Crystalline Structures – The Basics

• Crystal structure of a material is way in which atoms, ions, molecules are spatially arranged in 3-D space.

• **Crystal structure** = **lattice** (unit cell geometry) + **basis** (atom, ion, or molecule positions placed on lattice points within the unit cell).

• A **lattice** is used in context when describing crystalline structures, means a 3-D array of points in space. *Every lattice point must have identical surroundings.*

• **Unit cell**: smallest repetitive volume which contains the complete lattice pattern of a crystal. A unit cell is chosen to represent the highest level of geometric symmetry of the crystal structure. *It’s the basic structural unit or building block of crystal structure.*

- 7 crystal systems in 3-D
- 14 crystal lattices in 3-D

\[ a, b, \text{ and } c \text{ are the lattice constants} \]
\[ \alpha, \beta, \gamma \text{ are the interaxial angles} \]
Metallic Crystal Structures (the simplest)

- Recall, that:
  a) the coulombic attraction between delocalized valence electrons and positively charged cores is isotropic (non-directional),
  b) typically, only one element is present, so all atomic radii are the same,
  c) nearest neighbor distances tend to be small,
  d) electron cloud shields cores from each other.

- For these reasons, metallic bonding leads to close packed, dense crystal structures that maximize space filling and coordination number (number of nearest neighbors).

- Most elemental metals crystallize in the **FCC** (face-centered cubic), **BCC** (body-centered cubic), or **HCP** (hexagonal close packed) structures:

<table>
<thead>
<tr>
<th>Metallic Elements</th>
<th>Room temperature crystal structure</th>
<th>Crystal structure just before it melts</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>Sy, r.t.</td>
<td>Tm</td>
</tr>
<tr>
<td>IIA</td>
<td>f = fcc</td>
<td></td>
</tr>
<tr>
<td>IIIB</td>
<td>h = hcp</td>
<td></td>
</tr>
<tr>
<td>VB</td>
<td>b = bcc</td>
<td></td>
</tr>
<tr>
<td>VB</td>
<td>hc = hc (ABC)</td>
<td></td>
</tr>
<tr>
<td>VIIB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIB</td>
<td>x = complex</td>
<td></td>
</tr>
</tbody>
</table>

Lanthanides
Recall: Simple Cubic (SC) Structure

- Rare due to low packing density (only $\alpha$-Po has this structure)
- **Close-packed directions are cube edges.**

A hard sphere unit cell (each sphere represents an ion core with metallic bonding in between):

- **Coordination # = 6**
  (# of nearest neighbors)

Reduced-sphere unit cells (8 total: $2 \times 2 \times 2$)

- **Group V elements** (As, Sb and Bi) all crystallize in structures that can be thought of as distorted versions of the SC arrangement $\rightarrow$ trigonal (rhombohedral)$\rightarrow$
- **Three nearest-neighbors are close and three are further away.** These structures are more accurately described as $3 + 3$ arrangements.

SC: 1 2 3

body-diagonal (red line)

body-diagonal (green line)
APF for a simple cubic structure = 0.52

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

*assume hard spheres

• APF for a simple cubic structure = 0.52

Adapted from Fig. 3.42, Callister & Rethwisch 3e. (see next slide for calculation)
The number of lattice points is given by the equation:

\[ N = N_i + \frac{N_f}{2} + \frac{N_c}{8} + \ldots \]

- \(N_i\) = number of lattice points in cell interior (belong to 1 cell)
- \(N_f\) = number of lattice points on cell faces (shared by 2 cells)
- \(N_c\) = number of lattice points on cell corners (shared by 8 cells)
- \(N_e\) = number of lattice points on cell edges (shared by ? cells)

**Example:**

\[ N = 8 + \frac{0}{2} + \frac{8}{8} = 9 \text{ lattice points/unit cell} \]
Recall: Body Centered Cubic (BCC) Structure

- Atoms touch each other along cube (body) diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

Examples: Cr, W, α-Fe, Ta, Mo

- Coordination # = 8

2 atoms/unit cell = 1 center + 8 corners x 1/8

- In addition to the 8 N.N., there are 6 next N.N. (N.N.N.) only 15% (2/\sqrt{3}) further away.
- So this nearly 14 coordinate structure could also be described as having 8 + 6 coordination.

Adapted from Fig. 3.2, Callister & Rethwisch 3e.
Recall: BCC – APF

- APF for a body-centered cubic structure = 0.68

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

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

Adapted from Fig. 3.2(a), Callister & Rethwisch 3e.
Body Centered Tetragonal (BCT)

• Recall BCC:

The fact that the 6 next N.N. are so close suggests that tetragonal \((a=b\neq c)\) distortions could lead to the formation of 10 and 12 coordinate structures:

- If we compress the BCC structure along the \(c\)-axis, the atoms along the vertical axis become N.N., i.e. \(\text{CN}=10\) (BCT) when \(c/a=\sqrt{2}/\sqrt{3}\):

- Likewise if we shrink \(a\) and \(b\) with respect to \(c\), then the in-plane or equatorial atoms become N.N., i.e., \(\text{CN}=12\) when \(c/a=\sqrt{2}\).

- The equatorial atoms are now on the face centers (since height of cell is = diagonal of square base) the repeat unit is now identical to the Face Centered cubic (FCC) or cubic close packed (CCP):

• Only Protactinium (Pa) crystallizes in the BCT (CN=10) structure, but many crystal structures have BCT lattice.
Recall: Face Centered Cubic (FCC) Structure

- Atoms touch each other along face diagonals.

- Coordination # = 12
  - 12-fold coordination of each lattice point (same atom) is identical.

Exs.: Al, Cu, Au, Pb, Ni, Pt, Ag

- Note: All atoms are identical; the face atoms are shaded differently only for ease of viewing.

Extended unit cells

4 atoms/unit cell = 6 face x 1/2 + 8 corners x 1/8

Hard sphere unit cell  Reduced-sphere unit cell  2 unit cells (1 x 2)

Adapted from Fig. 3.1, Callister & Rethwisch 3e.
**Recall: FCC – APF**

- APF for a face-centered cubic structure = 0.74 which is maximum achievable APF for same diameter spheres, known as Kepler conjecture.

  FCC also known as cubic close packed (CCP) structure.

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

Where $R = \frac{a}{4}$

Atoms per unit cell:
- $4 \cdot \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3$

Volume per atom:
- $4 \cdot \frac{4}{3} \pi \left(\frac{\sqrt{2}a/4}{3}\right)$

APF = \[
\frac{\text{atoms/unit cell}}{a^3} = \frac{4 \cdot \frac{4}{3} \pi \left(\frac{\sqrt{2}a/4}{3}\right)}{a^3}
\]

Adapted from Fig. 3.1(a), Callister & Rethwisch 3e.
Recall: Hexagonal Closed Packed (HCP)

• Not all metals have unit cells with cubic symmetry, many metals have HCP crystal structures.

Alternately, the unit cell of HCP may be specified as a parallelepiped defined by atoms labeled A through H with J atom lying in unit cell interior (not at body center), it’s at $\left(\frac{1}{3} x, \frac{2}{3} y, \frac{1}{2} z\right)$.

- CN = 12
- Atoms/unit cell = 6
- APF = 0.74
- $c/a = 1.633$
Recall: Ideal \( c/a \) ratio for HCP is 1.633

A sketch of one-third of an HCP unit cell is shown:

Consider the tetrahedron labeled as \( JKLM \), which is reconstructed as:

The atom at point \( M \) is midway between the top and bottom faces of the unit cell--that is \( MH = c/2 \).

And, since atoms at points \( J, K, \) and \( M \), all touch one another, \( JM=JK=2R=a \), where \( R \) is the atomic radius.

Furthermore, from triangle \( JHM \),

\[
(JM)^2 = (JH)^2 + (MH)^2 \quad \text{or} \quad a^2 = JH^2 + \left(\frac{c}{2}\right)^2
\]

Now, we can determine the \( JH \) length by consideration of triangle \( JKL \), an equilateral triangle,

\[
\cos 30° = \frac{a/2}{JH} = \frac{\sqrt{3}}{2} \quad \text{or} \quad JH = \frac{a}{\sqrt{3}}
\]

Substituting this value for \( JH \) in the above expression yields

\[
a^2 = \frac{a^2}{3} + \frac{c^2}{4}
\]

Solving for \( c/a \)

\[
\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633
\]
How can we stack metal atoms to minimize empty space?

Which plane is more close-packed?

2-dimensions vs.

Now stack these 2-D layers to make 3-D structures
Stacking of HCP and FCC

• Most crystal structures in this class are described by comparing them to 1 of the 2 C.N.=12 HCP or FCC
• It is easiest to view HCP and FCC structures as stacked, close packed layers:

Single closest packed layer:

- 3-D structure is formed by stacking these layers upon one another.
- Atoms in the second layer fit into the valleys formed by 3 atoms of 1st layer:

Shaded spheres fit on top of the unshaded layer to maximize packing.

• There are two possible positions for the 3rd layer: #1: if the atoms take the positions labeled ‘1’, then they are directly above the atoms in the 1st layer thus the 3rd layer reproduces the 1st.
• If this pattern continues we have the AB|AB stacking sequence of the HCP structure.

• HCP Unit Cell:
  - 3D Projection

• 2D Projection

“equivalent”

Top layer
Middle layer
Bottom layer

Adapted from Fig. 3.3(a), Callister & Rethwisch 3e.
• #2: if, on the other hand, the atoms in the 3rd layer occupy the positions labeled ‘2’, then this layer is distinct from the 1st and the 2nd.
• The 4th layer must then repeat either 1st or the 2nd layer. If it repeats the 1st, then we have the ABC|ABC stacking sequence of the FCC (CCP) structure:
• If it repeats the 2nd, then ABCB|ABCB sequence such as in La, Nd, Pr and Pm (recall class7/slide 2: hc-packed)

• FCC Unit Cell:

Closed packed planes {111} of atoms
Corner has been removed to show stacking of close packed atoms

• ABC|ABC... Stacking Sequence
FCC – Stacking Sequence (continued)

2D Projections:

A sites

B sites

C sites
Comparing HCP and FCC

- The similarity of packing in these 2 structures is noteworthy, both have 12 CN, APF=0.74 and identical densities.
- The only significant difference between the structures is in the stacking sequence (ABC→AB), i.e. where the third close packed layer in FCC is positioned.
- Example, cobalt undergoes martensitic transformation from FCC to HCP at ~695 K.
- The lattice constant of FCC Co is 3.5446 Å, with a nearest-neighbor distance of 2.5064 Å.
- While for HCP Co, the lattice constants $a$ and $c$ are 2.5071 and 4.0695 Å, respectively, its nearest-neighbor distance is 2.4971 Å, and the ratio $c/a$ equals 1.623.
- Note that $AB$ in FCC would be equivalent to $AB$ in HCP, without the third close packed layer.