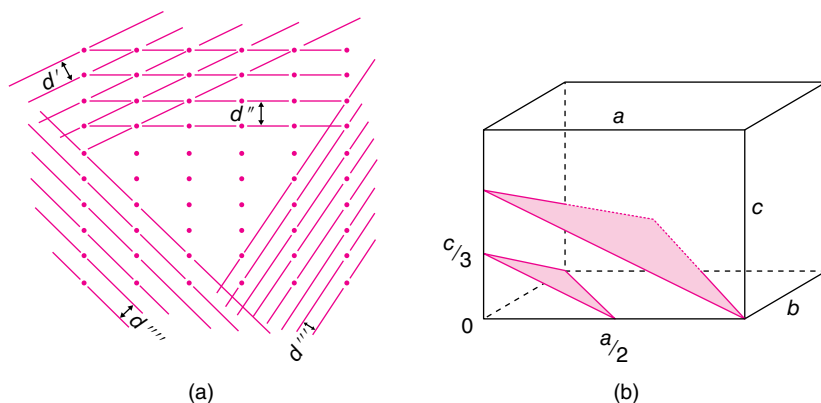


Figure 1.13 (a) Lattice planes (in projection); (b) derivation of Miller indices.

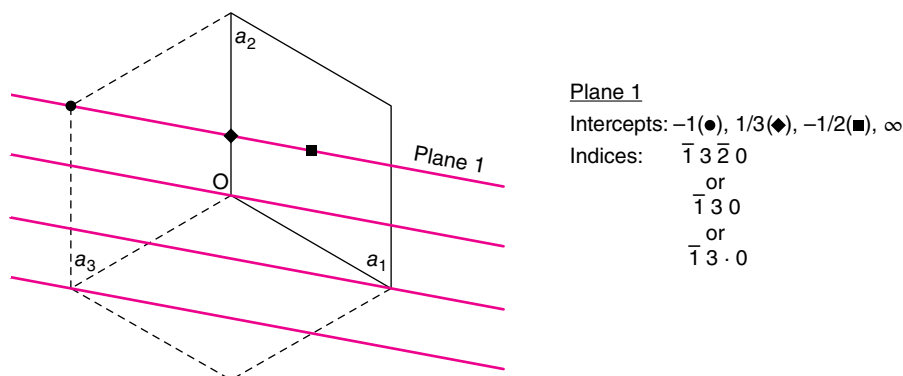


Figure 1.14 Miller indices for a hexagonal lattice.

In order to assign Miller indices to a set of planes, there are four stages:

1. From the array of lattice points, or the crystal structure, identify the unit cell, choose the origin and label the axes a , b , c and angles α (between b and c), β (between a and c) and γ (between a and b).
2. For a particular set of lattice planes, identify that plane which is adjacent to the one that passes through the origin.
3. Find the intersection of this plane on the three axes of the cell and write these intersections as fractions of the cell edges. The plane in question, Fig. 1.13(b), cuts the x axis at $a/2$, the y axis at b and the z axis at $c/3$; the fractional intersections are therefore $1/2$, 1 , $1/3$.
4. Take reciprocals of these fractions and write the three numbers in parentheses; this gives (213). These three integers, (213), are the Miller indices of the plane and all other planes parallel to it and separated from adjacent planes by the same d -spacing.

Some other examples are shown in Fig. 1.15. In (a), the shaded plane cuts x , y and z at $1a$, ∞b and $1c$, i.e. the plane is parallel to b . Taking reciprocals of 1 , ∞ and 1 gives us (101) for the Miller indices. A Miller index of 0 means, therefore, that the plane is parallel to that axis. In Fig. 1.15(b), the planes of interest comprise opposite faces of the unit cell. We cannot determine directly the indices of plane 1 as it passes through the origin. Plane 2 has intercepts of $1a$, ∞b and ∞c and Miller indices of (100).

Figure 1.15(c) is similar to (b) but there are now twice as many planes as in (b). To find the Miller indices, consider plane 2, which is the one that is closest to the origin but without passing through it. Its intercepts are $1/2$, ∞ and ∞ and the Miller indices are (200). A Miller index of 2, therefore indicates that the plane cuts the relevant axis at half the cell edge. This illustrates an important point. After taking reciprocals, do not divide through by the highest common factor. A common source of error is to regard, say, the (200) set of planes as those planes interleaved between the (100) planes, to give the sequence (100), (200), (100), (200), (100), ... The correct labelling is shown in Fig. 1.15(d). If extra planes are interleaved between adjacent (100) planes then *all* planes are labelled as (200).

The general symbol for Miller indices is (hkl). It is not necessary to use commas to separate the three letters or numbers and the indices are enclosed in parentheses, (). The brackets {} are used to indicate sets of planes that are equivalent; for example, the sets (100), (010) and (001) are equivalent in cubic crystals and may be represented collectively as {100}. In the examples chosen so far, all of the Miller indices are either 0 or positive but, as we shall see later, it is also important to define lattice planes that intersect axes in their negative directions. In these cases the relevant index has a bar above the number; thus planes ($\bar{h}, \bar{k}, \bar{l}$) are referred to as 'bar h , bar k , bar l '.

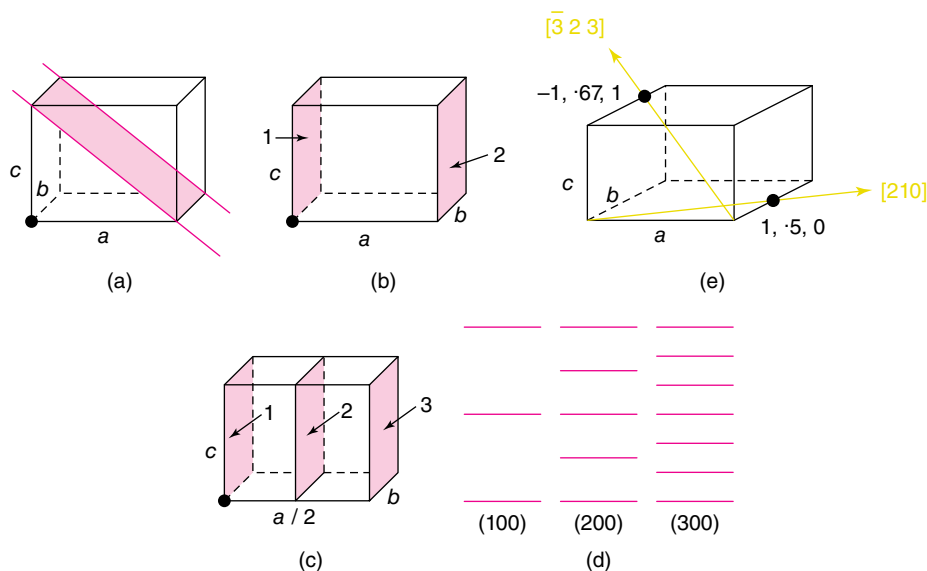


Figure 1.15 Examples of Miller indices: (a) (101) ; (b) (100) ; (c) (200) ; (d) $(h00)$; (e) indices of directions $[210]$ and $[\bar{3}23]$.

To label lattice planes in hexagonal unit cells, a modification to the method is required. For hexagonal unit cells, with $a = a \neq c$, there are three possible choices for the two a axes in the basal plane, a_1 , a_2 and a_3 , as shown in Fig. 1.14. Let us choose a_1 and a_2 to define the unit cell with the origin at O. Next, consider the set of planes shown, which are parallel to c ; assign Miller indices in the usual way but in this case, find the intercepts of plane 1 on all three a axes as well as the c axis; since these planes in Fig. 1.14 are parallel to c , plane 1 does not intersect the c axis. This leads to four indices for this set, representing the intercepts on a_1 , a_2 , a_3 and c , i.e. $\bar{1}3\bar{2}0$. The third index is redundant since, writing the indices as (hkl) , the condition

$$h + k + i = 0$$

holds (i.e. $-1 + 3 - 2 = 0$). Sometimes, all four indices are specified; sometimes, only three are specified (i.e. $\bar{1}30$ in the usual way); sometimes, the third index may be represented as a dot (i.e. $\bar{1}3 \cdot 0$).

1.6 Indices of Directions

Directions in crystals and lattices are labelled by first drawing a line that passes through the origin and parallel to the direction in question. Let the line pass through a point with general fractional coordinates x, y, z ; the line also passes through $2x, 2y, 2z$; $3x, 3y, 3z$, etc. These coordinates, written in square brackets, $[x, y, z]$, are the indices of the direction; x, y and z are arranged to be the set of smallest possible integers, by division or multiplication throughout by a common factor. Thus $[\frac{1}{2} \frac{1}{2} 0]$, $[110]$, $[330]$ all describe the same direction, but by convention $[110]$ is used.

For cubic systems, an $[hkl]$ direction is always perpendicular to the (hkl) plane of the same indices, but this is only sometimes true in non-cubic systems. Sets of directions which, by symmetry, are

equivalent, e.g. cubic [100], [010], are written using angle brackets, $\langle 100 \rangle$. Some examples of directions and their indices are shown in Fig. 1.15(e). Note that the [210] direction is defined by taking the origin at the bottom-left-front corner of the unit cell and taking the fractional coordinates: 1, 0.5, 0, to define the direction. For the direction $[\bar{3}23]$, where the bar sign indicates a negative direction, a different origin is chosen, at the bottom-right-front corner of the unit cell and passing through the fractional coordinates: -1, 0.67, 1.

1.7 *d*-Spacing Formulae

We have already defined the *d*-spacing of a set of planes as the perpendicular distance between any pair of adjacent planes in the set and it is this *d* value that appears in Bragg's law. For a cubic unit cell, the (100) planes simply have a *d*-spacing of *a*, the value of the cell edge, Fig. 1.15(b). For (200) in a cubic cell, $d = a/2$. For *orthogonal* crystals (i.e. $\alpha = \beta = \gamma = 90^\circ$), the *d*-spacing for any set of planes is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1.1)$$

The equation simplifies for tetragonal crystals, in which $a = b$, and still further for cubic crystals with $a = b = c$:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (1.2)$$

As a check, for cubic (200): $h = 2, k = l = 0$; $1/d^2 = 4/a^2$; $d = a/2$.

Monoclinic and, especially, triclinic crystals have much more complicated *d*-spacing formulae because each angle that is not equal to 90° is an additional variable. The formulae for *d*-spacings and unit cell volumes of all crystal systems are given in Appendix A.

1.8 Crystal Densities and Unit Cell Contents

The unit cell, by definition, must contain at least one formula unit, whether it be an atom, ion pair, molecule, etc. In centred cells, the unit cell contains more than one formula unit and more than one lattice point. A simple relation exists between cell volume, the number of formula units in the cell, the formula weight (FW) and the bulk crystal density (*D*):

$$D = \frac{\text{mass}}{\text{volume}} = \frac{\text{FW}}{\text{molar volume}} = \frac{\text{FW}}{\text{volume of formula unit} \times N}$$

where *N* is Avogadro's number. If the unit cell, of volume *V*, contains *Z* formula units, then

$$V = \text{volume of one formula unit} \times Z$$

Therefore,

$$D = \frac{\text{FW} \times Z}{V \times N} \quad (1.3)$$

V is usually expressed in $\text{\AA}^3$ and must be multiplied by 10^{-24} to convert V to cm^{-3} and to give densities in units of g cm^{-3} . Substituting for N , the equation reduces to

$$D = \frac{\text{FW} \times Z \times 1.66}{V} \quad (1.4)$$

and, if V is in $\text{\AA}^3$, the units of D are g cm^{-3} . This simple equation has a number of uses, as shown by the following examples:

- It can be used to check that a given set of crystal data is consistent and that, for example, an erroneous formula weight has not been assumed.
- It can be used to determine any of the four variables if the other three are known. This is most common for Z (which must be a whole number) but is also used to determine FW and D .
- By comparison of D_{obs} (the experimental density) and D_{calc} (calculated from the above equation), information may be obtained on the presence of crystal defects such as vacancies or interstitials, the mechanisms of solid solution formation and the porosity of ceramic pieces.

Considerable confusion often arises over the value of the contents, Z , of a unit cell. This is because atoms or ions that lie on corners, edges or faces are also shared between adjacent cells; this must be taken into consideration in calculating *effective* cell contents. For example, α -Fe [Fig. 1.11(e)] has $Z = 2$. The corner Fe atoms, of which there are eight, are each shared between eight neighbouring unit cells. Effectively, each contributes only $1/8$ to the particular cell in question, giving $8 \times 1/8 = 1$ Fe atom for the corners. The body centre Fe lies entirely inside the unit cell and counts as one. Hence $Z = 2$.

For Cu metal, Fig. 1.11(c), which is *fcc*, $Z = 4$. The corner Cu again counts as one. The face centre Cu atoms, of which there are six, count as $1/2$ each, giving a total of $1 + (6 \times 1/2) = 4$ Cu in the unit cell.

NaCl is also *fcc* and has $Z = 4$. Assuming the origin is at Na (Fig. 1.2) the arrangement of Na is the same as that of Cu in Fig. 1.11(c) and therefore, the unit cell contains 4 Na. Cl occupies edge centre positions of which there are 12; each counts as $1/4$, which, together with Cl at the body centre, gives a total of $(12 \times 1/4) + 1 = 4$ Cl. Hence the unit cell contains, effectively, 4 NaCl. If unit cell contents are not counted in this way, but instead all corner, edge- and face-centre atoms are simply counted as one each, then the ludicrous answer is obtained that the unit cell has 14 Na and 13 Cl!

1.9 Description of Crystal Structures

Crystal structures may be described in various ways. The most common and one which gives all the necessary information, is to refer the structure to the unit cell. The structure is given by the size and shape of the cell and the positions of the atoms, i.e. *atomic coordinates*, inside the cell. However, a knowledge of the unit cell and atomic coordinates alone is often insufficient to give a revealing picture of what the structure looks like in 3D. The latter is obtained only by considering a larger part of the structure, comprising perhaps several unit cells and by considering the arrangement of atoms relative to each other, their coordination numbers, interatomic distances, types of bonding, etc. It then becomes possible to find alternative ways of visualising structures and also to compare and contrast different types of structure.

Two of the most useful ways of describing structures are based on *close packing* and *space-filling polyhedra*. Neither can be applied to all types of structure and both have their limitations. They do, however, provide greater insight into crystal chemistry than is obtained using unit cells and their contents alone. It can be very useful to make your own crystal structure models, either from coloured

spheres or polyhedra, and tips for constructing models are given in Appendix B. In addition, all the structures described in this book, and many more, are available to view in the crystal viewer software package which can be downloaded, free of charge, from the Companion Wiley resource site. Using this, structures can be expanded, rotated, colours changed and key structural features highlighted by hiding selected atoms or polyhedra.

1.10 Close Packed Structures – Cubic and Hexagonal Close Packing

Many metallic, ionic, covalent and molecular crystal structures can be described using the concept of close packing. The guiding factor is that structures are usually arranged to have the maximum density. The principles involved can be understood by considering the most efficient way of packing equal-sized spheres in three dimensions.

The most efficient way to pack spheres in *two* dimensions is shown in Fig. 1.16(a). Each sphere, e.g. A, is surrounded by, and is in contact with, six others, i.e. each sphere has six *nearest neighbours* and its *coordination number*, *CN*, is six. By regular repetition, infinite sheets called *close packed layers* form. The coordination number of six is the maximum possible for a planar arrangement of contacting, equal-sized spheres. Lower coordination numbers are, of course, possible, as shown in Fig. 1.16(b), where each sphere has four nearest neighbours, but the layers are no longer close packed, *cp*. Note also that within a *cp* layer, three *close packed directions* occur. Thus, in Fig. 1.16(a) spheres are in contact in the directions xx' , yy' and zz' and sphere A belongs to each of these rows.

The most efficient way to pack spheres in *three* dimensions is to stack *cp* layers on top of each other. There are two simple ways to do this, resulting in *hexagonal close packed* and *cubic close packed* structures as follows.

The most efficient way for two *cp* layers A and B to be in contact is for each sphere of one layer to rest in a hollow between three spheres in the other layer, i.e. at P or R in Fig. 1.16(c) and (d). Two layers in such a position relative to each other are shown in Fig. 1.17. Atoms in the second layer may occupy

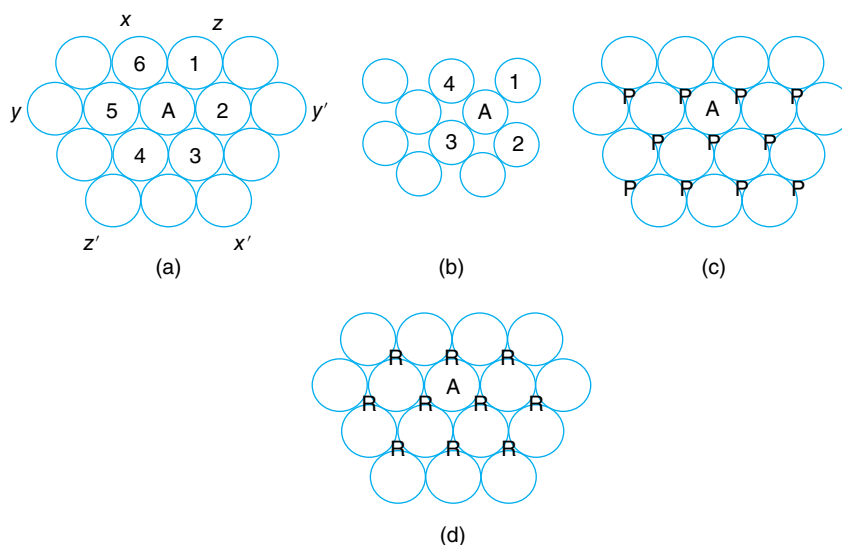


Figure 1.16 (a) A *cp* layer of equal-sized spheres; (b) a non-*cp* layer with coordination number 4; (c, d) alternative positions P and R for a second *cp* layer.

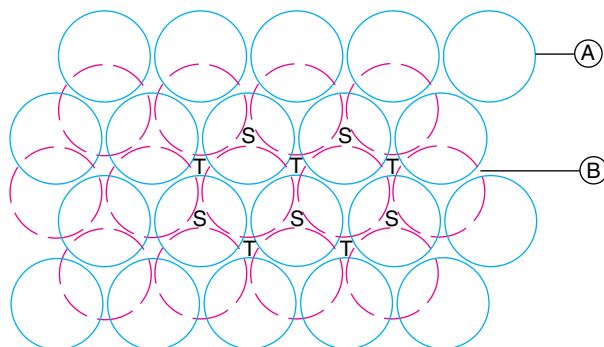


Figure 1.17 Two *cp* layers arranged in A and B positions. The B layer occupies the P positions of Fig. 1.16.

either P or R positions, but not both together, nor a mixture of the two. Any B (dashed) sphere is therefore seated between three A (solid) spheres, and vice versa.

Addition of a third *cp* layer to the two shown in Fig. 1.17 can also be done in two ways, and herein lies the distinction between hexagonal and cubic close packing. In Fig. 1.17, suppose that the A layer lies underneath the B layer and we wish to place a third layer on top of B. There is a choice of positions, as there was for the second layer: the spheres can occupy either of the new sets of positions S or T but not both together nor a mixture of the two. If the third layer is placed at S, then it is directly over the A layer. As subsequent layers are added, the following sequence arises:



This is known as *hexagonal close packing*, *hcp*. If, however, the third layer is placed at T, then all three layers are staggered relative to each other and it is not until the fourth layer is positioned (at A) that the sequence is repeated. If the position of the third layer is called C, this gives (Fig. 1.18)



This sequence is known as *cubic close packing* (*ccp*). The two simplest stacking sequences are *hcp* and *ccp* and these are by far the most important in structural chemistry. Other more complex sequences with larger repeat units, e.g. ABCACB or ABAC, occur in a few materials; some of these larger repeat units are responsible for the phenomenon of *polytypism*.

In a 3D *cp* structure, each sphere is in contact with 12 others, and this is the maximum coordination number possible for contacting and equal-sized spheres. [A common non-*cp* structure is the body centred cube, e.g. in α -Fe, with a coordination number of eight; see Fig. 1.11(e).] Six of these neighbours are coplanar with the central sphere, Fig. 1.16(a); from Fig. 1.17 and Fig. 1.18, the remaining six

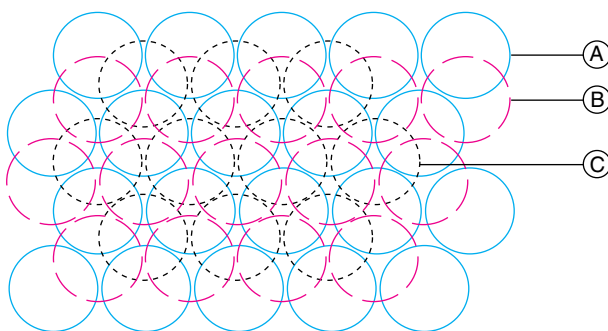


Figure 1.18 Three close packed layers in *ccp* sequence.

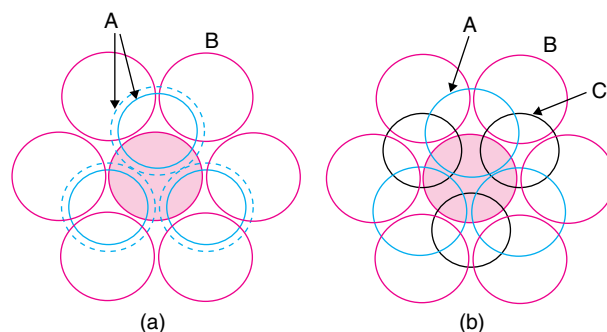


Figure 1.19 Coordination number 12 of shaded sphere in (a) hcp and (b) ccp structures. The shaded sphere is in the B layer, the layer underneath is A, and the layer above is either (a) A or (b) C.

are in two groups of three spheres, one in the plane above and one in the plane below (Fig. 1.19); *hcp* and *ccp* differ in the relative orientations of these two groups of three neighbours.

Many structures, not just of metals and alloys, but also ionic, covalent and molecular structures, can be described using close packing ideas. Sometimes the atoms that form the *cp* array are as closely packed as possible, but in other cases their arrangement is as in *cp* but the atoms are clearly not touching. Such structures are known as *eutactic* structures. Some guidelines as to whether it is appropriate to consider a structure in terms of a *cp* arrangement are given in Appendix D.

1.11 Relationship Between Cubic Close Packed and Face Centred Cubic

The unit cell of a *ccp* arrangement is the familiar face centred cubic (*fcc*) unit cell, Fig. 1.11(c), with spheres at corner and face centre positions. The relation between *ccp* and *fcc* is not immediately obvious since the faces of the *fcc* unit cell do not correspond to *cp* layers. The *cp* layers are, instead, parallel to the $\{111\}$ planes of the *fcc* unit cell. This is shown in Fig. 1.20 and Appendix B. The spheres labelled 2–7 in Fig. 1.20(a) form part of a *cp* layer, as revealed by removing a corner sphere 1 in (b) and comparing (b) with Fig. 1.16(a). The orientations of (a) and (b) in Fig. 1.20 are the same but the spheres in (b) are shown larger. A similar arrangement to that shown in (b) would be seen on removing any corner sphere in (a) and, therefore, in a *ccp* structure, *cp* layers occur in four orientations. These orientations are perpendicular to the body diagonals of the cube (the cube has eight corners but only four body diagonals and, hence, four different orientations of the *cp* layers). The *cp* layers in one orientation are seen edge-on in (c) and in another orientation, perpendicular to the layers in (d); (c) is the same as (a) but rotated slightly; similarly, (d) is the same as (b) but also rotated slightly. In (d), all atoms of the unit cell, spanning four *cp* layers, ABCA, are shown in projection down a $\langle 111 \rangle$ direction.

1.12 Hexagonal Unit Cell and Close Packing

An *hcp* arrangement of spheres has a hexagonal unit cell (Fig. 1.21). The *basal plane* of the cell coincides with a *cp* layer of spheres (b). The unit cell contains two spheres, one at the origin (and hence at all corners) and one inside the cell at positions $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ [pink circle in (a) and (b)]. Note that although the two *a* axes of the basal plane are equal, we need to distinguish them by a_1 and a_2 for the purpose of describe atomic coordinates of the positions $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$. The use of such *fractional coordinates* to represent positions of atoms inside a unit cell is discussed later.

cp layers occur in only one orientation in an *hcp* structure. These are parallel to the basal plane, as shown for one layer in Fig. 1.21(b). The two axes in the basal plane are of equal length; $a = 2r$, if the spheres of radius r touch; the angle γ is 120° (Table 1.1).

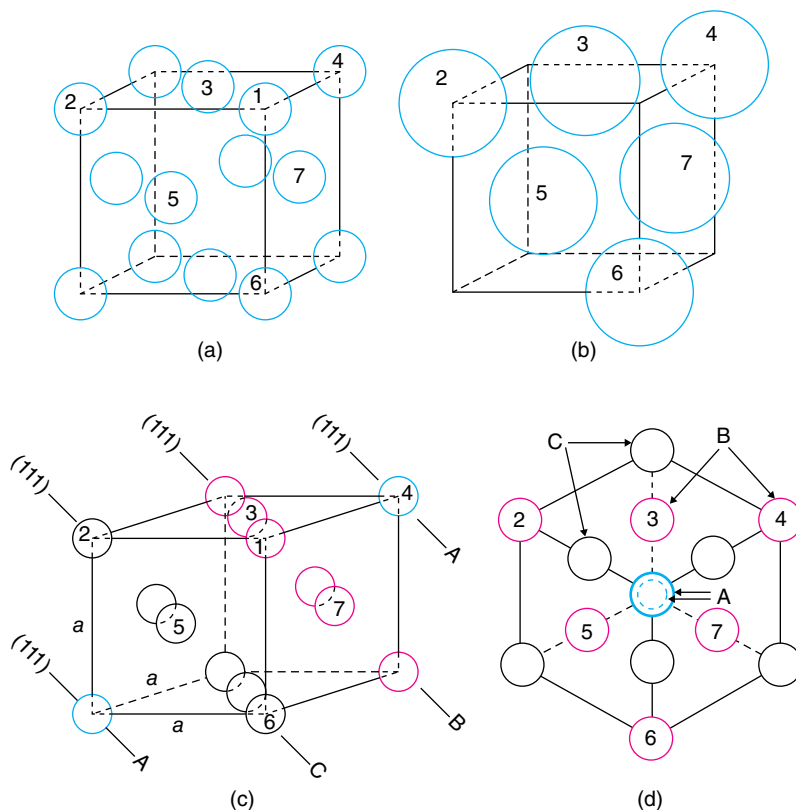


Figure 1.20 Face centred cubic, fcc, unit cell of a ccp arrangement of spheres.

The symmetry of the hexagonal unit cell is deceptively simple. The basal plane in isolation has a sixfold rotation axis but the adjacent B layer along the c axis reduces this to threefold rotational symmetry, as shown in Fig. 1.21(c): note the crystallographic symbol for a threefold axis, which is a solid triangle.

The structure does, however, possess a 6_3 screw axis parallel to c and passing through the basal plane at the coordinate position $\frac{1}{3}, \frac{2}{3}, 0$, as shown in Fig. 1.21(d). This symmetry axis involves a combined step of translation by $c/2$ and rotation by 60° ; atoms labelled 1–6 lie on a spiral with increasing c height above the basal plane; thus, atom 3 is on the top face of the unit cell whereas 4 and 5 are in the next unit cell in the c direction. Hence the *hcp* crystal structure has both a sixfold screw axis and a threefold rotation axis.

The *hcp* crystal structure has many other symmetry elements as well, including a nice example of a glide plane as shown in Fig. 1.21(e); the components of this c -glide involve displacement in the c direction by $c/2$ and reflection across the a_1c plane that passes through the unit cell with a_2 coordinate $\frac{2}{3}$, as shown by the dotted line (crystallographic symbol for a c -glide plane). Thus, atoms labelled 1, 2, 3, 4, etc. are related positionally to each other by this glide plane.

1.13 Density of Close Packed Structures

In *cp* structures, 74.05% of the total volume is occupied by spheres. This is the maximum density possible in structures constructed of spheres of only one size. This value may be calculated from the volume and contents of the unit cell. In a *ccp* array of spheres, the *fcc* unit cell contains four

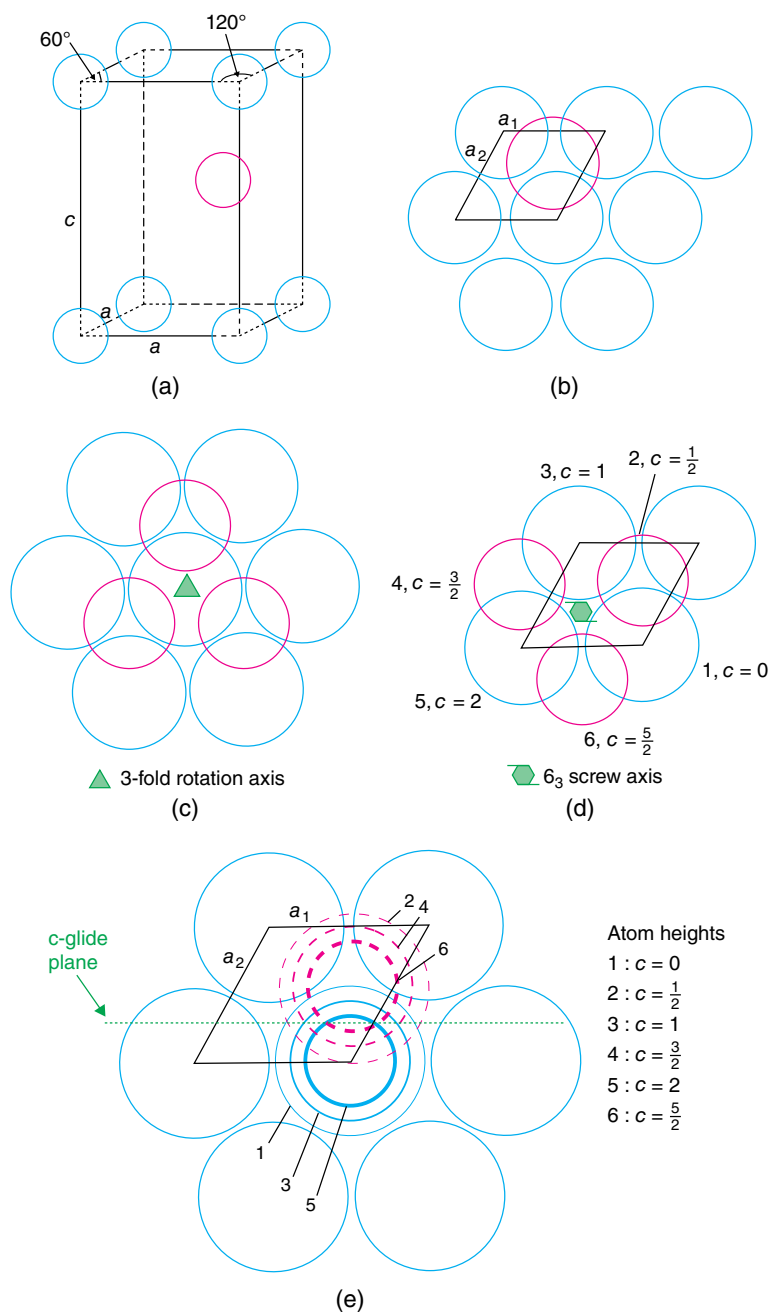


Figure 1.21 (a, b) Hexagonal unit cell of an hcp arrangement of spheres showing (c) a threefold rotation axis, (d) a 6_3 screw axis, and (e) a c -glide plane.

spheres, one at a corner and three at face centre positions, Fig. 1.20 (this is equivalent to the statement that a *fcc* unit cell contains four lattice points). *cp* directions [xx' , yy' , zz' in Fig. 1.16(a)], in which spheres are in contact, occur parallel to the face diagonals of the unit cell, e.g. spheres 2, 5 and 6 in Fig. 1.20(b) form part of a *cp* row. The length of the face diagonal is therefore $4r$. From the Pythagoras theorem, the length of the cell edge is then $2\sqrt{2}r$ and the cell volume is $16\sqrt{2}r^3$, Fig. 1.22

(a). The volume of each sphere is $1.33\pi r^3$ and so the ratio of the total sphere volume to the unit cell volume is given by

$$\frac{4 \times 1.33\pi r^3}{16\sqrt{2}r^3} = 0.7405 \quad (1.5)$$

Similar results are obtained for *hcp* by considering the contents and volume of the appropriate hexagonal unit cell, Fig. 1.21.

In non-*cp* structures, densities lower than 0.7405 are obtained, e.g. the density of body centred cubic, *bcc*, is 0.6802 (to calculate this it is necessary to know that the *cp* directions in *bcc* are parallel to the body diagonals, $\langle 111 \rangle$, of the cube).

1.14 Unit Cell Projections and Atomic Coordinates

In order to give 3D perspective to crystal structures, they are often drawn as oblique projections, as in Fig. 1.20(a). For accurate and unambiguous descriptions, it is necessary, however, to project them down particular crystallographic directions and/or onto unit cell faces, as shown for a face centred cube in Fig. 1.22(b) projected down the *z* axis onto the *ab* unit cell face. In this representation, the

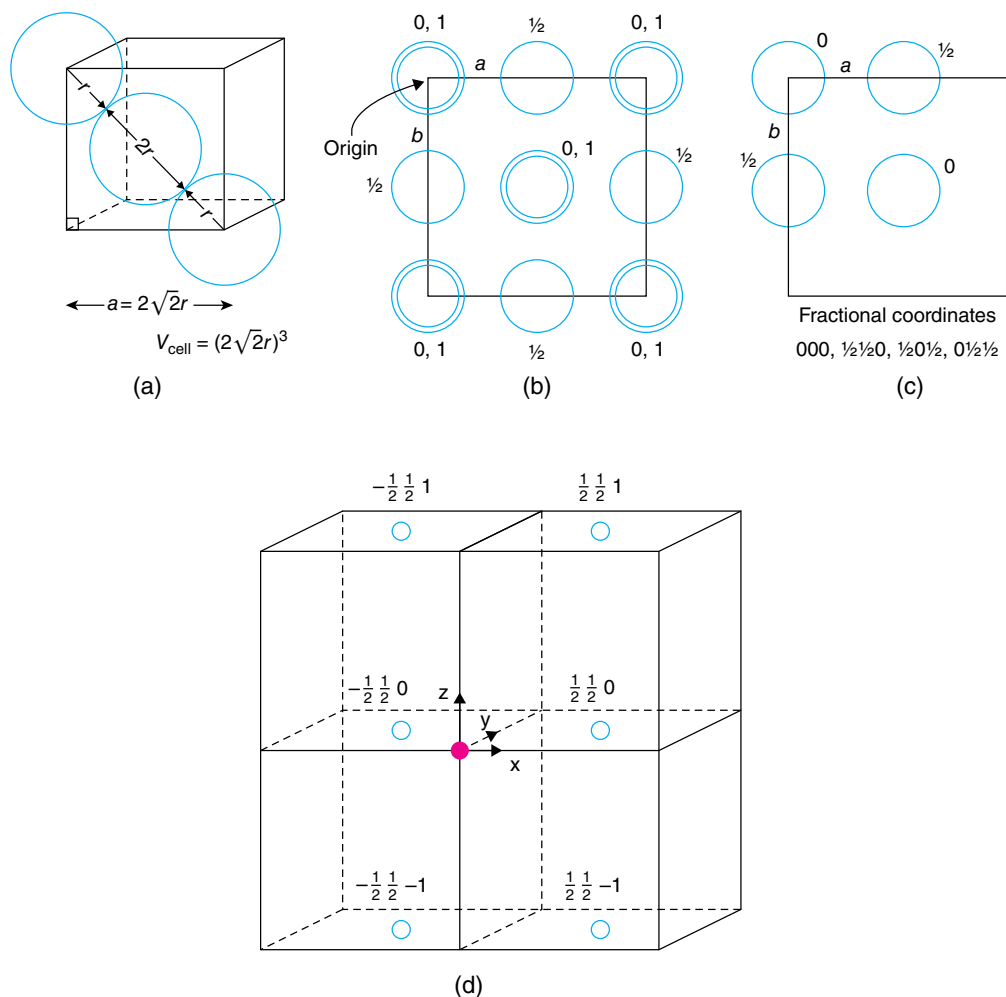


Figure 1.22 (a) Unit cell dimensions for a face centred cubic unit cell with spheres of radius r in contact along face diagonals. (b) Projection of a face centred cubic structure onto a unit cell face. (c) Unit cell contents. (d) Positive and negative atomic coordinates of the C face centre positions in four adjacent unit cells are given.

structure is projected onto a plane and so all sense of vertical perspective is lost. In order to restore some vertical perspective and to specify atomic positions fully, their vertical height in the unit cell is given, in this case as a fraction of c , beside each atom. It is not necessary to specify the x, y coordinates of each atom if the structure is drawn to scale; in this projection (b), the origin is shown as the top left-hand corner. There are two atoms at each corner, with z coordinates of 0 and 1. Similarly, atoms at the top and bottom face centres are shown with $z = 0, 1$ in the middle of the projection. The four side face centre positions are shown as single circles, each with $z = \frac{1}{2}$.

It is important to be able to use diagrams such as that in Fig. 1.22(b) and to relate these to listings of fractional atomic coordinates. Thus, a face centred cube contains, effectively, four positions in the unit cell, one corner and three face centres; their coordinates are $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$: each coordinate specifies the fractional distance of the atom from the origin in the directions a, b and c , respectively of the unit cell. These four positions are shown in Fig. 1.22(c) and it should be clear that the more complete structure shown in (b) is obtained simply by the addition of extra, *equivalent positions* in adjacent unit cells.

The diagrams in Fig. 1.22(b) and (c) both, therefore, represent the unit cell of a face centred cube; if we wish to use the cell shown in (b), we must remember that only $1/8$ of each corner atom belongs to this unit cell with the remaining $7/8$ associated with surrounding unit cells. Similarly, edge centre atoms belong to four adjacent unit cells and, therefore, only $1/4$ of each is counted. Finally, face centred atoms are split between two adjacent unit cells and therefore, each counts as half an atom. If we use diagram (c) to represent our unit cell contents, then all of the four atoms shown belong entirely to this unit cell and, for instance, other corner atoms are simply the corner atoms of adjacent unit cells. Diagram (c) shows the bare minimum that is necessary to illustrate the crystal structure whereas diagram (b) is more informative and gives a much clearer perspective of the structure in 3D.

In assigning fractional coordinates to the positions of atoms in a unit cell, it is customary to include in the cell those atoms whose coordinates lie between 0 and 0.999. Atoms with negative coordinates or with coordinates ≥ 1 then lie in adjacent unit cells. This is illustrated in Fig. 1.22(d), in which four unit cells are drawn. Let us consider the top right cell; its origin is given as the solid circle and positive directions of x, y and z are indicated by arrows. The diagram shows the coordinates of one pair of opposite, C-face Centre positions in each of the four cells. Relative to the origin of our chosen cell, all the C-centre positions shown at the right-hand side have $x = \frac{1}{2}$ and those at the left have $x = -\frac{1}{2}$. All positions in the diagram have a positive y value of $\frac{1}{2}$. The z values are in three sets, with values of 1, 0 and -1 . In considering the contents of the top right cell, the position at $\frac{1}{2}\frac{1}{2}0$ is regarded as belonging to the cell, but all other positions shown belong to neighbouring cells.

1.15 Materials that can be Described as Close Packed

1.15.1 Metals

Most metals crystallise in one of the three arrangements, *ccp*, *hcp* and *bcc*, the first two of which are *cp* structures. The distribution of structure type among the metals is irregular (Table 1.3), and no clear-cut trends are observed. It is still not well understood why particular metals prefer one structure type to another. Calculations reveal that the lattice energies of *hcp* and *ccp* metal structures are comparable and, therefore, the structure observed in a particular case probably depends on fine details of the bonding requirements or band structures of the metal. Structural details of elements not included in Table 1.3 are given in Appendix D.

1.15.2 Alloys

Alloys are intermetallic phases or solid solutions and, as is the case for pure metals, many have *cp* structures. For example, Cu and Au have *ccp* structures, both as pure elements and when mixed to

Table 1.3 Structures, unit cell dimensions, and metallic radii of some common metals

ccp			hcp				bcc		
Metal	$r/\text{\AA}$	$a/\text{\AA}$	Metal	$r/\text{\AA}$	$a/\text{\AA}$	$c/\text{\AA}$	Metal	$r/\text{\AA}$	$a/\text{\AA}$
Cu	1.28	3.6147	Be	1.12	2.2856	3.5842	Fe	1.24	2.8664
Ag	1.45	4.0857	Mg	1.60	3.2094	5.2105	Cr	1.25	2.8846
Au	1.44	4.0783	Zn	1.37	2.6649	4.9468	Mo	1.36	3.1469
Al	1.43	4.0495	Cd	1.52	2.9788	5.6167	W	1.37	3.1650
Ni	1.24	3.5240	Ti	1.47	2.9506	4.6788	Ta	1.43	3.3026
Pb	1.75	4.9502	Zr	1.60	3.2312	5.1477	Ba	2.17	5.019

form Cu–Au alloys. At high temperatures, a complete range of *solid solutions* between Cu and Au forms. In these the Cu and Au atoms are distributed statistically over the lattice points of the *fcc* unit cell and therefore the *ccp* layers contain a random mixture of Cu and Au atoms. On annealing the compositions AuCu and AuCu₃ at lower temperatures, the Au and Cu atoms *order* themselves; *ccp* layers still occur but the arrangement within the layers is no longer statistical. Such *order–disorder phenomena* occur commonly in both metallic and ionic structures.

1.15.3 Ionic structures

The structures of materials such as NaCl, Al₂O₃, Na₂O and ZnO, in which the anion is larger than the cation, are built of *cp* layers of anions with the cations placed in *interstitial sites*. Many structures are possible in which the variables are the anion stacking sequence, either *hcp* or *ccp*, and the number and type of interstitial sites occupied by cations. The cations are, however, often too large for the prescribed interstitial sites and the structure can accommodate them only by expanding the anion array. Consequently, the anion arrangement is the same as in *cp*, but the anions may not be in contact. O’Keeffe suggested the term *eutactic* for structures such as these. In the discussions that follow, use of the terms *hcp* and *ccp* for the anion arrays does not necessarily imply that the anions are in contact but rather that the structures are eutactic. A further complication, as we shall see later, is that the rigid sphere model is an oversimplification of reality since, in ionic structures, it can be difficult to specify ion sizes exactly.

It is useful at this stage to identify the criteria for an ionic structure to be regarded as close packed, since both cation and anion arrangements are involved. As with metal structures, the first criterion is that close packed anions exist with a coordination number, *by other anions*, of twelve. Six of these should be co-planar, forming *cp* layers, as in Fig. 1.16(a). The other six form part of two *cp* layers to either side; the relative orientation of these two layers determines the overall stacking sequence, whether *ccp* or *hcp*.

Various departures from ideal *cp* structures occur. Thus, in some structures, such as solid solutions or doped materials, anion vacancies may be present, within the overall *cp* array. These vacancies are usually at random throughout the anion array, such as in the perovskite (La_{1-x}Sr_x)(Ga_{1-x}Mg_x)O_{3-x}, but the ordering of oxygen vacancies may occur as in, for example, the beta alumina family of structures in which every fifth layer in a *cp* oxide sequence has $\frac{3}{4}$ of the oxygens missing, Fig. 8.23. In other *cp* structures, particularly those containing large cations such as K⁺, Sr²⁺ or La³⁺ in perovskites, mixed *cp* layers are present because these cations are large enough to be surrounded by 12 anion neighbours. Thus, in SrTiO₃, Sr and O together form a *ccp* sequence in which the Sr and O positions are ordered rather than randomised, Fig. 1.41(e). And in some other structures, especially fluorite, the *cations* rather than the anions form a *cp* array. Finally, the structures may be eutactic in that the *cp* arrangement of one type of ion is clearly present, but the ions are pushed apart and therefore, the structures are not *closest* packed.

Within a *cp* anion array, interstitial sites for cations are restricted to either tetrahedral or octahedral, as discussed next. For the anion coordination number, however, there is no such limitation. Although the anion–anion coordination number (above) is twelve, this refers to the second coordination sphere around a particular anion whereas the anion–cation coordination number refers to the primary coordination sphere, with the smallest interatomic distances. Various examples of anion–cation coordination numbers and arrangements are given throughout this chapter, as well as examples of structures that are distorted away from an ideal *cp* arrangement. First, we consider the cases of the standard tetrahedral and octahedral coordinations.

1.15.3.1 Tetrahedral and octahedral sites

Two types of interstitial site, tetrahedral and octahedral, are present in *cp* structures, Fig. 1.23. These may be seen by considering the nature of the interstitial space between any pair of adjacent *cp* layers. For the tetrahedral sites, three anions that form the base of the tetrahedron belong to one *cp* layer with

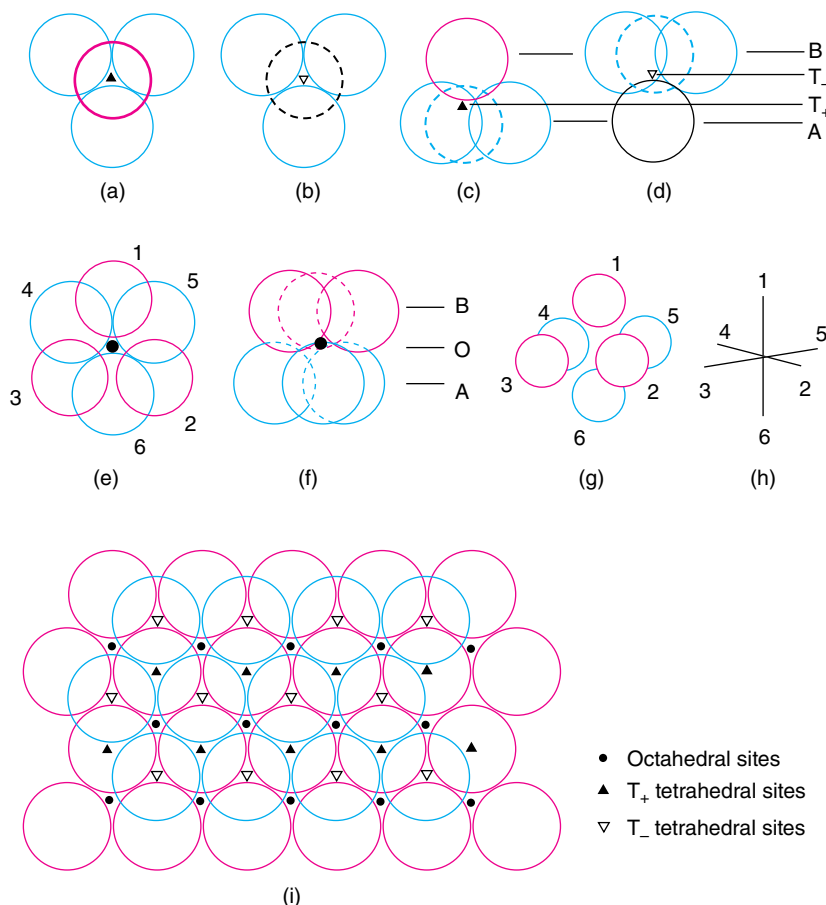


Figure 1.23 Tetrahedral and octahedral sites between two *cp* anion layers, seen from different perspectives. (a, b) Projection down threefold axis of T_+ , T_- sites. (c, d) Tetrahedral sites edge-on. (e) Projection down threefold axis of octahedral site and (f) seen edge-on. (g, h) Conventional representation of octahedral site. (i) Distribution of T_+ , T_- , O sites between two *cp* layers. The labelling of tetrahedral sites as T_+ and T_- is arbitrary and is only to indicate that there are two possible different orientations for these sites.

the apex of the tetrahedron either in the layer above (a) or below (b). This gives two orientations of tetrahedral sites, T_+ and T_- , in which the apex is up and down, respectively, and is illustrated further in (c) and (d) with the layers seen edge-on. Because the centre of gravity of a tetrahedron is nearer to the base than the apex (see Appendix C), cations in tetrahedral sites are not located midway between adjacent anion layers but are nearer one layer than the other. In *ccp* structures, there are four equivalent orientations of *cp* layers and therefore, four equivalent orientations of T_+ , T_- sites

Octahedral sites, O, are coordinated to three anions in each layer, Fig. 1.23(e) and are midway between the anion layers (f). A more common way to regard octahedral coordination is as four coplanar atoms with one atom at each apex above and below the plane. In (e), atoms 1, 2, 4 and 6 are coplanar; 3 and 5 form apices of the octahedron. Also, atoms 2, 3, 4, 5 and 1, 3, 5, 6 are coplanar. This is further illustrated in Fig. 1.23(g) and (h), which are similar to (e) but seen from a different and more conventional perspective.

The distribution of interstitial sites between any two adjacent layers of *cp* anions is shown in Fig. 1.23(i). We can see that below every red sphere in the upper layer is a T_+ site; likewise above every blue sphere in the lower layer is a T_- site. There are also as many O sites as either T_+ or T_- sites. A similar distribution to that in (i) is seen between each pair of *cp* anion layers. Counting up the numbers of each, then, for every anion there is one octahedral site and two tetrahedral sites, one T_+ and one T_- .

It is rare that all the interstitial sites in a *cp* structure are occupied; often one set is full or partly occupied and the remaining sets are empty. A selection of *cp* ionic structures, classified according to the anion layer stacking sequence and the occupancy of the interstitial sites, is given in Table 1.4. Individual structures are described later. Here we simply note how a wide range of structures are grouped into one large family; this helps to bring out similarities and differences between them. For example:

- (a) The rock salt and nickel arsenide structures both have octahedrally coordinated cations and differ only in the anion stacking sequence. Similarly, there are other pairs of structures with similar cation coordination numbers that differ only in the anion stacking sequence, e.g. olivine and spinel, wurtzite and zinc blende, CdI_2 and $CdCl_2$.

Table 1.4 Some close packed structures

Anion arrangement	Interstitial sites			Examples
	T_+	T_-	O	
<i>ccp</i>	–	–	1	NaCl, rock salt
	1	–	–	ZnS, blende, or sphalerite
	1/8	1/8	1/2	$MgAl_2O_4$, spinel
	–	–	1/2	$CdCl_2$
	–	–	1/3	$CrCl_3$
<i>hcp</i>	1	1	–	K_2O , antifluorite
	–	–	1	NiAs
	1	–	–	ZnS, wurtzite
	–	–	1/2	CdI_2
	–	–	1/2	TiO_2 , rutile ^a
<i>ccp</i> 'BaO ₃ ' layers	–	–	2/3	$\alpha-Al_2O_3$, corundum
	1/8	1/8	1/2	Mg_2SiO_4 , olivine
	–	–	1/4	$BaTiO_3$, perovskite

^a The *hcp* oxide layers in rutile are not planar but are buckled; the oxide arrangement may alternatively be described as *tetragonal packed, tp*.

- (b) Rutile, TiO_2 , and CdI_2 both have *hcp* anions (although the layers are buckled in rutile) with half the octahedral sites occupied by cations but they differ in the manner of occupancy of these octahedral sites. In rutile, half the octahedral sites between any pair of *cp* anion layers are occupied by Ti. In CdI_2 , layers of fully occupied octahedral sites alternate with layers in which all sites are empty; this gives CdI_2 a layered structure.
- (c) In a few structures, it is useful to regard the *cation* as forming the *cp* layers with the anions occupying the interstitial sites. The fluorite structure, CaF_2 , may be regarded as *ccp* Ca with all T_+ and T_- sites occupied by F. The antiferrofluorite structure of K_2O is the exact inverse of fluorite with *ccp* layers of O and K in T_+ , T_- sites; it is included in Table 1.4.
- (d) The *cp* concept may be extended to structures in which a mixture of anions and large cations form the packing layers and smaller cations occupy interstitial sites. In perovskite, BaTiO_3 , *ccp* layers of composition ' BaO_3 ' occur and one-quarter of the octahedral sites between these layers are occupied by Ti, although only those sites in which all six corners are O^{2-} ions.
- (e) Some structures are anion-deficient *cp* structures in which the anions form an incomplete *cp* array. The ReO_3 structure has *ccp* oxide layers with one-quarter of the O sites empty. It is analogous to perovskite just described in which Ti is replaced by Re and Ba sites are left vacant. The structure of β -alumina, nominally of formula $\text{NaAl}_{11}\text{O}_{17}$, contains *cp* oxide layers in which every fifth layer has approximately three-quarters of the O^{2-} ions missing.

1.15.3.2 *Relative sizes of tetrahedral and octahedral sites*

A general guideline is that tetrahedra are smaller than octahedra which, in turn, are smaller than polyhedra of higher coordination number; for a given anion array, the relative sizes of sites may be obtained quantitatively by geometric calculations (see the next section). In ionic structures, cations M occupy those sites or polyhedra of most suitable size. Cations may occupy sites which, at first sight, appear too small, by pushing apart anions and expanding the structure (as in eutactic structures). By contrast, cations tend not to occupy sites that are too large, unless the structure can adjust itself, by twisting or distorting the anion array so as to reduce the size of the sites; this happens in many distorted perovskite structures in which cations are too small to occupy large 12-coordinate sites and a partial structural collapse occurs (see Section 1.17.7). Thus, cations do not occupy large sites in which they can 'rattle'. An interesting intermediate situation occurs in some structures in which a cation site is marginally too large. The cation can then undergo small off-centre displacements giving rise to high polarisability, high permittivity and the phenomenon of ferroelectricity (Section 8.7).

1.15.3.3 *Location of tetrahedral and octahedral sites in an fcc unit cell; bond length calculations*

We have seen how T_+ , T_- and O sites occur between pairs of *cp* layers, Fig. 1.23, and how *fcc* and *ccp* structures are often equivalent, Fig. 1.20. We can now see where the T_+ , T_- and O sites are located within an *fcc* unit cell that has anions, X, at corners and face centres (A, B, C, and D), Fig. 1.24. The octahedral sites are easiest to locate; they are at edge-centre 1, 2, 3 and body-centre 4 positions. If the unit cell has length a , the M–X distance for octahedral sites is $a/2$.

In order to see the T_+ , T_- sites clearly, it is convenient to divide the unit cell into eight minicubes by bisecting each cell edge (dashed lines). These minicubes contain anions at only four of the eight corners; in the middle of each minicube is a tetrahedral site, either T_+ or T_- . There are two orientations for the minicubes, and therefore for the T sites, as shown in Fig. 1.25; relative to the parent unit cell, Fig. 1.24, the T_- tetrahedra have their apices pointing in the $[\bar{1}\bar{1}\bar{1}]$ direction and the T_+ sites in the $[111]$ direction.

At this point, we note that it is exceptionally useful to be able to regard a tetrahedral site as occupying the centre of a cube with alternate corners absent, Fig. 1.25(a) and (b). For such an arrangement, it is

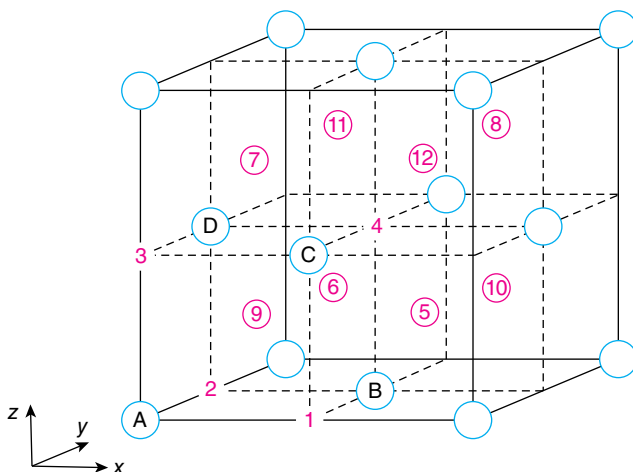


Figure 1.24 Available cation sites, 1–12, in an fcc anion array.

easy to calculate bond lengths and bond angles (c) and to demonstrate the various symmetry elements associated with a tetrahedron. Thus, for the minicube of edge dimension $a/2$,

$$M-X = \frac{1}{2} \left[3(a/2)^2 \right]^{\frac{1}{2}} = a\sqrt{3}/4$$

Twofold rotation axes and fourfold inversion axes run parallel to minicube edges but pass through pairs of opposite faces; there are three of these in total (see also Fig. 1.7c); mirror planes occur parallel to the set of lattice planes with indices $\{110\}$, and there are six of these in total [as in Fig. 1.9(c)]; threefold axes run parallel to $\langle 111 \rangle$ directions, four in total, Fig. 1.9(a); further details are in Appendix C.

1.15.3.4 Description of crystal structures; fractional atomic coordinates

In order to describe crystal structures, it is necessary to specify (a) the unit cell type, (b) its dimensions and (c) the fractional coordinates of the atoms in the unit cell. As described earlier, an fcc unit cell

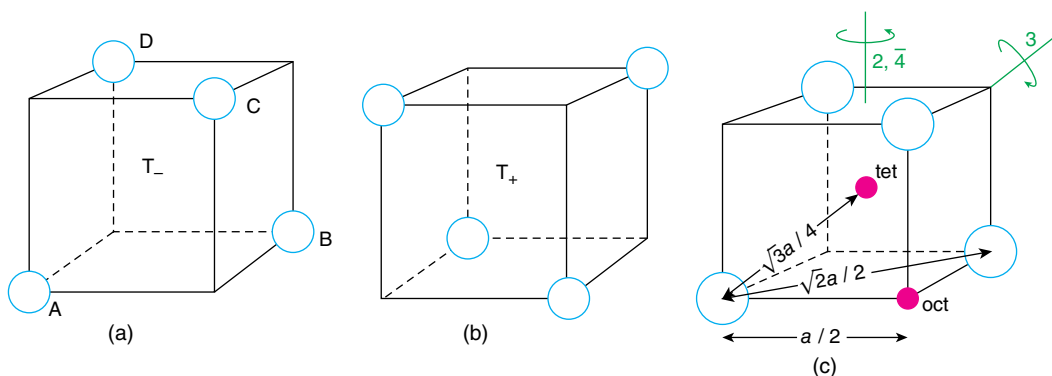


Figure 1.25 (a, b) Tetrahedral sites T_+ , T_- and their relation to a cube. (c) Bond length calculations and some symmetries of a tetrahedron.

containing anions at corner and face centre positions has, effectively, four anions in the unit cell, one at a corner and three at face centres. The fractional coordinates of the four anions A–D in the unit cell, Fig. 1.24, are

$$000, \frac{1}{2} \frac{1}{2} 0, \frac{1}{2} 0 \frac{1}{2}, 0 \frac{1}{2} \frac{1}{2}$$

Only one corner, at 000, is included since the other seven, e.g. at 100, 010, etc., are equivalent and can be regarded as the corner atoms of adjacent cells. The alternative would be to list all eight corner atoms, with the qualification that only 1/8 of each belonged to the unit cell in question. This would be equivalent to, but much more cumbersome than, regarding one corner only as specifically belonging, completely, to our unit cell. Likewise, for each pair of opposite faces, e.g. $\frac{1}{2} \frac{1}{2} 0$ and $\frac{1}{2} \frac{1}{2} 1$, it is most convenient to regard $\frac{1}{2} \frac{1}{2} 0$ as belonging completely to our unit cell; $\frac{1}{2} \frac{1}{2} 1$ then becomes the bottom face centre in the cell above.

The various cation positions in Fig. 1.24 have the following coordinates:

octahedral	1 : $\frac{1}{2} 00$	2 : $0 \frac{1}{2} 0$	3 : $00 \frac{1}{2}$	4 : $\frac{1}{2} \frac{1}{2} \frac{1}{2}$
tetrahedral, T ₊	5 : $\frac{3}{4} \frac{1}{4} \frac{1}{4}$	6 : $\frac{1}{4} \frac{3}{4} \frac{1}{4}$	7 : $\frac{1}{4} \frac{1}{4} \frac{3}{4}$	8 : $\frac{3}{4} \frac{3}{4} \frac{3}{4}$
tetrahedral, T ₋	9 : $\frac{1}{4} \frac{1}{4} \frac{1}{4}$	10 : $\frac{3}{4} \frac{3}{4} \frac{1}{4}$	11 : $\frac{1}{4} \frac{3}{4} \frac{3}{4}$	12 : $\frac{3}{4} \frac{1}{4} \frac{3}{4}$

Note that there are four of each type of cation site, O, T₊, T₋, in the unit cell, together with four anions. When different sites are fully or partially occupied by the cations, different structures are generated, as indicated in Table 1.4 and discussed later.

1.15.4 Covalent network structures

Materials such as diamond and silicon carbide, which have very strong, directional, covalent bonds, can also be described as *cp* structures or eutactic structures; many have the same structures as ionic compounds. Thus, one polymorph of SiC has the wurtzite structure and it is immaterial whether Si or C is regarded as the packing atom since the net result, a 3D framework of corner-sharing tetrahedra, is the same. Diamond can be regarded as a sphalerite structure in which half of the C atoms form a *ccp* array and the other half occupy T₊ sites, but again the two types of atom are equivalent. Classification of diamond as a eutactic structure is useful since in diamond all atoms are of the same size and it is unrealistic to distinguish between packing atoms and interstitial atoms.

Many structures have mixed ionic–covalent bonding, e.g. ZnS and CrCl₃; one advantage of describing them in terms of *cp* is that this can be done, if necessary, without reference to the type of bonding that is present.

1.15.5 Molecular structures

Since *cp* structures provide an efficient means of packing atoms, many molecular compounds crystallise as *cp* structures even though the bonding forces between adjacent molecules are weak van der Waals forces. If the molecules are roughly spherical or become spherical because they can rotate or occupy different orientations at random, then simple *hcp* or *ccp* structures result, e.g. in crystalline H₂, CH₄ and HCl. Non-spherical molecules, especially if they are built of tetrahedra and octahedra, can also fit into a *cp* arrangement. For example, Al₂Br₆ is a dimer with two AlBr₄ tetrahedra sharing a common edge, Fig. 1.26(a). In crystalline Al₂Br₆, the Br atoms form an *hcp* array and Al atoms occupy one-sixth of the available tetrahedral sites. One molecule, with the Br atoms in heavy outline is shown in Fig. 1.26(b); Al atoms occupy one pair of adjacent T₊ and T₋ sites. Br atoms 3 and 5 are

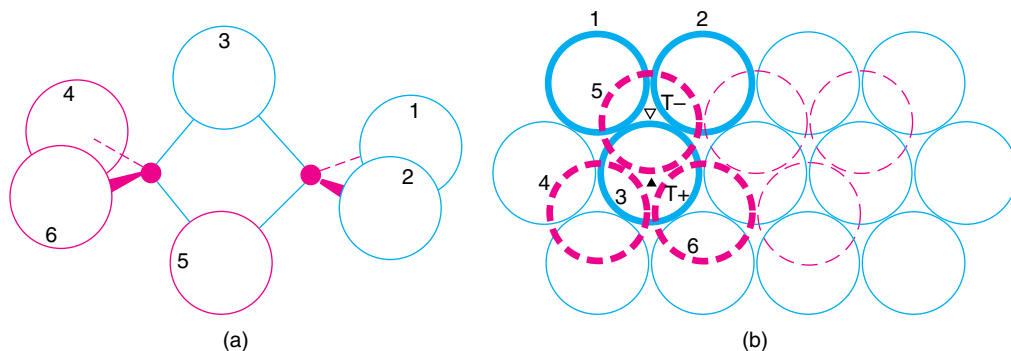


Figure 1.26 (a) hcp arrangement of Br atoms in crystalline Al_2Br_6 ; (b) Al atoms occupy T_+ and T_- sites. Dashed circles are below the plane of the paper.

common to both tetrahedra and are the bridging atoms in (a). Adjacent Al_2Br_6 molecules are arranged so that each Br in the hcp array belongs to only one molecule. SnBr_4 is a tetrahedral molecule and also crystallises with an hcp Br array, but only one-eighth of the tetrahedral sites are occupied.

1.15.6 Fullerenes and fullerides

The simplest, best known and symmetrical *fullerene* is C_{60} whose discovery led to the 1996 Nobel Prize in Chemistry awarded to Kroto, Curl and Smalley. It is a hollow, spherical cage of diameter $7.1 \text{ \AA}$ formed from 3-coordinate (approximately sp^2 hybridised) C atoms which link to form a network of 12 pentagons and 20 hexagons, Fig. 1.27(a), that match exactly the pattern on a soccer ball (hence the alternative, colloquial, American name ‘buckyball’; the name ‘fullerene’ is in honour of Buckminster Fuller, who designed the geodesic dome that has the same network structure as C_{60}).

Not surprisingly, in crystalline C_{60} , the C_{60} molecules arrange themselves according to the principles of close packing. At room temperature, crystalline C_{60} is face centred cubic, $Z = 4$ (C_{60}), $a = 14.17 \text{ \AA}$,

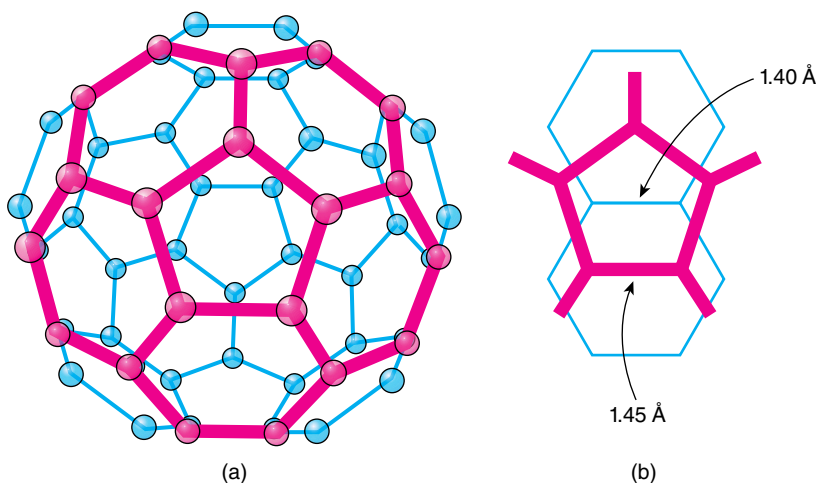


Figure 1.27 (a) The C_{60} molecule; one pentagon surrounded by five hexagons is shown in bold. (b) Parts of two C_{60} molecules in the region of closest contact showing a short C-C bond separating two hexagons in one molecule pointing towards the middle of a pentagon in an adjacent molecule. Adapted from W. I. R. David et al., Nature 353, 147 (1991).

and the C_{60} molecules are orientationally disordered. The separation of adjacent C_{60} molecules can be calculated with the aid of Fig. 1.22(a); a cube face diagonal corresponds to a *cp* direction from which we calculate that the centres of adjacent molecules are separated by 10.0 Å. The ‘hard diameter’ of a C_{60} molecule is calculated to be 7.1 Å which leaves a gap of 2.9 Å between adjacent molecules for van der Waals bonding.

Because the C_{60} molecules are not perfectly spherical, Fig. 1.27(a), they settle into an ordered arrangement below 249 K. The driving force for this ordering is optimisation of the bonding between adjacent C_{60} molecules. In particular, in a given [110] *cp* direction, the short electron-rich C–C bond that links two hexagons in one C_{60} molecule points directly at the centre of an electron-deficient pentagon, on an adjacent C_{60} molecule, as shown for two ring fragments in Fig. 1.27(b).

This arrangement minimises direct C–C overlap but maximises donor–acceptor electronic interactions between adjacent molecules. The C–C bonds in fullerene fall into two groups, 1.40 Å for C–C bonds linking two hexagons and 1.45 Å for bonds linking one hexagon and one pentagon; pentagons are isolated in C_{60} . Comparing these with typical single and double bond lengths in organic compounds, 1.54 and 1.33 Å, respectively, we can see that the C–C bonds in C_{60} are of intermediate bond order.

Some other fullerenes, such as C_{70} , also form *cp* structures, even though the molecules are not spherical. Thus, the C_{70} molecule is an ellipsoid (shaped like a rugby ball with a long axis of 8.34 Å and a short axis of 7.66 Å), but in crystalline C_{70} at room temperature the ellipsoids are able to rotate freely to give quasispherical molecules on a time average which form an *fcc* structure, $a = 15.01$ Å.

cp structures have, of course, tetrahedral and octahedral interstitial sites and in C_{60} these may be occupied by a range of large alkali metal cations to give materials known as *fullerides*. The most studied C_{60} fullerides have general formula A_3C_{60} as in Rb_3C_{60} or K_2RbC_{60} , in which all T_+ , T_- and O sites are occupied. These materials are metallic since the alkali metals ionise and donate their electrons to the conduction band of the C_{60} network, which is half full in A_3C_{60} . At low temperatures, many of these fullerides become superconducting. The highest T_c (the temperature at which the metal–superconductor transition occurs on cooling, Chapter 8) to date in the fullerides is 45 K in Tl_2RbC_{60} .

Other fullerides exist with different patterns of occupancy of interstitial sites, e.g. rock salt or zinc blende analogues in AC_{60} and fluorite analogues in A_2C_{60} . It is also possible to increase the number of A ions per C_{60} beyond 3; in A_4C_{60} ($A = Na$), A_4 clusters form in the octahedral sites. In A_6C_{60} , the packing arrangement of the C_{60} molecules changes from *ccp* to *bcc*; the *bcc* structure has a large number of interstitial sites, e.g. twelve distorted tetrahedral sites, distributed over the cube faces in the *bcc* array of anions (discussed in Chapter 8, for α -AgI, Fig. 8.28). This wide range of formulae arises because the C_{60} molecule can accept a number of electrons to give anions C_{60}^{n-} : $n = 1, 2, 3, 4, \dots$ Part of the excitement in C_{60} chemistry is that the electronic properties range from insulating to metallic/superconducting, depending on the value of n .

1.16 Structures Built of Space-Filling Polyhedra

This approach to describing crystal structures emphasises the coordination number of cations. Structures are regarded as built of polyhedra, formed by the cations with their immediate anionic neighbours, which link by sharing corners, edges or faces. For example, in NaCl each Na has six Cl nearest neighbours arranged octahedrally; this is represented as an octahedron with Cl at the corners and Na at the centre. A 3D overview of the structure is obtained by looking at how neighbouring octahedra link to each other. In NaCl, each octahedron edge is shared between two octahedra (Fig. 1.31, see later), resulting in an infinite framework of edge-sharing octahedra. In perovskite, $SrTiO_3$, TiO_6 octahedra link by

Table 1.5 Some structures built of space-filling polyhedra

Structure	Example
<i>Octahedra only</i>	
12 edges shared	NaCl
6 corners shared	ReO ₃
3 edges shared	CrCl ₃ , BiI ₃
2 edges and 6 corners shared	TiO ₂
4 corners shared	KAlF ₄
<i>Tetrahedra only</i>	
4 corners shared (between 4 tetrahedra)	ZnS
4 corners shared (between 2 tetrahedra)	SiO ₂
1 corner shared (between 2 tetrahedra)	Si ₂ O ₇ ⁶⁻
2 corners shared (between 2 tetrahedra)	(SiO ₃) _n ²ⁿ⁻ , chains, or rings

corner-sharing to form a 3D framework (Fig. 1.41, see later). These are just two examples; there are very many others, involving mainly tetrahedra and octahedra, leading to a wide diversity of structures. Some are listed in Table 1.5.

Although it is legitimate to estimate the efficiency of packing spheres in *cp* structures, we cannot do this for space-filling polyhedra since the anions, usually the largest ions in the structure, are represented by points at the corners of the polyhedra. In spite of this obvious misrepresentation, the space-filling polyhedron approach shows the topology or connectivity of a framework structure and indicates clearly the location of empty interstitial sites.

A complete scheme for classifying polyhedral structures has been developed by Wells and others. The initial problem is a geometric one: what types of network built of linked polyhedra are possible? The variables are as follows. Polyhedra may be tetrahedra, octahedra, trigonal prisms, etc. Polyhedra may share some or all of their corners, edges and faces with adjacent polyhedra, which may or may not be of the same type. Corners and edges may be common to two or more polyhedra (obviously only two polyhedra can share a common face). An enormous number of structures are feasible, at least theoretically, and it is an interesting exercise to categorise real structures on this basis.

The topological approach to arranging polyhedra in various ways takes no account of the bonding forces between atoms or ions. Such information must come from elsewhere. Also, the description of structures in terms of polyhedra does not necessarily imply that such entities exist as separate species. Thus, in NaCl, the bonding is mainly ionic, and physically distinct NaCl₆ octahedra do not occur. Similarly, SiC has a covalent network structure and separate SiC₄ tetrahedral entities do not exist. Polyhedra *do* have a separate existence in structures of (a) molecular materials, e.g. Al₂Br₆ contains pairs of edge-sharing tetrahedra, and (b) compounds that contain complex ions, e.g. silicate structures built of SiO₄ tetrahedra which form complex anions ranging in size from isolated monomers to infinite chains, sheets and 3D frameworks.

In considering the polyhedral linkages that are likely to occur, Pauling's third rule for the structures of complex ionic crystals (see Chapter 3 for other rules) provides a useful guideline. This states that shared edges and, especially, shared faces decrease the stability of a structure, particularly for cations of high valence and small coordination number, i.e. for small polyhedra, especially tetrahedra, that contain highly charged cations. When polyhedra share edges and, particularly, faces, the cation–cation distances (i.e. the distances between the centres of the polyhedra) decrease and the cations repel each other electrostatically. In Fig. 1.28 are shown pairs of (a) corner-sharing and (b) edge-sharing octahedra. The cation–cation distance is clearly less in the latter and for face-sharing octahedra, not shown, the cations are even closer. Comparing edge-shared octahedra and edge-shared tetrahedra (b, c), the

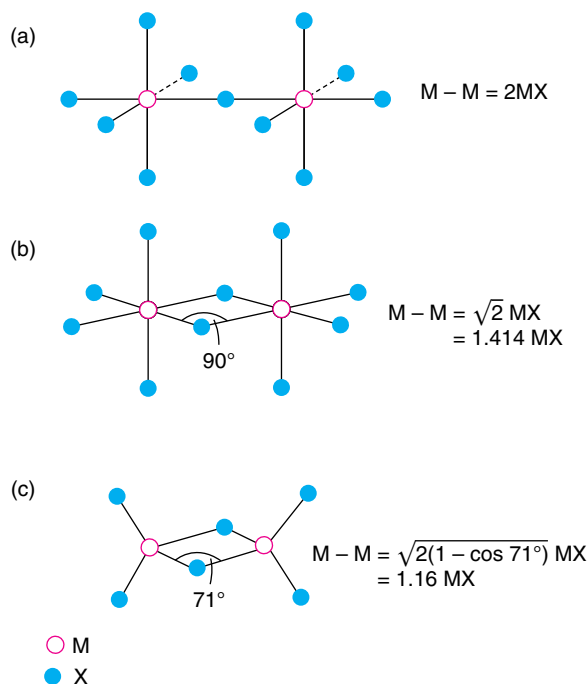


Figure 1.28 Cation–cation separation in octahedra which share (a) corners and (b) edges and in (c) tetrahedra which share edges.

cation–cation distance $M-M$ (relative to the cation–anion distance $M-X$) is less between the tetrahedra because the MXM bridging angle is 71° for them and 90° for the octahedra. A similar effect occurs for face-sharing tetrahedra and octahedra. In Table 1.6, the $M-M$ distances for various polyhedral linkages are given as a function of the $M-X$ distance. The $M-M$ distance is greatest for corner-sharing tetrahedra or octahedra and is least for face-sharing tetrahedra. For the sharing of corners and edges, the $M-M$ distances given are the maximum possible. Reduced distances occur if the polyhedra are rotated about the shared corner or edge (e.g. so that the $M-X-M$ angle between corner-shared polyhedra is less than 180°).

From Table 1.6, the $M-M$ distance in face-shared tetrahedra is considerably *less than* the $M-X$ bond distance. This therefore represents an unstable situation, because of the large cation–cation repulsions which would arise, and does not normally occur. A good example of the non-occurrence of face-sharing tetrahedra is provided by the absence of any crystal whose structure is the *hcp* equivalent of the fluorite (or antfluorite) structure. In Na_2O , which has the antfluorite structure, the oxide ions are in a *ccp* array and the NaO_4 tetrahedra share edges. However, in a structure with an *hcp* anion array and all the tetrahedral cation sites occupied, the MX_4 tetrahedra would share faces. Edge sharing of

Table 1.6 The $M-M$ distance between MX_4 or MX_6 groups sharing X atom(s)

	Corner sharing	Edge sharing	Face sharing
Two tetrahedra	$2.00 MX(\text{tet.})^a$	$1.16 MX(\text{tet.})^a$	$0.67 MX(\text{tet.})$
Two octahedra	$2.00 MX(\text{oct.})^a$	$1.41 MX(\text{oct.})^a$	$1.16 MX(\text{oct.})$

^a Maximum possible value.

tetrahedra, in which the M–M separation is only 16% larger than the M–X bond distance (Table 1.6) is energetically acceptable, as shown by the common occurrence of compounds with a fluorite structure, but face sharing of tetrahedra is generally unacceptable.

For tetrahedra containing cations of high charge, edge sharing may be energetically unacceptable and only corner sharing occurs. For example, in silicate structures which are built of SiO_4 tetrahedra, edge sharing of SiO_4 tetrahedra never occurs. (*Note:* In an ideally ionic structure, the charge on Si would be 4+, but the actual charges are considerably less due to partial covalency of the Si–O bonds.) In SiS_2 , however, edge sharing of SiS_4 tetrahedra does occur; the Si–S bond is longer than the Si–O bond and consequently the Si–Si distance in edge-shared SiS_4 tetrahedra is also greater and appears to be within the acceptable range for interatomic separations.

1.17 Some Important Structure Types

1.17.1 Rock salt (NaCl), zinc blende or sphalerite (ZnS), fluorite (CaF_2), antifluorite (Na_2O)

These structures are considered together because they all have *ccp/fcc* anions and differ only in the positions of the cations. In Fig. 1.24 are shown the anions in a *fcc* unit cell with all possible O , T_+ and T_- sites for the cations. There is no rule as to which sites should be labelled T_+ and T_- ; the choice is yours. The choice of origin is also arbitrary; for present purposes, it is more convenient to place the anions at the origin and also, therefore, at face centre positions. The different structures are generated as follows:

- rock salt: O occupied; T_+ and T_- empty
- zinc blende: T_+ (or T_-) occupied; O , T_- (or T_+) empty
- antifluorite: T_+ , T_- occupied; O empty.

Unit cells are shown in Fig. 1.29, in oblique projection (a–c) and as projections on the *ab* face of the unit cell in (d–f). Each is described in more detail later.

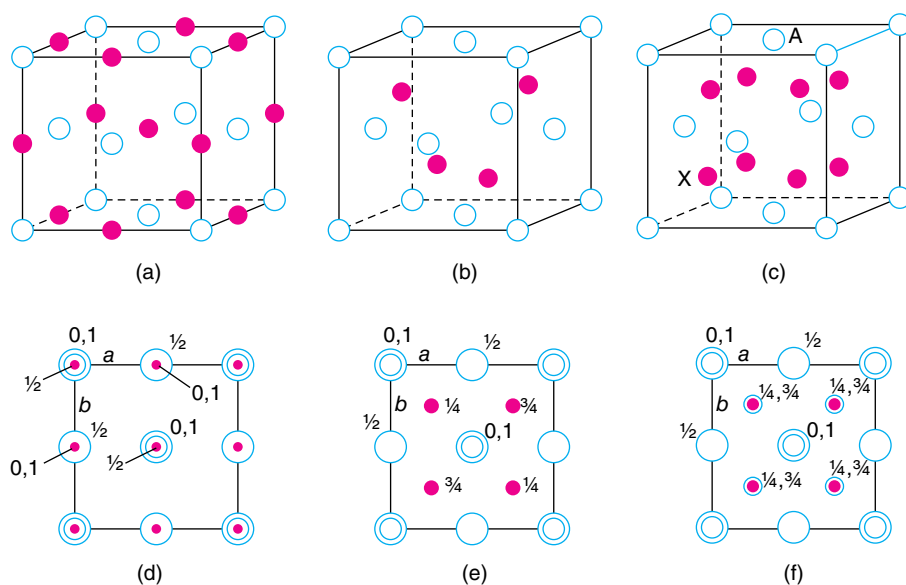


Figure 1.29 Unit cell of (a, d) NaCl, (b, e) ZnS, sphalerite, and (c, f) Na_2O . Closed circles are cations; open circles are anions.

Table 1.7 Two ways to describe the antifluorite structure

	Old cell	New cell
Anions	$000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$	$\frac{3}{4}\frac{3}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{1}{4}$
Cations	$\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{1}{4}$ $\frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{3}{4}$	$000, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00$ $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}\frac{1}{2}\frac{1}{2}$

A general rule regarding coordination numbers is that in any structure of formula A_xX_y , the coordination numbers of A and X must be in the ratio of $y:x$. In both rock salt and zinc blende, $x = y$ and therefore, in each, anions and cations have the same coordination number.

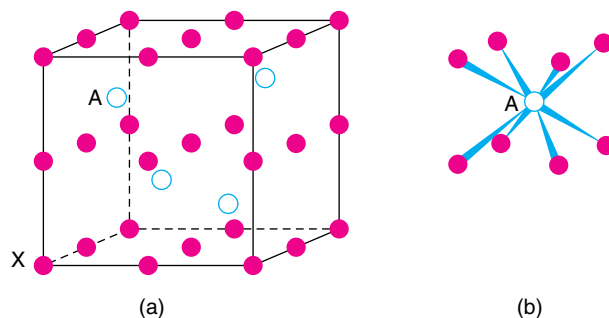
In antifluorite, of formula A_2X , the coordination numbers of cation and anion must be in the ratio of 1:2. Since the cations occupy tetrahedral sites, the anion coordination number must be eight. In order to see this, it is convenient to redefine the origin of the unit cell to coincide with a cation rather than an anion. This is done by displacing the unit cell along a body diagonal by one-quarter of the length of the diagonal. The cation at X in Fig. 1.29(c), with coordinates $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, may be chosen as the new origin of the unit cell. The coordinates of all atoms in the new cell are given by subtracting $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ from their coordinates in the old cell, as in Table 1.7.

In cases where negative coordinates occur as a result of this subtraction, e.g. $-\frac{1}{4}-\frac{1}{4}-\frac{1}{4}$, the position lies outside the new unit cell and it is necessary to find an equivalent position within the unit cell. In this particular case, 1 is added to each coordinate, giving $\frac{3}{4}\frac{3}{4}\frac{3}{4}$. Addition of 1 to, say, the x coordinate is equivalent to moving to a similar position in the next unit cell in the x direction. The new unit cell of antifluorite with its origin at cation X, is shown in Fig. 1.30(a). It contains cations at corners, edge centres, face centres and body centre.

In order to see the anion coordination more clearly, the unit cell may be imagined as divided into eight minicubes (as in Fig. 1.24). Each minicube in Fig. 1.30(a) has cations at all eight corners and at the centre of each is an eight-coordinate site. Anions occupy four of these eight minicubes such that parallel to the cell axes the eight-coordinate sites are alternately occupied and empty. The eightfold coordination for one anion, A, is shown in Fig. 1.30(b).

In the antifluorite structure, the effect of changing the origin from an anion to a cation is to show the structure in a completely different light. This does not happen with the rock salt and zinc blende structures. In these, the cation and anion positions are interchangeable and it is immaterial whether the origin coincides with an anion or a cation.

So far, the NaCl, ZnS and Na₂O structures have been described in two ways: (a) as *cp* structures and (b) in terms of their unit cells. A third way is to regard them as built of space-filling polyhedra. Each ion

**Figure 1.30** Alternative view of the antifluorite structure.

and its nearest neighbours may be represented by the appropriate polyhedron, e.g. in zinc blende a tetrahedron represents one Zn with four S neighbours (or vice versa). It is then necessary to consider how neighbouring polyhedra are linked in 3D. Let us now consider each of these structures in more detail.

1.17.1.1 Rock salt structure

To summarise, the rock salt structure has *ccp/fcc* anions with octahedral sites fully occupied by cations and tetrahedral sites empty. Each cation is surrounded by six anions, as shown for cations 1, 2 and 3 in Fig. 1.31; similarly, each anion is octahedrally coordinated by cations (to see this, consider the anion at the top face centre, $\frac{1}{2}\frac{1}{2}1$, which is coordinated to the four edge centre cations in the top face, to the cation at the body centre, shown, and to a sixth cation at the body centre of the unit cell above).

The (NaCl_6) or (ClNa_6) octahedra share common edges, Fig. 1.31. Since each has 12 edges and each edge is common to two octahedra, it is difficult to represent this satisfactorily in a drawing; Fig. 1.31 shows just two such linkages. A perspective which focuses on the 3D array of octahedra is shown in Fig. 1.32; the structure may be regarded as layers of octahedra, which also have an ABC stacking sequence similar to the anions. Each octahedron face is parallel to a *cp* layer of anions, as emphasised by the numbering or shading of coplanar faces. Parts of four different sets of faces are seen, corresponding to the four *cp* orientations in a *ccp/fcc* array. Also shown, arrowed, in Fig. 1.32 are the empty tetrahedral sites.

A large number of AB compounds possess the rock salt structure. A selection is given in Table 1.8 together with values of the *a* dimension of the cubic unit cell. Most halides and hydrides of the alkali metals and Ag^+ have this structure, as do a large number of chalcogenides (oxides, sulphides, etc.) of divalent metals. Many are ionic but others are either metallic, e.g. TiO , or covalent, e.g. TiC .

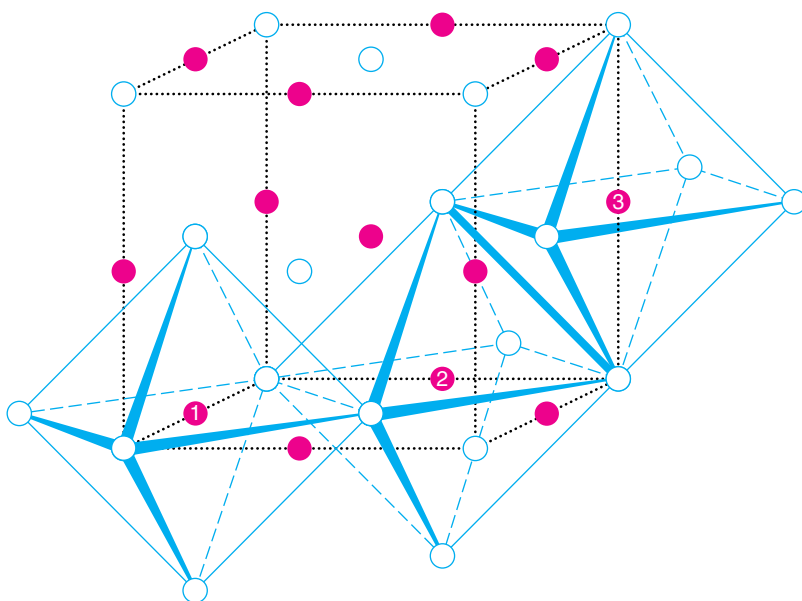


Figure 1.31 Unit cell of the rock salt structure showing edge-sharing octahedra.

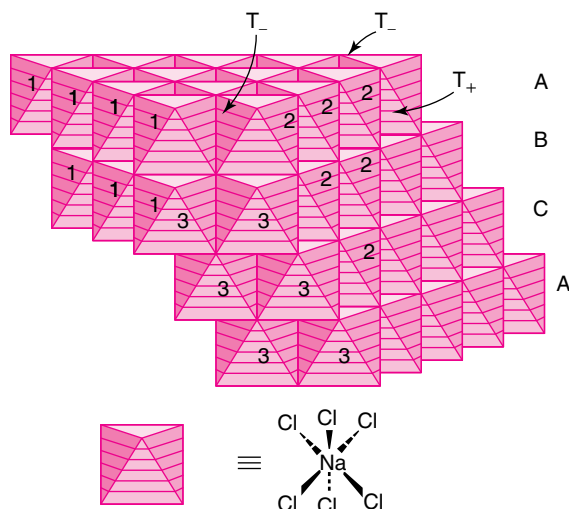


Figure 1.32 The rock salt structure as an array of edge-sharing octahedra.

1.17.1.2 Zinc blende (sphalerite) structure

The zinc blende structure has *ccp/fcc* anions with cations in one set of tetrahedral sites, either T_+ or T_- . The ZnS_4 tetrahedra are linked at their corners and each corner is common to four such tetrahedra. The unit cell of zinc blende, Fig. 1.29(b), is shown again in Fig. 1.33(a), but in terms of corner-sharing ZnS_4 tetrahedra. The faces of the tetrahedra are parallel to the *cp* anion layers, i.e. the $\{111\}$ planes; this is emphasised in a more extensive model in Fig. 1.33(b), which is oriented so that one set of tetrahedron faces is approximately horizontal. Conventionally, ZnS is regarded as built of *cp* layers of sulphides anions with the smaller zinc cations in tetrahedral sites. Since the same structure is generated by interchanging the Zn and S, the structure could also be described as a *cp* array of Zn with S occupying one set of tetrahedral sites. A third, equivalent description is as an array of *ccp* ZnS_4 (or SZn_4) tetrahedra.

Some compounds with the zinc blende structure are listed in Table 1.9. The bonding is less ionic than in compounds with the rock salt structure. Thus, oxides do not usually have the zinc blende structure (ZnO , not included in Table 1.9, is an exception; it is dimorphic with zinc blende and wurtzite structure polymorphs). Chalcogenides of the alkaline earth metals (but not Be) have the rock salt structure, whereas the chalcogenides of Be, Zn, Cd, and Hg have the zinc blende structure, as do Cu(I) halides

Table 1.8 Some compounds with the NaCl structure, $a/\text{\AA}$

MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	α -MnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	RbBr	6.889
CoO	4.260	SrSe	6.246	NaBr	5.9772	RbI	7.342
NiO	4.1769	BaSe	6.600	NaI	6.473	AgF	4.92
CdO	4.6953	CaTe	6.356	TiN	4.240	AgCl	5.549
TiC	4.3285	LaN	5.30	UN	4.890	AgBr	5.7745

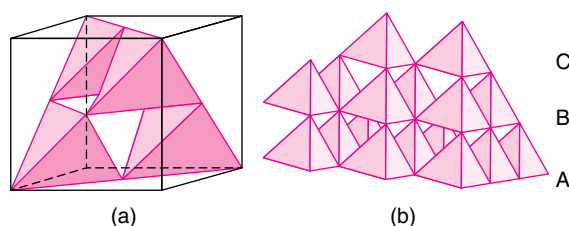


Figure 1.33 The sphalerite (zinc blende) structure showing (a) the unit cell contents and (b) a more extended network of corner-sharing tetrahedra.

and γ -AgI. A range of III–V compounds (i.e. elements from Groups III and V of the Periodic Table) have the zinc blende structure and some, e.g. GaAs, are important semiconductors.

1.17.1.3 Antifluorite/fluorite structure

The antifluorite structure has *ccp/fcc* anions with cations in all (T_+ and T_-) tetrahedral sites. The difference between antifluorite and fluorite is that antifluorite refers to an anion array with tetrahedral cations, whereas fluorite has the inverse arrangement with a *ccp* cation array and tetrahedral anions. Since the cation:anion ratio is 2:1 in antifluorite and the cation coordination is 4, the anion coordination must be 8, Fig. 1.30.

The very different coordination environments of anions and cations leads to two entirely distinct descriptions of the structure in terms of a 3D network of either tetrahedra or cubes, Fig. 1.34; (a) corresponds to the arrangement shown in Fig. 1.29(c) and the tetrahedra are highlighted; (b) corresponds to the arrangement in Fig. 1.30(b) in which the cubic coordination arrangement is highlighted. A more extended network of corner- and edge-sharing cubes is shown in Fig. 1.34(c). This must surely rate as one of the world's largest models of the antifluorite structure!

The *antifluorite* structure is shown by a large number of oxides and other chalcogenides of the alkali metals (Table 1.10), i.e. compounds of general formula $A_2^+ X^{2-}$. A group of fluorides of large, divalent cations and oxides of large tetravalent cations have the inverse, *fluorite*, structure, i.e. $M^{2+}F_2$ and $M^{4+}O_2$.

From Fig. 1.34(b) and (c), an alternative way of describing the fluorite structure is as a primitive cubic array of anions in which the eight-coordinate sites at the cube body centres are alternately empty and occupied by a cation. It should be stressed that the true lattice type of fluorite is *fcc* and not primitive cubic, since the primitive cubes represent only a small part (one-eighth) of the *fcc* unit cell. Description of fluorite as a primitive cubic array of anions with alternate cube body centres occupied by cations shows a similarity to the CsCl structure (see later). This also has a primitive cubic array of anions, but, instead, cations occupy *all* the body centre sites.

Table 1.9 Some compounds with the zinc blende (sphalerite) structure, $a/\text{\AA}$

CuF	4.255	BeS	4.8624	β -CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.07	CdSe	6.077	BP	4.538	GaAs	5.6534
γ -CuBr	5.6905	BeTe	5.54	CdTe	6.481	BAs	4.777	GaSb	6.095
γ -CuI	6.051	β -ZnS	5.4060	HgS	5.8517	AlP	5.451	InP	5.869
γ -AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β -MnS, red	5.600	β -SiC	4.358	HgTe	6.453	AlSb	6.1347	InSb	6.4782
C ^a	3.5667	Si	5.4307	Ge	5.6574	α -Sn (grey)	6.4912		

^a Diamond structure.

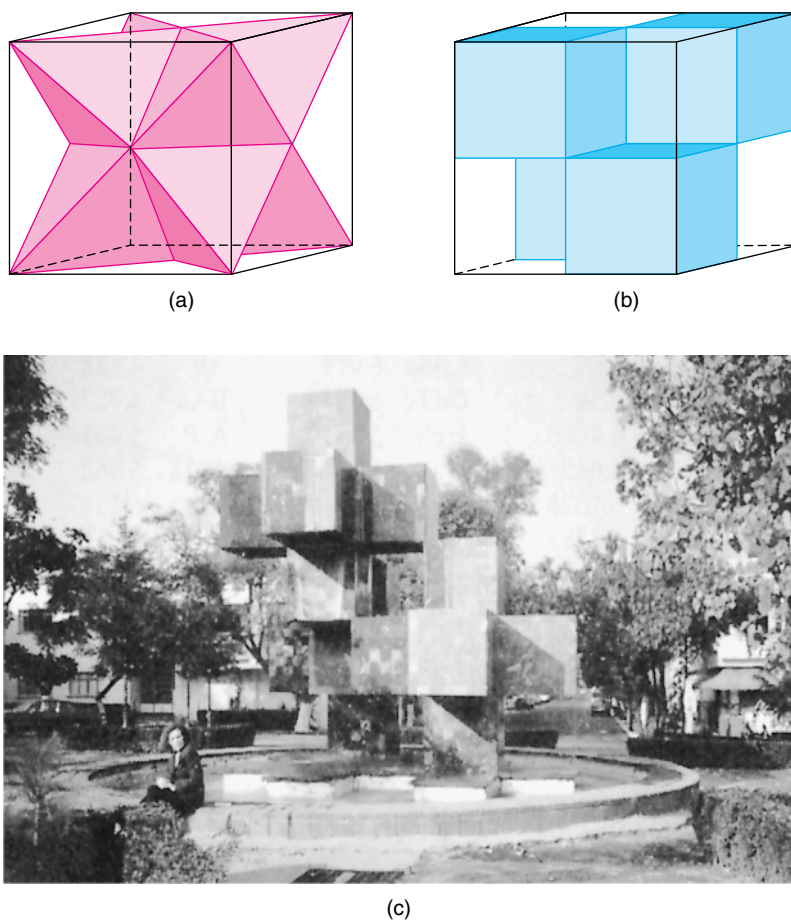


Figure 1.34 The antifluorite structure of Na_2O showing the unit cell in terms of (a) NaO_4 tetrahedra and (b) ONa_8 cubes. A more extended array of cubes is shown in (c); this model resides on a roundabout in Mexico City.

Most fluorite structures are eutactic in terms of descriptions as both a primitive cubic array of anions and an *fcc* array of cations. Thus, the anions are usually too large to occupy tetrahedral holes in a fully dense *ccp* cation array and, conversely, cations are too large to occupy eight-coordinate sites in a fully dense primitive cubic anion array. A compound that approaches maximum density is Li_2Te

Table 1.10 Some compounds with fluorite or antifluorite structure, $a/\text{\AA}$

Fluorite structure				Antifluorite structure			
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
SrCl_2	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
CdF_2	5.3895	UO_2	5.372	Na_2O	5.55	Rb_2O	6.74
$\beta\text{-PbF}_2$	5.940	NpO_2	5.4334	Na_2S	6.539	Rb_2S	7.65

containing the smallest alkali metal and largest chalcogen and for which the Te–Te distance, 4.6 Å, is only slightly greater than the diameter of the Te^{2+} ion, 4.4 Å.

In this section, we have described the ideal cubic fluorite structure, A_2X . A number of closely related structures with a range of formulae, including the pyrochlore structure, is described in Section 1.17.12.

1.17.1.4 Cuprite structure, Cu_2O

This structure is related to fluorite, CaF_2 but only 1/4 of the tetrahedral positions are occupied by anions. Cu forms an *fcc* array; two tetrahedral sites, at 1/4, 1/4, 1/4 and 3/4, 3/4, 3/4, are occupied by O. Consequently, the CN of Cu is twofold linear, rather than 8-fold for Ca in fluorite and 4-fold for Zn in sphalerite. Another way to view the structure is as two interpenetrating lattices, *fcc* Cu and *bcc* O, giving a structure that, overall, is primitive cubic, $a = 4.267$ Å. The linear, or ‘dumbbell’ coordination of 2 is unusual for a reasonably sized cation but is a common feature in structures of monovalent Cu $3d^{10}$ and may be rationalised in terms of *sp* hybridisation giving two Cu *sp* hybrid orbitals, arranged linearly.

1.17.1.5 Bond length calculations

It is very often desirable to be able to calculate interatomic distances in crystal structures. This is usually straightforward for crystals which have *orthogonal* unit cells (i.e. $\alpha = \beta = \gamma = 90^\circ$), and involves simple trigonometric calculations. For example, in the rock salt structure, the anion–cation distance is $a/2$ and the anion–anion distance is $a/\sqrt{2}$. The main interatomic distances involving cations in T/O sites in an *fcc/ccp* anion array are shown in Fig. 1.25(c) and are summarised in Table 1.11 for the important structure types. These may be used together with the tables of unit cell dimensions, Table 1.9, etc., for calculations on specific compounds. Typical values of bond distances (to oxygen and fluorine) for all the elements are given in Appendix F, where relevant values for different coordination numbers and oxidation states are also given.

Consideration of atom arrangements in the three structure types described above shows that the concept of *cp* anions with cations in interstitial sites begins to break down in the fluorite structure. Thus, while the antifluorite structure of Na_2O may be regarded as containing *ccp* O^{2-} ions with Na^+ ions in tetrahedral sites, in the fluorite structure of CaF_2 , it is necessary to regard the Ca^{2+} ions as forming the *ccp* array with F^- ions in tetrahedral sites. In CaF_2 the Ca^{2+} ions have a eutactic *ccp* arrangement, but are well separated from each other; from Table 1.9 and Table 1.10, $\text{Ca}–\text{Ca} = 3.86$ Å, which is much larger than the diameter of a Ca^{2+} ion (depending on which table of ionic radii is consulted, the diameter of Ca^{2+} is in the range $\sim 2.2–2.6$ Å).

The F–F distance in CaF_2 is 2.73 Å, which indicates that the fluorines are approximately contacting ($r_{\text{F}^-} = 1.2–1.4$ Å). Although the array of F^- ions in CaF_2 is not *cp* but is primitive cubic, this is perhaps a more realistic way of describing the structure than as containing a eutactic *ccp* array of Ca^{2+} ions; nevertheless, both descriptions are used widely.

1.17.2 Diamond

This structure type, so important to the semiconductor industry, has already been described, as the zinc blende or sphalerite structure, Fig. 1.29 and Fig. 1.33. The diamond structure is obtained when the two elements in zinc blende are identical, as in diamond. It may therefore be described as a *ccp* array of carbon atoms, with one set of tetrahedral sites (either T_+ or T_-) occupied also by carbon atoms. It is, however, rather artificial to make a distinction between packing and interstitial atoms since structurally they are identical. Most Group IV elements crystallise with the diamond structure, Table 1.9.

Table 1.11 *Calculation of interatomic distances in some simple structures*

Structure type	Distance	Number of such distances	Magnitude of distance in terms of unit cell dimensions
Rock salt (cubic)	Na–Cl	6	$a/2 = 0.5a$
	Cl–Cl	12	$a/\sqrt{2} = 0.707a$
	Na–Na	12	$a/\sqrt{2} = 0.707a$
Zinc blende (cubic)	Zn–S	4	$a\sqrt{3}/4 = 0.433a$
	Zn–Zn	12	$a/\sqrt{2} = 0.707a$
	S–S	12	$a/\sqrt{2} = 0.707a$
Fluorite (cubic)	Ca–F	8	$a\sqrt{3}/4 = 0.433a$
	Ca–Ca	12	$a/\sqrt{2} = 0.707a$
	F–F	6	$a/2 = 0.5a$
Wurtzite ^a (hexagonal)	Zn–S	4	$a\sqrt{3}/8 = 0.612a = 3c/8 = 0.375c$
	Zn–Zn	12	$a = 0.612c$
	S–S	12	$a = 0.612c$
Nickel arsenide ^a (hexagonal)	Ni–As	6	$a/\sqrt{2} = 0.707a = 0.433c$
	As–As	12	$a = 0.612c$
	Ni–Ni	2	$c/2 = 0.5c = 0.816a$
	Ni–Ni	6	$a = 0.612c$
Caesium chloride (cubic)	Cs–Cl	8	$a\sqrt{3}/2 = 0.866a$
	Cs–Cs	6	a
	Cl–Cl	6	a
Cadmium iodide (hexagonal)	Cd–I	6	$a/\sqrt{2} = 0.707a = 0.433c$
	I–I	12	$a = 0.612c$
	Cd–Cd	6	$a = 0.612c$

^aThese formulae do not necessarily apply when c/a is different from the ideal value of 1.633.

1.17.3 Wurtzite (ZnS) and nickel arsenide (NiAs)

These structures have in common an *hcp* arrangement of anions and differ only in the positions of the cations, as follows:

- wurtzite: T_+ (or T_-) sites occupied; T_- (or T_+), O empty
- nickel arsenide: O sites occupied; T_+ , T_- empty.

These structures are the *hcp* analogues of the *ccp* sphalerite and rock salt structures, respectively. Note that there is no hexagonal equivalent of the fluorite and antifluorite structures.

Both wurtzite and nickel arsenide have hexagonal symmetry and unit cells. A unit cell containing *hcp* anions is shown in Fig. 1.35(a). It is less easy to visualise and draw on paper than a cubic cell because of the γ angle of 120° . The unit cell contains two anions, one at the origin and one inside the cell:

$$0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$$

In Fig. 1.35(b) is shown a projection down c of the same structure. Close packed layers occur in the basal plane, i.e. at $c = 0$ (blue circles), at $c = 1$ (not shown) and at $c = \frac{1}{2}$ (pink circles). The layer stacking arrangement is repeated every other layer ... ABABA. ... The contents of one unit cell are shown in (c). Dashed circles represent atoms at the top four corners of the unit cell, i.e. at $c = 1$.

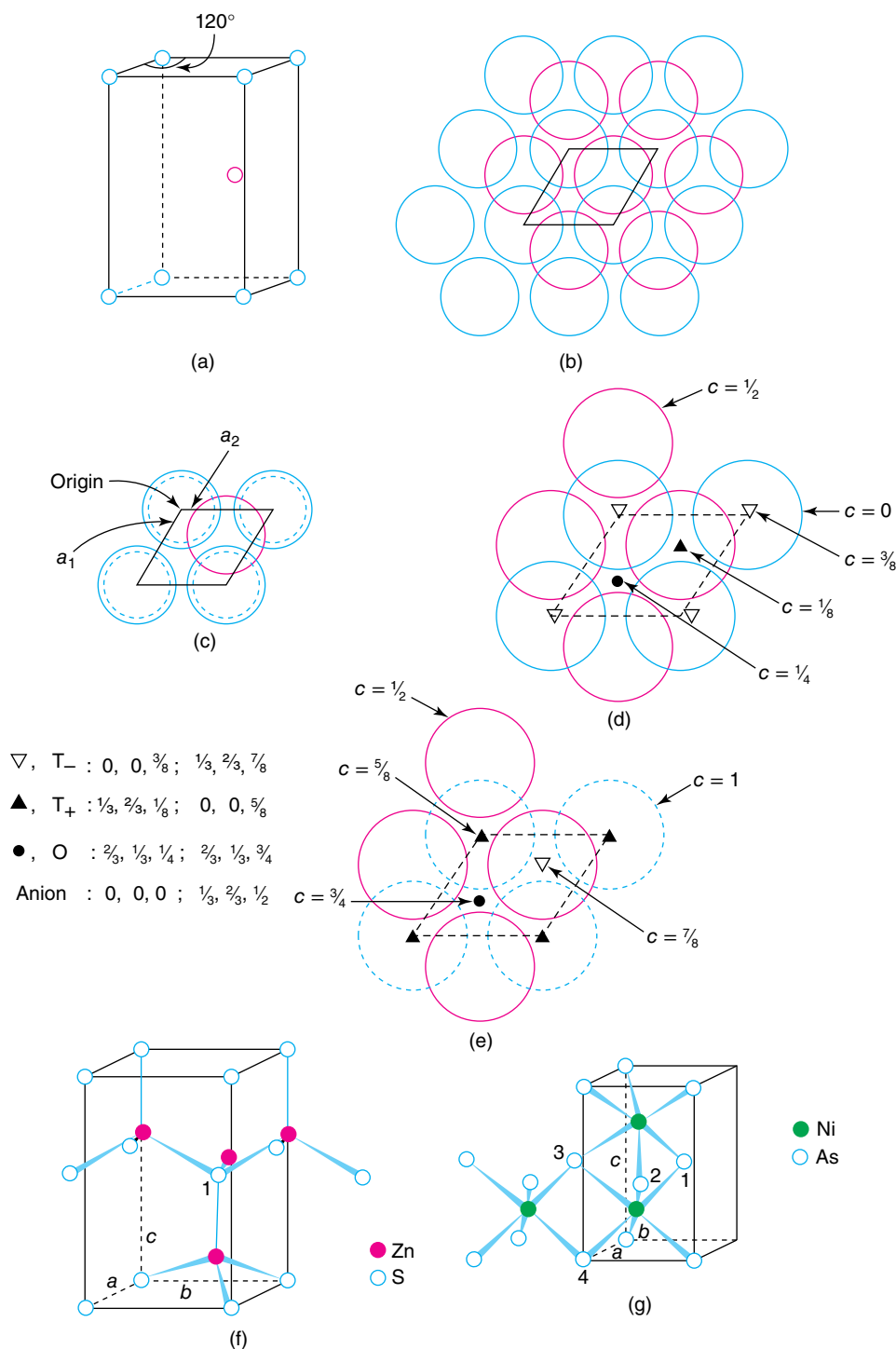
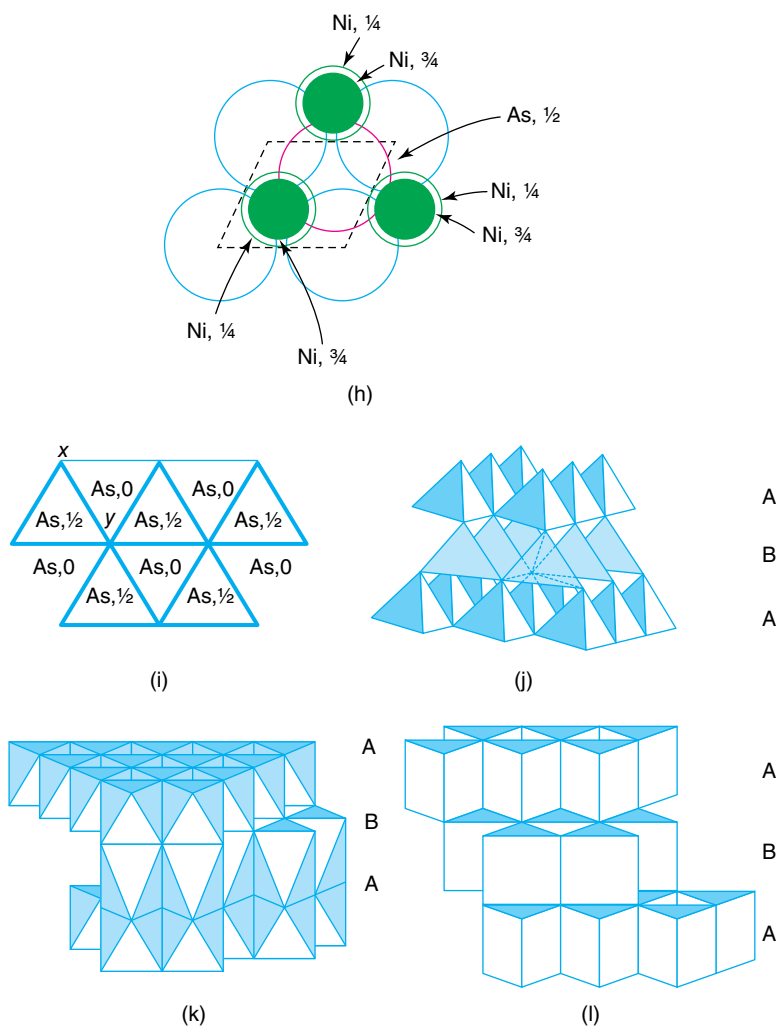


Figure 1.35 The wurtzite and nickel arsenide structures: (a–c) the hexagonal unit cell of an hcp anion array; (d, e) interstitial sites in an hcp array; (f, g) structures of wurtzite and NiAs; (h, i) trigonal prismatic coordination of arsenic in NiAs; (j–l) models of the ZnS and NiAs structures showing the arrangement and linkages of the polyhedra.

**Figure 1.35** (Continued)

In metals which have *hcp* structures, adjacent metal atoms are in contact, e.g. along a_1 and a_2 ($\equiv b$) edges of the unit cell (b, c). In eutactic *cp* ionic structures, however, the anions may be pushed apart by the cations in the interstitial sites. Assuming for the moment that the anions are in contact, then the hexagonal unit cell has a definite shape given by the ratio $c/a = 1.633$. This is because a is equal to the shortest distance X–X, i.e. the diameter of an anion, and c is equal to twice the vertical height of a tetrahedron comprising four anions. The ratio c/a may then be calculated by geometry (see Appendix C).

The interstitial sites available for cations in an *hcp* anion array are shown in Fig. 1.35(d) for the bottom half of the unit cell between $c = 0$ and $c = \frac{1}{2}$ and in (e) for the top half of the unit cell. Since the cell contains two anions, there must be two each of T_+ , T_- and O.

A detailed description of the sites that are occupied in wurtzite and NiAs is now given for completeness; such a degree of detail may, however, not be necessary to gain an overview of these two structures and is not compulsory reading! In Fig. 1.35(d), a T_- site occurs along the c edge of the cell at height $\frac{3}{8}$ above the anion at the origin. This T_- site is coordinated to three anions at $c = \frac{1}{2}$ and one anion at the

Table 1.12 Some compounds with the wurtzite structure

Compound	$a/\text{\AA}$	$c/\text{\AA}$	u	c/a	Compound	$a/\text{\AA}$	$c/\text{\AA}$	u	c/a
ZnO	3.2495	5.2069	0.345	1.602	AgI	4.580	7.494		1.636
ZnS	3.811	6.234		1.636	AlN	3.111	4.978	0.385	1.600
ZnSe	3.98	6.53		1.641	GaN	3.180	5.166		1.625
ZnTe	4.27	6.99		1.637	InN	3.533	5.693		1.611
BeO	2.698	4.380	0.378	1.623	TaN	3.05	4.94		1.620
CdS	4.1348	6.7490		1.632	NH ₄ F	4.39	7.02	0.365	1.600
CdSe	4.30	7.02		1.633	SiC	3.076	5.048		1.641
MnS	3.976	6.432		1.618	MnSe	4.12	6.72		1.631

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corner, $c = 0$. The tetrahedron so formed, therefore, points downwards. The position of the T_- site inside this tetrahedron is at the centre of gravity, i.e. at one-quarter of the vertical distance from base to apex (see Appendix C). Since the apex and base are at $c = 0$ and $c = \frac{1}{2}$, this T_- site is at $c = \frac{3}{8}$. In practice, the occupant of this T_- site in the wurtzite structure may not be at exactly $0.375c$. For those structures which have been studied accurately, Table 1.12, values range from 0.345 to 0.385; the letter u represents the fractional c value.

The three anions at $c = \frac{1}{2}$ that form the base of this T_- site also form the base of a T_+ site shown in Fig. 1.35(e) centred at $0, 0, \frac{5}{8}$. The apex of this tetrahedron is the anion at the top corner with coordinates $0, 0, 1$. Another T_+ site at $\frac{1}{3}, \frac{2}{3}, \frac{1}{8}$ is coordinated to three anions in the basal plane and an anion at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ (d). The triangular base of this site, at $c = 0$, is shared with a T_- site underneath (not shown) at $\frac{1}{3}, \frac{2}{3}, -\frac{1}{8}$. The equivalent T_- site that lies inside the unit cell is at $\frac{1}{3}, \frac{2}{3}, \frac{7}{8}$ (e).

The octahedral site in Fig. 1.35(d) is coordinated to three anions at $c = 0$ and three anions at $c = \frac{1}{2}$. The centre of gravity of the octahedron lies midway between these two groups of anions and has coordinates $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$. The second octahedral site lies immediately above the octahedral site shown in (d) and has coordinates $\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$ (e). The three anions at $c = \frac{1}{2}$ are therefore common to the two octahedra, which means that octahedral sites share opposite faces.

The coordination environments of the cations in wurtzite and NiAs are emphasised in Fig. 1.35(f) and (g). Zinc is shown in T_+ sites and forms ZnS_4 tetrahedra (f), linked at their corners to form a 3D network, as in (j). A similar structure results on considering the tetrahedra formed by four Zn atoms around a S. The tetrahedral environment of S (1) is shown in (f). The SZn_4 tetrahedron which it forms points down, in contrast to the ZnS_4 tetrahedra, all of which point up; on turning the SZn_4 tetrahedra upside down, however, the same structure results.

Comparing larger scale models of zinc blende [Fig. 1.33(b)] and wurtzite [Fig. 1.35(j)], they are clearly very similar and both can be regarded as networks of tetrahedra. In zinc blende, layers of tetrahedra form an ABC stacking sequence and the orientation of the tetrahedra within each layer is identical. In wurtzite, the layers form an AB sequence and alternate layers are rotated by 180° about c relative to each other.

The $NiAs_6$ octahedra in NiAs are shown in Fig. 1.35(g). They share one pair of opposite faces (e.g. the face formed by arsenic ions 1, 2 and 3) to form chains of face-sharing octahedra that run parallel to c . In the ab plane, however, the octahedra share only edges: As atoms 3 and 4 are shared between two octahedra such that chains of edge-sharing octahedra form parallel to b . Similarly, chains of edge-sharing octahedra form parallel to a (not shown). A more extended view of the octahedra and their linkages is shown in (k).

The NiAs structure is unusual in that the anions and cations have the same coordination number but different coordination environments. Since the cation:anion ratio is 1:1 and the Ni coordination is

octahedral, As must also be six-coordinate. However, the six Ni neighbours are arranged as in a trigonal prism and not octahedrally. This is shown for As at $c = \frac{1}{2}$ in Fig. 1.35(h), which is coordinated to three Ni at $c = \frac{1}{4}$ and three at $c = \frac{3}{4}$. The two sets of Ni are superposed in projection down c and give trigonal prismatic coordination for As. [Note that in a similar projection for octahedral coordination, the two sets of three coordinating atoms are staggered relative to each other, as in (e).]

The NiAs structure may also be regarded as built of AsNi_6 trigonal prisms, therefore, which link up by sharing edges to form a 3D array. In Fig. 1.35(i), each triangle represents a prism in projection down c . The prism edges that run parallel to c , i.e. those formed by Ni at $c = \frac{1}{4}$ and $\frac{3}{4}$ in (h), are shared between three prisms. Prism edges that lie in the ab plane are shared between only two prisms, however. In (i), the edge xy is shared between As at $c = \frac{1}{2}$ and $c = 0$. The structure therefore has layers of prisms arranged in an ... ABABA ... hexagonal stacking sequence, as shown further in (1).

The NiAs structure can be described as *hcp* As with Ni in fully occupied octahedral interstitial sites. However, unlike the case of NaCl where Na and Cl positions are interchangeable, we cannot simply exchange Ni, As and arrive at the same structural description. If we consider the arrangement of Ni alone, it still forms *cp* layers but the stacking sequence along c is identical because Ni atoms are superposed in projection, Fig. 1.35(h). Since both As and Ni form *cp* layers, we may describe the combined layer stacking sequence parallel to c as **ACBCACBC...** where Ni atoms in C positions (red) separate the A and B layers of As (black).

A selection of compounds with wurtzite and NiAs structures is given in Table 1.12 and Table 1.13 with values of their hexagonal cell parameters a and c . The wurtzite structure is formed mainly by chalcogenides of divalent metals and is a fairly ionic structure. The NiAs structure is more metallic and is adopted by a variety of intermetallic compounds and some transition metal chalcogenides (S, Se, and Te). The value of the ratio c/a is approximately constant in the wurtzite structures but varies considerably in compounds with the NiAs structure. This is associated with the presence of metallic bonding which arises from metal–metal interactions in the c direction, as follows. First consider the environment of Ni and As:

- Each As is surrounded by (Table 1.11):
 - 6 Ni in a trigonal prism at distance $0.707a$
 - 12 As, *hcp* arrangement, at distance a .

Table 1.13 *Some compounds with the NiAs structure*

Compound	$a/\text{\AA}$	$c/\text{\AA}$	c/a	Compound	$a/\text{\AA}$	$c/\text{\AA}$	c/a
NiS	3.4392	5.3484	1.555	CoS	3.367	5.160	1.533
NiAs	3.602	5.009	1.391	CoSe	3.6294	5.3006	1.460
NiSb	3.94	5.14	1.305	CoTe	3.886	5.360	1.379
NiSe	3.6613	5.3562	1.463	CoSb	3.866	5.188	1.342
NiSn	4.048	5.123	1.266	CrSe	3.684	6.019	1.634
NiTe	3.957	5.354	1.353	CrTe	3.981	6.211	1.560
FeS	3.438	5.880	1.710	CrSb	4.108	5.440	1.324
FeSe	3.637	5.958	1.638	MnTe	4.1429	6.7031	1.618
FeTe	3.800	5.651	1.487	MnAs	3.710	5.691	1.534
FeSb	4.06	5.13	1.264	MnSb	4.120	5.784	1.404
δ -NbN ^a	2.968	5.549	1.870	MnBi	4.30	6.12	1.423
PtB ^a	3.358	4.058	1.208	PtSb	4.130	5.472	1.325
PtSn	4.103	5.428	1.323	PtBi	4.315	5.490	1.272

^a Anti-NiAs structure.

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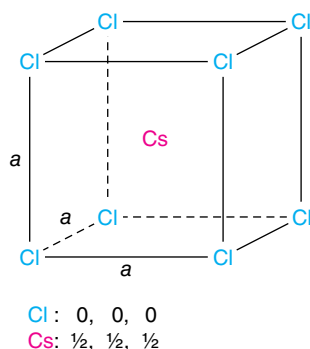


Figure 1.36 The primitive cubic unit cell of CsCl.

- Each Ni is surrounded by:
 - 6 As, octahedrally, at distance $0.707a$
 - 2 Ni, linearly, parallel to c , at distance $0.816a$ (i.e. $c/2$)
 - 6 Ni, hexagonally, in ab plane at distance a .

The main effect of changing the value of the c/a ratio is to alter the Ni–Ni distance parallel to c . Thus, in FeTe, $c/a = 1.49$, and the Fe–Fe distance is reduced to $0.745a$ [i.e. $c/2 = \frac{1}{2}(1.49a)$], thereby bringing these Fe atoms into close contact and increasing the metallic bonding in the c direction. Simple quantitative calculations of the effect of changing the c/a ratio are difficult to make since it is not readily possible to distinguish between, for example, an increase in a and a decrease in c , either of which could cause the same effect on the c/a ratio.

1.17.4 Caesium chloride (CsCl)

The unit cell of CsCl is shown in Fig. 1.36. It is a primitive cube, containing Cl at corners and Cs at the body centre, or vice versa (note that it is *not* body centred cubic since there are different ions at corner and body centre positions). The coordination numbers of both Cs and Cl are eight with inter-atomic distances of $0.866a$, Table 1.11. The CsCl structure is not *cp*. In a *cp* structure, each anion has 12 other anions as next nearest neighbours whereas in CsCl, each Cl has only six Cl^- ions as next nearest neighbours (arranged octahedrally). Some compounds with the CsCl structure are given in Table 1.14. They fall into two groups, halides of large monovalent elements and a variety of intermetallic compounds.

Lanthanum hexaboride, LaB_6 , has the CsCl structure in which Cl is replaced by the octahedral cluster anion B_6^{3-} . LaB_6 has a low work function (i.e. it ionises easily) of 2.5 eV, very high electron

Table 1.14 Some compounds with the CsCl structure

Compound	$a/\text{\AA}$	Compound	$a/\text{\AA}$	Compound	$a/\text{\AA}$	Compound	$a/\text{\AA}$
CsCl	4.123	NH_4Br	4.0594	CuPd	2.988	AlNi	2.881
CsBr	4.286	TlCl	3.8340	AuMg	3.259	LiHg	3.287
CsI	4.5667	TlBr	3.97	AuZn	3.19	MgSr	3.900
CsCN	4.25	TlI	4.198	AgZn	3.156		
NH_4Cl	3.8756	CuZn	2.945	LiAg	3.168		

emissivity, metallic conductivity and is stable in vacuum. These properties enable it to be used as a hot cathode in the electron gun in electron microscopes: advantages are that it has higher brightness and longer lifetime than traditional tungsten filament cathodes.

Although CsCl is not a *cp* structure, there is a link between it and the fluorite structure, which can be described as a primitive cubic array of anions with cations in *alternate* cube body centres, Fig. 1.34; in CsCl, *all* body centres are occupied.

1.17.5 Other AX structures

There are five main AX structure types, rock salt, CsCl, NiAs, sphalerite and wurtzite, each of which is found in a large number of compounds. There are also several less common AX structures. Some are distorted variants of one of the main structure types, e.g.:

- FeO at low temperatures, <90 K, has a rock salt structure with a slight rhombohedral distortion (the α angle is increased from 90 to 90.07° by a slight compression along one threefold axis). This rhombohedral distortion is associated with magnetic ordering in FeO at low temperatures (see Chapter 9).
- TiF has a rock salt-related structure in which the *fcc* cell is distorted into a face centred orthorhombic cell by changing the lengths of all three cell axes by different amounts. The distortion arises because, in this structure, Ti^+ (Xe core) $4f^{14}5d^{10}6s^2$ is a non-spherical cation exhibiting a stereochemically-active inert (or lone) pair effect.
- NH_4CN has a distorted CsCl structure (as in NH_4Cl) in which the CN^- ions do not assume spherical symmetry but are oriented parallel to face diagonals. This distorts the symmetry to tetragonal and effectively increases *a* relative to *c*.

Other AX compounds have completely different structures, e.g.:

- Compounds of the d^8 ions, Pd and Pt (in PdO, PtS, etc.), often have a square planar coordination for the cation, associated with the Jahn-Teller effect; d^9 ions also show this effect, e.g. Cu in CuO.
- Compounds of heavy *p*-block atoms in their lower oxidation states (e.g. Ti^+ , Pb^{2+} , Bi^{3+}) often have distorted polyhedra in which the cation exhibits the *inert pair effect*, as with TiF, above. Thus, in PbO and SnO the M^{2+} ion has four O^{2-} neighbours to one side giving a square pyramidal arrangement, Fig. 3.14. InBi is similar with Bi^{3+} showing the inert pair effect and irregular coordination.

1.17.6 Rutile (TiO_2), cadmium iodide (CdI_2), cadmium chloride (CdCl_2) and caesium oxide (Cs_2O)

The title structures, together with fluorite, represent the main AX_2 structure types. The unit cell of rutile is tetragonal $a = b = 4.594 \text{ \AA}$, $c = 2.958 \text{ \AA}$, and is shown in Fig. 1.37(a). The Ti positions, two per cell, are fixed at the corner 0, 0, 0 and body centre $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The O positions, four per cell, have general coordinates $x, x, 0$; $1-x, 1-x, 0$; $\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}$; $\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}$, with a variable parameter, *x*, whose value must be determined experimentally. Crystal structure determination and refinement gave the *x* values listed beneath Fig. 1.37(a) for the four oxygens in the unit cell, i.e. with $x \simeq 0.3$.

The body centre Ti at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is coordinated octahedrally to six oxygens. Four of these, two at $z = 0$ and two at $z = 1$ directly above the two at $z = 0$, are coplanar with Ti. Two oxygens at $z = \frac{1}{2}$ are collinear with Ti and form the axes of the octahedron. The corner Ti are also octahedrally coordinated but the orientation of their octahedra is different, Fig. 1.37(b). The oxygens are coordinated trigonally to three Ti, e.g. oxygen at 0 in (a) is coordinated to Ti at the corner, at the body centre and at the body centre of the cell below.

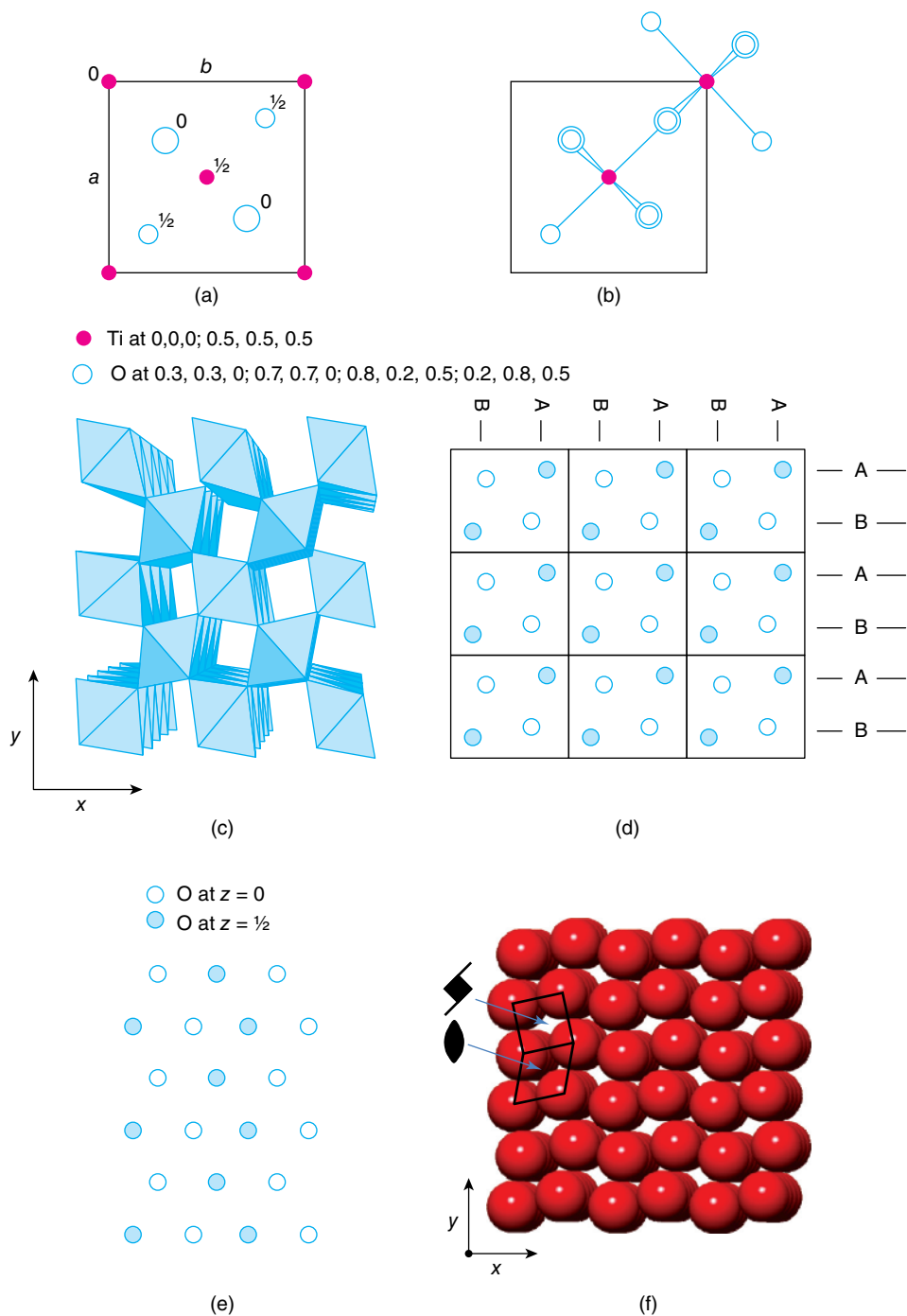


Figure 1.37 The rutile structure, TiO_2 : (a) the unit cell; (b) TiO_6 octahedra in two orientations in the unit cell; (c) an array of octahedra in 3D; (d) oxygen atoms in zig-zag arrangement; (e) oxygen atoms in an ideal hcp structure in projection; (f) [001] projection of the structure showing fourfold screw axes and twofold rotation axes.

The TiO_6 octahedra link by sharing edges and corners to form a 3D framework. Consider the TiO_6 octahedron in the centre of the cell in Fig. 1.37(b); a similar octahedron in identical orientation occurs in the cells above and below such that octahedra in adjacent cells share edges to form infinite chains parallel to c . For example, Ti at $z = +\frac{1}{2}$ and $-\frac{1}{2}$ in adjacent cells are both coordinated to two oxygens at $z = 0$. Chains of octahedra are similarly formed by the octahedra centred at the corners of the unit cell. The two types of chains, which differ in orientation about c by 90° and which are $c/2$ out of step with each other, link by their corners to form a 3D framework, Fig. 1.37(c).

The rutile structure is also commonly described as a distorted *hcp* oxide array with half the octahedral sites occupied by Ti. A 3×3 block of unit cells is shown in Fig. 1.37(d) with only the oxygen positions marked. Corrugated *cp* layers occur, both horizontally and vertically. This contrasts with the undistorted *hcp* arrangement (e), in which the layers occur in one orientation only (horizontally).

The octahedral sites between two *cp* layers in an ideal *hcp* anion array are shown in the projection in Fig. 1.38(a). While all these sites are occupied in NiAs [Fig. 1.35(h)], only half are occupied in rutile and in such a manner that alternate horizontal rows of octahedral sites are full and empty. The orientation of the tetragonal unit cell in rutile is shown. Parallel to the tetragonal c axis, horizontally, the TiO_6 octahedra share edges. This is shown in Fig. 1.38(b) for two octahedra with oxygens 1 and 2 forming the common edge.

An alternative, and more accurate, way to describe the packing arrangement of oxide ions in rutile is as a slightly distorted version of a different type of packing called *tetragonal packing* (*tp*), characterised by a sphere coordination number of 11 which contrasts with *hcp* and *ccp* which have a packing sphere coordination number of 12. The symmetry of *tp* is quite different to that of *hcp* since *tp* is characterised by fourfold rotational symmetry without any threefold symmetry whereas *hcp* has no fourfold symmetry but is characterised by threefold (or sixfold) symmetry. An [001] projection of the rutile structure is shown in Fig. 1.37(f); the fourfold symmetry shown is not a simple rotation axis but is a fourfold screw axis in which the structure rotates by 90° and translates by half the unit cell in the [001] direction.

The bond lengths in TiO_2 may be calculated readily; for the Ti–O bond between Ti at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and O at $(0.3, 0.3, 0)$ the difference in both x and y coordinates of Ti and O is $(\frac{1}{2} - 0.3)a = 0.92 \text{ \AA}$. From a right-angled triangle calculation, the Ti–O distance in projection down c [Fig. 1.37(a)] is $(0.92^2 + 0.92^2)^{1/2}$. However, Ti and O have a difference in c height of $(\frac{1}{2} - 0)c = 1.48 \text{ \AA}$ and

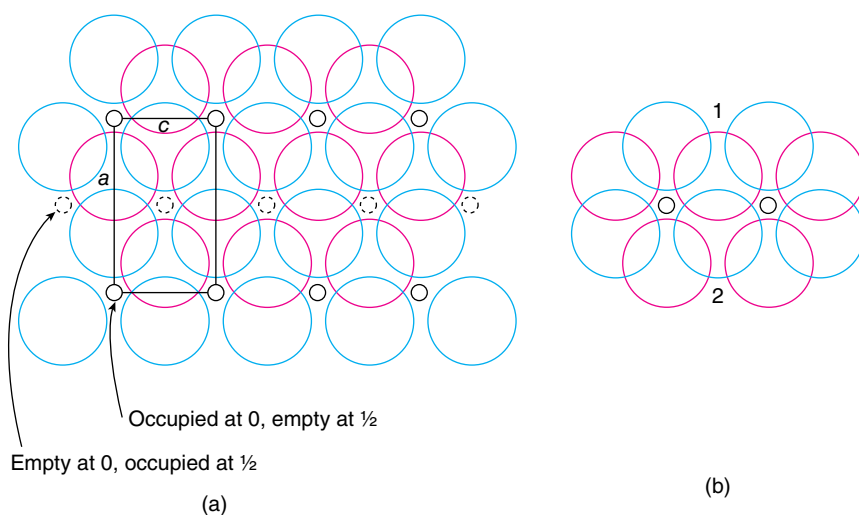


Figure 1.38 (a) Octahedral sites in an ideal *hcp* array; (b) edge-sharing octahedra.

Table 1.15 Some compounds with the rutile structure

Compound	<i>a</i> /Å	<i>c</i> /Å	<i>x</i>	Compound	<i>a</i> /Å	<i>c</i> /Å	<i>x</i>
TiO ₂	4.5937	2.9581	0.305	CoF ₂	4.6951	3.1796	0.306
CrO ₂	4.41	2.91		FeF ₂	4.6966	3.3091	0.300
GeO ₂	4.395	2.859	0.307	MgF ₂	4.623	3.052	0.303
IrO ₂	4.49	3.14		MnF ₂	4.8734	3.3099	0.305
β-MnO ₂	4.396	2.871	0.302	NiF ₂	4.6506	3.0836	0.302
MoO ₂	4.86	2.79		PdF ₂	4.931	3.367	
NbO ₂	4.77	2.96		ZnF ₂	4.7034	3.1335	0.303
OsO ₂	4.51	3.19		SnO ₂	4.7373	3.1864	0.307
PbO ₂	4.946	3.379		TaO ₂	4.709	3.065	
RuO ₂	4.51	3.11		WO ₂	4.86	2.77	

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the Ti–O bond length is therefore equal to $(0.92^2 + 0.92^2 + 1.48^2)^{1/2} = 1.97$ Å. The axial Ti–O bond length between, for example, Ti($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and O(0.8, 0.2, 0.5) is easier to calculate because both atoms are at the same *c* height. It is equal to $[2(0.3 \times 4.594)^2]^{1/2} = 1.95$ Å.

Two main groups of compounds exhibit the rutile structure, Table 1.15: oxides of tetravalent metals and fluorides of divalent metals. In both cases, the metals are too small to have eight coordination and form the fluorite structure. The rutile structure may be regarded as essentially ionic.

The CdI₂ structure is nominally similar to that of rutile because it has an *hcp* anion array with also, half of the octahedral sites occupied by M²⁺ ions. The manner of occupancy of the octahedral sites is quite different, however; entire layers of octahedral sites are occupied and these alternate with layers of empty sites, Fig. 1.39. CdI₂ is therefore a layered material in both its crystal structure and properties, in contrast to rutile, which has a more rigid, 3D character.

Two I layers in a *hcp* array are shown in Fig. 1.39(a) with the octahedral sites in between occupied by Cd. To either side of the I layers, the octahedral sites are empty. Compare this with NiAs [Fig. 1.35(d) and (h)] which has the same anion arrangement but with all octahedral sites occupied. The layer stacking sequence along *c* in CdI₂ is shown schematically in Fig. 1.39(b) and emphasises the layered nature of the CdI₂ structure: I layers form an ... ABABA ... stacking sequence. Cd occupies octahedral sites which may be regarded as the C positions relative to the AB positions for I. The CdI₂ structure is, effectively, a sandwich structure in which Cd²⁺ ions are sandwiched between layers of I[−] ions; adjacent sandwiches are held together by weak van der Waals bonds between the I layers. In this sense, CdI₂ has certain similarities to molecular structures. For example, solid CCl₄ has strong C–Cl bonds *within* the molecule but only weak Cl–Cl bonds *between* adjacent molecules. Because the intermolecular forces are weak, CCl₄ is volatile with low melting and boiling points. In the same way, CdI₂ may be regarded as an infinite sandwich ‘molecule’ in which there are strong Cd–I bonds within the molecule but weak van der Waals bonds between adjacent molecules.

The coordination of I in CdI₂ is shown in Fig. 1.39(c). An I at $c = \frac{1}{4}$ (shaded) has three close Cd neighbours to one side at $c = 0$. The next nearest neighbours are 12 I that form the *hcp* array: six are in the same plane, forming a hexagonal ring, at $c = \frac{1}{4}$; three are at $c = -\frac{1}{4}$ and three at $c = \frac{3}{4}$.

The layered nature of CdI₂ is emphasised further in a model of polyhedra: CdI₆ octahedra link at their edges to form infinite sheets, Fig. 1.39(d), but there are no direct polyhedral linkages between adjacent sheets. A self-supporting, 3D model of octahedra cannot be made for CdI₂, therefore. Some compounds which have the CdI₂ structure are listed in Table 1.16. It occurs mainly in transition metal iodides, bromides, chlorides and hydroxides. TiS₂ has the CdI₂ structure and was considered as a potential

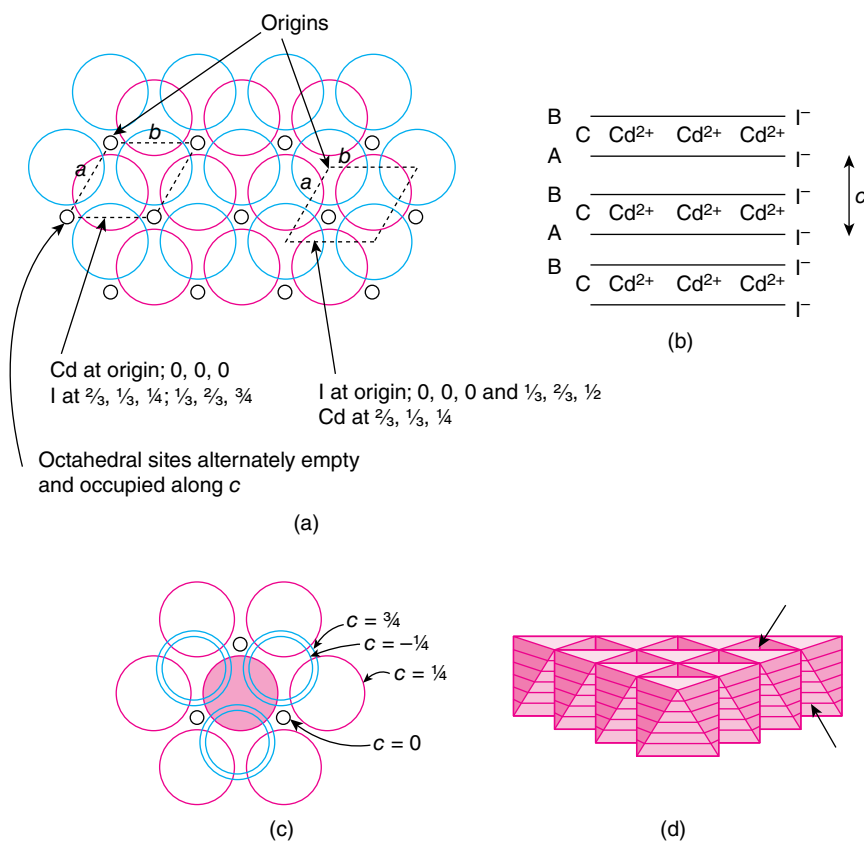


Figure 1.39 The CdI_2 structure: (a) the basal plane of the hexagonal unit cell is outlined, with two possible choices of origin; (b) the layer stacking sequence; (c) the coordination environment of I; (d) a layer of close packed octahedra; empty tetrahedral sites are arrowed.

Table 1.16 Some compounds with the CdI_2 structure

Compound	$a/\text{\AA}$	$c/\text{\AA}$	Compound	$a/\text{\AA}$	$c/\text{\AA}$
CdI_2	4.24	6.84	VBr_2	3.768	6.180
CaI_2	4.48	6.96	TiBr_2	3.629	6.492
CoI_2	3.96	6.65	MnBr_2	3.82	6.19
FeI_2	4.04	6.75	FeBr_2	3.74	6.17
MgI_2	4.14	6.88	CoBr_2	3.68	6.12
MnI_2	4.16	6.82	TiCl_2	3.561	5.875
PbI_2	4.555	6.977	VCl_2	3.601	5.835
ThI_2	4.13	7.02	Mg(OH)_2	3.147	4.769
TiI_2	4.110	6.820	Ca(OH)_2	3.584	4.896
TmI_2	4.520	6.967	Fe(OH)_2	3.258	4.605
VI_2	4.000	6.670	Co(OH)_2	3.173	4.640
YbI_2	4.503	6.972	Ni(OH)_2	3.117	4.595
$\text{ZnI}_2(\text{l})$	4.25	6.54	Cd(OH)_2^2	3.48	4.67

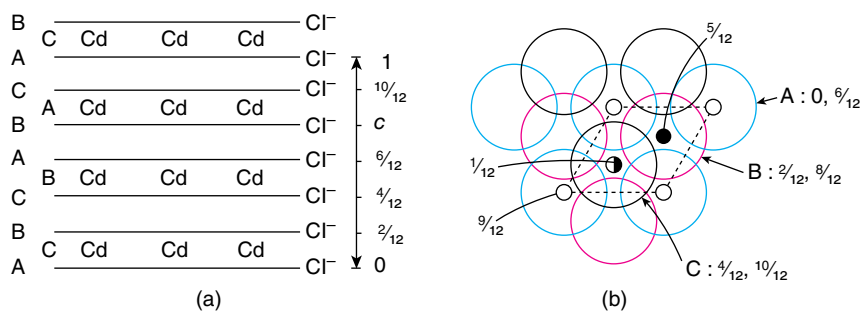


Figure 1.40 The CdCl_2 structure.

intercalation host cathode for use in lithium batteries (see Section 8.4): Li^+ ions are able to diffuse into the empty layers that separate adjacent TiS_2 sheets at the same time as electrons enter, and migrate through, the $3d$ band composed of d_{xy} orbitals on Ti.

The CdCl_2 structure is closely related to that of CdI_2 and differs only in the nature of the anion packing: Cl^- ions are *ccp* in CdCl_2 whereas I^- is *hcp* in CdI_2 .

The CdCl_2 structure may be represented by a hexagonal unit cell, although a smaller rhombohedral cell can also be chosen. The base of the hexagonal cell is of similar size and shape to that in CdI_2 but its c axis is three times longer than c in CdI_2 . This is because in CdCl_2 , the Cd positions, and the CdCl_6 octahedra, are staggered along c and give rise to a three-layer repeat for Cd (CBA) and a six-layer repeat for Cl (ABCABC), Fig. 1.40. In contrast, in CdI_2 , the Cd positions and the CdI_6 octahedra are stacked on top of each other and the c repeat contains only two I layers (AB) and one Cd layer (C).

The unit cell of CdCl_2 in projection down c is shown in Fig. 1.40(b). Cl layers occur at $c = 0$ (A), $2/12$ (B) and $4/12$ (C), and this sequence is repeated at $c = 6/12$, $8/12$ and $10/12$. Between those Cl layers at 0 and $2/12$, Cd occupies octahedral sites at $1/12$. However, the octahedral sites between Cl layers at $2/12$ and $4/12$ are empty (these sites, at $c = 3/12$, are directly below Cd at $9/12$).

The CdCl_2 structure is layered, similarly to CdI_2 , and many of the comments made about structure and bonding in CdI_2 apply equally well. It also occurs with a variety of transition metal halides (Table 1.17).

The structure of Cs_2O is most unusual as it is anti- CdCl_2 . Cs forms *ccp* layers and O occupies the octahedral sites between alternate pairs of Cs layers. This raises some interesting questions because Cs is the most electropositive element and Cs salts are usually regarded as highly ionic. However, the structure of Cs_2O clearly shows that Cs is not surrounded by oxygens, as expected for an ionic structure, but has only three O neighbours, all located at one side. The structure is held together, in 3D, by bonding between Cs in adjacent layers.

Table 1.17 Some compounds with the CdCl_2 structure

Compound	$a/\text{\AA}$	$c/\text{\AA}$	Compound	$a/\text{\AA}$	$c/\text{\AA}$
CdCl_2	3.854	17.457	NiCl_2	3.543	17.335
CdBr_2	3.95	18.67	NiBr_2	3.708	18.300
CoCl_2	3.544	17.430	NiI_2	3.892	19.634
FeCl_2	3.579	17.536	ZnBr_2	3.92	18.73
MgCl_2	3.596	17.589	ZnI_2	4.25	21.5
MnCl_2	3.686	17.470	Cs_2O^a	4.256	18.99

^a Cs_2O has an anti- CdCl_2 structure.

R. W. G. Wyckoff, *Crystal Structures*, Vols 1 to 6, Wiley (1971).

It may be that the structure of Cs_2O does not reflect any peculiar type of bonding but rather that it is the only structural arrangement which is feasible for a compound of this formula and for ions of this size. Thus, from the formula, the coordination numbers of Cs and O must be in the ratio of 1:2; since Cs^+ is considerably larger than O^{2-} , the maximum possible coordination number of O by Cs may be six, which then leads to a coordination number of three for Cs.

A related question arises with the structures of the other alkali metal oxides, in particular K_2O and Rb_2O . These are antifluorites with coordination numbers of four and eight for M and O, respectively. These are unusual since Rb is normally far too large to enter into tetrahedral coordination with O. However, if there is no feasible alternative structure, then perhaps Rb has no choice but to enter the tetrahedral sites. With Cs_2O , tetrahedral coordination of Cs by O is probably impossible, hence its structure is anti- CdCl_2 rather than antifluorite. Thermodynamic data qualitatively support these observations; neither Cs_2O nor Rb_2O is very stable: instead, they oxidise readily to give peroxides, M_2O_2 , and superoxides, MO_2 , which contain much larger anions. Further details of alkali oxides, including suboxides, are given in Chapter 16.

1.17.7 Perovskite

This very important structure type, of general formula ABX_3 and typified by SrTiO_3 , has a primitive cubic unit cell, shown in Fig. 1.41 as a projection down one axis (a, b) and as an oblique projection (c, d). There are two ways of drawing the unit cell of perovskite. One, (a), contains Ti at the cube corners (coordinates 0, 0, 0), Sr at the body centre ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and O at the edge centres ($\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2}$). The other, (b), contains Sr at the corners, Ti at the body centre and O at the face centres. These two descriptions are interchangeable and are simply related by translation of the origin half way along the cube body diagonal. The octahedral coordination environment of Ti is seen in (c, d) and interatomic distances calculated by simple geometry. The bond distance $\text{Ti}-\text{O} = a/2 = 1.953 \text{ \AA}$. Sr is equidistant from 12 oxygens and the $\text{Sr}-\text{O}$ distance equals half the diagonal of any cell face, i.e. $a/\sqrt{2}$ or $2.76 \text{ \AA}$.

Each O has two Ti as its nearest cationic neighbours, at $1.953 \text{ \AA}$, and four Sr, coplanar with O at $2.76 \text{ \AA}$. However, eight other oxygens are at the same distance, $2.76 \text{ \AA}$, as the four Sr. It is debatable whether the O coordination number is best regarded as two (linear) or as six (a grossly squashed octahedron with two short and four long distances) or as 14 (six cations and eight oxygens). No firm recommendation is made!

Having arrived at the unit cell of SrTiO_3 , the atomic coordinates, coordination numbers and bond distances, we now wish to view the structure on a rather larger scale and ask the following questions. Does it have *cp* anions? Is it a framework structure? Answers are as follows.

Perovskite does not contain *cp* oxide ions as such but O and Sr, considered together, do form a *ccp* array with the layers parallel to the $\{111\}$ planes, Fig. 1.41(c) and (e). To see this, compare the perovskite structure with Sr at the origin, (d), with that of NaCl (Fig. 1.2). The latter contains Cl (or Na, depending on the choice of origin) at the corner and face centre positions of the cell and is *ccp*. By comparison, perovskite contains O at the face centres and Sr at the corner. The structure of the mixed Sr, O *cp* layers in perovskite is such that one-quarter of the atoms are Sr, arranged in a regular fashion, Fig. 1.41(e). It is quite common for fairly large cations, such as Sr^{2+} ($r = 1.1 \text{ \AA}$), to play apparently different roles in different structures, i.e. as 12-coordinate packing ions, as in SrTiO_3 perovskite, or as octahedrally coordinated cations within a *cp* oxide array, as in SrO (rock salt structure).

The formal relation between rock salt and perovskite also includes the Na and Ti cations as both occupy octahedral sites: in NaCl, all octahedral sites are occupied (corners and face centres), but in perovskite only one-quarter [the corner sites in (a)] are occupied. The other octahedral sites at the face

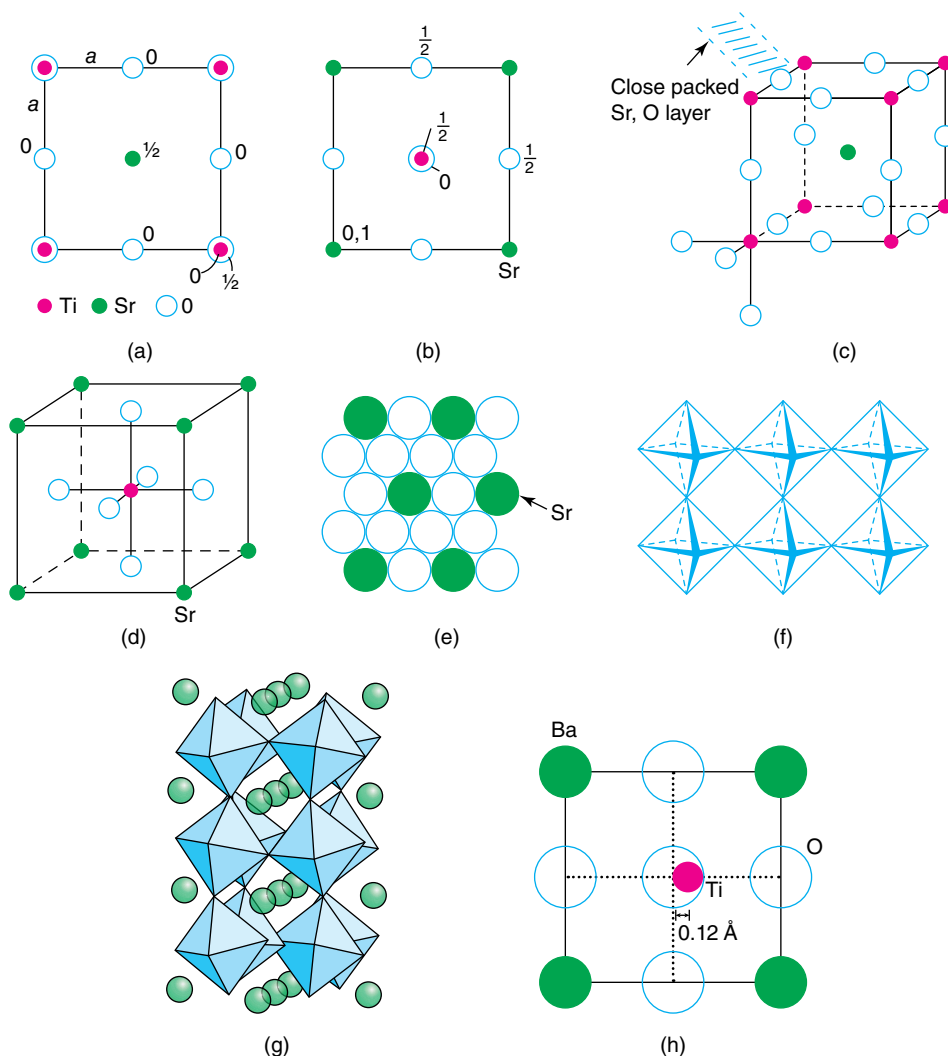
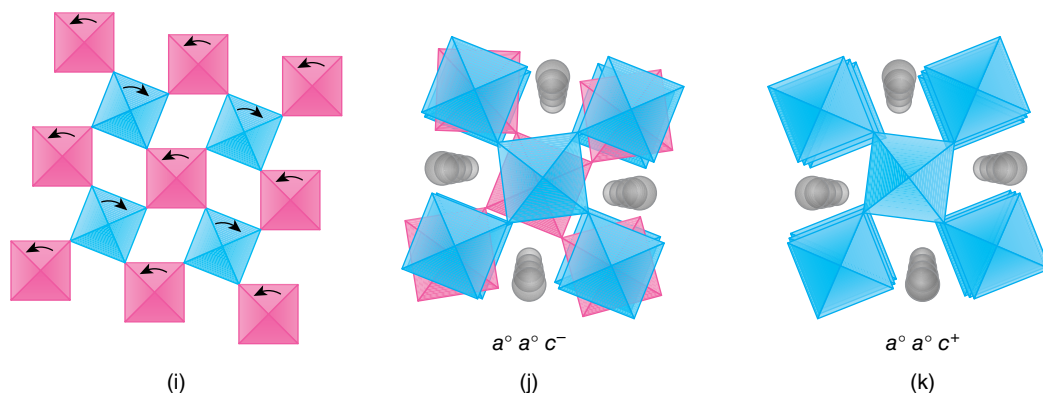


Figure 1.41 (a–d) The perovskite structure of SrTiO_3 . (e) A close packed Sr, O layer. (f) A layer of corner-sharing octahedra. (g) GdFeO_3 structure. (h) Structure of tetragonal BaTiO_3 projected onto the ac plane. Note, the origin of the unit cell is shifted to coincide with Ba rather than with Ti as in (b). Adapted with permission from M. T. Weller, *Inorganic Materials Chemistry*, © 1994 Oxford University Press. (i) Coupled rotation of octahedra in 2D corner-sharing sheets. (j, k) View looking down the c axis of $a^0a^0c^-$ and $a^0a^0c^+$ with the A-site cations shown as spheres and the B-site cations located at the centre of the octahedra. Based on M. W. Lufaso and P. M. Woodward, *Acta Cryst. Sect. B Struct. Sci.* 57, 725 (2001).

centres (c) have oxygen atoms at four corners but Sr at the other two corners and therefore, these sites are rarely occupied in perovskite-related structures.

Perovskite is also regarded as a framework structure with corner-sharing TiO_6 octahedra and with Sr in 12-coordinate interstices. The octahedral coordination of one Ti is shown in Fig. 1.41(c) and (d); each O of this octahedron is shared with one other octahedron, such that the Ti–O–Ti arrangement is linear. Thus, octahedra link at their corners to form sheets (f), and neighbouring sheets link similarly to form a 3D framework.

**Figure 1.41 (Continued)**

Several hundred oxides and halides form the perovskite structure; a selection is given in Table 1.18. The oxides contain two cations whose combined oxidation state is six. Thus, possible combinations are +I, +V as in KNbO_3 , +II, +IV as in CaTiO_3 and +III, +III as in LaGaO_3 . The 12-coordinate A site cations are, of course, much larger than the six-coordinate B site cations.

As well as the cubic perovskite structure, described so far, a variety of distorted, non-cubic structures exist. These lower-symmetry structures often form on cooling the high-temperature cubic structure and the framework of octahedra may be slightly twisted or distorted. An example is shown in Fig. 1.41(g) for the structure of GdFeO_3 . The reasons for the structural distortions are associated with the size requirements of the 12-coordinate A and six-coordinate B sites and whether adjustments to the structure are required to accommodate different-sized cations. Also, more complex perovskite structures form in which two different cations may occupy either the A or B sites, giving a range of cation ordering possibilities.

1.17.7.1 Tolerance factor

The reason why structural distortions occur in many perovskites is that the A and/or B atoms are not exactly the right size to fit the sites generated by the remainder of the structure. In an oxide with the ideal, cubic perovskite structure, the bond lengths are related to the unit cell dimension, a , by

$$a = \sqrt{2}r_{\text{A-O}} = 2r_{\text{B-O}} \quad (1.6)$$

Since bond lengths for each element, oxidation state and coordination number usually fall within closely defined ranges (Appendix F), it is possible to use equation (1.6) to see how well the sizes

Table 1.18 Some compounds with the perovskite structure

Compound	$a/\text{\AA}$	Compound	$a/\text{\AA}$	Compound	$a/\text{\AA}$
KNbO_3	4.007	LaFeO_3	3.920	CsCaF_3	4.522
KTaO_3	3.9885	LaGaO_3	3.875	CsCdBr_3	5.33
KIO_3	4.410	LaVO_3	3.99	CsCdCl_3	5.20
NaNbO_3	3.915	SrTiO_3	3.9051	CsHgBr_3	5.77
NaWO_3	3.8622	SrZrO_3	4.101	CsHgCl_3	5.44
LaCoO_3	3.824	SrHfO_3	4.069		
LaCrO_3	3.874	SrSnO_3	4.0334		

of a particular A, B combination meet the requirements for an undistorted, ideal perovskite. The degree to which the sizes depart from equation (1.6) is given by a *tolerance factor*, t :

$$t = \frac{\sqrt{2}r_{A-O}}{2r_{B-O}} \quad (1.7)$$

In practice, there is some flexibility over bond lengths and usually, a cubic perovskite forms with t in the range $0.9 < t < 1.0$.

For $t > 1$, the B site is larger than required. If t is only slightly greater than 1.0, the structure distorts but is still basically a perovskite as in BaTiO_3 , $t = 1.06$. There may also be a change in the stacking sequence of the AX_3 close packed layers from *ccp* to *hcp* to give the family of hexagonal perovskites typified by BaNiO_3 . For larger departures from $t = 1.0$, however, the B ion demands a smaller site, of lower coordination number, and the structure changes completely, as in BaSiO_3 which has tetrahedral Si.

For smaller tolerance factors, $0.85 < t < 0.90$, several different kinds of structural distortion occur because now, as in GdFeO_3 , the A cation is too small for its site. These distortions generally involve tilting and rotation of the BO_6 octahedra as shown in Fig. 1.41(g). Consequently some, or all, of the B–O–B linkages are no longer linear but are zig-zag, which has the effect of reducing the size of the A cation site.

1.17.7.2 BaTiO_3

BaTiO_3 is tetragonal at room temperature, $a = 3.995$, $c = 4.034$ Å, with the structure shown in projection on the ac plane in Fig. 1.41(h). Since Ti is slightly too small for its octahedral site, it displaces by about 6% of the Ti–O distance towards one of the corner oxygens; Ba^{2+} ions also undergo a smaller displacement in the same direction. This reduces the coordination of Ti to five (square pyramidal) and, to have reasonable Ti–O bond lengths, the structure also contracts slightly in the ab plane [not shown in (h)].

Ti atoms in adjacent unit cells undergo a similar displacement in the same direction and the resulting structure has a large dipole moment due to the separation of positive and negative charge centres. It is possible to flip the orientation of the dipoles: under the action of an applied electric field, the Ti atoms move through the centre of the octahedral site towards one of the other corner oxygens. This ready reversibility gives the structure high polarisability and a high permittivity (or dielectric constant) and is responsible for the property of ferroelectricity (see Section 8.7).

1.17.7.3 Tilted perovskites: Glazer notation

We saw in Fig. 1.41(g) how octahedra can tilt or rotate cooperatively leaving the BO_6 octahedra essentially unchanged but reducing the size of the A site and its coordination number. Thus, in GdFeO_3 , the A site is eight-coordinate instead of 12-coordinate. Such structural distortions occur when the A cation is too small to occupy comfortably the 12 coordinate sites created by the array of corner-sharing BO_6 octahedra and, consequently, the octahedral rotations allow a reduction in the A–O bond length.

A wide variety of structural distortions occur in perovskites whose tolerance factor is less than unity. The most common distortion involves tilting or rotation of octahedra about one or more of the three axes of the octahedron. This is a cooperative process since octahedra link at their corners to adjacent octahedra in the 3D framework and, for instance, clockwise rotation of an octahedron about one axis causes anticlockwise rotation of the adjacent octahedra, Fig. 1.41(i). For the example shown, octahedra which form sheets in the xy plane undergo coupled rotations about the z axis.

Similar coupled rotations may or may not also occur about x and y axes. Within a given sheet of octahedra, the octahedral rotations cannot occur independently of each other since clockwise rotation of one octahedron demands anticlockwise rotation of the four adjacent, corner-linked octahedra. However, between adjacent planes in, for instance, the z direction there is no automatic coupling between adjacent planes. This gives rise to two commonly observed possibilities in which the octahedral rotations in adjacent planes are identical or the exact opposite.

These two possibilities are illustrated in Fig. 1.41(j) and (k). Detailed analysis has shown that 15 different tilt systems are theoretically possible and classification schemes have been developed by Glazer and Alexandrov. The widely used Glazer method is as follows:

1. Starting with the undistorted cubic perovskite, the three axes of the octahedron are given the letters a , b and c . If the degree of any rotation about all three axes is the same, they are labelled. aaa ; if rotation about one axis is different, for example about c , the labelling is aac .
2. Each of the three letters carries a superscript; if there is no rotation about that axis, the superscript is ^{0} ; if the rotation between adjacent planes of octahedra is the same, and in-phase, the superscript is $^+$; if the rotation between adjacent planes is in the opposite sense, the superscript is $^-$.

For the examples shown in Fig. 1.41(j) and (k), rotation of octahedra about only one axis is shown and therefore the two possibilities are labelled $a^0a^0c^-$ and $a^0a^0c^+$. These are easy to appreciate since the rotations are about one axis only. For cases involving rotation about all three axes, detailed scrutiny of the structures may be needed; thus for GdFeO_3 , the tilt system is $a^-b^+a^-$ although this may not be readily apparent from diagram (g). The different tilt systems give rise to structures with unit cells that are usually no longer cubic. For instance, GdFeO_3 has a larger orthorhombic unit cell with $a \approx c \approx \sqrt{2}a_p$; $b = 2a_p$, where a_p refers to the parent cubic perovskite cell. Hence the unit cell of GdFeO_3 is four times larger than the cubic perovskite cell and contains four formula units. The $a^-b^+a^-$ tilt system is the most commonly observed distorted perovskite structure. Another common tilt system is $a^-a^-a^-$, which leads to a trigonal unit cell; it is shown by phases such as LaBO_3 ; $B = \text{Co}, \text{Ni}, \text{Cu}, \text{Al}, \text{and Ga}$.

An interesting tilt system which retains cubic symmetry is $a^+a^+a^+$ and is shown by a family of phases with general formula $A'A''_3\text{B}_4\text{O}_{12}$ with $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ as the most studied example. The TiO_6 octahedra undergo similar coupled rotations about all three axes; a consequence of this is that three-quarters of the A sites change their coordination from 12-coordinate to square planar. This structure is shown by a number of compounds in which Cu, Mn and Ni occupy the square planar A'' sites, Fig. 1.42(a) discussed next.

1.17.7.4 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, CCTO

There is much recent interest in a family of perovskite-related phases typified by $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ because of the possibility that they exhibit a giant dielectric constant. It is now known that the measured high permittivities are not a property of the bulk crystals but are associated with the grain–grain contacts in ceramics. The high permittivity is a consequence of the geometry of the regions responsible since the capacitance of a region is proportional to its area but inversely proportional to its thickness. CCTO has a most unusual crystal structure since the A sites of perovskite contain intermediate-size Ca cations whose coordination number is reduced to eight by tilting of TiO_6 octahedra together with square planar CuO_4 units. The crystal structure is shown in Fig. 1.42(a) in which the left-hand diagram emphasises tilting of the TiO_6 octahedra and the right-hand diagram shows the square planar Cu-based units which have three equivalent orientations in the cubic unit cell. In Glazer notation, the tilt system for CCTO is $a^+a^+a^+$.

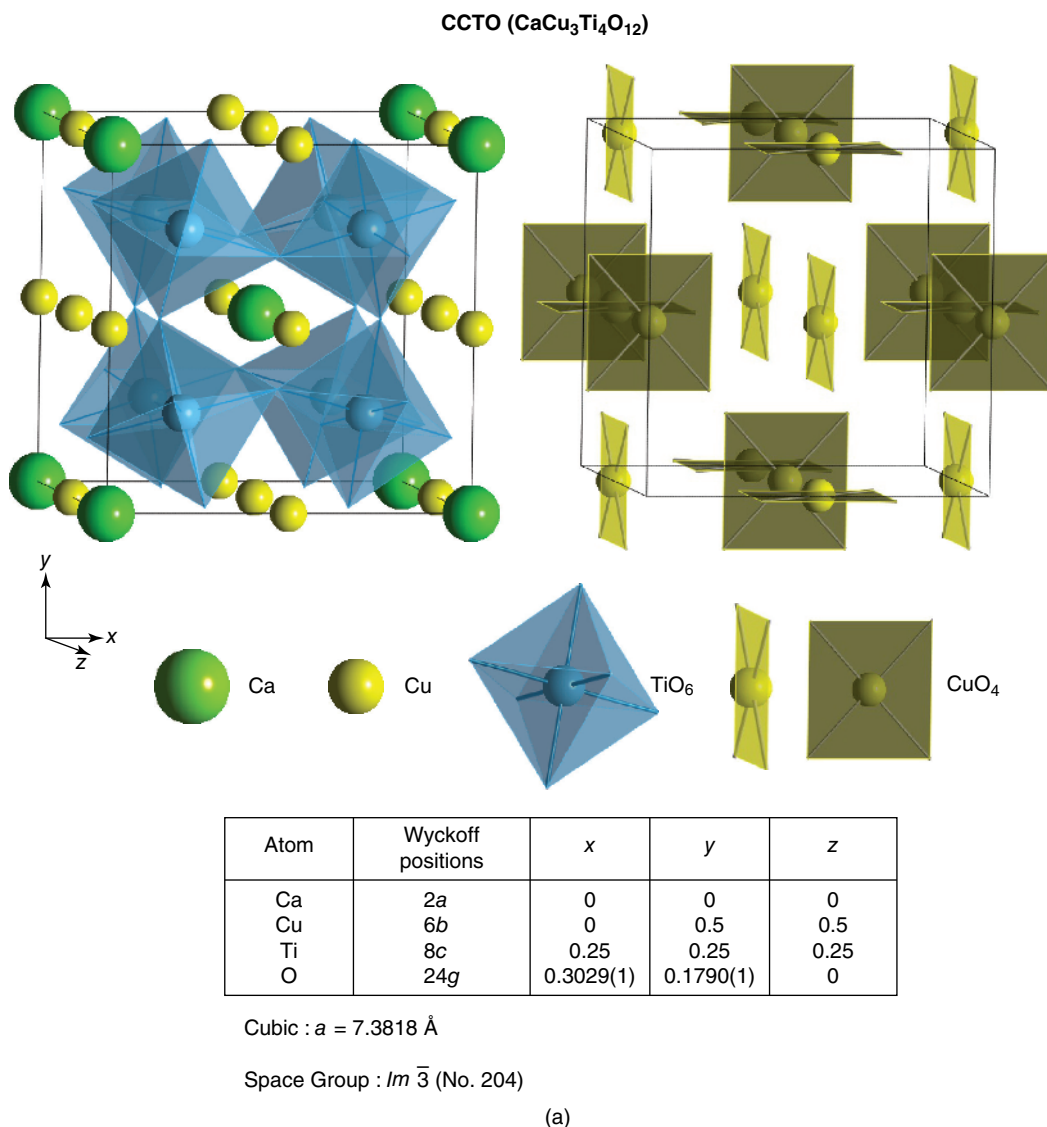
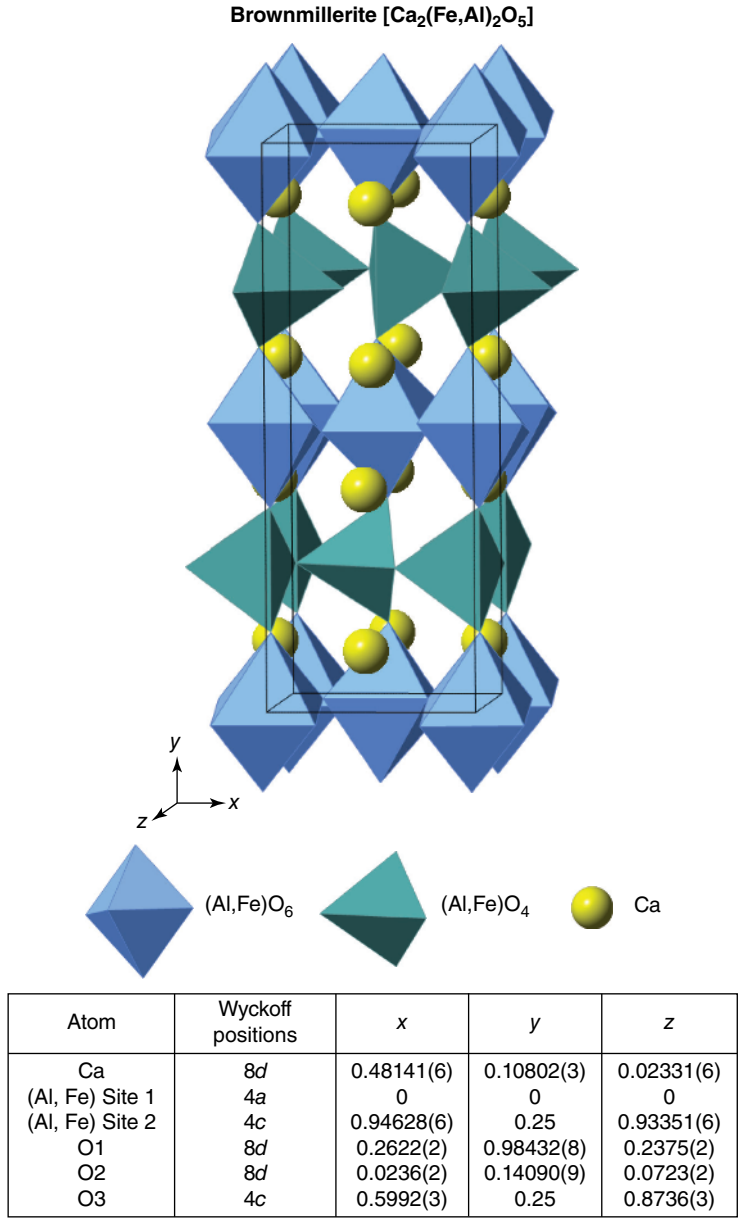


Figure 1.42 (a) Crystal structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Modified from E. S. Bozin et al., J. Phys. Condens. Matter 16, S5091 (2004). (b) The brownmillerite structure. Modified from G. J. Redhammer et al., Amer. Miner. 89, 405 (2004). (c) The $\text{La}_2\text{Ni}_2\text{O}_5$ structure. Modified from J. A. Alonso et al., J. Phys. Cond. Matter 9, 6417 (1997). (d, e) A 2D section through the perovskite structure showing corner-linked BO_6 octahedra in which different cations B, B' may be either (d) disordered or (e) ordered: A-site cations are omitted for clarity; (f) structure-field map showing the effect of A and B sizes on structure type; (g) crystal structure of BaNiO_3 as an [001] projection with some NiO_6 octahedra emphasised: space group $P6_3/\text{mmc}$; $a = 5.629$, $c = 4.811 \text{ \AA}$; atomic positions Ba (2d) $1/3, 2/3, 3/4; 2/3, 1/3, 1/4$; Ni (2a) $0, 0, 0; 0, 0, 1/2$; O 6(h) $x, 2x, 1/4$; $x = 0.1462$; (h) one column of face-sharing octahedra parallel to c. O and Ba positions together form BaO_3 layers; (i–l) different polytypes and labelling notations. For each, h and c layers and the number of layers in the unit cell are shown: (i) $(\text{ch})_2 \text{BaRuO}_3$, (j) $(\text{cch})_2 \text{BaTiO}_3$, (k) $(\text{cchc})_2 \text{Ba}_8\text{Ta}_4\text{Ti}_3\text{O}_{24}$, (l) $(\text{cchcc})_2 \text{Ba}_{10}\text{Ta}_{7.04}\text{Ti}_{1.2}\text{O}_{30}$.



Orthorhombic : $a = 5.4217$, $b = 14.7432$, $c = 5.5960 \text{ \AA}$

Space Group : $Pnma$ (No. 62)

(b)

Figure 1.42 (Continued)

A wide range of compositions, $\text{AA}'_3\text{B}_4\text{O}_{12}$ form the same structure as CCTO. A is an intermediate-sized alkali, alkaline earth or rare earth cation such as Na^+ , Ca^{2+} , La^{3+} , Pr^{3+} , Nd^{3+} or a lone pair p -block cation Pb^{2+} , Bi^{3+} that occupies the 8-coordinate sites; A' is either of the Jahn-Teller active ions Cu^{2+} or Mn^{3+} that occupies the square planar sites; B is a transition metal such as Ti, V, Mn, Fe, Co, Rh,

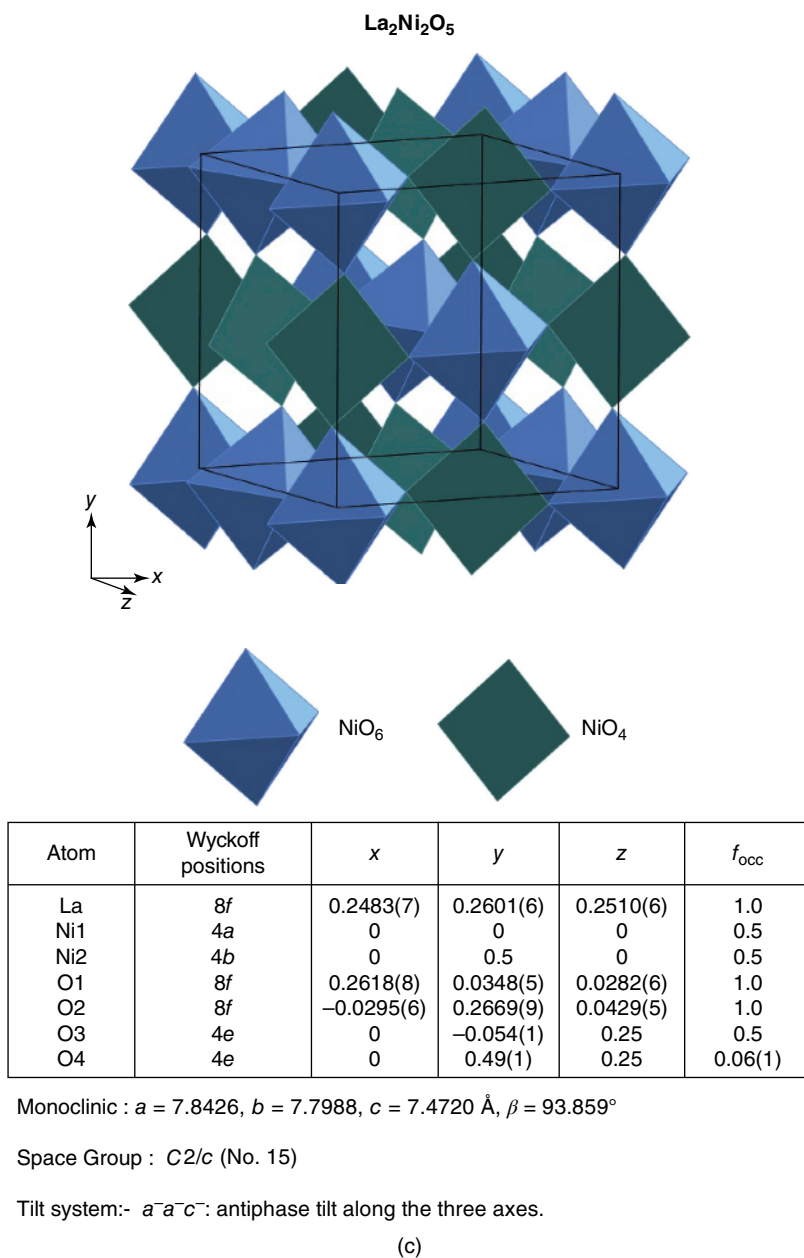


Figure 1.42 (Continued)

Ir, or a *p*-block element Ga, Ge, Sn, Sb that occupies the octahedral sites. The structures are cubic with $a = 2a_p$, where a_p is the lattice parameter of the perovskite subcell.

The electrical and magnetic properties of these materials depend on the valence states of the transition metal cations that occupy A' and B sites. These may change if charge disproportionation phenomena occur, such as disproportionation at low temperatures of Fe⁴⁺ into Fe³⁺ and Fe⁵⁺ in the Fe analogue of CCTO or if temperature-dependent local electron transfer or redox reaction occurs

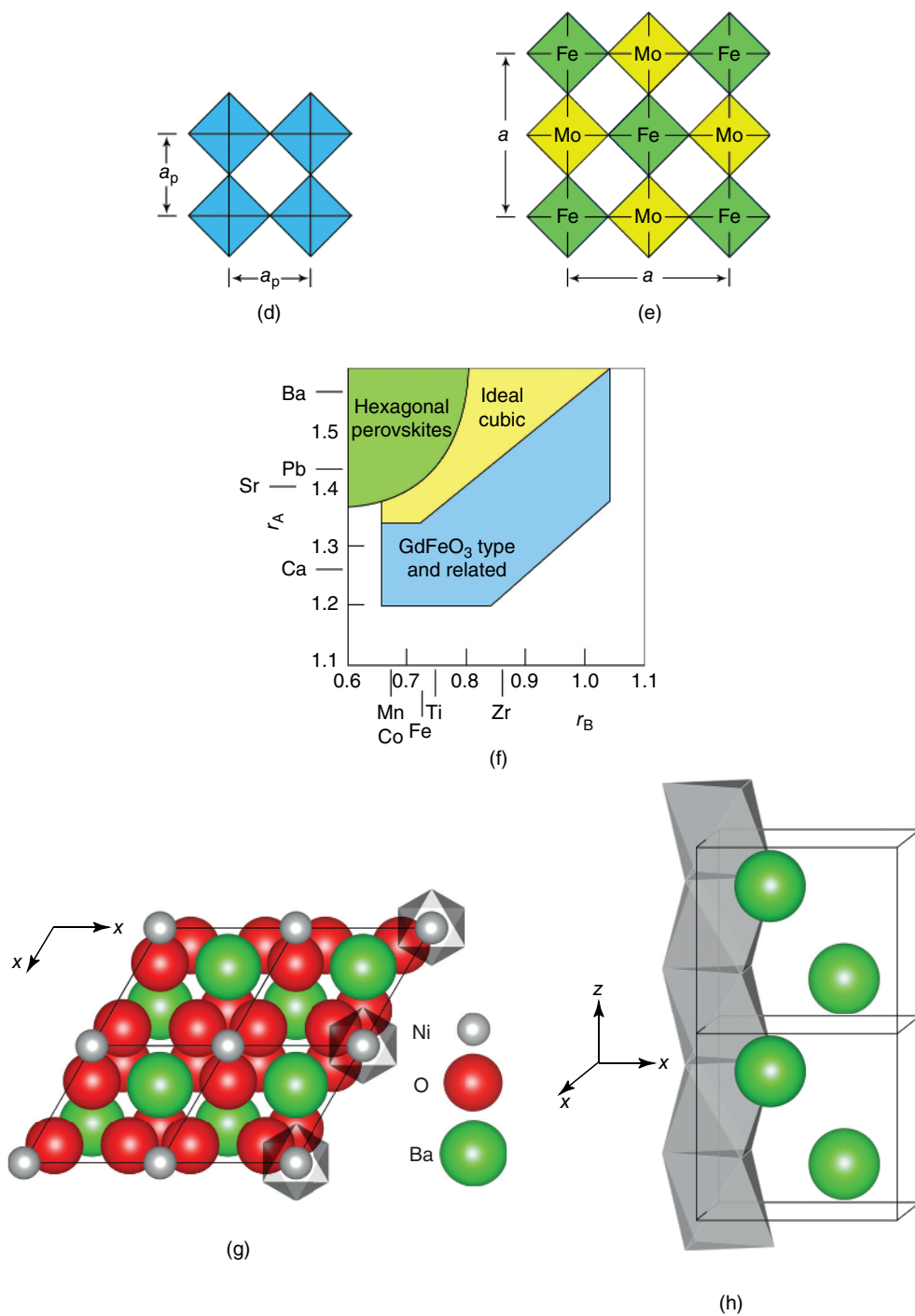


Figure 1.42 (Continued)

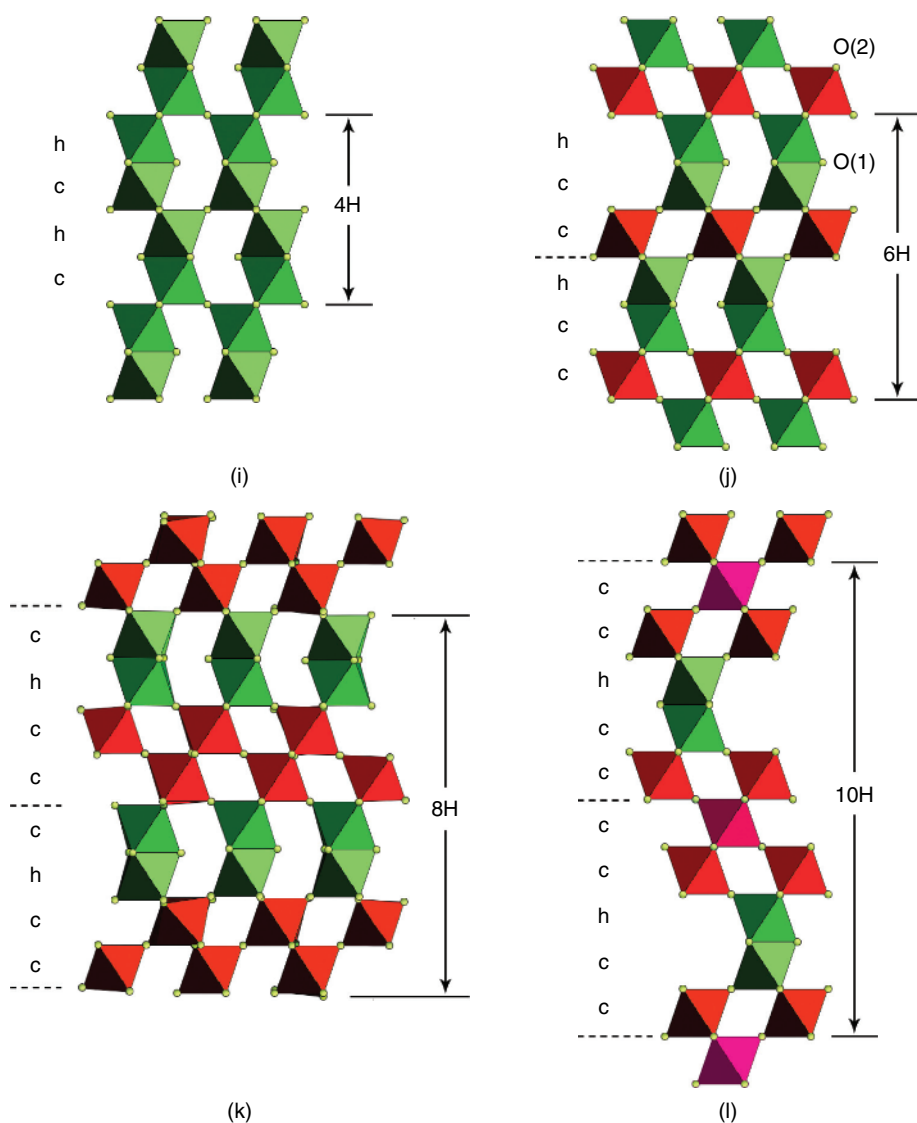


Figure 1.42 (Continued)

between cations such as $\text{Cu}^{2+}/\text{Fe}^{4+}$ and $\text{Cu}^{3+}/\text{Fe}^{3+}$ in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. Novel phenomena and properties may be anticipated following in-depth studies of structure–property correlations in such materials.

1.17.7.5 Anion-deficient perovskites

Anion-deficient perovskites occur commonly and, in cases where the anions are ordered, a variety of more complex structures are generated. As a consequence of anion deficiency, the B site coordination number must reduce from six on average. In the brownmillerite structure, $\text{Ca}(\text{Fe},\text{Al})\text{O}_{2.5}$, Fig. 1.42(b), the average B site coordination number is expected to be five and this is achieved in a layered structure with alternating sheets of tetrahedra and octahedra. In $\text{LaNiO}_{2.5}$, Fig. 1.42(c), the Ni

coordination is a mixture of NiO_6 octahedra and NiO_4 square planes which are ordered to give a $2 \times 2 \times 2$ supercell relative to the perovskite subcell. In the a and b directions, octahedra and square planes alternate but in the c direction chains of corner-sharing octahedra form which are connected to adjacent chains by the square planar units. The Ni polyhedra exhibit antiphase tilting along the three unit cell axes and therefore, may be described in Glazer notation as $a^-a^-c^-$. This material was produced from LaNiO_3 by hydrogen reduction, but a residual amount of oxygen remained in the O(4) sites, giving a composition, for the particular material that was studied, of $\text{LaNiO}_{2.56(1)}$; possibly, using different preparative conditions, materials with different oxygen contents could be prepared.

The above are two examples of anion-ordered crystal structures which occur at specific compositions. Other anion ordering arrangements are known both at these and other compositions. In addition, solid solutions form in many systems in which the anion content is variable and can be represented by the general formula $\text{ABO}_{3-\delta}$. In these, the oxygen vacancies may be distributed at random through the perovskite structure or locally ordered structures may form in which small domains of a particular structure type are distributed at random through a disordered perovskite network.

1.17.7.6 Stoichiometry–property relations

The perovskite structure, with two different-sized cations and several possible cation charge combinations, occurs with a very wide range of compositions. In addition, defect perovskites form in which there are either cation or anion vacancies. Defects, solid solutions and various kinds of properties are all considered in later chapters. All we wish to note here is the incredible range of properties found in materials with perovskite-related structure whose composition has been adjusted to optimise a particular property. Almost every physical property imaginable has been found in materials with the perovskite structure by changing their composition and/or defect structure; for this reason, perovskite is sometimes referred to as an inorganic chameleon! A selection of perovskites and their properties is listed in Table 1.19.

1.17.7.7 Cation-ordered perovskites

Oxide perovskites ABO_3 have an overall cation charge of 6+ which allows the possibility of different cation charge combinations. Since the A and B sites are also very different in size, most elements in the

Table 1.19 *Perovskites: some composition–property correlations*

Composition	Property
CaTiO_3	Dielectric
BaTiO_3	Ferroelectric
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	Relaxor ferroelectric
$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$	Piezoelectric
$(\text{Ba}_{1-x}\text{La}_x)\text{TiO}_3$	Semiconductor
$(\text{Y}_{1/3}\text{Ba}_{2/3})\text{CuO}_{3-x}$	Superconductor
Na_xWO_3	Mixed conductor (Na^+ , e^-); electrochromic
$\text{SrCeO}_3\text{:H}$	Proton conductor
RE TM O_{3-x}	Mixed conductor (O^{2-} , e^-)
$\text{Li}_{0.5-3x}\text{La}_{0.5+x}\text{TiO}_3$	Li^+ ion conductor
$\text{A MnO}_{3-\delta}$	Giant magnetoresistance

RE = rare earth; TM = transition metal.

periodic table can be found, somewhere, in a perovskite structure. In complex perovskites with more than two cations, many examples are known of cation ordered arrangements on A and/or B sites, such as in *double perovskites* with general formula $A_2(BB')O_6$. In these, two different cations are arranged on the B sites in the same way that the anions and cations are arranged in the rock salt structure. A 2D section through the structure of Ba_2FeMoO_6 , Fig. 1.42(e), shows FeO_6 and MoO_6 octahedra that alternate in an *fcc* arrangement. In ordered, undistorted structures such as this, the structure is still cubic but the unit cell edge, a , is twice the length of the perovskite subcell lattice parameter, a_p .

Whether the B site cation arrangement is ordered, Fig. 1.42(e) or disordered, (d) depends on whether the increased entropy associated with cation disorder would offset the loss in enthalpy on forming a disordered structure containing dis-similar cations. This is because cations of dissimilar size and charge are more likely to segregate into clusters or to form an ordered arrangement over two sets of lattice sites than to randomise over a single set of lattice sites, leading to a higher lattice energy or more negative enthalpy of formation for an ordered structure than for a disordered one. The reason why partial or complete disorder is observed in many structures, especially at high temperatures, is because of the increasing influence of the $T\Delta S$ term in the overall free energy, ΔG (from $\Delta G = \Delta H - T\Delta S$), which offsets the increased lattice energy of an ordered structure. One effect of increasing temperature is therefore to introduce structural disorder through the term $T\Delta S$. A similar result may arise by compositional change, or doping. For example, Ca_2FeReO_6 has B-site order of Fe and Re, but partial substitution of La onto the A sites, in the solid solution $Ca_{2-x}La_xFeReO_6$, causes (indirectly) the B cations to disorder.

Two additional complications in seeking to rationalise ordered vs disordered cation arrangements are first, many perovskites become non-stoichiometric through oxygen loss at high temperatures. In this process, electrons are released by the O^{2-}/O_2 reaction but are retained in the perovskite lattice and are associated with transition metal ions that therefore have a reduced valence state, leading to the mixed valence of transition metals on the B sites. Second, synthesis temperature may be important, especially if kinetically stable but thermodynamically metastable structures are obtained at moderate synthesis temperatures. There is no simple way to tell whether a particular structure is thermodynamically stable or metastable until follow-on experiments are performed to investigate its thermal stability and possible polymorphic transitions, Chapter 7. Many cases are known in which a partially ordered or fully disordered structure may be synthesised as a consequence of the moderate synthesis temperatures or conditions that are used, although the fully ordered structure would be the true, thermodynamically stable, low temperature polymorph.

The significance of the lattice energy component associated with BB' order in double perovskite structures is illustrated well by three $Ba_2BB'O_6$ phases in which the BB' combinations, and the extra lattice energy calculated to be associated with BB' order, are: $Sc^{III}Re^V$, 594 kJ mol⁻¹; $Ni^{II}Re^{VI}$, 2414 kJ mol⁻¹; Li^IRe^{VII} , 5381 kJ mol⁻¹ [data taken from Rosenstein and Schor, *J. Chem. Phys.* **38**, 1789 (1963)]. Note, these all contain octahedrally coordinated Re but unusually, in three different valence states. The three structures have similar-sized unit cells and therefore, charge difference rather than size difference between B and B' appears to be the main factor that determines their increased lattice energy.

Many different structural and compositional variations are observed within the family of cation-ordered double perovskites. The A site is frequently occupied by Ca, Sr or Ba, but the B sites may contain a wide range of, mainly transition metals, in III/V, II/VI and I/VII combinations, as shown by the above examples. The A site may also be occupied by larger, trivalent rare earth cations with II/IV BB' combinations, as in La_2MgHfO_6 and I/V, as in La_2LiIrO_6 . Some compositions, such as Ba_2BiIrO_6 , are polymorphic and exhibit both a cation-disordered cubic structure at a high temperature and a non-cubic ordered structure(s) at a lower temperature.

In addition to thermodynamic considerations of the enthalpy and entropy of possible ordered or disordered arrangements of dis-similar cations on the B sites, tolerance factor considerations influence

whether a particular structure is undistorted or tilted in some way and many non-cubic structural variations have been found. It is difficult to give clear guidelines as to which distorted or tilted structure may form for a particular composition because other factors may also be involved, including possible oxygen non-stoichiometry and distortions of cation-oxygen octahedra containing either Jahn-Teller active cations or lone pair *p*-block cations

As well as the rock salt arrangement of B site cations, other ordered arrangements occur, especially in materials in which the B:B' ratio is different from 1:1. Ideal 1:2 double perovskites typified by $\text{Ba}_3\text{SrTa}_2\text{O}_9$ have layered BB' arrangements that are ordered along $[111]_p$. The AO_3 layers are separated by alternating layers of, in this case, Sr and Ta cations in octahedral sites. The ordering causes the structure to show a small rhombohedral distortion from the cubic symmetry of the parent perovskite. This ordered structure has a nine-layer repeat consisting of six BaO_3 layers, two Ta layers and one Sr layer. Other members of the 1:2 family also show partial disorder of the BB' sites and/or various tilted arrangements. A particularly important example is $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, referred to as PMN, in which the BB' cations are neither fully ordered nor disordered but instead, form nanoscale ordered domains within a disordered lattice, resulting in a very high and temperature-independent permittivity, leading to applications of PMN as a relaxor ferroelectric.

The above examples concern B site order; A site order also occurs, as in NaLaMgWO_6 , $\text{CaMnTi}_2\text{O}_6$ (Mn^{2+} on A sites) and notably, in the oxygen-deficient superconducting phase $\text{YBa}_2\text{Cu}_3\text{O}_7$, Fig. 8.8, in which the Cu coordination number is reduced from 6 to a mixture of 5 and 4. A strongly tilted arrangement with 1:3 A site order is shown by $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, Section 1.17.7.4, which has aroused recent interest as a supposed 'giant dielectric'; however, the greatly reduced tolerance factor associated with Ca and Cu as A-site cations causes extensive tilting, leading to square planar coordination for Cu.

1.17.7.8 *Hybrid organic–inorganic halide perovskites*

So far, we have considered A sites to be occupied, fully or partially, by large cations such as K^+ , Ba^{2+} and La^{3+} . In a family of hybrid organic–inorganic perovskites, the A sites are large enough to contain ammonium, NH_4^+ and small organic derivative cations such as methylammonium, $\text{MA} (\text{CH}_3\text{NH}_3)^+$, tetramethylammonium, $\text{TMA} [(\text{CH}_3)_4\text{N}]^+$ and formamidinium, $\text{FA} (\text{NH}_2=\text{CHNH})^+$. The inorganic BX_3 framework of corner-sharing octahedra typically consists of the divalent cations of Ge, Sn or Pb with the larger halogens Cl, Br and I. These hybrid perovskites display a range of structural variants, including (i) tilted structures based on the BX_3 octahedra and (ii) ordered arrangements, based on the non-spherical A cations, which may undergo phase transitions to disordered cubic structures with increasing temperature. In recent years, there has been great interest in these hybrid perovskites for high efficiency, solar cell applications.

A very extensive family of hybrid layered or intergrowth perovskites has been reported which contain large organic cations that cannot fit within the A-site cages. Instead the structures consist of BX_3 layers in various orientations: $[100]$, $[110]$ or $[111]$, separated by layers of organic cations. The inorganic BX_3 component may be either a single layer or a multilayer block, similar to those found in the $[100]$ orientation in the Ruddlesden–Popper family of perovskite-rock salt intergrowth structures, Section 1.17.14. The polar, NH_3^+ end of the organic component is bonded ionically to the anions of the inorganic layer and usually, the organic component consists of double layers in a head-to-head arrangement for bonding to the inorganic layers to either side. Given the many possible compositions for the organic component, which usually consists of chains of different lengths and with various side groups attached, there is great scope for generating novel hybrid layered perovskites. This provides one way to modify the properties that are associated primarily with the inorganic component of the structure.

1.17.7.9 Anti-perovskites

The anti-perovskites have the inverse of the expected cation–anion distribution. In these: X sites contain large atoms such as alkaline earth and rare earth elements; the octahedral B sites contain anions or small atomic species; a range of metallic elements or larger halogens occupy the A sites. However, it is difficult to give a description of a typical anti-perovskite material. Some are best regarded as interstitial alloys, such as Fe_3NPt in which N occupies octahedral sites within the cubic close packed Fe_3Pt lattice. Others have metallic elements on the A sites and have properties and bonding that are intermediate between ionic and metallic, such as BiNCa_3 , SnNnd_3 and MgCNi_3 . Another group is a range of oxy-compounds such as Na_3OCl , K_3OBr , Ag_3IS , Ca_3NAs and Cs_3OAu . Most have undistorted cubic structures analogous to SrTiO_3 , but distorted structures also occur.

1.17.7.10 Mixed anion perovskites: oxynitrides and oxyfluorides

The oxide O^{2-} , nitride N^{3-} and fluoride, F^- ions are of similar size and can readily substitute for each other in crystal structures, other although the number of mixed anion systems that have been studied and reported in the literature are far fewer than those of mixed cation-based materials. The reasons for this are that first, oxynitrides do not usually have the same thermal stability as corresponding oxides since metal-oxygen bonds are usually stronger than metal-nitrogen bonds. Controlling the N stoichiometry presents difficulties during synthesis if N_2 gas is lost in an ‘open’ reaction. Second, the synthesis of oxyfluorides requires stringent safety precautions if F_2 gas is involved.

A range of oxynitride perovskites are known with a 2:1 ratio of O:N and an overall cation charge of 7+. These include II/V cation charge combinations in ATaO_2N : A=Ca, Sr, Eu and III/IV combinations in ATiO_2N : A=Ce, Pr, Nd. Oxynitride perovskites with a 1:2 ratio of O:N form, such as LaTaON_2 and EuWON_2 . Given the similar sizes but different valencies of O^{2-} and N^{3-} , there is also much scope for the preparation of non-stoichiometric oxynitrides that have variable O:N ratios together with different cation combinations, including mixed valence cations, to maintain charge balance.

O and N are either disordered or ordered, fully or partially, in these perovskites and similar tilted or distorted structures occur to those found in oxide perovskites. For instance, LaZrO_2N , $\text{Ca}(\text{Ta},\text{Nb})\text{O}_2\text{N}$ and NdTiO_2N adopt the GdFeO_3 structure with tilt system $a^+b^-b^-$, whereas LaTiO_2N adopts the $a^-b^-c^-$ tilt system. In ordered 2:1 oxynitrides such as $\text{Sr}(\text{Nb},\text{Ta})\text{O}_2\text{N}$, the $[(\text{Nb},\text{Ta})\text{O}_4\text{N}_2]$ octahedra show strong preference for a *cis* arrangement of the two N positions. Each N forms a linear B–N–B segment in the linkage of corner-sharing octahedra; additional bonding interactions involving the transition metal *d* orbitals are believed to be responsible for the commonly observed *cis* configurations.

Oxide perovskites exhibit a very wide range of electrical, magnetic and optical properties and these may be modified by substitution of N for O in oxynitrides. The property modifications are associated with the lower electronegativity of N than O which leads to (i) more covalent metal-nitrogen bonds compared with the more ionic metal-oxygen bonds and (ii) a consequent reduction in the band gap of oxynitrides and nitrides. The band gap is frequently in the visible part of the electromagnetic spectrum and can be fine-tuned by adjusting the O:N ratio, leading to a range of brightly coloured materials with applications as non-toxic pigments and in visible light, photocatalytic water-splitting processes.

A similar story can be told for oxyfluoride perovskites. The ones prepared so far have large A-site cations, especially Ca, Sr and Ba, exhibit various tilted structures and the possibility of variable O:F ratio, especially in fluorinated cuprate phases that exhibit superconductivity.

1.17.7.11 Hexagonal perovskites

Hexagonal perovskites form when the tolerance factor is somewhat greater than unity. This is summarised schematically in the structure – field map, Fig. 1.42(f), in which A and B cation radii form

the two axes. The crossover between different phase fields is not a rigid boundary, but is also a rich source of polymorphic structures, such as shown by BaTiO_3 which exhibits both hexagonal and cubic perovskite polymorphs at temperatures above and below about 1450°C , respectively.

The cubic perovskites considered so far may be regarded as layer structures in which *cp* AO_3 layers are arranged in a *ccp* stacking sequence. Hexagonal perovskites also contain *cp* AO_3 layers in which A is usually Ba, but the stacking sequence is either *hcp* or a more complex structure with a combination of *ccp* and *hcp* stacking. A useful and simple nomenclature to describe these mixed stacking sequences is to label a particular AO_3 layer according to whether, in combination with the layers on either side, the local arrangement is *hcp* or *ccp*. Thus, if the layers on either side are in a similar position, the sequence is labelled *h* but if the layers to either side are in different positions, it is labelled *c*.

A major, and significant, difference between structures containing *ccp* and *hcp* anions concerns the relative positions of available tetrahedral and octahedral sites for occupancy by cations. In an *hcp* anion array, the octahedral cation sites form face-sharing columns in one direction, as shown by NiAs, giving rise to short metal-metal distances across the shared faces (and metallic bonding in NiAs). Face-sharing of octahedral sites does not usually occur in ionic structures unless there is some kind of positive bonding interaction between the cations involved. In cubic perovskite, by contrast, the BO_6 octahedra are well-separated and share corners since only $\frac{1}{4}$ of the available octahedral sites that are suitable for cation occupancy have oxygen at all six corners (however, in a *ccp* structure such as rock salt in which all octahedral sites are occupied by cations, the octahedra share edges, Fig. 1.32).

Hexagonal perovskites form because their tolerance factor has a value greater than unity which means that, in a corresponding cubic perovskite, the B–O bonds would be somewhat elongated, as in Fig. 1.41(h). There is, therefore, a competitive energy balance between having either elongated B–O bonds or reduced B–B distances respectively, in the cubic and hexagonal perovskite structure types. The balance can be tipped in favour of one or other structure by either changes in temperature or doping, as observed with BaTiO_3 in which either increased temperature or certain dopants lead to a transition from a cubic to a hexagonal structure.

The short metal-metal distances in hexagonal perovskites appear to be facilitated by positive bonding interactions involving the *d* electrons of the transition metal B cations that act to counteract the effects of cation-cation charge repulsion. The common occurrence of polytypism in the family of hexagonal perovskites, with mixed *h,c* stacking sequences of the AO_3 layers, can be related to the formation of localised metal-metal pair interactions. Strictly, the term polytypism refers to different stacking arrangements for the same composition (such as found with the many stacking sequences shown by silicon carbide) but here, it is convenient to use the term to allow compositional differences as well since there is a very large family of hexagonal perovskite compositions that are characterised mainly by different stacking sequences. Two other ways which illustrate reduced cation-cation repulsions are observed in (i) structures that contain a low valence cation in some of the B sites, as in $\text{Ba}_4\text{Nb}_3\text{LiO}_{12}$ and (ii) structures with some B site vacancies, as in $\text{Ba}_5\text{Ta}_4\text{O}_{15}$.

The simplest hexagonal perovskite structure is that of BaNiO_3 which is entirely *hcp*. It contains infinite chains of face-sharing NiO_6 octahedra running perpendicular to the BaO_3 layers, with Ni in the 4+ valence state. An [001] projection of four unit cells is shown in Fig. 1.42(g). Two face-sharing octahedra form the repeat unit along the *c* cell edge; the octahedra are highlighted at the right hand side in (g) and shown from a different perspective in (h) together with some of the Ba atoms that form the *cp* BaO_3 layers. Other oxides that have a similar structure with *h* stacking of layers are BaMnO_3 , BaCoO_3 and SrCoO_3 .

In most other hexagonal perovskites, the metal-metal pair interactions do not extend as far as forming infinite columns of face-sharing octahedra in a complete *hcp* anion array, as in BaNiO_3 . Thus, pairs of face-sharing octahedra occur in BaRuO_3 which are linked by corner-sharing to adjacent pairs to give the *ch* sequence, as shown in (i); this may be written more completely as $(ch)_2$ to indicate that two pairs form the repeat in the *c* unit cell direction and is alternately given the label 4H, referring to a 4-layer

repeat unit with overall hexagonal symmetry. In hexagonal BaTiO_3 , face-sharing pairs are separated by single layers of a cubic structure, (j), to give the polytype $(cch)_2$. In $\text{Ba}_8\text{Ta}_4\text{Ti}_3\text{O}_{12}$, (k), the stacking sequence is $(cchc)_2$ and in $\text{Ba}_{10}\text{Ta}_{7.04}\text{Ti}_{1.2}\text{O}_{30}$ (l), the sequence is $(cchcc)_2$. Many materials with more complex polytypic sequences have also been synthesised; overviews of these and other perovskite-derivative structures, including those containing two types of *cp* layers which introduce an additional structural complexity, are given in the books by Tilley and Mitchell.

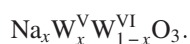
A recent development that has given fresh impetus to the study of hexagonal perovskite derivative phases is the discovery of a high level of oxide ion conductivity in $\text{Ba}_3\text{MnNbO}_{8.5}$; $\text{M} = \text{Mo}, \text{W}$. The structure is a hybrid of two separate structures: first, a 9-layer hexagonal perovskite, $(hhc)_3$ of formula $\text{A}_3\text{B}_2\text{O}_9$ that contains face-sharing trimers of octahedra linked through their corners; second, a structurally related, but oxygen-deficient palmierite structure in which (i) one of the AO_3 layers has instead the stoichiometry AO_2 , (ii) the B cations are displaced from their octahedral sites to form layers of tetrahedra and (iii) the overall formula is $\text{A}_3\text{B}_2\text{O}_8$. Given the wide range of hexagonal perovskites and their derivatives that are already known, many of which are similarly oxygen-deficient, the discovery of other new oxide ion conducting materials in this family, as well as possible mixed conductors, may be anticipated.

1.17.8 Rhenium trioxide (ReO_3), perovskite tungsten bronzes, tetragonal tungsten bronzes and tunnel structures

The structure of cubic ReO_3 is closely related to the perovskite described above. It is the same as the ' TiO_3 ' framework of perovskite, SrTiO_3 , but without the Sr atoms. Its unit cell is the same as that shown in Fig. 1.41(a) with Re at corners and O at edge centres. A few oxides and halides form the ReO_3 structure, Table 1.20, together with an example of the anti- ReO_3 structure in Cu_3N .

A wide variety of oxide and oxyfluoride structures, often with complex formulae, can be derived from the ReO_3 structure by coupled rotation of groups of octahedra. To see this, we start with the ideal cubic ReO_3 structure shown in Fig. 1.43(a). Each octahedron shares its six corners with other octahedra and in 2D, layers of corner-sharing octahedra are obtained. In the cubic perovskite structure, large 12-coordinate cavities are occupied by A cations, ideally without modification of the array of octahedra, (b).

The *perovskite tungsten bronze* structures are intermediate between ReO_3 and perovskite. They occur in series such as Na_xWO_3 and have a 3D framework of WO_6 octahedra, as in ReO_3 , but with some ($0 < x < 1$) of the large A sites occupied by Na. To accommodate a variation in stoichiometry, x , the oxidation state of tungsten is a mixture of, or intermediate between, V and VI. The formula of the bronzes may be written more completely as



These materials have interesting colours and electrical properties. At low x , they are pale green/yellow in colour and semiconducting. As x rises and electrons begin to occupy the $5d$ band of tungsten, they become brightly coloured and metallic, hence the name 'bronze'.

Table 1.20 Some compounds with the ReO_3 structure

Compound	$a/\text{\AA}$	Compound	$a/\text{\AA}$
ReO_3	3.734	NbF_3	3.903
UO_3	4.156	TaF_3	3.9012
MoF_3	3.8985	Cu_3N	3.807

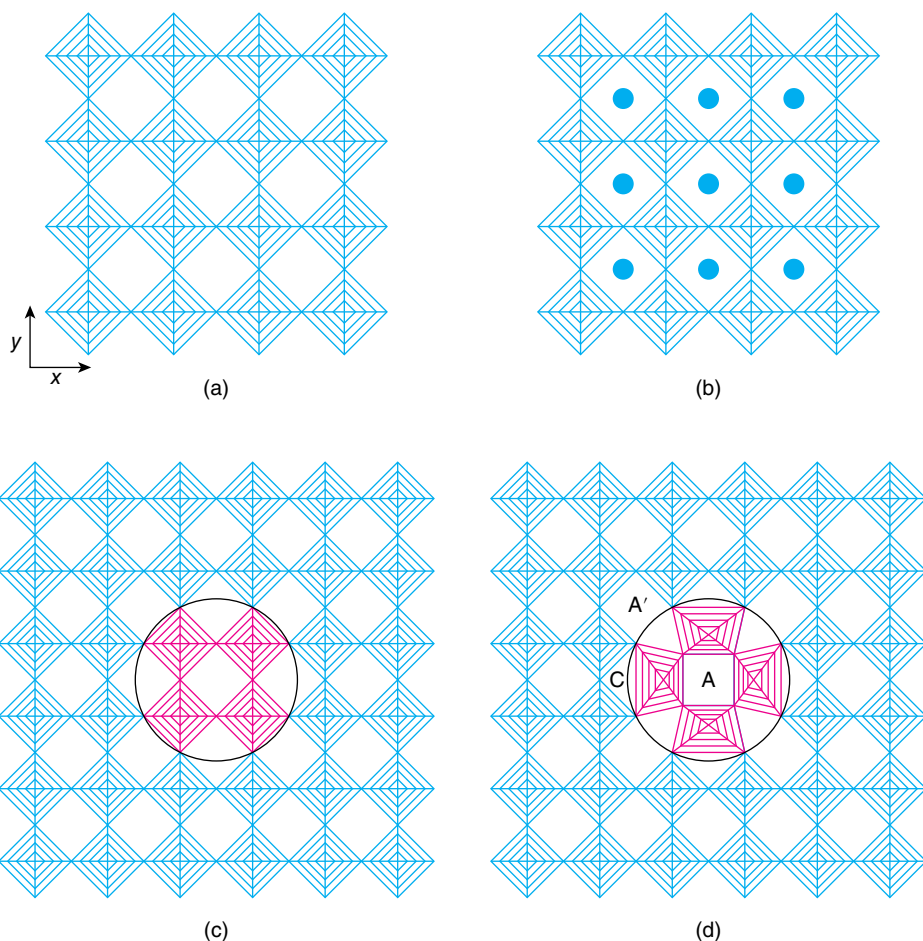


Figure 1.43 The structure of (a) ReO_3 , (b) tungsten bronze Na_xWO_3 , (c, d) bronze and tunnel structures derived from ReO_3 by rotation of blocks of four octahedra and (e, f) the tetragonal tungsten bronze structure. Adapted from B. G. Hyde and M. O’Keeffe, *Acta Cryst. Sect. A* 29, 243 (1973). (g) The TTB structure of $\text{Ba}_2\text{LaTi}_2\text{Nb}_3\text{O}_{15}$. Adapted from G. C. Miles et al., *J. Mater. Chem.* 15, 798 (2005). (h, i) Tunnel structure of Mo_5O_{14} .

A variety of monovalent cations enter the tungsten bronze structure; similar series also occur with MoO_3 in the *molybdenum bronzes*. Many other highly conducting bronzes based on oxides MO_2 or MO_3 form in which M is a transition metal, such as Ti, V, Nb, Ta, Mo, W, Re, Ru or Pt, that is capable of existing in mixed oxidation states.

Thus far, we have not modified the arrangement of octahedra. Different arrays of octahedra are, however, obtained by rotation of columns of four octahedra by 90° and reconnecting them with the parent structure as shown in Fig. 1.43(c) and (d). This has major consequences for the size and coordination number of the A cation sites. Some, A, retain their coordination number of 12 and in projection may be perceived as ‘square tunnels’; a second set of sites, A’, has a coordination number which is increased to 15 and in projection may be regarded as ‘pentagonal tunnels’. A third set, C, has coordination number reduced to nine and is referred to as ‘triangular tunnels’. We now have the building blocks for the *tetragonal tungsten bronze*, TTB, structure. This contains an important family of ferroelectric materials although, since they are insulating, it is rather a misnomer to call them bronzes.

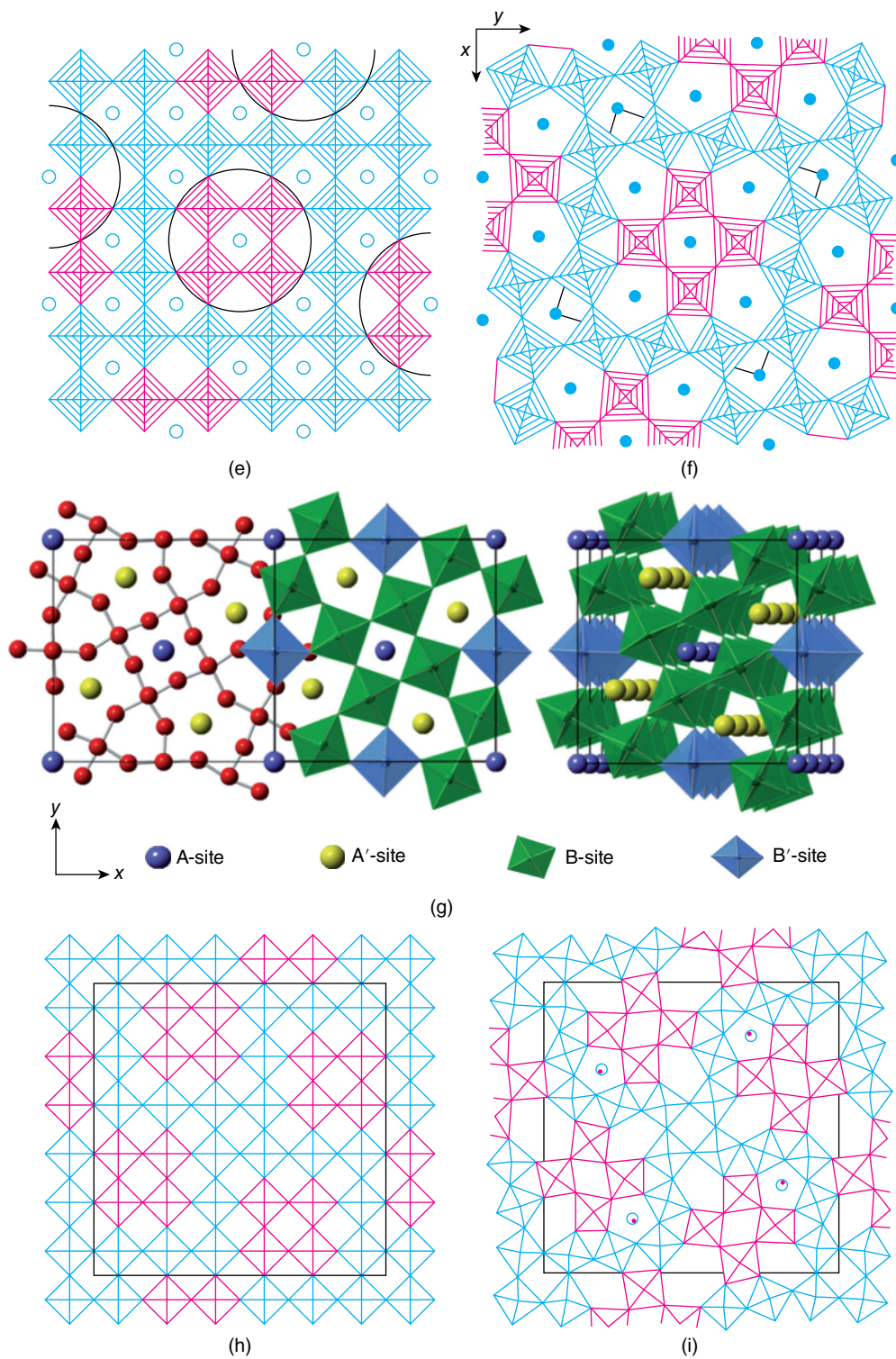


Figure 1.43 (Continued)

Table 1.21 *Some compounds with the tetragonal tungsten bronze, TTB, structure. Unit cell: tetragonal $a \approx 12.4$, $c \approx 3.9$ Å*

A_2	A'	B_4B'	O_{15}
Ba_2	RE^a	Ti_2, Nb_3	O_{15}
Sr_2	Na or K	Nb_5	O_{15}
Ba_2	Na	Nb_5	O_{15}
Ba_2 or Sr_2	Ba or Sr	Ti, Nb_4	O_{15}
$Sr_{2.5}$		Nb_5	O_{15}
$K_{0.4-0.6}$		W	O_3

^a RE = La, ..., Dy, Bi.

The general formula of the ideal TTB structure is $A_2A'B_4B'O_{15}$ or $A_2A'B_3B'_2O_{15}$, depending on the oxidation states of A, A', B, and B'. The structure is built of corner-sharing BO_6 and $B'O_6$ octahedra; the B,B':O ratio is 1:3, as in ReO_3 , but the linkage of the octahedra is different from that in ReO_3 . In the TTB structure, blocks of octahedra which form four-membered rings are rotated by 90° relative to the parent ReO_3 structure to give a framework containing triangular, square and pentagonal columns, Fig. 1.43(e) and (f). In the c direction, the unit cell is only one octahedron thick. In principle, all the sites are available for cation occupancy. In practice, large cations such as K^+ and Ba^{2+} occupy the pentagonal tunnels with a coordination number to the oxygen of 15, whereas somewhat smaller cations such as La^{3+} occupy square tunnels with coordination number 12; the triangular tunnels, C in the formula, remain either empty or occupied by smaller ions such as Li^+ .

A selection of compounds with the TTB structure is shown in Table 1.21. The structure is versatile since cations on the A and A' sites can be either fully ordered, disordered or only partially occupied. In addition, there are two crystallographically distinct, octahedral B and B' sites, which can be occupied by one species or a mixture. As with all crystal structures, it may be useful to view them in different ways and the TTB structure is shown from three different perspectives in Fig. 1.43(g).

The structure of Mo_5O_{14} is based on the same principles but is rather different to the TTB structure, Fig. 1.43(h) and (i). Pentagonal columns are again present and these are occupied by rows of Mo and O atoms, as shown by open and closed circles in (i). Because of the extra oxygens in the columns, Mo occupies small sites whose coordination number is reduced greatly from 15 to 7. Other pentagonal columns, and triangular columns, remain empty. In addition, new hexagonal columns are created by the array of octahedra and these remain empty in Mo_5O_{14} . Many other complex structures are built using similar principles, for example, $NaNb_6O_{15}F$, $Nb_{16}W_{18}O_{94}$, $Bi_6Nb_{34}O_{94}$ and Ta_3O_7F .

1.17.9 Spinel

Several commercially important magnetic oxides have the spinel structure. The parent spinel is $MgAl_2O_4$. It has *ccp* oxide ions with Mg^{2+} , Al^{3+} in tetrahedral and octahedral interstices, respectively. Many oxides, sulphides, and halides have the spinel structure and different cation charge combinations are possible, namely:

2, 3	as in	$MgAl_2O_4$
2, 4	as in	Mg_2TiO_4
1, 3, 4	as in	$LiAlTiO_4$
1, 3	as in	$Li_{0.5}Al_{2.5}O_4$
1, 2, 5	as in	$LiNiVO_4$
1, 6	as in	Na_2WO_4

Similar cation combinations occur with sulphides, e.g. 2,3 as in ZnAl_2S_4 and 2,4 as in Cu_2SnS_4 . With halides, cations are limited to charges of 1 and 2, in order to give an overall cation:anion ratio of 3:4, e.g. Li_2NiF_4 .

MgAl_2O_4 has a large, cubic unit cell with $a = 8.08 \text{ \AA}$. The cell contents are eight formula units ($Z = 8$) corresponding to ' $\text{Mg}_8\text{Al}_{16}\text{O}_{32}$ '. In the *ccp* oxide array, half of the octahedral sites are occupied by Al and one-eighth of the tetrahedral sites, both T_+ and T_- , by Mg.

The unit cell of the spinel structure is a large cube, eight times (i.e. $2 \times 2 \times 2$) the size of a typical face centred cube, and it is almost impossible to give a comprehensible 3D drawing of the complete unit cell and its contents. We can, however, easily understand how the structure arises and draw structural fragments to illustrate certain features.

Writing the general formula of a *normal spinel* as $\text{A}^{\text{tet}}\text{B}_2^{\text{oct}}\text{O}_4$, let us first consider the $\text{B}_2^{\text{oct}}\text{O}_4$ part. This is simply the rock salt structure with *ccp* O^{2-} ions but with only alternate octahedral sites occupied by B cations. Two such rock salt-derivative subcells are shown in Fig. 1.44(a) and (b) (each subcell forms one octant of the spinel unit cell); the bottom face of the subcell in (a) is the same as the top face of the subcell in (b). Oxygens are shown at corners and face centres (as in Fig. 1.24). Some octahedral positions are shown as occupied (solid circles) but alternate ones in any of the three unit cell directions are empty (small squares).

The base of the spinel unit cell is shown in (c); it is formed by the base of (b), dashed, and that of three adjacent subcells. The alternating, empty–occupied–empty sequence of octahedral sites is clearly seen and also occurs similarly in the third dimension (a, b).

To complete the structure, we need to locate the tetrahedral A cations. In an *fcc* anion array, Fig. 1.24, the eight tetrahedral sites, 5–12, are located as shown. These tetrahedral sites are equidistant from oxygen atoms but also from the octahedral cation sites (e.g. distances 9–A and 9–3 in Fig. 1.24 are equal). Cation–cation repulsions do not allow adjacent tetrahedral and octahedral sites to be occupied simultaneously (this would be equivalent to tetrahedra and octahedra sharing a common face). We therefore need to find those tetrahedral sites for which all four neighbouring octahedral sites are empty. In Fig. 1.44(a), *all* of the tetrahedral sites (5–12 in Fig. 1.20) have at least one neighbouring octahedral cation and so none of the tetrahedral sites in this octant is occupied. The octant immediately below (or above) that in (a) is shown in (b); note that its top face is the same as the bottom face in (a). In this octant, two of the tetrahedral sites (positions 8 and 9 in Fig. 1.24) have no octahedral cation neighbours and, therefore, both of these contain an A cation. Taking the spinel structure as a whole, the eight octants fall into two structural groups, as represented by (a) and (b). The A cations are located in the four octants of type (b).

The two types of octant are arranged such that they alternate in any of the three unit cell directions. They are, in fact, arranged in exactly the same way as anions and cations in the rock salt structure, Fig. 1.44(d). A projection of the unit cell onto one face, showing cation positions only, is shown in (e). The orientation is exactly the same as in (b) and (c) but now atom heights, above the plane of the paper, are given as multiples of $c/8$. Octahedral positions are solid circles; occupied tetrahedral positions are represented by A. You should be able to see that the octahedral atoms O' in the base (height 0) are the same as in (b) and (c). An alternative view of the structure of MgAl_2O_4 spinel is shown in (f). It consists of a framework of edge-sharing AlO_6 octahedra with isolated MgO_4 tetrahedra inside channels formed by the octahedral array.

The above description of the spinel structure is somewhat idealised. In practice, the anions are displaced slightly from their corner and face centre positions. The degree of displacement varies slightly from compound to compound, which means that the bond lengths to A and B cations can change so as to fit best those required by the particular A and B ions. The origin of the spinel structure is usually shifted to coincide with a tetrahedral A cation. We need not pursue this any further as it may lead to confusion, but it does lead to alternative descriptions of the spinel structure (e.g. the A cations alone are arranged in the same way as the carbon atoms in the diamond structure!).

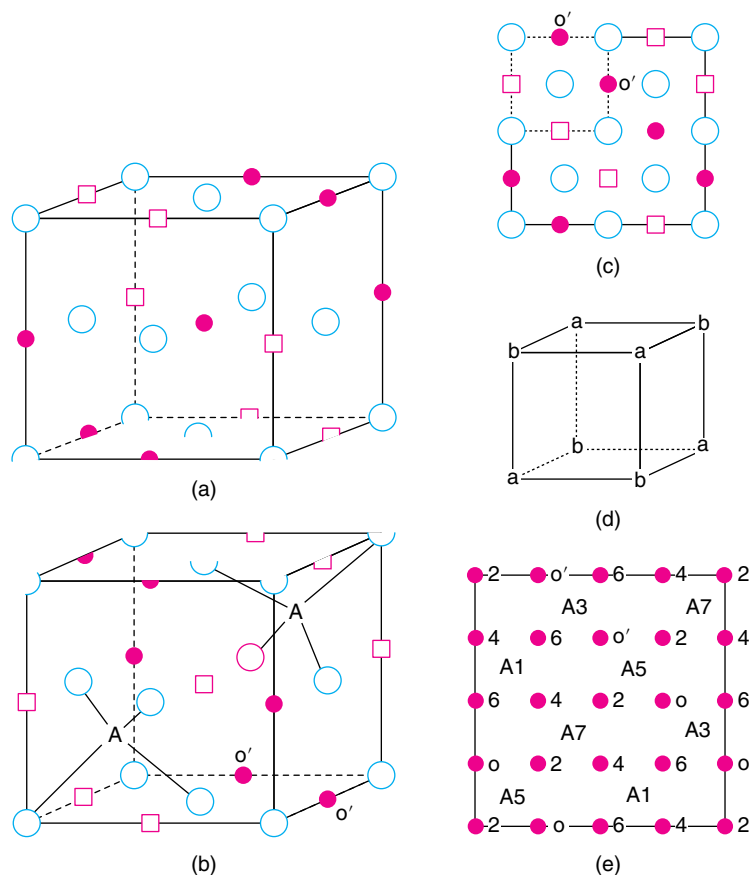


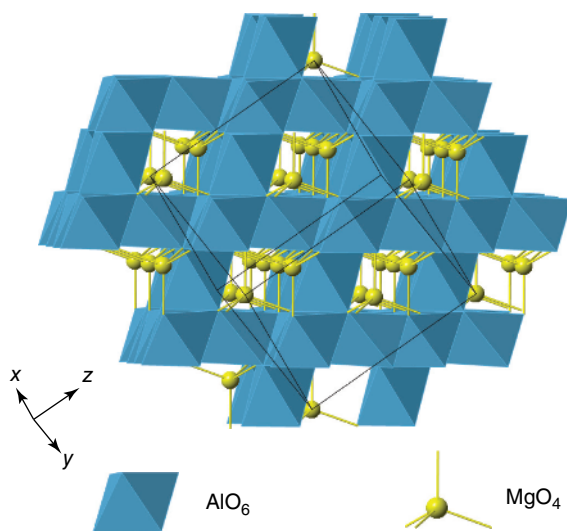
Figure 1.44 Representative parts of the spinel structure. (a) One octant of the unit cell showing oxygens at corner and face centres, empty (□) and occupied (●) octahedral sites. (b) A second octant, underneath the one in (a), showing in addition the occupation of two tetrahedral sites, A. (c) One face of the cubic unit cell of the spinel structure. The dashed part coincides with the base of the subcell shown in (b). (d) Alternating arrangement of the two types of octant (a) and (b). (e) Cation positions in spinel. Numbers refer to fractional heights, as multiples of $c/8$. Octahedral cation sites O' are also shown in (b) and (c). (f) Two perspectives of the spinel structure of $MgAl_2O_4$ showing a framework of AlO_6 octahedra with MgO_4 tetrahedra in channel sites.

A complicating factor in some spinel structures is that the cation distribution may vary. Two extreme types of behaviour may be distinguished. In *normal* spinels, the cations occupy sites given by the formula



i.e. with A in tetrahedral sites and B in octahedral sites. Examples of normal spinels are $MgAl_2O_4$ and $MgTi_2O_4$. In *inverse* spinels, half of the B ions occupy tetrahedral sites, leaving the remaining B ions and all the A ions in octahedral sites, i.e.

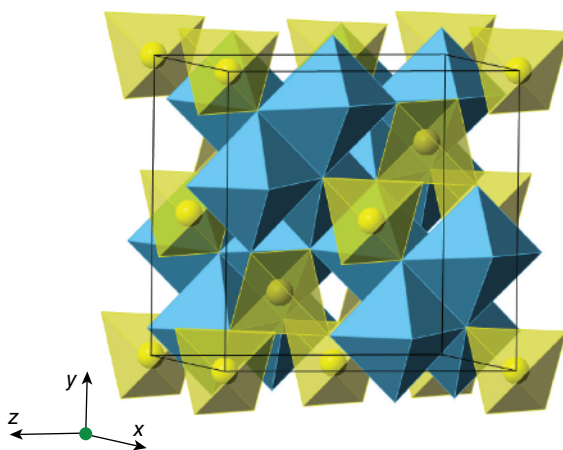


Spinel (MgAl_2O_4)

Atom	Wyckoff positions	x	y	z
Mg	8a	0	0	0
Al	16d	0.625	0.625	0.625
O	32e	0.3873(1)	0.3873(1)	0.3873(1)

Cubic : $a = 8.0806 \text{ \AA}$

Space Group : $Fd \bar{3}m$ (No. 227)



(f)

Figure 1.44 (Continued)

Table 1.22 *Some compounds with the spinel structure*

Compound	Type	$a/\text{\AA}$	Structure	Compound	Type	$a/\text{\AA}$	Structure
MgAl ₂ O ₄	2, 3	8.0800	Normal	MgIn ₂ O ₄	2, 3	8.81	Inverse
CoAl ₂ O ₄	2, 3	8.1068	Normal	MgIn ₂ S ₄	2, 3	10.708	Inverse
CuCr ₂ S ₄	2, 3	9.629	Normal	Mg ₂ TiO ₄	2, 4	8.44	Inverse
CuCr ₂ Se ₄	2, 3	10.357	Normal	Zn ₂ SnO ₄	2, 4	8.70	Inverse
CuCr ₂ Te ₄	2, 3	11.051	Normal	Zn ₂ TiO ₄	2, 4	8.467	Inverse
MgTi ₂ O ₄	2, 3	8.474	Normal	LiAlTiO ₄	1, 3, 4	8.34	Li in tet
Co ₂ GeO ₄	2, 4	8.318	Normal	LiMnTiO ₄	1, 3, 4	8.30	Li in tet
Fe ₂ GeO ₄	2, 4	8.411	Normal	LiZnSbO ₄	1, 2, 5	8.55	Li in tet
MgFe ₂ O ₄	2, 3	8.389	Inverse	LiCoSbO ₄	1, 2, 5	8.56	Li in tet
NiFe ₂ O ₄	2, 3	8.3532	Inverse				

Usually the A and B cations in octahedral sites are disordered. Examples of inverse spinels are MgFe₂O₄ and Mg₂TiO₄.

In addition to normal and inverse spinels, a complete range of intermediate cation distributions is possible and, in some cases, the distribution changes with temperature. The cation distribution may be quantified using a parameter, γ , which is the fraction of A ions on the octahedral sites:

- normal: $[A]^{tet}[B_2]^{oct}O_4$ $\gamma = 0$
- inverse: $[B]^{tet}[A, B]^{oct}O_4$ $\gamma = 1$
- random: $[B_{0.67}A_{0.33}]^{tet}[A_{0.67}B_{1.33}]^{oct}O_4$ $\gamma = 0.67$.

The cation distribution in spinels and the *degree of inversion*, γ , have been studied in considerable detail. Several factors influence γ , including the site preferences of ions in terms of size, covalent bonding effects and crystal field stabilisation energies (see Chapter 2). The γ value in any particular spinel is given by the net effect of these various parameters taken together. Some compounds with the spinel structure are given in Table 1.22.

1.17.10 Olivine

The olivine structure, typified by the minerals forsterite, Mg₂SiO₄, and triphylite, LiFePO₄, is the *hcp* analogue of the spinel structure. One-eighth of the tetrahedral sites are occupied by Si or P and half of the octahedral sites by Mg or Li, Fe within an *hcp* oxide array. There are two crystallographically distinct octahedral sites in olivine, which are occupied in ordered fashion by Li and Fe in LiFePO₄. The crystal structure is shown in Fig. 1.45 and some olivines are listed in Table 1.23. Olivines occur mainly with oxides but also with sulphides, selenides and some fluorides. Various cation charge combinations occur, such that in oxides the three cations have a net charge 8+.

Olivines (mainly forsterite and fayalite) are believed to be the main mineralogical constituent of the Earth's upper mantle. At high pressures, many olivines transform to the spinel structure and spinels are probably the main constituent of the Earth's lower mantle. Volume changes associated with the olivine to spinel phase transformation may have had fundamental geological consequences during the evolution of the Earth, involving the formation of mountain ranges and under-sea ridges. When spinel material from the lower mantle was pushed upwards to the Earth's surface, it transformed to olivine due to the reduction in pressure. The reverse transformation, olivine to spinel, with a volume contraction may be a contributing factor to earthquakes.

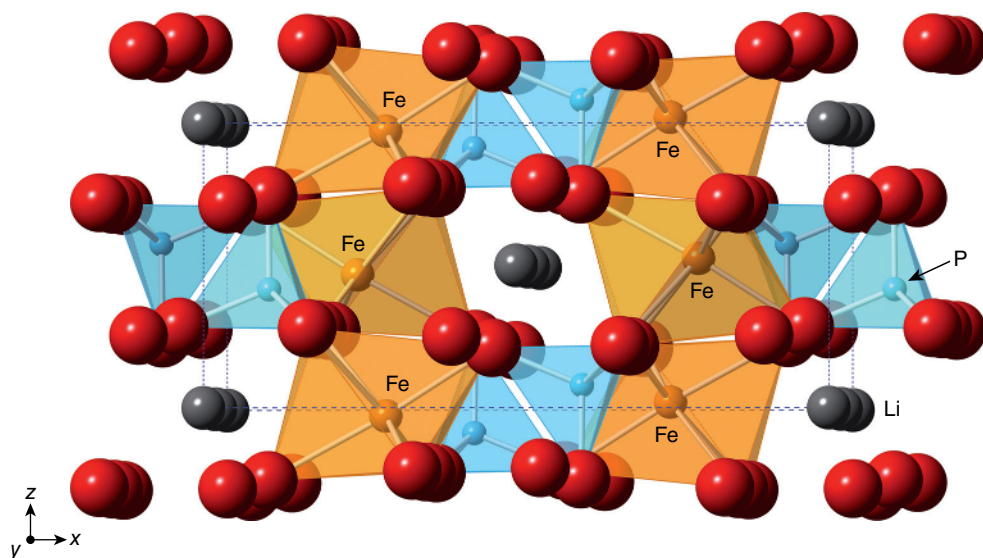


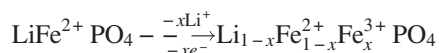
Figure 1.45 Olivine structure of LiFePO_4 . Modified from J. J. Biendicho and A. R. West, *Solid State Ionics* 203, 33 (2011).

Table 1.23 Some compounds with the olivine structure

General formula			
Octahedral site	Tetrahedral site	hcp anion	Examples
II_2	IV	O_4	Mg_2SiO_4 (forsterite)
			Fe_2SiO_4 (fayalite)
			CaMgSiO_4 (monticellite)
			$\gamma\text{-Ca}_2\text{SiO}_4$
			A_2GeO_4 : A = Mg, Ca, Sr, Ba, Mn
III_2	II	O_4	Al_2BeO_4 (chrysoberyl)
			Cr_2BeO_4
II, III	III'	O_4	MgAlBeO_4
			LiFePO_4 (triphylite)
I, II	V	O_4	LiMnPO_4 (lithiophyllite)
			LiRESiO_4 : RE = Ho, ..., Lu
I, III	IV	O_4	NaREGeO_4 : RE = Sm, ..., Lu
			LiREGeO_4 : RE = Dy, ..., Lu
II_2	IV	S_4	Mn_2SiS_4
			Mg_2SnS_4
			Ca_2GeS_4
			$\gamma\text{-Na}_2\text{BeF}_4$
I_2	II	F_4	

Unit cell: orthorhombic; for LiFePO_4 , $a = 10.33$, $b = 6.01$, $c = 4.70$ Å; $Z = 4$.

There is much current interest in LiFePO_4 as the cathode material in rechargeable lithium batteries. On charging, Li deintercalates from the structure and a corresponding amount of Fe is oxidised from Fe^{2+} to Fe^{3+} , as follows:



Lithium ions occupy channels parallel to the y axis, Fig. 1.45, which allows them to leave and enter the structure readily during cell charge and discharge. This is an example of a solid state redox reaction with a cell potential of about 3.08 V. LiFePO_4 , and associated LiMnPO_4 , are of interest because the redox reaction and the process of lithium removal and insertion are reversible over many cycles, giving a high cell capacity, and the materials are cheap, non-toxic and environmentally friendly.

1.17.11 Corundum, ilmenite and LiNbO_3

These three closely related structure types can be regarded, ideally, as *hcp* oxide ions with cations occupying two-thirds of the octahedral sites. Conceptually, they are related to the NiAs structure in which all the octahedral sites are occupied, and to the CdI_2 structure in which only half the octahedral sites are occupied, Table 1.4. The crystal structures are shown in Fig. 1.46 and some compounds adopting these structures are listed in Table 1.24. Corundum contains only one cation, Al^{3+} , whereas ilmenite contains two cations that are ordered over the octahedral sites that are occupied by Al in corundum. In LiNbO_3 , the same octahedral sites are occupied but the cation ordering arrangement is different.

The unit cell of all three structures is hexagonal and has six *cp* oxygen layers parallel to the basal plane, shown in Fig. 1.46(a) at c heights 1/12, 3/12, 5/12, 7/12, 9/12 and 11/12. Cations are in octahedral sites mid-way between the oxygen layers; alternate layers of cation sites are occupied by Fe and Ti in ilmenite, Fig. 1.46(b). Pairs of octahedra share a common face in the c direction and cation repulsion between the cation pairs causes distortion from an ideal *hcp* structure. In all cases, the cation octahedra are distorted with three long and three short bonds. Repulsion between Nb^{5+} and Li^+ in LiNbO_3 causes displacement of Li to a position near the triangular face at the opposite side of the octahedron. LiNbO_3 and LiTaO_3 are ferroelectric materials and cation displacements within the face-sharing octahedra are responsible for the polar crystal structures and dipole reorientation in an applied electric field, which is a characteristic feature of ferroelectrics.

The cation ordering sequence in LiNbO_3 is different to that in ilmenite, Fig. 1.46(c) and (d). Li and Nb are both present, ordered, between any pair of close packed oxide ion layers whereas Fe and Ti occupy alternate sets of layers in ilmenite. An alternative view of the LiNbO_3 structure is given in (d), which illustrates that LiNbO_3 can also be regarded as a grossly distorted perovskite structure. Tilting and rotation of the NbO_6 octahedra (B sites) reduce the coordination of the A sites from 12 to distorted octahedral, and these are occupied by Li. If we regard LiNbO_3 as a distorted perovskite, its tolerance factor is 0.78, which, in practice, represents the lower limit for materials that can be regarded as distorted perovskites.

1.17.12 Fluorite-related structures, pyrochlore, weberite and rare earth sesquioxides

The fluorite structure of CaF_2 can be described as eutactic *ccp* Ca^{2+} ions with F^- ions occupying all tetrahedral sites, Fig. 1.29. A number of more complex fluorite-related structures occur with an excess or deficiency of anions or with cation ordering.

A remarkable anion-excess fluorite is LaH_3 ; LaH_2 forms the basic fluorite structure and extra hydrogens occupy fully the octahedral sites. The structure therefore has all tetrahedral and octahedral sites occupied by H within a *ccp* La array, Fig. 1.24. A similar structure is observed in intermetallics such as

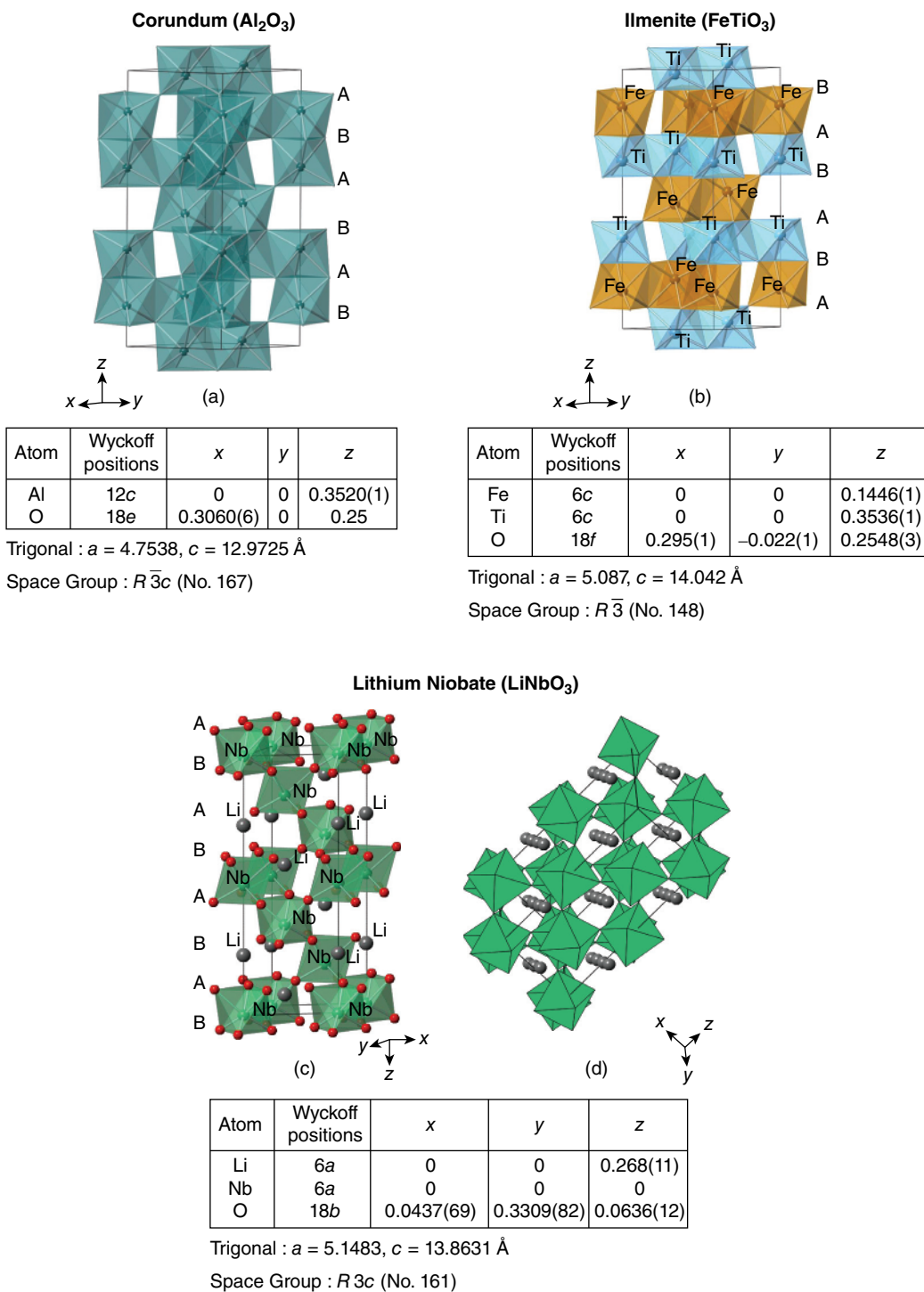


Figure 1.46 Crystal structures of (a) corundum, (b) ilmenite and (c, d) LiNbO_3 .

Table 1.24 *Some compounds with corundum-related structures*

Corundum (α -alumina)	M ₂ O ₃ : M = Al, Cr, Fe (hematite), Ti, V, Ga, Rh Al ₂ O ₃ : with Cr dopant (ruby) Al ₂ O ₃ : with Ti dopant (sapphire)
Ilmenite	MTiO ₃ : M = Mg, Mn, Fe, Co, Ni, Zn, Cd MgSnO ₃ , CdSnO ₃ NiMnO ₃ NaSbO ₃
LiNbO ₃ , LiTaO ₃	

Li₃Bi and Fe₃Al. These structures represent an extreme with full occupancy of all tetrahedral and octahedral sites. Partial tetrahedral site occupancies occur in the lanthanum hydrides which form a continuous solid solution between LaH_{1.9} and LaH₃.

Oxygen-excess fluorites occur in UO_{2+x} (see Fig. 2.10); the structure is distorted locally and the extra oxide ions are displaced off cube body centres. This has a knock-on effect in which some of the corner oxide ions are displaced onto interstitial sites. The UO_{2+x} system has been studied in considerable detail because of its importance in the nuclear industry as a fuel in nuclear reactors.

Mixed anion oxyfluorides such as LaOF and SmOF form the fluorite structure in which similarly sized O²⁻ and F⁻ ions are disordered over the tetrahedral sites. Various examples of mixed-cation fluorites are known in which two different cations are ordered, as shown for several examples in Fig. 1.47. These structures are rather idealised, however, since the anions are displaced off the centres of the tetrahedral sites in various ways to give, for instance, a distorted tetrahedral environment for Cr²⁺ in SrCrF₄ and distorted octahedral coordination for both Ti and Te in TiTe₃O₈.

Li₂O has the antifluorite structure and various Li-deficient antifluorites are good Li⁺ ion conductors; for instance, Li₉N₂Cl₃ has 10% of the Li⁺ sites vacant, giving rise to high Li⁺ ion mobility.

The *pyrochlore* structure may be regarded as a distorted, anion-deficient fluorite with two different-sized cations A and B. Its formula is written as either A₂B₂X₇ or A₂B₂X₆X'. The unit cell is cubic with a ~11 Å and contains eight formula units. In principle, the structure is simple since, ideally, it is a fluorite with one-eighth of the tetrahedral anion sites empty. Also, there is only one variable positional parameter, the *x* fractional coordinate of the 48 X atoms in the position (*x*, 1/8, 1/8), etc., Fig. 1.48. Various compounds form the pyrochlore structure and their differences depend on the value of *x*, which is usually in the range 0.31–0.36. In the extreme case that *x* = 0.375, the structure is derived from an undistorted fluorite with 8-coordinate A cations, as in fluorite, but grossly distorted BX₆ octahedra. As *x* decreases, the 48 X atoms move off their regular tetrahedral sites and the cubic coordination of A becomes distorted: six X neighbours form a puckered hexagon and two X' atoms are at a different distance, in apical positions, on either side of the puckered hexagon.

At *x* = 0.3125, the B coordination becomes undistorted octahedral and the BX₆ octahedra link by sharing corners to form a 3D network. The A coordination may be described as 2X' + 6X, with short A–X' bonds. These A–X' bonds form a 3D network, A₂X', that interpenetrates the network of BX₆ octahedra, of stoichiometry B₂X₆. The A₂X' net, with linear X'–A–X units and X'A₄ tetrahedra, is similar to that in cuprite, Cu₂O. The B₂X₆ and A₂X' networks, that together form the pyrochlore structure, are shown separately in Fig. 1.48.

Pyrochlore-based oxides have a range of interesting properties and applications. La₂Zr₂O₇ is an electronic insulator whereas Bi₂Ru₂O_{7-δ} is metallic and Cd₂Re₂O₇ is a low temperature superconductor. (Gd_{1.9}Ca_{0.1})Ti₂O_{6.9} is an oxide ion conductor and Y₂Mo₂O₇ is a spin glass. As indicated in some of the above examples, the anion content is not always 7 and indeed the amount of X' in the general formula can have values between 0 and 1 in different pyrochlores.

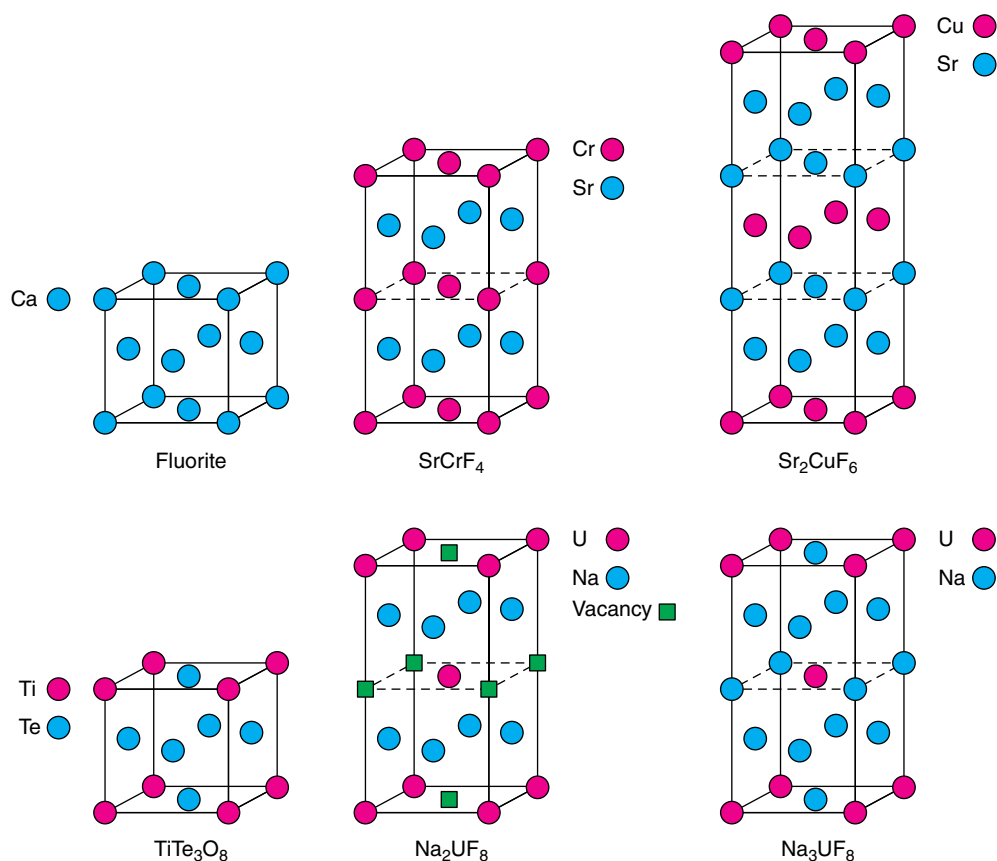


Figure 1.47 Some cation-ordered fluorites showing cation positions relative to those in fcc fluorite. A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press (2012).

The *rare earth oxides* RE_2O_3 have structures derived from oxygen-deficient fluorite in which the rare earth CN is reduced to 7 or 6. There are three structure types stable below 2000 °C: hexagonal A, monoclinic B and cubic C (or bixbyite) with A favoured by larger cations La to Pm, C by the smaller cations Gd to Lu and B by those of intermediate size. Some oxides are polymorphic and transform in the sequence C to B to A with increasing temperature, although most do not form all three polymorphs. Structure types and polymorphisms are summarised in Fig. 1.48(b) with part of the structure of A-type La_2O_3 in (c) showing 7-fold coordination of La in the form of a distorted cube with one corner missing. The B structure is a monoclinic distortion of A giving rise to a mixture of 6- and 7-coordinate RE cations whereas the C structure has 6-coordinate cations. The mineral name of the C structure is bixbyite, $(\text{Fe},\text{Mn})_2\text{O}_3$ and it is essentially cubic fluorite with $\frac{1}{4}$ of the oxygens missing.

The *weberite* structure, $\text{Na}_2\text{MgAlF}_7$, is another anion-deficient fluorite superstructure, closely related to pyrochlore that is shown by a range of fluorides and oxides of general formula $\text{A}_2\text{B}_2\text{X}_7$. The ideal symmetry of weberite is orthorhombic, space group *Imma*, but several structurally-related polymorphs occur, depending on composition. The anion-deficiency relative to fluorite leads to an overall reduction in cation coordination number with two types of distorted AX_8 polyhedra and two sets of BX_6 octahedra. It may be regarded as a 3D network of corner-sharing BX_6 octahedra, but also as a complex interpenetrating network of corner- and edge-sharing AO_8 polyhedra within

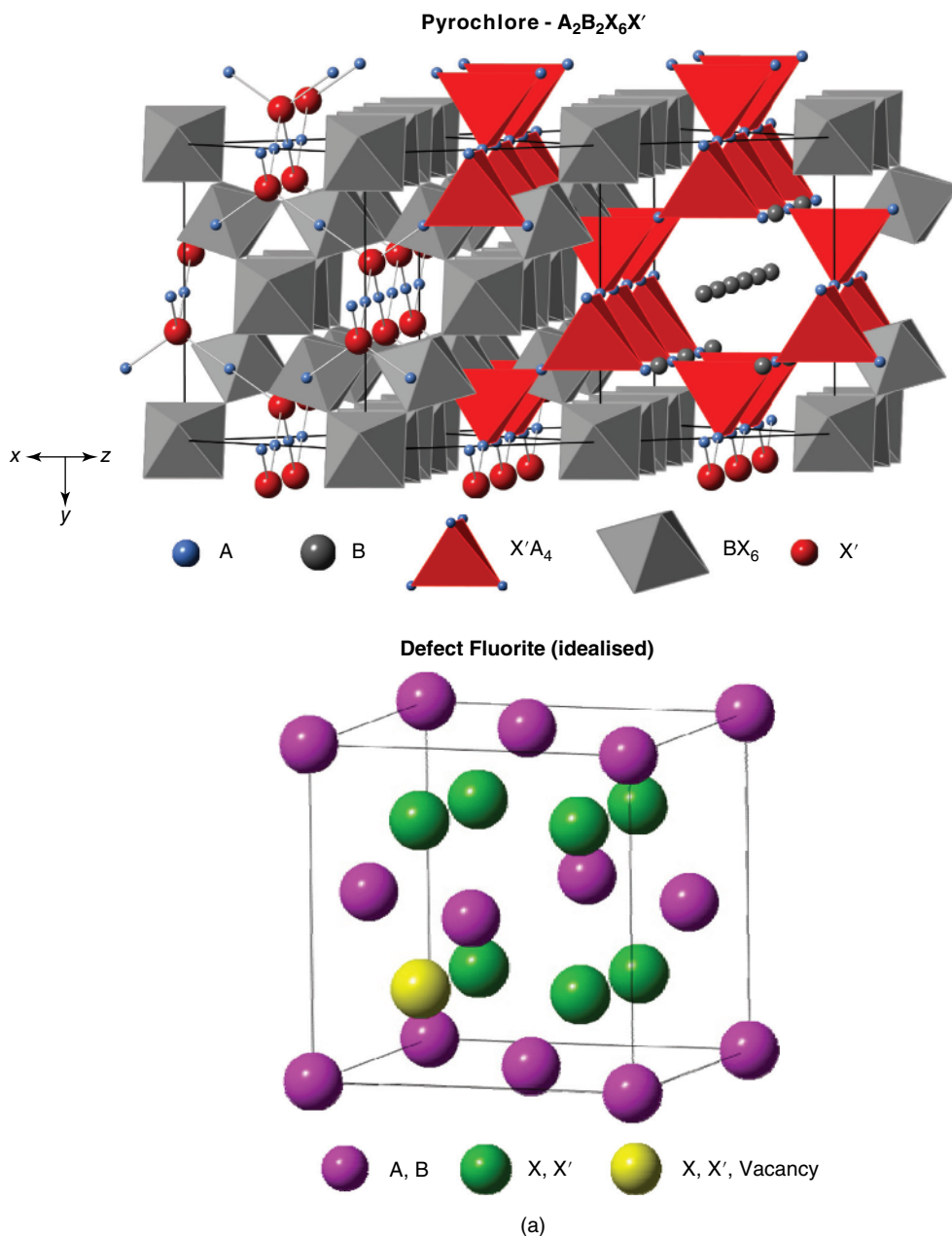


Figure 1.48 The pyrochlore structure, which may be regarded as a distorted, $2 \times 2 \times 2$ superstructure of a cation-ordered, anion-deficient fluorite. Anions in eightfold positions, e.g. $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in fluorite split into two groups in pyrochlore, with one group, X, in 48-fold positions at e.g. $(x, \frac{1}{8}, \frac{1}{8})$. (b) Temperature-dependent polymorphism of the rare earth sesquioxides. G. Adachi and N. Imanaka, *Chem. Rev.* 98, 1479 (1998). (c) part of the C-type La_2O_3 crystal structure showing 7-coordinate La.

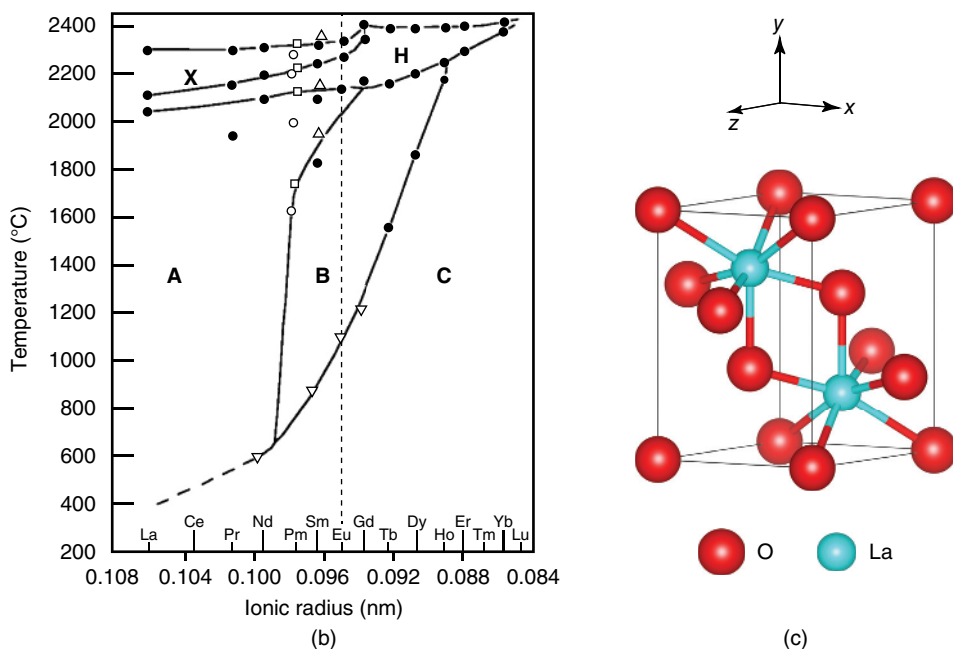


Figure 1.48 (Continued)

which the anions occupy three sets of crystallographically-distinct tetrahedral sites. The cations in isolation form ccp layers, equivalent to those in the (111) orientation in fluorite and pyrochlore, but have two stoichiometries, A_3B and AB_3 , that alternate. The A components of these layers also form a so-called Kagome network of interlinked hexagons and triangles which may be regarded as cp layers with $\frac{1}{4}$ of the packing atoms absent.

A range of complex oxides have weberite structures, in compositional families such as Ln_3NbO_7 , better written more informatively as $Ln_2(Ln, Nb)O_7$; $Ln = La, Nd, Gd, Dy$; $Ln_2B_2O_7$: $LnB = NdZr, SmTi$; $A_2Sb_2O_7$: $A = Ca, Sr, Pb$ and $Ca_2(Ta, Nb)_2O_7$ (see L Cai and JC Nino, *Acta Cryst B* **65**, 269 (2009) for more details). Weberite oxides are of interest, showing a diverse range of electrical properties. Various weberite fluorides are known, with Na or Ag as the A-cations and different divalent, trivalent B cation combinations such as B^{2+} : Mg, Mn, Fe, Co, Ni, Cu, Zn and B^{3+} : Sc, V, Cr, Fe, Al, Ga, In, Tl; most interest is in the magnetic interactions associated with the different transition metal combinations in the B sites within the Kagome A sublattice.

1.17.13 Garnet

The garnets are a large family of complex oxides, including both minerals and synthetic materials, some of which are important ferromagnetic materials; yttrium aluminium garnet (YAG) is used as a synthetic gemstone and when doped with neodymium is the key component in YAG lasers; more recently, garnets with high Li^+ ion conductivity have been synthesised; garnets have hardness 6.5–7.5 on the Mohs scale and are used industrially as an abrasive on sandpaper. They have the general formula $A_3B_2X_3O_{12}$: $A = Ca, Mg, Fe$, etc.; $B = Al, Cr, Fe$, etc.; $X = Si, Ge, As, V$, etc. A is a large ion with a radius of $\sim 1 \text{ \AA}$ and has a coordination number of eight in a distorted cubic environment. B and X are smaller ions which occupy octahedral and tetrahedral sites, respectively. Garnets with $A = Y$ or a

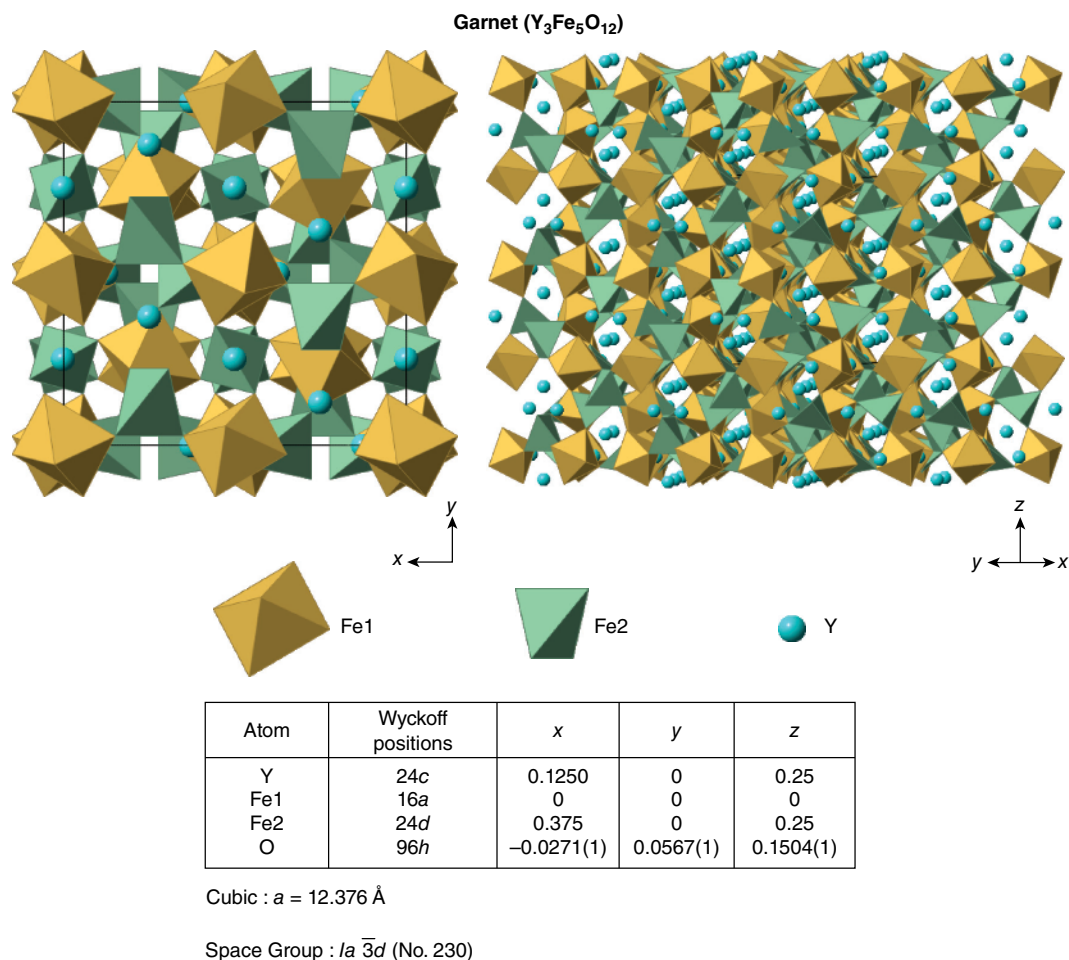


Figure 1.49 *The garnet crystal structure.*

rare earth: Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu and B, X = Fe^{3+} have interesting magnetic properties. One of the most important is yttrium iron garnet (YIG), $\text{Y}_3\text{Fe}_5\text{O}_{12}$, the structure of which is shown in Fig. 1.49. Many other A, B, X combinations are possible, such as those in Table 1.25.

The unit cell of garnet is body centred cubic, $a \approx 12.4 \text{ \AA}$, and contains eight formula units. The structure may be regarded as a framework built of corner-sharing BO_6 octahedra and XO_4 tetrahedra. The larger A ions occupy eight-coordinate cavities within this framework. In YIG and the rare earth garnets, the B and X ions are the same, Fe^{3+} .

1.17.14 Perovskite-rock salt intergrowth structures: K_2NiF_4 , Ruddlesden–Popper, Aurivillius and Dion Jacobsen phases and layered cuprate superconductors

The K_2NiF_4 structure is the simplest structure of a large family of related materials that has attracted much attention in recent years because several of them are superconductors. The structure may be regarded as alternating layers of perovskite and rock salt structures, as shown in Fig. 1.50. The formula K_2NiF_4 could be written in expanded form as $\text{KNiF}_3 \cdot \text{KF}$ to indicate the perovskite and rock salt

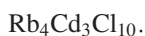
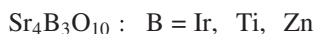
Table 1.25 Examples of A, B, X combinations in garnets

Garnet	A	B	X	O
Grossular	Ca ₃	Al ₂	Si ₃	O ₁₂
Uvarovite	Ca ₃	Cr ₂	Si ₃	O ₁₂
Andradite	Ca ₃	Fe ₂	Si ₃	O ₁₂
Pyrope	Mg ₃	Al ₂	Si ₃	O ₁₂
Almandine	Fe ₃	Al ₂	Si ₃	O ₁₂
Spessartine	Mn ₃	Al ₂	Si ₃	O ₁₂
	Ca ₃	CaZr	Ge ₃	O ₁₂
	Ca ₃	Te ₂	Zn ₃	O ₁₂
	Na ₂ Ca	Ti ₂	Ge ₃	O ₁₂
	NaCa ₂	Zn ₂	V ₃	O ₁₂

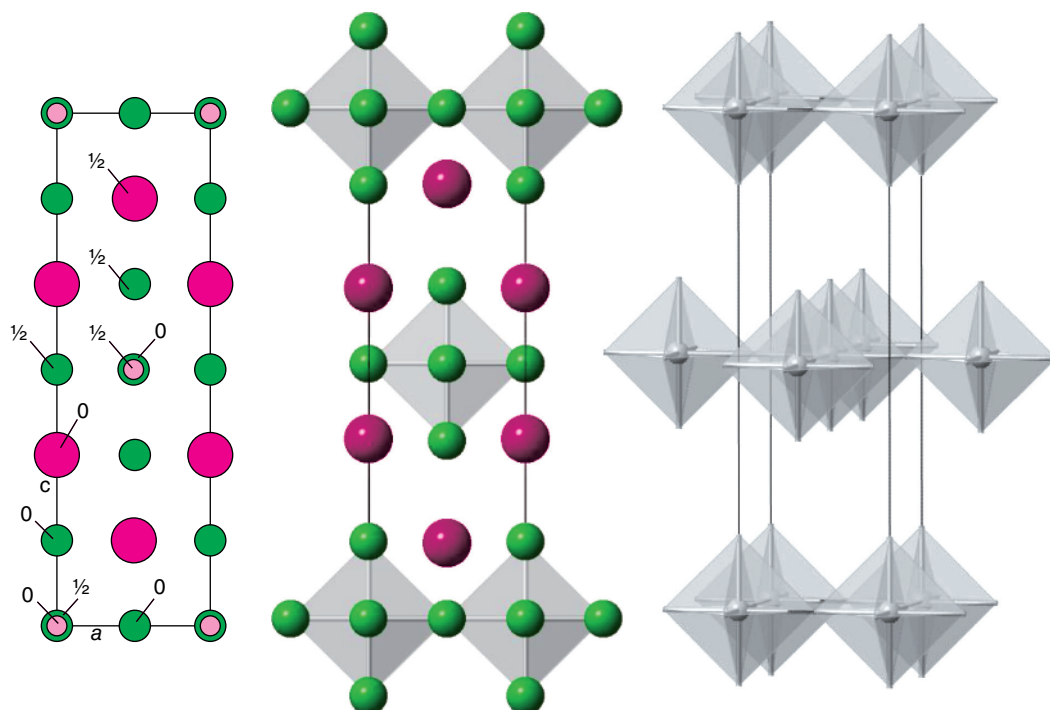
components. The structure is body centred tetragonal with perovskite-like layers of octahedra centred at $c = 0$ and $c = \frac{1}{2}$. K⁺ ions lie at the interface between rock salt and perovskite blocks and have a coordination number of 9. The coordination number of K in rock salt would be 12 but the rock salt blocks are less than one unit cell thick and the K coordination in rock salt is interrupted by the atomic displacements that generate perovskite blocks. The K₂NiF₄ structure occurs with a range of fluorides and chlorides containing small divalent cations, Table 1.26, and with a range of oxides with different charge combinations such as A₂⁺B⁶⁺O₄, A₂²⁺B⁴⁺O₄, A₂³⁺B²⁺O₄, A²⁺A'³⁺B³⁺O₄ and A₂³⁺B_{1/2}⁺B'_{1/2}³⁺O₄ containing large A and small B cations; probably other cation combinations are also possible.

A-site cation ordering occurs in A⁺A'³⁺B⁴⁺O₄: A = Na, A' = La → Lu, B = Ti; Na and the lanthanides occupy different layers in the c direction. Anion-deficient and anion-excess K₂NiF₄ structures exist. For example, in Sr₂XO₃: X = Cu, Pd, one-quarter of the oxygens are removed, giving square planar coordination for X and seven-coordinate Sr, whereas in La₂NiO_{4+x}, interstitial oxygens are present.

The *Ruddlesden–Popper* series of compounds have the K₂NiF₄ structure as their simplest family member; other family members exist with more layers in the perovskite blocks. Thus, with strontium titanates, a family of phases exists with general formula Sr_{*n*+1}Ti_{*n*}O_{3*n*+1} and consist of *n*SrTiO₃ perovskite blocks interleaved with SrO rock salt layers. Two members of this family are Sr₃Ti₂O₇ ($n = 2$) and Sr₄Ti₃O₁₀ ($n = 3$). The $n = \infty$ member corresponds to SrTiO₃ perovskite. These phases retain a tetragonal unit cell with similar a dimensions but have much longer c axes. A similar family of phases forms for La_{*n*+1}Ni_{*n*}O_{3*n*+1}: $n = 1, 2, 3, \infty$. In most cases, only one or two members of the Ruddlesden–Popper series are known, with examples such as



A large and diverse family of Cu-based perovskite-rock salt intergrowth phases contains many examples of the *high T_c cuprate superconductors*. The key element for the superconductivity is Cu and it shows enormous structural diversity in the cuprates with coordination numbers ranging from



● Ni: $0\ 0\ 0; \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$

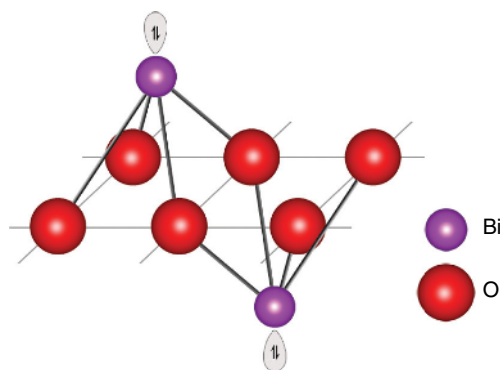
● K: $\pm\ 0\ 0\ z; \pm\ \frac{1}{2}\ \frac{1}{2}\ z + \frac{1}{2}; z = 0.35$

● F(1): $\frac{1}{2}\ 0\ 0; 0\ \frac{1}{2}\ 0; 0\ \frac{1}{2}\ \frac{1}{2}, \frac{1}{2}\ 0\ \frac{1}{2}$
 F(2): $\pm\ 0\ 0\ z; \pm\ \frac{1}{2}\ \frac{1}{2}\ z + \frac{1}{2}; z = 0.15$

Tetragonal: $a = 4.006\ \text{\AA}, c = 13.076\ \text{\AA}$

Space group: $I4/mmm$ (No. 139)

(a)



(b)

Figure 1.50 (a) The K_2NiF_4 structure. (b) The Bi_2O_2 layers that form part of the intergrowth structure of Aurivillius phases.

Table 1.26 Some compounds with the K_2NiF_4 structure

Compound ^a	a/Å	c/Å	z (M ⁺ ion)	z (anion)
K ₂ NiF ₄	4.006	13.076	0.352	0.151
K ₂ CuF ₄	4.155	12.74	0.356	0.153
Ba ₂ SnO ₄	4.140	13.295	0.355	0.155
Ba ₂ PbO ₄	4.305	13.273	0.355	0.155
Sr ₂ SnO ₄	4.037	12.53	0.353	0.153
Sr ₂ TiO ₄	3.884	12.60	0.355	0.152
La ₂ NiO ₄	3.855	12.652	0.360	0.170
K ₂ MgF ₄	3.955	13.706	0.35	0.15
Other examples ^b				
M ₂ Y ⁶⁺ O ₄ : M = K, Rb, Cs; Y = U, Np				
Ln ₂ YO ₄ : Ln = La → Nd; Y = Ni, Cu				
CaLnAlO ₄ : Ln = La → Er, Y				
SrLnFeO ₄ : Ln = La → Tb				
SrLnCrO ₄ : Ln = La → Dy				
BaLnFeO ₄ : Ln = La → Eu				
La ₂ Li _{1/2} Y _{1/2} O ₄ : Y = Ni, Co				
A ₂ BF ₄ : A = K, Rb, Tl; B = Mg, Ni, Zn, Co, Fe				
A ₂ BCl ₄ : A = Rb, Cs; B = Cr, Mn, Cd				
Sr ₂ BO ₄ : B = Ti, Sn, Zr, Hf, Mo, Tc, Ir, Ru, Rh, Mn				

^a R. W. G. Wyckoff, *Crystal Structures*, Vols 1 to 6, Wiley (1971).^b O. Muller and R. Roy, *The Major Ternary Structural Families*, Springer-Verlag (1974).

2 (linear) to 4 (square planar), 5 (pyramidal) and 6 (octahedral), as discussed in Section 8.3.6. In addition to YBa₂Cu₃O₇ and related materials which are basically oxygen-deficient perovskites, Bi- and Tl-based cuprates are perovskite–rock salt intergrowth phases with considerable compositional and structural complexity. The BiSCCO superconductors consist of three phases that are labelled according to their Bi:Sr:Ca:Cu ratios: 2201, 2212 and 2223. The 2212 phase (80 K superconductor), Bi₂Sr₂CaCu₂O₈ has rock salt-like layers, Bi₂O₂, that separate double perovskite layers containing Cu in octahedral sites, whereas the 2223 phase (110 K superconductor) has triple perovskite layers. In these structures, SrO layers form a coherent interface between rock salt and perovskite components.

The *Aurivillius* family of phases are ordered intergrowth structures consisting of one or more perovskite layers of corner-sharing octahedra separated by single layers of formula Bi₂O₂. The Bi₂O₂ layers are formed by a single, 2D square planar net of oxygens in which each square is capped on one side only by Bi³⁺ to give sheets of pyramids in an alternating ‘up’ and ‘down’ arrangement, Fig. 1.50(b). Bi³⁺ is a lone pair-active, heavy *p*-block cation and the spatial disposition of the lone pairs acts to separate the Bi₂O₂ layers from the perovskite blocks. This Bi₂O₂ structural arrangement is different to the octahedral rock salt arrangement of Bi in the BiSCCO phases.

The general formula of Aurivillius phases is Bi₂O₂[A_{m-1}M_mO_{3m+1}]. Examples include: M=Mo, *m* = 1 for Bi₂O₂[MoO₄] with a single layer of perovskite-like octahedra; Bi₂O₂[SrNb₂O₇] with a double perovskite layer of NbO₆ octahedra and Sr in 12-coordinate cages; Bi₂O₂[Bi₂Ti₃O₁₀] with triple perovskite layers and Bi in the 12-coordinate perovskite A sites as well as in the Bi₂O₂ layers.

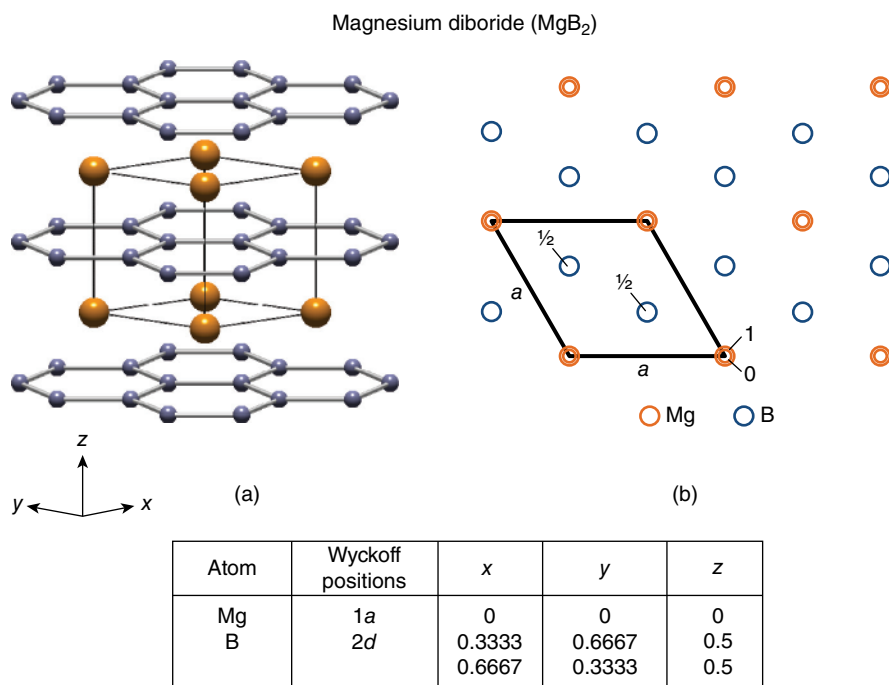
The *Dion-Jacobsen* phases are related to Aurivillius phases but the Bi₂O₂ layers are replaced by layers of alkali cations to give the general formula A'[A_{m-1}M_mX_{3m+1}]. Examples include K[LaNb₂O₇] that has double perovskite layers and Cs[La₂Ti₂NbO₁₀] with triple layers.

1.17.15 The aluminium diboride structure (AlB₂)

The aluminium diboride family of crystal structures shot to prominence in 2000 when isostructural MgB₂ was discovered to be a superconductor with $T_c = 39$ K. It has a relatively simple crystal structure, shown in Fig. 1.51, in which Mg atoms form close packed layers stacked in an AAA sequence, which may be referred to as primitive hexagonal packing, *hp*. The *cp* Mg layers are separated by B layers arranged as in graphite; hence Mg is 12-coordinate with hexagonal rings of B atoms above and below. Each B has three B nearest neighbours in a trigonal planar arrangement and six Mg next nearest neighbours arranged in a trigonal prism.

Numerous borides and silicides have the AlB₂ structure, including MB₂: M = Ti, Zr, Nb, Ta, V, Cr, Mo, Mg, U, and MSi₂: M = U, Pu, Th. The crystal structure of some metal hydroxides such as Cd(OH)₂ is also closely related.

The AlB₂ structure is closely related to the NiAs structure. In both structures, the metal atoms form a primitive hexagonal array but only half the trigonal prismatic sites are occupied by As in NiAs whereas all trigonal prismatic sites are occupied by B in AlB₂. Consequently, the coordination of Ni is octahedral in NiAs instead of 12-coordinate Al in AlB₂.



Hexagonal : $a = 3.08489$, $c = 3.52107$ Å

Space Group : $P6/mmm$ (No. 191)

Figure 1.51 The crystal structure of MgB₂ as (a) an oblique projection showing hexagonal rings of B atoms with 12-coordinate Mg situated between pairs of rings and (b) [001] projection of the crystal structure.

1.17.16 Silicate structures – some tips to understanding them

Silicates, especially many minerals, often have complex formulae and structures. The purpose of this section is not to give a review of their structures but simply to show that a considerable amount of structural information may be obtained from their chemical formulae. Using certain guidelines, one can appreciate, without the necessity of remembering a large number of complex formulae, whether a particular silicate is a 3D framework structure, sheet-like, chain-like, etc.

It is common practice to regard silicate structures as composed of cations and silicate anions. Various silicate anions are possible, ranging from the extremes of isolated SiO_4^{4-} tetrahedra in orthosilicates such as olivine (Mg_2SiO_4), to infinite 3D frameworks, as in silica itself (SiO_2). The structures of silicate anions are based on certain principles:

1. Almost all silicate structures are built of SiO_4 tetrahedra.
2. The tetrahedra may link by sharing corners to form larger polymeric units.
3. No more than two SiO_4 tetrahedra may share a common corner (i.e. oxygen).
4. SiO_4 tetrahedra never share edges or faces with each other.

Exceptions to (1) are structures in which Si is octahedrally coordinated to O as in one polymorph of SiP_2O_7 and in high-pressure polymorphs of SiO_2 (coesite, stishovite). The number of these exceptions is very small, however, and we can regard SiO_4 tetrahedra as the normal building block in silicate structures. Guidelines (3) and (4) are concerned, respectively, with maintaining local electroneutrality and with ensuring that highly charged cations, such as Si^{4+} , are not too close together.

The important factor in relating the formula to structure type is the Si:O ratio. This ratio is variable since two types of O may be distinguished in the silicate anions: *bridging oxygens* and *non-bridging oxygens*. Bridging oxygens are those that link two tetrahedra, Fig. 1.52. Effectively, they belong half to one Si and half to another Si. In evaluating the net Si:O ratio, bridging oxygens count as $\frac{1}{2}$. Non-bridging oxygens are linked to only one Si or silicate tetrahedron as in (b). They are also called *terminal oxygens*. In order to maintain charge balance, non-bridging oxygens must of course also be linked to other cations in the crystal structure. In evaluating the overall Si:O ratio, non-bridging oxygens count as 1.

The overall Si:O ratio in a silicate structure depends on the relative number of bridging and non-bridging oxygens. Some examples are given in Table 1.27; they are all straightforward and one may deduce the type of silicate anion directly from the chemical formula.

Many more complex examples could be given. In these, although the detailed structure cannot be deduced from the formula, one can at least get an approximate idea of the type of silicate anion. For example, in $\text{Na}_2\text{Si}_3\text{O}_7$, the Si:O ratio is 1:2.33. This corresponds to a structure in which, on average, two-thirds of an O per SiO_4 is non-bridging. Clearly, therefore, some SiO_4 tetrahedra must be composed entirely of bridging oxygens whereas others contain one non-bridging oxygen. The structure of the silicate anion would therefore be expected to be something between an infinite sheet and a 3D framework. In fact, it is an infinite, double-sheet silicate anion in which two-thirds of the silicate tetrahedra have one non-bridging O.

The relation between formula and anion structure is more complex when Al is present. In some cases, Al substitutes for Si, in the tetrahedra; in others, it occupies octahedral sites. In the plagioclase feldspars typified by albite, $\text{NaAlSi}_3\text{O}_8$, and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, Al partly replaces Si in the silicate anion. It is therefore appropriate to consider the overall ratio (Si + Al):O. In both cases, this ratio is 1:2 and, therefore, a 3D framework structure is expected, as in SiO_2 itself, Fig 1.52(c). Framework structures also occur in orthoclase, KAlSi_3O_8 , kalsilite, KAlSiO_4 , eucryptite, LiAlSiO_4 , and spodumene, $\text{LiAlSi}_2\text{O}_6$.

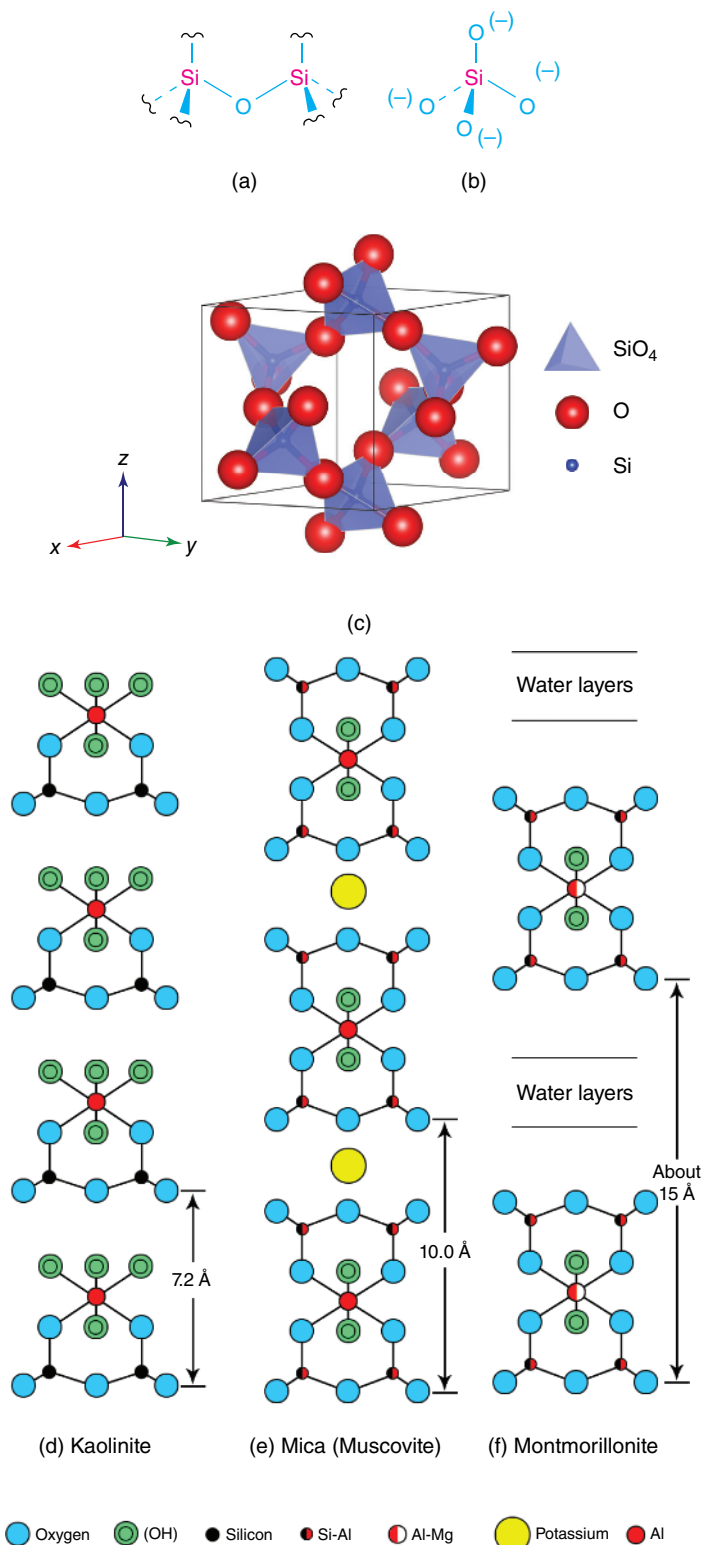


Figure 1.52 Silicate anions with (a) bridging and (b) non-bridging oxygens. (c) The quartz structure formed by a 3D network of corner-sharing silicate tetrahedra, within which, 6-membered rings can be identified. These rings enclose cavities that can accommodate interstitial cations such as Li^+ , Section 2.3.3.1. (d, e, f) Building blocks, schematically, of clay mineral structures. Adapted from W. M. Carty, Bull. Amer. Ceram. Soc. 72 (1999).

Table 1.27 Relation between chemical formula and silicate anion structure

Si:O ratio	Number of oxygens per Si		Type of silicate anion	Examples
	Bridging	Non-bridging		
1:4	0	4	Isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	Dimer $\text{Si}_2\text{O}_7^{6-}$	$\text{Ca}_3\text{Si}_2\text{O}_7$ rankinite, $\text{Sc}_2\text{Si}_2\text{O}_7$ thortveite
1:3	2	2	Chains $(\text{SiO}_3)_n^{2n-}$	Na_2SiO_3 , MgSiO_3 pyroxene
			Rings, e.g. $\text{Si}_3\text{O}_9^{6-}$	CaSiO_3^a , $\text{BaTiSi}_3\text{O}_9$ benitoite
			$\text{Si}_6\text{O}_{18}^{12-}$	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ beryl
1:2.5	3	1	Sheets $(\text{Si}_2\text{O}_5)_n^{2n-}$	$\text{Na}_2\text{Si}_2\text{O}_5$
1:2	4	0	3D framework	SiO_2^b

^a CaSiO_3 is dimorphic. One polymorph has $\text{Si}_3\text{O}_9^{6-}$ rings and the other has infinite $(\text{SiO}_3)_n^{2n-}$ chains.

^b The three main polymorphs of silica, quartz, tridymite, and cristobalite, each have a different kind of 3D framework structure.

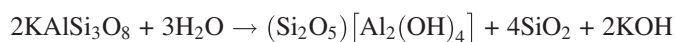
Substitution of Al for Si occurs in many sheet structures such as micas and clay minerals. Talc has the formula $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$ and, as expected for an Si:O ratio of 1:2.5, the structure contains infinite silicate sheets. In the mica phlogopite, one-quarter of the Si in talc is effectively replaced by Al and extra K is added to preserve electroneutrality. Hence phlogopite has the formula $\text{KMg}_3(\text{OH})_2(\text{Si}_3\text{Al})\text{O}_{10}$. In talc and phlogopite, Mg occupies octahedral sites between silicate sheets; K occupies 12-coordinate sites.

The mica muscovite, $\text{KAl}_2(\text{OH})_2(\text{Si}_3\text{Al})\text{O}_{10}$, is more complex; it is structurally similar to phlogopite, with infinite sheets, $(\text{Si}_3\text{Al})\text{O}_{10}$. However, two other Al^{3+} ions replace the three Mg^{2+} ions of phlogopite and occupy octahedral sites. By convention, only ions that replace Si in tetrahedral sites are included as part of the complex anion. Hence octahedral Al^{3+} ions are formally regarded as cations in much the same way as alkali and alkaline earth cations, Table 1.27.

With a few exceptions, silicate structures cannot be described as *cp*. However, this disadvantage is offset by the clear identification of the silicate anion component which facilitates classification and description of a very wide range of structures. In addition, the Si–O bond is strong and partially covalent and the consequent stability of the silicate anion is responsible for many of the properties of silicates.

Many examples of silicate crystal structures are given in the minerals section of the CrystalViewer Companion website. To facilitate viewing of the silicate anion, the remaining cations in the structures can be hidden; you can check out the numbers of bridging and non-bridging oxygens for consistency with the Si–O ratio in the mineral formulae.

The structural building blocks of clay minerals are illustrated in Fig. 1.52(d, e, f). They consist of layers of silicate or aluminosilicate tetrahedra which all have the same orientation; their apices are connected to layers of Al, Mg octahedra to form either (d) double- or (e,f) triple-layered sheets. Clay minerals form in nature by the decomposition of feldspars such as microcline or orthoclase to give kaolinite:



Kaolinite has a two layer, 1:1, structure (d) whose opposite surfaces are the basal planes of $\text{Si}_2\text{O}_5^{2-}$ layers and $\text{Al}_2(\text{OH})_4^{2+}$ layers. These double layers are stacked together and separated by weak van der Waals bonds, that give rise to the softness and easy cleavage of such clay minerals. Other layered minerals such as muscovite (e), montmorillonite (f), talc, bentonite and pyrophyllite have a three layer, 2:1, structure in which the layer of octahedra is sandwiched between two layers of tetrahedra. If the overall structure is electrically neutral, then the interlayer, van der Waals space may contain only water

molecules (f), but if the layers have a net negative charge then cations such as K^+ also occupy the interlayer space, as in micas (e).

Kaolinite clays have long-standing industrial uses as the fundamental components of whitewares and traditional ceramics. The interlayer bonding forces control the rheological properties and viscosity of slips during processing and formation of the green bodies. In a kaolin particle, the opposite faces of the sheets have different chemical properties and respond differently in an aqueous environment. The bases of the silicate tetrahedra are weakly acidic whereas those of the hydroxide octahedra are weakly basic. Further, the effective surface charges change sign at a different pH for the two particle surfaces. Thus, the silicate surface has an *isoelectric point*, *IEP* at pH ~ 3 at which the surface charge, or *zeta potential*, changes sign, whereas the *IEP* for the hydroxide surface is at pH ~ 10 . This means that at neutral pH, for instance, the two surfaces are oppositely charged. Control of surface charges is vital to the dispersion/agglomeration of particles during slip casting and therefore, for the quality of the ceramic product.

There is increasing interest in the synthesis of new functional materials by starting with layered structures such as clay minerals and modifying the components – ionic or molecular – that occupy the interstitial space between the layers. A wide range of materials and properties can be synthesised by *chimie douce* methods, such as pillared clays that have novel porous structures and magnetic hybrid materials. Such materials are kinetically stable, although thermodynamically metastable and cannot be prepared by the usual high temperature solid state reaction methods (Section 4.3.7.2).

1.18 Point Groups and Space Groups

A working knowledge of point groups and space groups is invaluable for anyone interested in crystal chemistry and structure-property relations. Without such knowledge, one is entirely dependent for information about crystal structures on the availability of 3D models, crystal structure libraries, or good quality drawings in the literature. Once the basic principles of space groups are grasped, however, it is possible to make drawings of a structure for oneself, from different orientations if required, or even to construct one's own 3D models. All that is needed is a listing of the atomic coordinates in the structure and details of the relevant space group. There are also various excellent commercial software packages, such as Crystal-Maker, available which take away much of the hard work involved in preparing structural drawings.

This section is written for the non-crystallographer; short-cuts are made and many of the complications and subtleties of space groups are avoided. The main objective is to show the relation between space groups and sets of atomic coordinates on the one hand and 3D crystal structures on the other. A familiarity with unit cells, crystal systems, Bravais lattices and the elements of point and space symmetry, summarised in Sections 1.1–1.6, is essential background knowledge. We begin with a discussion of *point groups*. Point groups are much simpler than *space groups* because the elements of translational symmetry are absent from point groups. They therefore provide a relatively painless introduction to the subject while introducing the necessary concepts at an early stage. We then look at a few selected examples of space groups and finish with two examples that show the derivation of crystal structures from space group and atomic coordinates information.

1.18.1 Point groups

The elements of point symmetry which may be observed in crystals are the rotation axes 1, 2, 3, 4 and 6, the inversion axes $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$, and the mirror plane, m (which is equivalent to $\bar{2}$). These symmetry elements may occur either alone or in various possible combinations with each other to give a total of 32 possible *crystallographic point groups*. The method of drawing and labelling point groups used here is the same as that recommended in *International Tables for X-ray Crystallography*, Vol 1. The

Table 1.28 Point symmetry elements

Symmetry element	Written symbol	Graphical symbol
Rotation axes	1	None
	2	
	3	
	4	
	6	
Inversion axes	$\bar{1}$	None ^a
	$\bar{2} (\equiv m)$	
	$\bar{3} (\equiv 3 + \bar{1})$	
	$\bar{4}$	
	$\bar{6} (= 3/m)$	
Mirror plane	m	

^a The inversion axis, $\bar{1}$, equivalent to a centre of symmetry, is represented as a small open circle, o , in space groups, but does not have a formal graphical representation in point groups, even though it is present in many point groups.

^b The inversion axis, $\bar{2}$ does not have a separate graphical symbol other than that of the mirror plane equivalent to it.

Table 1.29 The thirty-two point groups

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

symbols for the different point symmetry elements are given in Table 1.28. The thirty-two point groups, classified according to their crystal system, are listed in Table 1.29 and shown diagrammatically in Appendix E.

1.18.2 Stereographic projections and equivalent positions

Point groups are represented graphically as *stereographic projections*. These are used a lot, especially in geology and mineralogy, to represent, in 3D, the directions in crystals and to show the relative orientations of crystal faces. To construct a stereographic projection, the different symmetry elements in a point group are encapsulated within a sphere, which becomes a circle in the projection. Usually, one of the rotation or inversion axes of the point group is arranged to be perpendicular to the plane of the circle and passes through its centre. Each point group is represented by two diagrams: the right hand

one shows the symmetry elements; the left hand one shows the *equivalent positions* that are generated by the symmetry operations.

A simple point group that has only one symmetry element is the monoclinic point group 2, which consists of a single twofold rotation axis. It is shown as a stereographic projection in Fig. 1.52(b). The lens-shaped symbol in the centre of the circle represents the 2-fold rotation axis perpendicular to the plane of the circle and which passes through the centre of the sphere that the projection represents. The thin vertical line is a construction line; its significance can be seen in the companion drawing, (a) which shows the equivalent positions generated by the 2-fold rotational symmetry. We know that, if an object possesses a 2-fold rotation axis, it can be rotated by 180° about that axis to arrive at a position that is indistinguishable from the original position. This indistinguishable position or identical orientation is known, crystallographically, as an equivalent position and therefore, we can say that a 2-fold rotation axis generates two equivalent positions. In (a), if our original position is shown as the small dot symbol, 1, that is above the plane of the stereographic projection, the 2-fold axis generates an equivalent position at 2 which is also above the plane. On continuing with the rotation operation by a further 180° , position 2 moves around the circle to arrive back at starting position 1; hence, 1 and 2 are the two equivalent positions in this point group.

In Fig. 1.53(c, d), the trigonal point group, 3 is shown. This has a threefold axis perpendicular to the plane of the stereographic projection (d) and is represented by the solid triangle. Three equivalent

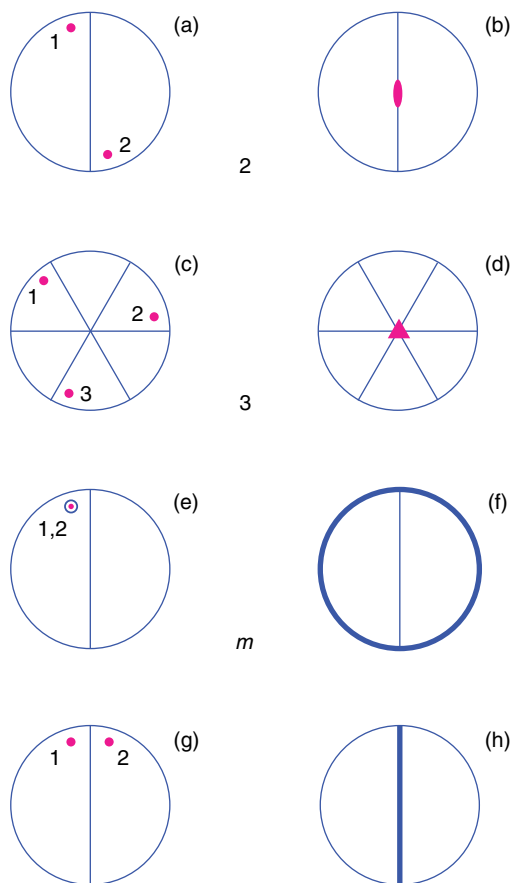


Figure 1.53 The point groups (a, b) 2, (c, d) 3, and (e–h) m.

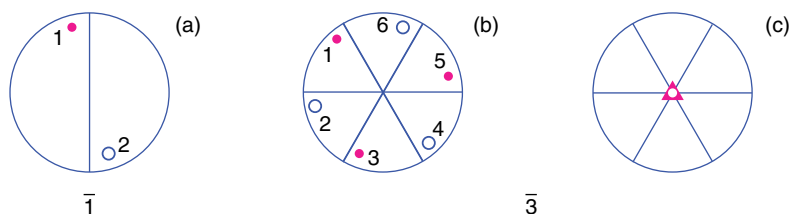


Figure 1.54 The point groups (a) $\bar{1}$ and (b, c) $\bar{3}$.

positions are generated by the operation steps that involve rotation by 120° , either clockwise or anti-clockwise, as shown in (c). Point groups 4 and 6 use the same principles as described for point groups 2 and 3 and are illustrated in Appendix E.

Monoclinic point group m is shown in Fig. 1.53(e, f) and in another orientation in (g, h). This has a single mirror plane which lies in the plane of the projection in (f) and is represented as a thick circle. Equivalent positions are generated by reflection across the mirror plane and hence, our starting position 1, above the plane generates an equivalent position 2, represented by an open circle, directly underneath the plane (e). In (h) the same point group, m , is shown but oriented vertically and perpendicular to the plane of the circle. It is represented by the thick line that bisects the projection that is shown; in this orientation, the equivalent positions are either side of the mirror and both are shown above the plane, (g); equally, they could both be below the plane.

The centre of symmetry in the point group, $\bar{1}$ is shown in Fig. 1.54(a). It does not have a symbolic representation and hence, only one diagram showing the equivalent positions is given. Recall that a centre of symmetry represents two identical positions that are equidistant from the centre of an object and lie on a straight line passing through its centre. This generates the two equivalent positions shown in (a): 1 lies above the plane; 2 lies on a straight line that passes through the centre, to an equal distance the other side and therefore, is below the plane.

The inversion axes, spoken as: *bar n*, i.e. $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$ are combined symmetry operations involving the rotation component, and inversion through the centre, as in $\bar{1}$. The trigonal point group $\bar{3}$ is shown in Fig. 1.54(b, c). The symbol for $\bar{3}$, in (c), is a solid triangle with an open circular centre. Six equivalent positions (b) are generated, 1–6, before finally returning to starting position 1. Point groups $\bar{2}$, $\bar{4}$ and $\bar{6}$ are shown in Appendix E; readers may like to confirm for themselves that point group $\bar{2}$ is equivalent to a mirror plane perpendicular to the 2-fold inversion axis.

So far, we have considered point groups that have a single symmetry element. The three orthorhombic point groups shown in Fig. 1.55 all have combinations of symmetry elements. For each, again, two diagrams are used. First, point group 222 has the three, mutually perpendicular twofold axes shown in (b): one is perpendicular to the plane of the projection, passes through the centre and is represented by the lens-shaped symbol in the centre of the projection; one runs vertically in the plane of the projection and is represented by two symbols on the circumference of the circle at the top and bottom; one runs horizontally in the plane of the projection and is represented by the two symbols at the left and right on the circle circumference.

In order to generate equivalent positions in point group 222, it is necessary to first, identify a starting position, shown in Fig. 1.56(a), and operate on that position with one of the symmetry elements, for example the 2-fold axis perpendicular to the plane of the projection. This generates a new equivalent position shown in (b). The operation is then repeated until arriving back at the starting position. The next step, 2 is to consider the effect of the symmetry operations associated with one of the other symmetry elements, which generates an additional set of equivalent positions. This is shown in (c) for the 2-fold axis running horizontally and in the plane of the paper; each of the equivalent positions

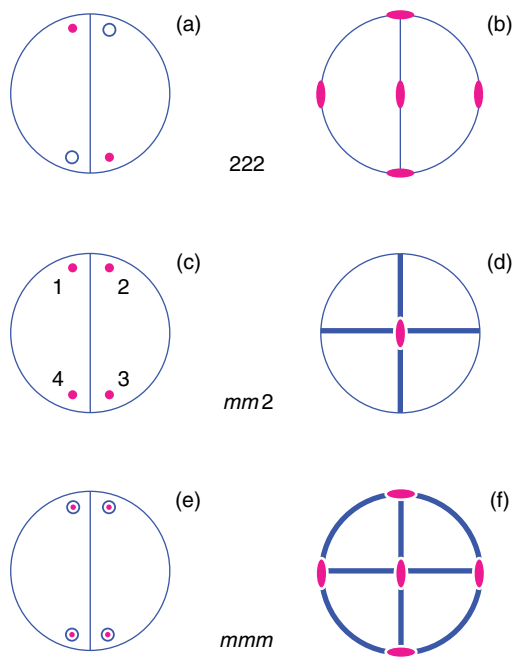


Figure 1.55 The three orthorhombic point groups 222, $mm2$, and mmm .

in (b), above the plane of the projection, generates a new position below the plane. Finally, the effect of the third symmetry element, step 3 is considered.

In this case, however, no new equivalent positions are generated in (d). The third 2-fold axis, shown vertically in the plane of the paper, is essentially redundant since it arises automatically from the presence of the other 2-fold axes. The point group 222 could therefore be represented in the shortest possible notation as 22 because the third twofold axis is not independent. The longer notation is used in order to show consistency with the essential symmetry requirements (Table 1.1) for orthorhombic unit cells. The order in which the symmetry axes are considered in Fig. 1.56 is unimportant and any two of the 2-fold axes together generate the third axis automatically.

Orthorhombic point group $mm2$, Fig. 1.55 contains two mirror planes at right angles to each other with a 2-fold axis passing along the line of intersection of the mirror planes (d). The 2-fold axis is perpendicular to the paper and the mirror planes are indicated in projection as the thick lines lying horizontally and vertically. This point group also has four equivalent positions, but all are at the same height relative to the plane of the paper (c). As in the previous example, the third symmetry element is not independent but is generated by the combined operation of any of the other two elements. The choice of order of the symmetry elements is again immaterial; any two out of the three, in combination, will generate the third element.

Orthorhombic point group mmm , Fig. 1.55, contains, as essential symmetry elements, three mirror planes mutually perpendicular to each other; as a consequence of the mirror planes, three mutually perpendicular 2-fold axes are generated. (Note: the reverse process does NOT occur; the three 2-fold axes in 222 do not lead to the automatic generation of mirror planes) These symmetry elements are shown in (f) with the 8 equivalent positions in (e). In this case, all three mirror planes are essential for the point group mmm .

Only three orthorhombic point groups are possible. If other combinations of 2-fold axes and mirror planes are considered, they will turn out to be equivalent to one of the three allowed point groups. For

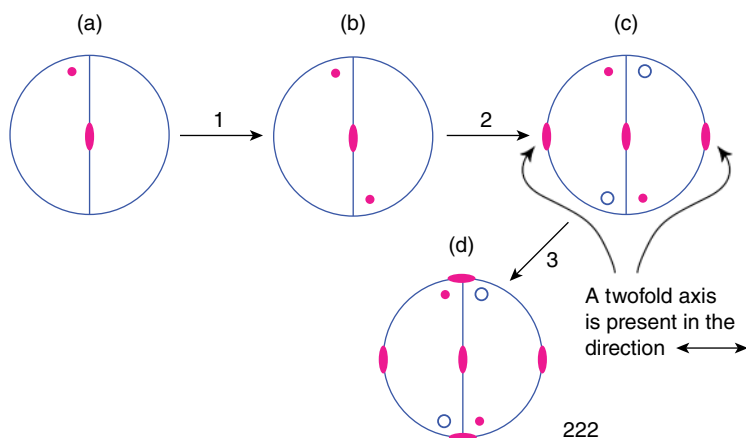


Figure 1.56 Equivalent positions in the point group 222. In step 1, a 2-fold axis perpendicular to the plane of the paper is added. In step 2, a second 2-fold axis, running horizontally in the plane of the paper is added. In step 3, a third 2-fold axis, running vertically in the plane of the paper has been added but is created automatically by step 2.

instance, the combination $22m$ can be shown to yield the same set of positions and symmetries as mmm . Of the three orthorhombic point groups, only mmm possesses a centre of symmetry (the equivalent positions created by a centre of symmetry are shown in Fig. 1.54(a) for the triclinic point group $\bar{1}$). Each position in mmm has a centrosymmetrically related partner, but this is not the case for 222 and $mm2$. The relevance of centrosymmetry is discussed in Section 1.18.4.

As a final example, consider the trigonal point group 32 which is characterised by a single 3-fold axis with a perpendicular 2-fold axis, Fig. 1.57. The 3-fold axis is oriented perpendicular to the plane of the paper (b). There are three 2-fold axes lying in the plane of the paper and at 60° to each other, but only one of these is independent. To demonstrate this and find the equivalent positions, start with position 1 and consider the effect of the 3-fold axis (rotation by 120°). Positions 3 and 5 result (a). Then consider the effect of one of the 2-fold axes, say XX' in (b). This generates three new positions: $1 \rightarrow 4$, $3 \rightarrow 2$ and $5 \rightarrow 6$; also, two more 2-fold axes YY' and ZZ' are automatically generated, e.g. YY' relates positions 1 and 6, 2 and 5, 3 and 4.

Of the 32 crystallographic point groups, 27 are non-cubic and we have looked at 9 of these. The remaining 18, Appendix E, can be treated along similar lines and should cause no problem for the reader. The main difficulty likely to be encountered concerns the orientation of the different symmetry elements in a point group. Some guidelines are as follows: (i) in monoclinic, hexagonal, trigonal and

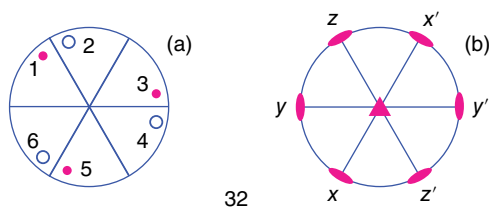


Figure 1.57 Trigonal point group 32.

tetragonal point groups, the unique axis is shown perpendicular to the plane of the paper (stereogram); (ii) an oblique line, as in $4/mmm$, indicates that, in this case, the 4-fold axis has a mirror plane perpendicular to it: it would be clearer if the symbol were written as $(4/m)mm$; (iii) in tetragonal, trigonal and hexagonal point groups, the 2-fold axes, as in $\bar{4}2m$, are always in the plane perpendicular to the unique axis (i.e. perpendicular to $\bar{4}$).

The 5 cubic point groups are rather more complicated to work with as they are difficult to represent by simple 2D projections. This is because (i) there are so many symmetry elements present and more importantly, (ii) many are not perpendicular to each other. Whereas for non-cubic point groups, the symmetry axes are either in the plane or perpendicular to the plane of the stereograms, this is not generally possible for cubic point groups and oblique projections are needed to represent the 3-fold axes. No further discussion of cubic point groups, which are shown in Appendix E, is given.

1.18.3 Point symmetry of molecules: general and special positions

The relationships between point symmetry and structure are best illustrated by examples of small molecules. The methylene dichloride molecule, CH_2Cl_2 , Fig. 1.58, possesses (i) a single 2-fold axis which bisects the $\text{H}-\text{C}-\text{H}$ and $\text{Cl}-\text{C}-\text{Cl}$ bond angles and (ii) two mirror planes (a). The 2-fold axis is parallel to the line of intersection of the mirror planes. These symmetry elements may be represented as in (b), in which the 2-fold axis is perpendicular to the plane of the paper and the mirror planes appear in projection as horizontal and vertical lines. From inspection of Fig. 1.55, it is seen that CH_2Cl_2 belongs to point group $mm2$. However, the number of equivalent positions in $mm2$ is four (c), which does not appear to tally with the realities of the CH_2Cl_2 molecule. Thus, if we place a H atom at one equivalent position, there should be only two possible equivalent positions in the molecule, as there are only two H atoms present. This apparent anomaly is resolved by letting the equivalent positions in Fig. 1.55(c) lie on the vertical mirror plane instead of to either side of the mirror. This yields the arrangement shown in Fig. 1.58(c), which now has only two equivalent positions. Thus, positions 1 and 2 in Fig. 1.55(c) become the single position A in Fig. 1.58(c). We can now distinguish between the *general equivalent positions* of a point group and the *special equivalent positions*; the latter arise when the general

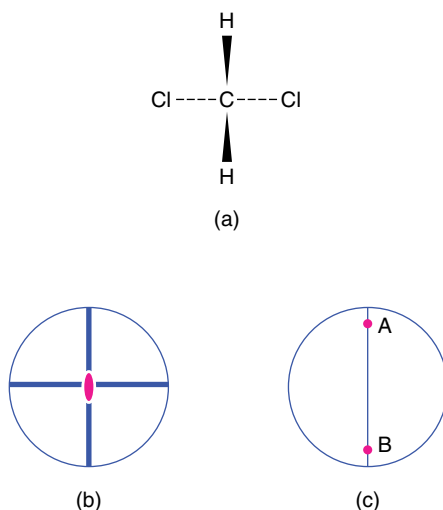


Figure 1.58 The symmetry of the methylene dichloride molecule, CH_2Cl_2 , point group $mm2$.

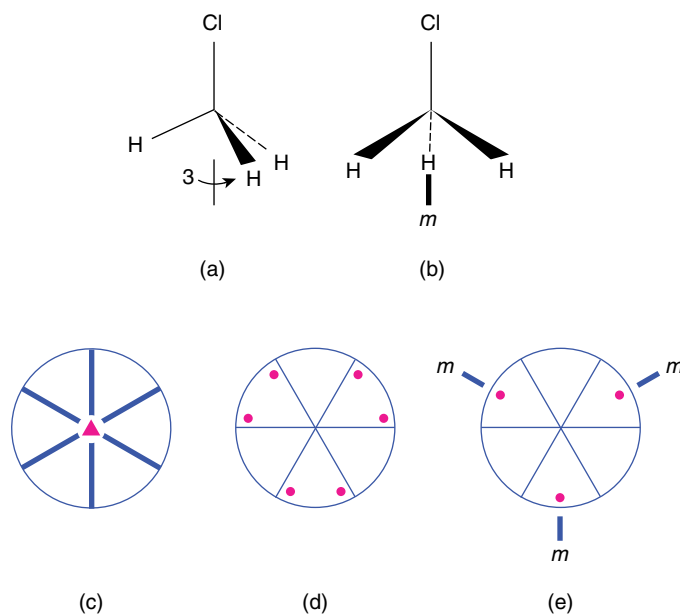


Figure 1.59 The symmetry of the methyl chloride molecule, CH_3Cl , point group $3m$.

positions lie on a symmetry element such as a mirror plane or rotation axis. Thus, A and B in Fig. 1.58 (c) are both special positions.

As a second example, the point symmetry of the methyl chloride molecule, CH_3Cl is shown in Fig. 1.59. The molecule possesses one 3-fold axis along the direction of the C–Cl bond (a). It has no 2-fold axes but has three mirror planes oriented at 60° to each other; one is shown in (b). The 3-fold axis coincides with the line of intersection of the mirror planes. The symmetry elements are shown as a stereogram in (c) and by comparison with Appendix E, we see that the point group is $3m$. The six general equivalent positions in $3m$ are given in (d). We again have the problem that there are more equivalent positions than possible atoms and this is overcome by allowing the general positions to lie on the mirror planes (e); the number of positions is thereby reduced to three.

1.18.4 Centrosymmetric and non-centrosymmetric point groups

Of the 32 point groups, 21 do not possess a centre of symmetry. The absence of a centre of symmetry is an essential but not sufficient requirement for the presence in crystals of optical activity, pyroelectricity and piezoelectricity (Chapters 8 and 10). Optical activity is confined to 15 of the 21 non-centrosymmetric point groups and piezoelectricity to 20 of these. This is of use in, for example, the search for new materials with piezoelectric activity; it is a waste of time trying to detect piezoelectricity in crystals whose point group is not among the 20 active groups! Crystallographers also make some use of the piezoelectric effect in structure determination. It is a considerable help in solving an unknown structure to know the space group at the outset. If a test for piezoelectricity is carried out with positive results, this limits the choice of space group to the non-centrosymmetric ones. The absence of piezoelectricity does not necessarily mean, however, that the point group and space group are centrosymmetric.

1.18.5 Space groups

The combination of the 32 possible point groups and the 14 Bravais lattices (which in turn are combinations of the 7 crystal systems, or unit cell shapes, and the different possible lattice types) gives rise to 230 possible space groups. All crystalline materials, apart from those showing either quasisymmetry, Section 1.2.2, or those that possess a superstructure with a different, incommensurate periodicity to that of the sublattice, have a structure which belongs to one of these space groups. This does not, of course, mean that only 230 different crystal structures are possible. For the same reason, the human body (from its external appearance) is not the only object to belong to point group $\bar{2}$: teapots also do!

Space groups are formed by adding elements of translation to the point groups. The space symmetry elements – screw axes and glide planes – are derived from their respective point symmetry elements – rotation axes and mirror planes – by adding a translation step in between each operation of rotation or reflection, Section 1.2.5. A complete tabulation of all possible screw axes and glide planes and their symbols is not given here; instead, symbols are explained as they arise. We also discuss only a few of the simpler space groups; however, once the basic rules have been learned, by working through these examples, there should be no difficulty in understanding and using any space group. The interested reader is recommended to consult the authoritative *International Tables for X-ray Crystallography*, Vol 1 (preferably an early edition as later additions contain extra material of relevance only to specialist crystallographers).

The written symbol of a space group contains between two and four characters. The first character is always a capital letter which corresponds to the lattice type: *P*, *I*, *A*, etc. The remaining characters correspond to some of the symmetry elements that are present. If the crystal system has a unique or principal axis (e.g. the 4-fold axis in tetragonal crystals), the symbol for this axis appears immediately after the lattice symbol. For the remaining characters, there appear to be different rules for different crystal systems. As these rules are not essential to an understanding of space groups, they are not repeated here.

Space groups are usually drawn as parallelograms to represent the unit cell, with the plane of the parallelogram corresponding to the *xy* plane of the unit cell. By convention, Fig. 1.60(a), the origin is taken as the top left-hand corner, with *y* horizontal, *x* downwards and the positive *z* direction out of the plane of the paper and pointing towards the reader. For each space group, two parallelograms are used, the left-hand one gives the equivalent positions; the right-hand one gives the symmetry elements. Let us see some examples. Each one introduces at least one new feature.

1.18.5.1 *Triclinic P* $\bar{1}$

This space group is primitive and centrosymmetric; it is shown in Fig. 1.60(b, c). The right-hand diagram shows the symmetry elements: there are centres of symmetry (shown as small open circles) at the origin (*t*), midway along the *a* and *b* edges and in the middle of the *C* face (i.e. the face bounded by *a* and *b*). Additional centres of symmetry, not shown, occur in the middle of the other faces, halfway along the *c* edge and at the body centre of the unit cell.

The left-hand diagram gives the equivalent positions in space group $\bar{1}$. These are represented by large open circles; a positive sign indicates that they are above the plane of the paper and a negative sign below. In the latter case, that position will lie in the unit cell below the one that has been defined. A comma inside the equivalent position symbol indicates an *enantiomorphic* relationship to a second, centrosymmetrically related equivalent position.

To find the equivalent positions in the space group, it is necessary, as with point groups, to choose a starting position and operate on this position with the various symmetry elements that are present. The conventional starting position is at 1, close to the origin and with small positive values of *x*, *y* and *z*. This position must be present in all other unit cells (definition of the unit cell); three are shown as 1', 1'' and 1'''.

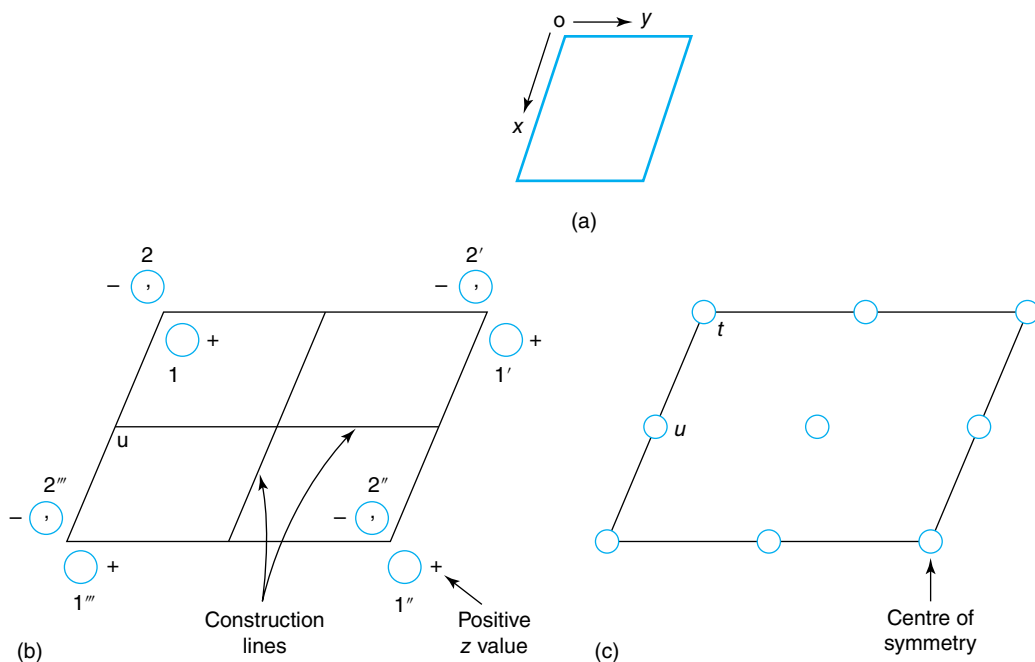


Figure 1.60 (a) The convention used to label axes and origin of space groups. (b, c) Triclinic space group $P\bar{1}$ (number 2); coordinates of equivalent positions: $x, y, z; \bar{x}, \bar{y}, \bar{z}$.

Consider now the effect of the centre of symmetry, t , at the origin of the unit cell. This acts upon position 1 to create position 2. The minus sign at 2 indicates a negative z height and the comma shows its enantiomorphic relation to position 1. Positions $2', 2''$ and $2'''$ in Fig. 1.60 are automatically generated from position 2 by translation because they are equivalent positions in adjacent cells.

To understand the meaning of an enantiomorphic relationship, the effect of an inversion operation is to convert a left-handed object into a right-handed one and vice versa. This is illustrated in Fig. 1.61 for two tetrahedra that are positioned so as to be related to each other by inversion through a centre of symmetry. Individual tetrahedra do not possess a centre of symmetry, whereas groupings of tetrahedra may possess one, such as shown in Fig. 1.61. In addition, if the tetrahedra themselves are chiral, such as the molecule CHFBrI with the four different corners represented by 1, 2, 3, 4 in Fig. 1.61, then the centrosymmetric partner in the configuration shown is a different isomer with the corner arrangement $1', 2', 3', 4'$.

The next step is to write down the coordinates of the equivalent positions in the unit cell. This is done in the form x, y, z where x, y and z are the fractional distances, relative to the unit cell edge dimensions, from the origin of the cell. Let position 1, Fig. 1.60, have fractional coordinates x, y, z ; positions $1', 1''$ and $1'''$ in adjacent unit cells are given by adding 1 to the relevant coordinates i.e. $x, 1 + y, z$ for $1'$, $1 + x, 1 + y, z$ for $1''$ and $1 + x, y, z$ for $1'''$. Position 2 is the centrosymmetric partner position of 1, i.e. $-x, -y, -z$. Position $2''$ is then in the next unit cell at $\cdots 1 - x, 1 - y, -z$, etc. Thus, if a position lies outside the unit cell under consideration, an equivalent position within the unit cell can be found, usually by adding or subtracting 1 from one or more of the fractional coordinates. Position $2''$ is outside the cell because it has a negative z value; the equivalent position inside the cell is given by a displacement of one unit cell length in the z direction to give coordinates $1 - x, 1 - y, 1 - z$. These coordinates are written in shorthand as $\bar{x}, \bar{y}, \bar{z}$.

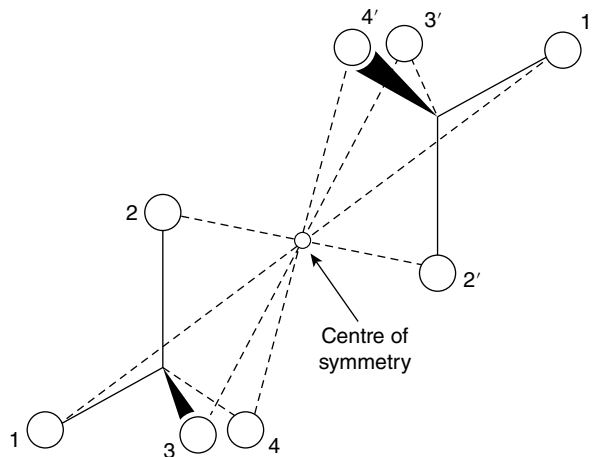


Figure 1.61 Two tetrahedra in a centrosymmetric arrangement.

In summary, therefore, the unit cell in space group $P\bar{1}$ has two equivalent positions that lie inside the unit cell: x, y, z (position 1) and $\bar{x}, \bar{y}, \bar{z}$ (the position at height c above $2''$ in Fig. 1.60).

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

The positions x, y, z and $\bar{x}, \bar{y}, \bar{z}$ are general positions and apply to any value of x, y, z between 0 and 1. In certain circumstances, x, y, z and $\bar{x}, \frac{1}{2}, \bar{z}$ coincide, for example, if $x = y = z = \frac{1}{2}$. In this case, there is only one position, $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ which is a special position. Special positions arise when the general position lies on a symmetry element, in this case a centre of symmetry, as discussed for point groups in Section 1.18.3. The coordinates of the *one-fold special positions* in $P\bar{1}$ are, therefore, $(0, 0, 0)$, $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and correspond to the corner, edge, face and body centres of the unit cell.

The coordinates of the general and special positions for each space group are listed in *International Tables for X-ray Crystallography* together with additional information, as shown in Table 1.30 for $P\bar{1}$. The general positions are listed first followed by the various special positions; for each, the first column gives the *multiplicity*, i.e. the number of equivalent positions. The second column is the so-called *Wyck-off notation* in inverse alphabetical sequence; the logic behind this labelling scheme is that those positions at the bottom of the list have highest point symmetry and the symmetry may decrease on moving upwards through the list. The third column specifies the point symmetry of the positions. In this case, all the special positions coincide with a centre of symmetry whereas the general position, labelled as 2(i), has no point symmetry.

1.18.5.2 Monoclinic $C2$

By common convention, the unique 2-fold axis in a monoclinic unit cell is labelled b . Unfortunately, this is different to the use of c as the unique axis in tetragonal, trigonal and hexagonal cells but this usage for monoclinic cells is now so well established that it is unlikely to be altered. With b as the

Table 1.30 Coordinates and labelling of equivalent positions in space group $P\bar{1}$

Number of positions	Wyckoff notation	Point symmetry	Coordinates of equivalent positions
2	l	1	$xyz, \bar{x}\bar{y}\bar{z}$
1	h	$\bar{1}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
1	g	$\bar{1}$	$0, \frac{1}{2}, \frac{1}{2}$
1	f	$\bar{1}$	$\frac{1}{2}, 0, \frac{1}{2}$
1	e	$\bar{1}$	$\frac{1}{2}, \frac{1}{2}, 0$
1	d	$\bar{1}$	$\frac{1}{2}, 0, 0$
1	c	$\bar{1}$	$0, \frac{1}{2}, 0$
1	b	$\bar{1}$	$0, 0, \frac{1}{2}$
1	a	$\bar{1}$	$0, 0, 0$

unique axis, the unit cell projects onto the xy plane as a rectangle (because $\gamma = 90^\circ$), as shown in Fig. 1.62. Since $\beta \neq 90^\circ$, the z axis is not perpendicular to the plane of the paper but is inclined to the vertical.

The C -centring in space group $C2$ means that if the Bravais lattice has a lattice point at the origin (with coordinates $0, 0, 0$), it also has an equivalent lattice point in the middle of the side bounded by a and b , at $\frac{1}{2}, \frac{1}{2}, 0$. For any position x, y, z in this space group, there will, therefore, be an equivalent position at $x + \frac{1}{2}, y + \frac{1}{2}, z$. This C -centring has no representation in the right-hand diagram of Fig. 1.62 but can be seen in the left-hand diagram; for example, positions 1 and 2 are related by the C -centring.

The main symmetry element present in space group $C2$ is a 2-fold rotation axis parallel to b ; it passes through the origin and is coincident with the y axis of the unit cell. The symbol for a 2-fold rotation axis in the plane of the paper is an arrow. In this case, it is parallel to and coincident with y , passes through the origin $x = 0, z = 0$, and is shown by arrow d in the right-hand diagram. The effect of the 2-fold rotation axis on position 1, left-hand diagram with coordinates x, y, z , is to generate the equivalent position shown as $3'$, with coordinates $-x, y, -z$.

Other symmetry elements are generated automatically by a combination of this 2-fold rotation axis and the C -centring. Thus, another 2-fold rotation axis, e , parallel to b , is created which cuts the x axis at $\frac{1}{2}$ and the z axis at 0; positions 1 and 3 are related by this 2-fold axis, as are positions $3'$ and $1''$, positions 4 and 2, etc.

We also find that 2-fold screw axes have been created automatically in this space group. A 2-fold screw axis, symbol 2_1 , involves a rotation component of 180° and a translation by $\frac{1}{2}$ in the direction of the screw axis. Two 2_1 screw axes, f and g , are shown which are parallel to b , cut the x axis at $\frac{1}{4}, \frac{3}{4}$ and are in the plane of the unit cell projection at $z = 0$. Screw axes in the plane of the paper are represented as half-arrows. Screw axis f relates positions 1, 4 and $1'$ on an imaginary spiral that passes through the unit cell. The 2_1 screw axis is a combined translation and rotation operation. Thus, position 1 is translated halfway along y , retaining its x and z values, to the position shown as the dashed circle and then rotated by 180° about the axis parallel to y and at $x = \frac{1}{4}, z = 0$, to arrive at position 4; it is important to recognise that the dashed circle is *not* an equivalent position but is drawn merely to show that two operations are involved in the screw axis. Positions $3', 2$, and $3''$ are similarly related by the same screw axis.

Space group $C2$ has four equivalent positions which are generated by a combination of the C -centring and a 2-fold rotation axis. Starting from position 1, the effect of C -centring is to create position 2 which is displaced by $(\frac{1}{2}, \frac{1}{2}, 0)$ from position 1. The effect of the 2-fold rotation axis, d is to rotate position 1 about the b edge by 180° and create position $3'$. As position 1 has a positive z coordinate, $3'$ must have a corresponding negative z value. The position equivalent to $3'$ that lies inside the unit cell is

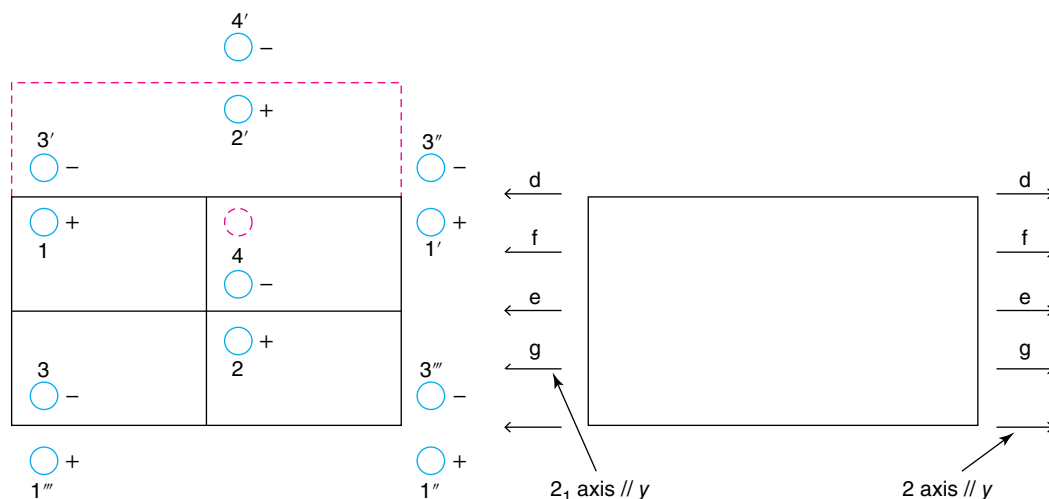


Figure 1.62 Monoclinic space group *C2* (No 5); coordinates of equivalent positions 4(c): x, y, z ; $\bar{x}y\bar{z}$; $x + \frac{1}{2}, y + \frac{1}{2}, z$; $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$. Special positions, point symmetry 2, 2(b): $0, \frac{1}{2}, z$; 2(a): $0, 0, z$.

found by translating to adjacent unit cells in both x and z directions to arrive at a position that is above 3 and is inside the unit cell, i.e. 3 has coordinates $1 - x, y, -z$ and therefore the equivalent position inside the unit cell is at $\bar{x}, y, \bar{z}$.

The same rotation axis d creates position $4'$ from position 2, whose equivalent position inside the unit cell is above position 4 with coordinates $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$. Hence, in summary, we may say that the C -centring creates a second equivalent position and the effect of the 2-fold axis is to create two more equivalent positions, to give a total of 4 equivalent positions in space group *C2*. All the other positions shown in Fig. 1.62 are created by translation to adjacent unit cells; the other 2-fold rotation and 2_1 screw axes are generated automatically and do not generate any extra equivalent positions.

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

The general positions in space group *C2* are 4-fold but if they lie on the 2-fold rotation axes, their number is reduced to two and they become special positions. Thus, if $x = z = 0$, the two positions have coordinates $0, y, 0$ and $\frac{1}{2}, y + \frac{1}{2}, 0$. A second set of special positions arises when $x = 0, z = \frac{1}{2}$ (the reader may like to check that there is a 2-fold axis parallel to b and at $x = 0, z = \frac{1}{2}$ that is not indicated in Fig. 1.62: it is at height $c/2$ above axis d).

1.18.5.3 Monoclinic *C2/m*

This space group, shown in Fig. 1.63, is also C -centred and has, as its principal symmetry elements, a mirror plane perpendicular ($\perp$) to a 2-fold axis. The 2-fold axis is parallel to b , by convention, and therefore the mirror plane is the xz plane. Two mirror planes are present in the cell; they intersect b at 0 and $\frac{1}{2}$ and are shown as thick vertical lines in Fig. 1.63. As in the space group *C2*, there are two 2-fold rotation

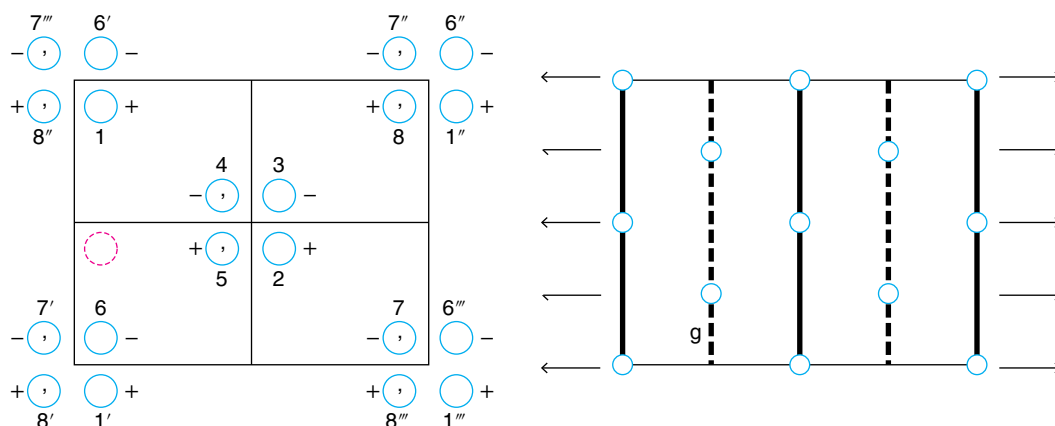


Figure 1.63 Monoclinic space group $C2/m$ (No 12). Coordinates of general equivalent positions 8(j): $x, y, z; x, \bar{y}, z; \bar{x}y\bar{z}, \bar{x}\bar{y}z$ and $\frac{1}{2}+x, \frac{1}{2}+y, z; \frac{1}{2}+x, \frac{1}{2}-y, z; \frac{1}{2}-x, \frac{1}{2}+y, \bar{z}; \frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$. Special positions with point symmetry $2/m$, 2(a): $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0$; 2(b): $0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0$; 2(c): $0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; 2(d): $0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}$; special positions with point symmetry $\bar{1}$, 4(e): $\frac{1}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{3}{4}, 0; \frac{3}{4}, \frac{3}{4}, 0; \frac{3}{4}, \frac{1}{4}, 0$; 4(f): $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, \frac{1}{2}; \frac{3}{4}, \frac{3}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, \frac{1}{2}$; special positions with point symmetry 2, 4(g): $0, y, 0; 0, \bar{y}, 0; \frac{1}{2}, \frac{1}{2}+y, 0; \frac{1}{2}, \frac{1}{2}-y, 0$; 4(h): $0, y, \frac{1}{2}; 0, \bar{y}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}$; special position with point symmetry m , 4(i): $x, 0, z; \bar{x}, 0, \bar{z}; \frac{1}{2}+x, \frac{1}{2}, z; \frac{1}{2}-x, \frac{1}{2}, \bar{z}$.

axes, parallel to b and intersecting a at 0 and $\frac{1}{2}$, and two 2_1 screw axes parallel to b and intersecting a at $\frac{1}{4}$ and $\frac{3}{4}$. All of these 2 and 2_1 axes are at c height equal to zero. An additional set of axes, not shown, occurs at $c = \frac{1}{2}$. Also present, as discussed later, are centres of symmetry and glide planes.

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

The coordinates of the eight equivalent positions within the cell, together with their number, if shown, are: x, y, z (1); $x + \frac{1}{2}, y + \frac{1}{2}, z$ (2); $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}; \frac{1}{2} - x, \frac{1}{2} - y, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, z$ (5); $\bar{x}, y, \bar{z}; \bar{x}, \bar{y}, \bar{z}; \bar{x}, y, z$ (8). These eight positions may be grouped into two sets of four positions that are related by the C -centring. The coordinates of both sets are given in Fig. 1.63. Several sets of special positions are possible in this space group, e.g. if $y = 0$, a 4-fold set occurs: $x, 0, z; \bar{x}, 0, \bar{z}; x + \frac{1}{2}, \frac{1}{2}, z; \frac{1}{2} - x, \frac{1}{2}, \bar{z}$. If $x = 0, y = 0$ and $z = \frac{1}{2}$, a 2-fold set arises: $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. All the special positions are listed in Fig. 1.63 caption.

The combination of a mirror plane perpendicular to a 2-fold axis, together with the C -centring, leads to the generation of several other symmetry elements. These include 2_1 screw axes parallel to b , centres of symmetry and glide planes. For example, the centre of symmetry created at the origin relates positions 1 and $7'''$, $6'$ and $8''$.

The thick dashed line g in the right-hand diagram indicates a glide plane for which the translation component is $a/2$ and reflection is across a plane perpendicular to b . Such a glide plane is called 'an a

glide perpendicular to b^* . Thus, position 1 is translated by $a/2$ to the position shown as the dashed circle; reflection across the plane, g , which cuts b at $\frac{1}{4}$ leads to position 5. Repetition of the process converts 5 into $1'$, which is equivalent to the starting position, 1. Similarly, positions 8, 2 and $8'''$ are related by the glide plane which cuts b at $\frac{3}{4}$.

1.18.5.4 Orthorhombic $P222_1$

This primitive orthorhombic space group has 2-fold rotation axes parallel to x and y and a 2_1 screw axis parallel to z . The feature of this space group, Fig. 1.64, which makes the generation of the equivalent positions a little difficult to visualise, is that the 2-fold rotation axes parallel to y occur at a c height of $\frac{1}{4}$. Consider first the axis parallel to y at $a = 0$ and $c = \frac{1}{4}$. The starting position 1 has a small positive z coordinate of $+z$; the twofold axis is at $z = \frac{1}{4}$. Therefore, position 1 is at $(\frac{1}{4} - z)$ below the 2-fold axis. The new position, $2'$, formed by rotation about this axis is, therefore, at $(\frac{1}{4} - z)$ above the 2-fold axis, i.e. it has z coordinate $\frac{1}{4} + (\frac{1}{4} - z) = \frac{1}{2} - z$. This is shortened to $\frac{1}{2} -$ in Fig. 1.64.

Consider now the 2-fold axis parallel to x and at $b = c = 0$ (i.e. passing through the origin). This axis generates positions $3''$ from 1 and $4'''$ (its equivalent in the cell below) from $2'$. With these two axes we have generated all four equivalent positions in this space group. The third axes, such as the 2_1 axis parallel to z , are automatically generated by the combined action of the other two axes and are not independent of them. This 2_1 axis relates, for example, positions 1 and $4'''$, (i.e. translation of position 1 by $c/2$ followed by 180° rotation about c gives $4'''$). Positions $2'$ and $3''$ are similarly related.

1.18.5.5 Orthorhombic $F222$

The new feature of this space group is that it has a face centred lattice which, as can be seen from Fig. 1.65, leads to a considerable increase in the number of symmetry elements and equivalent positions. The basic symmetry elements are three intersecting 2-fold axes, parallel to x , y and z and passing

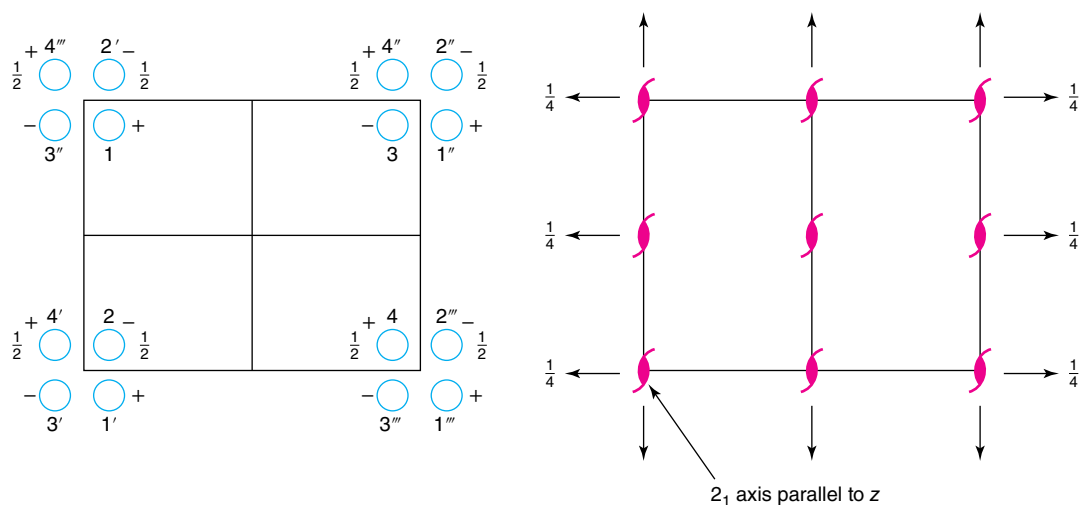


Figure 1.64 Orthorhombic space group $P222_1$ (No 17); Coordinates of equivalent positions 4(e): x, y, z ; $\bar{x}, y, \frac{1}{2} - z$; $x, \bar{y}, \bar{z}$; $\bar{x}, \bar{y}, \frac{1}{2} + z$. Special positions with point symmetry 2, 2(a): $x, 0, 0$; $\bar{x}, 0, \frac{1}{2}$; 2(b): $x, \frac{1}{2}, 0$; $\bar{x}, \frac{1}{2}, \frac{1}{2}$; 2(c): $0, y, \frac{1}{4}$; $0, \bar{y}, \frac{3}{4}$; 2(d): $\frac{1}{2}, y, \frac{1}{4}$; $\frac{1}{2}, \bar{y}, \frac{3}{4}$

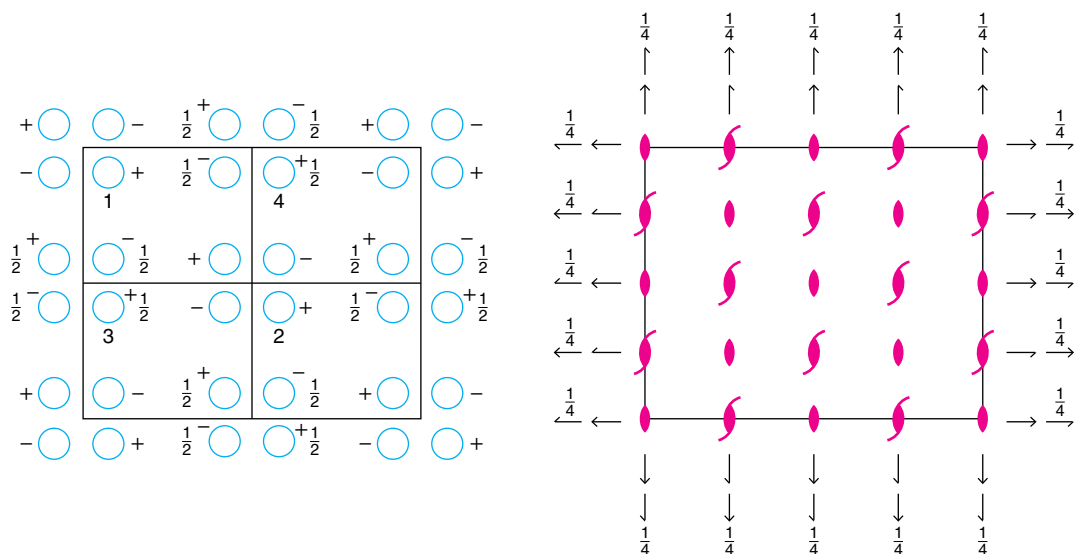


Figure 1.65 Orthorhombic space group $F222$ (No 22); coordinates of equivalent positions $16(k) 000 : xyz, \bar{x}\bar{y}z, x\bar{y}\bar{z}, \bar{x}y\bar{z}$

$$0\frac{1}{2}\frac{1}{2} : xy + \frac{1}{2}z + \frac{1}{2}\bar{x}_2^1 - y_2^1 + z, x_2^1 - y_2^1 - z, \bar{x}_2^1 + y_2^1 - z$$

$$\frac{1}{2}0\frac{1}{2} : \frac{1}{2} + xy_2^1 + z, \frac{1}{2} - x\bar{y}_2^1 + z, \frac{1}{2} + x\bar{y}_2^1 - z, \frac{1}{2} - xy_2^1 - z$$

$$\frac{1}{2}\frac{1}{2}0 : \frac{1}{2} + x_2^1 + yz, \frac{1}{2} - x_2^1 - yz, \frac{1}{2} + x_2^1 - y\bar{z}, \frac{1}{2} - x_2^1 + y\bar{z}$$

Special positions with point symmetry 222 , 4(a): only one position is given as the other three are generated by the face centring; $0, 0, 0$; **4(b):** $0, 0, \frac{1}{2}$; **4(c):** $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; **4(d):** $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$; **special positions with point symmetry 2 , 8(e):** $x, 0, 0$; $\bar{x}, 0, 0$; **8(f):** $0, y, 0$; $0, \bar{y}, 0$; **8(g):** $0, 0, z$; $0, 0, \bar{z}$; **8(h):** $\frac{1}{4}, \frac{1}{4}, z$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{2} - z$; **8(i):** $\frac{1}{4}, y, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{2} - y, \frac{1}{4}$; **8(j):** $x, \frac{1}{4}, \frac{1}{4}$; $\frac{1}{2} - x, \frac{1}{4}, \frac{1}{4}$.

through the origin. Many other 2-fold axes occur automatically, e.g. one intersecting the cell at $a = \frac{1}{4}$, $c = \frac{1}{4}$, parallel to b and another at $a = \frac{1}{4}$, $b = \frac{1}{4}$, parallel to c . Many 2_1 axes are also created, e.g. at $a = 0$, $b = \frac{1}{4}$, parallel to c and at $b = \frac{1}{4}$, $c = 0$, parallel to a .

There are sixteen general equivalent positions that fall into four groups related by the face-centring condition. The four sets are related as $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$; $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$. Thus, position 1, (x, y, z) , is related to positions 2–4: $(x + \frac{1}{2}, y + \frac{1}{2}, z)$; $(x + \frac{1}{2}, y, z + \frac{1}{2})$ and $(x, y + \frac{1}{2}, z + \frac{1}{2})$. Generation of the remaining equivalent positions by the action of the 2-fold axes should be straightforward.

1.18.5.6 Tetragonal $I4_1$

The principal axis in the space group $I4_1$, Fig. 1.66, is a 4_1 screw axis parallel to z . There are four such axes which intersect the unit cell at $x = \frac{1}{4}$, $y = \frac{1}{4}$; $x = \frac{3}{4}$, $y = \frac{1}{4}$; $x = \frac{1}{4}$, $y = \frac{3}{4}$ and $x = \frac{3}{4}$, $y = \frac{3}{4}$. The operation of a 4_1 screw axis involves translation of $\frac{1}{4}$ combined with rotation by 90° about the axis. The positions 1 to 4 are related to each other by the 4_1 axis at s , and it can be seen that these positions lie on a spiral about s . The symbols of screw axes s and t are reversed because their direction of rotation is different; s involves clockwise rotation and t an anticlockwise rotation (e.g. the sequence of positions $7', 2, 5, 4'$). The body-

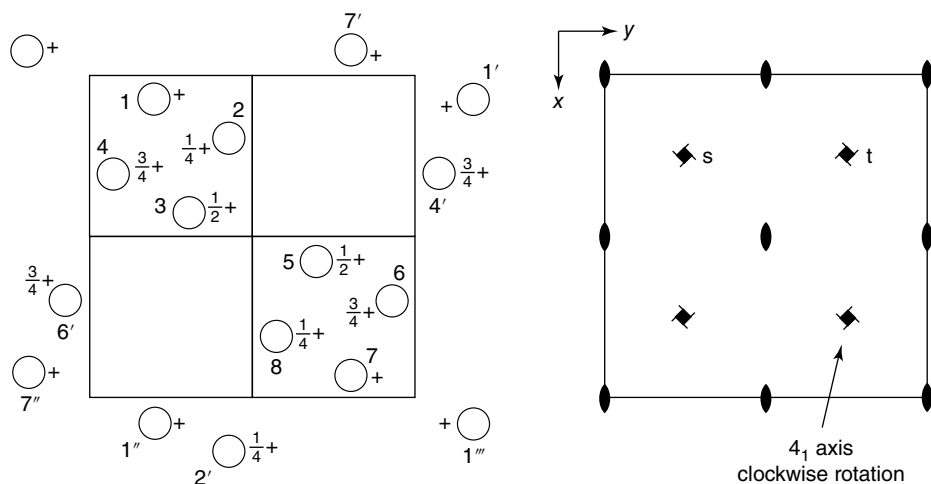


Figure 1.66 Tetragonal space group $I4_1$ (No 80); coordinates of equivalent positions 8(b):

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

$$\frac{111}{222} : x + \frac{1}{2}y + \frac{1}{2}z + \frac{1}{2}, \frac{1}{2} - x - y\frac{1}{2} + z, \frac{1}{2} - yx\frac{3}{4} + z, \frac{1}{2} + yx\frac{3}{4} + z$$

Special positions with point symmetry 2, 4(a): $0, 0, z; 0, \frac{1}{2}, \frac{1}{4} + z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z; \frac{1}{2}, 0, \frac{3}{4} + z$.

centring, I , relates positions 1–4 to 5–8 and the cell contains eight general equivalent positions. Several 2-fold axes parallel to z are also generated.

1.18.6 Space groups and crystal structures

The purpose of this section is to show the fundamental importance of space groups to crystal structures and how the atomic coordinates of a structure are related to the space group. As examples, two simple but important structures, which have already been described earlier in this chapter, are considered in some detail.

1.18.6.1 The perovskite structure, SrTiO_3

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

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

Space group: **$Pm\bar{3}m$** (number 221)

Atomic coordinates: Ti in 1(a) at $0, 0, 0$; Sr in 1(b) at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; O in 3(d) at $0, 0, \frac{1}{2}$

This is, in fact, a very simple example since although the space group $Pm\bar{3}m$ is complicated, as are all cubic space groups, all the atoms in perovskite lie on special positions. There are 48 general equivalent positions in this space group, but a large number of special positions arise when atoms lie on symmetry elements. Ti occupies a 1-fold special position at the origin of the unit cell; the symbol 1(a) indicates that there is only one position in this set and (a) the Wyckoff label, for this (set of) position(s). Sr also occupies a 1-fold special position, 1(b), at the body centre of the cell. Oxygen occupies a 3-fold special position 3(d); the coordinates of one of these positions, $0, 0, \frac{1}{2}$ are given and the only remaining information that is needed from the space group are the coordinates of the other two oxygen positions. From *International Tables*, these are $0, \frac{1}{2}, 0$ and $\frac{1}{2}, 0, 0$.

From this information, the unit cell and atomic positions may be drawn, first as a projection down one of the cubic cell axes, Fig. 1.41(a) and then as an oblique projection to show the atomic positions more clearly, Fig. 1.41(c). [Note: Fig. 1.41(b) shows an alternative unit cell with Sr at the origin, as discussed in Section 1.17.7.] The coordination environment of each atom may be seen in (c) and inter-atomic distances calculated by simple geometry, as detailed in Section 1.17.7, together with a more extended discussion of perovskites, structural distortions in some cases and structure–property relations.

1.18.6.2 The rutile structure, TiO_2

We need to know the following information:

Unit cell: tetragonal, $a = 4.594$, $c = 2.958 \text{ \AA}$

Space group: $P4_2/mnm$ (No 136)

Atomic coordinates: Ti in 2(a) at $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; O in 4(f) at $(x, x, 0)$; $(\bar{x}, \bar{x}, 0)$; $(\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2})$; $(\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2})$

As in the perovskite structure, only special positions are used to accommodate atoms and the 16-fold general positions are unoccupied. The Ti positions are fixed at the corner and body centre but O has a variable parameter, x , whose value must be determined experimentally. Crystal structure determination and refinement gives $x = 0.30$ for TiO_2 . The unit cell of rutile is shown projected onto the xy plane in Fig. 1.37(a) and the structure is described fully in Section 1.17.6.

The symmetry elements in space group $P4_2/mnm$ are shown in Fig. 1.67; most should also be readily apparent on inspection of the structural model shown in Fig. 1.37(a and f). Thus, the 4_2 axes are located halfway along the cell edges although no atoms lie on these 4_2 axes. The oxygen atoms are arranged on spirals around the 4_2 axes such that translation by $c/2$ and rotation by 90° convert one oxygen position to another. Centres of symmetry are present, for example, at the cell corners; also 2 and 2_1 axes and (not shown) mirror planes and glide planes are present.

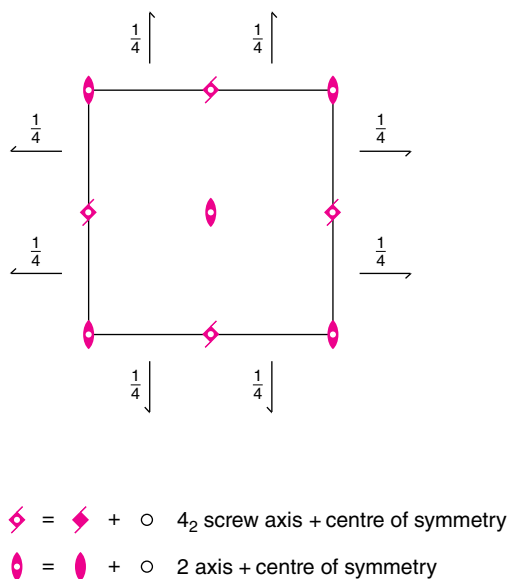


Figure 1.67 The symmetry elements in space group $P4_2/mnm$.

1.18.7 Systematic absences in diffraction patterns and space groups

We see in Chapter 5 how the presence of lattice centring or elements of space symmetry lead to systematically absent reflections from X-ray (but also electron and neutron) diffraction patterns. For example, in space group $C2$, the C -centring imposes the condition that only those reflections that satisfy the rule: for (hkl) : $h + k = 2n$ are allowed. The 2_1 screw axes parallel to b impose the condition for reflection: for $(0k0)$: $k = 2n$. However, this is also a consequence of the C -centring condition, for the special case that $h = l = 0$, and so does not lead to any extra *systematic absences*. Information on the conditions limiting possible reflections is given for every space group in *International Tables for X-ray Crystallography*. In the above case, since the 2_1 screw axes do not impose an extra set of conditions, they are often written in parentheses.

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

Two further examples: in space group $P222_1$, the only symmetry element which causes systematic absences is the 2_1 axis parallel to z , i.e. for $00l$ reflections, only those for which $l = 2n$ may be observed; there are no general conditions on hkl reflections since the space group is primitive. For space group $I4_1$, two conditions are imposed on the possible reflections: for the body centring, only the reflections hkl : $h + k + l = 2n$ may be observed; the 4_1 screw axis places the additional condition that: for $00l$ reflections, $l = 4n$.

