Extension 5: Crystal Structures

1. Prerequisites

The key ideas required to understand this section are:

Topic	Book page
Arrangement of ions in sodium chloride	52
Metallic bonding	74
Arrangement of molecules in iodine	77
Hydrogen bonding – the structure of ice	79
The structure of silica	200

2. Solid state structure

Types of solids

When most liquids are cooled, they freeze. Their particles arrange themselves in ordered positions and they form **crystalline** solids. Some solids, such as diamonds, sugar and grains of sand, are single crystals. Most crystalline solids, however, consist of many small crystals 'lumped together' – such as ice, granite and metals. **Amorphous** solids do not have an ordered structure – glass is an example of an amorphous solid.

In a crystalline solid the atoms, molecules or ions are arranged in a definite repeating pattern

Crystalline solids

Different types of crystalline solids include:

(i)   Ionic solids which contain positive and negative ions; e.g. potassium chloride, K^+Cl^-.

(ii)   Molecular solids which consist of individual molecules; e.g. iodine, I_2, and ice, H_2O.

(iii) Network solids have crystals in which all of the atoms are held together by covalent bonds and it is not possible to distinguish individual molecules; e.g. diamond, C, and silicon dioxide or sand, SiO_2.

(iv)   Metallic solids are composed of metal atoms in a giant lattice arrangement; e.g. copper, Cu, and zinc, Zn.

Metallic solids

Pure metals are crystalline solids, where the metal atoms pack closely together in a repeating pattern; the atoms pack together as though they were spheres. When spheres of equal size pack together as closely as possible in a plane, they arrange themselves as in Fig. 5.1; each sphere is in contact with six others. This arrangement is called close packing. Fig. 5.1 shows the arrangement in a single layer.
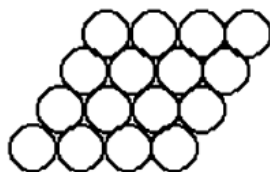

Fig. 5.1 A layer in close packing

The crystals of many metals consist of these layers stacked on top of each other. The layers can be stacked in one of two ways:
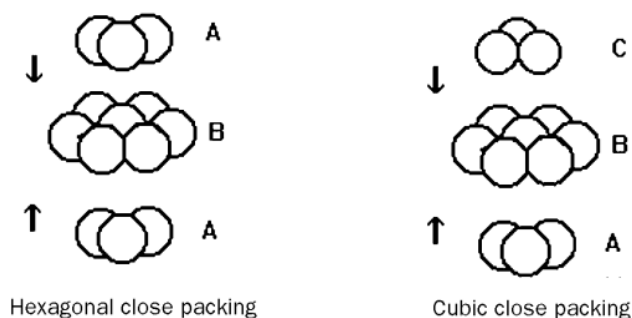
Fig. 5.2 Layers in close packing

In **hexagonal close packing**, each sphere in the third layer lies directly above a sphere in the first layer. These are labelled A layers. The second layer is labelled the B layer. The stacking arrangement is called ABAB. Examples of metals that crystallize in this way are: Mg and Zn.

In **cubic close packing**, the spheres in the third layer are not directly above spheres in layer A or layer B. This layer is type C. The arrangement is labelled ABCABC. Examples of metals that crystallize in this way are Al, Cu, Pb and Ag. This type of packing is also known as face-centred cube – if you make a model of a small unit and rotate it you will see a cube with a sphere in the centre of each face (see Fig. 5.12).

In both of these arrangements each atom touches twelve nearest neighbours: six in its own plane and three in each plane above and below the atom. The number of neighbours touching an atom is known as its coordination number – in these cases the coordination number is 12.

Some metals crystallise in a *body-centred cubic* structure which contains planes of spheres that are *not* close packed. Each sphere in a plane is surrounded by four nearest neighbours that do not touch. The second layer is stacked on top of the first layer such that a sphere in the second layer touches four spheres in the first layer. The spheres of the third layer are positioned directly above the spheres of the first layer, those of the fourth layer directly above the second . . . and so on. The bodycentred cubic arrangement is shown in Fig. 5.3. Examples of metals that crystallize in this way are: K, Rb and Cs.

A layer in a body centred cubic structure

Looking down at two layers stacked on top of each other

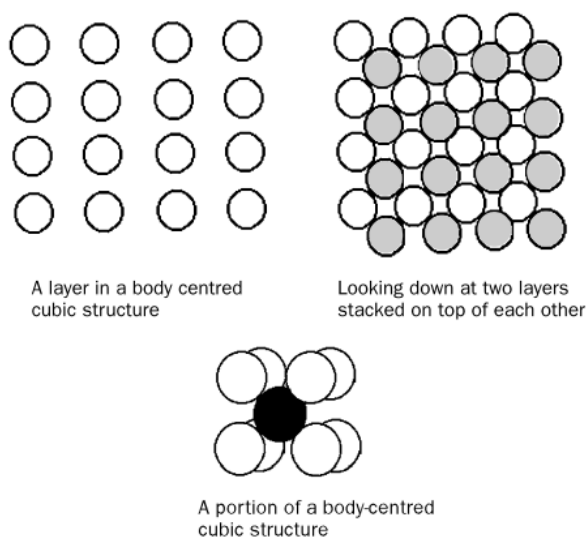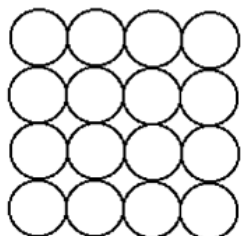A portion of a body-centred cubic structure
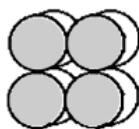
Fig. 5.3 Body-centred cubic structure

EXERCISE 5A

What is the coordination number of an atom in the body-centred cubic structure?

A *simple cubic structure* is not close packed and is quite rare for metals. It contains planes which each sphere *touches* its four nearest neighbours. Planes are stacked directly above each other, so that an atom in the first layer touches only one atom in the second layer. The coordination number of an atom is six; each atom touches four atoms in its own layer, as s one in the layer above and one in the layer below (see Fig. 5.4). Polonium is an example of a metal that crystallizes in this way.

A layer in a simple cubic structure

A portion of a simple cubic structure

Fig. 5.4 Simple cubic structure

EXAMPLE 1

Tungsten crystallizes in a body-centred cubic unit cell with an edge length of 317 pm.
   (i)   What is the atomic radius of tungsten in this structure?
   (ii) Calculate the density of tungsten. ($N_A = 6.022 \times 10^{23} \text{mol}^{-1}$ $m(W) = 184 \text{ u}$)

Answer

(i)   Look back at Fig. 5.3. A tungsten atom in a layer touches those atoms in layers above it, but not within layers: $z = 317$ pm.

$\frac{a}{2}$ is equal to half the diagonal of a cube of size z

From Pythagoras's theorem the length of the diagonal of the square is found from:

$$c^2 = z^2 + z^2$$
$$c^2 = 2z^2$$
$$c^2 = 200{,}978$$
$$c = 448 \text{ pm.}$$

And then, using another right-angled triangle:

$$a^2 = c^2 + z^2$$
$$a^2 = 448^2 + 317^2$$
$$a = 549 \text{ pm.}$$

Since the atoms touch along a, the radius of a single tungsten atom is a, quarter of a or 137 pm.

(ii)   Density is defined as mass/volume. Each unit cell contains one atom in the centre, which 'belongs' completely to that unit cell, and eight atoms in the corners of a unit cell, each of which is shared by eight other unit cells. Therefore, 1/8 of each corner atom, contributes to each unit cell. This makes a total of 1 + 1/8×8 = 2 atoms of tungsten 'belong' to each unit cell. Since one atom of tungsten has a mass of 184/6.022×10²³g, two atoms have a mass of 368/6.022×10²³g.

EXAMPLE 1 *(continued)*
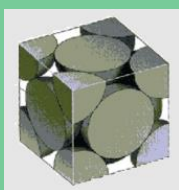
Density is often quoted in g cm^{-3}.

The volume of a unit cell is $(317 \times 10^{-10})^3$ cm³; the density of tungsten is therefore:

$$\frac{368}{(317 \times 10^{-10})^3 \times 6.022 \times 10^{23}}$$

= 19.2 g cm^{-3}.

EXERCISE 5B

Lead, atomic radius 175 pm, crystallizes in a face-centred cubic unit cell, with the nearest neighbours in contact (see the space filling diagram below).

(i) Calculate the edge length of the unit cell.
(ii) Calculate the density of lead. m(Pb) = 207 u

3. Ionic Bonding

Ionic crystals consist of two or more different ions that have different sizes.

In simple ionic structures, the anions (generally larger than the cations) are usually in a close packed arrangement. The spaces between the anions, which are called holes or interstices, are occupied by the cations. There are two common types of hole: Tetrahedral holes are found in the space formed between three spheres in one plane and one in another plane, and octahedral holes are found in the space formed between three spheres in one plane and three in another plane (see Fig. 5.5).
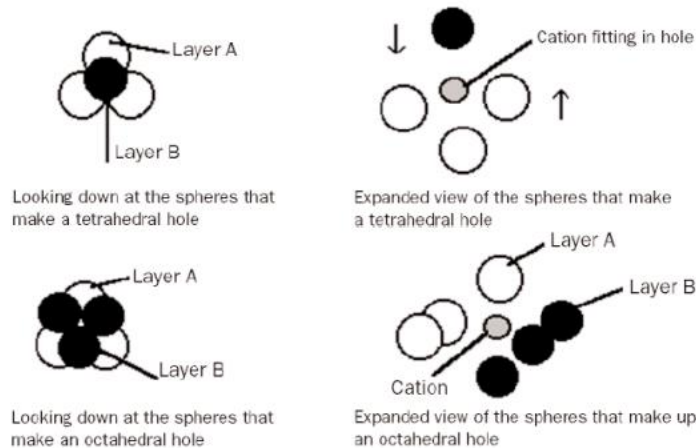

Fig. 5.5 Octahedral and tetrahedral holes

Whether the cations of an ionic compound occupy tetrahedral or octahedral holes, depends on their size relative to the anions. Relatively small cations go into tetrahedral holes, while relatively large cations go into octahedral holes. If the cations are too large to occupy octahedral holes, the packing of the anions may form a more open structure, such as a simple cubic arrangement, and the cations can then occupy larger spaces. See Fig. 5.6 overleaf.
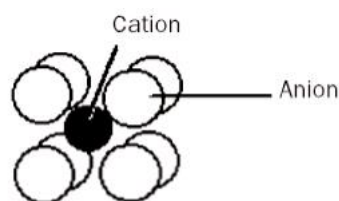
A cation in a cubic hole in a simple cubic arrangement of anions
Note that this is an expanded view (for clarity). The cation touches the anions.

Fig. 5.6 Cation in a cubic arrangement of anions

The ratio of octahedral holes to anions in a close-packed structure is 1:1. Compounds with cations in octahedral holes in a close packed arrangement of anions can have a maximum cation-to-anion ratio of 1:1, e.g. NaCl. The ratio of tetrahedral holes to anions in a close packed arrangement is 2:1 because there are two tetrahedral holes to each anion in the structure. Compounds such as Na_2O and CaF_2 (note that here the F – ions fill the holes!) crystallize in this way. Compounds with a cation-to-anion ratio of less than 2:1 may also crystallize this way, if the ionic sizes fit - in these cases, some of the tetrahedral holes remain vacant.

> ### EXERCISE 5C
>
> **(i)** Aluminium oxide crystals contain aluminium ions in 2/3 of the octahedral holes in a close-packed arrangement. Use this statement to work out the formula of aluminium oxide.
> **(ii)** What is the formula of an oxide of titanium that consists of a close packed arrangement of oxide ions with titanium atoms in ½ of the octahedral holes?

4. The radius ratio rule

The structure of a compound mostly depends on its stoichiometry and the relative sizes of the cation and anion. Determining the radius ratio enables us to predict the likely structure of an ionic compound:

radius ratio = $r+/r–$

r^+ = the radius of the cation; and

r^- = the radius of the anion.

There is a minimum ratio for each coordination number; below this ratio the structure is not stable. Limiting values for the radius ratio in ionic compounds are:

Coordination number	Type of packing	Limiting values of r^+/r^-
8	body-centred cubic	above 0.732
6	octahedral sites occupied	0.414 to 0.732
4	tetrahedral sites occupied	0.225 to 0.414

> ### EXERCISE 5D
>
> Predict the coordination number of Cs^+ (r^+ = 170 pm) in CsCl. The radius of a chloride ion is 181 pm.

5. Space lattices and crystal structures

The particles in a crystal are arranged in a definite repeating pattern. The collection of all the points in a crystal that have identical environments is called a **space lattice**. The basic 'building block' of a space lattice is called a **unit cell**. An entire crystal can be built up by repeating the unit cell in three dimensions. The unit cell of sodium chloride is shown in Fig. 5.7.
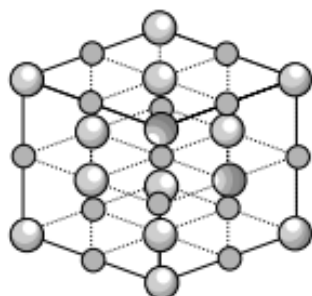

Fig. 5.7 A unit cell of sodium chloride

The unit cell is not always a cube-shape as in Fig. 5.7. In general, the unit cell is defined as follows. A unit cell is a parallelpiped for which the size and shape are defined by the lengths of three axes (a, b and c) and the angles (α, β and γ) between them (see Fig. 5.8). A unit cell will have one of seven basic shapes depending on the values of a, b and c and α, β and γ.
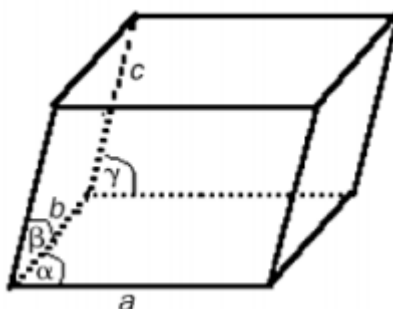

Fig. 5.8 A unit cell

Table 1 Seven crystal systems

Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90° \; \gamma \neq 120°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \; \beta \neq 90°$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$

6. The Bravais lattices

Bravais showed, in 1848, that there were only fourteen types of space lattice possible for the seven crystal systems. These are shown overleaf in Fig. 5.9. The letters P, C, I, F and R stand for primitive (P); face-centred in one of the faces (C); body-centred (I); face-centred (F); and rhombohedral (R).
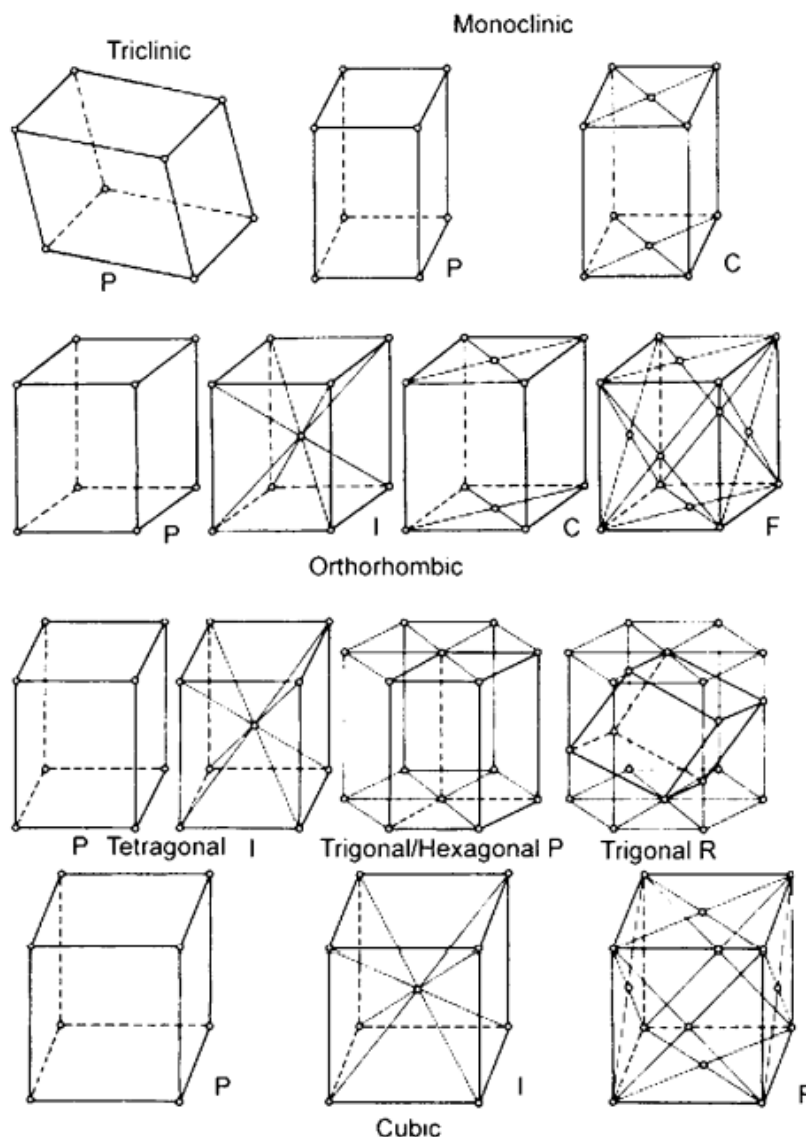
Fig. 5.9 Bravais lattices

7. Finding the number of atoms or ions per unit cell

Some of the atoms or ions in a unit cell may be shared by other unit cells and therefore *do not lie completely* within the unit cell shown. In order to work out how many particles are in a unit cell, use the following rules:

(i)   A particle lying completely within a unit cell belongs to that unit cell only and is counted as 1.

(ii) A particle lying on the face of a unit cell is shared equally by two unit cells and is counted as ½.

(iii) A particle lying on an edge is shared by four unit cells and is counted as ¼.

(iv) A particle lying on a corner is shared by eight unit cells and is therefore counted as 1/8.

The simple cubic unit cell

There is 1 net particle (8 x 1/8) within the unit cell. A unit cell containing one particle is called a *primitive cell*. See Fig. 5.10 overleaf.
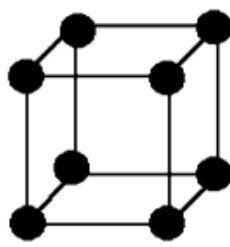
Fig. 5.10 Cubic unit cell

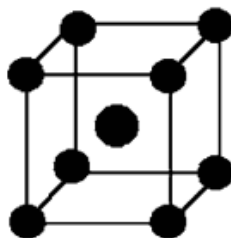## The body-centred cubic unit cell

Fig. 5.11 Body-centred cubic unit cell

EXERCISE 5E

How many particles are within the body-centred cubic unit cell?

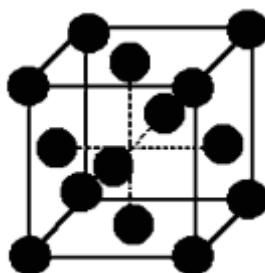## The face-centred cubic unit cell

Fig. 5.12 Face-centred cubic unit cell

EXERCISE 5F

How many particles are there in the face-centred cubic unit cell?

8. Calculation of ionic radii

If we know the edge length of a unit cell and the positions of the ions in it, we can calculate the ionic radii for the ions in the crystal lattice:

EXAMPLE 2

The edge length of a unit cell of LiCl (which has a structure like NaCl – see Fig. 5.7) is 514pm. Assuming anion-anion contact, calculate the ionic radius for the chloride ion.
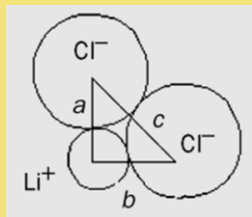
Answer

The LiCl structure contains a right-angled triangle involving two chloride ions and one lithium ion. The lithiom ion is so small that all the ions in the structure touch; *a* is the distance between the centre of a chloride ion and the centre of a lithium ion and is one

EXAMPLE 2   *(continued)*

half of the edge length of the unit cell; b represents the same.

So $a = \frac{514}{2}$ and $b = \frac{514}{2}$.
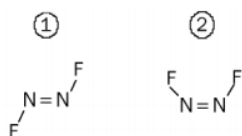
By Pythagoras: $c^2 = a^2 + b^2$

$c = 363$ pm.

Because it is assumed that the anions touch each other, c is twice the radius of one chloride ion.

So $r_{Cl^-} = 182$ pm.

Revision questions

1. There are two molecules with formula N_2F_2:

By considering the electronegativities of the atoms (see Box 4.6 on page 60 of the book) and the shape of the molecules, decide whether each molecule has a dipole. If a dipole is present, what is its direction?

2. By using electronegativity differences, predict which compound would have the higher boiling point: CaF_2 or OF_2?

**3.** What types of forces between molecules would you expect in:
   (i) tetrachloromethane, CCl_4;
   (ii) hydrogen sulphide, H_2S;
   (iii) sulphur, S_8; and
   (iv) methanol, CH_3OH – compare with water, (or HOH!).

4. Arrange the following elements in order of increasing melting point: magnesium, silicon (silicon's physical behaviour is similar to carbon), hydrogen. Explain your order.

5. In a zinc sulphide crystal, zinc ions occupy half of the tetrahedral holes in a close-packed arrangement of sulphide ions. What is the formula of zinc sulphide?

6. (i) Predict the coordination number of Na^+ ($r^+ = 102$ pm) in NaCl. The radius of a chloride ion is 181 pm. **(ii)** The edge length of the unit cell of KCl (NaCl-like structure) is 628 pm. Assuming anion is touching nearest cation, calculate the ionic radius of the potassium ion.

7. The following is a unit cell for potassium chloride:
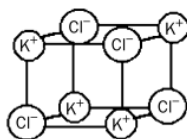
(i) How many ions of each type are there in one cell?
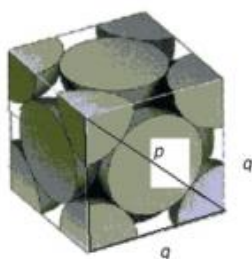(ii) What is the formula of potassium chloride?

Answers

Exercises

Exercise 5A

8

Exercise 5B

Look again at the face-centred cubic unit cell. The nearest neighbours are the atoms touching as follows:

(i) By Pythagoras: $2q^2 = p^2 = (175 \times 4)^2$.
(ii) q = 495 nm = edge length of unit cell.
(iii) Volume of unit cell = $(495 \times 10^{-10})^3 = 1.21 \times 10^{-22} cm^3$. Number of atoms that 'belong' to the unit cell = 8 corners $(8 \times 1/8)$ + 6 faces $(6 \times 1/2)$ = 4. Mass of these atoms = $(4 \times 207)/6.022 \times 10^{23} g = 1.38 \times 10^{-21} g$.
(iv) Density = mass/volume = $(1.38 \times 10^{-21})/(1.21 \times 10^{-22}) cm^3 = 11.4 \ g \ cm^{-3}$.

Exercise 5C

(i) The ratio of octahedral holes to anions in a close-packed structure is 1:1. The ratio of aluminium cations to anions in a close-packed structure is 2/3:1 (or 2:3). The formula is therefore Al_2O_3.

(ii) The ratio of octahedral holes to anions in a close-packed structure is 1:1. The ratio of titanium cations to anions is ½:1 or 1:2. The formula is TiO_2.

Exercise 5D

Radius ratio = 170/181 = 0.939. Coordination number is 8.

Exercise 5E

Number of particles that 'belong to' the cell : 8 corners shared by 8 other unit cells contribute 8 × 1/8 =1 and 1 atom in the middle that is not shared by any other cell. This makes a total of two particles.

Exercise 5F

Number of particles that 'belong to' the cell : 8 corners shared by 8 other unit cells contribute 8 × 1/8 = 1; and 6 faces each shared by two unit cells contribute 6 × ½ = 3. This makes a total of four particles.

Revision questions

1. There is a large electronegativity difference between N and F (1.0) so the N-F bond is polar. The molecule in ①, however, does not have an overall dipole because the symmetry of the molecule ensures that the fluorine atoms pull electron density in opposite directions. There is a dipole in ②:
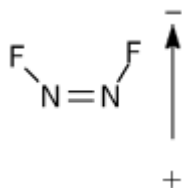
2. CaF_2 – the electronegativity difference between Ca and F is very large (3.0), indicating the substance is ionic; high boiling points are characteristic of ionic compounds because the ions are attracted to each other by strong electrostatic forces. On the other hand, OF_2 is covalent (electronegativity difference of 0.5) and consists of small, discrete molecules attracted to each other by weaker van der Waals' forces – the boiling point is much lower.

3.
   (i)   London dispersion forces only – even though there is a large electronegativity difference between C and Cl the molecule is tetrahedral and the symmetry ensures that it has no overall dipole.
   (ii) London dispersion forces and dipole-dipole interaction. There is an electronegativity difference between H and S, and the molecule is 'bent', like water, so it has an overall dipole.
   (iii) London dispersion forces only.
   (iv) London dispersion forces and hydrogen bonding:
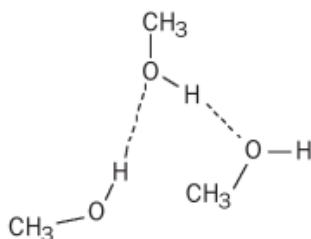
4. Hydrogen (molecules have no dipole, intermolecular forces London dispersion only) < magnesium (metallic bonding) < silicon (giant network solid consisting of Si-Si covalent bonds).

5. The ratio of tetrahedral holes to anions in a close packed arrangement is 2:1, but only half are occupied. Therefore the ratio of cations to anions is 1:1. The formula of zinc sulphide must be ZnS.

6.
   (i)   Radius ration is 102/181 = 0.563. Cations occupy octahedral holes and the coordination number is 6.
   (ii) Edge length of cell = 628 pm.
         This is equal to $2 \times rCl^- + 2 \times rK^+$
         $628 = 2 \times 181 + 2 \times rK^+$
         $rK^+ = 133$ pm.

7. There are four Cl^- corners and four K^+ corners in the unit cell. Each corner is shared by eight other unit cells, which contribute 1/8 of itself to the unit cell.
Total number of Cl^- ions per unit cell = $4 \times 1/8 = \frac{1}{2}$.
Total number of K^+ ions per unit cell = $4 \times 1/8 = \frac{1}{2}$.
This makes a ratio of $\frac{1}{2}:\frac{1}{2}$ or 1:1. The formula for potassium chloride is therefore KCl.