Chapter 3: The Structure of Crystalline Solids

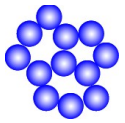
ISSUES TO ADDRESS...

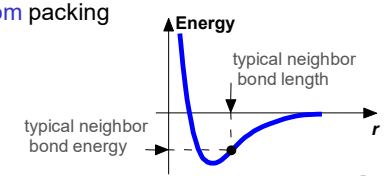
- How do atoms assemble into solid structures? (for now, focus on metals)
- How does the density of a material depend on its structure?
- When do material properties vary with the sample (i.e., part) orientation?

1

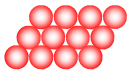
Energy and Packing

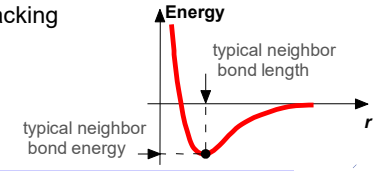
- Non dense, random packing





- Dense, ordered packing



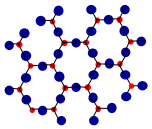


Dense, ordered packed structures tend to have lower energies.

2

Materials and Packing

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

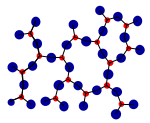


crystalline SiO_2
Adapted from Fig. 3.22(a), *Callister 7e.*

• 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.*

3

Section 3.3 – Crystal Systems

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

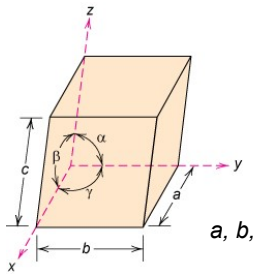


Fig. 3.4, *Callister 7e.*

7 crystal systems

14 crystal lattices

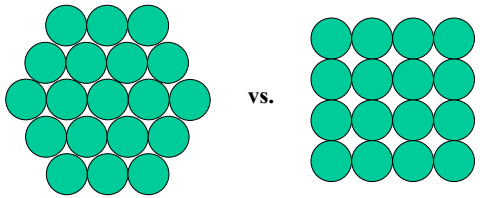
a, b, and *c* are the lattice constants

4

Section 3.4 – 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

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Metallic Crystal Structures

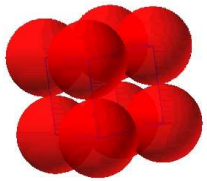
- Tend to be densely packed.
- Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - Electron cloud shields cores from each other
- Have the simplest crystal structures.

We will examine three such structures...

6

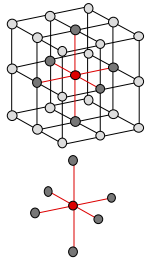
Simple Cubic Structure (SC)

- 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)



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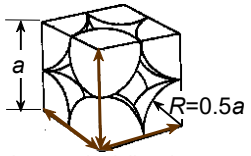
Atomic Packing Factor (APF)

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

*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.*

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

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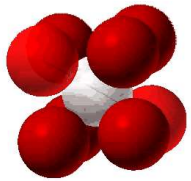
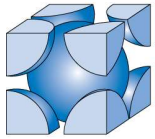
Body Centered Cubic Structure (BCC)

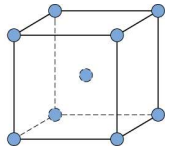
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

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

- Coordination # = 8







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

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

(Courtesy P.M. Anderson)

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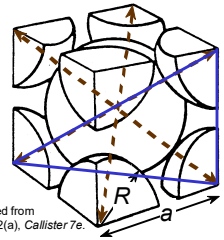
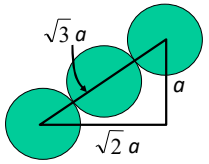
Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



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



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

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

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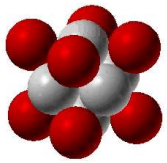
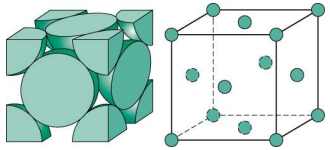
Face Centered Cubic Structure (FCC)

- 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)

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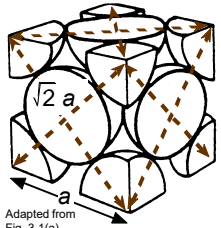
Atomic Packing Factor: FCC

- 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 x 1/2 + 8 x 1/8
= 4 atoms/unit cell

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

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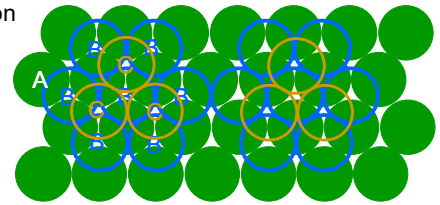
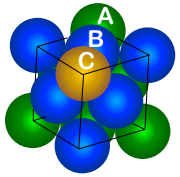
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection



- FCC Unit Cell



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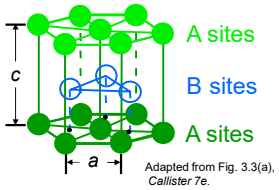
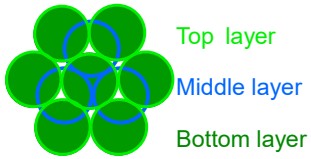
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



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

- 2D Projection



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

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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 x 10^{23} atoms/mol

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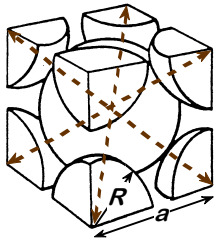
Theoretical Density, ρ



- Ex: Cr (BCC)
  A = 52.00 g/mol
  R = 0.125 nm
  n = 2

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

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{g}}{\text{mol}}}{\text{volume} \times \frac{\text{atoms}}{\text{mol}}} = \frac{2 \times 52.00}{a^3 \times 6.023 \times 10^{23}}$$

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

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Densities of Material Classes

In general

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

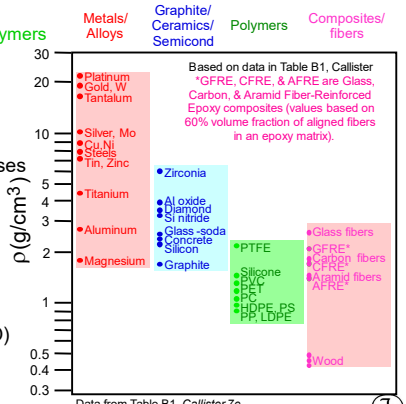
Why?

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 B1, *Callister 7e.*

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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. 8.33(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)

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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).

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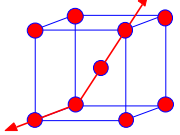
Single vs Polycrystals

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

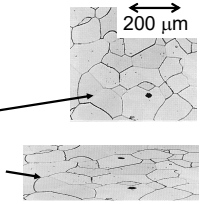
E (diagonal) = 273 GPa



E (edge) = 125 GPa

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. ($E_{poly\ iron}$ = 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].)

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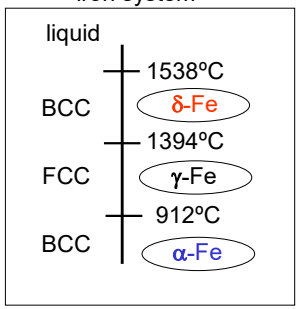
Section 3.6 – Polymorphism

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

titanium
α, β-Ti

carbon
diamond, graphite

iron system



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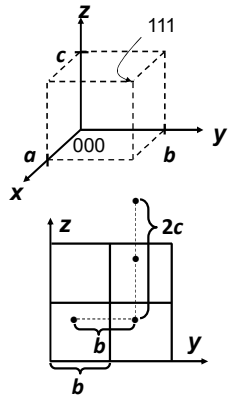
Section 3.8 Point Coordinates



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

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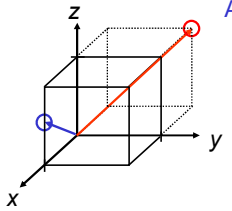
Crystallographic Directions



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*>

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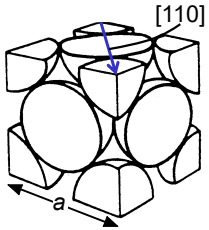
Linear Density

- Linear Density of Atoms ≡ LD = $\frac{\text{Number of atoms}}{\text{Unit length of direction vector}}$



ex: linear density of Al in [110] direction

a = 0.405 nm

atoms → 2

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

length → $\sqrt{2}a$

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