The Role
of
Crystal Structure - I

Smart Materials, Structures and Systems Laboratory
IIT Kanpur

ISSUES TO ADDRESS…

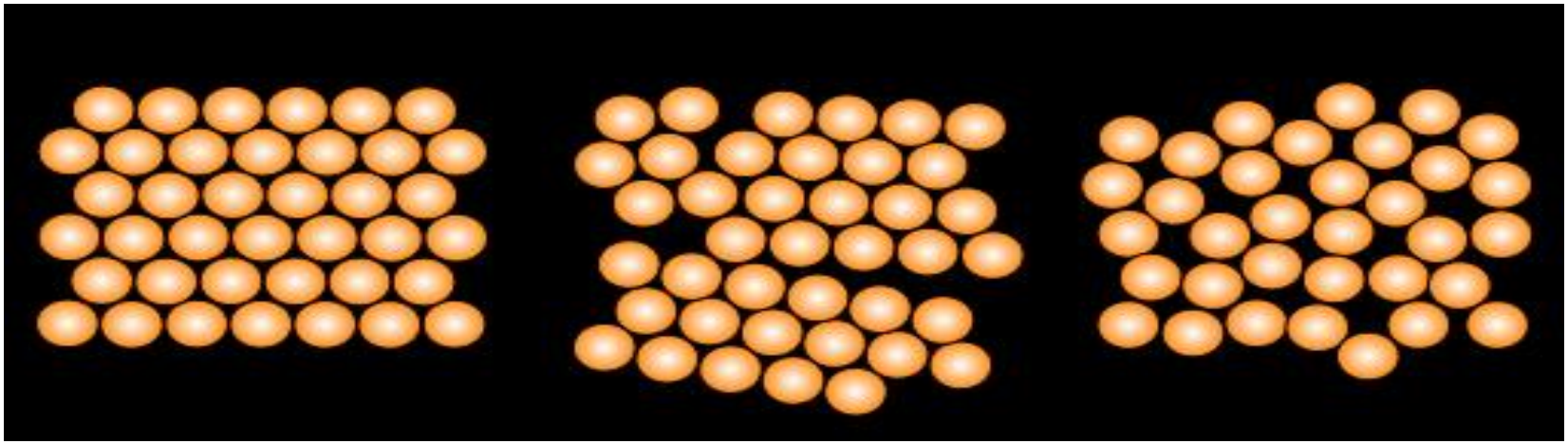
1. How do atoms assemble into solid structures?
2. When do material properties vary with sample (i.e., part) orientation?
3. How does density depend on the structure?

Importance of Crystallography

- **Crystallography** is the study of **atomic and molecular structure**.
- The study of crystal geometry helps to understand how the **atoms** in a material are **arranged** in order to interpret the **relationship** between **atomic structure** and **properties** of these materials namely-
  - ✓ Mechanical
  - ✓ Electrical
  - ✓ Magnetic
  - ✓ Optical
  - ✓ Metallurgical
- Common Technique: *X-ray* diffraction

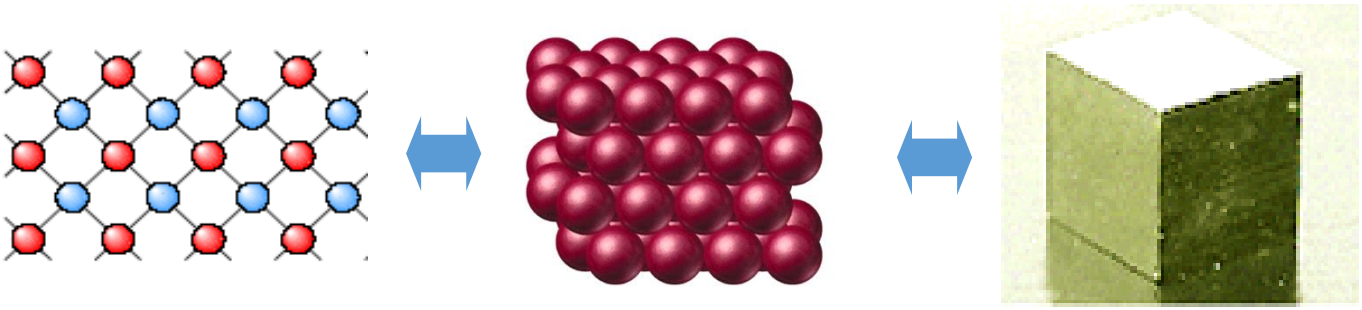
Solid Materials

- Crystalline
- Polycrystalline
- Amorphous



Crystalline Solid

- A **long range** structure exists in which **atoms** are **arranged** into unit cells and the **unit cells repeat** in a **regular orderly pattern**, forming a lattice (3-D).
- Directional properties - **Anisotropic** nature.
- **Sharp melting point**
- Example – Gold, Silver, Aluminum, etc.



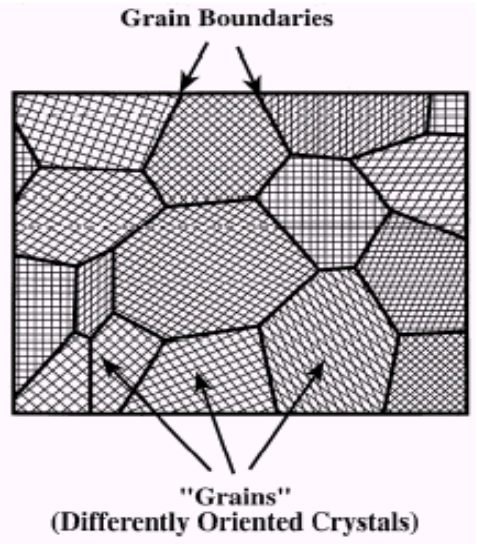
Crystalline solid

Polycrystalline Solid

- Made up of an **aggregate** of many small **single crystals** (also called crystallites or **grains**).
- **Across grain boundary**, the **orientation** of crystal **change**s.
- The grains are usually 100 nm - 100 microns in diameter.
- Polycrystalline material have a high degree of order over many atomic or molecular dimension.
- Polycrystals with grains that are <10 nm in diameter are called Nano-crystalline.
- Most engineering materials are polycrystalline.
- **Properties may or may not vary** with **direction**.
- Example – Common steel is polycrystalline.

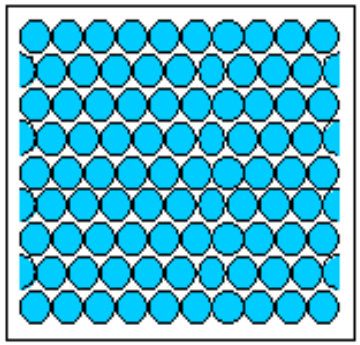
  If **grains** are "**textured** (due to rolling)", then **anisotropic.**

  If **grains** are **random**, then **isotropic** (E ≈ 210 GPa).

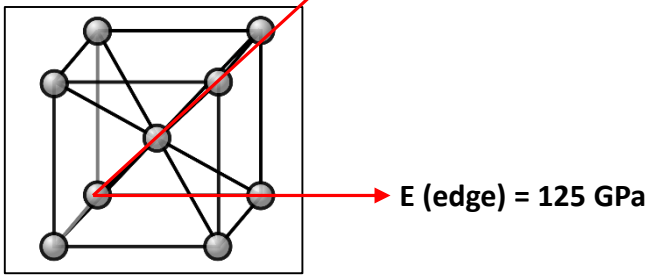


Reference: W.D Callister

Single Crystal



- Only one grain – no grain boundaries.
- Formed by uniform cooling of liquid material.
- Have **a high degree of order** throughout the ***entire volume of the material***
- Useful for applications where grain boundaries are harmful.
- For example, high temperature deformation or creep resistance (as **creep** takes place by **grain boundary sliding**) - single crystal turbine blades - Ni-based super alloy gas turbine blades (withstand creep at high temperature due to lack of grain boundaries).
- Other examples – Diamond, Semi-conductors.
- BCC* Iron

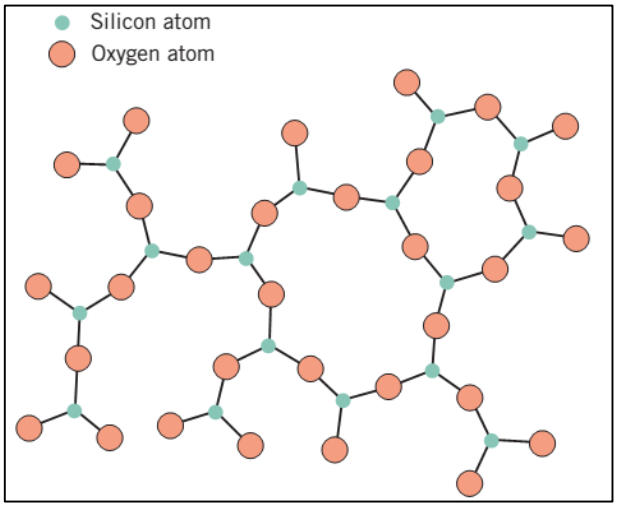


* BCC will be discussed in further slides

Amorphous Solid

- The atoms or molecules are arranged in an **irregular manner.**
- No periodic packing.
- **No directional properties** - Isotropic substances.
- Occurs for complex structures, rapid cooling.

Example : Glass, Plastic, rubber, etc.



Silica

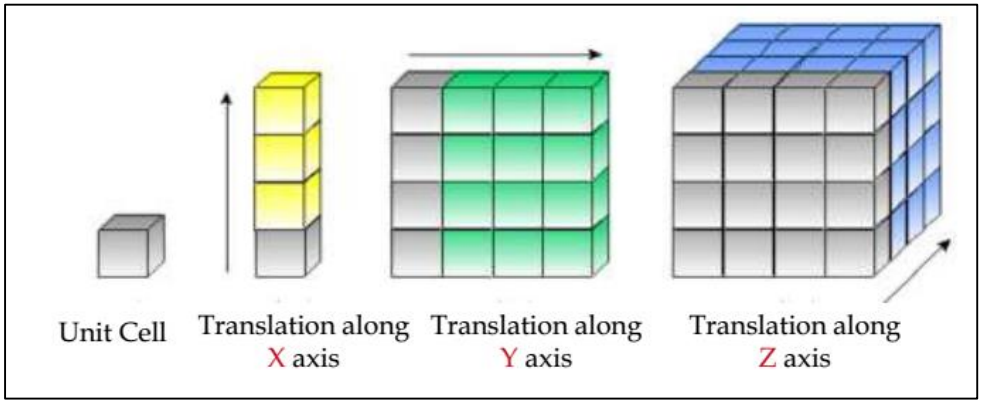
Reference: W.D Callister, 7Ed.

Unit Cell

- ✓ The **smallest block** or geometrical figure from which the crystal is build up by repetition in three dimensions.

  (or)

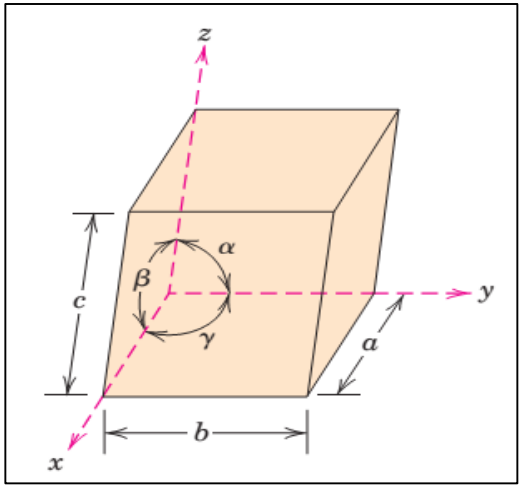
- ✓ The fundamental grouping of particles which are repeating entities.
- ✓ Unit cell is basic structural unit or building blocks of the crystal structure.
- ✓ A crystalline solid can be constructed from a **unit cell** plus **translation operators.**



3-D Unit Cell

- ✓ Defined by three vectors **a,b,c** and the angles **α, β, γ** between them.
- ✓ To define any crystal structure these 6 lattice parameters are essential.

α = angle between **b** and **c**
B = angle between **a** and **c**
γ = angle between **b** and **a**



A unit cell with *x*, *y*, and *z* coordinate axes, axial lengths (*a*, *b*, *c*) and interaxial angles α, β, γ

Reference: W.D Callister, 7Ed.

Lattice / Basis

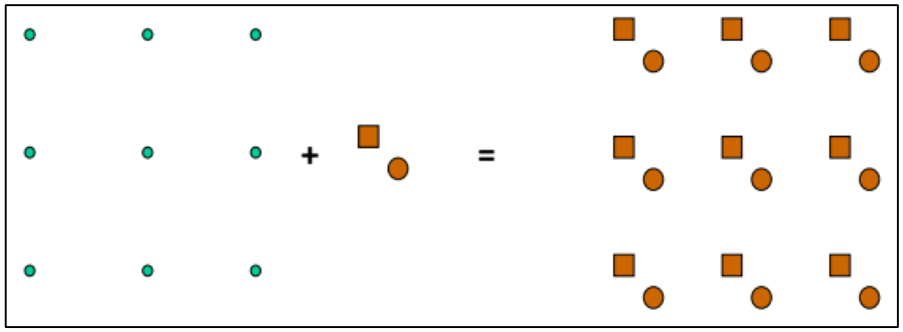
Lattice

Array of points in space, in which every point has identical environment with respect to all other points.

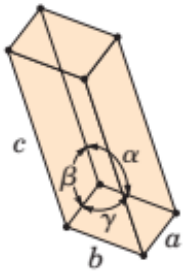
Basis

Single atom or group of atoms identical in composition and orientation in space

Lattice + Basis = Crystal Structure



Other types of Lattice

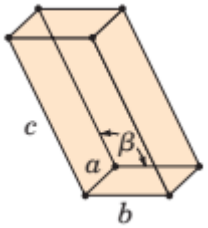


$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma$

$$V = abc\sqrt{1 - cos2\alpha - cos2\beta - cos2\gamma + 2cos\alpha cos\beta cos\gamma}$$

Triclinic

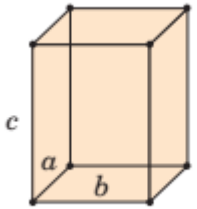


$a \neq b \neq c$

$\alpha = \gamma = 90^0, \beta \neq 90^0$

$V = abc \sin\beta$

Monoclinic



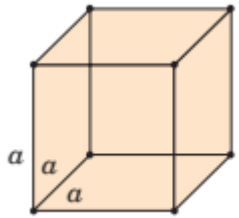
$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^0$

$V = abc$

Orthorhombic

Other types of Lattice



a = b = c

$\alpha = \beta = \gamma = 90^0$

$V = a^3$

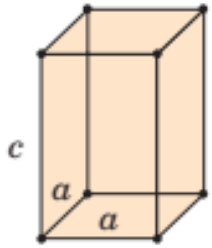
Cubic

a = b = c

$\alpha = \beta = \gamma \neq 90^0$

$V = a^3\sqrt{1 - 3cos^2\alpha + 2cos^3\alpha}$

Rhombohedral (Trigonal)

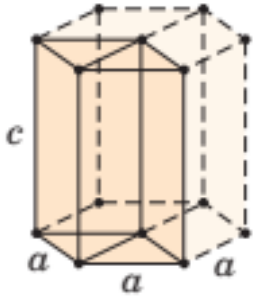


a = b ≠ c

$\alpha = \beta = \gamma = 90^0$

$V = a^2c$

Tetragonal



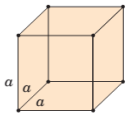
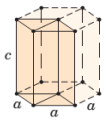
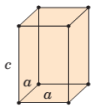
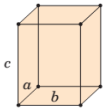
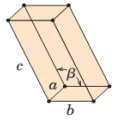
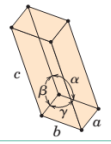
a = b ≠ c

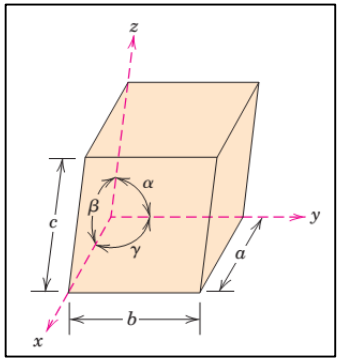
$\alpha = \beta = 90^0$, $\gamma = 120^0$

$V = \frac{\sqrt{3}}{2}a^2c$

Hexagonal

Lattice Parameter Relationships and Unit Cell Geometries for the 7 Crystal Systems

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

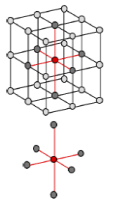


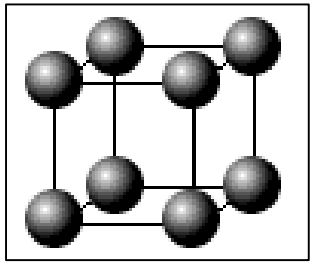
A unit cell with *x*, *y*, and *z* coordinate axes, axial lengths (*a*, *b*, *c*) and interaxial angles α, β, γ

Reference: W.D Callister, 7Ed.

Simple Cubic Structure (SCC)

- ✓ The unit cell consists of **eight corner atoms** and all these corner atoms contribute only one effective atom for the lattice.
- ✓ **Coordination No.** = the number of atoms immediately surrounding a central atom in a crystal = **6**
- ✓ Rare due to poor packing (only Polonium, Po).





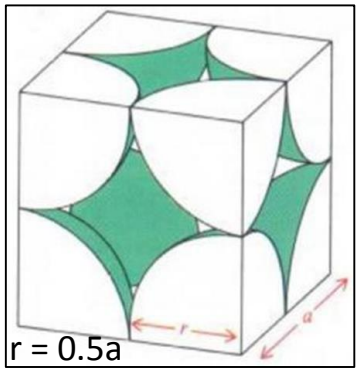
Reduced-sphere unit cell

Number of atoms per unit cell, n = (1/8) x 8 = 1

Atomic packing factor = $\frac{Volume\ of\ atoms\ in\ a\ unit\ cell}{Total\ unit\ cell\ volume}$

$$= \frac{(atoms/unit\ cell)\ x\ (volume/atom)}{a^3}$$

$$= \frac{1\ x\ \frac{4}{3}\pi(0.5a)^3}{a^3} = 0.52$$



r = 0.5a

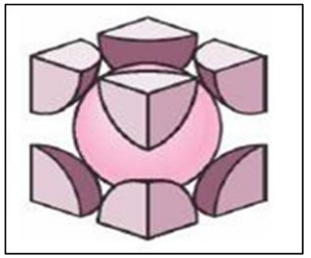
Hard –sphere unit cell

- The atoms in SCC occupy 52% of the space and the rest (48%) is void/interstitial space.

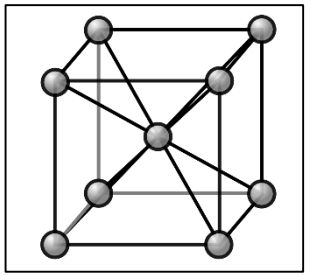
Reference: W.D Callister

Body-Centered Cubic Structure (BCC)

- ✓ BCC structure has 8 corner atoms and 1 body center atom.
- ✓ The center atom is not shared by any of the unit cells.
- ✓ Coordination No. = 8
- ✓ **Example :** Chromium(Cr) , Iron(Fe) , Molybdenum(Mo) , Potassium(K) , Sodium(Na) , Tantalum(Ta) , Vanadium(V)



Hard –sphere unit cell



Reduced-sphere unit cell

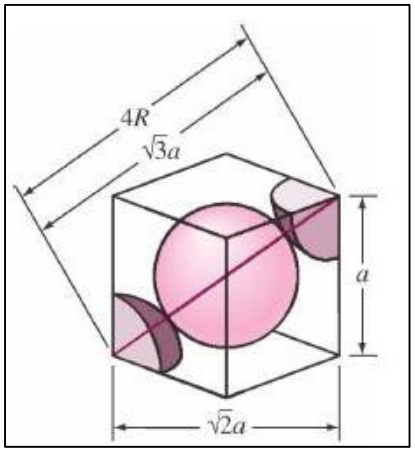
Number of atoms per unit cell, n = (1/8) x 8 + 1 = 2

Atomic packing factor = $\frac{Volume\ of\ atoms\ in\ a\ unit\ cell}{Total\ unit\ cell\ volume}$

$= \frac{(atoms/unit\ cell)\ x\ (volume/atom)}{a^3}$

$= \frac{2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3} = 0.68$

- The atoms in BCC occupy 68% of the space and the rest (32%) is void/interstitial space.
- BCC is tightly packed than simple cubic structure (52%).



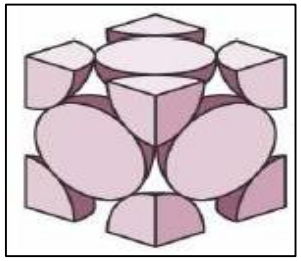
$4R = \sqrt{3}\,a$

BCC

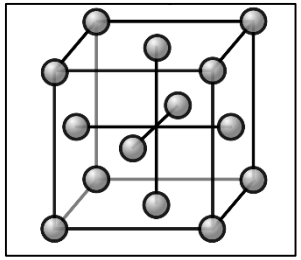
Reference: W.D Callister

Face-Centered Cubic Structure (FCC)

- ✓ FCC structure has 8 corner atoms and each **face has one center** atom.
- ✓ The center atom is not shared by any of the unit cells.
- ✓ Coordination No. = 12
- ✓ **Example :** Aluminum(Al), Copper(Cu), Gold(Au), Lead(Pb), Nickel(Ni), Platinum(Pt) , Silver(Ag)



Hard –sphere unit cell



Reduced-sphere unit cell

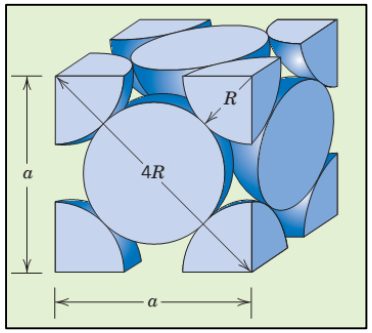
Number of atoms per unit cell, n = (1/8) x 8 + 6 x (1/2) = 4

Atomic packing factor = $\frac{Volume\ of\ atoms\ in\ a\ unit\ cell}{Total\ unit\ cell\ volume}$

$$= \frac{(atoms/unit\ cell)\ x\ (volume/atom)}{a^3}$$

$$= \frac{4\ x\ \frac{4}{3}\pi\left(\frac{\sqrt{2}\,a}{4}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

- The atoms in BCC occupy 74% of the space and the rest (26%) is void/interstitial space.
- FCC is tightly packed than BCC (68%).



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

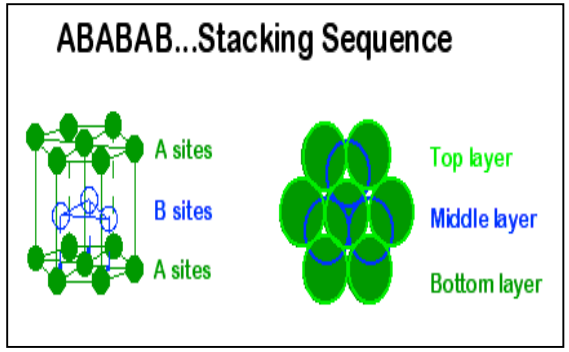
FCC

Reference: W.D Callister

Hexagonal Close Packing Structure (HCP)

- ✓ ABABAB…..stacking sequence
- ✓ The center atom is not shared by any of the unit cells.
- ✓ Coordination No. = 12

Example : Magnesium(Mg), Cobalt(Co), Zirconium(Zr), Titanium(Ti), Beryllium(Be), Zinc(Zn), Cadmium(Cd)



Number of atoms per unit cell, n = 12x(1/6) + 2x(1/2) + 3 = 6

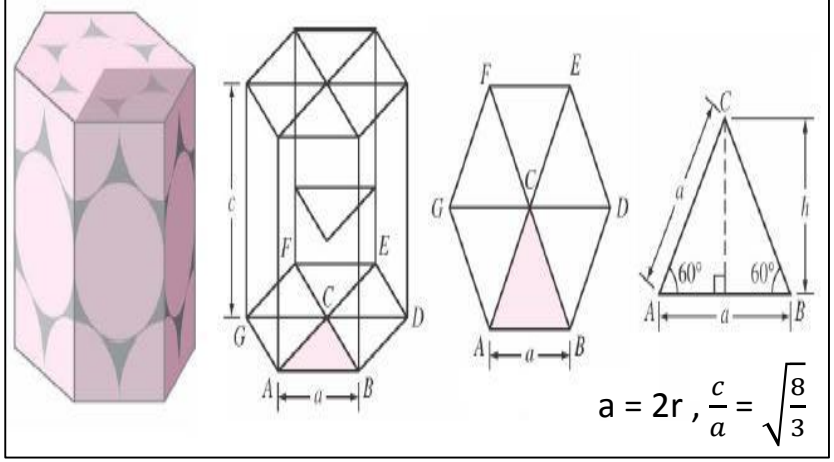
Atomic packing factor = $\frac{\textit{Volume of atoms in a unit cell}}{\textit{Total unit cell volume}}$

$$= \frac{(\textit{atoms/unit cell}) \times (\textit{volume/atom})}{c \times \textit{area of base}}$$

$$= \frac{6 \times \frac{4}{3}\pi(r)^3}{c \times (6 \times \frac{\sqrt{3}}{4}a^2)} = \frac{2\pi}{3\sqrt{3}}\frac{a}{c} = \frac{\pi}{3\sqrt{2}}$$

= 0.74

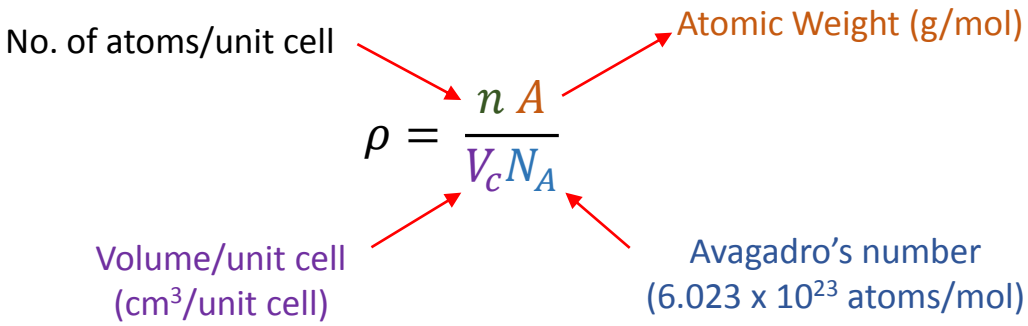
- The atoms in HCP occupy 74% of the space and the rest (26%) is void/interstitial space.



$a = 2r$, $\frac{c}{a} = \sqrt{\frac{8}{3}}$

Reference: W.D Callister

Theoretical Density



Example : Copper

- Crystal structure = FCC (4 atoms/unit cell)
- Atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- Atomic radius, R = 0.128 nm (1nm = 10^{-7} cm)
- $V_C = a^3$; For FCC : $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23}$ cm^3
- Result : Theoretical $\rho_{Cu} = 8.89$ g/cm^3

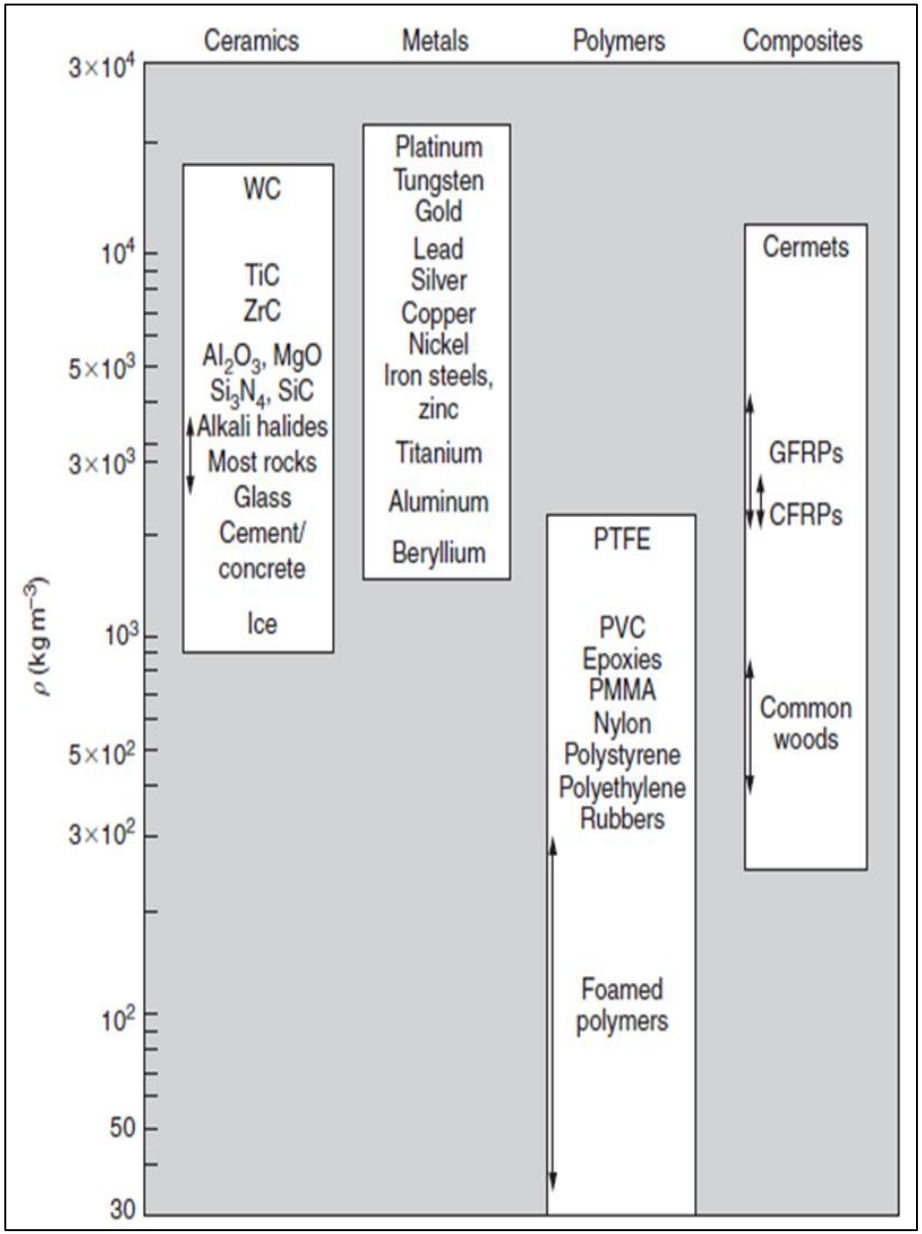
  Actual $\rho_{Cu} = 8.94$ g/cm^3

Density of Material Classes

$$\rho_{Metals} \geq \rho_{Ceramics} \geq \rho_{Polymers}$$

Why ?

- ✓ **Metals have**
  - **Close Packing (metallic bonding).**
  - **Large atomic masses.**
- ✓ **Ceramics have less dense packing (covalent bonding).**
- ✓ **Polymers have poor packing (often amorphous).**
- ✓ **Composites average values**



Reference: Engineering Materials 1: Ashby & Jones, 4th Ed.