9 Crystal Structures _____

Supporting interactive 3D images of crystal structures and more advanced material may be found at:http://www-teach.ch.cam.ac.uk/links/3Dindex.html

A   Introduction

Chemists are inspired by beauty and have long been fascinated by crystals, including snowflakes, minerals and gemstones.

Fig. 1 A snowflake

Fig.2 Fluorite
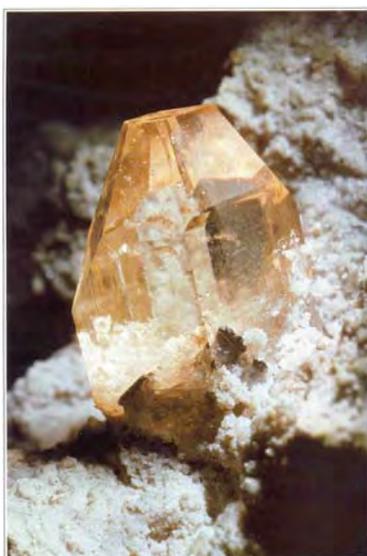
Fig. 3 Topaz

Fig. 4 Fool's gold

Fig. 1 Snowflakes commonly show six-fold symmetry. It is no coincidence that when water freezes, it forms a hexagonal lattice. [Image from www.SnowCrystals.com.]
Fig. 2 Fluorite is calcium fluoride, CaF_2. It is the compound chosen to exemplify its crystal structure type. Its symmetry at the atomic level is apparent from its crystalline form. [Image from "An illustrated guide to Rocks and Minerals" by Michael O'Donoghue, Thunder Bay Press.]

Fig. 3 Topaz has a complex structure: it is an aluminosilicate containing fluoride and hydroxide ions.

Fig. 4 Fool's gold is also known as pyrite and has formula FeS_2 (containing the Fe^{2+} and $^-S–S^-$ ions). The ions, perhaps not surprisingly given the picture, arrange themselves into a cubic lattice.
[Figures 3 and 4 from "Rocks and Minerals of the World: an illustrated encyclopedia" by Rudolf Ďuďa and Luboš Rejl, Tiger Books.]

The first attempt to relate the external shape of a crystal to its structure at the molecular level was made in a study of snowflakes by Johannes Kepler, in 1611. He related the six-fold symmetry of the snowflake to the hexagon formed when packing equally-sized balls into a densely packed layer. This work was extended by Robert Hooke who realised that balls could stack to form the different shapes that crystals were observed to adopt.

One of the triumphs of twentieth century science was the development by Max von Laue and Lawrence Bragg of the theory and practice of x-ray diffraction and how, from these experiments, crystal structures could be determined. One of the first x-ray diffraction photographs, taken in 1912 of zinc blende (ZnS), is shown below.
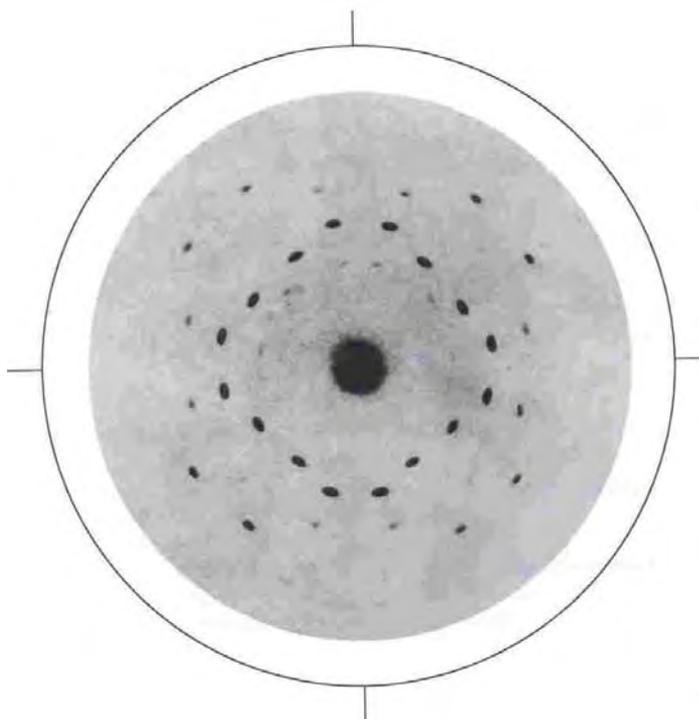
Fig. 5 One of the 'Laue diagrams' published by Friedrich, Knipping and Laue in 1912. This finally demonstrated the existence of internal atomic regularity in crystals and its relationship to external symmetry. [Image from "The Basics of Crystallography and Diffraction" by Christopher Hammond, OUP.]

The technique was made most famous 40 years later by Rosalind Franklin and Raymond Gosling whose x-ray photograph of DNA in May 1952 led to the elucidation of

the double helix structure of DNA by Francis Crick and James Watson in 1953. Their x-ray photograph of DNA is shown below.
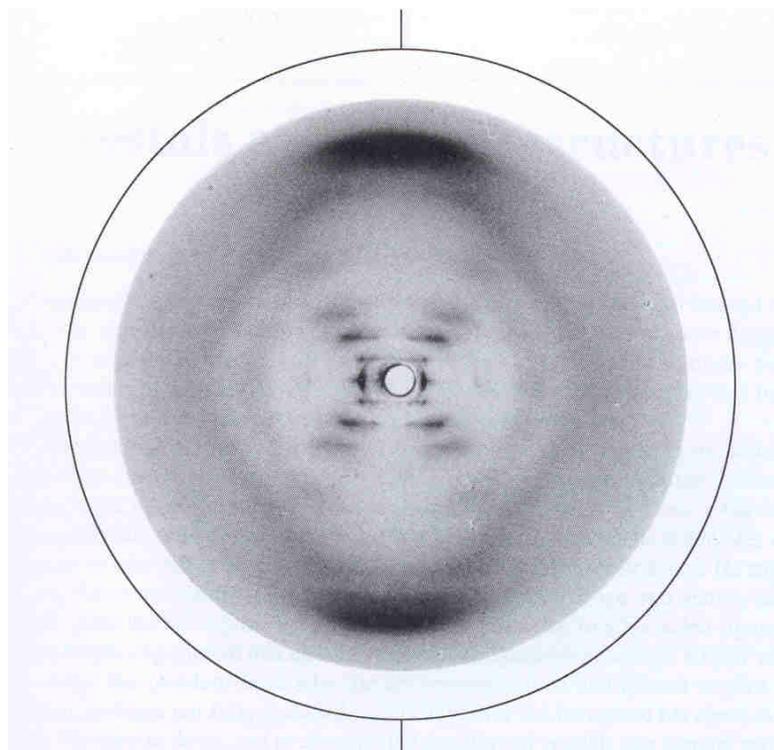
Fig. 6 X-ray photograph of DNA taken by Rosalind Franklin and Raymond Gosling in 1952 and published in the 25 April issue of *Nature*, vol 171, p737, 1953.

B   Close-packing

The simplest place to start with crystal structures is how to pack together as tightly as possible lots of atoms of the same size. We assume atoms to be spherical in shape, which keeps the problem simple. So it is rather like packing oranges into a box. First, if we consider balls sitting on a plane in a single layer we find that the most neighbours that a sphere can be touching simultaneously is six, as was suggested by Kepler in 1611 (see earlier). This can easily be appreciated by considering pennies in contact on the surface of a table.

With all the circles/balls being of equal sides the centres of all the objects form a grid of equilateral triangles sharing their edges with their neighbours. Given that the internal angle in an equilateral triangle is 60° one can see the origin of the hexagonal symmetry. The close packing of spheres in a plane is shown in Figure 7.
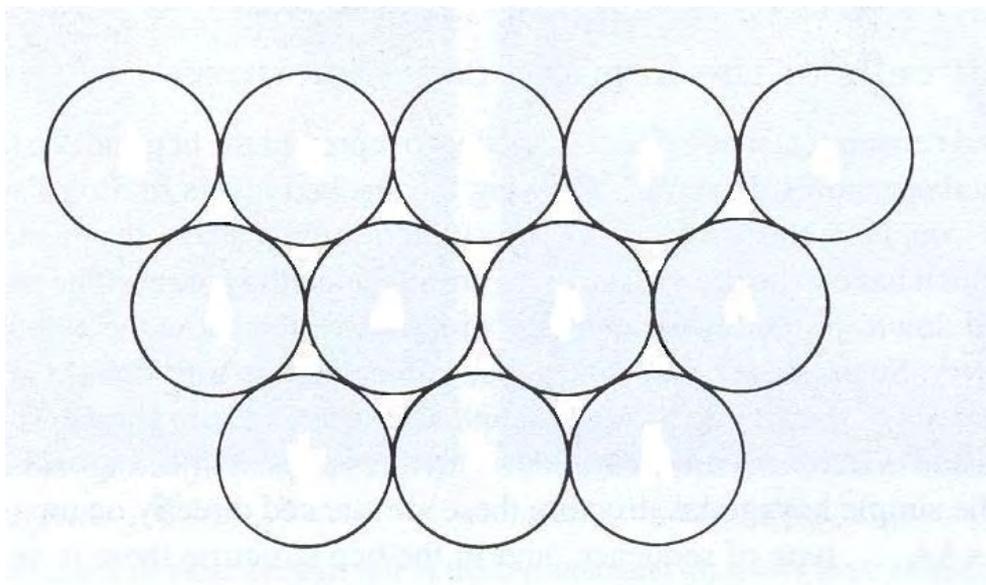
Fig. 7 The close-packing of spherical balls (or circles) in a plane. By considering one of the two central balls it is evident that there are six neighbours in contact in a hexagonal arrangement.

The above diagram shows close-packing in two dimensions. The next problem is to consider the third dimension. The most efficient way to pack together layers of these atoms is for one plane to nestle into the gaps in the plane below. By looking along a row of circles above you can see that there are twice as many gaps between them as there are circles. When placing a plane of atoms on top of a close-packed layer only there is only space for half of these gaps to have an atom right on top of it. In this way the gaps can be considered to be of two types, as shown below.
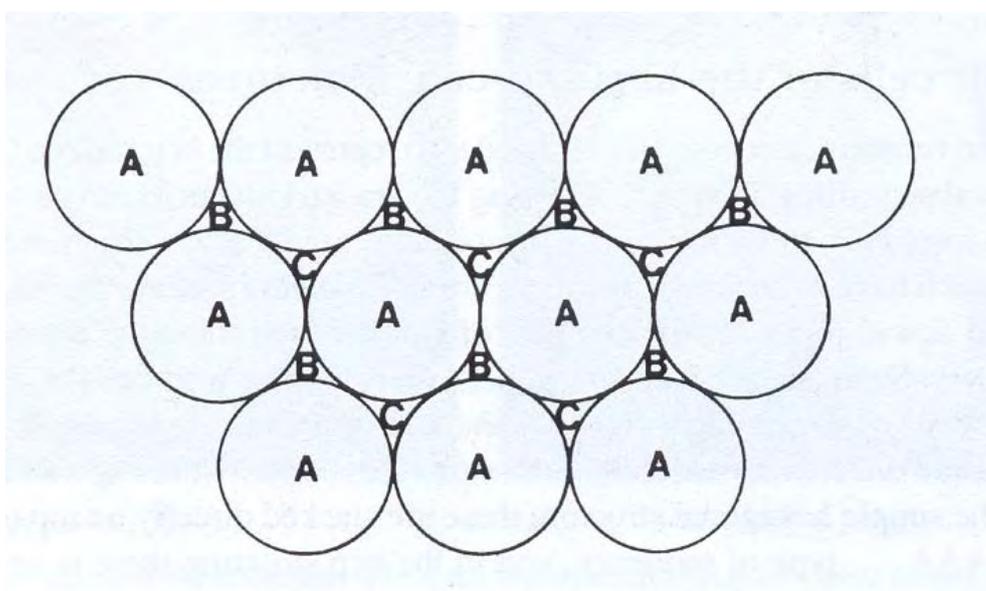
Fig. 8 A close-packed layer of atoms, showing two types of hole in the layer, labelled 'B' and 'C'. [Image from "The Basics of Crystallography and Diffraction" by Christopher Hammond, OUP.]

So a plane of close-packed atoms from above could sit on the holes labelled 'B' or the holes labelled 'C' but not both at once. Clearly the two different possibilities for the second plane are equivalent. However, when considering where to place a third plane of atoms, there really is a choice. If the second plane of atoms were to sit on the 'B' holes then the atoms in the third plane could either rest directly above the atoms in the first plane (in the 'A' position) or they could reside above the 'C' holes. These two possibilities are both equally efficient at filling space as the 'B' and 'C' holes are the same (as is evident from Figure 7). They are not, however, equivalent from the point of view of symmetry. But since both of the above methods of stacking planes of close-packed atoms are equally efficient, both are seen in nature – in metallic crystals. The two types are described separately below.

1. Hexagonal close-packing

The type where atoms only occupy the 'A' and 'B' positions in an alternating sequence is known as 'AB' packing or hexagonal close-packing, relating to the hexagonal symmetry discussed earlier. This arrangement is illustrated in the Figure 9 below. The atoms are shown at half actual radii, ie not actually in contact, to make the structure easier to interpret. While all of the atoms are identical, the atoms in alternating ('B') layers are shown in green to make the packing arrangement clear. Magnesium is an example of a metal that adopts this structure.
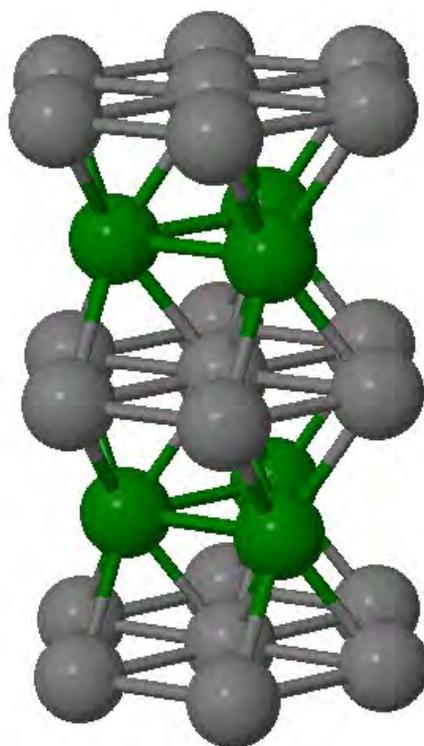
Fig. 9 The 'AB' close-packing arrangement of hexagonal close-packing. The 'B' layers are shown in green, even though all the atoms in the structure are actually identical. The bonds in the Figure connect atoms that are in contact in the structure.

Considering the central grey atom in Figure 9 it is evident that an atom in a hexagonal close-packed lattice will be in contact with 12 neighbours: six in the hexagonal

arrangement in the plane, and three in an equilateral triangle arrangement in the plane above and the plane below. The number of nearest neighbours with which an atom is in contact is known as the coordination number.

2. Cubic close-packing

The type where atoms occupy the 'A', 'B' and 'C' positions in that sequence is known as 'ABC' packing, or cubic close-packing. It is not particularly obvious at first that there is cubic symmetry in 'ABC' packing; we shall explore this in the next section. This arrangement is illustrated in the Figure below. Again, the atoms are shown not actually in contact to make the structure easier to see. Similarly, despite the colour coding of the 'A', 'B' and 'C' layers all of the atoms are identical. Copper is an example of a metal that adopts this structure.
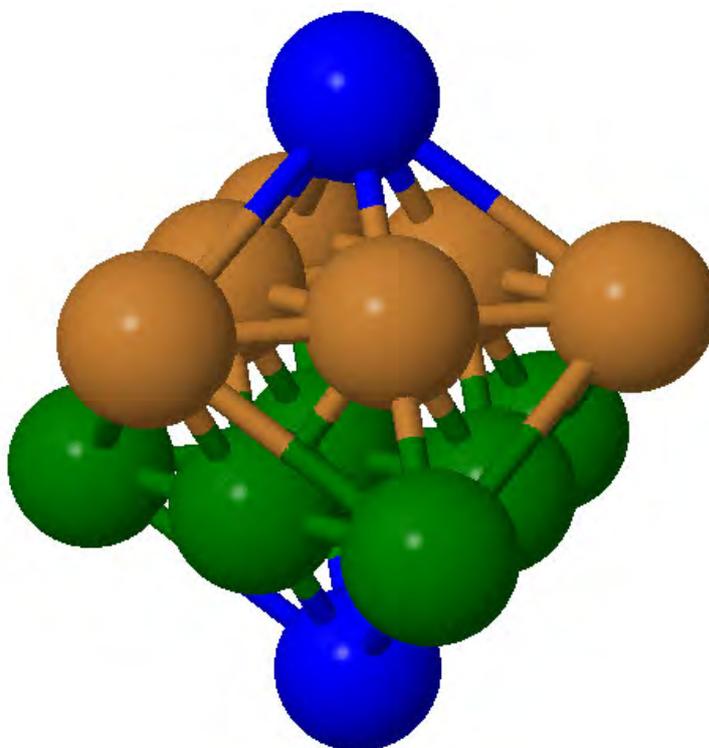
Fig. 10 The 'ABC' close-packing arrangement of cubic close-packing. The 'A', 'B' and 'C' layers are colour coded, even though all the atoms in the structure are actually identical. The bonds in the Figure connect atoms that are in contact in the structure.

In cubic close-packing there is also a coordination number of twelve. This isn't surprising in view of the equal efficiency of the lattices of filling space. The arrangement is similar to the one in the hexagonal close-packing case, except the triangles of atoms in contact in the layers above and below are at a different orientation to each other (rotated by 60°).

C   The unit cell

In a high quality crystal the structure is highly ordered and repeats itself countless times. The most convenient way to discuss the structure is to consider the smallest repeating unit of the structure that contains all the symmetry of the crystal. This is known as the unit cell. A crystal can be built up by stacking lots of unit cells together side-by-side. The only unit cells we shall consider here are those of cubic symmetry as these are the geometrically the most straightforward and the easiest to visualise.
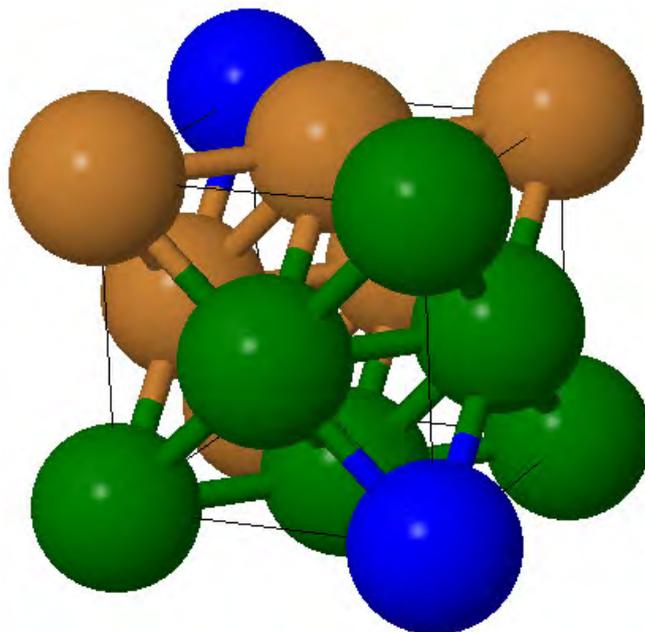
Fig. 11 The cubic close-packed unit cell, with colour-coded close-packed layers. The black wireframe depicts the cubic region that repeats itself in the structure. The coloured bonds in the Figure connect atoms that are in contact in the structure.

In the last section it was pointed out that the 'ABC' type of close-packing has cubic symmetry. Indeed the unit cell that describes the structure is cubic, and is shown in Figure 11. Again, the atoms are shown not actually in contact and the close-packed layers are colour coded. The unit cell cube is superimposed in black. The lines of the cube do not represent bonds but rather the region of space that repeats itself in the lattice. Note that the atoms below are just rotated in space compared to the earlier depiction of the cubic close-packed lattice.

Within the unit cell in Figure 11 we see atoms in one of two types of position. Atoms are either sitting on the corner of the cube or else they are in the centre of one of the faces. The eight corners and six faces are all associated with an atom. Each atom in a corner position is actually shared between the eight adjacent cubes that meet at that corner. These eight cubes are equivalent and so one eighth of a corner atom is within the unit cell. As there are eight corners on a cube that leads to a total cell occupancy of 1 for the corner atoms. Each atom at the centre of a face is shared with one other cube and so one half of a face-centre atom is within the unit cell. As there are six faces on a cube, there is a cell occupancy of 3 for the face-centre atoms. The total cell occupancy for the

cubic close-packed unit cell is therefore 4, despite the fact that 14 atoms are visible in Figure 11.

D   Compounds

The picture is more complicated in compounds because, with more than one element involved, there is more than one size of atom. The lattices for compounds that we encounter are commonly ionic (or considered to be ionic) and so the atoms involved will be referred to as ions from now on. A convenient way of considering the problem is for one ion to fit into the gaps of a lattice formed by the oppositely charged ion. Such an arrangement maximises the contact between oppositely charged ions, providing attractive forces, and minimises the contact between similarly charged ions, minimising the repulsive forces. In this way ionic compounds achieve the highest possible lattice energy and therefore the maximum possible energetic stability.

So we need to consider the gaps in a lattice of ions. One way of imagining the gaps, or holes, in a lattice is to refer back to Figure 8. Let us imagine that there is a second layer of ions above the 'A' layer (of the same type as the 'A' layer ions) that are all sitting on the 'B' gaps. In this picture we can find two types of hole in the lattice.

1. Tetrahedral holes

In Figure 8, below each ion in the 'B' layer there is a small hole. The centre of this hole is slightly above the level of the centres of the 'A' ions. Such a hole is surrounded by four neighbours – three 'A' ions arranged as an equilateral triangle just beneath and a 'B' ion immediately above. Because those 'A' and 'B' ions are all an equal distance from each other, their centres are at the corners of a tetrahedron, and so the hole is known as a tetrahedral hole.

An ion residing in such a hole will therefore have four nearest-neighbour ions of the other type. Since every ion in a close-packed lattice can be considered to be in a plane and fitting into a hole on the plane on either side, then every ion has a tetrahedral hole associated with it on either side. Therefore there are twice as many tetrahedral holes in a close-packed lattice as there are ions. An ion occupying a tetrahedral hole is shown in the Figure below.
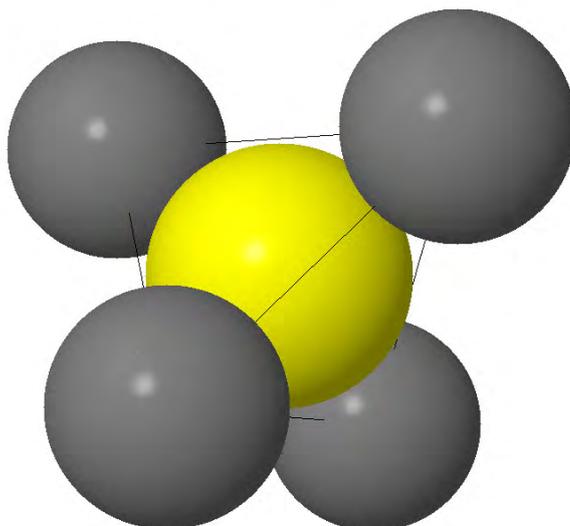
Fig. 12 Non-metal ion (shown in yellow) occupying the tetrahedral hole between four metal ions (shown in grey). The metal ions are nominally close-packed though in fact are not in contact due to the size of the non-metal ion. The black wireframe connects the centres of the four metal ions, illustrating the tetrahedral symmetry of the hole.

Let's assume that the grey ions are metal cations and the yellow ion is a non-metal anion. Three of the four metal cations can be considered to be in one close-packed layer with the fourth one in the adjacent layer. The non-metal ion is occupying the tetrahedral hole just above the layer with the three metal ions. Since the non-metal ion is larger than the hole itself it has forced the metal ions apart. Ions fitting into such holes are in fact larger than the holes for this reason: since the metal ions are of like charges, and like-charges repel, the added size of the non-metal ion compared to the hole reduces the electrostatic repulsion between the metal ions.

2. Octahedral holes

Going back to Figure 8 again, assuming there are ions in the 'A' and 'B' positions, we can also identify octahedral holes in the lattice. In this case the octahedral holes are the holes labelled 'C'. These are not quite so easy to see. The centre of the hole is half way between the 'A' and 'B' planes. Beneath it there is an equilateral triangle of 'A' ions and above it is an equilateral triangle of 'B' ions. The triangles have different orientations: one rotated 60° relative to the other. However, the corners of two such triangles connect together to form a regular octahedron. An ion inside an octahedral hole of counter-ions is shown in Figure 13.
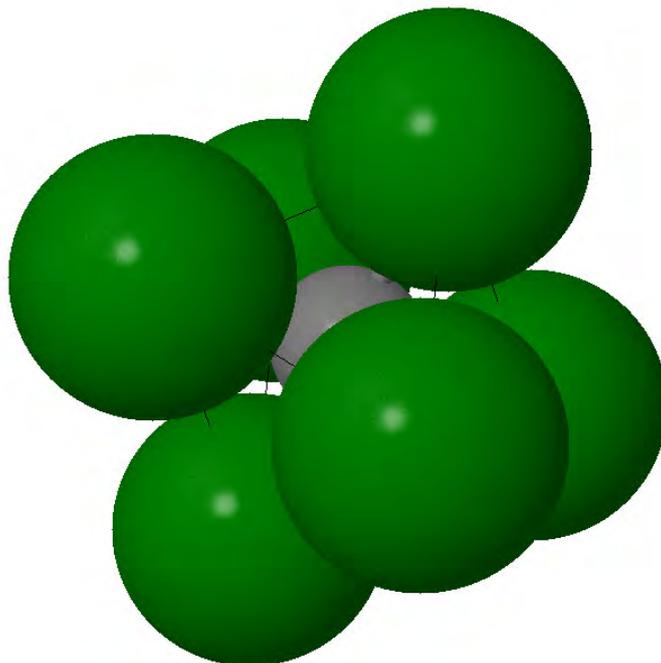
Fig. 13 Metal ion (shown in grey) occupying the octahedral hole between six non-metal ions (shown in green). The non-metal ions are nominally close-packed though in fact are not in contact due to the size of the non-metal ion. The black wireframe connects the centres of the six non-metal ions, illustrating the octahedral symmetry of the hole.

In the Figure above it is apparent how the octahedral hole relates to close-packed layers by considering the three non-metal ions above and to the left of the central metal ion to be in one close-packed layer and the three bottom-right ions to be of the adjacent close-packed layer of non-metal ions. Each group of three ions forms an equilateral triangle rotated 60° relative to the other.

An ion residing in such a hole will therefore have six nearest-neighbour ions of the other type. Referring back to Figure 8, since every 'C' hole in this model is an octahedral hole, and since inspection along rows of ions reveals that there is an equal number of 'C' holes compared to ions in a row, then there is the same number of octahedral holes in a close-packed lattice as there are ions.

Now that we have considered occupying tetrahedral and octahedral holes in close-packed lattices with counter-ions to form ionic compounds, we can go on to consider a couple of classic examples.

3. Sodium chloride, NaC*l*

In the sodium chloride lattice there is a 1:1 ratio (stoichiometry) between the two types of ion. The lattice can be considered as a close-packed arrangement of one type of ion with the other type of ion occupying all the octahedral holes in the lattice. This is consistent with the ratio of octahedral holes to ions arrived at earlier. The structure is illustrated in Figure 14.
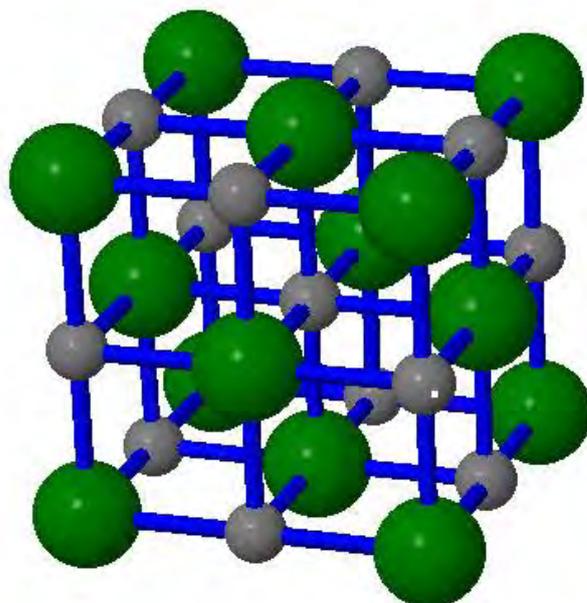
Figure 14 The unit cell of the sodium chloride lattice. The green ions are chloride ions and the grey ions are sodium ions. In this view the close-packed layers of the chloride ions are clearly visible. The bonds connect the ions that are in contact in the structure.

The symmetry of the above structure is very high. Indeed the sodium and chloride ions are in fact in equivalent lattices: the lattice can equally be considered as a close-packed lattice of sodium ions with chloride ions in all the octahedral holes. By considering a unit cell displaced by half of a cell length, a similar cell emerges but with the two types of ion having exchanged position in the cell.

By considering the central sodium ion in the unit cell it is apparent that the ions are sitting in octahedral holes: it has six nearest neighbours chloride ions which are arranged along the plus and minus directions of the x, y and z axes, assuming they are drawn along the bonds connecting the ion to the neighbours with which it is in contact. This is made clear in Figure 15.

It is unfortunate that only one ion in the unit cell for NaС*l* has all six of its nearest neighbours visible in the cell. However, when considering another of the sodium ions, which are all half-way along the edges of the unit cell cube, four of its nearest-neighbour chloride ions are visible in the cell. These ions can be found along the x, y and z axes (as defined in the last paragraph) and with a bit of imagination it can be seen that the other two nearest neighbours will lie in adjacent unit cells, and that therefore all the sodium ions are in octahedral holes.

Similarly, consideration of the chloride ions in the unit cell, which are at the corner and face-centre positions, reveals that they are all in octahedral holes of sodium ions. In the case of the corner chlorides, only three of the nearest-neighbour sodium ions are visible in the unit cell, but these are along the x, y and z axes; it is obvious by symmetry that there are three other nearest neighbours in adjacent unit cells, forming an octahedral arrangement. In the case of the face-centre chlorides, five of the nearest-neighbour

sodium ions are visible in the unit; it is clear that the sixth neighbouring sodium ion is in the adjacent unit cell, forming an octahedral arrangement.

Now that we have established that both sets of ions are in octahedral holes we can confirm that both ions are 6-coordinate, ie they each have six nearest neighbours. The fact that both ions have the same coordination number is consistent with their 1:1 stoichiometry in the compound.
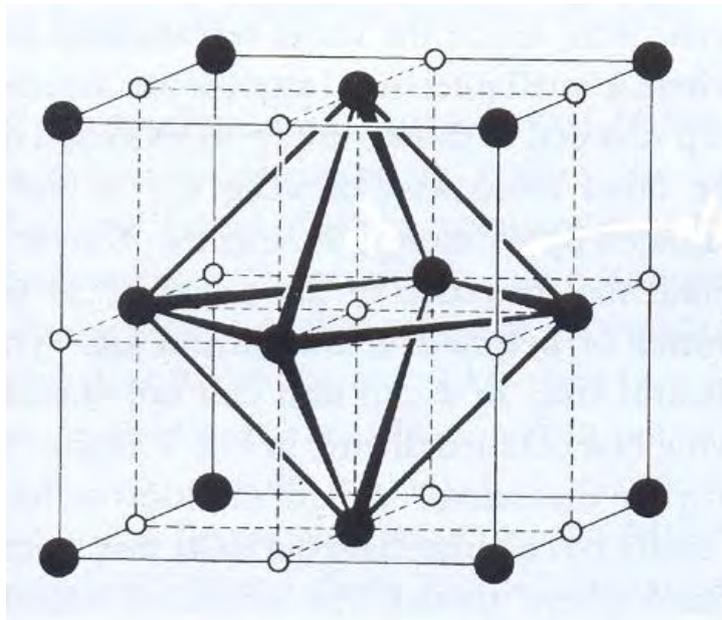
Figure 15 The unit cell for NaCl showing the octahedral coordination around the central ion. [Image adapted from "The Basics of Crystallography and Diffraction" by Christopher Hammond, OUP.]

It is good practice to consider the cell occupancy of each type of ion. The chloride ions in Figure 14 occupy the cubic-close-packed positions and so, according to the discussion in the Unit Cell section, have a cell occupancy of 4 (from the calculation $(8 \times 1/8) + (6 \times 1/2)$). As for the sodium ions they occupy the body-centre of the cube and the edge-centre positions. The edge-centre ions are shared by four unit cells, and since the cubes are equivalent each ion has an occupancy of 1/4. Since a cube has 12 edges, the total cell occupancy of sodium ions is $(12 \times 1/4) + 1 = 4$. The sodium and chloride ions therefore have the same cell occupancy of 4, which is consistent with their 1:1 stoichiometry in the compound.

4. Fluorite, CaF$_2$

In the fluorite (calcium fluoride) lattice there is a 1:2 stoichiometry between the two types of ion. The lattice can be considered as a close-packed arrangement of calcium ions with the fluoride ions occupying all the tetrahedral holes in the lattice. This is consistent with the ratio of tetrahedral holes to ions arrived at earlier. The structure is illustrated in Figure 16.
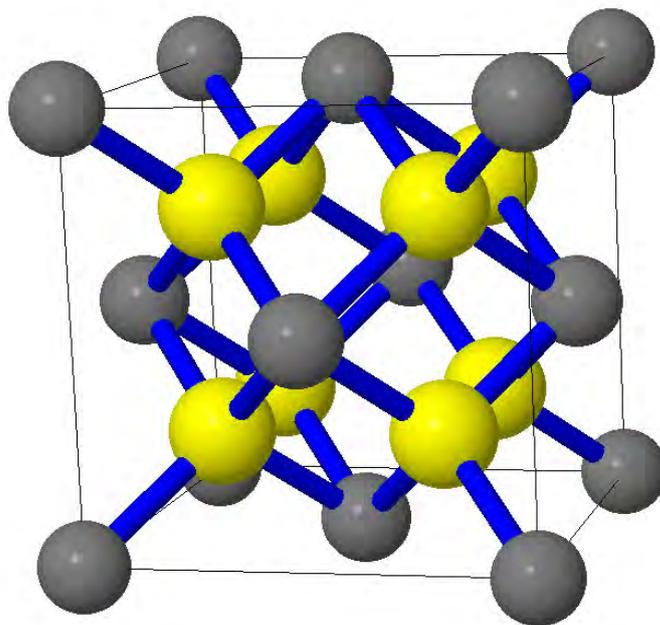
Figure 16 The unit cell of the fluorite (CaF_2) lattice. The grey ions are calcium ions and the yellow ions are fluoride ions. The blue bonds connect the ions that are in contact in the structure. The black wireframe depicts the cubic region that repeats itself in the structure.

Inspection of the yellow fluoride ions shows that they have four nearest neighbours (the blue bonds indicate which ions in the structure are in contact with them). It may not be obvious that these four neighbours are in a tetrahedral arrangement; this symmetry can be confirmed by thinking of the unit cell divided up into eight equal cubes, or octants. The cell length of the octant is half that of the unit cell. In three dimensions then the octant has a volume of $(1/2)^3 = 1/8$ of the unit cell. In each of these octants four of the eight corners have calcium ions at the corners, as shown in Figure 17 below. By symmetry the fluoride ion must be at the centre of the cube: since it is in contact with all four calcium ions, the distances between the fluoride ion and the calcium ions must be the same.
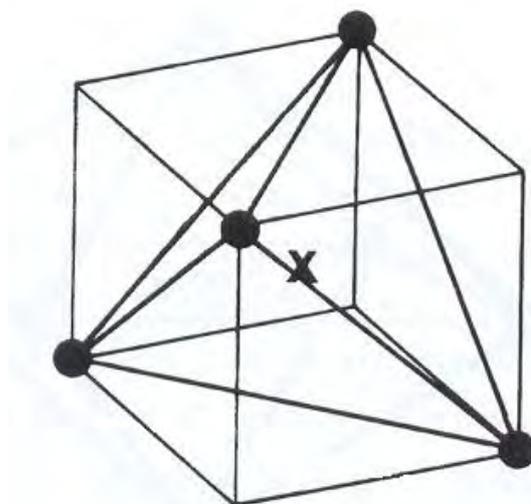
Fig. 17 The tetrahedral hole within an octant of the fluorite unit cell. X marks the centre of the hole and the centre of the octant. The arrangement of the four calcium ions at the alternating corners of a cube gives a tetrahedral arrangement: the distances between all four calcium ions are equal, by symmetry, which defines the tetrahedron.

A tetrahedral hole shown within the fluorite unit cell is given in the Figure below.
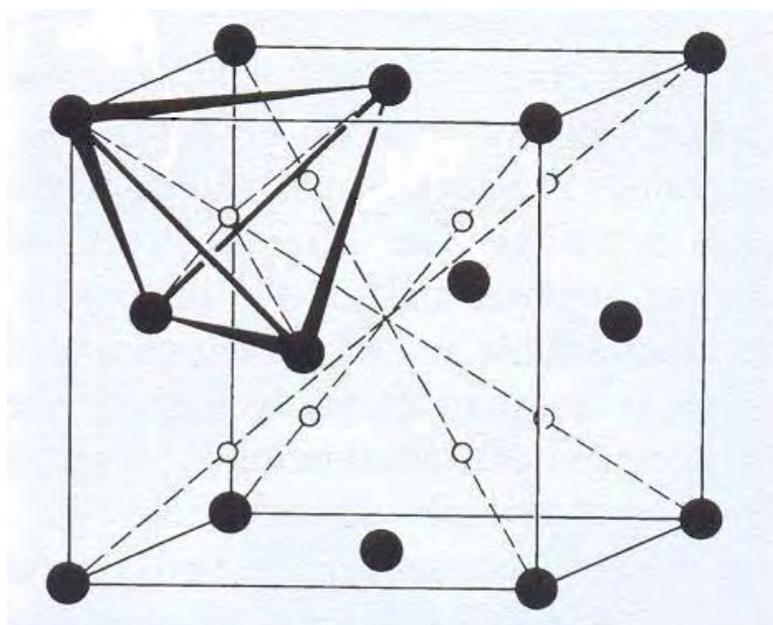
Fig. 18 The unit cell for CaF_2 showing the tetrahedral coordination around one of the fluoride ions. [Image adapted from "The Basics of Crystallography and Diffraction" by Christopher Hammond, OUP.]

Since every corner calcium ion is in contact with a fluoride ion in the unit cell, and since each corner calcium ion is shared between eight unit cells, it follows that the corner calcium ions have eight nearest neighbour fluoride ions, and therefore a coordination number of eight.

In Figure 18 above, it is apparent, by symmetry, that the calcium ion at the centre of the top face of the unit cell has four fluoride nearest neighbours in the unit cell – one in each of the four top octants. Since every face-centre calcium ion is shared between two unit cells, then by symmetry each of these face-centre calcium ions, like the corner calcium ions, has a coordination number of eight.

In summary, the fluoride ions have a coordination number of 4 and the calcium ions have a coordination number of 8. This is consistent with the 2:1 stoichiometry of the compound. [You may also be able to see that the calcium ions occupy cubic holes, half of which are occupied.]

It is good practice to consider the cell occupancy of each type of ion. The calcium ions occupy the cubic-close-packed positions and so, according to the discussion in the Unit Cell section, have a cell occupancy of 4 (from the calculation $(8 \times 1/8) + (6 \times 1/2)$). As for the fluoride ions they are all within the body of the cube and so have a cell occupancy of 8. This 1:2 ratio of cell occupancy is consistent with their 1:2 stoichiometry in the compound.

E   Sample exercises

1. This question is about the earliest general study of crystal structures

The first person to consider the structure of crystals as a general problem was Robert Hooke. The image below is from Scheme VII in his book *Micrographia*, published in 1665. Inspired by the regular shapes of crystalline specimens that he examined with his microscope, he proposed that these could arise from the packing together of "a company of bullets" as shown in his sketches A to L below. These are analogous to the unit cells that crystallographers refer to today.
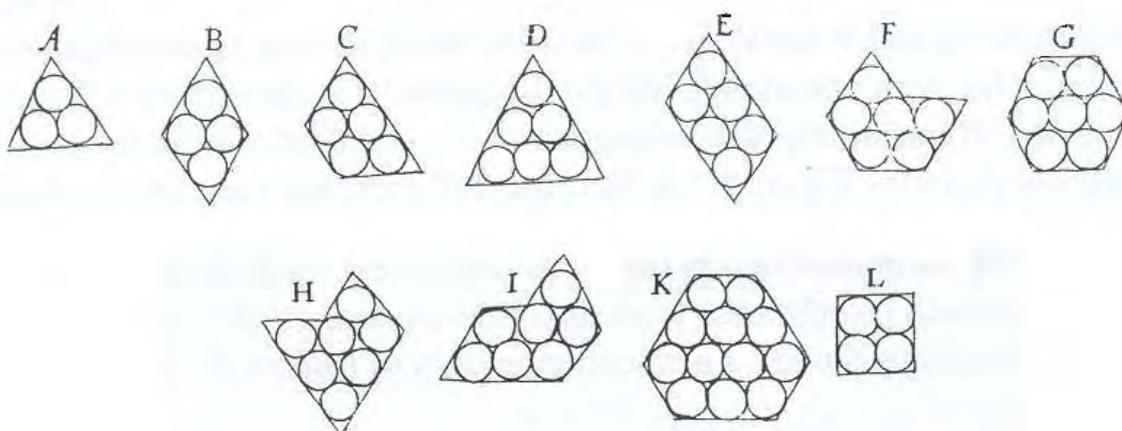
(a) All of the packing arrangements A to L can be considered to be close-packed within the plane of the paper with one exception. Which is the exception?

(b) Of the unit cells above, which one shows the greatest symmetry with respect to rotation?

(c) Calculate, in two dimensions, the percentage of space filled by the bullets in arrangement L.

2. This question is about gold nanoparticles

UK scientists have found a way to target cancer with gold (*Photochemical and Photobiological Sciences*, 2006).

Gold crystallises in the arrangement shown below.
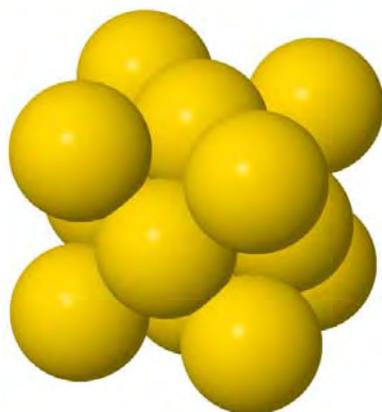
Jmol

The above structure is known as a *unit cell*. Running perpendicular to the body-diagonals in the unit cell are the close-packed layers. These are shown with colour-coding in the representation below.
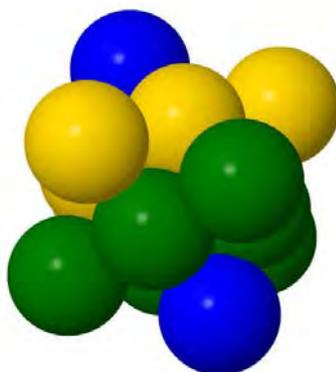
Jmol

An anti-cancer drug is bound to the gold nanoparticle. The drug-nanoparticle complex is attracted to cancer cells. In the presence of light, the cancer drug excites oxygen

molecules to a reactive form known as 'singlet oxygen', which causes apoptosis ('cell suicide') of the cancer cells.

(a) Gold is unusual in being made up of a single isotope, Au-197. Write down the number of protons, neutrons and electrons in an atom of Au-197. [A periodic table is available in the data booklet.]

(b) If a gold nanoparticle contains a million gold atoms, calculate its mass. [Hint: you will need Avogadro's number, which is in the data booklet.]

(c) Given that the radius of a gold atom is 0.135 nm (1 nm = 10^{-9} m), calculate the number of gold atoms in a gold nanoparticle that has dimensions 10 nm × 10 nm × 10 nm. Assume that 74% of the volume of the nanoparticle is taken up by spherical gold atoms. (The other 26% of the volume is the spaces between the atoms.) The volume of a sphere is $\frac{4}{3}\pi r3$ where r is the radius. [Hint: calculate the volume of the nanoparticle occupied by gold atoms, and the volume of one gold atom.]

(d) What is the name of the particular type of structure adopted by gold crystals?

(e) Given that atoms are located at the corners of the unit cell and in the centre of the faces, calculate the total number of atoms within the cell. [Hint: remember that the corners of the unit cell are in the *centres* of the atoms, so not all the atom is actually inside the cell.]

(f) Within the bulk of a gold nanoparticle how many neighbouring atoms are in contact with a gold atom?

(g) In the figure above, the close-packed layers are colour-coded. There is more than one direction in which the close-packed layer planes can be shown to be propagating. Given that the close-packed planes are perpendicular to a body-diagonal axis in the cube [a body-diagonal axis passes through two corners and the centre of the cube] deduce in how many different directions the close-packed layers can be drawn.

Sample question

4   In most metals the atoms pack in one of three possible ways. One of these is called *body-centred cubic (bcc)*, in which there is 32% empty space between the atoms. In the other two common metal structures there is only 26% empty space, so these structures are described as *close-packed*.

(a)   Give the coordination number of a metal atom in a *close-packed* metal structure.

.... [1]

(b)   Complete the table to give the names and layer structures of the two close-packed metal structures.

name	layer structure

[4]

(c)   Explain the differences between the lattice structures of sodium chloride, $NaCl$, and calcium fluoride, CaF_2, by completing the following sentences.

(i) $NaCl$ can be considered to consist of a close-packed structure of sodium ions with

chloride ions occupying the .... holes.   [1]

(ii) CaF_2 can be considered to consist of a close-packed lattice of

.... ions with .... ions

occupying the .... holes.   [2]