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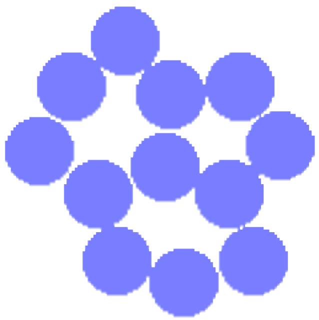
CHAPTER 3: CRYSTAL STRUCTURES & PROPERTIES

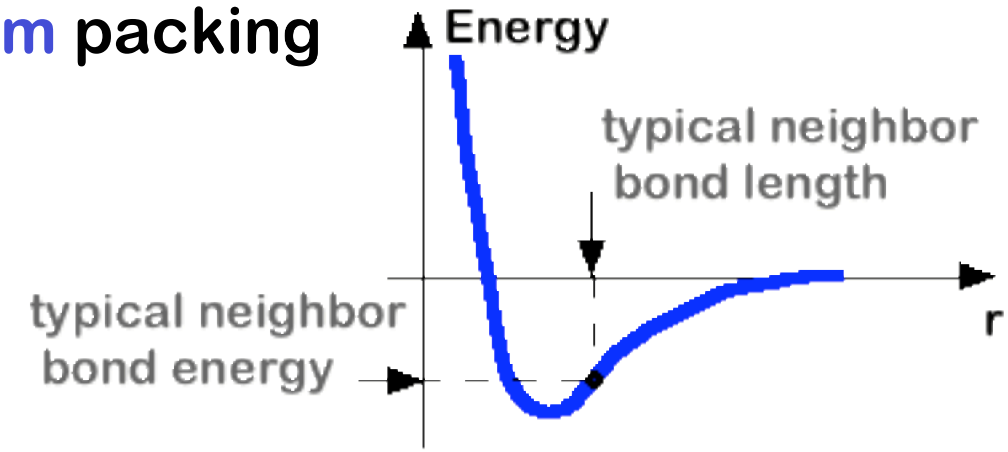
ISSUES TO ADDRESS...

- 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?

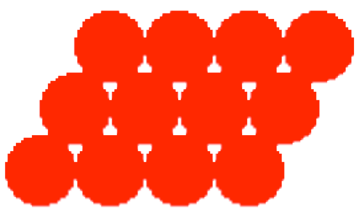
ENERGY AND PACKING

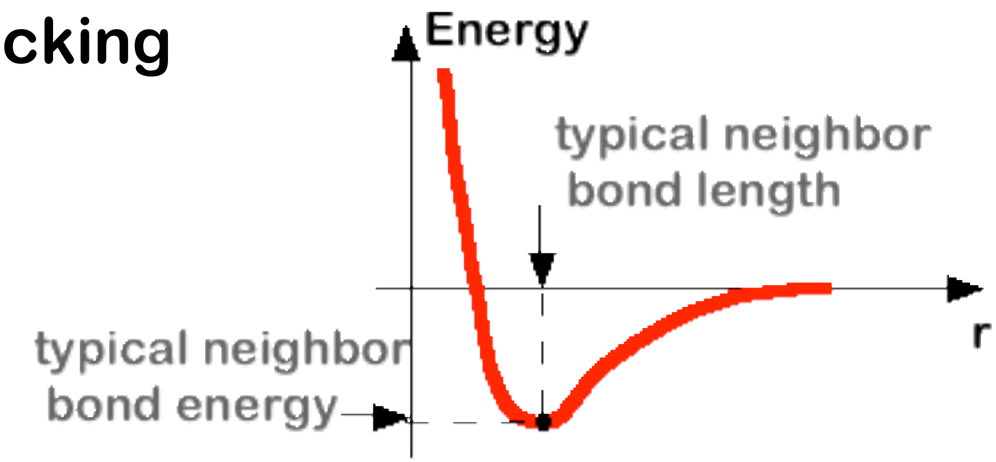
- Non dense, random packing





- Dense, regular packing



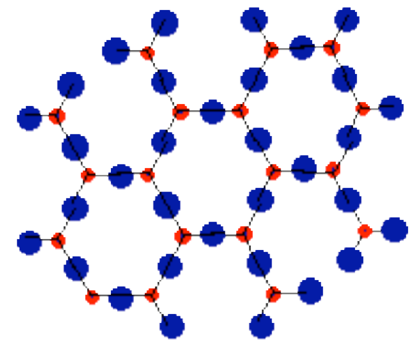


Dense, regular-packed structures tend to have lower energy.

MATERIALS AND PACKING

Crystalline materials...

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



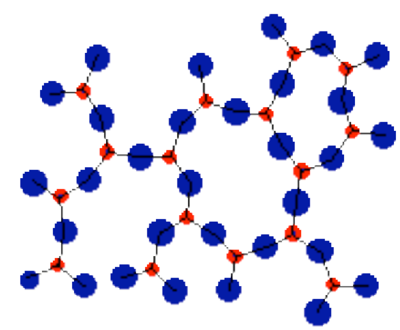
crystalline SiO_2
Adapted from Fig. 3.18(a), *Callister 6e.*

• Si • Oxygen

Noncrystalline materials...

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

"Amorphous" = Noncrystalline



noncrystalline SiO_2
Adapted from Fig. 3.18(b), *Callister 6e.*

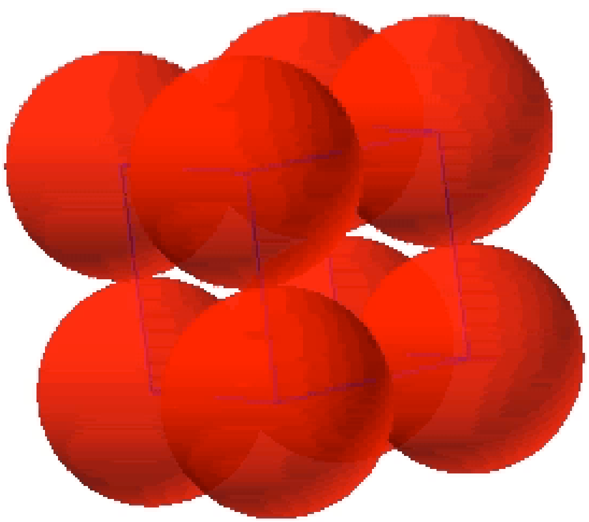
METALLIC CRYSTALS

- tend to be densely packed.
- have several 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.
- have the simplest crystal structures.

We will look at three such structures...

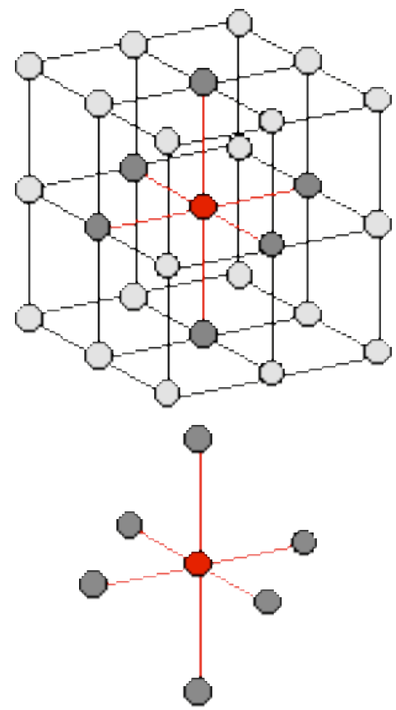
SIMPLE CUBIC STRUCTURE (SC)

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



(Courtesy P.M. Anderson)

- Coordination # = 6
  (# nearest neighbors)

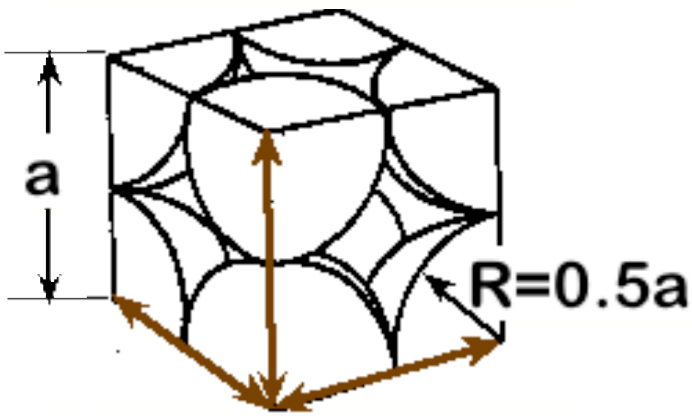


ATOMIC PACKING FACTOR

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

*assume hard spheres

- APF for a simple cubic structure = 0.52   **~50%!**



close-packed directions

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

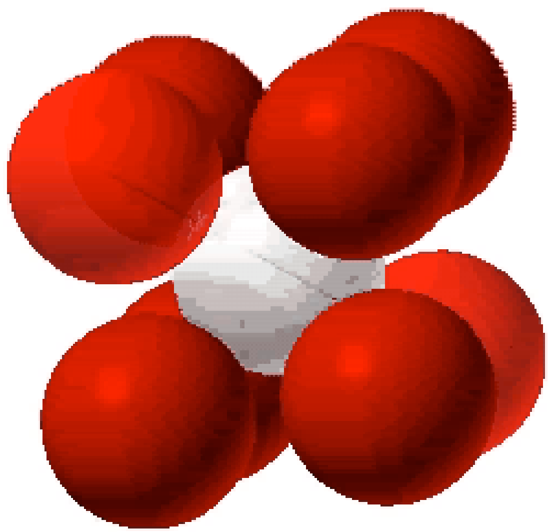
Adapted from Fig. 3.19, *Callister 6e.*

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

atoms / unit cell (the 1); volume / atom ($\frac{4}{3}\pi(0.5a)^3$); volume / unit cell (a^3)

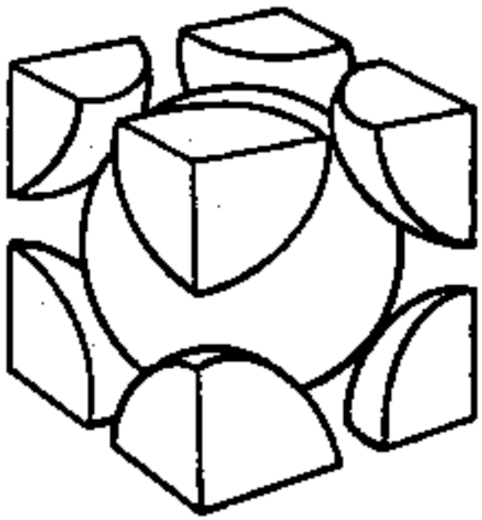
BODY CENTERED CUBIC STRUCTURE (BCC)

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



(Courtesy P.M. Anderson)

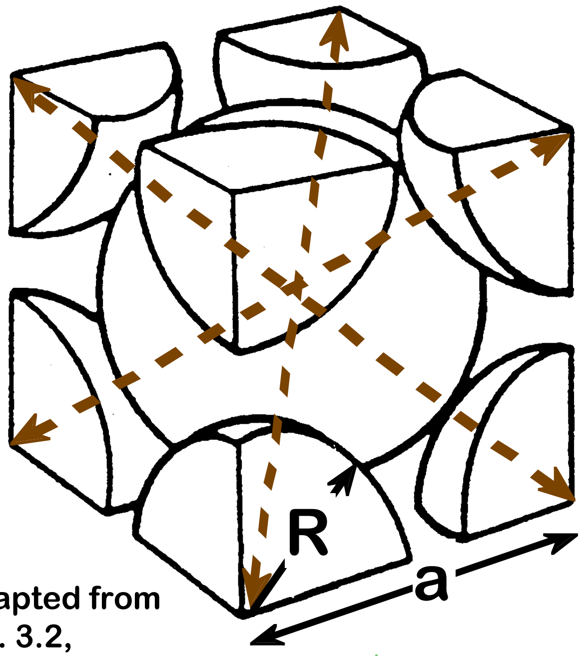
- Coordination # = 8



Adapted from Fig. 3.2, *Callister 6e.*

ATOMIC PACKING FACTOR: BCC

- **APF for a body-centered cubic structure = 0.68**



Adapted from Fig. 3.2, *Callister 6e.*

Close-packed directions:

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

Unit cell contains:

1 + 8 x 1/8

= 2 atoms/unit cell

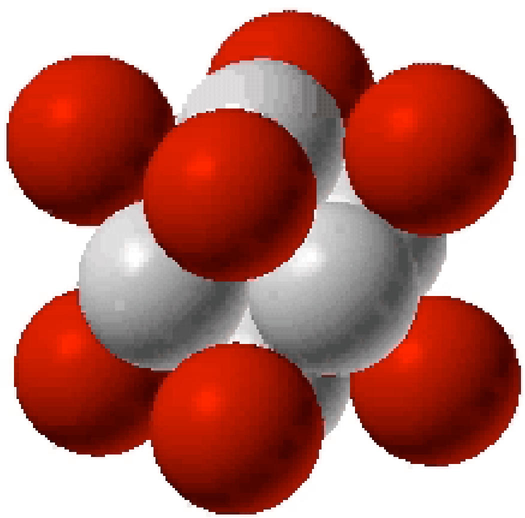
$$\text{APF} = \frac{2 \cdot \frac{4}{3}\pi\left(\sqrt{3}a/4\right)^3}{a^3}$$

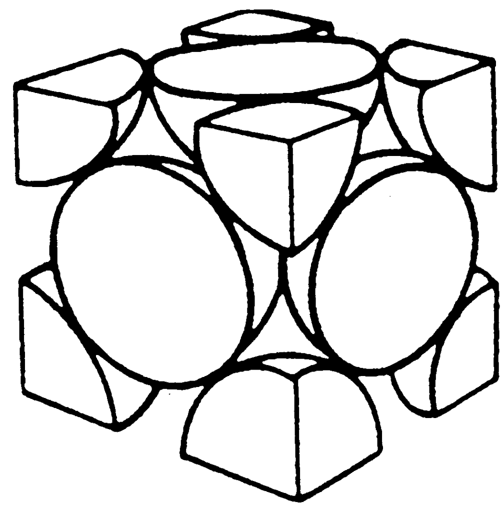
where 2 = $\frac{\text{atoms}}{\text{unit cell}}$, $\frac{4}{3}\pi\left(\sqrt{3}a/4\right)^3$ = $\frac{\text{volume}}{\text{atom}}$, a^3 = $\frac{\text{volume}}{\text{unit cell}}$

FACE CENTERED CUBIC STRUCTURE (FCC)

- **Close packed directions are face diagonals.**
  - **--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.**

- **Coordination # = 12**

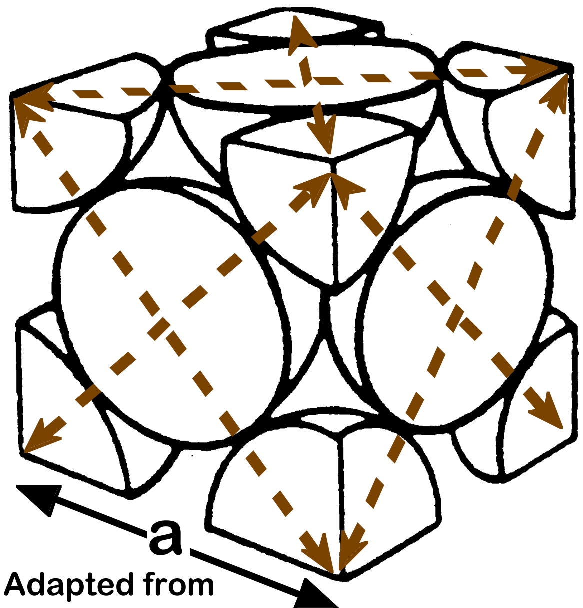




Adapted from Fig. 3.1(a), *Callister 6e.*

ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74



Adapted from Fig. 3.1(a), *Callister 6e.*

Close-packed directions:
length = 4R
$= \sqrt{2}\, a$

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

$$\text{APF} = \frac{4 \; \frac{4}{3}\pi\left(\sqrt{2}a/4\right)^3}{a^3}$$

- 4: atoms / unit cell
- $\frac{4}{3}\pi\left(\sqrt{2}a/4\right)^3$: volume / atom
- a^3: volume / unit cell

THEORETICAL DENSITY, ρ

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

- # atoms/unit cell → n
- Atomic weight (g/mol) → A
- Volume/unit cell (cm^3/unit cell) → V_C
- Avogadro's number (6.023×10^{23} atoms/mol) → N_A

Example: Copper

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius R = 0.128 nm (1 nm = 10^{-7}cm)

$V_C = a^3$; For FCC, $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23} cm^3$

Result: theoretical $\rho_{Cu} = 8.89\ g/cm^3$

Compare to actual: $\rho_{Cu} = 8.94\ g/cm^3$

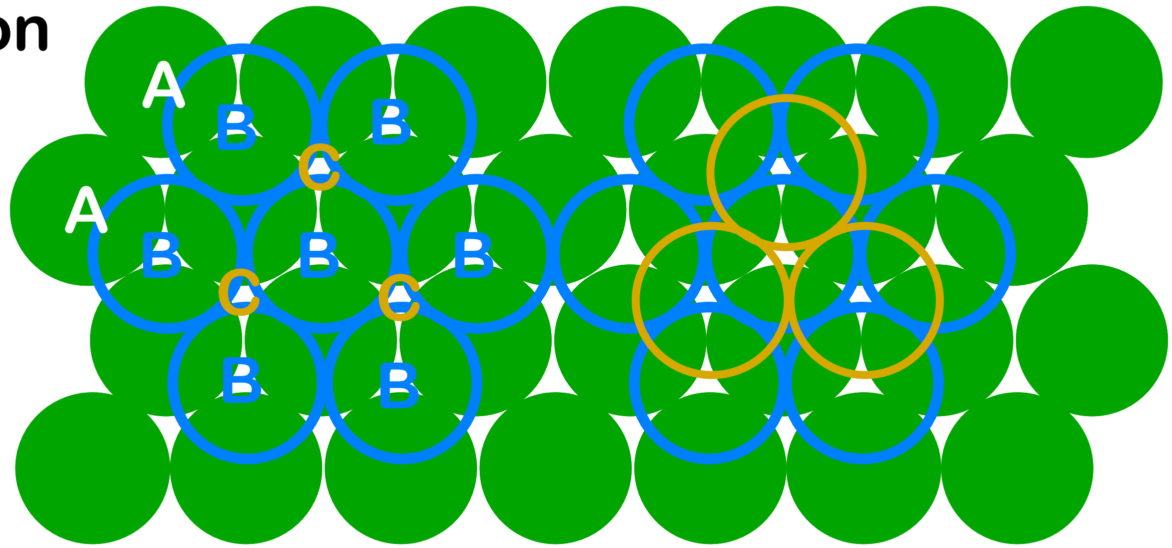
FCC STACKING SEQUENCE

- ABCABC... Stacking Sequence
- 2D Projection

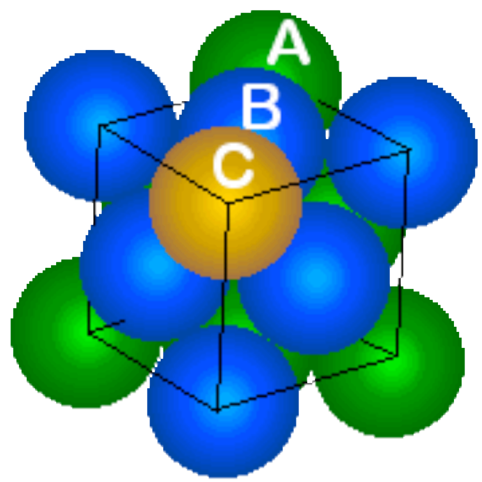
A sites

B sites

C sites

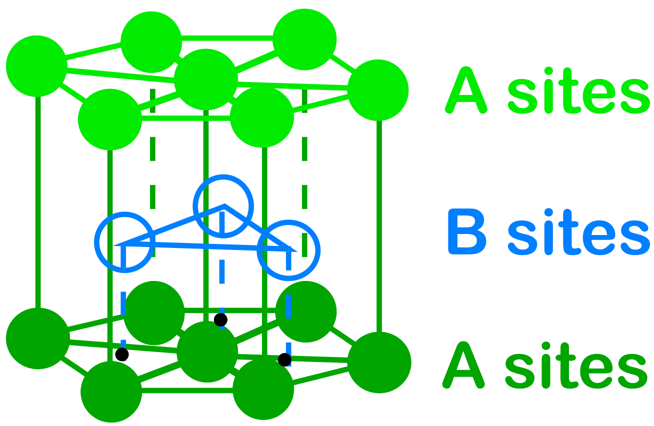


- FCC Unit Cell



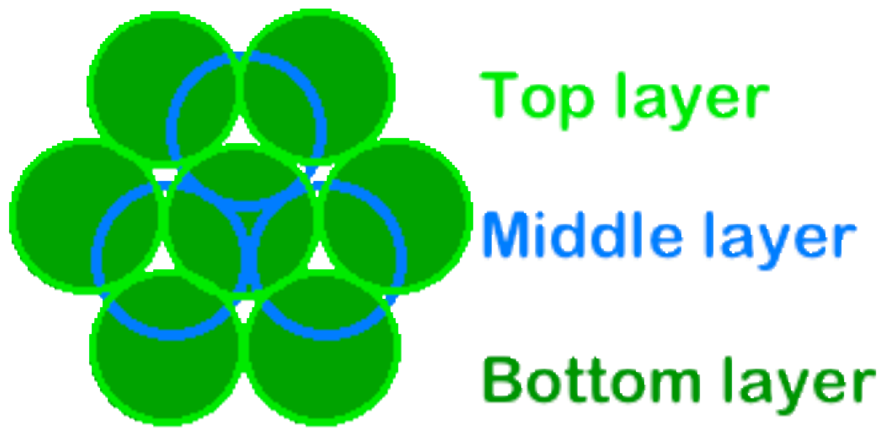
HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

- ABAB... Stacking Sequence
- 3D Projection

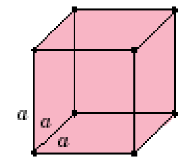
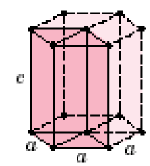
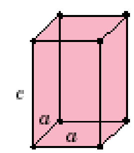
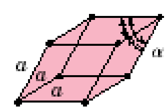
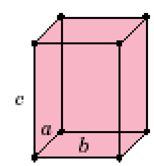
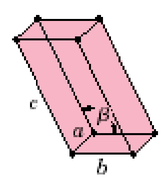
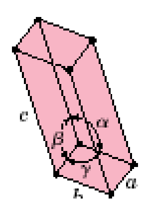


Adapted from Fig. 3.3, *Callister 6e.*

- 2D Projection



- Coordination # = 12
- APF = 0.74

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Characteristics of Selected Elements at 20C

Element	Symbol	At. Weight (amu)	Density (g/cm^3)	Crystal Structure	Atomic radius (nm)
Aluminum	Al	26.98	2.71	FCC	0.143
Argon	Ar	39.95	------	------	------
Barium	Ba	137.33	3.5	BCC	0.217
Beryllium	Be	9.012	1.85	HCP	0.114
Boron	B	10.81	2.34	Rhomb	------
Bromine	Br	79.90	------	------	------
Cadmium	Cd	112.41	8.65	HCP	0.149
Calcium	Ca	40.08	1.55	FCC	0.197
Carbon	C	12.011	2.25	Hex	0.071
Cesium	Cs	132.91	1.87	BCC	0.265
Chlorine	Cl	35.45	------	------	------
Chromium	Cr	52.00	7.19	BCC	0.125
Cobalt	Co	58.93	8.9	HCP	0.125
Copper	Cu	63.55	8.94	FCC	0.128
Flourine	F	19.00	------	------	------
Gallium	Ga	69.72	5.90	Ortho.	0.122
Germanium	Ge	72.59	5.32	Dia. cubic	0.122
Gold	Au	196.97	19.32	FCC	0.144
Helium	He	4.003	------	------	------
Hydrogen	H	1.008	------	------	------

Adapted from Table, "Characteristics of Selected Elements", inside front cover, *Callister 6e.*

DENSITIES OF MATERIAL CLASSES

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

Why?

Metals have...

- close-packing (metallic bonding)
- large atomic mass

Ceramics have...

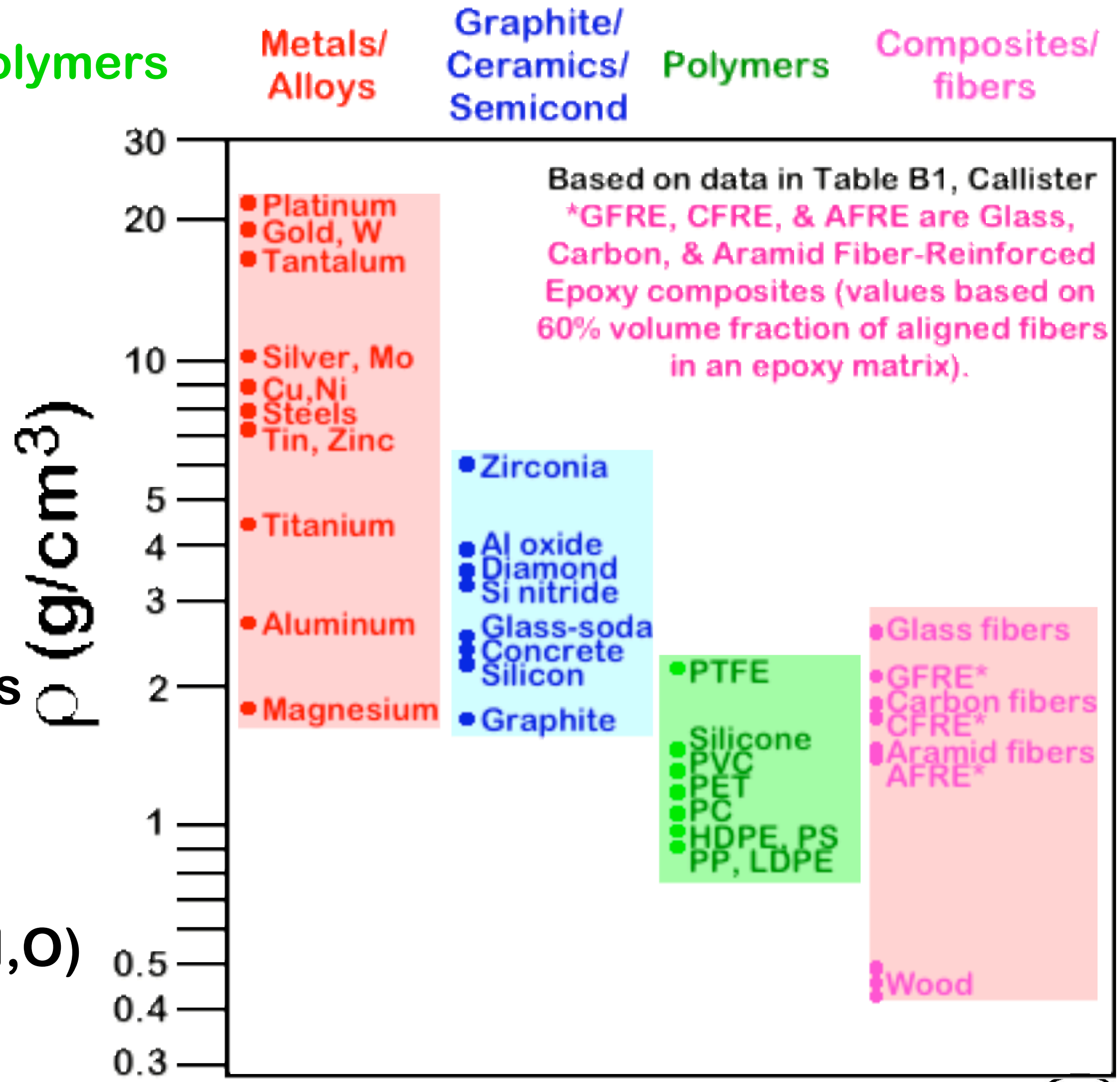
- less dense packing (covalent bonding)
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values



Data from Table B1, *Callister 6e.*

CERAMIC BONDING

- **Bonding:**
  - --Mostly ionic, some covalent.
  - --% ionic character increases with difference in electronegativity.
- **Large vs small ionic bond character:**

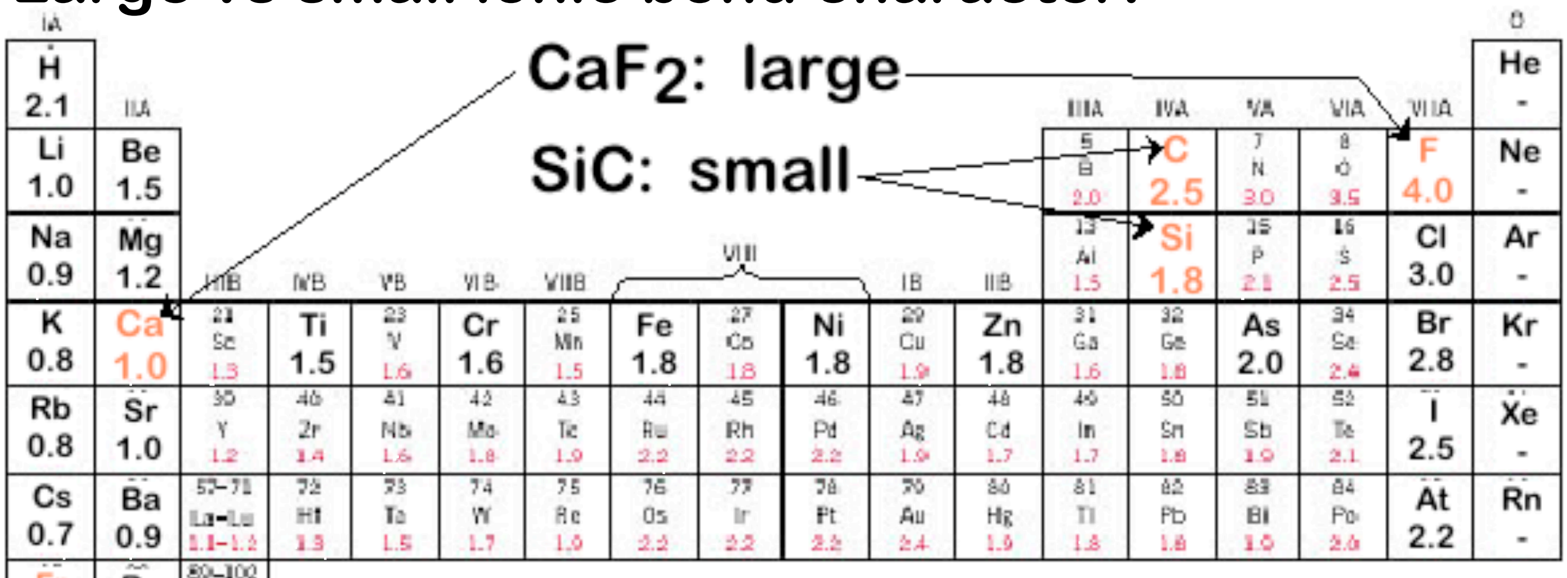
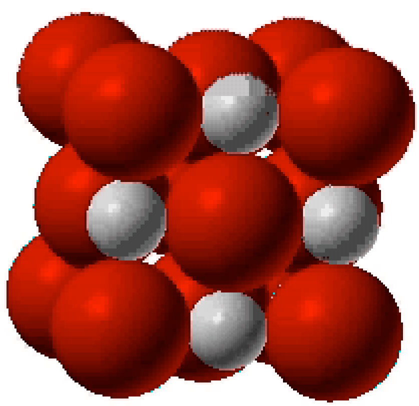


Table of Electronegativities

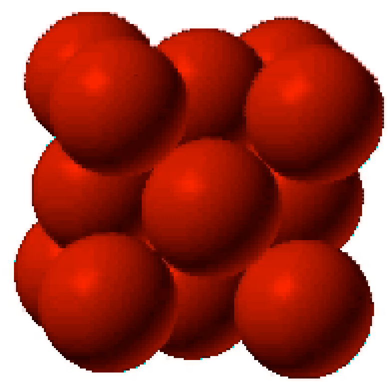
Adapted from Fig. 2.7, *Callister 6e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

STRUCTURE OF COMPOUNDS: NaCl

- Compounds: Often have similar close-packed structures.
- Structure of NaCl
- Close-packed directions
  --along cube edges.



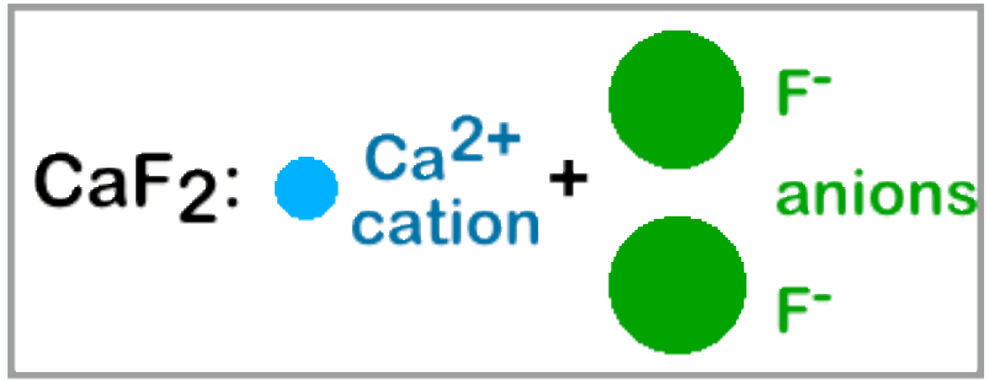
(Courtesy P.M. Anderson)



(Courtesy P.M. Anderson)

IONIC BONDING & STRUCTURE

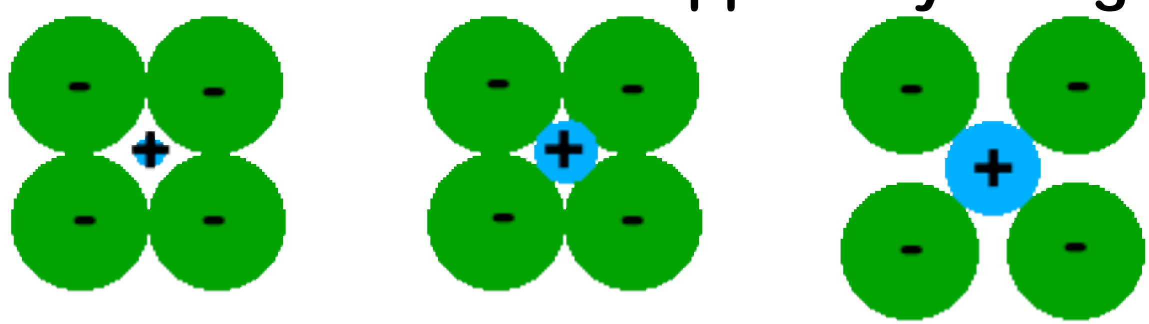
- Charge Neutrality:
  --Net charge in the structure should be zero.



--General form: A_mX_p

m, p determined by charge neutrality

- Stable structures:
  --maximize the # of nearest oppositely charged neighbors.



unstable stable stable

Adapted from Fig. 12.1, *Callister 6e.*

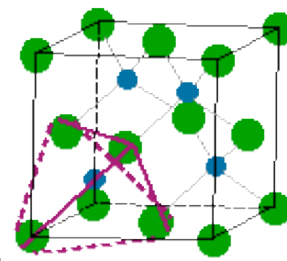
COORDINATION # AND IONIC RADII

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

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

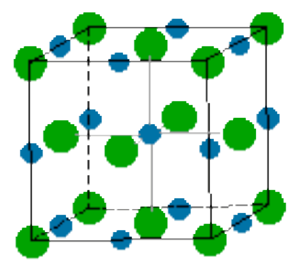
$\frac{r_{cation}}{r_{anion}}$	Coord #
< .155	2
.155-.225	3
.225-.414	4
.414-.732	6
.732-1.0	8

Adapted from Table 12.2, *Callister 6e.*



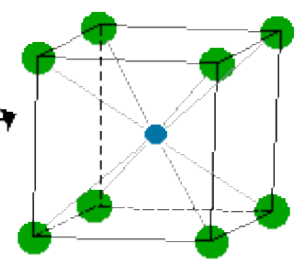
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 6e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 6e.*

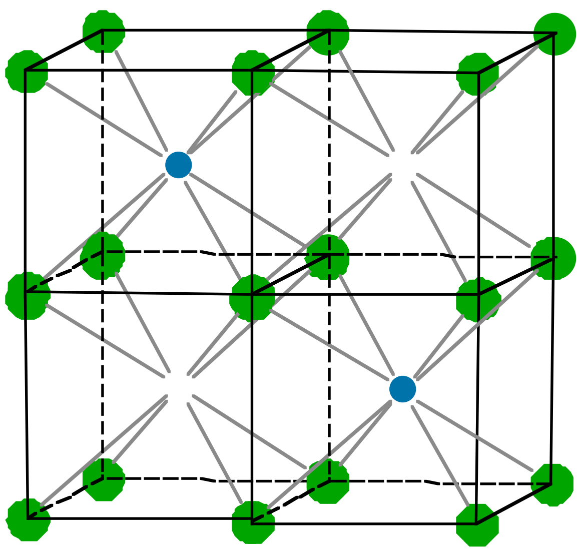


CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 6e.*

A_mX_p STRUCTURES

- Consider CaF_2 : $\frac{r_{cation}}{r_{anion}} = \frac{0.100}{0.133} \approx 0.8$
- Based on this ratio, coord # = 8 and structure = CsCl.
- Result: CsCl structure w/only half the cation sites occupied.



- Only half the cation sites are occupied since $\#Ca^{2+}$ ions = 1/2 # F^- ions.

Adapted from Fig. 12.5, *Callister 6e.*

EX: PREDICTING STRUCTURE OF FeO

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

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100
Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

Data from Table 12.3, *Callister 6e.*

- Answer:

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

$$= 0.550$$

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

Crystal Systems

Cubic:
Lead ore

Rhombic:
Topaz

Hexagonal:
Emerald

Tetragonal:
idocrase

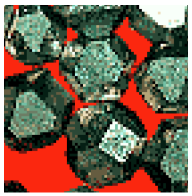
Monoclinic:
Gypsum

Triclinic:
Axinite

CRYSTALS AS BUILDING BLOCKS

- *Some* engineering applications require single crystals:

--diamond single crystals for abrasives



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

--turbine blades

Fig. 8.30(c), *Callister 6e.* (Fig. 8.30(c) courtesy of Pratt and Whitney).

- Crystal properties reveal features of atomic structure.

--Ex: Certain crystal planes in quartz fracture more easily than others.

(Courtesy P.M. Anderson)

POLYCRYSTALS

- *Most* engineering materials are polycrystals.

Adapted from Fig. K, color inset pages of *Callister 6e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

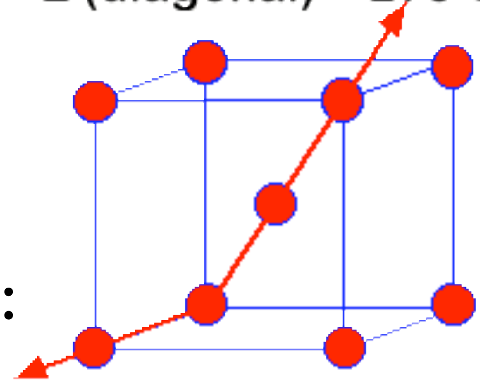
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If crystals are randomly oriented, overall component properties are not directional.
- Crystal sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

SINGLE VS POLYCRYSTALS

- Single Crystals

  -Properties vary with direction: anisotropic.

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



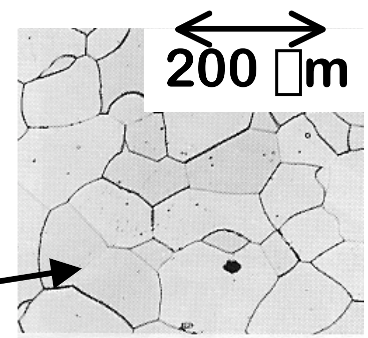
Data from Table 3.3, *Callister 6e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

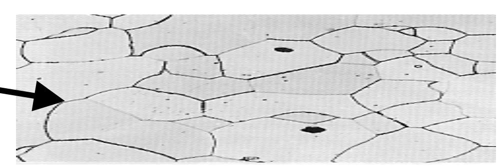
- Polycrystals

  -Properties may/may not vary with direction.

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

  -If grains are textured, anisotropic.





Adapted from Fig. 4.12(b), *Callister 6e*. (Fig. 4.12(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].)

SUMMARY

- Atoms may assemble into crystalline or amorphous 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).
- Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.