

Chapter 3: The Structure of Crystalline Solids

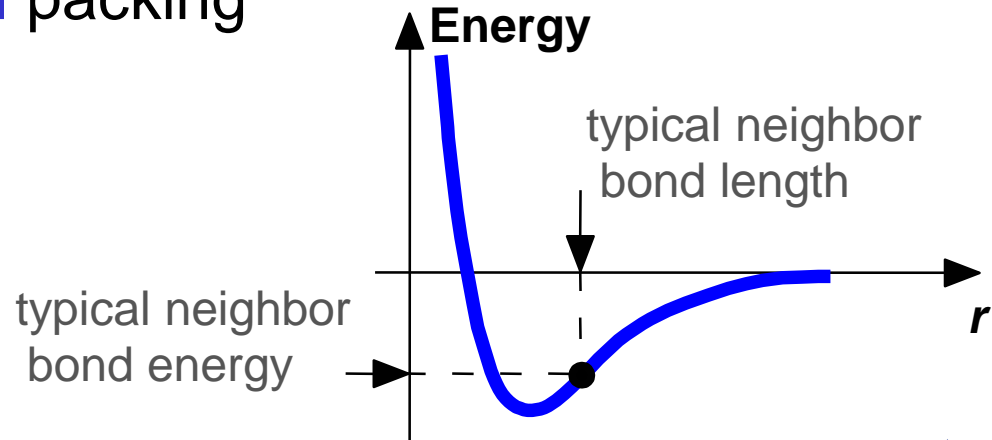
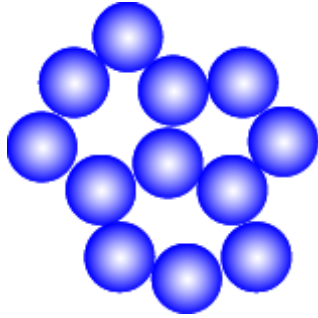
ISSUES TO ADDRESS...

- 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?

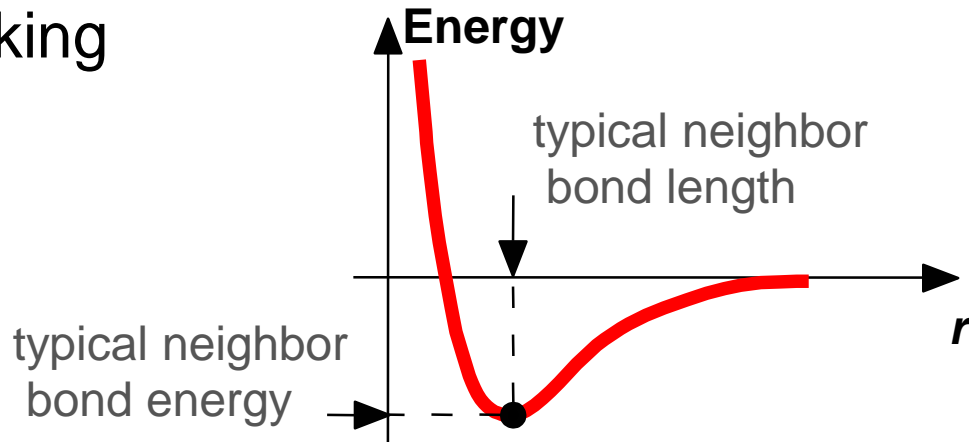
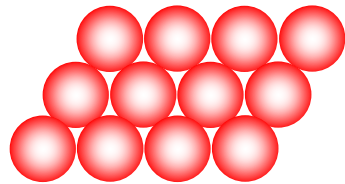


Energy and Packing

- Non dense, **random** packing



- Dense, **ordered** packing



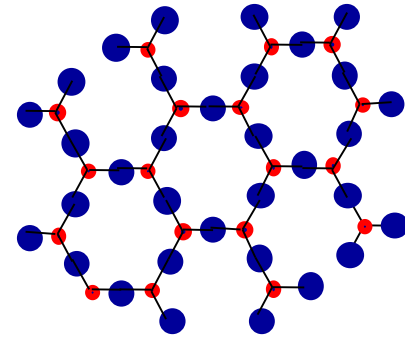
Dense, ordered packed structures tend to have lower energies.



Materials and Packing

Crystalline materials...

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



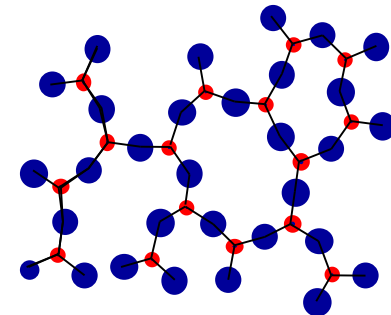
crystalline SiO₂

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

Noncrystalline materials...

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

• **Si** • **Oxygen**



noncrystalline SiO₂

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.

Lattice: three-dimensional array of points coinciding with atom position (or sphere centers)

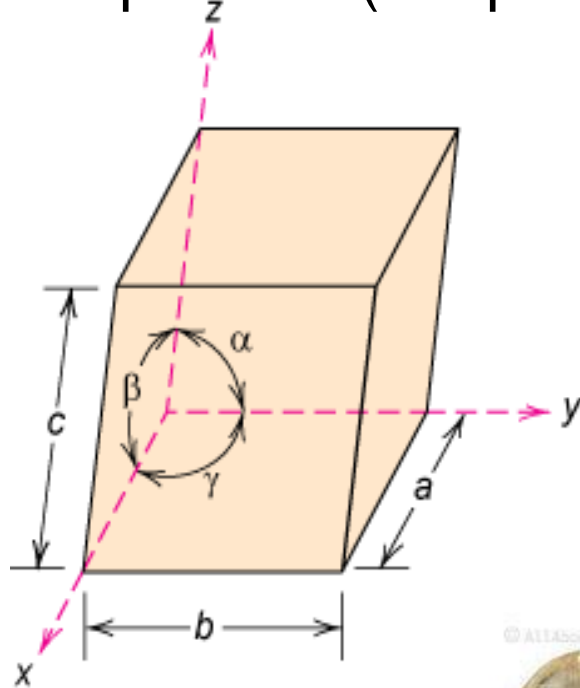


Fig. 3.4, Callister

7 crystal systems

14 crystal lattices

a , b , and c are the lattice constants

© AllAboutGemstones.com



Isometric



Hexagonal



Tetragonal



Trigonal



Orthorhombic



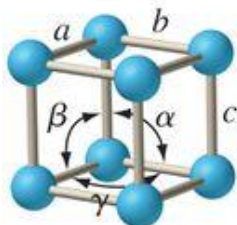
Monoclinic



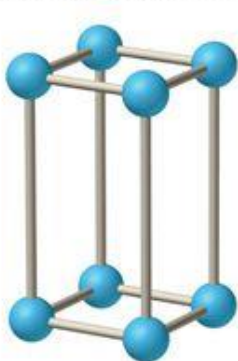
Triclinic

7 crystal systems

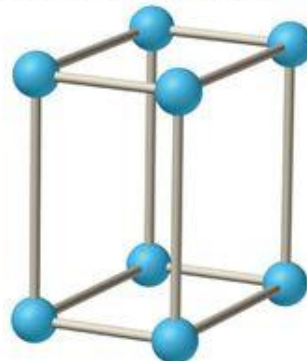
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



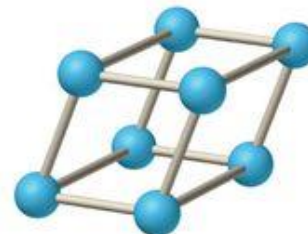
Simple cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



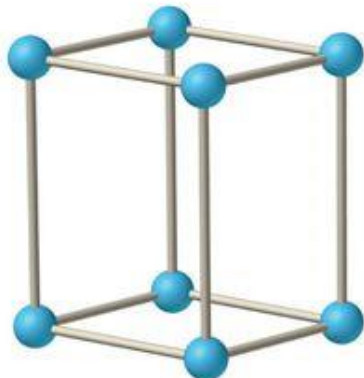
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



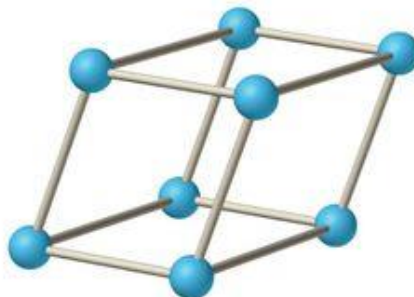
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



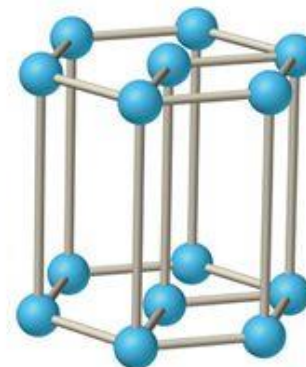
Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



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



Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



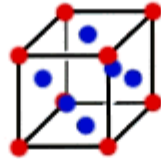
Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



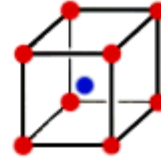
14 different crystal lattices, called **Bravais Lattices**. (3 different cubic types, 2 different tetragonal types, 4 different orthorhombic types, 2 different monoclinic types, 1 rhombohedral, 1 hexagonal, 1 triclinic).



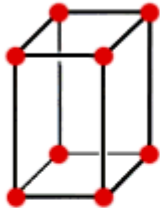
Simple cubic



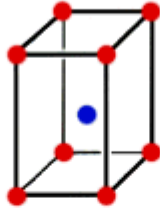
Face-centered cubic



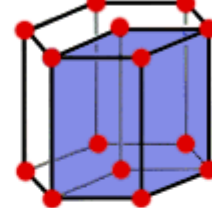
Body-centered cubic



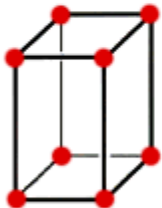
Simple tetragonal



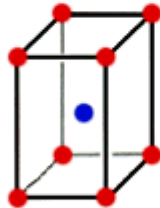
Body-centered tetragonal



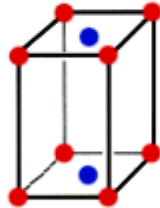
Hexagonal



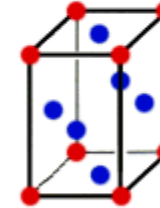
Simple orthorhombic



Body-centered orthorhombic



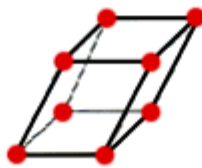
Base-centered orthorhombic



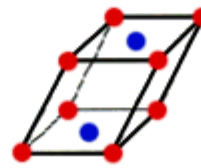
Face-centered orthorhombic



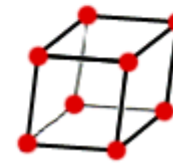
Rhombohedral



Simple Monoclinic



Base-centered monoclinic



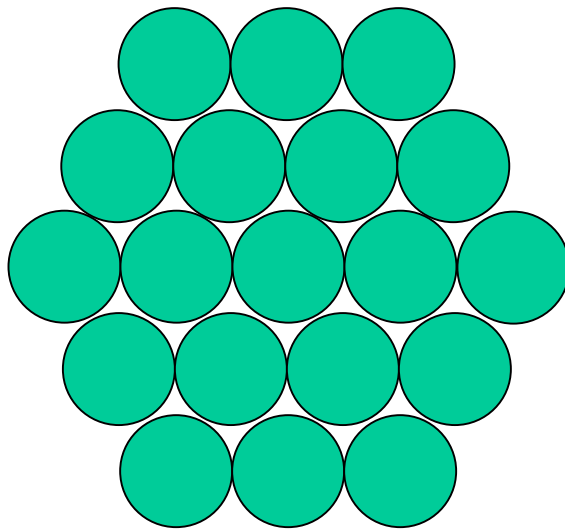
Triclinic



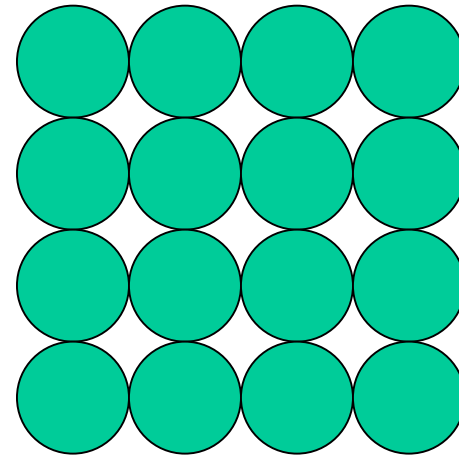
Section 3.4 – Metallic Crystal Structures

- 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.

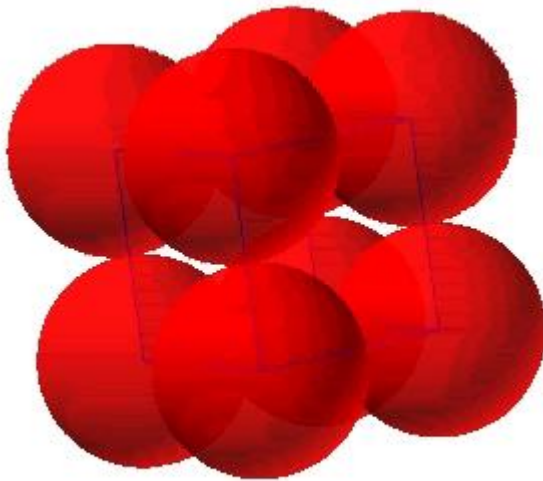
We will examine three such structures...



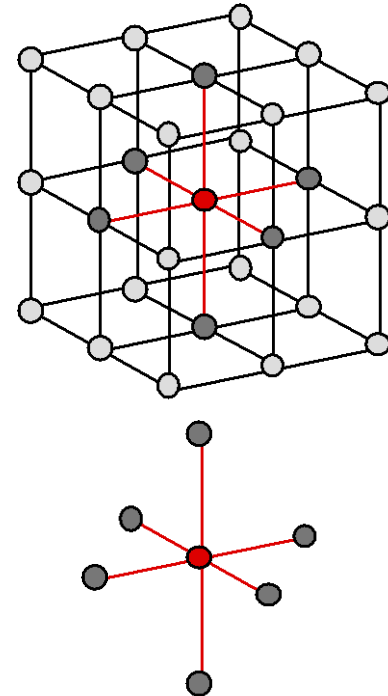
Simple Cubic Structure (SC)

- 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)

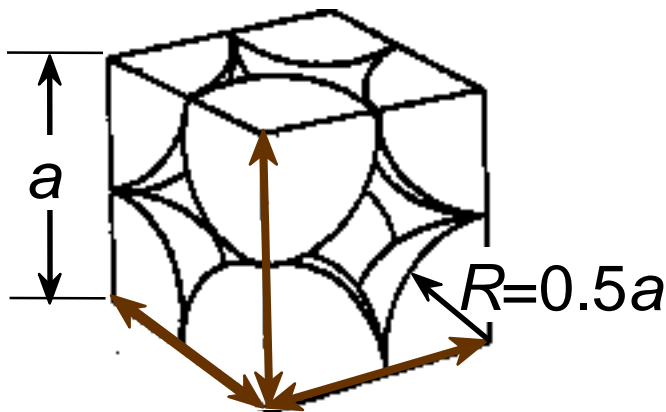


Atomic Packing Factor (APF)

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

*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.

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

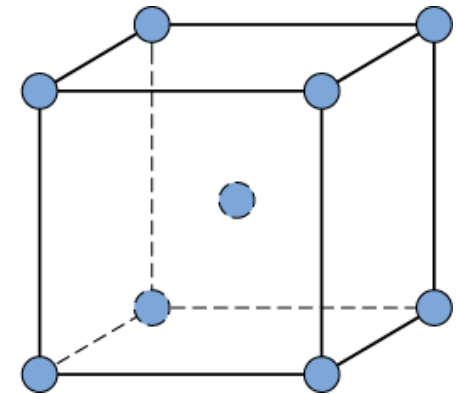
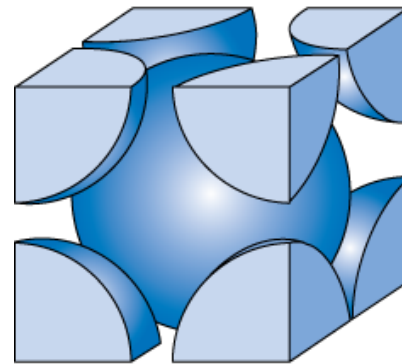
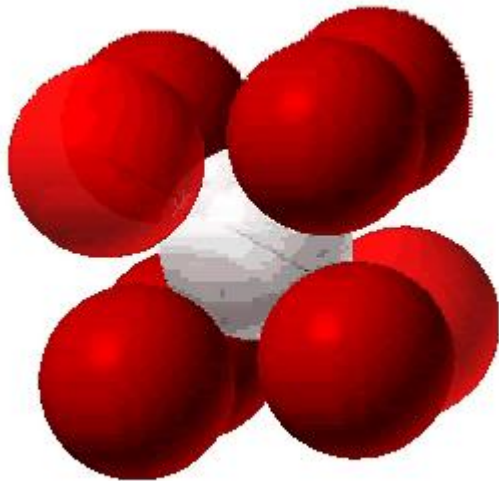


Body Centered Cubic Structure (BCC)

- 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 (α), Tantalum, Molybdenum

- Coordination # = 8



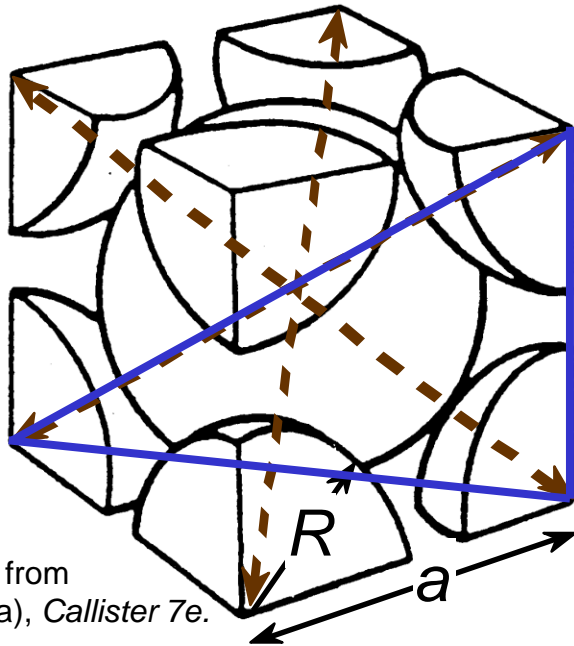
Adapted from Fig. 3.2,
Callister 7e.

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

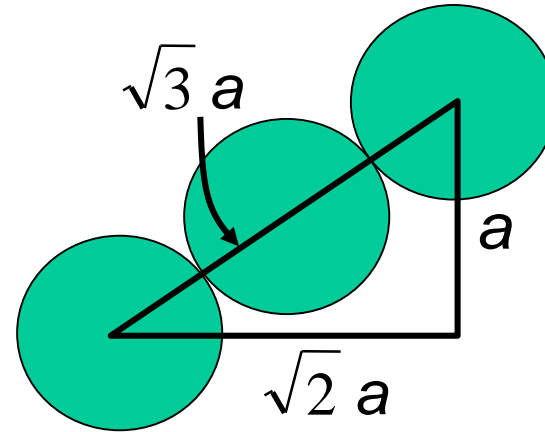


Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



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



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

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

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

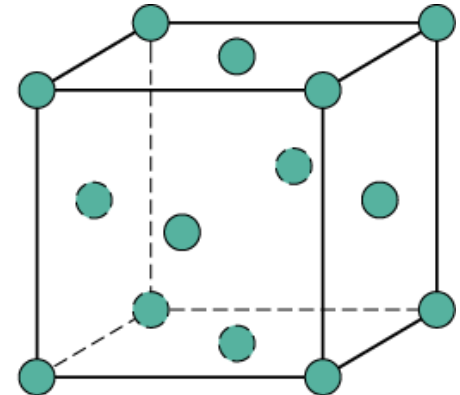
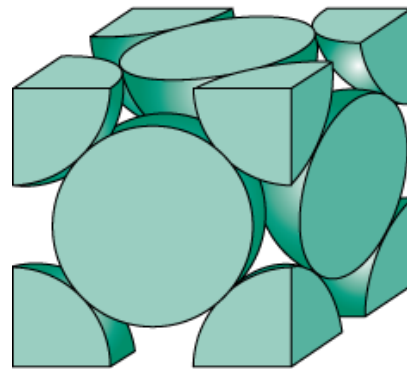
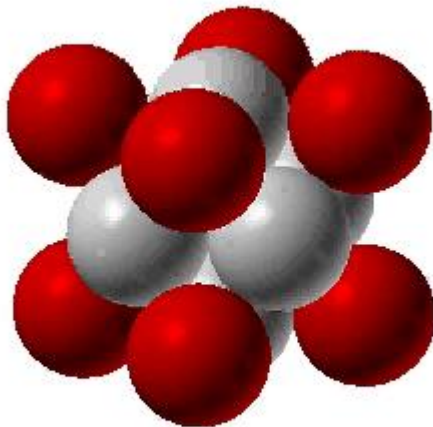


Face Centered Cubic Structure (FCC)

- 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



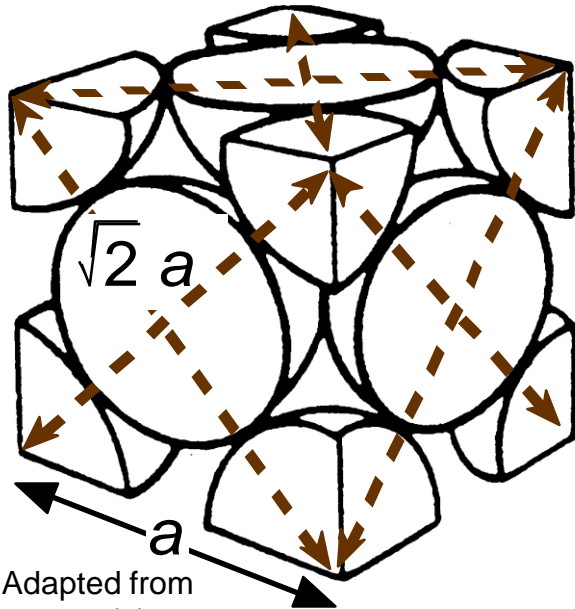
Adapted from Fig. 3.1, *Callister 7e*.

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



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**

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

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



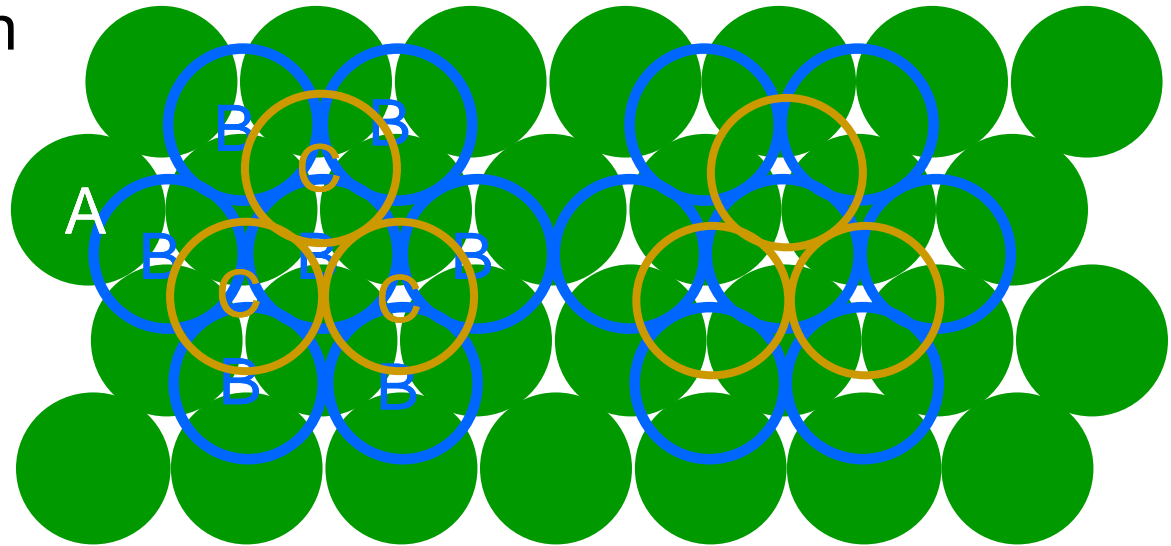
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

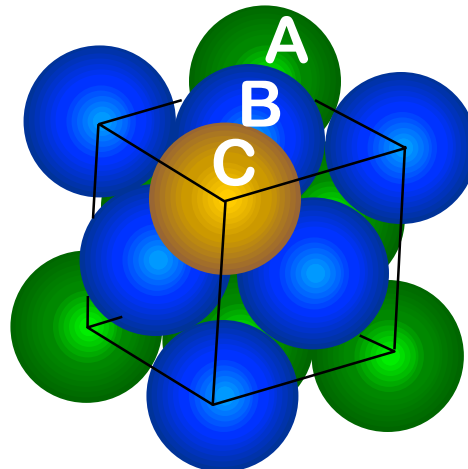
A sites

B sites

C sites

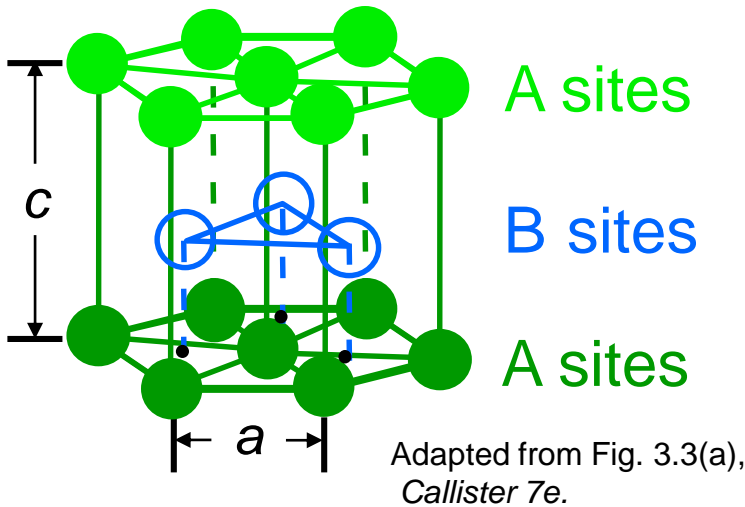


- FCC Unit Cell



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, ρ

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

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

where

n = number of atoms/unit cell

A = atomic weight

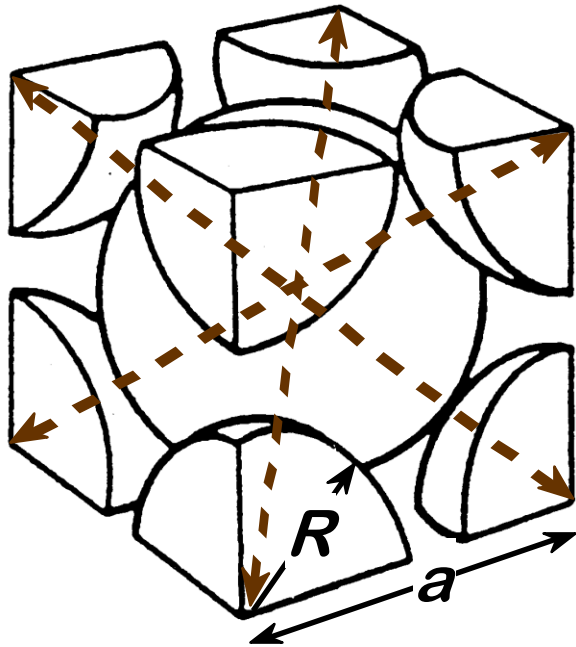
V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro's number

= 6.023×10^{23} atoms/mol



Theoretical Density, ρ



- Ex: Cr (BCC)

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

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

$$n = 2$$

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

$$\frac{\text{atoms}}{\text{unit cell}} \rightarrow \begin{array}{|c|c|} \hline 2 & 52.00 \\ \hline \end{array}$$

$$\frac{\text{g}}{\text{mol}}$$

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

$$\rho =$$

$$\frac{\begin{array}{|c|c|} \hline a^3 & 6.023 \times 10^{23} \\ \hline \end{array}}$$

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

$$\frac{\text{atoms}}{\text{mol}}$$



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...

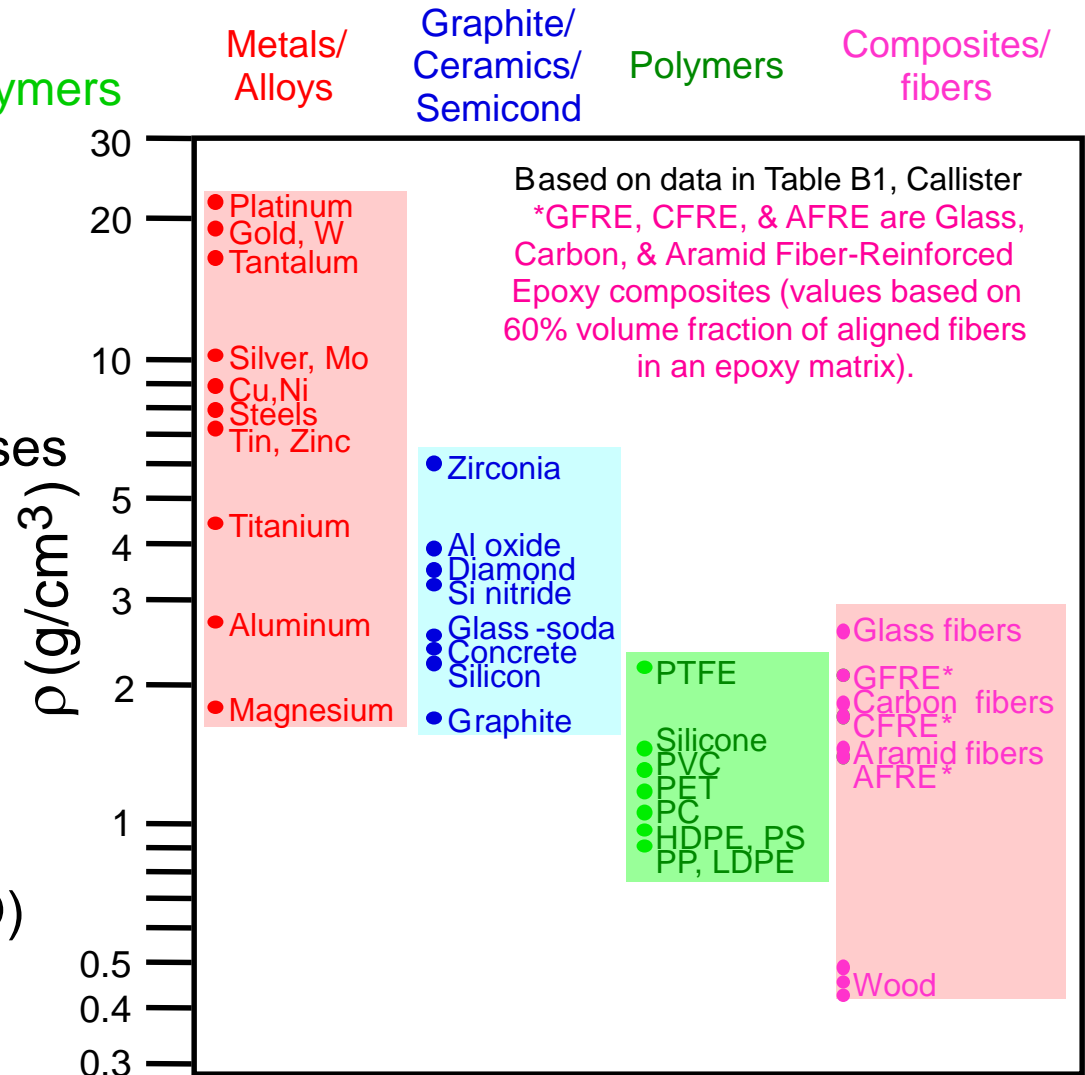
- less dense packing
- often lighter elements

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 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.

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)

Isotropic

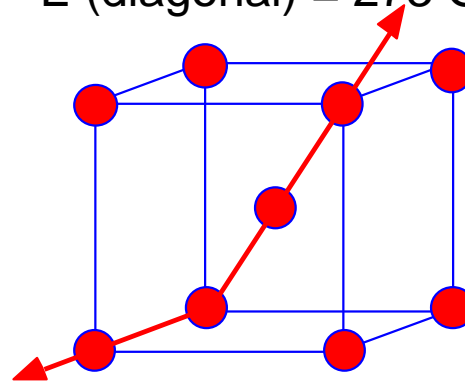
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented, overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

Single vs Polycrystals

- Single Crystals

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

E (diagonal) = 273 GPa

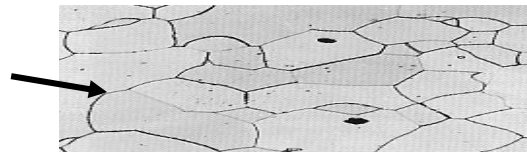
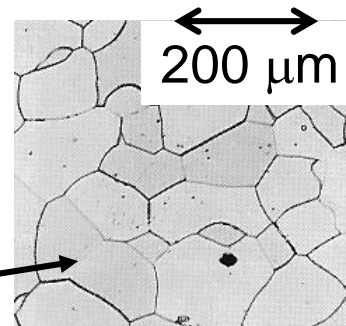


Data from Table 3.3, *Callister 7e*.
(Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

E (edge) = 125 GPa

- 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].)

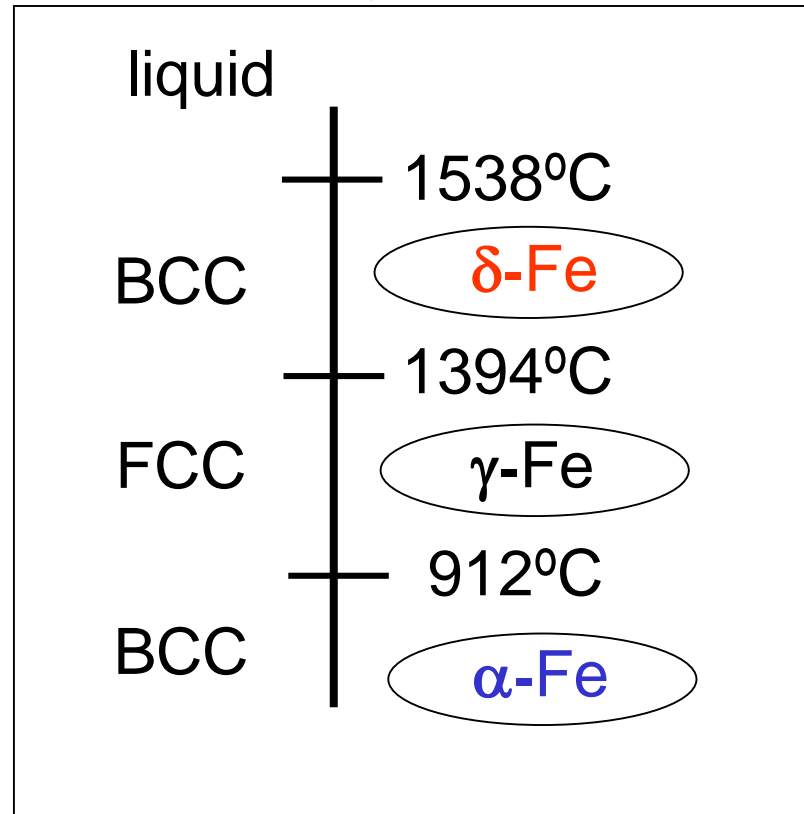
Section 3.6 – Polymorphism

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

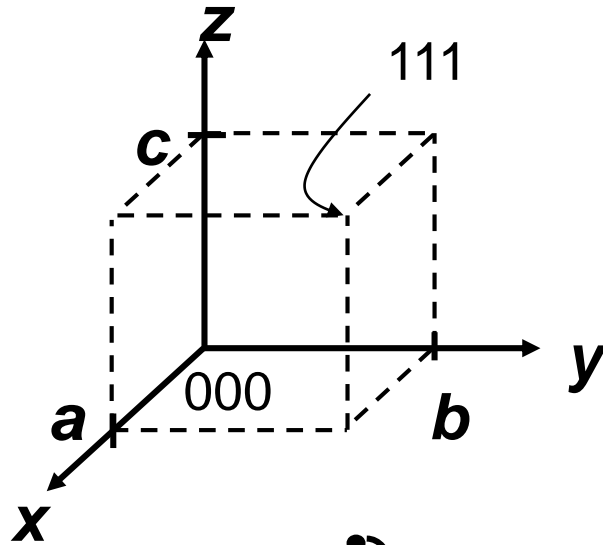
titanium
 α , β -Ti

carbon
diamond, graphite

iron system



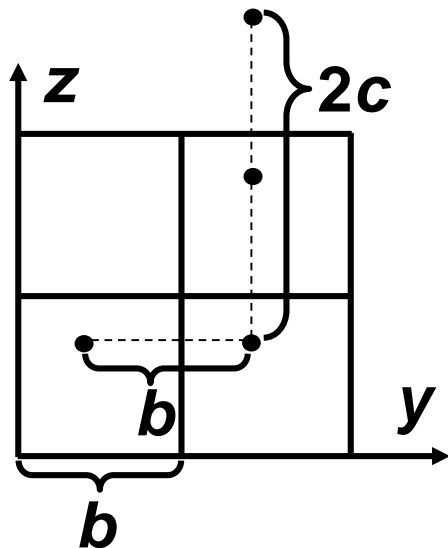
Section 3.8 Point Coordinates



Point coordinates for unit cell center are

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

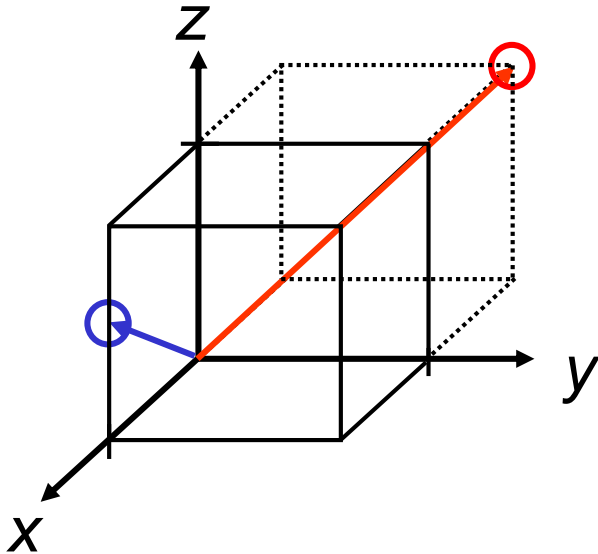
Point coordinates for unit cell corner are 111



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: $1, 0, \frac{1}{2} \Rightarrow 2, 0, 1 \Rightarrow [201]$

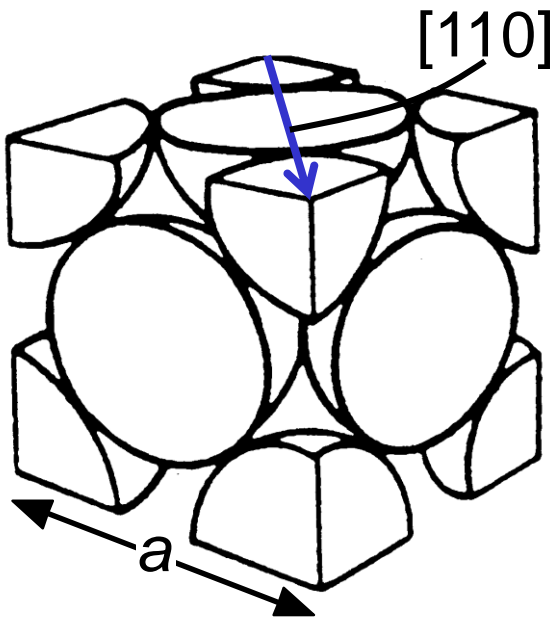
$-1, 1, 1 \Rightarrow [\bar{1}11]$ where overbar represents a negative index

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

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

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

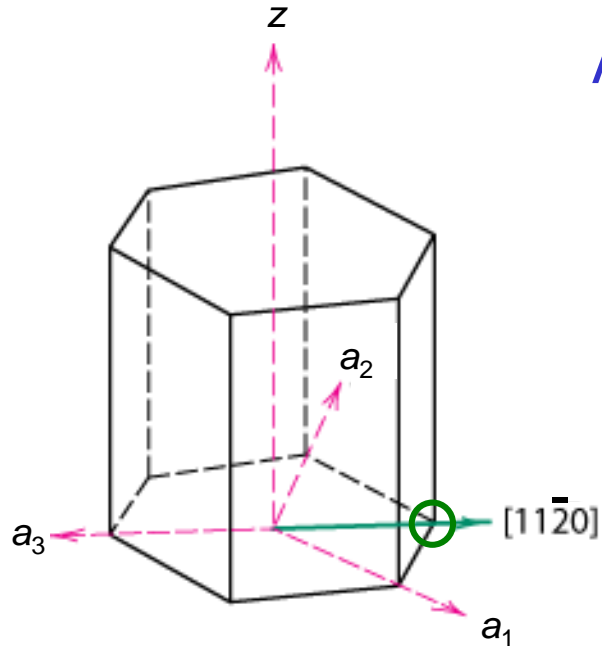


HCP Crystallographic Directions

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

$[uvw]$

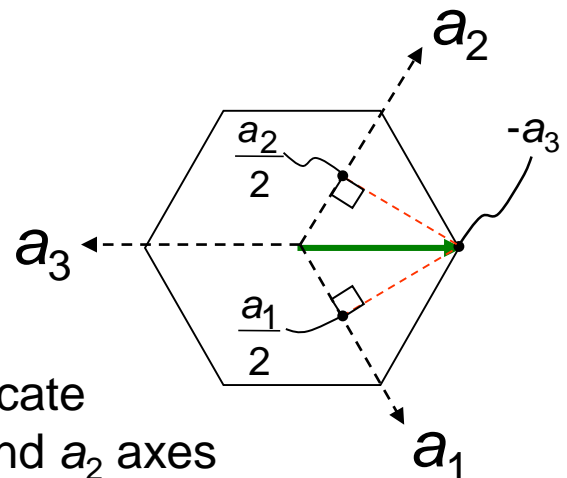


Adapted from Fig. 3.8(a), Callister 7e.

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.

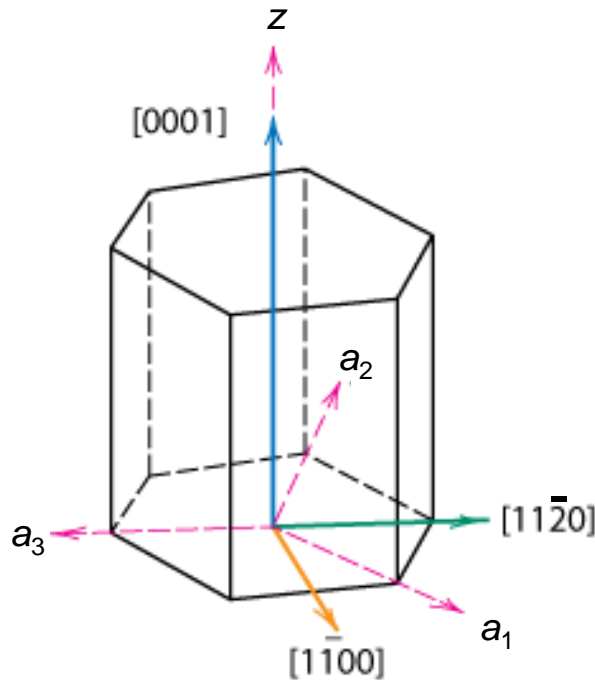


Fig. 3.8(a), Callister 7e.

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

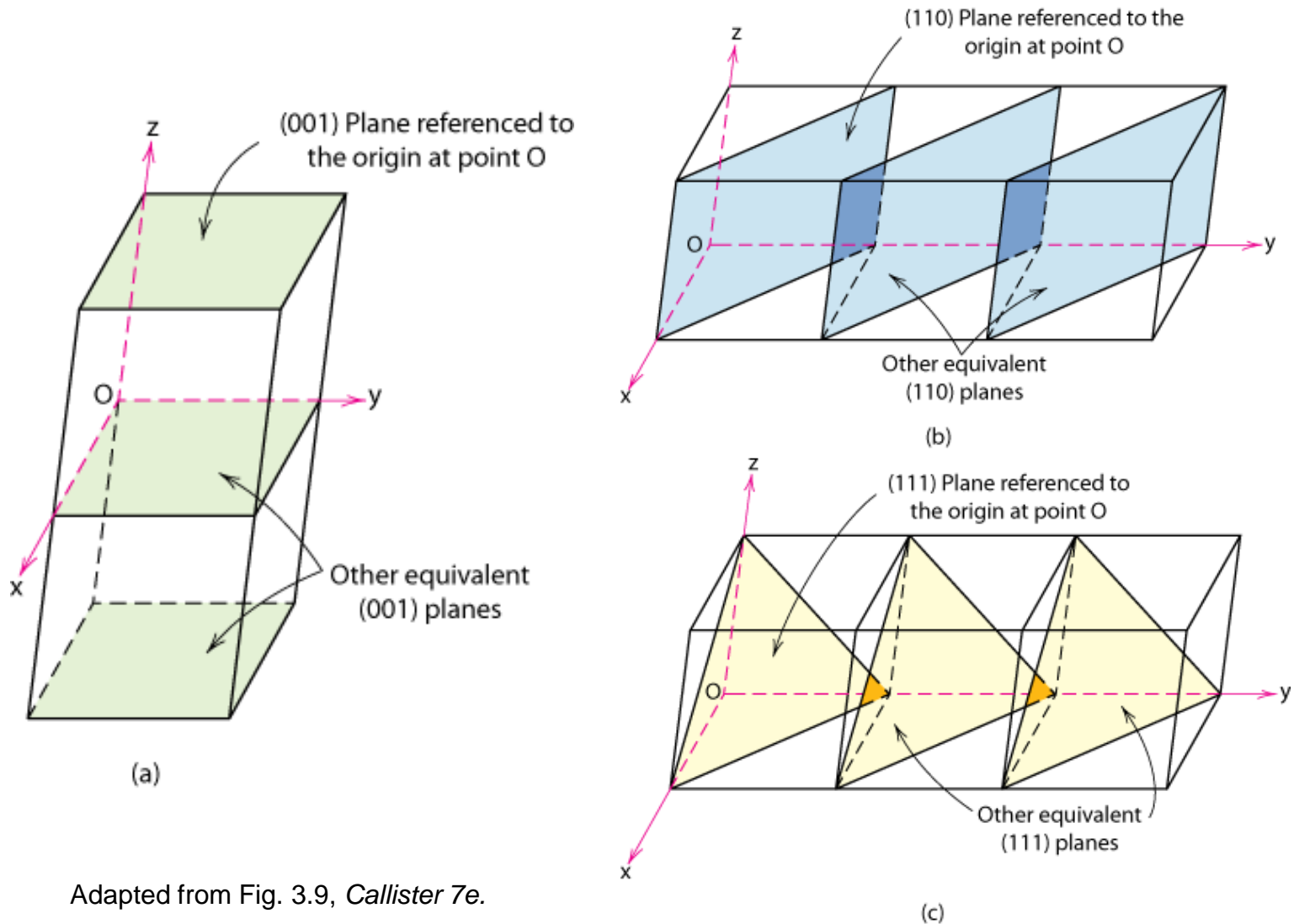
$$u = \frac{1}{3}(2u' - v')$$

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

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

$$w = w'$$

Crystallographic Planes



Adapted from Fig. 3.9, Callister 7e.

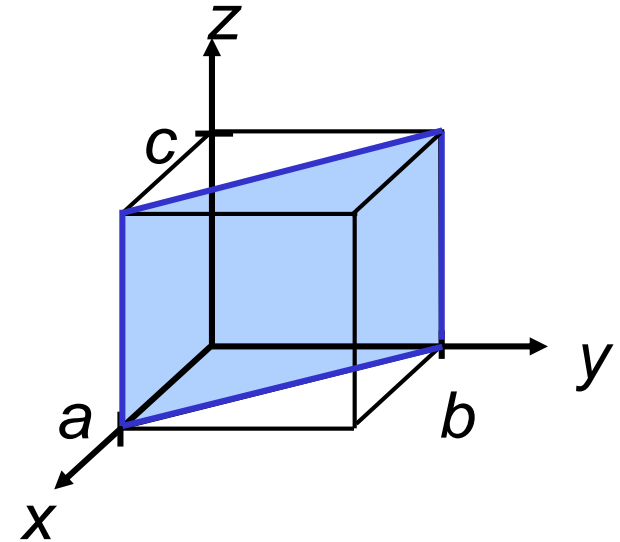
Crystallographic Planes

- 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)

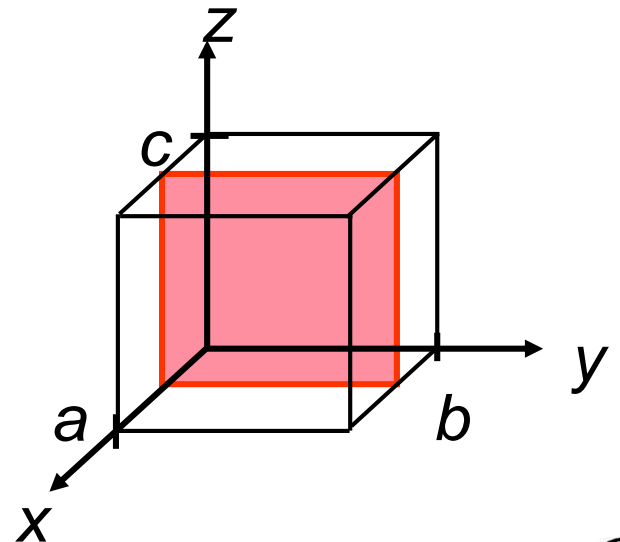


Crystallographic Planes

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

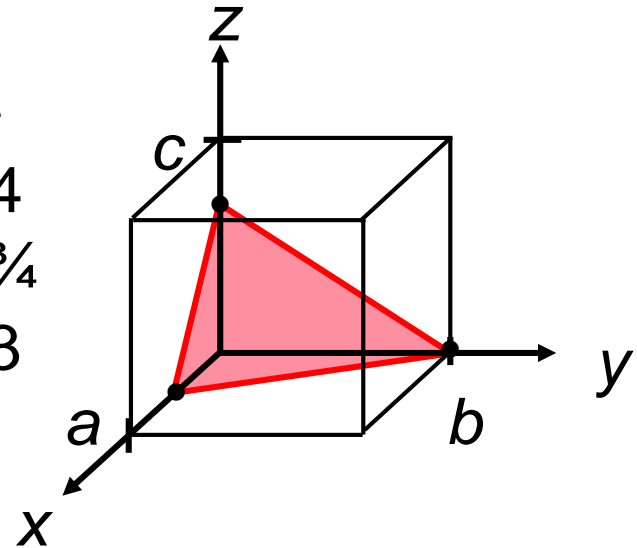


<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/1/2	1/ ∞	1/ ∞
	2	0	0
3. Reduction	2	0	0
4. Miller Indices	(100)		



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 $\{hkl\}$

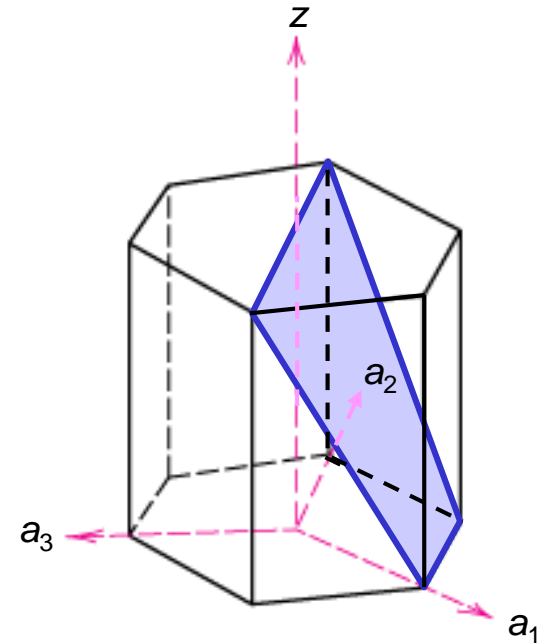
Ex: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$



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	∞	-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.

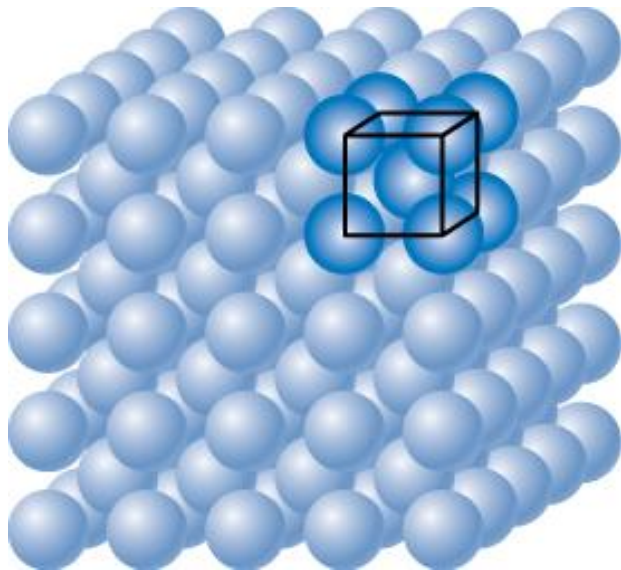
Crystallographic Planes

- 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.

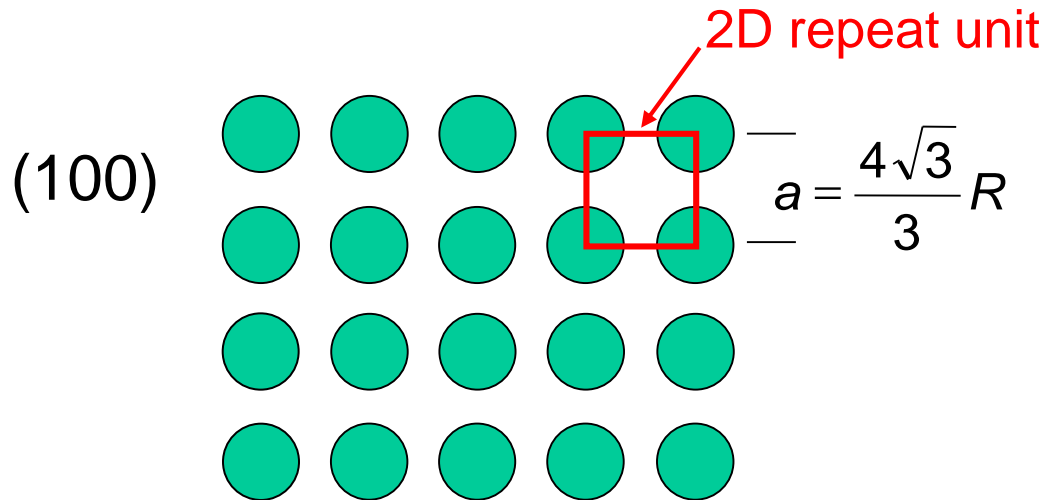


Planar Density of (100) Iron

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



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



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

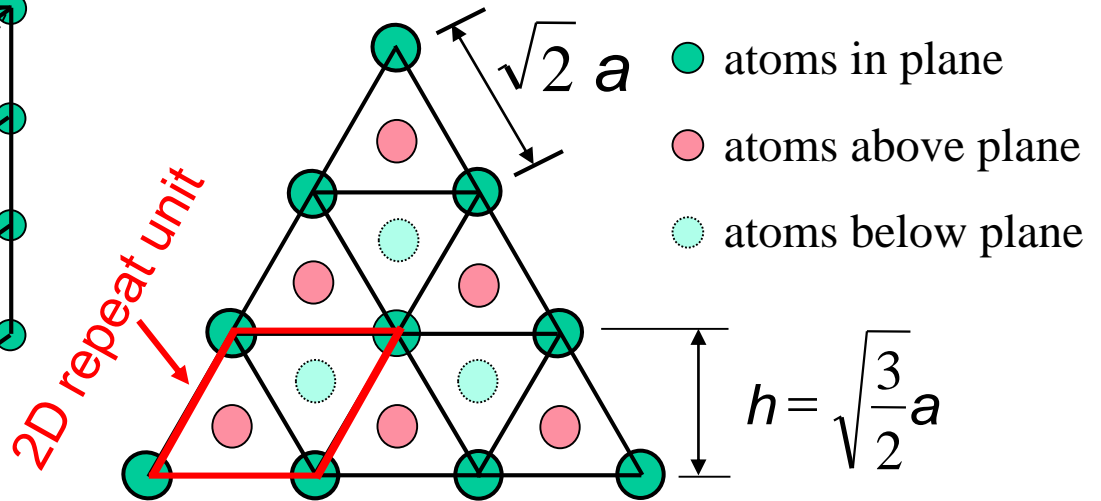
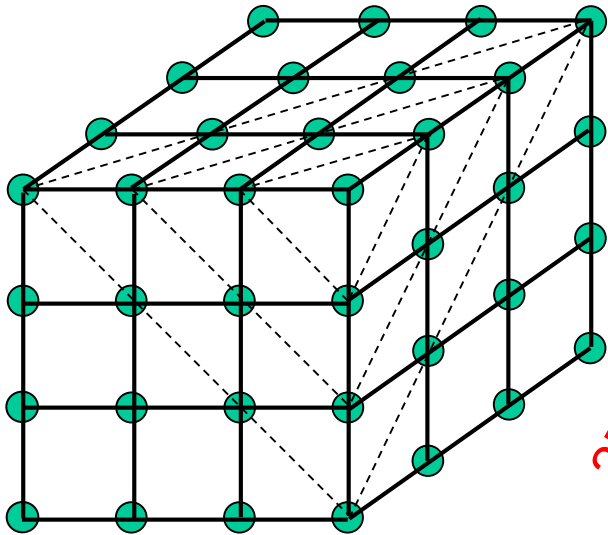
$$\text{Planar Density} = \frac{\text{atoms}}{\text{2D repeat unit}} \div \frac{\text{area}}{\text{2D repeat unit}} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$



Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell



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

atoms
2D repeat unit

Planar Density =

area
2D repeat unit

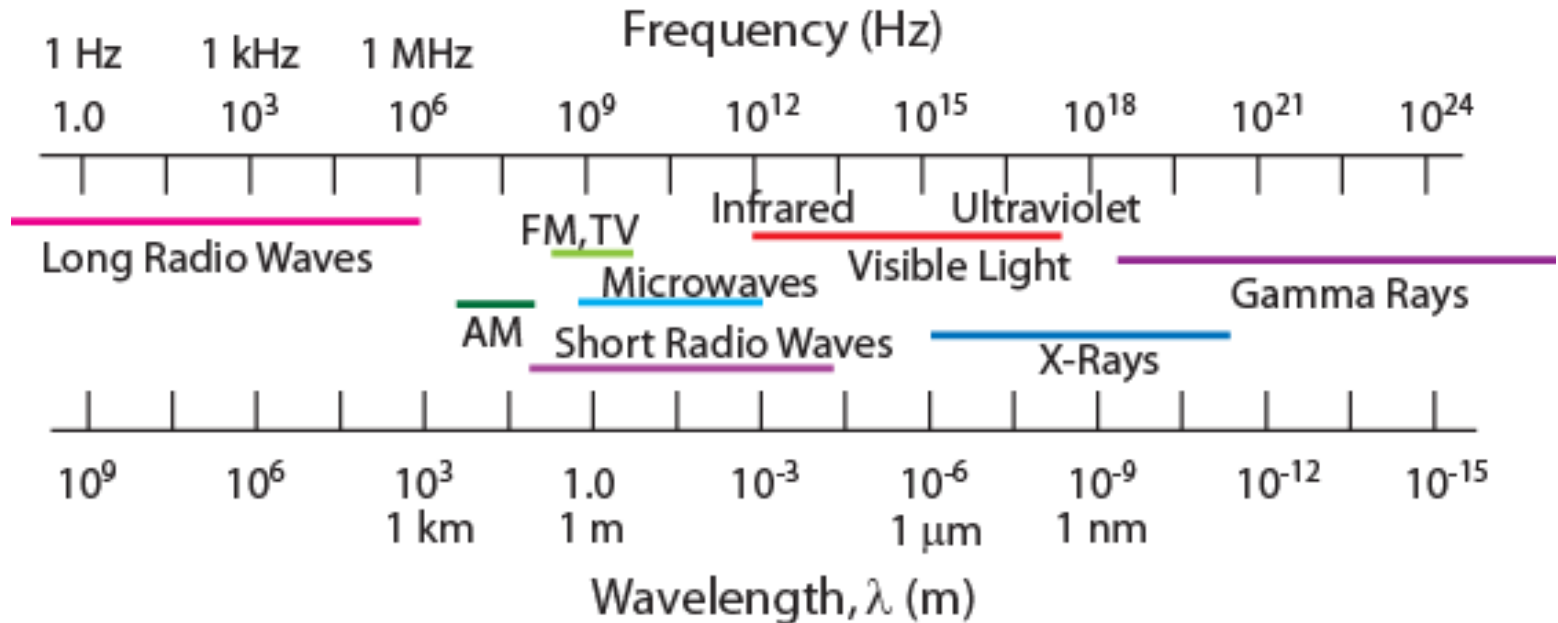
$$= \frac{1}{\frac{16\sqrt{3}}{3} R^2} = 7.0 \frac{\text{atoms}}{\text{nm}^2}$$

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



Section 3.16 - X-Ray Diffraction

Electromagnetic Spectrum

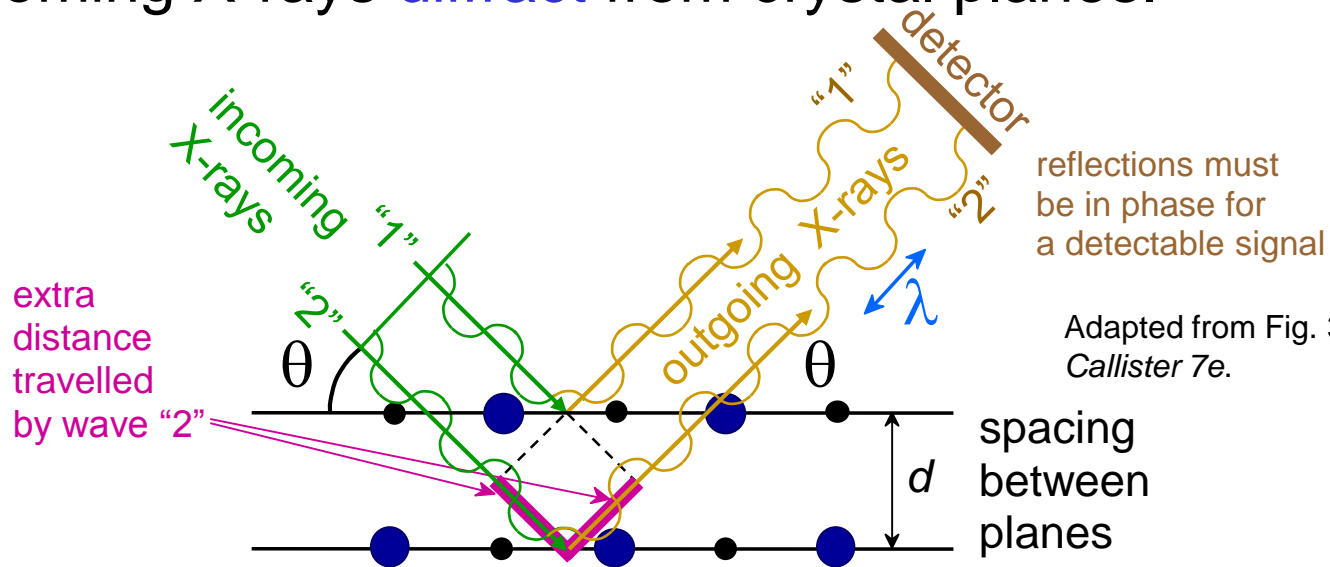


- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.



X-Rays to Determine Crystal Structure

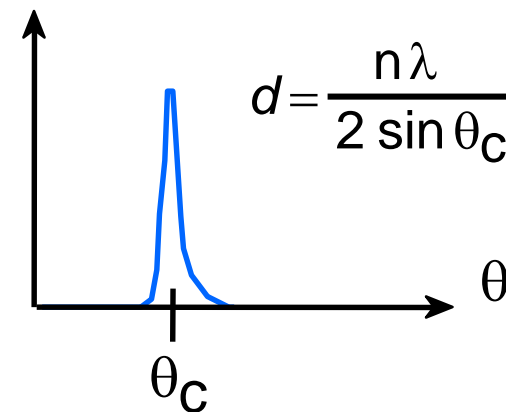
- Incoming X-rays **diffract** from crystal planes.



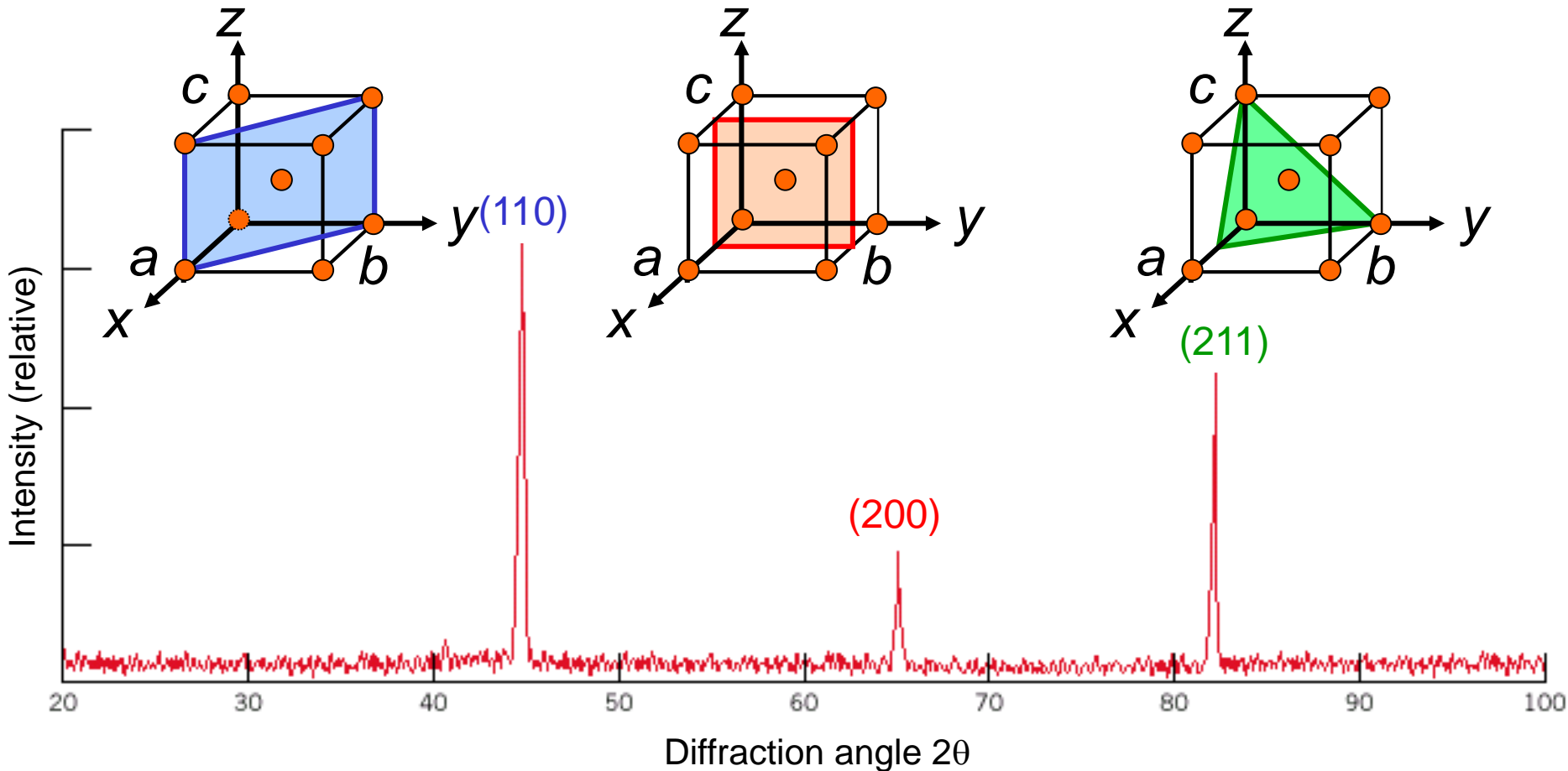
Adapted from Fig. 3.19,
Callister 7e.

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

X-ray intensity (from detector)



X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α -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.

