

# Chapter 3: The Structure of Crystalline Solids

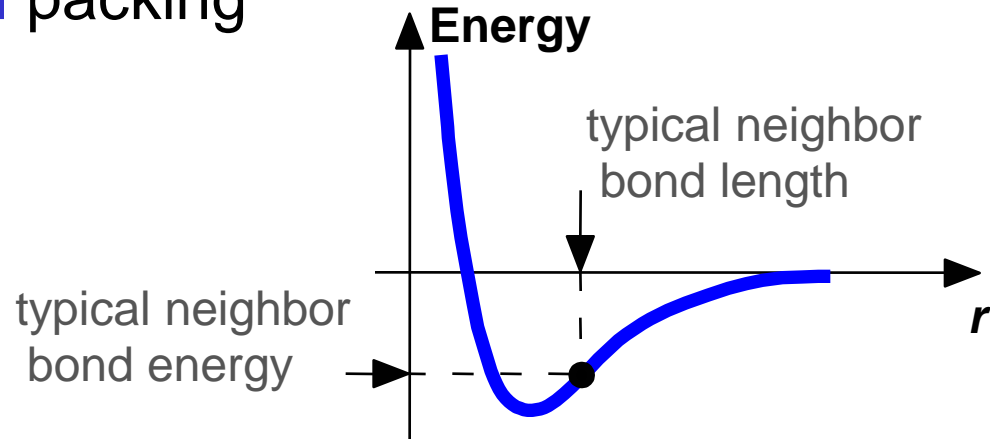
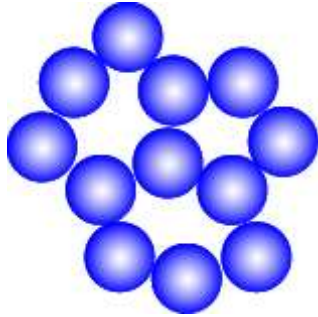
## ISSUES TO ADDRESS...

- 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?

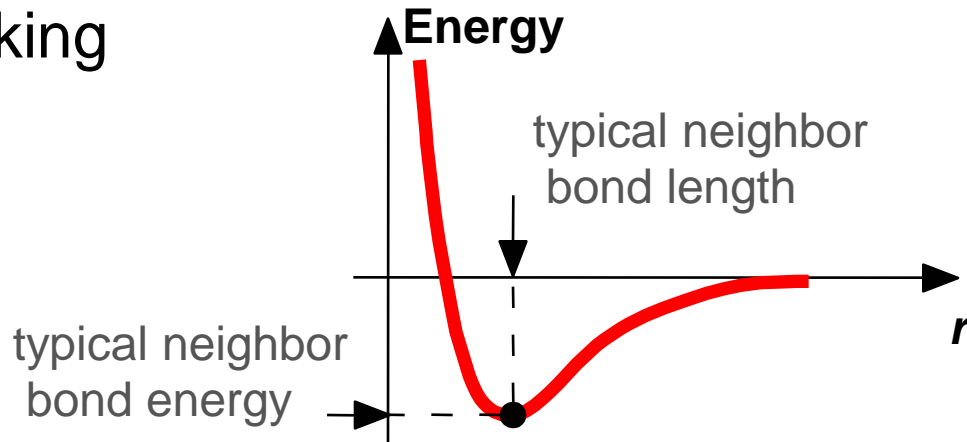
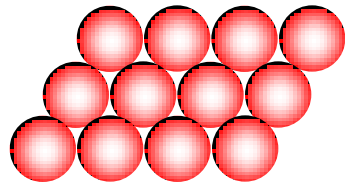


# Energy and Packing

- Non dense, **random** packing



- Dense, **ordered** packing



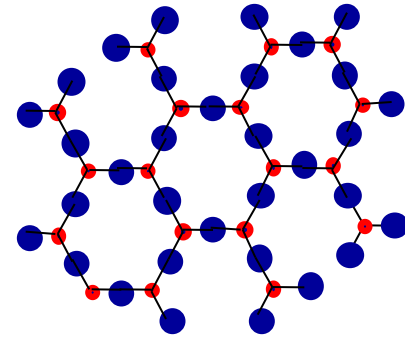
Dense, ordered packed structures tend to have lower energies.



# Materials and Packing

## Crystalline materials...

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



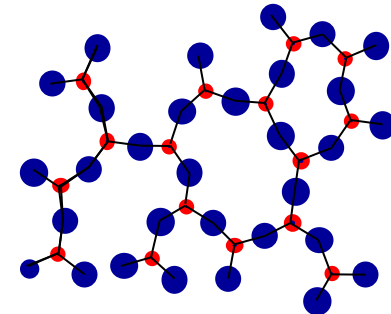
crystalline SiO<sub>2</sub>

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

• **Si**      • **Oxygen**

## Noncrystalline materials...

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



noncrystalline SiO<sub>2</sub>

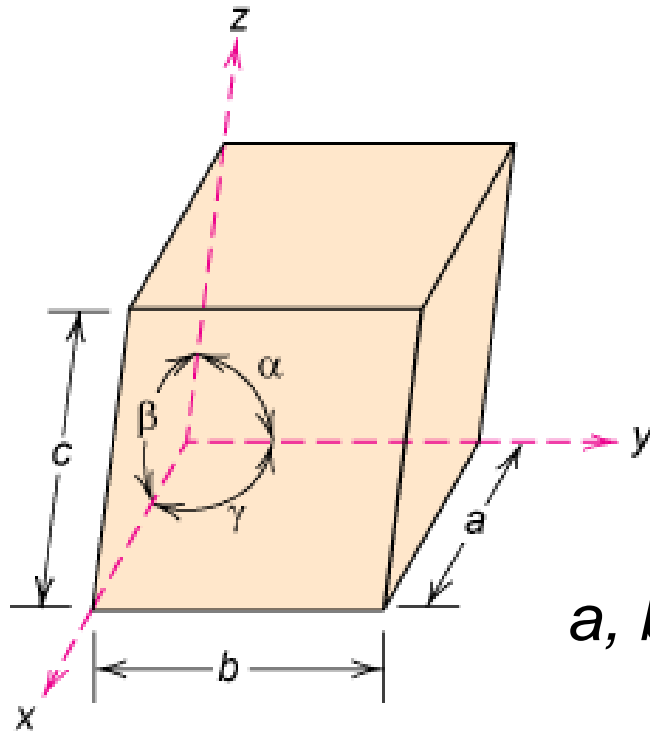
Adapted from Fig. 3.22(b),  
*Callister 7e.*

"Amorphous" = Noncrystalline



# Section 3.3 – 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

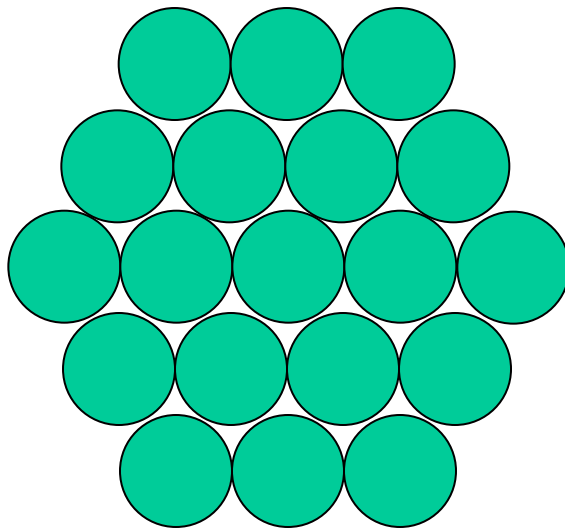
Fig. 3.4, Callister 7e.



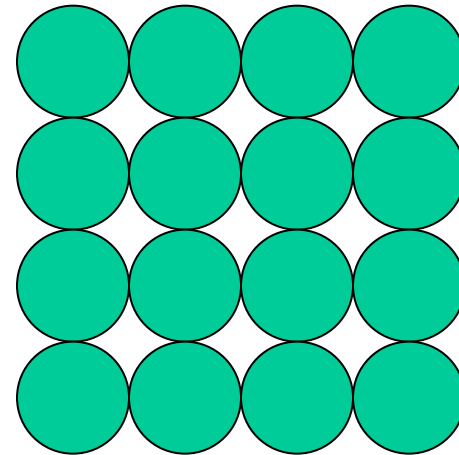
## Section 3.4 – Metallic Crystal Structures

- 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.

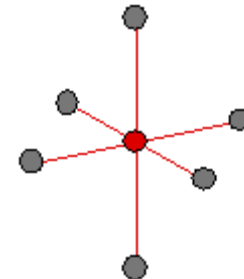
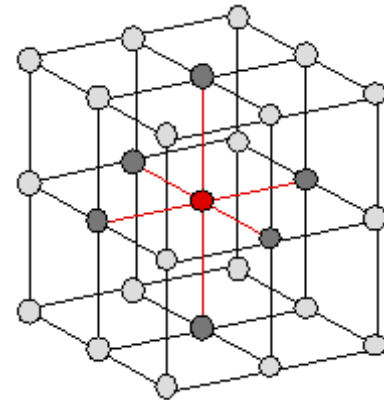
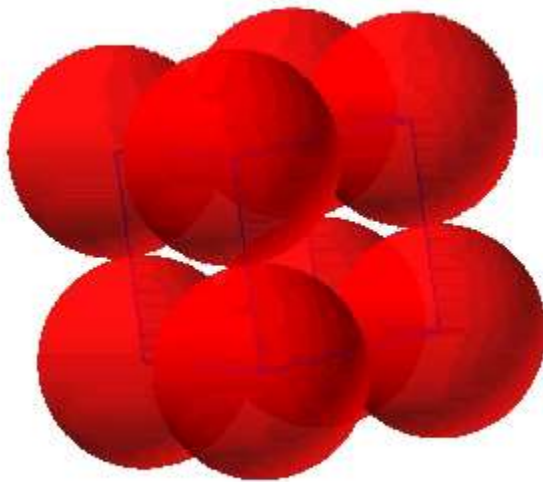
We will examine three such structures...



# Simple Cubic Structure (SC)

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

- Coordination # = 6  
(# nearest neighbors)



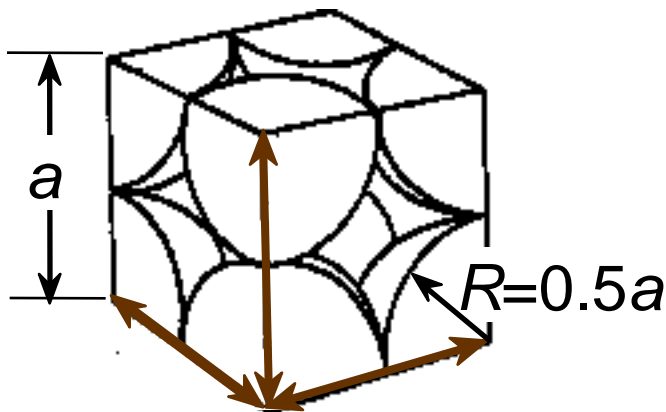
(Courtesy P.M. Anderson)

# 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  $8 \times 1/8 =$

**1 atom/unit cell**

Adapted from Fig. 3.23,  
Callister 7e.

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



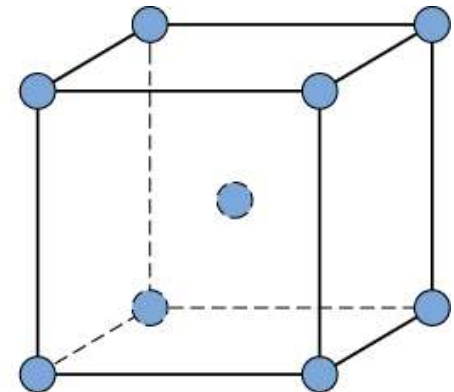
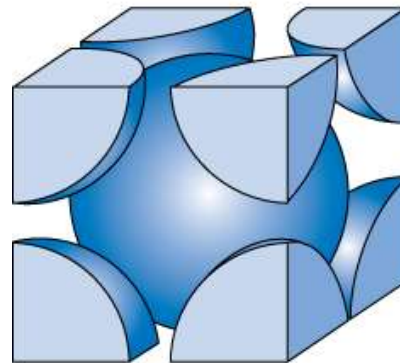
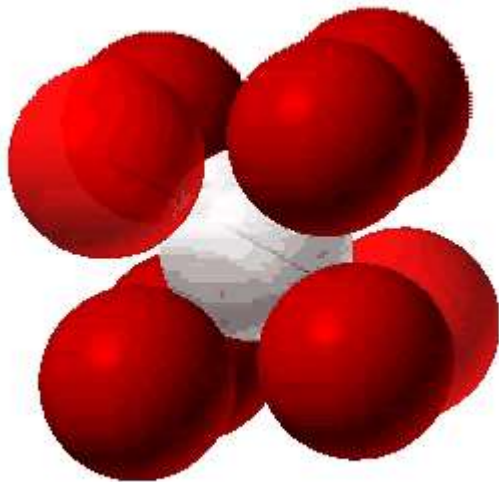
# Body Centered Cubic Structure (BCC)

- 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 ( $\alpha$ ), Tantalum, Molybdenum

- Coordination # = 8



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

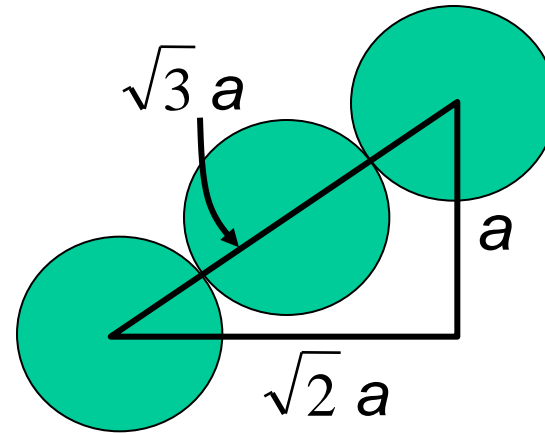
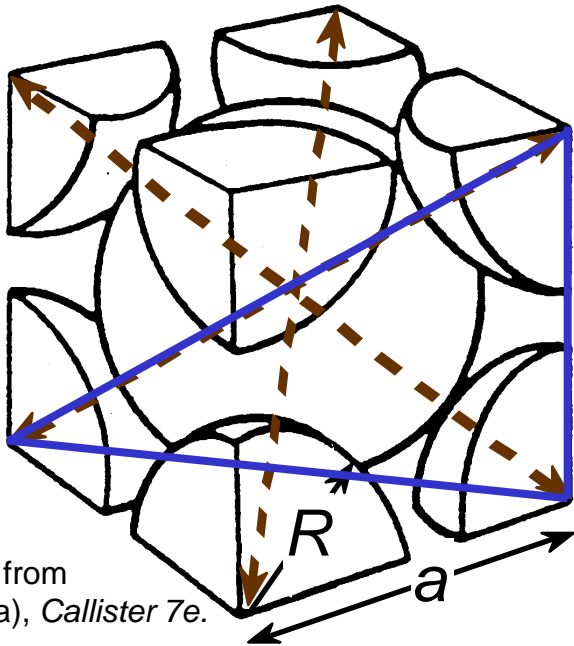
2 atoms/unit cell: 1 center + 8 corners  $\times$  1/8

(Courtesy P.M. Anderson)



# Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



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

$$\text{APF} = \frac{\text{atoms unit cell} \times \text{volume atom}}{\text{volume unit cell}}$$

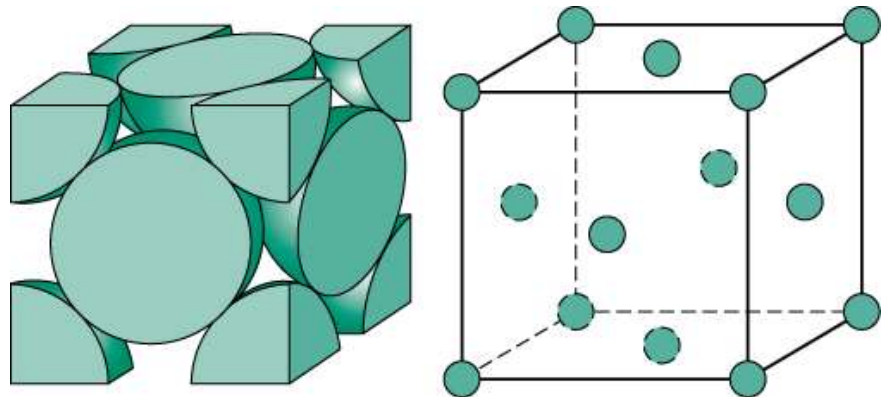
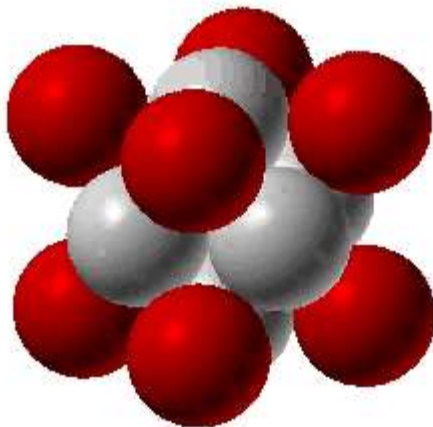
$$\text{APF} = \frac{2 \times \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3}$$

# 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

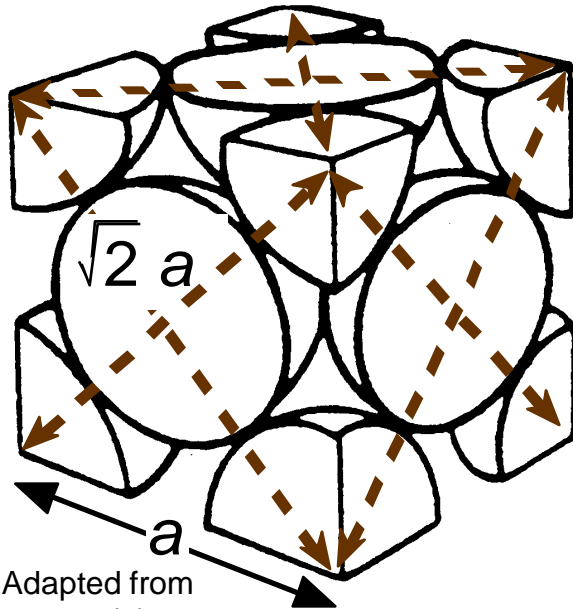


Adapted from Fig. 3.1, *Callister 7e*.

4 atoms/unit cell:  $6 \text{ face} \times \frac{1}{2} + 8 \text{ corners} \times \frac{1}{8}$

# Atomic Packing Factor: FCC

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



Adapted from  
Fig. 3.1(a),  
Callister 7e.

Close-packed directions:  
length =  $4R = \sqrt{2} a$

Unit cell contains:  
 $6 \times 1/2 + 8 \times 1/8$   
= 4 atoms/unit cell

$$\text{APF} = \frac{\begin{array}{c} \text{atoms} \\ \text{unit cell} \end{array} \rightarrow 4 \cdot \frac{4}{3} \pi \left( \frac{\sqrt{2}a}{4} \right)^3 \leftarrow \begin{array}{c} \text{volume} \\ \text{atom} \end{array}}{\begin{array}{c} a^3 \leftarrow \begin{array}{c} \text{volume} \\ \text{unit cell} \end{array} \end{array}}$$

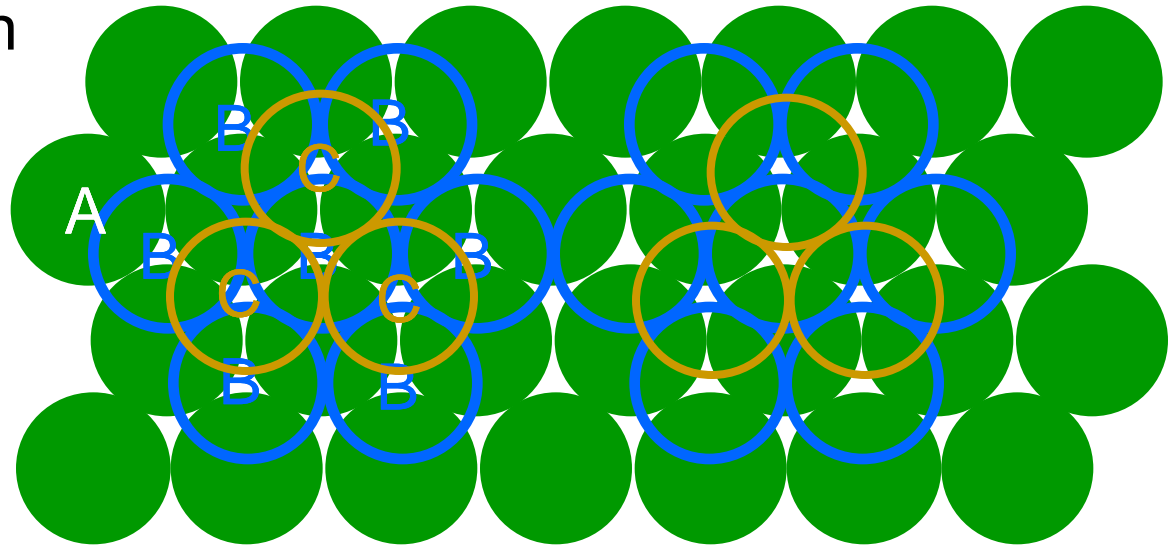
# FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

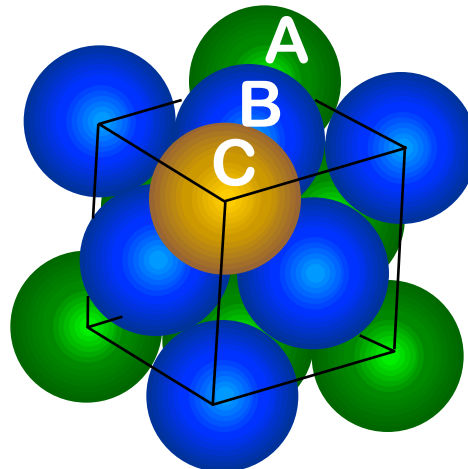
A sites

B sites

C sites

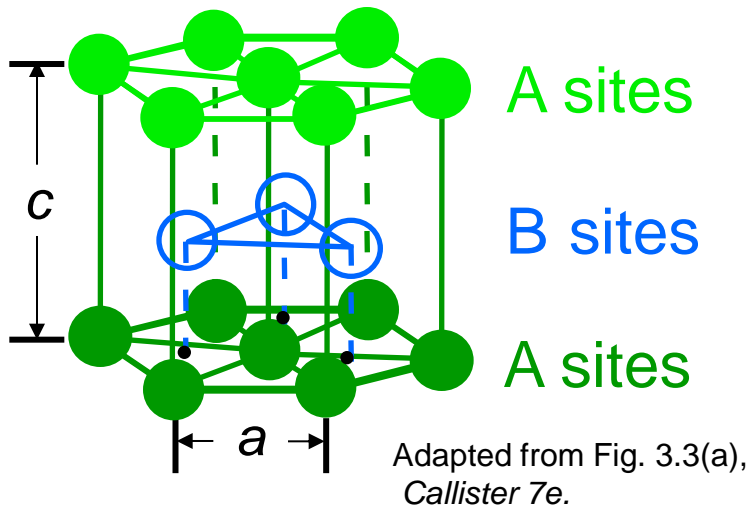


- FCC Unit Cell

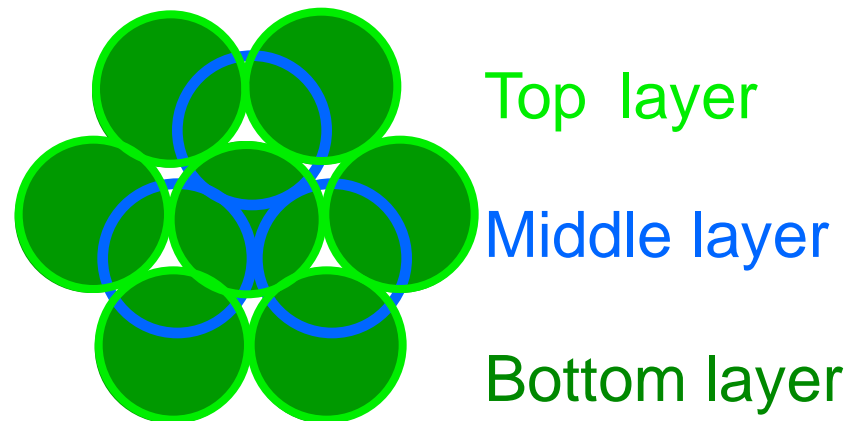


# Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



- 2D Projection



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

# Theoretical Density, $\rho$

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

$$\rho = \frac{n A}{V_C N_A}$$

where

$n$  = number of atoms/unit cell

$A$  = atomic weight

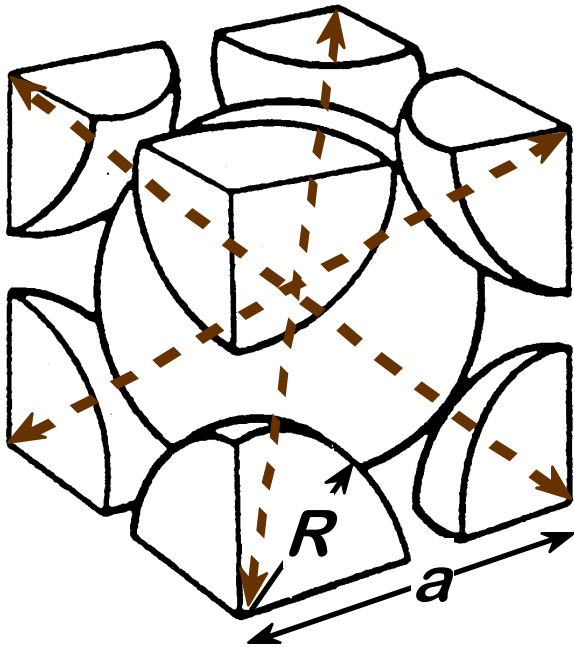
$V_C$  = Volume of unit cell =  $a^3$  for cubic

$N_A$  = Avogadro's number

=  $6.023 \times 10^{23}$  atoms/mol



# Theoretical Density, $\rho$



- Ex: Cr (BCC)

$$A = 52.00 \text{ g/mol}$$

$$R = 0.125 \text{ nm}$$

$$n = 2$$

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

atoms  
unit cell

2 52.00

g  
mol

$\rho =$

volume  
unit cell

$a^3$   $6.023 \times 10^{23}$

atoms  
mol

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

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





# Densities of Material Classes

In general

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

Why?

**Metals** have...

- close-packing (metallic bonding)
- often large atomic masses

**Ceramics** have...

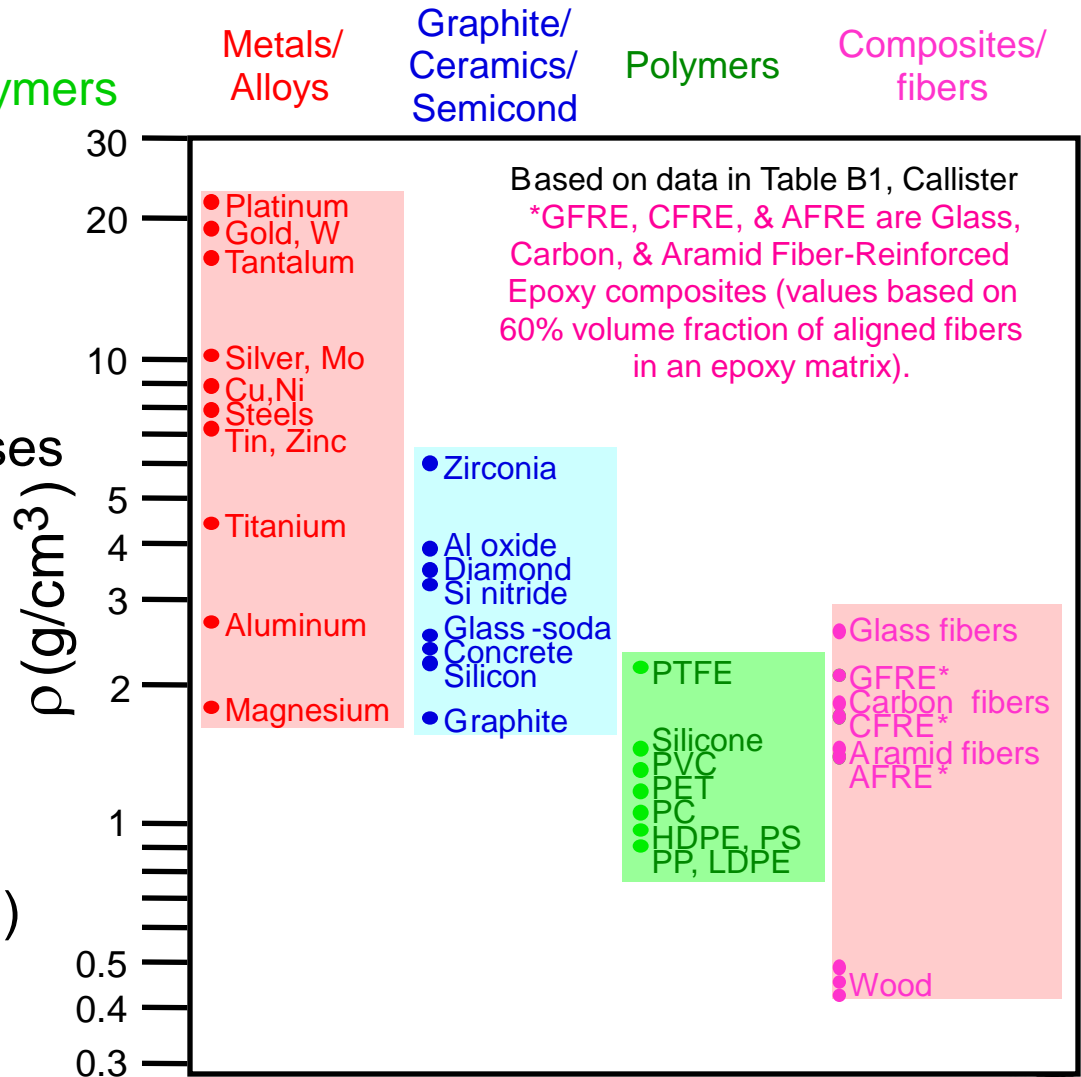
- less dense packing
- often lighter elements

**Polymers** have...

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

**Composites** have...

- intermediate values



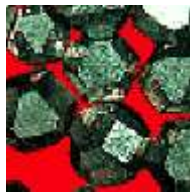
Data from Table B1, Callister 7e.



# Crystals as Building Blocks

- Some engineering applications require single crystals:
  - diamond single
  - turbine blades

crystals for abrasives



(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.

Fig. 8.33(c), *Callister 7e*.  
(Fig. 8.33(c) courtesy of Pratt and Whitney).



(Courtesy P.M. Anderson)

# 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)

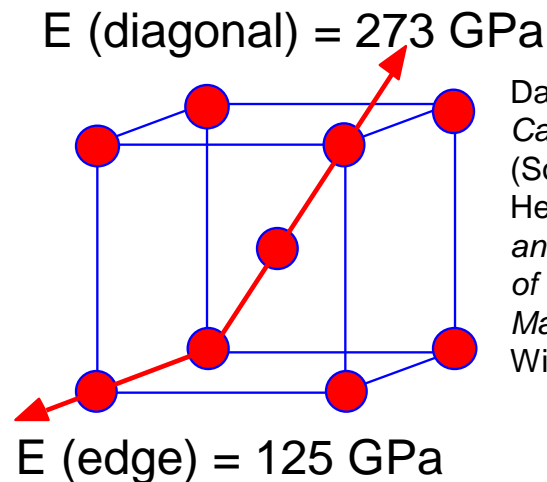
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented, overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

Isotropic

# Single vs Polycrystals

- Single Crystals

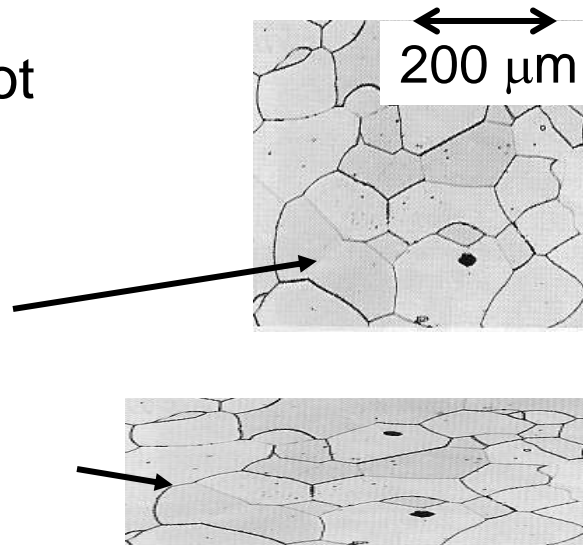
- Properties vary with direction: **anisotropic**.
- Example: the modulus of elasticity ( $E$ ) in BCC iron:



Data from Table 3.3, *Callister 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**.  
( $E_{\text{poly iron}} = 210 \text{ GPa}$ )
- 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].)

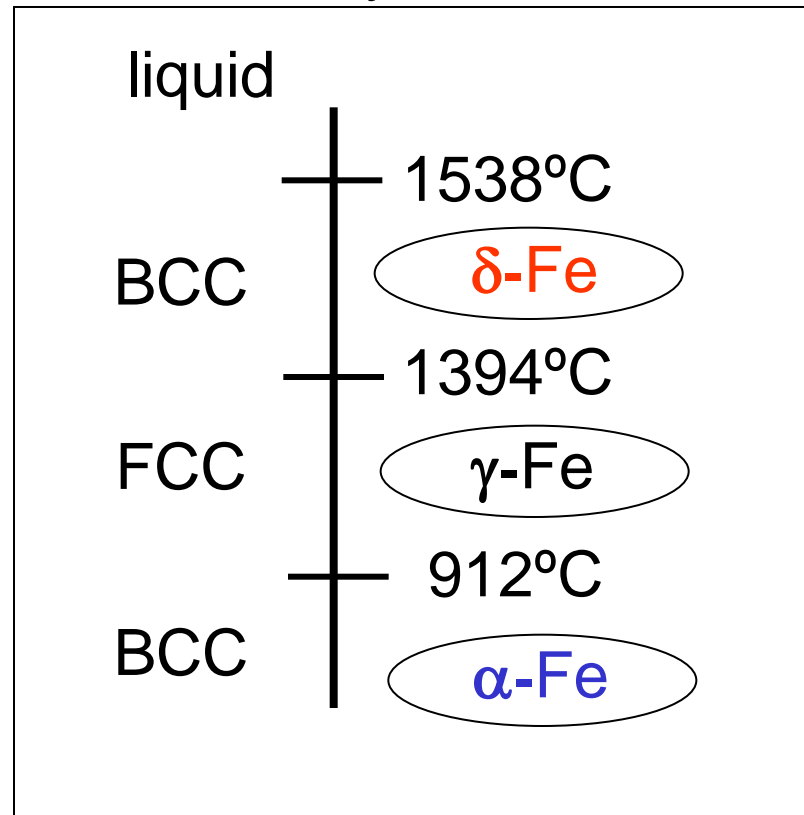
# Section 3.6 – Polymorphism

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

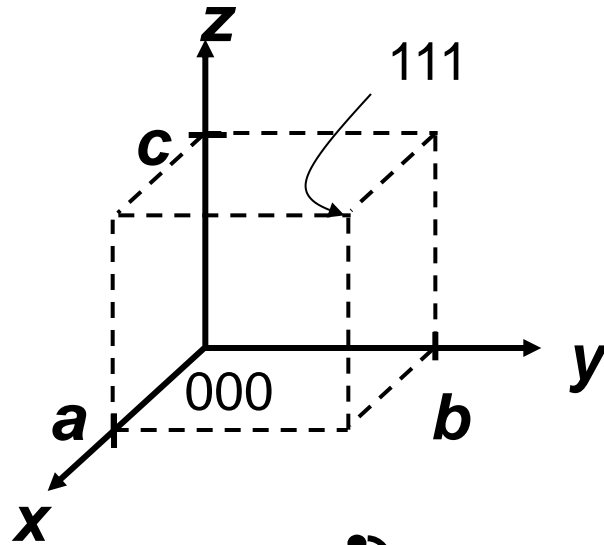
titanium  
 $\alpha$ ,  $\beta$ -Ti

carbon  
diamond, graphite

iron system



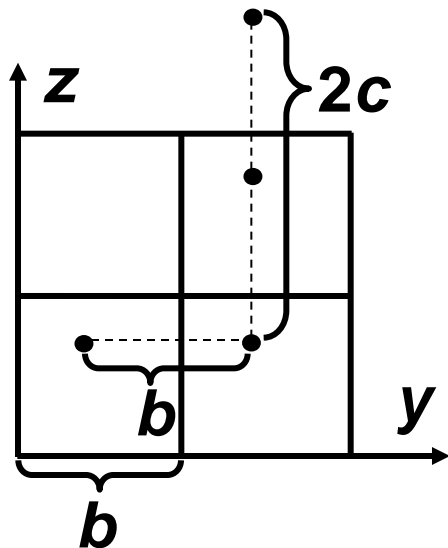
# Section 3.8 Point Coordinates



Point coordinates for unit cell center are

$$a/2, b/2, c/2 \quad \frac{1}{2} \frac{1}{2} \frac{1}{2}$$

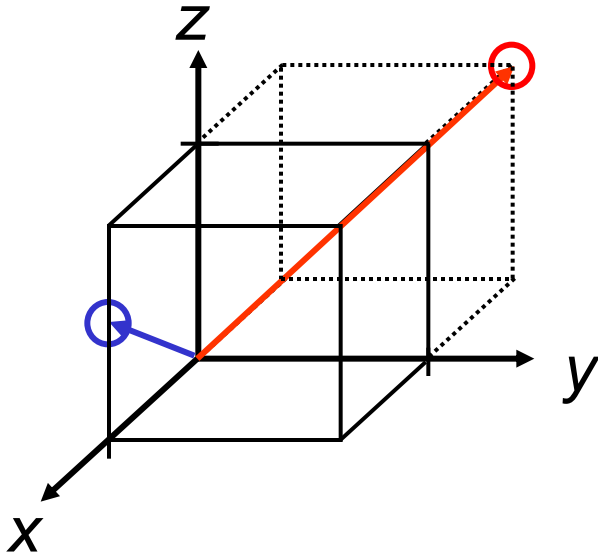
Point coordinates for unit cell corner are 111



Translation: integer multiple of lattice constants  $\rightarrow$  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:  $1, 0, \frac{1}{2} \Rightarrow 2, 0, 1 \Rightarrow [201]$

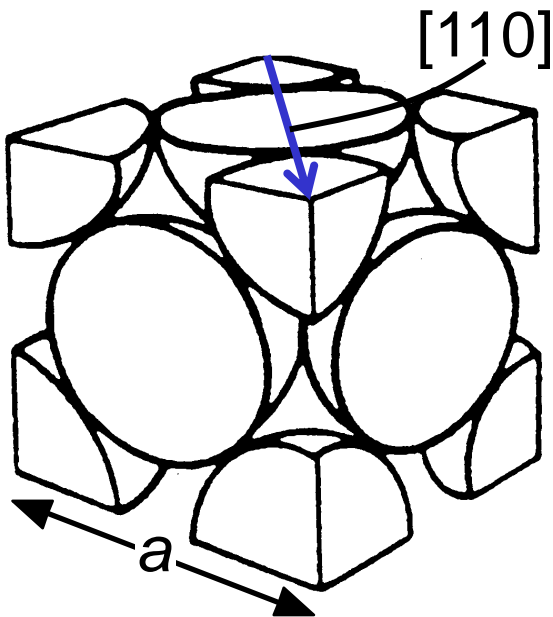
$-1, 1, 1 \Rightarrow [\bar{1}11]$  where overbar represents a negative index

families of directions  $\langle uvw \rangle$



# Linear Density

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



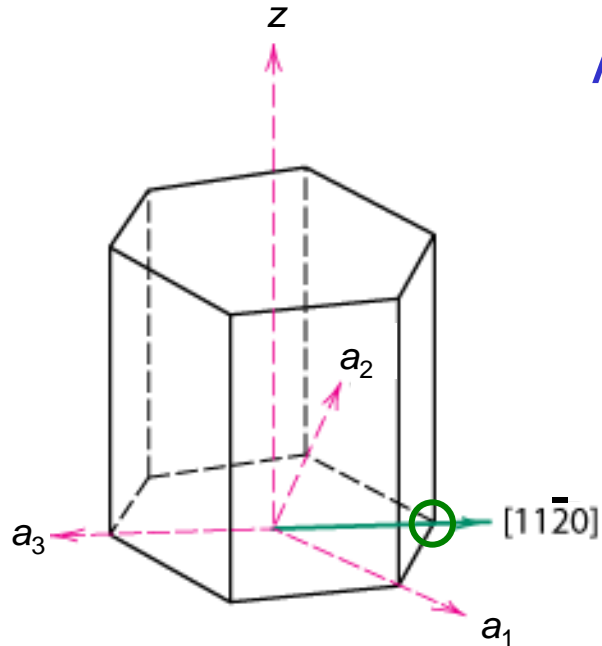
ex: linear density of Al in  $[110]$  direction

$$a = 0.405 \text{ nm}$$

$$\begin{array}{l} \text{\# atoms} \rightarrow 2 \\ \text{length} \rightarrow \sqrt{2}a \end{array} \quad LD = \frac{2}{\sqrt{2}a} = 3.5 \text{ nm}^{-1}$$



# HCP Crystallographic Directions



Adapted from Fig. 3.8(a), Callister 7e.

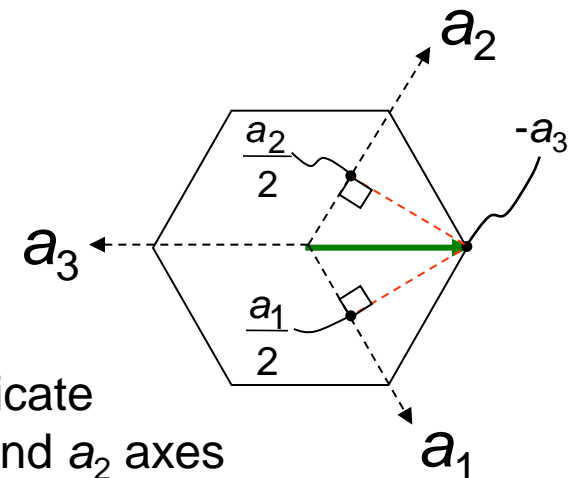
## Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions  $a_1$ ,  $a_2$ ,  $a_3$ , or  $c$
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$[uvw]$

ex:  $\frac{1}{2}, \frac{1}{2}, -1, 0$

$\Rightarrow [11\bar{2}0]$



dashed red lines indicate  
projections onto  $a_1$  and  $a_2$  axes

# HCP Crystallographic Directions

- Hexagonal Crystals

- 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e.,  $u'v'w'$ ) as follows.

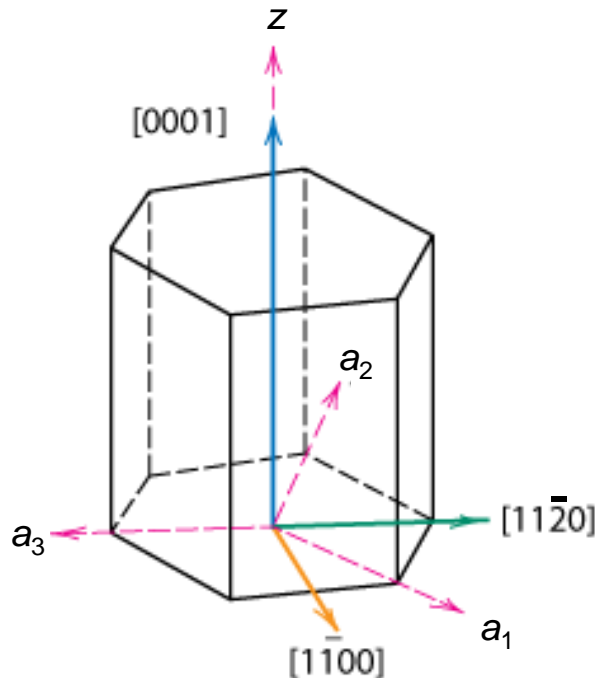


Fig. 3.8(a), Callister 7e.

$$[u'v'w'] \rightarrow [uvtw]$$

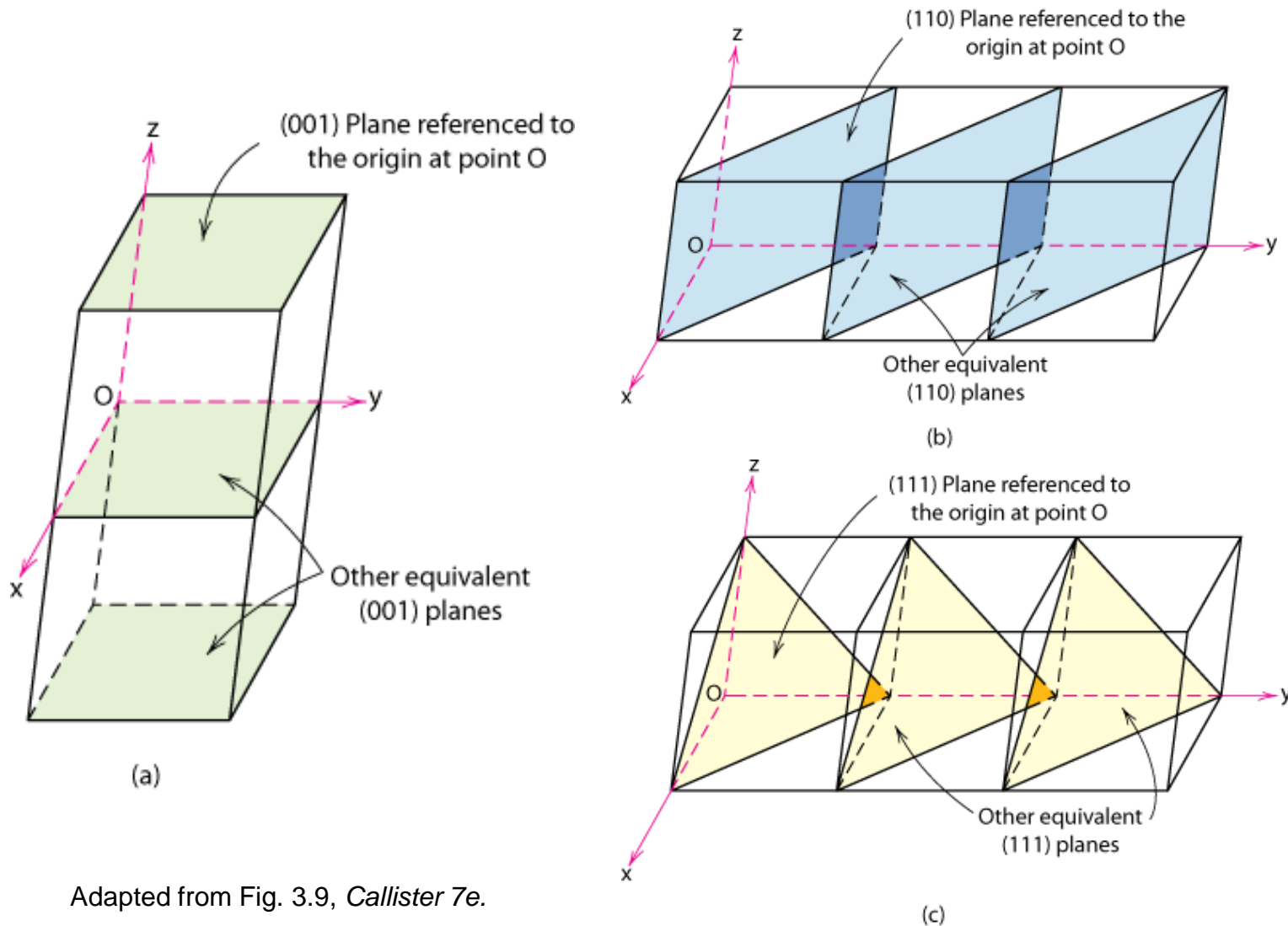
$$u = \frac{1}{3}(2u' - v')$$

$$v = \frac{1}{3}(2v' - u')$$

$$t = -(u + v)$$

$$w = w'$$

# Crystallographic Planes



Adapted from Fig. 3.9, *Callister 7e*.

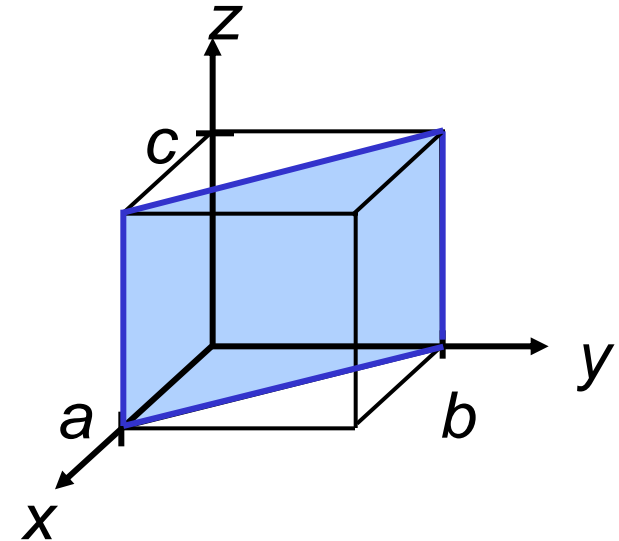
# Crystallographic Planes

- 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.,  $(hkl)$

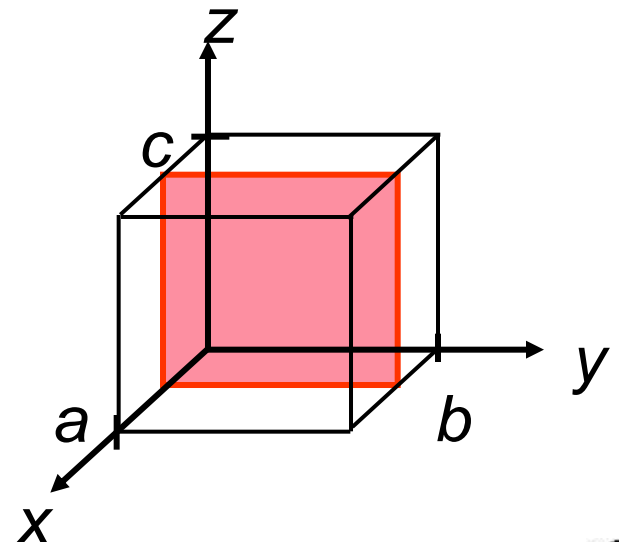


# Crystallographic Planes

<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1	1	$\infty$
2. Reciprocals	1/1	1/1	1/ $\infty$
	1	1	0
3. Reduction	1	1	0
4. Miller Indices	(110)		

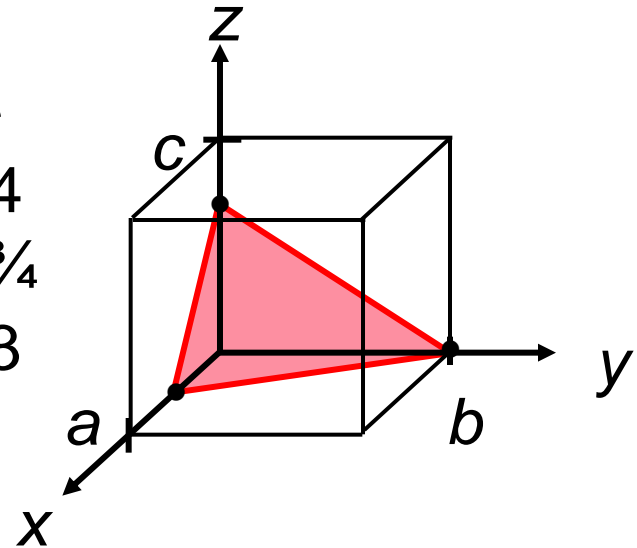


<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1/2	$\infty$	$\infty$
2. Reciprocals	1/1/2	1/ $\infty$	1/ $\infty$
	2	0	0
3. Reduction	2	0	0
4. Miller Indices	(100)		



# Crystallographic Planes

<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1/2	1	3/4
2. Reciprocals	1/1/2	1/1	1/3/4
	2	1	4/3
3. Reduction	6	3	4
4. Miller Indices	(634)		



Family of Planes  $\{hkl\}$

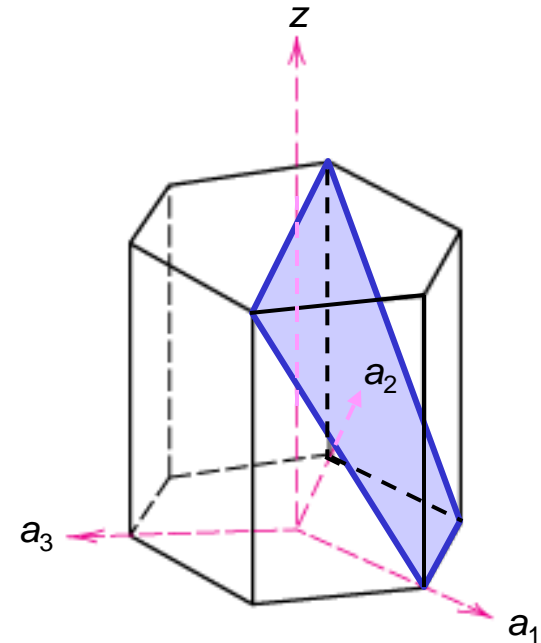
Ex:  $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$



# Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

<u>example</u>	$a_1$	$a_2$	$a_3$	$c$
1. Intercepts	1	$\infty$	-1	1
2. Reciprocals	1	$1/\infty$	-1	1
	1	0	-1	1
3. Reduction	1	0	-1	1
4. Miller-Bravais Indices	$(10\bar{1}1)$			



Adapted from Fig. 3.8(a), Callister 7e.

# Crystallographic Planes

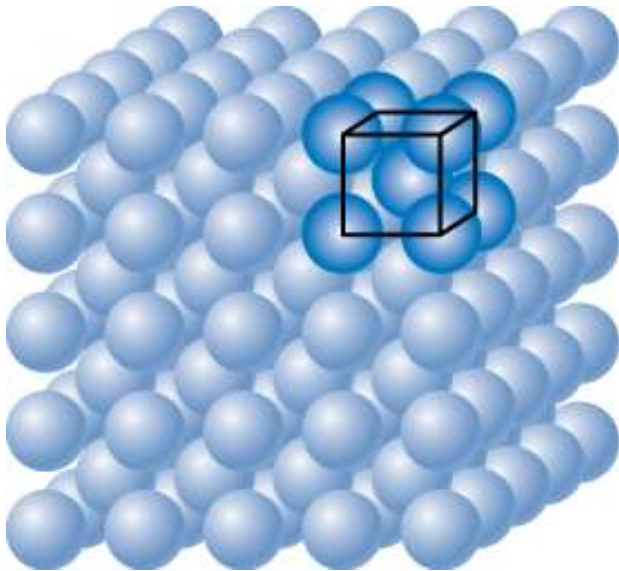
- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
  - a) Draw (100) and (111) crystallographic planes for Fe.
  - b) Calculate the planar density for each of these planes.





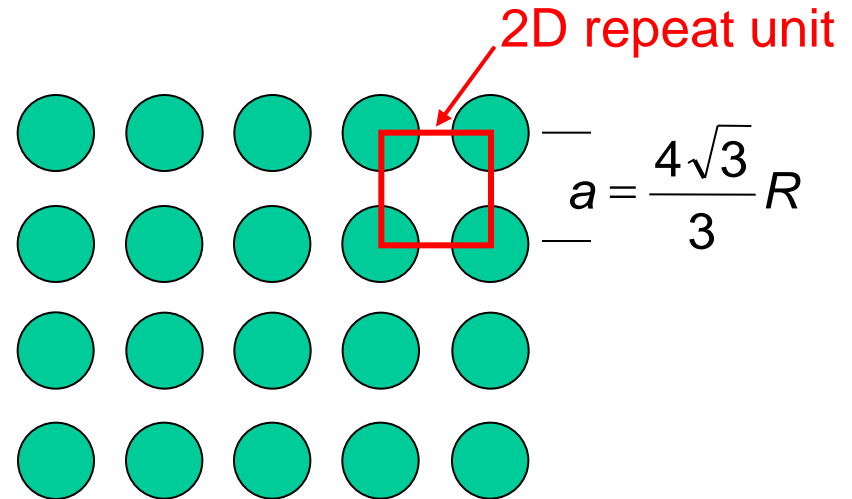
# Planar Density of (100) Iron

Solution: At  $T < 912^\circ\text{C}$  iron has the BCC structure.



Adapted from Fig. 3.2(c), Callister 7e.

(100)



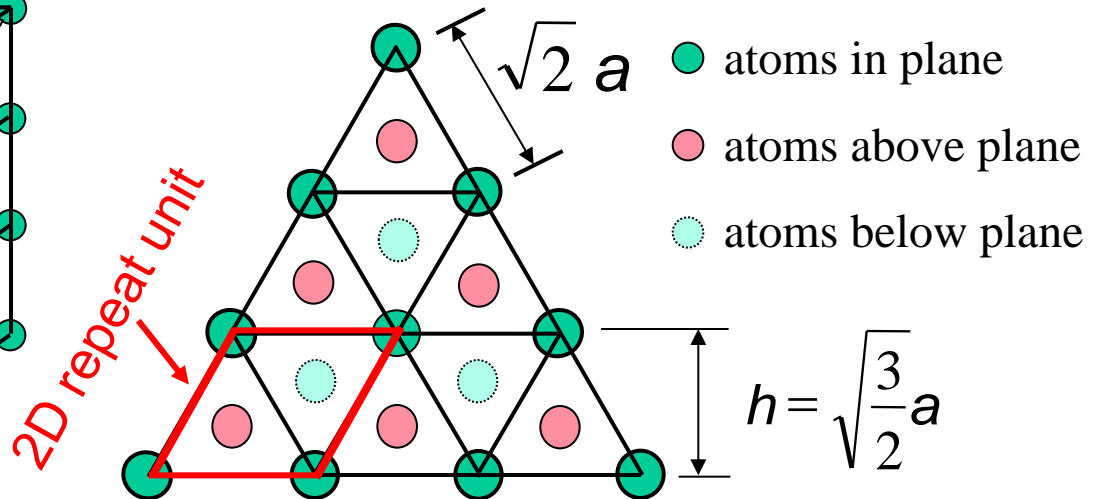
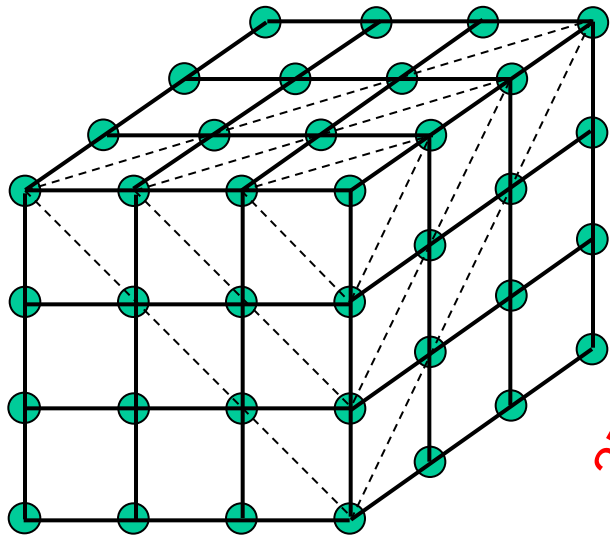
Radius of iron  $R = 0.1241 \text{ nm}$

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

# Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell



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

atoms  
2D repeat unit

1

Planar Density =

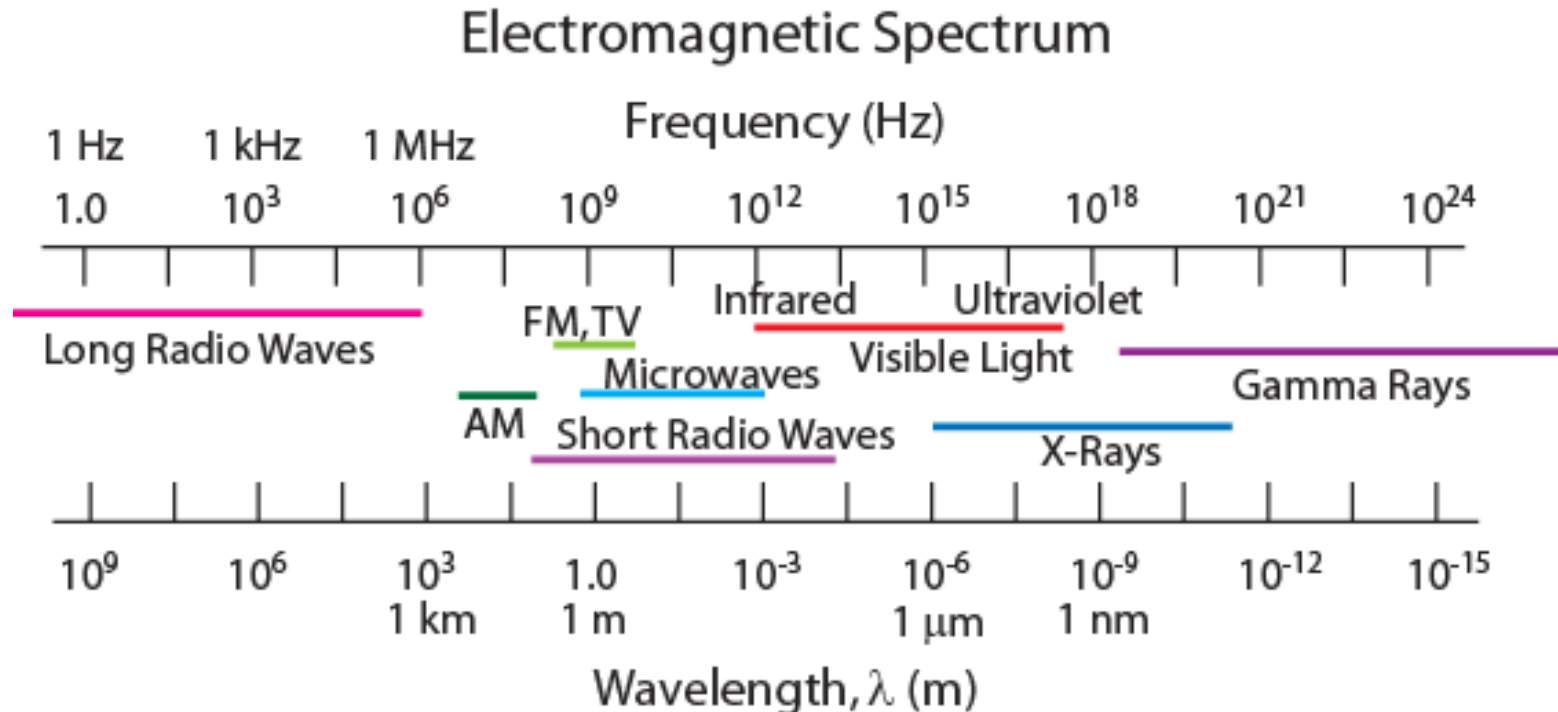
area  
2D repeat unit

$$\frac{1}{\frac{16\sqrt{3}}{3} R^2}$$

$$= 7.0 \frac{\text{atoms}}{\text{nm}^2} =$$

$$0.70 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

# Section 3.16 - X-Ray Diffraction

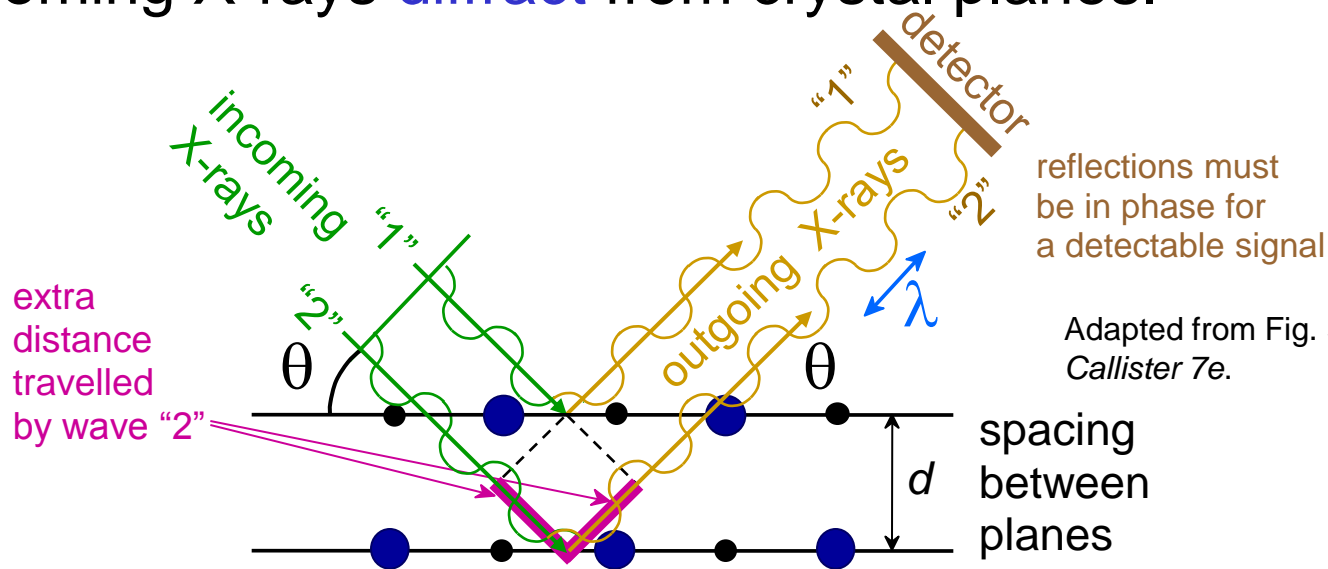


- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings  $< \lambda$
- Spacing is the distance between parallel planes of atoms.



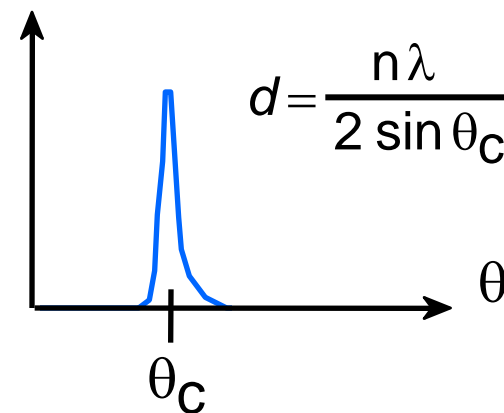
# X-Rays to Determine Crystal Structure

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

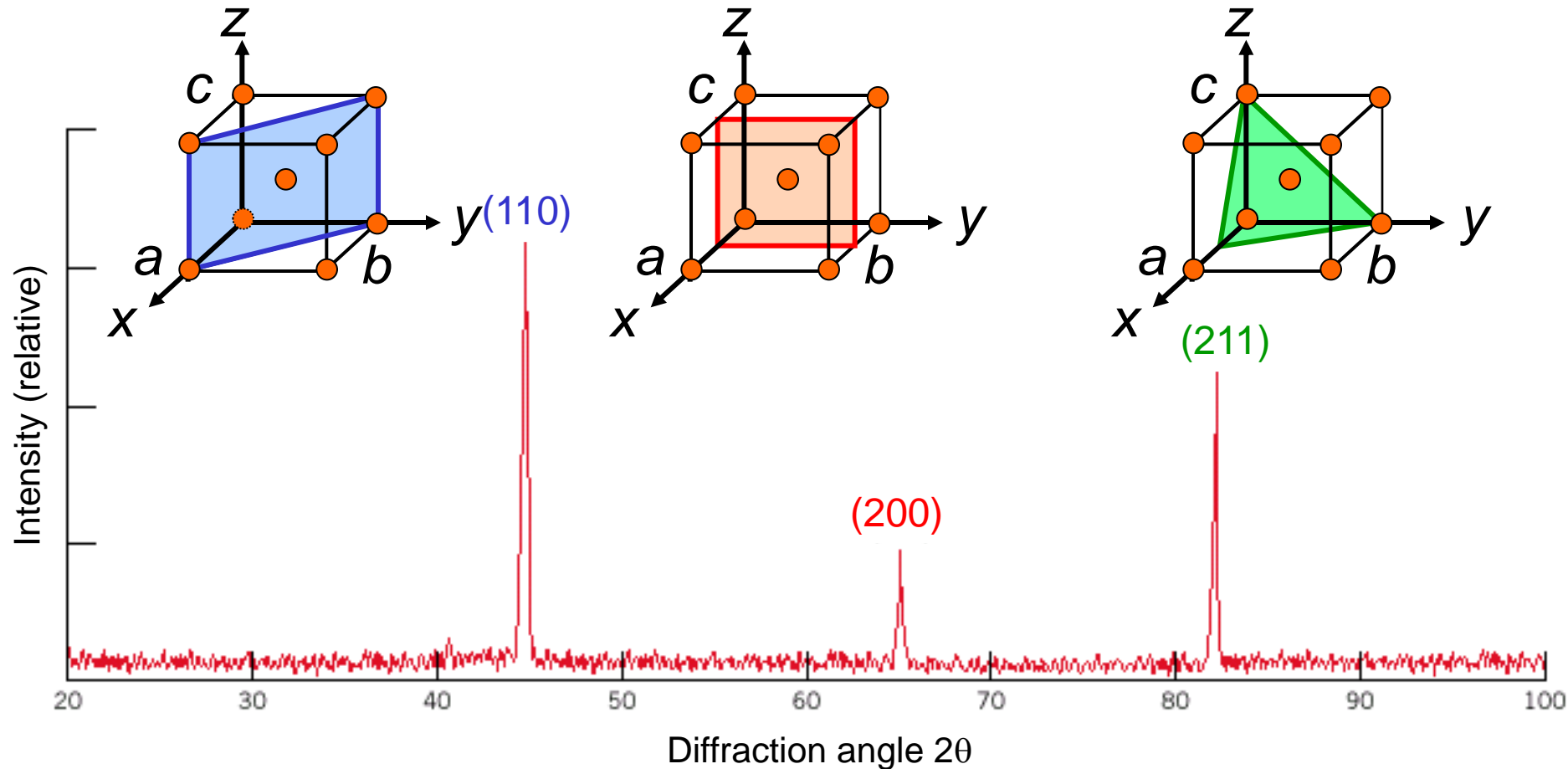


Measurement of critical angle,  $\theta_c$ , allows computation of planar spacing,  $d$ .

X-ray intensity (from detector)



# X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline  $\alpha$ -iron (BCC)

Adapted from Fig. 3.20, *Callister 5e*.



# 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.



# ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems:

