Bonding in Solids

There are four types of solid:

1. **Molecular** (formed from molecules) - usually soft with low melting points and poor conductivity.
2. **Covalent network** - very hard with very high melting points and poor conductivity.
3. **Ionic** (formed from ions) - hard, brittle, high melting points and poor conductivity.
4. **Metallic** (formed from metal atoms) - soft or hard, high melting points, good conductivity, malleable and ductile.

- NB: A solid with only one type of atom is also called ‘atomic’

---

Bonding in Solids

Covalent Network Solids

- Atoms held together in large networks.
- Examples: diamond, graphite, quartz (SiO₂), silicon carbide (SiC), and boron nitride (BN).
- In diamond:
  - each C atom has a coordination number of 4;
  - each C atom is tetrahedral;
  - there is a three-dimensional array of atoms.
  - Diamond is hard, and has a high melting point (3550 °C).

---

Bonding in Solids

Types of Crystalline Solids

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Form of Unit Particles</th>
<th>Forces Between Particles</th>
<th>Properties</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>Atoms or molecules</td>
<td>London dispersion, dipole-dipole, London dispersion, hydrogen bonds</td>
<td>Fairly soft, low to moderately high melting point, poor thermal and electrical conductivity</td>
<td>Argon, Ar; methane, CH₄; ammonia, NH₃; dry ice, CO₂</td>
</tr>
<tr>
<td>Covalent-network</td>
<td>Atoms connected in a network of covalent bonds</td>
<td>Covalent bonds</td>
<td>Very hard, very high melting point, high thermal and electrical conductivity</td>
<td>Diamond, C; quartz, SiO₂; silicon carbide, SiC; boron nitride, BN</td>
</tr>
<tr>
<td>Ionic</td>
<td>Positive and negative ion attractions</td>
<td>Electrostatic attractions</td>
<td>Hard and brittle, high melting point, poor thermal and electrical conductivity</td>
<td>Typical salts—for example, NaCl, KCl, Ca(NO₃)₂</td>
</tr>
<tr>
<td>Metallic</td>
<td>Atoms</td>
<td>Metallic bonds</td>
<td>Soft to very hard, low to very high melting point, excellent thermal and electrical conductivity, malleable and ductile</td>
<td>All metallic elements—for example, Cu, Fe, Al, W</td>
</tr>
</tbody>
</table>

---

Bonding in Solids

(a) Diamond

(b) Graphite
**Diamond**

- Hard Structure
- Tetrahedral atomic arrangement

What hybrid state do you think the carbon has?

---

**Bonding in Solids**

**Covalent Network Solids**

- In graphite
  - each C atom is arranged in a planar hexagonal ring;
  - layers of interconnected rings are placed on top of each other;
  - the distance between C atoms is close to benzene (1.42 Å vs. 1.395 Å in benzene);
  - the distance between layers is large (3.41 Å);
  - electrons move in delocalized orbitals (good conductor).

---

Copyright © Houghton Mifflin Company. All rights reserved.
Graphite

- Form planar sheets
- actually more stable than diamond

What hybrid state do you think the carbon has?

Fullerene-C$_{60}$
• Closely Related to Graphite Structure
• Both Six-membered and Five-membered Rings of Carbon are Found in the Fullerenes

Artists carbon nanotubes, multiwalled MWCNT

Forming Carbon Nanotubes
There are 7 basic crystal systems, but we are only concerned with **CUBIC**.

- **CUBIC**
  - All sides equal length
  - All angles are 90 degrees
X-rays scattered from two different atoms may reinforce (constructive interference) or cancel (destructive interference) one another.

Figure 16.11: Reflection of X rays of wavelength

\[ n \lambda = 2d \sin \theta \]

Reflection of X rays: Bragg equation

Father and son Bragg – Nobel prize 1915
Crystal Lattices

- Regular 3-D arrangements of equivalent LATTICE POINTS in space.
- Lattice points define UNIT CELLS – smallest repeating internal unit that has the symmetry characteristic of the solid.

Cubic Unit Cells of Metals

- **Simple cubic (SC)**
  - 1 atom/unit cell
- **Body-centered cubic (BCC)**
  - 2 atoms/unit cell
- **Face-centered cubic (FCC)**
  - 4 atoms/unit cell

Atom Sharing at Cube Faces and Corners

- Atom shared in corner
  --> 1/8 inside each unit cell
- Atom shared in face
  --> 1/2 inside each unit cell

Atoms in unit cell

1

1/2

1/4

1/8
### Number of Atoms per Unit Cell

<table>
<thead>
<tr>
<th>Unit Cell Type</th>
<th>Net Number Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>1</td>
</tr>
<tr>
<td>BCC</td>
<td>2</td>
</tr>
<tr>
<td>FCC</td>
<td>4</td>
</tr>
</tbody>
</table>

### Simple Ionic Compounds

CsCl has a SC lattice of Cs⁺ ions with Cl⁻ in the center.

1 unit cell has 1 Cl⁻ ion plus
(8 corners)(1/8 Cs⁺ per corner)
= 1 net Cs⁺ ion.

### Two Views of CsCl Unit Cell

Either arrangement leads to formula of 1 Cs⁺ and 1 Cl⁻ per unit cell

Cl⁻, radius = 181 pm
Cs⁺, radius = 165 pm

Cl⁻ ions at each cube corner = 1 net Cl⁻ ion in the unit cell.

Cs⁺ lattice and Cl⁻ in lattice hole

One Cs⁺ ion at each cube corner gives one net Cs⁺ ion in the unit cell.

### Simple Ionic Compounds

Salts with formula MX can have SC structure — but not salts with formula MX₂ or M₂X.
How many atoms are in the fcc unit cell?

Figure 16.17

6(atoms on faces) + 8(atoms on corners)
= 6(1/2) + 8(1/8)
= 3 + 1
= 4

Your eyes “see” 14 Cl\(^-\) ions and 13 Na\(^+\) ions in the figure

Ion Count for the Unit Cell: 4 Na\(^+\) and 4 Cl\(^-\) \(\text{Na}_4\text{Cl}_4 = \text{NaCl}\)

Can you see how this formula comes from the unit cell?

NaCl Construction

The Sodium Chloride Lattice

Many common salts have FCC arrangements of anions with cations in OCTAHEDRAL HOLES — e.g., salts such as CA = NaCl

- FCC lattice of anions \(\rightarrow\) 4 A\(^-\)/unit cell
- C\(^+\) in octahedral holes \(\rightarrow\) 1 C\(^+\) at center
  + [12 edges \(\times\) 1/4 C\(^+\) per edge]
  = 4 C\(^+\) per unit cell
Comparing NaCl and CsCl

- Even though their formulas have one cation and one anion, the lattices of CsCl and NaCl are different.
- The different lattices arise from the fact that a Cs\(^+\) ion is much larger than a Na\(^+\) ion.

Ionic Solids

- NaCl Structure
  - Each ion has a coordination number of 6.
  - Face-centered cubic lattice.
  - Cation to anion ratio is 1:1.
  - Examples: LiF, KCl, AgCl and CaO.
- CsCl Structure
  - Cs\(^+\) has a coordination number of 8.
  - Different from the NaCl structure (Cs\(^+\) is larger than Na\(^+\)).
  - Cation to anion ratio is 1:1.

The CsCl and NaCl Structures

CsCl

NaCl

Bonding in Solids

- NaCl Structure
  - Each ion has a coordination number of 6.
  - Face-centered cubic lattice.
  - Cation to anion ratio is 1:1.
  - Examples: LiF, KCl, AgCl and CaO.
- CsCl Structure
  - Cs\(^+\) has a coordination number of 8.
  - Different from the NaCl structure (Cs\(^+\) is larger than Na\(^+\)).
  - Cation to anion ratio is 1:1.
Figure 16.13: The closet packing arrangement of uniform spheres.

\[ \frac{4 \pi}{3} r^3 \times \frac{1}{4} \times \frac{2}{3} \frac{r^3}{V^3} = \frac{1}{2} \frac{\sqrt{2}}{2} \]

Figure 16.14: When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (aba), the unit cell is the hexagonal prism illustrated here in red.

Cubic Closest Packed Structure

(b) abc — Closest packing

An atom in every fourth layer lies over an atom in the first layer.
Figure 16.36: The holes that exist among closest packed uniform spheres

Figure 16.37: (a) The octahedral hole (shown in yellow) lies at the center of six spheres that touch along the edge (e) of the square.

\[ d = 2R\sqrt{2} \]
\[ 2r = 2R\sqrt{2} - 2R \]
\[ r = R(\sqrt{2} - 1) \]
\[ = R(0.414) \]

Figure 16.37: (b) The center of the octahedral hole

Figure 16.38: (a) The tetrahedral hole (b) The center of the tetrahedral hole

\[ r = R(0.225) \]
Figure 16.39: One packed sphere and its relationship to the tetrahedral hole

(a) A simple cubic array with X⁻ ions, with an M⁺ ion in the center (in the cubic hole).
(b) The body diagonal $b$ equals $r = R(0.732)$

\[ r = R(0.732) \]

### TABLE 16.6 Guidelines for Filling Various Types of Holes for the Ionic Solid $MX$

<table>
<thead>
<tr>
<th>Size of $M^+$</th>
<th>Type of Hole Filled</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.225R^- &lt; r^+$</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>$&lt; 0.414R^-$</td>
<td></td>
</tr>
<tr>
<td>$0.414R^- &lt; r^+$</td>
<td>Octahedral</td>
</tr>
<tr>
<td>$&lt; 0.732R^-$</td>
<td></td>
</tr>
<tr>
<td>$0.732R^- &lt; r^+$</td>
<td>Cubic</td>
</tr>
</tbody>
</table>