# Chapter 4: Structures of Crystalline Solids

ISSUES TO ADDRESS...

- How do atoms assemble into solid structures in metallic, ceramic and polymeric materials?

- How do the structures of ceramic materials differ from those of metals?

- How do polymeric crystals accommodate the polymer chain?

- How does the density of a material depend on its structure?
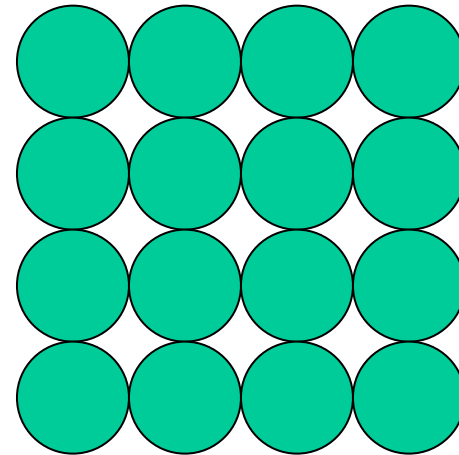
- How can we stack metal atoms to minimize empty space?

2-dimensions
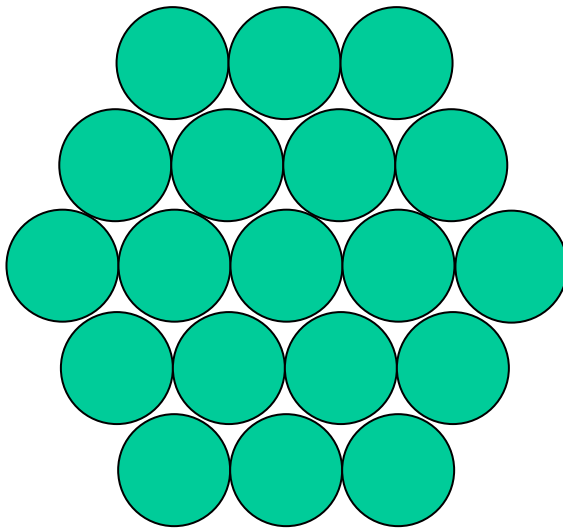
vs.

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.
  - 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.

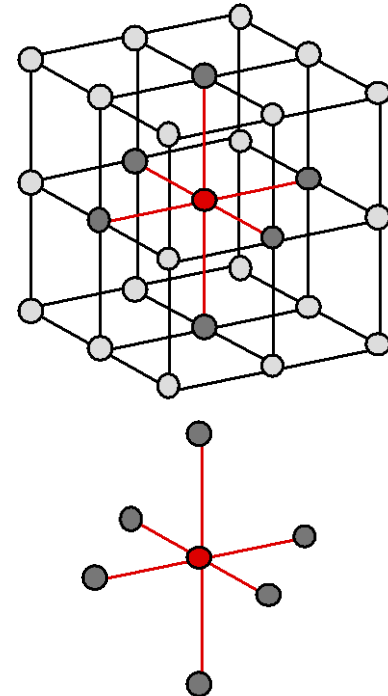 We will examine three such structures...

Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.
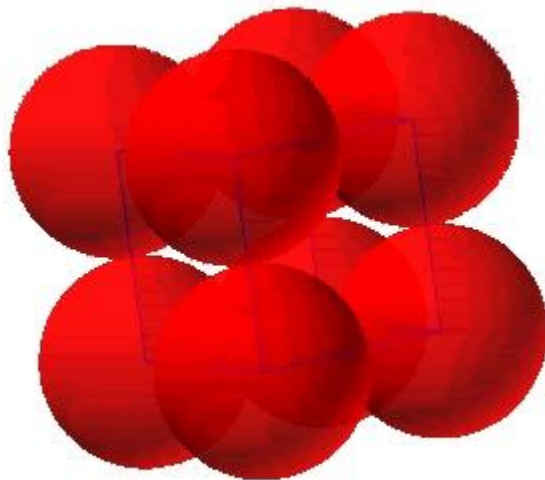
- Coordination # = 6
  (# nearest neighbors)
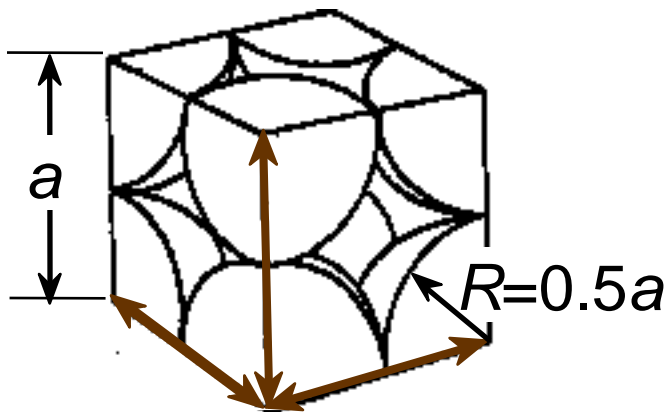
(Courtesy P.M. Anderson)

Atomic Packing Factor (APF)

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

*assume hard spheres

• APF for a simple cubic structure = 0.52

a

$R = 0.5a$

close-packed directions

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

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

$\dfrac{\text{atoms}}{\text{unit cell}}$

$\dfrac{\text{volume}}{\text{atom}}$

$\dfrac{\text{volume}}{\text{unit cell}}$

From Fig. 4.38
Callister's Materials Science and Engineering,
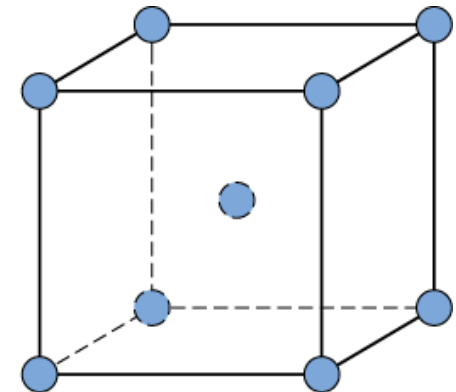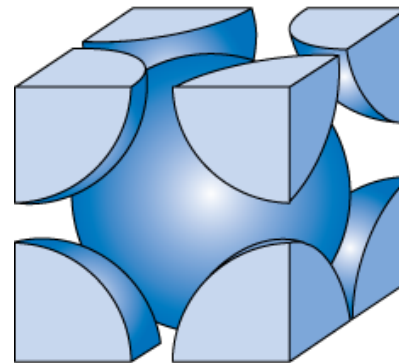*Adapted Version.*

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 (α), Tantalum, Molybdenum

• Coordination # = 8

From Fig. 4.2,
Callister's Materials Science and Engineering,
Adapted Version.

(Courtesy P.M. Anderson)

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

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68

$\sqrt{3}\,a$

a

$\sqrt{2}\,a$

From
Fig. 4.2(a)
*Callister's Materials
Science and
Engineering,
Adapted Version.*

R

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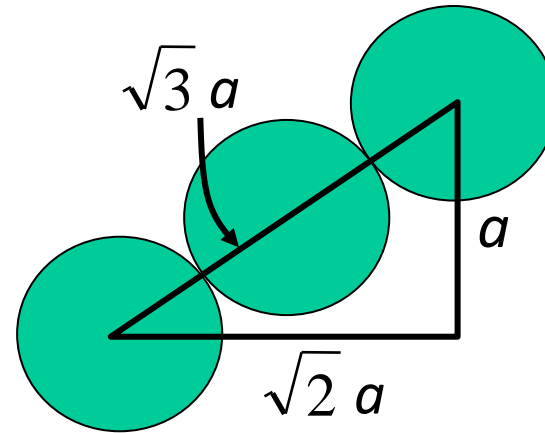
Close-packed directions:
length $= 4R = \sqrt{3}\,a$

$$APF = \dfrac{2\left[\dfrac{4}{3}\,\pi\,(\sqrt{3}a/4)^3\right]}{a^3}$$

$\dfrac{\text{atoms}}{\text{unit cell}}$

$\dfrac{\text{volume}}{\text{atom}}$

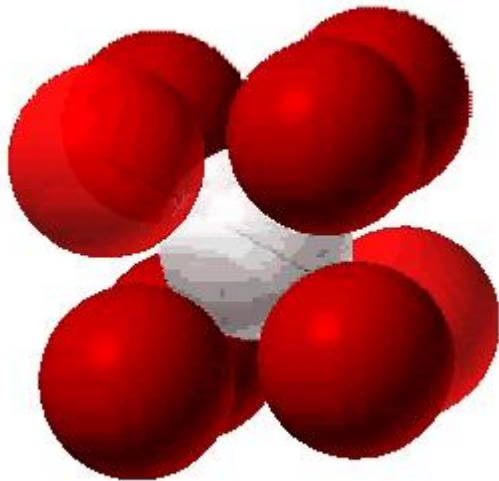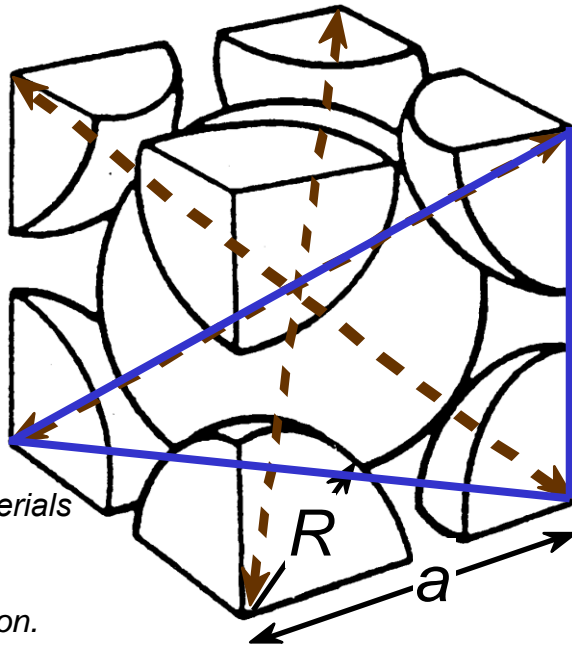$\dfrac{\text{volume}}{\text{unit cell}}$

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
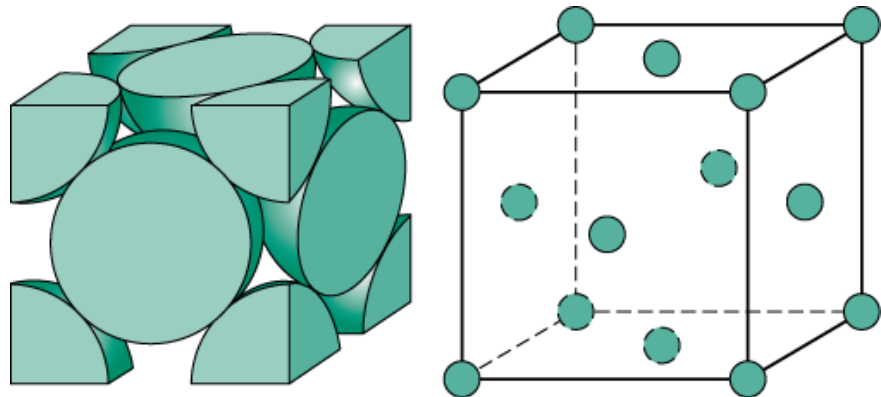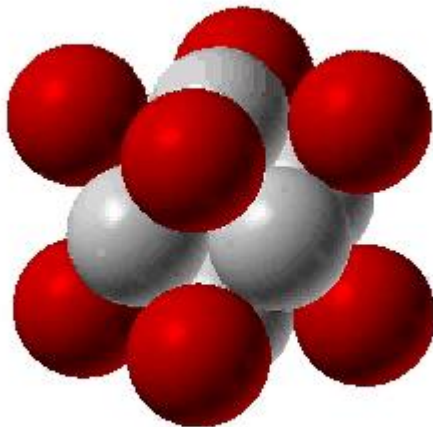
From Fig. 4.1
Callister's Materials Science and Engineering, Adapted Version.

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

(Courtesy P.M. Anderson)

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74
  maximum achievable APF

$\sqrt{2}\ a$

a

From
Fig. 4.1(a),
*Callister's Materials Science
and Engineering,
Adapted Version.*
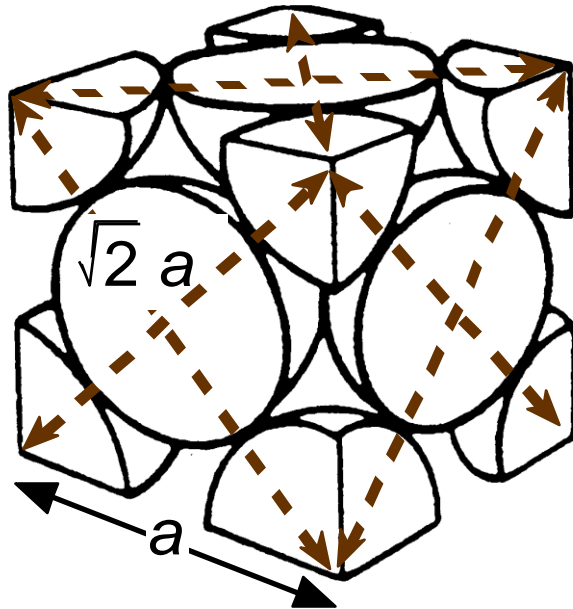
Close-packed directions:
  length = $4R = \sqrt{2}\ a$

Unit cell contains:
  6 x 1/2 + 8 x 1/8
  = 4 atoms/unit cell

$$\text{APF} = \frac{\overbrace{4}^{\frac{\text{atoms}}{\text{unit cell}}}\ \overbrace{\frac{4}{3}\ \pi\ (\sqrt{2}a/4)^3}^{\frac{\text{volume}}{\text{atom}}}}{\underbrace{a^3}_{\frac{\text{volume}}{\text{unit cell}}}}$$

FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

A sites

B sites

C sites
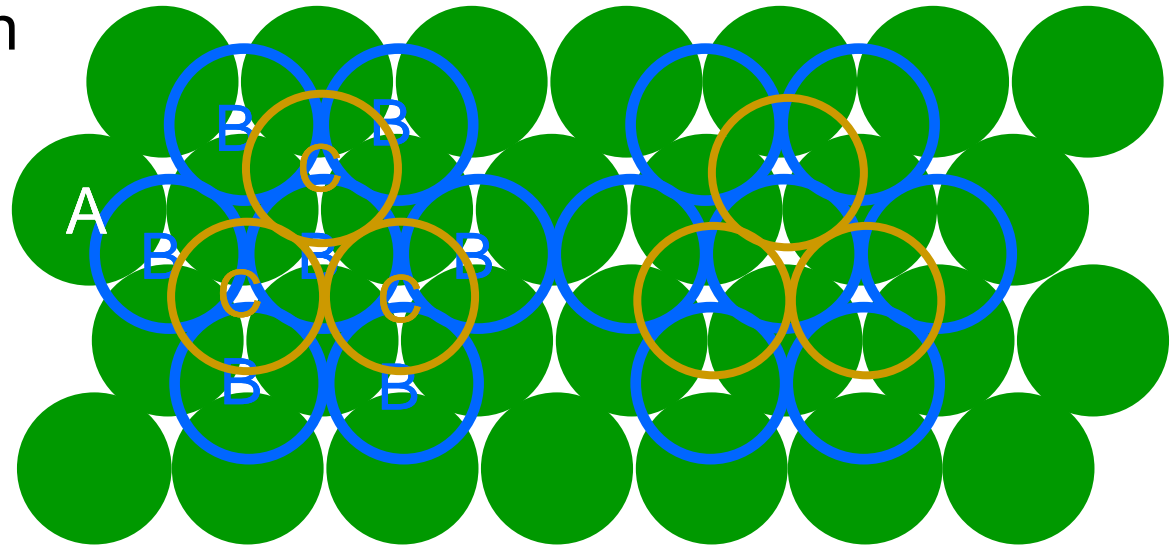
- FCC Unit Cell
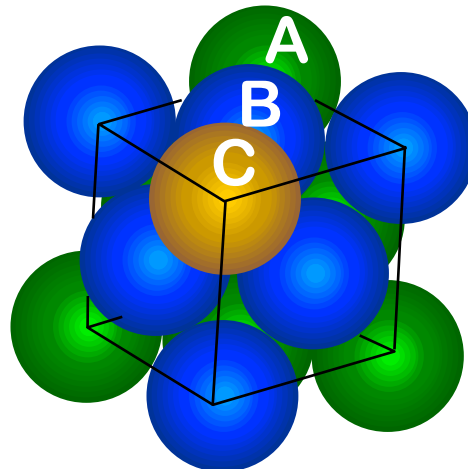
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence

- 3D Projection

A sites — Top layer

B sites — Middle layer

A sites — Bottom layer
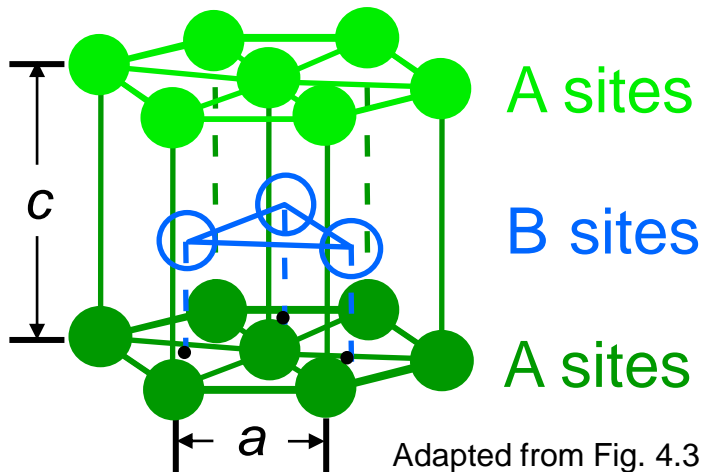
- 2D Projection

Adapted from Fig. 4.3(a),
*Callister's Materials Science and Engineering,
Adapted Version.*
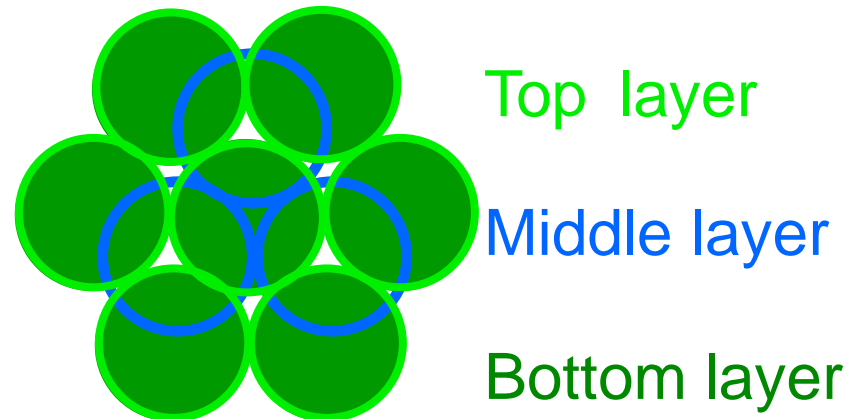
- Coordination # = 12

- APF = 0.74

- c/a = 1.633

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

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

   = 6.023×10^{23} atoms/mol

Theoretical Density, ρ
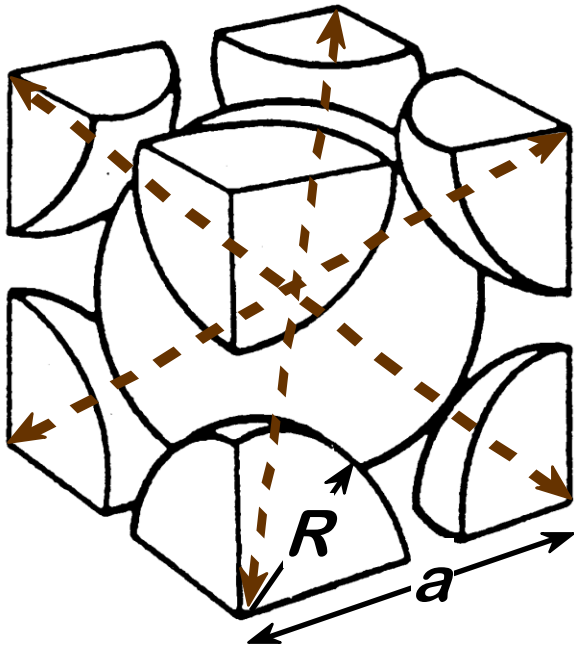
- Ex: Cr (BCC)

  $A = 52.00$ g/mol

  $R = 0.125$ nm

  $n = 2$

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

$$\rho = \cfrac{\overbrace{2}^{\frac{atoms}{unit\ cell}}\ \overbrace{52.00}^{\frac{g}{mol}}}{\underbrace{a^3}_{\frac{volume}{unit\ cell}}\ \underbrace{6.023 \times 10^{23}}_{\frac{atoms}{mol}}}$$

$\rho_{theoretical} = 7.18$ g/cm^3

$\rho_{actual} = 7.19$ g/cm^3

Densities of Material Classes

In general

ρ_{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

Metals/Alloys	Graphite/Ceramics/Semicond	Polymers	Composites/fibers

$\rho(g/cm^3)$

*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).

Metals/Alloys: Platinum; Gold, W; Tantalum; Silver, Mo; Cu,Ni; Steels; Tin, Zinc; Titanium; Aluminum; Magnesium

Graphite/Ceramics/Semicond: Zirconia; Al oxide; Diamond; Si nitride; Glass -soda; Concrete; Silicon; Graphite

Polymers: PTFE; Silicone; PVC; PET; PC; HDPE, PS; PP, LDPE

Composites/fibers: Glass fibers; GFRE*; Carbon fibers; CFRE*; Aramid fibers; AFRE*; Wood

Data from Table B1
Callister's Materials Science and Engineering, Adapted Version.

Linear Density

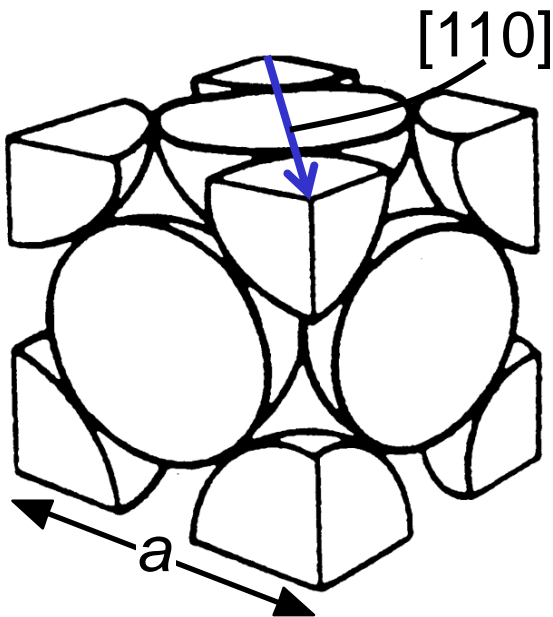- Linear Density of Atoms ≡ LD = $\dfrac{\text{Number of atoms}}{\text{Unit length of direction vector}}$

[110]

a

ex: linear density of Al in [110] direction

$$a = 0.405 \text{ nm}$$

\# atoms

length

$$LD = \dfrac{2}{\sqrt{2}a} = 3.5 \text{ nm}^{-1}$$

Atomic Packing of Crystallographic Planes

- We want to examine the atomic packing of crystallographic planes

- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.

  a) Draw (100) and (111) crystallographic planes for Fe.

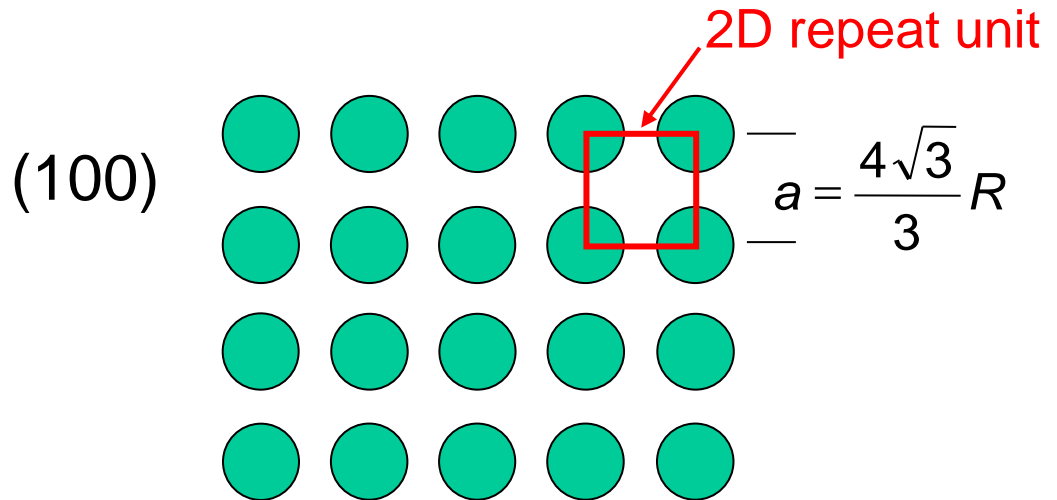 b) Calculate the planar density for each of these planes.

Planar Density of (100) Iron

Solution: At T < 912°C iron has the BCC structure.
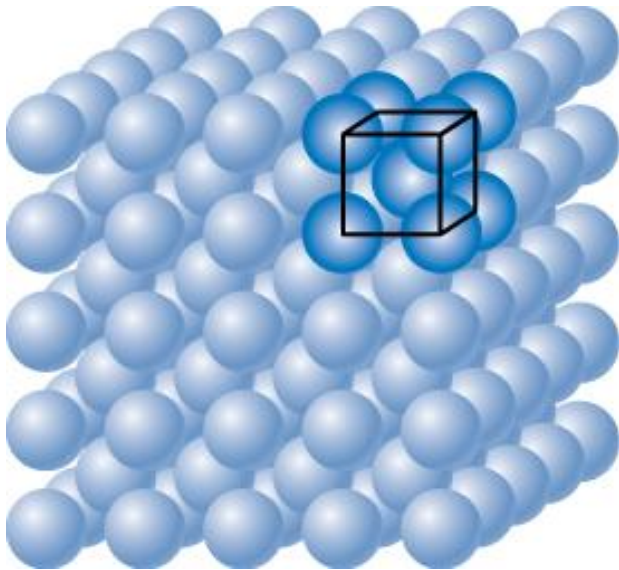
From Fig. 4.2(c), *Callister's Materials Science and Engineering, Adapted Version.*
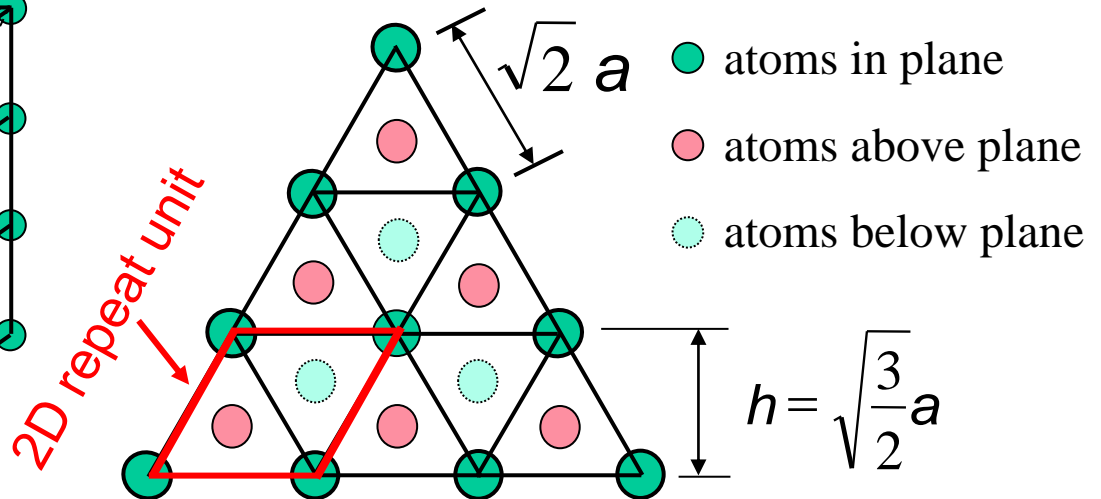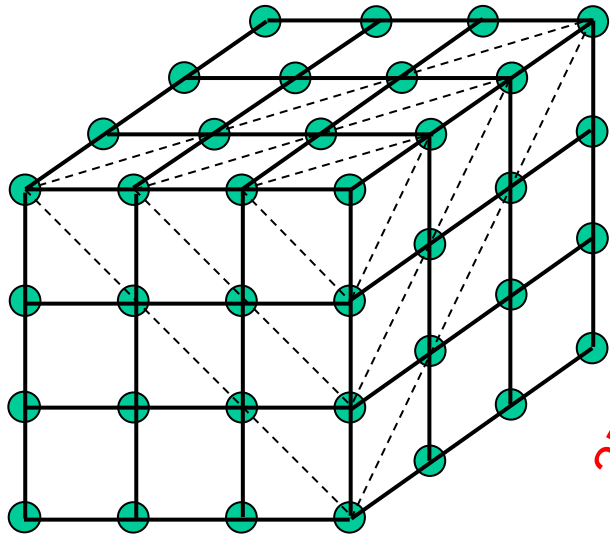
2D repeat unit

(100)

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

Radius of iron $R = 0.1241$ nm

$$\text{Planar Density} = \frac{\frac{\text{atoms}}{\text{2D repeat unit}} \to 1}{\frac{\text{area}}{\text{2D repeat unit}} \to a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1\frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19}\frac{\text{atoms}}{\text{m}^2}$$

Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell

- 🟢 atoms in plane
- 🔴 atoms above plane
- 🔵 atoms below plane

$$\text{area} = \sqrt{2}\ ah = \sqrt{3}\ a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$$

$$\text{Planar Density} = \dfrac{\dfrac{\text{atoms}}{\text{2D repeat unit}}\ \to\ 1}{\dfrac{\text{area}}{\text{2D repeat unit}}\ \to\ \dfrac{16\sqrt{3}}{3}R^2} = 7.0\frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19}\ \frac{\text{atoms}}{\text{m}^2}$$

Section 4.9 – Polymorphism

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

titanium

α, β-Ti

carbon

diamond, graphite

iron system

liquid

BCC — 1538ºC

δ-Fe

FCC — 1394ºC

γ-Fe

BCC — 912ºC

α-Fe
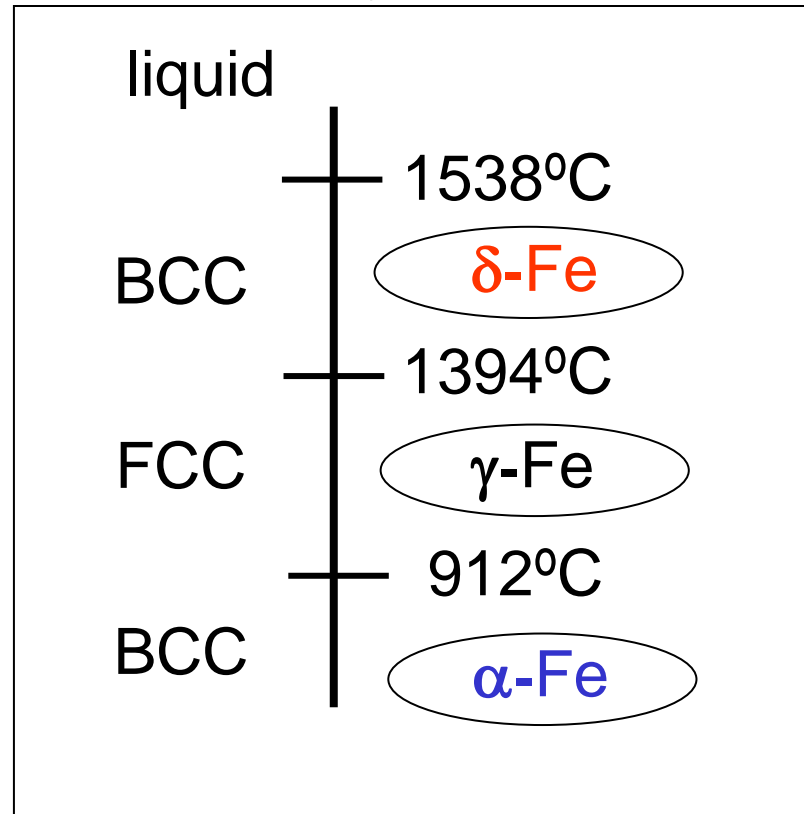
Ceramic Crystal Structures

Oxide structures

- oxygen anions much larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations in the holes of the oxygen lattice

Site Selection

Which sites will cations occupy?

1. Size of sites

    – does the cation fit in the site

2. Stoichiometry

    – if all of one type of site is full the remainder have to go into other types of sites.
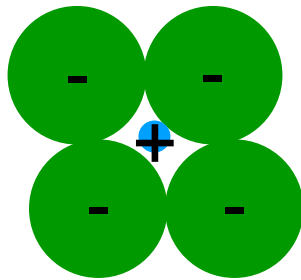
3. Bond Hybridization

Ionic Bonding & Structure

1. Size - Stable structures:

--maximize the # of nearest oppositely charged neighbors.
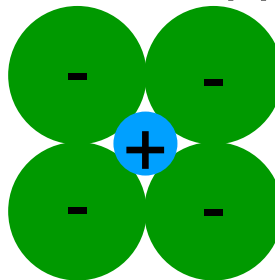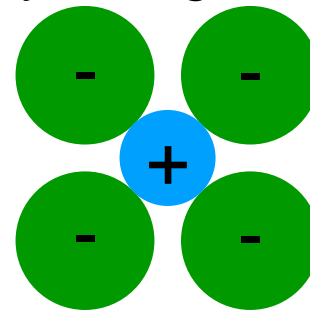
From Fig. 4.10
Callister's Materials Science and Engineering, Adapted Version.

unstable   stable   stable

- **Charge Neutrality**:
  --Net charge in the structure should be zero.

CaF_2: Ca^{2+} cation + F^- anions F^-
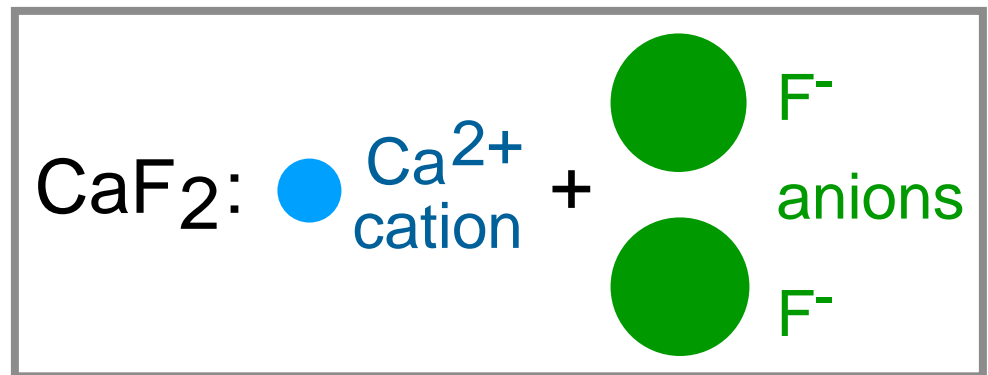
--General form: $A_m X_p$

m, p determined by charge neutrality

Coordination # and Ionic Radii

- Coordination # increases with $\dfrac{r_{cation}}{r_{anion}}$

Issue: How many anions can you arrange around a cation?

$\dfrac{r_{cation}}{r_{anion}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

Adapted from Table 4.3

ZnS
(zincblende)

From Fig. 4.13

NaCl
(sodium chloride)

From Fig. 4.11

CsCl
(cesium chloride)

From Fig. 4.12

Figures and table from Callister's Materials Science and Engineering, Adapted Version.
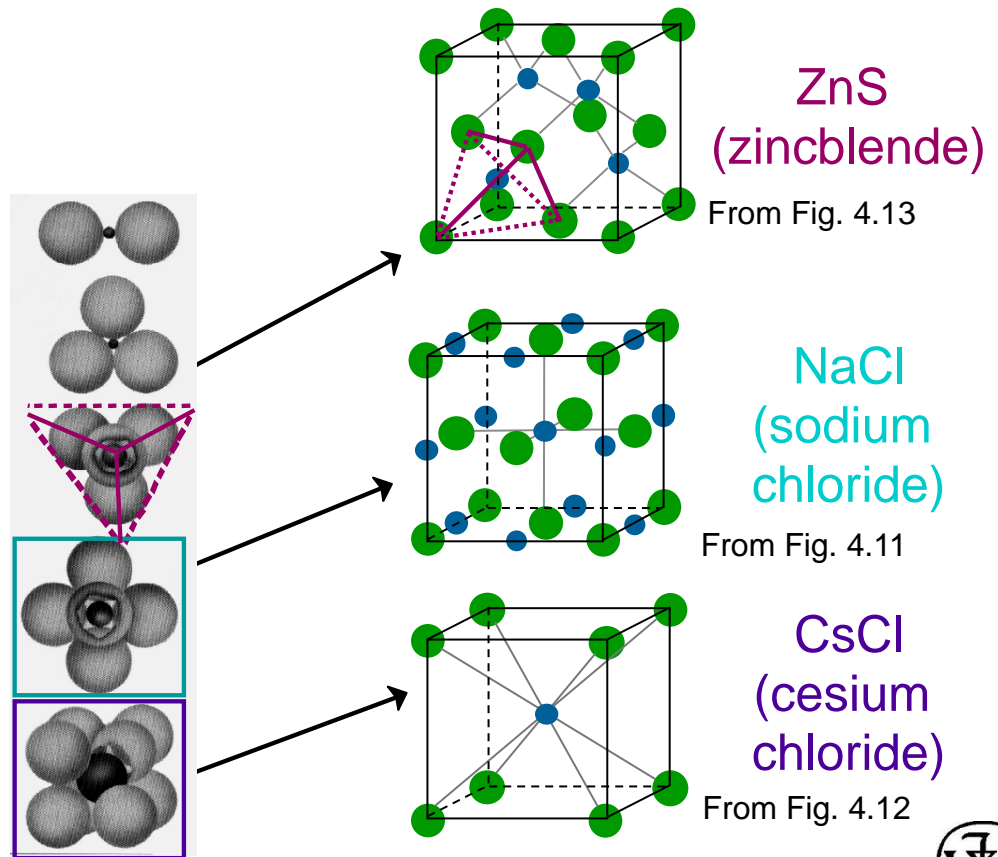
Cation Site Size

- **Determine minimum r_{cation}/r_{anion} for O_H site (C.N. = 6)**

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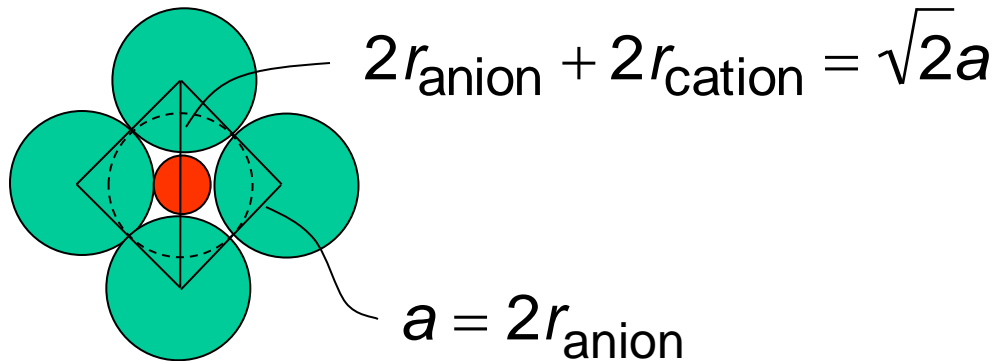
$$a = 2r_{anion}$$

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

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

$$\frac{r_{cation}}{r_{anion}} = 0.414$$

Site Selection II

2. Stoichiometry

- If all of one type of site is full the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 O_H and 8 T_D sites.

If for a specific ceramic each unit cell has 6 cations and the cations prefer O_H sites

4 in O_H

2 in T_D

Site Selection III

3. Bond Hybridization – significant covalent bonding

- the hybrid orbitals can have impact if significant covalent bond character present

- For example in SiC

  - $X_{Si} = 1.8$ and $X_C = 2.5$

$$\% \, ionic \, character = 100 \, \{1 - \exp[-0.25(X_{Si} - X_C)^2]\} = 11.5\%$$

  - ca. 89% covalent bonding
  - both Si and C prefer sp^3 hybridization
  - Therefore in SiC get T_D sites

Example: Predicting 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

- Answer:

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

$$= 0.550$$

based on this ratio,
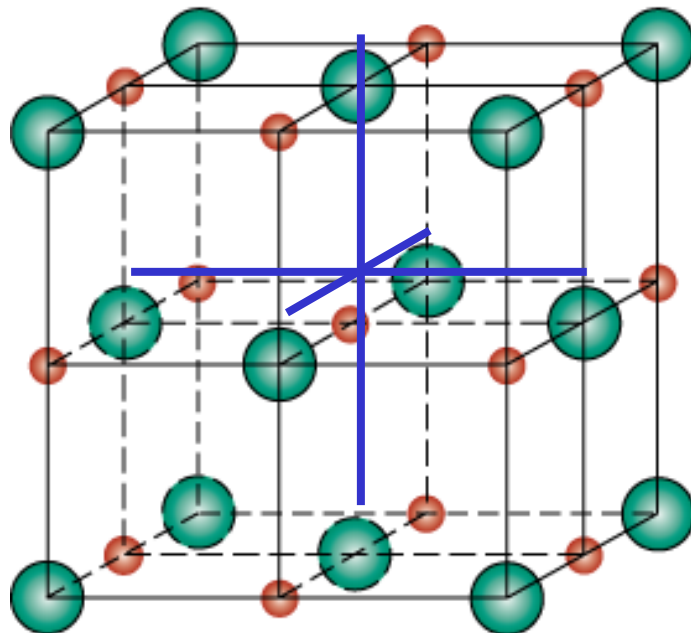--coord # = 6
--structure = NaCl

Data from Table 4.4
Callister's Materials Science and Engineering, Adapted Version.

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure

From Fig. 4.11
Callister's Materials Science and Engineering, Adapted Version.

Na+ $r_{Na} = 0.102$ nm

Cl− $r_{Cl} = 0.181$ nm

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

∴   cations prefer O_H sites

MgO and FeO

MgO and FeO also have the NaCl structure

From Fig. 4.11
Callister's Materials Science and Engineering, Adapted Version.

O²⁻ — $r_O = 0.140$ nm

Mg²⁺ — $r_{Mg} = 0.072$ nm
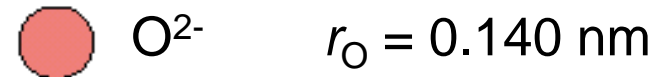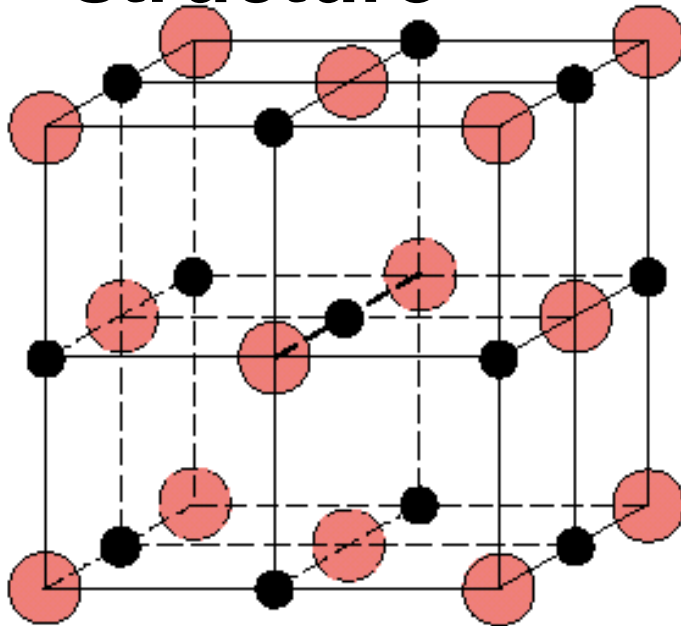
$r_{Mg}/r_O = 0.514$

$\therefore$ cations prefer O_H sites

So each oxygen has 6 neighboring Mg²⁺

AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:

Cs+

Cl−

$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$
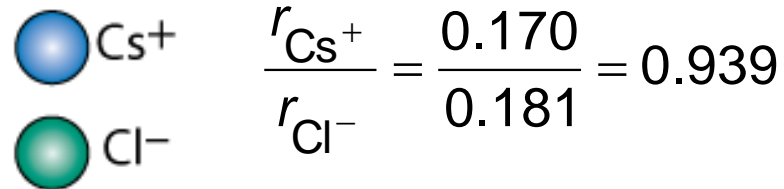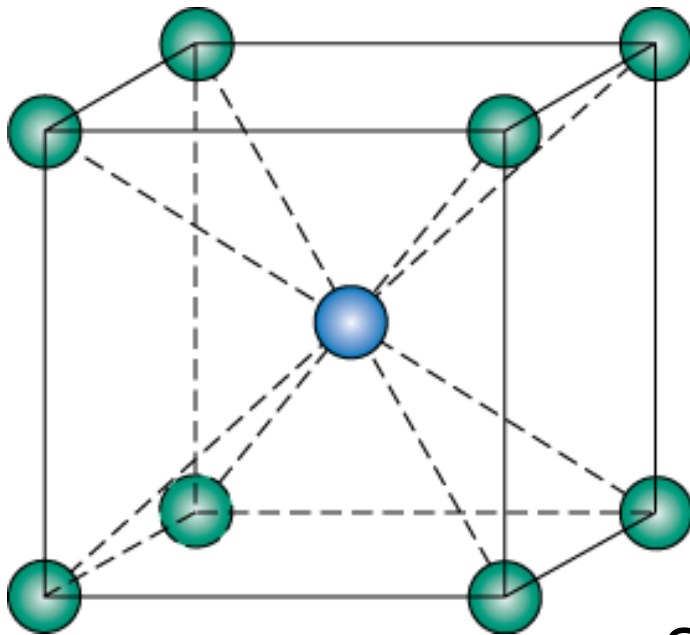
∴   cubic sites preferred

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

From Fig. 4.12
*Callister's Materials
Science and
Engineering,
Adapted Version.*

AX Crystal Structures

Zinc Blende structure
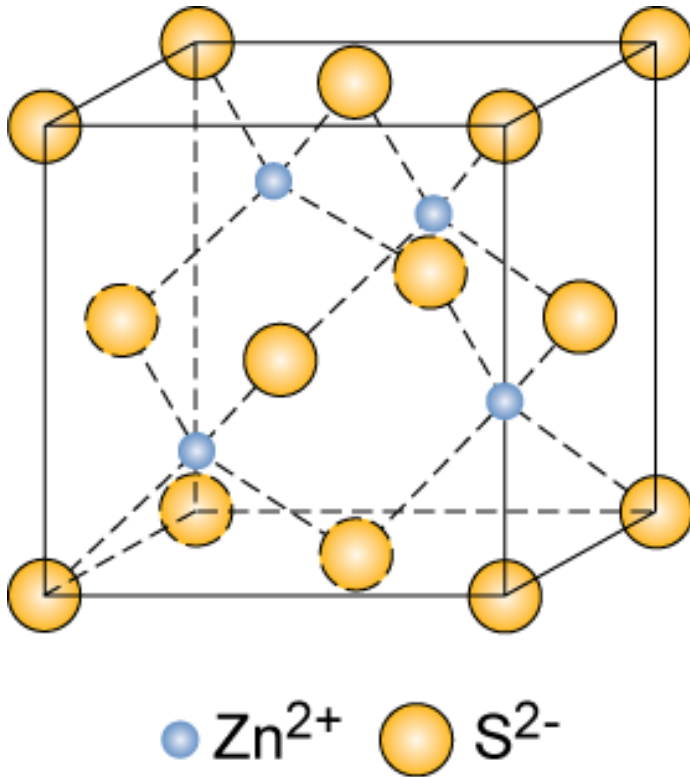
● Zn^{2+} ⬤ S^{2-}

Ex: ZnO, ZnS, SiC

$$\frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.074}{0.140} = 0.529 \implies O_H??$$

- Size arguments predict Zn^{2+} in O_H sites,
- In observed structure Zn^{2+} in T_D sites

- **Why is Zn^{2+} in T_D sites?**
  - **bonding hybridization of zinc favors T_D sites**

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

AX$_2$ Crystal Structures

Fluorite structure
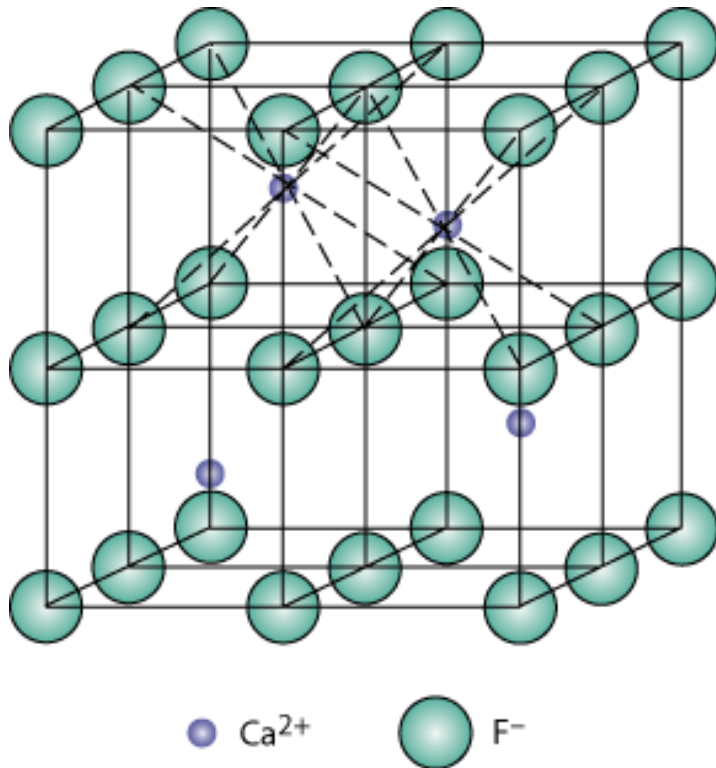
- Calcium Fluorite (CaF$_2$)
- cations in cubic sites

- UO$_2$, ThO$_2$, ZrO$_2$, CeO$_2$

- antifluorite structure – cations and anions reversed

○ Ca^{2+} ● F$^-$

From Fig. 4.14
Callister's Materials Science and Engineering Adapted Version.

ABX$_3$ Crystal Structures

Perovskite structure

Ex: complex oxide

BaTiO$_3$

• Ti^{4+} ● Ba^{2+} ● O^{2-}
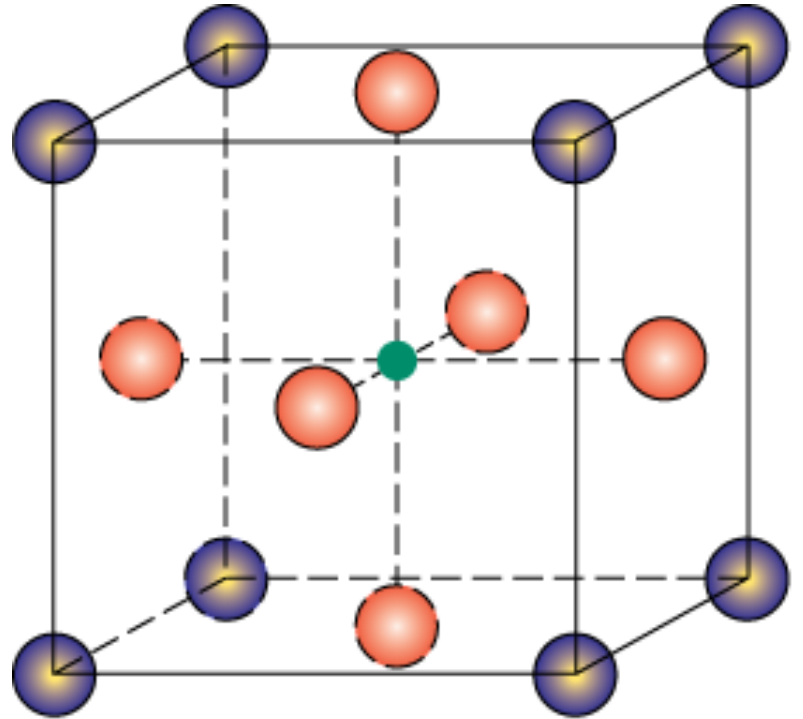
From Fig. 4.15
Callister's Materials Science and Engineering Adapted Version.

Mechanical Properties

We know that ceramics are more brittle than metals. Why?

- **Consider method of deformation (will learn later in chapters on mechanical properties – Chapter 9 and 10)**
    - **slippage along slip planes**
        - **in ionic solids this slippage is very difficult**
        - **too much energy needed to move one anion past another anion**

Ceramic Density Computation

Number of formula units/unit cell

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

Volume of unit cell

Silicate Ceramics

Most common elements on earth are Si & O

Si^{4+}

O^{2-}

From Figs. 4.18 and 4.19
*Callister's Materials Science
and Engineering
Adapted Version.*
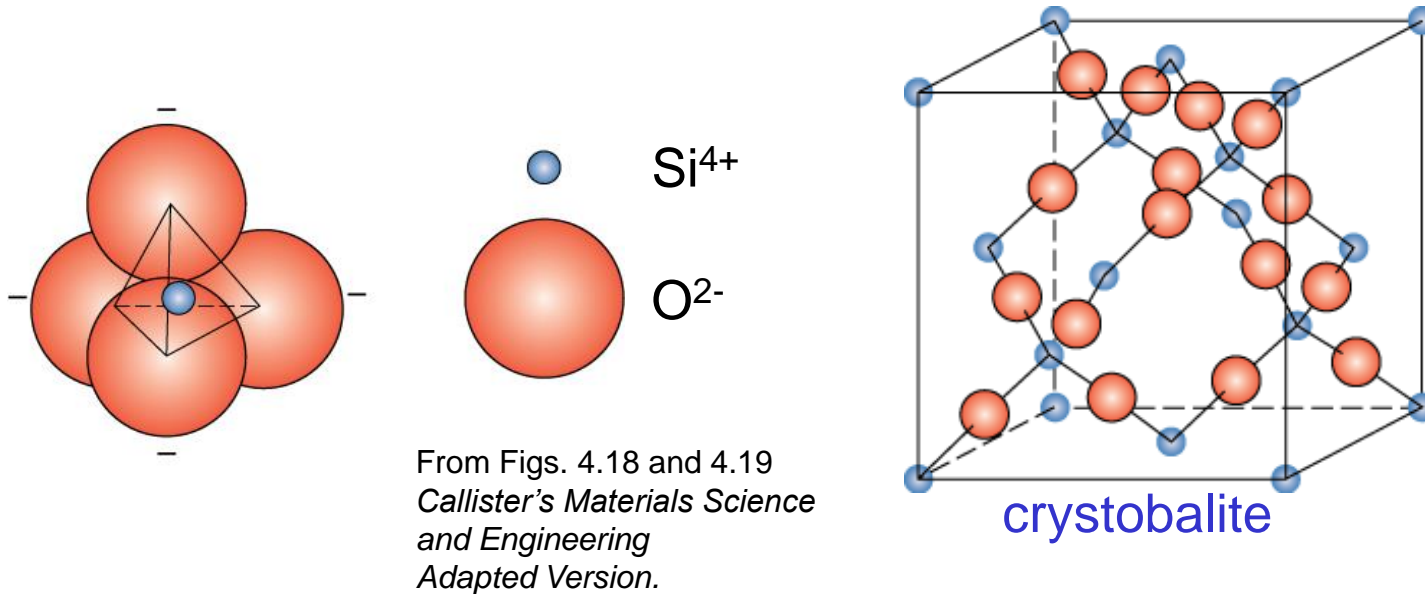
crystobalite

- **SiO_2 (silica) structures are quartz, crystobalite, & tridymite**

- **The strong Si-O bond leads to a strong, high melting material (1710ºC)**

Amorphous Silica

- **Silica gels - amorphous SiO$_2$**
  - **Si^{4+} and O^{2-} not in well-ordered lattice**
  - **Charge balanced by H$^+$ (to form OH$^-$) at "dangling" bonds**
    - **very high surface area > 200 m^2/g**
  - **SiO$_2$ is quite stable, therefore unreactive**
    - **makes good catalyst support**

From Fig. 4.20
*Callister's Materials Scie
and Engineering
Adapted Version.*

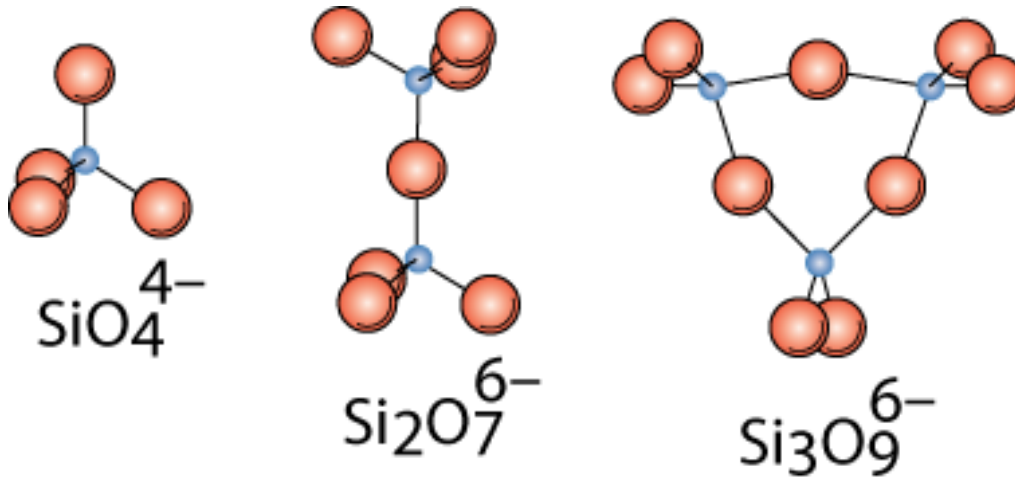• Si^{4+} • O^{2-} • OH$^-$
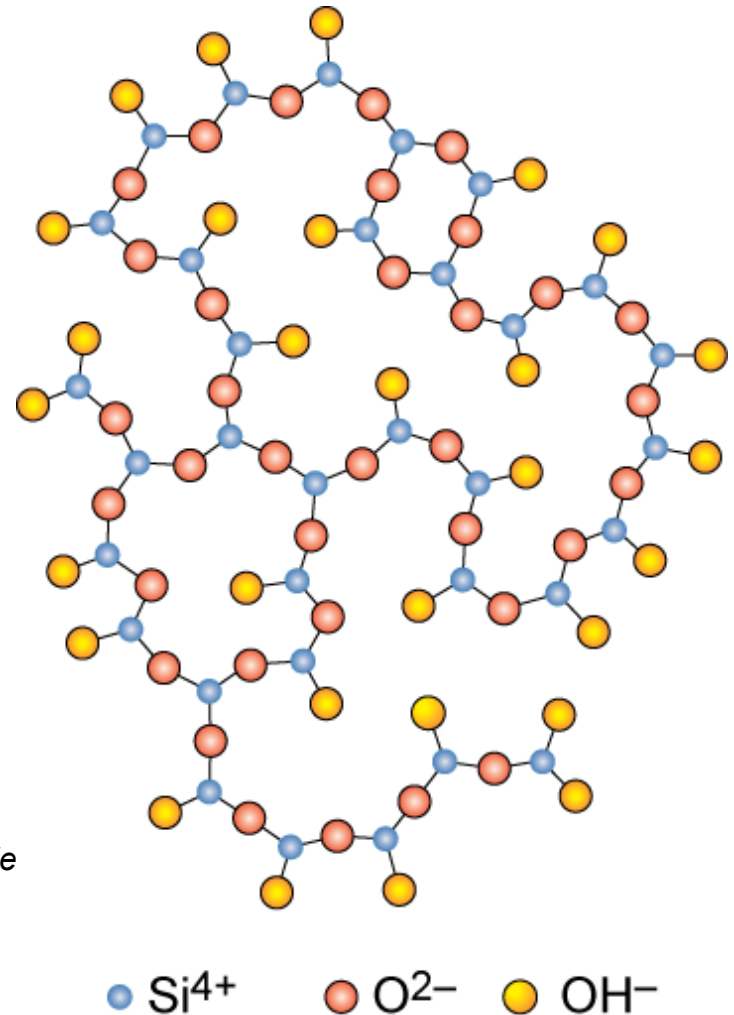
Silica Glass

- **Dense form of amorphous silica**
  - **Charge imbalance corrected with "counter cations" such as Na$^+$**
  - **Borosilicate glass is the pyrex glass used in labs**
    - better temperature stability & less brittle than sodium glass

Silicates

- Combine SiO_4^{4-} tetrahedra by having them share corners, edges, or faces

$$SiO_4^{4-}$$

$$Si_2O_7^{6-}$$

$$Si_3O_9^{6-}$$
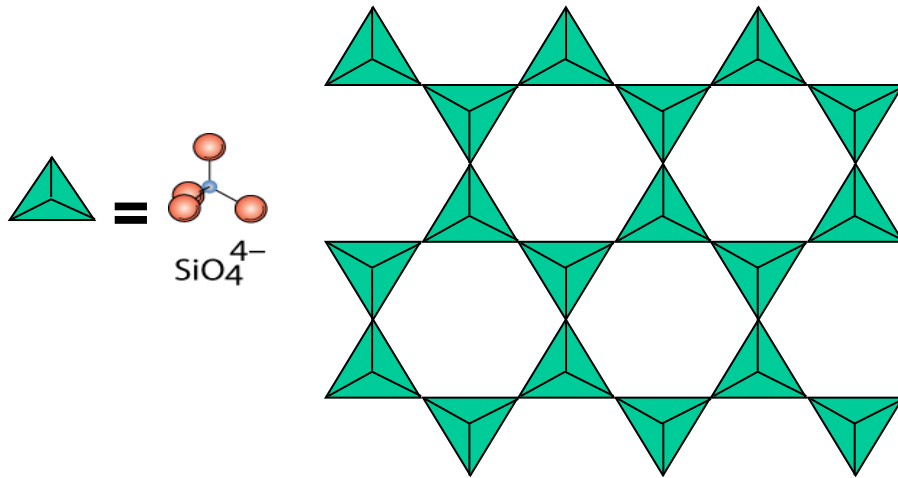
Mg_2SiO_4 $Ca_2MgSi_2O_7$

From Fig. 4.21
Callister's Materials Science and Engineering Adapted Version.
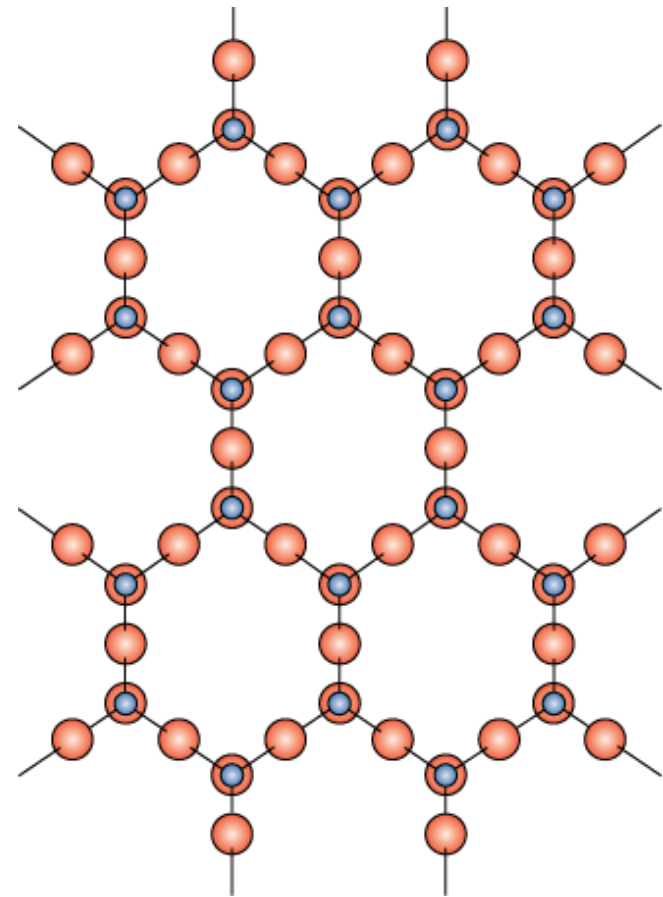
- Cations such as Ca^{2+}, Mg^{2+}, & Al^{3+} act to neutralize & provide ionic bonding

Layered Silicates

- **Layered silicates (clay silicates)**
  - **SiO_4 tetrahedra connected together to form 2-D plane**

- **$(Si_2O_5)^{2-}$**
- **So need cations to balance charge**

From Fig. 4.22
Callister's Materials Science and Engineering, Adapted Version.

Layered Silicates

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

$Al_2(OH)_4^{2+}$ Layer

Anion midplane

$(Si_2O_5)^{2-}$ Layer

- Si^{4+}
- Al^{3+}
- OH$^-$
- O^{2-}
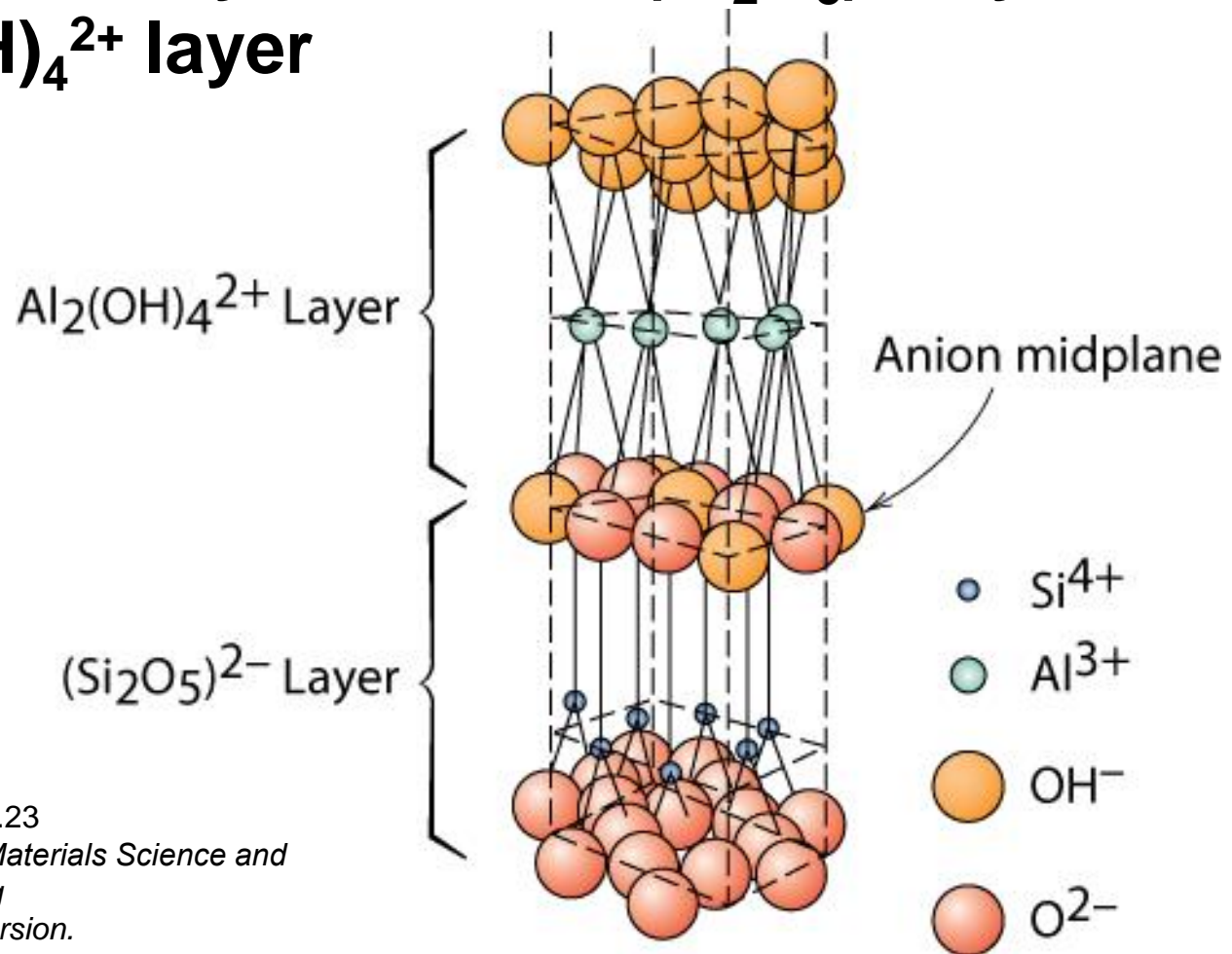
From Fig. 4.23
*Callister's Materials Science and Engineering
Adapted Version.*

Note: these sheets loosely bound by van der Waal's forces

Layered Silicates

- **Can change the counterions**
 - **this changes layer spacing**
  - **the layers also allow absorption of water**
- **Micas $KAl_3Si_3O_{10}(OH)_2$**
- **Bentonite**
  - **used to seal wells**
  - **packaged dry**
  - **swells 2-3 fold in H_2O**
  - **pump in to seal up well so no polluted ground water seeps in to contaminate the water supply.**

Carbon Forms

- **Carbon black – amorphous – surface area ca. 1000 m²/g**

- **Diamond**
  - **tetrahedral carbon**
    - **hard – no good slip planes**
    - **brittle – can cut it**
  - **large diamonds – jewelry**
  - **small diamonds**
    - **often man made - used for cutting tools and polishing**
  - **diamond films**
    - **hard surface coat – tools, medical devices, etc.**
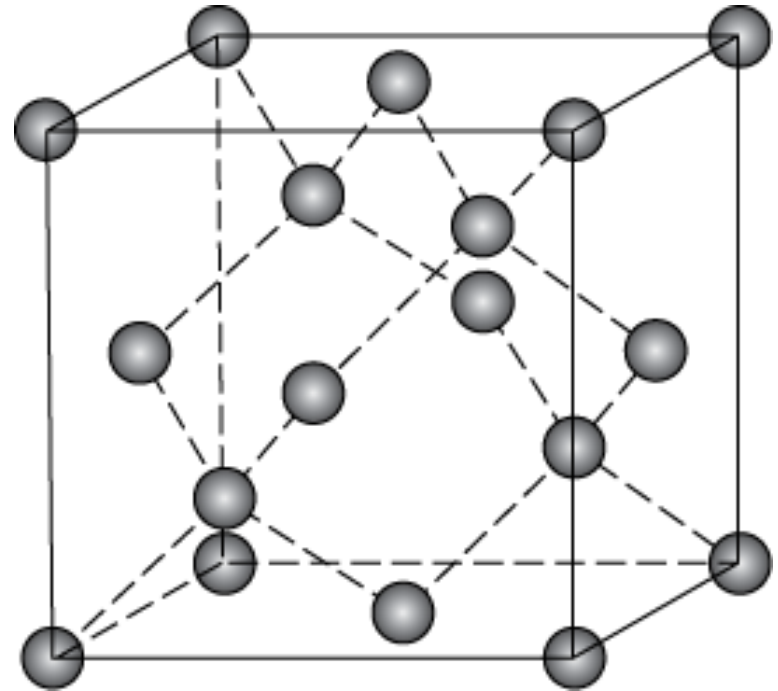
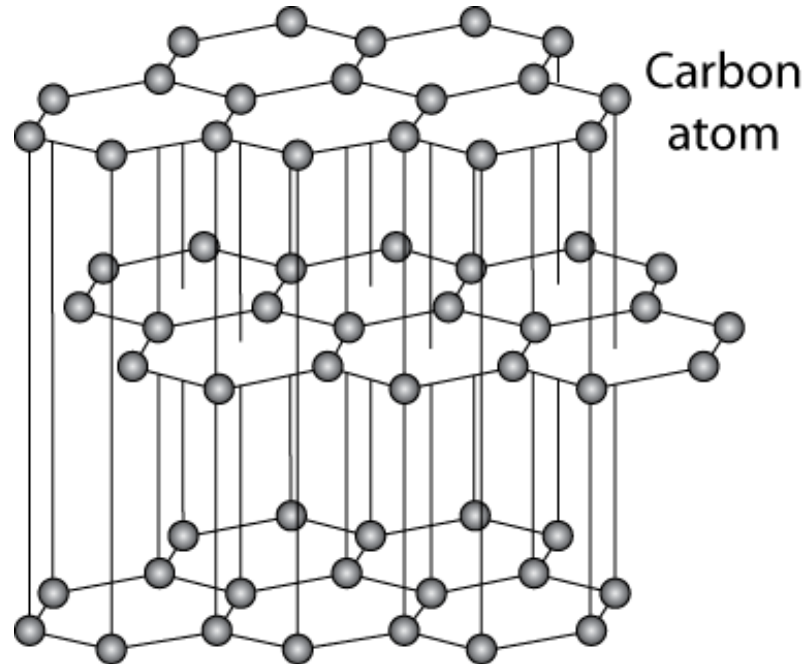From Fig. 4.24
Callister's Materials Science and Engineering Adapted Version.

Carbon Forms - Graphite

- **layer structure – aromatic layers**

Carbon atom

From Fig. 4.26
Callister's Materials Science and Engineering Adapted Version.

  - **weak van der Waal's forces between layers**
  - **planes slide easily, good lubricant**

Carbon Forms – Fullerenes and Nanotubes

- **Fullerenes or carbon nanotubes**
  - **wrap the graphite sheet by curving into ball or tube**
  - **Buckminister fullerenes**
    - **Like a soccer ball C_{60} - also C_{70} + others**
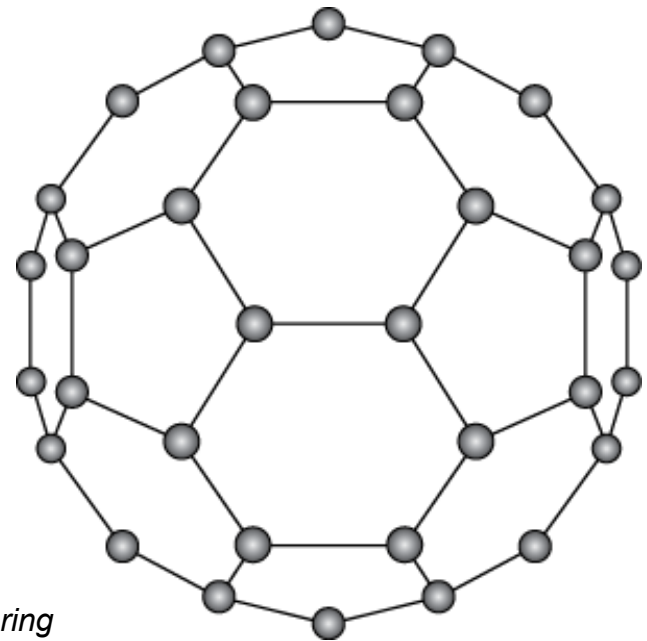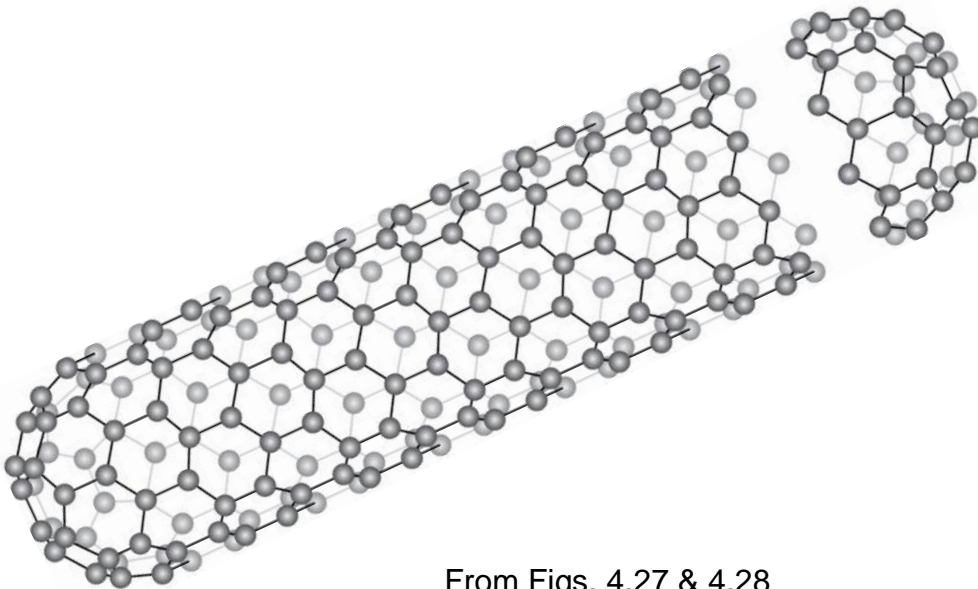
From Figs. 4.27 & 4.28
Callister's Materials Science and Engineering Adapted Version.

Polymer Crystallinity

Ex: polyethylene unit cell

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

10 nm
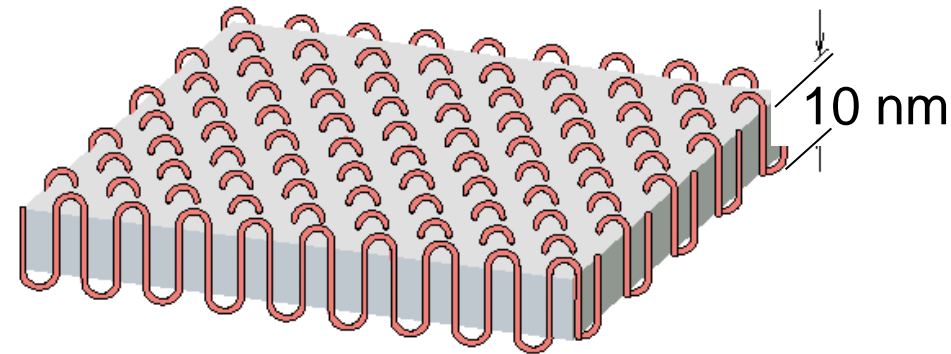
From Fig. 4.31
*Callister's Materials Science and Engineering
Adapted Version.*

0.255 nm

0.741 nm

0.494 nm

From Fig. 4.29
*Callister's Materials Science and Engineering
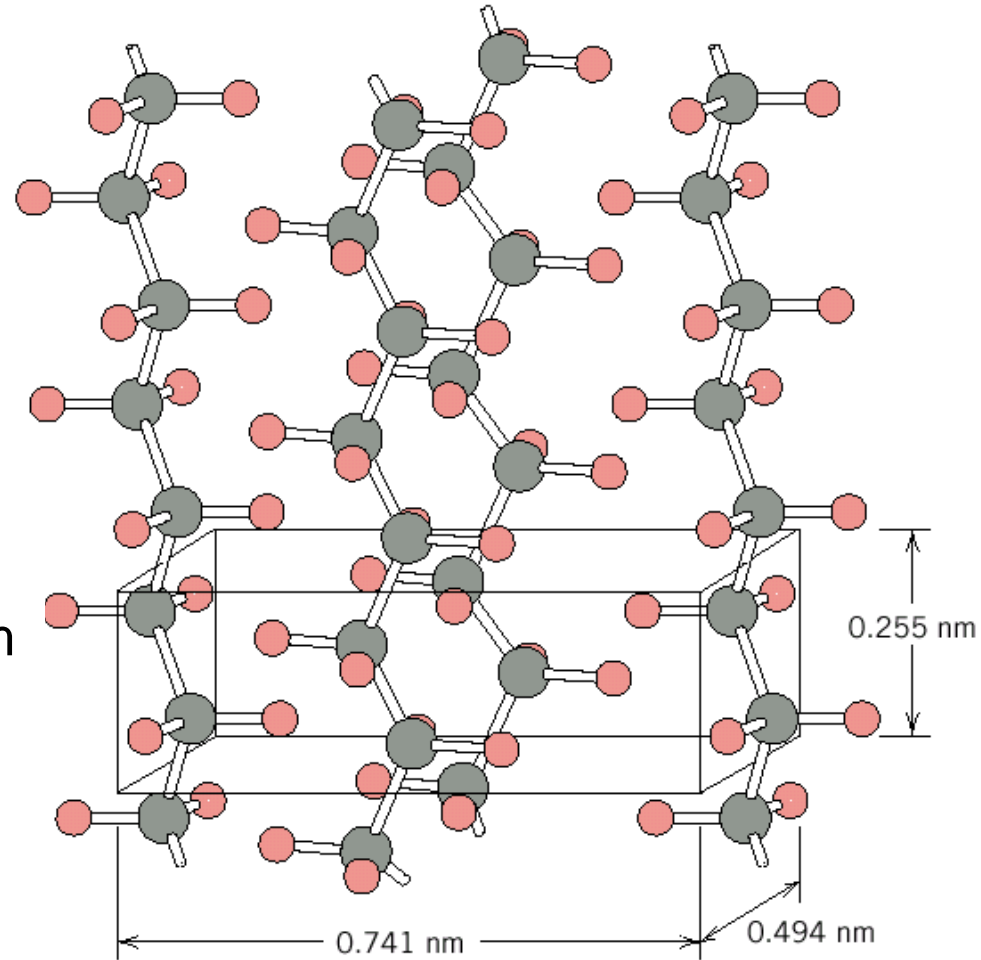Adapted Version.*

Polymer Crystallinity

Polymers rarely 100% crystalline

- **Too difficult to get all those chains aligned**

- **% Crystallinity: % of material that is crystalline.**
  -- *TS* and *E* often increase with % crystallinity.
  -- Annealing causes crystalline regions to grow. % crystallinity increases.

Region of high crystallinity

Amorphous region

crystalline region

amorphous region
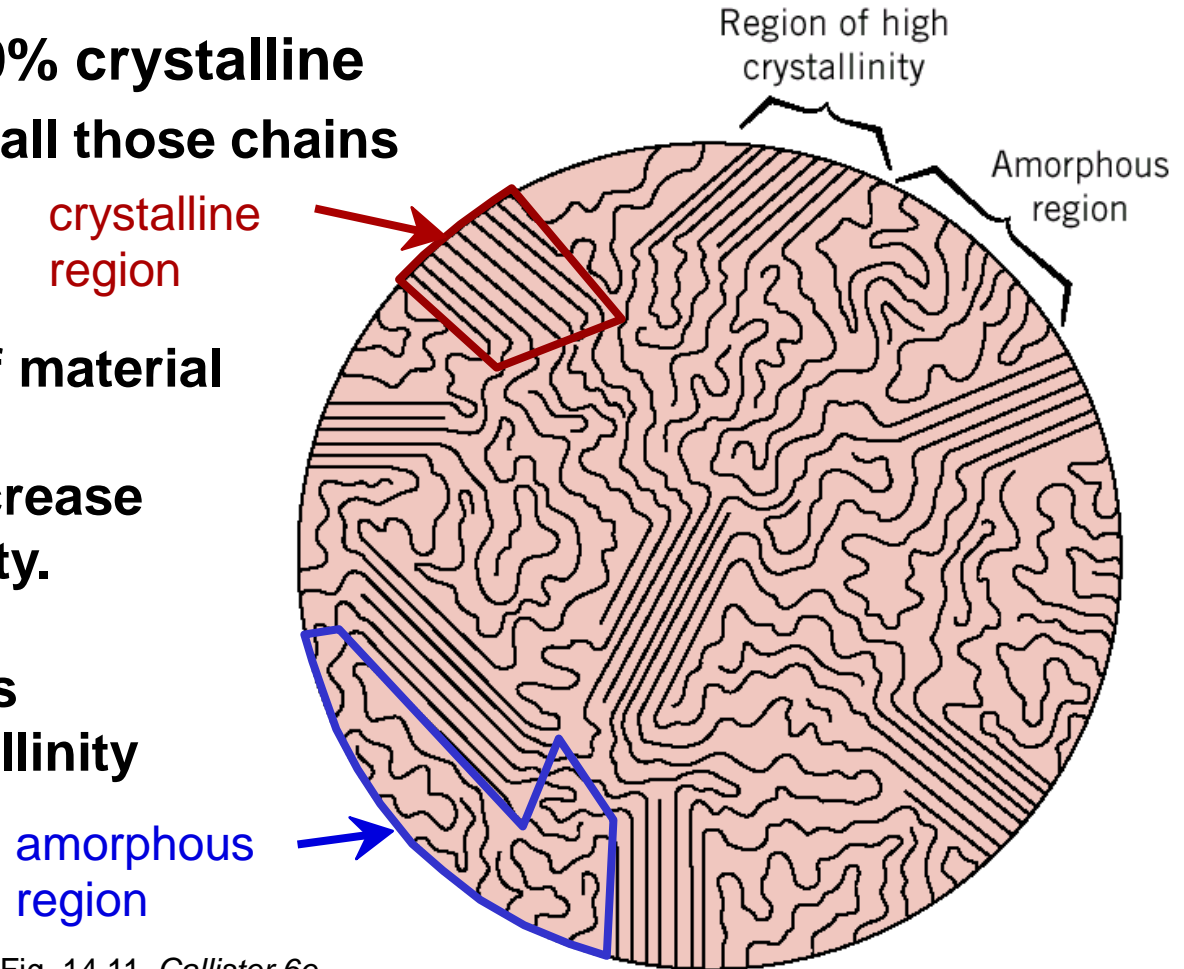
From Fig. 14.11, *Callister 6e.*
(Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

Polymer Crystal Forms

- **Single crystals** – **only if slow careful growth**
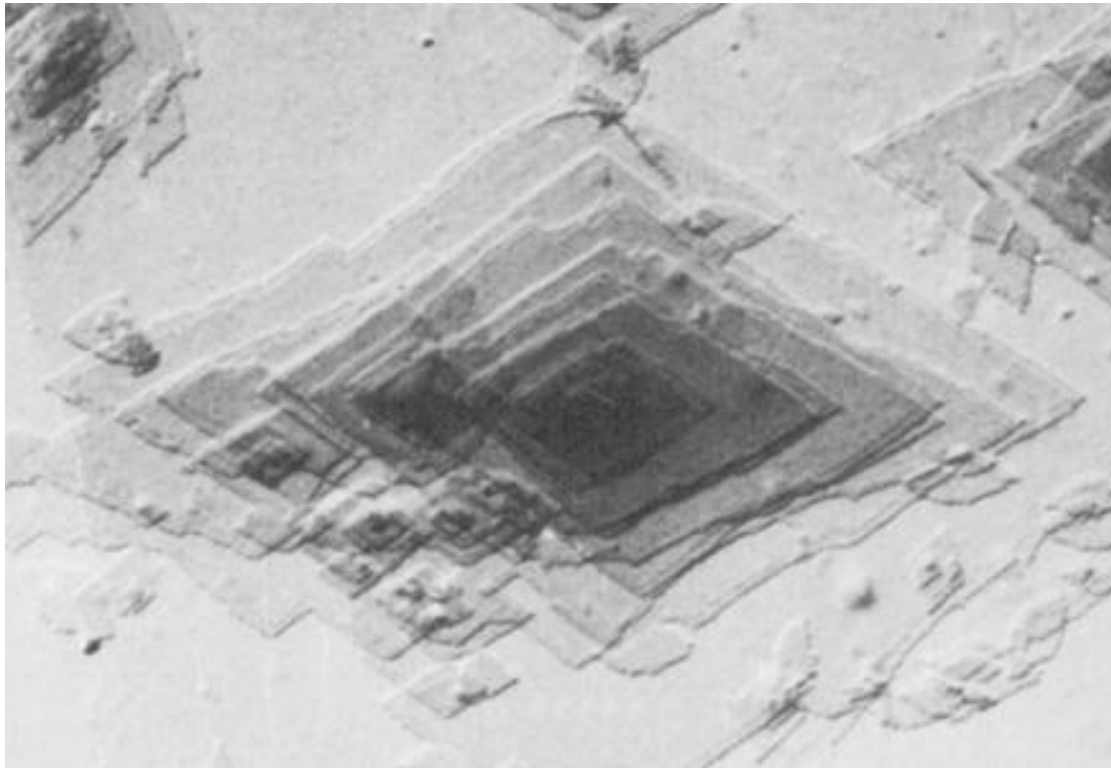
From Fig. 4.30
Callister's Materials Science and Engineering
Adapted Version

Polymer Crystal Forms

Direction of spherulite growth

Lamellar chain-folded crystallite

Amorphous material

Tie molecule

Nucleation Site

Interspherulitic boundary
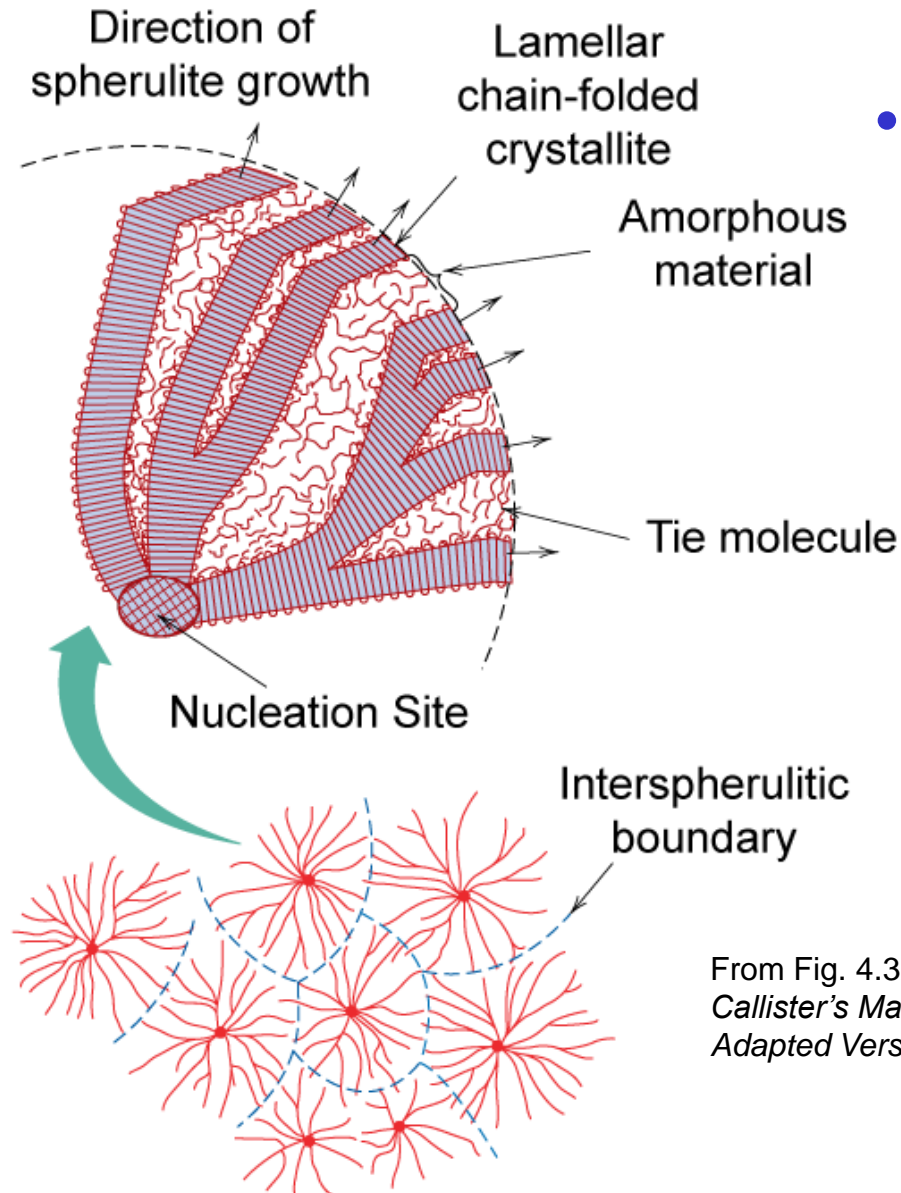
• **Spherulites – fast growth – forms lamellar (layered) structures**

From Fig. 4.32
Callister's Materials Science and Engineering Adapted Version.

Spherulites – crossed polarizers

Maltese cross

100 μ

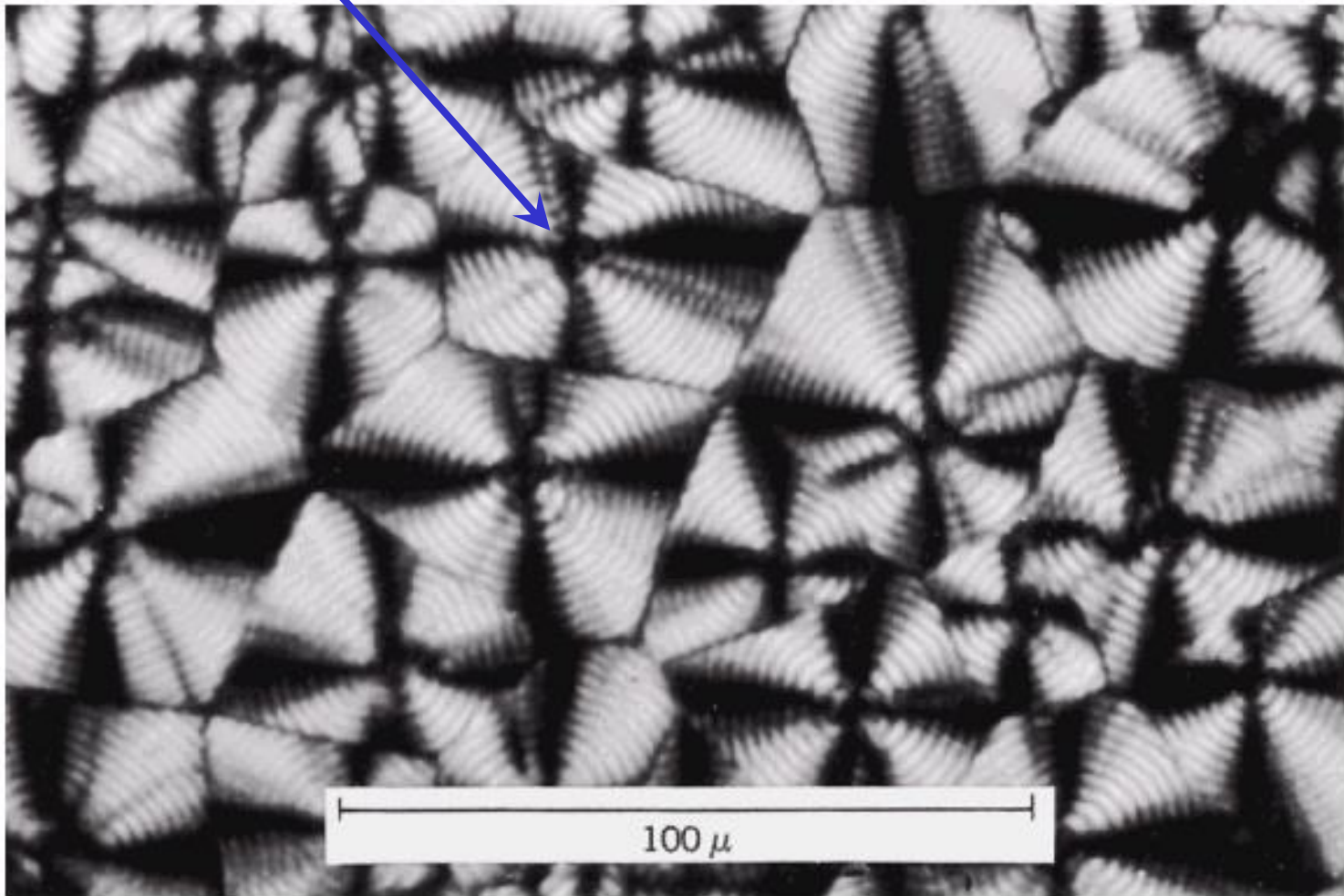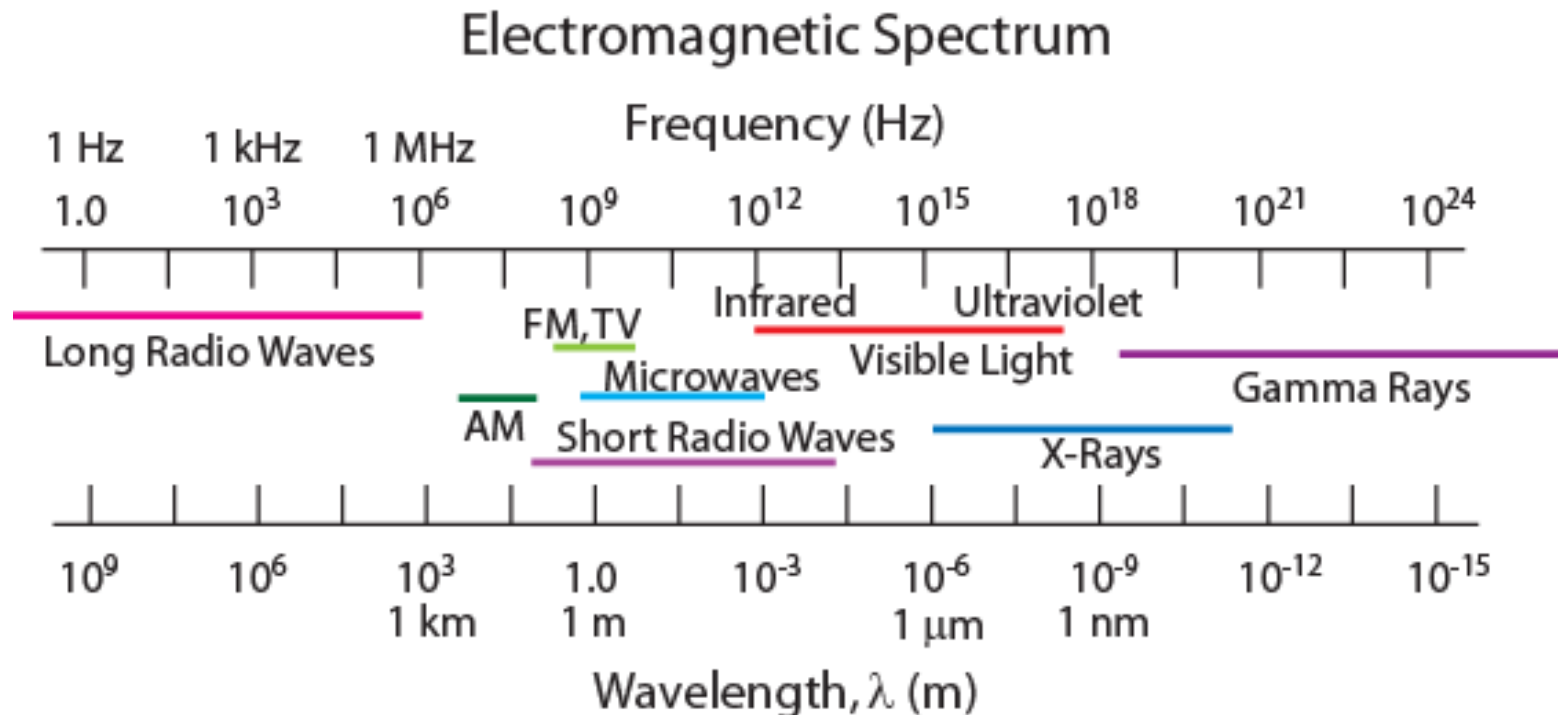From Fig. 4.33
*Callister's Materials Science and Engineering
Adapted Version*

Section 4.20 - X-Ray Diffraction

Electromagnetic Spectrum

Frequency (Hz)

1 Hz	1 kHz	1 MHz						
1.0	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

Long Radio Waves

FM,TV

Infrared   Ultraviolet

AM   Short Radio Waves   Microwaves   Visible Light

Gamma Rays

X-Rays

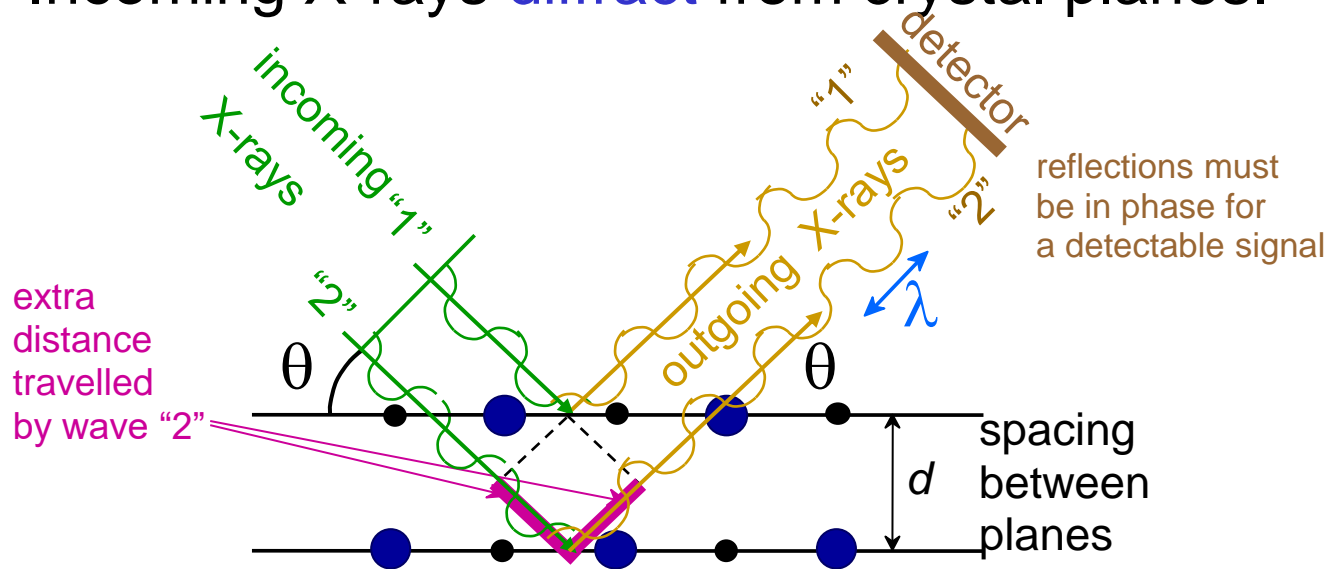| 10^9	10^6	10^3	1.0	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}
		1 km	1 m		1 μm	1 nm		

Wavelength, λ (m)

- 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.

incoming X-rays

incoming "1"

"2"

detector

"1"

"2"

outgoing X-rays

λ

reflections must be in phase for a detectable signal

extra distance travelled by wave "2"

θ θ

d spacing between planes

From Fig. 4.35
Callister's Materials Science and Engineering, Adapted Version.

Measurement of critical angle, θ_c, allows computation of planar spacing, *d*.

X-ray intensity (from detector)

$$d = \frac{n\lambda}{2\sin\theta_c}$$

θ

θ_c
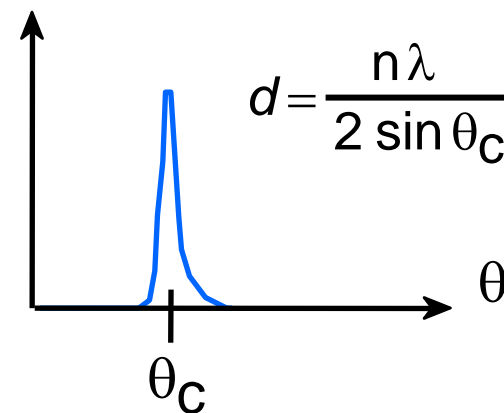
X-Ray Diffraction Pattern
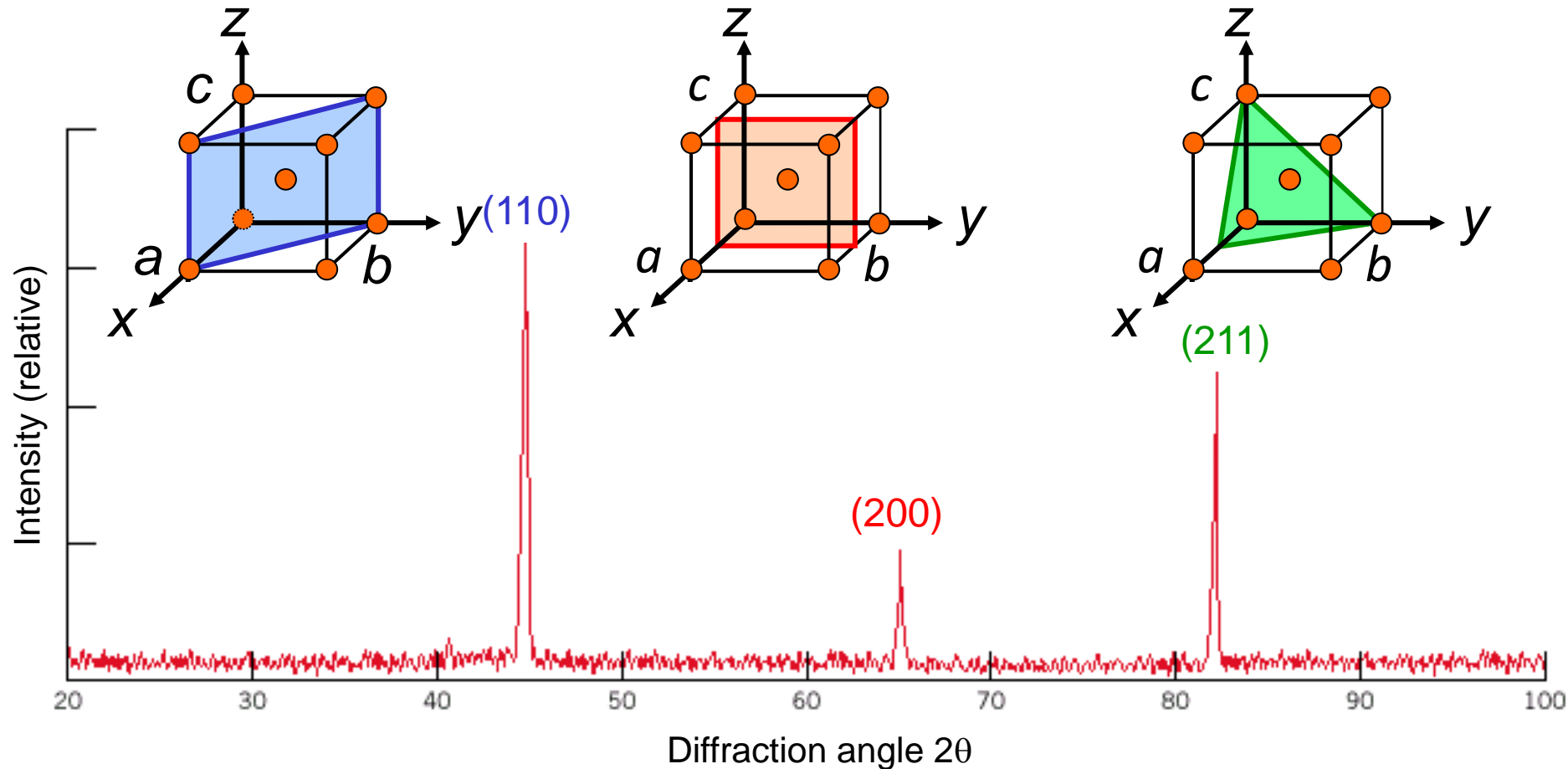
Diffraction pattern for polycrystalline α-iron (BCC)

From Fig. 3.20, *Callister 5e.*

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).

- Crystallographic directions and planes are related to atomic linear densities and planar densities.

- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).

SUMMARY

- Ceramic materials have covalent & ionic bonding.

- Ceramic structures are based on charge neutrality and maximizing # of nearest oppositely charged neighbors

- Ceramic structures may be predicted based on the ratio of the cation and anion radii

- Polymer structures were described, in particular the spherulitic structure of semicrystalline polymer

- X-ray diffraction is used for crystal structure and interplanar spacing determinations.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: