ENGINEERING MATERIALS (ME 281)

Structure of Crystalline Solids

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Lecture outline

➢ **Crystal Structure**

- Fundamental concepts

- Metallic crystal structures

- Computation of density in metals

- Crystal systems and types of solids

➢ **Crystallographic Directions and Planes**

- Miller indices

- Linear and planar densities

- Anisotropy

Learning Objectives

After this chapter, you should be able to do the following:

➢ Explain the common crystal structures in metals.

➢ Define the terms coordination number and atomic parking factor

➢ Identify specific directions and planes in crystals using Miller indices.

➢ Explain the concept of linear and planar densities

➢ Explain the terms polymorphism, allotropy, polycrystalline and amorphous solids

➢ Define Isotropy and Anisotropy

Crystal Structure

Fundamental concepts

➤ A **crystal** is a solid composed of atoms, ions, or molecules arranged in a repeated (periodic) pattern at regular intervals in three dimensions.

➤ A **crystal structure** is the ordered arrangement of atoms, ions or molecules in a crystalline material.

➤ A **crystalline material** consists of primarily organized crystal structure.

➤ *Atoms (or ions) are considered as hard spheres with well-defined radii.*
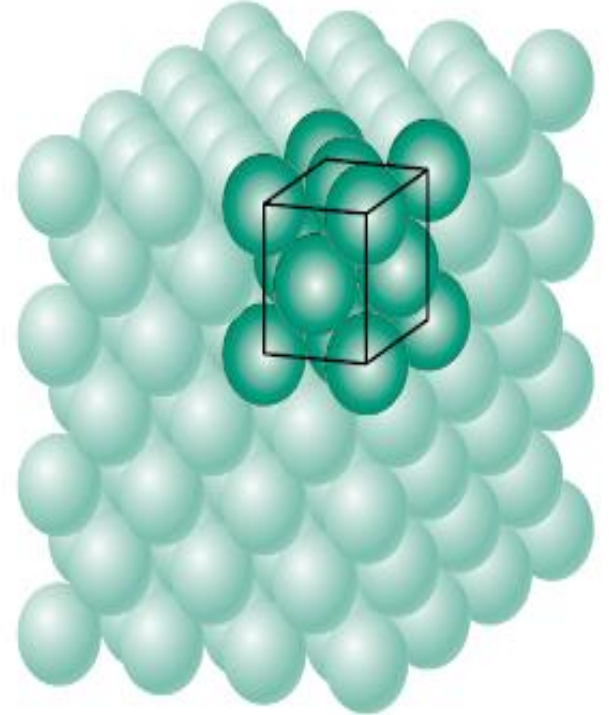
➤ The term **lattice** represent a three-dimensional periodic array of points that coincides with atom positions.

➤ *The **Unit cell** is the smallest repeatable entity that can be used to completely represent a crystal structure.*

Crystal Structure

The Unit cell is characterized by:

➢ Type of atoms and their radii, R

➢ Cell dimensions (lattice spacing a, b and c) in terms of R.

➢ Angle between the axis, α, β and γ

➢ n, number of atoms per unit cell.

➢ CN, the coordination number

➢ APF, the atomic packing factor

Unit Cell
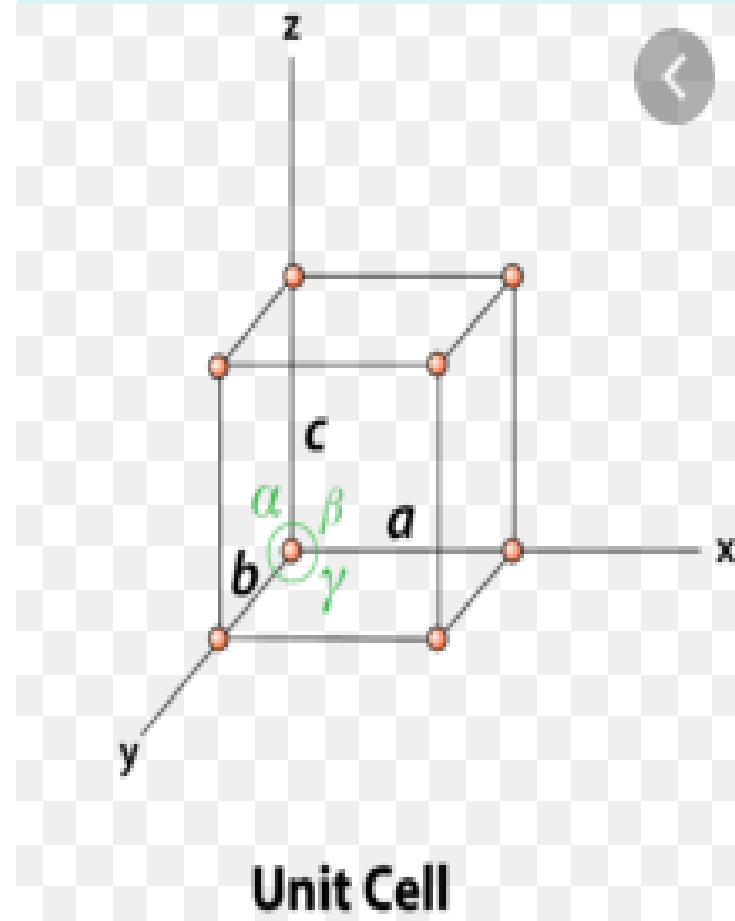
Crystal Structure: Metals

➤ The atomic bonding is metallic and non-directional in nature.

➤ For metals, each sphere represents an ion core with atomic radius, R (typically 0.1 - 0.2 nm).

➤ Common crystal structures for most metals:

• Simple cubic (SC)   Face-centered cubic (FCC)

• Body-centered cubic (BCC) Hexagonal close-packed (HCP)

➤ Two important characteristics: coordination number and atomic packing factor.

➤ The **coordination number** refers to the number of closest neighboring atoms to which an atom is bonded in a crystalline solid.

➤ The **atomic parking factor (APF)** is the ratio of total atomic volume to the unit cell volume.
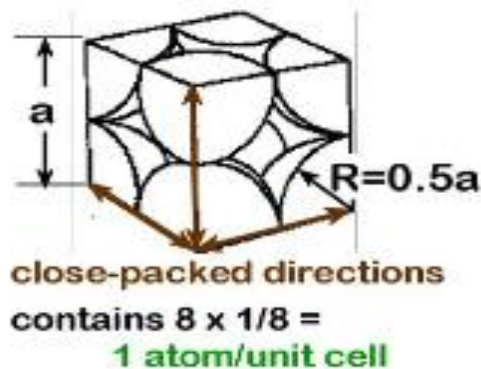
$$APF = \frac{Volume\ of\ atoms\ in\ unit\ cell}{Volume\ of\ unit\ cell} = \frac{V_s}{V_c}$$

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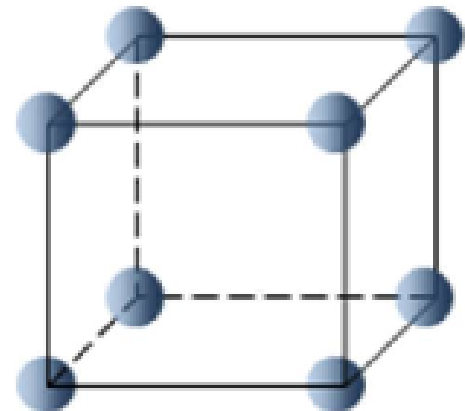# Crystal Structure: Metals

Simple Cubic (SC) Structure

➢ Eight atoms with one at each corner of the cubic unit cell.

➢ Polonium has this crystal structure.

➢ The hard spheres touch one another along cube edge (**cube edge length, a =2R**)

➢ **The coordination number, CN = 6**

➢ **Number of atoms per unit cell, n = 1**

• 8 corner atoms shared by eight cells, 8 x 1/8 = 1

➢ **Atomic packing factor, APF = 0.52**

➢ All atoms are equivalent.

• APF for a simple cubic structure = 0.52

$$APF = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

atoms / unit cell = 1

volume / atom = $\frac{4}{3}\pi (0.5a)^3$

volume / unit cell = a^3

R=0.5a

close-packed directions

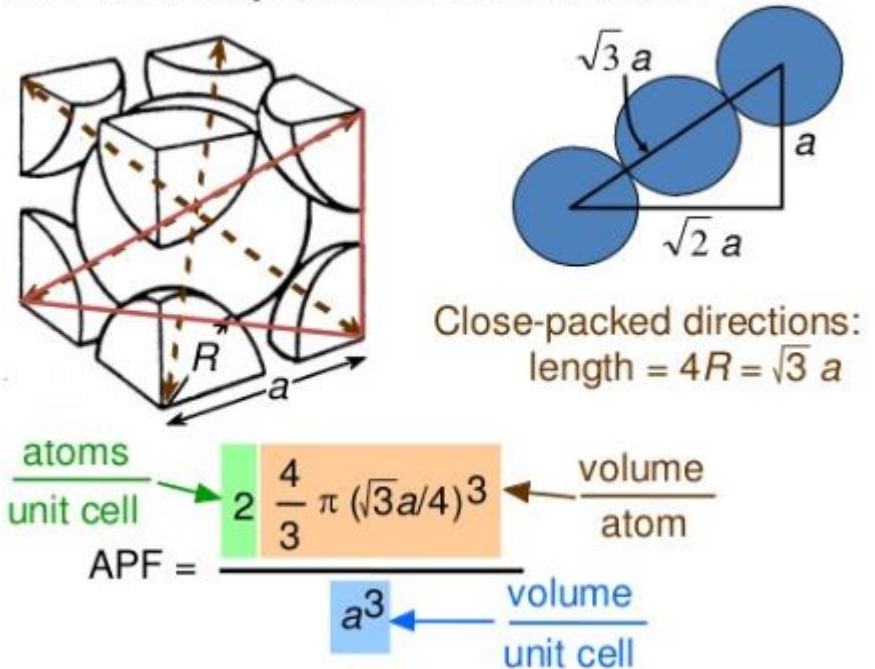contains 8 x 1/8 = 1 atom/unit cell

Crystal Structure: Metals

Body-Centered Cubic (BCC) Structure

➢ Atoms at each corners and at center of cubic unit cell

➢ Li, Na, K, Cr, Ba, α-Fe, etc. have this structure

➢ The hard spheres touch one another along cube diagonal (**cube edge length, a =4R/√3**)

➢ **The coordination number, CN = 8**

➢ **Number of atoms per unit cell, n = 2**

• Center atom shared by no other cells, 1 x 1 = 1

• 8 corner atoms shared by eight cells, 8 x 1/8 = 1

➢ **Atomic packing factor, APF = 0.68**

➢ Corner and center atoms are equivalent.

• APF for a body-centered cubic structure = 0.68

$$\sqrt{3}\,a$$

$$a$$

$$\sqrt{2}\,a$$

Close-packed directions:
length $= 4R = \sqrt{3}\,a$

$$\frac{atoms}{unit\ cell} \rightarrow \quad APF = \dfrac{2\ \dfrac{4}{3}\pi\,(\sqrt{3}a/4)^3 \leftarrow \dfrac{volume}{atom}}{a^3 \leftarrow \dfrac{volume}{unit\ cell}}$$
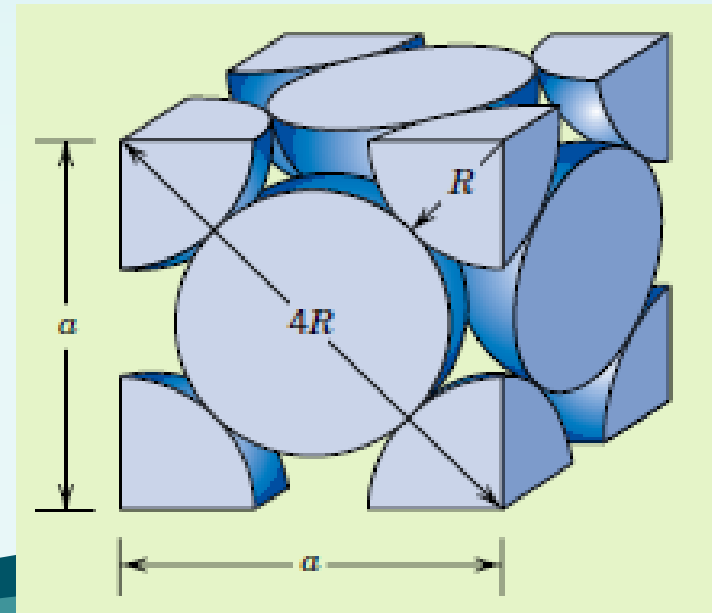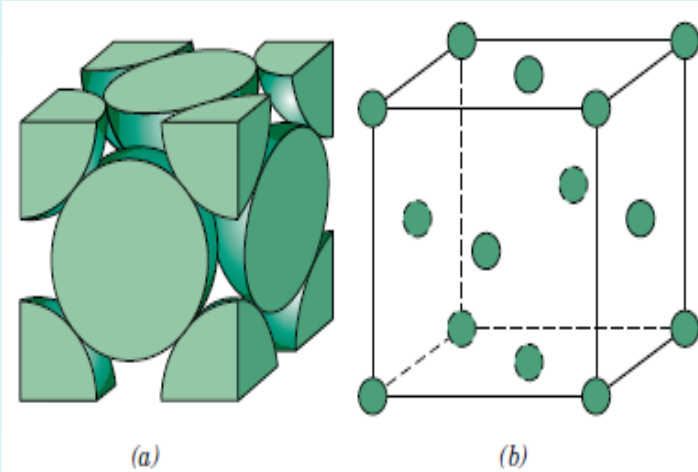
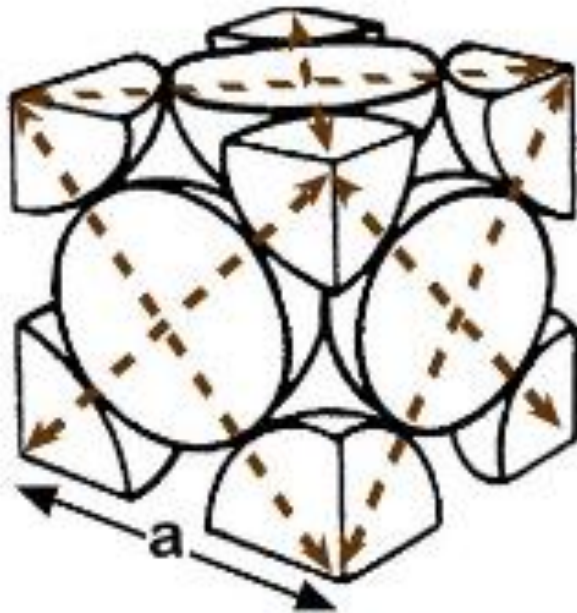# Crystal Structure: Metals

Face-Centered Cubic (FCC) Structure

➢ Atoms are located at each of the corners and on the centers of all the faces of the cubic unit cell

➢ Cu, Al, Ag, Au have this crystal structure.

➢ The hard spheres touch one another across a face diagonal (**cube edge length, a = 2R√2**)

(a)   (b)

➢ **The coordination number, CN = 12**

➢ **Number of atoms per unit cell, n = 4**

• 6 face atoms shared by two cells,

  6 x 1/2 = 3

• 8 corner atoms shared by eight cells,
  8 x 1/8 = 1

➢ **Atomic packing factor, APF = 0.74**

Crystal Structure: Metals

- **APF** for a Face-centered cubic structure = **0.74**

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

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

$$\frac{atoms}{unit\ cell} \rightarrow \qquad \frac{volume}{atom}$$

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

$$\frac{volume}{unit\ cell}$$

Crystal Structure: Metals

Hexagonal Closed-Packed (HCP) Structure

➢ HCP is one more common structure in metallic crystals

➢ Cd, Mg, Zn, Ti, etc. have this structure.

➢ 6 atoms form regular hexagon, surrounding one atom in center, another plane is situated halfway up unit cell (c-axis),with 3 additional atoms situated at interstices of hexagonal (closed-packed) plane.

(a)

(b)
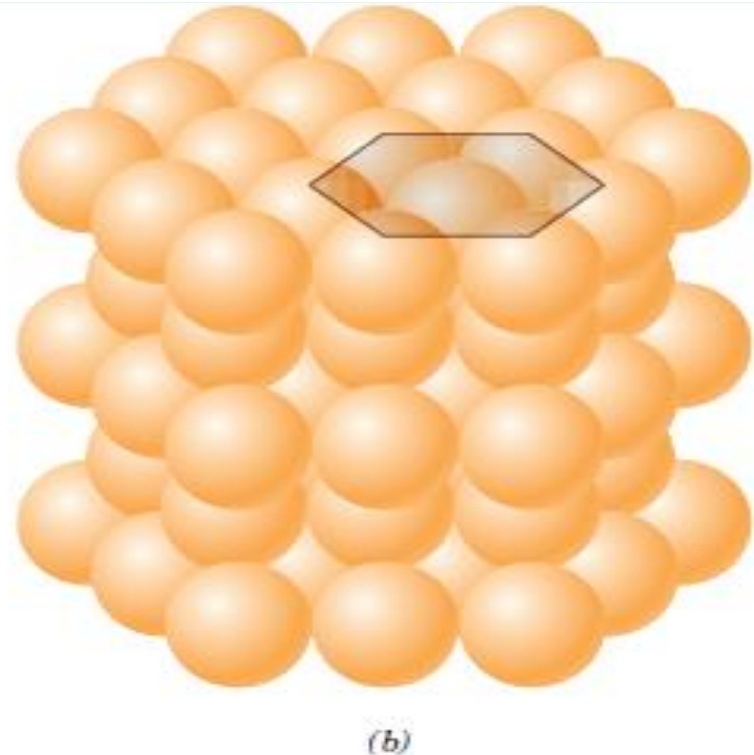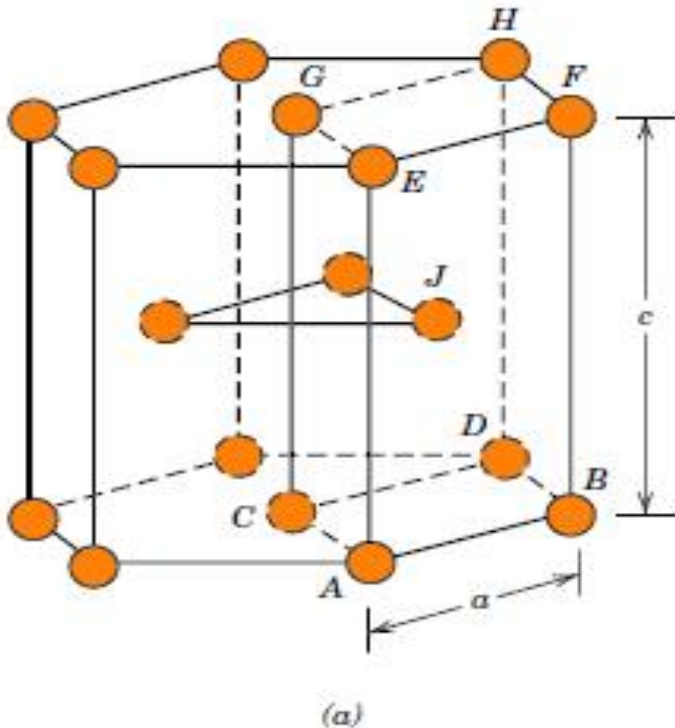
Density Computation: Metals

➢ Theoretical density of a metallic solid crystal structure is given by:

$$\rho = \frac{nA}{V_c N_A}$$

- n = number of atoms associated with each unit cell
- A = atomic weight
- Vc = volume of the unit cell
- N_A = Avogadro's number (6.022 x 10^{23} atoms/mol)

Density Computation: Metals

➢ Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density and compare answer with its measured density.

Solution

➢ The crystal structure is FCC. Therefore, number of atoms per unit cell, n, is 4. Also, atomic weight A copper (Cu) is given as 63.5 g/mol. The unit cell volume V_c for FCC is determined as $16\,R^3\sqrt{2}$ where R, the atomic radius, is 0.128 nm.

➢ Substituting the various parameters into equation gives

$$\rho = \frac{\left(4\,\frac{atoms}{unit\ cell}\right) \times \left(63.5\,\frac{g}{mol}\right)}{\left[16\sqrt{2}\,(1.28\,\times\,10^{-8})^3\,\frac{cm^3}{unit\ cell}\right] \times \left(6.022\,\times\,10^{23}\,\frac{atoms}{mol}\right)} = 8.89\ g/cm^3$$
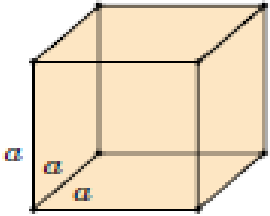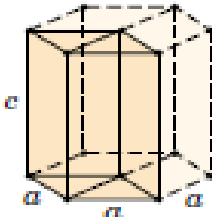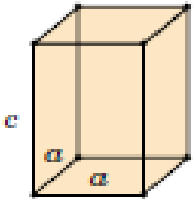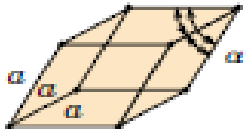
The density of copper in literature is 8.94 g/cm³, which is in very close to the calculated value obtained.
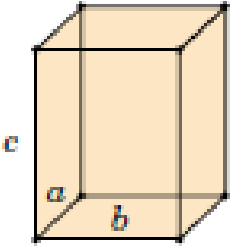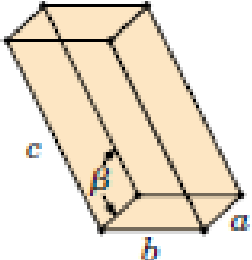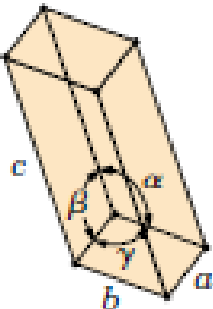
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Crystal Systems

➢ A crystal system is a set of groups into which crystals are commonly classified according to the relative lengths and inclinations of their axes or according to their respective symmetries.

➢ The unit cell geometry is defined completely in terms of six parameters: three edge lengths a, b, c, and three inter-axial angles α, β, γ and are referred to as the **lattice parameters** of a crystal structure.

➢ There exist seven different combinations of a, b, and c, and α, β, and γ, each representing a distinct crystal system.

➢ The seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic, and triclinic.

➢ Cubic system has the greatest degree of symmetry.

➢ Triclinic system has the least symmetry.
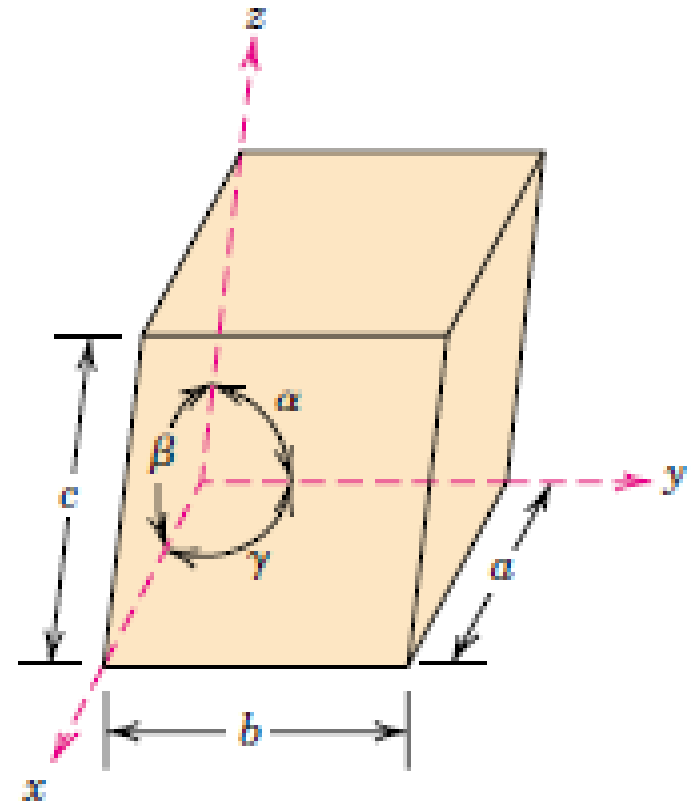
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Crystal Systems: Lattice Parameters

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)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	

Crystal Systems: Lattice Parameters

| Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Some Important Definitions

➢ **Polymorphism:** Metals, as well as non-metals, with more than one crystal structure. In elemental solids, it is often referred to as allotropy.

➢ **Single crystals:** solid with one whole crystal having regular geometric structure with flat faces.

➢ **Polycrystalline**: A solid composed of many crystalline grains, not aligned with each other. The grains can be more or less aligned with respect to each other. Where they meet is called a grain boundary.

➢ **Non-crystalline (Amorphous) solids**: A solid that lacks the long-range order that is characteristic of a crystal.

Crystallographic Directions and Planes

➤ **Miller Indices:** A system of notation required to identify a particular direction (s) or plane(s) to characterize the arrangement of atoms in a unit cell.
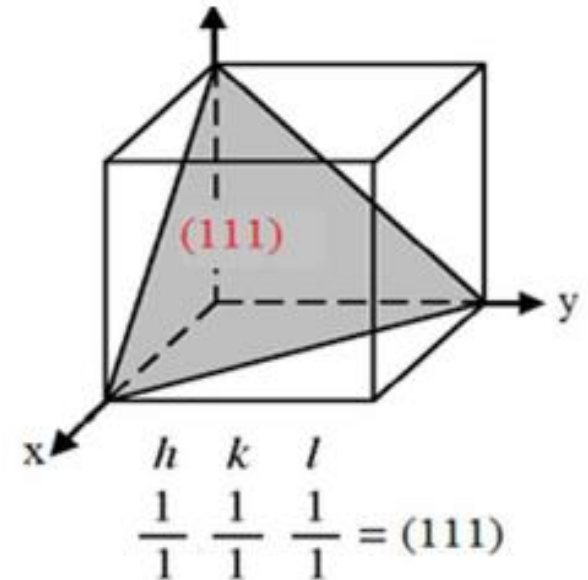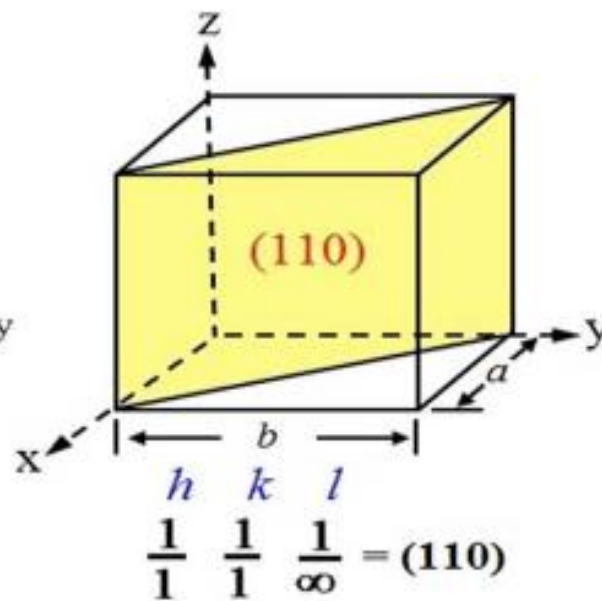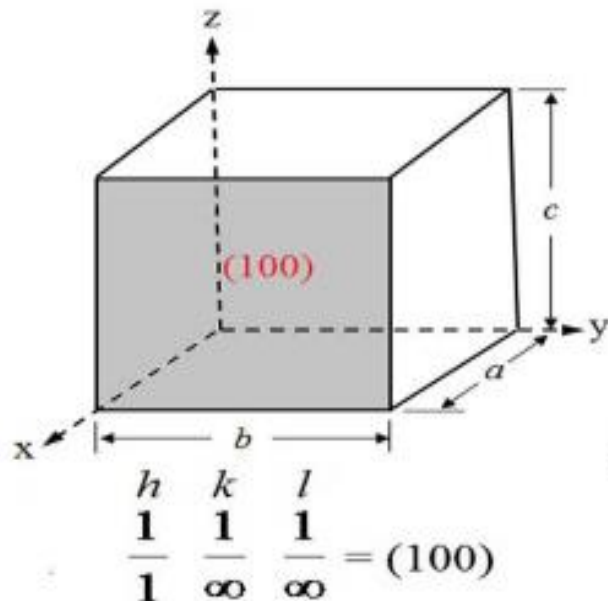
Steps to define crystallographic directions in cubic crystal

- A vector of convenient length is placed parallel to the required direction.

- The length of the vector projection on each of the three axes are measured in unit cell dimensions.

- The three numbers are converted to smallest integer values, known as indices, by multiplying or dividing by a common factor.

- The three indices are enclosed in square brackets, [hkl]. A family of directions is represented by <hkl>.
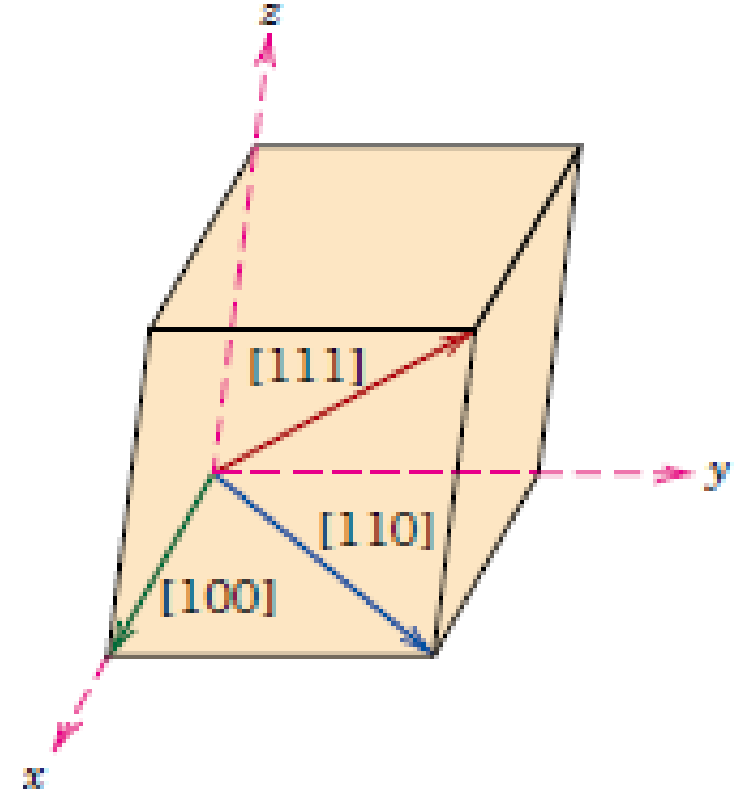
Crystallographic Planes

➢ Miller indices of a plane indicated by h k l are given by the reciprocal of the intercepts of the plane on the three axes.

➢ The plane, which intercepts the X at 1 (one lattice parameter) and is parallel to the Y and Z axes, has Miller indices h = 1/1 = 1, k = 1/∞ = 0, l = 1/∞ = 0.

➢ Formulas involving Miller indices are very similar to related formulas from analytical geometry.

$$\begin{array}{ccc} h & k & l \\ \dfrac{1}{1} & \dfrac{1}{\infty} & \dfrac{1}{\infty} \end{array} = (100)$$

$$\begin{array}{ccc} h & k & l \\ \dfrac{1}{1} & \dfrac{1}{1} & \dfrac{1}{\infty} \end{array} = (110)$$

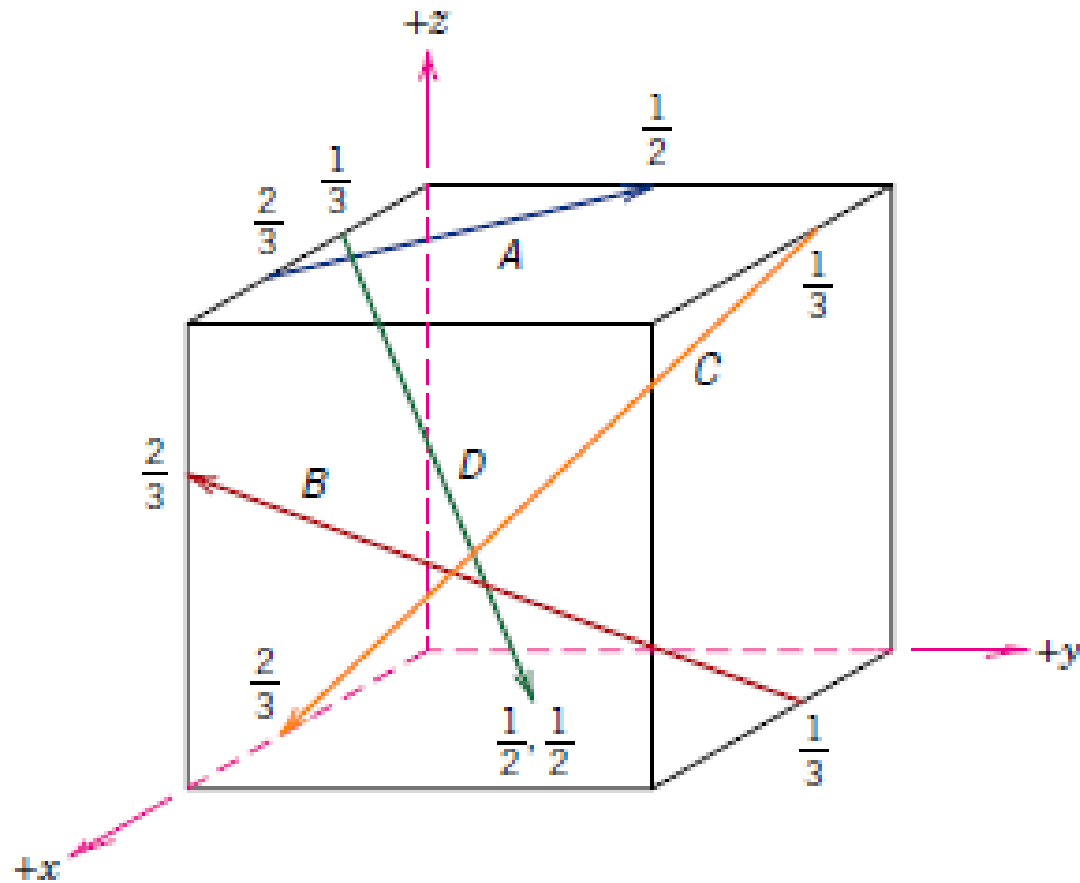$$\begin{array}{ccc} h & k & l \\ \dfrac{1}{1} & \dfrac{1}{1} & \dfrac{1}{1} \end{array} = (111)$$

Crystallographic Planes

Steps to define crystallographic planes in cubic crystal;

➤ Determine the intercepts of the plane along the crystallographic axes, in terms of unit cell dimensions.

➤ If plane is passing through origin, there is the need to construct a plane parallel to original plane.

➤ Take the reciprocals of these intercept numbers.

➤ Clear fractions.

➤ Reduce to set of smallest integers.

➤ The three indices are enclosed in parenthesis, (hkl).
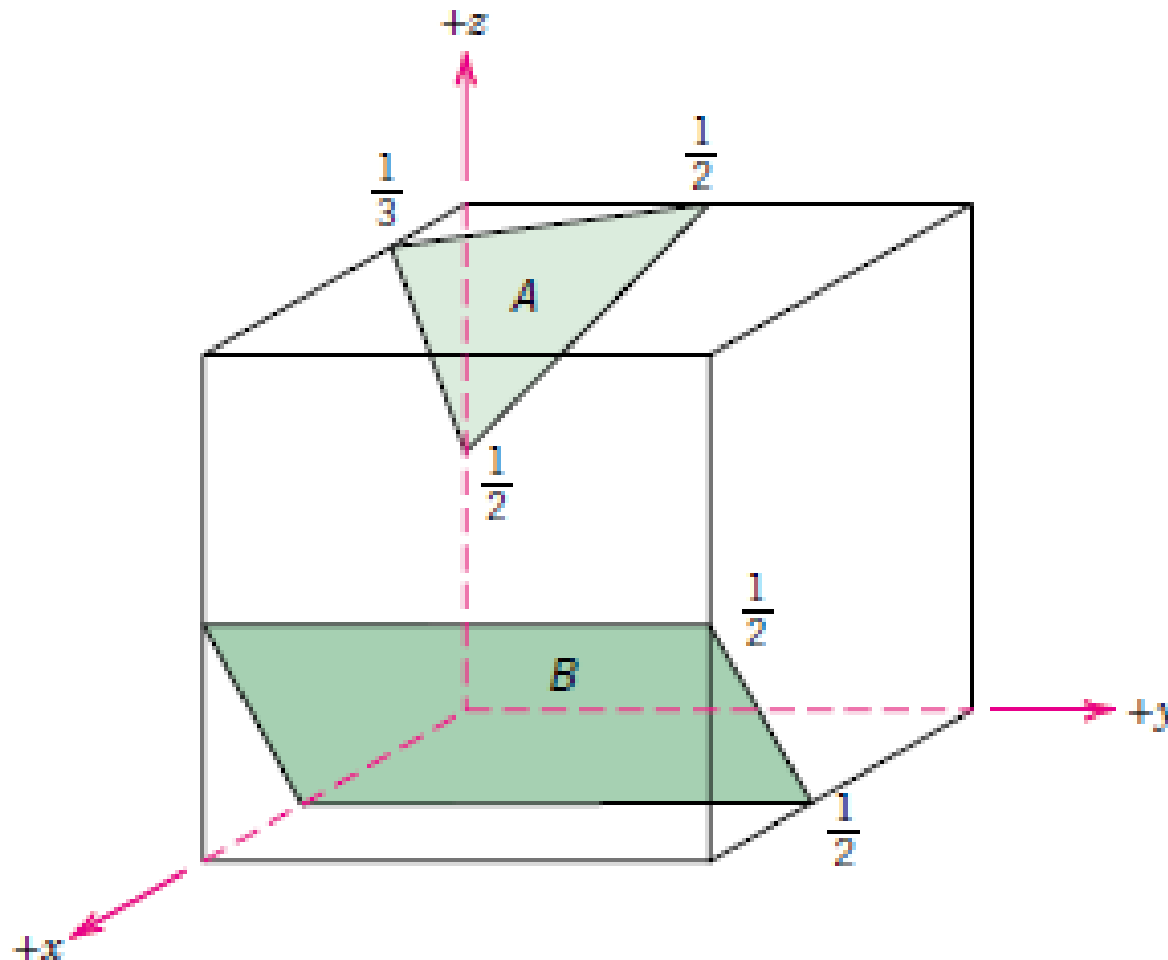
➤ A family of planes is represented by {hkl}

Crystallographic Directions: Example

➤ Determine the indices for the directions shown in the following cubic unit cell

➢ Determine the Miller indices for the planes shown in the following unit cell:
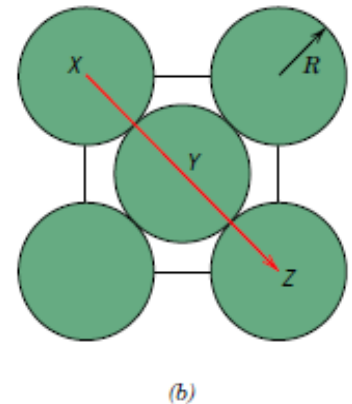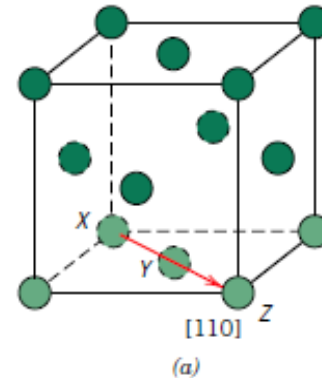
Linear and Planar Densities

Linear Density

➢ It is defined as the number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction.

$$LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$

➢ The units of linear density is reciprocal length (e.g., nm^{-1}, m^{-1}).

➢ Determine the linear density of the [110] direction for the FCC crystal structure.

Note

➢ It is necessary to take into account the sharing of atoms with adjacent unit cells

$$LD_{[110]} = \frac{\frac{1}{2} atom + 1\ atom + \frac{1}{2} atom}{R + R + R + R} = \frac{2\ atoms}{4R} = \frac{1}{2R}$$

Linear and Planar Densities

Planar Density

➤ It is defined as the number of atoms per unit area the number of atoms that are centered on a particular crystallographic plane.

$$PD = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$

➤ The units for planar density is reciprocal area (e.g., nm^{-2}, m^{-2}).

➤ Determine the planar density of the [110] direction for the FCC crystal structure.

➤ $Area\ of\ plane\ (110) = a \times fd = a \times$
$\sqrt{(a^2 + a^2)} = a \times \sqrt{2}a = \sqrt{2}a^2$

➤ $Cube\ edge\ length_{FCC}, a = 2R\sqrt{2} \Rightarrow a^2 = 8R^2$

➤ $Area\ of\ plane\ (110) = \sqrt{2}a^2 = 8R^2\sqrt{2}$

(a)   (b)
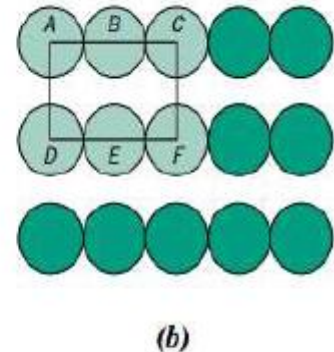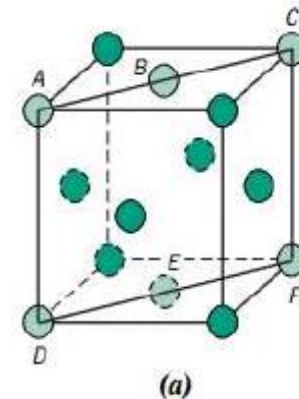
$$PD_{[110]} = \frac{\frac{1}{4} + \frac{1}{2} + \frac{1}{4} + \frac{1}{4} + \frac{1}{2} + \frac{1}{4}}{8R^2\sqrt{2}} = \frac{2}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}}$$

Anisotropy

➢ The properties of materials mostly depend on the crystal structure.

➢ However, crystals are not symmetric in all directions, or the crystal planes are not the same with respect to atomic density or packing.

➢ Hence, the physical properties of crystalline solids show different values when measured along different directions in the same crystals.

➢ This directionality of properties is termed as **Anisotropy**.

➢ It is associated with the variation of atomic or ionic spacing with crystallographic direction.

➢ Substances whereby the measured properties are independent of direction of measurement are **isotropic**.

Lecture Ends