• Crystal structure of a material is the 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.*

• Each crystal structure is built by stacking unit cells and placing objects (motifs, basis) on the lattice points:

7 crystal systems in 3-D

14 crystal lattices in 3-D

\[ \alpha, \beta, \gamma \text{ are the interaxial angles} \]
Metallic Crystal Structures
(the simplest)

• Recall, that a) 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, and 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:
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)

- 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.

Reduced-sphere unit cells (8 total: $2 \times 2 \times 2$)
Simple Cubic (SC) – Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52

Contains 8 x 1/8 = 1 atom/unit cell

(see next slide for calculation)
Number of Lattice points (e.g. atoms/ions) per Unit Cell

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

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

\[
N \quad P \quad Q
\]

\[
\sqrt{2}a \quad \sqrt{3}a
\]

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.

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

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

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

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

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 = $4R = \sqrt{2}a$

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.

- Basal plane examples: Zn, Mg, α-Ti (room temp)

  Alternatively, 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 \((1/3 \hat{x}, 2/3 \hat{y}, 1/2 \hat{z})\).

- \(CN = 12\)
- Atoms/unit cell = 6
- APF = 0.74
- \(c/a = 1.633\)
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 \( JHM \), \( (JM)^2 = (JH)^2 + (MH)^2 \) or

\[
 a^2 = JH^2 + \left( \frac{c}{2} \right)^2
\]

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

\[
 \cos 30^\circ = \frac{a/2}{JH} = \frac{\sqrt{3}}{2}
\]

or \( JH = \frac{a}{\sqrt{3}} \)

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

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

solving for \( c/a \)

\[
 \frac{c}{a} = \frac{\sqrt{8}}{\sqrt{3}} = 1.633
\]
• How can we stack metal atoms to minimize empty space?
• Which plane is more close-packed?

2-dimensions vs. 3-dimensions

Now stack these 2-D layers to make 3-D structures
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
  - AB|AB... Stacking Sequence

2D Projection
- "equivalent"
  - Top layer
  - Middle layer
  - Bottom layer

Adapted from Fig. 3.3(a), *Callister & Rethwisch 3e*. 

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FCC – Stacking Sequence

• #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

Triangle represents (111) plane
2D Projections:

A sites
B sites
C sites

FCC – Stacking Sequence (continued)
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.