

2019 Fall

Introduction to Materials Science and Engineering

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Contents for previous class

CHAPTER 3: Fundamentals of Crystallography

III. Crystalline \leftrightarrow Noncrystalline Materials

- Single crystals, Polycrystalline materials, Anisotropy
- Quasicrystals
- Noncrystalline solids : Amorphous solid

CHAPTER 4: The Structure of Crystalline Solids

I. METALLIC CRYSTALS _ APF , CN ...

- The face-centered cubic crystal structure (FCC)
- The body-centered cubic crystal structure (BCC)
- The hexagonal closed-packed crystal structure (HCP)

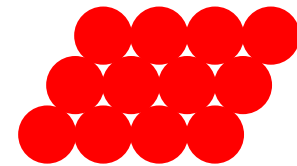
Contents for previous class

I. Atomic arrangement in the solid state

- Solid materials are classified according to the **regularity** with which atoms and ions are arranged with respect to one another.

- So, how are they arranged ?

(a) **periodically** – having long range order in 3-D

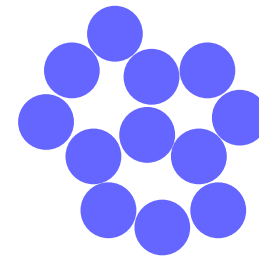


Crystal

(b) **quasi-periodically**

Quasicrystal

(c) **randomly** – having short range order with the characteristics of bonding type but losing the long range order



Amorphous

- **Crystal: Perfection → Imperfection**

Non-crystalline Materials

- **Amorphous materials**

a wide diversity of materials can
be rendered amorphous
indeed **almost all materials can**.

- metal, ceramic, polymer

ex) amorphous metallic alloy (1960)

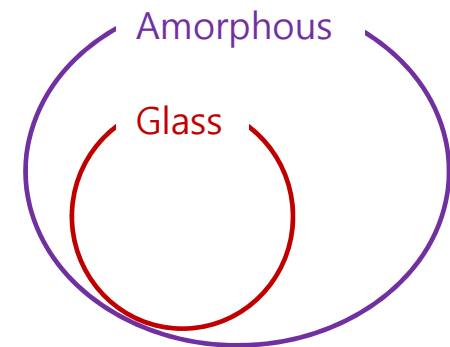
- **glassy/non-crystalline material**

cf) amorphous vs glass

- random atomic structure (short range order)
- showing glass transition.

- retain liquid structure

- rapid solidification from liquid state



QUASICRYSTALS

Similar to crystals, BUT...

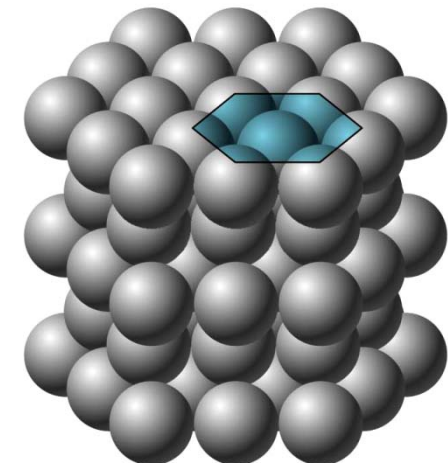
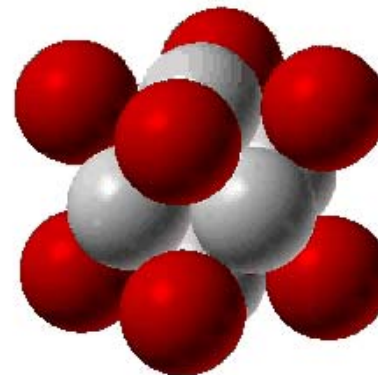
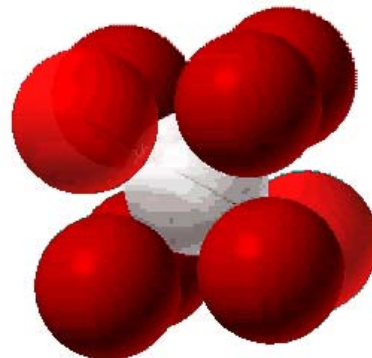
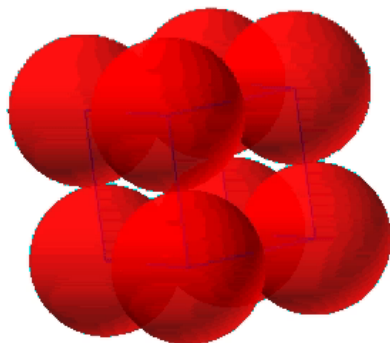
- Orderly arrangement . . .
But *QUASIPERIODIC* instead of *PERIODIC*
- Rotational Symmetry . . .
But with *FORBIDDEN* symmetry
- Structure can be reduced to a finite number
of repeating units

Contents for today's class

II. Metallic crystal system

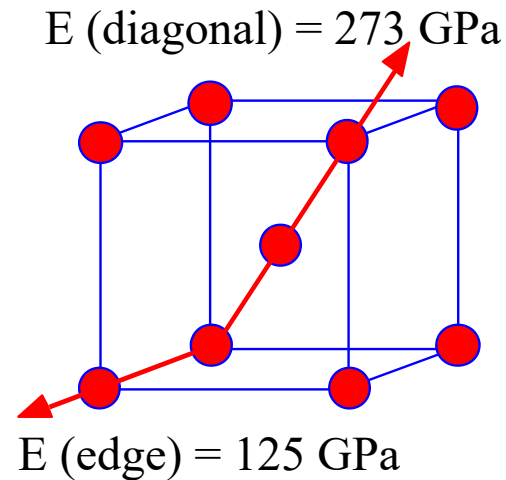
TABLE 3-2 ■ Crystal structure characteristics of some metals

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α -Mn
Body-centered cubic	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd



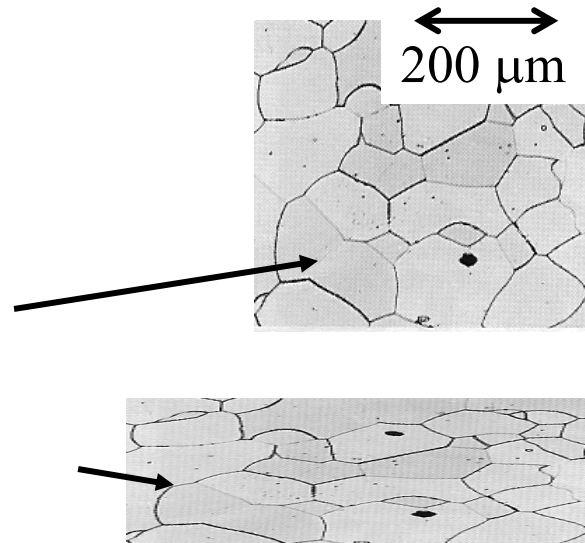
Single vs Polycrystals

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



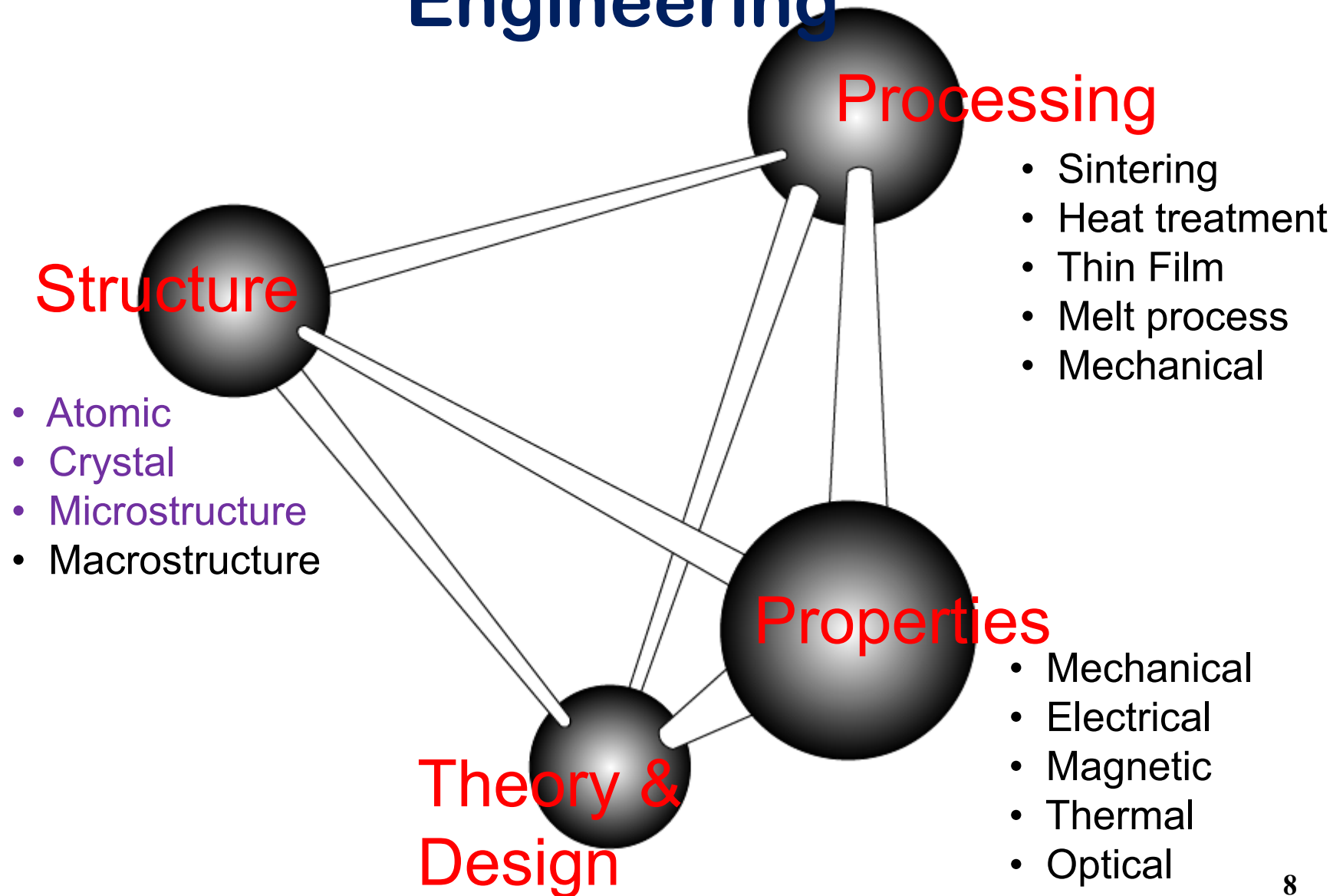
Data from Table 3.3,
Callister 7e.
(Source of data is R.W.
Hertzberg, *Deformation
and Fracture Mechanics of
Engineering Materials*, 3rd
ed., John Wiley and Sons,
1989.)

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



Adapted from Fig. 4.14(b),
Callister 7e.
(Fig. 4.14(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].)

Materials Science and Engineering



Contents for today's class

CHAPTER 4: The Structure of Crystalline Solids

I. METALLIC CRYSTALS _ APF , CN ...

- FCC, BCC, HCP

II. Ceramic Crystal Structure

- Ionic arrangement geometries
- Some common ceramic crystal structure
- Density computation-ceramics
- Silicate ceramics
- Carbon

III. Polymer Structure

IV. X-ray diffraction: Determination of crystal structures

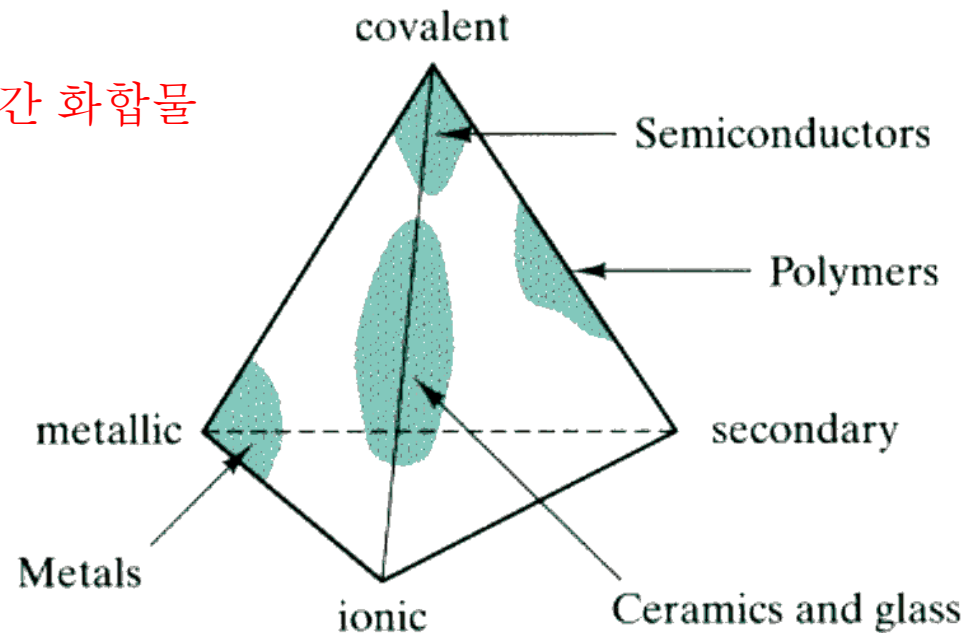
- The diffraction phenomenon
- X-diffraction and Bragg's law
- Diffraction techniques

Ceramic Crystal Structures

Materials-Bonding Classification

Material type	Bonding character	Example
Metal	Metallic	Iron (Fe) and the ferrous alloys
Ceramics and glasses	Ionic/covalent	Silica (SiO ₂): crystalline and noncrystalline
Polymers	Covalent and secondary	Polyethylene $(-C_2H_4)_n$
Semiconductors	Covalent or covalent/ionic	Silicon (Si) or cadmium sulfide (CdS)

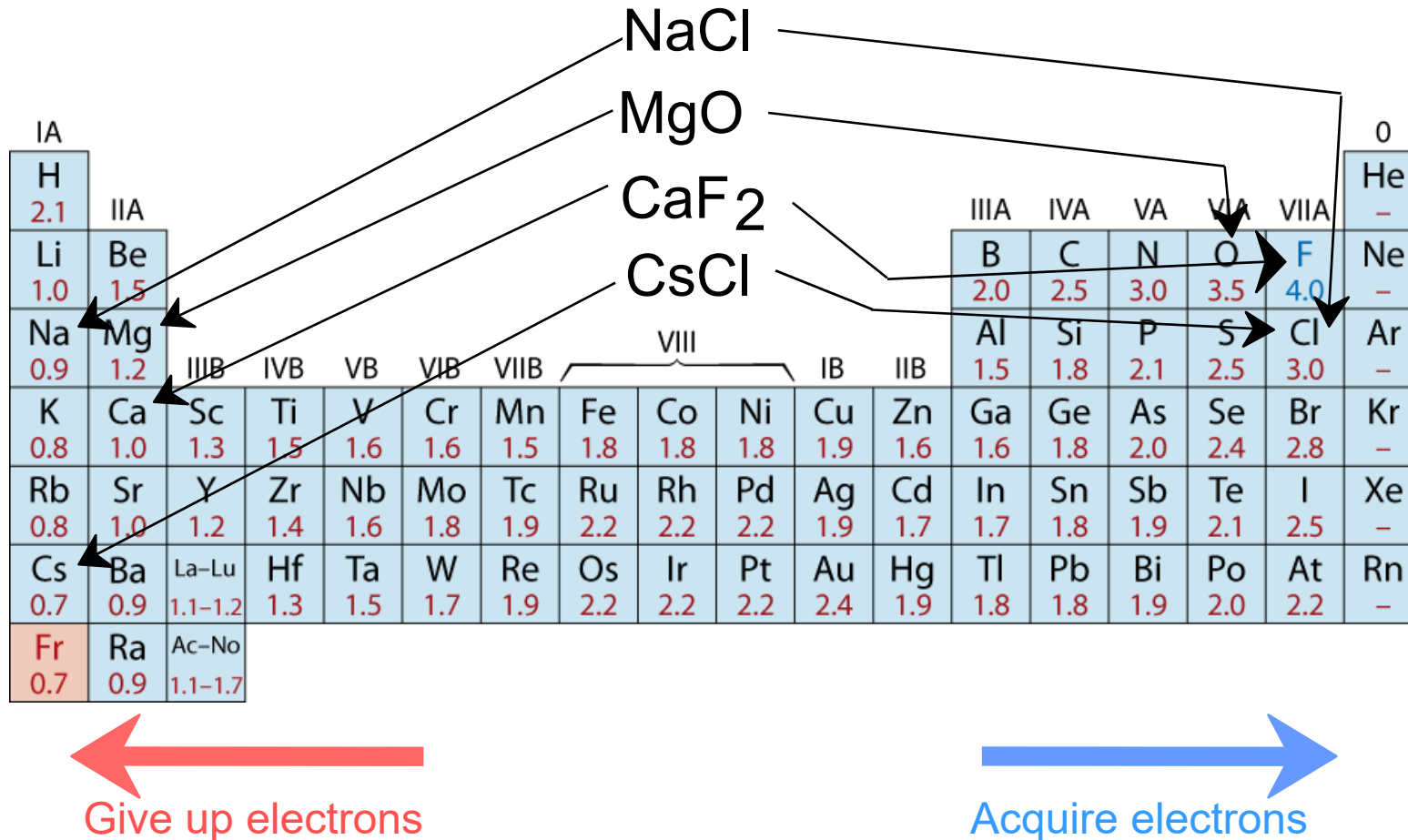
금속-비금속 원소간 화합물
'구운 것 (firing)'



< 실제 많은 재료는 2개 혹은 그 이상의 결합에 혼합 >

Ionic Bonding

- Predominant bonding in **Ceramics**



Adapted from Fig. 2.7, *Callister 7e*. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Covalent Bonding

Diagram illustrating covalent bonding in various molecules and solids, mapped onto the periodic table. Arrows indicate the elements involved in each substance:

- H₂**: Hydrogen (H, Group IA)
- H₂O**: Hydrogen (H, Group IA) and Oxygen (O, Group VIA)
- C(diamond)**: Carbon (C, Group IVA)
- SiC**: Silicon (Si, Group IVA) and Carbon (C, Group IVA)
- F₂**: Fluorine (F, Group VIIA)
- Cl₂**: Chlorine (Cl, Group VIIA)
- GaAs**: Gallium (Ga, Group IIIA) and Arsenic (As, Group VA)

The periodic table shows electronegativity values (in red) for various elements. A vertical green line highlights **column IVA**, which includes Carbon (C, 2.5), Silicon (Si, 1.8), Germanium (Ge, 1.8), and Tin (Sn, 1.8). Other elements shown include Hydrogen (2.1), Lithium (1.0), Beryllium (1.5), Sodium (0.9), Magnesium (1.2), Potassium (0.8), Calcium (1.0), Scandium (1.3), Titanium (1.5), Vanadium (1.6), Chromium (1.6), Manganese (1.5), Iron (1.8), Cobalt (1.8), Nickel (1.8), Copper (1.9), Zinc (1.8), Gallium (1.6), Germanium (1.8), Arsenic (2.0), Selenium (2.4), Bromine (2.8), Krypton (2.0), Rubidium (0.8), Strontium (1.0), Yttrium (1.2), Zirconium (1.4), Niobium (1.6), Molybdenum (1.8), Technetium (1.9), Ruthenium (2.2), Rhodium (2.2), Palladium (2.2), Silver (1.9), Cadmium (1.7), Indium (1.7), Tin (1.8), Antimony (1.9), Tellurium (2.1), Iodine (2.5), Xenon (2.0), Cesium (0.7), Barium (0.9), Lanthanum-Lutetium (1.1-1.2), Hafnium (1.3), Tantalum (1.5), Tungsten (1.7), Rhenium (1.9), Osmium (2.2), Iridium (2.2), Platinum (2.2), Gold (2.4), Mercury (1.9), Thallium (1.8), Lead (1.8), Bismuth (1.9), Polonium (2.0), Astatine (2.2), and Francium (0.7), Radium (0.9), Actinide-Neptunium (1.1-1.7).

- molecules with **nonmetals**
- molecules with **metals** and **nonmetals**
- elemental solids (RHS of Periodic Table)
- compound solids (about **column IVA**)

Ionic bond = metal + nonmetal

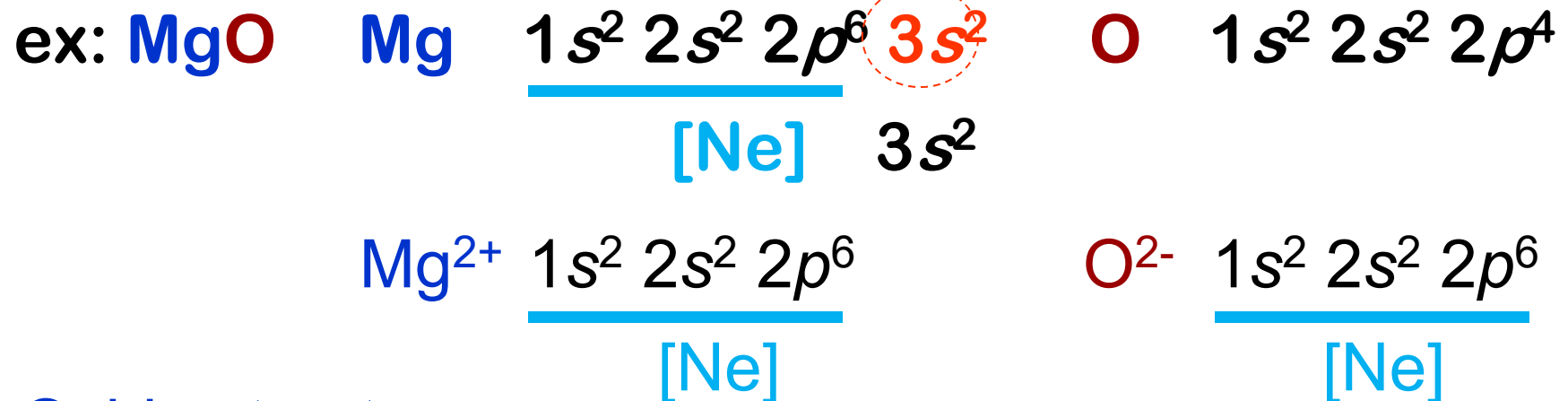


Accepts
electrons
(양이온)



Donates
electrons
(음이온)

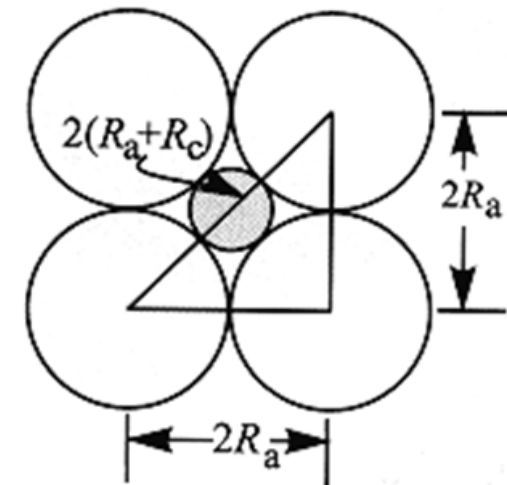
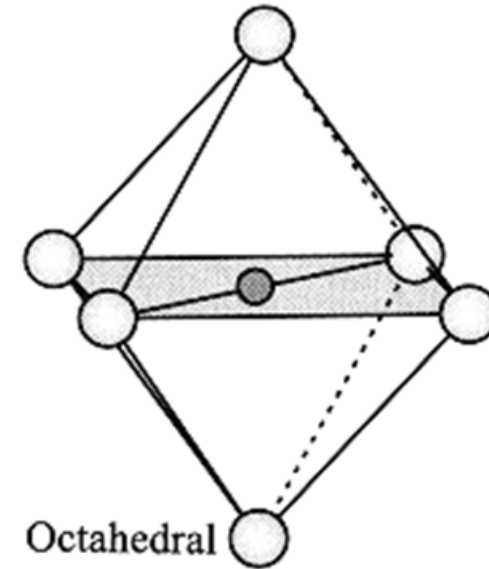
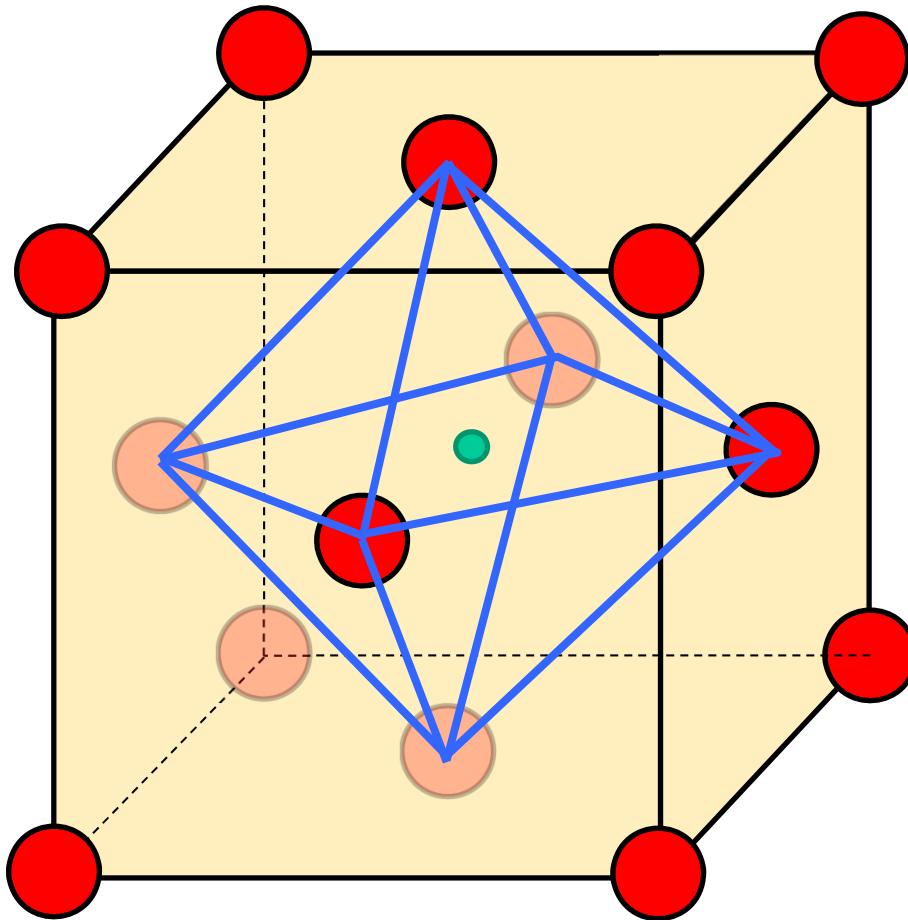
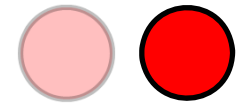
Dissimilar electronegativities



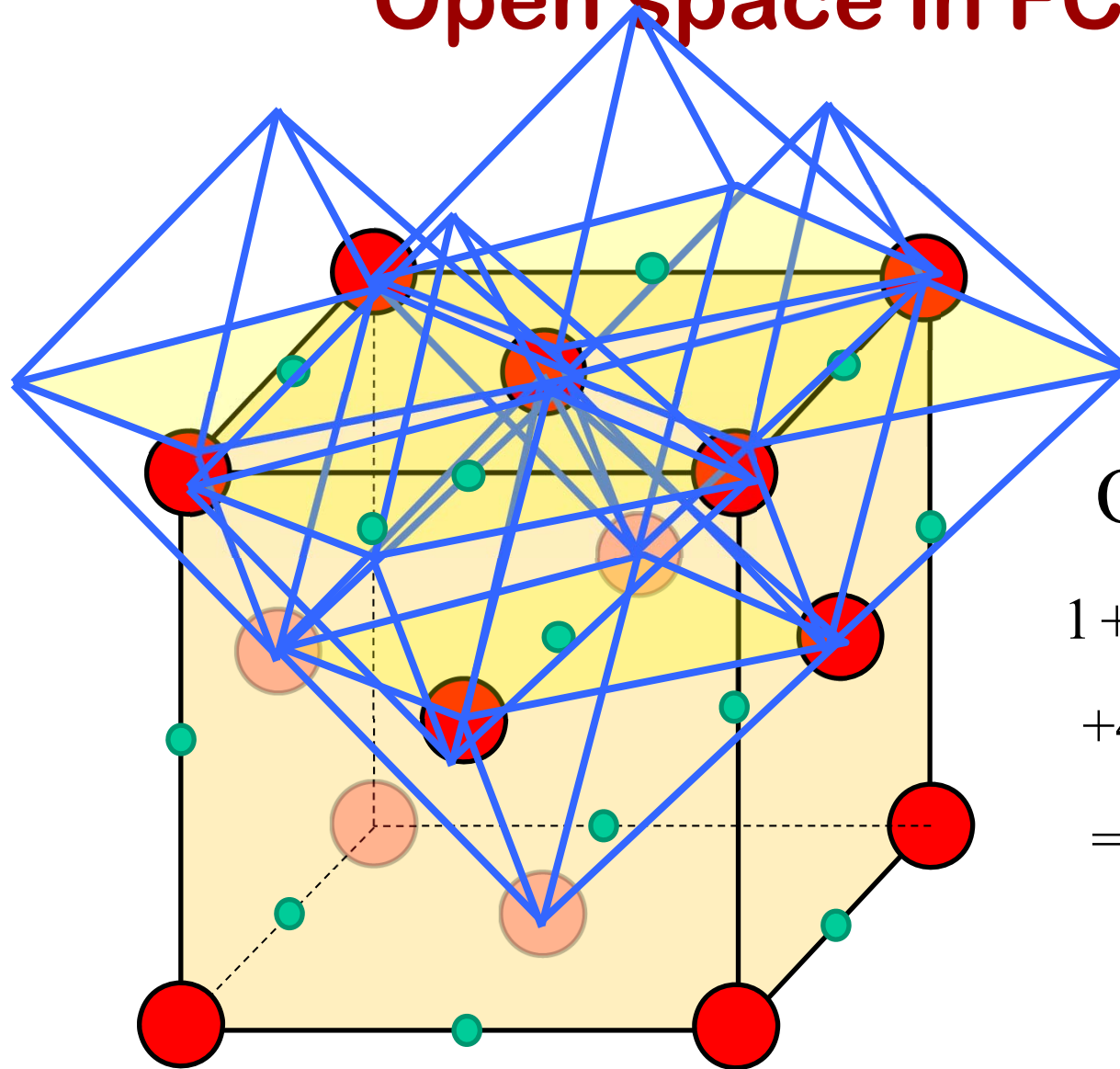
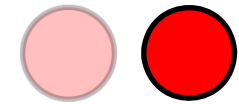
Oxide structures

- oxygen anions larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations fit into interstitial sites among oxygen ions

Open space in FCC 1



Open space in FCC 1



Octahedral sites

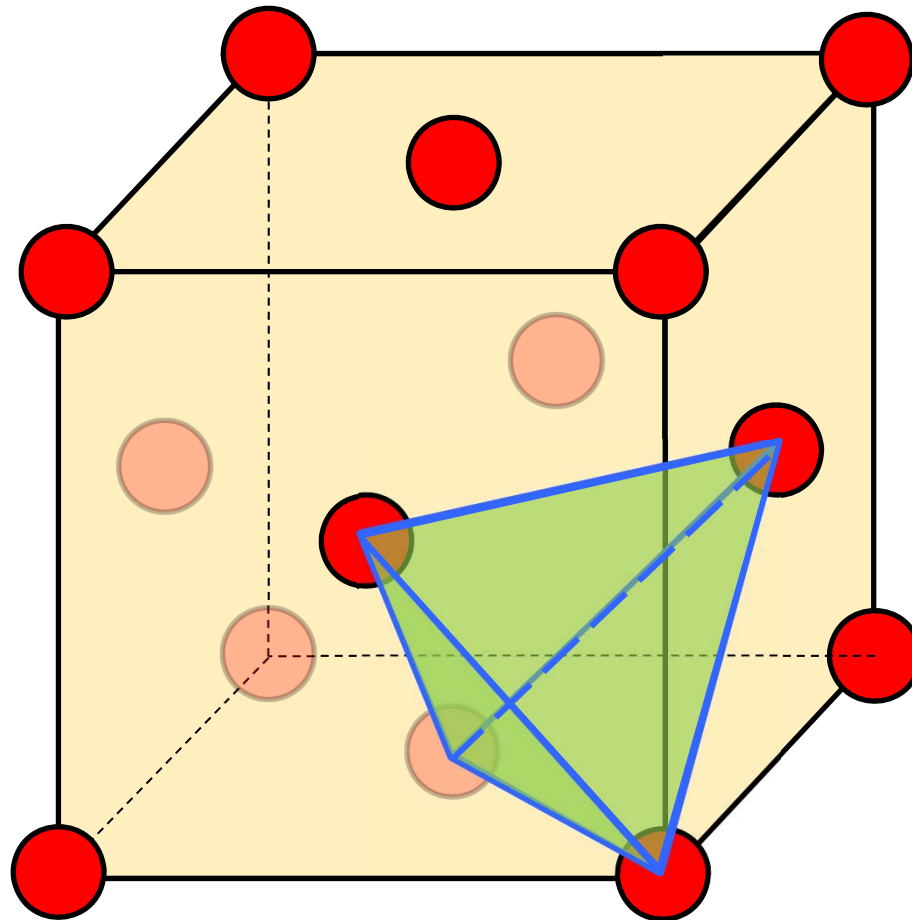
$$1 + 1/4 + 1/4 + 1/4 + 1/4$$

$$+ 4 * (1/4) + 4 * (1/4)$$

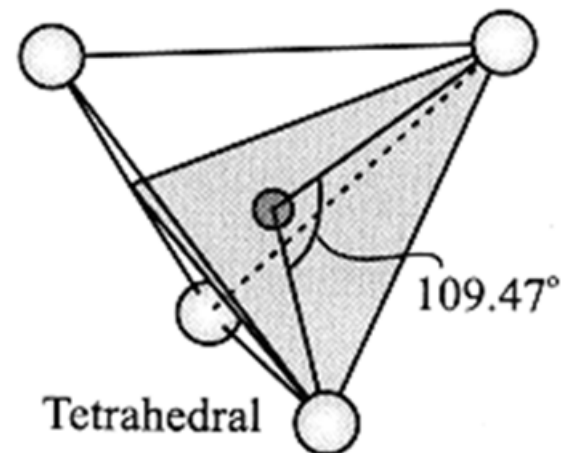
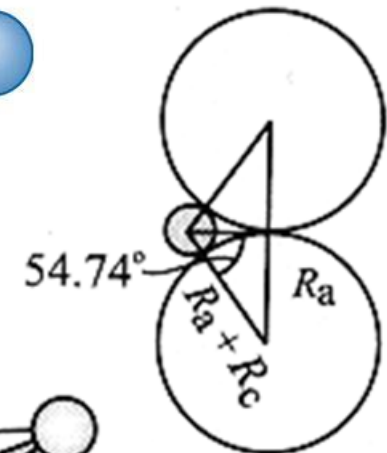
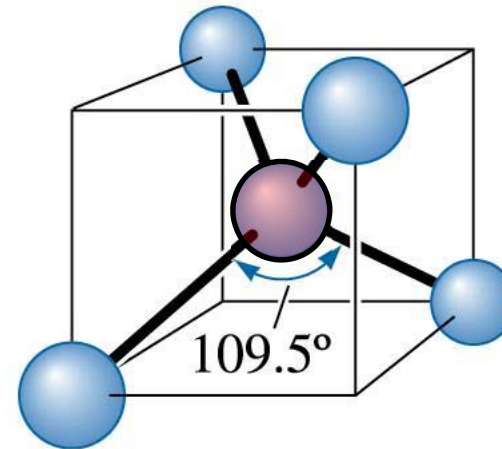
$$= 4$$

Open space in FCC 2

- Visible Atoms
- Atoms behind

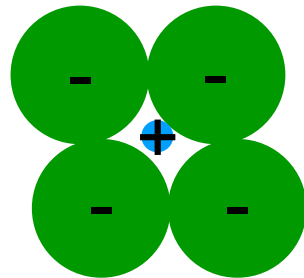


Tetrahedral sites = 8

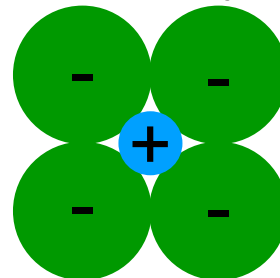


Factors that Determine Crystal Structure

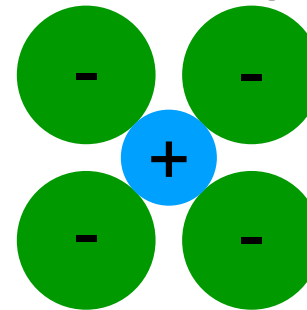
1. **Relative sizes of ions** – Formation of stable structures:
--maximize the # of oppositely charged ion neighbors.



unstable



stable

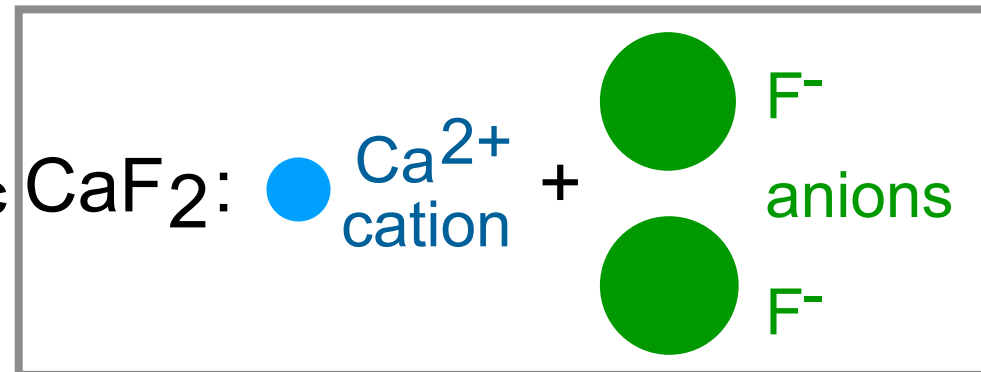


stable

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

2. **Maintenance of Charge Neutrality** :

- Net charge in ceramic should be zero.**
--Reflected in chemical formula:



m, p values to achieve
charge neutrality

Chapter 4.6

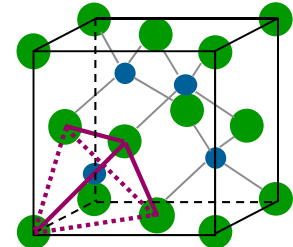
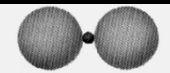
Coordination Number and Ionic Radii

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

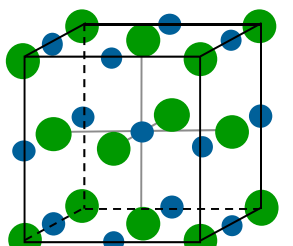

To form a stable structure, how many anions can surround around a cation?

surround a cation:

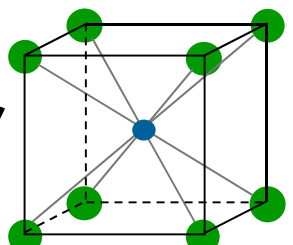

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord. Number	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic



ZnS
(zinc blende)
Adapted from Fig. 4.7,
Callister & Rethwisch 9e.



NaCl
(sodium chloride)
Adapted from Fig. 4.5,
Callister & Rethwisch 9e.

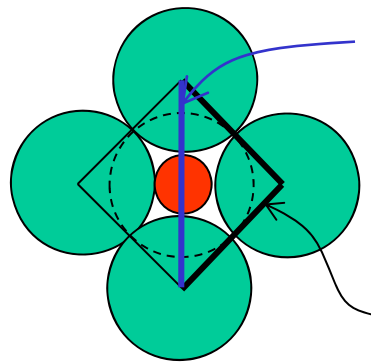


CsCl
(cesium chloride)
Adapted from Fig. 4.6,
Callister & Rethwisch 9e.

Adapted from Table 4.3,
Callister & Rethwisch 9e.

Computation of Minimum Cation-Anion Radius Ratio

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



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

$$a = 2r_{\text{anion}}$$

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

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

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

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)

Al³⁺ 0.053

Fe²⁺ 0.077

Fe³⁺ 0.069

Ca²⁺ 0.100

Anion

O²⁻ 0.140

Cl⁻ 0.181

F⁻ 0.133

- Answer:

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

based on this ratio,

-- coord # = 6 because

$$0.414 < 0.550 < 0.732$$

-- crystal structure is NaCl

Data from Table 4.4,
Callister & Rethwisch 9e.

Ceramic Structure

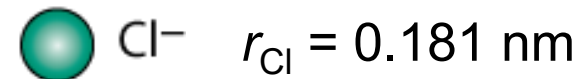
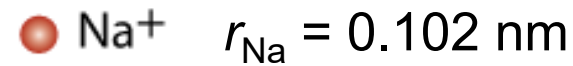
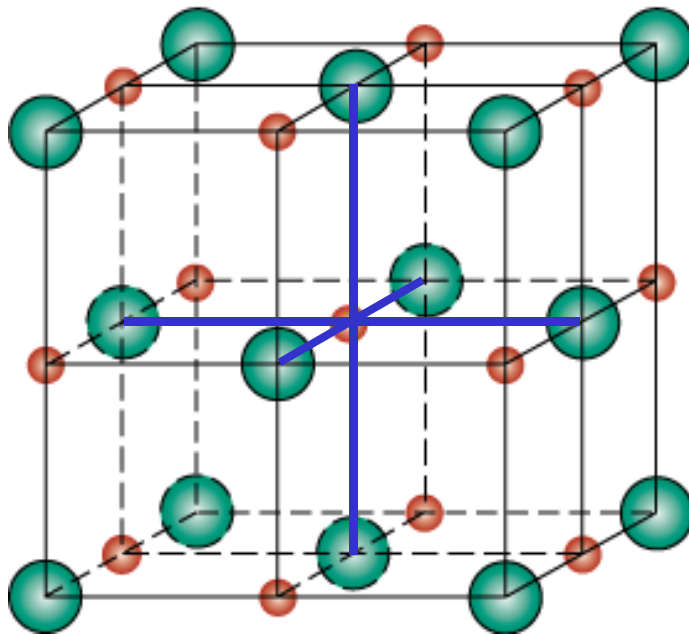
Summary of Some Common Ceramic Crystal Structures

<i>Structure Name</i>	<i>Structure Type</i>	<i>Anion Packing</i>	<i>Coordination Numbers</i>		<i>Examples</i>
			<i>Cation</i>	<i>Anion</i>	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX ₂	Simple cubic	8	4	CaF ₂ , UO ₂ , ThO ₂
Perovskite	ABX ₃	FCC	12(A) 6(B)	6	BaTiO ₃ , SrZrO ₃ , SrSnO ₃
Spinel	AB ₂ X ₄	FCC	4(A) 6(B)	4	MgAl ₂ O ₄ , FeAl ₂ O ₄

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure

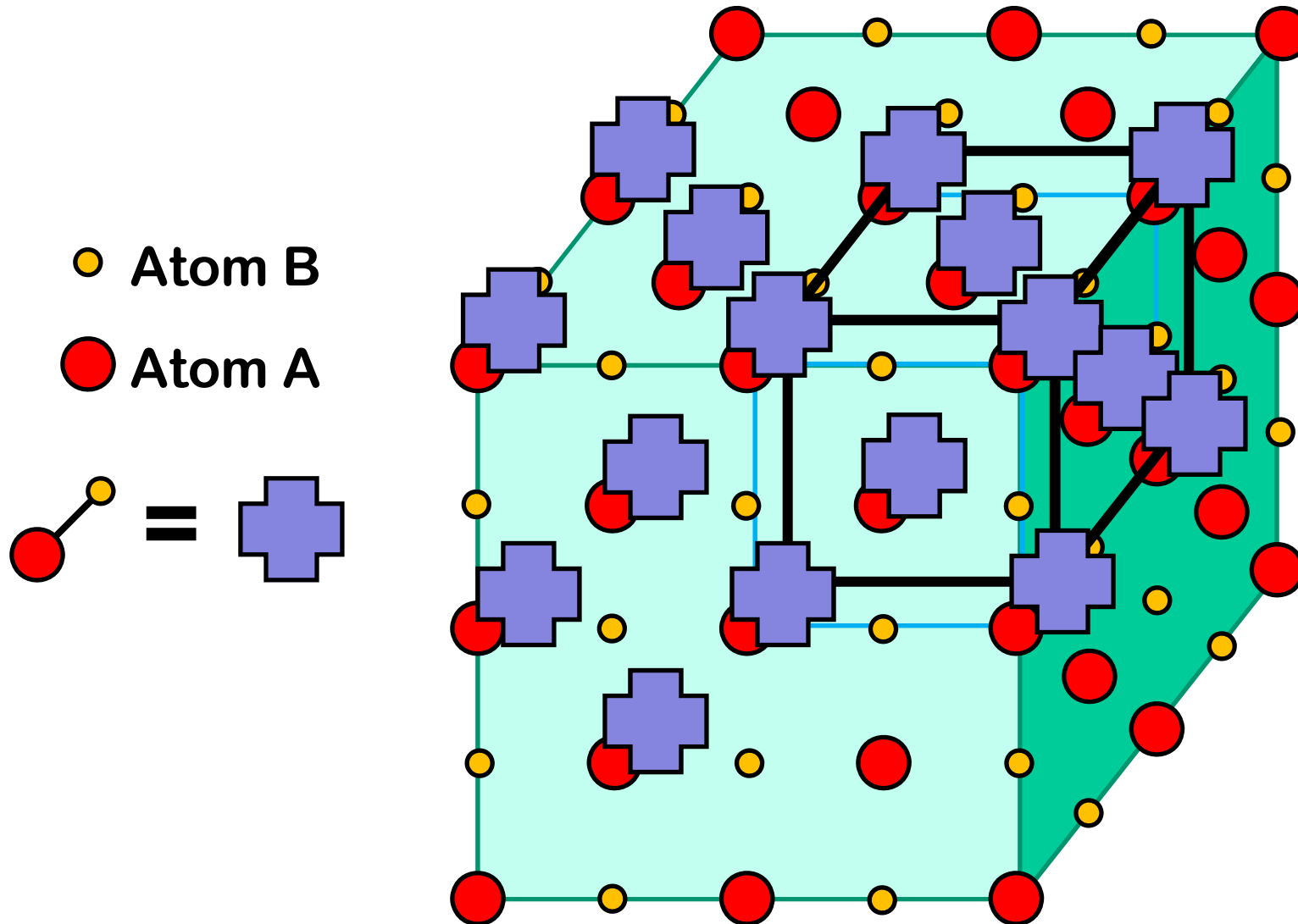


$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

∴ cations (Na⁺) prefer octahedral sites

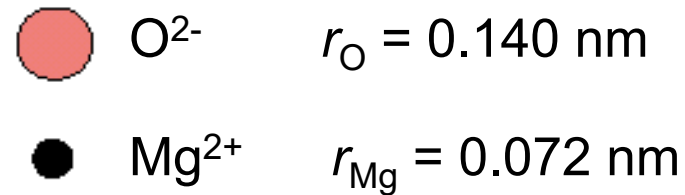
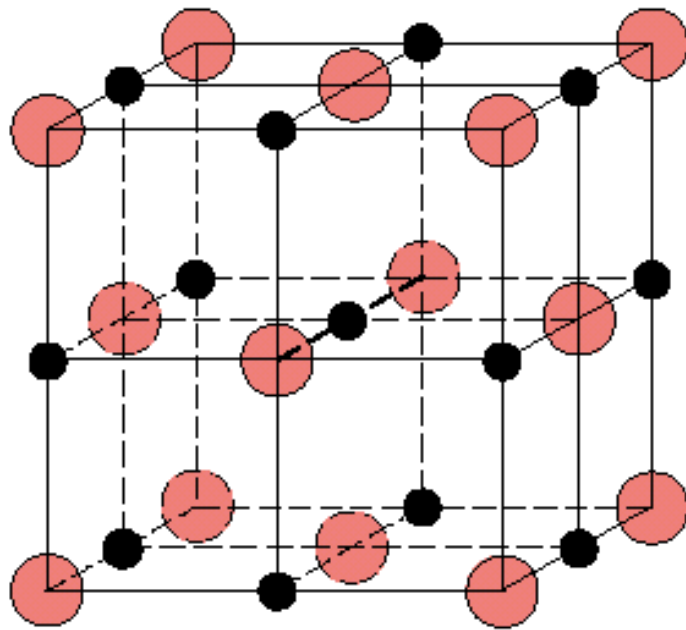
Adapted from Fig. 4.5,
Callister & Rethwisch 9e.

Show why NaCl is FCC



MgO and FeO

MgO and FeO also have the NaCl structure



$$r_{Mg}/r_O = 0.514$$

\therefore cations prefer octahedral sites

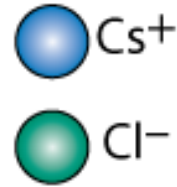
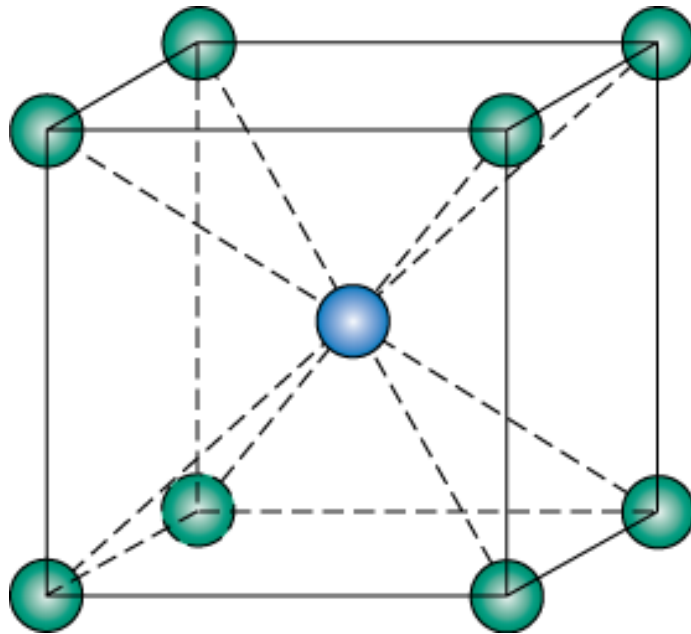
Adapted from Fig. 4.5,
Callister & Rethwisch 9e.

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

AX Crystal Structures

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

Cesium Chloride structure:



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

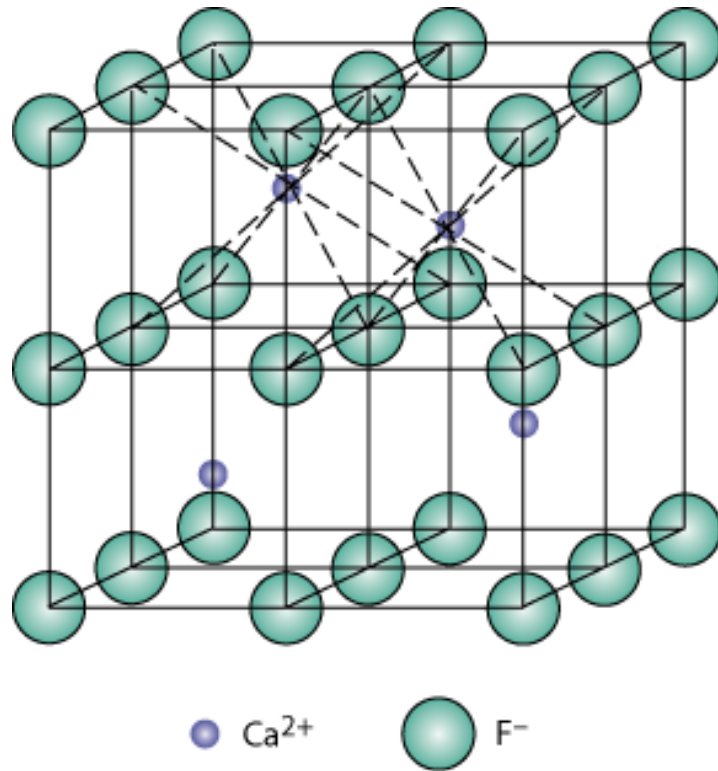
∴ Since $0.732 < 0.939 < 1.0$,
cubic sites preferred

So each Cs⁺ has 8 neighbor Cl⁻

Fig. 4.6, Callister & Rethwisch 9e.

AX₂ Crystal Structures

Fluorite structure



- Calcium Fluorite (CaF₂)
- Cations in cubic sites
- UO₂, ThO₂, ZrO₂, CeO₂
- Antifluorite structure – positions of cations and anions reversed

Fig. 4.8, Callister & Rethwisch 9e.

ABX₃ Crystal Structures

- Perovskite structure

Ex: complex oxide
 BaTiO_3

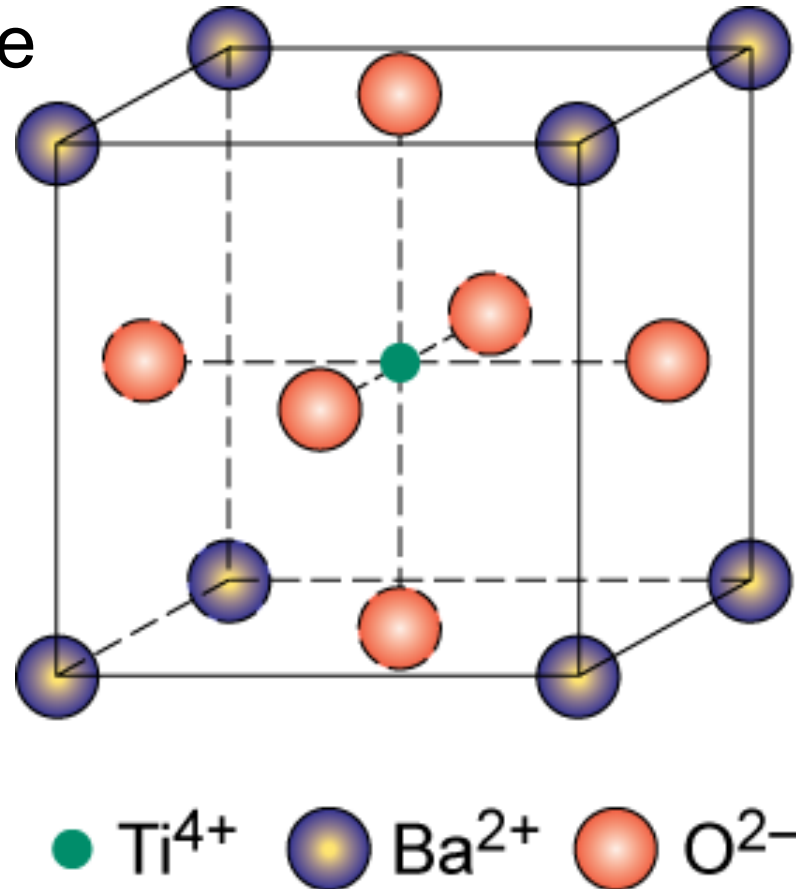


Fig. 4.9, Callister &
Rethwisch 9e.

Chapter 4.10

이론밀도

Density Computations for Ceramics

Number of formula units/unit cell

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

Volume of unit cell

Avogadro's number

ΣA_C = sum of atomic weights of all cations in formula unit

ΣA_A = sum of atomic weights of all anions in formula unit

Formular unit: 화학식 단위에 포함되어 있는 모든 이온

ex) BaTiO₃ Ba 이온 1개, Ti 이온 1개, 산소이온 3개

Densities of Material Classes

In general

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

Why?

Metals have...

- close-packing
(metallic bonding)
- often large atomic masses

Ceramics have...

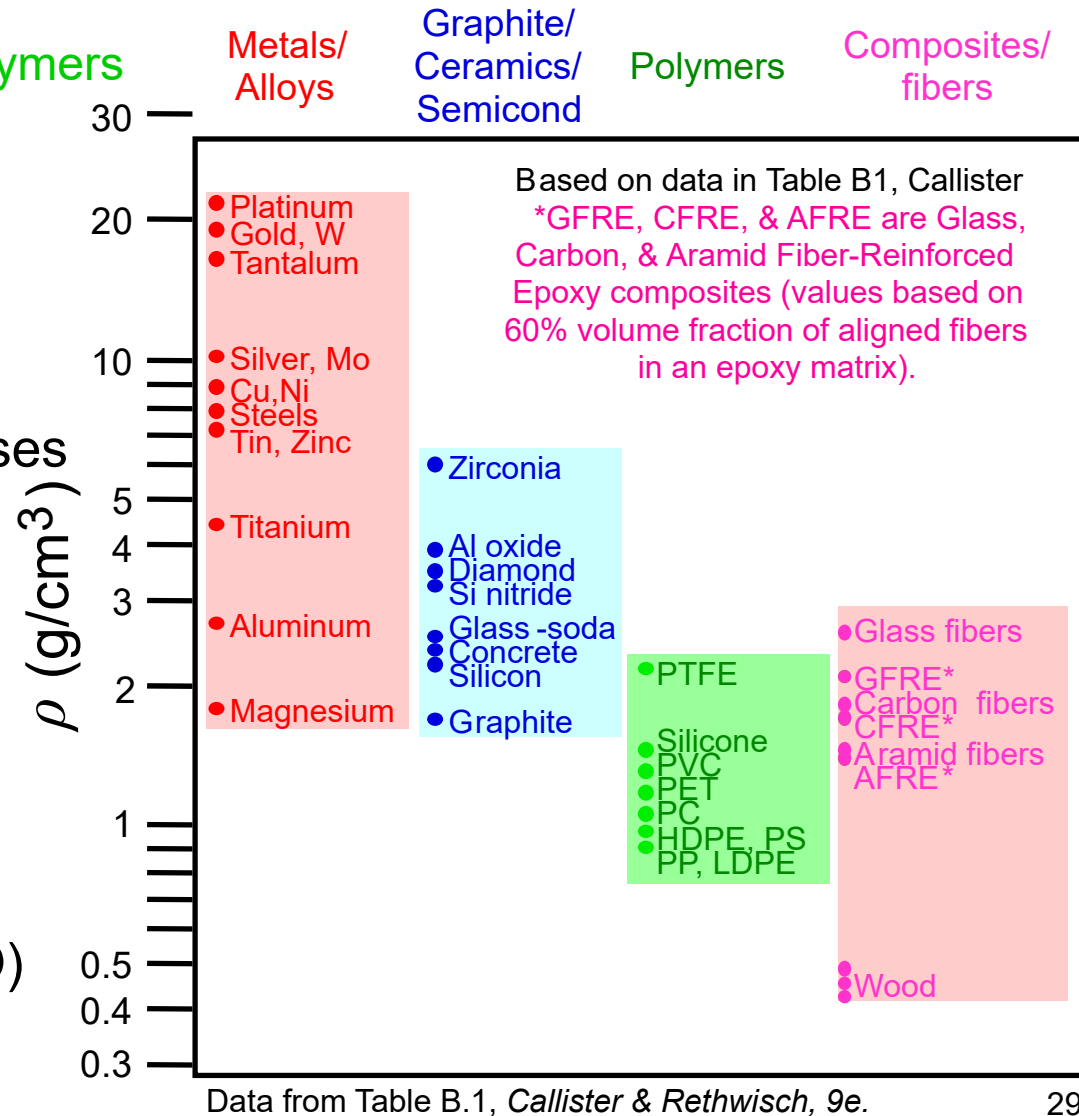
- less dense packing
- often lighter elements

Polymers have...

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

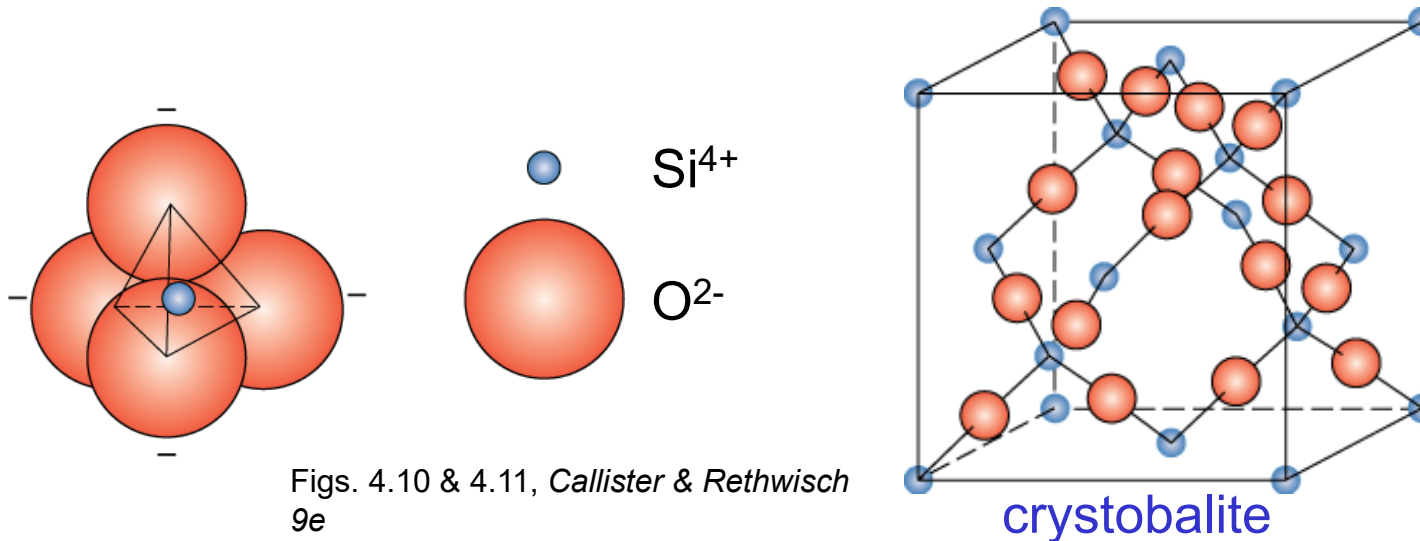
Composites have...

- intermediate values



Silicate Ceramics

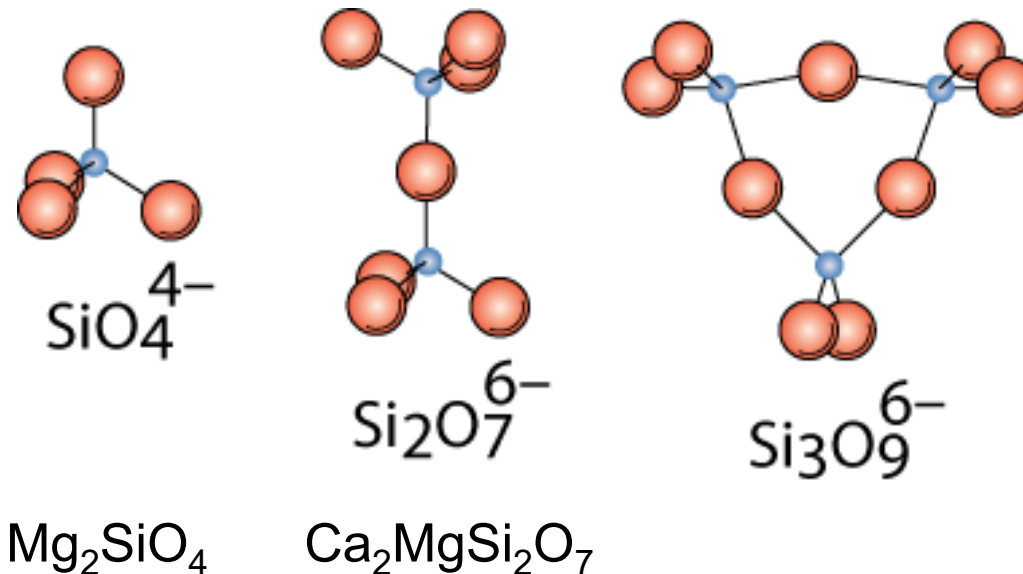
Most common elements on earth are Si & O



- SiO_2 (silica) **polymorphic** forms are **quartz, cristobalite, & tridymite**
- The strong Si-O bonds lead to a high melting temperature (1710°C) for this material

Silicates

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



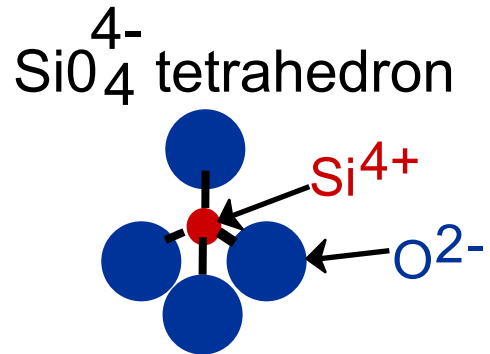
Adapted from Fig. 4.13, *Callister & Rethwisch 9e*.

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

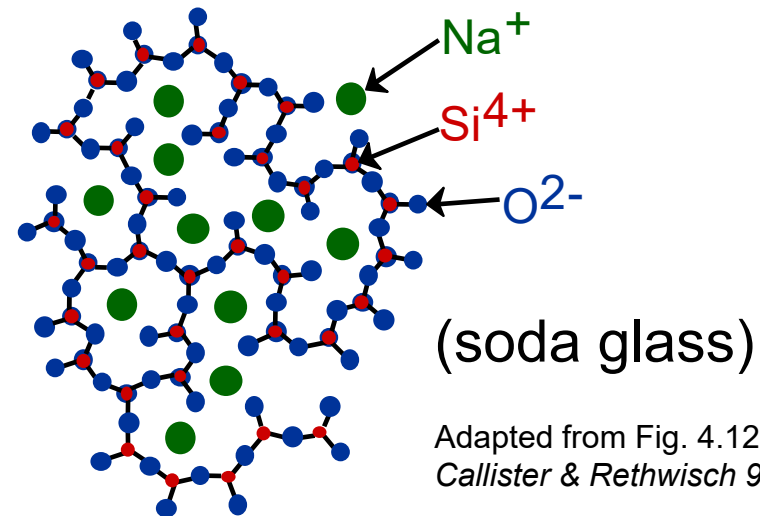
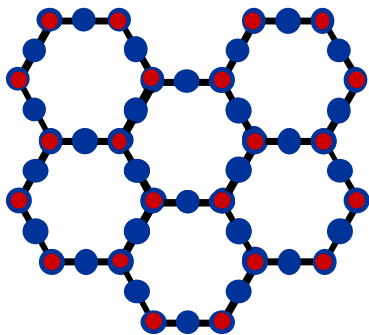
- Basic Unit:



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 :



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 $(\text{Si}_2\text{O}_5)^{2-}$ unit
- Negative charge balanced by adjacent plane rich in positively charged cations

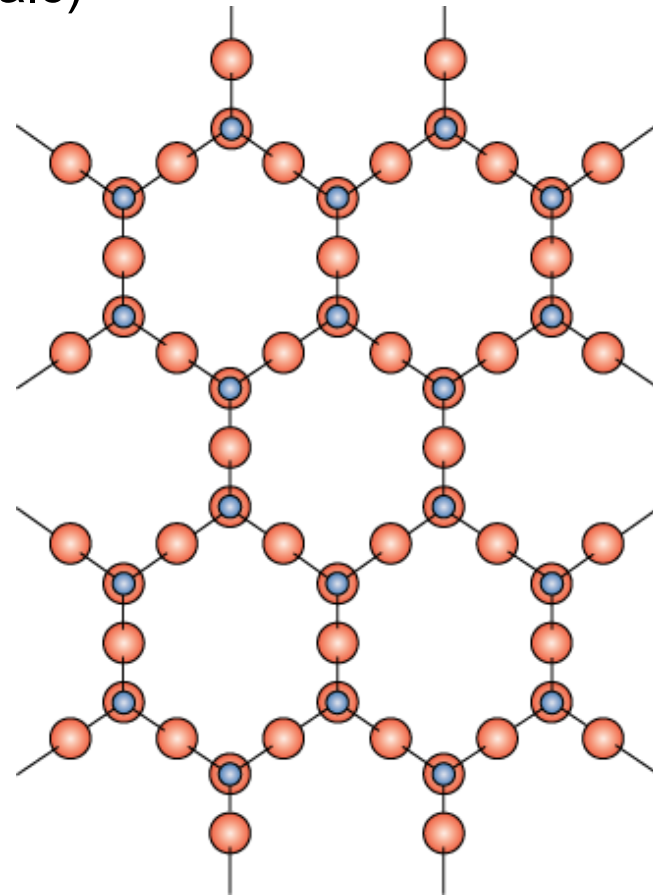


Fig. 4.14, Callister & Rethwisch 9e.

Layered Silicates (cont)

- **Kaolinite clay** alternates $(\text{Si}_2\text{O}_5)^{2-}$ layer with $\text{Al}_2(\text{OH})_4^{2+}$ layer

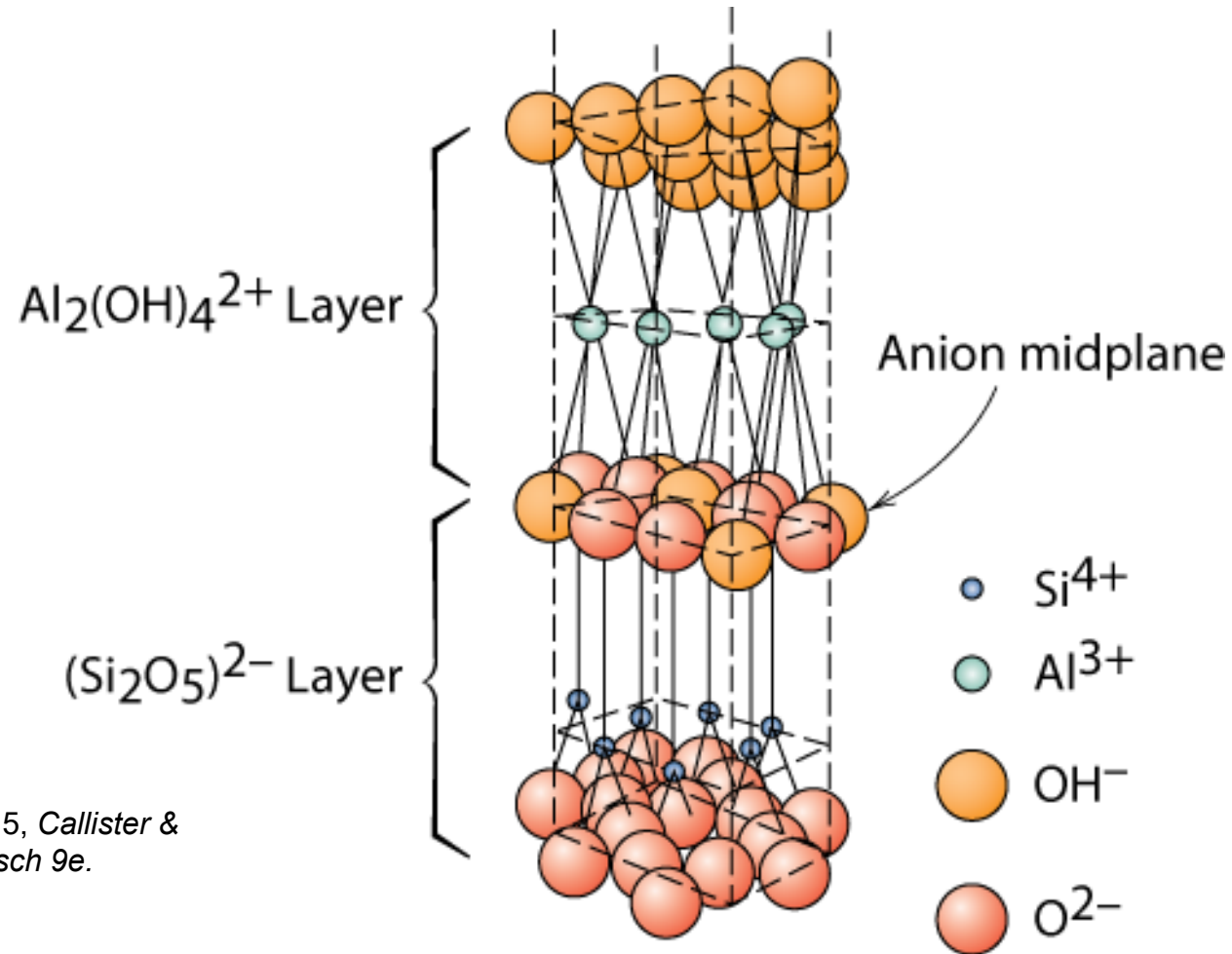


Fig. 4.15, Callister & Rethwisch 9e.

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

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.

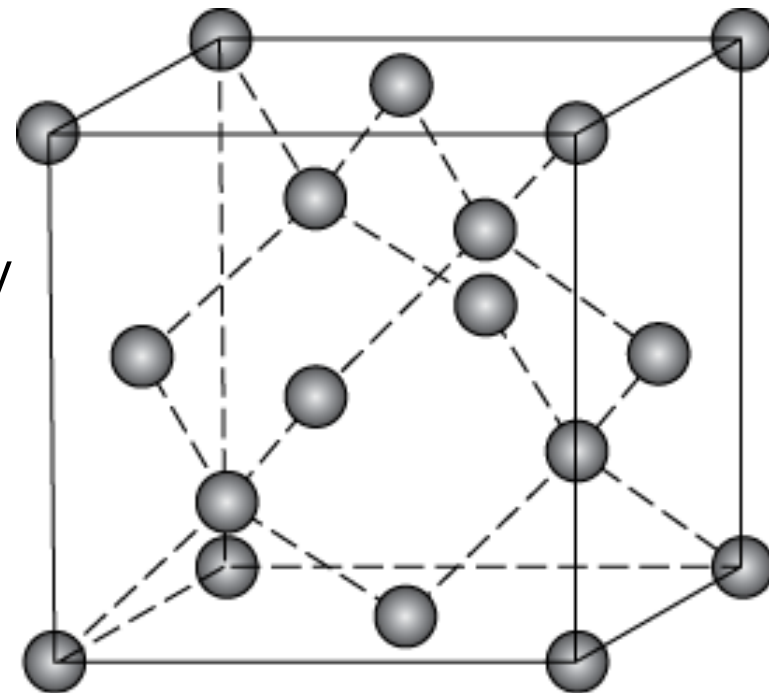


Fig. 4.17, Callister & Rethwisch 9e.

Polymorphic Forms of Carbon (cont)

Graphite

- layered structure – parallel hexagonal arrays of carbon atoms

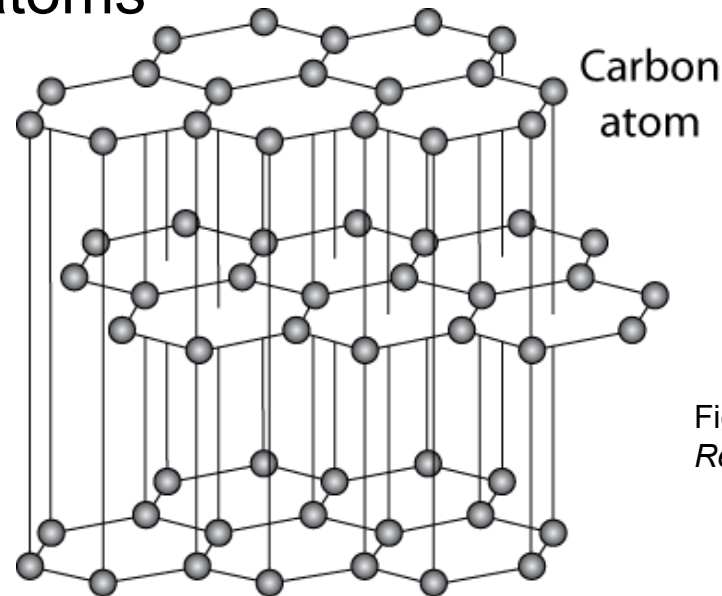


Fig. 4.18, Callister & Rethwisch 9e.

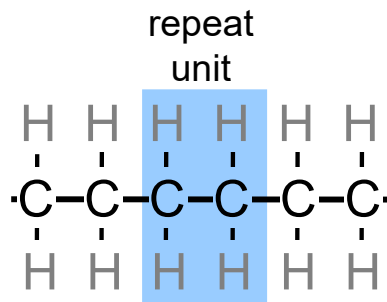
- weak van der Waal' s forces between layers
- planes slide easily over one another -- good lubricant

Chapter 5: Structures of Polymers

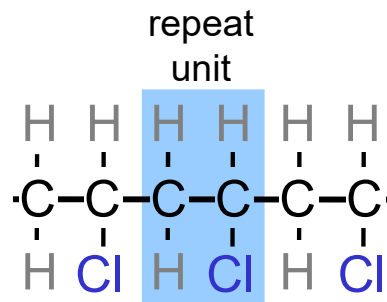
What is a Polymer?

Polymer (= many mer) : a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional repeating units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition of one or a few of the constitutional repeating units

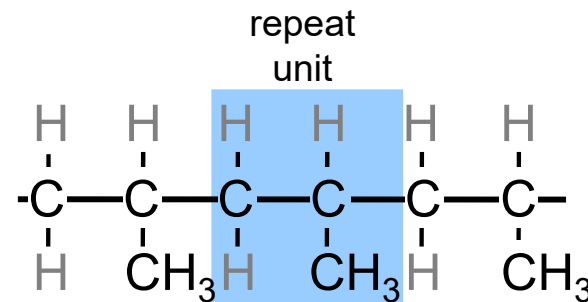
Poly **mer**
many repeat unit



Polyethylene (PE)



Poly(vinyl chloride) (PVC)



Polypropylene (PP)

Ancient Polymers

- Originally natural polymers were used
 - Wood
 - Rubber
 - Cotton
 - Wool
 - Leather
 - Silk
- Oldest known uses
 - Rubber balls used by Incas
 - Noah used pitch (a natural polymer) for the ark

Polymer Composition

Most polymers are hydrocarbons

- i.e., made up of H and C

1) Saturated hydrocarbons

- Each carbon singly bonded to four other atoms
- Example:
 - Ethane, C_2H_6

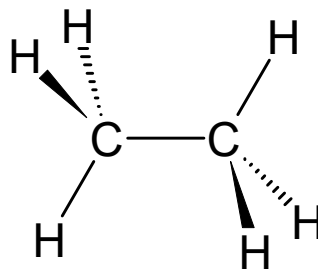


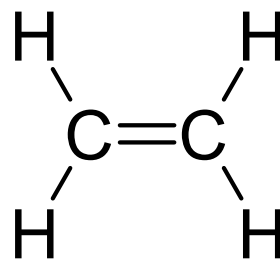
Table 5.1

Compositions and
Molecular Structures
for Some Paraffin
Compounds: C_nH_{2n+2}

<i>Name</i>	<i>Composition</i>	<i>Structure</i>	<i>Boiling Point (°C)</i>
Methane	CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	-164
Ethane	C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	-88.6
Propane	C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	-42.1
Butane	C ₄ H ₁₀		-0.5
Pentane	C ₅ H ₁₂		36.1
Hexane	C ₆ H ₁₄		69.0

2) Unsaturated Hydrocarbons

- Double & triple bonds somewhat unstable
 - can form new bonds
 - Double bond found in ethylene or ethene - C_2H_4



- Triple bond found in acetylene or ethyne - C_2H_2



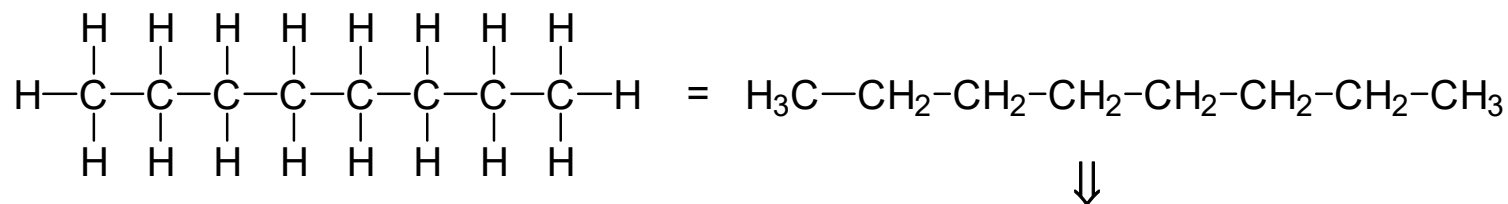
Isomerism

- Isomerism

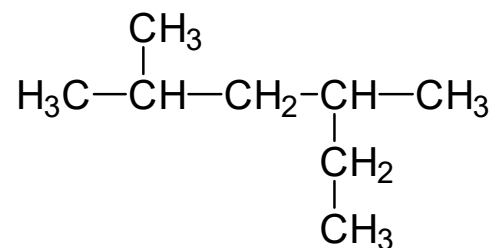
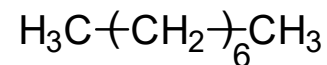
- **two compounds with same chemical formula**
can have quite different structures

for example: C_8H_{18}

- normal-octane

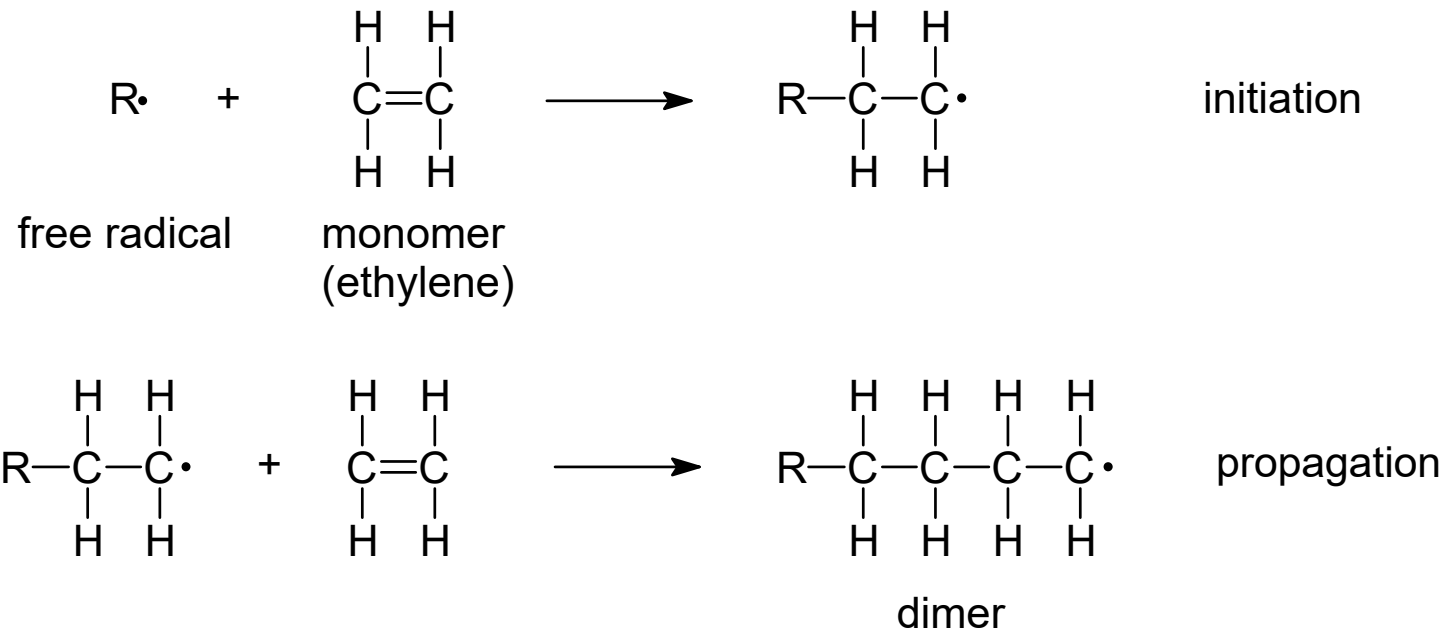


- 2,4-dimethylhexane

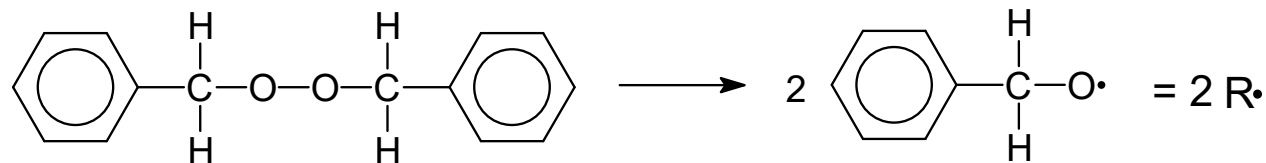


Polymerization and Polymer Chemistry

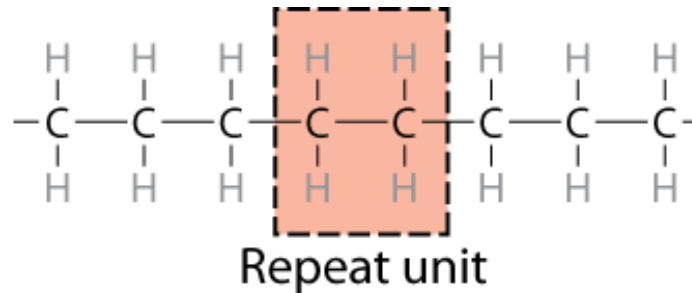
- Free radical polymerization



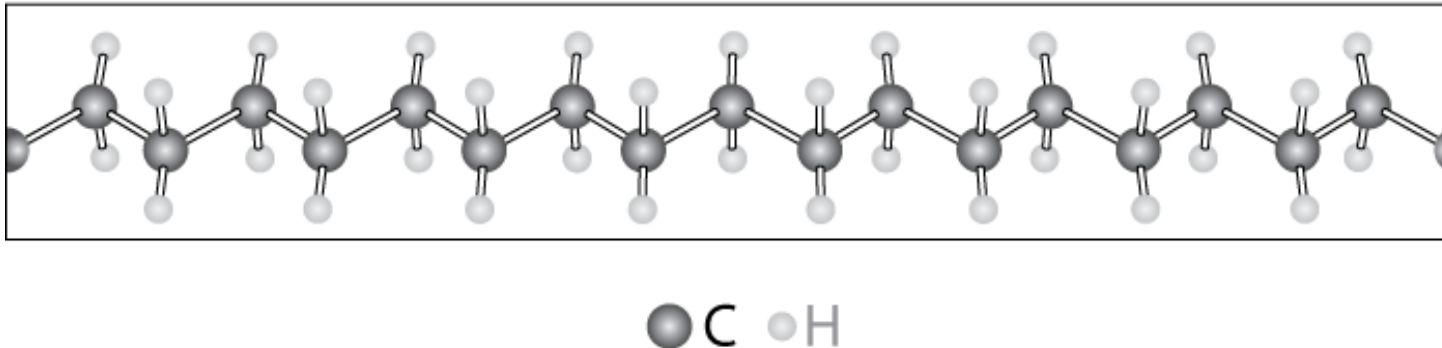
- Initiator: example - benzoyl peroxide



Chemistry and Structure of Polyethylene



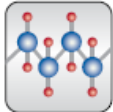
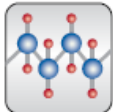

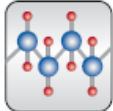

Adapted from Fig.
5.1, *Callister &
Rethwisch 9e.*



Note: polyethylene is a long-chain hydrocarbon
- paraffin wax for candles is short polyethylene

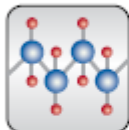
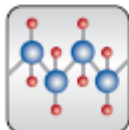
Bulk or Commodity Polymers

Table 5.3 Repeat Units for Ten of the More Common Polymeric Materials

<i>Polymer</i>	<i>Repeat Unit</i>
 <p>WileyPLUS: VMSE Repeat Unit Structures</p>	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$
 <p>WileyPLUS: VMSE</p>	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$
 <p>WileyPLUS: VMSE</p>	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$
 <p>WileyPLUS: VMSE</p>	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$
 <p>WileyPLUS: VMSE</p>	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$

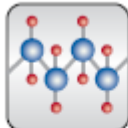
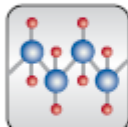
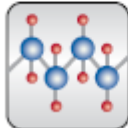
Bulk or Commodity Polymers (cont)

Table 5.3 (Continued)

<i>Polymer</i>	<i>Repeat Unit</i>
 WileyPLUS: VMSE	Poly(methyl methacrylate) (PMMA) $ \begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array} $
 WileyPLUS: VMSE	Phenol-formaldehyde (Bakelite) $ \begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{C}_6\text{H}_2-\text{CH}_2 \\ \\ \text{CH}_2 \end{array} $

Bulk or Commodity Polymers (cont)

Table 5.3 (Continued)

<i>Polymer</i>	<i>Repeat Unit</i>
 <p>WileyPLUS: VMSE</p>	<p>Poly(hexamethylene adipamide) (nylon 6,6)</p> $\text{—N—}\left[\begin{array}{c} \text{H} \\ \\ \text{—C—} \\ \\ \text{H} \end{array}\right]_6\text{—N—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\left[\begin{array}{c} \text{H} \\ \\ \text{—C—} \\ \\ \text{H} \end{array}\right]_4\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$
 <p>WileyPLUS: VMSE</p>	<p>Poly(ethylene terephthalate) (PET, a polyester)</p> $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\overset{a}{\text{C}_6\text{H}_4}\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O—}\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{—C—C—} \\ \quad \\ \text{H} \quad \text{H} \end{array}\text{—O—}$
 <p>WileyPLUS: VMSE</p>	<p>Polycarbonate (PC)</p> $\text{—O—}\overset{a}{\text{C}_6\text{H}_4}\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{—}\text{C}_6\text{H}_4\text{—O—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$

MOLECULAR WEIGHT

- **Molecular weight**, M : Mass of a mole of chains.



Low M



high M

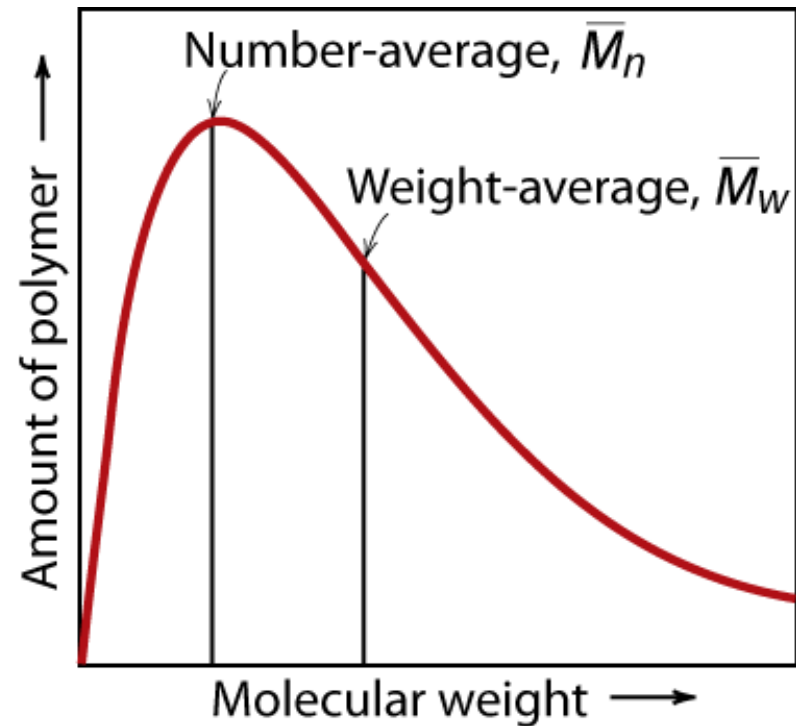
Not all chains in a polymer are of the same length
— i.e., there is a distribution of molecular weights

MOLECULAR WEIGHT DISTRIBUTION

Fig. 5.4, Callister & Rethwisch 9e.

$$\bar{M}_n = \frac{\text{total wt of polymer}}{\text{total \#of molecules}}$$

$$\bar{M}_n = \sum x_i M_i$$
$$\bar{M}_w = \sum w_i M_i$$



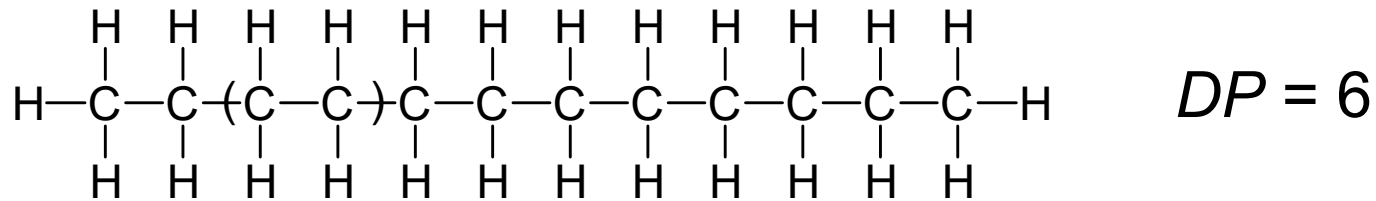
M_i = mean (middle) molecular weight of size range i

x_i = number fraction of chains in size range i

w_i = weight fraction of chains in size range i

Degree of Polymerization, *DP*

DP = average number of repeat units per chain



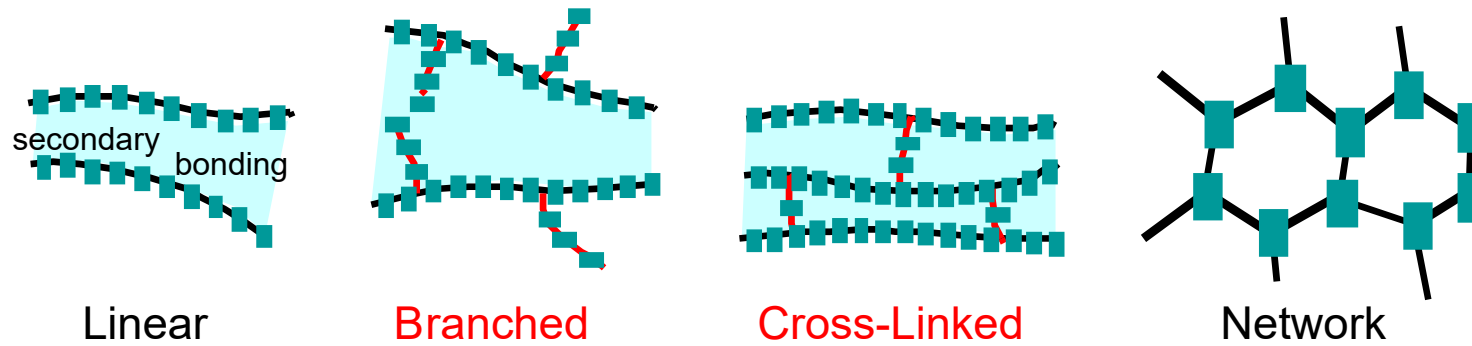
$$DP = \frac{\bar{M}_n}{\bar{m}}$$

where \bar{m} = average molecular weight of repeat unit
for copolymers this is calculated as follows:

$$\bar{m} = \sum f_i m_i$$

Chain fraction f_i mol. wt of repeat unit m_i

Molecular Structures for Polymers



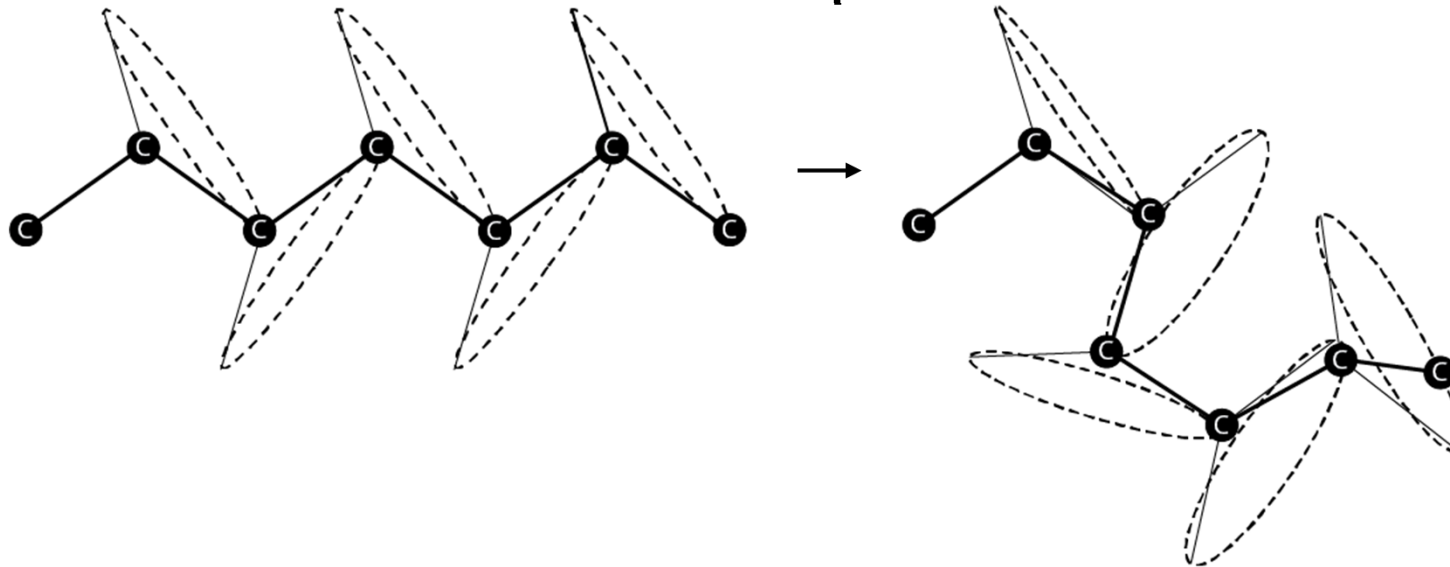
Adapted from Fig. 5.7, *Callister & Rethwisch 9e*.

Polymers – Molecular Shape

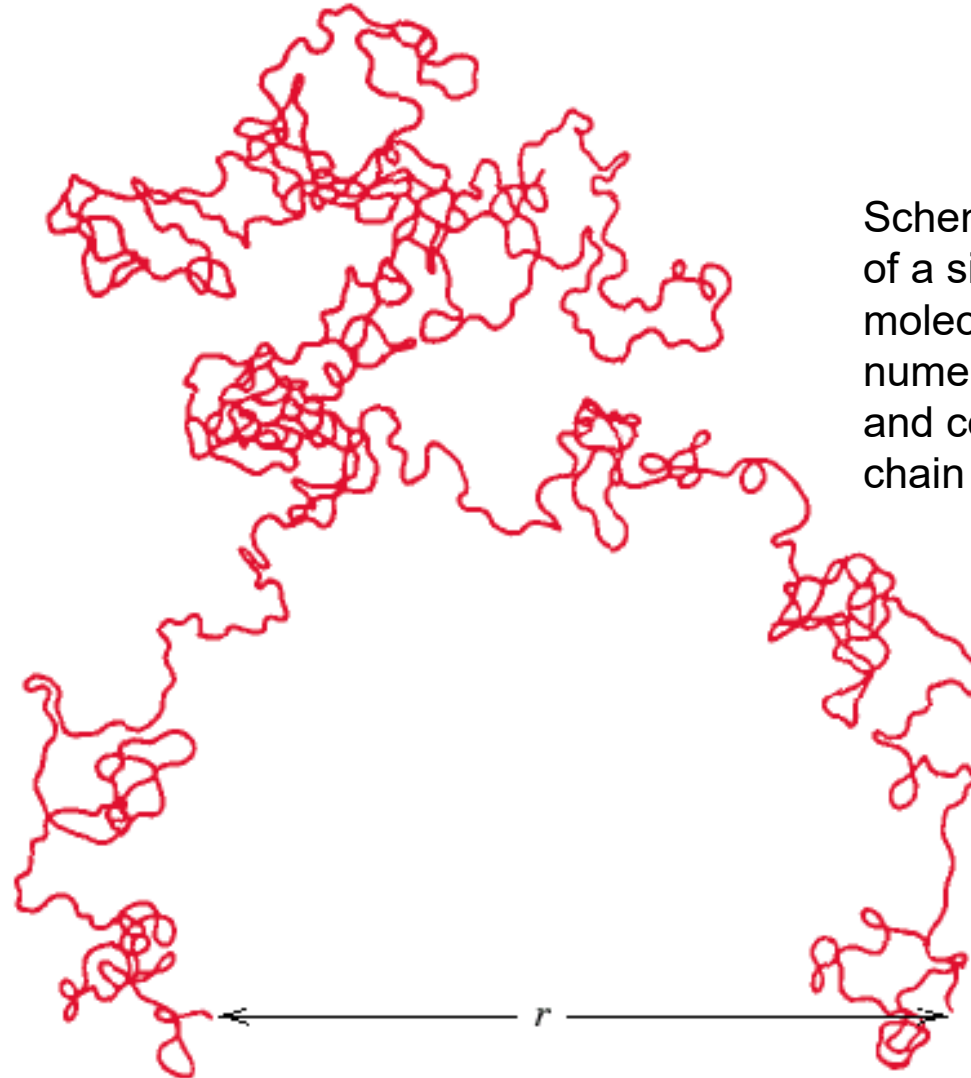
Molecular Shape (or **Conformation** 형태)

- chain bending and twisting are possible by rotation of carbon atoms around their chain bonds
- note: not necessary to break chain bonds to alter molecular shape

Adapted from Fig.
5.5, Callister &
Rethwisch 9e.



Chain End-to-End Distance, r

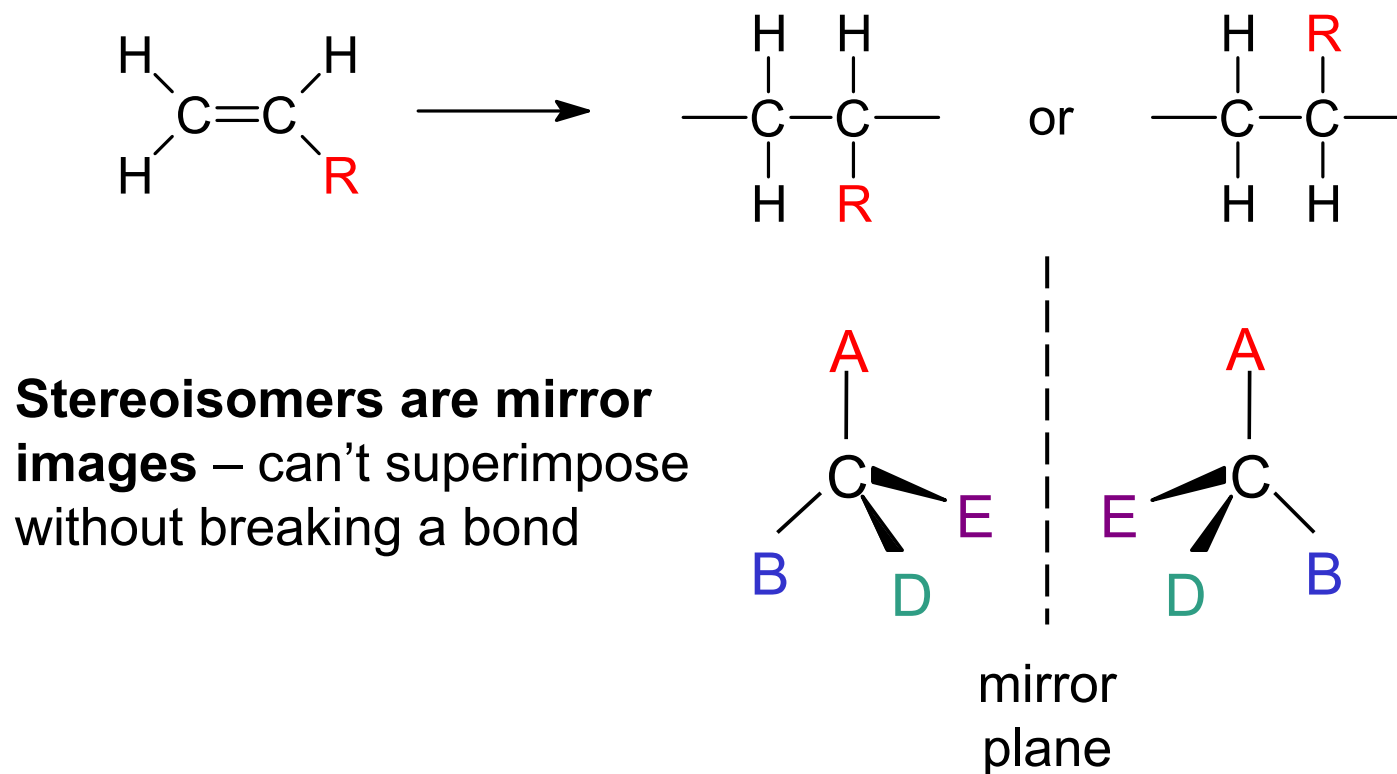


Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations.

Molecular Configurations for Polymers

Configurations – to change must break bonds

a) Stereoisomerism

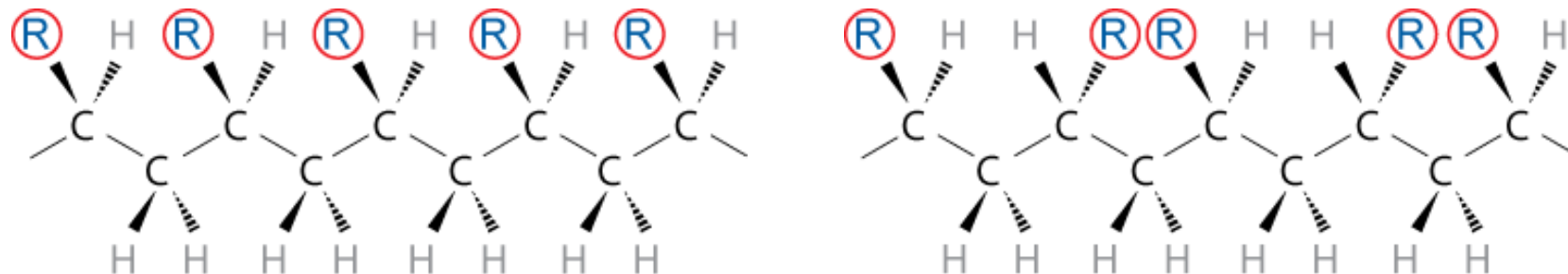
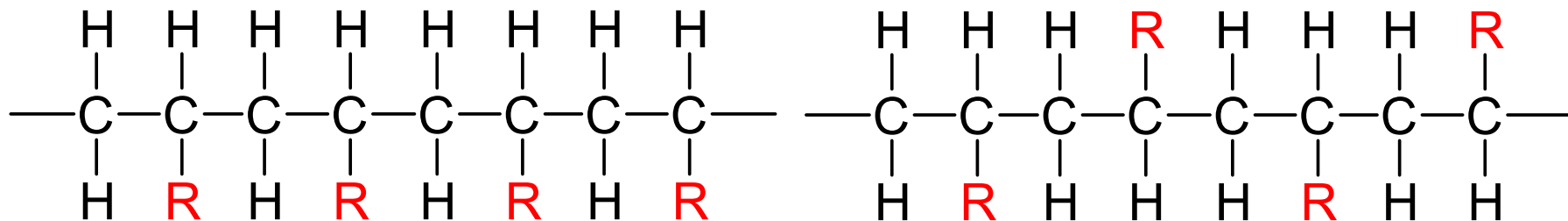


Tacticity

Tacticity — stereoregularity or spatial arrangement of **R** units along chain

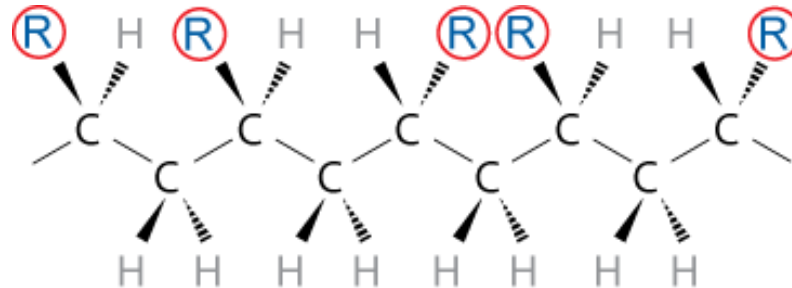
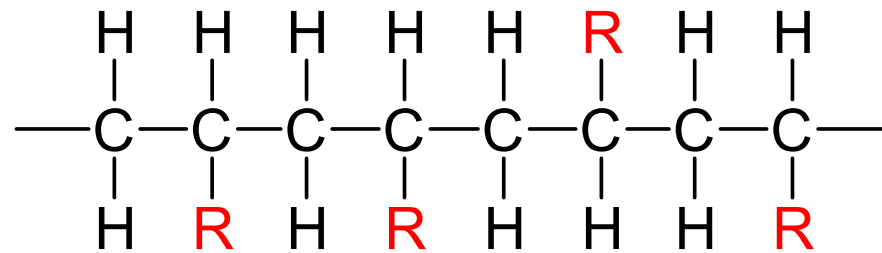
isotactic — all **R** groups on same side of chain

syndiotactic — **R** groups alternate sides



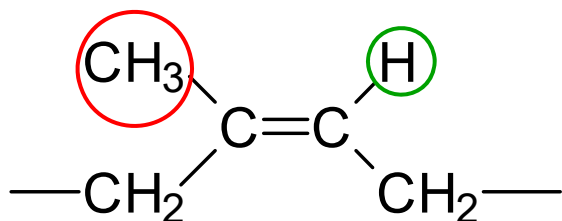
Tacticity (cont.)

atactic – R groups randomly positioned



b) Geometrical isomerism

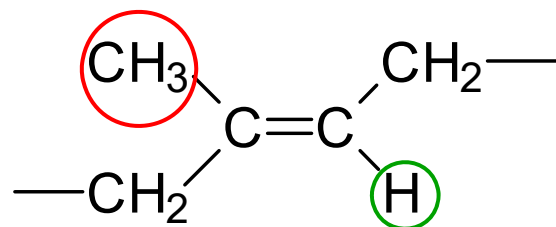
cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

**H atom and CH₃ group
on same side of chain**



trans

trans-isoprene
(gutta percha)

**H atom and CH₃ group on
opposite sides of chain**

Copolymers

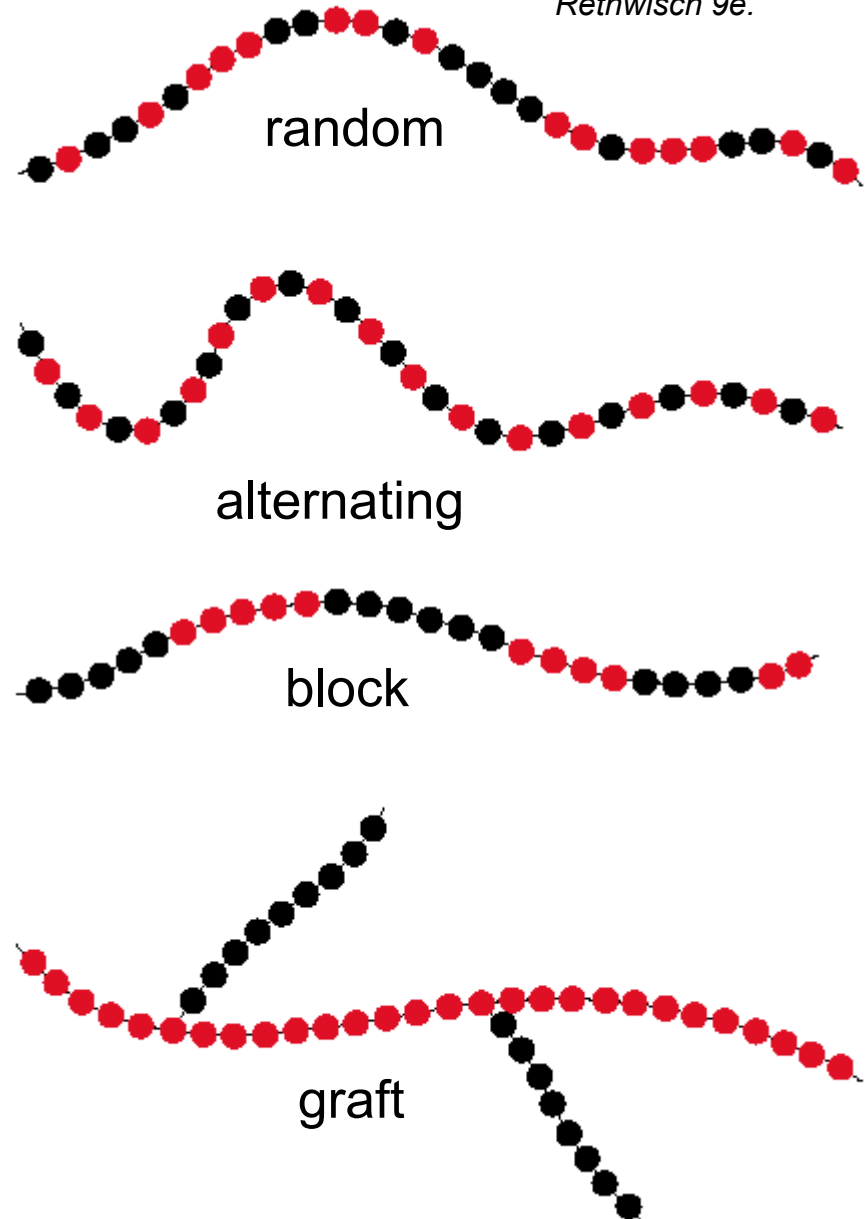
two or more monomers
polymerized together

- **random** – A and B randomly positioned along chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A units alternate with large blocks of B units
- **graft** – chains of B units grafted onto A backbone

A – ●

B – ●

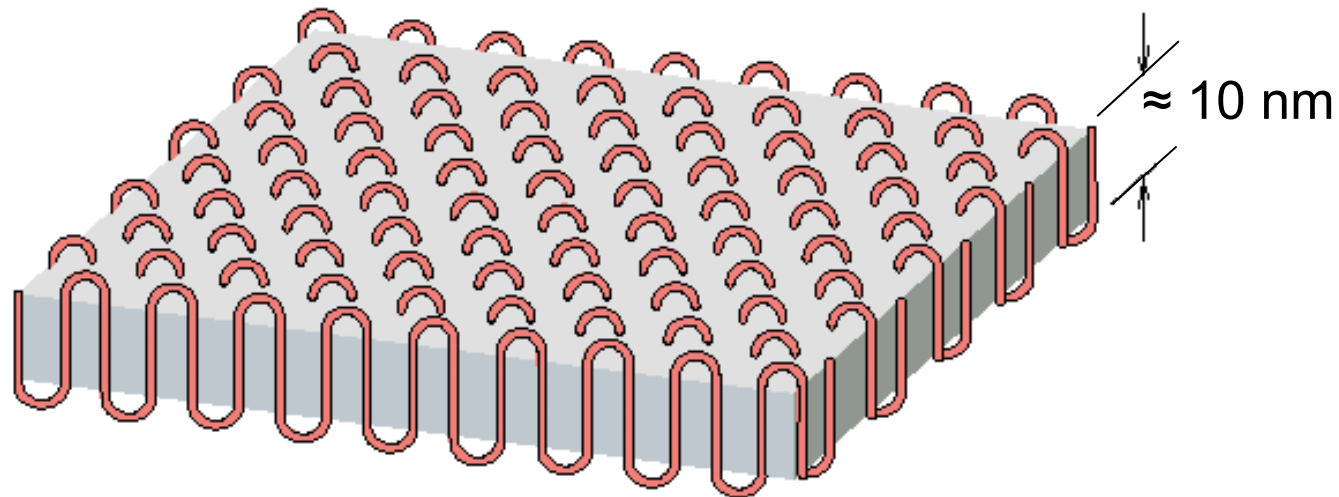
Fig. 5.9, Callister & Rethwisch 9e.



Polymer Crystals

- Crystalline regions
 - thin platelets with chain folds at faces
 - Chain folded structure

Fig. 5.11, Callister & Rethwisch 9e.



Polymer Crystals (cont.)

Polymers rarely 100% crystalline

- Difficult for all regions of all chains to become aligned
- Degree of crystallinity expressed as % crystallinity.
 - Some physical properties depend on % crystallinity.
 - Heat treating causes crystalline regions to grow and % crystallinity to increase.

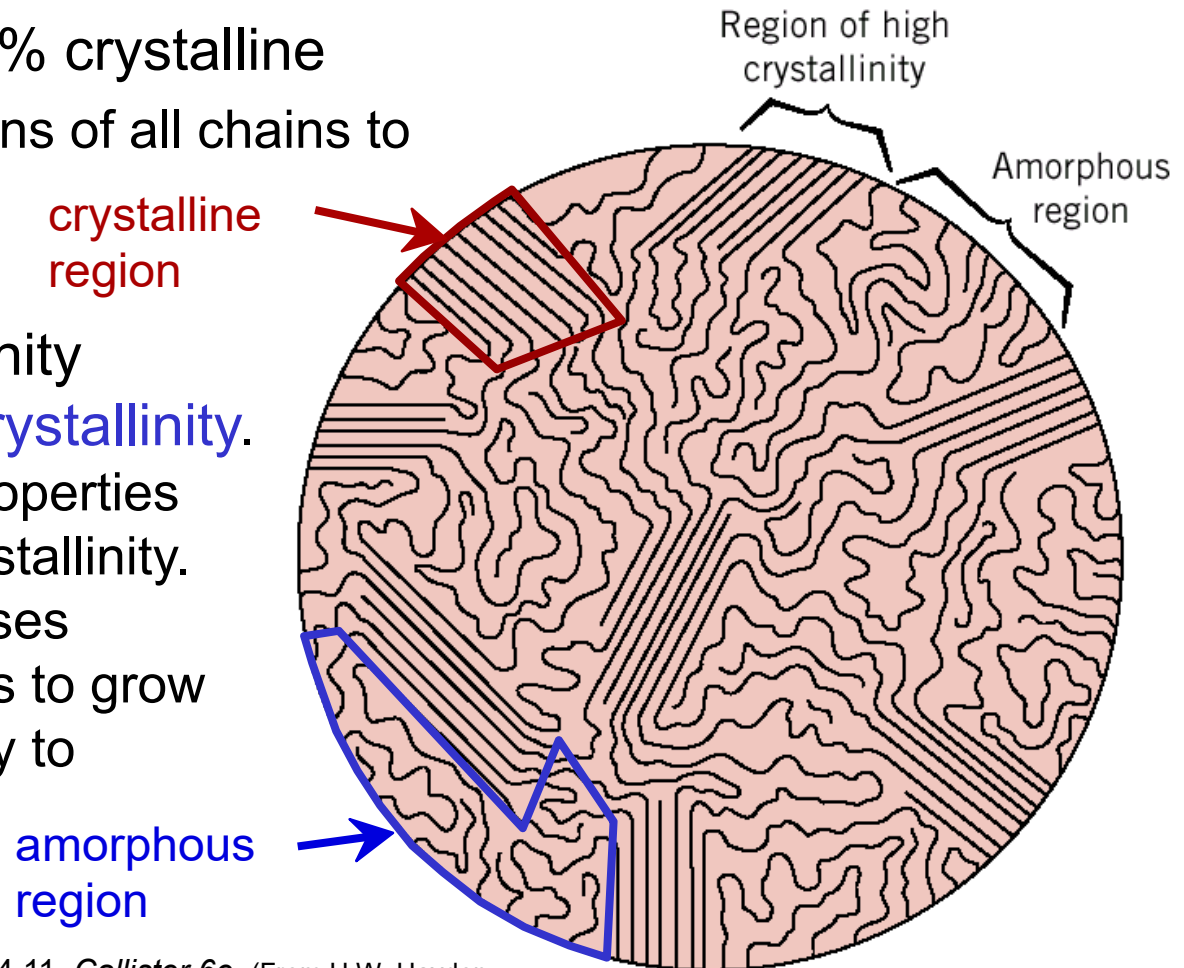


Fig. 14.11, *Callister 6e*. (From H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

Polymer Single Crystals

- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- **Single crystals** – only for slow and carefully controlled growth rates

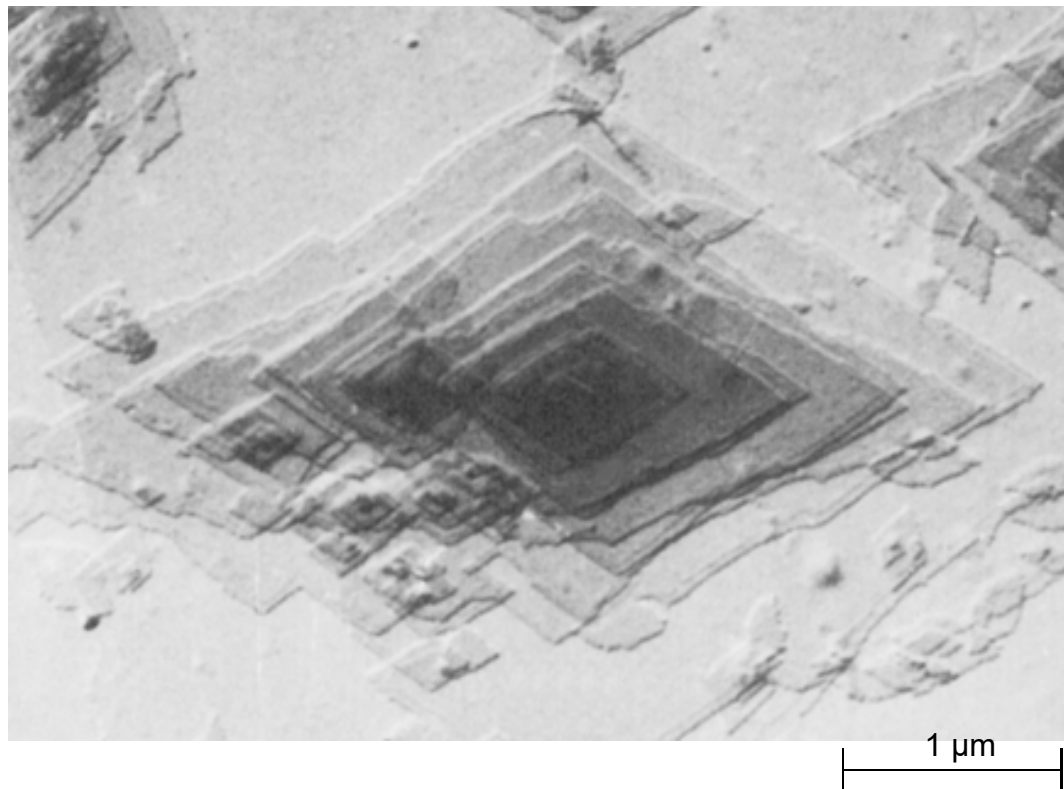
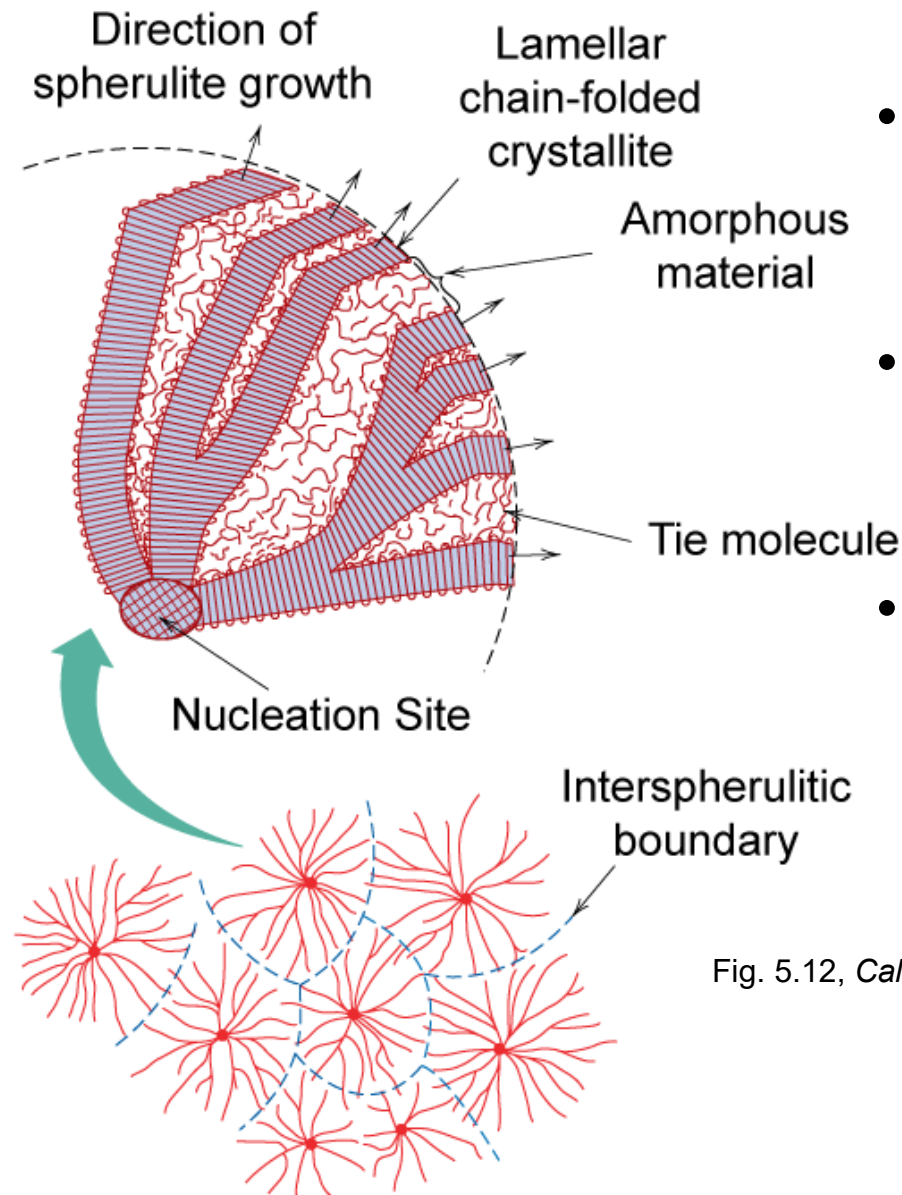


Fig. 5.10, *Callister & Rethwisch 9e*.

[From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Eds.), *Growth and Perfection of Crystals*. General Electric Company and John Wiley & Sons, Inc., 1958, p. 498. Reprinted with permission of John Wiley & Sons, Inc.]

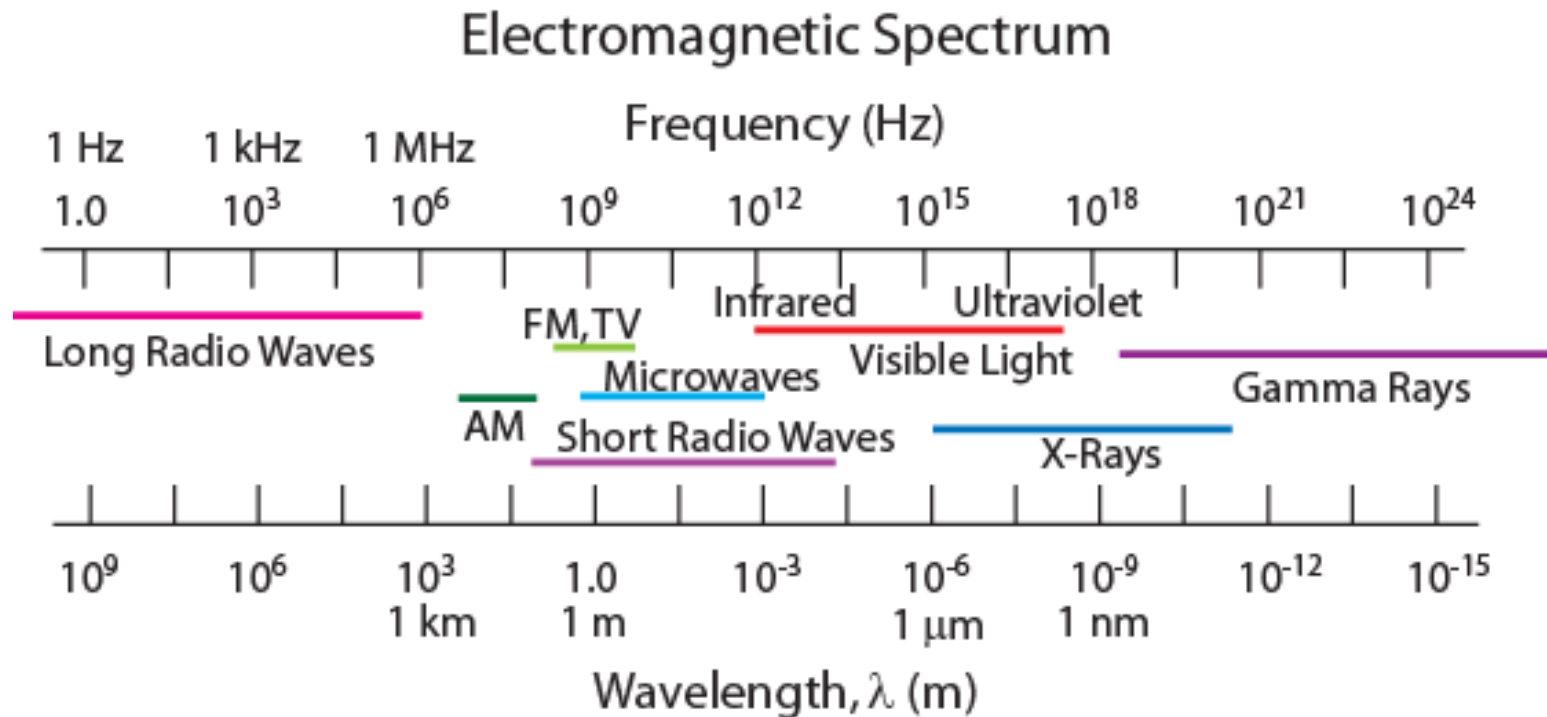
Semicrystalline Polymers



- Some semicrystalline polymers form **spherulite** structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

Fig. 5.12, Callister & Rethwisch 9e.

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-ray generation

- Intense electron beam hits the electrons in the outer shells to excite electrons to other levels (higher energy state)
- Excited electrons come down to lower level generating photon (X-ray)

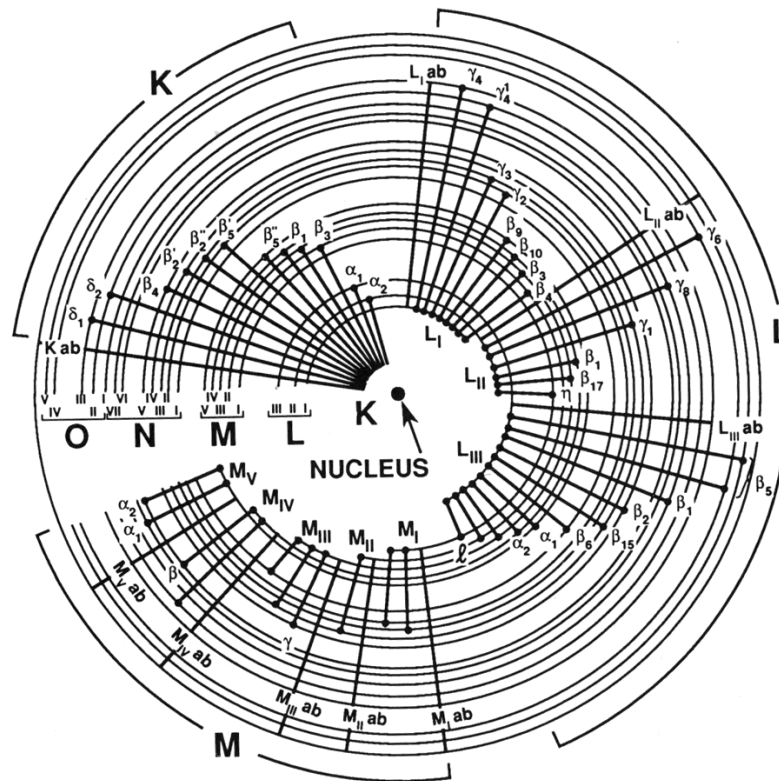
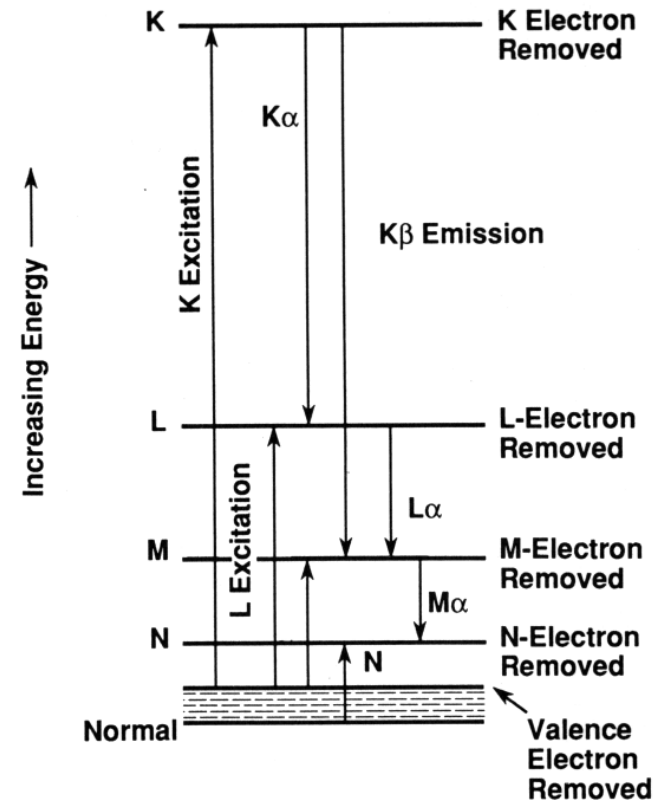
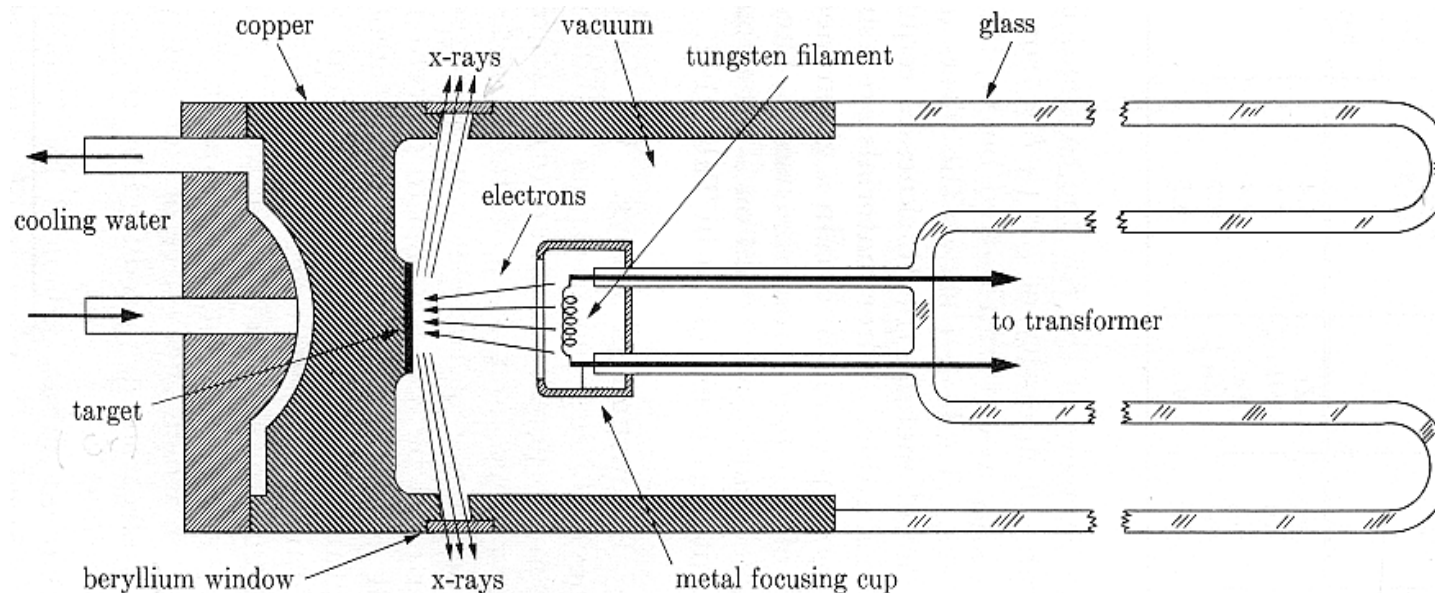


Figure 3.37. Comprehensive energy-level diagram showing all electron transitions which give rise to K, L, and M x rays (Woldseth, 1973).



X-Ray Production

- ❑ a voltage of 35,000 volts is applied between the cathode and anode target metal in the x-ray tube.
- ❑ when the electrons released from the W-filament strike the metal target (anode), x-rays are produced.
- ❑ Note: 98% of the energy is converted into heat.



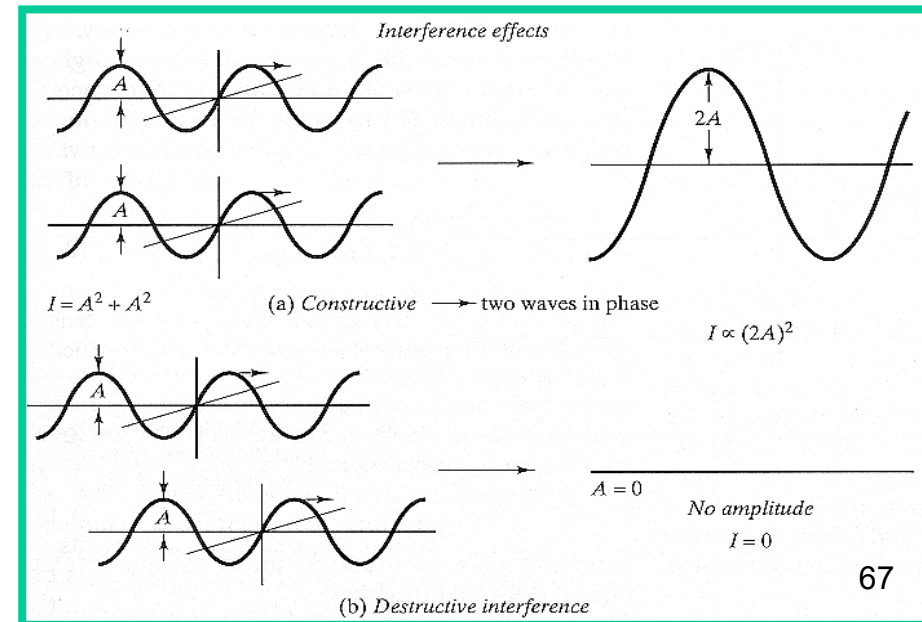
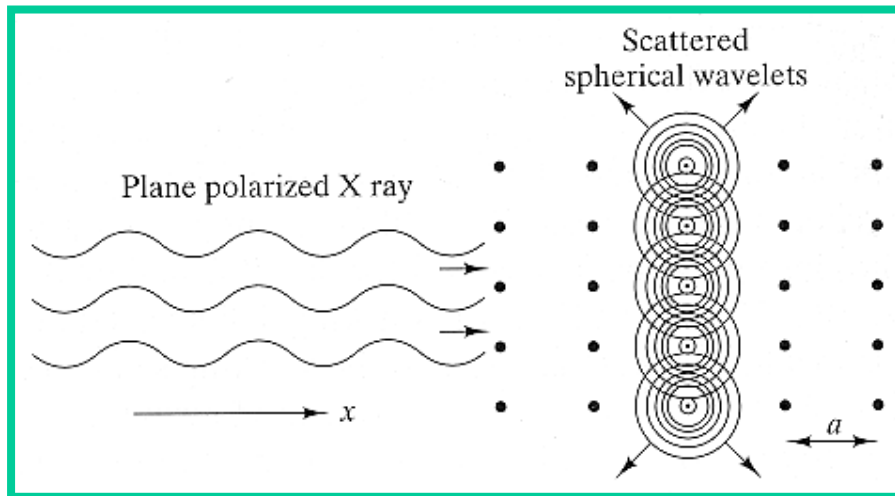
• Radiations used in Crystallography

□ average diffraction properties of X-rays, electrons, and neutron

	X-rays	Electrons	Neutrons
1) Charge	0	-1 e	0
2) Rest mass	0	9.11×10^{-31} kg	1.67×10^{-27} kg
3) Energy	10 keV	100 keV	0.03 eV
4) Wavelength	1.5 Å	0.04 Å	1.2 Å
5) Bragg angles	Large	1°	Large
6) Extinction length	10 μ m	0.03 μ m	100 μ m
7) Absorption length	100 μ m	1 μ m	5 cm
8) Width of rocking curve	5"	0.6°	5"
9) Refractive index $n=1+\delta$	$n < 1$ $\delta \approx -1 \times 10^{-5}$	$n > 1$ $\delta \approx +1 \times 10^{-4}$	$n \geq 1, n \leq 1$ $\delta \approx \pm 1 \times 10^{-6}$
10) Atomic scattering amplitudes f	10^{-3} Å	10 Å	10^{-4} Å
11) Dependence of f on the atomic number Z	$\sim Z$	$\sim Z^{2/3}$	Nonmonotonic
12) Anomalous dispersion	Common	-	Rare
13) Spectral length	1 eV $\Delta\lambda/\lambda \approx 10^{-4}$	3 eV $\Delta\lambda/\lambda \approx 10^{-5}$	500 eV $\Delta\lambda/\lambda \approx 2$

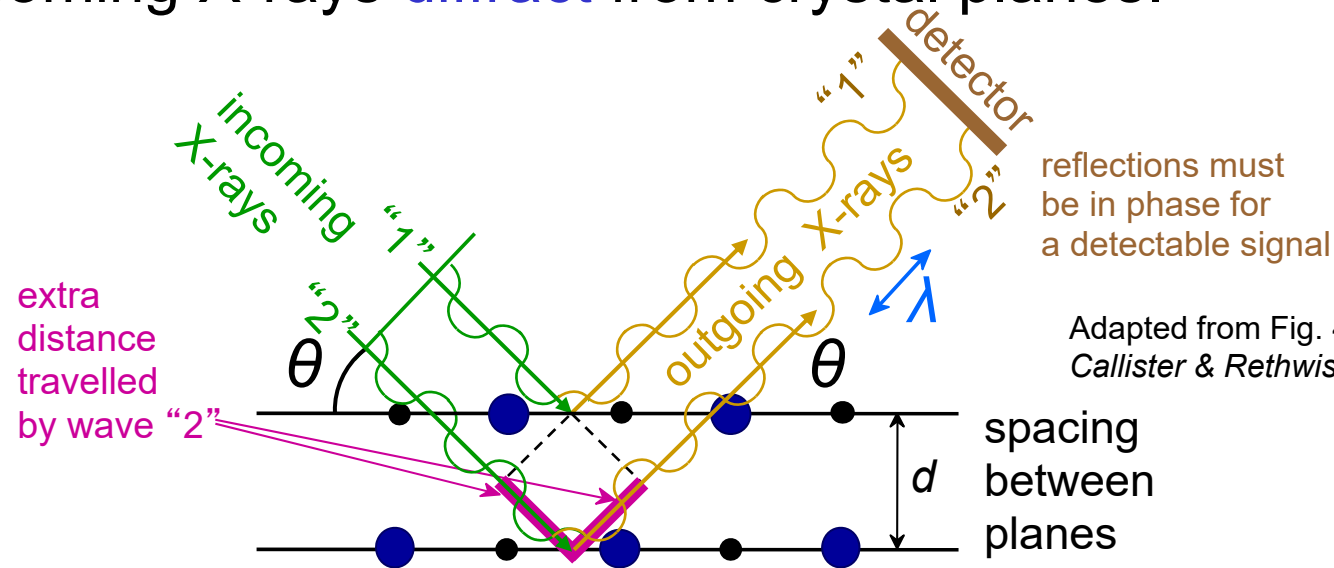
• Diffraction

- ❑ occurs as the wave encounters a series of regularly spaced obstacles which scatter the wave.
- ❑ these scattering centers (atoms), have spacing comparable in magnitude to the wavelength.
- ❑ diffraction results from specific phase relationships established between the waves scattered by the scattering atoms (centers).



X-Rays to Determine Crystal Structure

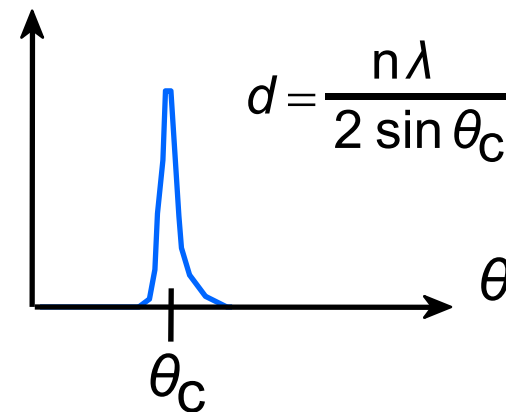
- Incoming X-rays **diffract** from crystal planes.



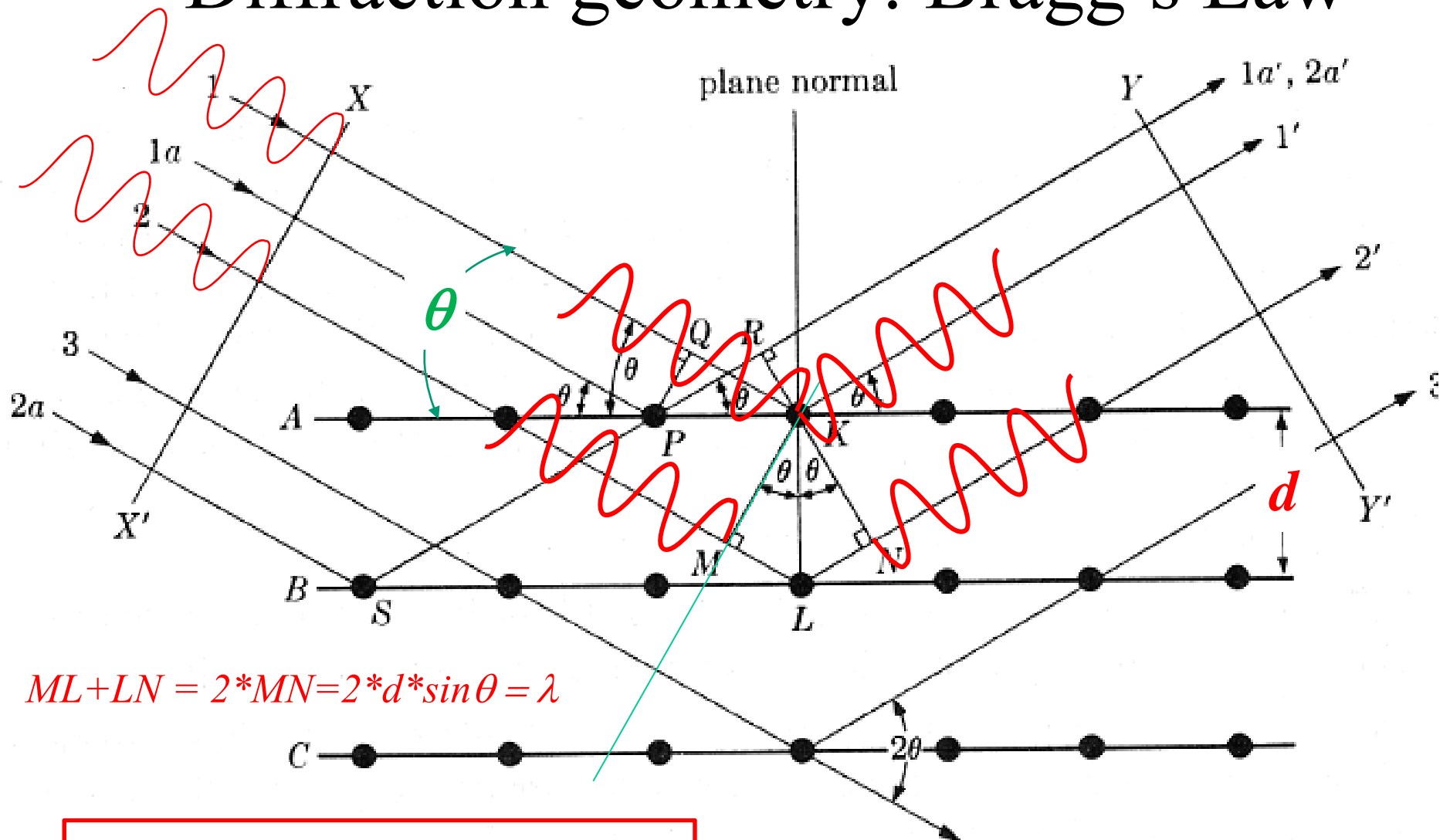
Adapted from Fig. 4.29,
Callister & Rethwisch 9e.

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

X-ray intensity (from detector)



Diffraction geometry: Bragg's Law



$$ML + LN = 2 * MN = 2 * d * \sin \theta = \lambda$$

$$\lambda = 2d \sin \theta_B$$

Structure Determination (X-Ray)

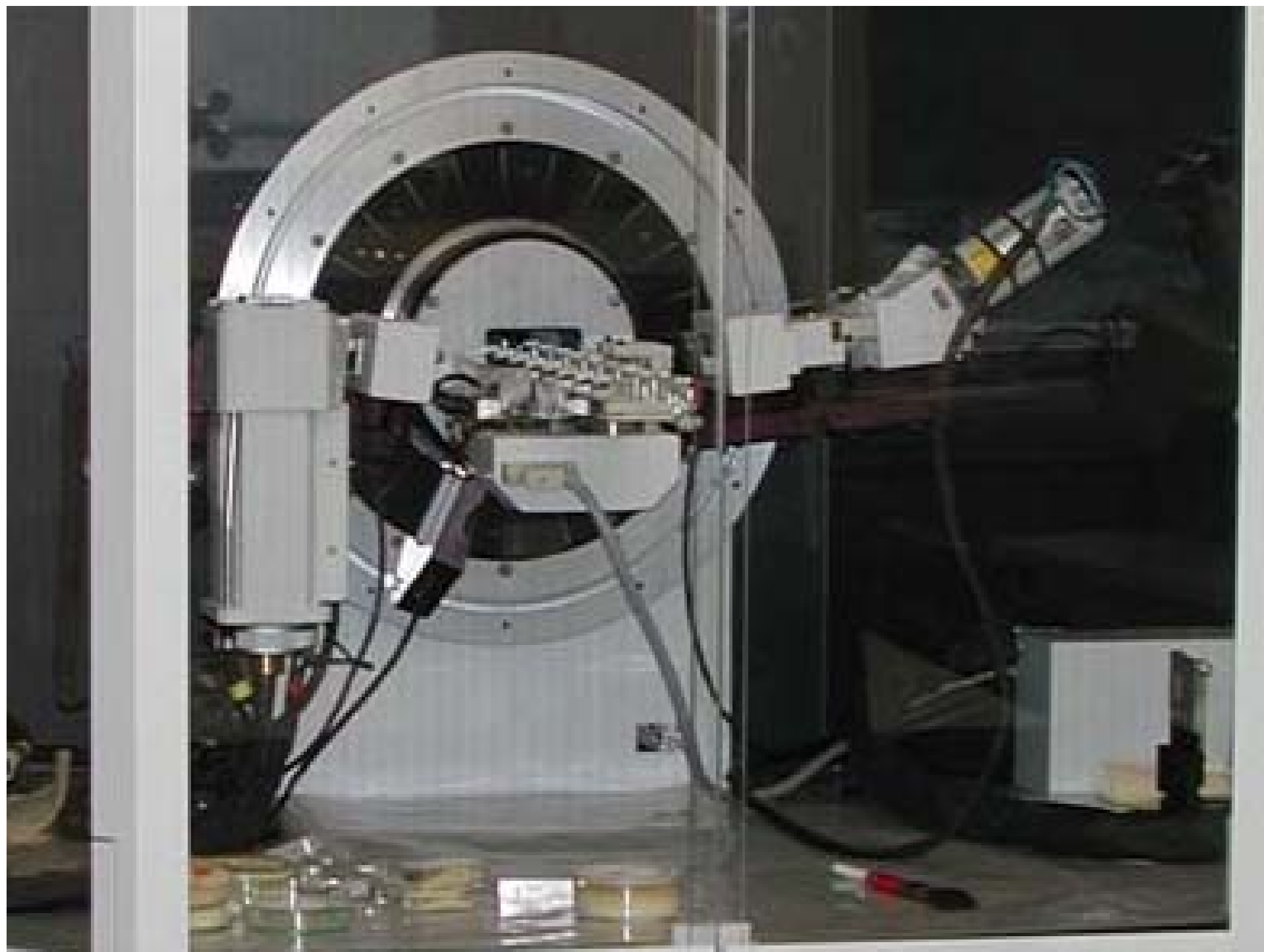
Crystal structure	Diffraction does not occur when	Diffraction occurs when
Body-centered cubic (bcc)	$h + k + l = \text{odd number}$	$h + k + l = \text{even number}$
Face-centered cubic (fcc)	h, k, l mixed (i.e., both even and odd numbers)	h, k, l unmixed (i.e., are all even numbers or all odd numbers)
Hexagonal close packed (hcp)	$(h + 2k) = 3n, l \text{ odd}$ (n is an integer)	All other cases

diffraction line	sc	$h^2+k^2+l^2$ (cubic)	bcc	fcc
100	1			
110	2	2		
111	3			3
200	4	4		4
210	5			
211	6	6		
220	8	8		8
221	9			

$$2d \sin \theta = \lambda$$

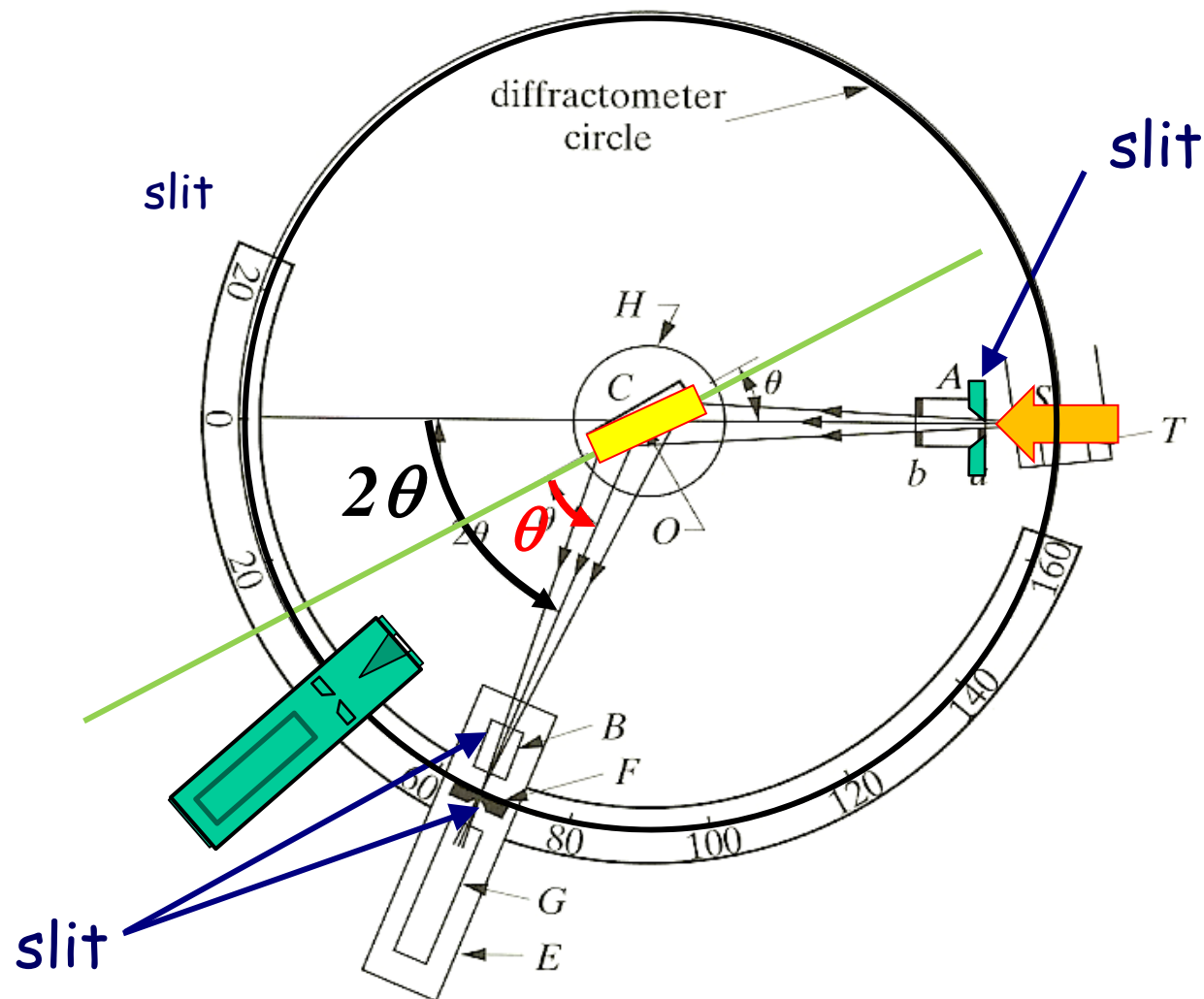
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

(interplanar spacing)



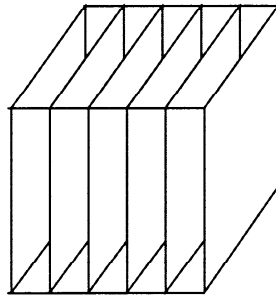
X-ray diffractometer

Bragg-Brentano Geometry

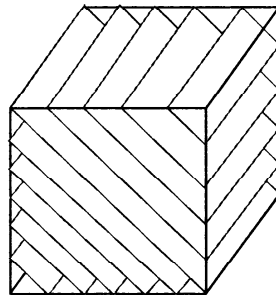


Lattice planes

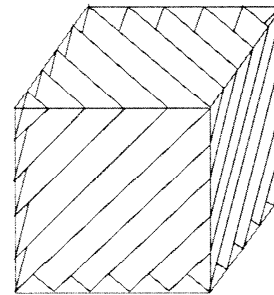
The following figures show the annotation of crystal surfaces.



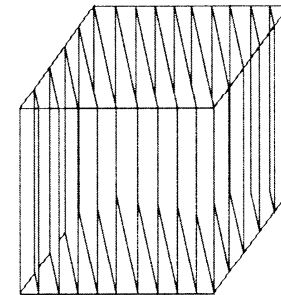
(100) planes



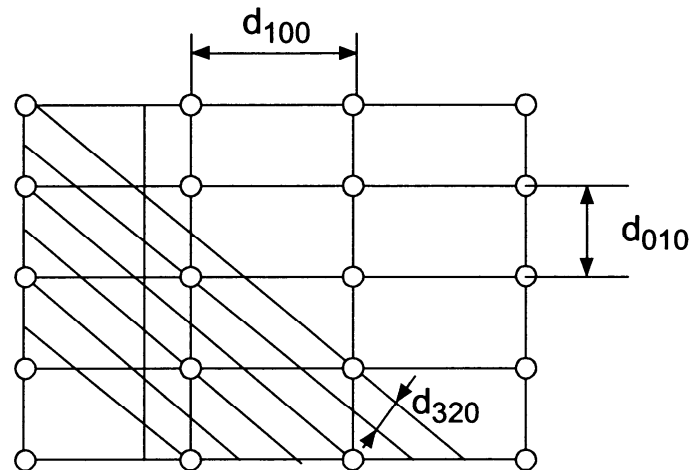
(110) planes



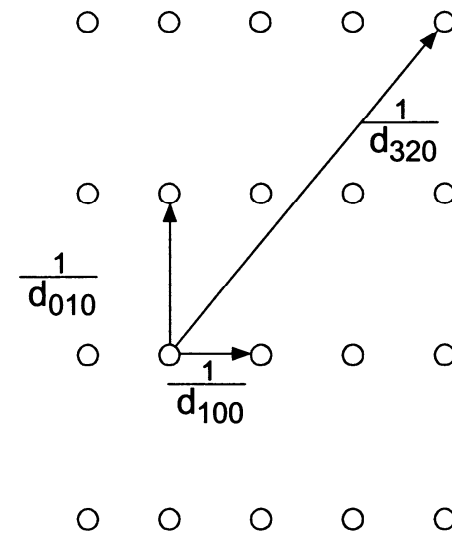
(111) planes



(210) planes

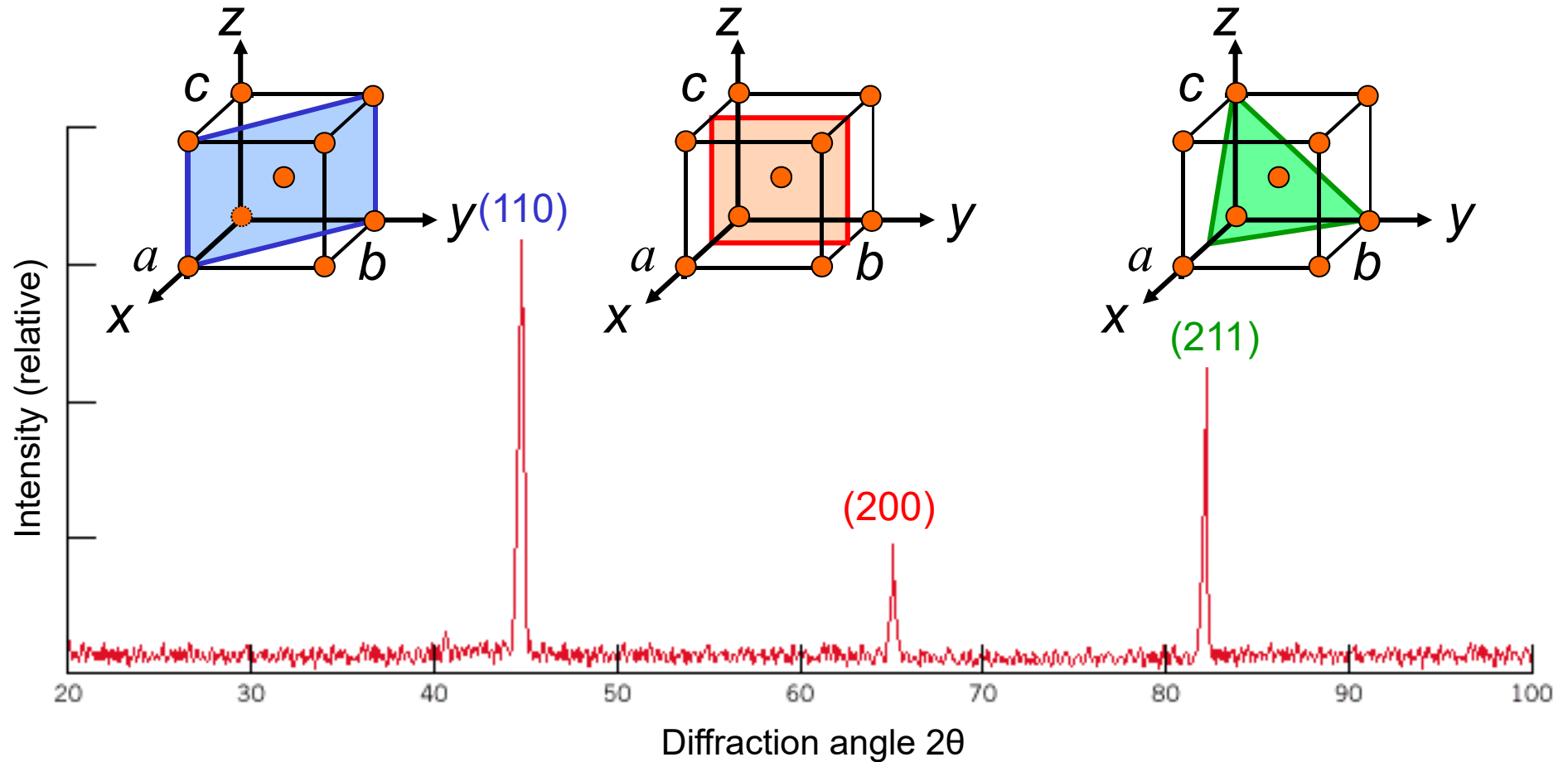


Crystal planes



Reciprocal crystal planes

Determination of crystal structure I



Diffraction pattern for polycrystalline α -iron (BCC)

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

Determination of crystal structure II

□ Problem: Determine the d-spacing for the (111) plane, the lattice parameter a_0 and the atomic radius for Al.

$$2\theta = 38^\circ \Rightarrow \theta = 19^\circ \text{ for (111)}$$

$$\lambda = 2 \cdot d \cdot \sin \theta \Rightarrow d_{(111)} = \frac{\lambda}{2 \cdot \sin \theta} = \frac{0.1542 \text{ nm}}{2 \cdot \sin 19^\circ} = 0.237 \text{ nm}$$

$$d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}} \Rightarrow a_o = d_{hkl} \cdot \sqrt{h^2 + k^2 + l^2}$$

$$a_o = 0.237 \times \sqrt{1^2 + 1^2 + 1^2} \text{ nm} = 0.237 \times \sqrt{3} \text{ nm}$$

$$a_o = 0.410 \text{ nm}; a_o = \frac{4 \cdot r}{\sqrt{2}} \Rightarrow r = \frac{a_o \cdot \sqrt{2}}{4} = 0.144 \text{ nm}$$

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.
- **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).
- **Polymer (= many mer)** is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional repeating units) linked to each other in amounts sufficient to provide a set of properties. Most polymers are hydrocarbons – i.e., made up of H and C.
- **X-ray diffraction** is used for crystal structure and interplanar spacing determinations.