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# Solids

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## 5.1 Covalent network structures

- Covalent network structures are infinite structures in which the atoms are linked by covalent bonds.
- Different structural forms of the same *element* are known as allotropes. Graphite, diamond, and buckminsterfullerene ( $C_{60}$ ) are three allotropes of carbon.
- Different structural forms of the same *compound* are known as polymorphs. Quartz and  $\beta$ -cristobalite are two polymorphs of  $SiO_2$ .
- Each different structural form of an element or compound is a different phase. The conversion of one phase to another is called a phase transition.

## 5.2 Structures based on the packing of spheres

- The most efficient manner in which atoms can pack is called close packing. There are two important types of close packing. Cubic close packing (ccp) has a layer repeat ABCABC... and hexagonal close packing (hcp) has a layer repeat of ABABAB....
- A unit cell is the smallest possible repeating unit for a structure.
- The cubic close-packed structure is also known as face-centred cubic (fcc).
- Close-packed structures contain octahedral and tetrahedral interstitial sites.
- Body-centred cubic (bcc) and primitive cubic structures can also be formed, but they have lower packing efficiencies.
- Packing efficiencies for structures can be calculated by dividing the volume of the atoms in a unit cell by the total volume of the unit cell. The value is usually quoted as a percentage.

### 5.3 Metallic bonding

- The bonding in metals and their conductivity can be explained using band theory, which is derived from molecular orbital theory.
- Alloys are materials containing a mixture of two or more metals, or a metal and a non-metal.
- Substitutional alloys, such as brass, have structures in which the atoms of one element are substituted by those of another.
- Interstitial alloys, such as the austenite phase of steel, have structures in which one element lies in the interstitial sites of another.

### 5.4 Structures of compounds

- Crystal structures can be determined by X-ray crystallography.
- The structures of many binary compounds can be described using a close-packed lattice of one atom or ion, with the other type occupying the octahedral or tetrahedral interstitial sites.
- The NaCl structure has a cubic close-packed array of chloride ions with the Na<sup>+</sup> ions occupying the octahedral sites.
- Structures can also be based on non-close-packed lattices. An example of this is the structure of CsCl, which consists of a primitive cubic lattice of Cl<sup>-</sup> ions with Cs<sup>+</sup> ions in the cubic sites.

### 5.5 The ionic model

- Coordination numbers and structures of ionic compounds can be predicted using the radius ratio rule, though this is not always reliable as it assumes the ionic radii cannot vary.
- Hess's law enables enthalpy changes to be determined by using Born–Haber cycles.
- The lattice enthalpy for the compound A<sub>x</sub>B<sub>y</sub> is the enthalpy change for the process
$$A_xB_y (s) \rightarrow x A^{y+} (g) + y B^{x+} (g)$$
- In a Born–Haber cycle, the enthalpy change with the largest magnitude is usually the lattice enthalpy.

## 5.6 Calculating lattice energy

- Lattice energies can be calculated using the Born–Landé equation.
- Compounds containing polarizable anions and polarizing cations have high covalent character.
- Compounds with a large degree of covalent character have higher lattice energies than anticipated from the Born–Landé equation.
- In the absence of full information, good estimates of lattice energies can be made using the Kapustinskii equation.

## 5.7 Predicting bond types

- The type of bonding present in a binary compound can be predicted by considering the electronegativities of the elements involved.
- This can be shown on a bond-type triangle, which plots the average electronegativity of the elements against the difference in electronegativity.

## Learning outcomes

By the end of this chapter you should be able to do the following.

- Use the terms allotrope, polymorph, and unit cell, giving examples of each.
- Understand the differences between cubic close packing (ccp) and hexagonal close packing (hcp).
- Draw unit cells and cell projection diagrams for ccp, hcp, body-centred cubic (bcc), and primitive cubic structures.
- Calculate packing efficiencies.
- Calculate the density of a substance and its empirical formula from a knowledge of its unit cell.
- Describe the bonding in metals using the free electron model and band theory.
- Describe the structures of binary compounds based on the packing of one type of ion or atom with the other type occupying interstitial sites.
- Predict the limiting radii for different geometries.

- Use the radius ratio rule to predict the structures of ionic compounds.
- Calculate lattice enthalpies using Born–Haber cycles.
- Understand how the Madelung constant can be calculated.
- Calculate lattice energies using the Born–Landé equation and the Kapustinskii equation.
- Predict the type of bonding in a compound from the electronegativities of the atoms.