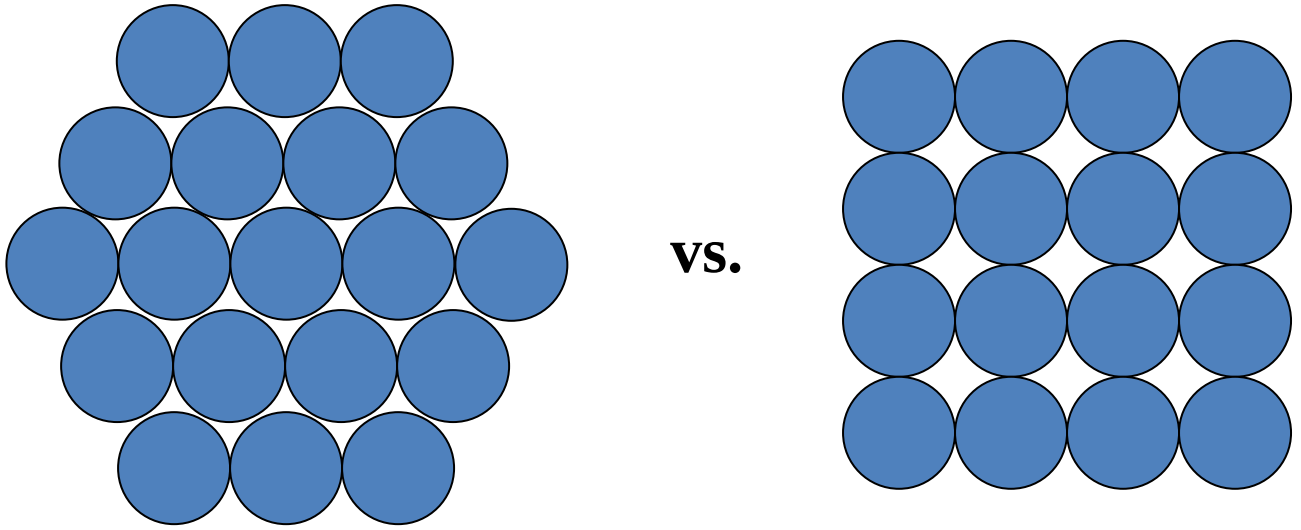
# CHAPTER 4

## THE STRUCTURE OF CRYSTALLINE SOLIDS

# METALLIC CRYSTAL STRUCTURES

- How can we stack metal atoms to minimize empty space?

2-dimensions




Now stack these 2-D layers to make 3-D structures

# METALLIC CRYSTAL STRUCTURES

- Tend to be densely packed.
- Reasons for dense packing:

  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional

  (*Strength of bond is equal in all directions )*.

  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - Electron cloud shields cores from each other
- Have the simplest crystal structures.

  We will examine three such structures...

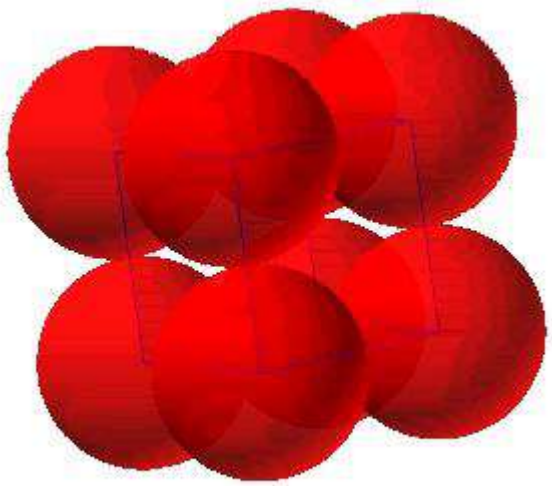
- Two important characteristics of a metal crystal structure

  - coordination number : number of nearest neighbour or touching atoms

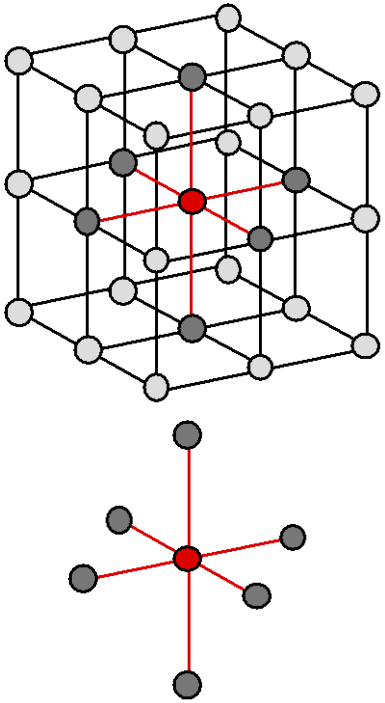
  - atomic packing factor (APF) : sum of the sphere volumes of all atoms within a unit cell

# SIMPLE CUBIC STRUCTURE (SC)

- Rare due to low packing density (only Po (polonium) has this structure)



- Coordination # = 6
  (# nearest neighbors)

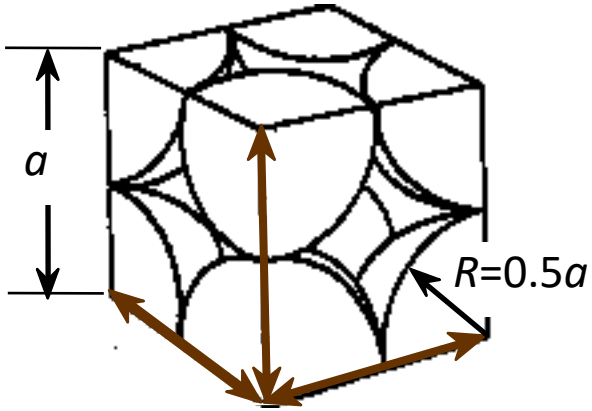


# ATOMIC PACKING FACTOR (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52




close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

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

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

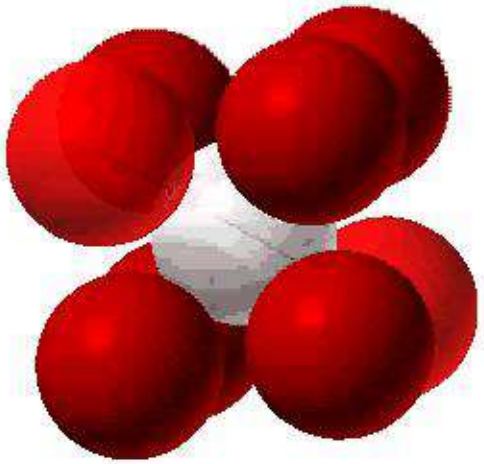
# BODY CENTERED CUBIC STRUCTURE (BCC)

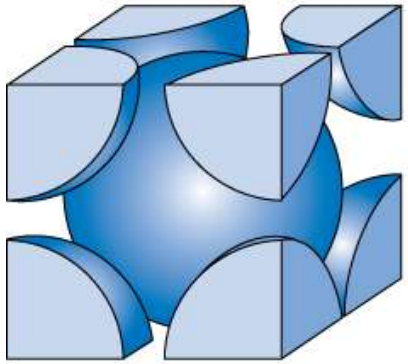
- Atoms touch each other along cube diagonals.

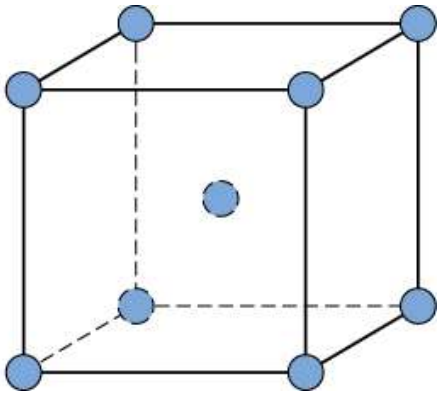
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe ($\alpha$), Tantalum, Molybdenum

- Coordination # = 8



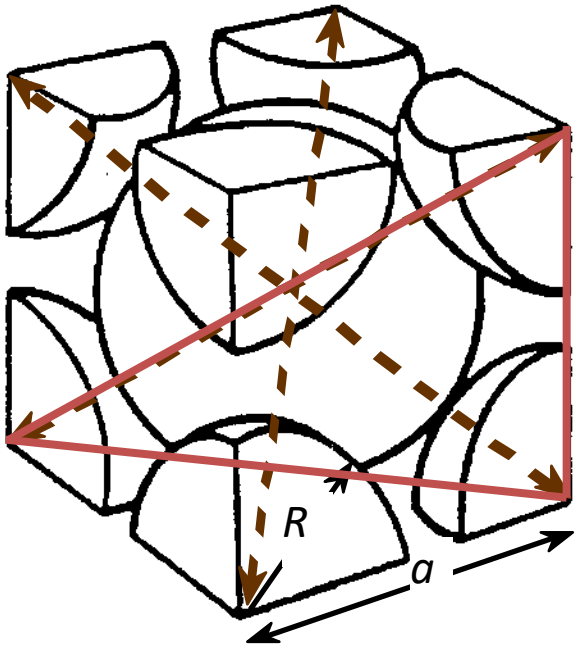


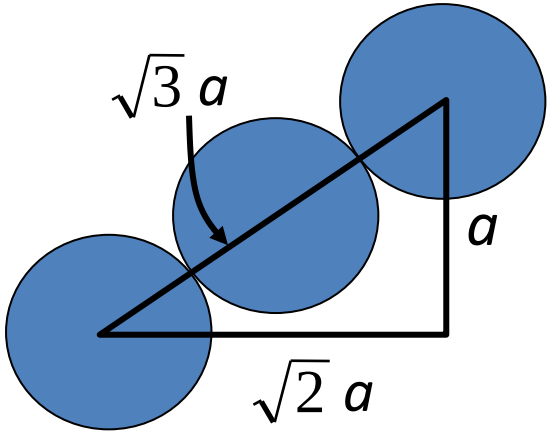


2 atoms/unit cell: 1 center + 8 corners x 1/8

# ATOMIC PACKING FACTOR (APF) - BCC

- APF for a body-centered cubic structure = 0.68




Close-packed directions:

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

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi\left(\sqrt{3}\,a/4\right)^3}{a^3}$$

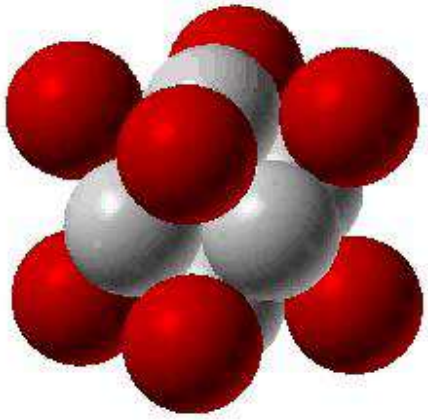
# FACE CENTERED CUBIC STRUCTURE (FCC)

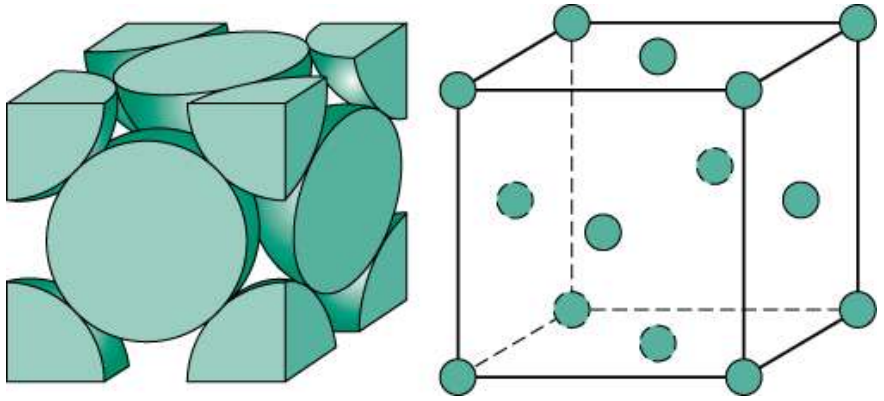
- Atoms touch each other along face diagonals.

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

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12

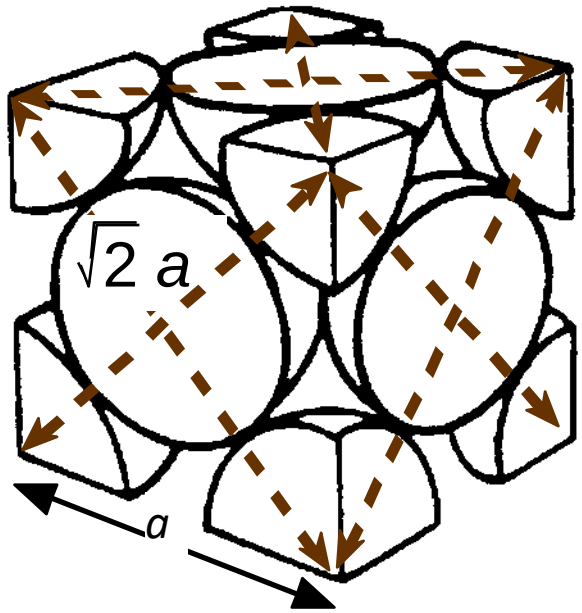




4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

# ATOMIC PACKING FACTOR (APF)- FCC

- APF for a face-centered cubic structure = 0.74




maximum achievable APF

Close-packed directions:

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

Unit cell contains:

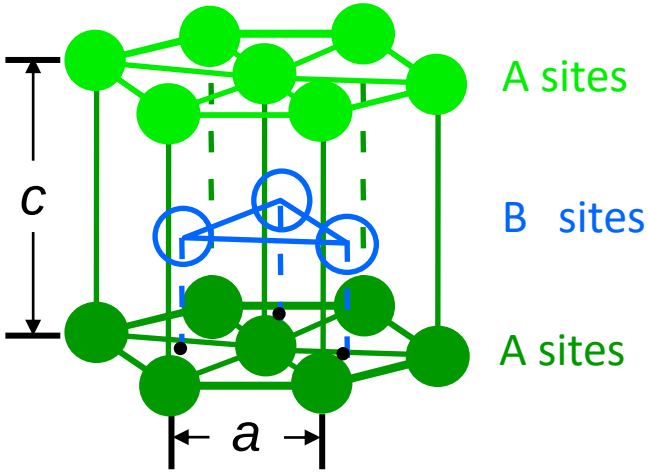
6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

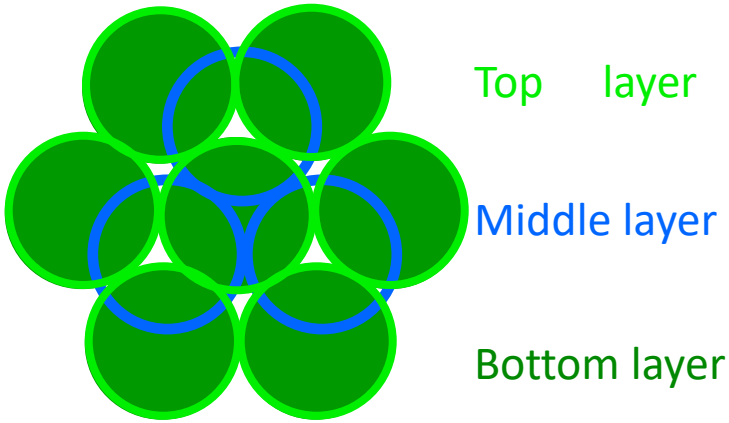
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}\,a}{4}\right)^3}{a^3}$$

# HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

- ABAB... Stacking Sequence
- 3D Projection




- 2D Projection

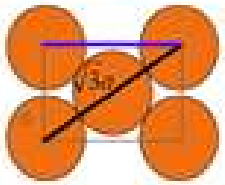
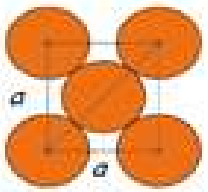



- Coordination # = 12
- APF = 0.74
- $c/a$ = 1.633

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

# Summary

| | a (lattice constant) | Atoms/unit cell | Coordi-nation No. | Examples |
|---|---|---|---|---|
| **Simple cubic** | a = 2R  | **1** | 6 | CsCl |
| **BCC** | a = 4R/√3  | **2** | 8 | Many metals: α-Fe, Cr, Mo, W |
| **FCC** | a = 4R/√2<br>or<br>a = 2R√2  | **4** | 12 | Many metals : Ag, Au, Cu, Pt |
| **HCP** | a = 2R<br>c = 1.633 a | **6** | 12 | Many metals : Co, Mg, Ti, Zn |

# EXAMPLE PROBLEM

1. Consider a BCC crystal structure. Given that length of the cube side is $a$, and the atomic radius is $R$. Calculate the atomic packing factor (APF) of BCC unit cell.

2. Show that the atomic packing factor for FCC crystal structure is 0.74.

# Crystal structure for some metals

| *Metal* | *Crystal Structure*[a] | *Atomic Radius*[b] *(nm)* | *Metal* | *Crystal Structure* | *Atomic Radius (nm)* |
|---|---|---|---|---|---|
| Aluminum | FCC | 0.1431 | Molybdenum | BCC | 0.1363 |
| Cadmium | HCP | 0.1490 | Nickel | FCC | 0.1246 |
| Chromium | BCC | 0.1249 | Platinum | FCC | 0.1387 |
| Cobalt | HCP | 0.1253 | Silver | FCC | 0.1445 |
| Copper | FCC | 0.1278 | Tantalum | BCC | 0.1430 |
| Gold | FCC | 0.1442 | Titanium ($\alpha$) | HCP | 0.1445 |
| Iron ($\alpha$) | BCC | 0.1241 | Tungsten | BCC | 0.1371 |
| Lead | FCC | 0.1750 | Zinc | HCP | 0.1332 |

# THEORETICAL DENSITY, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

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

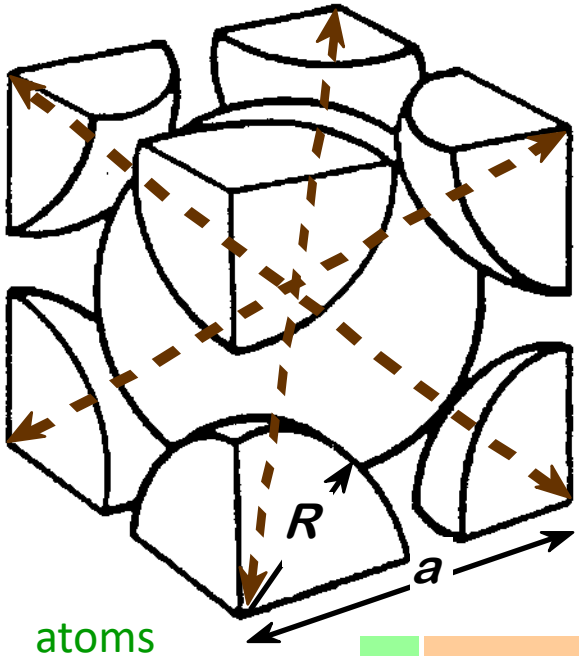
where $n$ = number of atoms/unit cell

$A$ = atomic weight

$V_C$ = Volume of unit cell = $a^3$ for cubic

$N_A$ = Avogadro's number

= $6.022 \times 10^{23}$ atoms/mol




- Ex: Cr (BCC)

  $A$ = 52.00 g/mol

  $R$ = 0.125 nm

  $n$ = 2 atoms/unit cell

$$a = 4R/\sqrt{3} = 0.2887 \text{ nm}$$

$$\rho = \frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{g}}{\text{mol}} \div \frac{\text{volume}}{\text{unit cell}} \times \frac{\text{atoms}}{\text{mol}}$$

$$\rho = \frac{2 \times 52.00}{a^3 \times 6.022 \times 10^{23}}$$

| | |
|---|---|
| $\rho_{theoretical}$ | = 7.18 g/cm$^3$ |
| $\rho_{actual}$ | = 7.19 g/cm$^3$ |

# EXAMPLE PROBLEM

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.

# CERAMIC CRYSTAL STRUCTURE

# Ceramic Materials

- *keramikos* - burnt stuff in Greek → desirable properties of ceramics are normally achieved through a high-temperature heat treatment process (*firing*).
- Usually a compound between metallic and non-metallic elements.
- Always composed of more than one element (e.g.,$Al_2O_3$, NaCl, SiC, $SiO_2$)
- Interaction bond either totally ionic or having some covalent character

Properties :

- • Generally hard and brittle
- • *Generally* electrical and thermal **insulators** (exceptions: graphite,
- diamond, AlN… and others)
- • Can be optically opaque, semi-transparent, or transparent
- High chemical stability and high melting temperature.

# Class of ceramic

Traditional Ceramics: primary raw materials is clay
Example: porcelain, bricks, tiles, glasses.

# Class of ceramic

Oxygen sensor


Now new generation of this materials have evolved

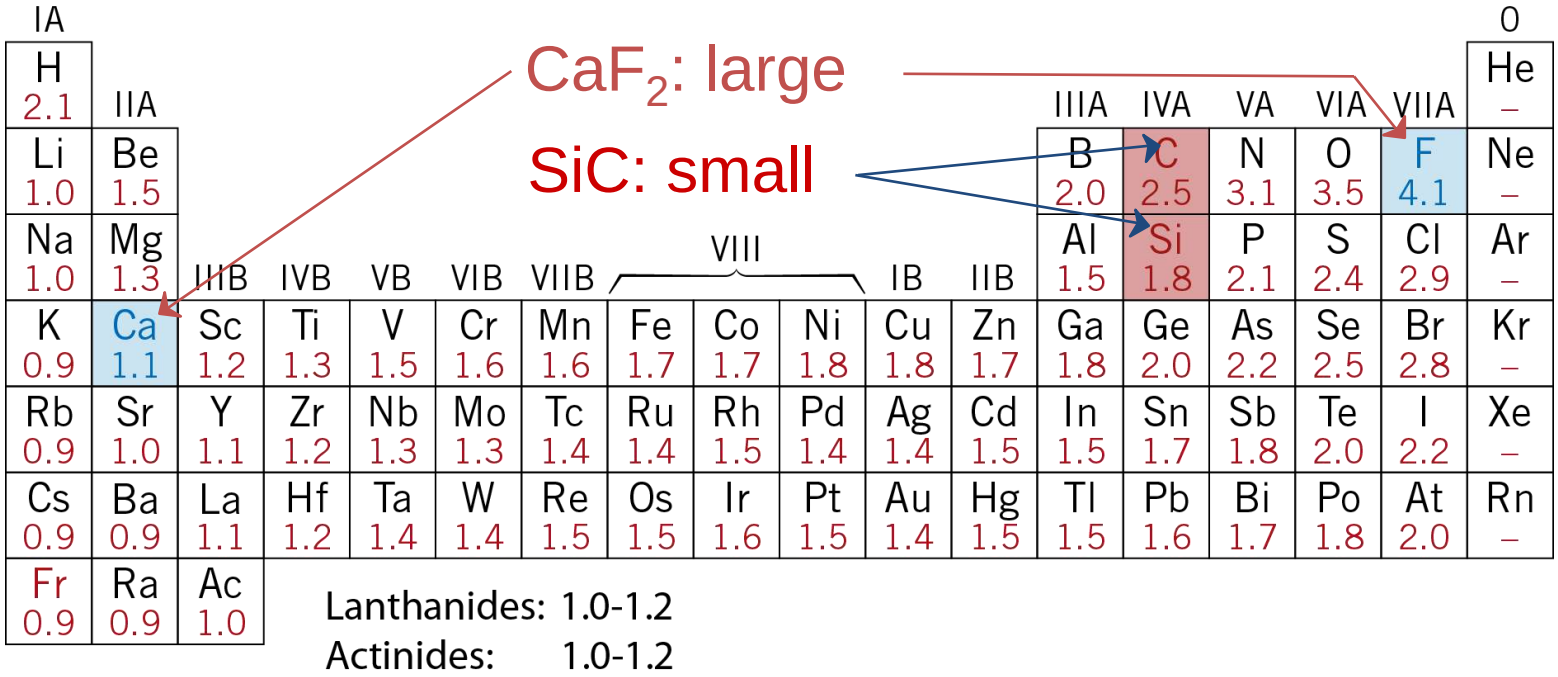
Engineering Ceramics

- High-temperature ceramic
- Advance ceramic
- Electroceramic

Aerospace product-Ni
Ti, Stainless steel

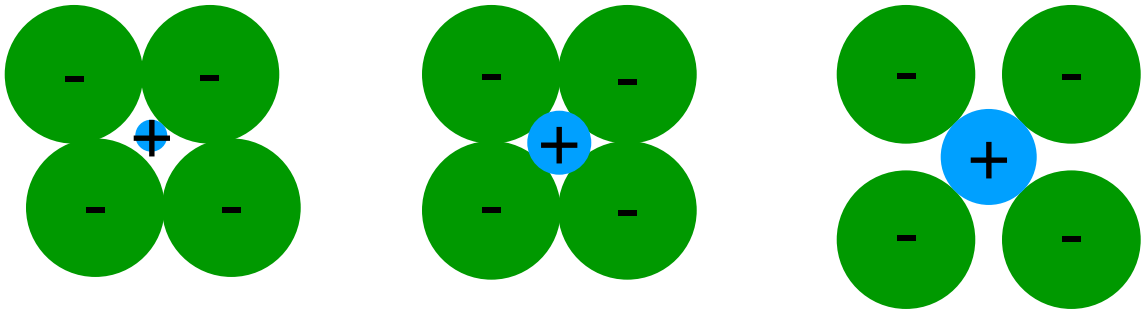
# Atomic Bonding in Ceramics

- Bonding:
  -- Can be ionic and/or covalent in character.
  -- % ionic character increases with difference in electronegativity of atoms.
- Degree of ionic character may be large or small:



# Factors that Determine Crystal Structure

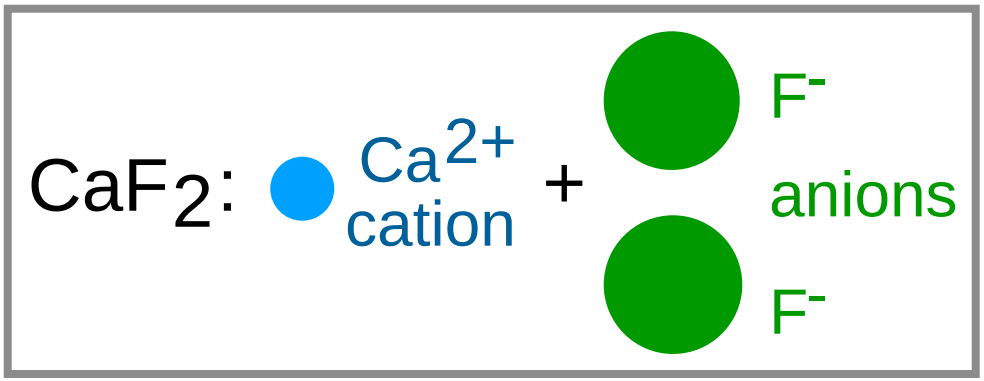
1. Relative sizes of ions – Formation of stable structures:
   --maximize the # of oppositely charged ion neighbors.




unstable stable stable

Adapted from Fig. 4.4, *Callister & Rethwisch 9e.*

2. Maintenance of Charge Neutrality :
   --Net charge in ceramic should be zero.
   --Reflected in chemical formula:




$A_mX_p$

m, p values to achieve charge neutrality

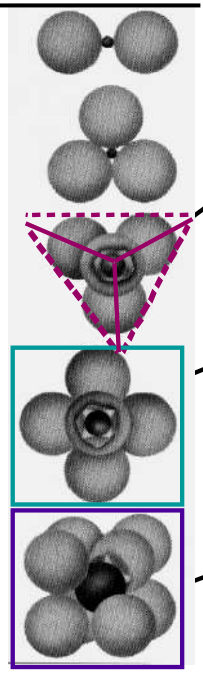
# Coordination Number and Ionic Radii

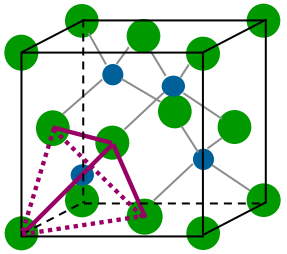
- Coordination Number increases with $\frac{r_{cation}}{r_{anion}}$

To form a stable structure, how many anions can surround around a cation?

| $\frac{r_{cation}}{r_{anion}}$ | Coord. Number | |
|---|---|---|
| < 0.155 | 2 | linear |
| 0.155 - 0.225 | 3 | triangular |
| 0.225 - 0.414 | 4 | tetrahedral |
| 0.414 - 0.732 | 6 | octahedral |
| 0.732 - 1.0 | 8 | cubic |

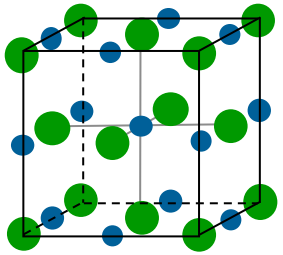
Adapted from Table 4.3, *Callister & Rethwisch 9e.*





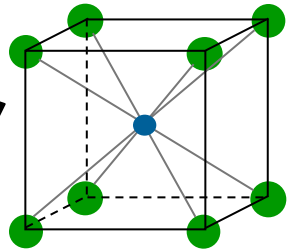
ZnS (zinc blende)

Adapted from Fig. 4.7, *Callister & Rethwisch 9e.*



NaCl (sodium chloride)

Adapted from Fig. 4.5, *Callister & Rethwisch 9e.*

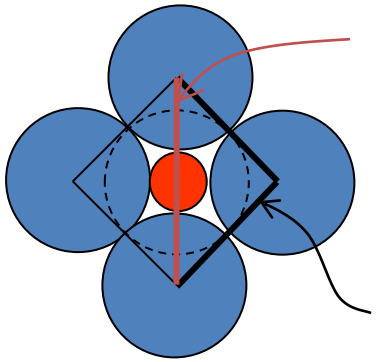


CsCl (cesium chloride)

Adapted from Fig. 4.6, *Callister & Rethwisch 9e.*

# Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum $r_{cation}/r_{anion}$ for an octahedral site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

$$a = 2r_{anion}$$

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion} \qquad r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414$$

# Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

| Cation | Ionic radius (nm) |
|---|---|
| $Al^{3+}$ | 0.053 |
| $Fe^{2+}$ | 0.077 |
| $Fe^{3+}$ | 0.069 |
| $Ca^{2+}$ | 0.100 |

| Anion | |
|---|---|
| $O^{2-}$ | 0.140 |
| $Cl^{-}$ | 0.181 |
| $F^{-}$ | 0.133 |

Data from Table 4.4, *Callister & Rethwisch 9e.*

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140} = 0.550$$

based on this ratio,
-- coord # = 6 because

$$0.414 < 0.550 < 0.732$$

-- crystal structure is NaCl

# Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what is the coordination number and coordination geometry would you predict for FeO?

| Cation | Ionic radius (nm) |
|---|---|
| $Al^{3+}$ | 0.053 |
| $Fe^{2+}$ | 0.077 |
| $Fe^{3+}$ | 0.069 |
| $Ca^{2+}$ | 0.100 |

| Anion | |
|---|---|
| $O^{2-}$ | 0.140 |
| $Cl^{-}$ | 0.181 |
| $F^{-}$ | 0.133 |

Data from Table 4.4, *Callister & Rethwisch 9e.*

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140} = 0.550$$

based on this ratio,
-- coord # = 6 because

$$0.414 < 0.550 < 0.732$$

-- Coordination geometry is octahedral

# Ceramic Crystal Structure

1. AX - Type Crystal Structures

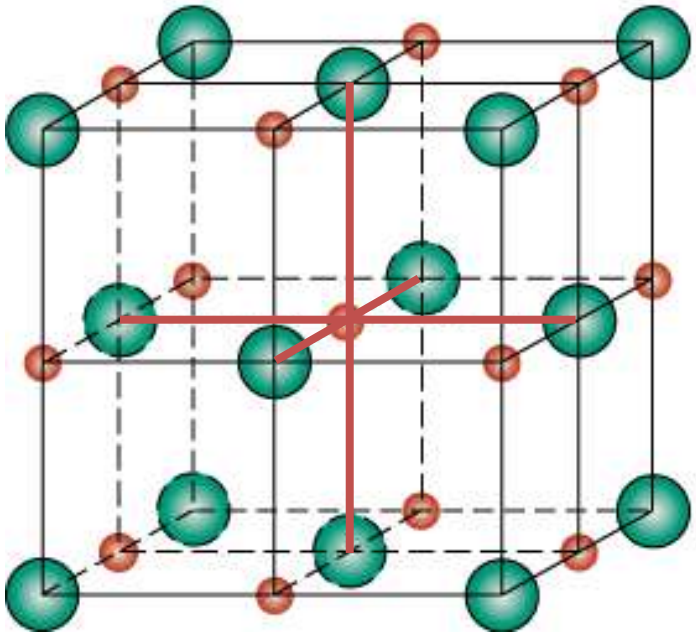
   Include: NaCl, CsCl, and zinc blende structures

2. $A_mX_p$ – Type Crystal Structures

3. $A_mB_nX_p$ Crystal Structures

# AX Crystal Structures

1. NaCl (rock salt) structure



Adapted from Fig. 4.5,
*Callister & Rethwisch 9e.*

$Na^+$ $r_{Na} = 0.102$ nm

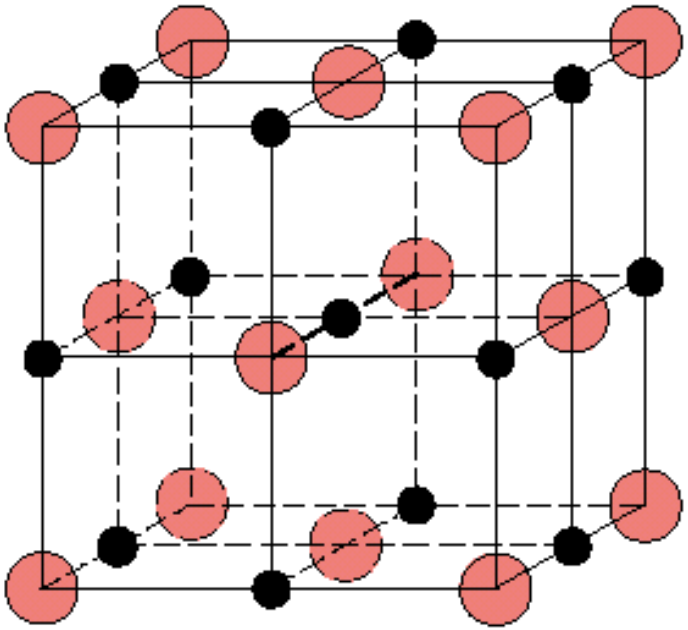
$Cl^-$ $r_{Cl} = 0.181$ nm

$r_{Na}/r_{Cl} = 0.564$

$\therefore$ cations ($Na^+$) prefer octahedral sites

# MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 4.5,
*Callister & Rethwisch 9e.*

$O^{2-}$ $r_O = 0.140$ nm

$Mg^{2+}$ $r_{Mg} = 0.072$ nm

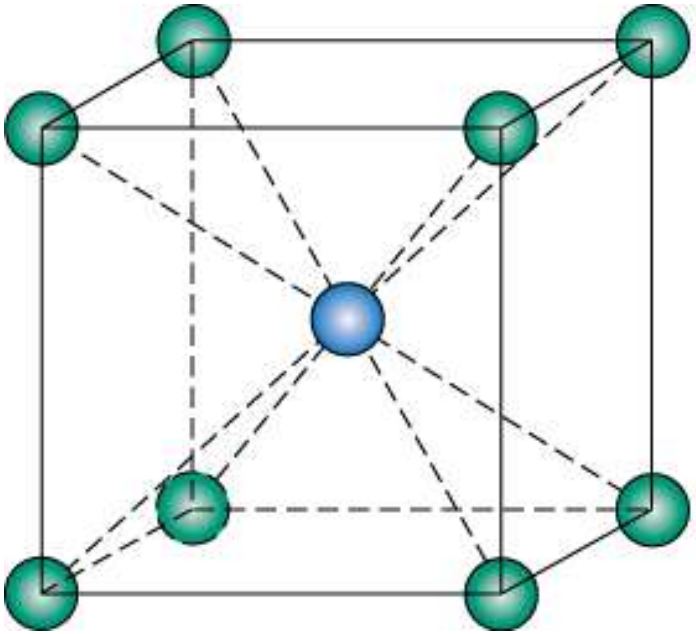
$r_{Mg}/r_O = 0.514$

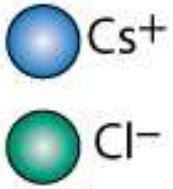
$\therefore$ cations prefer octahedral sites

So each $Mg^{2+}$ (or $Fe^{2+}$) has 6 neighbor oxygen atoms

# AX Crystal Structures

2. Cesium Chloride structure






$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

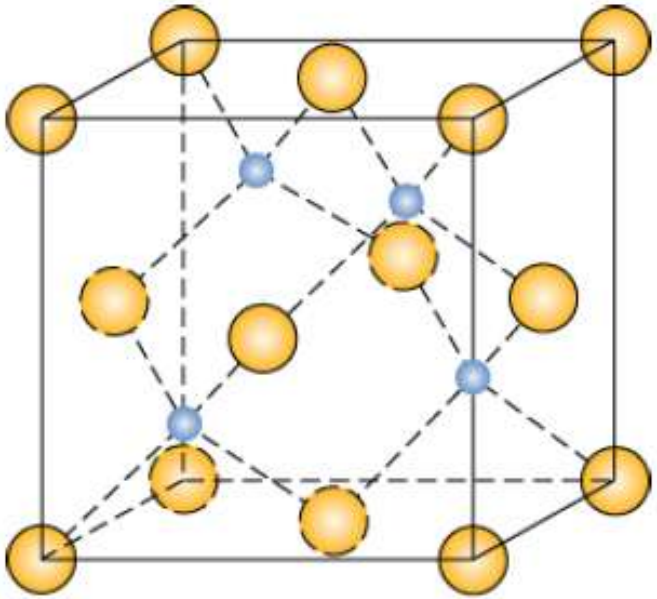
$\therefore$ Since 0.732 < 0.939 < 1.0, cubic sites preferred

So each $Cs^+$ has 8 neighbor $Cl^-$

Fig. 4.6, *Callister & Rethwisch 9e.*

# AX-type Crystal structure

## Zinc Blende structure (S atom at corner and face position, Zn fill interior tetrahedral position)



$Zn^{2+}$ $S^{2-}$

Example: ZnO, ZnS, SiC

$$\frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow \text{octahedron??}$$

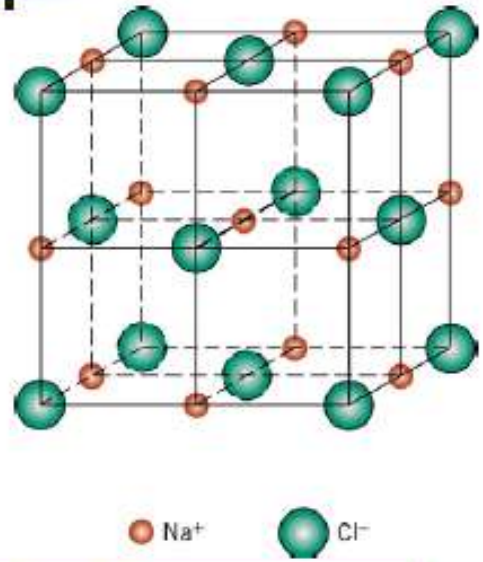
- Size arguments predict $Zn^{2+}$ in octahedron sites
- In observed structure $Zn^{2+}$ in tetrahedron sites

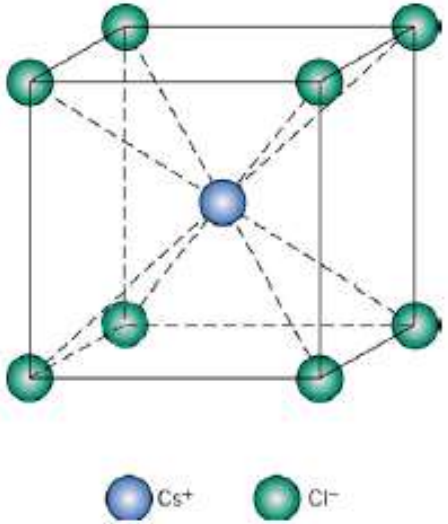
**Why is $Zn^{2+}$ in *tetrahedron* sites?**

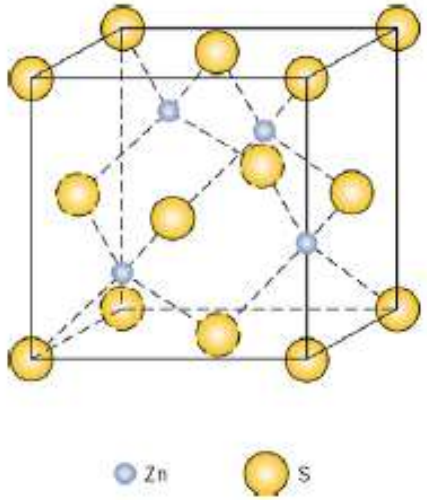
*bonding hybridization of zinc favors tetrahedron sites*

So each $Zn^{2+}$ has 4 neighboring $S^{2-}$

# Summary - AX




**Rock Salts**

Generated from FCC arrangement

Ceramics: NaCl, NiO, MgO, FeO

**Cesium Chloride**

Generated from BCC arrangement

Ceramics: CsCl, TlCl and TlBr

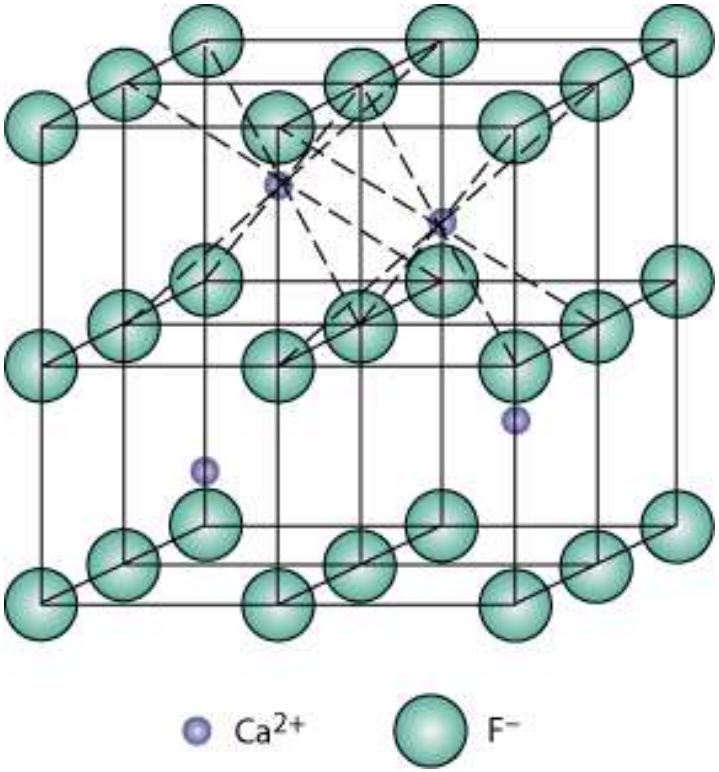
**Zinc Blende**

Generated from FCC arrangement

Ceramics: ZnO, CdS, InAs, GaAs, ZnSe, SiC

# $AX_2$ Crystal Structures

## Fluorite structure




- Calcium Fluorite ($CaF_2$)
- Cations in cubic sites

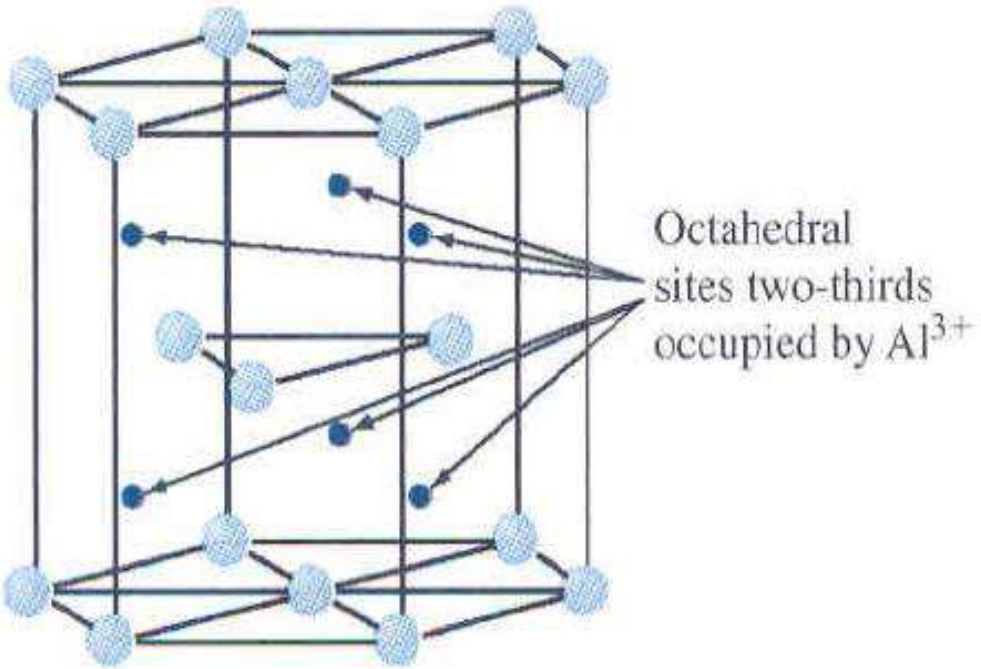
- $UO_2$, $ThO_2$, $ZrO_2$, $CeO_2$

- Antifluorite structure – positions of cations and anions reversed

Fig. 4.8, *Callister & Rethwisch 9e.*

# $A_yX_z$

- Corundum; $Al_2O_3$



# $ABX_3$ Crystal Structures

- Perovskite structure

Ex: complex oxide

$BaTiO_3$

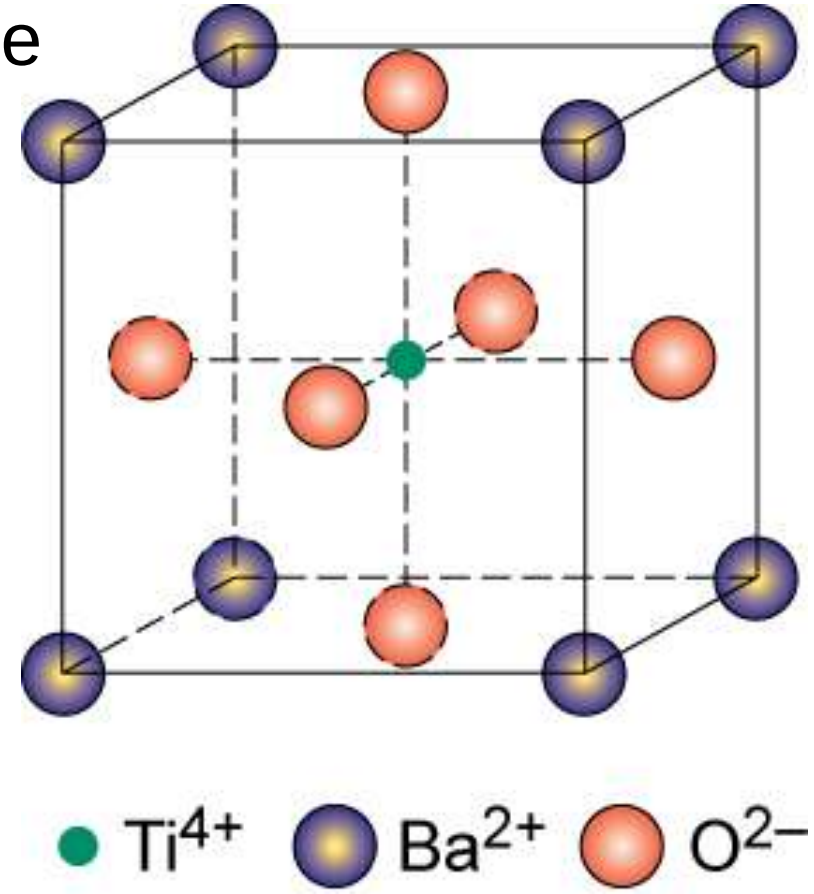



Fig. 4.9, *Callister & Rethwisch 9e.*

# Density Computations for Ceramics

Number of formula units/unit cell

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$

Avogadro's number

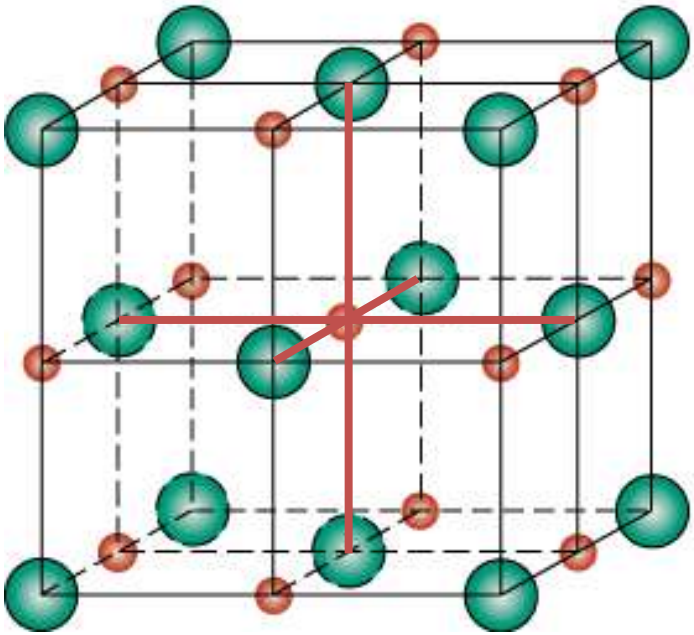
Volume of unit cell

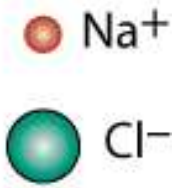
$\Sigma A_C$ = sum of atomic weights of all cations in formula unit

$\Sigma A_A$ = sum of atomic weights of all anions in formula unit

# Density Computations for Ceramics - Example

On the basis of the crystal structure, compute the theoretical density for sodium chloride. ($A_{Na}$ = 23 g/mol; $A_{Cl}$ = 35.5 g/mol)






$r_{Na}$ = 0.102 nm

$r_{Cl}$ = 0.181 nm

Adapted from Fig. 4.5,
*Callister & Rethwisch 9e.*

# Densities of Material Classes

In general

$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

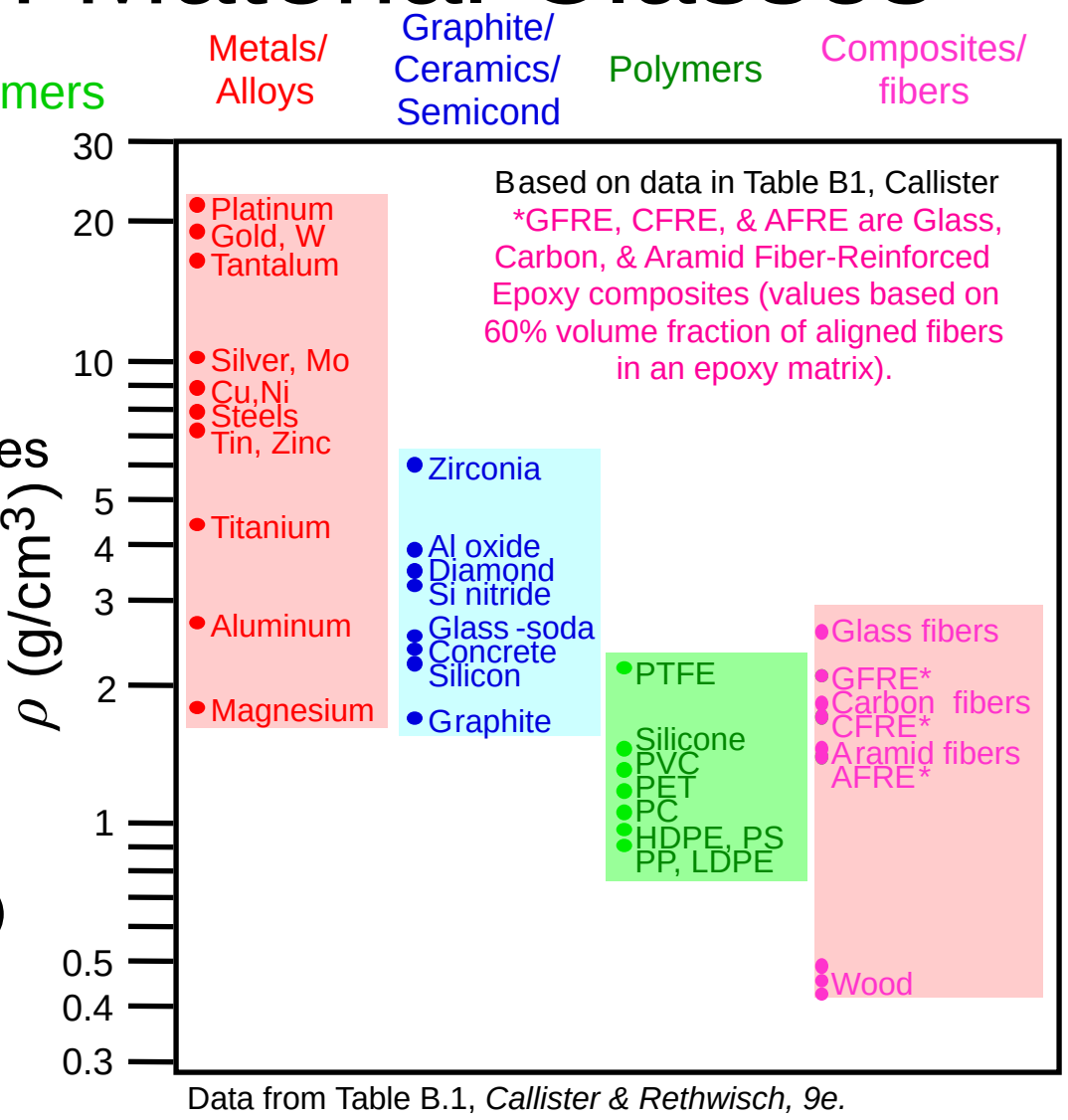
Why?

**Metals** have...
- close-packing (metallic bonding)
- often large atomic masses

**Ceramics** have...
- less dense packing
- often lighter elements

**Polymers** have...
- low packing density (often amorphous)
- lighter elements (C,H,O)

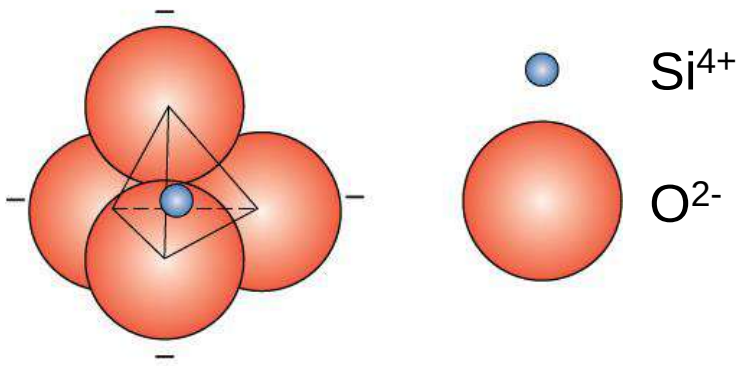
**Composites** have...
- intermediate values



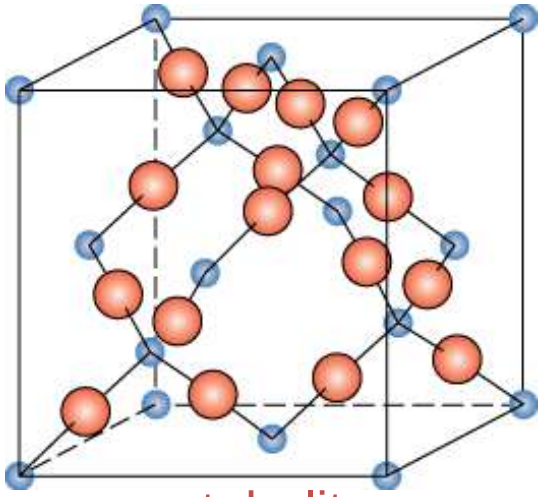

Data from Table B.1, *Callister & Rethwisch, 9e.*

# Silicate Ceramics – Crystalline Silica

Most common elements on earth are Si & O




Figs. 4.10 & 4.11, *Callister & Rethwisch 9e*

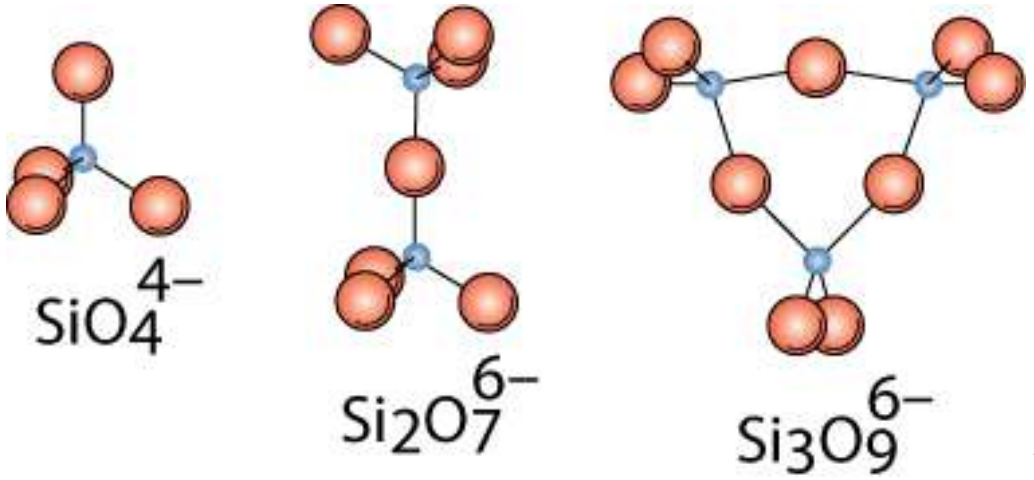


crystobalite

- $SiO_2$ (silica) polymorphic forms are quartz, crystobalite, & tridymite
- The strong Si-O bonds lead to a high melting temperature (1710ºC) for this material

# Silicates

Bonding of adjacent $SiO_4^{4-}$ accomplished by the sharing of common corners, edges, or faces




Adapted from Fig. 4.13, *Callister & Rethwisch 9e.*

$Mg_2SiO_4$ $Ca_2MgSi_2O_7$

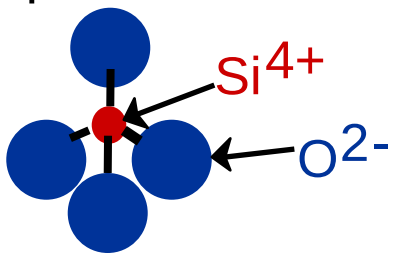
Presence of cations such as $Ca^{2+}$, $Mg^{2+}$, & $Al^{3+}$

1. maintain charge neutrality, and
2. ionically bond $SiO_4^{4-}$ to one another

# Glass Structure

- Basic Unit:

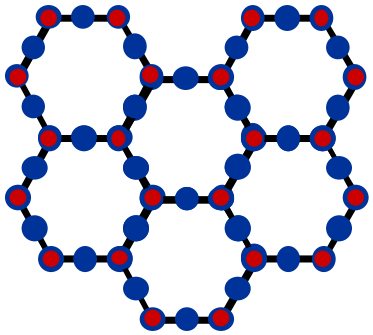
$SiO_4^{4-}$ tetrahedron

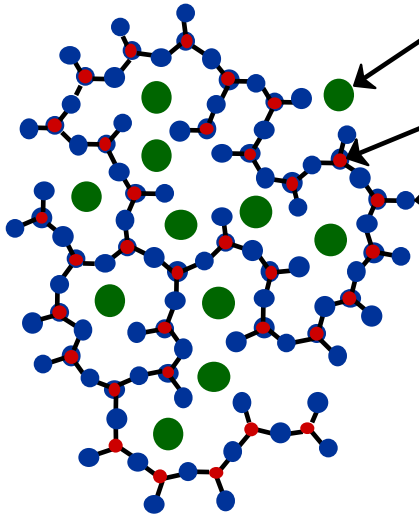



Glass is noncrystalline (amorphous)

- Fused silica is $SiO_2$ to which no impurities have been added
- Other common glasses contain impurity ions such as $Na^+$, $Ca^{2+}$, $Al^{3+}$, and $B^{3+}$

- Quartz is crystalline $SiO_2$:






(soda glass)

Adapted from Fig. 4.12, *Callister & Rethwisch 9e*.

# Layered Silicates

- Layered silicates (e.g., clays, mica, talc)
  - $SiO_4$ tetrahedra connected together to form 2-D plane

- A net negative charge is associated with each $(Si_2O_5)^{2-}$ unit
- Negative charge balanced by adjacent plane rich in positively charged cations

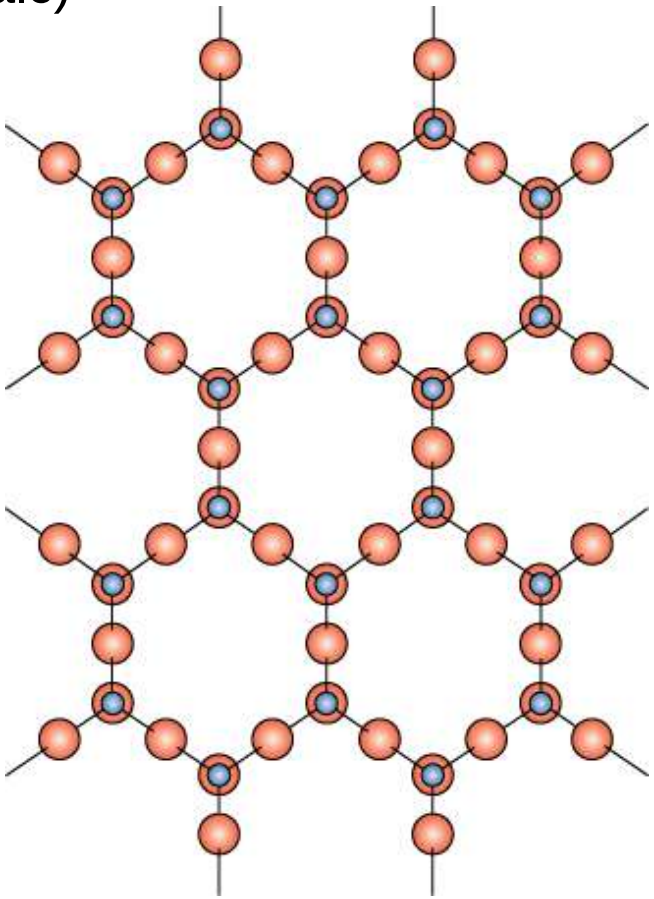


Fig. 4.14, *Callister & Rethwisch 9e.*

# Layered Silicates (cont)

- Kaolinite clay alternates $(Si_2O_5)^{2-}$ layer with $Al_2(OH)_4^{2+}$ layer

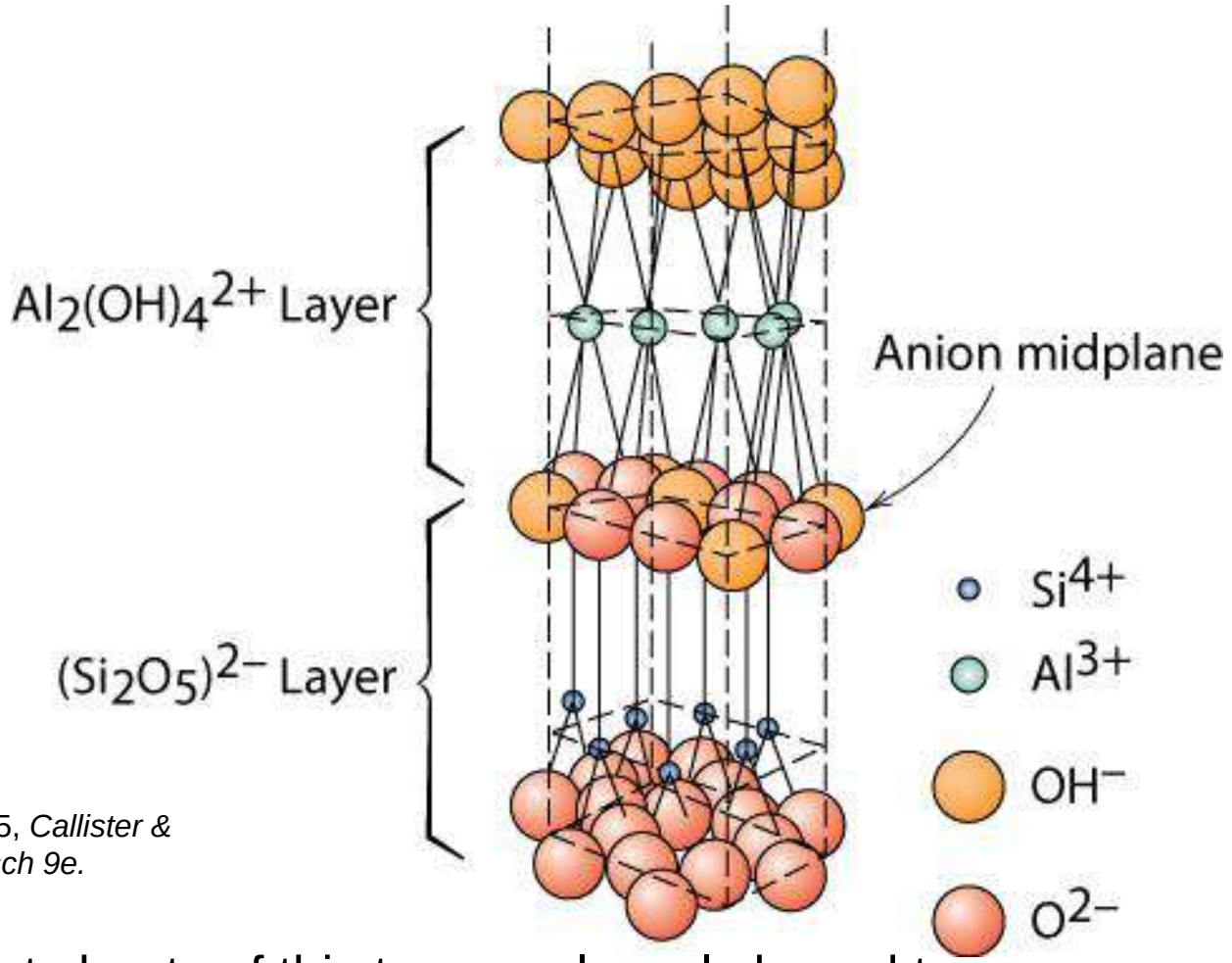


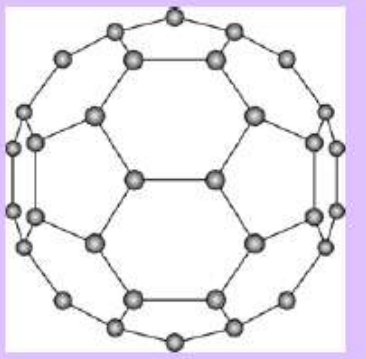

Fig. 4.15, *Callister & Rethwisch 9e.*

Note: Adjacent sheets of this type are loosely bound to one another by van der Waal's forces.

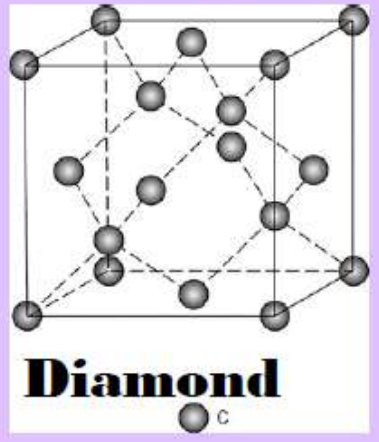
# Carbon- based materials

- Since graphite is often considered a ceramic material, and since the crystal structure of diamond is related to the zinc blende structure, discussion of carbon- based materials typically accompanies ceramics.

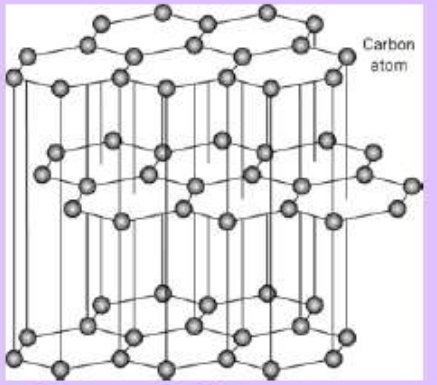
- We will review the crystal structure and major properties of the three known polymorphs of carbon:
- diamond (metastable)
- graphite (stable)
- fullerene (stable)



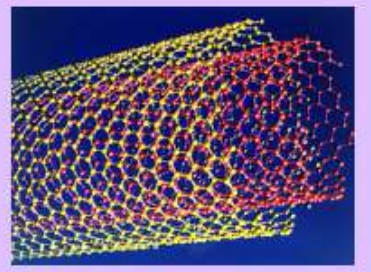
**Fullerenes**




**Diamond**




**Graphite**



**Carbon Nanotubes**

# Polymorphic Forms of Carbon

**Diamond**

- tetrahedral bonding of carbon
  - hardest material known
  - very high thermal conductivity
- large single crystals – gem stones
- small crystals – used to grind/cut other materials
- diamond thin films
  - hard surface coatings – used for cutting tools, medical devices, etc.

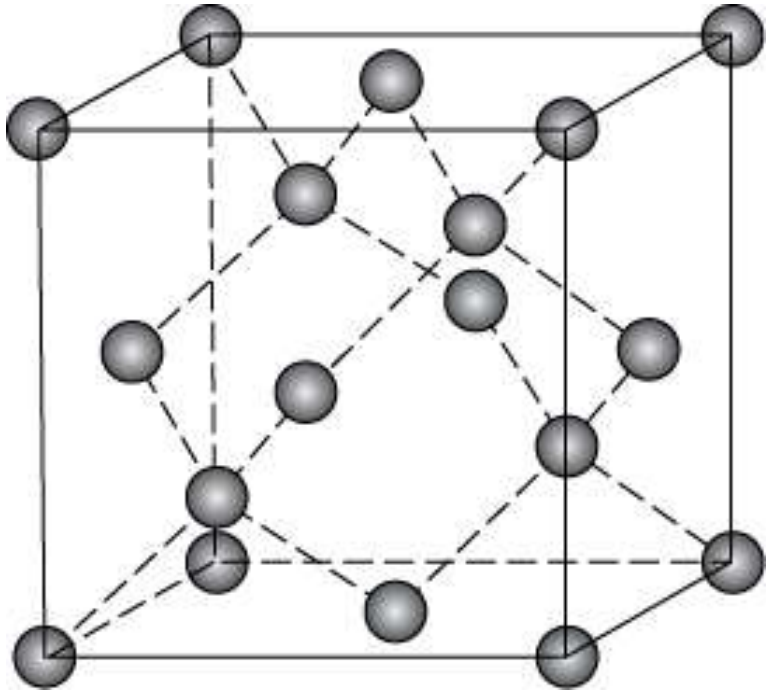


Fig. 4.17, *Callister & Rethwisch 9e.*

# Polymorphic Forms of Carbon (cont)

## Graphite

– layered structure – parallel hexagonal arrays of carbon atoms

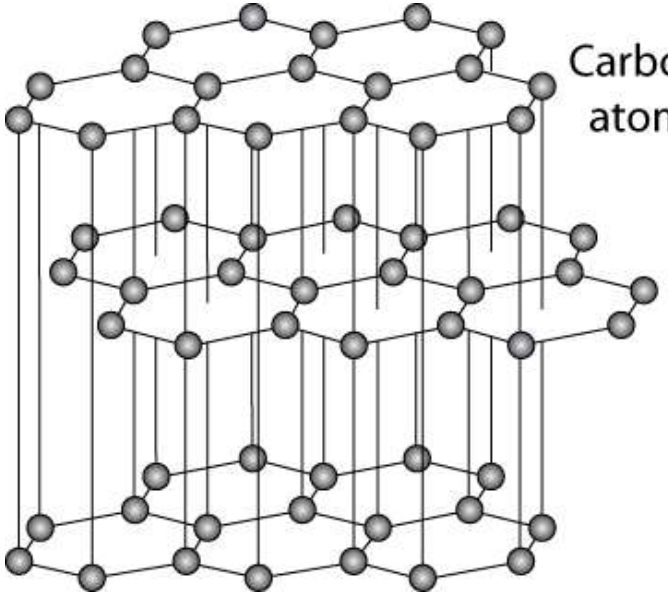


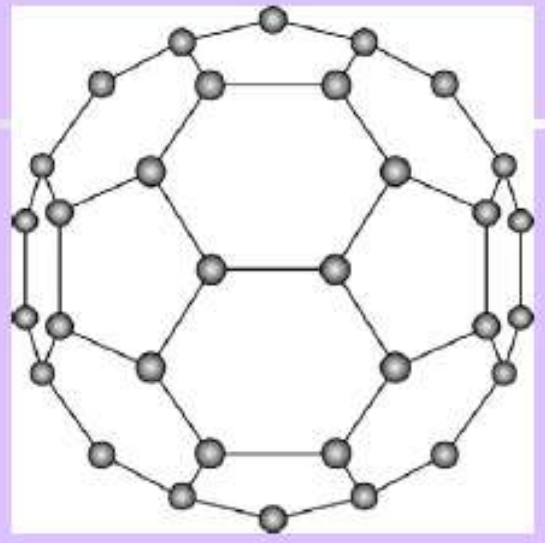

Fig. 4.18, *Callister & Rethwisch 9e.*

– weak van der Waal's forces between layers

– planes slide easily over one another -- good lubricant

# FULLERENE

- discovered in 1985 by spark synthesis
- carbon bond to form a hollow spherical molecule, each consisting of 60 carbon atoms
- commonly called *"Buckminsterfullerene"* after R. Buckminster Fuller, original designer of the geodesic dome.
- The highly symmetrical nature of the bonding gives rise to a highly stable molecule.
- Individual C60 molecules bond together to form a FCC lattice
- other forms have recently been discovered including tubes and rods *(buckytubes)*



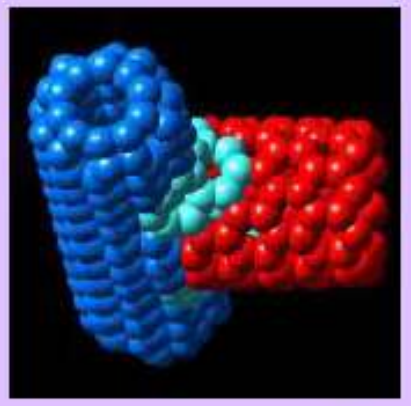
Buckminsterfullerenes (buckyballs)

Possible applications:

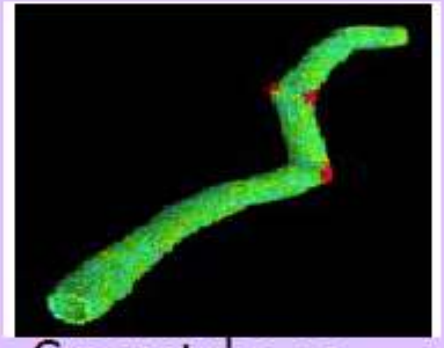
- drug delivery
- low mass structural members

# Carbon Nanotubes – single graphite atomic layer with conventional hexagonal structure being rolled into tubes and at both ends closed with 2 hemi fullerenes

Carbon Nanotubes
carbon nanotubes are expected to play an important role in future ***nanotechnology*** applications (nanoscale materials, sensors, machines, and computers)



Carbon nanotube T-junction



C nanotube as reinforcing fibre in nanocomposite

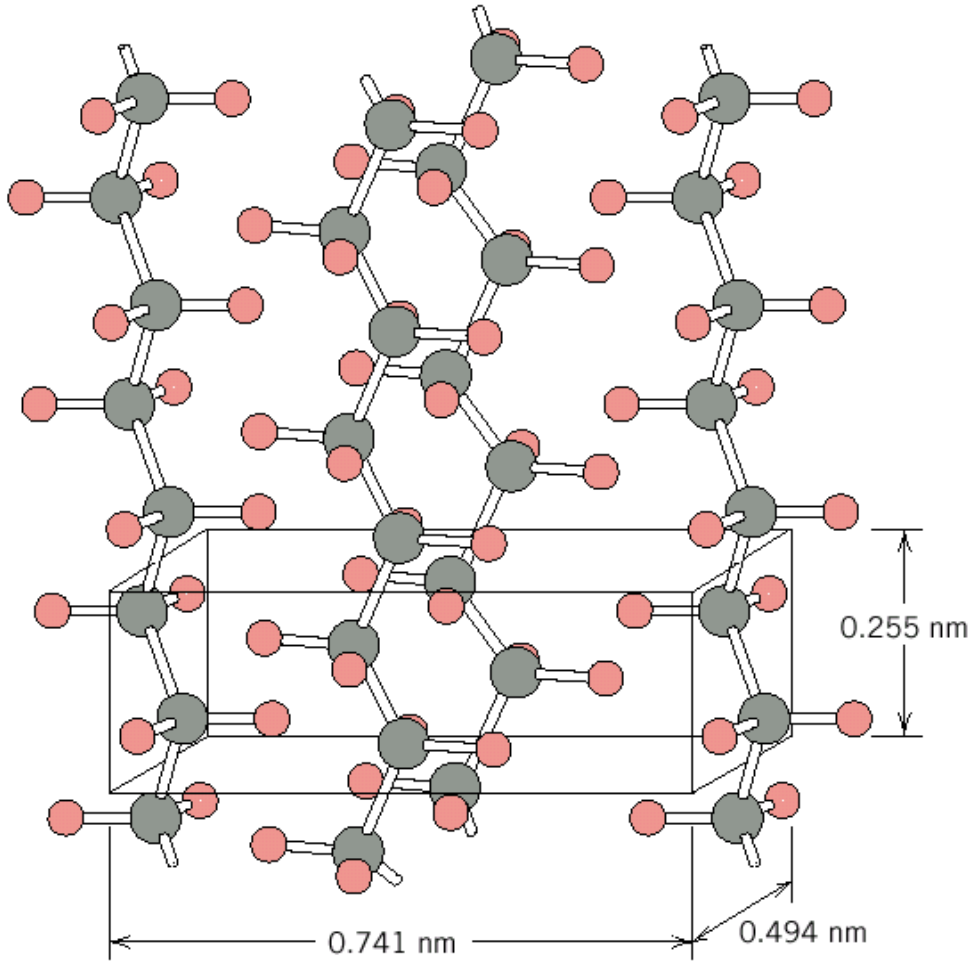
carbon nanotube gear

Properties:
- Have tensile strength 20 times than that of the strongest steel
- High elastic modulus
- Low density, conduct electricity, high heat conductivity

# Crystallinity in Polymers

- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown
  - polyethylene unit cell

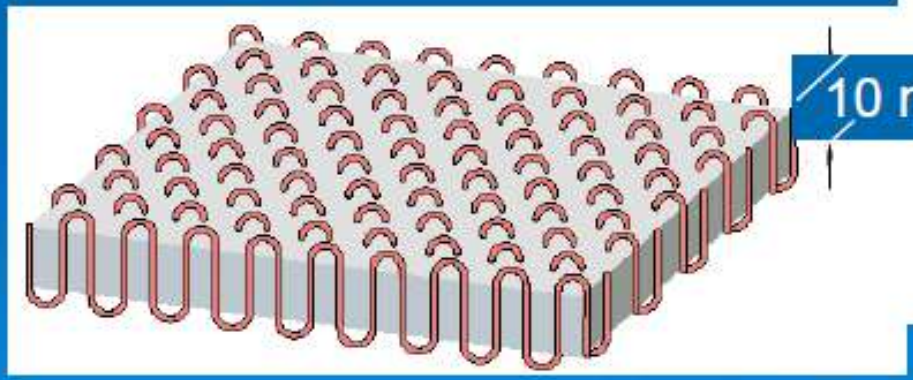
Fig. 4.19, *Callister & Rethwisch 9e.*

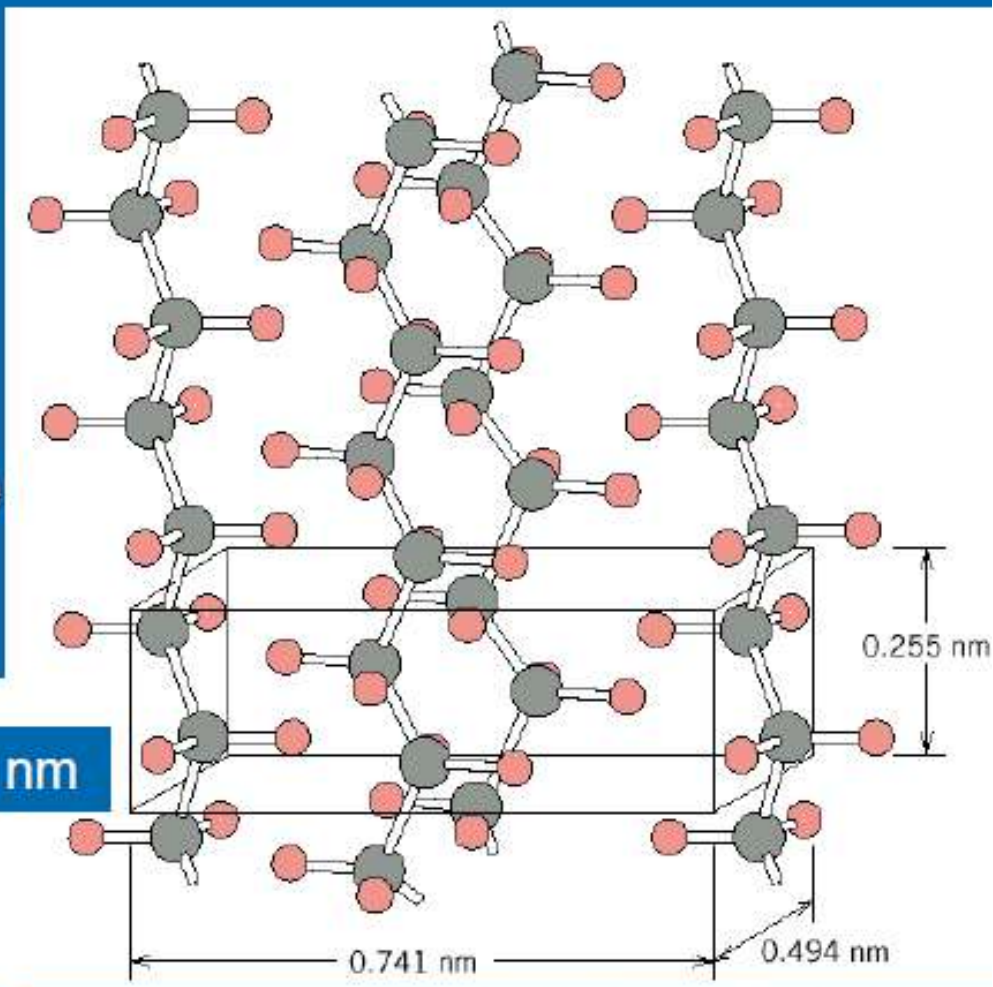


# Polymer Crystallinity

**Ex: polyethylene unit cell**

- **Crystals must contain the polymer chains in some way**
  - **Chain folded structure**



# Computation of Density and Percent Crystallinity

- Computation of Density
  (in relation with number of molecules inside a unit cell)

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

Where:

$n$ = number of repeat units within a unit cell

$A$ = repeat unit molecular weight

$V_C$ = volume of the unit cell

$N_A$ = Avogadro's number ($6.023 \times 10^{23}$ atoms/mol)

# Computation of Density and Percent Crystallinity

- Computation of Percent Crystallinity

$$\%\,\text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Where:

$\rho_s$ = density of polymer specimen
$\rho_a$ = density of totally amorphous polymer
$\rho_c$ = density of perfectly crystalline polymer

## Computations of the Density and Percent Crystallinity of Polyethylene

**(a)** Compute the density of totally crystalline polyethylene. The orthorhombic unit cell for polyethylene is shown in Figure 14.10; also, the equivalent of two ethylene repeat units is contained within each unit cell.

**(b)** Using the answer to part (a), calculate the percent crystallinity of a branched polyethylene that has a density of 0.925 $g/cm^3$. The density for the totally amorphous material is 0.870 $g/cm^3$.

# Crystals as Building Blocks

- *Some* engineering applications require single crystals:
  -- diamond single crystals for abrasives

(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

-- turbine blades

- Properties of crystalline materials often related to crystal structure.

  -- Ex: Quartz fractures more easily along some crystal planes than others.

(Courtesy P.M. Anderson)

# Polycrystals

- *Most* engineering materials are polycrystals.


Anisotropic

Isotropic

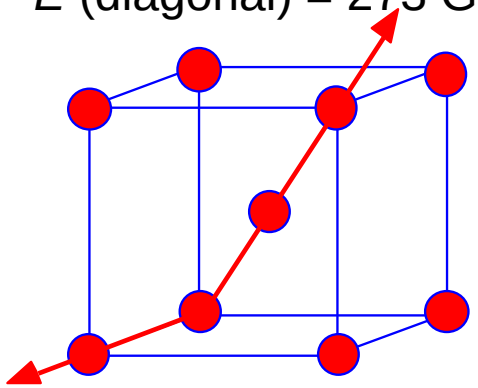
Fig. K, color inset pages of *Callister 5e*.
(Courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented,
  overall component properties are not directional.
- Grain sizes typically range from 1 nm to 2 cm
  (i.e., from a few to millions of atomic layers).

# Single vs Polycrystals

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

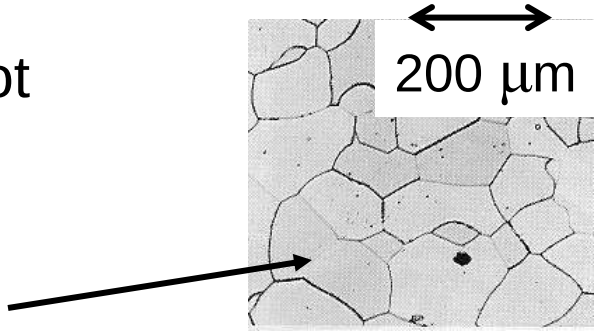
$E$ (diagonal) = 273 GPa

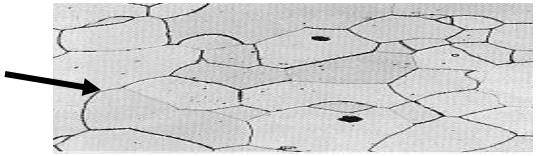


$E$ (edge) = 125 GPa

Data from Table 3.3, *Callister & Rethwisch 9e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

- 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.



Adapted from Fig. 6.19(b), *Callister & Rethwisch 9e*. [Fig. 6.19(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

# Polymorphism

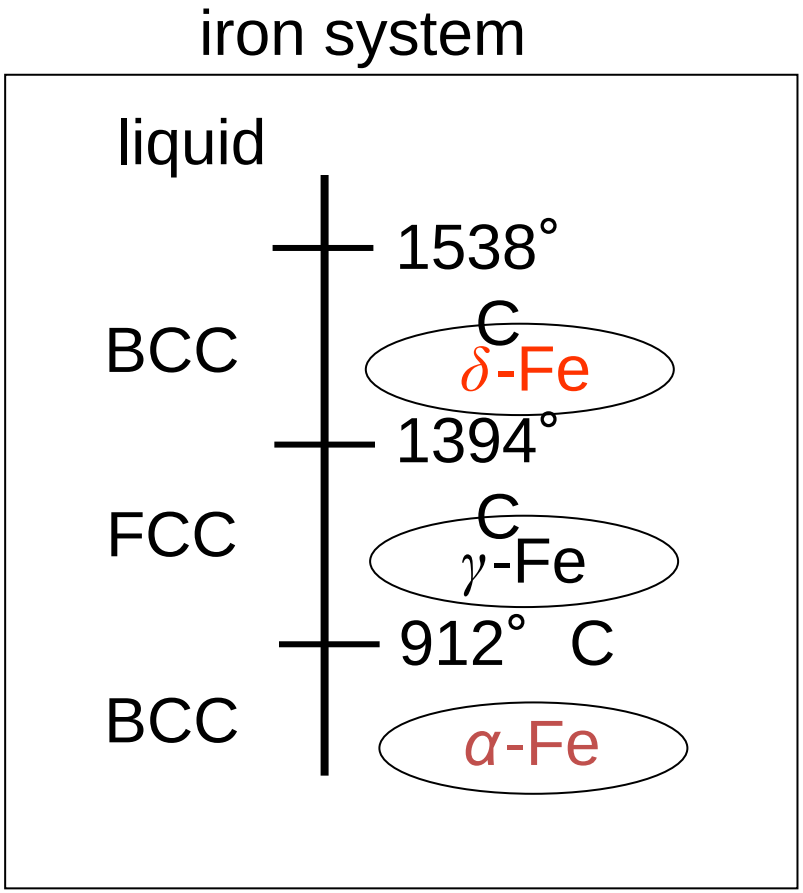
- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

titanium

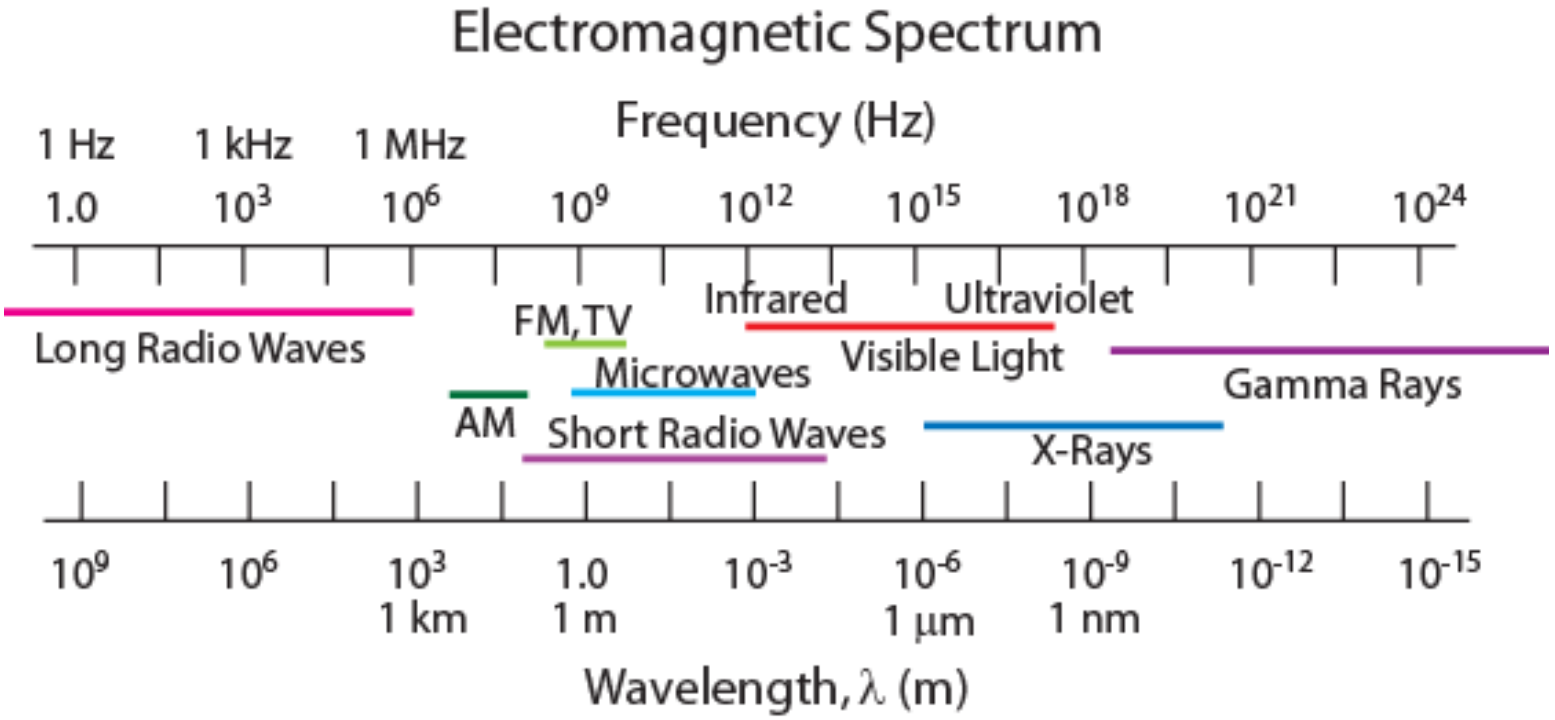
$\alpha$, $\beta$ -Ti

carbon

diamond, graphite



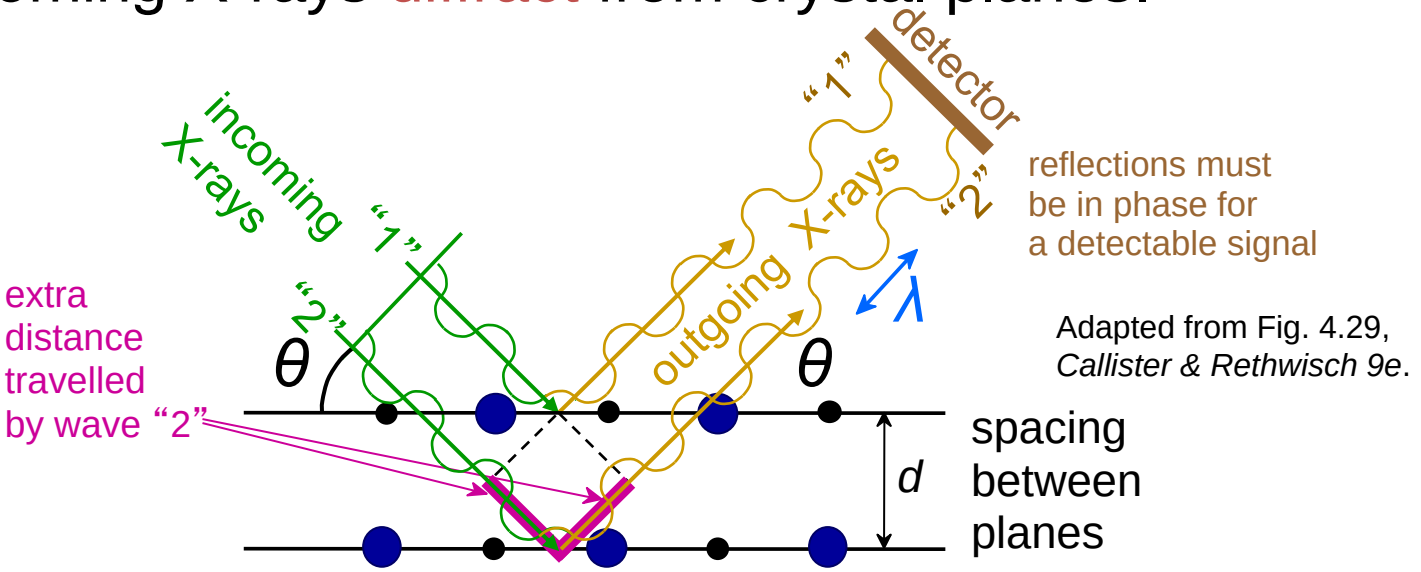
# X-Ray Diffraction




- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

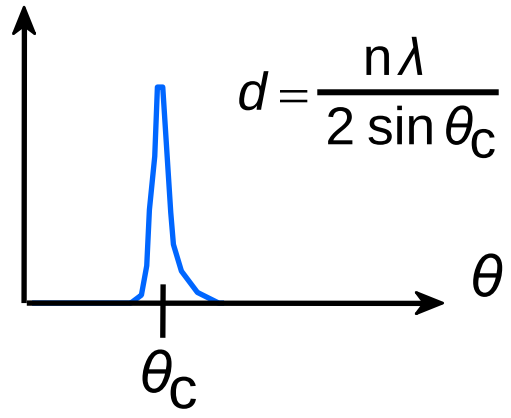
# X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.

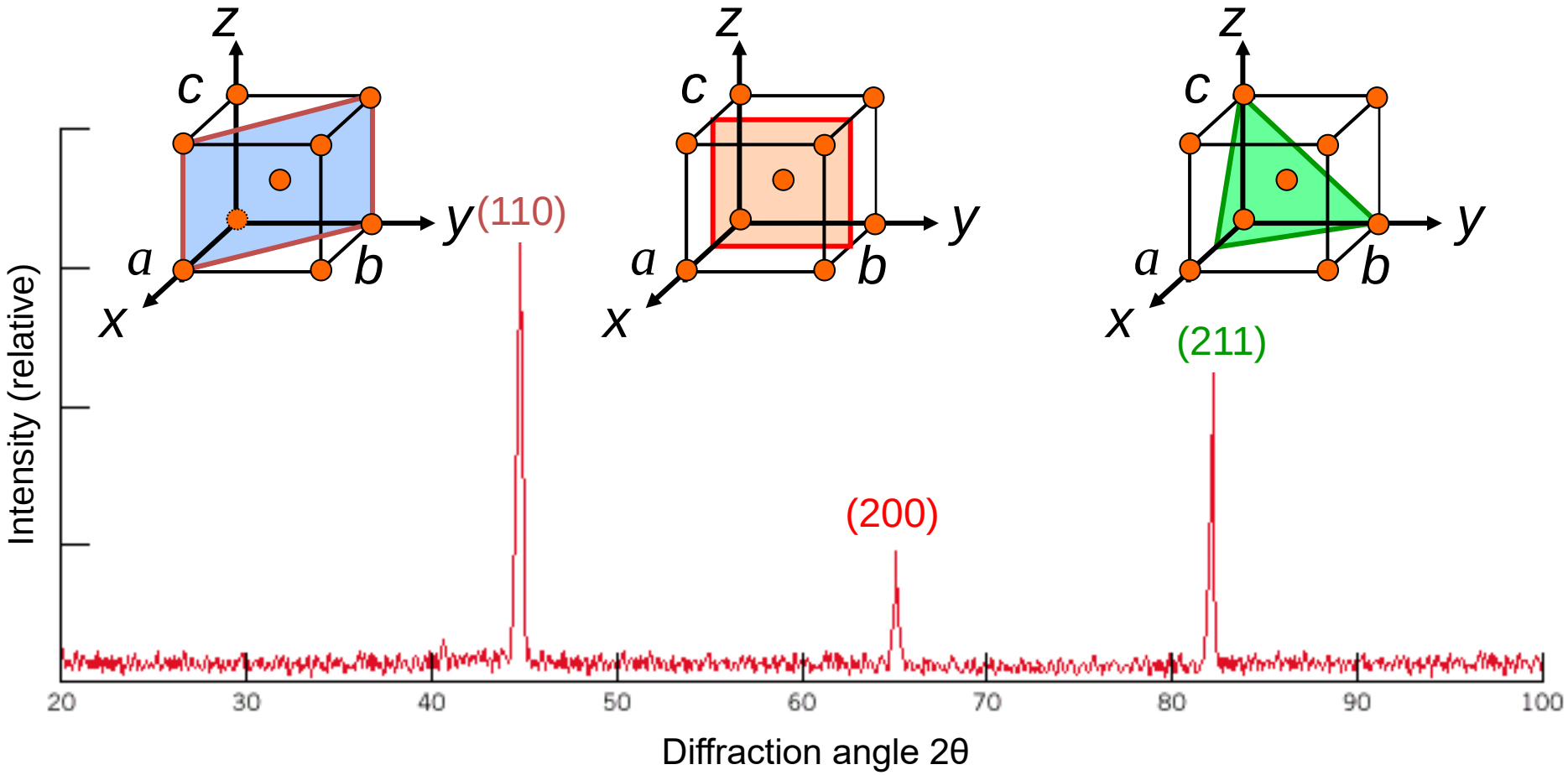



Adapted from Fig. 4.29, *Callister & Rethwisch 9e*.

Measurement of critical angle, $\theta_c$, allows computation of planar spacing, $d$.



# X-Ray Diffraction Pattern




Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.22, *Callister 8e.*

# Summary

- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal 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).
- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.