Chapter 3: The Structure of Crystalline Solids

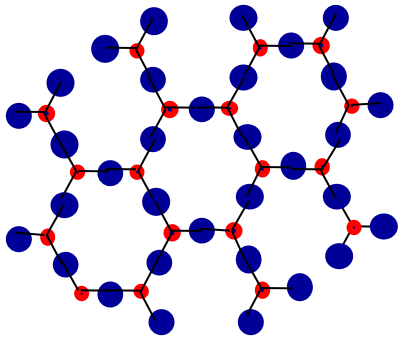
ISSUES TO ADDRESS...

- How do atoms assemble into solid structures?
- Examples of dependence of material property on its crystal structure

Crystalline vs. Noncrystalline (Amorphous) Materials

Crystalline materials...

- atoms pack in periodic, 3D arrays with long-range translational symmetry
- typical of:
  - Most metals
  - Many ceramics
  - Some polymers



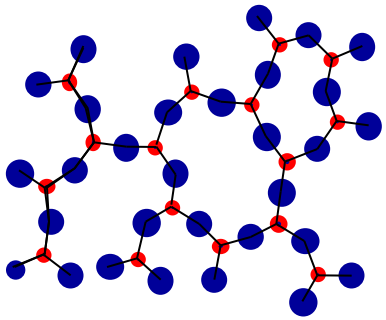
crystalline SiO_2

Adapted from Fig. 3.23(a), *Callister & Rethwisch 8e.*

• **Si** ● **Oxygen**

Noncrystalline materials...

- atoms have no long-range periodic packing
- occurs for:
  - All glasses
  - Some polymer



noncrystalline SiO_2

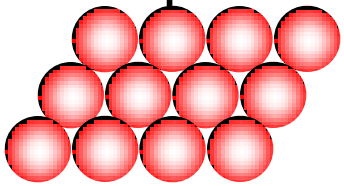
Adapted from Fig. 3.23(b), *Callister & Rethwisch 8e.*

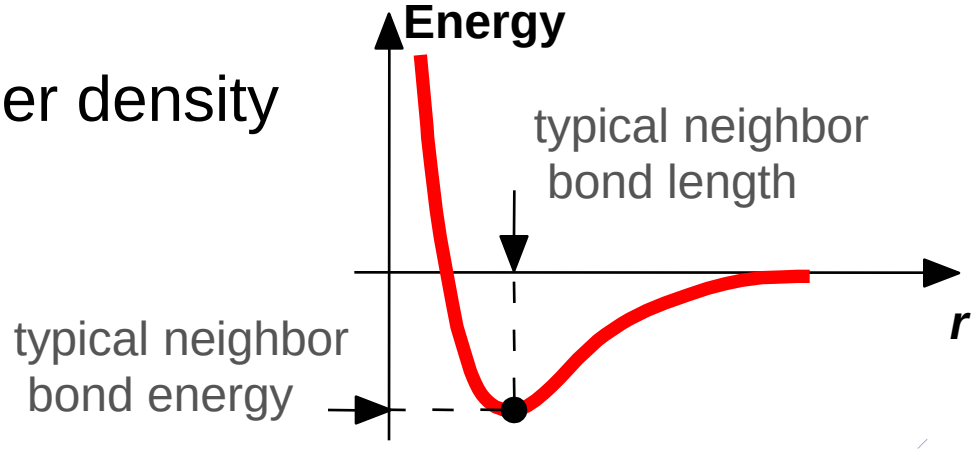
"Amorphous" = Noncrystalline

Energy & Packing for Crystalline vs. Noncrystalline (Amorphous) Materials

- Crystalline material

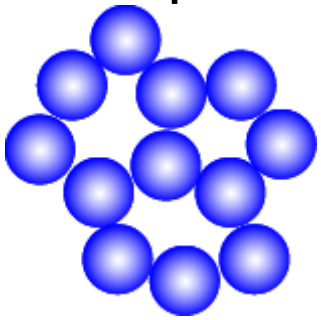
Ordered packing, higher density

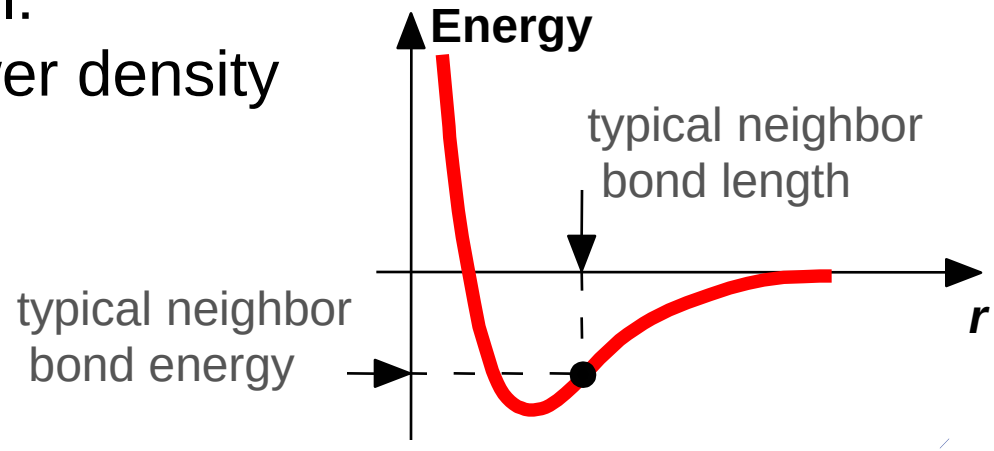




- Amorphous material:

Random packing, lower density



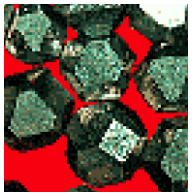


Orderly packed crystalline structures tend to have higher density and **lower** energies (**more stable**)

Single Crystal Materials

- Periodic arrangement of atoms throughout the entire material

-- diamond single crystals for industrial abrasives



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

-- Single crystal silicon wafer for semiconductor

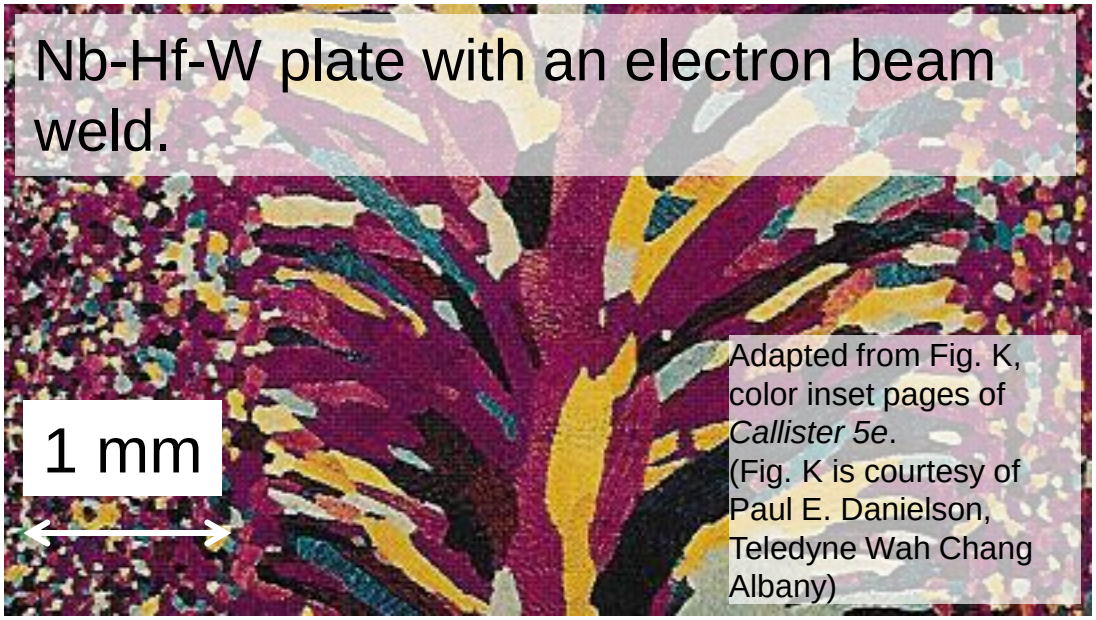
http://www.sumcosi.com/english/products/lineup.html

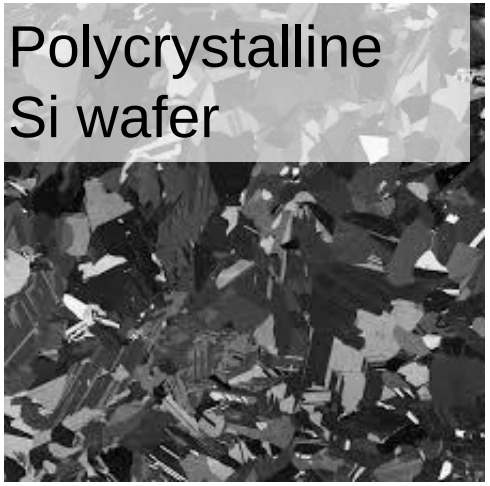
-- turbine blades

Fig. 8.33(c), *Callister & Rethwisch 8e.* (Fig. 8.33(c) courtesy of Pratt and Whitney).

Polycrystalline Materials

- *Most* engineering materials are polycrystalline, i.e., they contain many individual grains or small crystals





http://pveducation.org

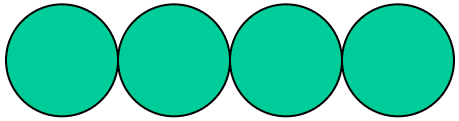
- Each "**grain**" is a single crystal

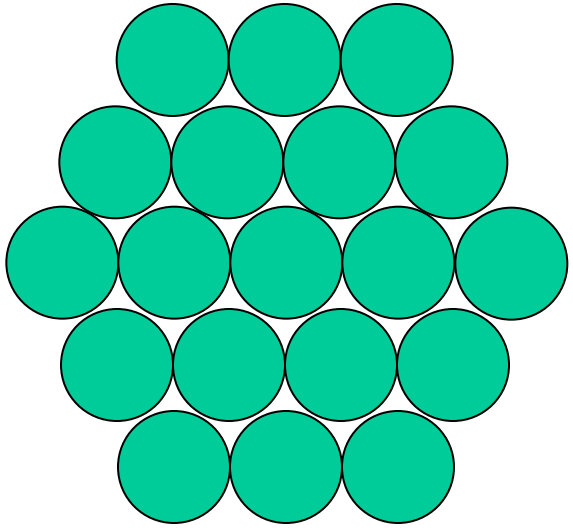
- Grain size ranges from ~1 nm to ~1 cm

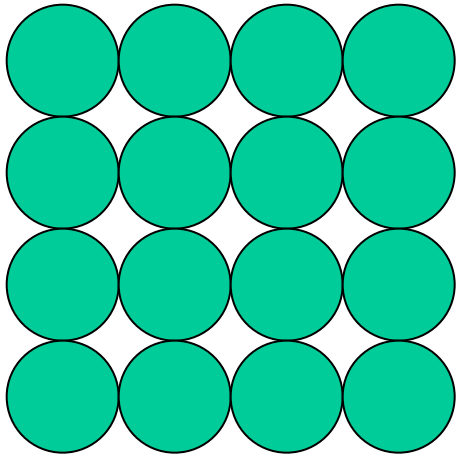
Polycrystalline Materials

Hard Sphere Model for Crystal Structures

- Hard-sphere model
  - Atoms are hard spheres
  - Atoms “touch” nearest neighbors
  - **Periodic** with **translational symmetry**
- Exercise:
  - Draw 1D arrangement
  - Draw 2D arrangement

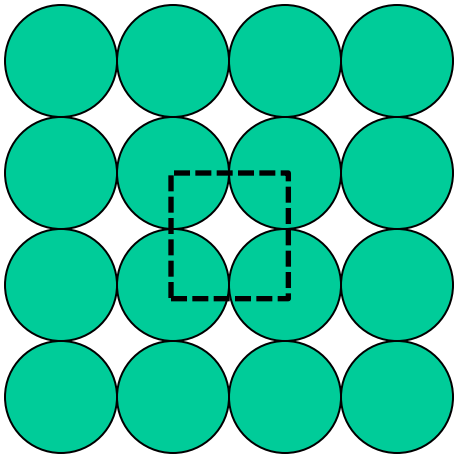


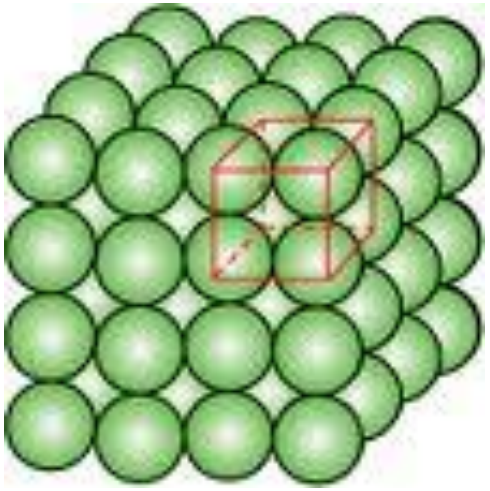




Crystal Lattice, Unit Cell, & Coordination Number (CN)

- **Crystal lattice**: an array of points coincide with atoms (or a certain set of atoms or molecules) representing geometric configuration in crystals
- **Unit cell:**
  Smallest (simplest) repeating unit in a lattice that satisfy the followings:
  - Represent/reflect symmetry in crystal
    - Translational
    - Rotational
    - Mirror
  - Opposite faces (for 3D)/edges are parallel
  - Each point is identical in its environment
- **Coordination Number (CN)**
  - Number of nearest (or touching) neighboring atoms for an atom within a crystal





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Crystal Systems

Unit cell in 3D typically parallelepipeds

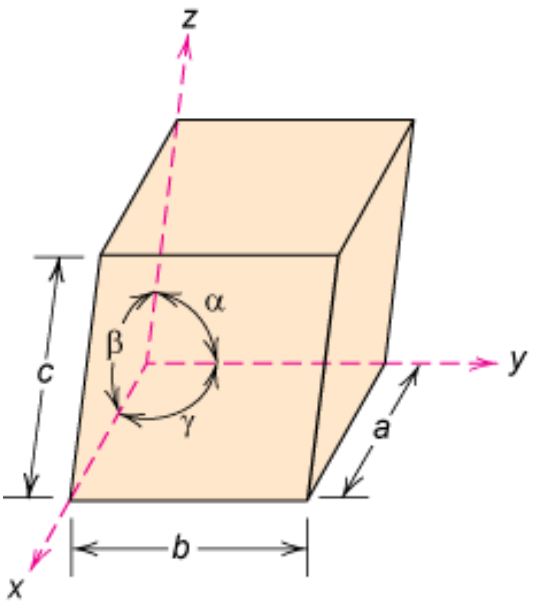


Fig. 3.4, *Callister & Rethwisch 8e.*

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

α, β, γ are angles

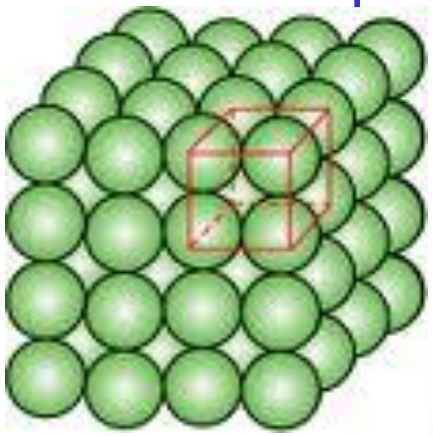
7 Crystal Systems

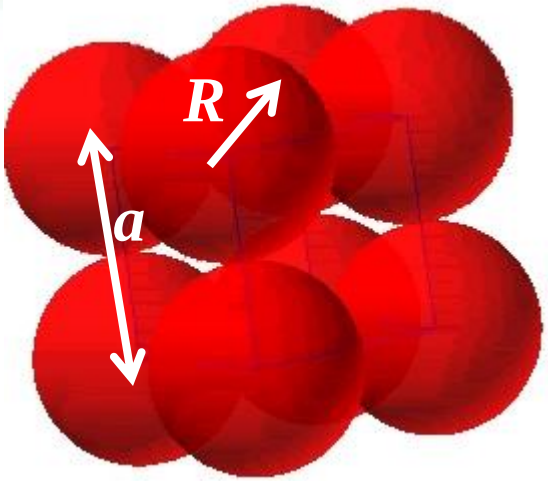
4 3-fold axis of rotation	1 4-fold axis of rotation	3 2-fold axis of rotation			
Cubic	**Tetragonal**	**Orthorhombic**	**Monoclinic**	**Triclinic**	**Rhombohedral (Trigonal)**	**Hexagonal**
			1 mirror plane	None	1 3-fold axis of rotation	1 6-fold axis of rotation

Adapted with changes from http://crystalinehealing.blogspot.com/2014/06/blog-post_11.html

Simple Cubic Structure (SC)

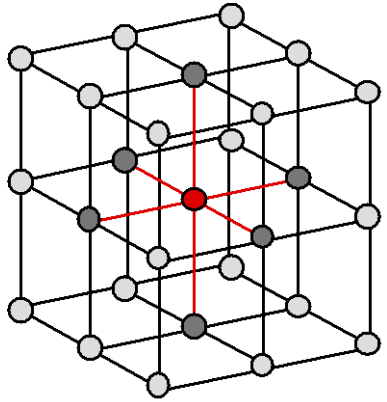
- Cubic crystal system
- Simple
- Rare for metals (only Po has this structure)
- Close-packed directions are cube edges

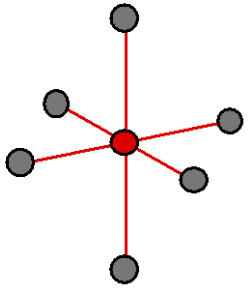




(Courtesy P.M. Anderson)

- Coordination number (CN, or the # nearest/touching neighbors) = 6





- If same types of atoms (e.g., pure metal)
  - Edge length a
  - Atom radius R

$$a = 2R$$

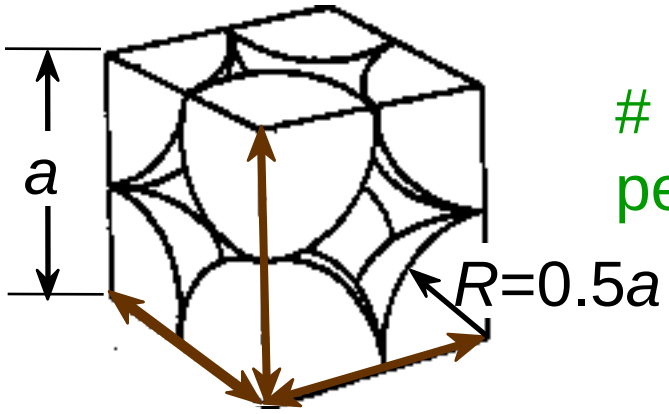
On average: 1 atoms per unit cell: 8 corners x 1/8 = 1

Crystal Structure Application Problem 2
Atomic Packing Factor (APF) for Simple Cubic Structure

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

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

# of atoms per unit cell

Volume of each atom

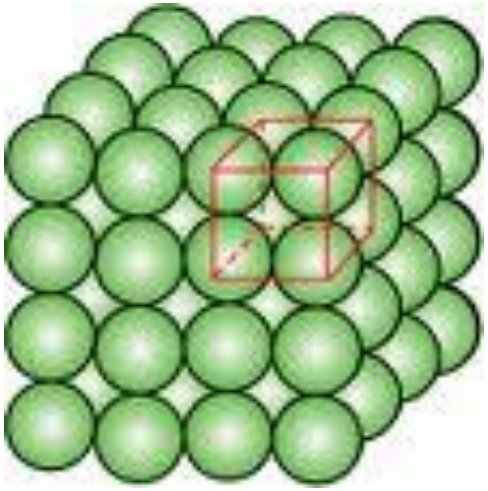
$$APF = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3} = \frac{\pi}{6} \cong 0.52$$

a^3 ← Volume of an unit cell

Adapted from Fig. 3.24, *Callister & Rethwisch 8e.*

Visualizing Simple Cubic (SC) Lattice

Filling balls for SC lattice



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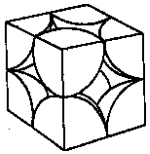


Unit cell for SC lattice

Ball-Stick model for SC lattice

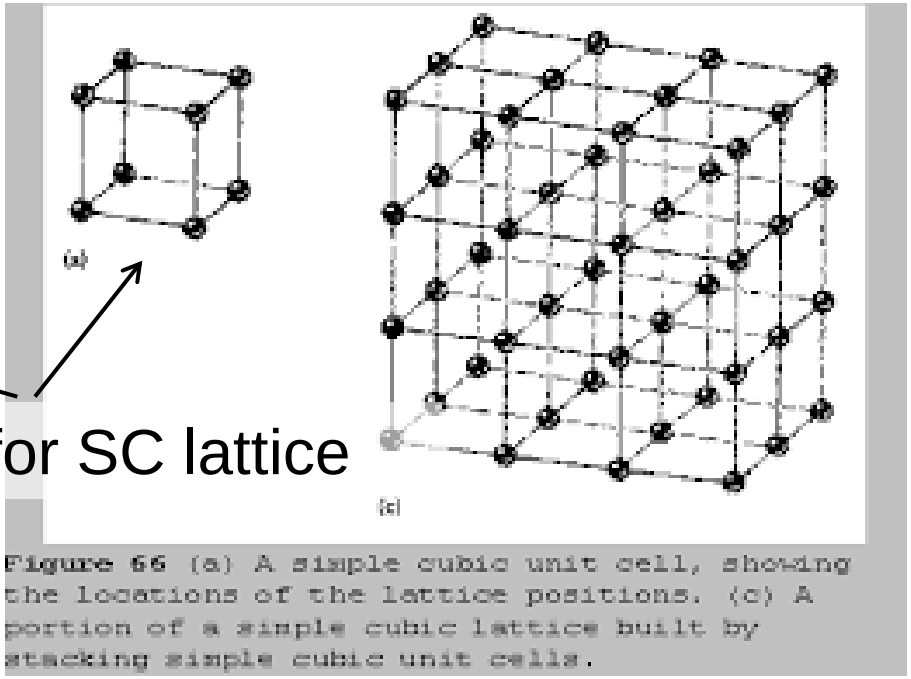


Figure 66 (a) A simple cubic unit cell, showing the locations of the lattice positions. (c) A portion of a simple cubic lattice built by stacking simple cubic unit cells.

http://www2.ucdsb.on.ca/tiss/stretton/CHEM2/arch19.htm

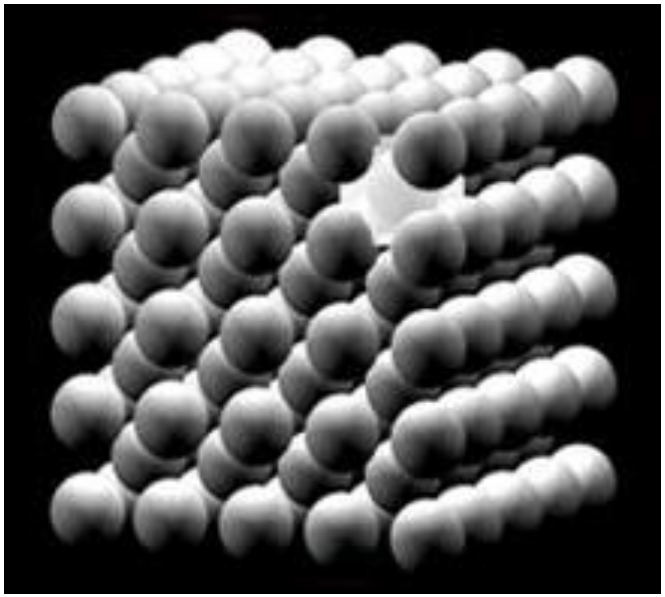
Body Centered Cubic (BCC) Structure

- Atoms touch each other along cube diagonals.

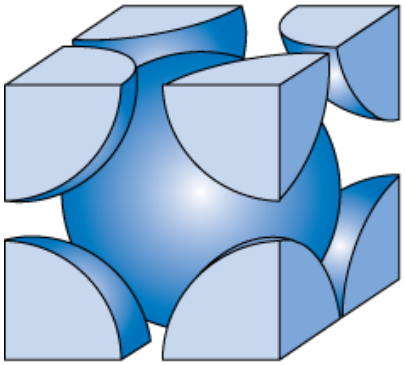
--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

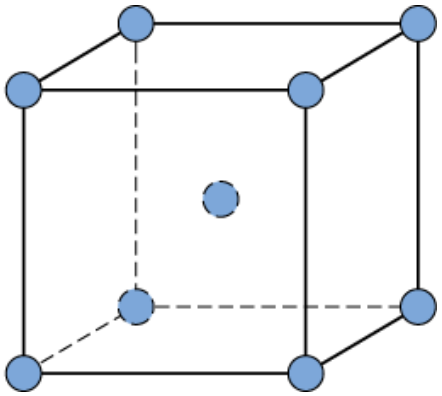
ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination number **CN = 8**



https://www.nde-ed.org/EducationResources/CommunityCollege/Materials/Structure/metallic_structures.htm



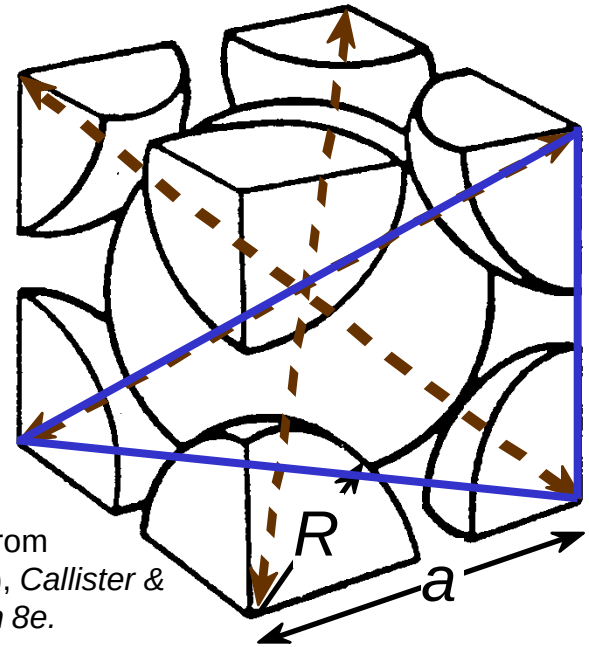


Adapted from Fig. 3.2, *Callister & Rethwisch 8e.*

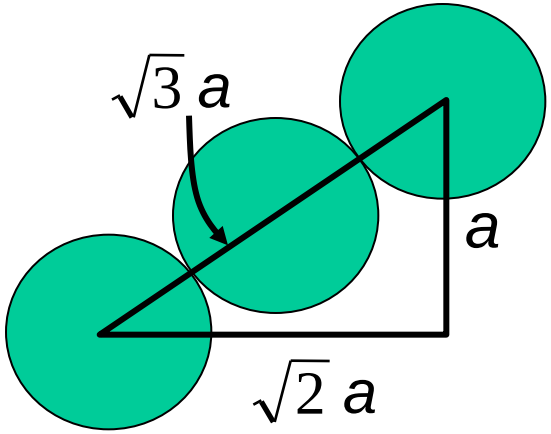
On average, 2 atoms per unit cell: 1 center + 8 corners x 1/8

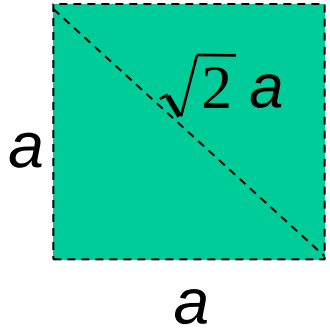
Crystal Structure Application Problem 2
Atomic Packing Factor (APF) for BCC

- APF for a body-centered cubic structure = 0.68



Adapted from Fig. 3.2(a), *Callister & Rethwisch 8e.*



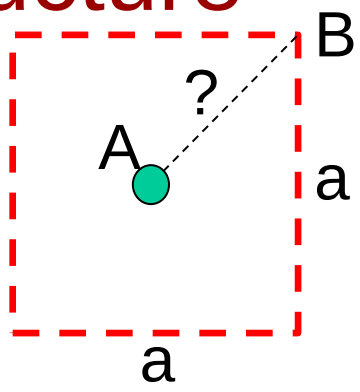


Along close-packed direction:

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

$$\text{APF} = \frac{\text{\# of atoms per unit cell} \times \text{Volume of each atom}}{\text{Volume of an unit cell}} = \frac{2 \cdot \frac{4}{3}\pi (\sqrt{3}a/4)^3}{a^3} = \frac{\sqrt{3}\pi}{8} \cong 0.68$$

Face Centered Cubic (FCC) Structure

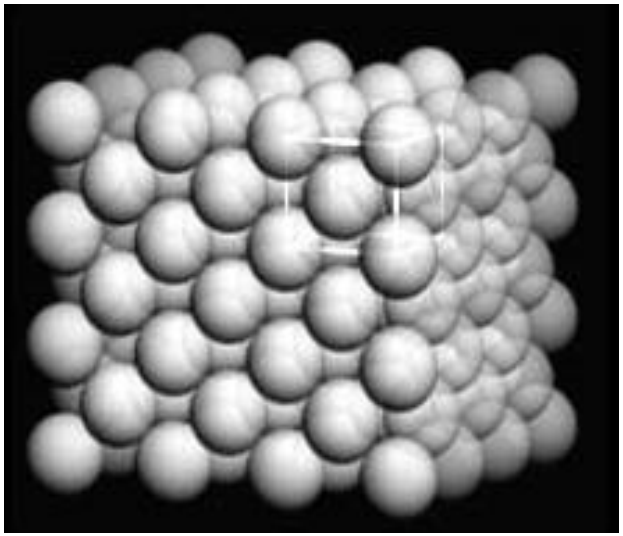


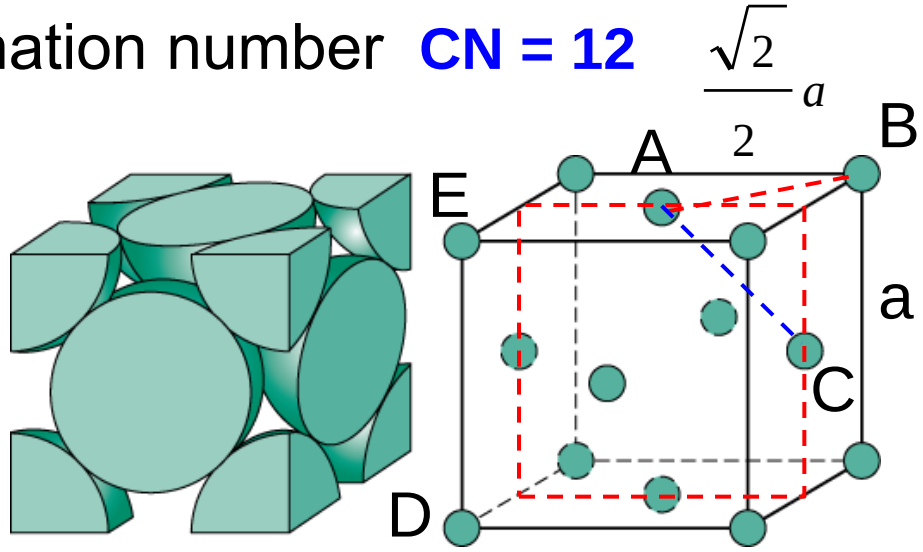
- Atoms touch each other along face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

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

https://www.nde-ed.org/EducationResources/CommunityCollege/Materials/Structure/metallic_structures.htm

- Coordination number **CN = 12**



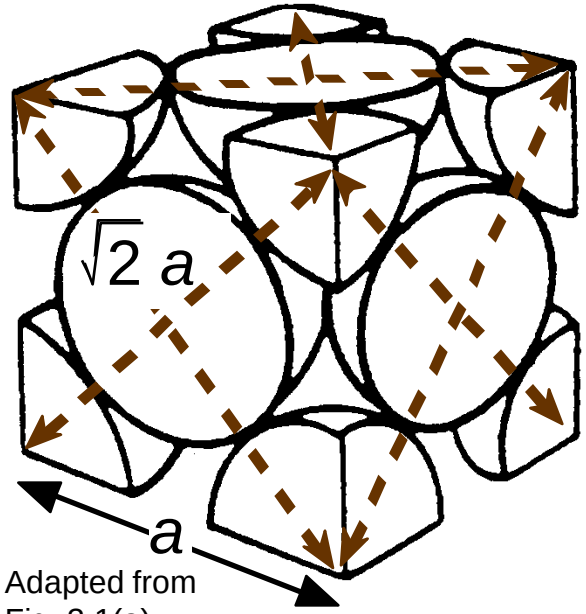


Adapted from Fig. 3.1, *Callister & Rethwisch 8e.*

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

Crystal Structure Application Problem 2
Atomic Packing Factor (APF) for FCC

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



Adapted from Fig. 3.1(a), *Callister & Rethwisch 8e.*

Close-packed directions:

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

$$APF = \frac{\text{\# of atoms per unit cell} \times \text{Volume of each atom}}{\text{Volume of an unit cell}} = \frac{4\left(\frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3\right)}{a^3} = \frac{\sqrt{2}\pi}{6} \cong 0.74$$

Densities of Material Classes

In general

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

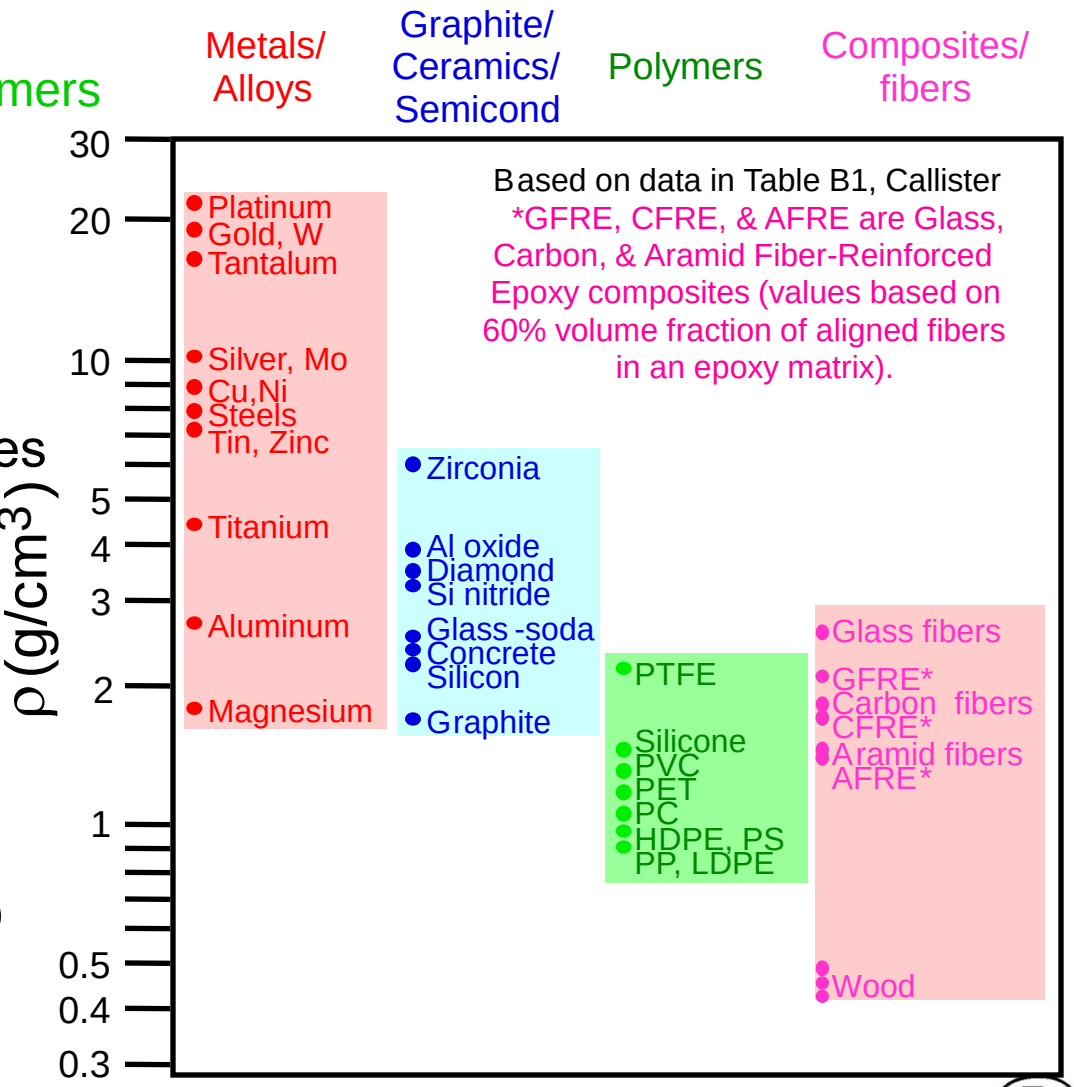
Why?

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



Data from Table B.1, *Callister & Rethwisch, 8e.*