

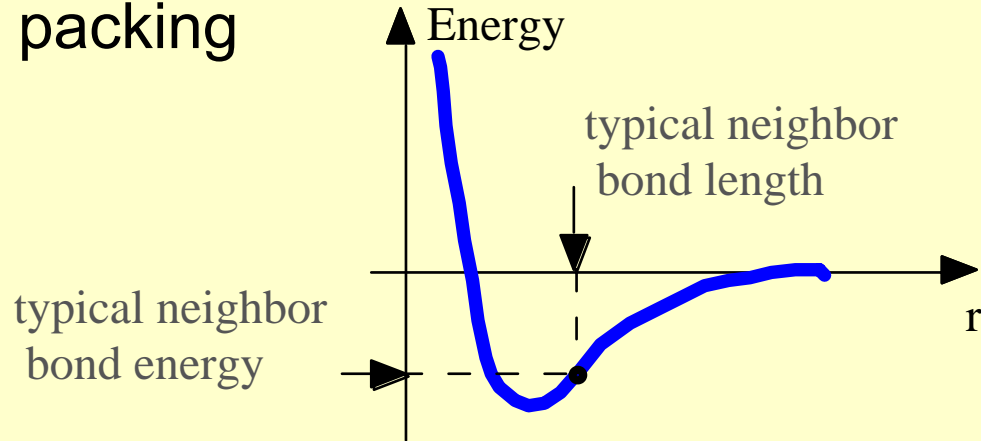
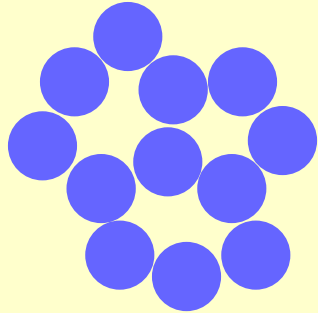
CHAPTER 3: Crystal structures and properties

ISSUES TO ADDRESS...

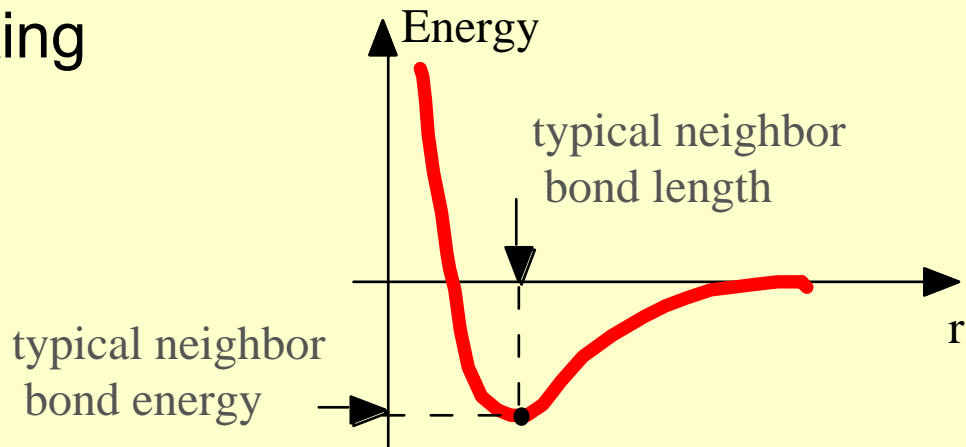
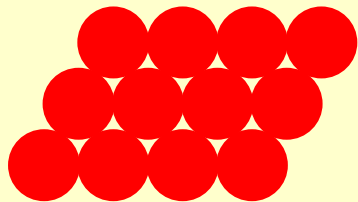
- How do atoms assemble into solid structures? (for now, focus on metals)
- How does the density of a material depend on its structure?
- When do material properties vary with the sample (i.e., part) orientation?

Energy and packing

- Non dense, **random** packing



- Dense, **regular** packing

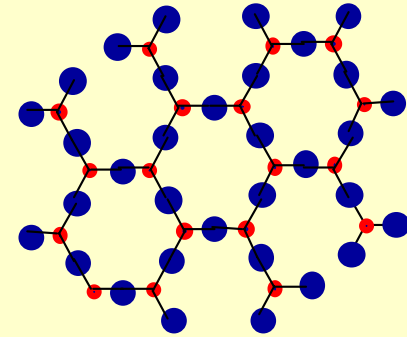


Dense, regular-packed structures tend to have lower energy.

Materials and packing

Crystalline materials...

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



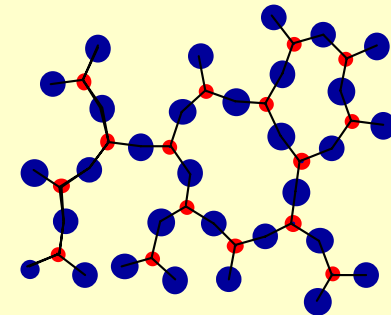
crystalline SiO₂

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

• Si • Oxygen

Noncrystalline materials...

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



noncrystalline SiO₂

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

"Amorphous" = Noncrystalline

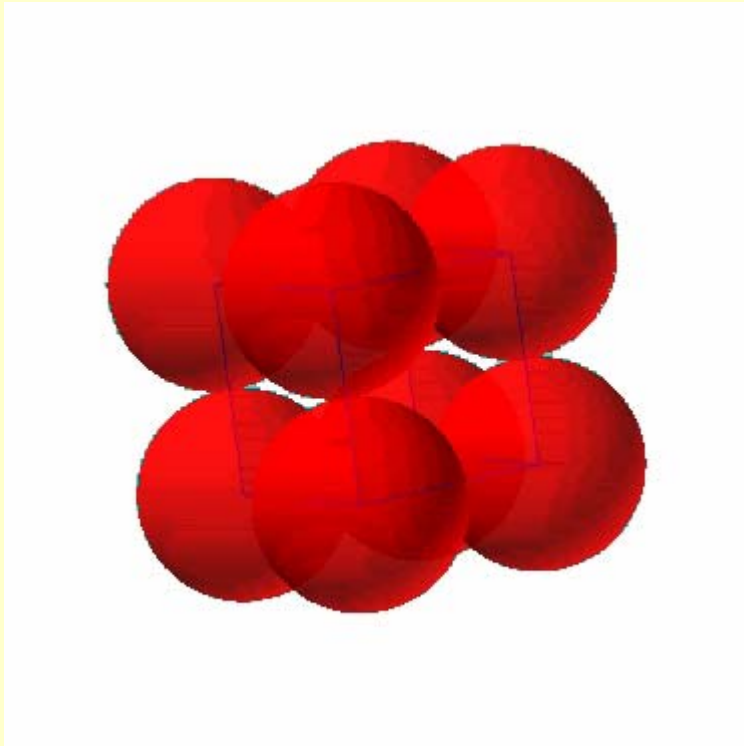
Metallic crystals

- 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...

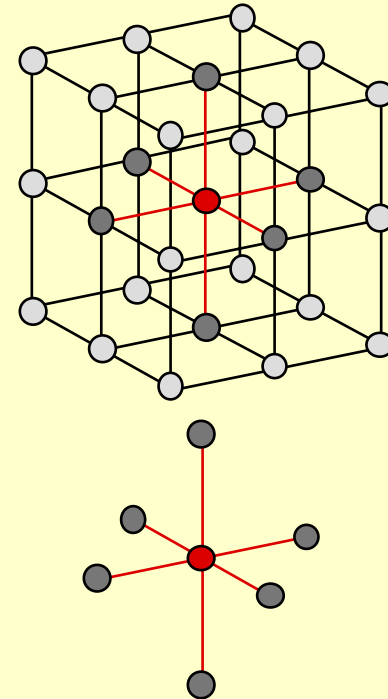
Simple Cubic (SC) structure

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



(Courtesy P.M. Anderson)

- **Coordination #** = 6
(# nearest neighbors)

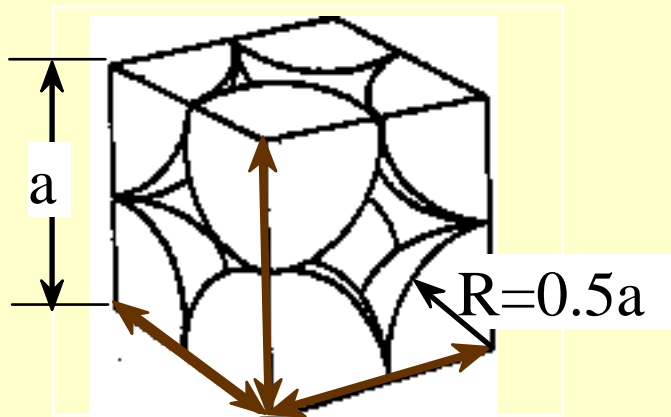


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains $8 \times 1/8 =$

1 atom/unit cell

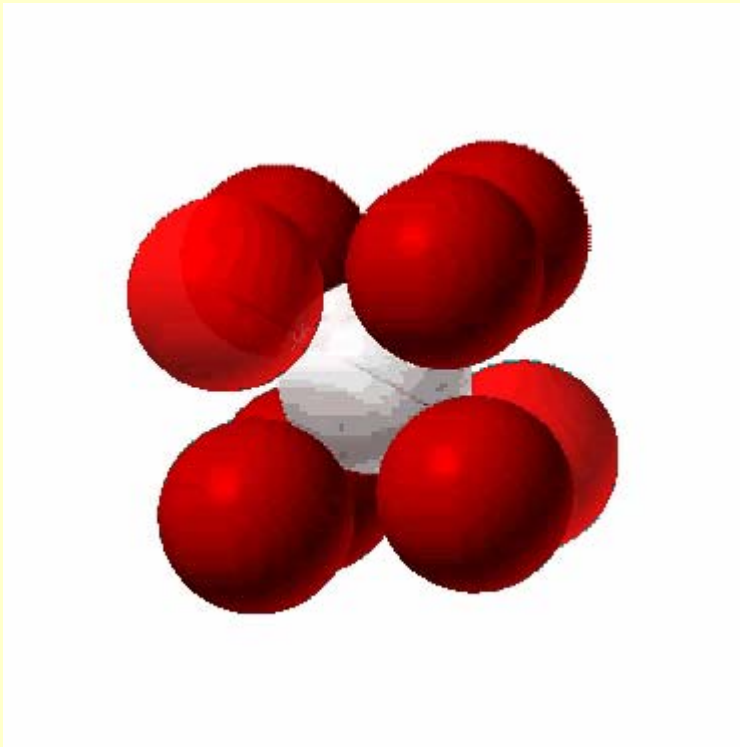
Adapted from Fig. 3.19,
Callister 6e.

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

volume atom
volume unit cell

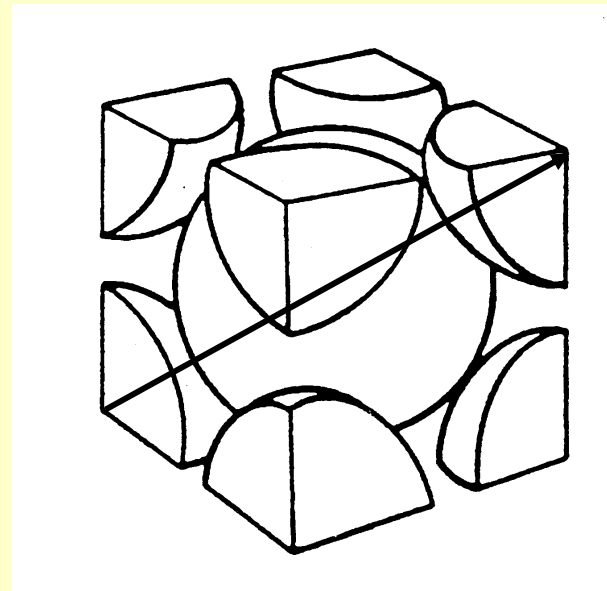
Body Centered Cubic (BCC) structure

- 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)

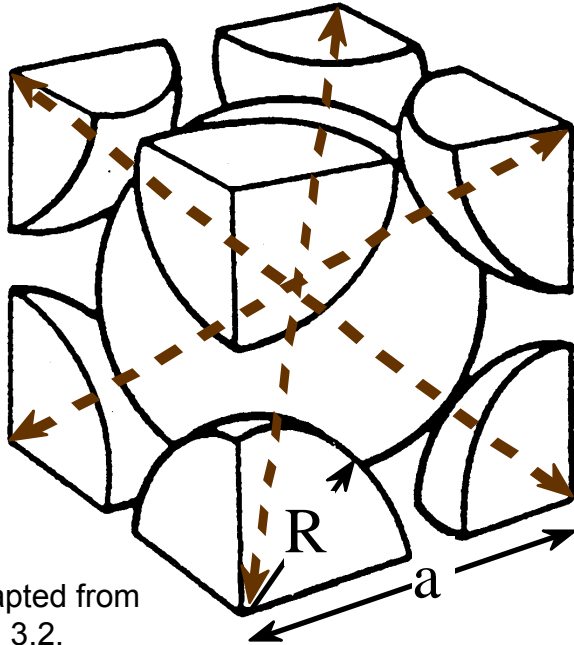
- Coordination # = 8



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:

$$\begin{aligned} \text{length} &= 4R \\ &= \sqrt{3} a \end{aligned}$$

Unit cell contains:

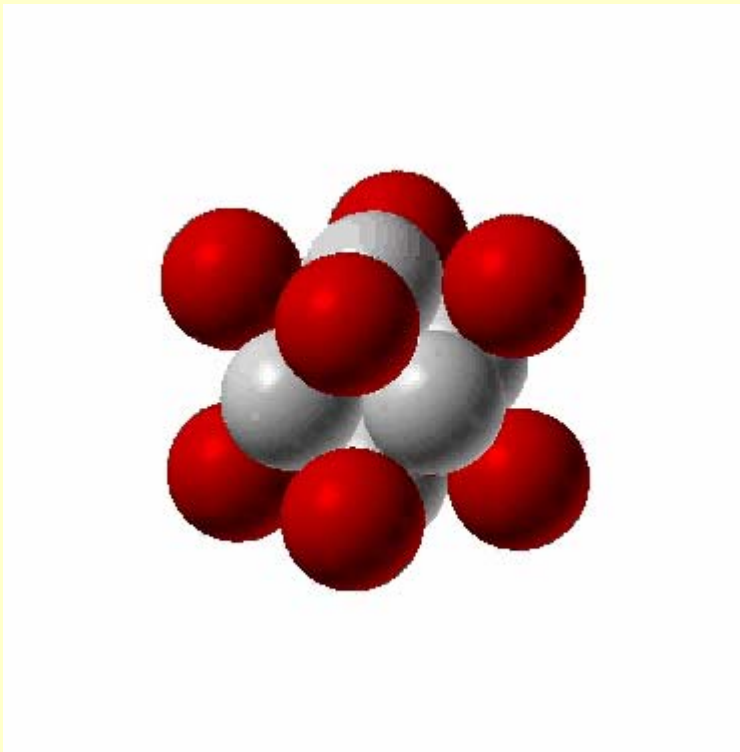
$$\begin{aligned} &1 + 8 \times 1/8 \\ &= \mathbf{2 \text{ atoms/unit cell}} \end{aligned}$$

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

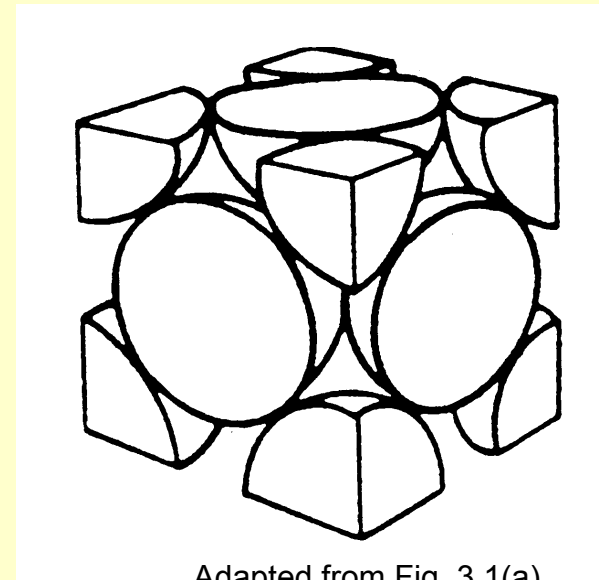
Face Centered Cubic (FCC) structure

- 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



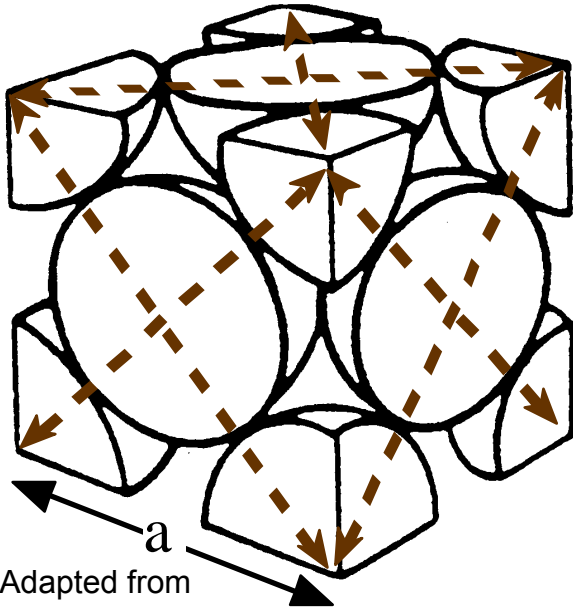
(Courtesy P.M. Anderson)



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:

$$\begin{aligned} \text{length} &= 4R \\ &= \sqrt{2} a \end{aligned}$$

Unit cell contains:

$$\begin{aligned} &6 \times 1/2 + 8 \times 1/8 \\ &= 4 \text{ atoms/unit cell} \end{aligned}$$

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

atoms
unit cell

volume
atom

volume
unit cell

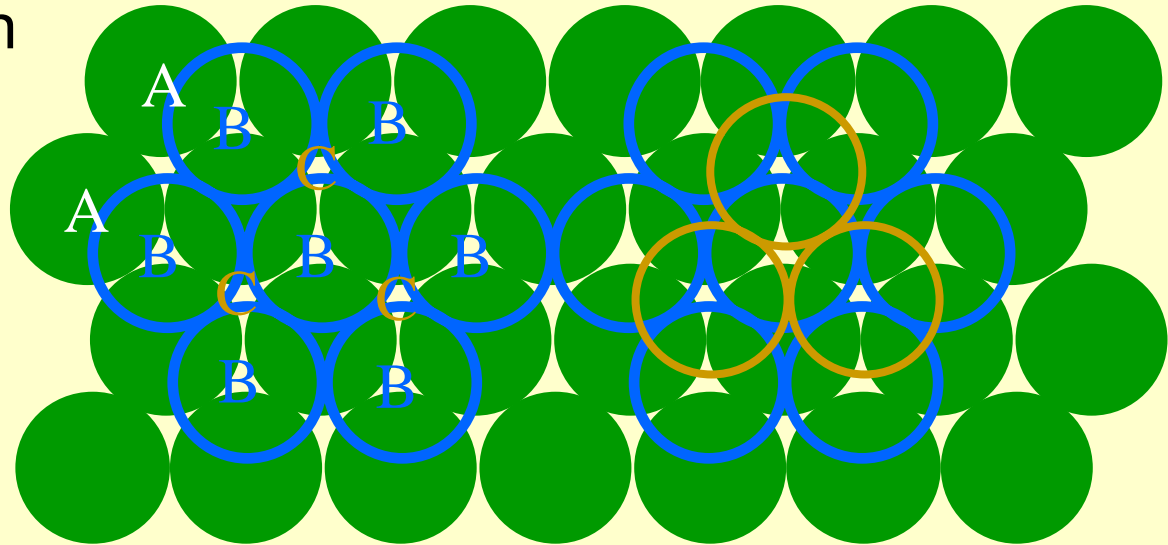
FCC stacking sequence

- ABCABC... Stacking Sequence
- 2D Projection

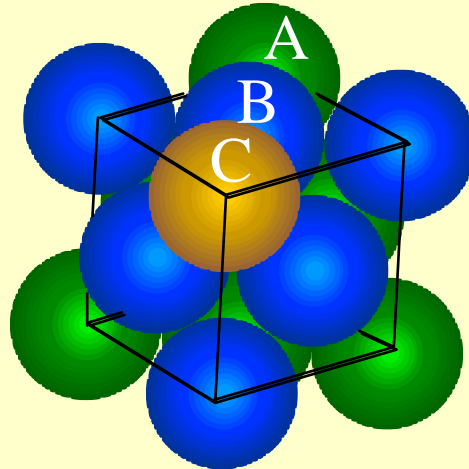
A sites

B sites

C sites

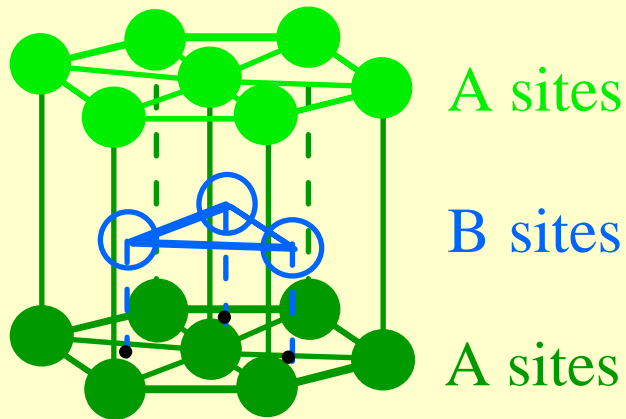


- FCC Unit Cell



Hexagonal Close-Packed (HCP) structure

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3,
Callister 6e.

- 2D Projection



- Coordination # = 12
- APF = 0.74

Theoretical density, ρ

atoms/unit cell

Atomic weight (g/mol)

$$\rho = \frac{n A}{V_c N_A}$$

Volume/unit cell
(cm³/unit cell)

$$V_c N_A$$

Avogadro's number

(6.023 x 10²³ atoms/mol)

Example: Copper

Data from Table inside front cover of Callister (see next slide):

- 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)

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

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

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

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

ρ_{metals} ρ_{ceramics} ρ_{polymers} Metals/Alloys Graphite/Ceramics/Semicond Polymers Composites/fibers

Why?

Metals have...

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

Ceramics have...

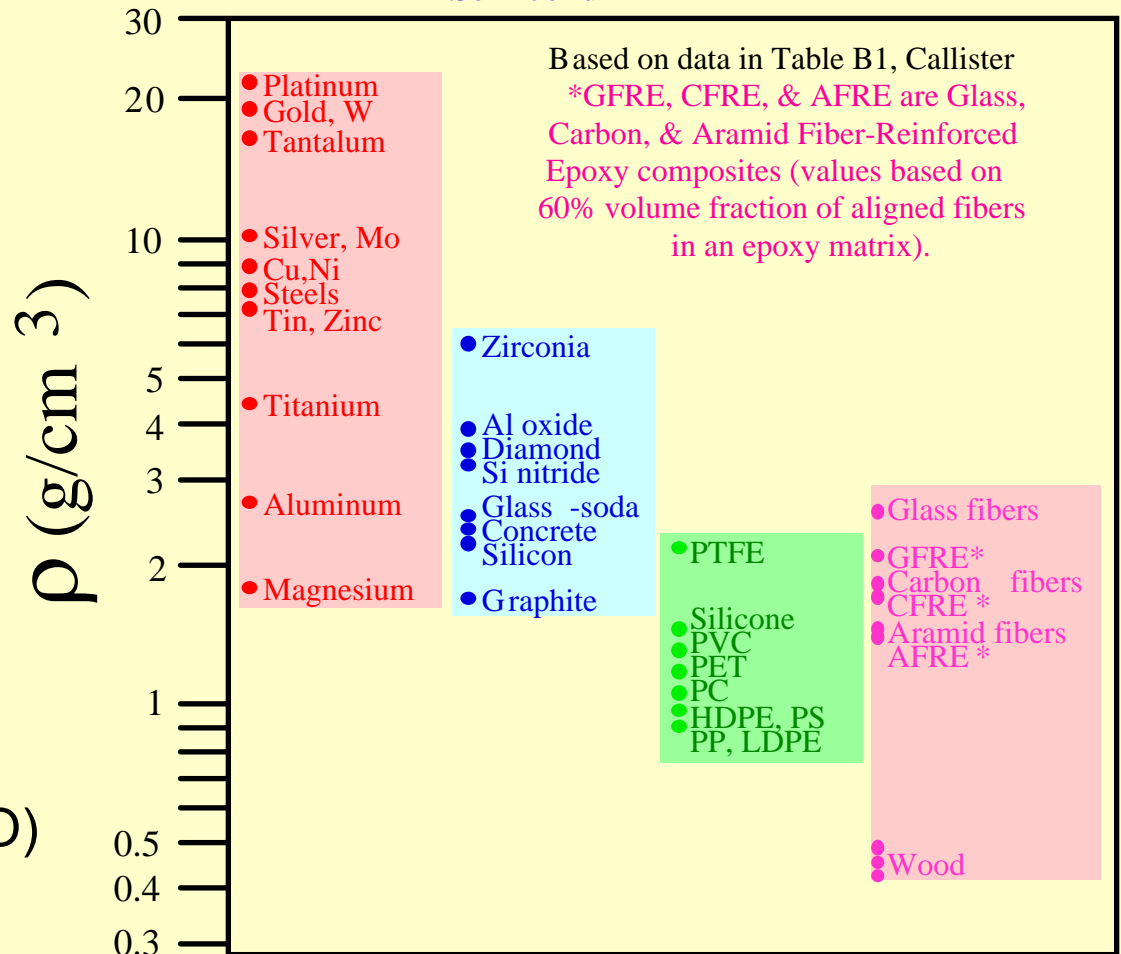
- less dense packing (covalent bonding)
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values



Data from Table B1, Callister 6e.

Polycrystals

- Most engineering materials are **polycrystals**.



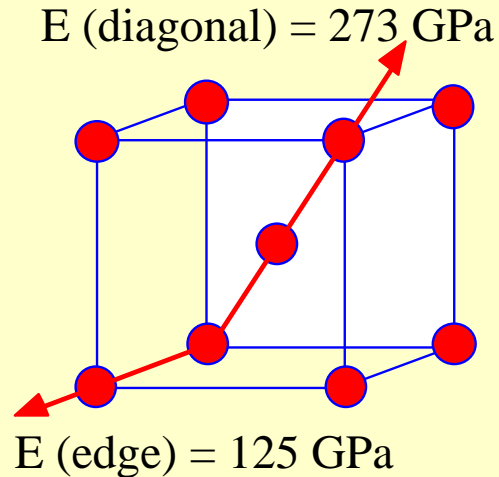
Adapted from Fig. K, color inset pages of *Callister 6e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

- 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

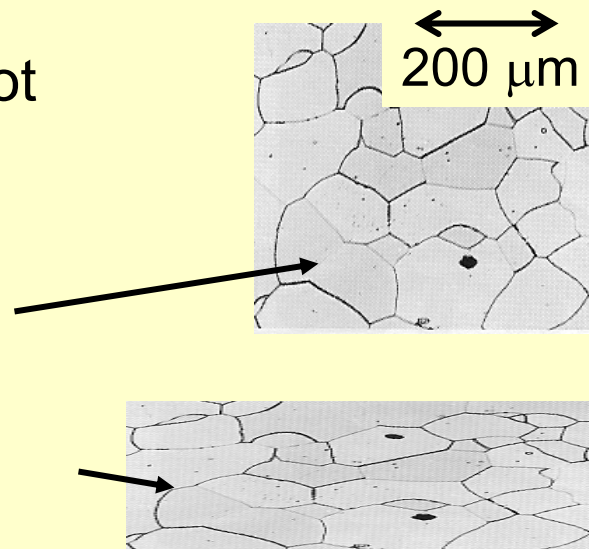
- Properties vary with direction: **anisotropic**.
- Example: the modulus of elasticity (E) in BCC iron:



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**. ($E_{\text{poly iron}} = 210 \text{ GPa}$)
- 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].)

Anisotropy

Table 3.3 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

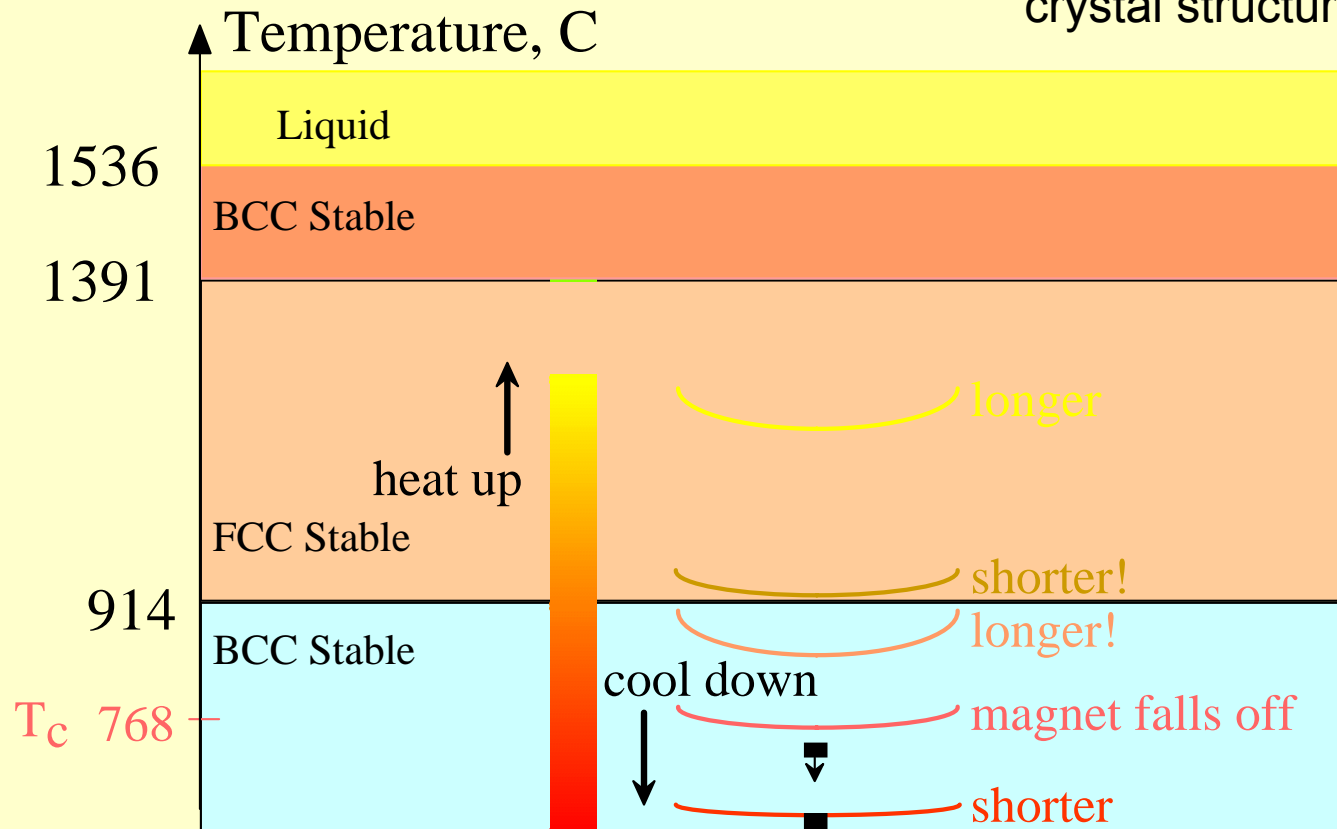
<i>Metal</i>	<i>Modulus of Elasticity (GPa)</i>		
	<i>[100]</i>	<i>[110]</i>	<i>[111]</i>
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

Demo: Heating and cooling of iron wire

- Demonstrates "polymorphism"

← The same atoms can have more than one crystal structure.



CHAPTER 12: Structure of ceramics

ISSUES TO ADDRESS...

- Structures of ceramic materials:
How do they differ from that of metals?

CERAMIC BONDING

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

IA	IIA															III A	IV A	V A	VIA	VII A	0		
H 2.1																B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	He -		
Li 1.0	Be 1.5															Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ne -		
Na 0.9	Mg 1.2	Ca 1.0															Zn 1.8	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Ar -
K 0.8	Sr 1.0	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 1.8	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-100 1.1-1.7																					

CaF₂: large

SiC: small

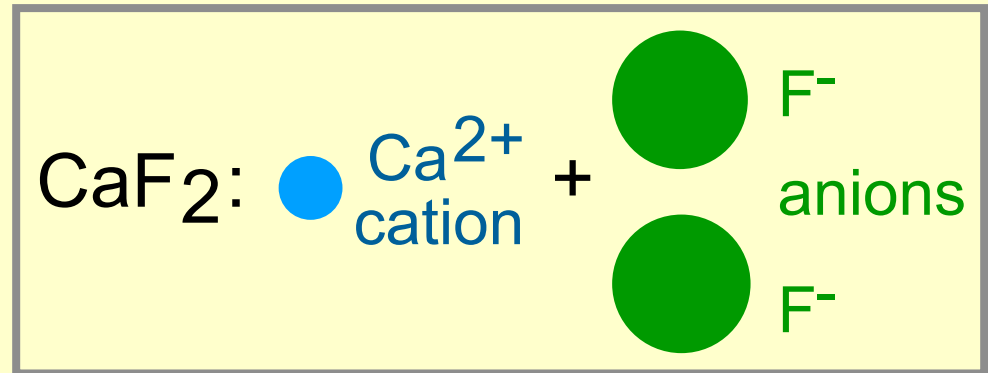
Table of Electronegativities

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.

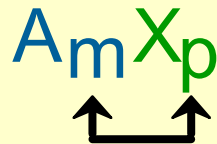
Ionic bonding & structure

- **Charge Neutrality:**

--Net charge in the structure should be zero.



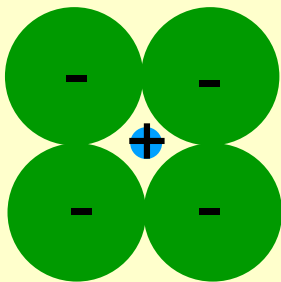
--General form:



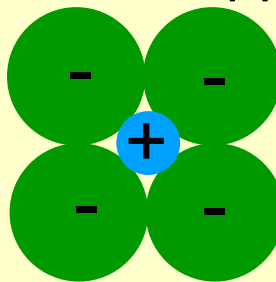
m, p determined by charge neutrality

- **Stable structures:**

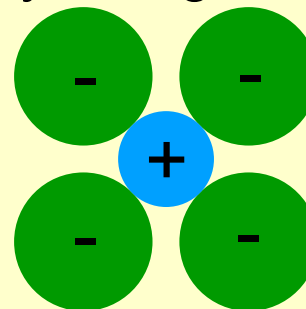
--maximize the # of nearest oppositely charged neighbors.



unstable



stable



stable

Adapted from Fig. 12.1,
Callister 6e.

Coordination # and ionic radii

- Coordination # increases with
Issue: How many anions can you
arrange around a cation?

$$\frac{r_{\text{cation}}}{r_{\text{anion}}}$$

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$
< .155

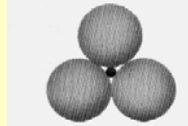
Coord #

2



.155-.225

3



.225-.414

4



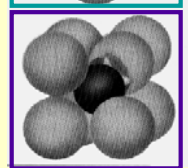
.414-.732

6

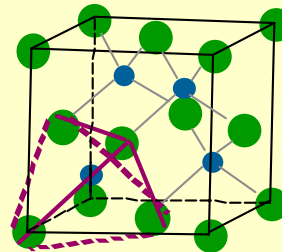


.732-1.0

8

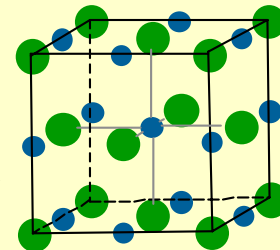


Adapted from Table 12.2,
Callister 6e.



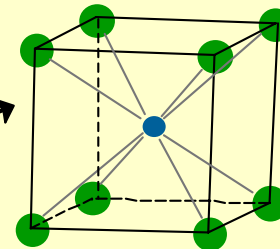
ZnS
(zincblende)

Adapted from Fig. 12.4,
Callister 6e.



NaCl
(sodium
chloride)

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

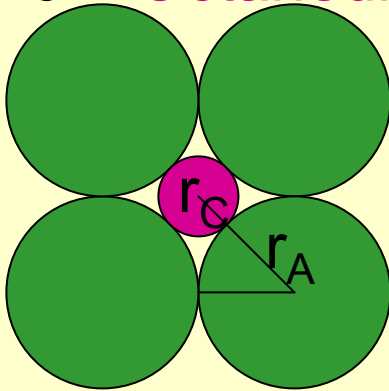


CsCl
(cesium
chloride)

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

Sample calculations of radii ratios

CN = 6 – Octahedral site

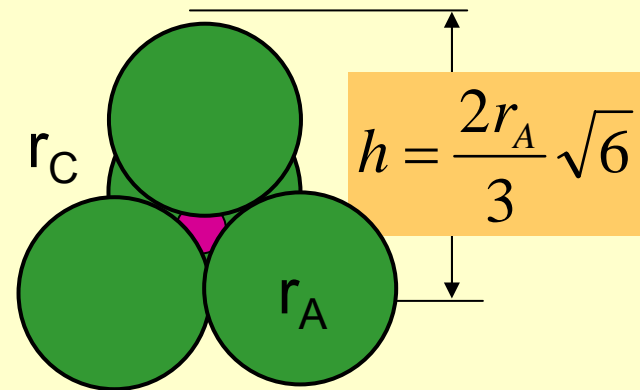


$$r_C + r_A \geq r_A \sqrt{2}$$

$$\frac{r_C}{r_A} + 1 \geq \sqrt{2}$$

$$\frac{r_C}{r_A} \geq \sqrt{2} - 1 = 0.414$$

CN = 4 – tetrahedral site



$$r_C + r_A \geq \frac{h}{2}$$

$$r_C + r_A \geq \frac{r_A}{3} \sqrt{6}$$

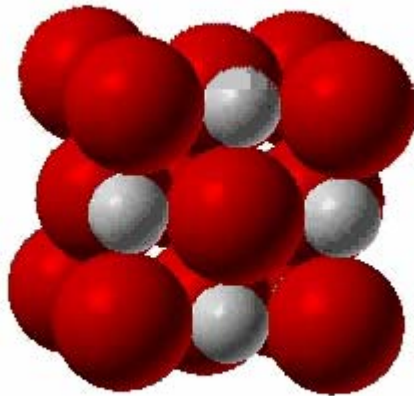
$$\frac{r_C}{r_A} + 1 \geq \frac{\sqrt{6}}{3}$$

$$\frac{r_C}{r_A} \geq \frac{\sqrt{6}}{3} - 1 = 0.225$$

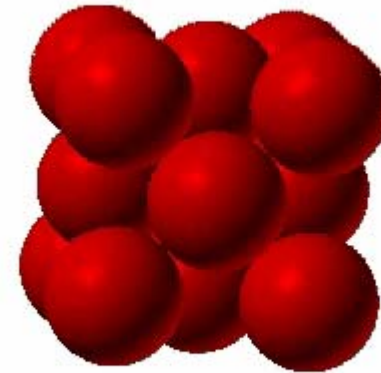
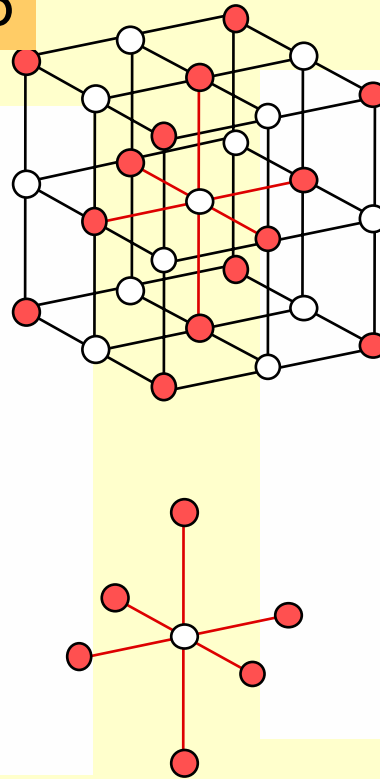
Structure of compounds: NaCl

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

CN = 6



(Courtesy P.M. Anderson)



(Courtesy P.M. Anderson)

Example: Predicting 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:

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

Data from Table 12.3,
Callister 6e.

Example: Predicting 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:

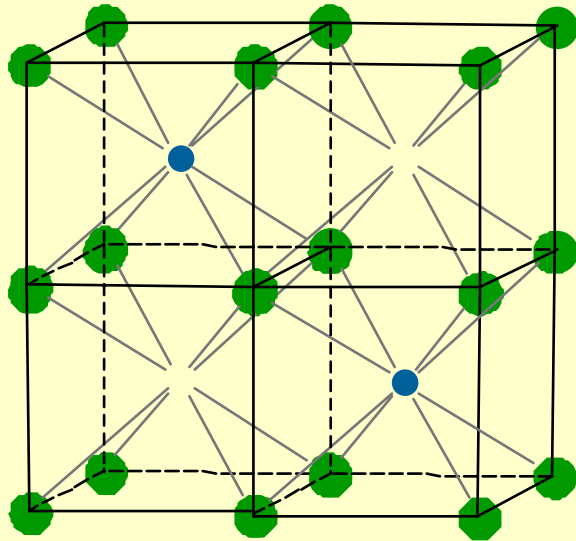
$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550$$

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

Data from Table 12.3,
Callister 6e.

A_mX_p structures

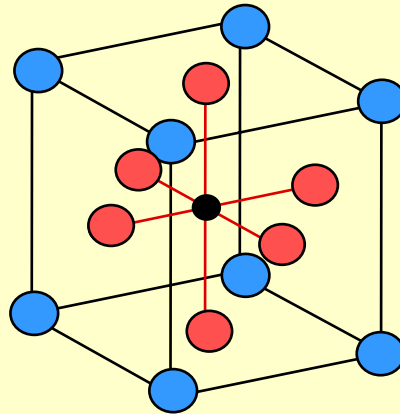
- Consider CaF_2 : $\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.100}{0.133} \approx 0.8$
- Based on this ratio, coord # = 8 and structure = CsCl.
- Result: CsCl structure w/only half the **cation** sites occupied.



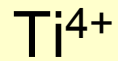
- Only half the **cation** sites are occupied since $\# \text{Ca}^{2+} \text{ ions} = 1/2 \# \text{F}^- \text{ ions}$.

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

$A_m B_n X_p$ structures

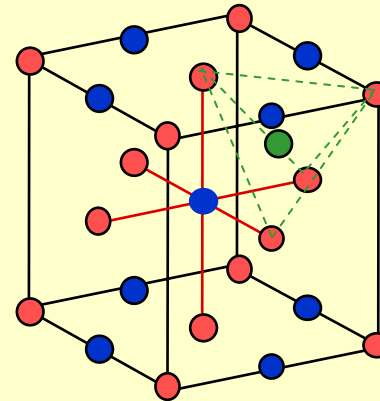


Perovskite

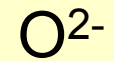
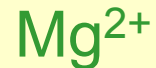


CN=6

CN=12



Spinel



CN=4

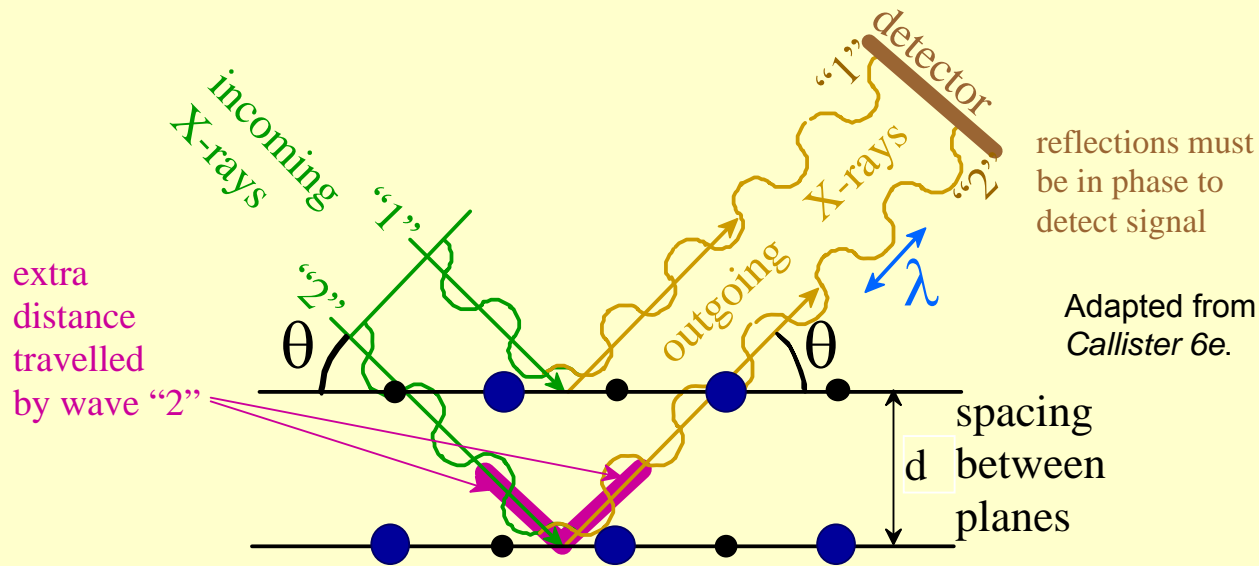
CN=6

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)
- Different structures of the same material are called **polymorphs**; the material is said to display **polymorphism**
- 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

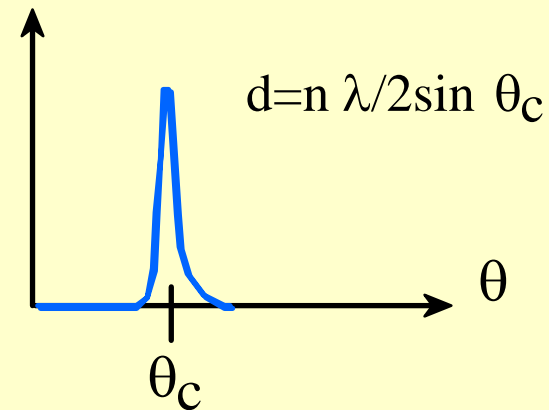
X-RAYS TO CONFIRM CRYSTAL STRUCTURE

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



- Measurement of:
Critical angles, θ_c ,
for X-rays provide
atomic spacing, d .

x-ray
intensity
(from
detector)

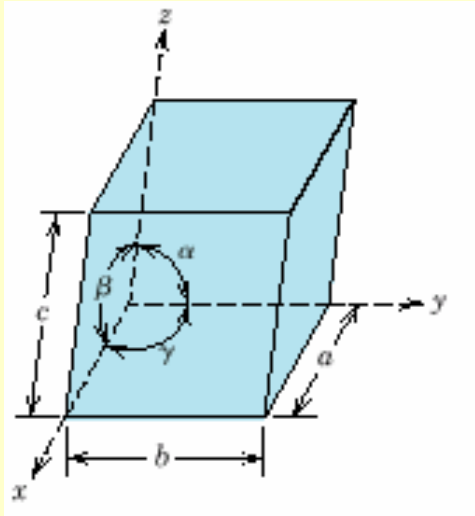


Crystallographic directions and planes

Objectives

- To be able to sketch directions corresponding to indices or vice versa in a cubic crystal system
- Specify Miller indices for planes drawn into a unit cell
- Compute planar and linear densities

Crystal systems



Cubic system

- 3 mutually \perp axes; $\alpha = \beta = \gamma = 90$
- 3 equal edges; $a = b = c$ (**lattice constants**)

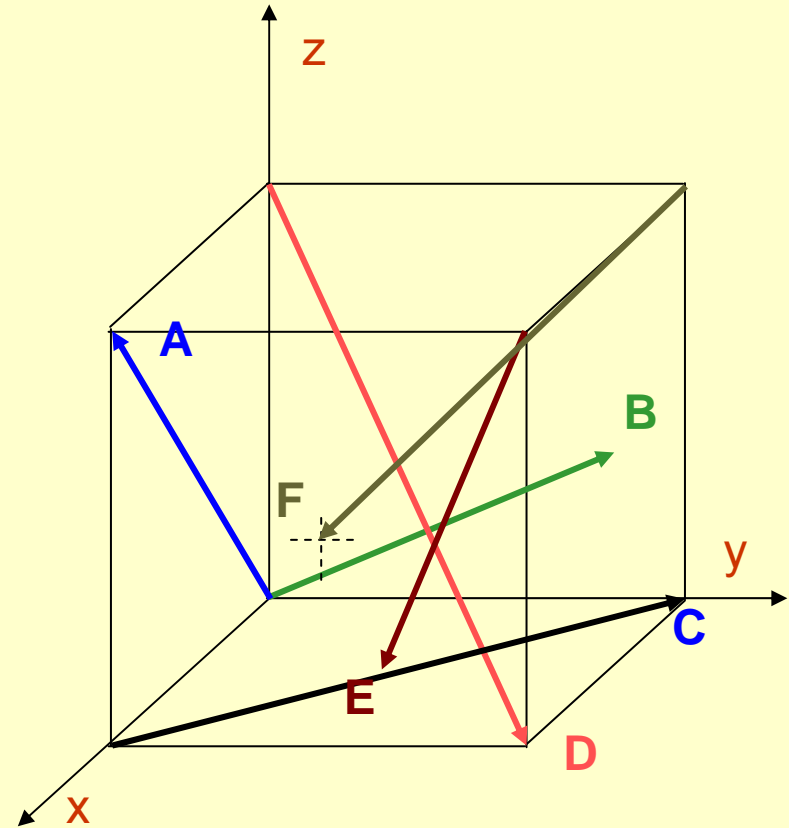
Cubic system is only one of **seven** crystal systems!

(3) Cubic	$a = b = c$	All angles = 90
(2) Tetragonal	$a = b \neq c$	All angles = 90
(4) Orthorhombic	$a \neq b \neq c$	All angles = 90
(2) Monoclinic	$a \neq b \neq c$	2 angles = 90; one $\neq 90$
(1) Triclinic	$a \neq b \neq c$	All angles \neq ; none = 90
(1) Hexagonal	$a = b \neq c$	2 Angles = 90; one = 120
(1) Rhombohedral	$a = b = c$	All angles equal $\neq 90$

Seven crystal systems are results from the arrangement of **14** different ways of arranging equivalent points in space – **Bravais lattices**

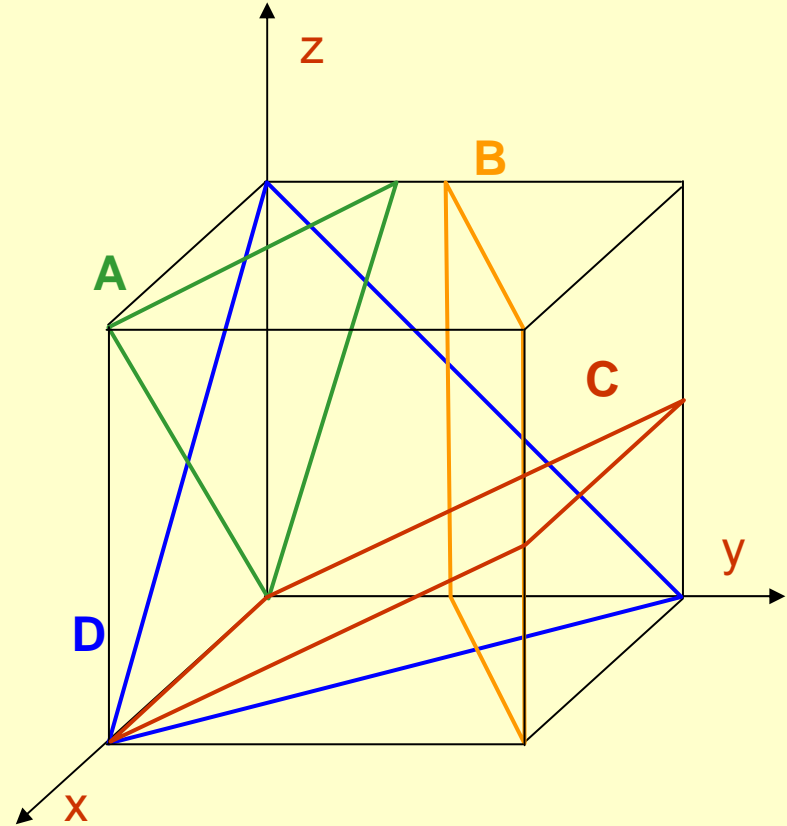
Crystal directions

- **Crystal Directions** – a vector - can be identified in a xyz coordinate system
 - 1. Choose an origin so that vector passes through it
 - 2. Write the coordinate of the end of the direction vector
 - 3. Write the coordinate of the origin of the direction vector
 - 4. Subtract the coordinate of the end from the coordinate from the origin
 - 5. Multiply all numbers by a common integer, as necessary, to reduce fractions
 - 6. Write the crystal direction enclosed by brackets without commas
- Generally designated by $[uvw]$
- Negatives are represented with a bar above the number



Miller Indices (crystal planes)

- **Crystal Planes** can also be defined within a cell.
 - 1. Select a convenient origin for the coordinate system so that the plane **does not** pass through it
 - 2. Find the coordinate of the points where the plane intersects the 3 major axes. **(If the plane does not intersect a particular axis, the intercept is infinity!)**
 - 3. Take the reciprocal (inverse) of the intercepts
 - 4. The plane indices are the final numbers obtained
- Generally designated as $(h\ k\ l)$ also called **Miller indices**



Family of directions

Directions in cubic system $[100]$, $[010]$, $[001]$, $[\bar{1}00]$, etc. are equivalent

The family is represented by $\langle 100 \rangle$

All combinations of $[12\bar{3}]$ directions regardless of signs are also equivalent – they are part of the $\langle 123 \rangle$ family

All combinations of $(11\bar{1})$ planes, regardless of signs are equivalents

The family is represented by $\{111\}$

Not true in non-cubic systems!!!

Planes and direction relationships

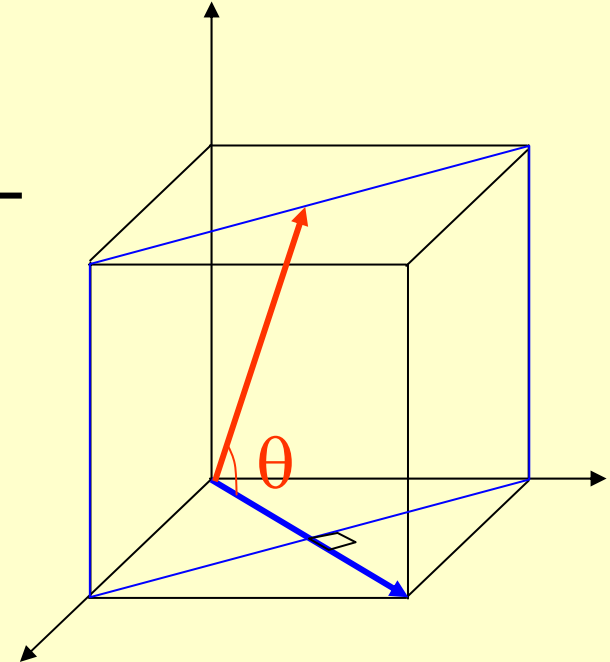
Make a note, we will be using this later

Planes and directions that share the indices are perpendicular

$[hkl]$ is perpendicular to (hkl)

$$\text{Cosine } \theta = \frac{(h.u + k.v + l.w)}{(h^2 + k^2 + l^2)^{1/2} \cdot (u^2 + v^2 + w^2)^{1/2}}$$

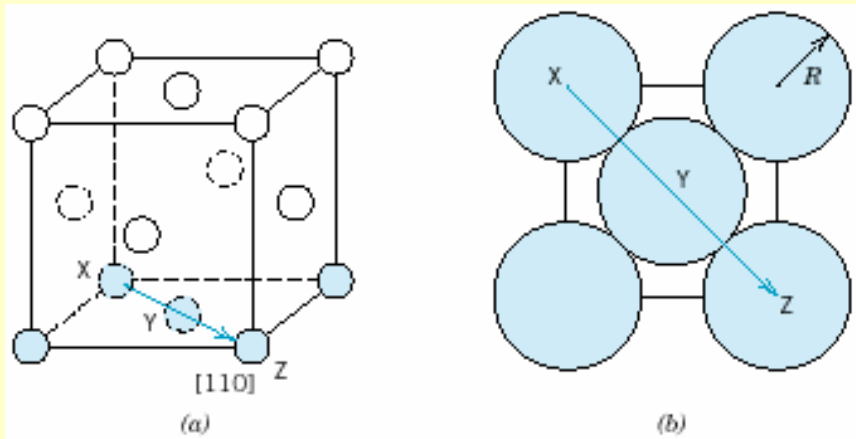
Not true in non-cubic systems!!!



Linear density

- We saw that many properties depended on crystal directions

Linear density =
$$\frac{\text{Number of atoms centered on a segment}}{\text{Length of segment}}$$

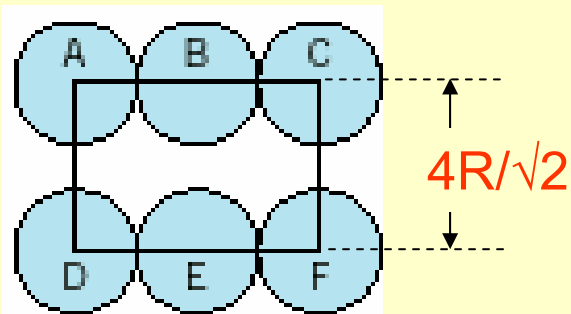


$$LD_{110} = \frac{2 \text{ atoms}}{4R} ; (\text{m})^{-1}$$

Planar density

Properties of crystals can be dependent on the specific plane (chemical, mechanical, magnetic etc.)

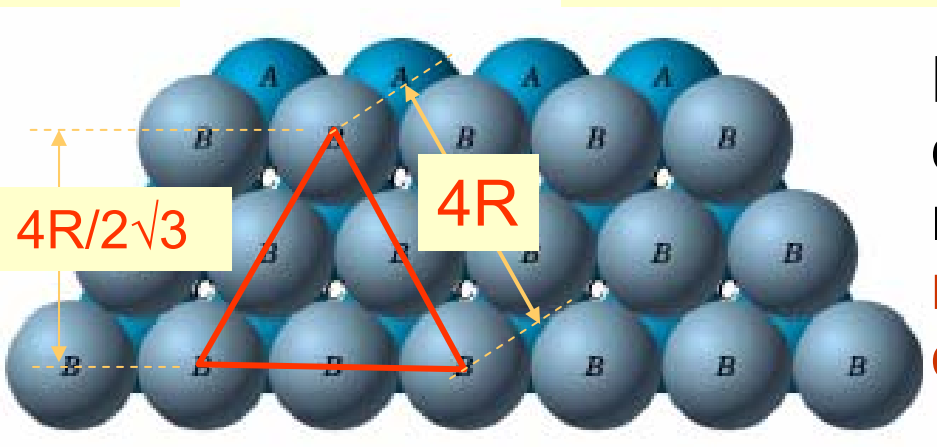
$$\text{Planar density} = \frac{\text{Number of atoms centered on a plane}}{\text{Area of plane}}$$



Example: Find FCC (lead) with Pb radius of 1.750 Å

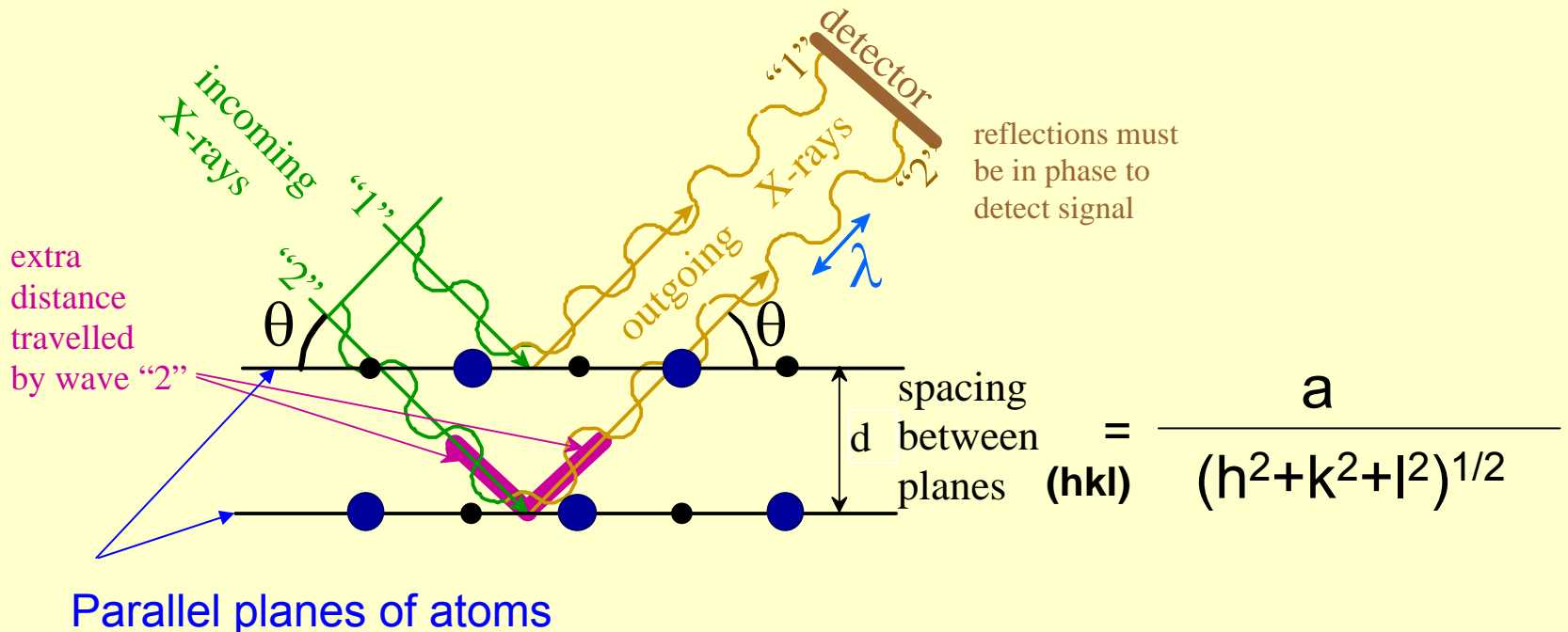
$$-PD_{110} = 2\text{atoms}/8R^2\sqrt{2}; (\text{m})^{-2}$$

$$-PD_{111} = 2\text{atoms}/4R^2\sqrt{2}; (\text{m})^{-2}$$



Both directions and planes (their densities) are important to the mechanism of **slip**. **It is the mechanism of metal deformation!!!**

Use of interplanar spacing



Bragg's Law: $n\lambda = 2d \sin \theta$

Allows the determination of

- Crystal structure
- Crystal orientation
- Lattice parameter
- Compound identification

ANNOUNCEMENTS

Reading: All of Chapter 3

Core Problems: due today 2:17, 20, 22; 3:1, 13; 12: 1, 5, 25

Self-help Problems: Examples problems in text