Chapter 3: The structure of crystalline solids

Outline

- Fundamental concepts
- Unit cells
- Metallic crystal structure
- Density and polymorphism
- Crystal systems

Fundamental concepts

- Crystalline materials: atoms are situated in a repeating or periodic array over large atomic distances
- Crystalline structure: how atoms, ions, or molecules are arranged spatially
- Lattice: a three-dimensional array of points coinciding with atom position

Fig 3.1 (a) a hard sphere unit cell (b) a reduced-sphere unit cell, (c) an aggregate of many atoms
Unit cells

- Small repeating units in a crystal
- Basic structural unit or building block of the crystal structure
- Not unique
- A highest level of geometrical symmetry

Simple cubic structure (SC)

- Close-packed directions are cube edges.
- Atoms per unit cell = 8 x 1/8 = 1
- Coordination # (nearest neighbors) = 6
- Rare due to low packing density (only Po has this structure)
Atomic packing factor (APF)

\[
\text{APF} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}
\]

*assume hard spheres

- APF for a simple cubic structure = 0.52

Metallic crystal structure

- Features of metallic crystal structure
  - non-directional in nature
  - no restriction on the number and position of nearest-neighbor atoms
  - close-packed: low energy
  - common type: face-centered cubic (FCC), body-centered cubic (BCC), hexagonal closed-packed (HCP)

Adapted from Fig. 3.23, Callister 7e.
The FCC crystal structure

- Total atoms per unit cell = 4
  - 8x1/8 atoms at corner + 6x1/2 face-centered atoms = 4
- The relation between cubic edge $a$ and the radius $R$
  \[ a = 2\sqrt{2}R \]
- Coordination number = 12
  - the number of nearest-neighbor or touching atoms
- Atomic packing factor (APF)
  - APF = 0.74

Atomic packing factor: FCC

- APF for a face-centered cubic structure = 0.74
  - maximum achievable APF
  - Close-packed directions:
    - length = $4R = \sqrt{2}a$
  - Unit cell contains:
    - $6 \times 1/2 + 8 \times 1/8$
    - = 4 atoms/unit cell

\[
\text{APF} = \frac{\frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3} = \frac{4}{3} \pi (\sqrt{2}a/4)^3
\]
**FCC stacking sequence**

- ABCABC... Stacking Sequence
- 2D Projection

**The BCC crystal structure**

- Total atoms per unit cell
  8x1/8 atoms at corner + 1 body-centered atoms = 2
- Coordination number = 8
Atomic packing factor: BCC

• APF for a body-centered cubic structure = 0.68

\[
\text{APF} = \frac{4}{3} \pi \left(\frac{3a}{4}\right)^3
\]

Close-packed directions:
length = \(4R = \sqrt{3} a\)

Hexagonal close-packed structure (HCP)

• ABAB... Stacking Sequence
• 3D Projection
• 2D Projection

\[c/2a = 1.633\]

ex: Cd, Mg, Ti, Zn

• 6 atoms/unit cell
• Coordination # = 12
• APF = 0.74
• c/a = 1.633
Theoretical density and polymorphism

• Density computation

\[
\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}
\]

\[
\rho = \frac{nA}{V_C N_A}
\]

where
- \(n\) = number of atoms/unit cell
- \(A\) = atomic weight
- \(V_C\) = Volume of unit cell = \(a^3\) for cubic
- \(N_A\) = Avogadro’s number
  = \(6.023 \times 10^{23}\) atoms/mol

• Polymorphism: a phenomenon that material has more than one crystal structure

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Theoretical density (example)

- Ex: Cr (BCC)
- \(A = 52.00\) g/mol
- \(R = 0.125\) nm
- \(n = 2\)

\[
a = 4R/\sqrt[3]{3} = 0.2887\ \text{nm}
\]

\[
\rho_{\text{theoretical}} = \frac{2 \times 52.00}{6.023 \times 10^{23}} = 7.18\ \text{g/cm}^3
\]

\[
\rho_{\text{actual}} = 7.19\ \text{g/cm}^3
\]
Densities of material classes

In general
\[ \rho_{\text{metals}} > \rho_{\text{ceramics}} > \rho_{\text{polymers}} \]

Why?
- **Metals** have...
  - close-packing (metallic bonding)
  - often large atomic masses
- **Ceramics** have...
  - less dense packing
  - often lighter elements
- **Polymers** have...
  - low packing density (often amorphous)
  - lighter elements (C,H,O)
- **Composites** have...
  - intermediate values

Based on data in Table B1, Callister 7e. *GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).

Crystal systems

- 7 crystal systems
- 14 crystal lattices

\[ a, b, \text{and} c \] are the lattice constants

Fig. 3.4, Callister 7e.
# Crystal systems

## Table 5.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Axial Relationships</th>
<th>Interaxial Angles</th>
<th>Unit Cell Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image1" alt="Cubic Unit Cell" /></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = 90^\circ; \gamma = 120^\circ$</td>
<td><img src="image2" alt="Hexagonal Unit Cell" /></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image3" alt="Tetragonal Unit Cell" /></td>
</tr>
</tbody>
</table>

## Crystal systems

- **Rhombohedral**
  - $a = b = c$
  - $\alpha = \beta = \gamma 
eq 90^\circ$
  - ![Rhombohedral Unit Cell](image4)

- **Orthorhombic**
  - $a \neq b \neq c$
  - $\alpha = \beta = \gamma = 90^\circ$
  - ![Orthorhombic Unit Cell](image5)

- **Monoclinic**
  - $a \neq b \neq c$
  - $\alpha = \gamma = 90^\circ \neq \beta$
  - ![Monoclinic Unit Cell](image6)

- **Triclinic**
  - $a \neq b \neq c$
  - $\alpha \neq \beta \neq \gamma = 90^\circ$
  - ![Triclinic Unit Cell](image7)
### Crystal Systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic: Lead ore</td>
<td><img src="image" alt="Cubic: Lead ore" /></td>
</tr>
<tr>
<td>Rhombic: Topaz</td>
<td><img src="image" alt="Rhombic: Topaz" /></td>
</tr>
<tr>
<td>Hexagonal: Emerald</td>
<td><img src="image" alt="Hexagonal: Emerald" /></td>
</tr>
<tr>
<td>Tetragonal: idocrase</td>
<td><img src="image" alt="Tetragonal: idocrase" /></td>
</tr>
<tr>
<td>Monoclinic: Gypsum</td>
<td><img src="image" alt="Monoclinic: Gypsum" /></td>
</tr>
<tr>
<td>Triclinic: Axinite</td>
<td><img src="image" alt="Triclinic: Axinite" /></td>
</tr>
</tbody>
</table>