CHAPTER 3: CRYSTAL STRUCTURES & PROPERTIES

- Crystalline
  - Single Xtal
  - Poly-Xtal
- Non-crystalline
- Materials
MATERIALS AND PACKING

Crystalline materials...
- atoms pack in periodic, 3D arrays
- typical of:  - metals
  - many ceramics
  - some polymers

Noncrystalline materials...
- atoms have no periodic packing
- occurs for:  - complex structures
  - rapid cooling

"Amorphous" = Noncrystalline
METALLIC CRYSTALS

• tend to be densely packed.
• have several reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
• have the simplest crystal structures.

We will look at three such structures...
Table 3.2

*The 14 Crystal (Bravais) Lattices.*
<table>
<thead>
<tr>
<th>System</th>
<th>Axial lengths and angles</th>
<th>Unit cell geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c, \alpha = \beta = \gamma = 90^\circ$</td>
<td>![Cubic Unit Cell]</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td>![Tetragonal Unit Cell]</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td>![Orthorhombic Unit Cell]</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$</td>
<td>![Rhombohedral Unit Cell]</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td>![Hexagonal Unit Cell]</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$</td>
<td>![Monoclinic Unit Cell]</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
<td>![Triclinic Unit Cell]</td>
</tr>
</tbody>
</table>

*The lattice parameters $a$, $b$, and $c$ are unit-cell edge lengths. The lattice parameters $\alpha$, $\beta$, and $\gamma$ are angles between adjacent unit-cell axes, where $\alpha$ is the angle viewed along the $a$ axis (i.e., the angle between the $b$ and $c$ axes). The inequality sign ($\neq$) means that equality is not required. Accidental equality occasionally occurs in some structures.*

Table 3.1

*The Seven Crystal Systems.*
SIMPLE CUBIC STRUCTURE (SC)

- Rare due to poor packing (only Po has this structure)
- Close-packed directions are cube edges.

\[ \text{Coordination } # = 6 \]  
(# nearest neighbors)

(Courtesy P.M. Anderson)
Total number of atoms = 1
Why?

\[ \frac{8 \times \frac{1}{8}}{8} = 1 \]
ATOMIC PACKING FACTOR

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

*assume hard spheres

- APF for a simple cubic structure = 0.52

Adapted from Fig. 3.19, Callister 6e.
BODY CENTERED CUBIC STRUCTURE (BCC)

- Close packed directions are cube diagonals.
  
  Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

- Coordination # = 8

(Courtesy P.M. Anderson)
Total number of atoms = 2
Why?

\[
8 \times \frac{1}{8} = 1
\]

\[
1 \times 1 = 1
\]

\[
\frac{1}{2}
\]
ATOMIC PACKING FACTOR: BCC

- APF for a body-centered cubic structure = 0.68

Close-packed directions:
length = 4R
\[ = \sqrt{3} a \]

Unit cell contains:
\[ 1 + 8 \times \frac{1}{8} \]
\[ = 2 \text{ atoms/unit cell} \]

ATOMIC PACKING FACTOR (APF):

\[
\text{APF} = \frac{2 \times \frac{4}{3} \pi (\sqrt{3} a/4)^3}{a^3}
\]

Adapted from Fig. 3.2, Callister 6e.
FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

- Coordination # = 12

(Courtesy P.M. Anderson)

Adapted from Fig. 3.1(a), Callister 6e.
Total number of atoms = 4
Why?

\[ \frac{8}{8} = 1 \]
\[ \frac{6}{2} = \frac{3}{4} \]
ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74

Close-packed directions:
length = 4R
= $\sqrt{2} a$

Unit cell contains:
$6 \times \frac{1}{2} + 8 \times \frac{1}{8}$
= 4 atoms/unit cell

APF = $\frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3$

= $\frac{a^3}{volume\ atom}$

= $\frac{a^3}{volume\ unit\ cell}$

Adapted from Fig. 3.1(a), Callister 6e.
FCC STACKING SEQUENCE

- ABCABC... Stacking Sequence
- 2D Projection

A sites
B sites
C sites

- FCC Unit Cell
HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

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

- Coordination # = 12
- APF = 0.74

Adapted from Fig. 3.3, *Callister 6e.*
STRUCTURE OF COMPOUNDS: NaCl

- Compounds: Often have similar close-packed structures.
- Structure of NaCl
  - Close-packed directions --along cube edges.
THEORETICAL DENSITY, $\rho$

\[
\rho = \frac{n \cdot A}{V_{c} \cdot N_{A}}
\]

- $n$: # atoms/unit cell
- $A$: Atomic weight (g/mol)
- $V_{c}$: Volume/unit cell (cm$^3$/unit cell)
- $N_{A}$: Avogadro's number ($6.023 \times 10^{23}$ atoms/mol)
Example: Copper

Data from Table inside front cover of Callister (see next slide):

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius \( R = 0.128 \text{ nm} \) (1 nm = \( 10^{-7} \text{ cm} \))

\[
V_c = a^3; \text{ For FCC, } a = \frac{4R}{\sqrt{2}}; \quad V_c = 4.75 \times 10^{-23} \text{ cm}^3
\]

Result: theoretical \( \rho_{Cu} = 8.89 \text{ g/cm}^3 \)

Compare to actual: \( \rho_{Cu} = 8.94 \text{ g/cm}^3 \)

Why are they different?
## Characteristics of Selected Elements at 20°C

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>At. Weight (amu)</th>
<th>Density (g/cm³)</th>
<th>Crystal Structure</th>
<th>Atomic radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>26.98</td>
<td>2.71</td>
<td>FCC</td>
<td>0.143</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>39.95</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>137.33</td>
<td>3.5</td>
<td>BCC</td>
<td>0.217</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>9.012</td>
<td>1.85</td>
<td>HCP</td>
<td>0.114</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>10.81</td>
<td>2.34</td>
<td>Rhomb</td>
<td>-----</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>79.90</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>112.41</td>
<td>8.65</td>
<td>HCP</td>
<td>0.149</td>
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<tr>
<td>Calcium</td>
<td>Ca</td>
<td>40.08</td>
<td>1.55</td>
<td>FCC</td>
<td>0.197</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>12.011</td>
<td>2.25</td>
<td>Hex</td>
<td>0.071</td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs</td>
<td>132.91</td>
<td>1.87</td>
<td>BCC</td>
<td>0.265</td>
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<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>35.45</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>52.00</td>
<td>7.19</td>
<td>BCC</td>
<td>0.125</td>
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<tr>
<td>Cobalt</td>
<td>Co</td>
<td>58.93</td>
<td>8.9</td>
<td>HCP</td>
<td>0.125</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>63.55</td>
<td>8.94</td>
<td>FCC</td>
<td>0.128</td>
</tr>
<tr>
<td>Flourine</td>
<td>F</td>
<td>19.00</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga</td>
<td>69.72</td>
<td>5.90</td>
<td>Ortho.</td>
<td>0.122</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge</td>
<td>72.59</td>
<td>5.32</td>
<td>Dia. cubic</td>
<td>0.122</td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>196.97</td>
<td>19.32</td>
<td>FCC</td>
<td>0.144</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>4.003</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1.008</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

Adapted from Table, "Characteristics of Selected Elements", inside front cover, Callister 6e.
DENSITIES OF MATERIAL CLASSES

Why?
Metals have...
  • close-packing (metallic bonding)
  • large atomic mass
Ceramics have...
  • less dense packing (covalent bonding)
  • often lighter elements
Polymers have...
  • poor packing (often amorphous)
  • lighter elements (C, H, O)
Composites have...
  • intermediate values

Based on data in Table B1, Callister 6e.
*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).

Data from Table B1, Callister 6e.
CRYSTALS AS BUILDING BLOCKS

• *Some* engineering applications require single crystals:
  --diamond single crystals for abrasives
  --turbine blades

(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

• Crystal properties reveal features of atomic structure.
  --Ex: Certain crystal planes in quartz fracture more easily than others.

(Courtesy P.M. Anderson)
Demo:

- Minerals

- Single / Poly
POLYCRYSTALS

• Most engineering materials are polycrystalline.
Effect of grain size, an example

Figure 7.22 The influence of annealing temperature on the tensile strength and ductility of a brass alloy. Grain size as a function of annealing temperature is indicated. Grain structures during recovery, recrystallization, and grain growth stages are shown schematically. (Adapted from G. Sachs and K. R. Van Horn, Practical Metallurgy, Applied Metallurgy and the Industrial Processing of Ferrous and Nonferrous Metals and Alloys, American Society for Metals, 1940, p. 139.)
SINGLE VS POLYCRYSTALS

- Single Crystals
  - Properties vary with direction: anisotropic.
  - Example: the modulus of elasticity (E) in BCC iron:
    - E (diagonal) = 273 GPa
    - E (edge) = 125 GPa

- Polycrystals
  - Properties may/may not vary with direction.
  - If grains are randomly oriented: isotropic.
    - \( E_{\text{poly iron}} = 210 \text{ GPa} \)
  - If grains are textured, anisotropic.

Adapted from Table 3.3, Callister 6e.

Adapted from Fig. 4.12(b), Callister 6e.
(Fig. 4.12(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)
Figure 3.17

Transmission electron micrograph (see Section 4.7) of the structure of clay platelets. This microscopic-scale structure is a manifestation of the layered crystal structure shown in Figure 3.16.

(Courtesy of I. A. Aksay.)
• Bar of Vanadium
Growing Crystals

https://www.youtube.com/watch?v=1_USYub3djY
Lattice Positions

Example: cubic system

\[ A = 1, 0, 0 \]
\[ B = \frac{1}{2}, \frac{1}{2}, 1 \]
\[ C = 1, 1, \frac{1}{2} \]
Figure 3.26

Notation for lattice positions.
Procedure for finding direction:

- Select two points on the line
- End point - Start point
- Clear fraction
- Put in [hkl] format

Note: negative sign goes above the number
Example:

- Select two points on the line
- End point - Start point
- Clear fraction
- Put in \([hkl]\) format

\( \begin{align*}
\begin{pmatrix} 0 \end{pmatrix} - 0,0,1 &= 1,0,0 &= [100]
\end{align*}
\)
Example:

- Select two points on the line
- End point - Start point
- Clear fraction
- Put in [hkl] format

\[
\begin{align*}
\frac{1}{2}, 0, 0, 1 &= \frac{1}{2}, 1, 1, 1 \\
1, 2, 1, -2 &= \left[1 2 \frac{1}{2}\right]
\end{align*}
\]
Family of directions, \( \langle 111 \rangle \), representing all body diagonals for adjacent unit cells in the cubic system.
Procedure for finding planes:

• Find plane’s intercept with X, Y and Z axis
• Inverse the numbers
• Clear fraction
• Put in (hkl) format

Note: negative sign goes above the number
Find plane’s intercept with X, Y and Z axis
Inverse the numbers
Clear fraction
Put in (hkl) format
Find plane's intercept with X, Y and Z axis
Inverse the numbers
Clear fraction
Put in (hkl) format

\[
\begin{align*}
x & = 1 \\
y & = 10 \\
z & = 2 \\
(102)
\end{align*}
\]
Planar Spacing (parallel planes only)

\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

Example: find spacing \( b/\omega \) (110) planes if \( a = 0.5 \) nm

\[ d = \frac{0.5 \times 10^{-9}}{\sqrt{1^2 + 1^2 + 0}} = \frac{0.5 \times 10^{-9}}{\sqrt{2}} \]

\[ d = 0.35 \times 10^{-9} \text{ m} \]
The previous equation of planar spacing is only for **CUBIC** systems.
Angle between two directions:

$$\cos(\theta) = \frac{A \cdot B}{|A| \times |B|}$$

$$\vec{A} = h\hat{i} + k\hat{j} + l\hat{k}$$  $$\vec{B} = h\hat{i} + k\hat{j} + l\hat{k}$$

**Example:** Find angle $\gamma$ between $[021]$ and $[211]$

$$A = \sqrt{1+0+4} = \sqrt{5}$$  $$B = \sqrt{4+1+1} = \sqrt{6}$$

$$\cos \theta = \frac{2+0+2}{\sqrt{5} \times \sqrt{6}} \Rightarrow \theta = 43^\circ$$
Figure 3.30

Notation for lattice planes. (a) The (210) plane illustrates Miller indices \((hkl)\). (b) Additional examples.
Family of planes, \{100\}, representing all faces of unit cells in the cubic system.
Atomic Linear density, $LD = \text{(number of atoms/unit length)}$

**Slip Direction (more later)**

Calculate $LD$ if cube is BCC

Number of atoms on line:

$2 \times \frac{1}{2} = 1$

$LD = \frac{1}{a \sqrt{2}} = \frac{1}{0.5 \times 10^{-9} \sqrt{2}}$

$LD = 1.4 \times 10^9$ atoms $\text{nm}^{-1}$

$a = 0.5 \text{nm}$
Calculate LD if cube is FCC

\[ 2 \times \frac{1}{2} + 1 = 2 \]

\[ L = \frac{2}{a\sqrt{2}} = 2.8 \times 10^9 \text{ atoms/\(m\)} \]
Atomic Planar density, $PD = \frac{\text{number of atoms/unit area}}{a^2\sqrt{2}}$

Slip plane (more later)

Calculate PD if cube is BCC

Number of atoms = 4 \times \frac{1}{4} + 1 = 2

$PD = \frac{2}{a^2\sqrt{2}} = \ldots$
Calculate PD if cube is FCC

\[ \# \text{ of atoms} = 4 \times \frac{1}{4} + 2 \times \frac{1}{2} = 2 \]

\[ PD = \frac{2}{a^2 \sqrt{2}} = \ldots \]
Atomic Volume density, \( VD = \text{(number of atoms/unit volume)} \)

Calculate \( VD \) if cube is BCC

\[ \text{Number of atoms} \]

\[ 8 \times \frac{1}{8} + 1 = 2 \]

\[ VD = \frac{2}{a^3} = \ldots \]
Atomic Volume density, $VD = \text{(number of atoms/unit volume)}$

Calculate $VD$ if cube is FCC

\[ \text{# of atoms} \]
\[ 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \]
\[ VD = \frac{4}{a^3} = \ldots \]
Converting from/to cubic to hexagonal, Directions

\([hkl]\) and \([uvtw]\)

\[u = \frac{n}{3}(2h-k)\]
\[v = \frac{n}{3}(2k-h)\]
\[t = -(u+v)\]
\[w = nl\]

Example: covert \([102]\) to hexagonal system

\[U = \frac{n}{3}(2-0) = \frac{2n}{3}\]
\[V = \frac{n}{3}(0-1) = -\frac{n}{3}\]
\[t = -(\frac{2n}{3} + \frac{n}{3}) = -\frac{n}{3}\]
\[W = n(2) = 2n\]

\([102]\) \rightarrow \([2\overline{1}1\overline{6}]\)
Converting from/to cubic to hexagonal, plane

(hkl) to/from (hkil)
i = -(h+k)

Example: convert (213) to hexagonal system

\[ i = -(2 + 1) = 3 \]

\( (213) \rightarrow (21\bar{3}3) \)
<table>
<thead>
<tr>
<th>#atoms/UC</th>
<th>$a_0$</th>
<th>C.N</th>
<th>P.F</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>2R</td>
<td>6</td>
<td>0.52</td>
<td>Fe, W, Mo, Cr,…</td>
</tr>
<tr>
<td>BCC</td>
<td>$\frac{4R}{\sqrt{3}}$</td>
<td>8</td>
<td>0.68</td>
<td>Fe, Cu, Al, Au, Ag, Pb, Ni,…</td>
</tr>
<tr>
<td>FCC</td>
<td>$\frac{4R}{\sqrt{2}}$</td>
<td>12</td>
<td>0.74</td>
<td>Fe, Cu, Al, Au, Ag, Pb, Ni,…</td>
</tr>
<tr>
<td>HCP</td>
<td>$a_0 = 2R$</td>
<td>12</td>
<td>0.74</td>
<td>Ti, Mg, Zn, Be, Co, Zr,…</td>
</tr>
</tbody>
</table>
Electromagnetic radiation spectrum. X-radiation represents that portion with wavelengths around 0.1 nm.
X-RAYS TO CONFIRM CRYSTAL STRUCTURE

- Incoming X-rays diffract from crystal planes.

- Measurement of:
  Critical angles, $\theta_c$, for X-rays provide atomic spacing, $d$.

  x-ray intensity (from detector)

  $$d = n\lambda / 2\sin\theta_c$$
\[ n\lambda = 2d \cdot \sin \theta \]

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]
Watch this video:
Graphical Methods

The diffraction pattern on the left was made by a beam of x-rays passing through thin aluminum foil. The diffraction pattern on the right was made by a beam of electrons passing through the same foil.

Poly x-tal
Small grains

Single x-tal
Large grains
X-Ray: Another Method

- Incident beam
- Film
Detection method

\[ n\lambda = 2dsin(\theta) \]
Figure 3.22  Diffraction pattern for polycrystalline α-iron, \( a=0.29 \text{ nm} \)

\[ n\lambda=2ds\sin(\theta) \]

Example: Find wavelength of the x-ray used to generate the above graph.

From graph, for \((110)\) \(2\theta=45, \theta=22.5\)

\[
d=\frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{0.29 \text{ nm}}{\sqrt{2}} = 0.205 \text{ nm}
\]

\[
\sin(22.5)=\frac{\lambda}{2 \times 0.205}, \quad \lambda=0.157 \text{ nm}=1.57\text{Å}
\]
Pyrite (done with SEM at SSU)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>5.18</td>
<td>15.23</td>
</tr>
<tr>
<td>Si K</td>
<td>0.67</td>
<td>1.13</td>
</tr>
<tr>
<td>S K</td>
<td>23.14</td>
<td>33.96</td>
</tr>
<tr>
<td>Fe K</td>
<td>4.80</td>
<td>4.04</td>
</tr>
<tr>
<td>Cu K</td>
<td>43.28</td>
<td>32.05</td>
</tr>
<tr>
<td>Zn K</td>
<td>6.20</td>
<td>4.46</td>
</tr>
<tr>
<td>As L</td>
<td>11.03</td>
<td>6.93</td>
</tr>
<tr>
<td>Sb L</td>
<td>5.71</td>
<td>2.21</td>
</tr>
</tbody>
</table>
SUMMARY

- Atoms may assemble into crystalline or amorphous structures.

- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).

- Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.