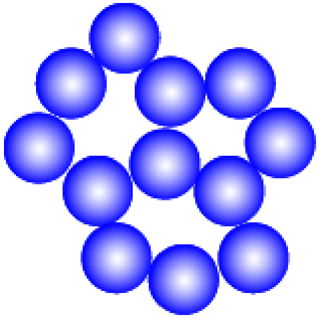
Chapter 3: The Structure of Crystalline Solids

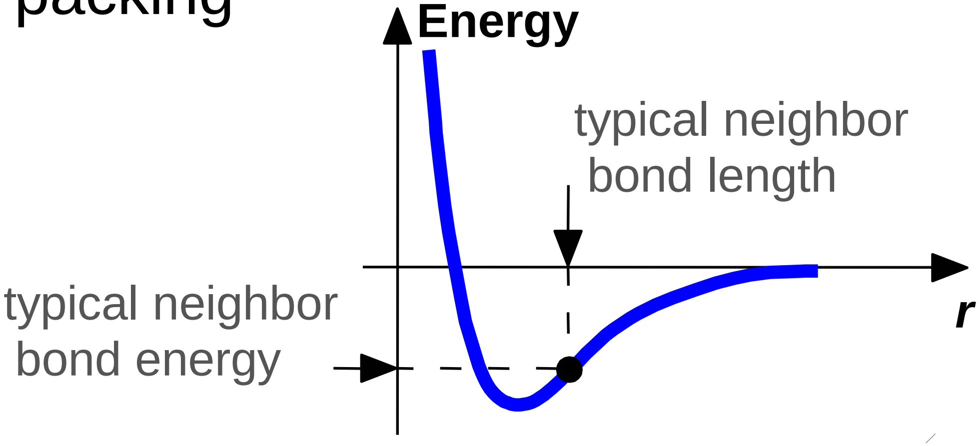
ISSUES TO ADDRESS...

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

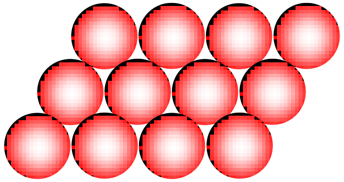
Energy and Packing

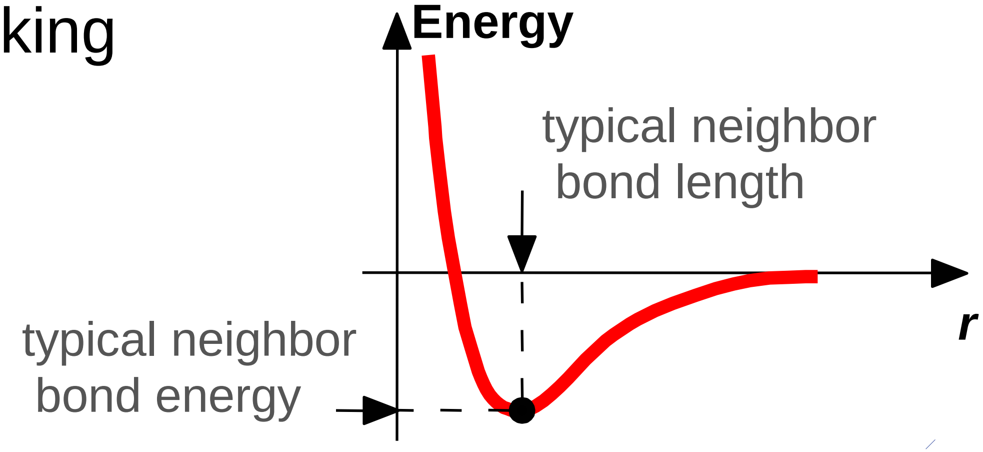
- Non dense, random packing





- Dense, ordered packing



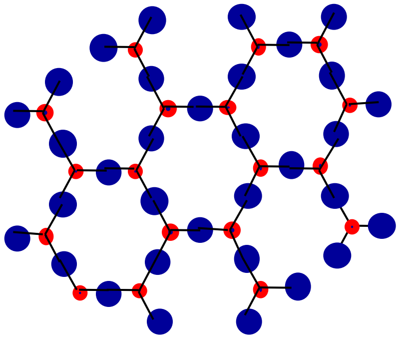


Dense, ordered packed structures tend to have lower energies.

Materials and Packing

Crystalline materials...

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



crystalline SiO_2

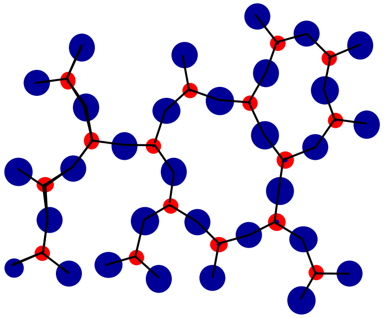
Adapted from Fig. 3.23(a), *Callister & Rethwisch 8e.*

• Si ● Oxygen

Noncrystalline materials...

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

"Amorphous" = Noncrystalline



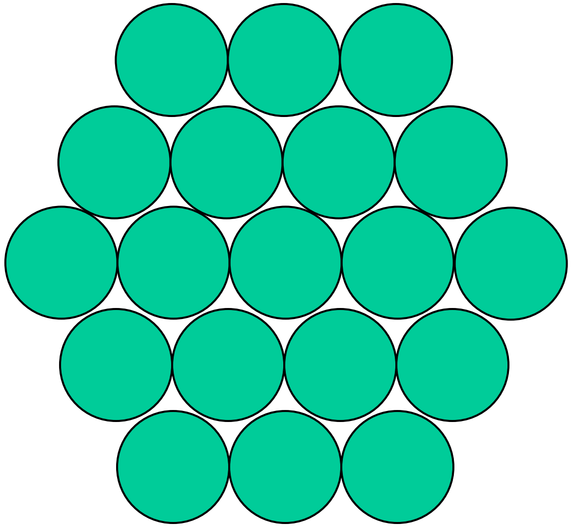
noncrystalline SiO_2

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

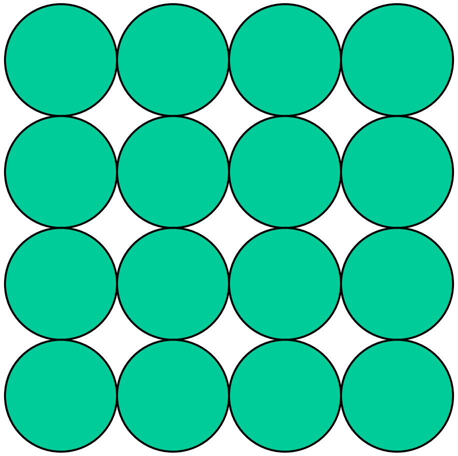
Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

2-dimensions



vs.



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

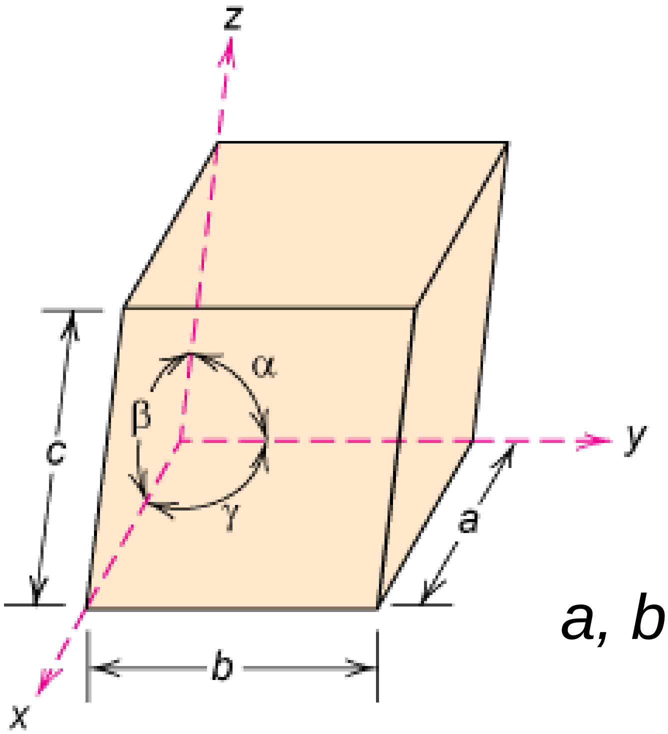
Metallic Crystal Structures

- 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
- Have the simplest crystal structures.

We will examine three such structures...

Crystal Systems

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



7 crystal systems

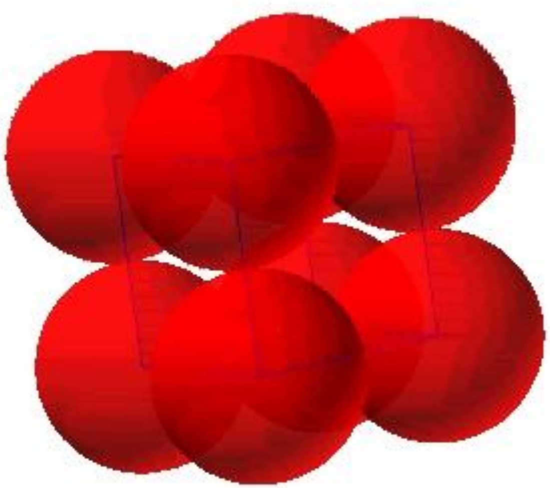
14 crystal lattices

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

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

Simple Cubic Structure (SC)

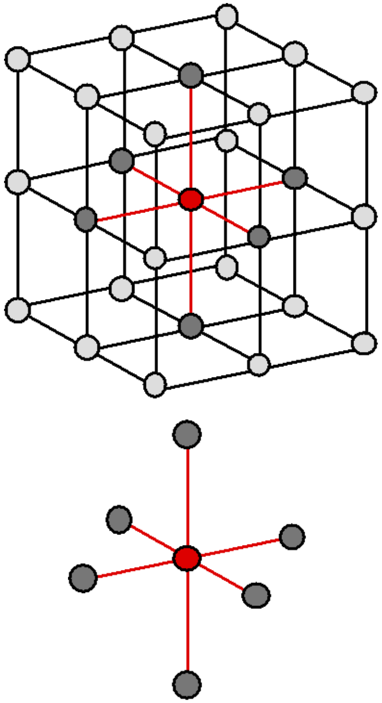
- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.



Click once on image to start animation

(Courtesy P.M. Anderson)

- Coordination # = 6
  (# nearest neighbors)

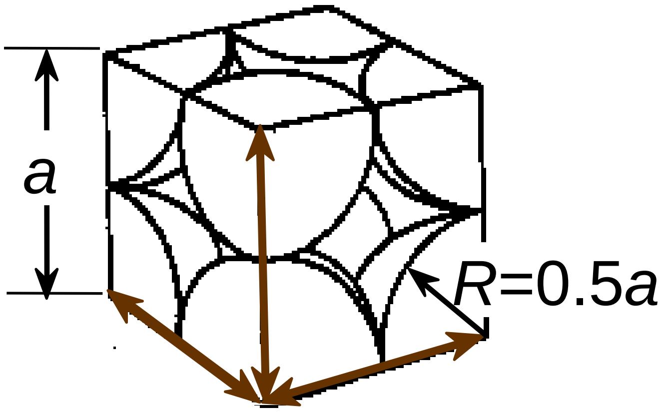


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

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

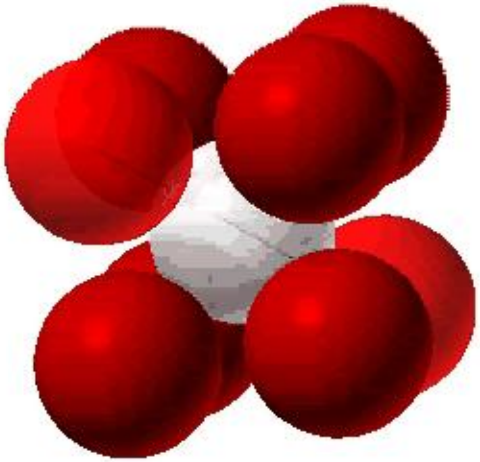
$$\text{APF} = \frac{\overset{\frac{\text{atoms}}{\text{unit cell}}}{1}\ \overset{\frac{\text{volume}}{\text{atom}}}{\frac{4}{3}\pi\,(0.5a)^3}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{a^3}}$$

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



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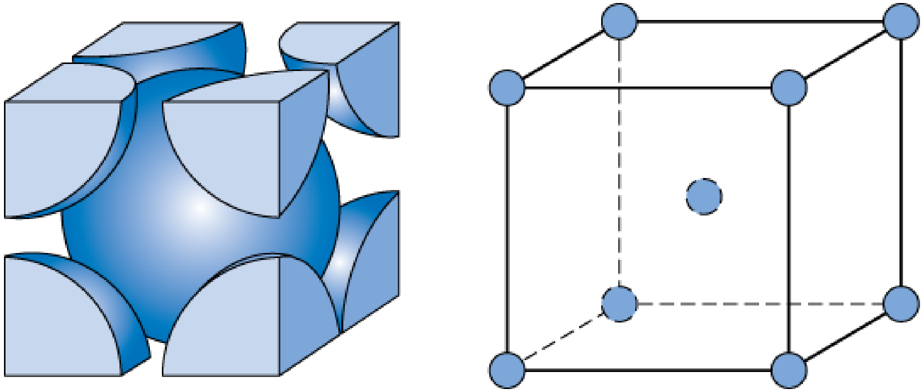
(Courtesy P.M. Anderson)

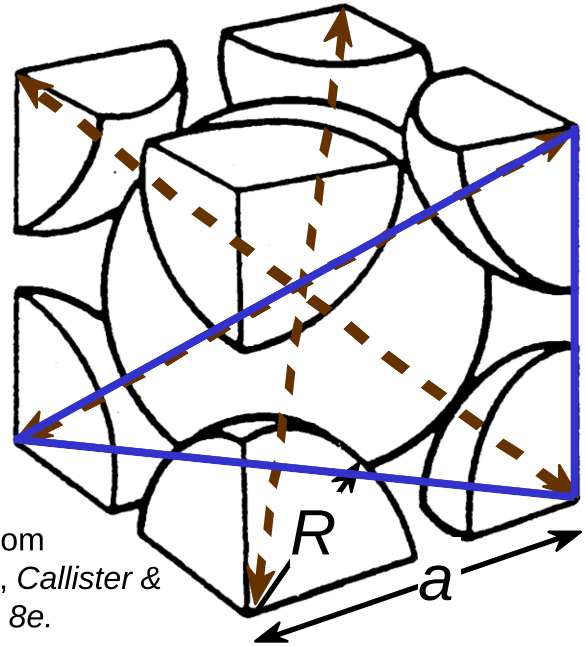


Adapted from Fig. 3.2, *Callister & Rethwisch 8e.*

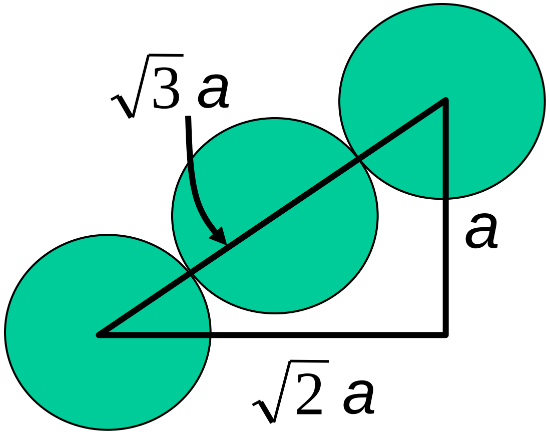
2 atoms/unit cell: 1 center + 8 corners x 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



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



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

$\frac{\text{atoms}}{\text{unit cell}}$

$\frac{\text{volume}}{\text{atom}}$

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

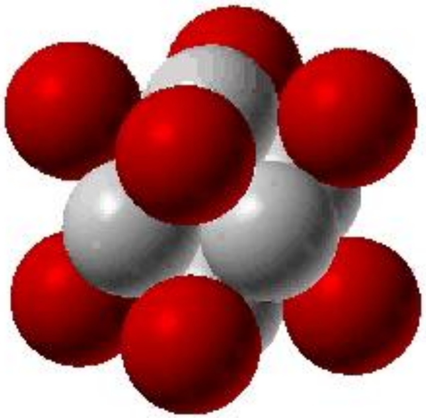
$\frac{\text{volume}}{\text{unit cell}}$

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



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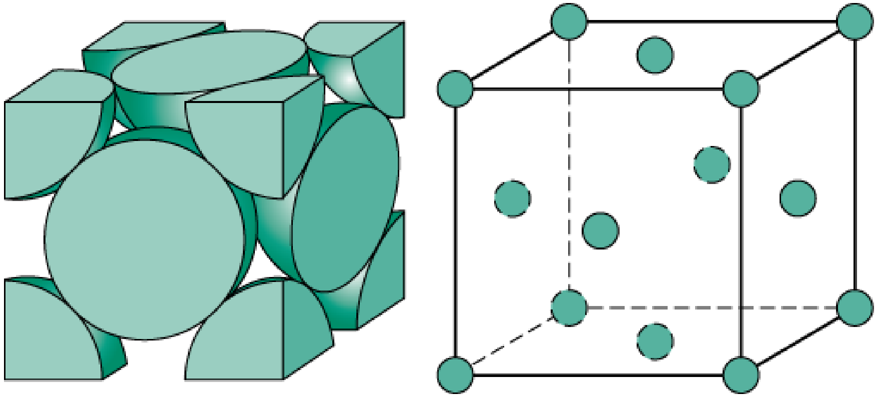
(Courtesy P.M. Anderson)



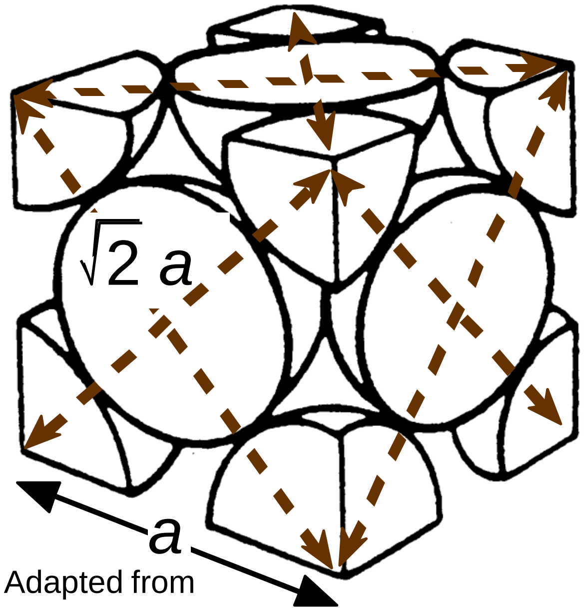
Adapted from Fig. 3.1, *Callister & Rethwisch 8e.*

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

Atomic Packing Factor: 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:

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

Unit cell contains:

$6 \times 1/2 + 8 \times 1/8$

= 4 atoms/unit cell

$$\text{APF} = \frac{4 \;\; \frac{4}{3}\pi\,(\sqrt{2}a/4)^3}{a^3}$$

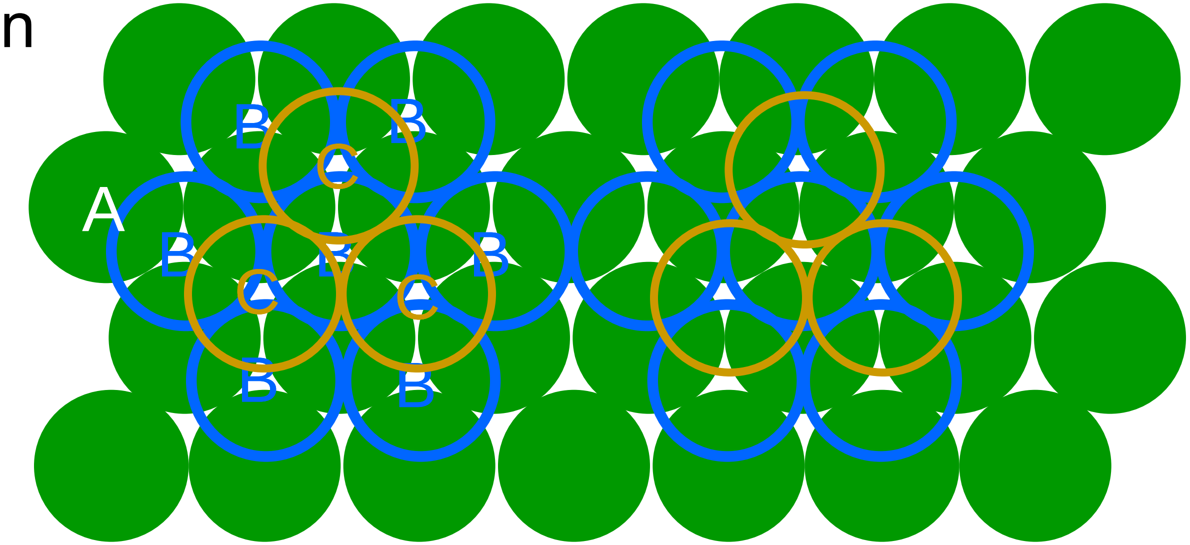
4: $\frac{\text{atoms}}{\text{unit cell}}$

$\frac{4}{3}\pi\,(\sqrt{2}a/4)^3$: $\frac{\text{volume}}{\text{atom}}$

a^3: $\frac{\text{volume}}{\text{unit cell}}$

FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

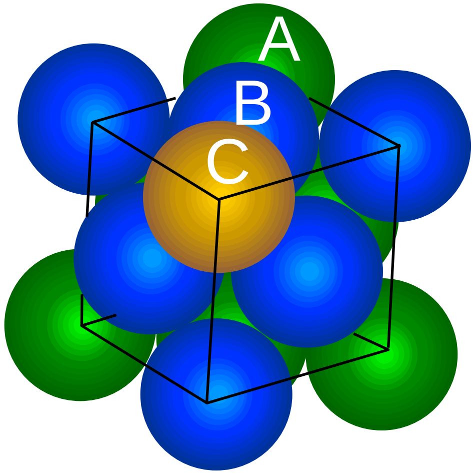


A sites

B sites

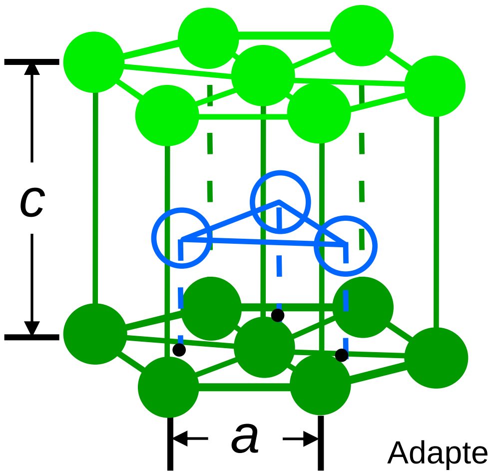
C sites

- FCC Unit Cell

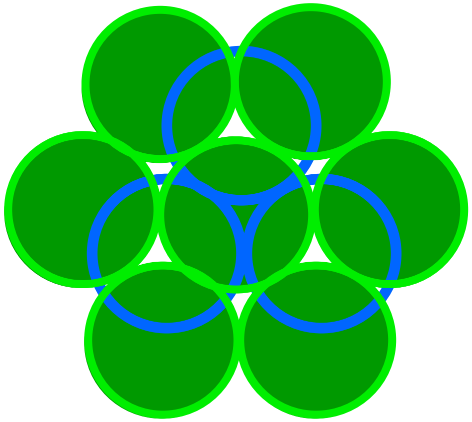


Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection
- 2D Projection



Adapted from Fig. 3.3(a), *Callister & Rethwisch 8e.*



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

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

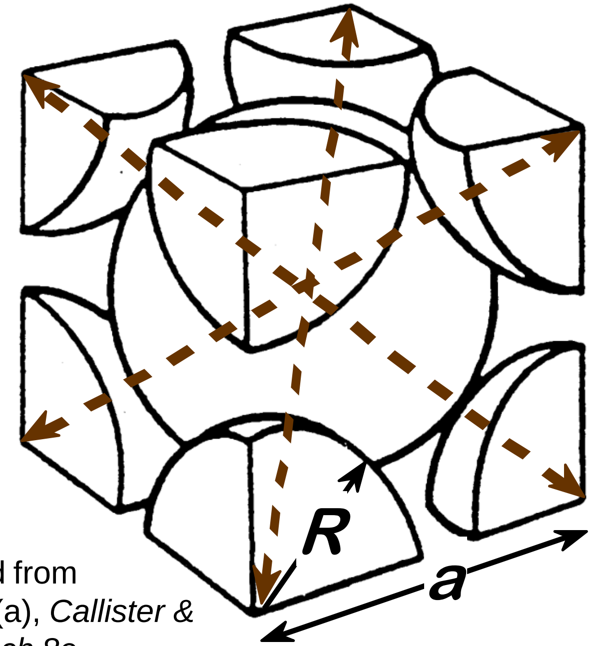
A = atomic weight

V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro’s number

= 6.022×10^{23} atoms/mol

Theoretical Density, ρ



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

- Ex: Cr (BCC)

  $A = 52.00$ g/mol

  $R = 0.125$ nm

  $n = 2$ atoms/unit cell

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

$$\rho = \frac{\overset{\frac{\text{atoms}}{\text{unit cell}}}{2}\;\;\overset{\frac{\text{g}}{\text{mol}}}{52.00}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{a^3}\;\;\underset{\frac{\text{atoms}}{\text{mol}}}{6.022 \times 10^{23}}}$$

$\rho_{\text{theoretical}} = 7.18 \text{ g/cm}^3$

$\rho_{\text{actual}} = 7.19 \text{ g/cm}^3$

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...

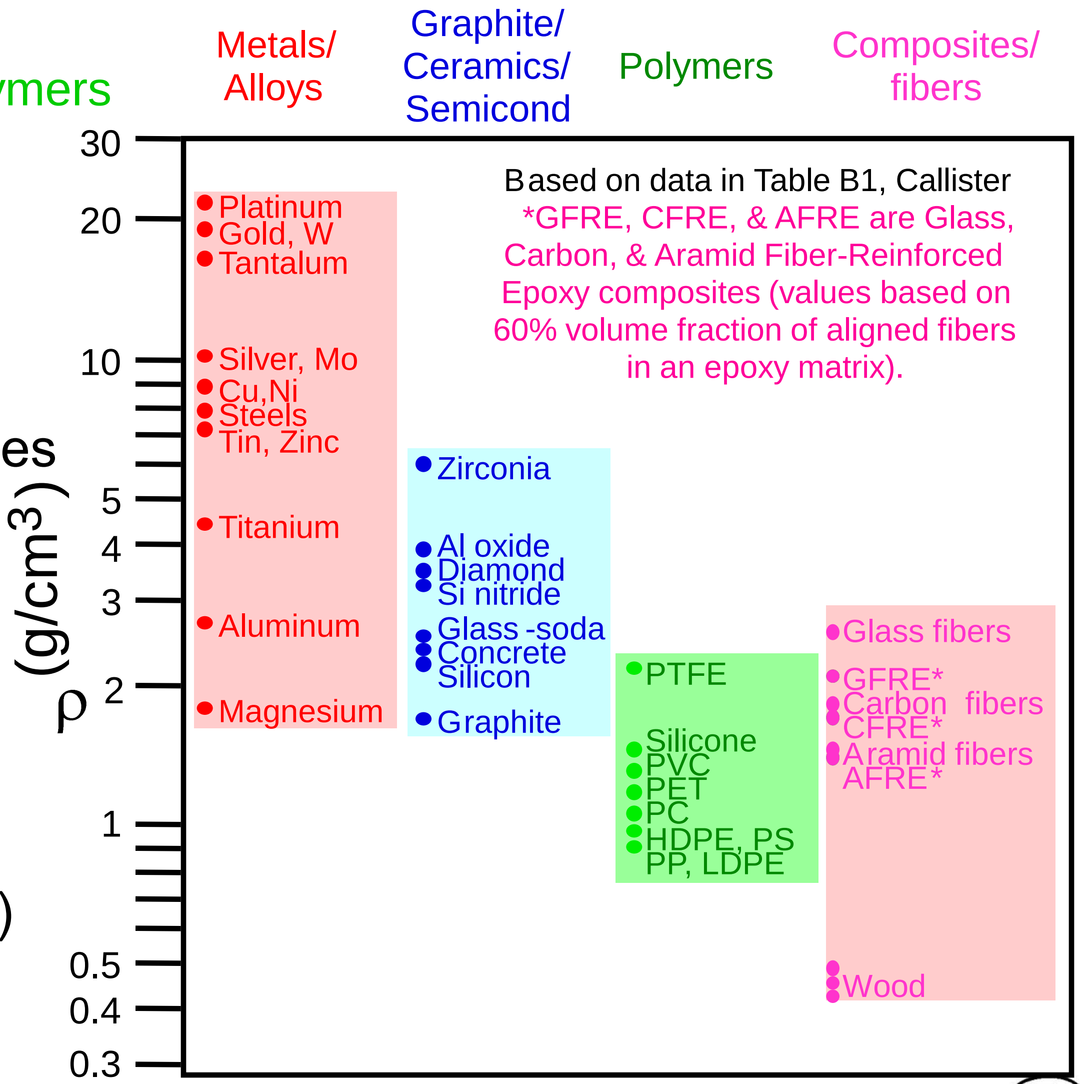
- less dense packing
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values



Based on data in Table B1, Callister

*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).

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

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.)

Fig. 8.33(c), *Callister & Rethwisch 8e.* (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)

Polycrystals

- *Most* engineering materials are polycrystals.

Anisotropic

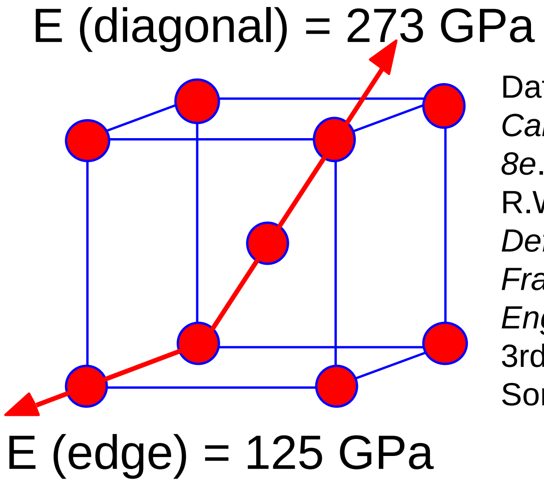
Isotropic

Adapted from Fig. K, color inset pages of *Callister 5e*. (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 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).

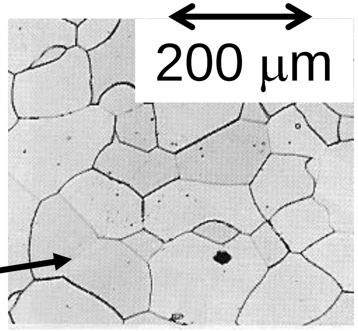
Single vs Polycrystals

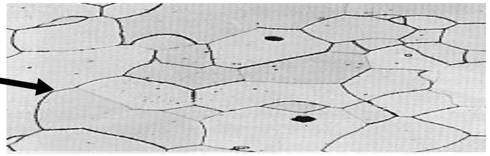
- Single Crystals
  - -Properties vary with direction: anisotropic.
  - -Example: the modulus of elasticity (E) in BCC iron:



Data from Table 3.3, *Callister & Rethwisch 8e*. (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. ($E_{\text{poly iron}} = 210$ GPa)
  - -If grains are textured, anisotropic.





Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e*. (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].)

Polymorphism

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

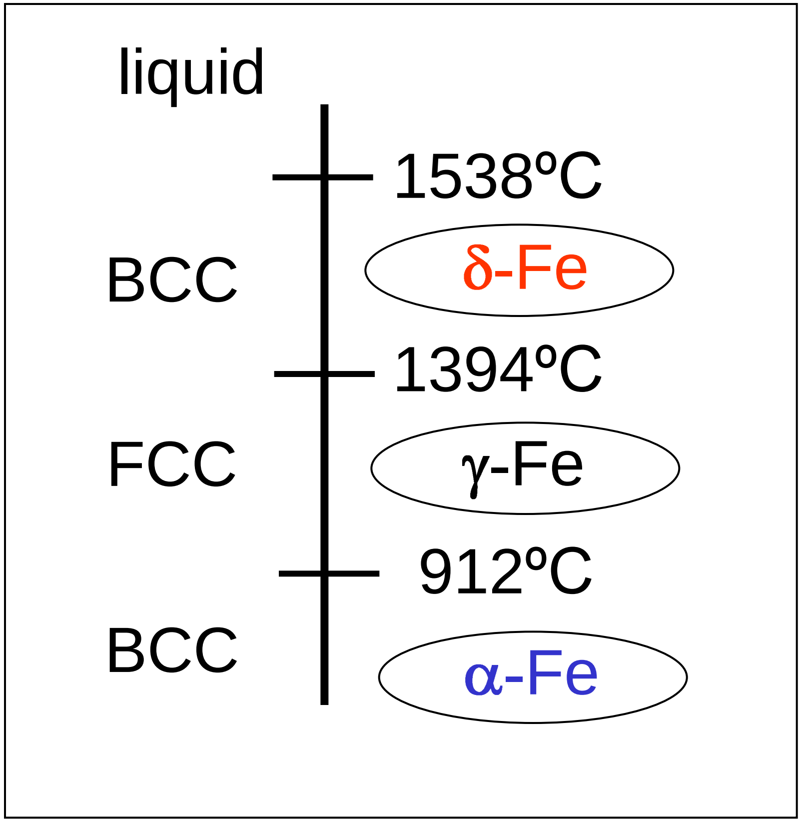
titanium

α, β-Ti

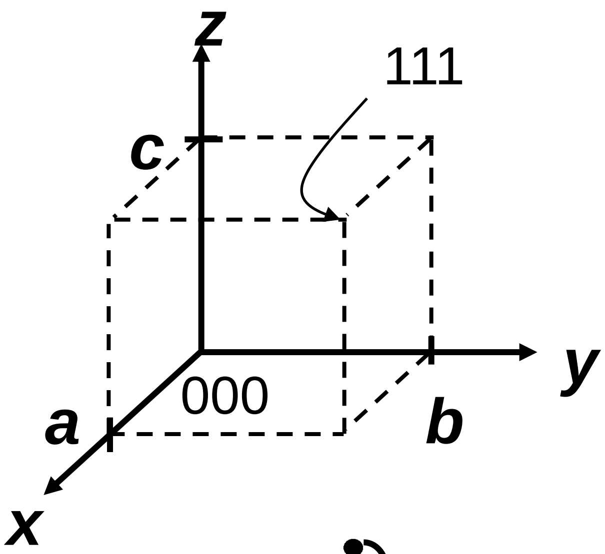
carbon

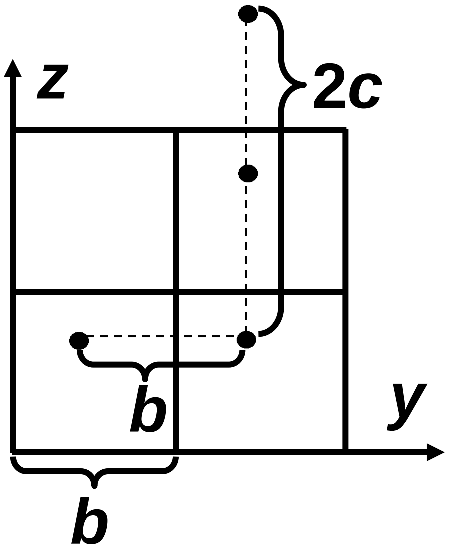
diamond, graphite

iron system



Point Coordinates





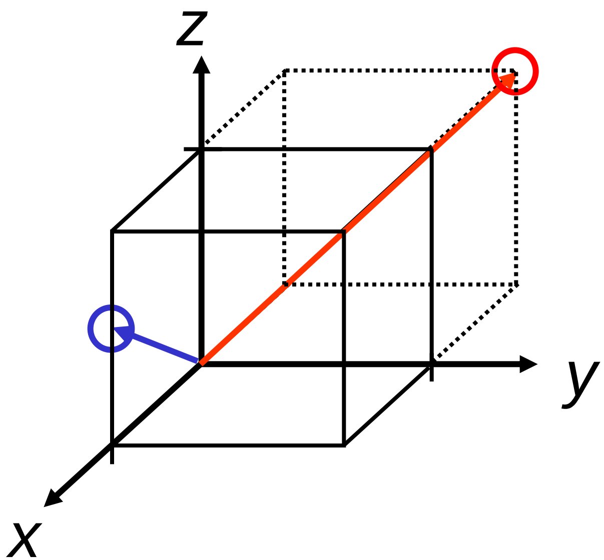
Point coordinates for unit cell center are

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

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*]

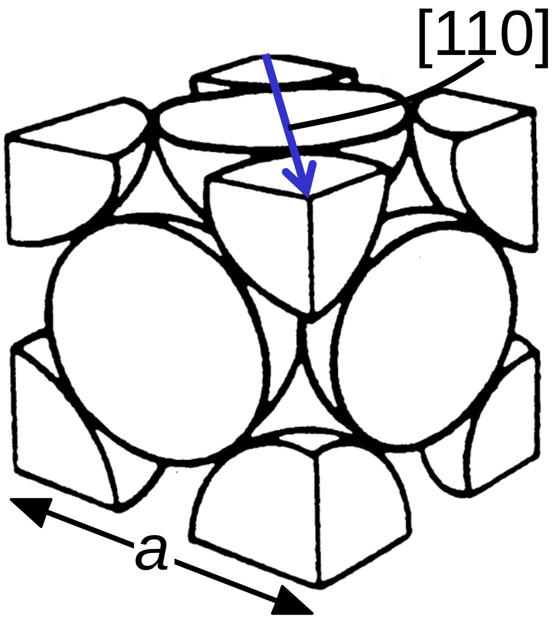
ex: 1, 0, ½ => 2, 0, 1 => [201]

-1, 1, 1 => $[\bar{1}11]$ where overbar represents a negative index

families of directions <*uvw*>

Linear Density

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



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

ex: linear density of Al in [110] direction

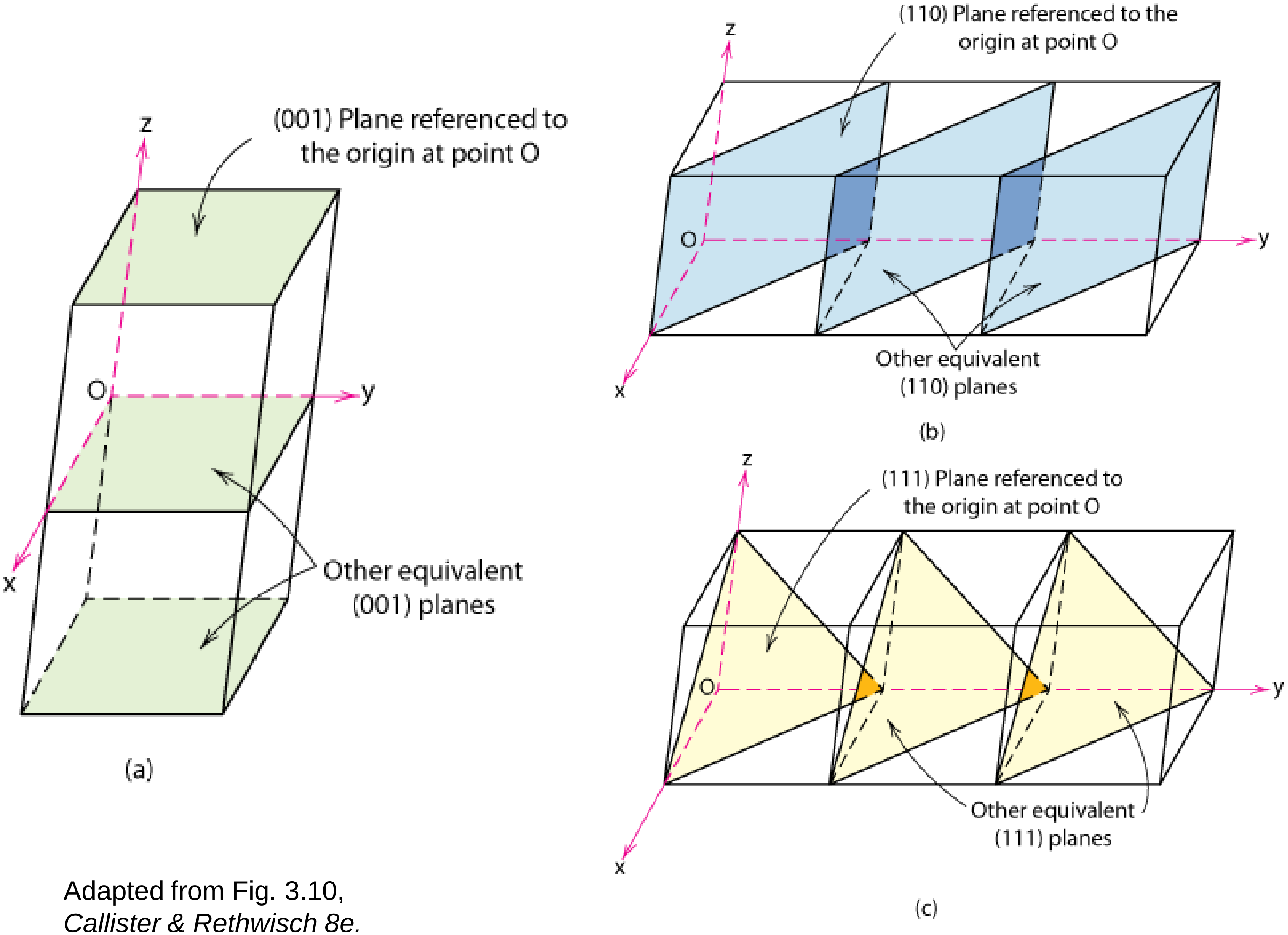
$a = 0.405$ nm

atoms

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

length

Crystallographic Planes



Adapted from Fig. 3.10,
Callister & Rethwisch 8e.

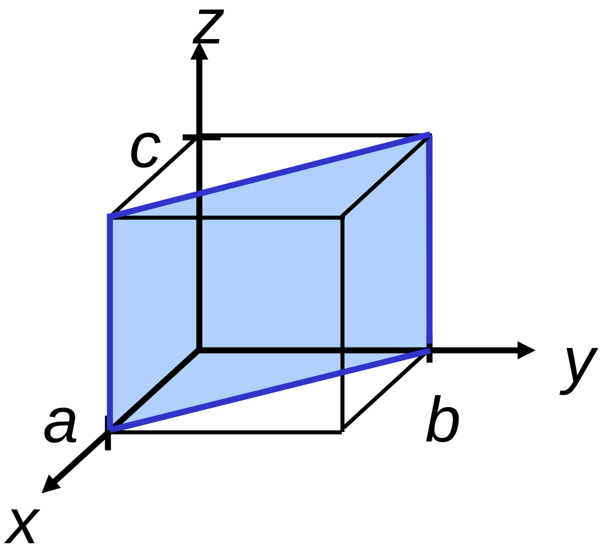
Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

- Algorithm
    1. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
    2. Take reciprocals of intercepts
    3. Reduce to smallest integer values
    4. Enclose in parentheses, no commas i.e., (*hkl*)

Crystallographic Planes

<u>example</u>		*a*	*b*	*c*
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		



Family of Planes {*hkl*}

Ex: {100} = (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$

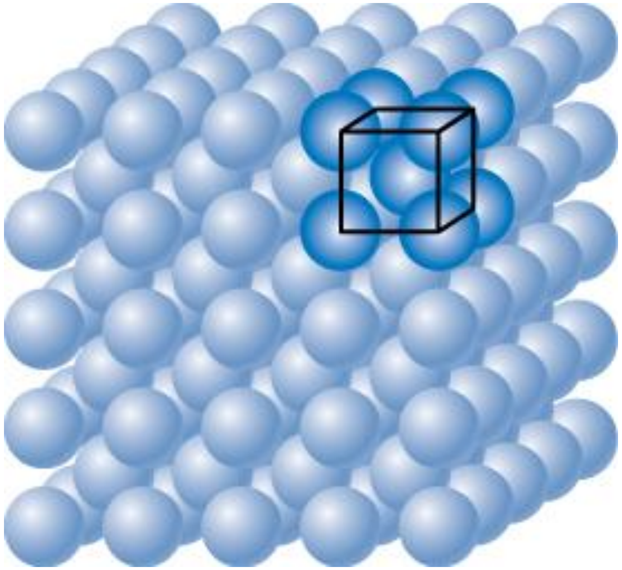
Planar Density of Atoms ≡ PD = $\dfrac{\text{Number of atoms}}{\text{Unit area of plane}}$

Crystallographic Planes

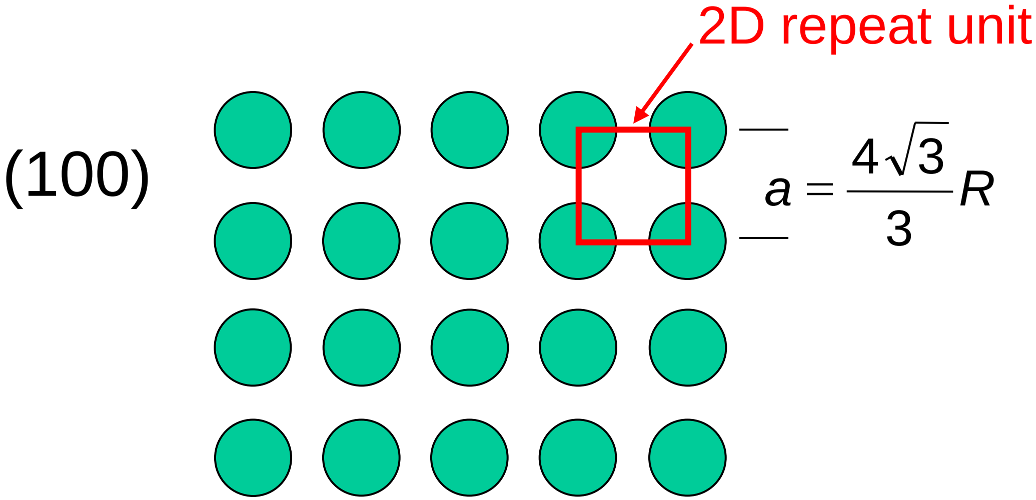
- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
  a) Draw (100) and (111) crystallographic planes for Fe.
  b) Calculate the planar density for each of these planes.

Planar Density of (100) Iron

Solution: At T < 912ºC iron has the BCC structure.



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



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

Radius of iron $R = 0.1241$ nm

$\dfrac{\text{atoms}}{\text{2D repeat unit}}$ → 1

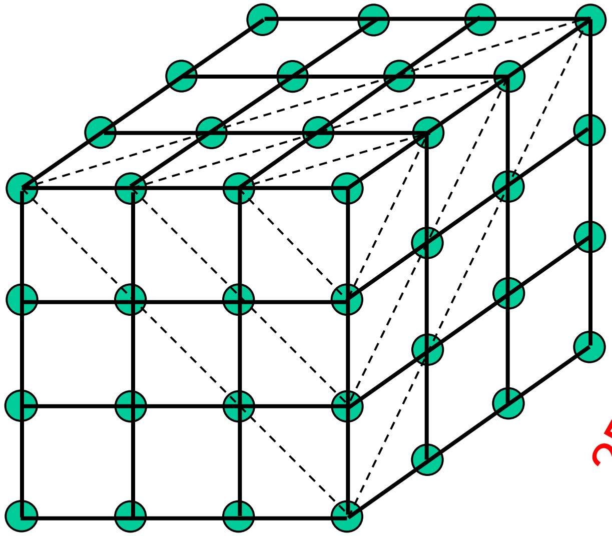
$\dfrac{\text{area}}{\text{2D repeat unit}}$ → a^2

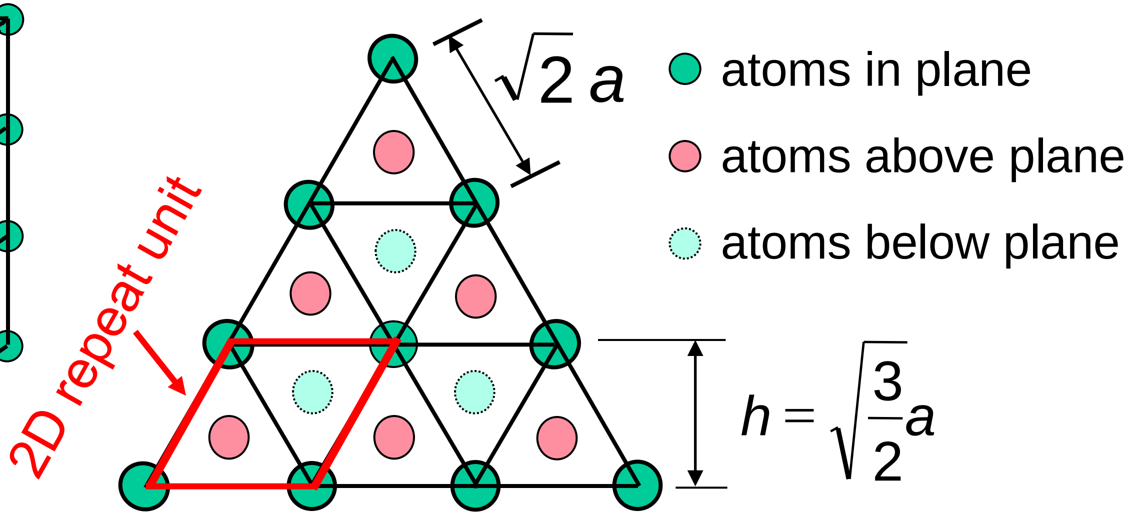
$$\text{Planar Density} = \frac{1}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1\,\frac{\text{atoms}}{\text{nm}^2} = \boxed{1.2 \times 10^{19}\,\frac{\text{atoms}}{\text{m}^2}}$$

Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell





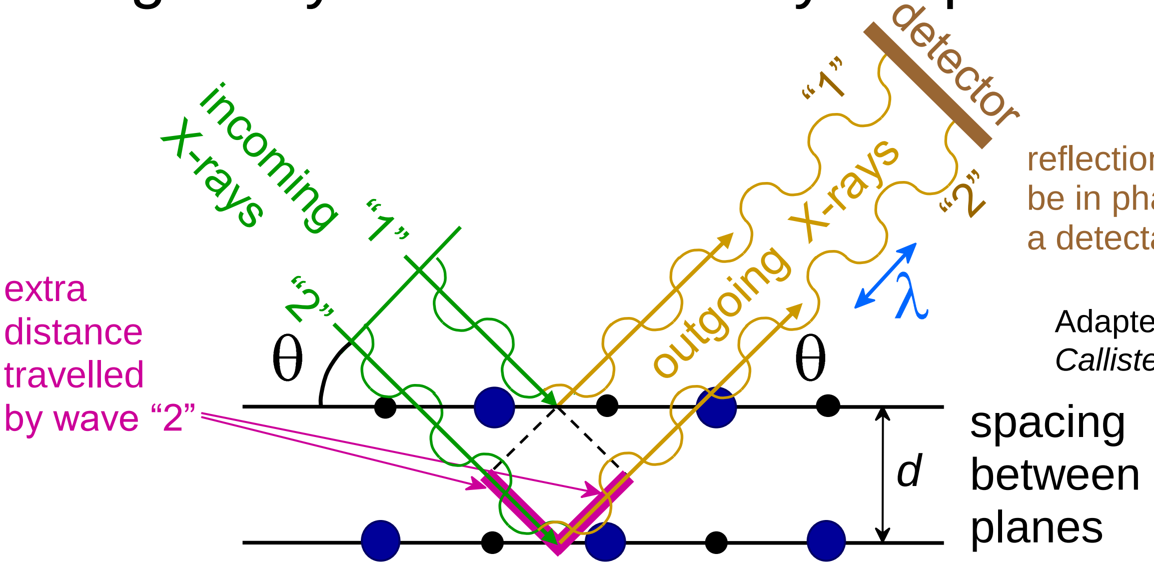
$$h = \sqrt{\frac{3}{2}}\,a$$

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

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

X-Rays to Determine Crystal Structure

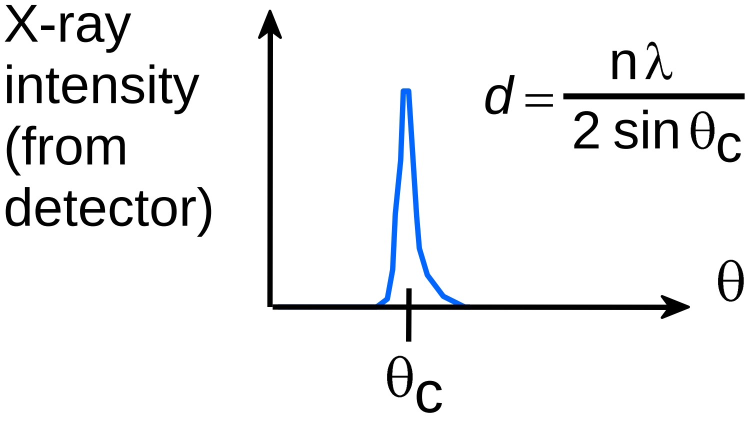
- Incoming X-rays diffract from crystal planes.



reflections must be in phase for a detectable signal

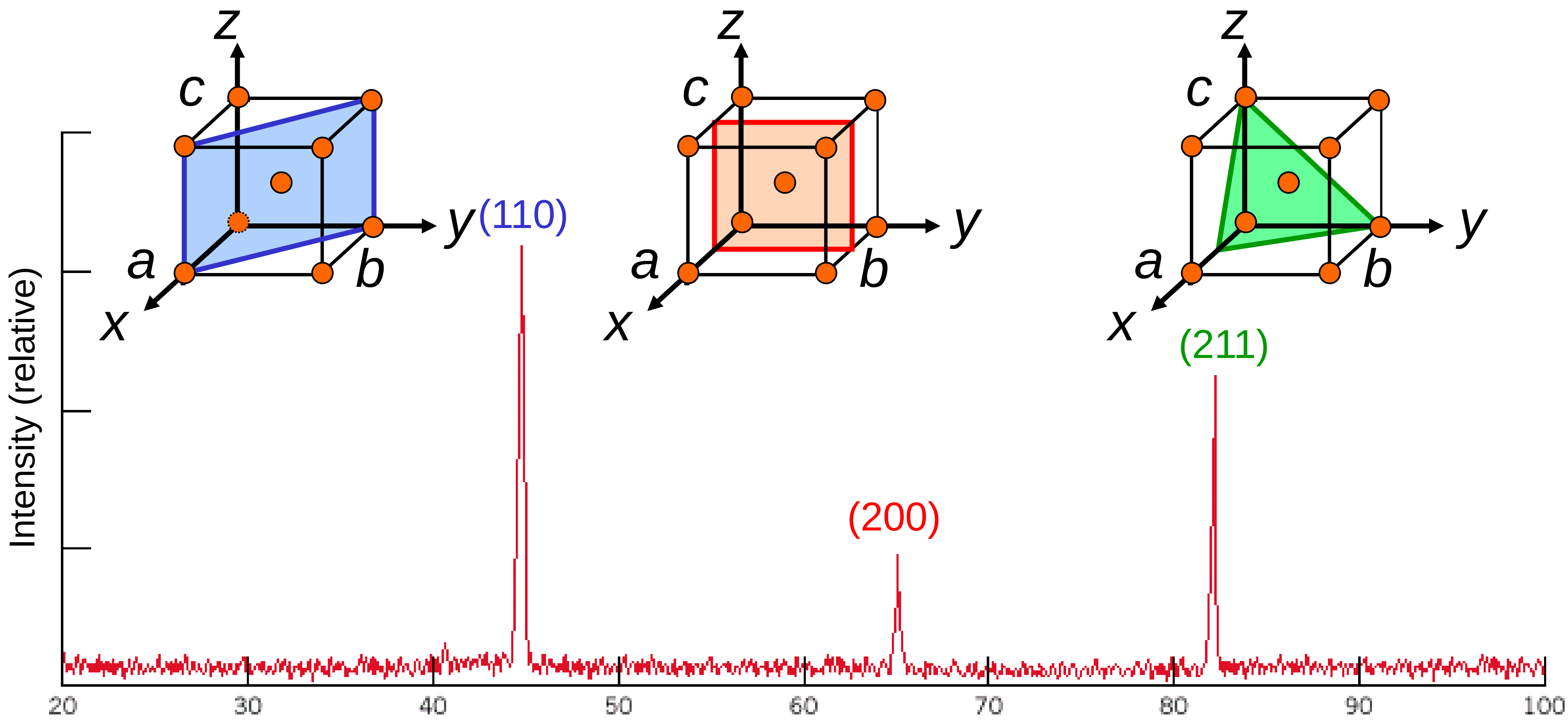
Adapted from Fig. 3.20, *Callister & Rethwisch 8e*.

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



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

X-Ray Diffraction Pattern



Diffraction angle 2θ

Diffraction pattern for polycrystalline α-iron (BCC)

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

SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal 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).
- Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.