2. Crystal Structure

- **crystalline solid** – the atoms or ions arrange in a pattern that repeats itself in three dimensions to form a solid which has long-range order
- **amorphous solid** – materials with only short-range order
- **space lattice** – a network composed of an infinite three-dimensional array of points
- **unit cell** – the repeating unit in a space lattice

![space lattice and unit cell diagram]

- **lattice constants**
  - lattice vector – \(a, b, c\)
  - interaxial angle – \(\alpha, \beta, \gamma\)
crystal system

only 7 different types of unit cells
14 standard (Bravais) unit cells could
describe all possible lattice networks

crystal system | axial lengths & interaxial angles | space lattice
--|---|---
cubic | \(a = b = c\) | simple cubic
| \(\alpha = \beta = \gamma = 90^\circ\) | body-centered cubic
| | face-centered cubic
tetragonal | \(a = b \neq c\) | simple tetragonal
| \(\alpha = \beta = \gamma = 90^\circ\) | body-centered tetragonal
orthorhombic | \(a \neq b \neq c\) | simple orthorhombic
| \(\alpha = \beta = \gamma = 90^\circ\) | body-centered orthorhombic
| | base-centered orthorhombic
| | face-centered orthorhombic
rhombohedral | \(a = b = c\) | simple rhombohedral
| \(\alpha = \beta = \gamma \neq 90^\circ\) | 
hexagonal | \(a = b \neq c\) | simple hexagonal
| \(\alpha = \beta = 90^\circ\) | \(\gamma = 120^\circ\) |
monoclinic | \(a \neq b \neq c\) | simple monoclinic
| \(\alpha = \gamma = 90^\circ \neq \beta\) | base-centered monoclinic
triclinic | \(a \neq b \neq c\) | simple triclinic
| \(\alpha \neq \beta \neq \gamma \neq 90^\circ\) |
metallic crystal structures
90% elemental metals crystallize into three crystal structures:

- **body-centered cubic (BCC)**

<table>
<thead>
<tr>
<th></th>
<th>(a) (nm)</th>
<th>(R) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.289</td>
<td>0.125</td>
</tr>
<tr>
<td>Fe</td>
<td>0.287</td>
<td>0.124</td>
</tr>
<tr>
<td>Mo</td>
<td>0.315</td>
<td>0.136</td>
</tr>
<tr>
<td>K</td>
<td>0.533</td>
<td>0.231</td>
</tr>
<tr>
<td>Na</td>
<td>0.429</td>
<td>0.186</td>
</tr>
<tr>
<td>Ta</td>
<td>0.330</td>
<td>0.143</td>
</tr>
<tr>
<td>W</td>
<td>0.316</td>
<td>0.137</td>
</tr>
<tr>
<td>V</td>
<td>0.304</td>
<td>0.132</td>
</tr>
</tbody>
</table>

- **face-centered cubic (FCC)**

<table>
<thead>
<tr>
<th></th>
<th>(a) (nm)</th>
<th>(R) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.405</td>
<td>0.143</td>
</tr>
<tr>
<td>Cu</td>
<td>0.3615</td>
<td>0.128</td>
</tr>
<tr>
<td>Au</td>
<td>0.408</td>
<td>0.144</td>
</tr>
<tr>
<td>Pb</td>
<td>0.495</td>
<td>0.175</td>
</tr>
<tr>
<td>Ni</td>
<td>0.352</td>
<td>0.125</td>
</tr>
<tr>
<td>Pt</td>
<td>0.393</td>
<td>0.139</td>
</tr>
<tr>
<td>Ag</td>
<td>0.409</td>
<td>0.144</td>
</tr>
</tbody>
</table>

- **hexagonal close-packed (HCP)**

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(c) (nm)</th>
<th>(R) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.2973</td>
<td>0.5618</td>
<td>0.143</td>
</tr>
<tr>
<td>Zn</td>
<td>0.2665</td>
<td>0.4947</td>
<td>0.133</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3209</td>
<td>0.5209</td>
<td>0.160</td>
</tr>
<tr>
<td>Co</td>
<td>0.2507</td>
<td>0.4069</td>
<td>0.125</td>
</tr>
<tr>
<td>Zr</td>
<td>0.3231</td>
<td>0.5148</td>
<td>0.160</td>
</tr>
<tr>
<td>Ti</td>
<td>0.2950</td>
<td>0.4683</td>
<td>0.147</td>
</tr>
<tr>
<td>Be</td>
<td>0.2286</td>
<td>0.3584</td>
<td>0.113</td>
</tr>
</tbody>
</table>
BCC

coordination number = 8
total 2 atoms per unit cell

\[ \sqrt{3} a = 4 \, R \quad a = \frac{4 \, R}{\sqrt{3}} \]

atomic packing factor (APF)

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

\[ APF = 0.68 \]

FCC
coordination number = 12
total 4 atoms per unit cell

\[ \sqrt{2} a = 4 \text{ R} \quad a = \frac{4 \text{ R}}{\sqrt{2}} \]

APF = 0.74

the closest packing possible of spherical atoms cubic closest-packed

HCP

coordination number = 12
total 2 atoms per unit cell

APF = 0.74

the closest packing possible of spherical atoms

c/a ratio for ideal HCP structure is 1.633
the closest packing

HCP \(ababa\) ....

FCC \(abcabc\) ....
atom positions in cubic unit cell

BCC unit cell
coordinates of eight corners:
(0, 0, 0) (1, 0, 0) (0, 1, 0) (0, 0, 1)  
(1, 1, 0) (1, 0, 1) (0, 1, 1) (1, 1, 1)  
coordinate of the center: \( \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \)

direction index – the vector components of the direction resolved along each of the coordinate axes and reduced to the smallest integers

all parallel direction vectors have the same direction indices
directions are *crystallographically equivalent* if the atom spacing along each direction is the same.

ex. cubic edge directions:

\[
[100] \ [010] \ [001] \ [0\bar{1}0] \ [00\bar{1}] \ [\bar{1}00]
\]

\[\equiv <100>\]

equivalent directions are called *indices of a family or form*.

ex. draw the following directions:

(a) \([112]\)

(b) \([\bar{1}10]\)

(c) \([\bar{3}2\bar{1}]\)
Miller indices for crystallographic planes

Miller notation system \((hkl)\)

Miller index – the reciprocals of the fractional intercepts that the plane makes with the \(x\), \(y\), and \(z\) axes of the three nonparallel edges of the cubic unit cell

procedure for determining Miller index:
(1) choose a plane not pass through \((0, 0, 0)\)
(2) determine the intercepts of the plane with \(x\), \(y\), and \(z\) axes
(3) form the reciprocals of these intercepts
(4) find the smallest set of whole numbers that are in the same ratio as the intercepts

ex.
ex. draw the following crystallographic planes in cubic unit cell:

(a) (101)  
(b) (110)  
(c) (221)

planes of a family or form \{hkl\}

ex. (100), (010), (001) are a family \{100\}

an important relationship for cubic system, the direction indices of a direction perpendicular to a crystal plane are the same as the Miller indices of that plane
interplanar spacing between two closest parallel planes with the same Miller indices is designated \( d_{hkl} \) (\( h, k, l \) are the Miller indices)

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

\( a \): = lattice constant

ex. determine the Miller indices of the planes shown as follow:

(a) \((5120)\)  
(b) \((646)\)
hexagonal structure

**Miller-Bravais indices** – HCP crystal plane

indices \((hkl)\) \(h + k + i = 0\)

three basal axes \(a_1, a_2, a_3\) and \(c\) axis

basal planes \((0001)\)

prism planes

\((ABCD)\) \((10\bar{1}0)\)

\((ABEF)\) \((1\bar{1}00)\)

\((CDGH)\) \((0\bar{1}10)\)
direction indices in HCP unit cell
four indices \([uvtw]\) \(u + v + t = 0\)
\(u = \frac{1}{3}(2u - v)\) \(v = \frac{1}{3}(2u - v)\) \(t = -(u + v)\)
directions \(a_1, a_2, a_3\)

+\(a_3\) direction incorporating \(c\) axis
directions on the upper basal planes
volume, planar, linear density

volume density

\[ \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \]

ex. Cu has FCC structure, atomic radius of 0.1278 nm, atomic mass of 63.54 g/mol
calculate the density of Cu in Mg/m\(^3\).

FCC structure \( \sqrt{2} a = 4 R \)
\[ a = 2 \sqrt{2} R = 2 \sqrt{2} (1.278 \times 10^{-10}) \]
\[ = 3.61 \times 10^{-10} \text{m} \]
\[ V = (3.61 \times 10^{-10} \text{m})^3 = 4.70 \times 10^{-29} \text{m}^3 \]
4 Cu per unit cell
\[ m = 4 \times 63.54 \times 1.66 \times 10^{-30} \text{Mg} = 4.22 \times 10^{-28} \text{Mg} \]
\[ \rho_v = \frac{4.22 \times 10^{-28} \text{Mg}}{4.70 \times 10^{-29} \text{m}^3} \]
\[ = 8.98 \text{Mg/m}^3 \quad \text{(exp. = 8.96 Mg/m}^3 \) \]

planar atomic density

\[ \rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}} \]

ex. calculate planar atomic density \( \rho_p \) on (110) plane of the \( \alpha \)-Fe in BCC lattice in atoms/mm\(^2\). (lattice constant \( a = 0.287 \text{nm} \))
1 atom (center) + \( \frac{1}{4} \) atom (corner) \times 4 = 2 atoms

\[
\text{area} = a \times \sqrt{2} a = \sqrt{2} a^2 = \sqrt{2} \left(2.87 \times 10^{-7}\right)^2 = 1.164 \times 10^{-13} \text{ mm}^2
\]

\[
\rho_p = \frac{2 \text{ atoms}}{1.164 \times 10^{-13} \text{ mm}^2} = 1.72 \times 10^{13} \text{ atoms/mm}^2
\]

linear atomic density

\[
\rho_l = \frac{\text{no. of atoms diam. intersected by selected length of line in direction of interest}}{\text{selected length of line}}
\]

ex. calculate linear atomic density \( \rho_l \) in [110] direction in Cu crystal lattice in atoms/mm. (Cu is FCC and lattice constant \( a = 0.361 \text{ nm} \))
no. of atoms = \( \frac{1}{2} + 1 + \frac{1}{2} = 2 \) atoms

length = \( \sqrt{2} a = \sqrt{2} (3.61 \times 10^{-7}) \)
\[ = 5.104 \times 10^{-7} \text{ mm} \]

2 atoms

\[ \rho_l = \frac{2}{5.104 \times 10^{-7} \text{ mm}} = 3.92 \times 10^6 \text{ atoms/mm} \]

**polymorphism** or **allotropy**

element or compound exists in more than one crystalline form under different conditions of temperature and pressure

ex.

<table>
<thead>
<tr>
<th>metal</th>
<th>crystal structure at room temperature</th>
<th>at other temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>FCC</td>
<td>BCC (&gt; 447°C)</td>
</tr>
<tr>
<td>Co</td>
<td>HCP</td>
<td>FCC (&gt; 427°C)</td>
</tr>
<tr>
<td>Hf</td>
<td>HCP</td>
<td>BCC (&gt; 1742°C)</td>
</tr>
<tr>
<td>Fe</td>
<td>BCC (( \alpha ))</td>
<td>FCC (912-1394°C) (( \gamma )) BCC (&gt; 1394°C) (( \delta ))</td>
</tr>
<tr>
<td>Li</td>
<td>BCC</td>
<td>HCP (&lt; -193°C)</td>
</tr>
<tr>
<td>Na</td>
<td>BCC</td>
<td>HCP (&lt; -233°C)</td>
</tr>
<tr>
<td>Tl</td>
<td>HCP</td>
<td>BCC (&gt; 234°C)</td>
</tr>
<tr>
<td>Ti</td>
<td>HCP</td>
<td>BCC (&gt; 883°C)</td>
</tr>
<tr>
<td>Y</td>
<td>HCP</td>
<td>BCC (&gt; 1481°C)</td>
</tr>
<tr>
<td>Zr</td>
<td>HCP</td>
<td>BCC (&gt; 872°C)</td>
</tr>
</tbody>
</table>
Crystal structure analysis

X-ray sources

X-rays used for diffraction are radiations with wavelengths 0.05 ~ 0.25 nm

A voltage of 35 kV is applied between cathode (W filament) and anode (Mo target)

X-ray spectrum 0.2 ~ 1.4 nm

Wavelength of Kα line 0.07 nm
X-ray diffraction
reflected wave patterns of beam are not in phase, no reinforced beam will be produced
destructive interference occurs

\[ n\lambda = MP + PN \]

reflected wave patterns of beam are in phase, reinforcement of the beam or constructive interference occurs

\[ n\lambda = 2d_{hkl} \sin \theta \]
ex. BCC Fe placed in an x-ray diffractometer using x-ray with $\lambda = 0.1541$ nm. diffraction from \{110\} planes was obtained at $2\theta = 44.704^\circ$. calculate lattice constant $a$.

\[
\lambda = 2 \, d_{110} \sin \theta
\]

\[
d_{110} = \frac{\lambda}{2 \sin \theta} = \frac{0.1541 \text{ nm}}{2 \sin(22.352^\circ)} = 0.2026 \text{ nm}
\]

\[
a = d_{hkl} \sqrt{h^2 + k^2 + l^2} = 0.2026 \sqrt{2} = 0.287 \text{ nm}
\]

X-ray diffraction analysis of crystal structures
powder diffraction method
diffractometer
diffraction pattern for cubic unit cell

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{and} \quad \lambda = 2d \sin \theta \]

\[ \lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \]

rules for determining the diffracting \( \{hkl\} \) planes in cubic crystals

<table>
<thead>
<tr>
<th>Reflection Present</th>
<th>Reflection Absent</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC ((h + k + l) = \text{even})</td>
<td>((h + k + l) = \text{odd})</td>
</tr>
<tr>
<td>FCC ((h, k, l) \text{ all odd or all even})</td>
<td>((h, k, l) \text{ not all odd or all even})</td>
</tr>
</tbody>
</table>

ex. Diffraction pattern for W sample by the use of a diffractometer with Cu radiation

W : BCC structure
\[ \lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \]

\[
\sin^2 \theta = \frac{\lambda^2(h^2 + k^2 + l^2)}{4a^2}
\]

\[
\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{h^2_A + k^2_A + l^2_A}{h^2_B + k^2_B + l^2_B}
\]

Miller indices of the diffracting planes for BCC and FCC

<table>
<thead>
<tr>
<th>{hkl}</th>
<th>(\Sigma[h^2 + k^2 + l^2])</th>
<th>FCC</th>
<th>BCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>{100}</td>
<td>1</td>
<td>.....</td>
<td>.....</td>
</tr>
<tr>
<td>{110}</td>
<td>2</td>
<td>.....</td>
<td>110</td>
</tr>
<tr>
<td>{111}</td>
<td>3</td>
<td>111</td>
<td>.....</td>
</tr>
<tr>
<td>{200}</td>
<td>4</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>{210}</td>
<td>5</td>
<td>.....</td>
<td>.....</td>
</tr>
<tr>
<td>{211}</td>
<td>6</td>
<td>.....</td>
<td>211</td>
</tr>
</tbody>
</table>

First two sets of diffraction planes

FCC \{111\} and \{200\}

\[
\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{h^2_A + k^2_A + l^2_A}{h^2_B + k^2_B + l^2_B} = 0.75
\]
BCC {110} and {200}

\[
\frac{\sin^2 \theta_A}{h^2_A + k^2_A + l^2_A} = 0.5
\]

\[
\frac{\sin^2 \theta_B}{h^2_B + k^2_B + l^2_B} = 0.5
\]

ex. an element that has either BCC or FCC structure shows diffraction peaks at following 2θ angles: 40, 58, 73, 86.8, 100.4 and 114.7. wavelength of x-ray \( \lambda = 0.154 \)

a. BCC or FCC?
b. determine the lattice constant \( a \).
c. identify the element.

<table>
<thead>
<tr>
<th>2θ</th>
<th>θ</th>
<th>\sin θ</th>
<th>\sin^2 θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>20</td>
<td>0.3420</td>
<td>0.1170</td>
</tr>
<tr>
<td>58</td>
<td>29</td>
<td>0.4848</td>
<td>0.2350</td>
</tr>
<tr>
<td>73</td>
<td>36.5</td>
<td>0.5948</td>
<td>0.3538</td>
</tr>
<tr>
<td>86.8</td>
<td>43.4</td>
<td>0.6871</td>
<td>0.4721</td>
</tr>
<tr>
<td>100.4</td>
<td>50.2</td>
<td>0.7683</td>
<td>0.5903</td>
</tr>
</tbody>
</table>

first and second angles
\[
\frac{0.1170}{0.3420} = 0.5 \quad \text{BCC structure}
\]

(b)

\[
a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta} = \frac{0.154 \sqrt{2}}{2 \cdot 0.342} = 0.318 \text{ nm}
\]

(c) W