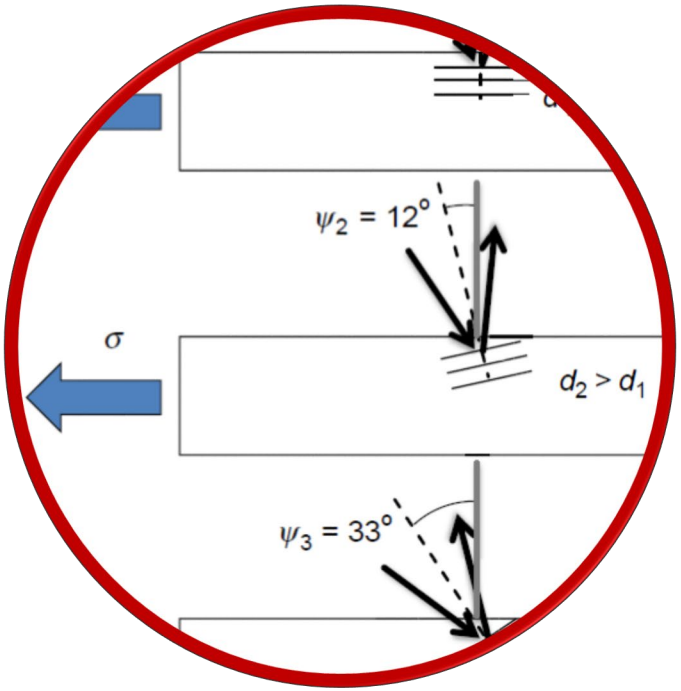
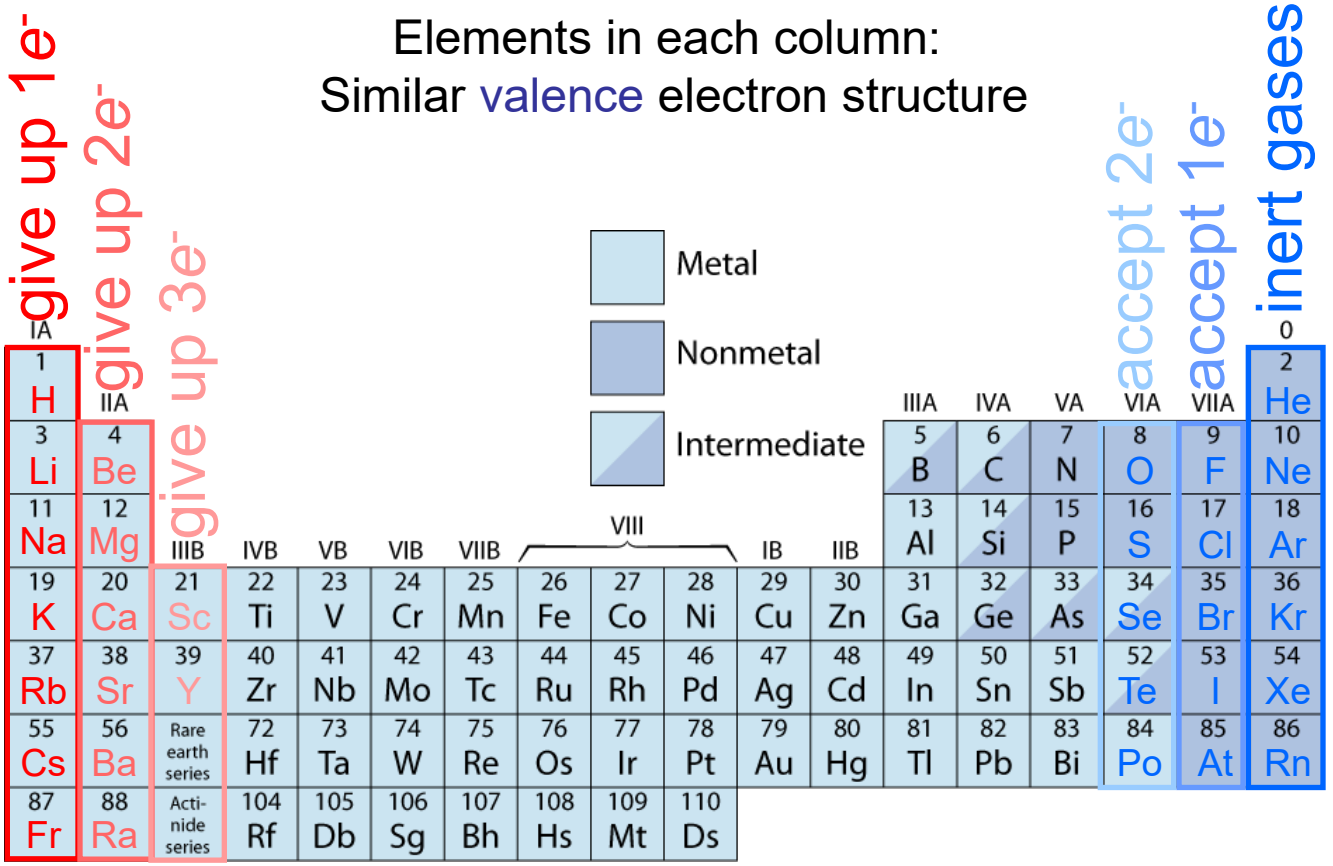
2. Microstructure of materials



The Periodic Table

Elements in each column:
Similar valence electron structure

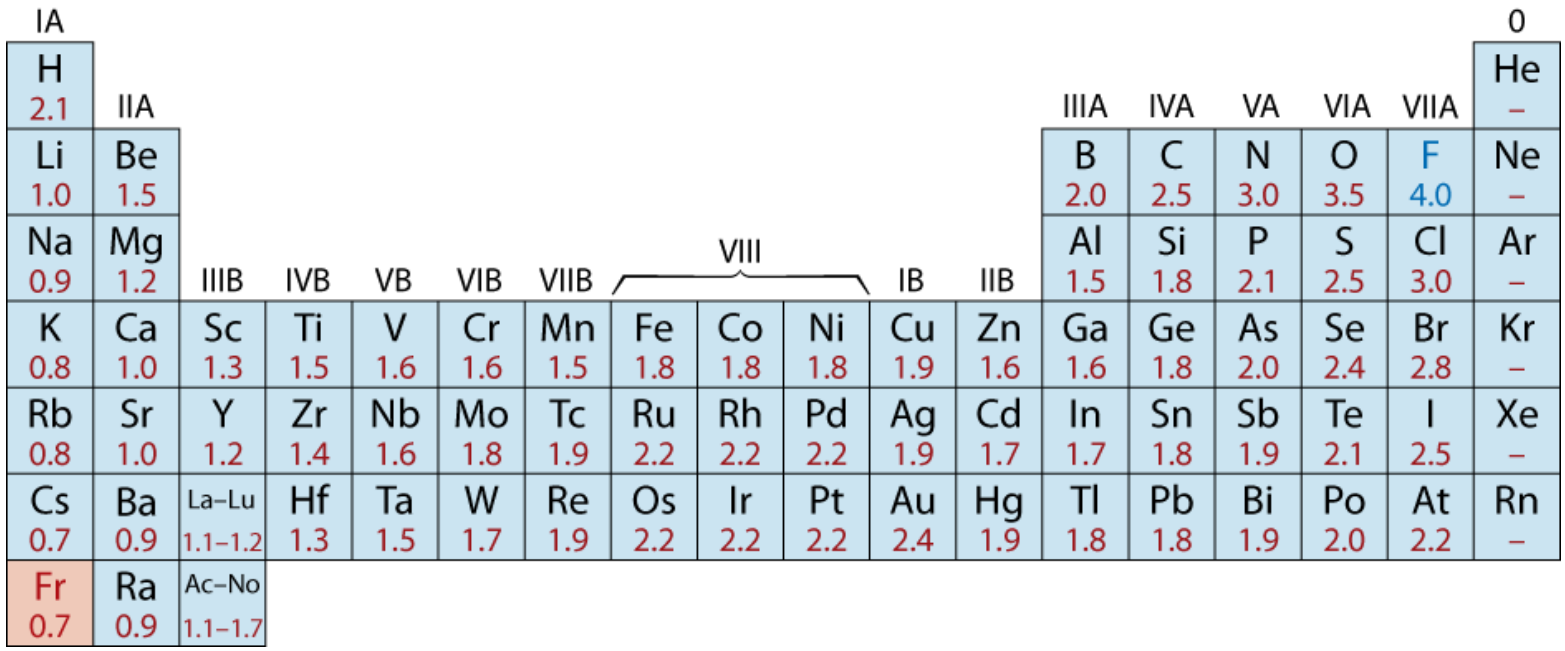


Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions.

Electronegativity

- Ranges from 0.7 to 4.0,
- Large values: tendency to acquire electrons.



Ionization Process

metal atom + nonmetal atom

donates electrons

accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ or [Ne] $3s^2$

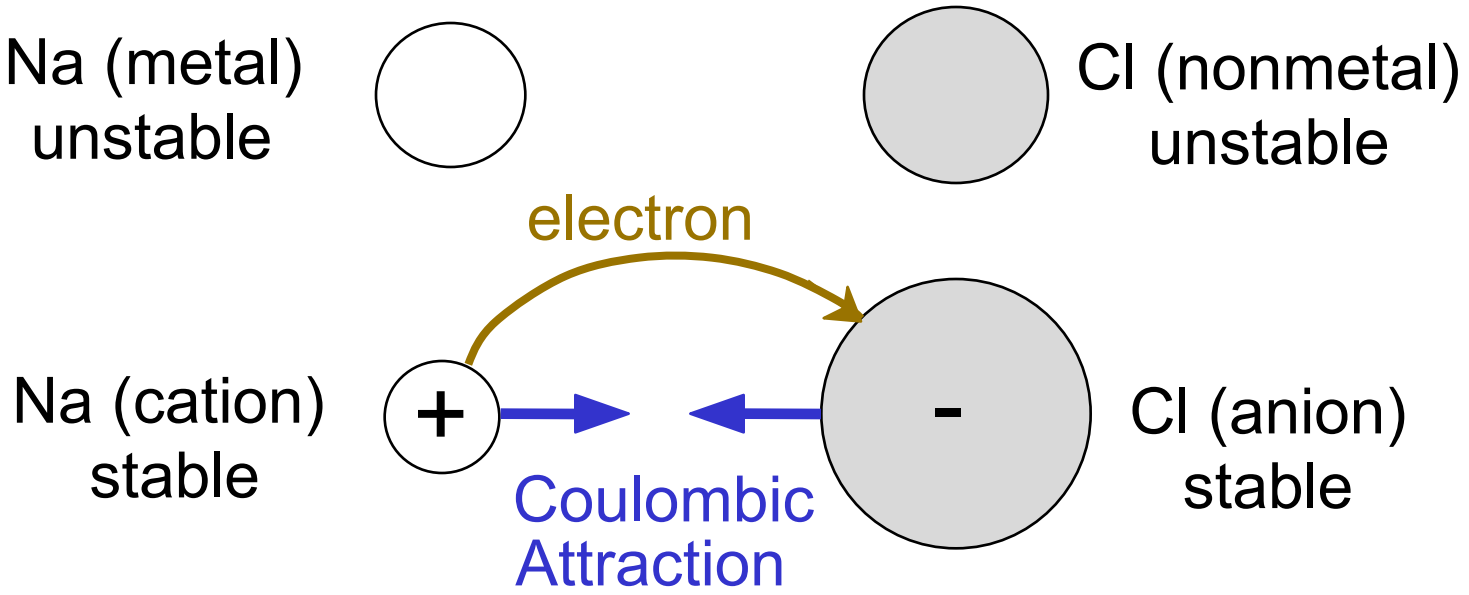
O $1s^2\ 2s^2\ 2p^4$

Mg^{2+} $1s^2\ 2s^2\ 2p^6$ or [Ne]

O^{2-} $1s^2\ 2s^2\ 2p^6$ or [Ne]

Ionic Bonding

- Occurs between + and - ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl



Ionic Bonding (cont.)

- Energy – minimum energy most stable
  - Net energy = sum of attractive and repulsive energies
  - Equilibrium separation when net energy is a minimum

$$E_N = E_A + E_R = -\frac{A}{r} + \frac{B}{r^n}$$

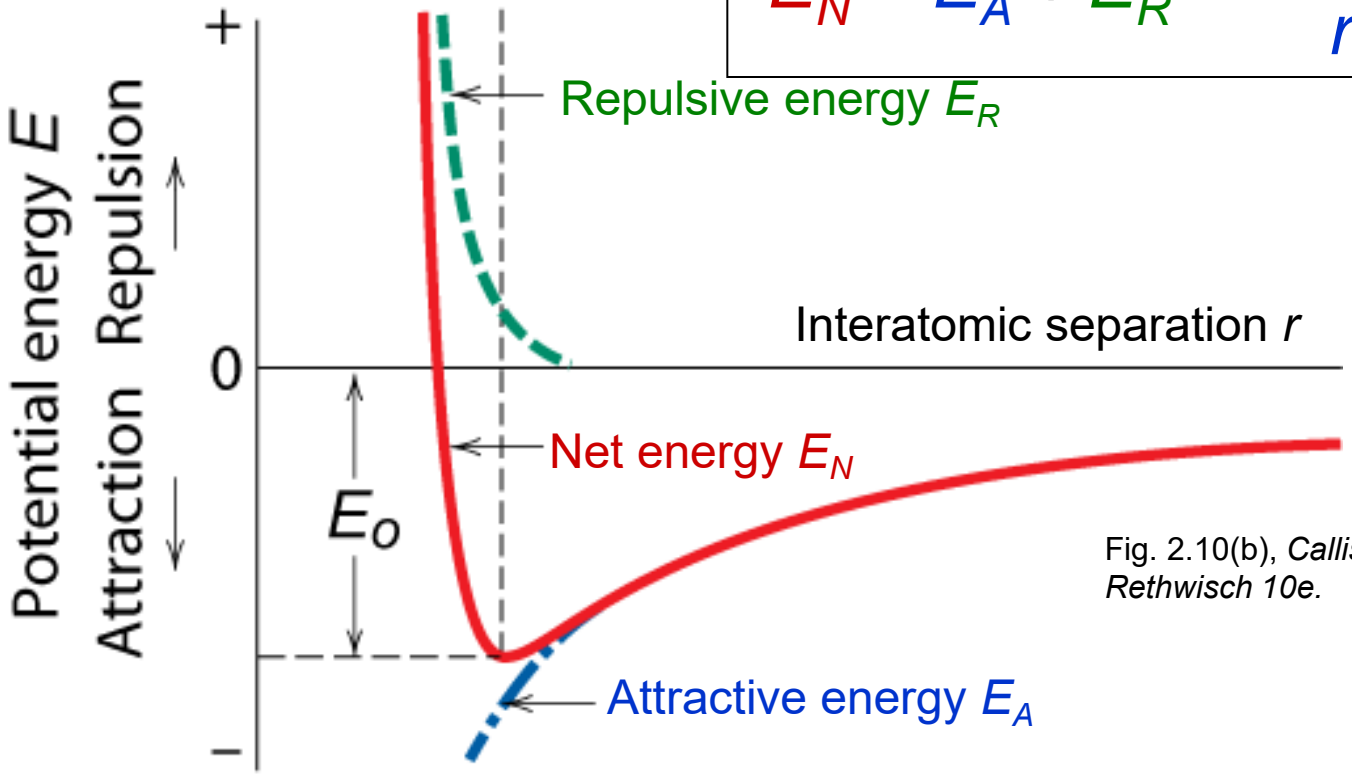
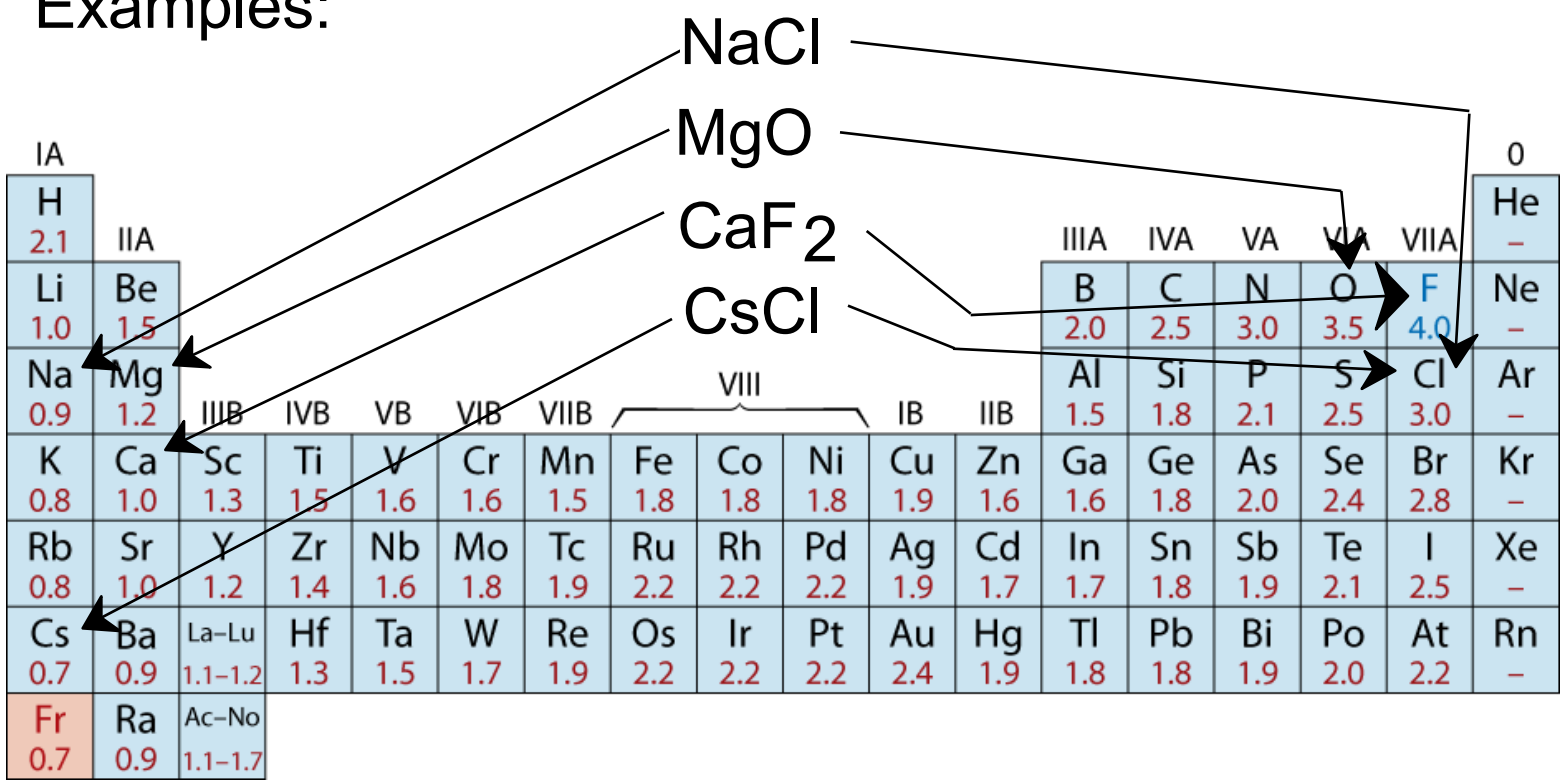


Fig. 2.10(b), *Callister & Rethwisch 10e.*

Ionic Bonding (cont.)

Predominant bonding in Ceramics

Examples:



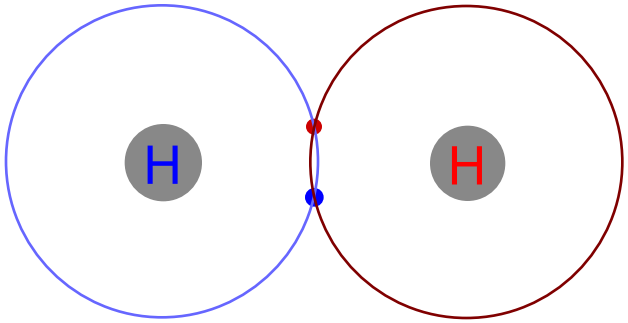
Covalent Bonding

- Similar electronegativities ∴ share electrons
- Bonds involve valence electrons – normally *s* and *p* orbitals are involved
- Example: H_2

Each H: has 1 valence e^-, needs 1 more

Electronegativities are the same.

H_2



- shared 1*s* electron from 1st hydrogen atom
- shared 1*s* electron from 2nd hydrogen atom

Fig. 2.12, *Calliser & Rethwisch 10e.*

Covalent Bonding: Bond Hybrization

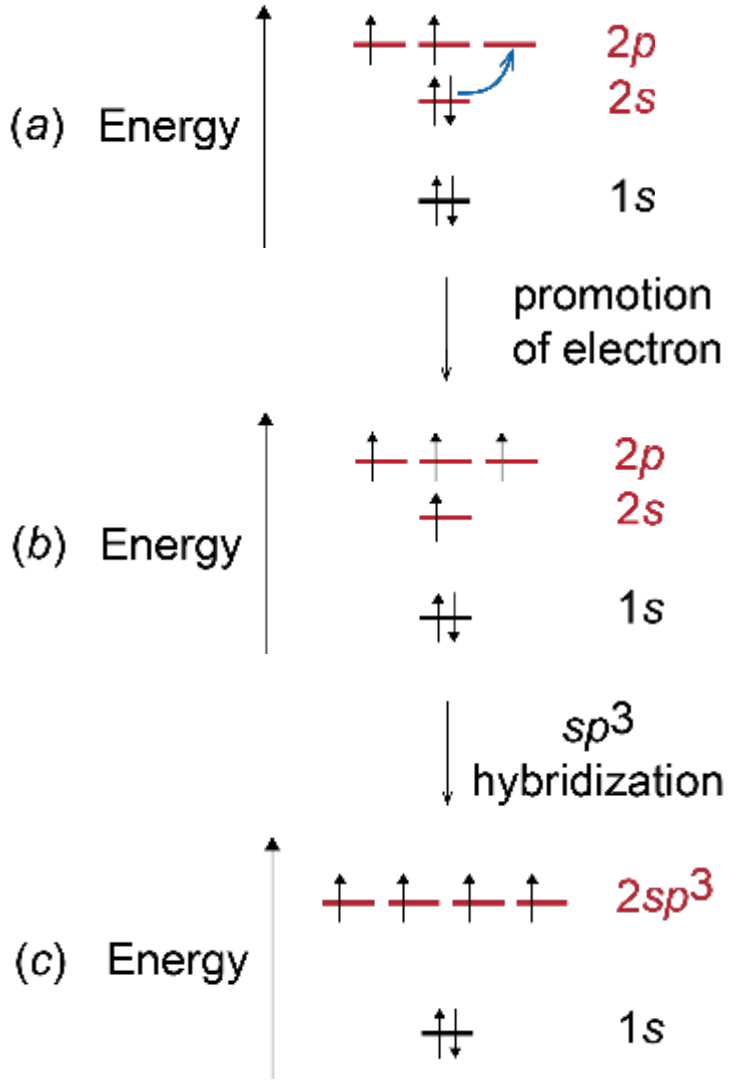


Fig. 2.13, *Callister & Rethwisch 10e.*

- Carbon can form sp^3 hybrid orbitals

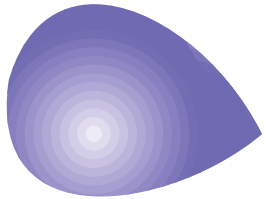


Fig. 2.14, *Callister & Rethwisch 10e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Covalent Bonding (cont.)

Hybrid sp^3 bonding involving carbon

Example: CH_4

C: each has 4 valence electrons, needs 4 more

H: each has 1 valence electron, needs 1 more

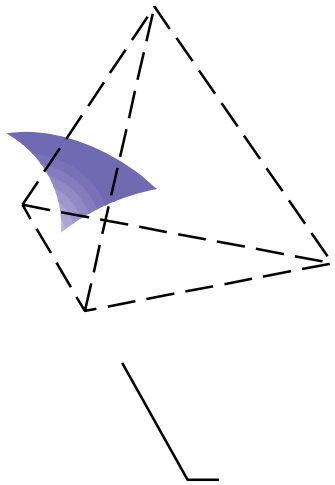


Fig. 2.15, *Callister & Rethwisch 10e.* (Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Electronegativities of C and H are similar so electrons are shared in sp^3 hybrid covalent bonds.

Metallic Bonding

- Electrons delocalized to form an "electron cloud"

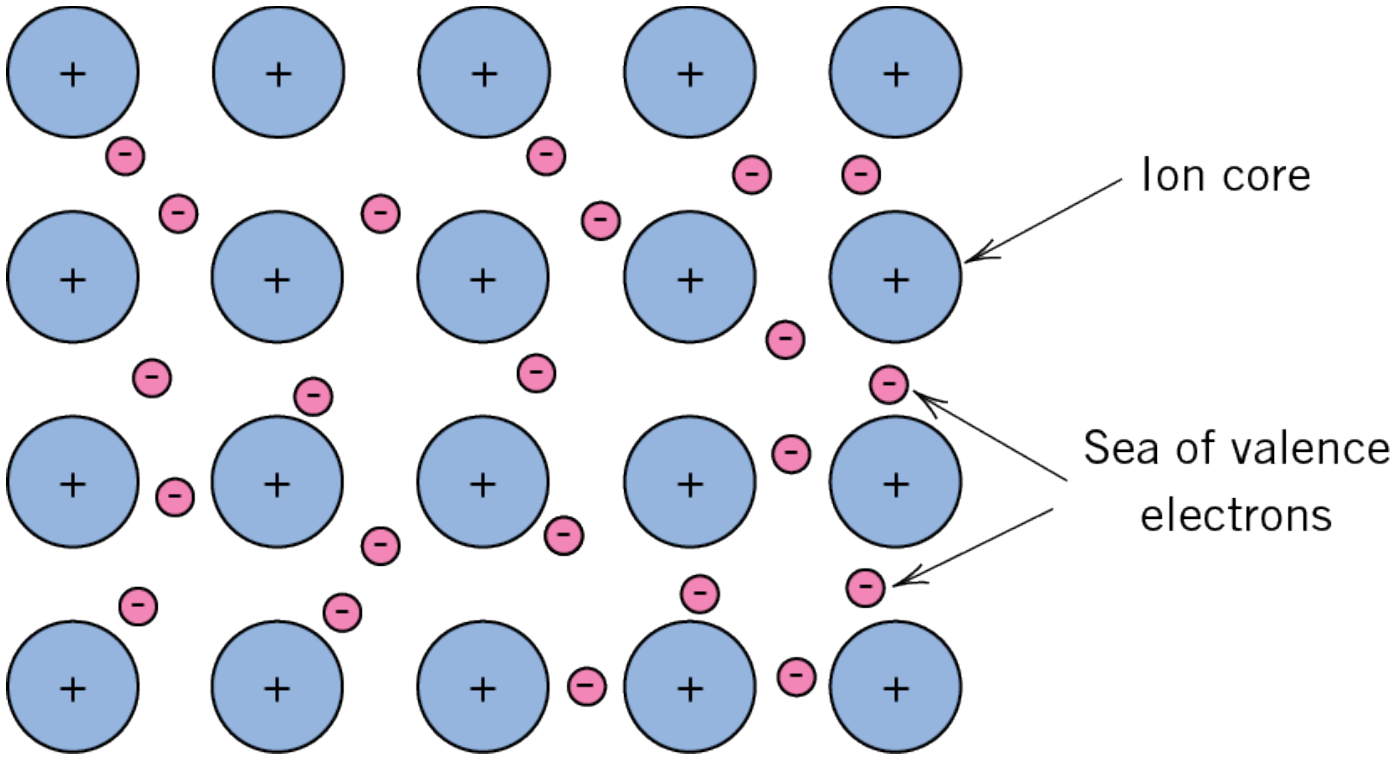


Fig. 2.19*b*, *Callister & Rethwisch 10e.*

Mixed Bonding

- Most common mixed bonding type is Covalent-Ionic mixed bonding

$$\%\ \text{ionic character} = \left(1 - e^{-\frac{(X_A - X_B)^2}{4}}\right) x\,(100\%)$$

where X_A & X_B are electronegativities of the two elements participating in the bond

Ex: MgO

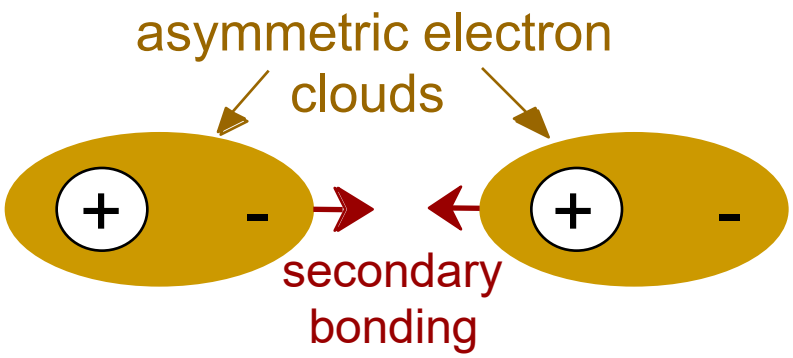
$X_{Mg} = 1.2$
$X_O = 3.5$

$$\%\ \text{ionic character} = \left(1 - e^{-\frac{(3.5-1.2)^2}{4}}\right) x\,(100\%) = 73.3\%$$

Secondary Bonding

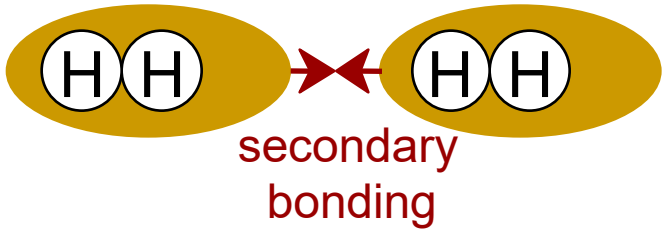
Arises from attractive forces between dipoles

- Fluctuating dipoles



ex: liquid H_2

H_2 → ← H_2

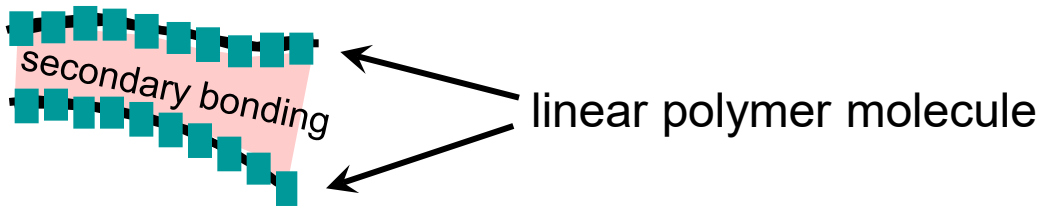


- Permanent dipoles

-general case:

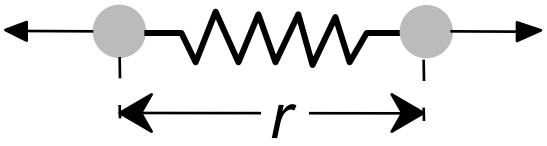
-ex: liquid HCl

-ex: polymer

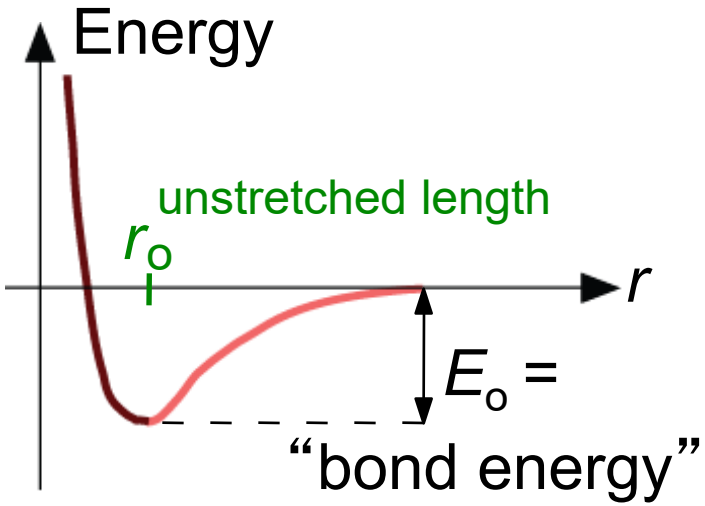


Properties Related to Bonding I: Melting Temperature (T_m)

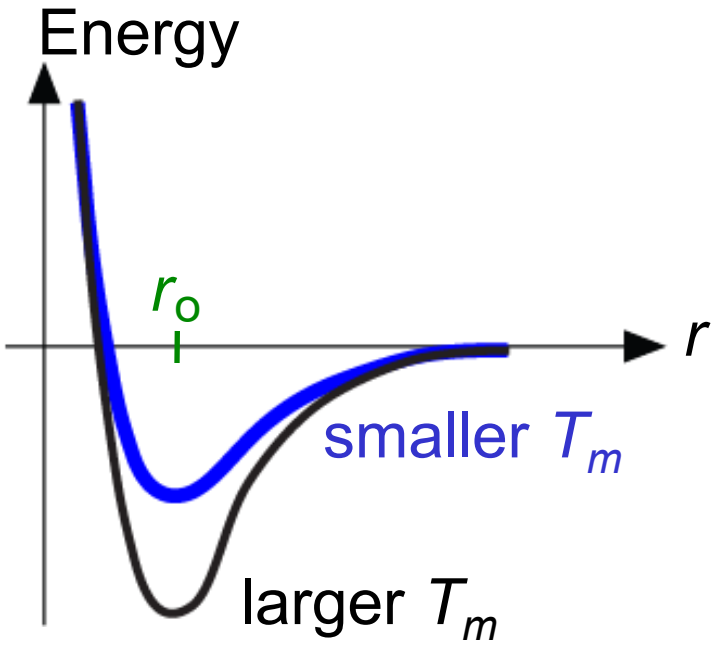
- Bond length, r



- Bond energy, E_o



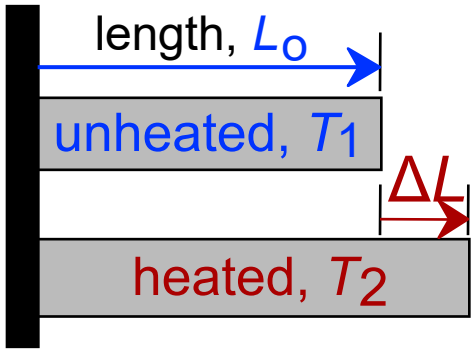
- Melting Temperature, T_m



The larger E_o, the higher T_m

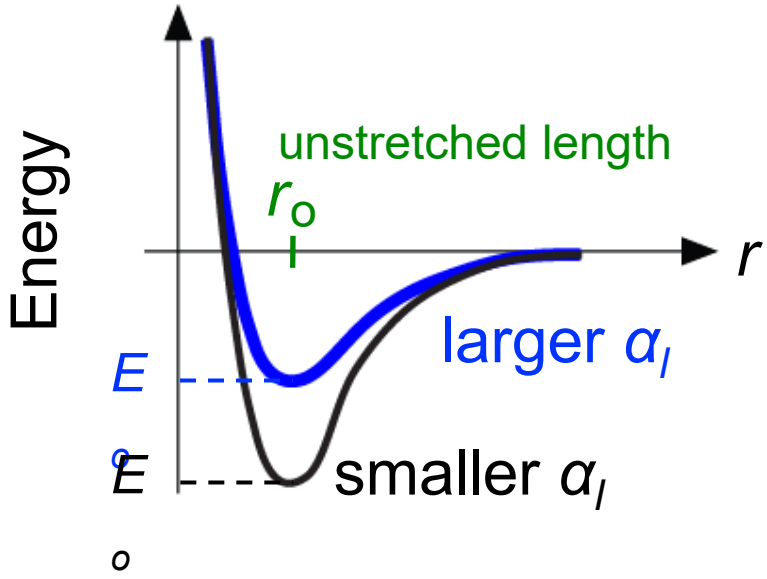
Prop. Related to Bonding II: Coeff. of Thermal Expansion (α_l)

- Coefficient of thermal expansion, α_l



$$\frac{\Delta L}{L_o} = \alpha_l (T_2 - T_1)$$

The smaller E_o, the larger α_l.



- Increase in bond length is due to asymmetry of the E vs. r curve. This results in an increase in α_l.
- As E_0 increases this asymmetry decreases.

Summary: Bonding Type and Bonding Energy

Ceramics

(Ionic & covalent bonding):

Large bond energy

high T_m
large E
small α_l

Metals

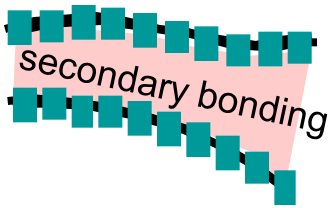
(Metallic bonding):

Variable bond energy

moderate T_m
moderate E
moderate α_l

Polymers

(Covalent & Secondary):



Weak bond energy (between chains)
Secondary bonding responsible for most physical properties

low T_m
small E
large α_l

summary

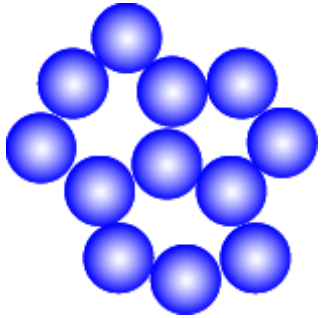
- A material's chemical, electrical, thermal, and optical properties are determined by electronic configuration.
- Valence electrons occupy the outermost unfilled electron shell.
- Primary bonding types include covalent, ionic, and metallic bonding.
- Secondary or van der Waals bonds are weaker than the primary bonding types.
- The percent ionic character of a covalent-ionic mixed bond between two elements depends on their electronegativities.

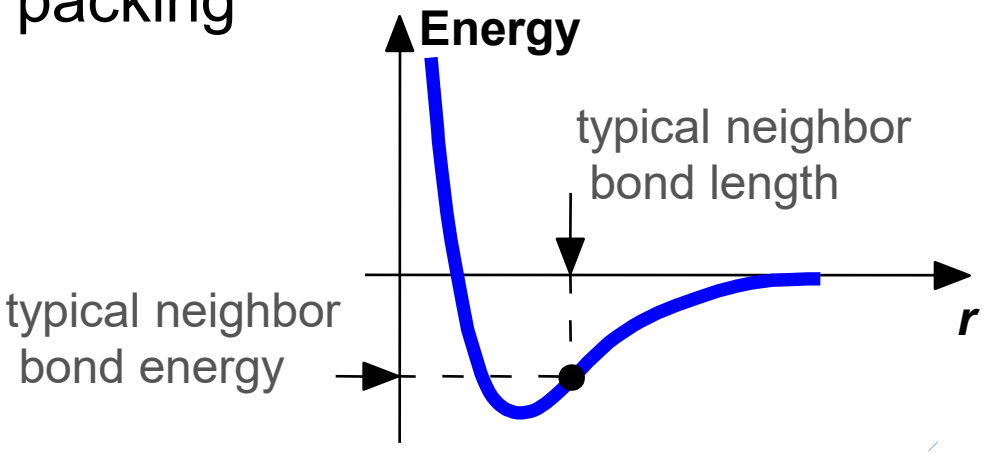
ISSUES TO EXPLORE...

- What is the difference in atomic arrangement between crystalline and noncrystalline solids?
- What are the crystal structures of metals?
- What are the characteristics of crystal structures?
- How are crystallographic points, directions, and planes specified?
- What characteristics of a material's atomic structure determine its density?

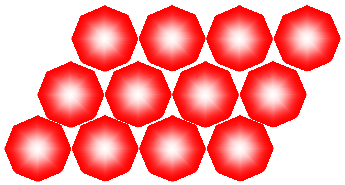
Energy and Packing

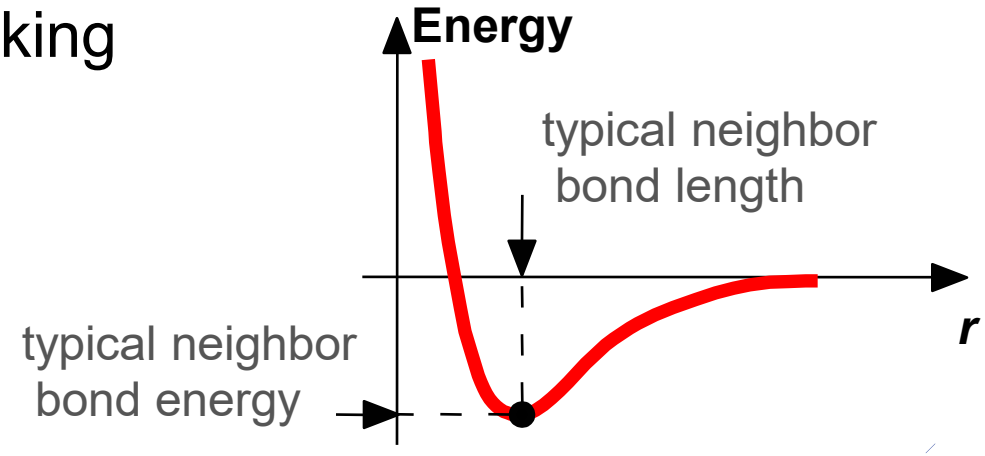
- Non dense, random packing





- Dense, ordered packing



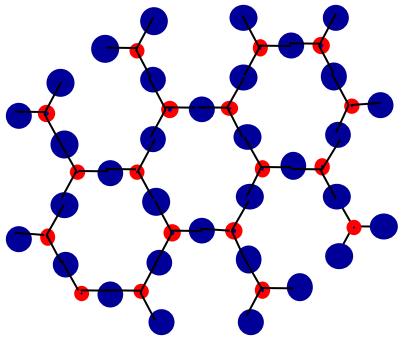


Ordered structures tend to be nearer the minimum in bonding energy and are more stable.

Materials and Atomic Arrangments

Crystalline materials...

- atoms arranged in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers



crystalline SiO_2

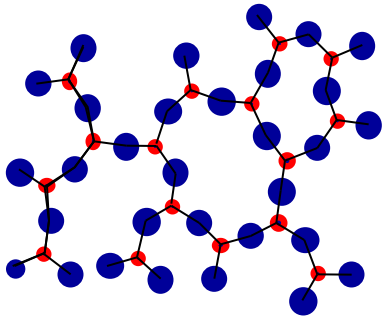
Adapted from Fig. 3.24(a), *Callister & Rethwisch 10e.*

• Si • Oxygen

Noncrystalline materials...

- atoms have no periodic arrangement
- occurs for: -complex structures
  -rapid cooling

"Amorphous" = Noncrystalline



noncrystalline SiO_2

Adapted from Fig. 3.24(b), *Callister & Rethwisch 10e.*

Metallic Crystal Structures: Atomic Packing

- Dense atomic packing for crystal structures of metals.
- Reasons for dense packing:
  - Bonds between metal atoms are nondirectional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - High degree of shielding (of ion cores) provided by free electron cloud.
- Crystal structures for metals simpler than structures for ceramics and polymers.

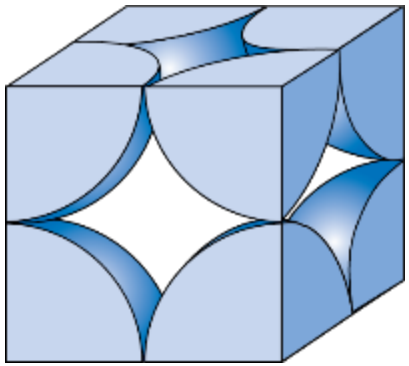
We will examine three such structures for metals...

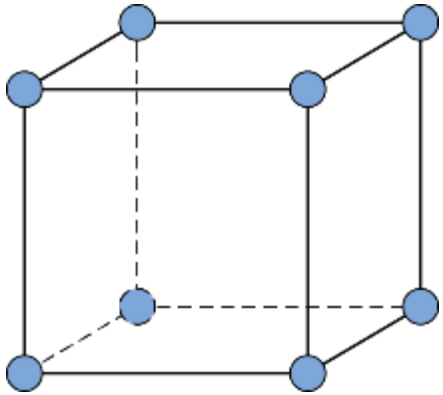
Simple Cubic (SC) Crystal Structure

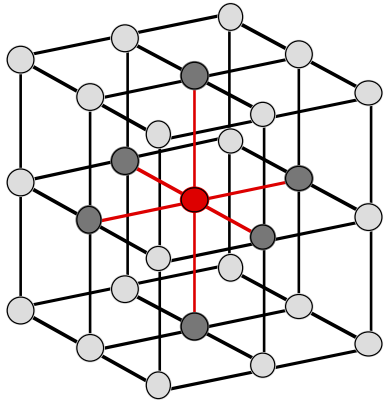
- Centers of atoms located at the eight corners of a cube
- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.

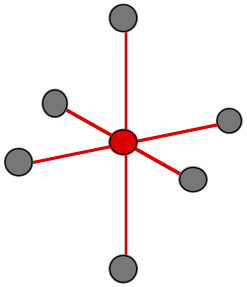
ex: Po

- Coordination # = 6
  (# nearest neighbors)









Adapted from Fig. 3.3, *Callister & Rethwisch 10e.*

Coordination Number

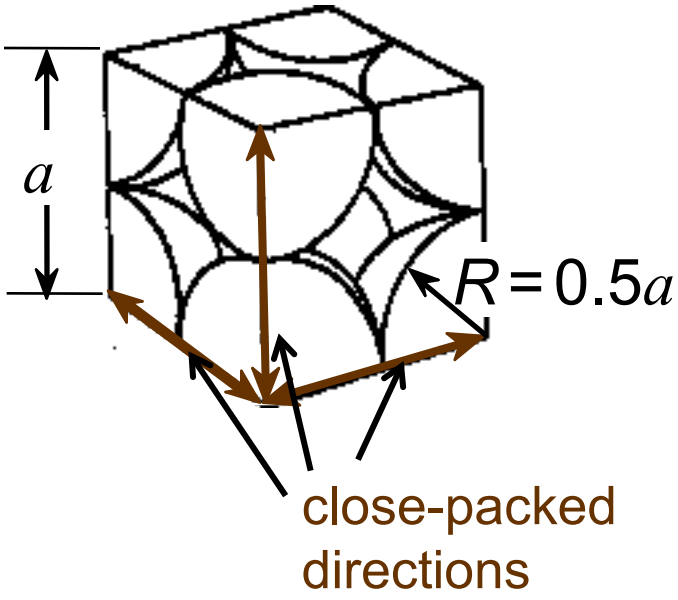
Coordination Number = number of nearest-neighbor or touching atoms

Atomic Packing Factor (APF)

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

*assume hard spheres

Atomic Packing Factor (APF) for Simple Cubic



$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3} = 0.52$$

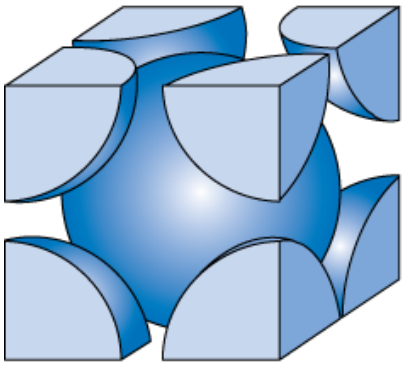
Unit cell contains 1 atom = 8 x 1/8 = 1 atom/unit cell

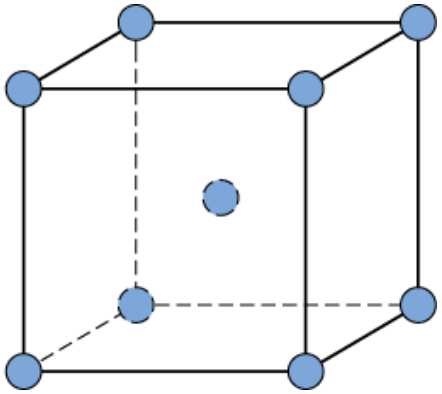
Body-Centered Cubic Structure (BCC)

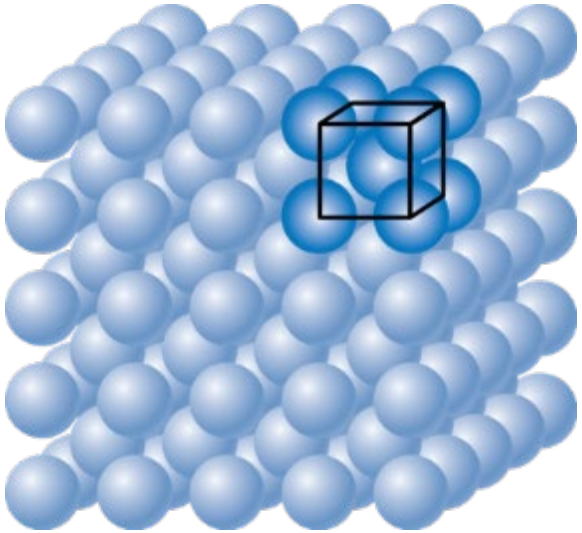
- Atoms located at 8 cube corners with a single atom at cube center.
  --Note: All atoms in the animation are identical; the center atom is shaded differently for ease of viewing.

ex: Cr, W, Fe (α), Ta, Mo

- Coordination # = 8



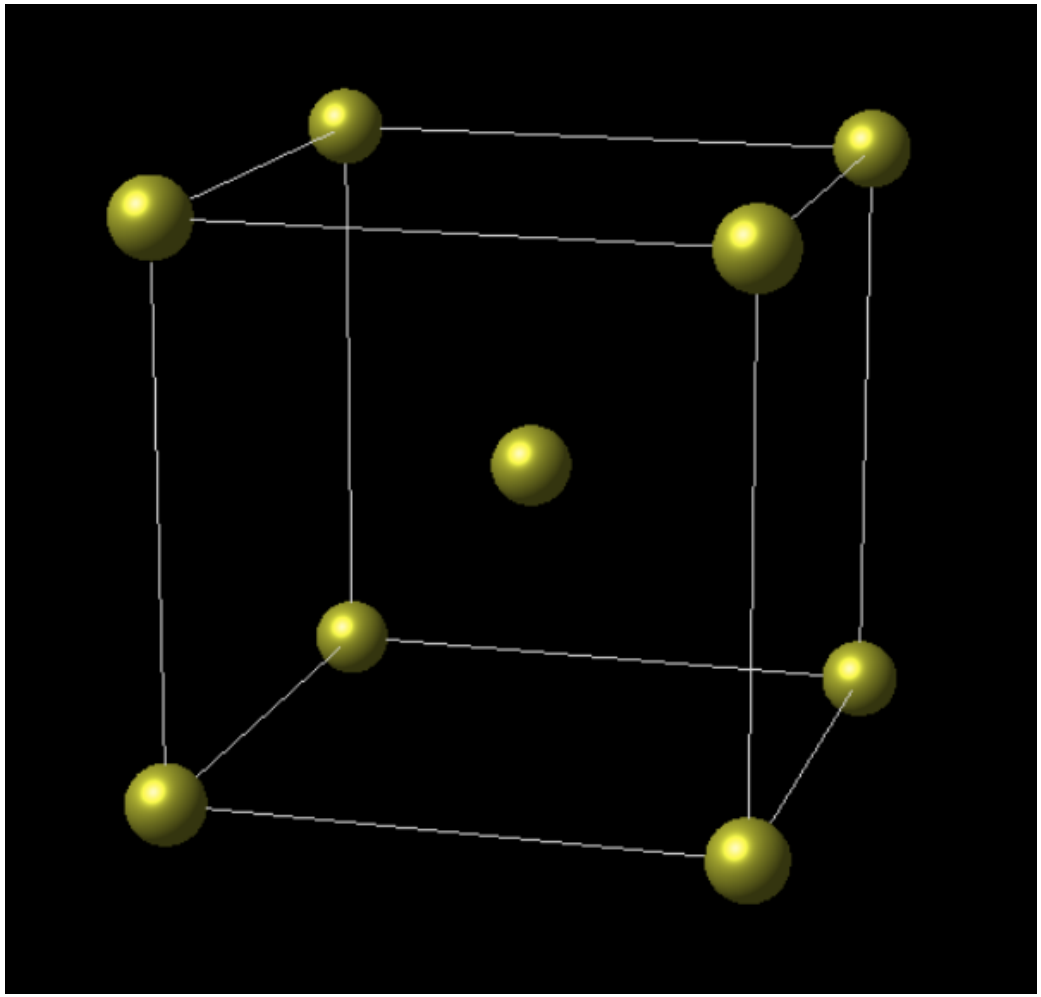




Adapted from Fig. 3.2, *Callister & Rethwisch 10e.*

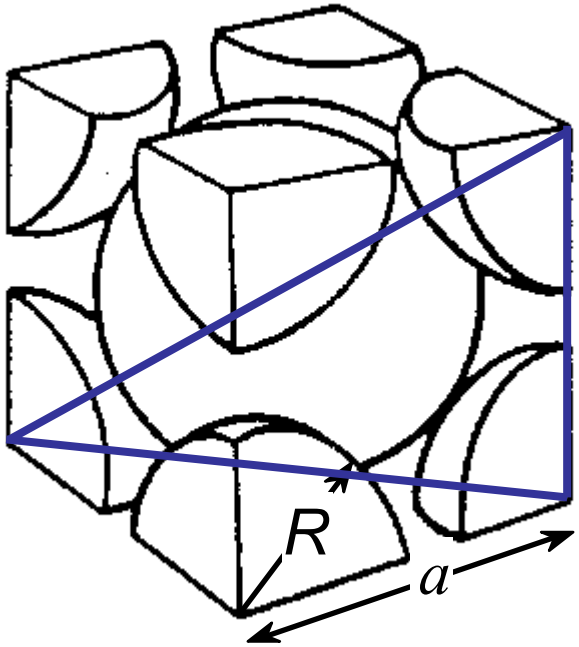
2 atoms/unit cell: 1 center + 8 corners x 1/8

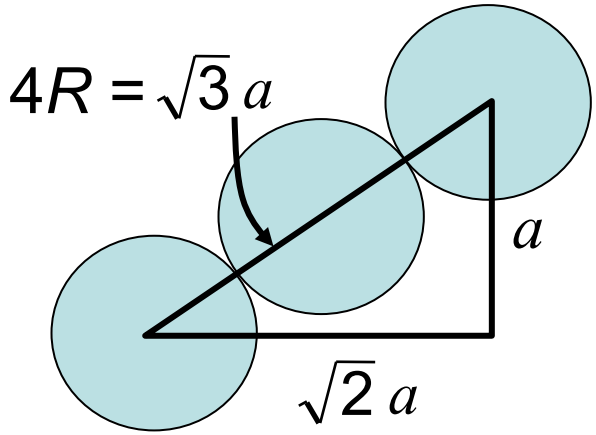
VMSE Screenshot – BCC Unit Cell



Atomic Packing Factor: BCC

- APF for the body-centered cubic structure = 0.68





For close-packed directions

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

$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \cdot \dfrac{\text{volume}}{\text{atom}}}{\dfrac{\text{volume}}{\text{unit cell}}} = \frac{2\left(\frac{4}{3}\pi\left(\sqrt{3}a/4\right)^3\right)}{a^3} = \frac{8}{3}\pi\left(\frac{\sqrt{3}}{4}\right)^3 = 0.68$$

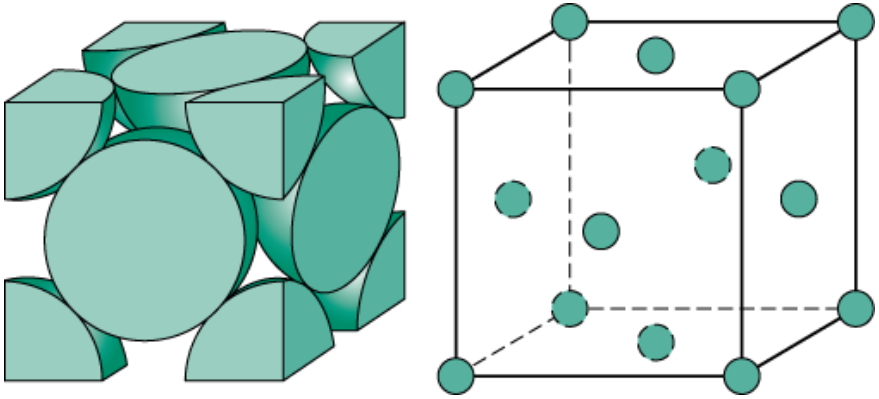
Face-Centered Cubic Structure (FCC)

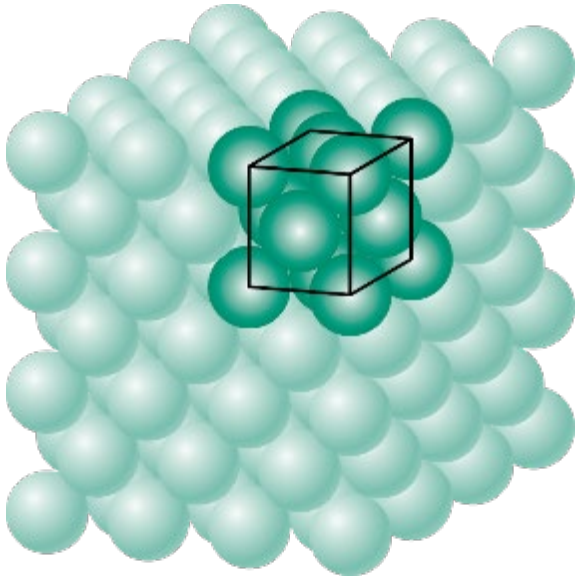
- Atoms located at 8 cube corners and at the centers of the 6 faces.

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

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

- Coordination # = 12



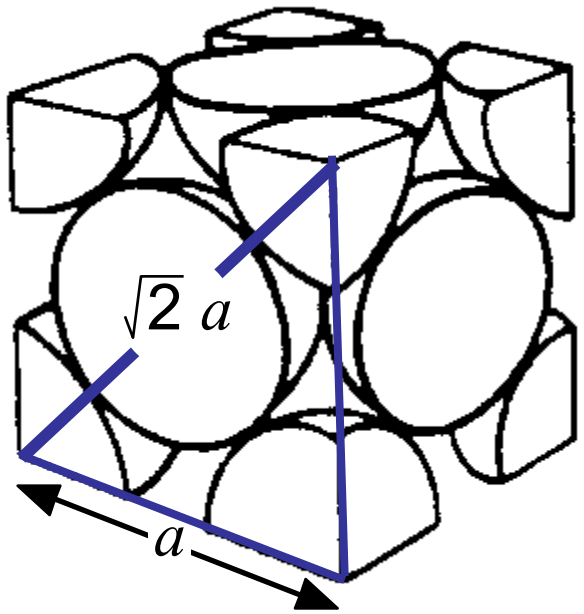


Adapted from Fig. 3.1, *Callister & Rethwisch 10e.*

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

Atomic Packing Factor: FCC

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



For close-packed directions:

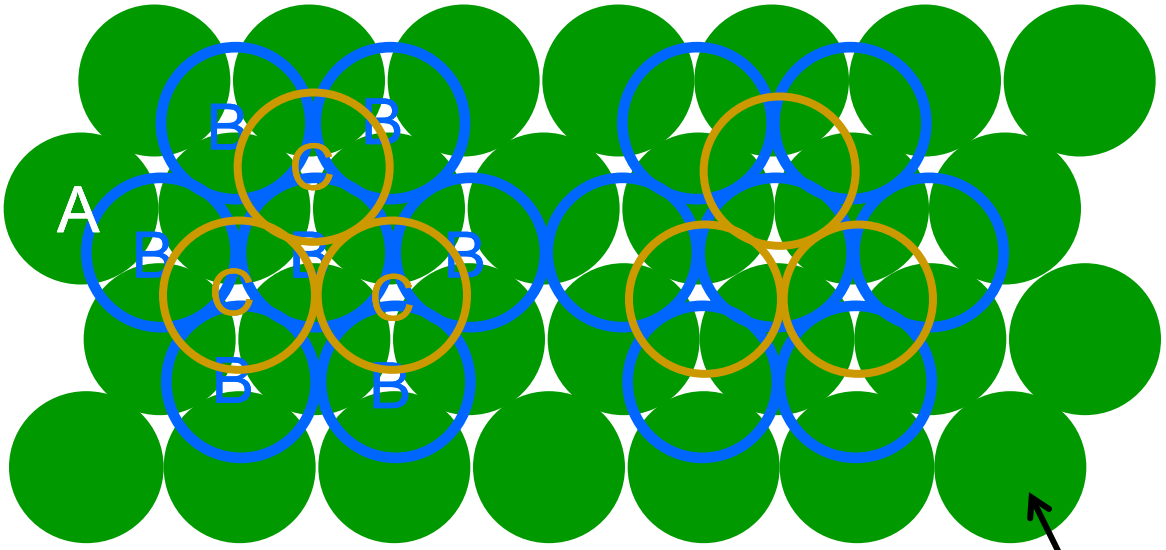
$$4R = \sqrt{2}\,a \quad \left(\text{i.e., } R = \frac{\sqrt{2}a}{4}\right)$$

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

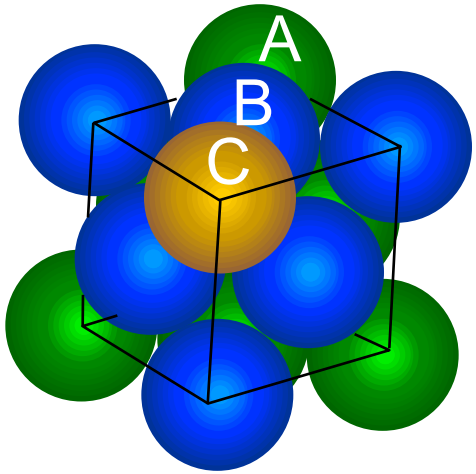
$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \cdot \dfrac{\text{volume}}{\text{atom}}}{\dfrac{\text{volume}}{\text{unit cell}}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3} = 0.74$$

FCC Plane Stacking Sequence

- ABCABC... Stacking Sequence–Close-Packed Planes of Atoms
- 2D Projection

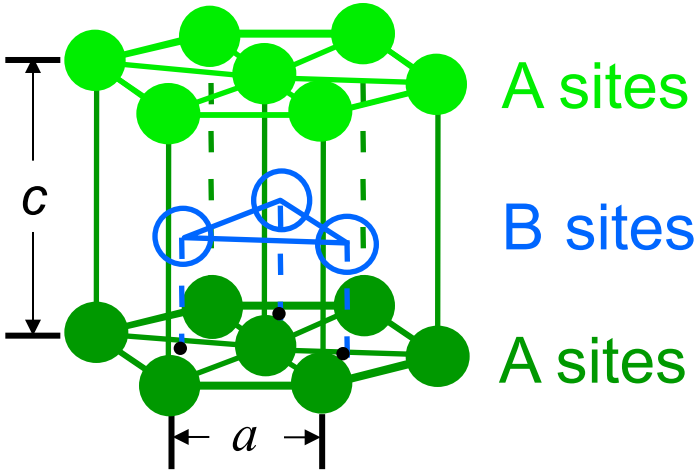


- Stacking Sequence Referenced to an FCC Unit Cell.

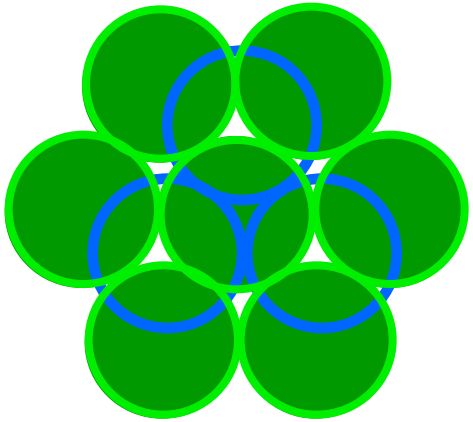


Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence–Close-Packed Planes of Atoms
- 3D Projection



- 2D Projection



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

Theoretical Density for Metals, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}} = \frac{(nA / N_A)}{V_C}$$

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

where n = number of atoms/unit cell

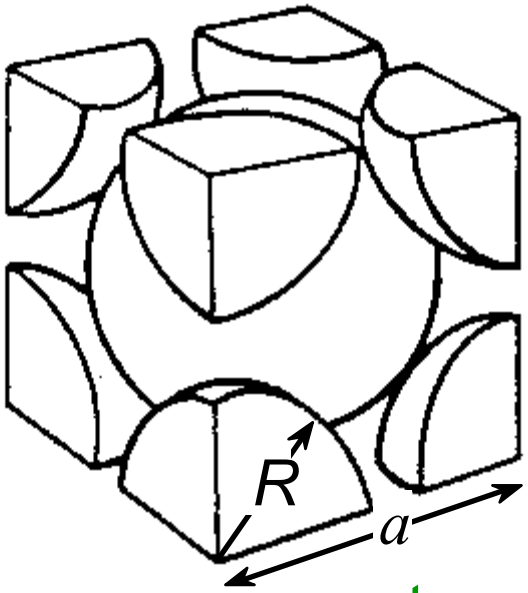
A = atomic weight

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

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol

Theoretical Density Computation for Chromium



- Cr has BCC crystal structure

A = 52.00 g/mol

R = 0.125 nm

n = 2 atoms/unit cell

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

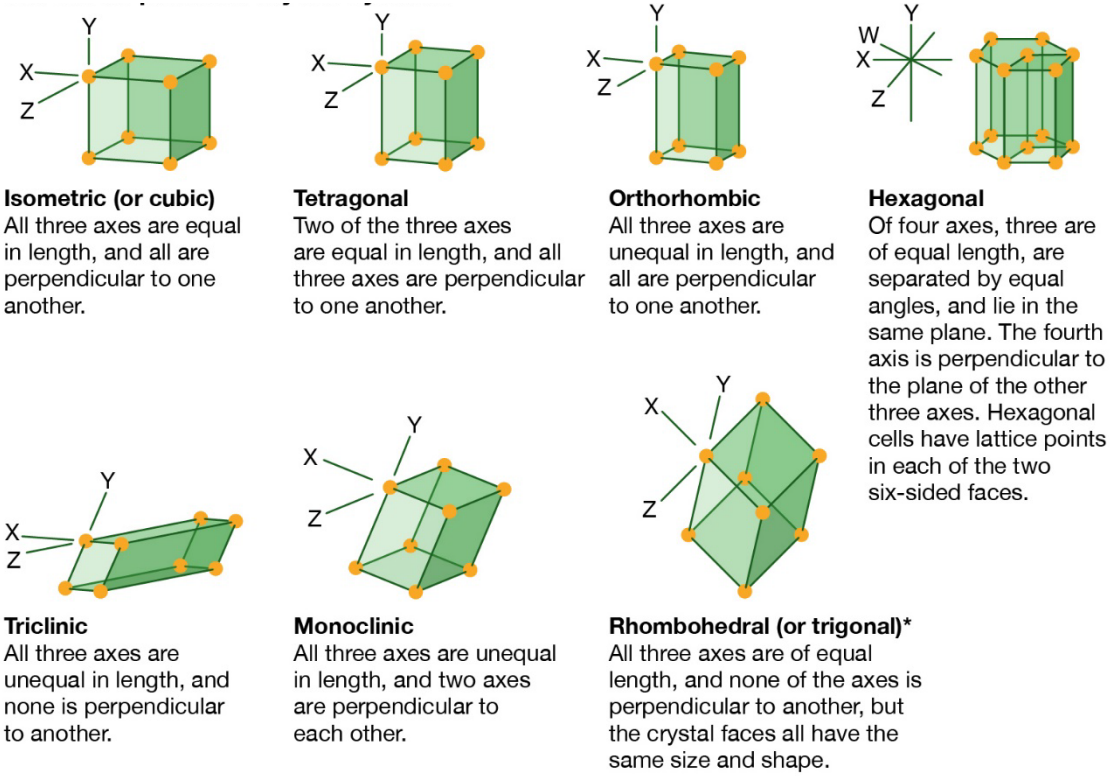
$V_C = a^3 = 2.406 \times 10^{-23}$ cm^3

$$\rho = \frac{n\,A}{V_C\,N_A} = \frac{\frac{\text{atoms}}{\text{unit cell}}\;\frac{\text{g}}{\text{mol}}}{\frac{\text{volume}}{\text{unit cell}}\;\frac{\text{atoms}}{\text{mol}}} = \frac{2 \;\; 52.00}{2.406 \times 10^{-23} \;\; 6.022 \times 10^{23}} = 7.19 \text{ g/cm}^3$$

ρ_{actual} = 7.15 g/cm^3

Crystalline systems

In crystallography, we distinguish 7 crystalline systems that correspond to groups of symmetry:



Densities Comparison for Four Material Types

In general

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

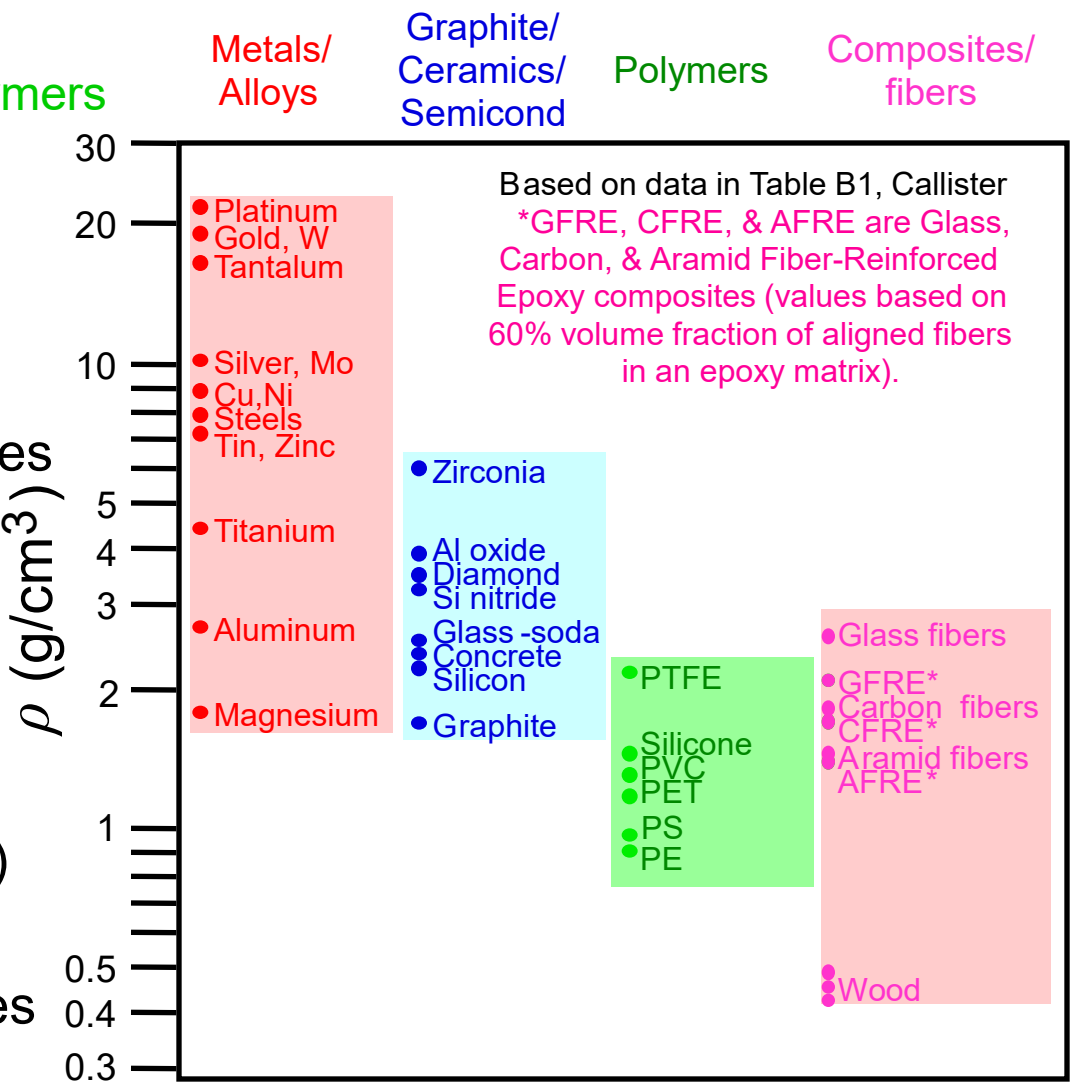
Why?

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

Ceramics have...
- often lighter elements

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

Composites have...
- moderate to low densities



Single Crystals

- When the periodic arrangement of atoms (crystal structure) extends without interruption throughout the entire specimen.

-- diamond single crystals for abrasives

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

-- Quartz single crystal

(Courtesy P.M. Anderson)

-- single crystal for turbine blade

Fig. 8.35(c), *Callister & Rethwisch 10e.*
(courtesy of Pratt and Whitney)

Polycrystalline Materials

- *Most* engineering materials are composed of many small, single crystals (i.e., are *polycrystalline*).

Courtesy of Paul E. Danielson, Teledyne Wah Chang Albany

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- Grain sizes typically range from 1 nm to 2 cm

  (i.e., from a few to millions of atomic layers).

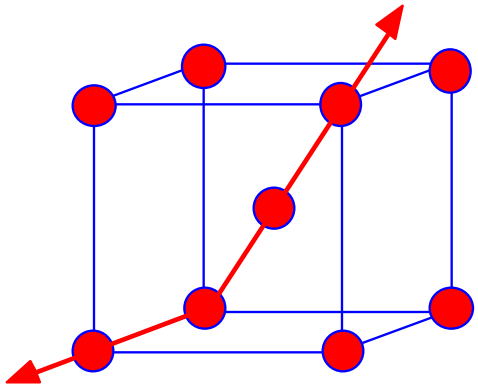
Anisotropy

- Anisotropy — Property value depends on crystallographic direction of measurement.

  - Observed in single crystals.
  - Example: modulus of elasticity (*E*) in BCC iron

$$E(\text{edge}) \neq E(\text{diagonal})$$

E (diagonal) = 273 GPa



E (edge) = 125 GPa

Unit cell of BCC iron

Isotropy

- Polycrystals
  - Properties may/may not vary with direction.
  - If grains randomly oriented: properties isotropic. ($E_{\text{poly iron}}$ = 210 GPa)
  - If grains textured (e.g., deformed grains have preferential crystallographic orientation): properties anisotropic.

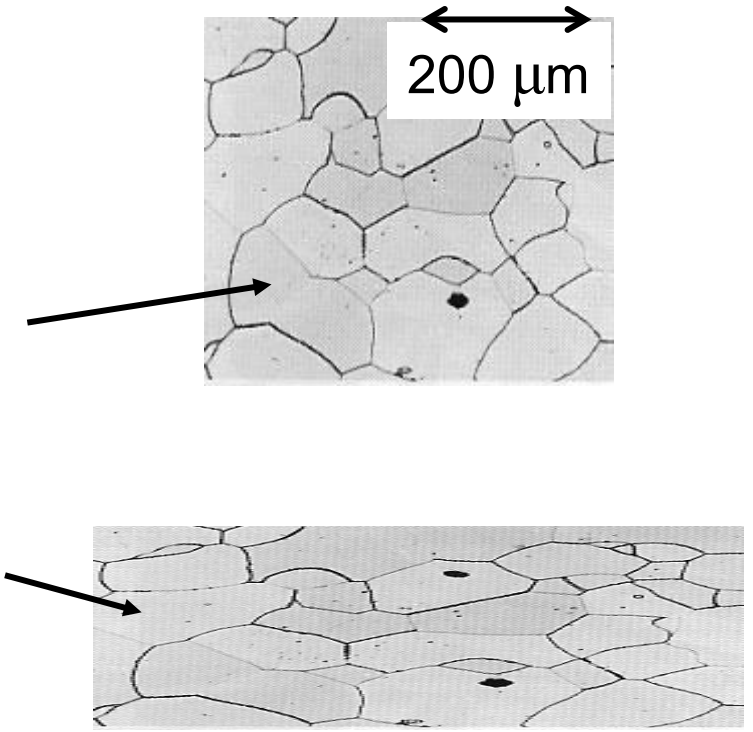


Fig. 4.15(b), *Callister & Rethwisch 10e*.
[Fig. 4.15(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

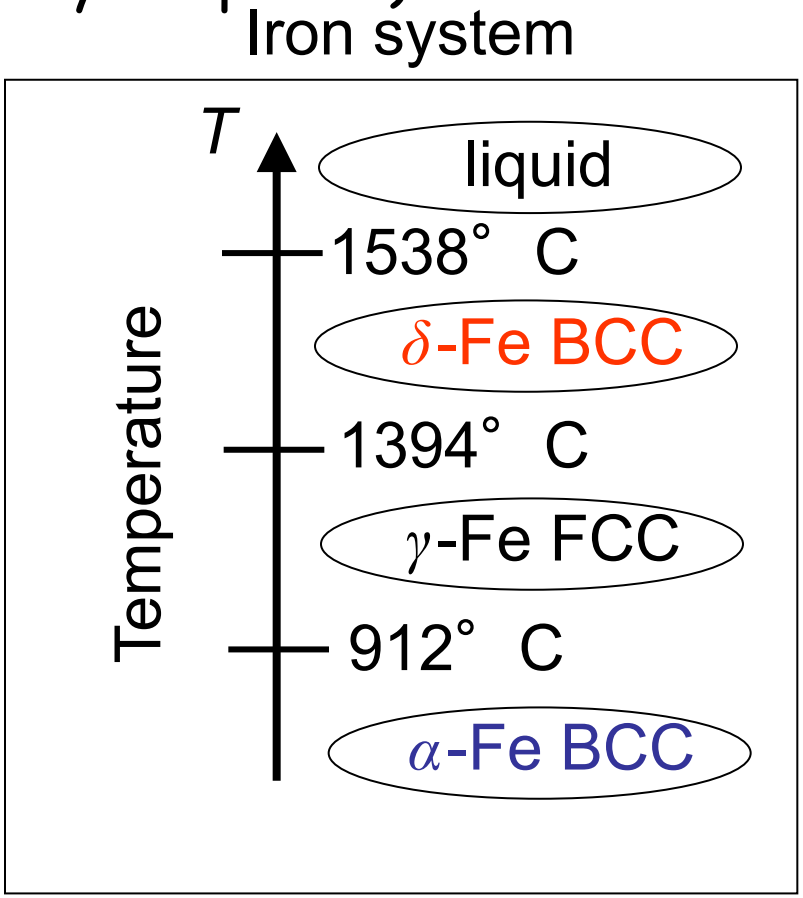
Polymorphism/Allotropy

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

Titanium: α or β forms

Carbon:

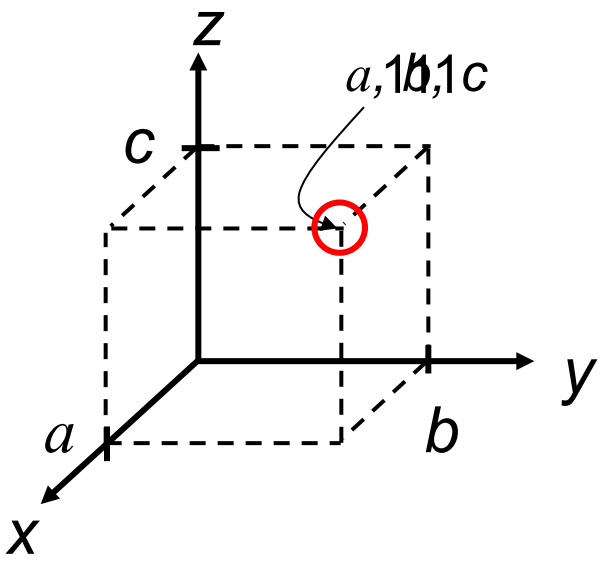
diamond, graphite



Point Coordinates

A point coordinate is a lattice position in a unit cell

Determined as fractional multiples of a, b, and c unit cell edge lengths



Example: Unit cell upper corner

1. Lattice position is

$$a,\ b,\ c$$

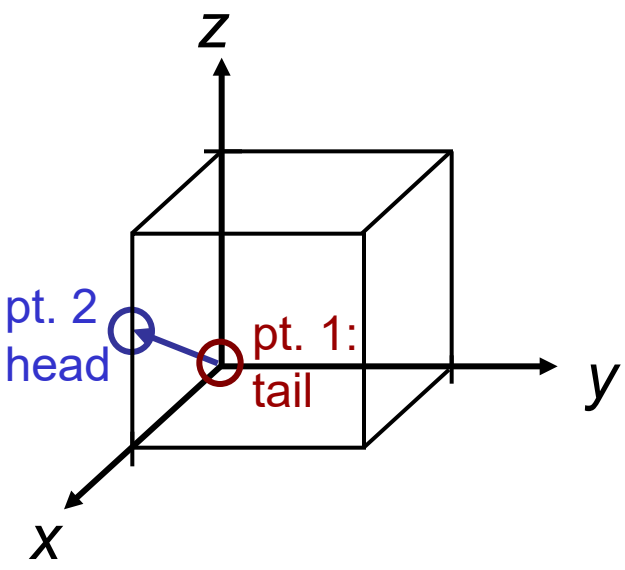
2. Divide by unit cell edge lengths (a, b, and c) and remove commas

$$\frac{a}{a}\ \frac{b}{b}\ \frac{c}{c} = 111$$

3. Point coordinates for unit cell corner are 111

Crystallographic Directions I.

Example Problem I



ex:

pt. 1 $x_1 = 0,\ y_1 = 0,\ z_1 = 0$

pt. 2 $x_2 = a,\ y_2 = 0,\ z_2 = c/2$

$$\frac{a-0}{a} \quad \frac{0-0}{b} \quad \frac{c/2-0}{c}$$

Algorithm – determine direction indices

1. Determine coordinates of vector tail, pt. 1: x_1, y_1, & z_1; and vector head, pt. 2: x_2, y_2, & z_2.
2. Tail point coordinates subtracted from head point coordinates.
3. Normalize coordinate differences in terms of lattice parameters a, b, and c:

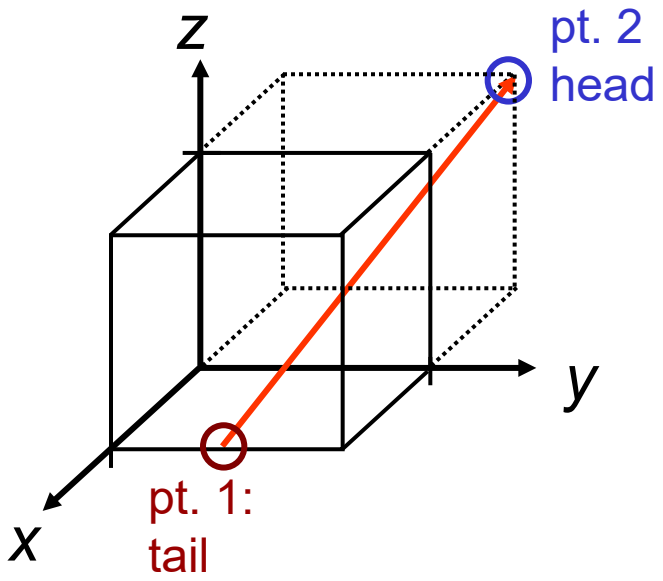
$$\frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}$$

4. Reduce to smallest integer values
5. Enclose indices in square brackets, no commas [*uvw*]

=> 1, 0, 1/2 => 2, 0, 1

=> [201]

Crystallographic Directions II: Example Problem 2



1. Point coordinates of tail and head

tail pt. 1 $x_1 = a$, $y_1 = b/2$, $z_1 = 0$

head pt. 2 $x_2 = -a$, $y_2 = b$, $z_2 = c$

2 & 3. Subtract and normalize

$$\frac{-a-a}{a} = -2; \quad \frac{b-b/2}{b} = 1/2; \quad \frac{c-0}{c} = 1$$

=> -2, 1/2, 1

4 & 5. Multiply by 2 to eliminate the fraction, then place in square brackets (no commas)

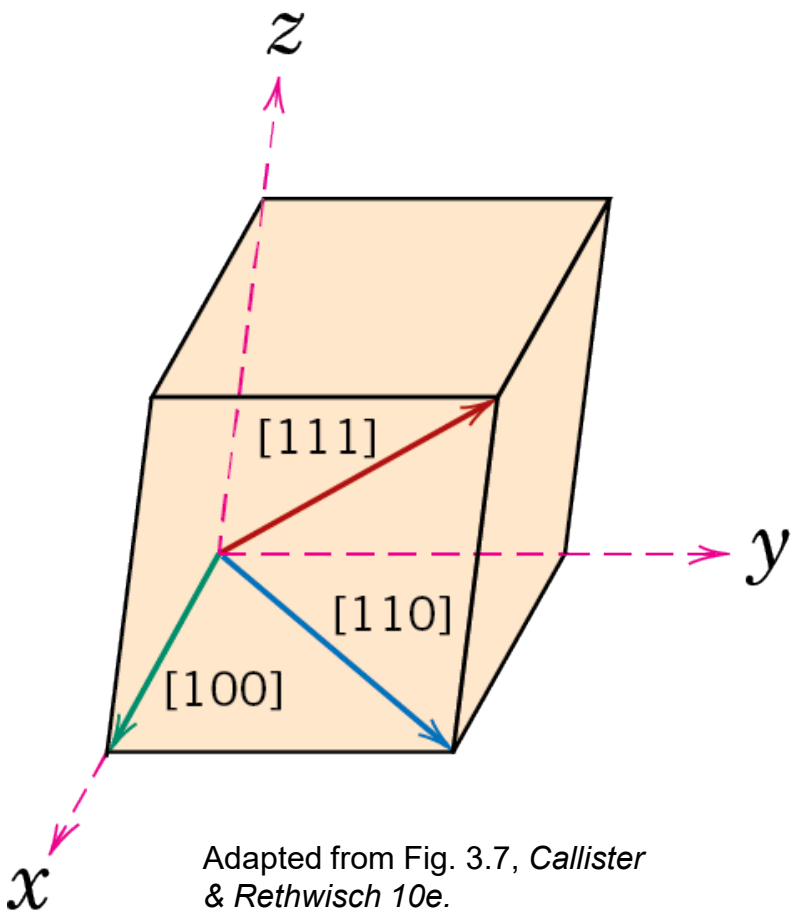
-4, 1, 2 => $[\bar{4}12]$

where the overbar represents a negative index

Family of directions – all directions that are crystallographically equivalent (have the same atomic spacing) – indicated by indices in angle brackets

Ex: <100> = [100], [010], [001], $[\bar{1}00]$, $[0\bar{1}0]$, $[00\bar{1}]$

Common Crystallographic Directions



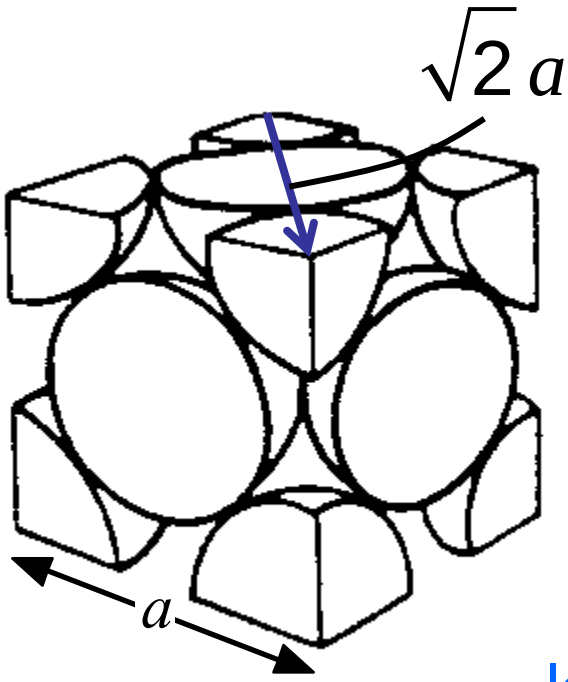
Adapted from Fig. 3.7, *Callister & Rethwisch 10e.*

Linear Density of Atoms (LD)

$$LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$

ex: linear density of Al in [110] direction

There are 2 half atoms and 1 full atom
= 2 atoms centered on vector



a = 0.405 nm

atoms

$$LD = \frac{2}{\sqrt{2}a} = \frac{2}{\sqrt{2}\,(0.405\ \text{nm})} = 3.5\ \text{nm}^{-1}$$

length

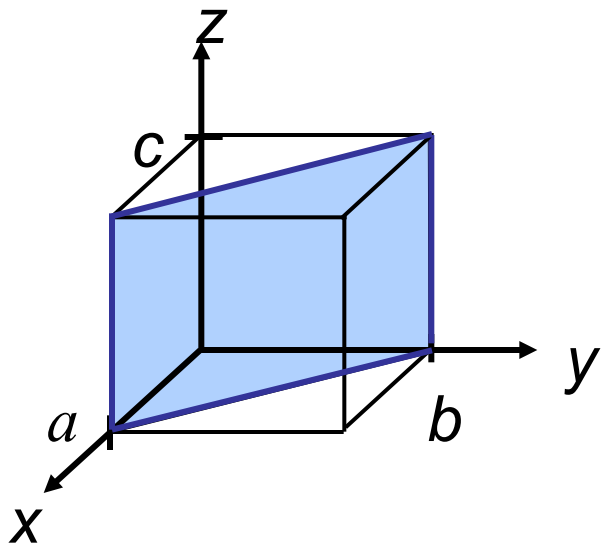
Crystallographic Planes

Algorithm for determining the Miller Indices of a plane

1. If plane passes through selected origin, establish a new origin in another unit cell
2. Read off values of intercepts of plane (designated *A*, *B*, *C*) with *x*, *y*, and *z* axes in terms of a, *b*, *c*
3. Take reciprocals of intercepts
4. Normalize reciprocals of intercepts by multiplying by lattice parameters a, *b*, and *c*
5. Reduce to smallest integer values
6. Enclose resulting Miller Indices in parentheses, no commas i.e., (*hkl*)

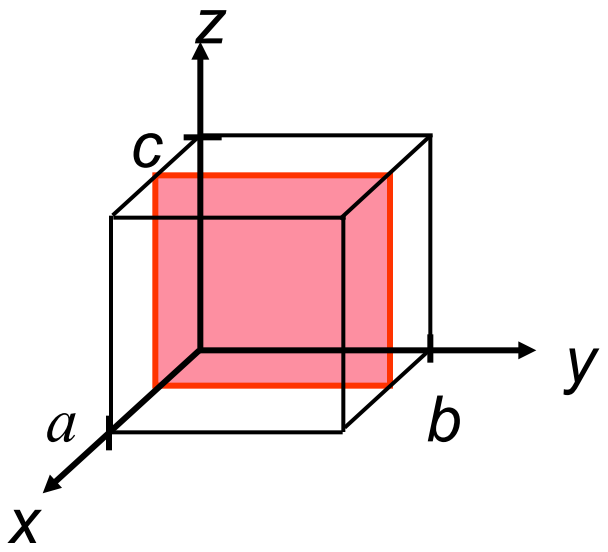
Example Problem I

		x	*y*	*z*
1.	Relocate origin – not needed			
2.	Intercepts	a	b	∞c
3.	Reciprocals	$1/a$	$1/b$	$1/\infty c$
4.	Normalize	a/a	b/b	$c/\infty c$
		1	1	0
5.	Reduction	1	1	0
6.	Miller Indices	(110)		



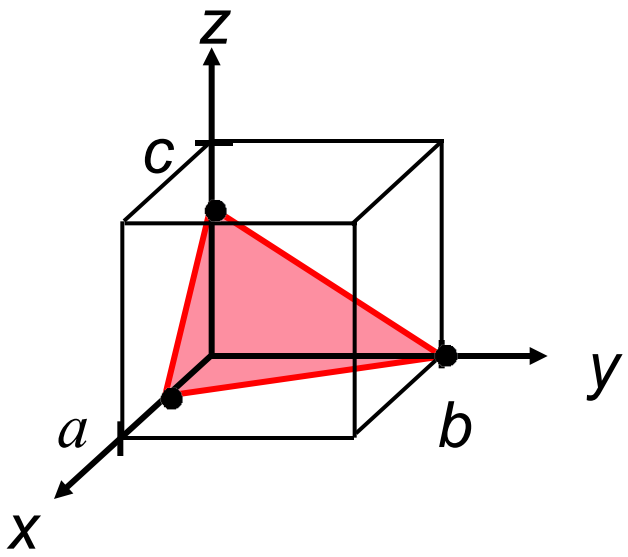
Example Problem II

		x	y	z
1.	Relocate origin – not needed			
2.	Intercepts	$a/2$	∞b	∞c
3.	Reciprocals	$2/a$	$1/\infty b$	$1/\infty c$
4.	Normalize	$2a/a$	$b/\infty b$	$c/\infty c$
		2	0	0
5.	Reduction	2	0	0
6.	Miller Indices	(200)		



Example Problem III

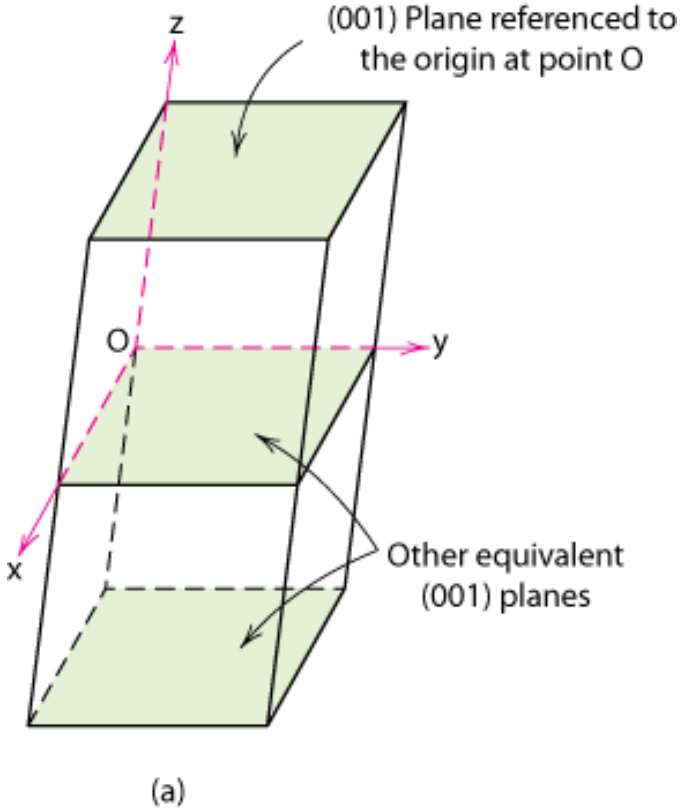
		x	*y*	*z*
1.	Relocate origin – not needed			
2.	Intercepts	$a/2$	b	$3c/4$
3.	Reciprocals	$2/a$	$1/b$	$4/3c$
4.	Normalize	$2a/a$	b/b	$4c/3c$
		2	1	4/3
5.	Reduction (x3)	6	3	4
6.	Miller Indices	(634)		

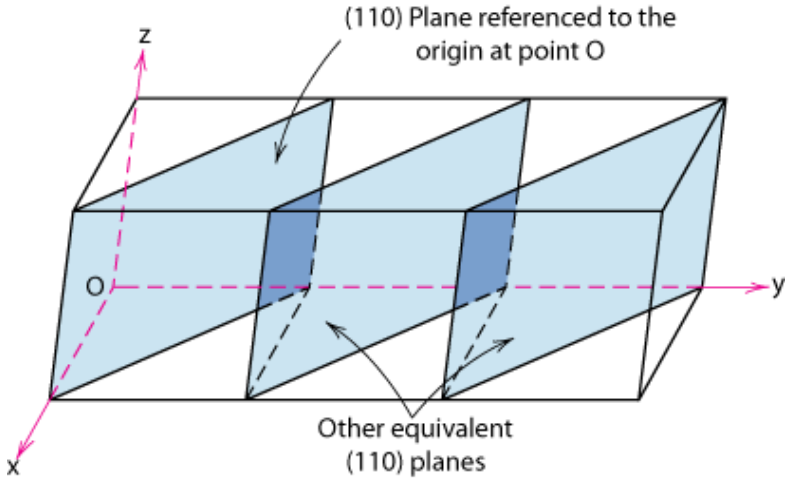


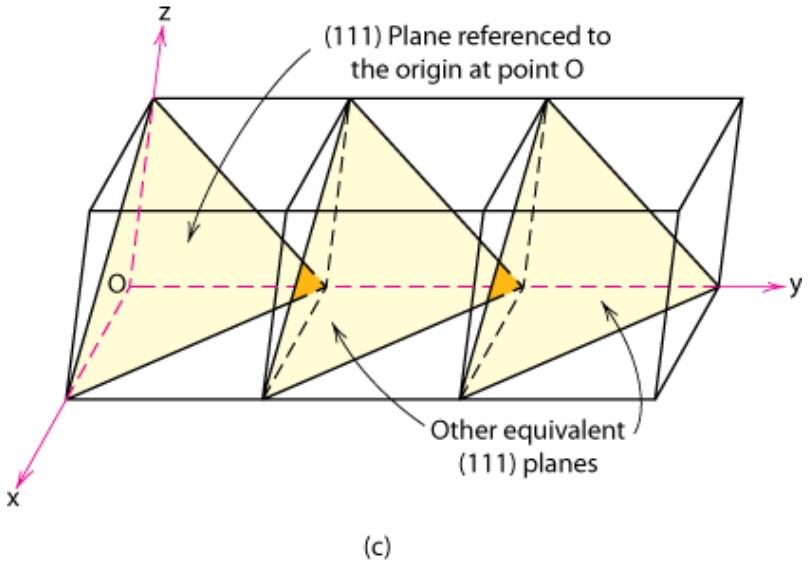
Family of planes – all planes that are crystallographically equivalent (have the same atomic packing) – indicated by indices in braces

Ex: {100} = (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$

Common Crystallographic Planes

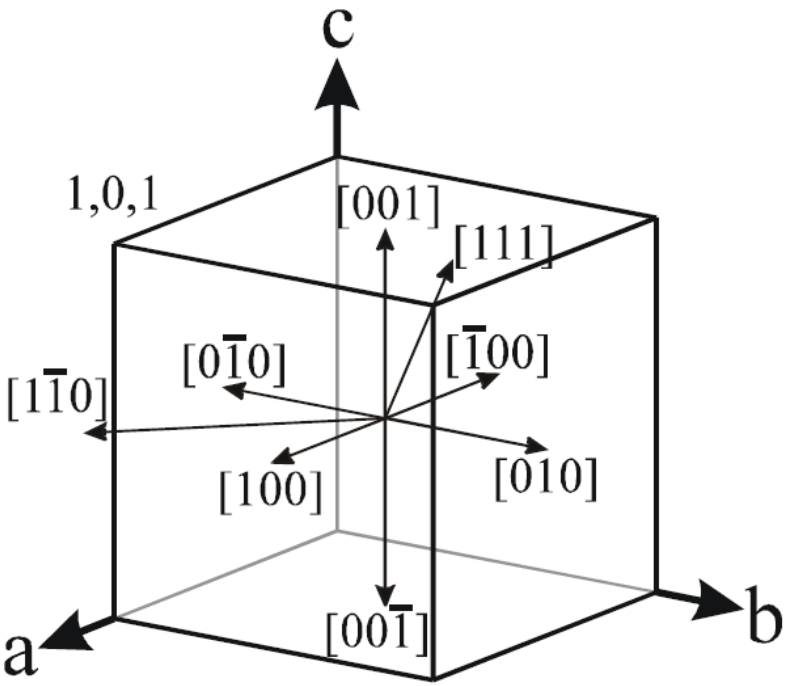


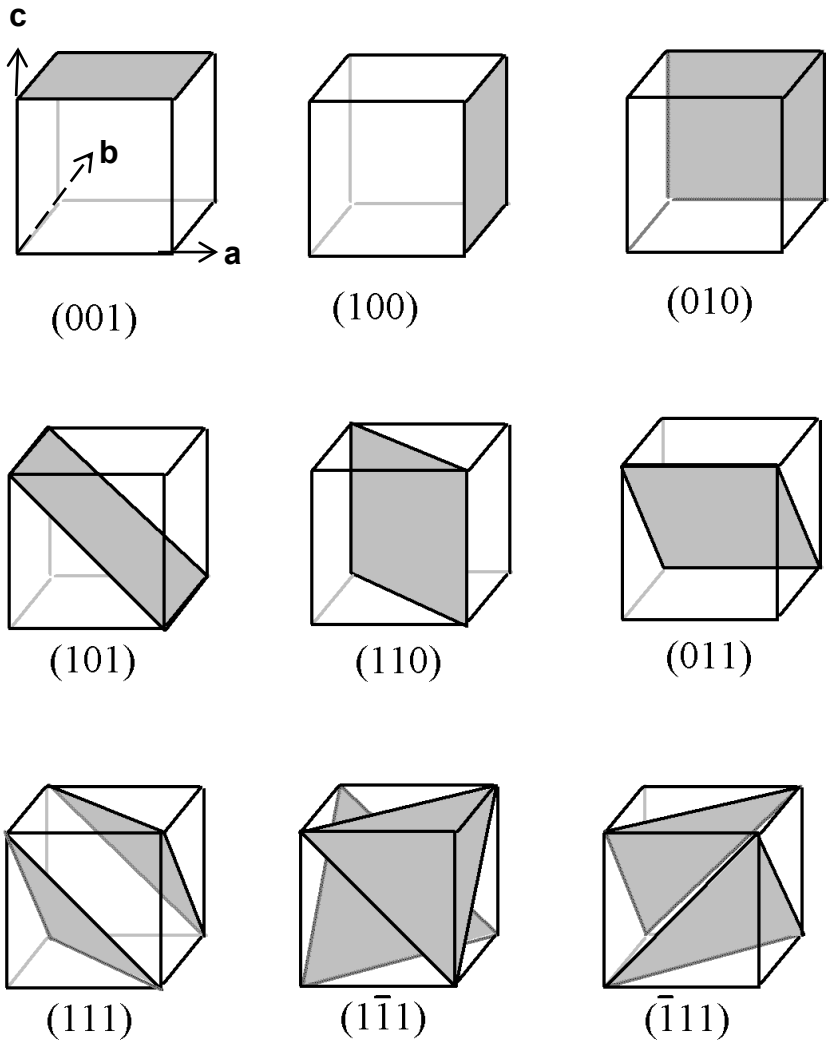




Adapted from Fig. 3.11,
Callister & Rethwisch 9e.

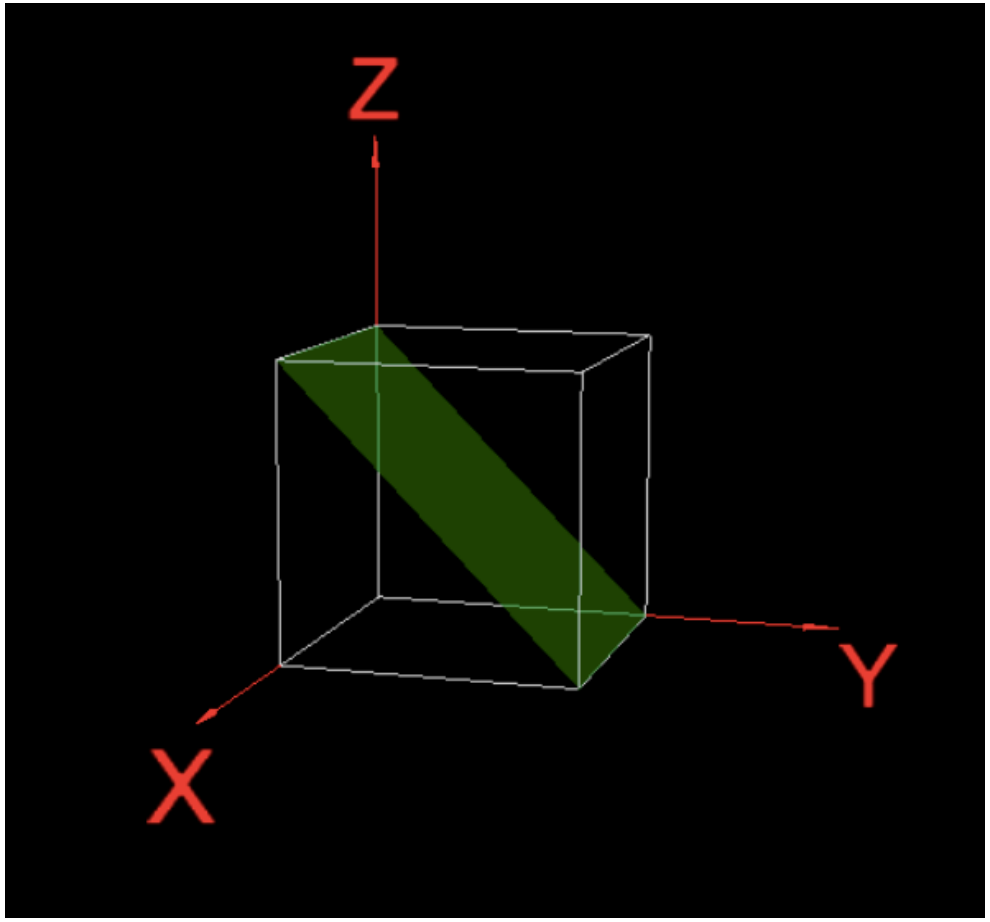
Miller indices





[uvw] is a crystal direction,
<uvw> is a family of directions
(hkl) is a crystal plane,
{hkl} is a family of planes.

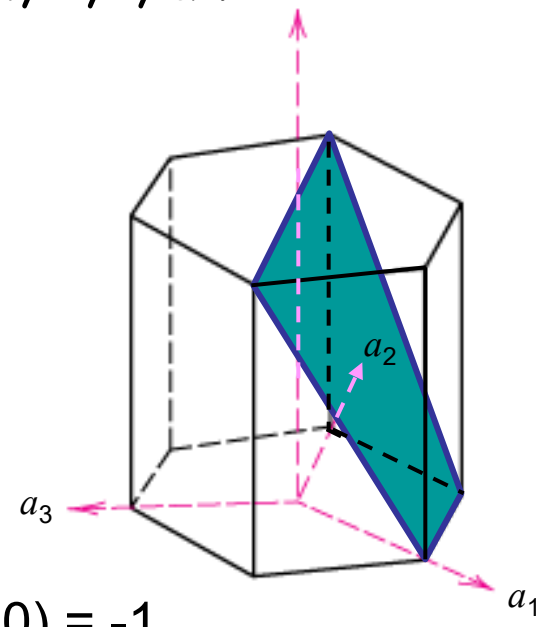
VMSE Screenshot – Crystallographic Planes



Additional practice on indexing crystallographic planes

Crystallographic Planes (HCP)

- For hexagonal unit cells a similar procedure is used
  - Determine the intercepts with the a_1, a_2, and z axes, then determine the Miller-Bravais Indices h, k, i, and l_z



example	a_1	a_2	c
1. Relocate origin – not needed			
2. Intercepts	a	∞a	c
3. Reciprocals	$1/a$	$1/\infty a$	$1/c$
4. Normalize	a/a	$a/\infty a$	c/c
	1	0	1
5. Reduction	$h = 1$	$k = 0$	$l = 1$

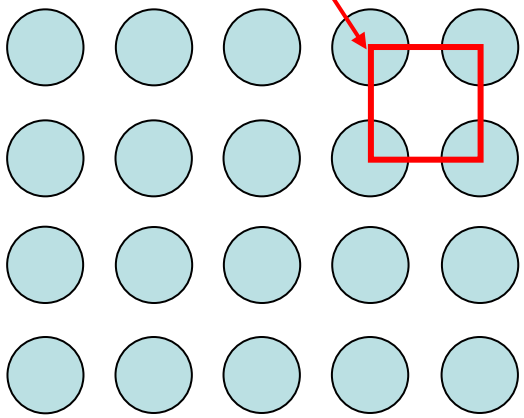
6. Determine index $i = -(h + k)$ $\quad i = -(1 + 0) = -1$
7. Miller-Bravais Indices $(10\bar{1}1)$

Planar Density of Atoms (PD)

$$\text{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$

ex: planar density of (100) plane of BCC Fe

2D repeat unit



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

There are 4 quarter atoms
= 1 atom centered on plane

$$a = \frac{4}{\sqrt{3}} R = \frac{4}{\sqrt{3}} (0.1241 \text{ nm}) = 0.287 \text{ nm}$$

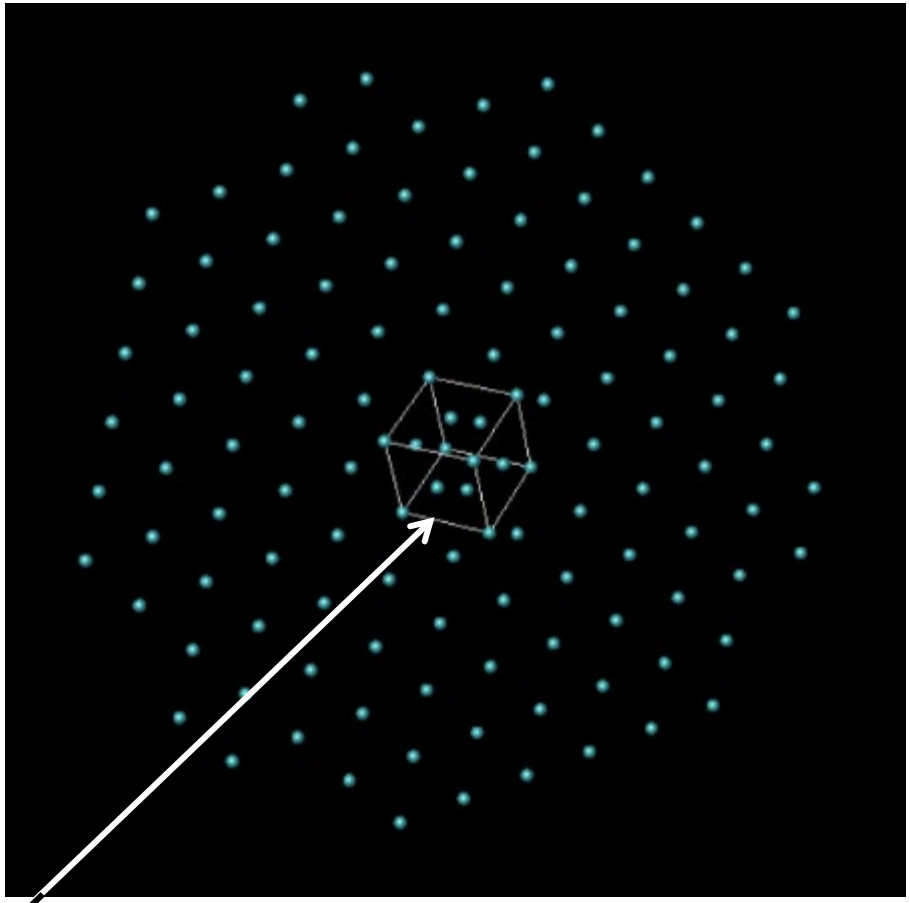
Radius of iron,
R = 0.1241 nm

atoms

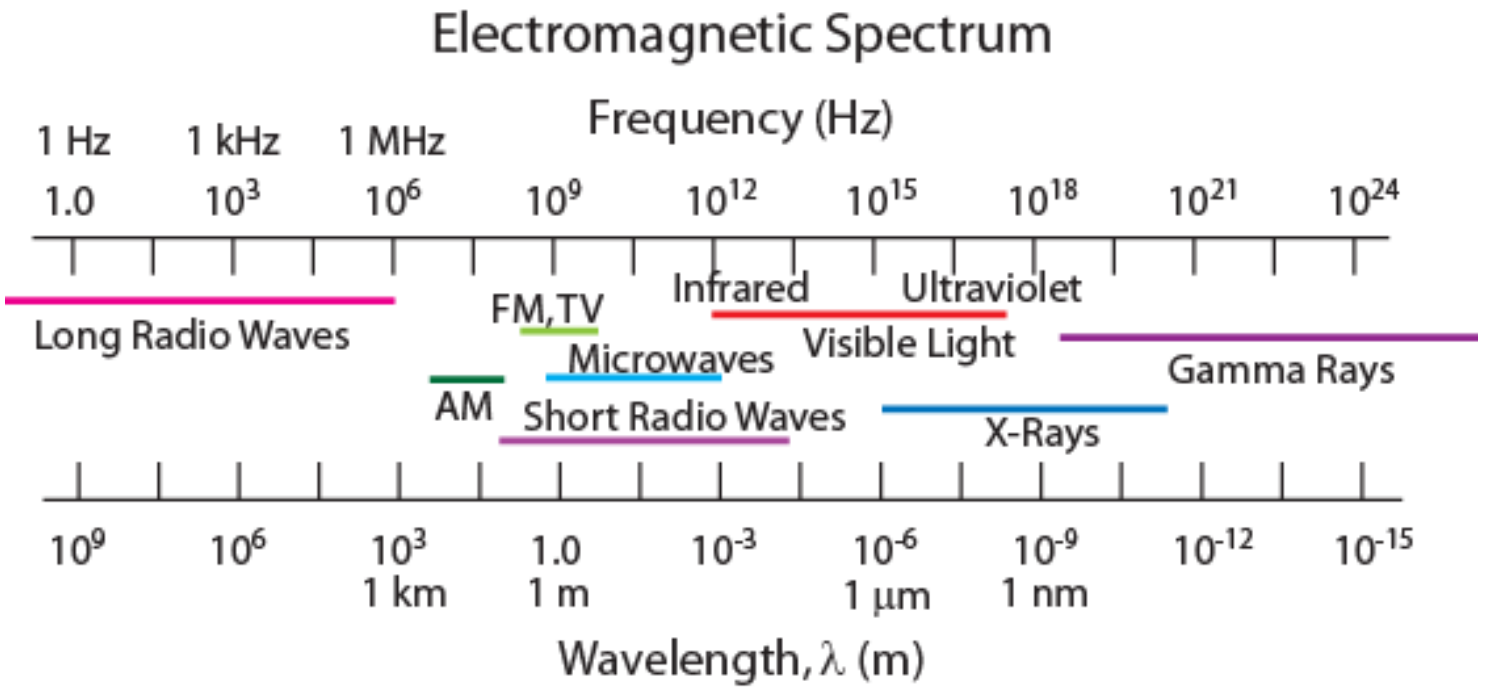
$$\text{PD} = \frac{1}{a^2} = \frac{1 \text{ atom}}{(0.287 \text{ nm})^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2}$$

area

VMSE Screenshot – Atomic Packing – (111) Plane for FCC



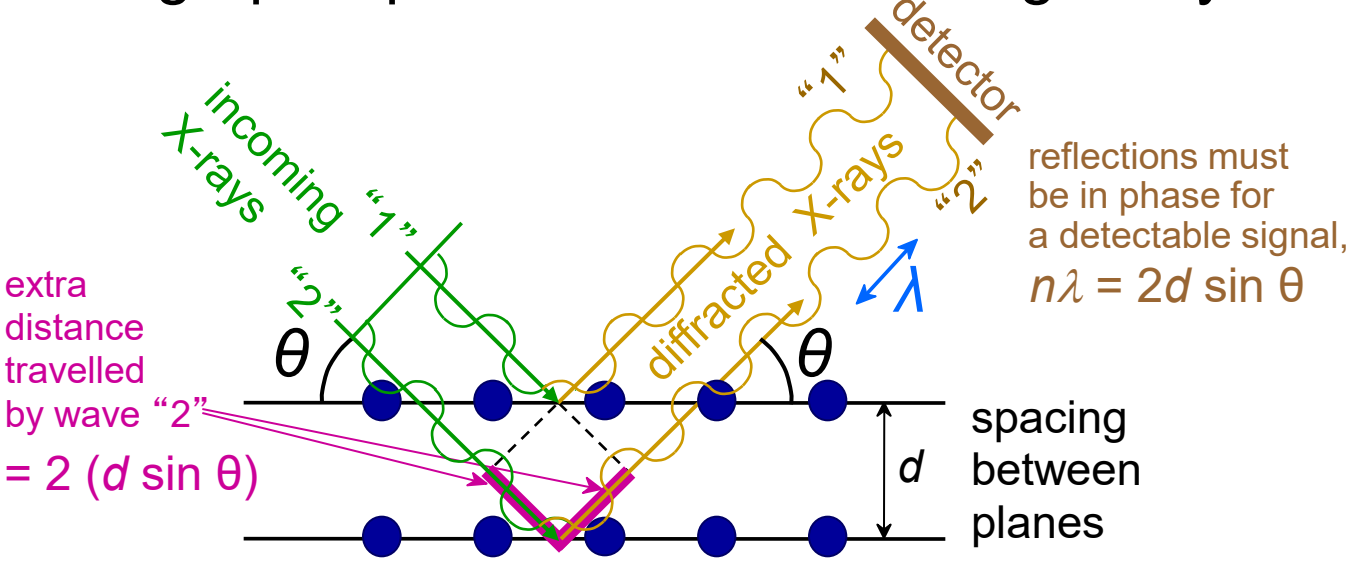
X-Ray Diffraction



- To diffract light, the diffraction grating spacing must be comparable to the light wavelength.
- X-rays are diffracted by planes of atoms.
- Interplanar spacing is the distance between parallel planes of atoms.

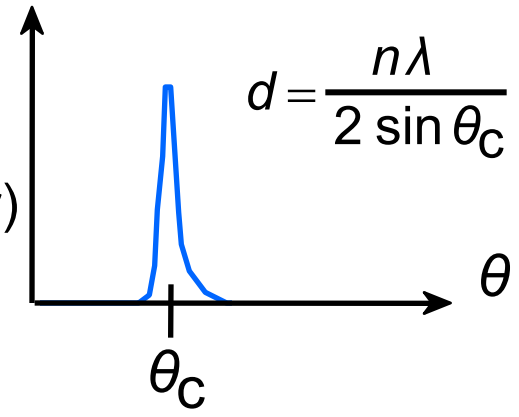
X-Rays to Determine Crystal Structure

- Crystallographic planes diffract incoming X-rays

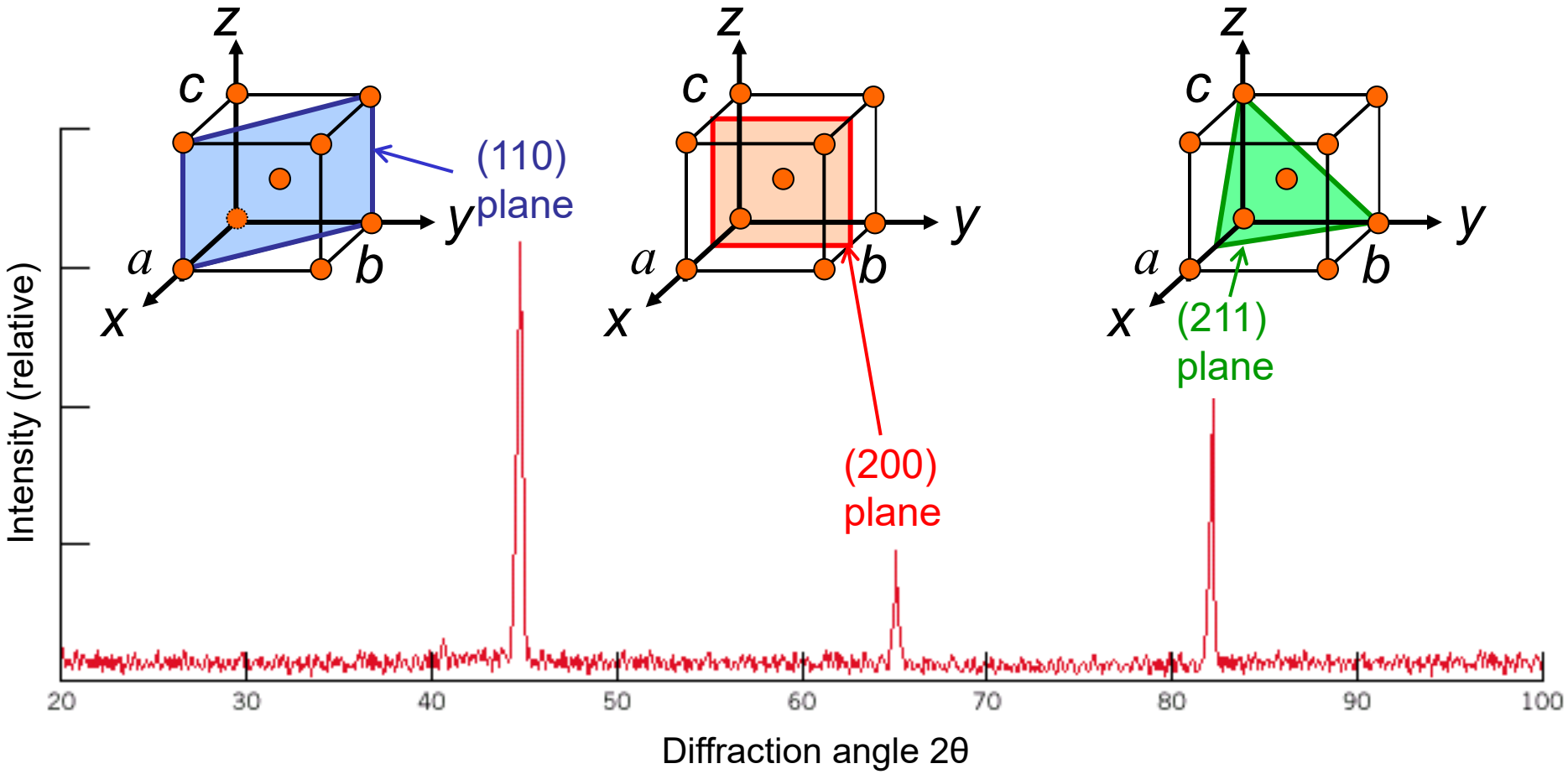


Measurement of diffraction angle, θ_c, allows computation of interplanar spacing, d.

Diffraction occurs when $\theta = \theta_c$



X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Summary

- Atoms may assemble into crystalline (ordered) or amorphous (disordered) structures.
- 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 calculate the theoretical density of a metal, given its crystal structure, atomic weight, and unit cell lattice parameters.
- Crystallographic points, directions and planes may be specified in terms of indexing schemes.
- Atomic and planar densities are related to crystallographic directions and planes, respectively.

Summary (continued)

- Materials can exist as single crystals or polycrystalline.
- For most single crystals, properties vary with crystallographic orientation (i.e., are anisotropic).
- For polycrystalline materials having randomly oriented grains, properties are independent of crystallographic orientation (i.e., they are isotropic).
- 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.