# Chapter 6

## Structures and energetics of metallic and ionic solids

<table>
<thead>
<tr>
<th>Packing of spheres and applications of the model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymorphism</td>
</tr>
<tr>
<td>Alloys and intermetallic compounds</td>
</tr>
<tr>
<td>Band Theory</td>
</tr>
<tr>
<td>Semiconductors</td>
</tr>
<tr>
<td>Ionic lattices and lattice energy, Born-Haber cycle</td>
</tr>
<tr>
<td>Defects</td>
</tr>
</tbody>
</table>

## Solids

Chemistry is traditionally described as the study of molecules.

- Except for helium, all substances form a solid if sufficiently cooled.
- Solid State Chemistry, a sub discipline of Chemistry, primarily involves the study of extended solids.
  - The vast majority of solids form one or more crystalline phases – where the atoms, molecules, or ions form a regular repeating array (unit cell).
  - The primary focus will be on the structures of metals, ionic solids, and extended covalent structures, where extended bonding arrangements dominate.
  - The properties of solids are related to its structure and bonding.
  - In order to modify the properties of a solid, we need to know the structure of the material.
  - Crystal structures are usually determined by a technique of X-ray crystallography.
  - Structures of many inorganic compounds may be initially described in terms of simple packing of spheres.
Close-Packing

Square array of spheres. Close-packed array of spheres.

Considering the packing of spheres in only 2-dimensions, how efficiently do the spheres pack for the square array compared to the close packed array?

Fig. 6.1 Part of one layer of a close packed arrangement of equal sized spheres. It contains hexagonal motifs.

**Fig. 5.2**  
(a) One layer (layer A) of close-packed spheres contains hollows that exhibit a regular pattern. (b) A second layer (layer B) of close-packed spheres can be formed by occupying every other hollow in layer A. In layer B, there are two types of hollow; one lies over a sphere in layer A, and three lie over hollows in layer A. By stacking spheres over these different types of hollow, two different third layers of spheres can be produced. The blue spheres in diagram (c) form a new layer C; this gives an ABC sequence of layers. Diagram (d) shows that the second possible third layer replicates layer A; this gives an ABA sequence.
hexagonal close packed (hcp)
ABABAB
Space Group:
P6\textsubscript{3}/mmc

cubic close packed (ccp)
ABCABC
Space Group:
Fm\overline{3}m
Face centered cubic (fcc) has cubic symmetry.

A unit cell is the smallest repeating unit in a solid state lattice.

Atom is in contact with three atoms above in layer A, six around it in layer C, and three atoms in layer B.

A ccp structure has a fcc unit cell.
Fig. 6.4  Unit cells of (a) a cubic close-packed (face-centred cubic) lattice and (b) a hexagonal close-packed lattice.

Fig. 6.5  Two layers of close-packed atoms shown (a) with the spheres touching, and (b) with the sizes of the spheres reduced so that connectivity lines are visible. In (b), the tetrahedral and octahedral holes are indicated.
Holes in CCP and HCP lattices are either tetrahedral or octahedral.

**Tetrahedral hole**

**Octahedral hole**

Fig. 5.6 Unit cells of (a) a simple cubic lattice and (b) a body-centred cubic lattice.
Body Centered Cubic (bcc)

The fraction of space occupied by spheres is 0.68

Coordination Number = 8

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting point / K</th>
<th>$\Delta_{\text{mp}} H / \text{kJ mol}^{-1}$</th>
<th>Boiling point / K</th>
<th>$\Delta_{\text{bp}} H / \text{kJ mol}^{-1}$</th>
<th>van der Waals radius ($r_v$) / pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>1</td>
<td>-</td>
<td>4.2</td>
<td>0.08</td>
<td>99</td>
</tr>
<tr>
<td>Neon</td>
<td>24.5</td>
<td>0.34</td>
<td>27</td>
<td>1.71</td>
<td>160</td>
</tr>
<tr>
<td>Argon</td>
<td>84</td>
<td>1.12</td>
<td>87</td>
<td>6.43</td>
<td>191</td>
</tr>
<tr>
<td>Krypton</td>
<td>116</td>
<td>1.37</td>
<td>120</td>
<td>9.08</td>
<td>197</td>
</tr>
<tr>
<td>Xenon</td>
<td>161</td>
<td>1.81</td>
<td>165</td>
<td>12.62</td>
<td>214</td>
</tr>
<tr>
<td>Radon</td>
<td>202</td>
<td>-</td>
<td>211</td>
<td>18</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Helium cannot be solidified under atmospheric pressure, the pressure condition for which all other phase changes in the table are considered.

Table 6.1 Selected physical data for group 18 elements.
The majority of the elements crystallize in hcp, bcc, or ccp (fcc). Polonium adopts a simple cubic structure.

Other sequences include ABAC (La, Pr, Nd, Am), and ABACACBCB (Sm). Actinides are more complex.
Fig. 6.7 A pressure–temperature phase diagram for iron
Fig. 5.8  In a substitutional alloy, some of the atom sites in the host lattice (shown in grey) are occupied by solute atoms (shown in red).

Calculate radius ratio for trigonal hole

\[
\cos(30°) = \frac{r^+}{r^+ + r^-} = \frac{\sqrt{3}}{2}
\]

\[
\frac{r^+}{r^-} = 0.155
\]

Relatively uncommon coordination environment.

Calculate the radius ratio for tetrahedral, octahedral, and cubic...
For example, consider the ionic compound NaCl.

The ionic radius of Na\(^+\) is 1.16\(\text{Å}\) and Cl\(^-\) is 1.67\(\text{Å}\).

The radius ratio is 1.16/1.67\(\text{Å}\) = 0.695, therefore falls in the range 0.414 to 0.732 so the Na\(^+\) is expected to occupy an octahedral hole.

The Cl\(^-\) is expected to form an A-type lattice – it has a ccp type.

-the sodium cations occupy the octahedral holes in that lattice.

<table>
<thead>
<tr>
<th>Type of hole</th>
<th>r^+/r^-</th>
<th>Max. C.N. possible</th>
<th>Cation r_+ / pm</th>
<th>Anion r_- / pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal</td>
<td>0.155</td>
<td>3</td>
<td>Li(^+) 76</td>
<td>F(^-) 133</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>0.225</td>
<td>4</td>
<td>Na(^+) 102</td>
<td>Cl(^-) 181</td>
</tr>
<tr>
<td>Octahedral</td>
<td>0.414</td>
<td>6</td>
<td>K(^+) 138</td>
<td>Br(^-) 196</td>
</tr>
<tr>
<td>Cubic</td>
<td>0.732</td>
<td>8</td>
<td>Rb(^+) 149</td>
<td>I(^-) 220</td>
</tr>
</tbody>
</table>
Radius Ratios

What are the relative sizes and coordination numbers of the cubic, octahedral, and tetrahedral holes?

<table>
<thead>
<tr>
<th>Size of hole</th>
<th>cubic</th>
<th>octahedral</th>
<th>tetrahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coord. no.</td>
<td>8</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

If a cation were to occupy one of these holes, it would have the coordination number indicated.

-the coordination number is proportional to the size of the hole.

Alloy

Intermetallic compound
An electrical conductor offers a low resistance (ohms) to the flow of electrical current (amperes).

Resistance (in $\Omega$) = \( \frac{\text{resistivity (in } \Omega \text{m}) \times \text{length of wire (in m)}}{\text{cross-sectional area of wire}} \)

**Fig. 6.9** A metal is characterized by the fact that its electrical resistivity increases as the temperature increases, i.e. its electrical conductivity decreases as the temperature increases.

A semiconductor, such as germanium, is characterized by the fact that its electrical resistivity decreases as the temperature increases. Its electrical conductivity increases as the temperature increases.
A **band** is a group of MOs, the energy differences between which are so small that the system behaves as if a continuous, non-quantized variation of energy within the band is possible.

**Fig. 6.11** The interaction of two 2s atomic orbitals in Li₂ leads to the formation of two MOs. With three Li atoms, three MOs are formed, and so on. For Liₙ, there are n molecular orbitals, but because the 2s atomic orbitals are all of the same energy, the energies of the MOs are very close together and constitute a band of orbitals.

Lattice at low temperature

As the temperature rises, the atoms vibrate, acting as though they are larger.

Lattice at high temperature
A **band gap** occurs when there is a significant energy difference between the bands.

\[1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}\]

The **Fermi level** is the energy level of the highest occupied orbital in the metal at absolute zero.

Conductivity of **intrinsic semiconductors** (e.g. Si or Ge) *increases* with temperature.

- Conduction can only occur if electrons are promoted to a higher s/p band known as the **conduction band**, because only then will there be a partially full band.

- The current in semiconductors will depend on \(n\), which is the number of electrons free to transport charge.

- The number of electrons able to transport charge is given by the number of \(e^-\) promoted to the conduction band plus the number of \(e^-\) in the valence band that were freed to move.
Extrinsic semiconductors

Deliberate introduction of a very low concentration of certain impurities alters the properties in a beneficial way.

- These semiconductors are known as doped or extrinsic semiconductors.
  - Consider introduction of boron (B) to Si. For every B, there is an electron missing from the valence band and this enables electrons near the top of the band to conduct better than pure Si.
  - A semiconductor doped with fewer valence electrons than the bulk is known as a p-type semiconductor.
  - Consider introduction of phosphorous (P) to Si. For every P, there is an extra electron and this forms energy levels that lie in the band gap between the valence and conduction band. Electrons are therefore close to the bottom of the conduction band and are easily promoted, enabling better conduction than pure Si.
  - A semiconductor doped with more valence electrons than the bulk is known as an n-type semiconductor. The n stands for negative charge carriers or electrons.

![p-type and n-type semiconductors](image)

**Fig. 8.13** (a) In a p-type semiconductor (e.g. Ga-doped Si), electrical conductivity arises from thermal population of an acceptor level which leaves vacancies (positive holes) in the lower band. (b) In an n-type semiconductor (e.g. As-doped Si), a donor level is close in energy to the conduction band.
How does one determine when one atom ends and another ends?
- easy for the same atom, ½ of the distance between the atoms.
- what about Na⁺-Cl⁻ (for example)?

High Resolution X-ray diffraction contour map of electron density.
- the minimum of electron density along the interionic distances enables accurate determination of the values of the radius for the cation and anion.

The effective ionic radii vary depending on coordination number.
Fig. 6.14 Trends in ionic radii $r_{\text{ion}}$ within the metal ions of groups 1 and 2, the anions of group 17 and metal ions from the first row of the $d$-block.
Trends in sizes of ions

1. The radii of ions within a group increase with atomic number Z. More electrons are present and the outer electrons are further away from the nucleus.

2. In a series of isoelectronic cations (e.g. Na⁺, Mg²⁺, Al³⁺) the radius decreases with increasing positive charge.

3. In a series of isoelectronic anions (e.g. F⁻, O²⁻) the radius increases with increasing negative charge.

4. For elements with more than one oxidation state (e.g. Ru⁴⁺, Ru⁵⁺), the radii decrease as the oxidation state increases.

5. As you move from left to right across a row of the periodic table, there is an overall decrease in radius for an similar ions with the same charge. See also the lanthanide contraction.

6. The spin state (high or low spin) affects the ionic radius of transition metals.

7. The radii increase with an increase in coordination number.

These trends in the sizes of ions may be explained by consideration of the shielding and effective nuclear charge. \( Z_{\text{eff}} = Z - S \) (See Gen. Chemistry)

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X-ray diffraction

X-rays were discovered by Wilhelm Rontgen, a German physicist in 1895. To generate x-rays, three things are needed.
• a source of electrons
• a means of accelerating the electrons at high speeds
• a target material to receive the impact of the electrons and interact with them.

Typical cathode element is W.
Potential difference is 20-50 kV.
Anode must be water cooled.

Frequency depends on the anode metal, often Cu, Mo, Co.

Lines occur because bombarding electrons knock out e⁻ from K shell \((n = 1)\), which are filled by electrons in higher shells. Electrons falling from L shell \((n = 2)\) give rise to \(K\) lines, whereas e⁻ from M shell \((n = 3)\) give the \(K\alpha\) lines. \((K\alpha_1\) and \(K\alpha_2\) doublets, etc.)
Diffraction of X-rays

Max von Laue used a crystal of copper sulfate as the diffraction grating (Nobel Prize 1914).

Crystalline solids consist of regular arrays of atoms, ion, or molecules with interatomic spacing on the order of 100 pm or 1 Å.

- The wavelength of the incident light has to be on the same order as the spacing of the atoms.
- W.H. and W.L. Bragg determined crystal structures of NaCl, KCl, ZnS, CaF₂, CaCO₃, C (diamond).
- Reflection of X-rays only occurs when the conditions for constructive interference are fulfilled.

\[
\text{Difference in path length} = BC + CD = d_{hkl} \sin \theta_{hkl}
\]

Difference in path length = 2d_{hkl}\sin \theta_{hkl}

Must be an integral number of wavelengths, \( n\lambda = 2d_{hkl}\sin \theta_{hkl} \) 

\( n = 1, 2, 3, \ldots \)

\[
\lambda = 2d_{hkl}\sin \theta
\]

Bragg Equation

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Box 6.6 Determination of structure: X-ray diffraction.
**NaCl structure type**

Fig. 6.15 Two representations of the unit cell of NaCl: (a) shows a space-filling representation and (b) shows a ‘ball-and-stick’ representation which reveals the coordination environments of the ions. The Cl\(^-\) ions are shown in green and the Na\(^+\) ions in purple; since both types of ion are in equivalent environments, a unit cell with Na\(^+\) ions in the corner sites is also valid. There are four types of site in the unit cell: central (not labelled), face, edge and corner positions.

**CsCl structure type**

Fig. 6.16 (a) The unit cell of CsCl: Cs\(^+\) ions are shown in yellow and Cl\(^-\) in green, but the unit cell could also be drawn with the Cs\(^+\) ion in the central site. The unit cell is defined by the yellow lines. (b) One way to describe the CsCl structure is in terms of interpenetrating cubic units of Cs\(^+\) and Cl\(^-\) ions.
Fig. 6.17 The \([\text{NH}_4]^+\) ion can be treated as a sphere in descriptions of solid-state lattices; some other ions (e.g. \([\text{BF}_4]^-\), \([\text{PF}_6]^-\)) can be treated similarly.

CaF\(_2\) - fluorite structure type

Fig. 6.18 (a) The unit cell of CaF\(_2\); the Ca\(^{2+}\) ions are shown in red and the F\(^-\) ions in green. (b) The unit cell of zinc blende (ZnS): the zinc centres are shown in grey and the sulfur centres in yellow. Both sites are equivalent and the unit cell could be drawn with the S\(^{2-}\) ions in the grey sites.
**diamond**  
β-cristobalite (SiO₂)

![Diamond and β-cristobalite structures](image)

**Fig. 6.19**  
(a) A typical representation of the diamond structure. (b) Recreation of the network shown in (a) provides a representation that can be compared with the unit cell of zinc blende (Figure 6.18b). The atom labels correspond to those in diagram (a). This structure type is also adopted by Si, Ge and α-Sn. (c) The unit cell of β-cristobalite, SiO₂, colour code: Si, purple; O, red.

wurtzite (ZnS)

![Wurtzite structure](image)

**Fig. 6.20**  
Three unit cells of wurtzite (a second polymorph of ZnS) define a hexagonal prism, the Zn²⁺ ions are shown in grey and the S²⁻ ions in yellow. Both ions are tetrahedrally shed and an alternative unit cell could be drawn by interchanging the ion positions.
rutile (TiO$_2$)

Fig. 8.21 The unit cell of rutile (one polymorph of TiO$_2$); the titanium centres are shown in grey and the oxygen centres in red.

CdI$_2$ and CdCl$_2$ – layer structures

Fig. 8.22 Parts of two layers of the CdI$_2$ lattice; Cd$^{2+}$ ions are shown in pale grey and I$^-$ ions in gold. The I$^-$ ions are arranged in an hcp array.
Perovskite (CaTiO$_3$) structure type

By accounting for three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics of the enthalpy of formation of an ionic solid.
**Lattice Energy**

$\Delta U(0K)$, The change in internal energy that accompanies the formation of one mole of a solid ionic compound from its gaseous ions at 0 K.

**Coulomb’s Law**

(ion pair $M^+$, $X^-$)

$$E = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$\Delta U = \left(\frac{|Z_+| |Z_-| e^2}{4\pi\varepsilon_0 r}\right)$

$e$ is the electronic charge, $1.6\times10^{-19}$ C

$\varepsilon_0$ is the permittivity of vacuum, $8.854\times10^{-12}$ F m$^{-1}$

The energy due to the coulombic interactions in a crystal is calculated for a particular structure by summing all the ion-pair interactions, thus producing an infinite series.

---

**NaCl**

From a Na$^+$,
- Six Cl$^-$ a distance of $r_0$
- Twelve Na$^+$ at a distance of $\sqrt{2}r_0$
- Eight Cl$^-$ at a distance of $\sqrt{3}r_0$
- Six Cl$^-$ a distance of $2r_0$

$$E_c = -\frac{e^2}{4\pi\varepsilon_0 r}(6 \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{2}} + \frac{24}{\sqrt{5}})$$

or

$$E_c = -\frac{e^2}{4\pi\varepsilon_0 r}\left(\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}}\right)$$
The term (series) inside the brackets is known as the Madelung constant, $A$. For one mole of NaCl, the energy due to the coulombic interactions is:

$$E_C = -\frac{N_A Ae^2}{4\pi\varepsilon_0 r}$$

$N_A$ = Avogadro’s number

Madelung constants have been computed for many of the simple ionic structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Madelung Constant, $A$</th>
<th>Number of ions in formula unit, $\nu$</th>
<th>$A/\nu$</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cesium chloride, CsCl</td>
<td>1.763</td>
<td>2</td>
<td>0.882</td>
<td>8:8</td>
</tr>
<tr>
<td>Sodium chloride, NaCl</td>
<td>1.748</td>
<td>2</td>
<td>0.874</td>
<td>6:6</td>
</tr>
<tr>
<td>Fluorite, CaF$_2$</td>
<td>2.519</td>
<td>3</td>
<td>0.840</td>
<td>8:4</td>
</tr>
<tr>
<td>Zinc Blende, ZnS</td>
<td>1.638</td>
<td>2</td>
<td>0.819</td>
<td>4:4</td>
</tr>
<tr>
<td>Wurtzite, ZnS</td>
<td>1.641</td>
<td>2</td>
<td>0.821</td>
<td>4:4</td>
</tr>
<tr>
<td>Corundum, Al$_2$O$_3$</td>
<td>4.172</td>
<td>5</td>
<td>0.835</td>
<td>6:4</td>
</tr>
<tr>
<td>Rutile, TiO$_2$</td>
<td>2.408</td>
<td>3</td>
<td>0.803</td>
<td>6:3</td>
</tr>
</tbody>
</table>

**Born exponent**

Ions are not point charges, but consist of positively charged nuclei surrounded by electron clouds.

- repulsion needs to be taken into account at small distances

repulsion can be expressed by:

$$E_R = \frac{B}{r^n}$$

where $B$ is a constant and $n$ (the Born exponent) is large and also a constant.

$$L = E_C + E_R = -\frac{N_A AZ e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$$

**Derivation elsewhere**

$$L = -\frac{N_A AZ e^2}{4\pi\varepsilon_0 r} \left(1 - \frac{1}{n}\right)$$

**Born-Landé Equation**

$$L = -\frac{1.389\times10^7 AZ e^2}{r_0} \left(1 - \frac{1}{n}\right)$$

Calculate average ($n$), e.g. RbCl is 9.5 (Average of 9 and 10)

$r_0$ in pm, units of $L$ are kJ/mol
Notice the large dependence on the charge of the ions:

\[ L = -\frac{1.389 \times 10^5 AZZ_n}{r_0} \left( 1 - \frac{1}{n} \right) \]

Multiply charged ions tend to have larger lattice energies.

It was noted by A.F. Kapustinskii that the Madelung constant divided by the number of ions in one formula unit of the structure \((A/\nu)\) was almost constant (0.88 to 0.80).

- A general equation can be developed to set up a general lattice energy equation and use the resulting equation to calculate the lattice energy of an unknown structure.

\[ L(kJ/mol) = -\frac{1.214 \times 10^5 vZZ_n}{r_+ + r_-(in\_pm)} \left( 1 - \frac{1}{n} \right) \quad \text{Kapustinskii equations} \]

Considering all of the approximations, there is good agreement with values obtained using a Born-Haber cycle, except with large polarizable ions.

It is not possible to measure lattice energy directly. Typically a thermochemical cycle is involved, but not all of the data (electron affinities, etc.) is necessarily available. Estimations are useful.

- Neil Bartlett used a similar approach to prepare XePtF₆.

<table>
<thead>
<tr>
<th>Electronic configuration of the ions in an ionic compound MX</th>
<th>Examples of ions</th>
<th>(n) (no units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[He][He]</td>
<td>H⁺, Li⁺</td>
<td>5</td>
</tr>
<tr>
<td>[Ne][Ne]</td>
<td>F⁻, O²⁻, Na⁺, Mg²⁺</td>
<td>7</td>
</tr>
<tr>
<td>[Ar][Ar] or [3d⁰][Ar]</td>
<td>Cl⁻, S²⁻, K⁺, Ca²⁺, Cu⁺</td>
<td>9</td>
</tr>
<tr>
<td>[Kr][Kr] or [4d⁰][Kr]</td>
<td>Br⁻, Rb⁺, Br²⁻, Ag⁺</td>
<td>10</td>
</tr>
<tr>
<td>[Xe][Xe] or [5d⁰][Xe]</td>
<td>I⁻, Cs⁺, Ba²⁺, Au⁺</td>
<td>12</td>
</tr>
</tbody>
</table>

**Table 6.3** Values of the Born exponent, \(n\), given for an ionic compound MX in terms of the electronic configuration of the ions \([M⁺][X⁻]\). The value of \(n\) for an ionic compound is determined by averaging the component values, e.g., for MgO, \(n = \frac{5 + 9}{2} = 7\); for LiCl, \(n = \frac{5 - 9}{2} = 7\).
**Fig. 6.25** The trend in the values of the first ionization energies of the noble gases (group 18).

**Schottky defect**

**Fig. 6.26** (a) Part of one face of an ideal NaCl structure, compare this with Figure 6.15. (b) A Schottky defect involves vacant cation and anion sites; equal numbers of cations and anions must be absent to maintain electrical neutrality. Colour code: Na, purple; Cl, green.
Silver bromide adopts an NaCl structure. (a) An ideal lattice can be described in terms of Ag⁺ ions occupying octahedral holes in a cubic close-packed array of bromide ions. (b) A Frenkel defect in AgBr involves the migration of Ag⁺ ions into tetrahedral holes; in the diagram, one Ag⁺ ion occupies a tetrahedral hole which was originally vacant in (a), leaving the central octahedral hole empty. Colour code: Ag, pale grey; Br, gold.