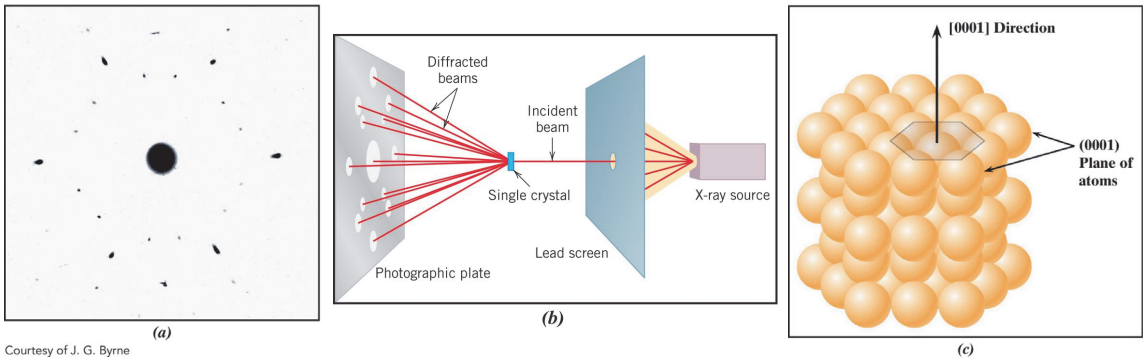
Chapter 4: The Structures of Crystalline Solids

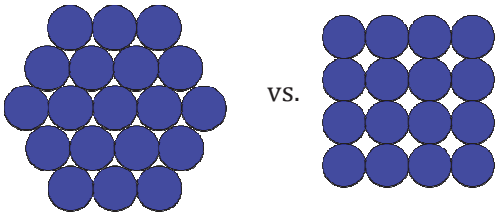
- **ISSUES TO ADDRESS...**
  - What are common crystal structures for metals and ceramics?
  - What features of a metal's/ceramic's atomic structure determine its density?
  - How do the crystal structures of ceramic materials differ from those for metals?



(a) X-ray diffraction photograph for a single crystal of magnesium.
(b) Schematic diagram illustrating how the spots in (a) are produced.
(c) Magnesium's hexagonal close-packed crystal structure

Metallic Crystal Structures

- **How can we stack metal atoms to minimize empty space?**
  - In 2-dimensions,

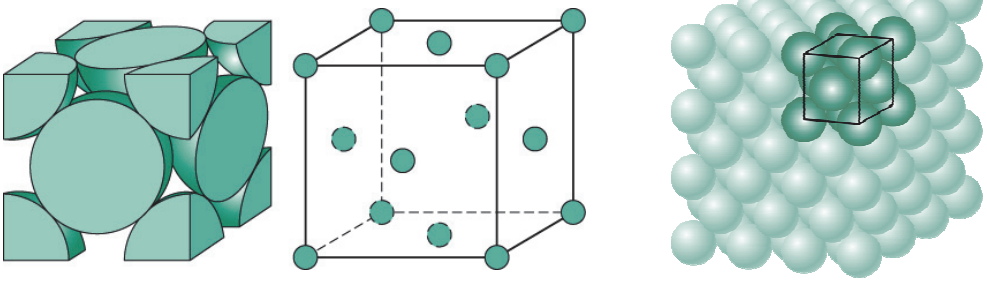


  - Now stack these 2-D layers to make 3-D structures.

- **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.
- **Metals have the simplest crystal structures.**
- **We will examine three such structures: FCC, BCC, HCP**

4.2 The Face-Centered Cubic (FCC) Crystal Structure

- **Face-Centered Cubic (FCC) Crystals**
  - Atoms are located at each of the corners and the centers of all the cube faces.
  - Atoms touch each other along face diagonals.
  - Example: Al, Cu, Au, Ni, Pt, Ag
  - Unit cell edge length for FCC: $a = 2R\sqrt{2}$ (R=atomic radius)
- **The number of atoms per unit cell, *N***
  - $N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$, where N_i= the number of interior atoms
    N_f= the number of face atoms
    N_c= the number of corner atoms
  - For FCC crystals, N_i= 0, N_f= 6, and N_c= 8, therefore N= 4.

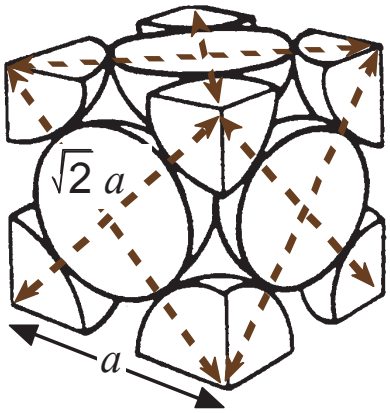


4.2 The Face-Centered Cubic (FCC) Crystal Structure

- **Coordination Number = the number of nearest neighbor or touching atoms**
  - For FCC, the coordination number is 12.
- **Atomic Packing Factor (APF)**
  - $APF = \dfrac{Volume\ of\ atoms\ in\ a\ unit\ cell}{Total\ unit\ cell\ volume}$
- **For FCC crystals, APF = 0.74**
  - Close-packed directions: length = $4R = \sqrt{2}a$
  - Unit cell contains 4 atoms (N= 4).
  - $APF = \dfrac{N \times (4/3)\pi R^3}{a^3}$

    $= \dfrac{4 \times (4/3)\pi(\sqrt{2}a/4)^3}{a^3}$

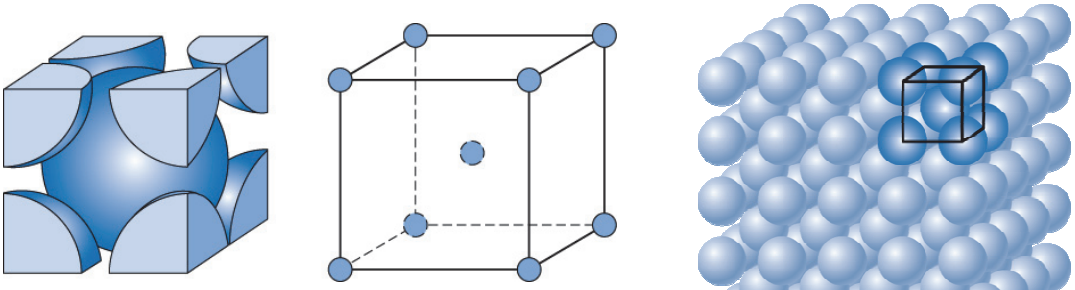
    = 0.74 (maximum achievable APF)



Adapted from Fig. 3.1(a), *Callister & Rethwisch 9e.*

4.3 The Body-Centered Cubic (BCC) Crystal Structure

- **Body-Centered Cubic (BCC) Crystals**
  - Atoms are located at all eight corners and a single atom at the cube center.
  - Atoms touch each other along cube diagonals.
  - Example: Cr, W, Fe (α), Tantalum, Molybdenum
  - Unit cell edge length for BCC: $a = 4R/\sqrt{3}$ (R=atomic radius)
- **The number of atoms per unit cell, *N***
  - For BCC crystals, $N_i = 1$, $N_f = 0$, and $N_c = 8$, therefore $N = N_i + \frac{N_f}{2} + \frac{N_c}{8} = 2$.
- **For BCC, the coordination number is 8.**



Adapted from Fig. 4.1,
Callister & Rethwisch 9e.

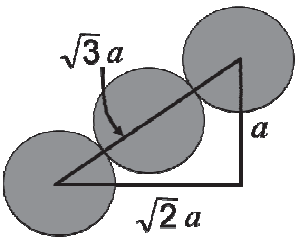
4.3 The Body-Centered Cubic (BCC) Crystal Structure

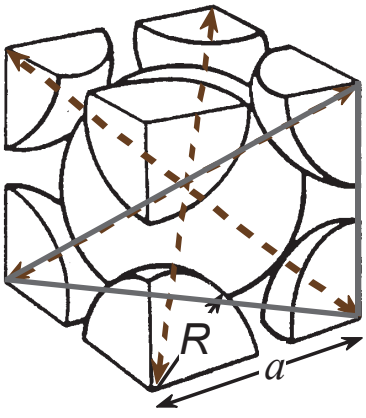
- **APF for a body-centered cubic structure = 0.68**
  - Close-packed directions: length = $4R = \sqrt{3}a$
  - Unit cell contains 2 atoms ($N = 2$).
  - APF = $\dfrac{\text{Volume of atoms in a unit cell}}{\text{Total unit cell volume}}$

$$= \frac{N \times (4/3)\pi R^3}{a^3}$$

$$= \frac{2 \times (4/3)\pi(\sqrt{3}a/4)^3}{a^3}$$

$$= 0.68 \quad \text{(maximum achievable APF)}$$



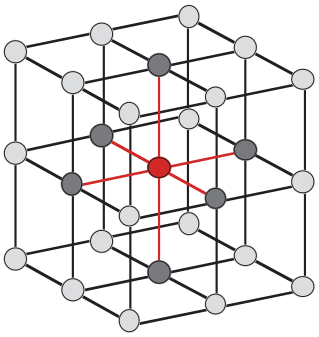


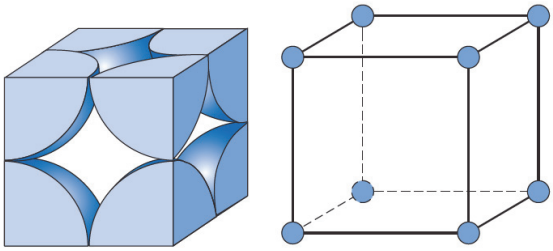
Adapted from Fig. 4.1(a),
Callister & Rethwisch 9e.

Simple Cubic (SC) Crystal Structure

- **Rare due to low packing density (only Po has this structure)**
- **Close-packed directions are cube edges.**
- **The coordination number of SC crystals is 6.**
- **APF for a simple cubic structure = 0.52**
  - Close-packed directions: length = $2R = a$
  - Unit cell contains 1 atoms (N= 1).
  - $\text{APF} = \dfrac{\text{N}\times(4/3)\pi\text{R}^3}{\text{a}^3} = \dfrac{1\times(4/3)\pi(0.5\text{a})^3}{\text{a}^3}$

  = 0.52 (maximum achievable APF)





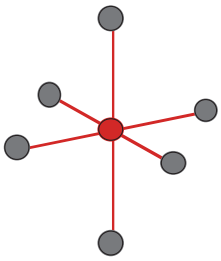
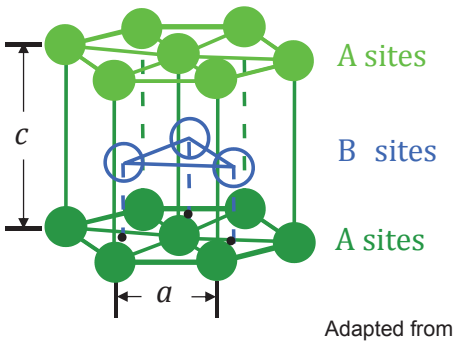


Fig. 4.2, *Callister & Rethwisch 9e.*

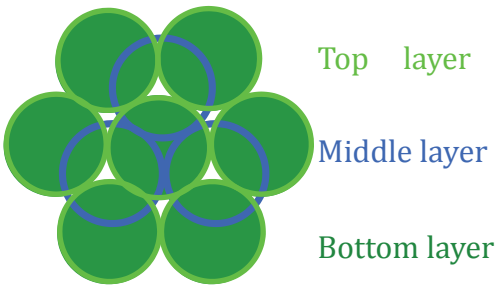
4.4 Hexagonal Close-Packed (HCP) Structure

- **ABAB... Stacking Sequence**
- **Example: Cd, Mg, Ti, Zn**
- **The coordination number of HCP crystals is 12.**
- **The number of atoms per unit cell, N, is 6.**
- **APF for a HCP structure = 0.74.**
- **c/a = 1.633**

• 3D Projection



• 2D Projection



Adapted from Fig. 4.3(a), *Callister & Rethwisch 9e.*

4.5 Density Calculations-Metals

- **Theoretical Density for Metals, ρ**

$$\text{Density} = \rho = \frac{\text{Mass of atoms in unit cell}}{\text{Total volume of unit cell}} = \frac{n\,A}{V_C\,N_A}$$

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
= 6.022×10^{23} atoms/mol

Adapted from Fig. 4.1(a), *Callister & Rethwisch 9e.*

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

- **Ex: Cr (BCC)**
  - A (atomic weight) = 52.00 g/mol
  - R (atomic radius) = 0.125 nm
  - n = 2 atoms/unit cell

$$\text{Density} = \rho = \frac{2 \times 52.00}{a^3 \times N 6.022 \times 10^{23}}$$

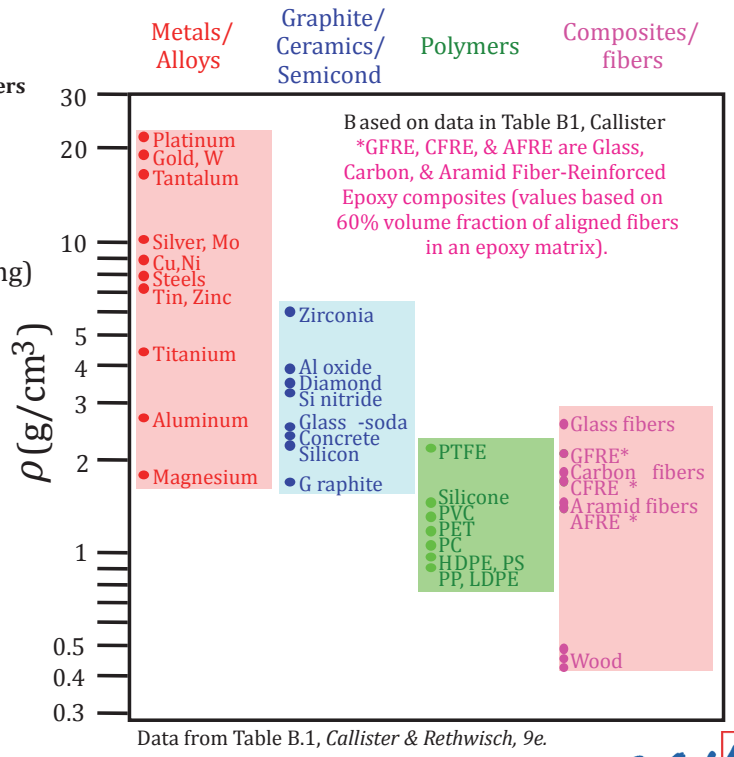
  - $\rho_{theoretical} = 7.18\ g/cm^3$
  - $\rho_{actual} = 7.19\ g/cm^3$

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 B.1, *Callister & Rethwisch, 9e.*

4.12 Polymorphic Forms of Carbon

- **Diamond**
  - tetrahedral bonding of carbon atoms
    - hardest material known
    - very high thermal conductivity
  - large single crystals – gem stones
  - small crystals – used to grind/cut other materials
  - diamond thin films
    - hard surface coatings – used for cutting tools, medical devices, etc.

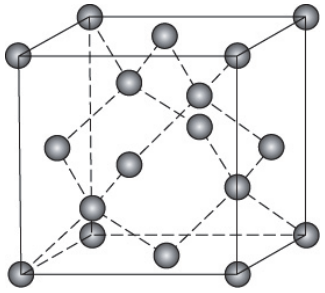


Fig. 4.17, *Callister & Rethwisch 9e.*

- **Graphite**
  - layered structure → parallel hexagonal arrays of carbon atoms
  - weak van der Waal's forces between layers
  - planes slide easily over one another → good lubricant

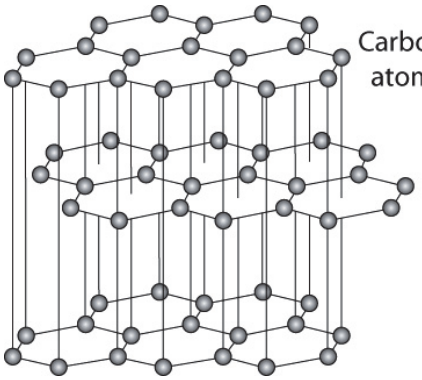
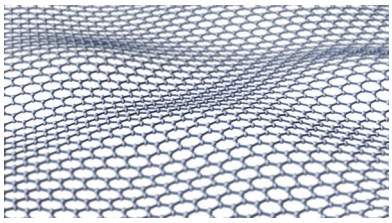


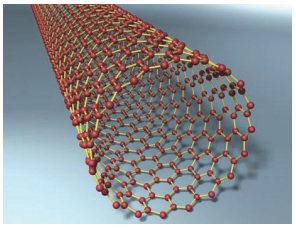
Fig. 4.18, *Callister & Rethwisch 9e.*

4.12 Polymorphic Forms of Carbon

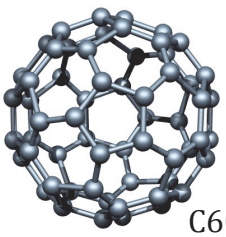
- **Graphene**
  - Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex.
- **Carbon Nanotube (CNT)**
  - Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure.
- **C60 (Bucky-Ball)**
  - Buckminsterfullerene (or bucky-ball) is a spherical fullerene molecule with the formula C60. It has a cage-like fused-ring structure (truncated icosahedron) which resembles a soccer ball (football), made of twenty hexagons and twelve pentagons, with a carbon atom at each vertex of each polygon and a bond along each polygon edge.



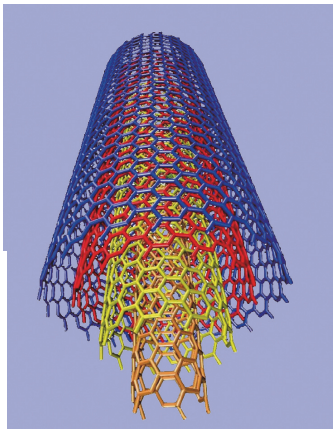
Graphene



Single-Walled CNT



C60



Multi-Walled CNT

4.13 Polymer Crystallinity

- **Ordered atomic arrangements involving molecular chains**
- **Polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material.**
- **Percent crystallinity**

$$\% \text{ Crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

  - ρ_s: density of a specimen
  - ρ_a: density of the totally amorphous polymer
  - ρ_s: density of the perfectly crystalline polymer

- **The degree of crystallinity of a polymer depends on the rate of cooling during solidification as well as on the chain configuration.**

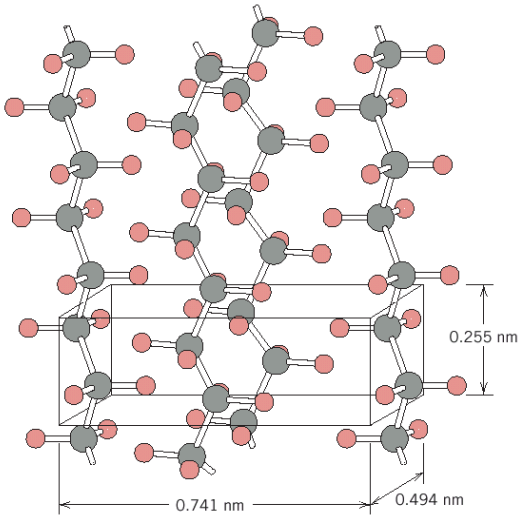
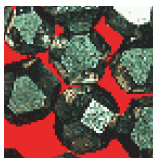


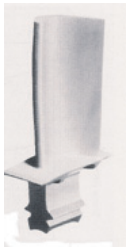
Fig. 4.19 Arrangement of molecular chains in a unit cell for polyethylene.

Crystals as Building Blocks

- **Some engineering applications require single crystals:**
  - diamond single crystals for abrasives
  - turbine blades



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



- **Properties of crystalline materials often related to crystal structure.**
  - Ex: Quartz fractures more easily along some crystal planes than others.

- **Polycrystals**
  - Most engineering materials are polycrystals.
  - Each "grain" is a single crystal.
  - If grains are randomly oriented, overall component properties are not directional.
  - Grain sizes typically range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

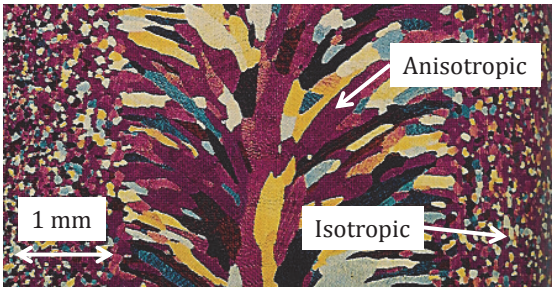
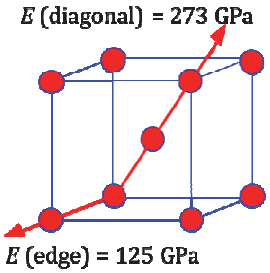


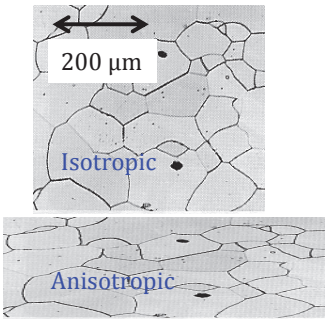
Fig. K, color inset pages of *Callister 5e.*
(Courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

Single vs. Polycrystals & Polymorphism

- **Single Crystals**
  - Properties vary with direction: anisotropic
  - Example: E (Young's modulus) in BCC iron
- **Polycrystals**
  - Properties may/may not vary with direction.
  - If grains are randomly oriented: isotropic (E (polycrystalline iron) = 210 GPa)
  - If grains are textured: anisotropic

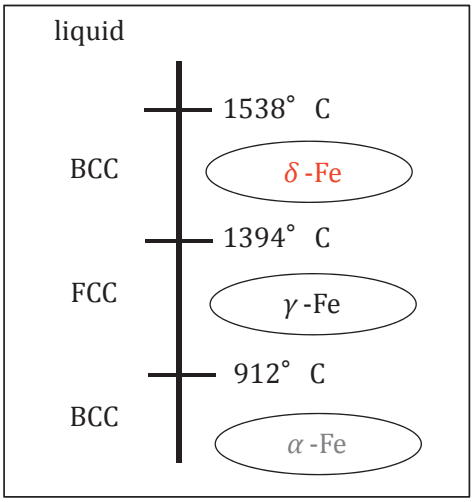


Data from Table 3.3, *Callister & Rethwisch 9e.*



Adapted from Fig. 6.19(b), *Callister & Rethwisch 9e.*

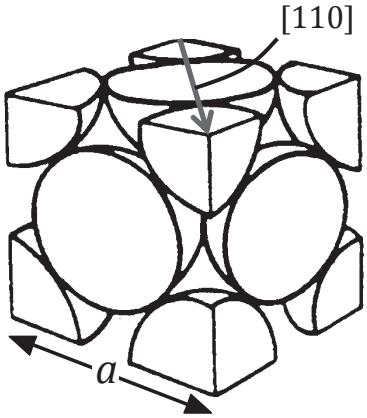
- **Polymorphism**
  - Two or more distinct crystal structures for the same material (allotropy/polymorphism)
  - Ex: Titanium, α, β –Ti, Carbon, Iron



Iron system

4.16 Linear and Planar Densities

- **Linear Density of Atoms ≡ LD =** $\dfrac{\text{Number of atoms centered on direction vector}}{\text{Unit length of direction vector}}$



Adapted from Fig. 3.1(a), *Callister & Rethwisch 9e.*

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 →

4.16 Linear and Planar Densities

- **Planar Density of (100) Iron: At T < 912°C iron has the BCC structure.**

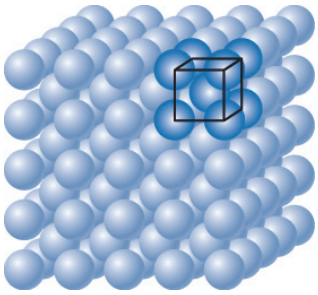
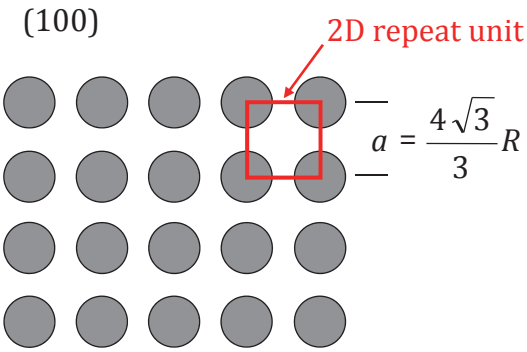


Fig. 4.2(c), *Callister & Rethwisch 9e* [from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]



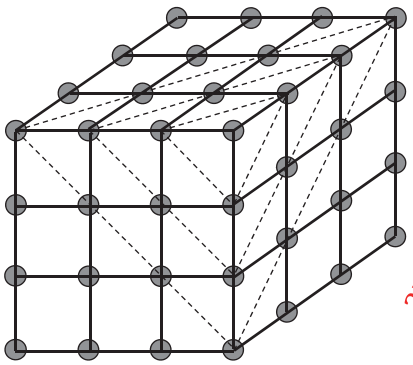
Radius of iron $R = 0.1241$ nm

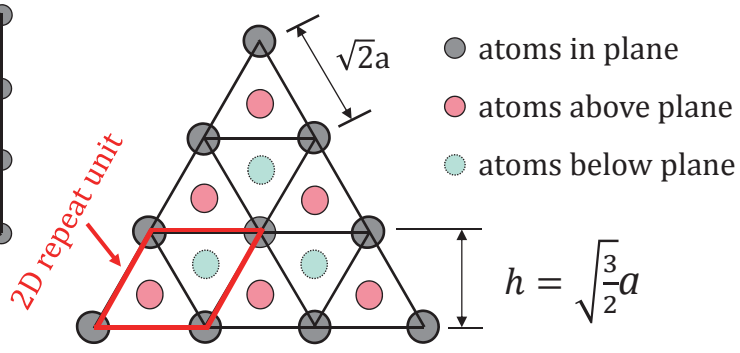
$$\text{Planar Density} = x = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

4.16 Linear and Planar Densities

- **Planar Density of (111) Iron**

1 atom in plane/unit surface cell





$$area = \sqrt{2}ah = \sqrt{3}a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$$

$$\text{Planar Density} = x = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{\frac{16\sqrt{3}}{3}R^2} = 7.0 \frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

4.17 Close-Packed Crystal Structures

- **FCC & HCP crystal structures**
  - Coordination Number = 12
  - APF = 0.74
- **FCC Stacking Sequence**
  - Close-Packed Plane: (111) plane
  - ABCABC Stacking Sequence
- **HCP Stacking Sequence**
  - Close-Packed Plane: (0001) plane
  - ABAB Stacking Sequence

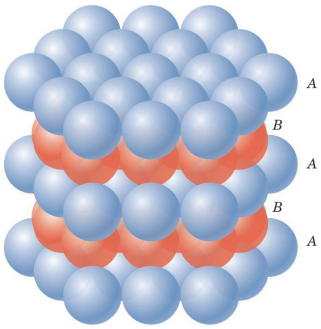
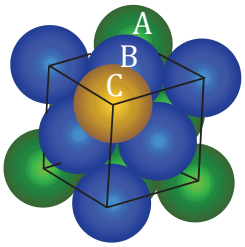
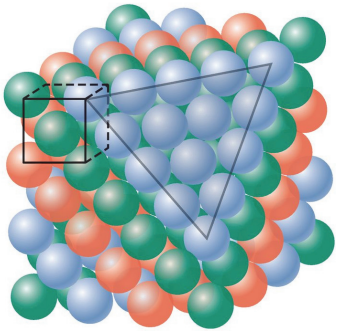
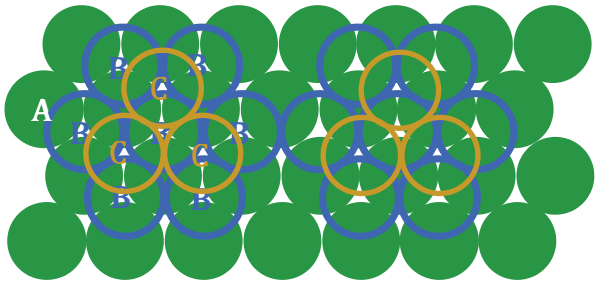


Fig. 4.24 Close-packed plane stacking sequence for the HCP structure.

- FCC Unit Cell



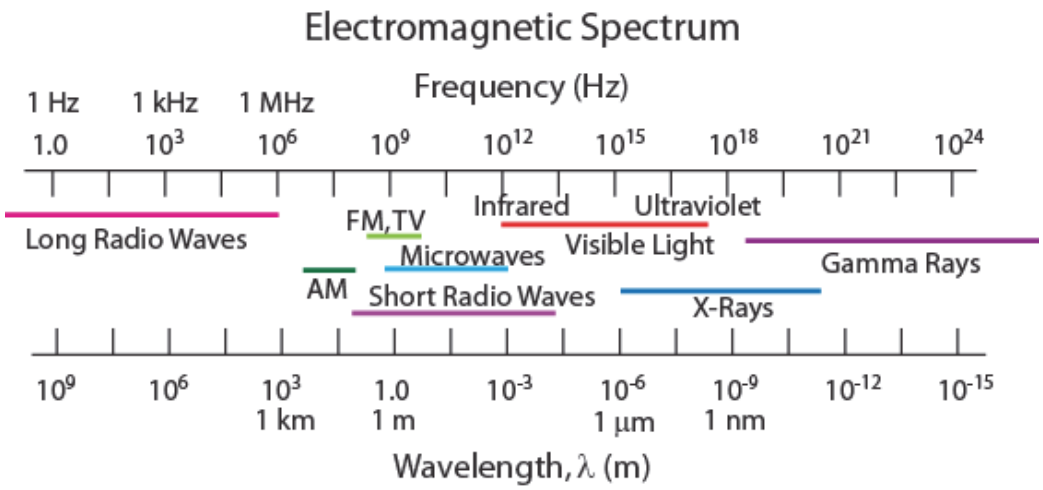




A sites B sites C sites

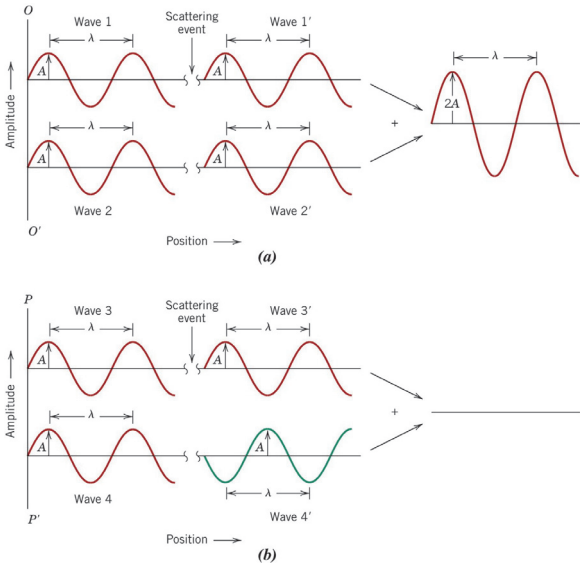
X-Ray Diffraction

- **Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.**
- **Can't resolve spacings < λ**
- **Spacing is the distance between parallel planes of atoms.**

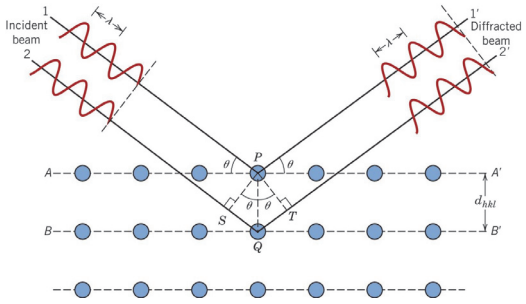


Interference and Bragg's Law

- **Constructive interference vs. destructive interference**



- **Bragg's Law**



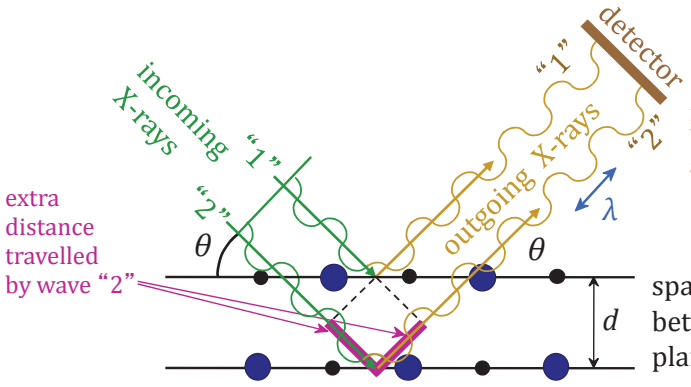
$$n\lambda = \overline{SQ} + \overline{QT}$$
$$= d_{hkl}\sin\theta + d_{hkl}\sin\theta$$
$$= 2d_{hkl}\sin\theta$$

$$\therefore n\lambda = 2d_{hkl}\sin\theta$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

X-Rays to Determine Crystal Structure

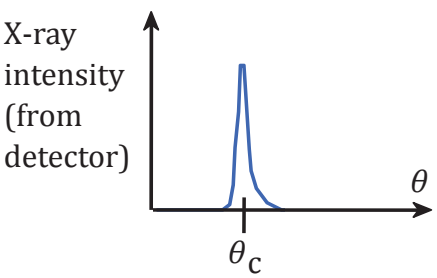
- **Incoming X-rays diffract from crystal planes.**



reflections must be in phase for a detectable signal

Adapted from Fig. 4.29, *Callister & Rethwisch 9e.*

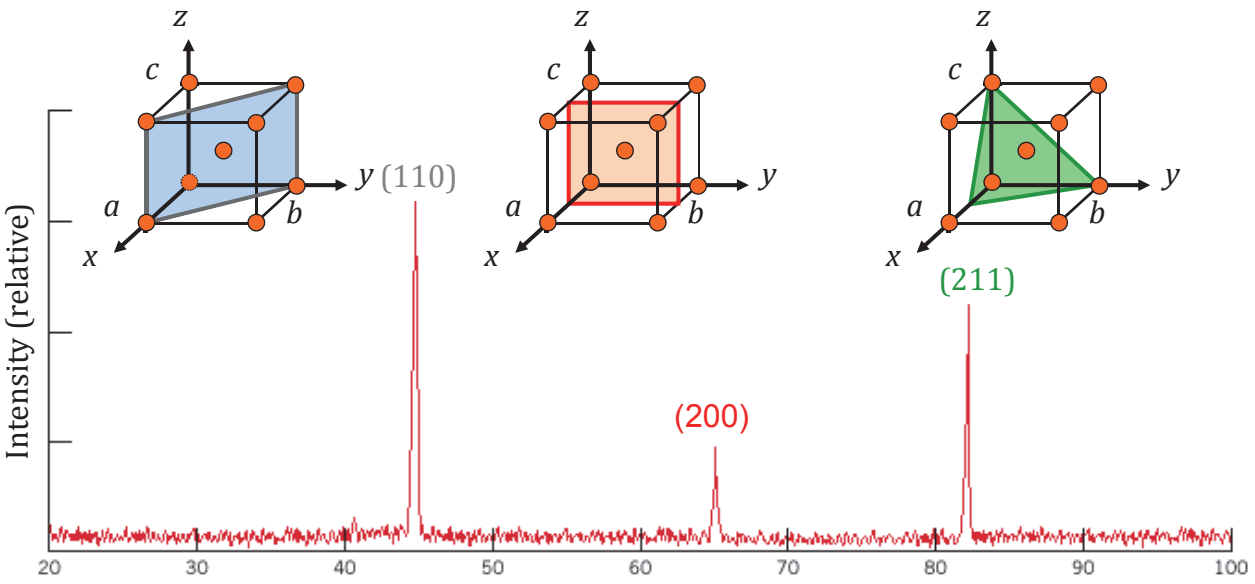
Measurement of critical angle, θ_c, allows computation of planar spacing, d.



Bragg's law

$$d = \frac{n\lambda}{2\sin\theta_c}$$

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.22, *Callister 8e.*