Chapter 3: The structure of crystalline solids

Outline

- Fundamental concepts
- Unit cells
- Metallic crystal structure
- Density and polymorphism
- Crystal systems

Fundamental concepts

- Crystalline materials: atoms are situated in a repeating or periodic array over large atomic distances
- Crystalline structure: how atoms, ions, or molecules are arranged spatially
- Lattice: a three-dimensional array of points coinciding with atom position

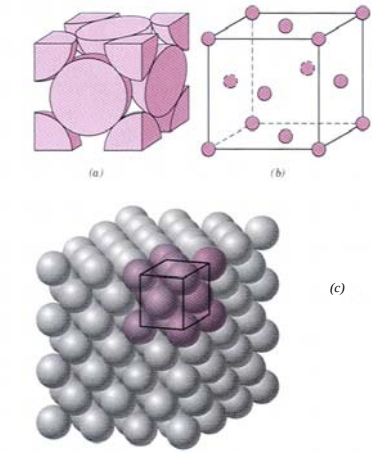
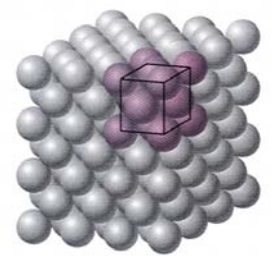


Fig 3.1 (a) a hard sphere unit cell (b) a reduced-sphere unit cell, (c) an aggregate of many atoms

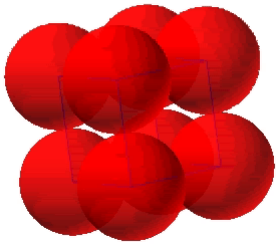
Unit cells

- Small repeating units in a crystal
- Basic structural unit or building block of the crystal structure
- Not unique
- A highest level of geometrical symmetry

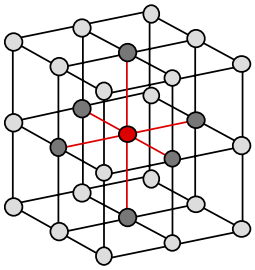


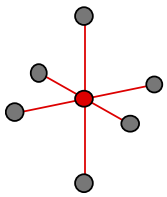
Simple cubic structure (SC)

- Close-packed directions are cube edges.
- Atoms per unit cell = 8 x 1/8 =1
- Coordination # (nearest neighbors) = 6
- Rare due to low packing density (only Po has this structure)



(Courtesy P.M. Anderson)



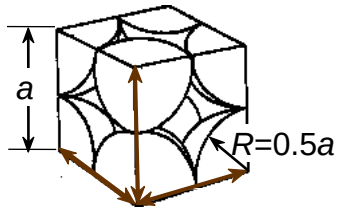


Atomic packing factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

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

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

Metallic crystal structure

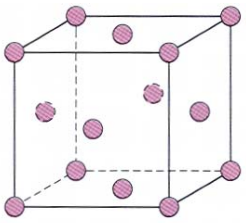
- Features of metallic crystal structure
  - non-directional in nature
  - no restriction on the number and position of nearest-neighbor atoms
  - close-packed: low energy
  - common type: face-centered cubic (FCC), body-centered cubic (BCC), hexagonal closed-packed (HCP)

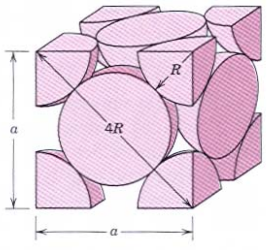
The FCC crystal structure

- Total atoms per unit cell=4
  - 8x1/8 atoms at corner+6x1/2 face-centered atoms=4
- The relation between cubic edge a and the radius R

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

- Coordination number=12
  - the number of nearest-neighbor or touching atoms
- Atomic packing factor (APF)
  - APF=0.74

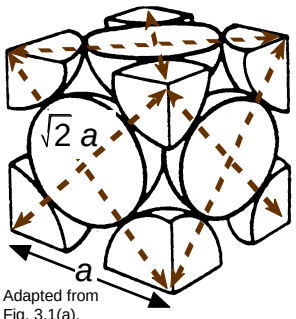




Atomic packing factor: FCC

- 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

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

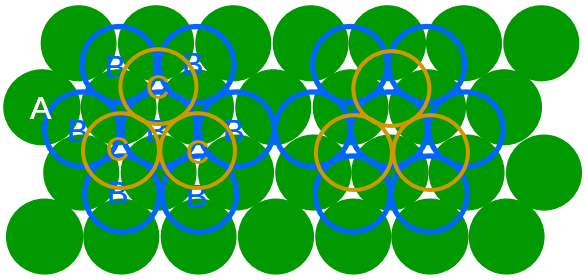
FCC stacking sequence

- ABCABC... Stacking Sequence
- 2D Projection

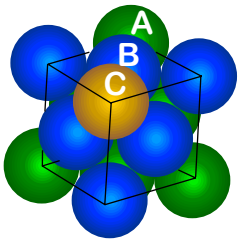
A sites

B sites

C sites

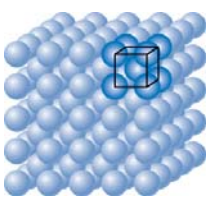


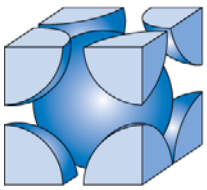
- FCC Unit Cell

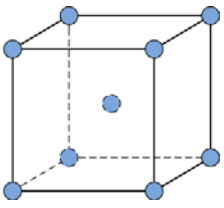


The BCC crystal structure

- Total atoms per unit cell
  8x1/8 atoms at corner+1 body-centered atoms=2
- Coordination number=8

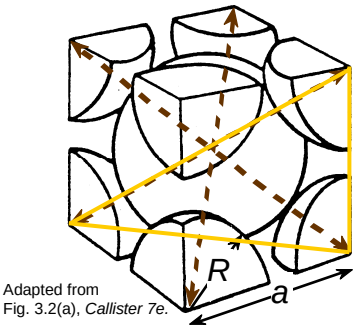




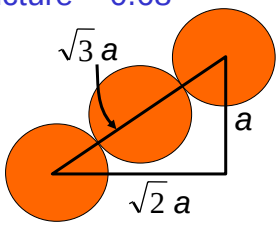


Atomic packing factor: BCC

- APF for a body-centered cubic structure = 0.68



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

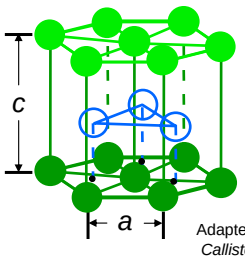


Close-packed directions:
length = $4R = \sqrt{3}\,a$

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

Hexagonal close-packed structure (HCP)

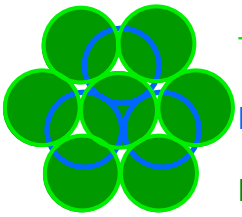
- ABAB... Stacking Sequence
- 3D Projection



A sites
B sites
A sites

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

- 2D Projection



Top layer
Middle layer
Bottom layer

- 6 atoms/unit cell
- Coordination # = 12
- APF = 0.74
- *c*/*a* = 1.633

ex: Cd, Mg, Ti, Zn

Theoretical density and polymorphism

- **Density computation**

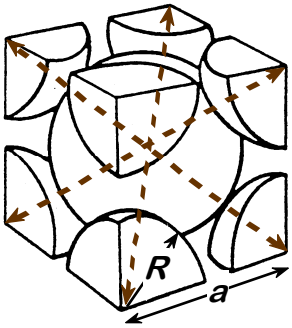
$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{nA}{V_C N_A}$$

where n = number of atoms/unit cell
A = atomic weight
VC = Volume of unit cell = $a3$ for cubic
NA = Avogadro's number
= 6.023 x 1023 atoms/mol

- **Polymorphism: a phenomenon that material has more than one crystal structure**

Theoretical density (example)



- 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

Densities of material classes

In general

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

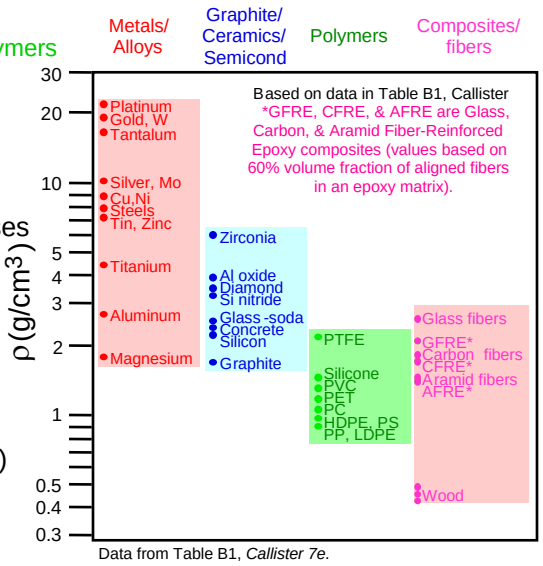
Why?

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.*

Crystal systems

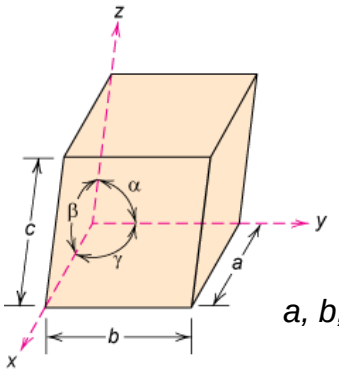


Fig. 3.4, *Callister 7e.*

- 7 crystal systems
- 14 crystal lattices

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

Crystal systems

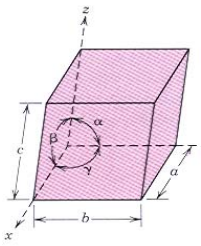
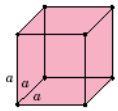
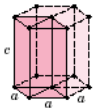
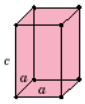
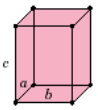
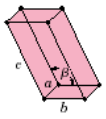
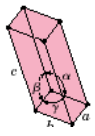
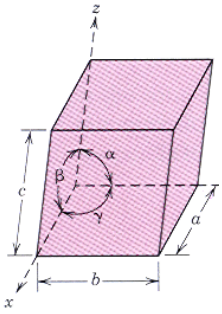


Table 3.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	

Crystal systems

Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	



Crystal Systems

Cubic:
Lead ore

Rhombic:
Topaz

Hexagonal:
Emerald

Tetragonal:
idocrase

Monoclinic:
Gypsum

Triclinic:
Axinite