

# Bonding of Atoms into Solid Structures

## - Primary Bond Types

- Ionic
- Covalent (*semiconductors*)
- Metallic (*metals*)
- Mixed ionic + covalent (*ceramics*)

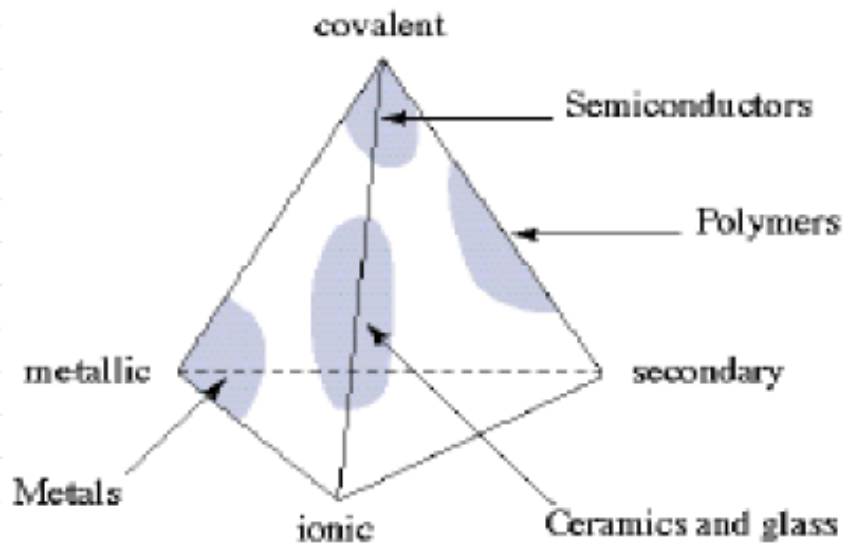
## - Secondary Bond

- Polar or van der Waals

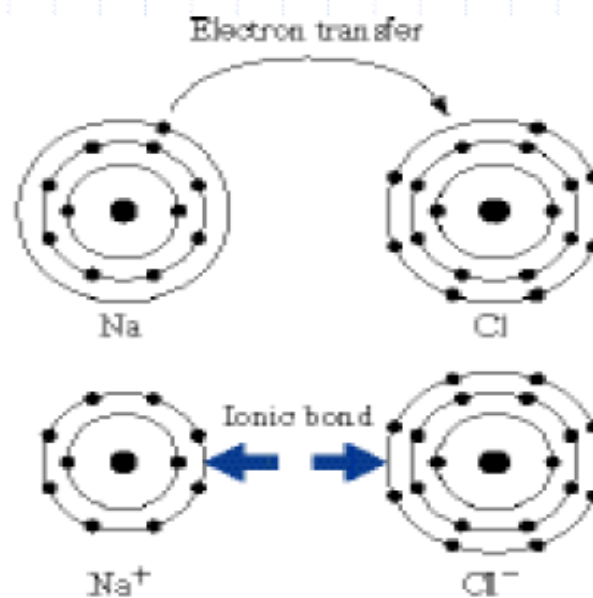
(*polymers*)



## Bonding Types for various Materials



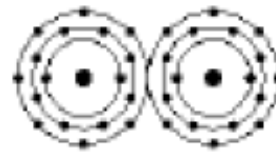
## Ionic Bonding by Electron Transfer



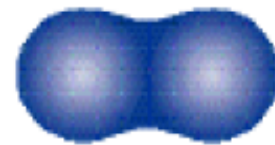
Ex: NaCl . Ionically Bonded Solid

## Covalent Bonding

- Sharing of electrons to achieve “stable electronic configuration”
- Small electronegativity
- Bond energy; weak to strong
- Directional bond; between specific atoms in specific directions



(a)



(b)



(c)



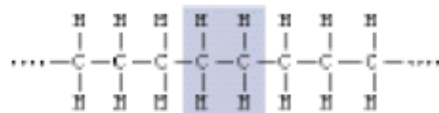
(d)

## Covalent Bonding in Polymers



Ethylene molecule

(a)

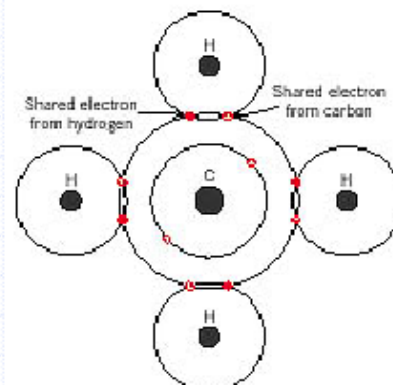


Ethylene unit

Polyethylene molecule

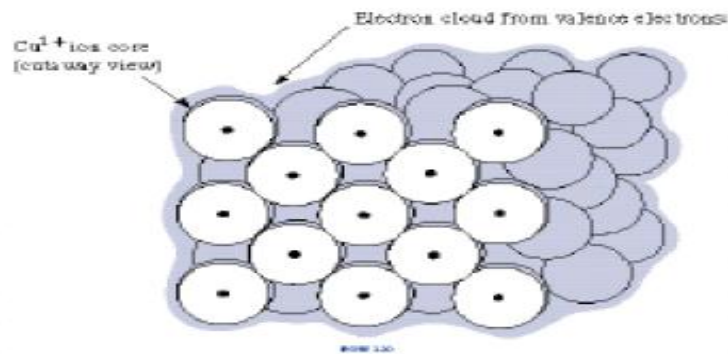
(b)

Ethylene ( $\text{C}_2\text{H}_4$ )



Methan ( $\text{CH}_4$ )

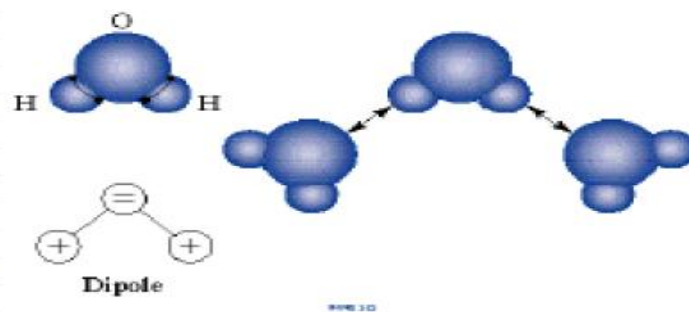
## Metallic Bonding



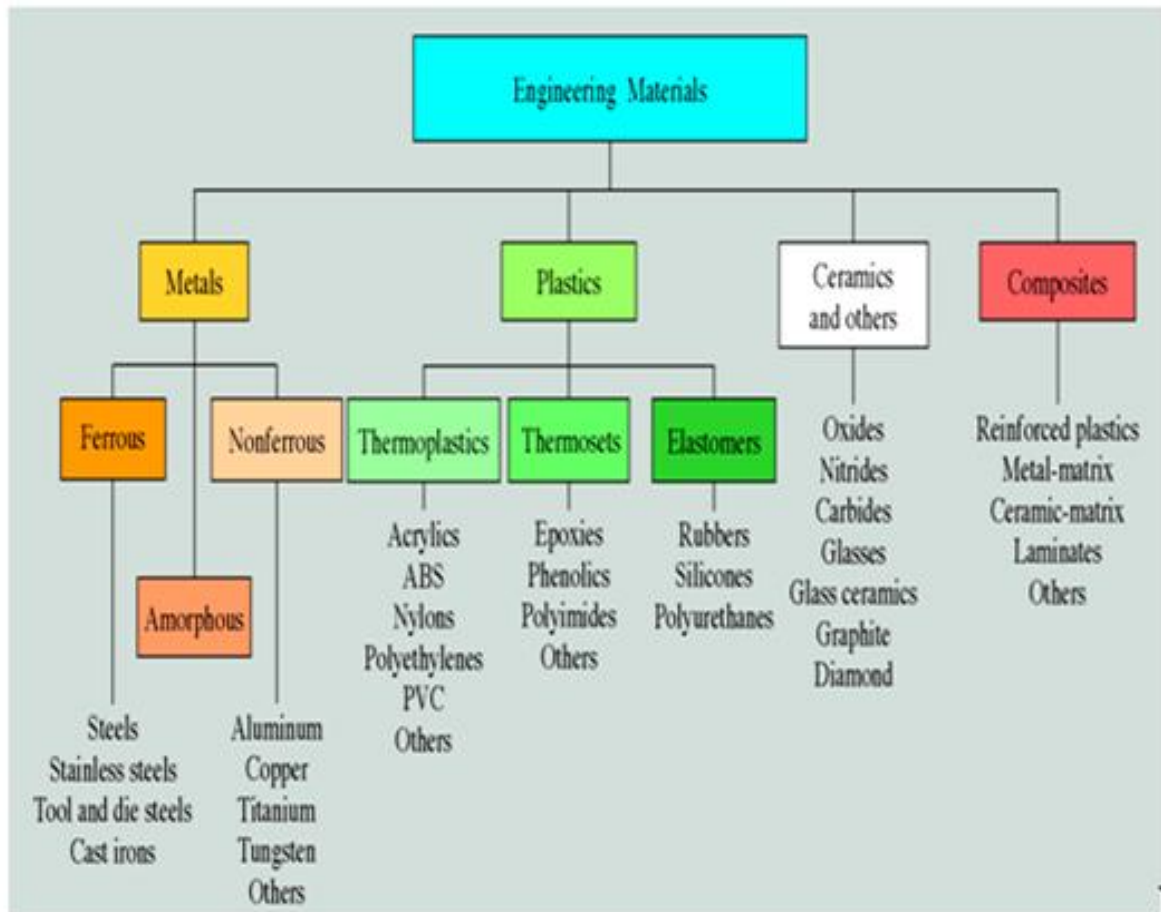
## Secondary (van der Waals) bonding

- Physical bonds, not chemical
- Bond energy is very weak compared to others
- Exists between almost all atoms and molecules
- Arise from atomic or molecular dipoles

## Secondary bonding of water molecules



# Classification of engineering materials



# Lecture 2

## THE STRUCTURE OF CRYSTALLINE SOLIDS

### 3.2 FUNDAMENTAL CONCEPTS

#### SOLIDS

##### AMORPHOUS

Atoms in an amorphous solid are arranged randomly- No Order

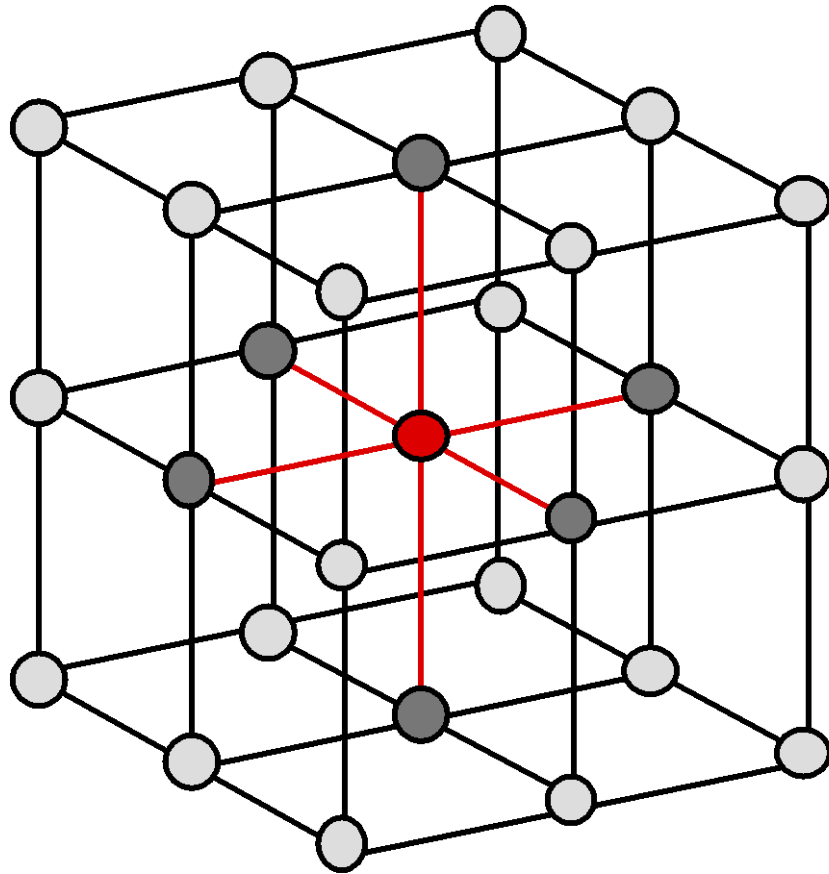
##### CRYSTALLINE

Atoms in a crystalline solid are arranged in a repetitive three dimensional pattern  
Long Range Order

All metals are crystalline solids

Many ceramics are crystalline solids

Some polymers are crystalline solids

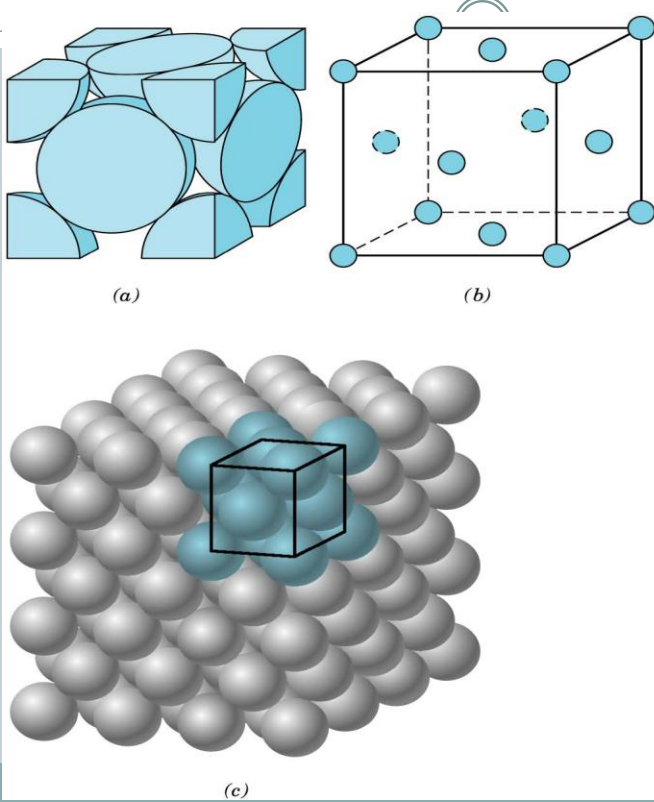


### 3.3 UNIT CELL

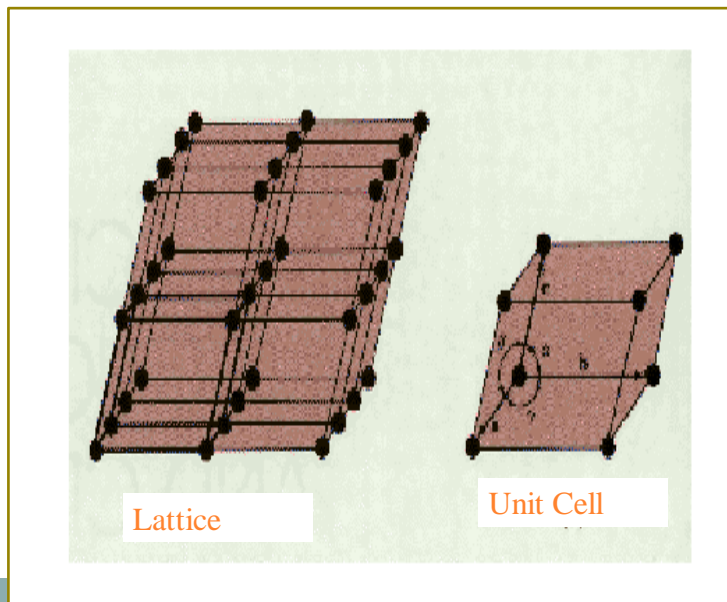
- **Unit cell** -- smallest grouping which can be arranged in three dimensions to create the lattice. Thus the **Unit Cell** is basic structural unit or building block of the crystal structure



# Unit cell & Lattice



**FIGURE 3.1** For the face-centered cubic crystal structure: (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Figure c adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

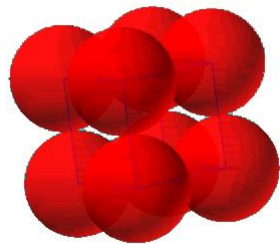




## 3.4 METALLIC CRYSTALS

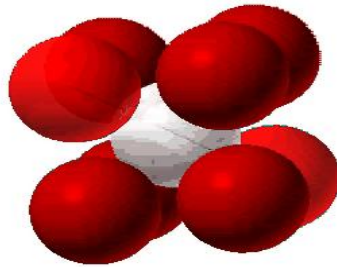
- Tend to be densely packed.
- Have several reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to have lower bonding energy.
- **Have the simplest crystal structures.**
  - Let us look at three such structures...

4



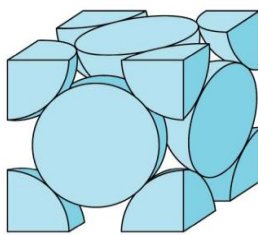
SC structure

## BODY CENTERED CUBIC STRUCTURE (BCC)

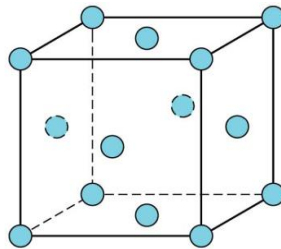


Cr, Fe, W, Nb, Ba, V

## FACE CENTERED CUBIC STRUCTURE (FCC)

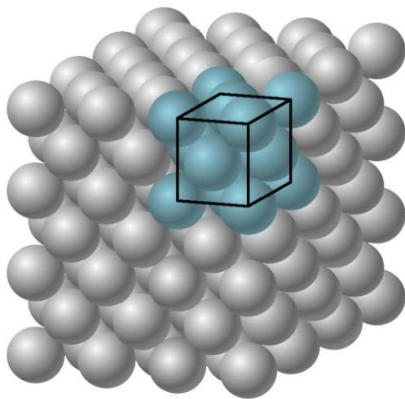


(a)



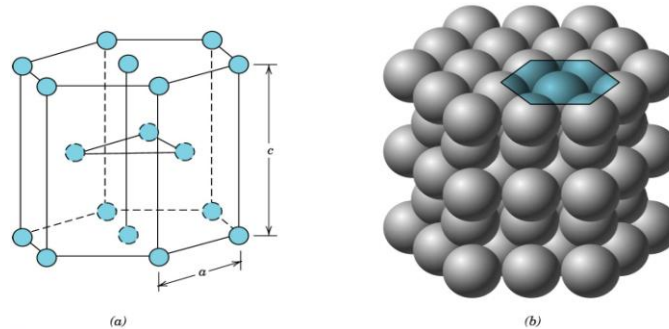
(b)

**FIGURE 3.1** For the face-centered cubic crystal structure: (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Figure c adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



(c)

## HEXAGONAL CLOSE-PACKED STRUCTURE HCP



**FIGURE 3.3** For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell ( $a$  and  $c$  represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms. (Figure b from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

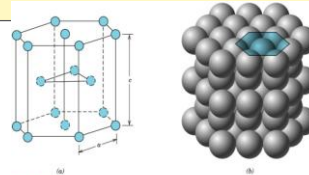
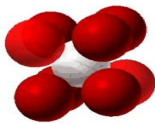
Mg, Zn, Cd, Zr, Ti, Be

## Number of atoms per unit cell

**BCC**  $1/8$  corner atom  $\times$  8 corners + 1 body center atom  
**= 2 atoms/uc**

**FCC**  $1/8$  corner atom  $\times$  8 corners +  $1/2$  face atom  $\times$  6 faces  
**= 4 atoms/uc**

**HCP** 3 inside atoms +  $1/2$  basal atoms  $\times$  2 bases +  $1/6$  corner atoms  $\times$  12 corners  
**= 6 atoms/uc**



**FIGURE 3.3** For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell ( $a$  and  $c$  represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms. (Figure b from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

## Relationship between atomic radius and edge lengths

**For FCC:**  $a = 2R\sqrt{2}$

**For BCC:**  $a = 4R/\sqrt{3}$

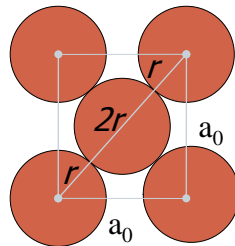
**For HCP**  $a = 2R$

$c/a = 1.633$  (for ideal case)

**Note:**  $c/a$  ratio could be less or more than the ideal value of 1.633

## Face Centered Cubic (FCC)

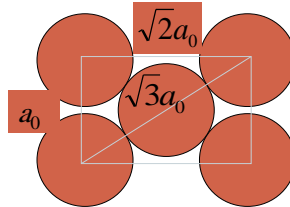
$$\sqrt{2}a_0 = 4r$$



## Body Centered Cubic (BCC)



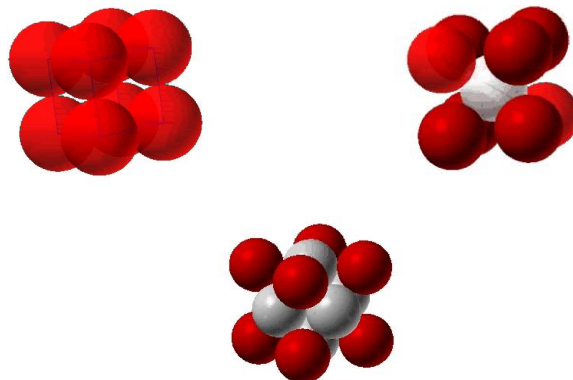
$$\sqrt{3}a_0 = 4r$$



## Coordination Number



- The number of touching or nearest neighbor atoms
- SC is 6
- BCC is 8
- FCC is 12
- HCP is 12

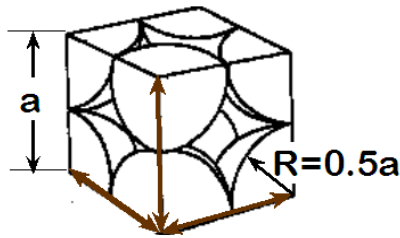


# ATOMIC PACKING FACTOR

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

\*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions  
contains  $8 \times 1/8 =$   
**1 atom/unit cell**

$$\text{APF} = \frac{\text{atoms unit cell} \times \frac{4}{3} \pi (0.5a)^3}{a^3}$$

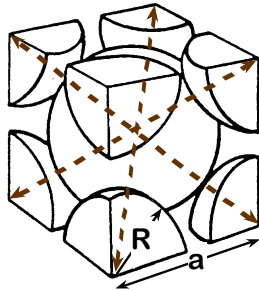
← volume atom

← volume unit cell

6

# ATOMIC PACKING FACTOR: BCC

- APF for a body-centered cubic structure = 0.68



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

Unit cell contains:  
 $1 + 8 \times 1/8$   
**= 2 atoms/unit cell**

$$\text{APF} = \frac{\text{atoms unit cell} \times \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3}$$

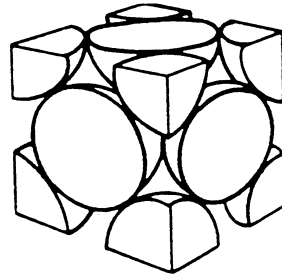
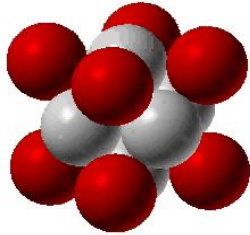
← volume atom

← volume unit cell



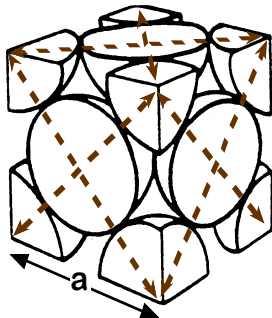
## FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are face diagonals.  
--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.
- Coordination # = 12



## ATOMIC PACKING FACTOR: FCC

- APF for a face-centered cubic structure = 0.74



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

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

$$\text{APF} = \frac{\text{atoms/unit cell} \times \text{volume/atom}}{\text{volume/unit cell}}$$

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

## 3.5 Density Computations

- Density of a material can be determined theoretically from the knowledge of its crystal structure (from its Unit cell information)
- Density = mass/Volume
- Mass is the mass of the unit cell and volume is the unit cell volume.
- mass = ( number of atoms/unit cell) “n” x mass/atom
- mass/atom = atomic weight “A”/Avogadro’s Number “N<sub>A</sub>”
- Volume = Volume of the unit cell “V<sub>c</sub>”

## THEORETICAL DENSITY

$$\rho = \frac{n A}{V_c N_A}$$

# atoms/unit cell → n

Atomic weight (g/mol) → A

Volume/unit cell (cm<sup>3</sup>/unit cell) → V<sub>c</sub>

Avogadro's number (6.023 x 10<sup>23</sup> atoms/mol) → N<sub>A</sub>

### Example problem on Density Computation

**Problem:** Compute the density of Copper

**Given:** Atomic radius of Cu = 0.128 nm ( $1.28 \times 10^{-8}$  cm)

Atomic Weight of Cu = 63.5 g/mol

Crystal structure of Cu is FCC

**Solution:**  $\rho = n A / V_c N_A$

$$n = 4$$

$$V_c = a^3 = (2R\sqrt{2})^3 = 16 R^3 \sqrt{2}$$

$$N_A = 6.023 \times 10^{23} \text{ atoms/mol}$$

$$\rho = 4 \times 63.5 \text{ g/mol} / 16 \sqrt{2} (1.28 \times 10^{-8} \text{ cm})^3 \times 6.023 \times 10^{23} \text{ atoms/mol}$$

$$\text{Ans} = 8.98 \text{ g/cm}^3$$

Experimentally determined value of density of Cu = 8.94 g/cm<sup>3</sup>

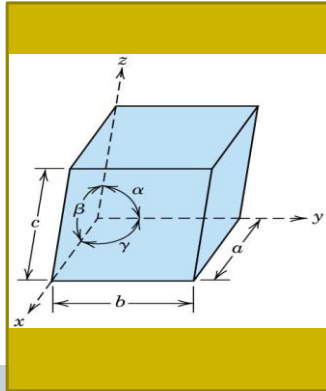
## 3.6 Crystal Systems

- Since there are many different possible crystal structures, it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic arrangements.
- One such scheme is based on the unit cell geometry, i.e. the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell.
- Within this framework, an x, y, and z coordinate system is established with its origin at one of the unit cell corners; each x, y, and z-axis coincides with one of the three parallelepiped edges that extend from this corner, as illustrated in Figure.

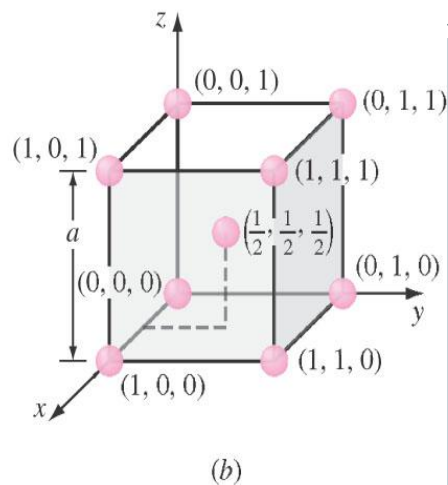
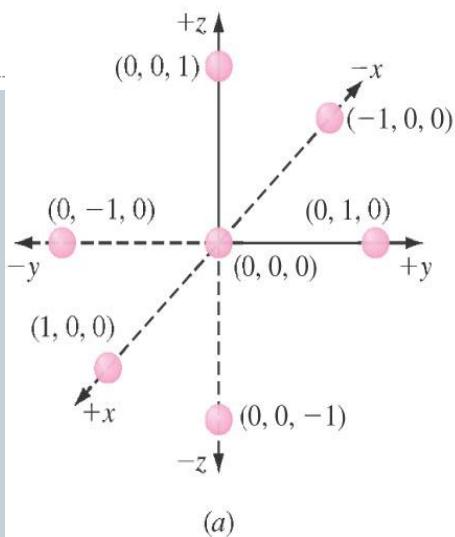
# The Lattice Parameters

## Lattice parameters

$a, b, c, \alpha, \beta, \gamma$  are called the lattice Parameters.



## 3.7 Point Coordinates in an Orthogonal Coordinate System Simple Cubic

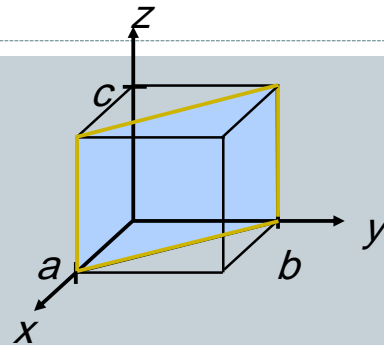


### 3.8 MILLER INDICES FOR CRYSTALLOGRAPHIC PLANES

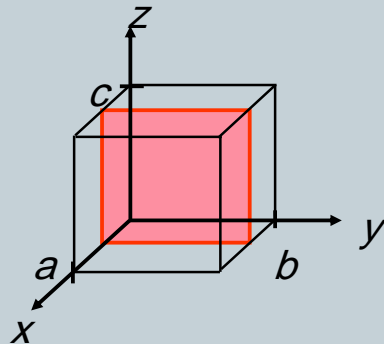
- **Miller Indices for crystallographic planes are the reciprocals of the fractional intercepts (with fractions cleared) which the plane makes with the crystallographic x,y,z axes of the three nonparallel edges of the cubic unit cell.**
- 4-Step Procedure:
  1. Find the **intercepts** that the plane makes with the three axes **x,y,z**. If the plane passes through origin change the origin or draw a parallel plane elsewhere (e.g. in adjacent unit cell)
  2. Take the **reciprocal** of the **intercepts**
  3. Remove fractions
  4. Enclose in ( )

### Crystallographic Planes

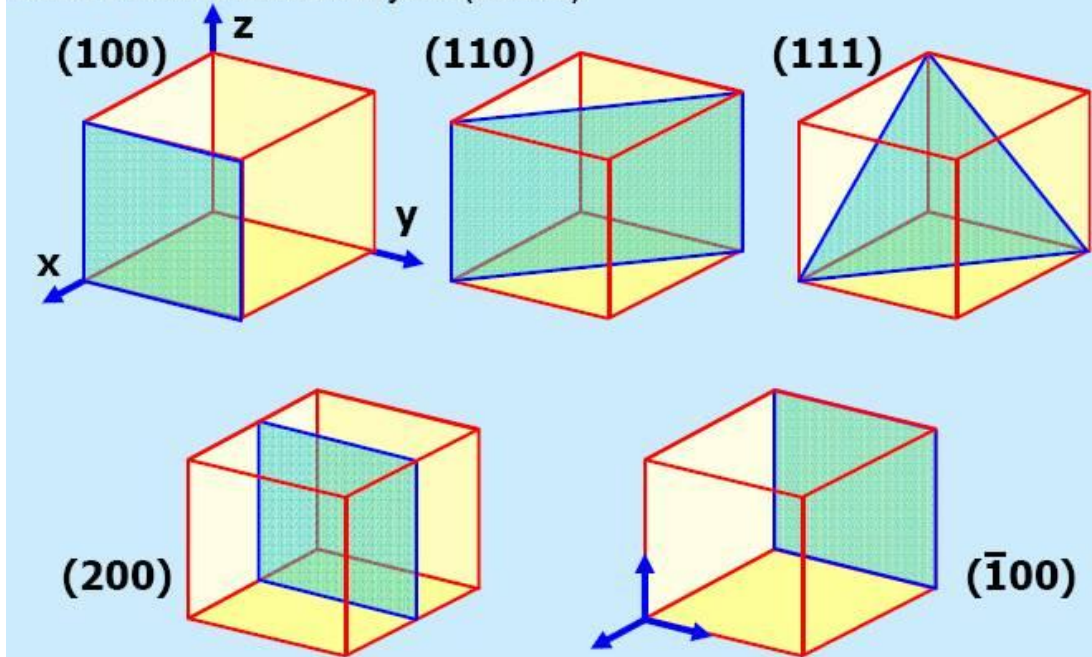
<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1	1	$\infty$
3. Reduction	1	1	0
4. Miller Indices	(110)		



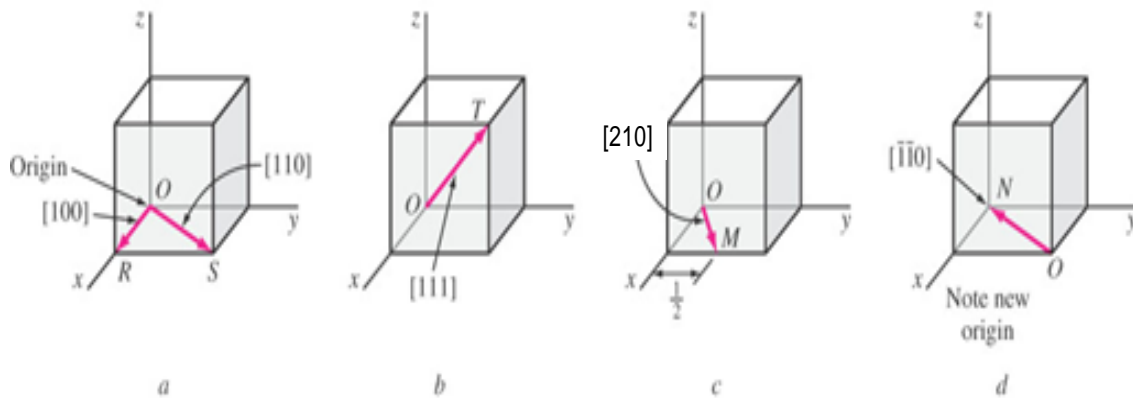
<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1/2	$\infty$	$\infty$
3. Reduction	2	0	0
4. Miller Indices	(200)		



Miller's indices in cubic crystal (Silicon)

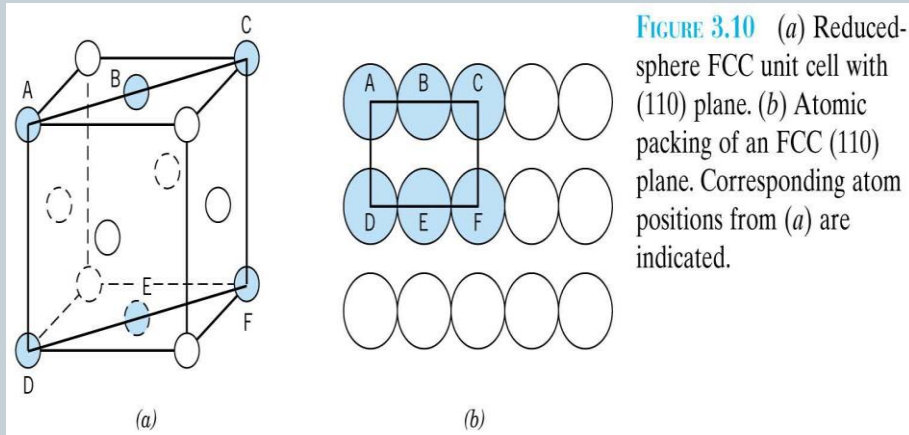


## Crystallographic Directions in Cubic System



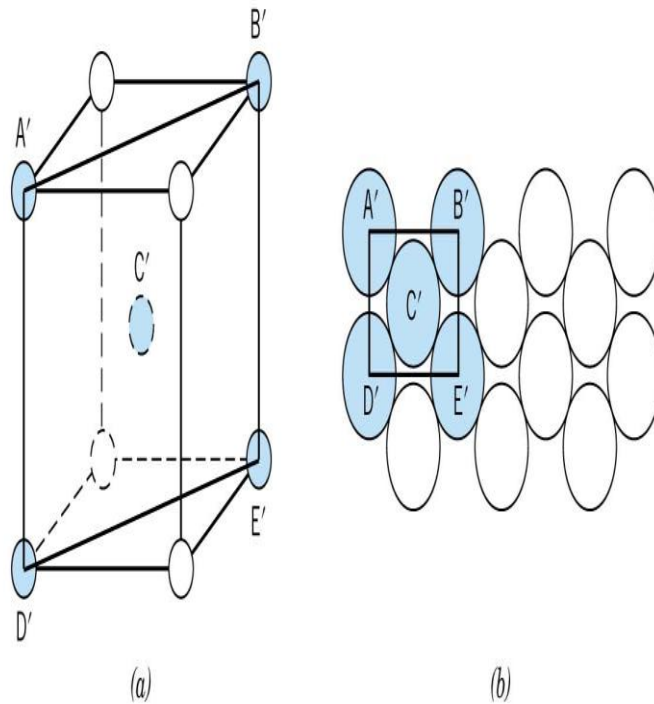


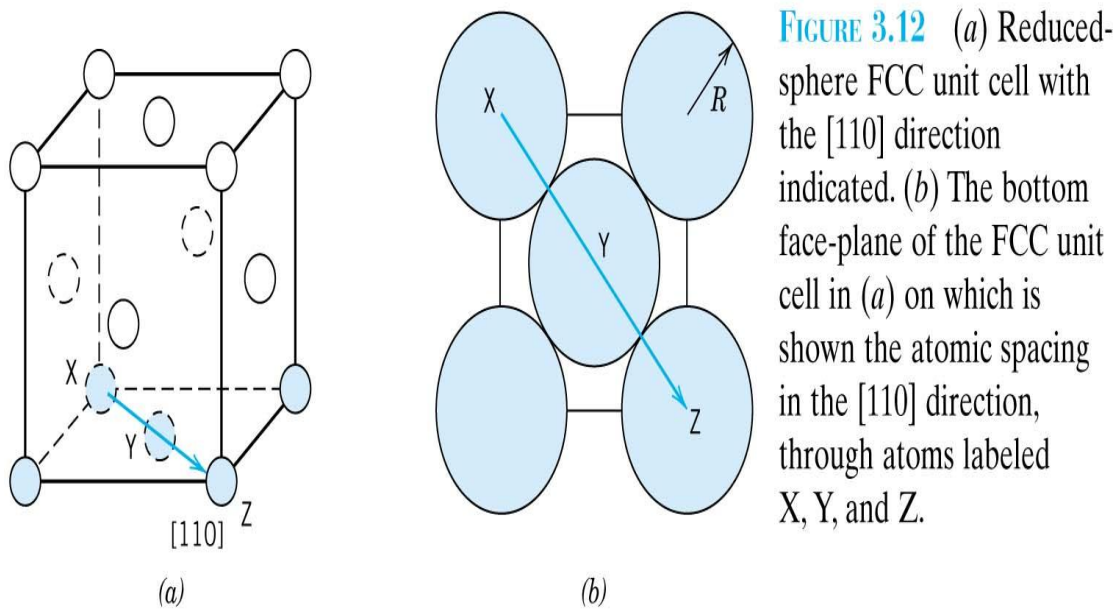
## Atomic Arrangement on (110) plane in FCC



**FIGURE 3.10** (a) Reduced-sphere FCC unit cell with (110) plane. (b) Atomic packing of an FCC (110) plane. Corresponding atom positions from (a) are indicated.

**FIGURE 3.11** (a) Reduced-sphere BCC unit cell with (110) plane. (b) Atomic packing of a BCC (110) plane. Corresponding atom positions from (a) are indicated.





### 3.11 Linear and Planar Atomic Densities

- **Linear Density “LD”**

is defined as the number of atoms per unit length whose centers lie on the direction vector of a given crystallographic direction.

$$LD = \frac{\text{No. of atoms centered on direction}}{\text{Length of direction vector}}$$

# Linear Density

LD for [110] in BCC.

# of atom centered on the direction vector [110]

$$= 1/2 + 1/2 = 1$$

Length of direction vector [110] =  $\sqrt{2}a$

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

$$LD = \frac{1}{\sqrt{2}a} = \frac{1}{\sqrt{2}(4R/\sqrt{3})} = \frac{\sqrt{3}}{\sqrt{2}4R}$$

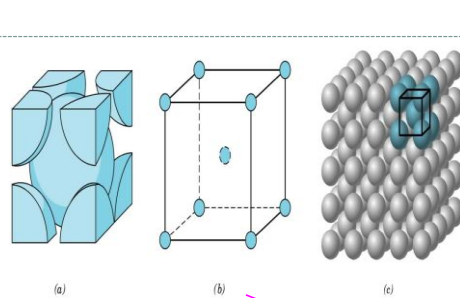
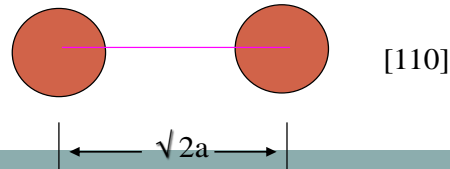


FIGURE 3.2 For the body-centered cubic crystal structure, (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Figure c from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, Structure, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



# Linear Density

• LD of [110] in FCC

# of atom centered on the direction vector [110] = 2 atoms

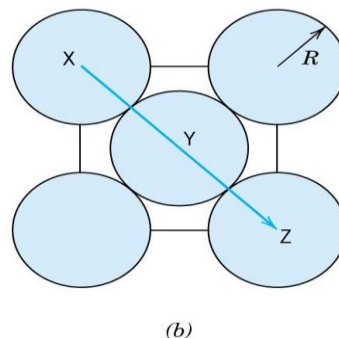
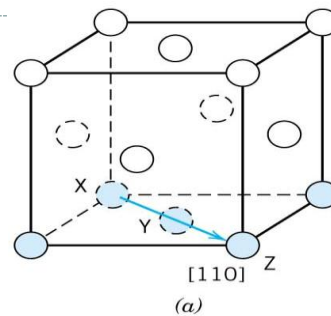
Length of direction vector [110] =  $4R$

$$LD = 2 / 4R$$

$$LD = 1/2R$$

Linear density can be defined as reciprocal of the repeat distance 'r'

$$LD = 1/r$$



## Planar Density

- Planar Density “PD” is defined as the number of atoms per unit area that are centered on a given crystallographic plane.

No of atoms centered on the plane

$$PD = \frac{\text{-----}}{\text{-----}}$$

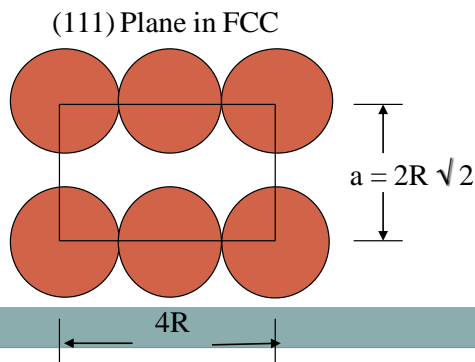
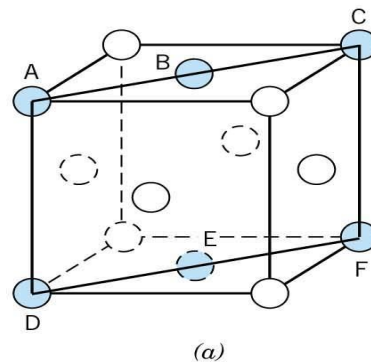
Area of the plane

## Planar Density of (110) plane in FCC

# of atoms centered on the plane (110)  
 $= 4(1/4) + 2(1/2) = 2$  atoms

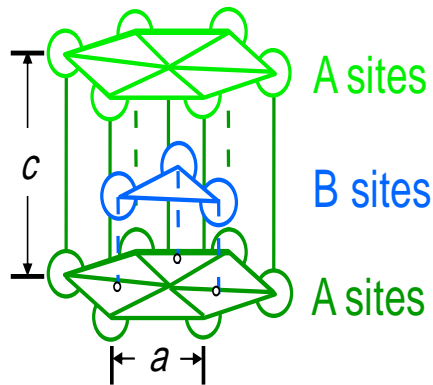
Area of the plane  
 $= (4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$

$$PD_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}}$$

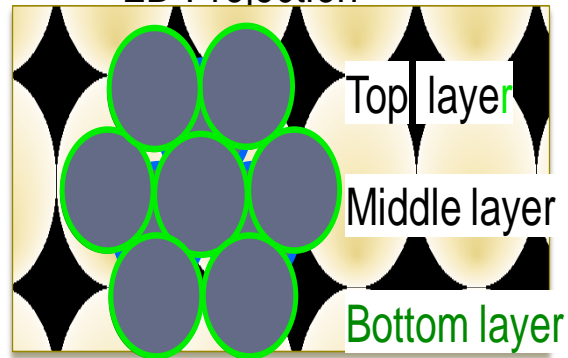


# Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



- 2D Projection



- Coordination # = 12

6 atoms/unit cell

- APF = 0.74

ex: Cd, Mg, Ti, Zn

- $c/a = 1.633$

## Crystalline and Noncrystalline Materials

### Single Crystals



- For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a single crystal.
- All unit cells interlock in the same way and have the same orientation.
- Single crystals exist in nature, but may also be produced artificially.
- They are ordinarily difficult to grow, because the environment must be carefully controlled.
- Example: Electronic microcircuits, which employ single crystals of silicon and other semiconductors.



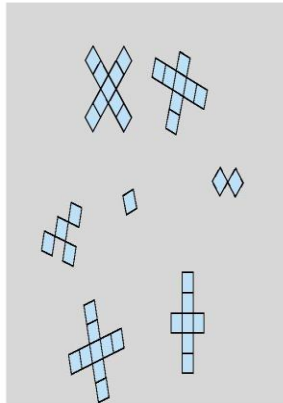
# Polycrystalline Materials

## 3.13 Polycrystalline Materials

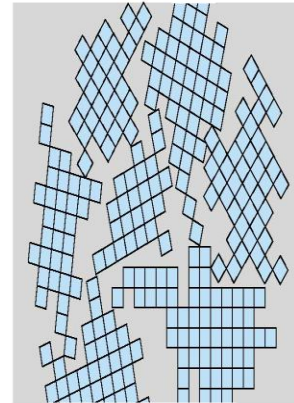
**Polycrystalline** → crystalline solids composed of many small crystals or grains.

**Various stages in the solidification :**

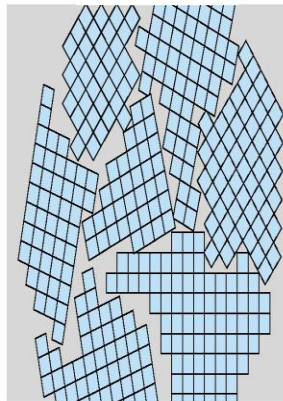
- a) Small crystallite nuclei Growth of the crystallites.
- b) Obstruction of some grains that are adjacent to one another is also shown.
- c) Upon completion of solidification, grains that are adjacent to one another is also shown.
- d) Grain structure as it would appear under the microscope.



(a)



(b)



(c)



(d)

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- **Defects in Solids**

- **0D, Point defects**

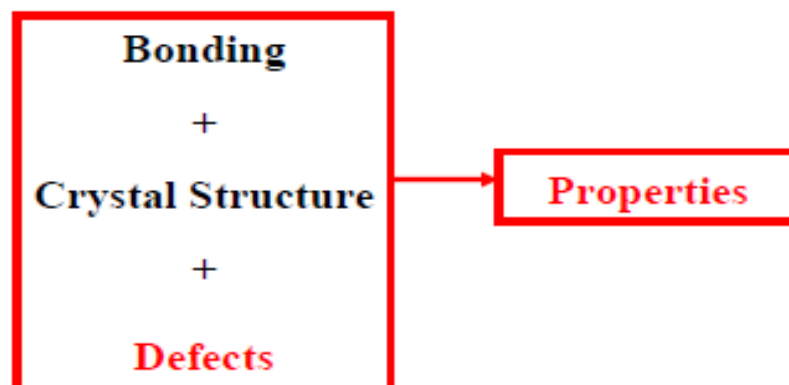
- ✓ vacancies
- ✓ interstitials
- ✓ impurities, weight and atomic composition

- **1D, Dislocations**

- ✓ edge
- ✓ screw

- **2D, Grain boundaries**

### **Why are defects important?**



Defects have a profound impact on the various properties of materials:

Production of advanced semiconductor devices require not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample.

Defects are responsible for color (& price) of a diamond crystal.

Forging a metal tool introduces defects ... and increases strength of the tool.

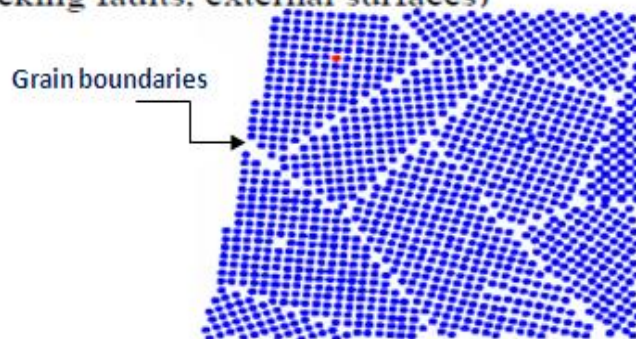
## Types of Defects

Defects may be classified into four categories depending on their dimension:

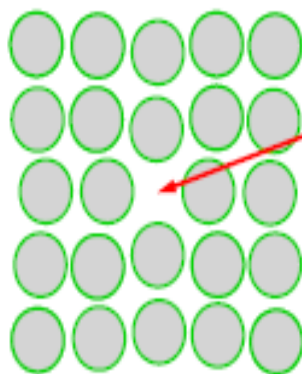
➤ **0D, Point defects:** atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials)

➤ **1D, Linear defects:** groups of atoms in irregular positions (e.g. screw and edge dislocations)

➤ **2D, Planar defects:** the interfaces between homogeneous regions of the material (e.g. grain boundaries, stacking faults, external surfaces)



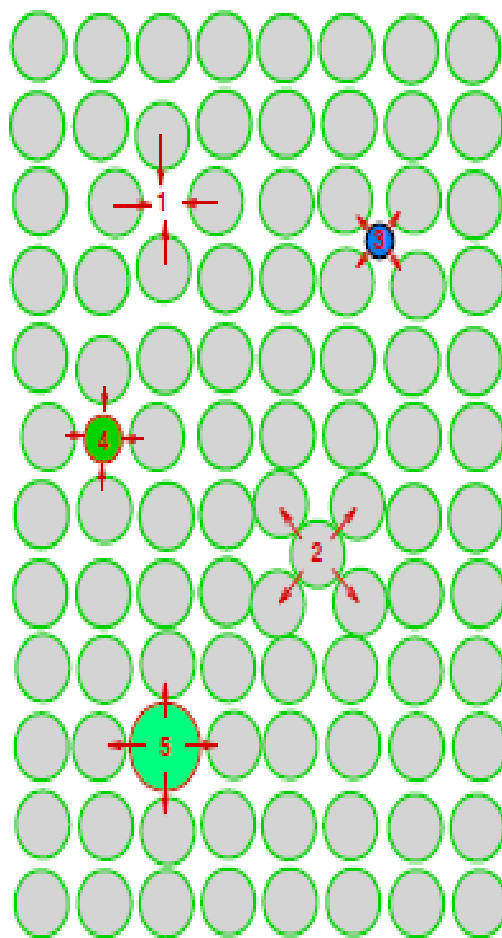
## Point Defects: Vacancies



**Vacancy = absence of an atom from its normal location in a perfect crystal structure**

Vacancies are always present in crystals and they are particularly numerous at high temperatures, when atoms are frequently and randomly change their positions leaving behind empty lattice sites (vacancies).

## Other point defects: self-interstitials, impurities



Schematic representation of different point defects:

- (1) vacancy;
- (2) self-interstitial;
- (3) interstitial impurity;
- (4,5) substitutional impurities

The arrows show the local stresses introduced by the point defects.

Due to the local stresses introduced by point defects, they can feel each other (interact) and feel external stresses.

The interactions can give a directionality to otherwise random jumps of atoms.

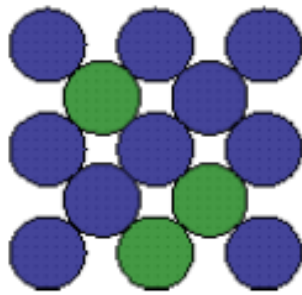
### Self-interstitials:

Self-interstitials in metals introduce large distortions in the surrounding lattice  $\Rightarrow$  the energy of self-interstitial formation is  $\sim 3$  times larger as compared to vacancies ( $Q_i \sim 3 \times Q_v$ )  $\Rightarrow$  equilibrium concentration of self-interstitials is very low (less than one self-interstitial per  $\text{cm}^3$  at room T).

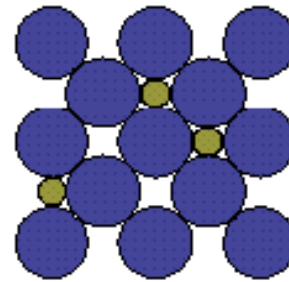
## Impurities

### Impurities - atoms which are different from the host

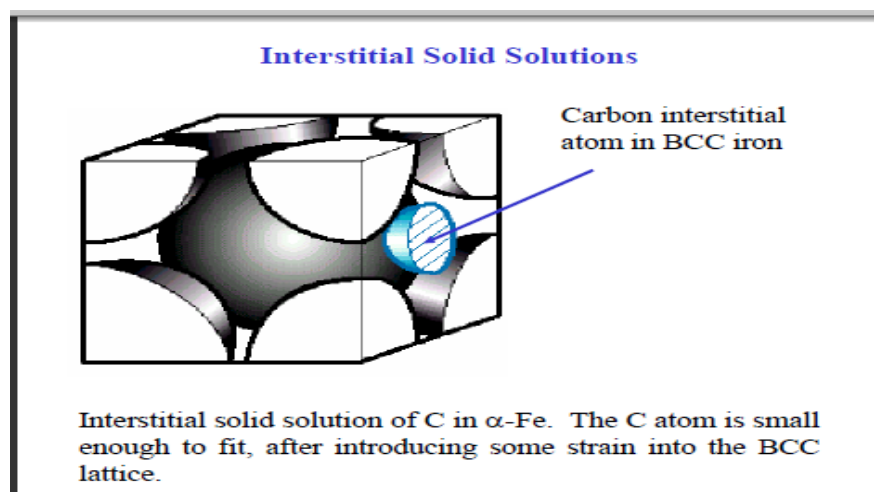
- All real solids are impure. Very pure metals 99.9999% - one impurity per  $10^6$  atoms
- May be intentional or unintentional  
Examples: carbon added in small amounts to iron makes steel, which is stronger than pure iron. Boron added to silicon change its electrical properties.
- **Alloys** - deliberate mixtures of metals  
Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.



substitutional impurity



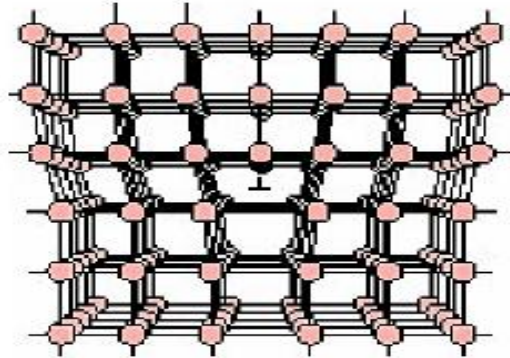
interstitial impurities





## Dislocations—Linear Defects

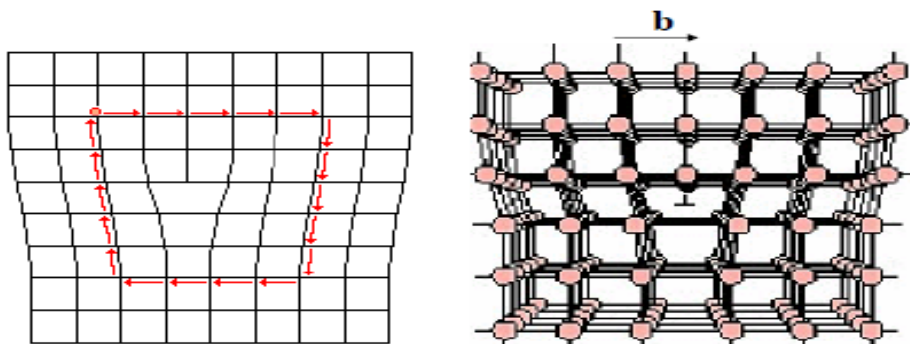
**Dislocations are linear defects:** the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**. Dislocations also create small elastic deformations of the lattice at large distances.



Dislocations are very important in mechanical properties of material (Chapters 6, 7, 8). Introduction/discovery of dislocations in 1934 by Taylor, Orowan and Polanyi marked the beginning of our understanding of mechanical properties of materials.

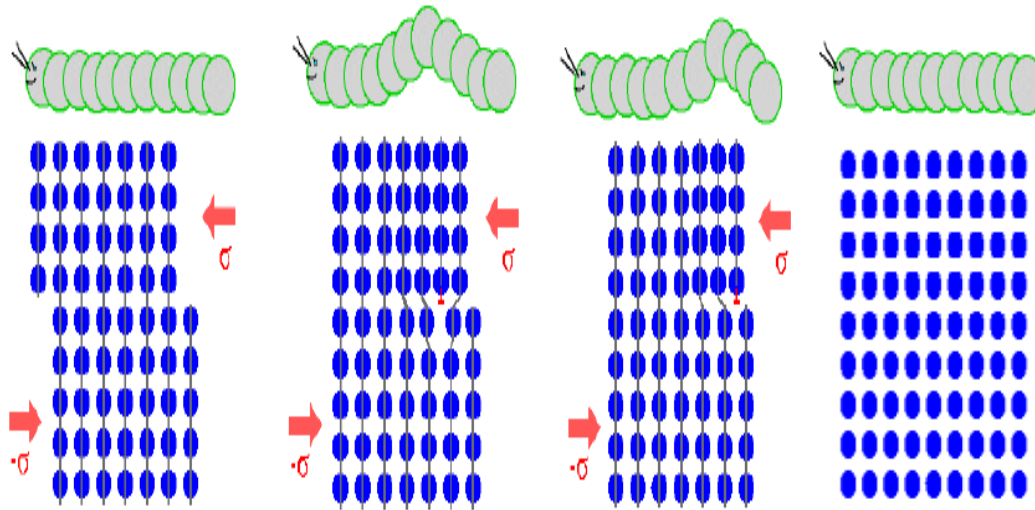
## Description of Dislocations—Burgers Vector

To describe the size and the direction of the lattice distortion caused by a dislocation we should introduce so-called **Burgers vector  $\mathbf{b}$** . To find the Burgers vector, we should make a circuit from atom to atom counting the same number of atomic distances in all directions. If the circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector  $\mathbf{b}$ .



Dislocations shown above have **Burgers vector directed perpendicular to the dislocation line**. These dislocations are called **edge dislocations**.

Shear occurs by dislocation movement producing permanent (plastic) deformation by “slip”

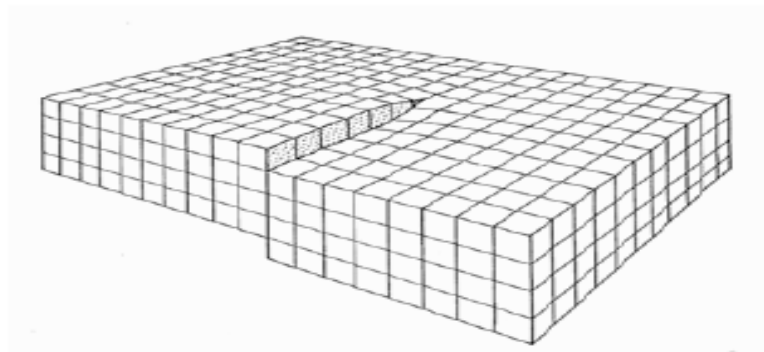


تمثيل حركة الانخلاء بحركة (دودة القز).

### Edge and screw dislocations

Dislocations shown in previous slide are **edge dislocations**. They have Burgers vector directed perpendicular to the dislocation line.

There is a second basic type of dislocation, called **screw dislocation**. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).



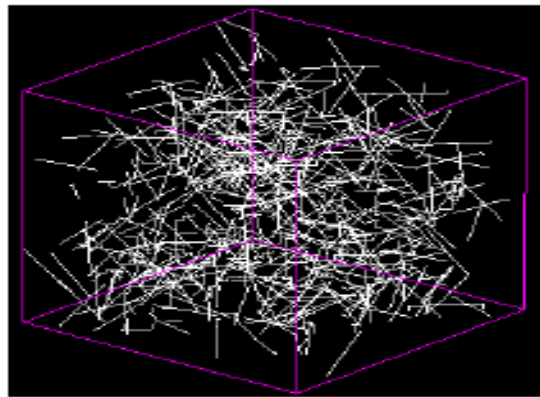
## Where do dislocations come from ?

The number of dislocations in a material is expressed as the **dislocation density** - the total dislocation length per unit volume or the number of dislocations intersecting a unit area. Dislocation densities can vary from  $10^5 \text{ cm}^{-2}$  in carefully solidified metal crystals to  $10^{12} \text{ cm}^{-2}$  in heavily deformed metals.

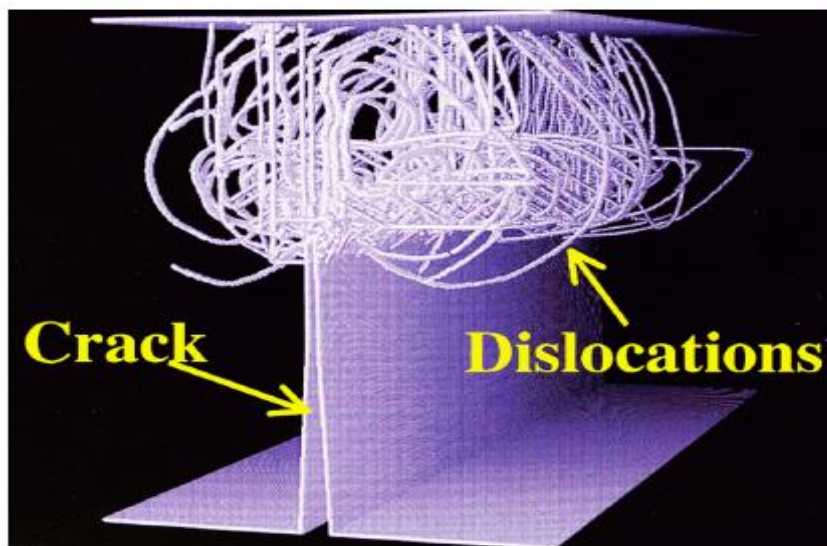
Most crystalline materials, especially metals, have dislocations in their as-formed state, mainly as a result of stresses (mechanical, thermal...) associated with the forming process.

The number of dislocations increases dramatically during plastic deformation (Ch.7). Dislocations spawn from existing dislocations, grain boundaries & surfaces

This picture is a snapshot from simulation of plastic deformation in a fcc single crystal (Cu) of linear dimension 15 micrometers.



## Atomistic simulation of crack propagation





## Planar (interfacial) defects

### External Surfaces

Surface atoms have unsatisfied atomic bonds, and higher energies than the bulk atoms  $\Rightarrow$  Surface energy,  $\gamma$  ( $\text{J}/\text{m}^2$ )

- Minimization of surface areas reduces the energy of the system (e.g. liquid drop)
- Solid surfaces can “reconstruct” to satisfy atomic bonds at surfaces.

### Grain Boundaries

Polycrystalline material comprised of many small crystals or grains. The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.

