

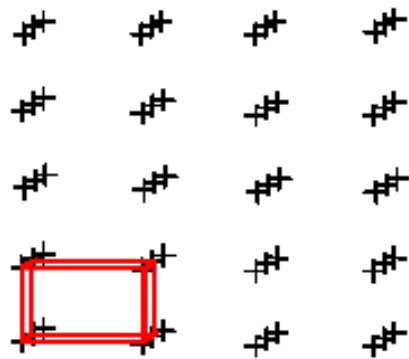
# CHAPTER 3: CRYSTAL STRUCTURES & PROPERTIES

## ISSUES TO ADDRESS...

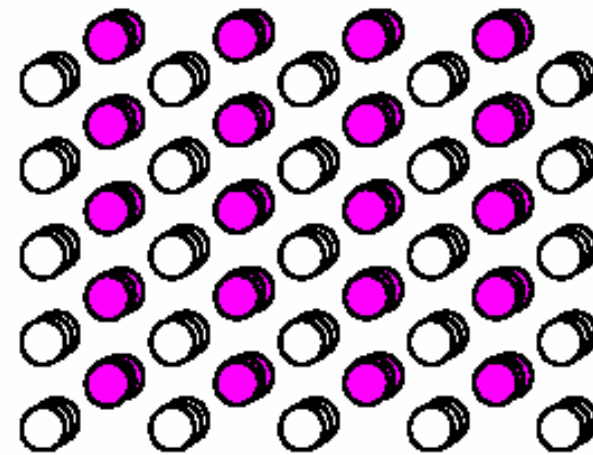
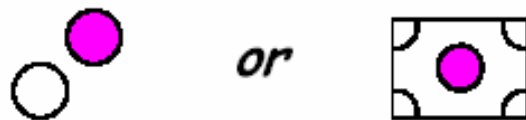
- How do atoms assemble into solid structures?  
(for now, focus on metals)
- How does the density of a material depend on  
its structure?
- When do material properties vary with the  
sample (i.e., part) orientation?

# Lattice and Basis

The Lattice



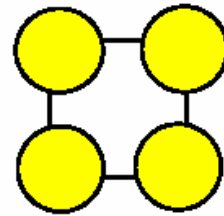
The Basis



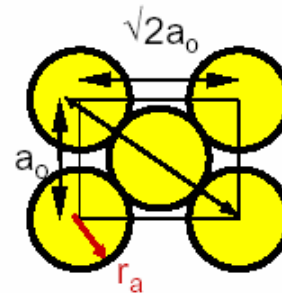
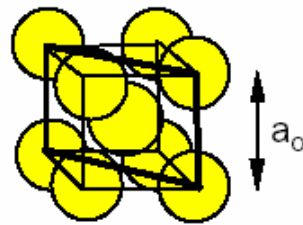
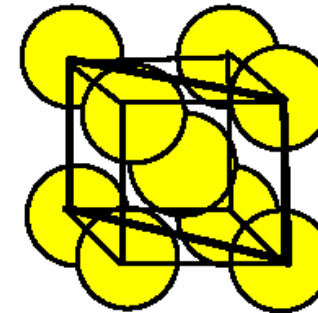
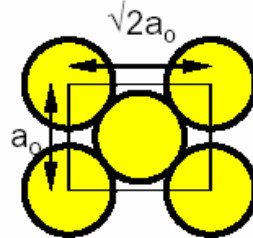
The Crystal

# Important Planes in BCC Structure

{100}: No atoms "touch" (are bonded!)



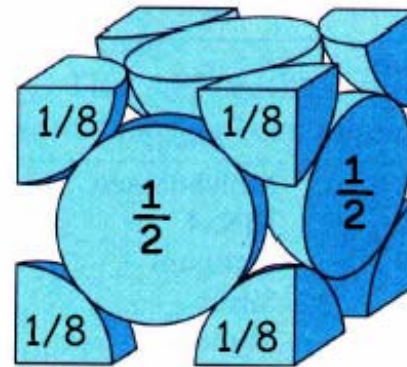
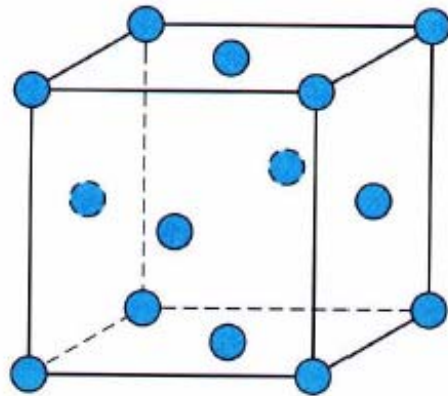
- {110}: Closest Packed:  
Atoms touch along  $\langle 111 \rangle$



$$\sqrt{2a_0^2 + a_0^2} = 4r_a$$

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

# Number of Atoms per Unit Cell



$$(8 \times 1/8) + (6 \times \frac{1}{2}) = 4 \text{ Lattice Points/Unit Cell}$$

$$4 \text{ Lattice Points/Unit Cell} \times 1 \text{ Atom/Latt. Point} = 4 \text{ Atoms/Cell!}$$

# *APF: FCC Cubic*

APF = vol. of atomic spheres in unit cell  
total unit cell vol.

How many spheres (i.e. atoms)? **4/cube**

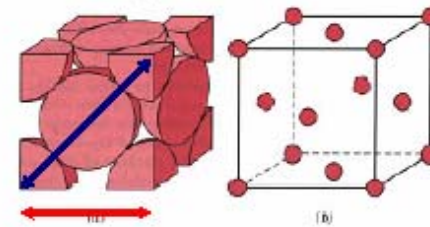
What is their volume?  **$4 \times 4\pi R^3/3$**

What is cube volume?  **$a^3$**

How is "R" related to "a"?  **$a = (2\sqrt{2}) R$**

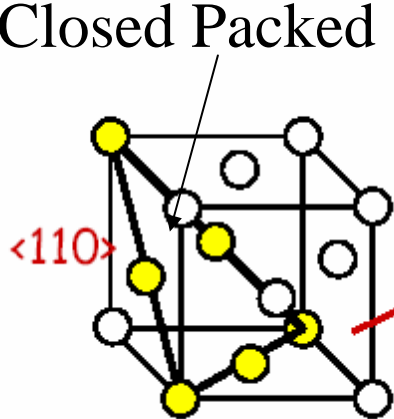
Therefore, independent of R **APF =  $(16\pi R^3/3)/a^3 = 0.74$**

Atomic configuration in  
**Face-Centered-Cubic**  
Arrangement

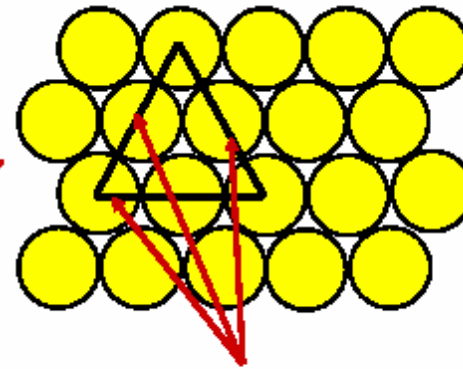


# Important Planes in FCC Structure

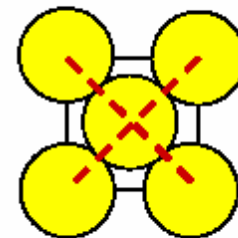
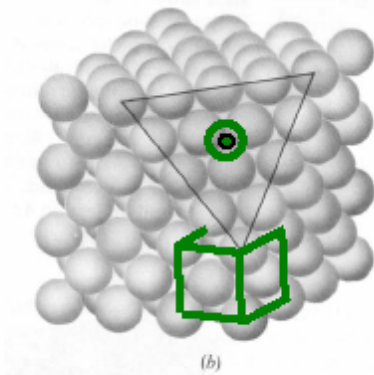
Closed Packed



(111)



Atoms "touch" (= are bonded) along the  $\langle 110 \rangle$ 's



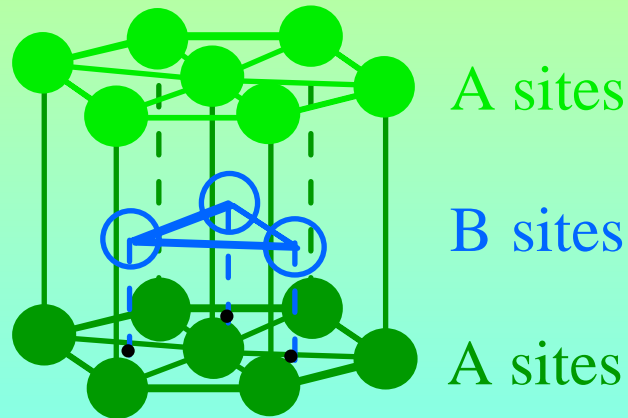
Bonds on {100}

Along  $\langle 110 \rangle$

Not Along  $\langle 100 \rangle$

# *Hexagonal Close-Packed (HCP) Structure*

- ABAB... Stacking Sequence
- 3D Projection

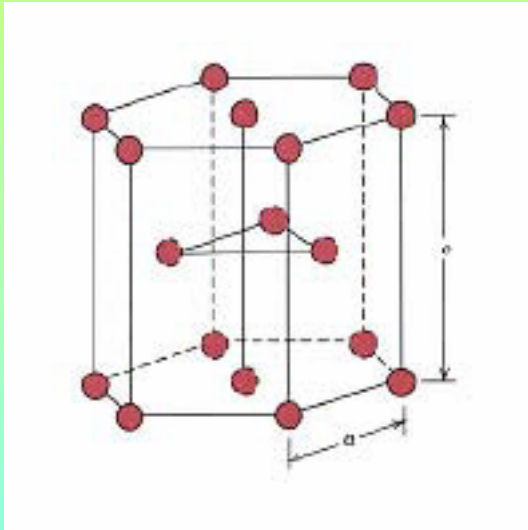


- 2D Projection



The top and the bottom faces consist of six atoms which form regular hexagon, surrounding one atom in center. Another plane with 3 additional atoms located in between.

# Hexagonal Close-Packed (HCP) Structure



The unit cell has two lattice parameters **a** and **c**.

- Six atoms per unit cell
  - Mid-plane atoms (3) shared by no other cells:  
 $3 \times 1 = 3$
  - hexagonal corner atoms (12) shared by six cells:  
 $12 \times 1/6 = 2$
  - top/bottom plane center atoms (2) shared by two cells:  
 $2 \times 1/2 = 1$
  - *Note: all atoms are equivalent*
- Ideal ratio  $c/a = 1.633$

**Example:** Mg, Ti, Zn

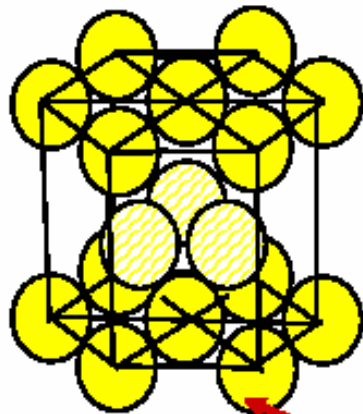
- APF = 0.74



# Important Planes in HCP Structure

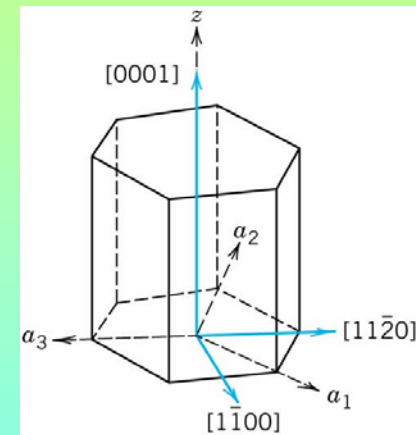
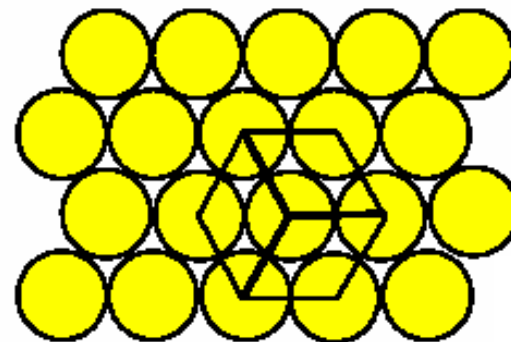
Close-packed Planes and Directions

(0001) Plane



$$a = 2R$$

(0001) close-packed plane



[1000], [0100],  
and [0010]

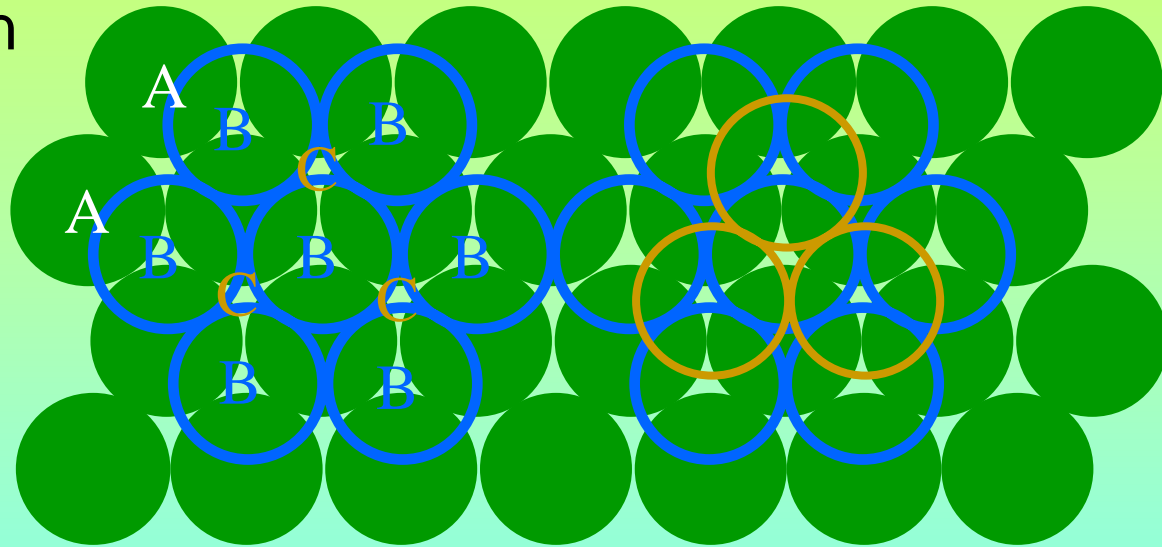
# *FCC STACKING SEQUENCE*

- ABCABC... Stacking Sequence
- 2D Projection

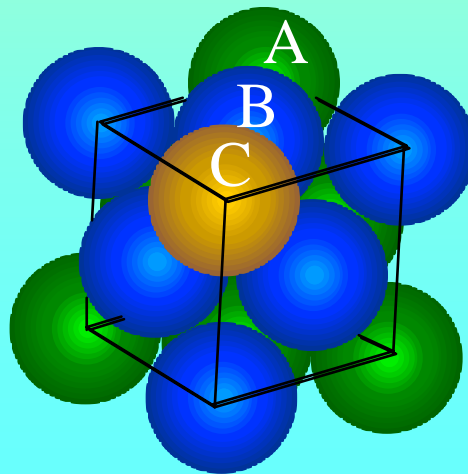
A sites

B sites

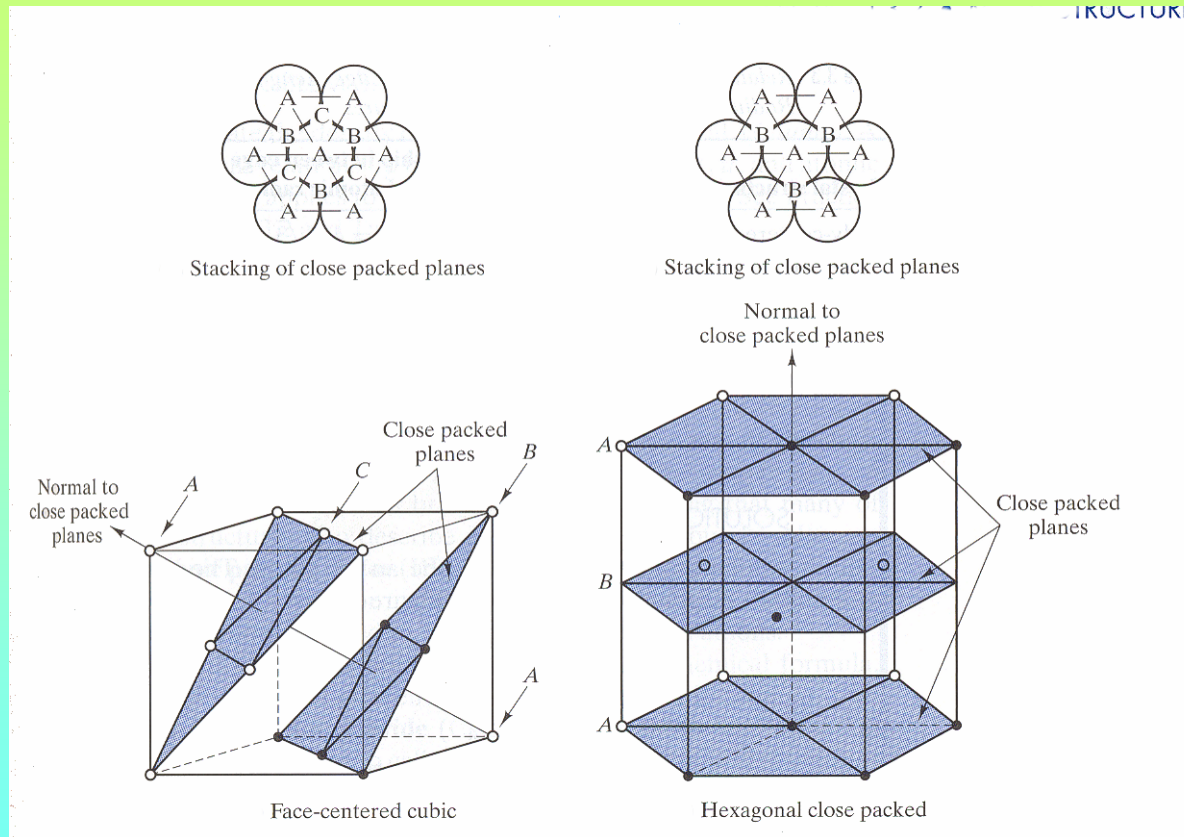
C sites



- FCC Unit Cell



# Comparing FCC and HCP Structures



The difference between the two structures lies in the different stacking sequences

# CLOSE-PACKED CRYSTALLOGRAPHIC DIRECTIONS AND PLANES

- In BCC, the close-packed planes are the  $\{110\}$  planes, and the close-packed directions are the  $\langle 111 \rangle$
- In FCC, the close-packed planes are the  $\{111\}$  planes, and the close-packed directions are the  $\langle 110 \rangle$  direction
- In HCP, the close-packed planes are the (0001) basal plane, and the close-packed directions are the  $[1000]$ ,  $[0100]$ , and  $[0010]$  directions and their negatives.
- We will see later the 'cp' planes and directions define *slip systems*

# *Characteristics of Selected Elements at 20 °C*

Element	Symbol	At. Weight (amu)	Density (g/cm <sup>3</sup> )	Crystal Structure	Atomic radius (nm)
Aluminum	Al	26.98	2.71	FCC	0.143
Argon	Ar	39.95	-----	-----	-----
Barium	Ba	137.33	3.5	BCC	0.217
Beryllium	Be	9.012	1.85	HCP	0.114
Boron	B	10.81	2.34	Rhomb	-----
Bromine	Br	79.90	-----	-----	-----
Cadmium	Cd	112.41	8.65	HCP	0.149
Calcium	Ca	40.08	1.55	FCC	0.197
Carbon	C	12.011	2.25	Hex	0.071
Cesium	Cs	132.91	1.87	BCC	0.265
Chlorine	Cl	35.45	-----	-----	-----
Chromium	Cr	52.00	7.19	BCC	0.125
Cobalt	Co	58.93	8.9	HCP	0.125
<b>Copper</b>	<b>Cu</b>	<b>63.55</b>	<b>8.94</b>	<b>FCC</b>	<b>0.128</b>
Flourine	F	19.00	-----	-----	-----
Gallium	Ga	69.72	5.90	Ortho.	0.122
Germanium	Ge	72.59	5.32	Dia. cubic	0.122
Gold	Au	196.97	19.32	FCC	0.144
Helium	He	4.003	-----	-----	-----
Hydrogen	H	1.008	-----	-----	-----

# Theoretical Density, $\rho$

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

# atoms/unit cell  $\rightarrow$   $n$       Atomic weight (g/mol)  $\rightarrow$   $A$   
 Volume/unit cell  $\rightarrow$   $V_c$       Avogadro's number  $\rightarrow$   $N_A$   
 ( $\text{cm}^3/\text{unit cell}$ )      ( $6.023 \times 10^{23}$  atoms/mol)

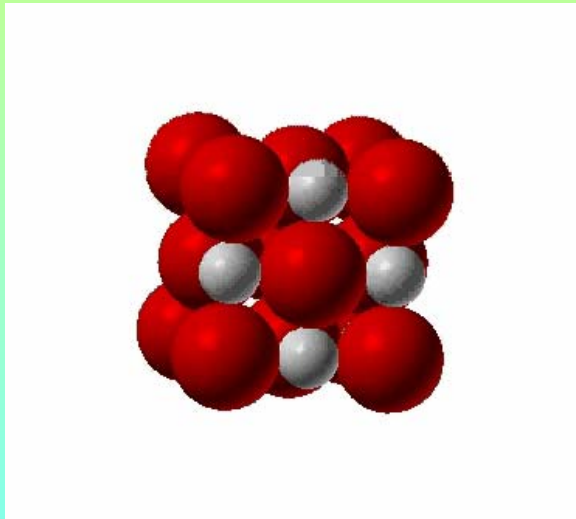
## Example: Copper

- crystal structure **FCC**
- # atoms/unit cell = **4**
- atomic weight = **63.55 g/mol**
- atomic radius  $R = \mathbf{0.128 \text{ nm}}$
- for FCC  $\mathbf{a = 2R\sqrt{2}}$ ;  $V_c = a^3$ ;  $V_c = 4.75 \times 10^{-23} \text{ cm}^3$

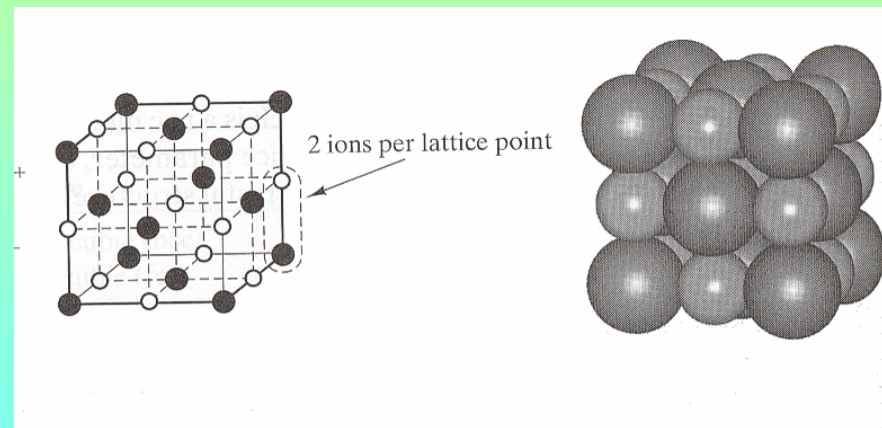
Result: theoretical	$\rho_{\text{Cu}} = 8.89 \text{ g/cm}^3$
Compare to actual:	$\rho_{\text{Cu}} = 8.94 \text{ g/cm}^3$

# CERAMIC STRUCTURE (1)

- Ceramics with chemical formula MX :
- Structure of NaCl



This structure can be described as having FCC Bravais lattice with two ions (1Na<sup>+</sup> and 1Cl<sup>-</sup>) associated with each lattice point.



- Close-packed directions --along cube edges.
- Eight ions per unit cell: (4Mg<sup>2+</sup> and 4O<sup>2-</sup>)

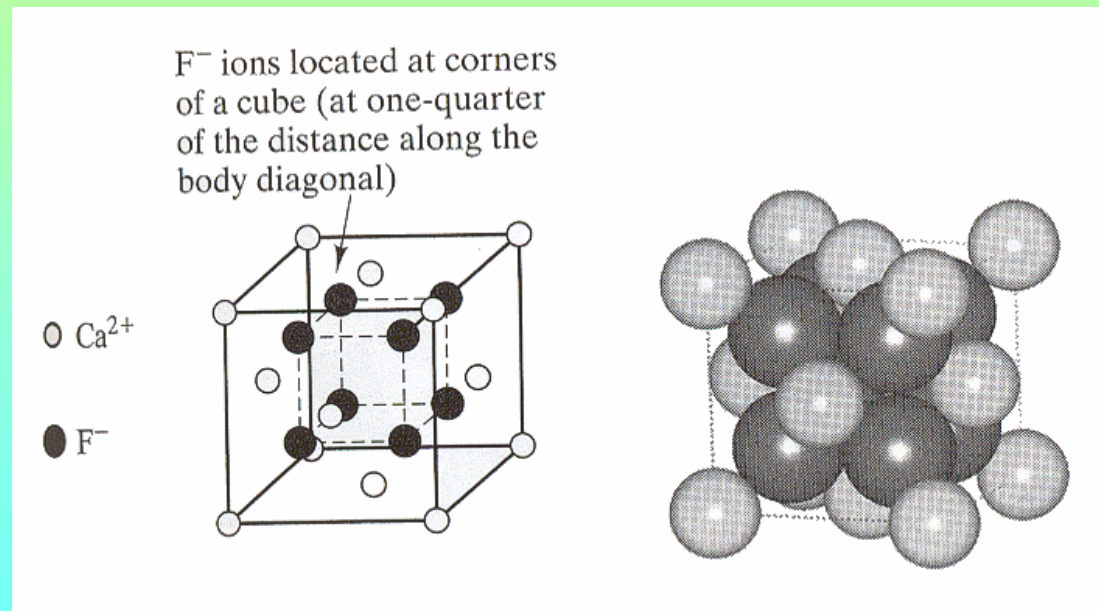
**Ionic Packing Factor (IPF): 0.627**

**Examples: MgO; CaO; FeO**

# *CERAMIC STRUCTURE (2)*

- The chemical formula  $\text{MX}_2$ : e.g. fluorite ( $\text{CaF}_2$ ) structure

This structure is built on the an FCC Bravais lattice with three ions ( $1\text{Ca}^{+2}$  and  $2\text{F}^-$ ) associated with each lattice point.



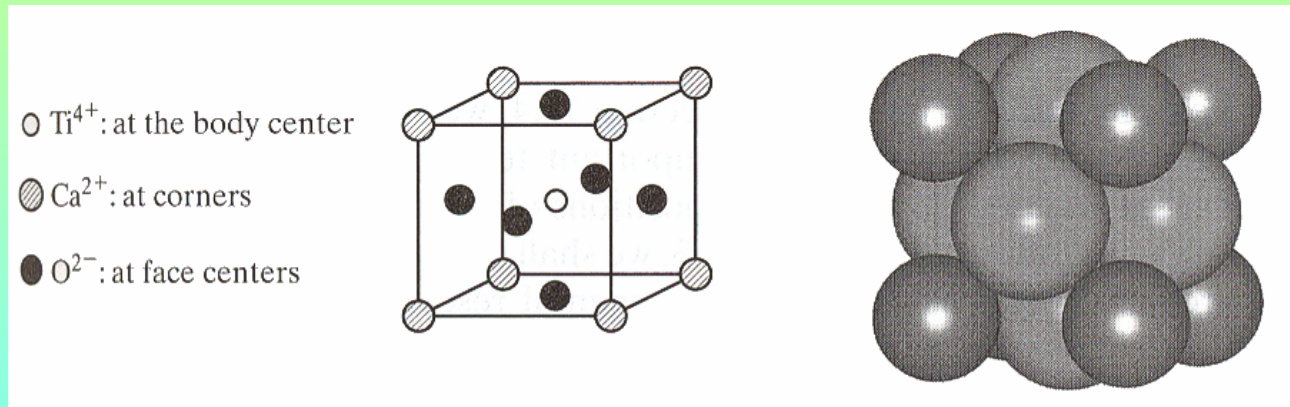
- 12 ions ( $4\text{Ca}^{2+}$  and  $8\text{F}^-$ ) per unit cell

**Examples:**  $\text{UO}_2$ ;  $\text{ThO}_2$ ;  $\text{TeO}_2$



# *CERAMIC STRUCTURE (3)*

- **Perovskite** - the chemical formula  $MM'O_3$ : e.g.  $CaTiO_3$  structure
- Structure of  $CaTiO_3$



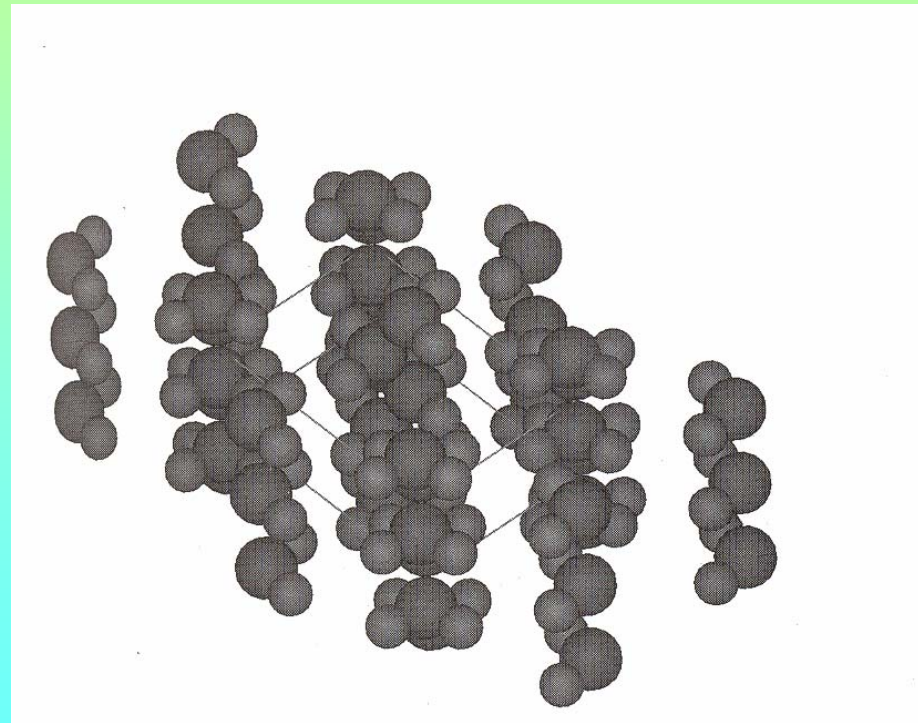
- 5 ions ( $1Ca^{2+}$ ,  $1Ti^{4+}$  and  $3O^{2-}$ ) per unit cell

**Examples:**  $BaTiO_3$ ;  $SrRuO_3$

# Polymeric Structures

- Polymers – the chain-like structures of long polymeric molecules, which arrangement into a regular and repeating patterns is difficult. Thus most commercial plastics are noncrystalline.
- One example of the unit cell for common polymer, i.e. **polyethylene**, consisting of  $C_2H_4$  molecules chains

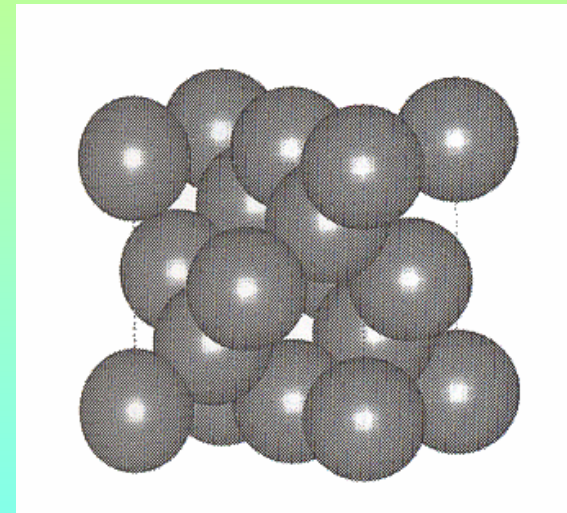
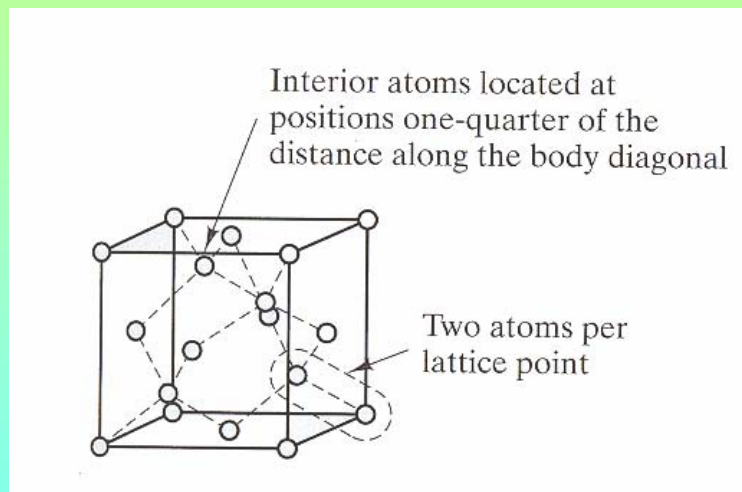
The darker larger sphere are **carbon** atoms, while lighter small ones are **hydrogen** atoms. The *unit cell dimensions* are 0.225nm x 0.494nm x 0.741nm



The orthorhombic unit cell, which is common for polymeric crystals

# Semiconductor Structures

- A single structure dominates the semiconductor industry: **the diamond cubic structure** (Examples: Si, Ge and gray Sn).



**Atoms/unit cell:**  $4+6 \times 1/2+8 \times 1/8=8$

**APF** = 0.340

This structure is built on the FCC Bravais lattice with two atoms associated with each lattice point and eight atoms per unit cell.

# Densities of Materials Classes

$\rho_{\text{metals}}$

$\rho_{\text{ceramics}}$

$\rho_{\text{polymers}}$

Metals/  
Alloys

Graphite/  
Ceramics/  
Semicond

Polymers

Composites/  
fibers

Why?

Metals have...

- close-packing  
(metallic bonding)
- large atomic mass

Ceramics have...

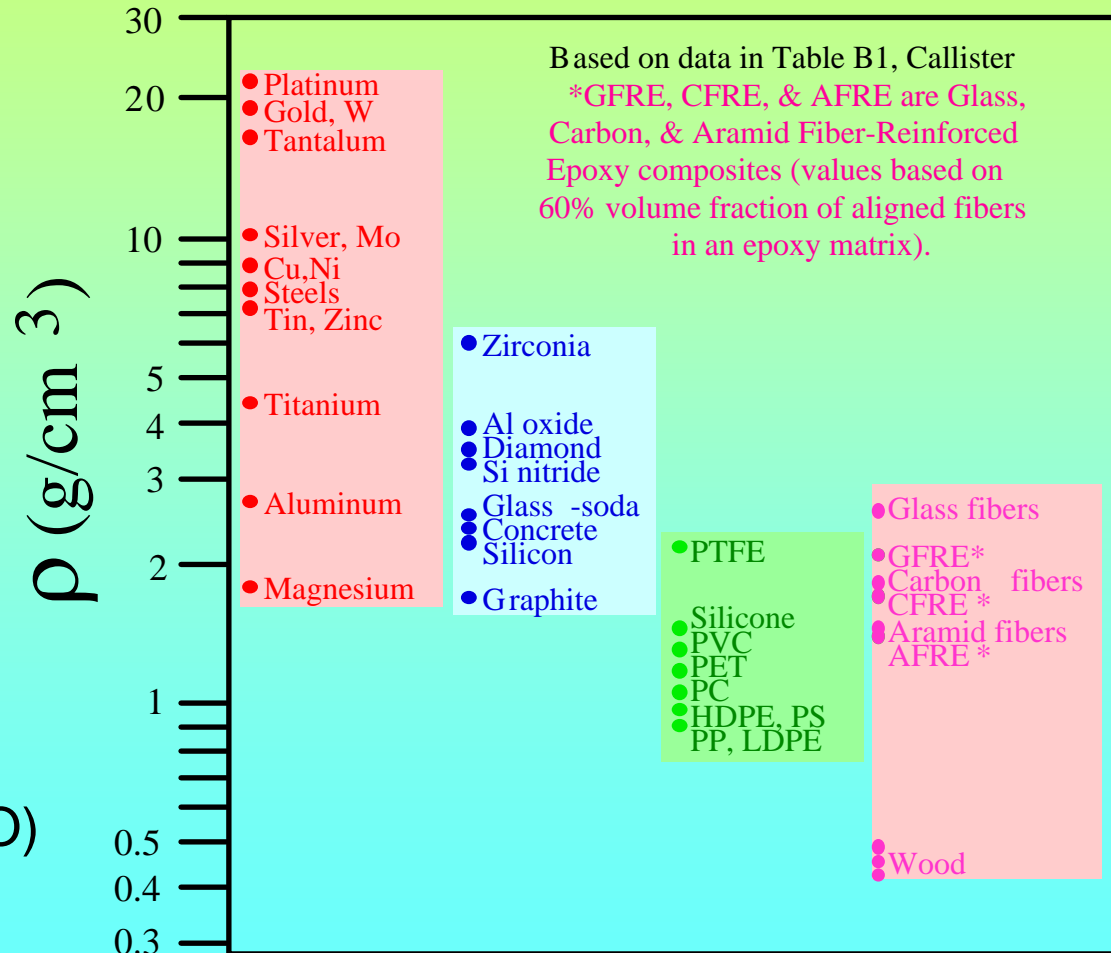
- less dense packing  
(covalent bonding)
- often lighter elements

Polymers have...

- poor packing  
(often amorphous)
- lighter elements (C,H,O)

Composites have...

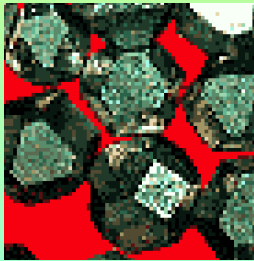
- intermediate values



# ***CRYSTALS AS BUILDING BLOCKS***

- *Some* engineering applications require single crystals:

--diamond single  
crystals for abrasives



--turbine blades



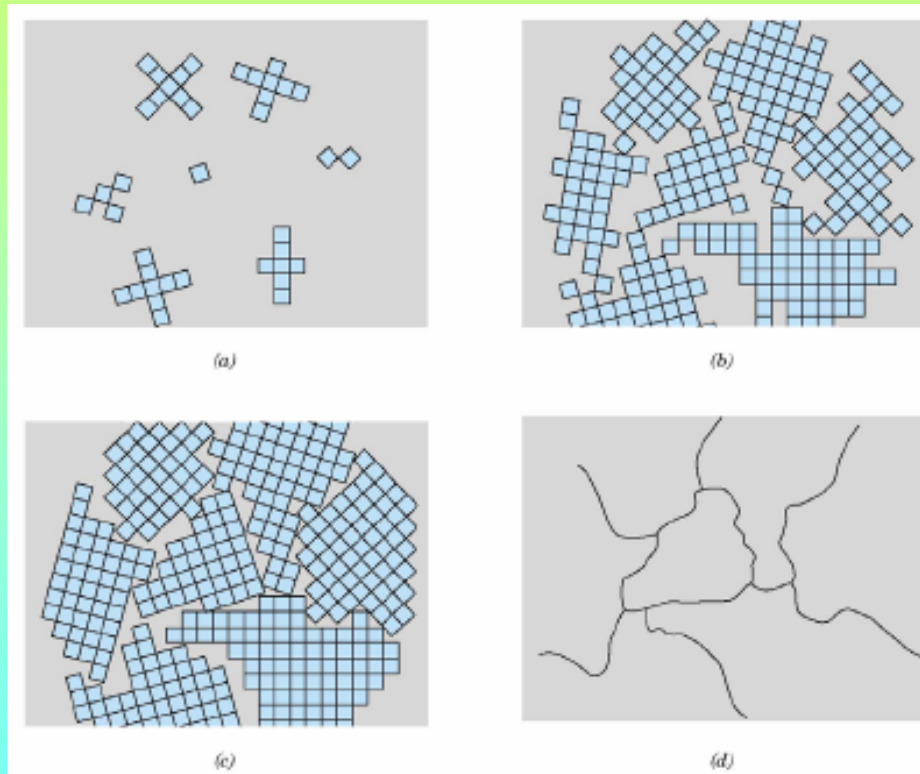
- Crystal properties reveal features of atomic structure.

--Ex: Certain crystal planes in quartz fracture more easily than others.



# ***POLYCRYSTALS (1)***

- Most engineering materials are polycrystals.



- Each "grain" is a single crystal.
- If crystals are randomly oriented, overall component properties are not directional.
- Crystal sizes range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

The square grids depicts unit cells. (a) Small crystalline nuclei; (b) Growth of the crystallites; (c) Irregular shape grains upon completion of solidification; (d) Grain boundaries.

# *POLYCRYSTALS (2)*

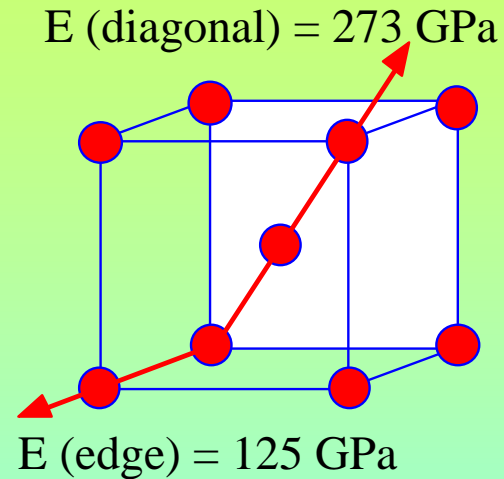


- Nb-Hf-W plate with an electron beam weld.
  - Each "grain" is a single crystal.

# *SINGLE VS POLYCRYSTALS*

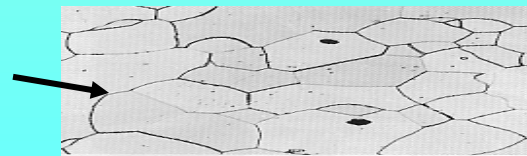
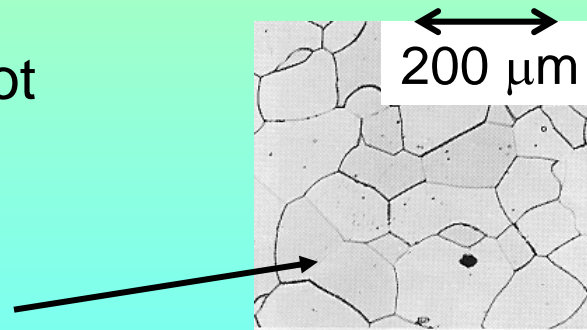
- **Single Crystals**

- Properties vary with direction: **anisotropic**.
- Example: the modulus of elasticity ( $E$ ) in BCC iron:



- **Polycrystals**

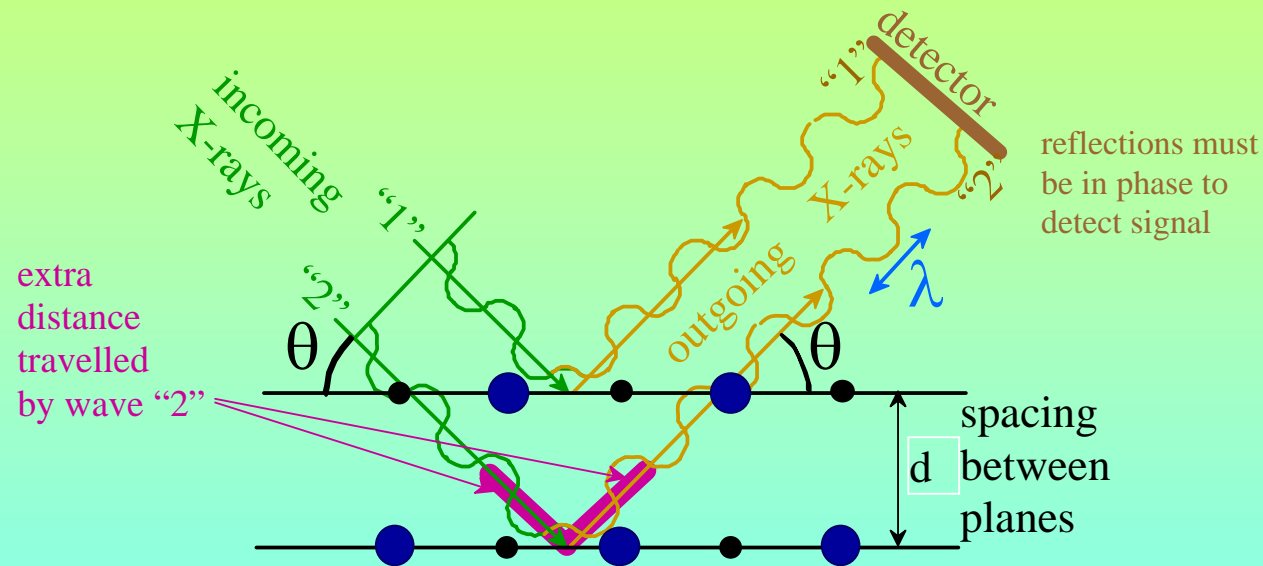
- Properties may/may not vary with direction.
- If grains are randomly oriented: **isotropic**.  
( $E_{\text{poly iron}} = 210$  GPa)
- If grains are **textured**, anisotropic.





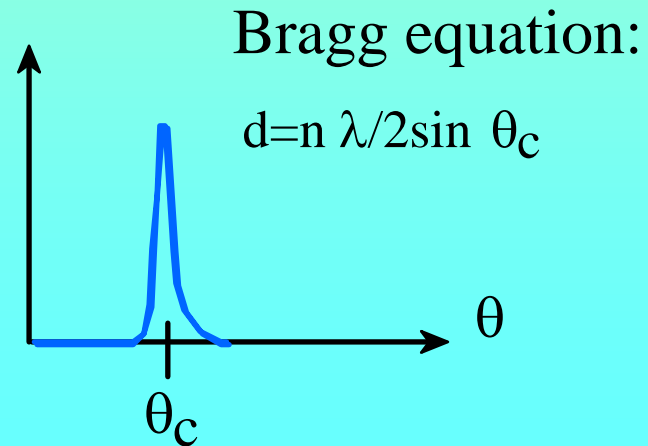
# X-RAYS TO CONFIRM CRYSTAL STRUCTURE

- Incoming X-rays **diffract** from crystal planes.



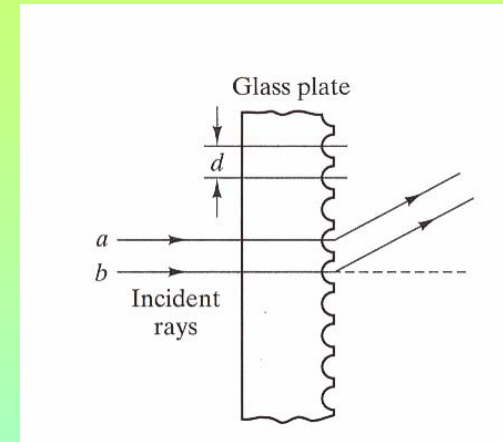
- Measurement of:  
Critical angles,  $\theta_c$ ,  
for X-rays provide  
atomic spacing,  $d$ .

x-ray  
intensity  
(from  
detector)



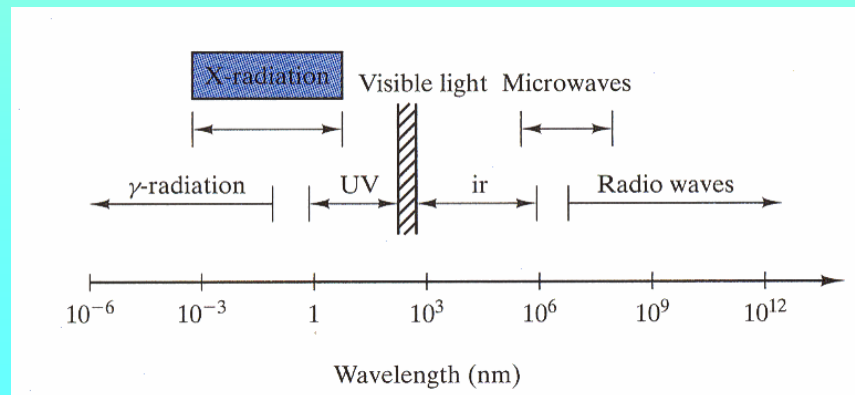
# X-RAY DIFFRACTION

- **Diffraction** is the preferential radiation scattering in some specific directions, which occurs as a result of photons being interact with some regular array of scattering centers, whose spacing is on the order of the wavelength of the radiation



Diffraction grating for visible light

- The 3-D array of atoms in crystalline lattice are the scattering centers
- The atoms size is  $\sim 0.1$  nm, thus to observe diffraction we have to use X-rays ( $10^{-3}$  to 1nm; e.g.  $\text{CuK}_{\alpha}$ -radiation  $\lambda = 0.1542$  nm))



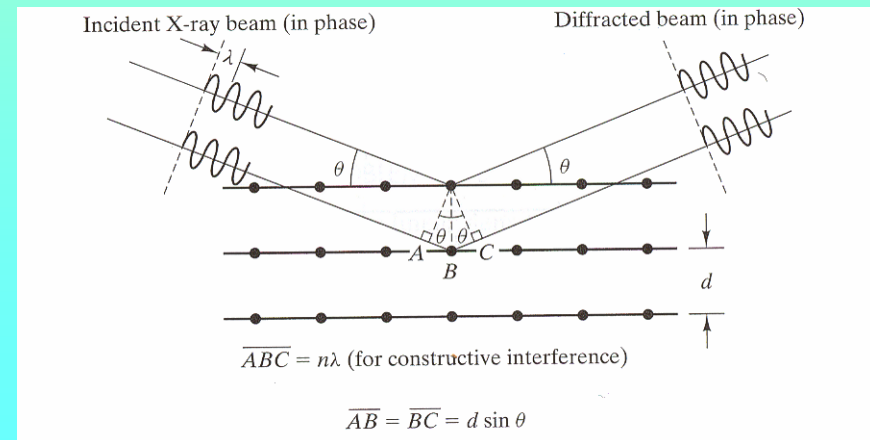
# BRAGG EQUATION

- For diffraction occurs x-ray beams scattered from the adjacent crystal planes must be in phase.
- The relationship that demonstrates this condition is the Bragg equation:

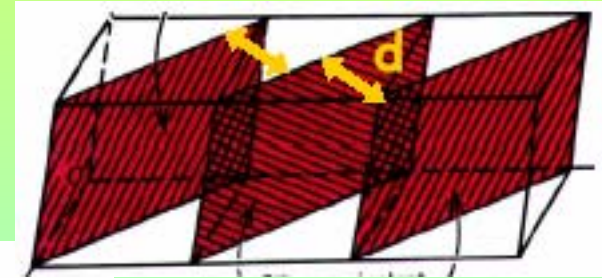
$$n\lambda = 2d \sin \Theta$$

$d$  – the spacing between adjacent crystal planes,  $\Theta$  – scattering angle,  $n$ - some integer number

For constructive interference of waves the difference in path length between the adjacent x-ray beams should be  $\sim$  to some integer number ( $n$ ) of radiation wavelength ( $\lambda$ )



# Inter-Planer Spacing



Cubics: 
$$\frac{1}{d_{hkl}^2} = \frac{(h^2+k^2+l^2)}{a^2}$$

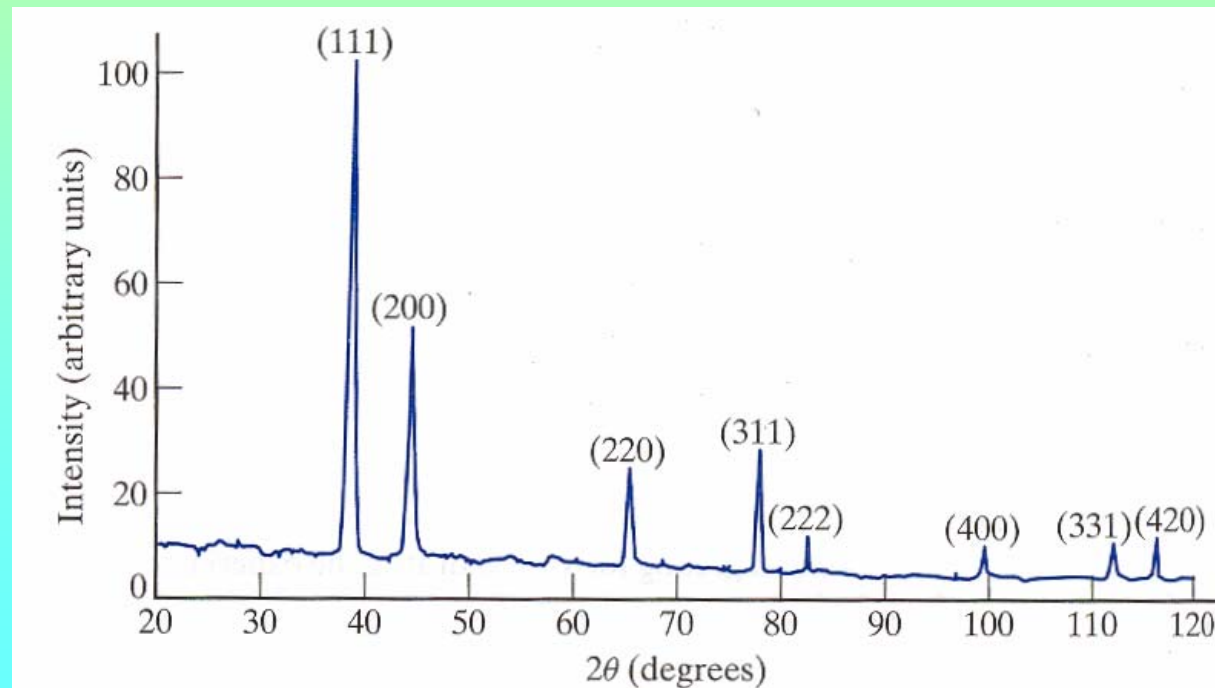
Tetragonal: 
$$\frac{1}{d_{hkl}^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic: 
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal: 
$$\frac{1}{d_{hkl}^2} = + \frac{4}{3} \frac{(h^2+hk+l^2)}{a^2} + \frac{l^2}{c^2}$$

# Example: Diffraction Patterns

- Each peak represents the solution to Bragg's law for known radiation wavelength ( $\lambda = 0.154\text{nm}$ )
- The unique relationship between such patterns and crystal structures provide a powerful tool for identification of the phase composition of powders and polycrystalline materials.



# ***SUMMARY***

- Atoms may assemble into **crystalline** or **amorphous** structures.
- We can predict the **density** of a material, provided we know the **atomic weight**, **atomic radius**, and **crystal geometry** (e.g., FCC, BCC, HCP).
- Material properties generally vary with single crystal orientation (i.e., they are **anisotropic**), but properties are generally non-directional (i.e., they are **isotropic**) in polycrystals with randomly oriented grains.