BONDING AND PROPERTIES

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Atomic Structure (Freshman Chem.)

- atom – electrons – 9.11×10^{-31} kg
  protons
  neutrons } 1.67×10^{-27} kg

- atomic number = # of protons in nucleus of atom
  = # of electrons of neutral species

- A [=] atomic mass unit = amu = 1/12 mass of ^{12}C

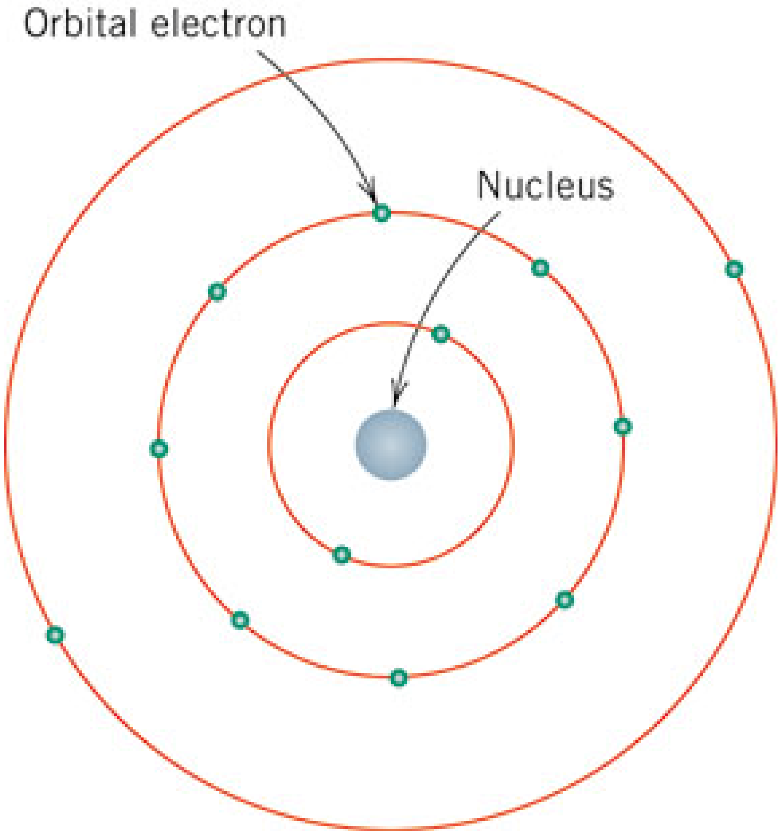
  Atomic wt = wt of 6.023×10^{23} molecules or atoms

  1 amu/atom = 1g/mol

  C 12.011
  H 1.008 etc.

Atomic Structure

- Valence electrons determine all of the following properties
    1) Chemical
    2) Electrical
    3) Thermal
    4) Optical



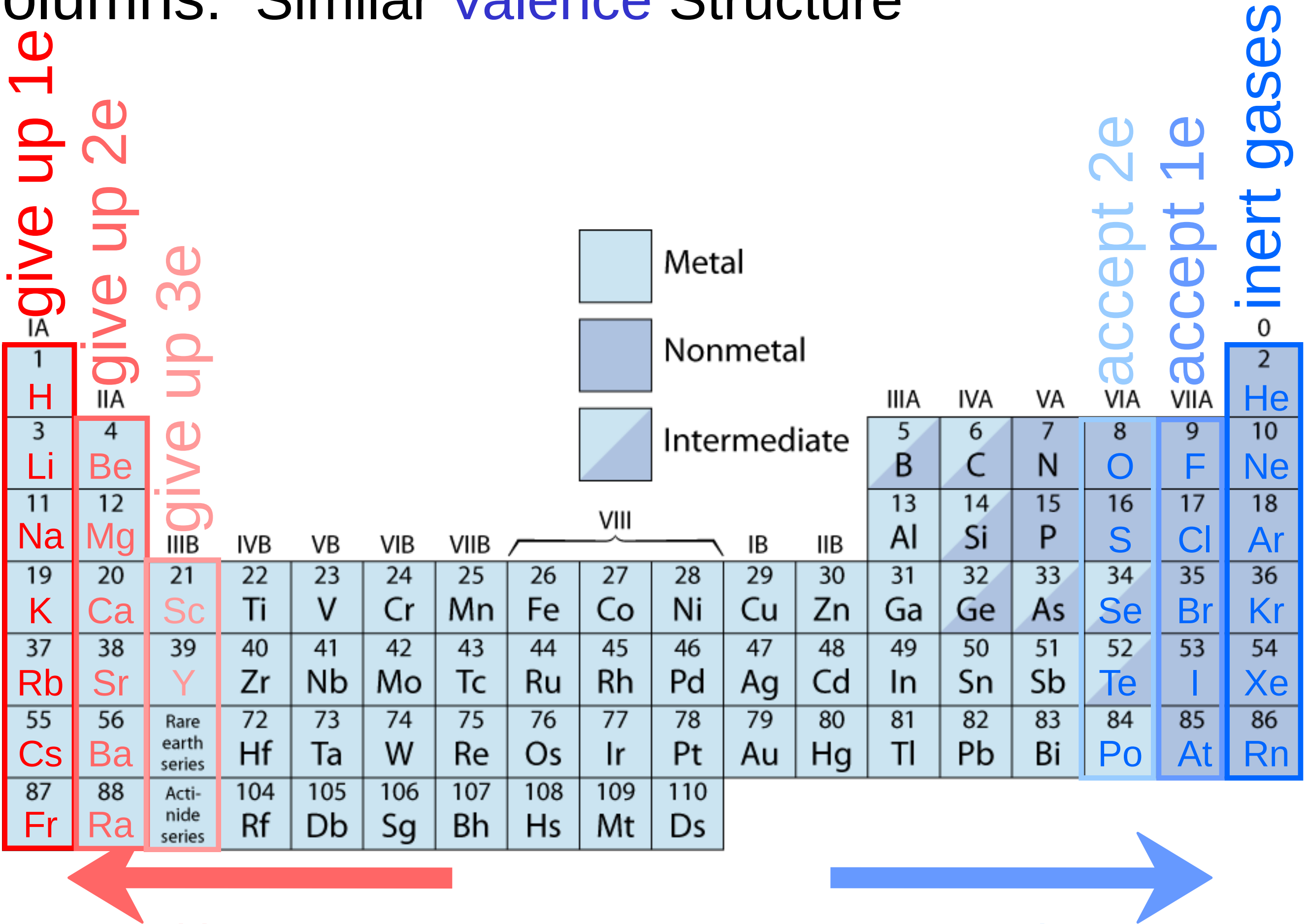
Electron Configurations

- Valence electrons – those in unfilled shells
- Filled shells more stable
- Valence electrons are most available for bonding and tend to control the chemical properties
  - example: C (atomic number = 6)

$$1s^2 \ \underbrace{\boxed{2s^2\ 2p^2}}_{\boxed{\text{valence electrons}}}$$

The Periodic Table

- Columns: Similar Valence Structure



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	Rare earth series	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	Acti-nide series	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds								

Adapted from Fig. 2.6, *Callister 7e.*

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

Electronegative elements:
Readily acquire electrons
to become - ions.

Ionic bond – metal + nonmetal

metal: donates electrons

nonmetal: accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$

[Ne] $3s^2$

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

Mg^{2+} $1s^2\ 2s^2\ 2p^6$

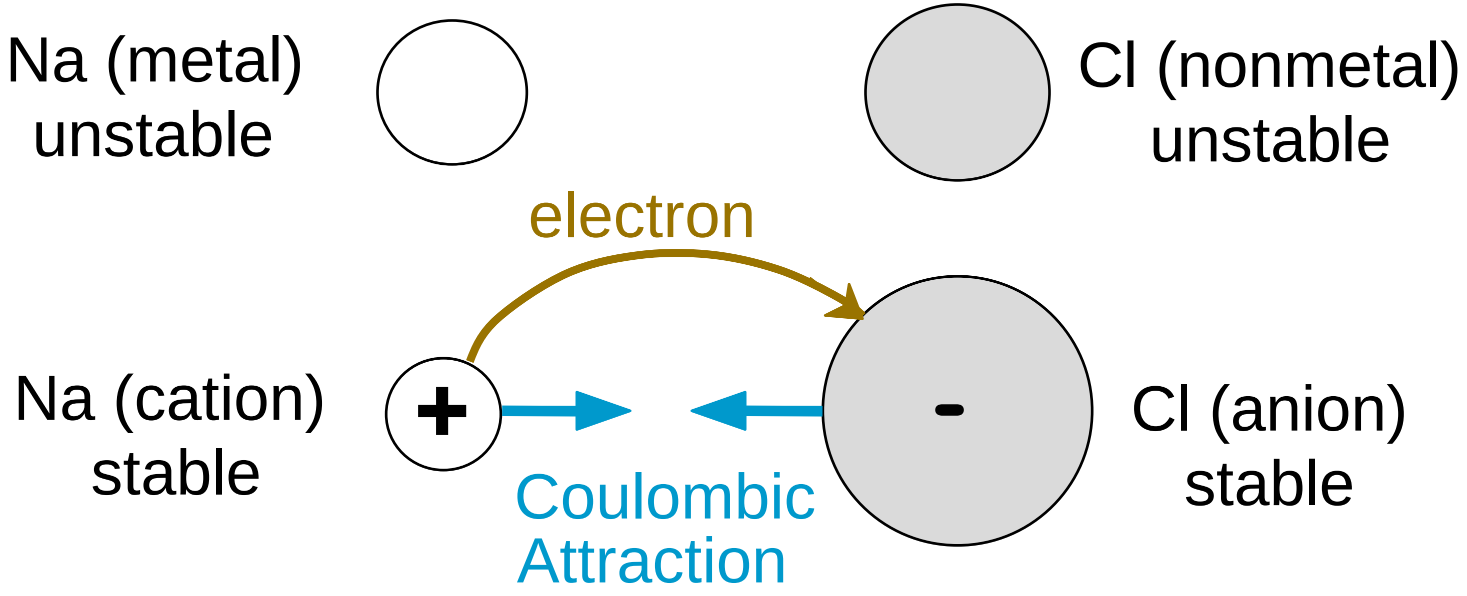
[Ne]

O^{2-} $1s^2\ 2s^2\ 2p^6$

[Ne]

Ionic Bonding

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



Na (metal)
unstable

Cl (nonmetal)
unstable

electron

Na (cation)
stable

+

-

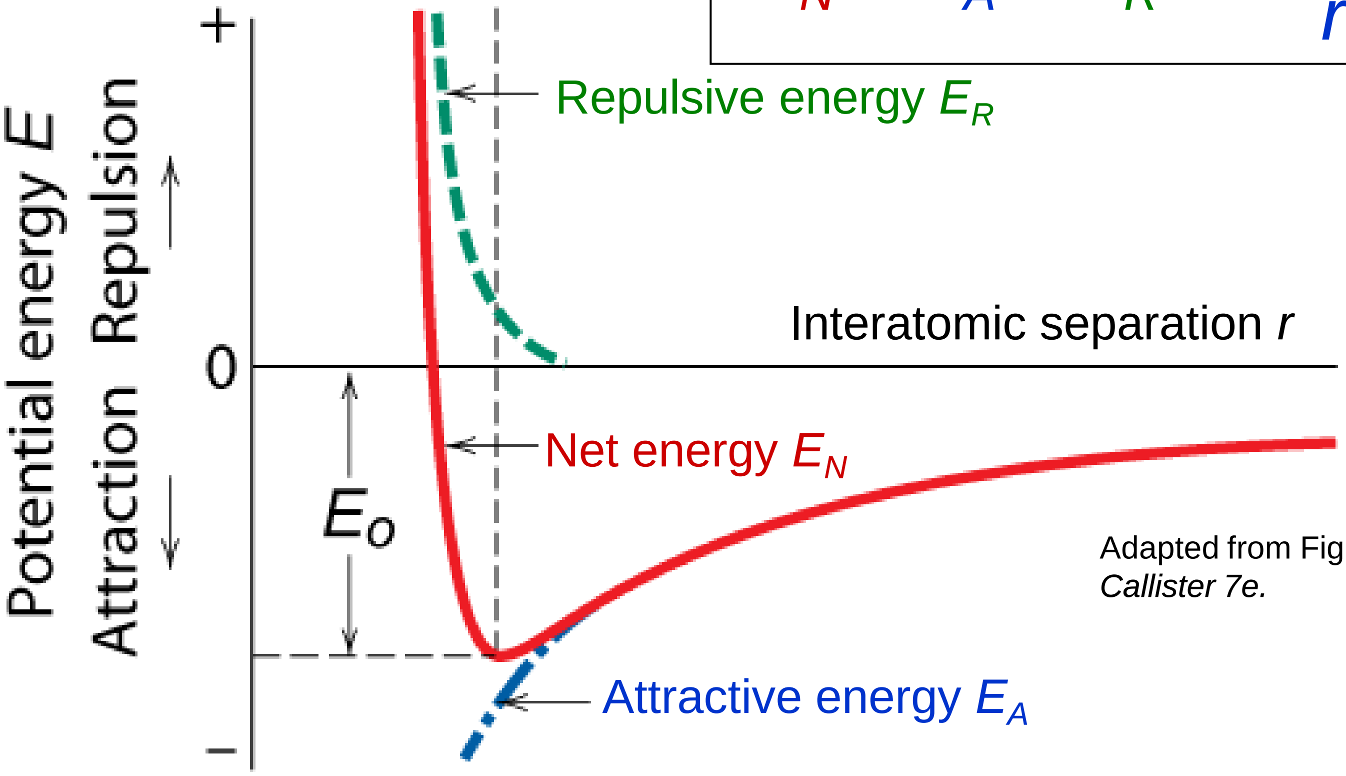
Cl (anion)
stable

Coulombic
Attraction

Ionic Bonding

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

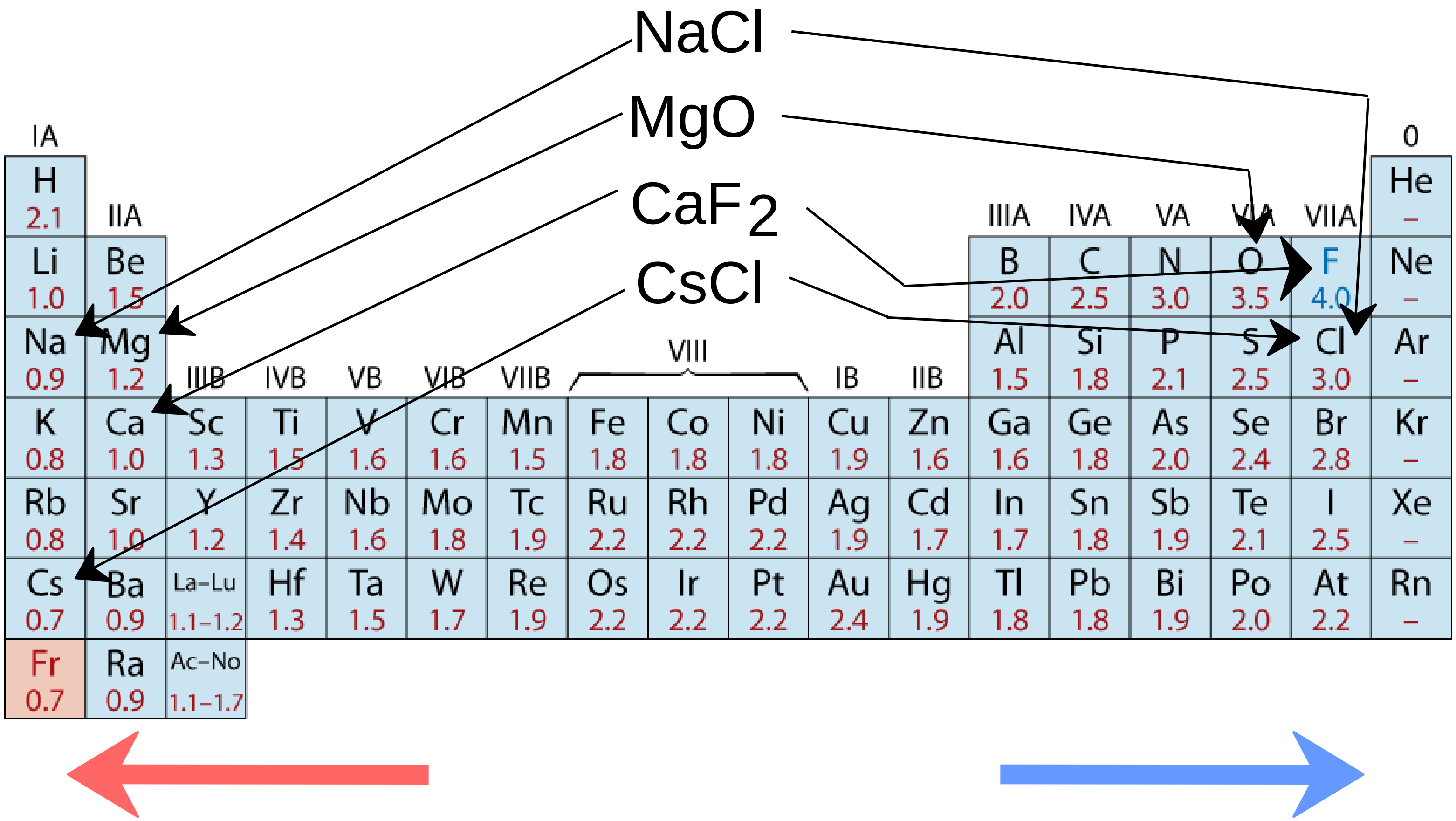
$$E_N = E_A + E_R = -\frac{A}{r} - \frac{B}{r^n}$$



Adapted from Fig. 2.8(b), *Callister 7e.*

Examples: Ionic Bonding

- Predominant bonding in Ceramics



NaCl

MgO

CaF_2

CsCl

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Give up electrons

Acquire electrons

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.

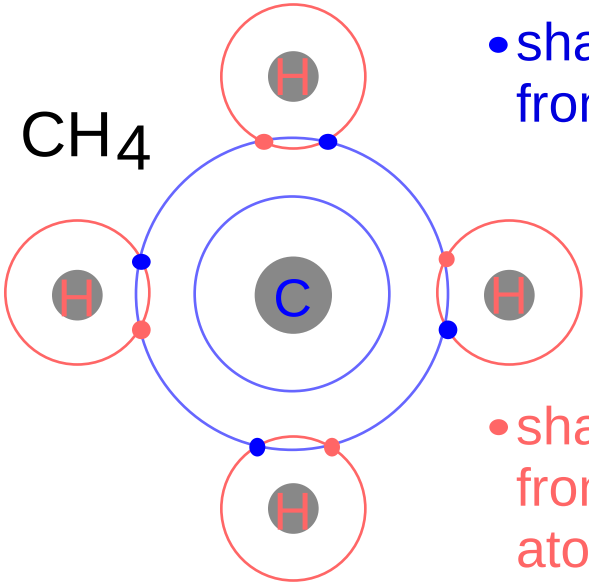
Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: CH_4

C: has 4 valence e^-,
needs 4 more

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

Electronegativities
are comparable.



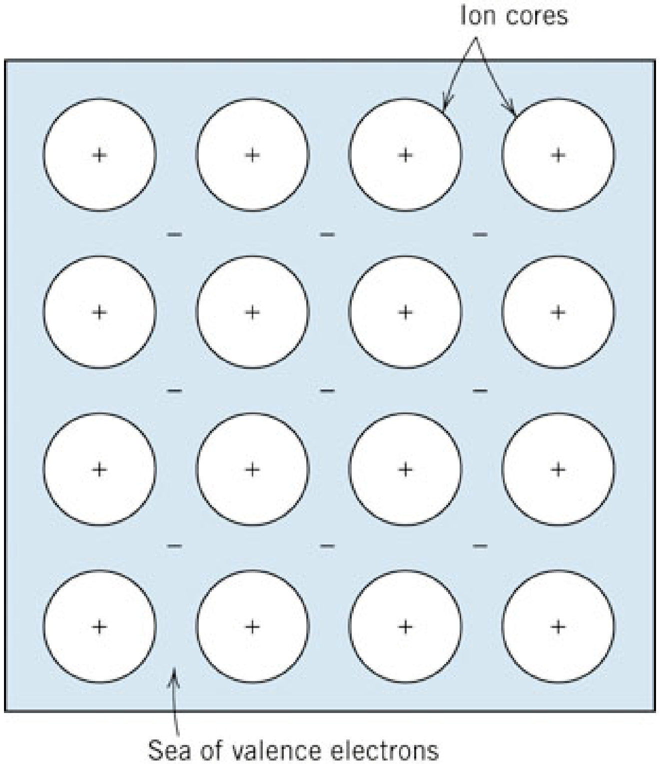
● shared electrons from carbon atom

● shared electrons from hydrogen atoms

Adapted from Fig. 2.10, *Callister 7e.*

Metallic Bonding

- Occurs between Metallic elements
- Ion Cores (+) surrounded by delocalized electrons (-)
- High electrical and thermal conductivity from “free electrons”



Adapted from Fig. 2.11, *Callister 7e.*

Primary Bonding

- Metallic Bond -- delocalized as electron cloud

- Ionic-Covalent Mixed Bonding

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

where X_A & X_B are Pauling electronegativities

Ex: MgO

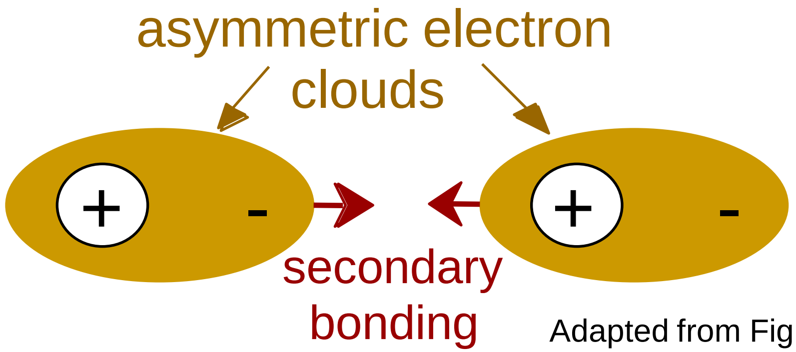
$X_{Mg} = 1.3$
$X_O = 3.5$

$$\% \text{ ionic character} = \left(1 - e^{-\frac{(3.5 - 1.3)^2}{4}}\right) \text{x} \, (100\%) = 70.2\% \text{ ionic}$$

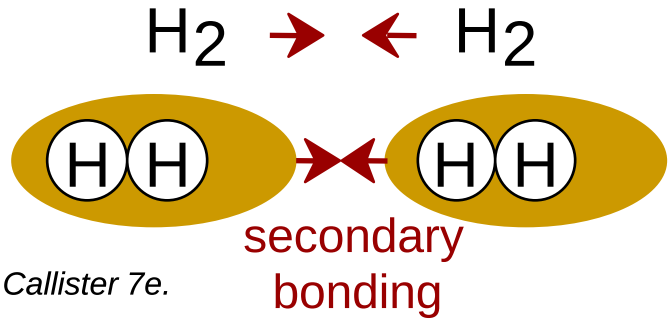
SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles



ex: liquid H_2



Adapted from Fig. 2.13, *Callister 7e.*

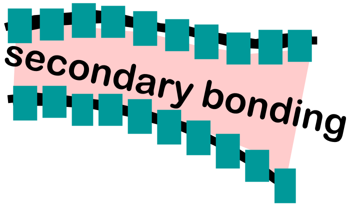
- Permanent dipoles-molecule induced

-general case:

Adapted from Fig. 2.14, *Callister 7e.*

-ex: liquid HCl

-ex: polymer



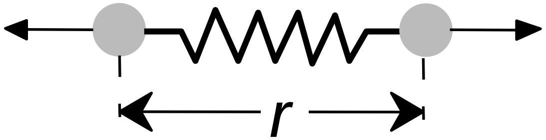
secondary bonding

Summary: Bonding

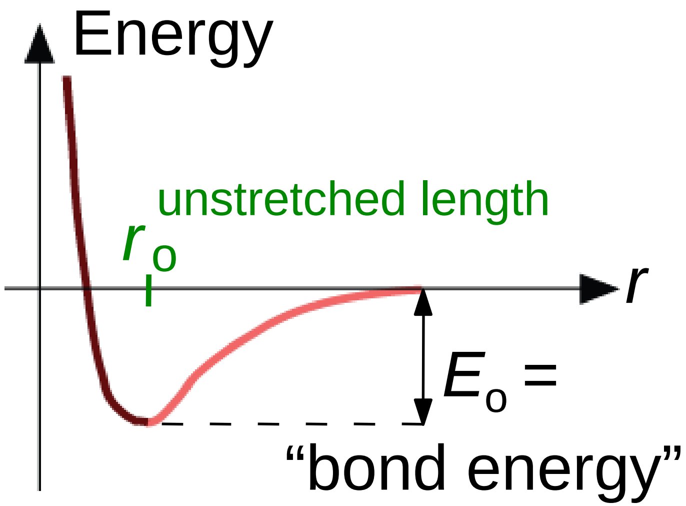
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Properties From Bonding: T_m

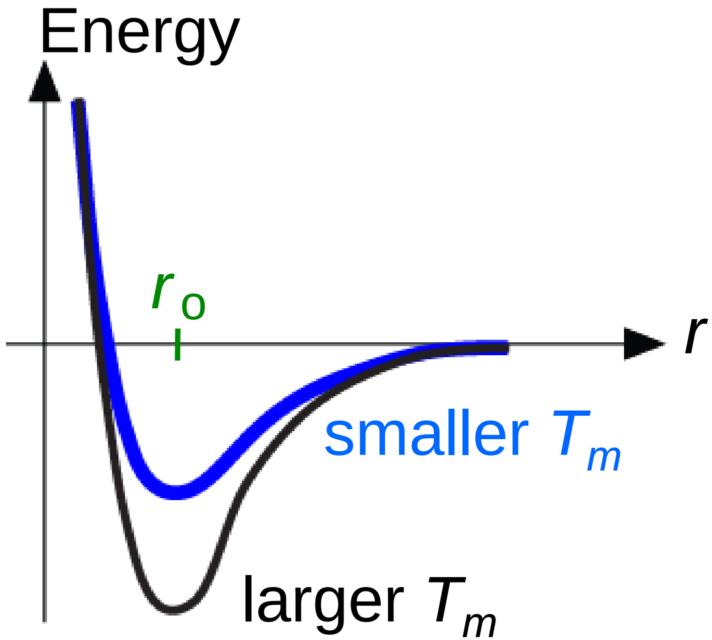
- Bond length, r



- Bond energy, E_o



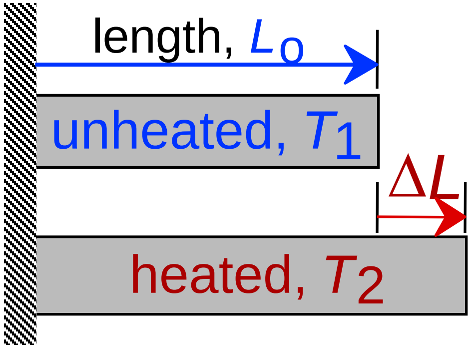
- Melting Temperature, T_m



T_m is larger if E_o is larger.

Properties From Bonding : α

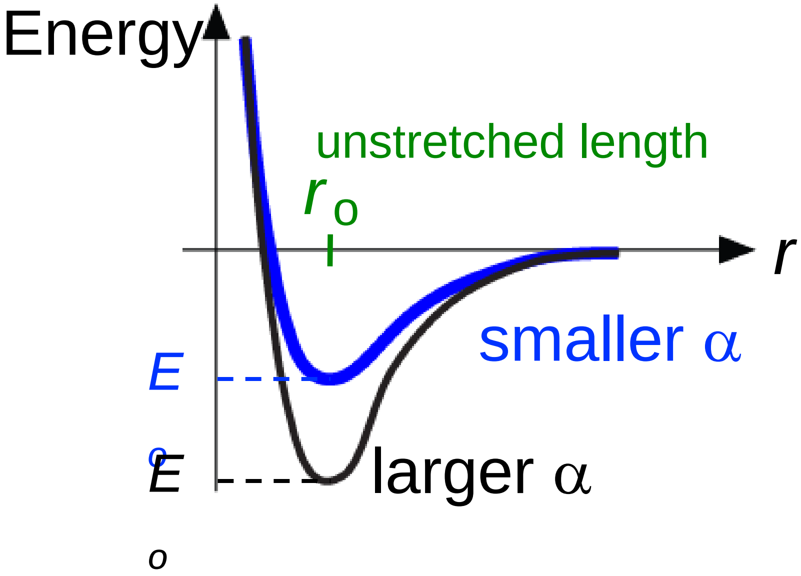
- Coefficient of thermal expansion, α



coeff. thermal expansion

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

- α ~ symmetry at r_o



α is larger if E_o is smaller.

Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m

large E

small α

Metals

(Metallic bonding):

Variable bond energy

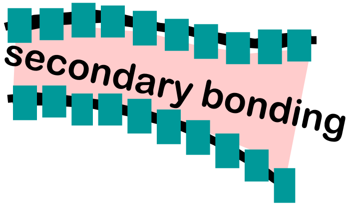
moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m

small E

large α

The Structure of Crystalline Solids

ISSUES TO ADDRESS...

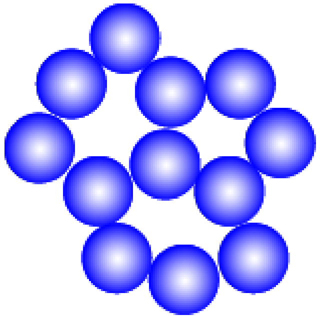
- How do atoms assemble into solid structures? (for now, focus on metals)

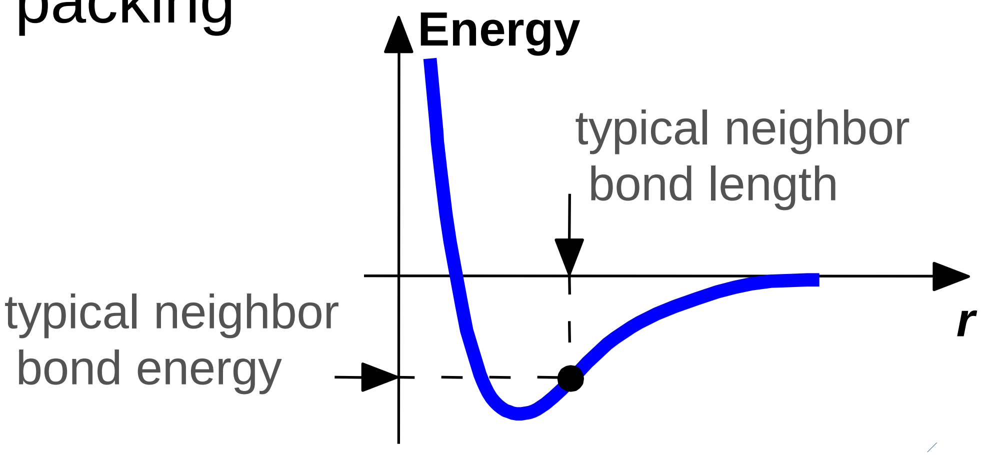
- How does the density of a material depend on its structure?

- When do material properties vary with the sample (i.e., part) orientation?

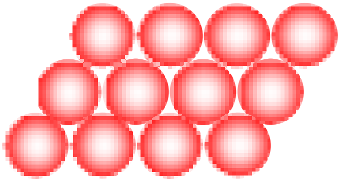
Energy and Packing

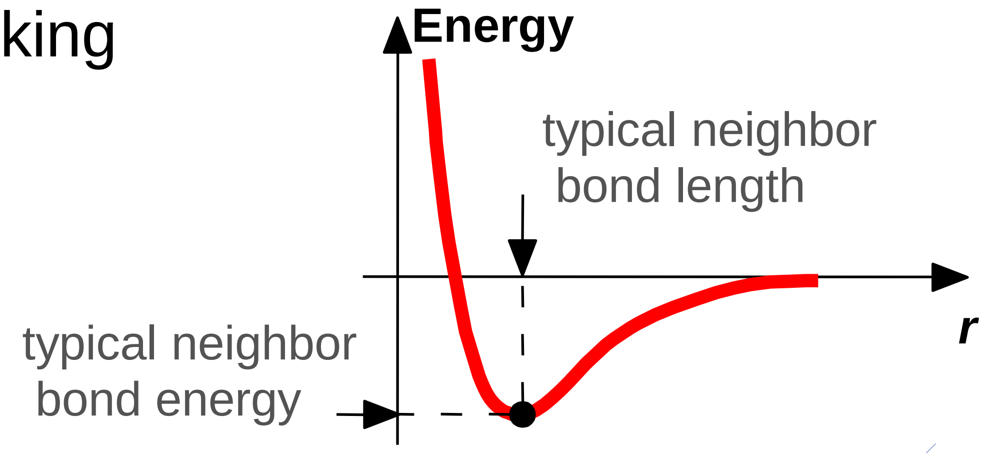
- Non dense, random packing





- Dense, ordered packing





Dense, ordered packed structures tend to have lower energies.

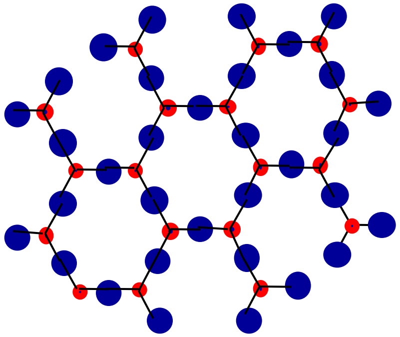
Materials and Packing

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals

  -many ceramics

  -some polymers



crystalline SiO_2

Adapted from Fig. 3.22(a), *Callister 7e.*

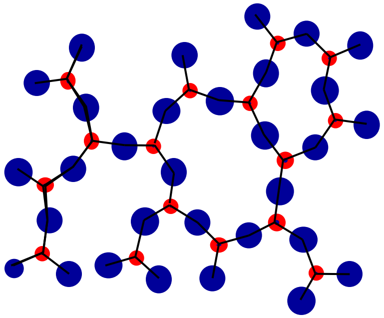
• Si **● Oxygen**

Noncrystalline materials...

- atoms have no periodic packing
- occurs for: -complex structures

  -rapid cooling

"Amorphous" = Noncrystalline



noncrystalline SiO_2

Adapted from Fig. 3.22(b), *Callister 7e.*

Crystal Systems

Unit cell: smallest repetitive volume which contains the complete lattice pattern of a crystal.

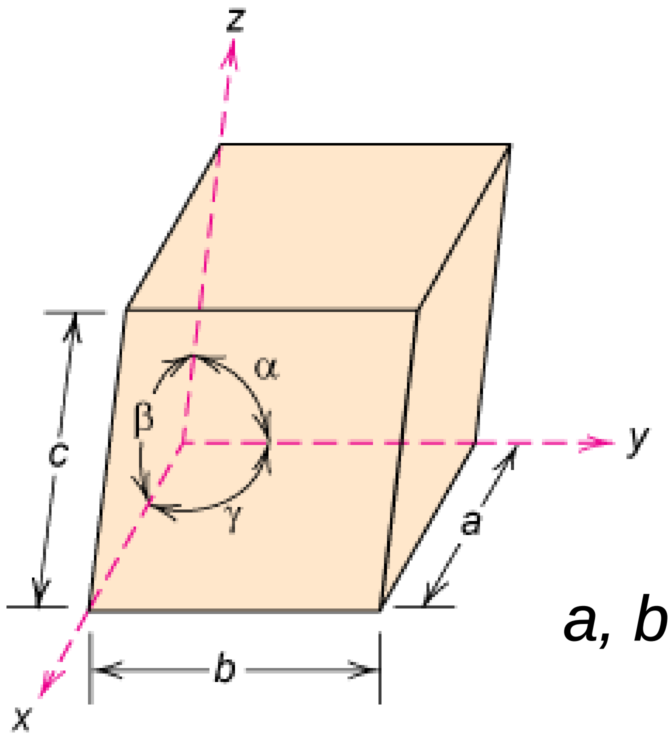


Fig. 3.4, *Callister 7e.*

7 crystal systems

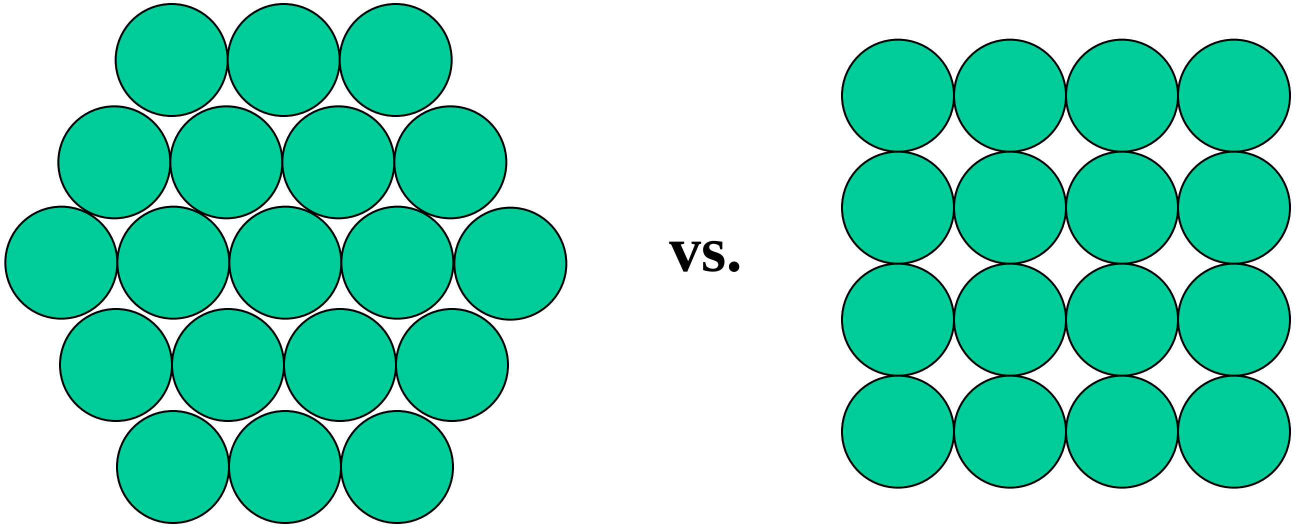
14 crystal lattices

a, *b*, and *c* are the lattice constants

Metallic Crystal Structures

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

2-dimensions



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

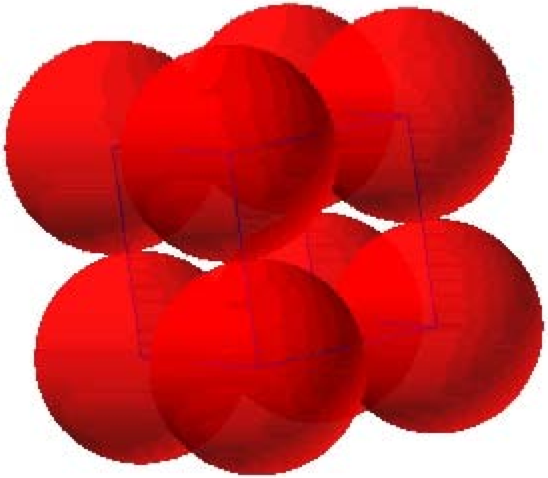
Metallic Crystal Structures

- Tend to be densely packed.
- Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - 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...

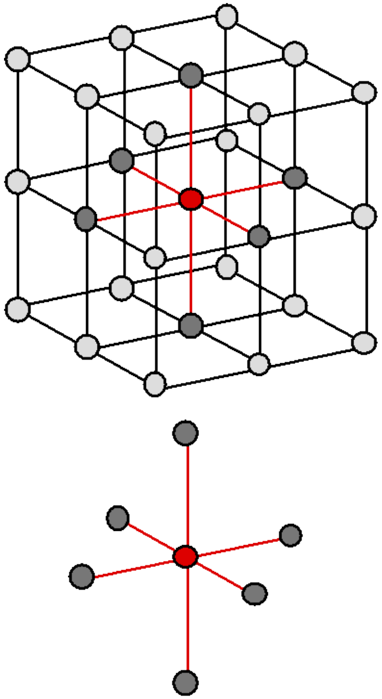
Simple Cubic Structure (SC)

- Rare due to low packing denisty (only Po has this structure)
- Close-packed directions are cube edges.



(Courtesy P.M. Anderson)

- Coordination # = 6
  (# nearest neighbors)

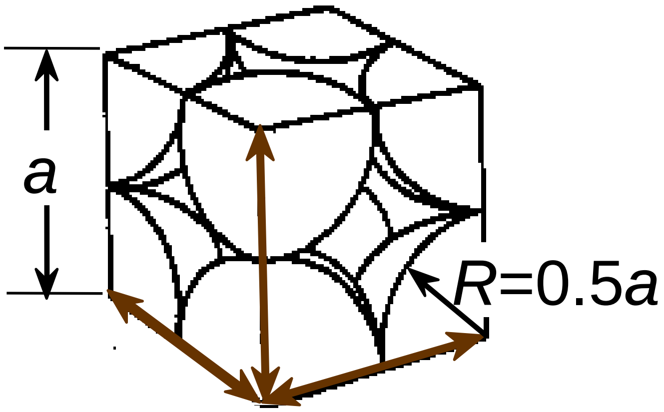


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.23, *Callister 7e.*

$$\frac{\text{atoms}}{\text{unit cell}} \qquad \frac{\text{volume}}{\text{atom}}$$

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

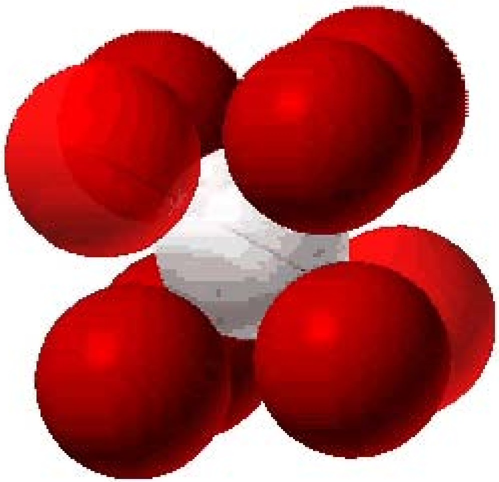
$$\frac{\text{volume}}{\text{unit cell}}$$

Body Centered Cubic Structure (BCC)

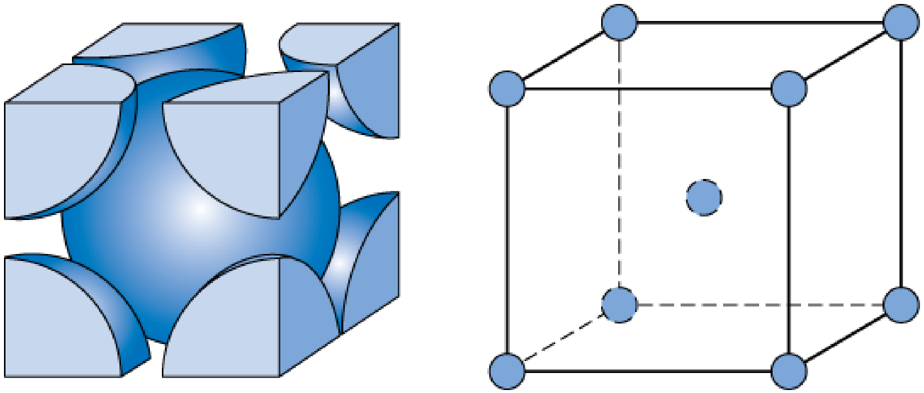
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8



(Courtesy P.M. Anderson)

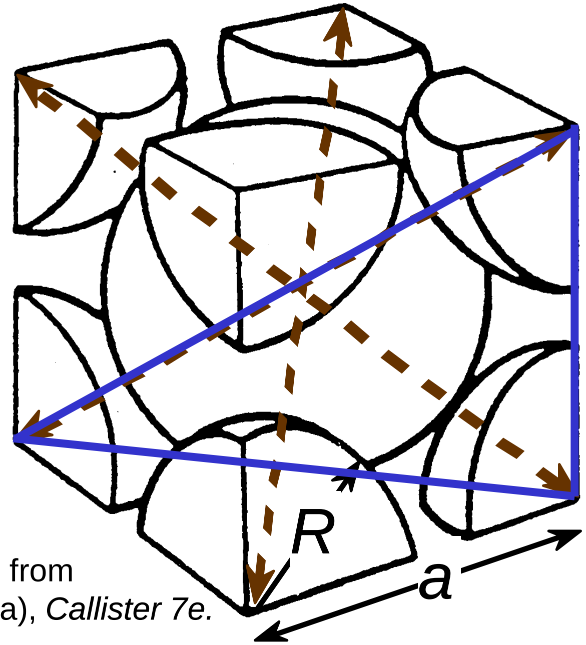


Adapted from Fig. 3.2, *Callister 7e.*

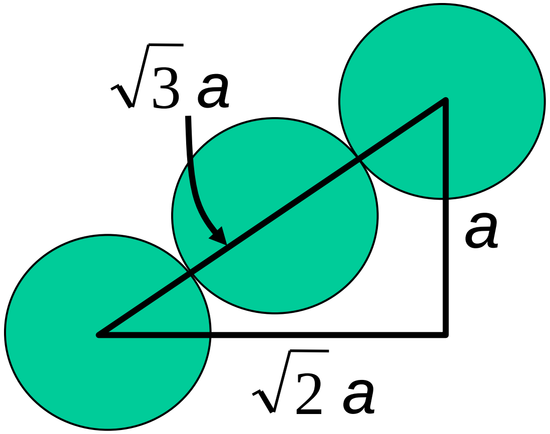
2 atoms/unit cell: 1 center + 8 corners x 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Adapted from
Fig. 3.2(a), *Callister 7e.*



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

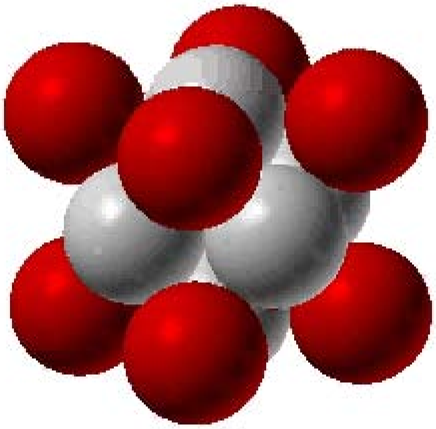
$$\text{APF} = \frac{\overset{\frac{\text{atoms}}{\text{unit cell}}}{2}\;\overset{\frac{\text{volume}}{\text{atom}}}{\frac{4}{3}\pi(\sqrt{3}a/4)^3}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{a^3}}$$

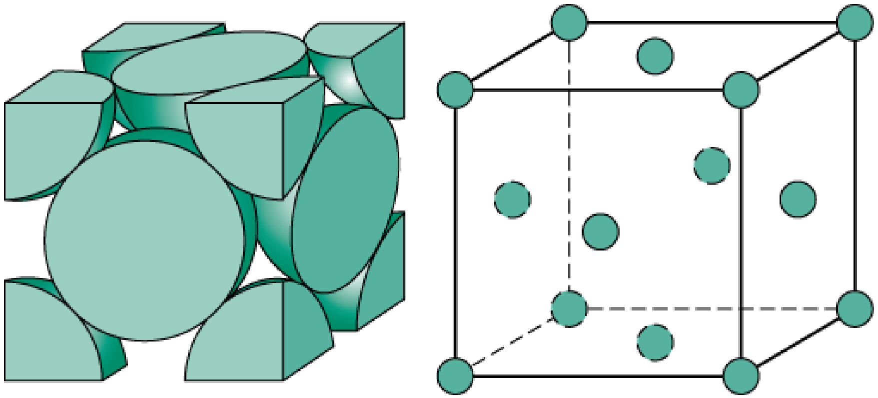
Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.
  - --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

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

- Coordination # = 12





Adapted from Fig. 3.1, *Callister 7e.*

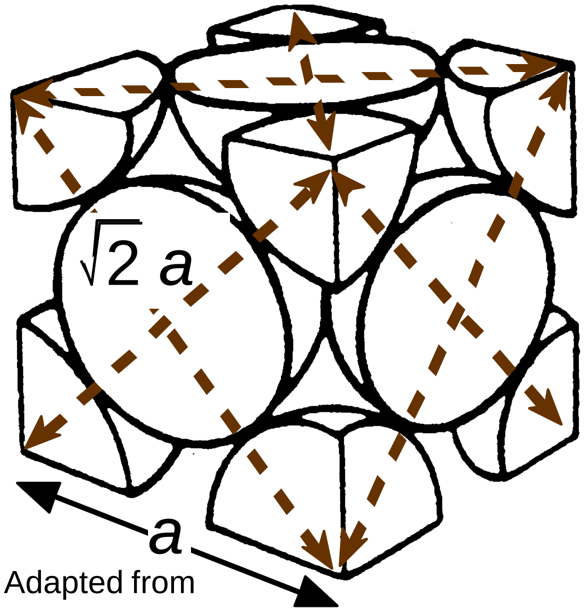
4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

(Courtesy P.M. Anderson)

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74

maximum achievable APF



Adapted from Fig. 3.1(a), *Callister 7e.*

Close-packed directions:

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

Unit cell contains:

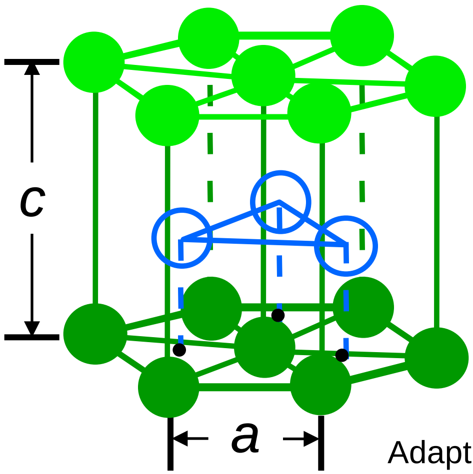
$6 \times 1/2 + 8 \times 1/8$

= 4 atoms/unit cell

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

Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



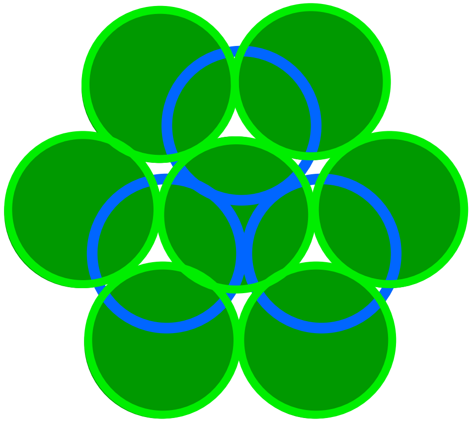
A sites

B sites

A sites

Adapted from Fig. 3.3(a), *Callister 7e.*

- 2D Projection



Top layer

Middle layer

Bottom layer

- 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

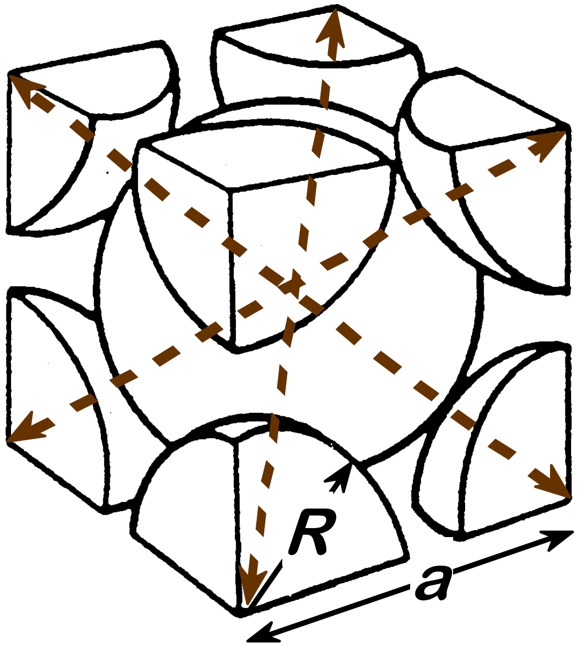
A = atomic weight

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

$$\rho = \frac{2 \quad 52.00}{a^3 \quad 6.023 \times 10^{23}}$$

$\frac{\text{atoms}}{\text{unit cell}}$ → 2

$\frac{\text{g}}{\text{mol}}$ → 52.00

$\frac{\text{volume}}{\text{unit cell}}$ → a^3

$\frac{\text{atoms}}{\text{mol}}$ → 6.023×10^{23}

$\rho_{\text{theoretical}}$	$= 7.18$ g/cm^3
ρ_{actual}	$= 7.19$ g/cm^3

Densities of Material Classes

In general

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

Why?

Metals have...

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

Ceramics have...

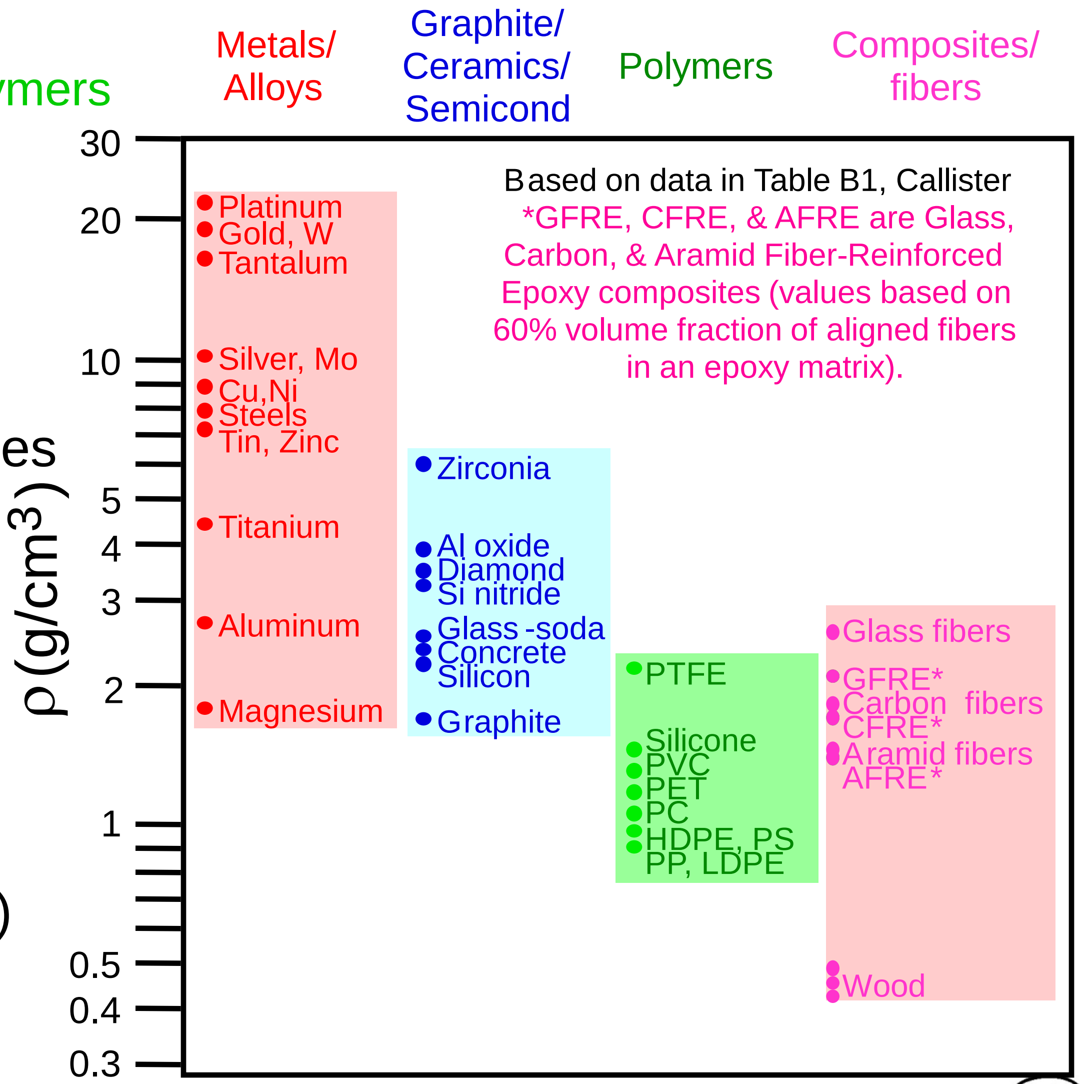
- less dense packing
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values



Based on data in Table B1, Callister

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

Data from Table B1, *Callister 7e.*

Crystals as Building Blocks

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

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

Fig. 8.33(c), *Callister 7e.* (Fig. 8.33(c) courtesy of Pratt and Whitney).

- Properties of crystalline materials often related to crystal structure.
  - --Ex: Quartz fractures more easily along some crystal planes than others.

(Courtesy P.M. Anderson)

Polycrystals

- *Most* engineering materials are polycrystals.

Anisotropic

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

Isotropic

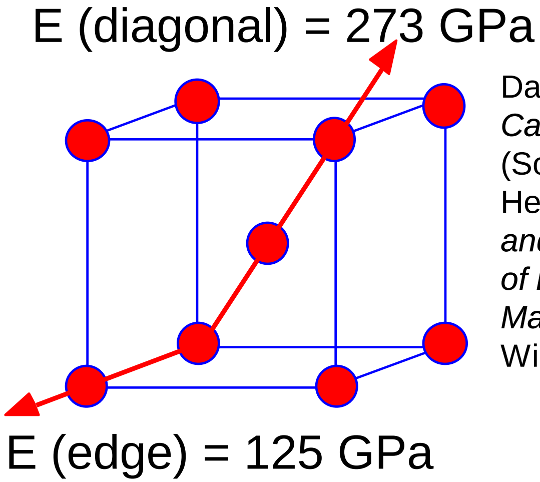
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented,
  overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm
  (i.e., from a few to millions of atomic layers).

Single vs Polycrystals

- Single Crystals

  -Properties vary with direction: anisotropic.

  -Example: the modulus of elasticity (E) in BCC iron:



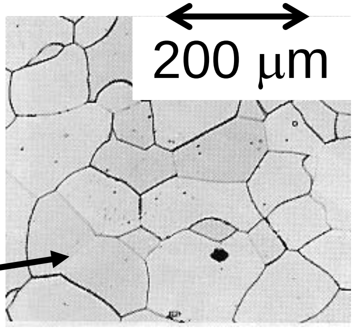
Data from Table 3.3, *Callister 7e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

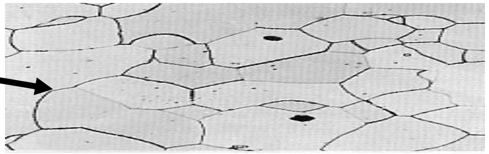
- Polycrystals

  -Properties may/may not vary with direction.

  -If grains are randomly oriented: isotropic. ($E_{\text{poly iron}}$ = 210 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].)

Polymorphism

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

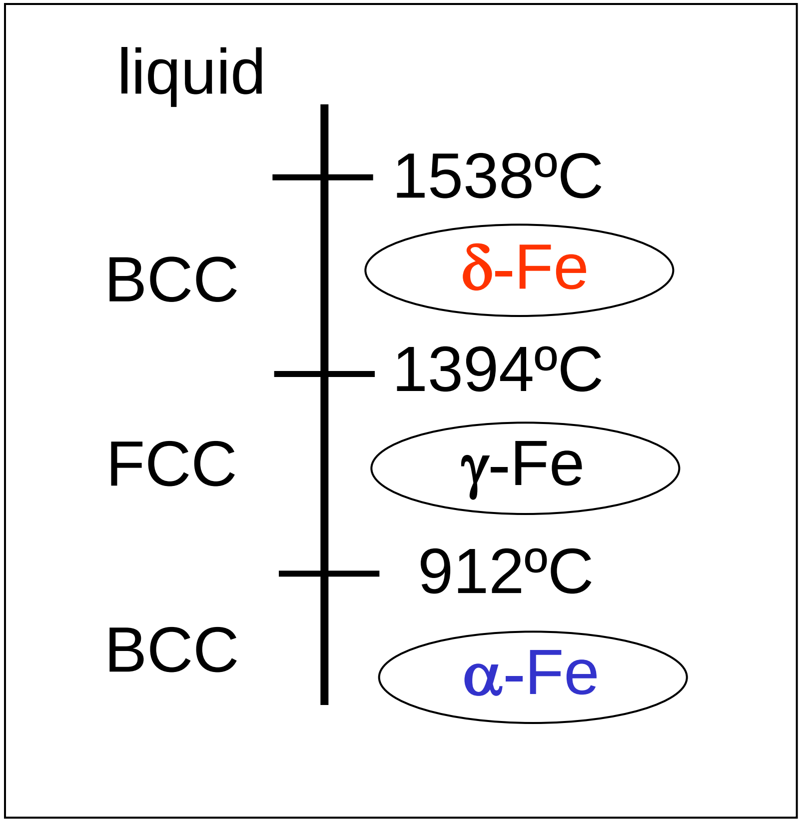
titanium

carbon

α, β-Ti

diamond, graphite

iron system



liquid

1538^{o}C

BCC δ-Fe

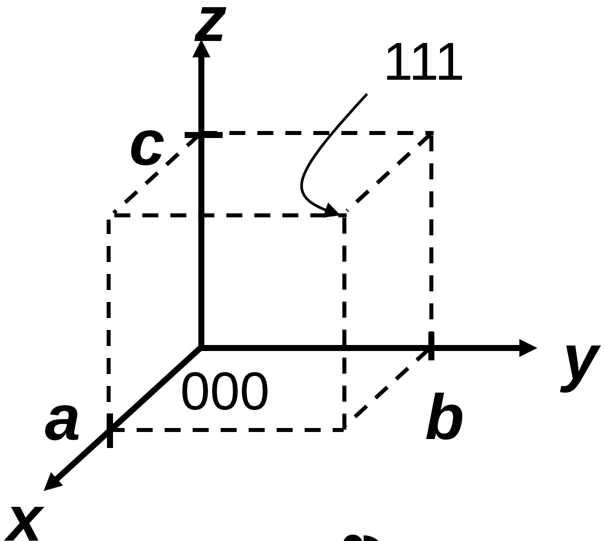
1394^{o}C

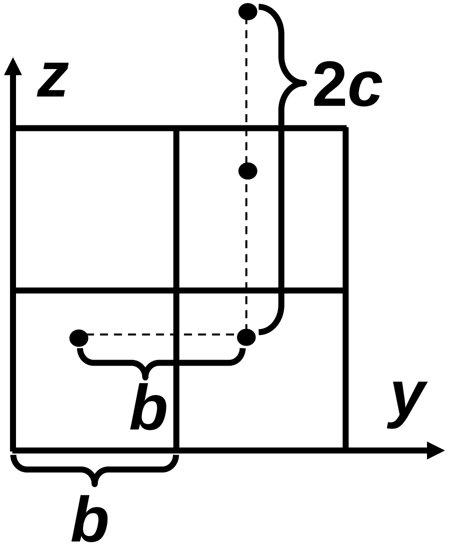
FCC γ-Fe

912^{o}C

BCC α-Fe

Point Coordinates





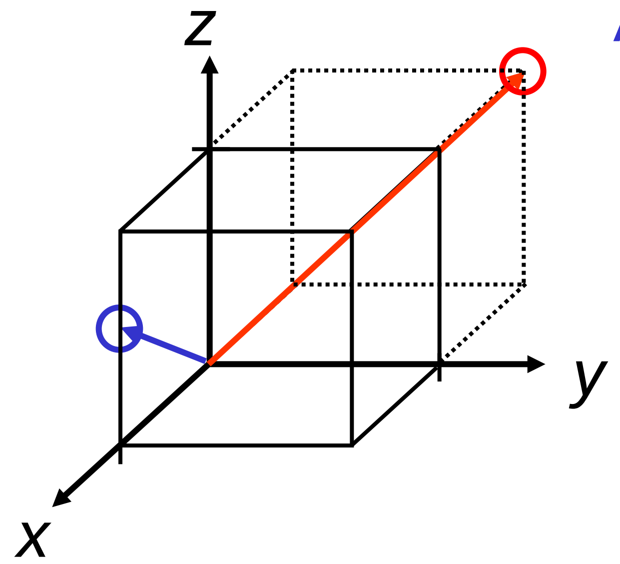
Point coordinates for unit cell center are

a/2, *b*/2, *c*/2 ½ ½ ½

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants → identical position in another unit cell

Crystallographic Directions



Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions *a*, *b*, and *c*
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

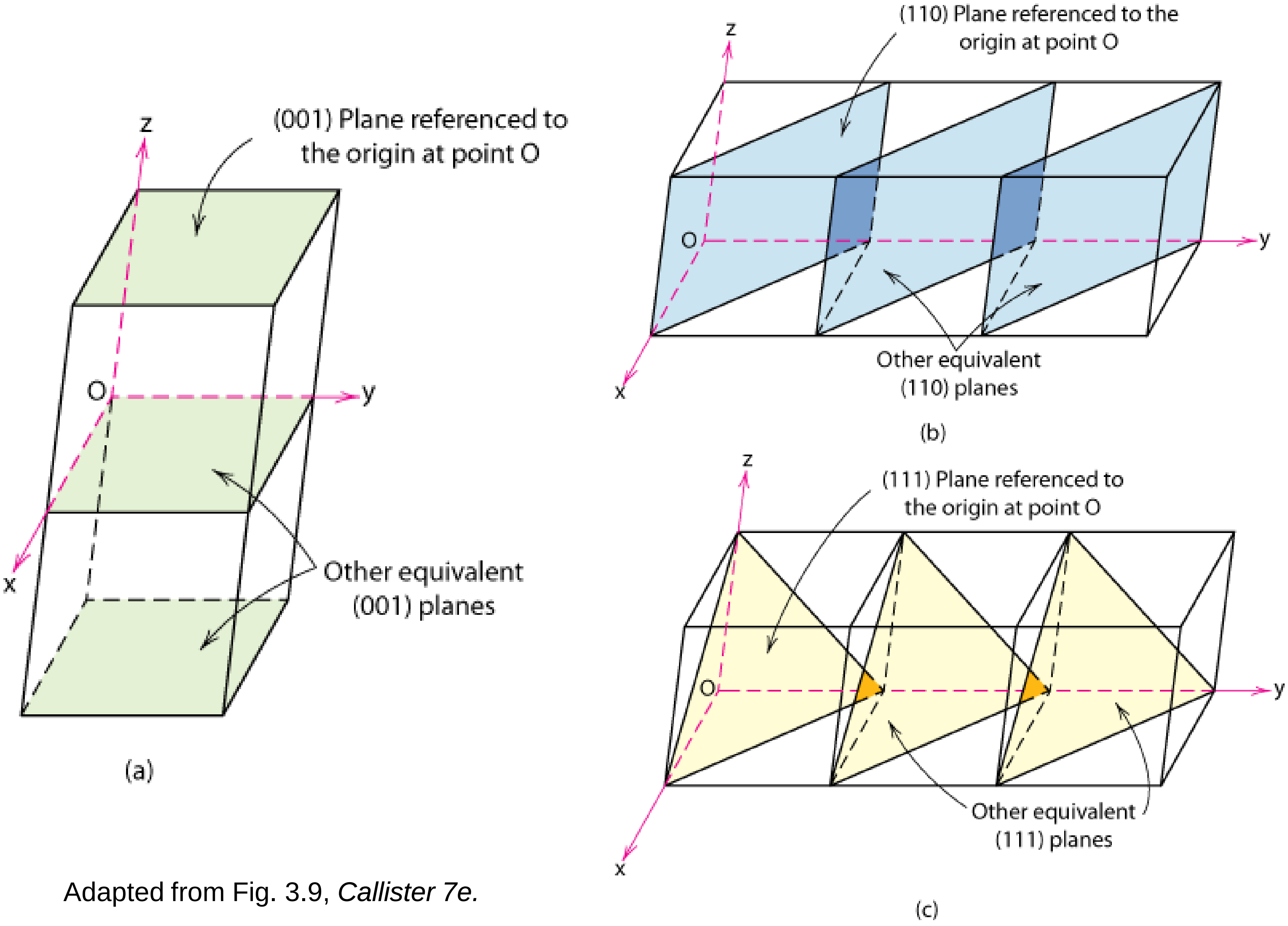
[*uvw*]

ex: 1, 0, ½ => 2, 0, 1 => [201]

-1, 1, 1 => $[\bar{1}11]$ where overbar represents a negative index

families of directions <*uvw*>

Crystallographic Planes



Adapted from Fig. 3.9, *Callister 7e.*

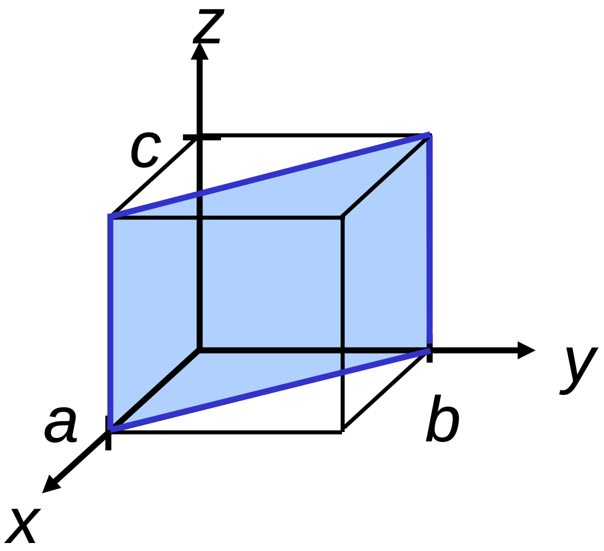
Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

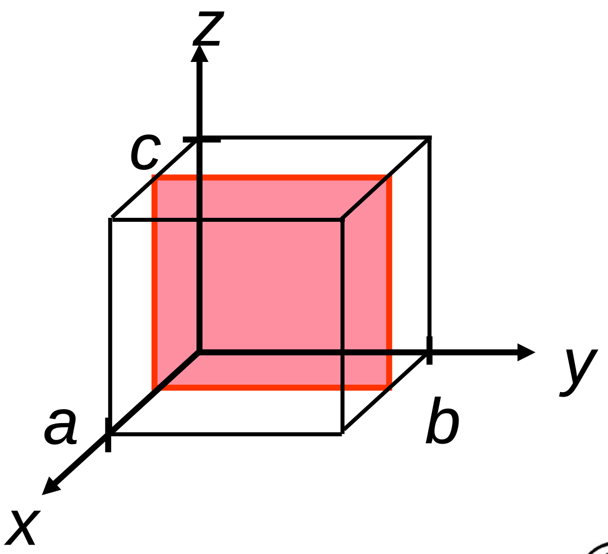
- Algorithm
  1. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
  2. Take reciprocals of intercepts
  3. Reduce to smallest integer values
  4. Enclose in parentheses, no commas i.e., (*hkl*)

Crystallographic Planes

example	a	b	c
1. Intercepts	1	1	∞
2. Reciprocals	1/1	1/1	1/∞
	1	1	0
3. Reduction	1	1	0
4. Miller Indices	(110)		

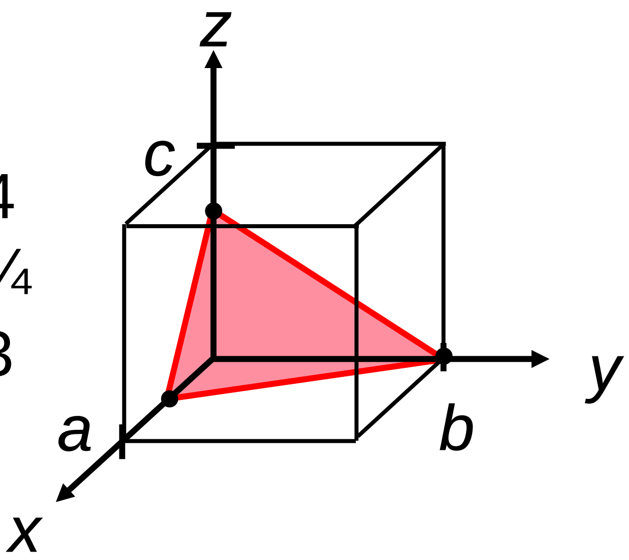


example	a	b	c
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/½	1/∞	1/∞
	2	0	0
3. Reduction	2	0	0
4. Miller Indices	(100)		



Crystallographic Planes

	<u>example</u>	*a*	*b*	*c*
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		



Family of Planes {*hkl*}

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

SUMMARY

- Atoms may assemble into crystalline or amorphous 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 predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).