Solid Crystals

There are 4 types of solid crystal:

1. Ionic Crystals
2. Metallic Crystals
3. Molecular Crystals
4. Macromolecular crystals

X-ray diffraction

X-ray diffraction provides information about the arrangement of atoms or ions in a crystal and the distances between them.

X-rays are electromagnetic radiation with wavelength of the same order of magnitude as the distance between atoms/ions in a crystal (approx. $^{-10}$m). For this reason a crystal will produce a diffraction pattern when bombarded with X-rays.

The diffraction pattern is then fed into a computer which calculates the distance between atoms/ions and bond angles.
An electron density map may be plotted. These maps join points of equal electron density by contours and so give a pattern which represents the structure of the substance:

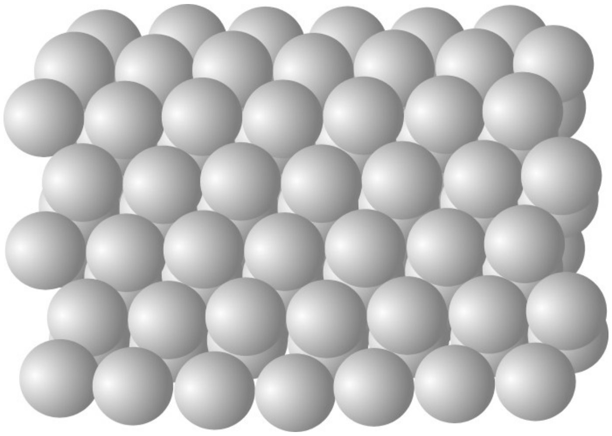
Bond lengths, bond angles and variation in electron density in the substance can be worked out from these maps.

Limitations of X-ray diffraction

a) Atoms of low relative atomic mass are difficult to detect because it is the electrons in the atoms/ions which affect X-rays.
b) Only solids can be analysed in form of crystals or powders.

Metallic Crystals

The metal cations are held in place by a sea of delocalised electrons. The cations are packed as closely as possible.



Typical properties of metals

- High melting points (metallic bonding is a strong type of bonding)
- Malleable
- Conductors of electricity (the delocalised electrons will flow when a potential difference is applied across it)
- Shiny (due to delocalised electrons causing light to be reflected)

Metals are malleable because the positive ions in the lattice are all identical. So the planes of ions can slide easily over one another. The attractive forces in the lattice are the same whichever ions are adjacent.

Metallic Lattices

Some of the simplest crystal structures are those of metals where all particles are identical. There are three major types of metallic lattice. Two of these involve the close packing of particles; the third involves cubic packing of particles :

Almost all metals crystallise in one or more of these systems. The close packed structures account for about 50 metals; cubic packing accounts for about 20 metals.

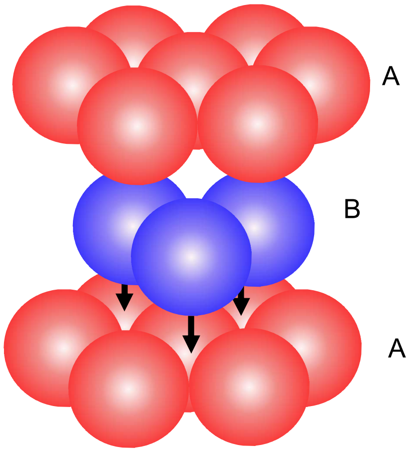
CLOSE PACKING → HEXAGONAL CLOSE PACKING (HCP)
→ CUBIC CLOSE PACKING (CCP)

CUBIC PACKING → BODY CENTRED CUBIC (BCC)

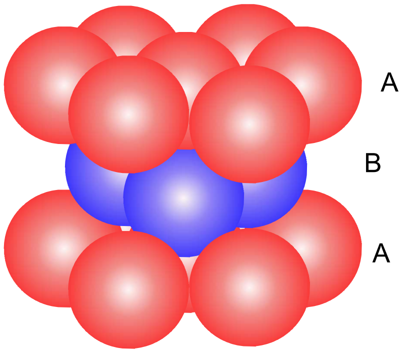
There is no obvious relationship between structural type and position in the periodic table.

In the both close packed arrangements a given sphere has 12 other spheres in contact with it. It is said to have 12 co-ordination or a co-ordination number of 12.

Hexagonal Close Packing (HCP)



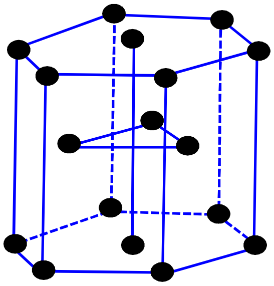
In hexagonal close packing the metal ions are arranged in layers. The second layer (B) sits in the holes above the first layer(A).
The pattern continues ABABAB



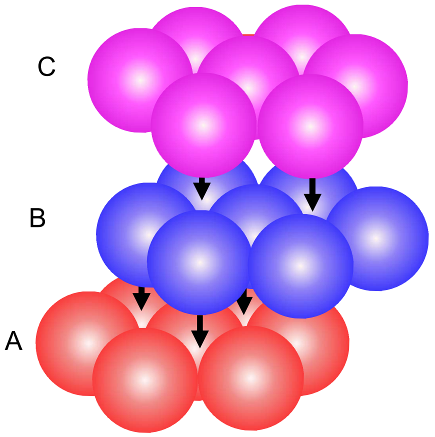
Mg, Zn, Cd all have HCP structures

The **unit-cell representation** is defined as the simplest repeating unit of the lattice which displays the full symmetry of the crystal

This is unit-cell representation for hexagonal close packing

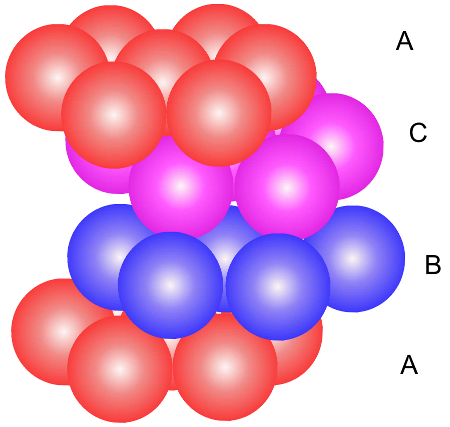


Cubic Close Packing CCP

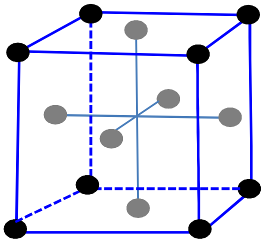


In Cubic Close Packing the layer are arranged differently from hexagonal close packing. The second layer (B) sits in the holes above the first layer(A)in the same way but the third layer does not sit above the first. The third layer is displaced over and is called layer (C).

The pattern continues ABCABCABC

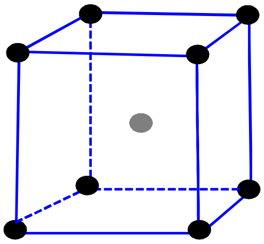


This is unit-cell representation for cubic close packing. This packing is also called face centred cubic packing. You can see there are particles at the centre of each face of the unit cell.



Cu, Ag, Au, Al, Pb all have CCP packing

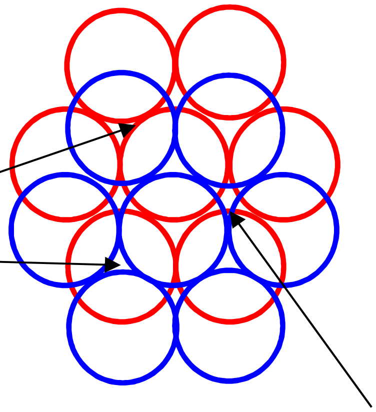
In body centred packing each sphere is in contact with 8 others and is said to have 8 co-ordination or a co-ordination number of 8.



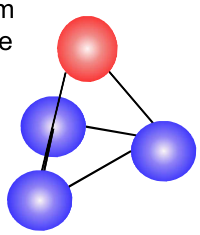
Examples: Group1 metals
many transition metals

Octehedral and Tetrahedral holes

In close cubic arrangements, in both the BCC and HCP arrangements, there are holes between neighbouring atoms/ions. There are two types of holes (or sites): octahedral and tetrahedral



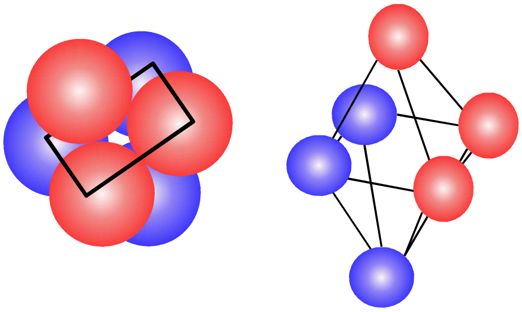
A tetrahedral site exists when 3 atoms from one layer touch each other. The centres of these three atoms, together with the centre of the atom in the next layer which touches all three form the corners of a tetrahedron. At the centre of this tetrahedron is a space known as a tetrahedral site.



A tetrahedral site appears in a lattice at a ratio of **two** per atom.

An octahedral site exists when 3 atoms from one each of two layers in the lattice touch each other.

It is also possible to describe the octahedral site existing because 4 atoms in a layer in the lattice touch each other. The centres of these 4 atoms, together with the centres of the atoms above and below the layer form the corners of an octahedron. (You have to look at an angle to see the layer of 4) At the centre of this octahedron is a space known as an octahedral site.



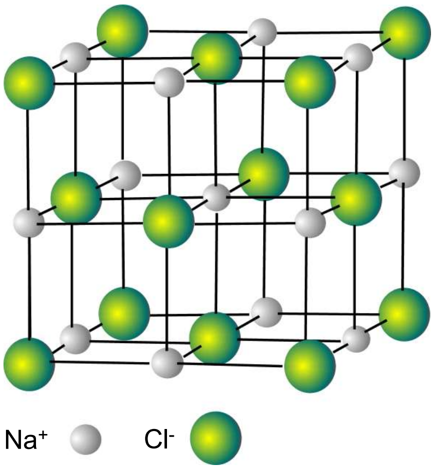
Octahedral sites are larger than tetrahedral sites.

An octahedral site appears in a lattice at a ratio of **one** per atom.

Ionic Crystal Lattices

Ionic lattices are variations of the metal lattice structures. If a close packed metal lattice structure is adopted by one type of ion and some or all the tetrahedral or octahedral sites are occupied by ions of opposite charge, an ionic lattice is formed.

In a sodium chloride lattice, the chloride ions are arranged a cubic close packed (BCC) arrangement and the sodium ions occupy the octahedral sites between the chloride ions.



Coordination no of Na$^+$ = 6
Coordination no of Cl$^-$ = 6
Type of structure =6:6

Ionic bonding is between ions and all their surrounding oppositely charged ions. Each sodium ion in this structure is surrounded and equally attracted by six chloride ions. The ionic bond is the attraction between all these ions

Structure of Ionic Substances

An ionic bond is the electrostatic force of attraction between oppositely charged ions in a lattice.

Electron density maps obtained through X-ray diffraction also give evidence for the existence of ions and also the structure of ionic substances

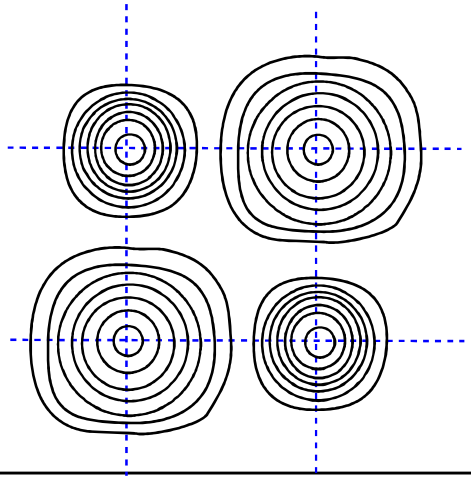
These maps show the likelihood of finding electrons in a region

The contours are lines of equal electron density, with greater electron densities being on contours closer to the nucleus

The maps show that for NaCl

- The ions are arranged in a regular pattern.
- The chloride ions are larger than the sodium ions

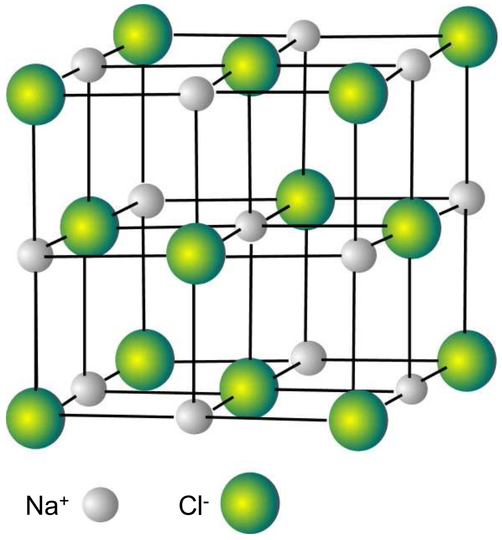
X-ray diffraction: Electron density map of NaCl



The ions are discrete or separate, because the electron density falls to zero between the ions.

The electron density map does not, however, show the edge of the ion and so it is difficult to measure the radius of the ion from an electron density map.

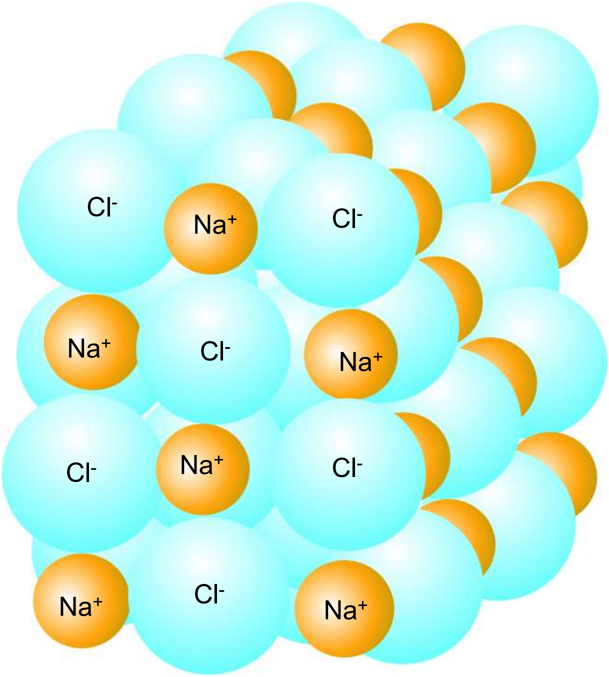
The ions in an ionic solid are arranged in a regular 3D pattern called a giant ionic lattice



The sticks in this diagram are there to help show the arrangements of the ions. They do not represent the ionic bonds.

Ionic bonding is between ions and all their surrounding oppositely charged ions. Each sodium ion in this structure is surrounded and equally attracted by six chloride ions. The ionic bonding is the attraction between all these ions

Space filling model of the ions showing the packing together of ions

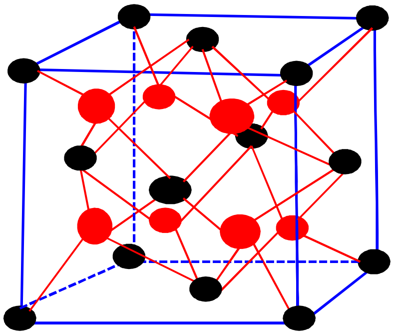


This is a more realistic representation of the arrangement of sodium ions (Na^+) and chloride ions (Cl^-) in the ionic compound sodium chloride.

Not all ionic substances have the same arrangement of ions in their lattices.

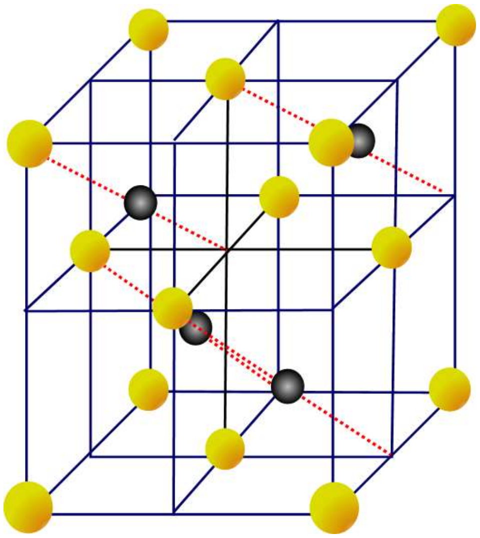
Calcium Fluoride Structure

Calcium ions form a BCC lattice and the fluoride ions occupy tetrahedral sites between the calcium ions.



Coordination no of Ca^{2+} = 8 Coordination no of F^{-} = 4
Type of structure = 8:4

Zinc Blende



Zinc Blende has another arrangement of ions

Sulfide ions form a BCC lattice and the zinc ions occupy half the tetrahedral sites between the sulfide ions. It is a similar structure to the diamond structure.

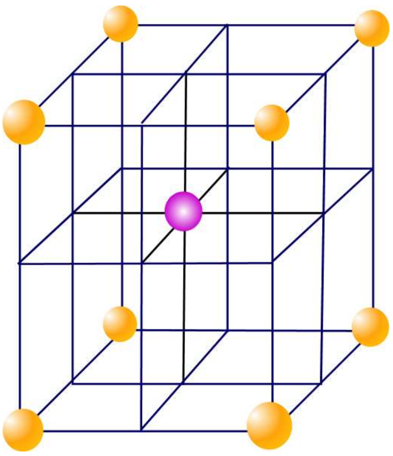
● S^{2-} ● Zn^{2+}

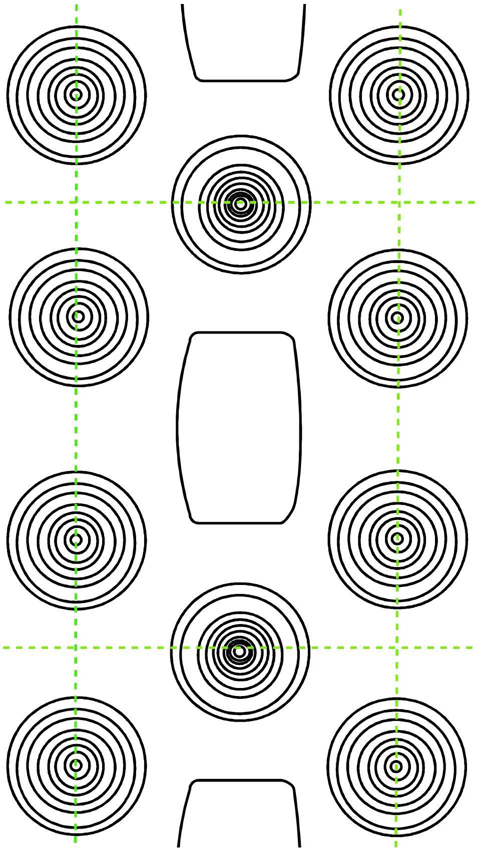
Coordination no of Zn^{2+} = 4
Coordination no of S^{2-} = 4
Type of structure = 4:4

Caesium chloride

The electron density map of caesium chloride shows a different arrangement of the ions

Chloride ions form the corners of a cube. Caesium ions form the corners of another cube. The cubes penetrate each other so that e.g. Cs^{+} ions are at the centres of e.g. Cl^{-} ion cube
Coordination no of Cs^{+} = 8
Coordination no of Cl^{-} = 8
Type of structure = 8:8





Carbon Allotropes

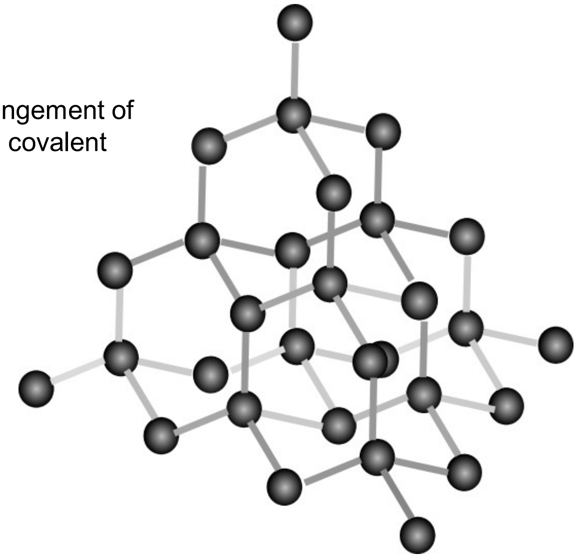
Carbon can form macromolecular compounds because it can form 4 covalent bonds, whereas iodine can only form one bond so only forms simple molecules

Macromolecular: diamond

The covalent bonds that join the atoms are very strong. This makes diamond very hard, with a high melting point.

Diamond cannot conduct electricity because all 4 electrons per carbon atoms are involved in covalent bonds. They are localised and cannot move.

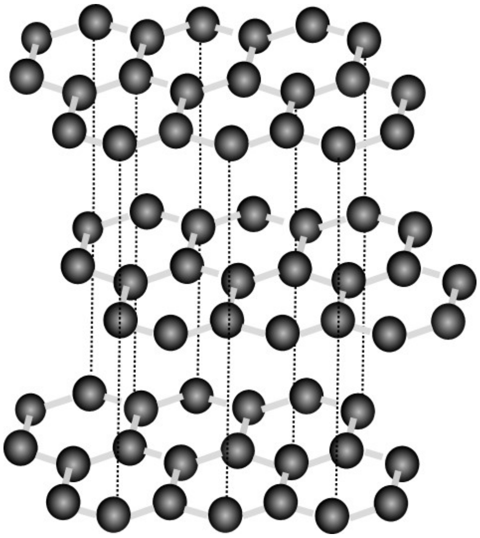
Tetrahedral arrangement of carbon atoms. 4 covalent bonds per atom



Macromolecular: Graphite

Graphite has a planar arrangement of carbon atoms in layers. There are 3 covalent bonds per atom in each layer. The 4th outer shell electron per atom is delocalised.

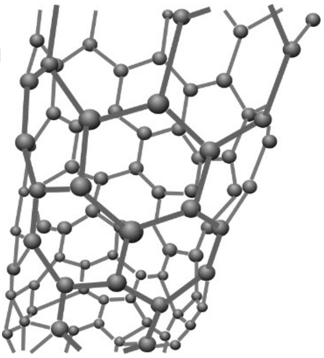
The layers have weak intermolecular forces between them. This means that the layers can easily slide over each other. Graphite therefore has a lubricating action (and is soft).

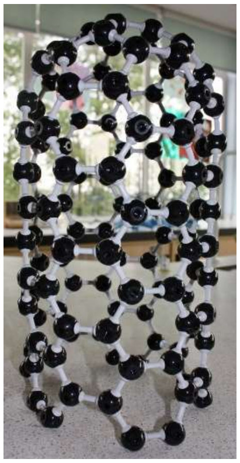


Graphite can conduct electricity well along the layers because one electron per carbon is free and delocalised, so electrons can move easily along layers.
It does not conduct electricity from one layer to the next because the energy gap between the layers is too large for easy electron transfer.

Both these macromolecular structures have very high melting points because of strong covalent forces in the giant structure. It takes a lot of energy to break the **many strong** covalent bonds.

Carbon nanotubes





These have very high tensile strength because of the strong structure of many strong covalent bonds.

Nanotubes can conduct electricity well along the tube because one electron per carbon is free and delocalised, so electrons can move easily along the tube.

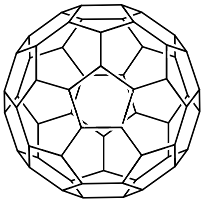
Nanotubes have potentially many uses. One being the potential to us as vehicles to deliver drugs to cells.

Graphene

Graphene is a new substance that is a one layer of graphite i.e. 3 covalent bonds per atom and the 4th outer electron per atom is delocalised.
Graphene has a very high tensile strength because of the strong structure of many strong covalent bonds.
Graphene can conduct electricity well along the structure because one electron per carbon is free and delocalised, so electrons can move easily along the structure.

Buckminsterfullerene

There are delocalized electrons in buckminsterfullerene, which is a molecule of C_{60} .



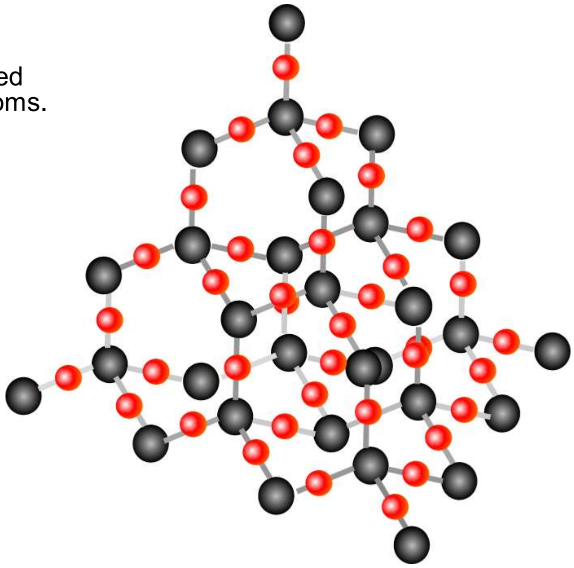
Macromolecular: Silicon dioxide

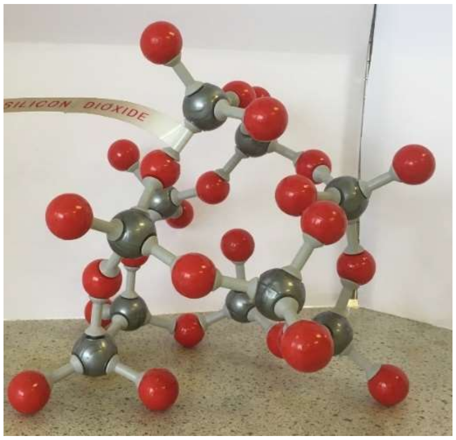
Silicon dioxide has a high melting point. The very strong silicon-oxygen covalent bonds have to be broken throughout the structure before melting occurs.

It is hard. This is due to the very strong covalent bonds.

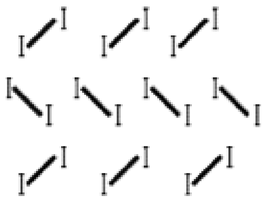
It does not conduct electricity. There are not any delocalised electrons. All the electrons are held tightly between the atoms.

It is insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and the silicon or oxygen atoms which could overcome the covalent bonds in the giant structure.



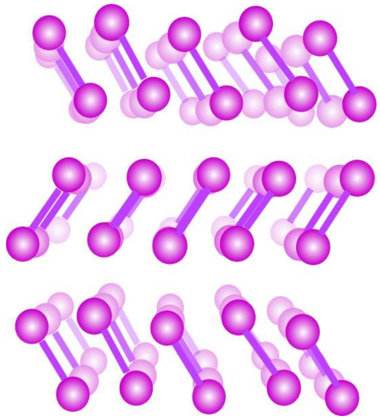


Molecular: Iodine



The crystals contain a regular arrangement of I_2 molecules held together by weak van der waals intermolecular forces

There are covalent bonds between the iodine atoms in the I_2 molecule



Properties of molecular crystals

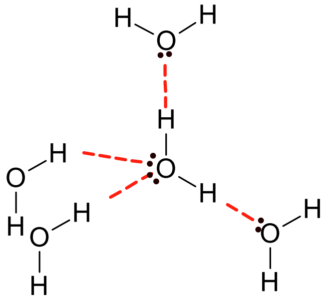
Low melting and boiling points because the van der waals forces between the molecules are weak.

Non conductor of electricity in any state because no charged particles are present.

Low solubility in water because iodine cannot form strong forces (hydrogen bonds) with water.

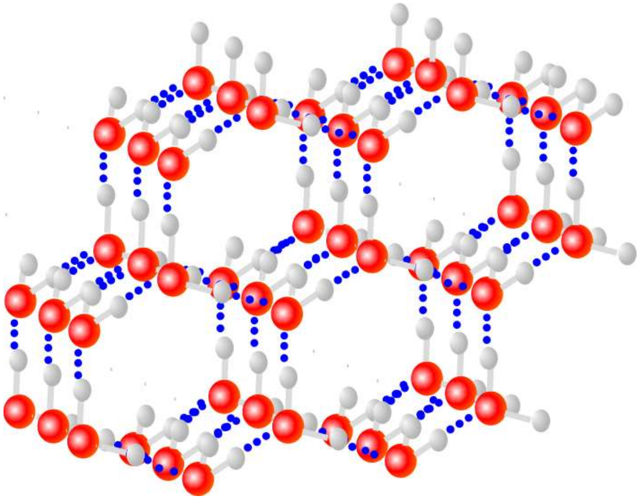
Molecular: Ice

In ice the hydrogen bonds hold the water molecules together in a regular structure



This is a difficult diagram to draw.

The main point to show is a central water molecule with two ordinary covalent bonds and two hydrogen bonds in a tetrahedral arrangement



The molecules are held further apart than in liquid water and this explains the lower density of ice