# Chapter 3: The Structure of Crystalline Solids
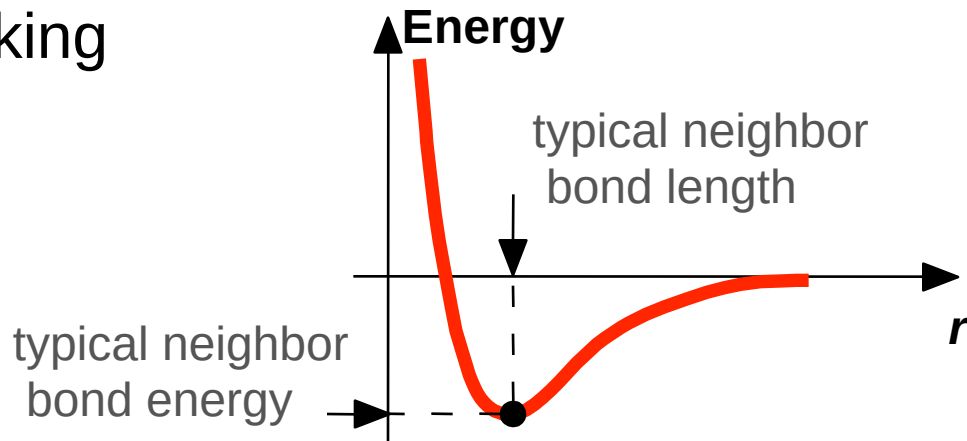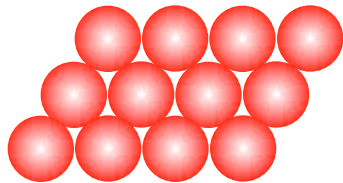
ISSUES TO ADDRESS...

- What is the difference in atomic arrangement between crystalline and noncrystalline solids?

- What features of a material's atomic structure determine its density?

- Under what circumstances does a material property vary with the measurement direction?

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Energy and Packing

- Non dense, random packing

Energy

typical neighbor
bond length

typical neighbor
bond energy

r
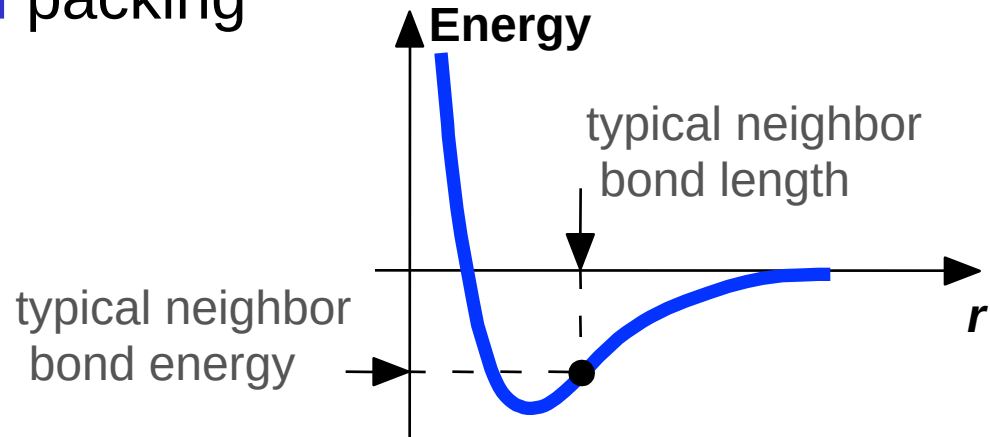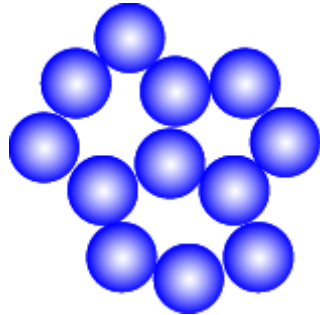
- Dense, ordered packing

Energy

typical neighbor
bond length
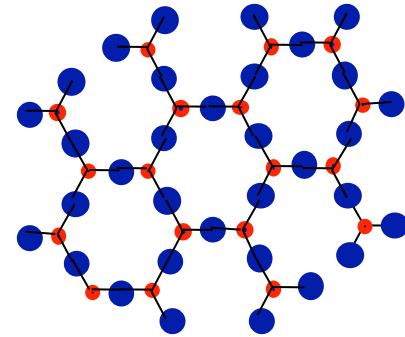
typical neighbor
bond energy

r

Dense, ordered packed structures tend to have lower energies.

Materials and Packing

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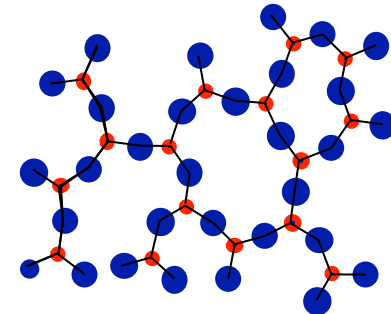 - -many ceramics
  - -some polymers

crystalline SiO_2
Adapted from Fig. 3.25(a),
Callister & Rethwisch 9e.

• **Si**   • **Oxygen**

Noncrystalline materials...

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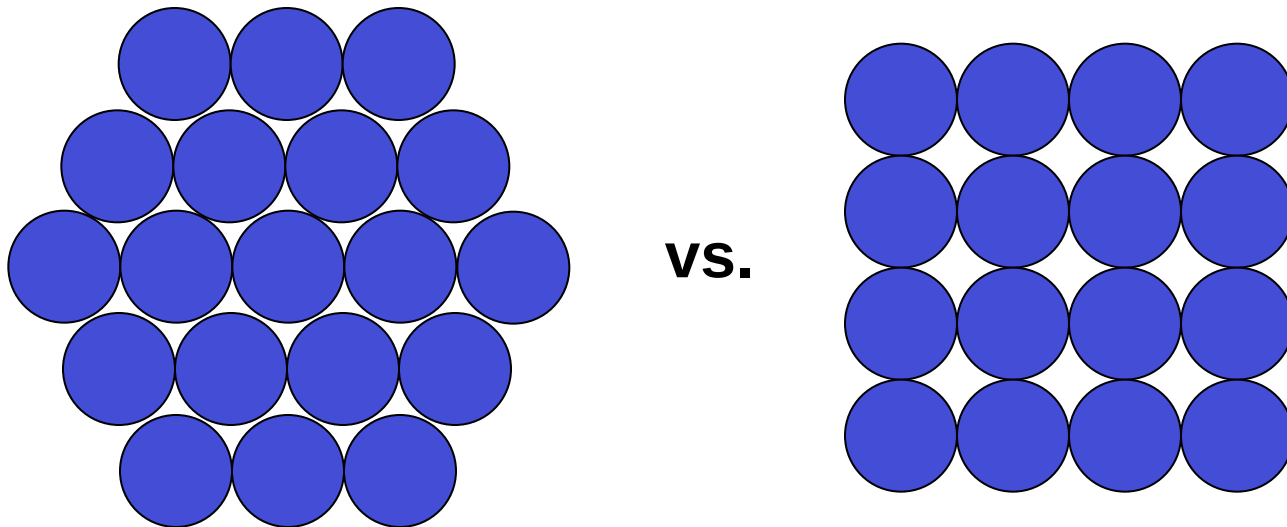- occurs for:
  - -complex structures
  - -rapid cooling

"Amorphous" = Noncrystalline

noncrystalline SiO_2
Adapted from Fig. 3.25(b),
Callister & Rethwisch 9e.

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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

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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.

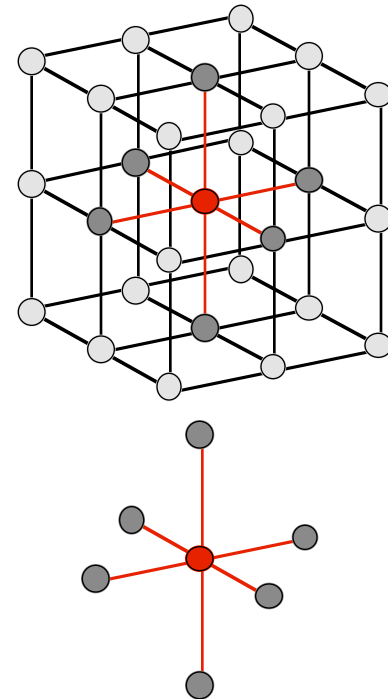 We will examine three such structures...

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)
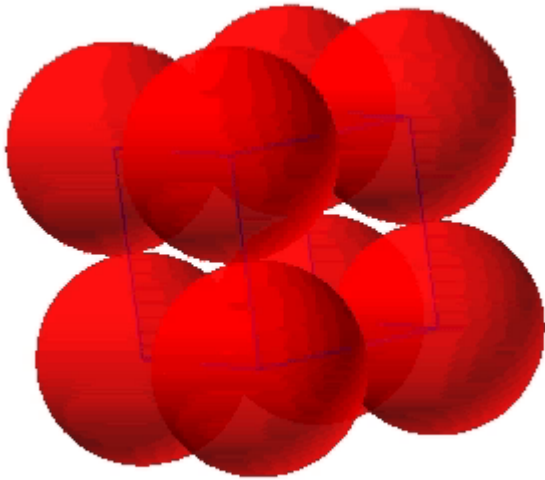
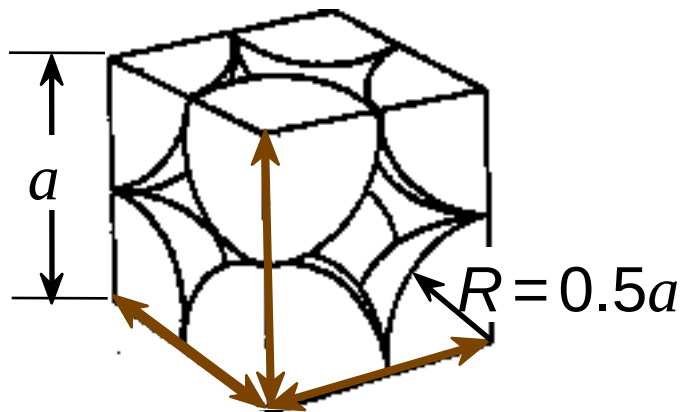Click once on image to start animation

(Courtesy P.M. Anderson)

Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52

a

$R = 0.5a$

close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.3 (a),
Callister & Rethwisch 9e.

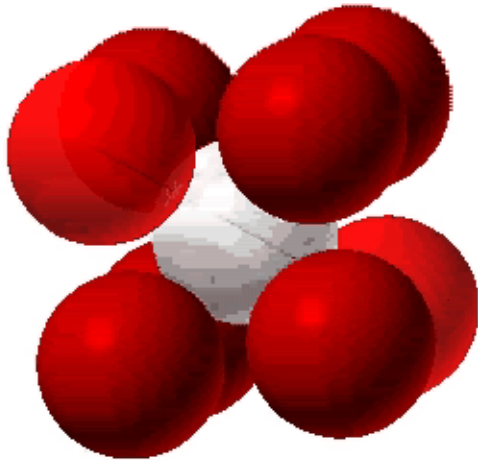$$APF = \frac{1 \cdot \frac{4}{3}\pi(0.5a)^3}{a^3}$$

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

$\dfrac{\text{volume}}{\text{atom}}$

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

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.
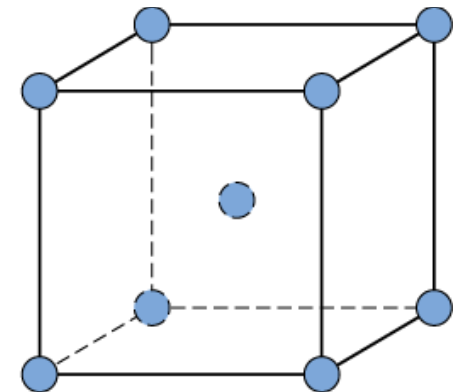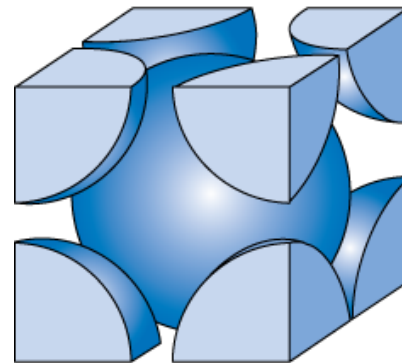
ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8

Click once on image to start animation

(Courtesy P.M. Anderson)

Adapted from Fig. 3.2, *Callister & Rethwisch 9e.*

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

VMSE Screenshot – BCC Unit Cell

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68
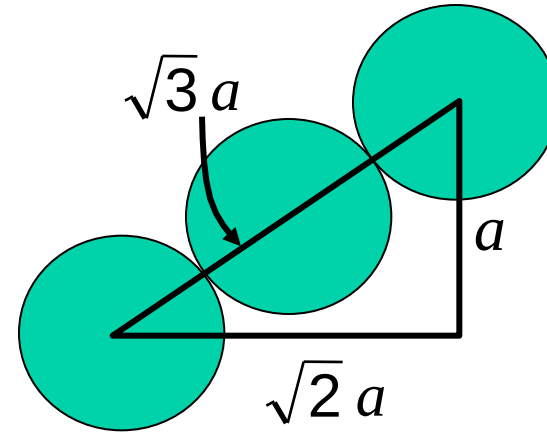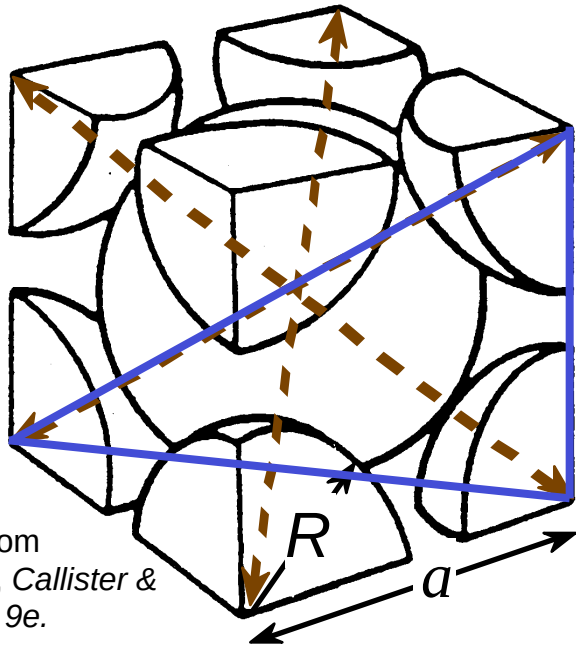
Adapted from Fig. 3.2(a), *Callister & Rethwisch 9e.*

R

a

$\sqrt{3}\,a$

a

$\sqrt{2}\,a$

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

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

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

$\dfrac{\text{volume}}{\text{atom}}$

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

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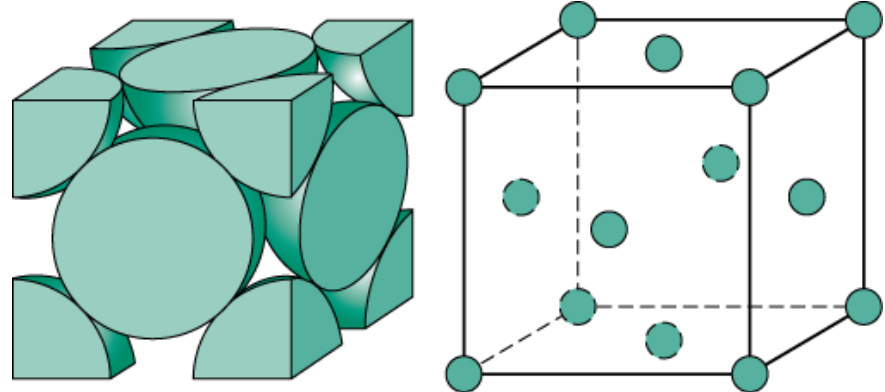
Adapted from Fig. 3.1, *Callister & Rethwisch 9e.*

Click once on image to start animation

(Courtesy P.M. Anderson)

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

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Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74

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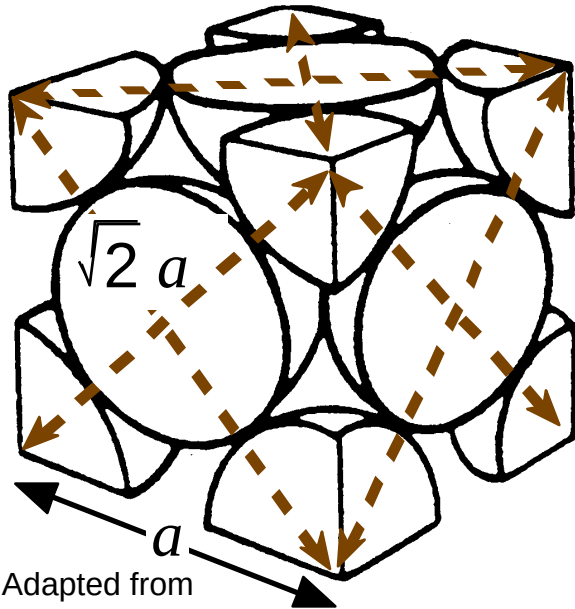
Close-packed directions:
length = $4R = \sqrt{2}\,a$

$\sqrt{2}\,a$

a

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

Unit cell contains:
6 x 1/2 + 8 x 1/8
= 4 atoms/unit cell

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

$\dfrac{\text{volume}}{\text{atom}}$

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

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

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FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

A sites

B sites

C sites
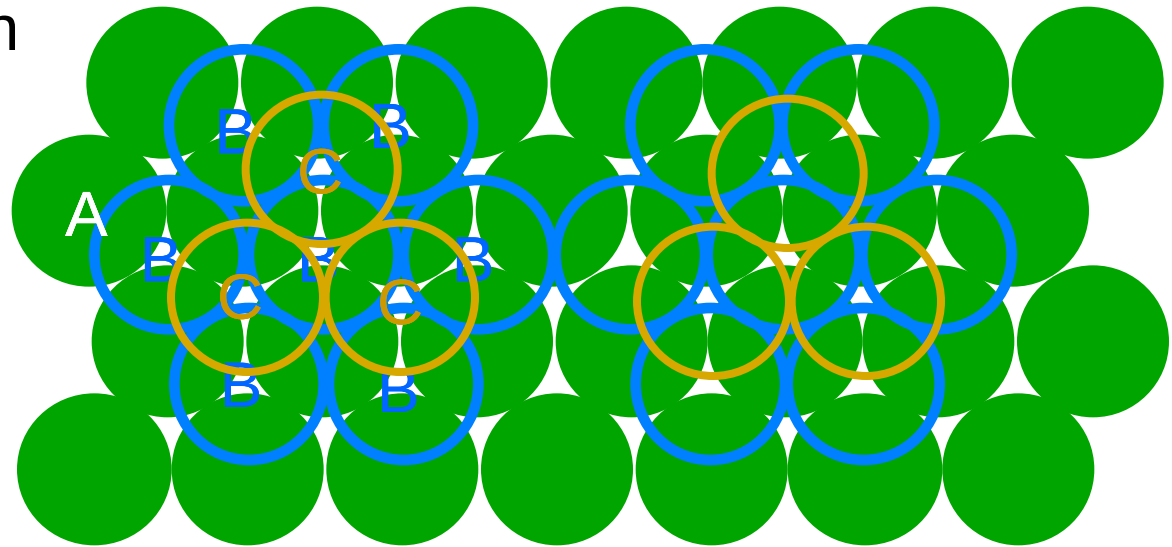
- FCC Unit Cell
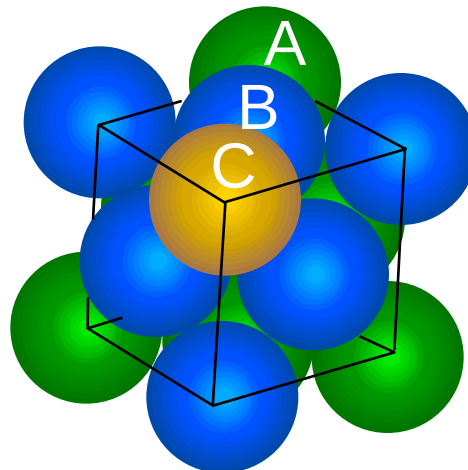
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence

- 3D Projection

A sites

B sites

A sites

Adapted from Fig. 3.4(a),
Callister & Rethwisch 9e.

- 2D Projection

Top layer

Middle layer

Bottom layer
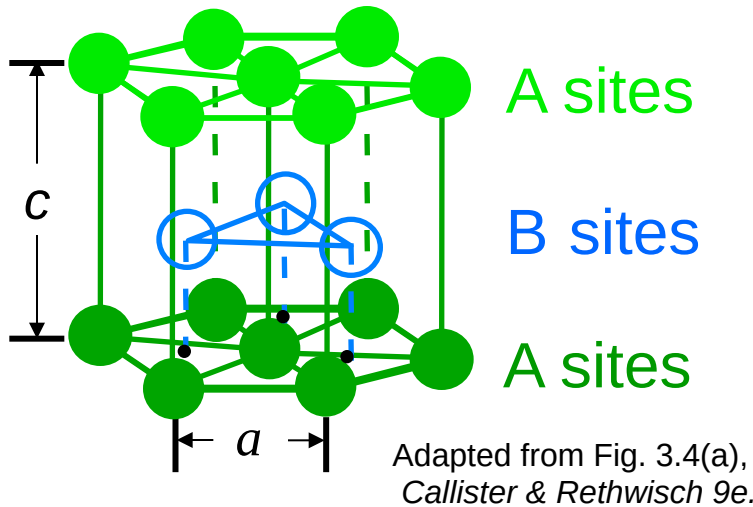
- Coordination # = 12

- APF = 0.74

- c/a = 1.633

6 atoms/unit cell
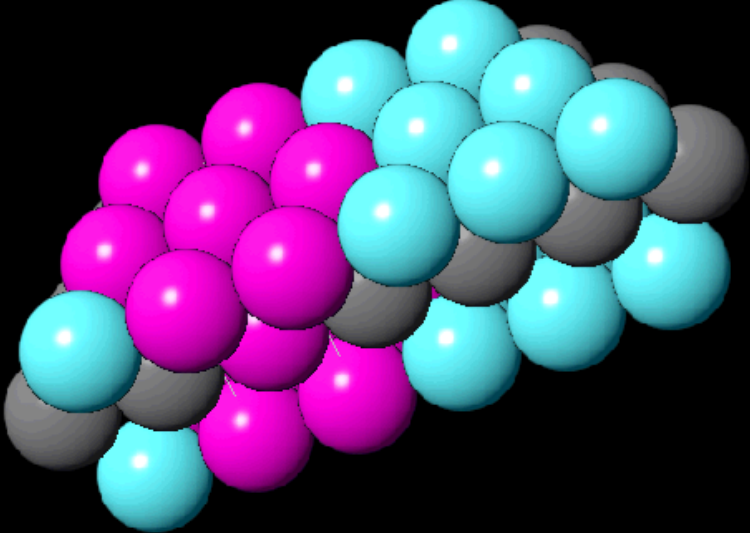
ex: Cd, Mg, Ti, Zn

VMSE Screenshot – Stacking Sequence and Unit Cell for HCP

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

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Theoretical Density, ρ
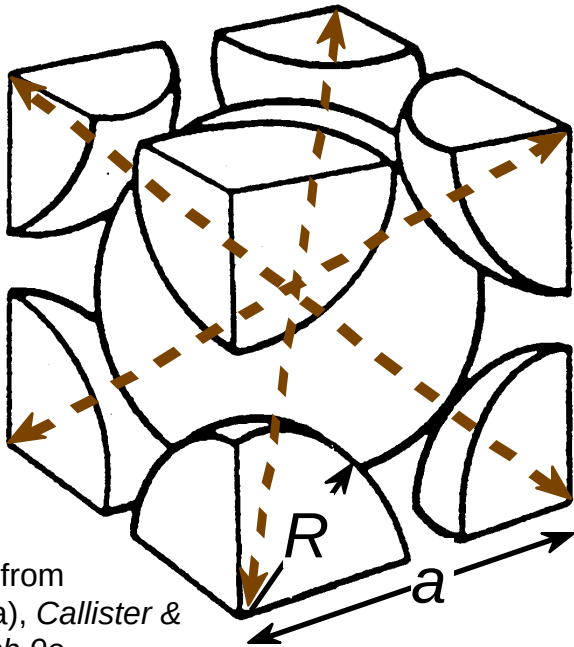
Adapted from Fig. 3.2(a), *Callister & Rethwisch 9e.*

- Ex: Cr (BCC)

  A = 52.00 g/mol

  R = 0.125 nm

  n = 2 atoms/unit cell

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

$$\frac{atoms}{unit\ cell} \rightarrow \rho = \frac{2 \quad 52.00 \quad \leftarrow \frac{g}{mol}}{a^3 \quad 6.022 \times 10^{23}}$$

$\frac{volume}{unit\ cell}$ $\frac{atoms}{mol}$

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

ρ_{actual} = 7.19 g/cm^3

Densities of Material Classes

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

Why?

Metals have...
- close-packing
  (metallic bonding)
- often large atomic masses

Ceramics have...
- less dense packing
- often lighter elements

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

Composites have...
- intermediate values

Metals/ Alloys | **Graphite/ Ceramics/ Semicond** | **Polymers** | **Composites/ fibers**

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).

ρ (g/cm^3)

30
20
10
5
4
3
2
1
0.5
0.4
0.3

Metals/Alloys:
- Platinum
- Gold, W
- Tantalum
- Silver, Mo
- Cu,Ni
- Steels
- Tin, Zinc
- Titanium
- Aluminum
- Magnesium

Graphite/Ceramics/Semicond:
- Zirconia
- Al oxide
- Diamond
- Si nitride
- Glass -soda
- Concrete
- Silicon
- Graphite

Polymers:
- PTFE
- Silicone
- PVC
- PET
- PC
- HDPE, PS
- PP, LDPE

Composites/fibers:
- Glass fibers
- GFRE*
- Carbon fibers
- CFRE*
- Aramid fibers
- AFRE*
- Wood

Data from Table B.1, *Callister & Rethwisch, 9e.*

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Crystals as Building Blocks

- *Some* engineering applications require single crystals:

  -- diamond single crystals for abrasives

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

  -- turbine blades

  Fig. 8.34(c), *Callister & Rethwisch 9e.*
  (courtesy of Pratt and Whitney)
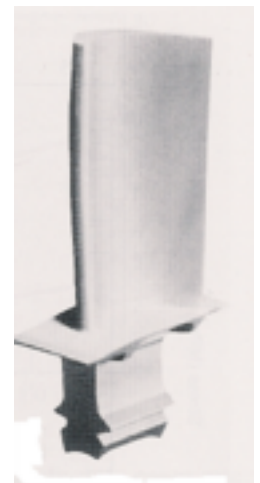
- Properties of crystalline materials often related to crystal structure.

  -- Ex: Quartz fractures more easily along some crystal planes than others.

  (Courtesy P.M. Anderson)

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Polycrystals

- *Most* engineering materials are polycrystals.

Anisotropic

1 mm

Fig. K, color inset pages of *Callister 5e*.
(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 typically range from 1 nm to 2 cm
  (i.e., from a few to millions of atomic layers).

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Single vs Polycrystals

- Single Crystals

  -Properties vary with direction: anisotropic.

 -Example: the modulus of elasticity (E) in BCC iron:

E (diagonal) = 273 GPa
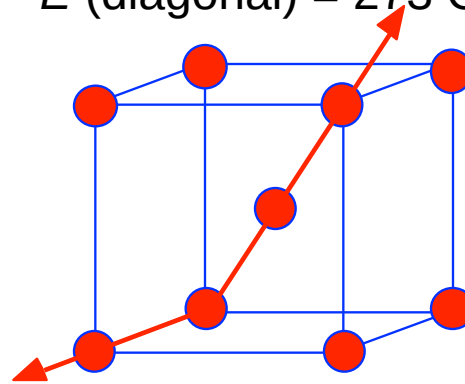
E (edge) = 125 GPa

Data from Table 3.4, *Callister & Rethwisch 9e*. (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.

200 µm
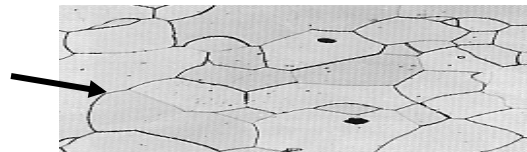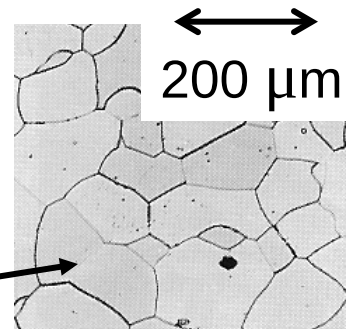
Adapted from Fig. 4.15(b), *Callister & Rethwisch 9e*. [Fig. 4.15(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

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Polymorphism

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

titanium

α, β -Ti

carbon

diamond, graphite

iron system

liquid

BCC	δ-Fe
	1538°C
	1394°C
FCC	γ-Fe
	912°C
BCC	α-Fe

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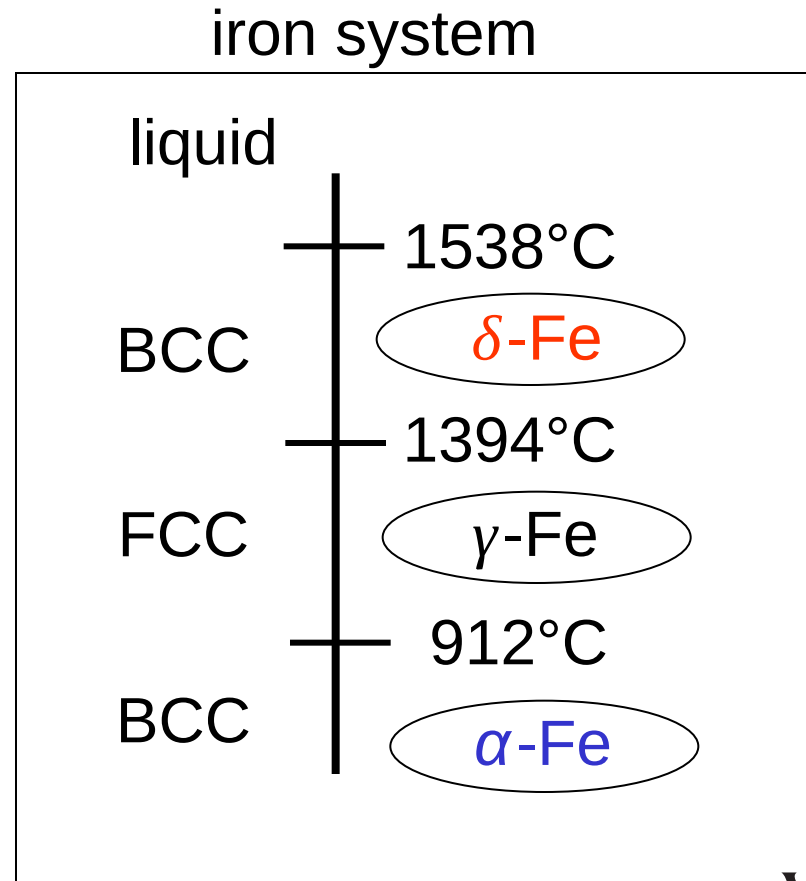
Crystal Systems

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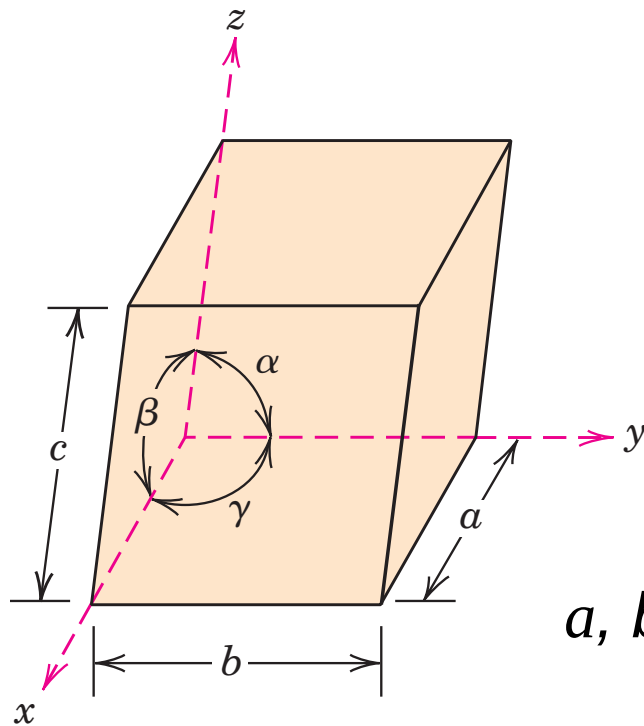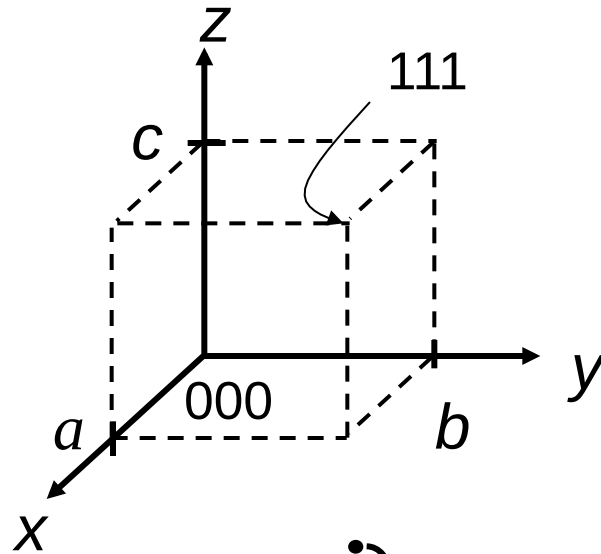
7 crystal systems

14 crystal lattices

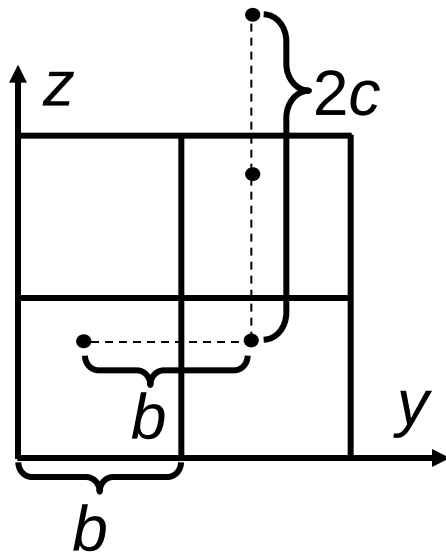*a, b,* and *c* are the lattice constants

Point Coordinates

Point coordinates for unit cell center are

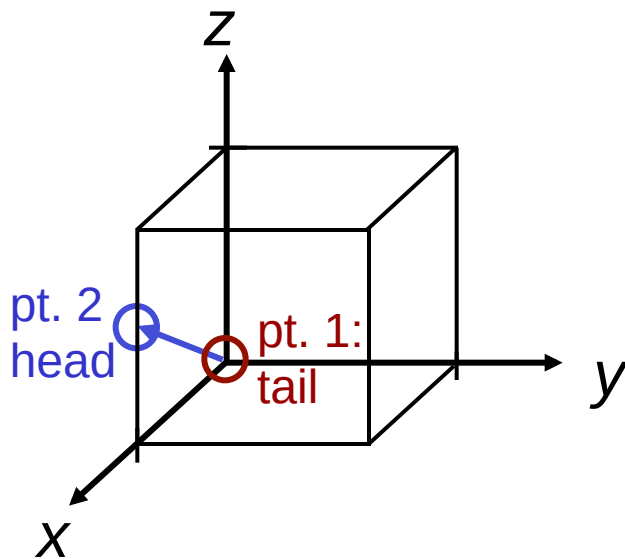$$a/2, \ b/2, \ c/2 \qquad \tfrac{1}{2} \ \tfrac{1}{2} \ \tfrac{1}{2}$$

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants → identical position in another unit cell

Crystallographic Directions

Algorithm

1. Determine coordinates of vector tail, pt. 1: x_1, y_1, & z_1; and vector head, pt. 2: x_2, y_2, & z_2.
2. Tail point coordinates subtracted from head point coordinates.
3. Normalize coordinate differences in terms of lattice parameters a, b, and c:

$$\frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}$$

4. Adjust to smallest integer values
5. Enclose in square brackets, no commas

$$[uvw]$$
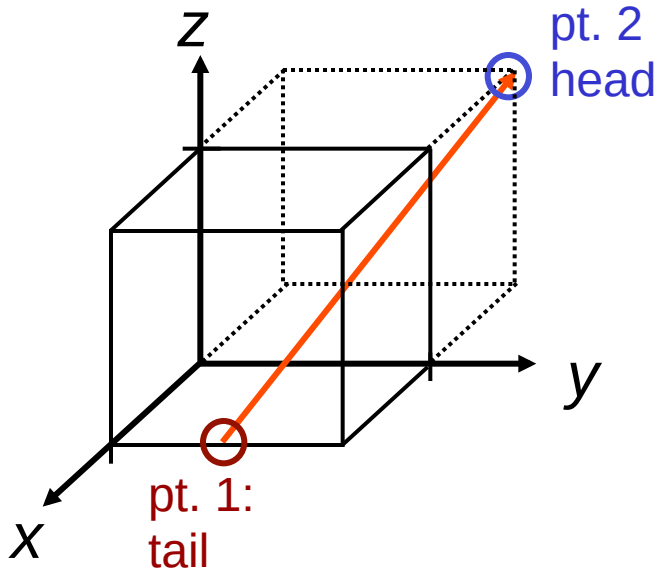
ex:

pt. 1 $x_1 = 0, y_1 = 0, z_1 = 0$

pt. 2 $x_2 = a, y_2 = 0, z_2 = c/2$

$$\frac{a - 0}{a} \quad \frac{0 - 0}{b} \quad \frac{c/2 - 0}{c}$$

=> 1, 0, 1/2   => 2, 0, 1

=> [201]

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Crystallographic Directions

z

pt. 2 head

pt. 1: tail

x

y

Example 2:

pt. 1 $\quad x_1 = a, \quad y_1 = b/2, \quad z_1 = 0$

pt. 2 $\quad x_2 = -a, \quad y_2 = b, \quad z_2 = c$

$$\frac{-a-a}{a} \quad \frac{b-b/2}{b} \quad \frac{c-0}{c}$$

=> -2, 1/2, 1

Multiplying by 2 to eliminate the fraction

-4, 1, 2 => $[\overline{4}12]$ where the overbar represents a negative index

families of directions *<uvw>*

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Chapter 3 - 26

VMSE Screenshot – [10$\bar{1}$] Direction

Linear Density

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

[110]

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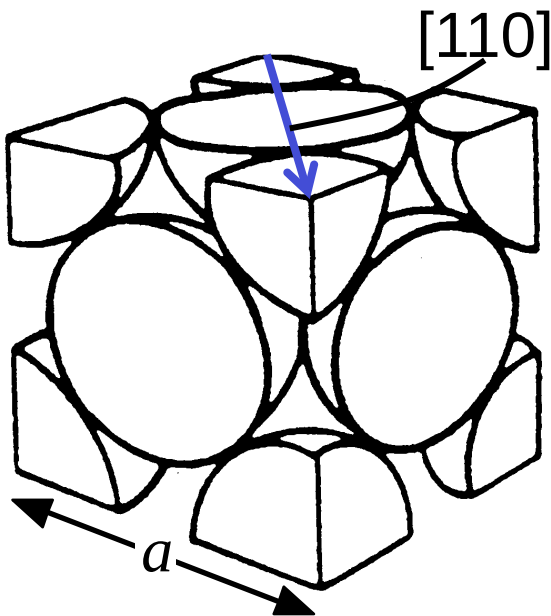
Adapted from Fig. 3.1(a), *Callister & Rethwisch 9e.*

ex: linear density of Al in [110] direction

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

\# atoms

length

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

Drawing HCP Crystallographic Directions (i)

Adapted from Figure 3.10,
Callister & Rethwisch 9e.
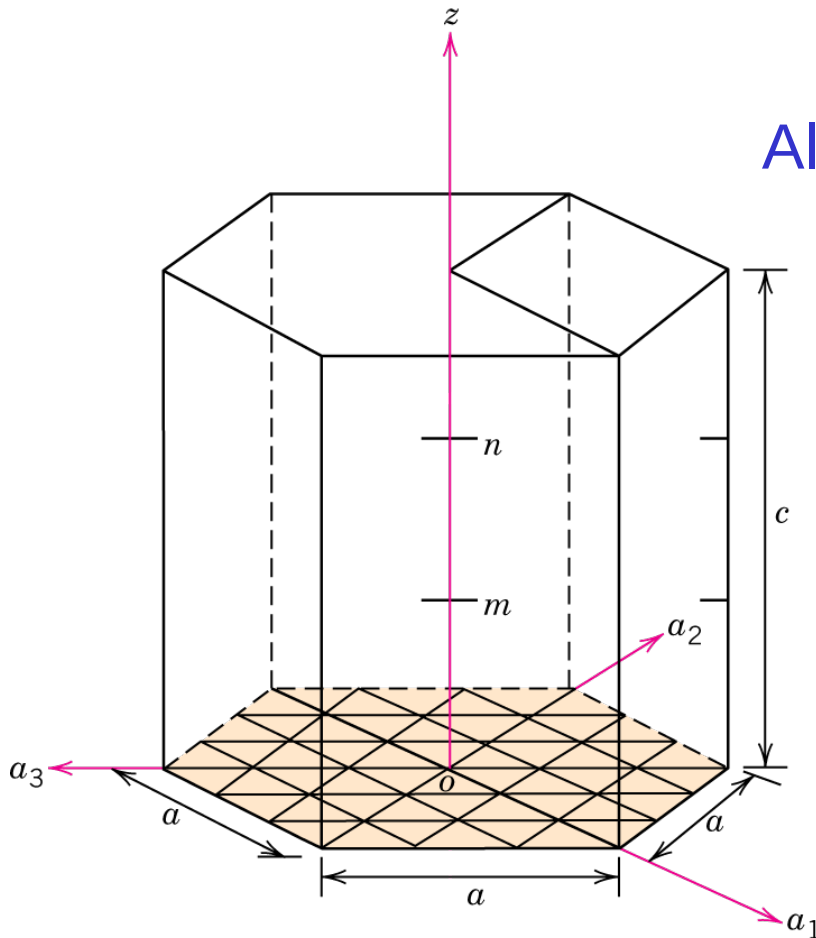
Algorithm (Miller-Bravais coordinates)

1. Remove brackets
2. Divide by largest integer so all values are ≤ 1
3. Multiply terms by appropriate unit cell dimension a (for a_1, a_2, and a_3 axes) or c (for z-axis) to produce projections
4. Construct vector by placing tail at origin and stepping off these projections to locate the head

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Drawing HCP Crystallographic Directions (ii)

- Draw the $[\bar{1}\,\bar{2}13]$ direction in a hexagonal unit cell.

Adapted from p. 72, *Callister & Rethwisch 9e.*

$[\bar{1}\bar{2}13]$

Algorithm

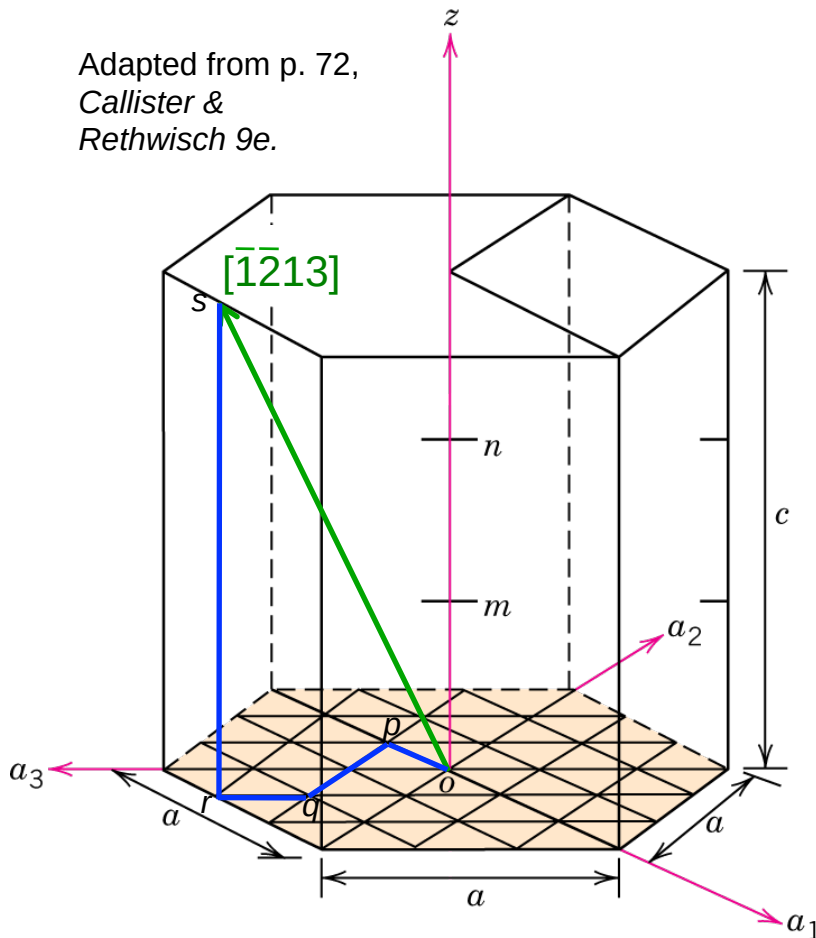|	a_1	a_2	a_3	z
1. Remove brackets	-1	-2	1	3
2. Divide by 3	$-\dfrac{1}{3}$	$-\dfrac{2}{3}$	$\dfrac{1}{3}$	1
3. Projections	$-\dfrac{a}{3}$	$-\dfrac{2a}{3}$	$\dfrac{a}{3}$	c

4. Construct Vector

    start at point o

    proceed $-a/3$ units along a_1 axis to point p

    $-2a/3$ units parallel to a_2 axis to point q

    $a/3$ units parallel to a_3 axis to point r

    c units parallel to z axis to point s

$[\bar{1}\bar{2}13]$ direction represented by vector from point o to point s

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Determination of HCP Crystallographic Directions (ii)
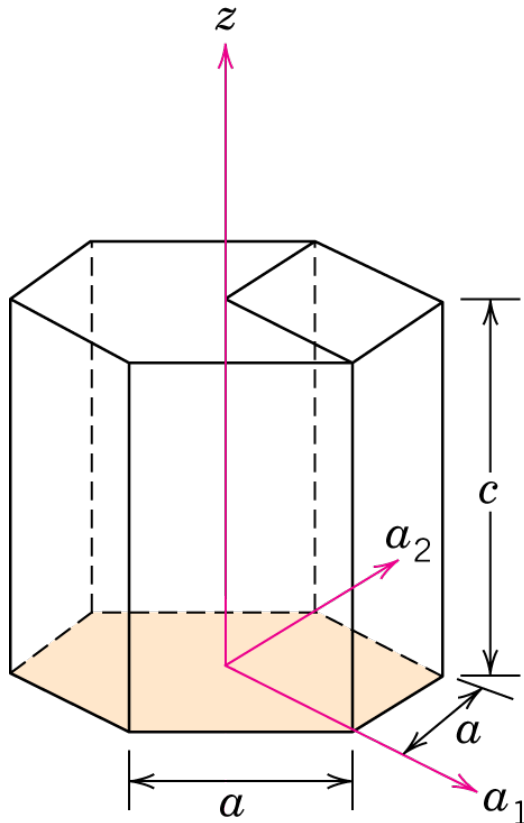
Adapted from p. 72, *Callister & Rethwisch 9e.*

Algorithm

1. Determine coordinates of vector tail, pt. 1: x_1, y_1, & z_1; and vector head, pt. 2: x_2, y_2, & z_2. in terms of three axis (a_1, a_2, and z)
2. Tail point coordinates subtracted from head point coordinates and normalized by unit cell dimensions a and c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas, for three-axis coordinates $[u'v'w']$
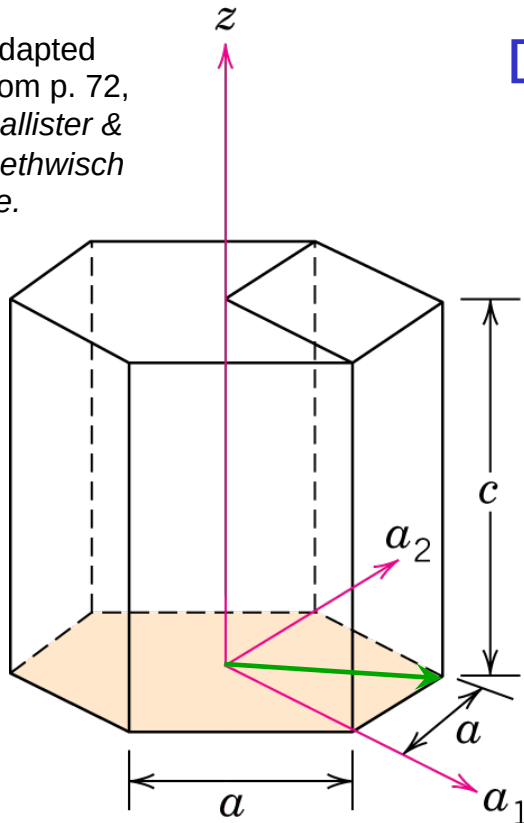5. Convert to four-axis Miller-Bravais lattice coordinates using equations below:

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

$$t = -(u + v) \qquad w = w'$$

6. Adjust to smallest integer values and enclose in brackets [*uvtw*]

Determination of HCP Crystallographic Directions (ii)

Determine indices for green vector

Example	a_1	a_2	z
1. Tail location	0	0	0
Head location	a	a	$0c$
2. Normalized	1	1	0
3. Reduction	1	1	0
4. Brackets		[110]	

5. Convert to 4-axis parameters
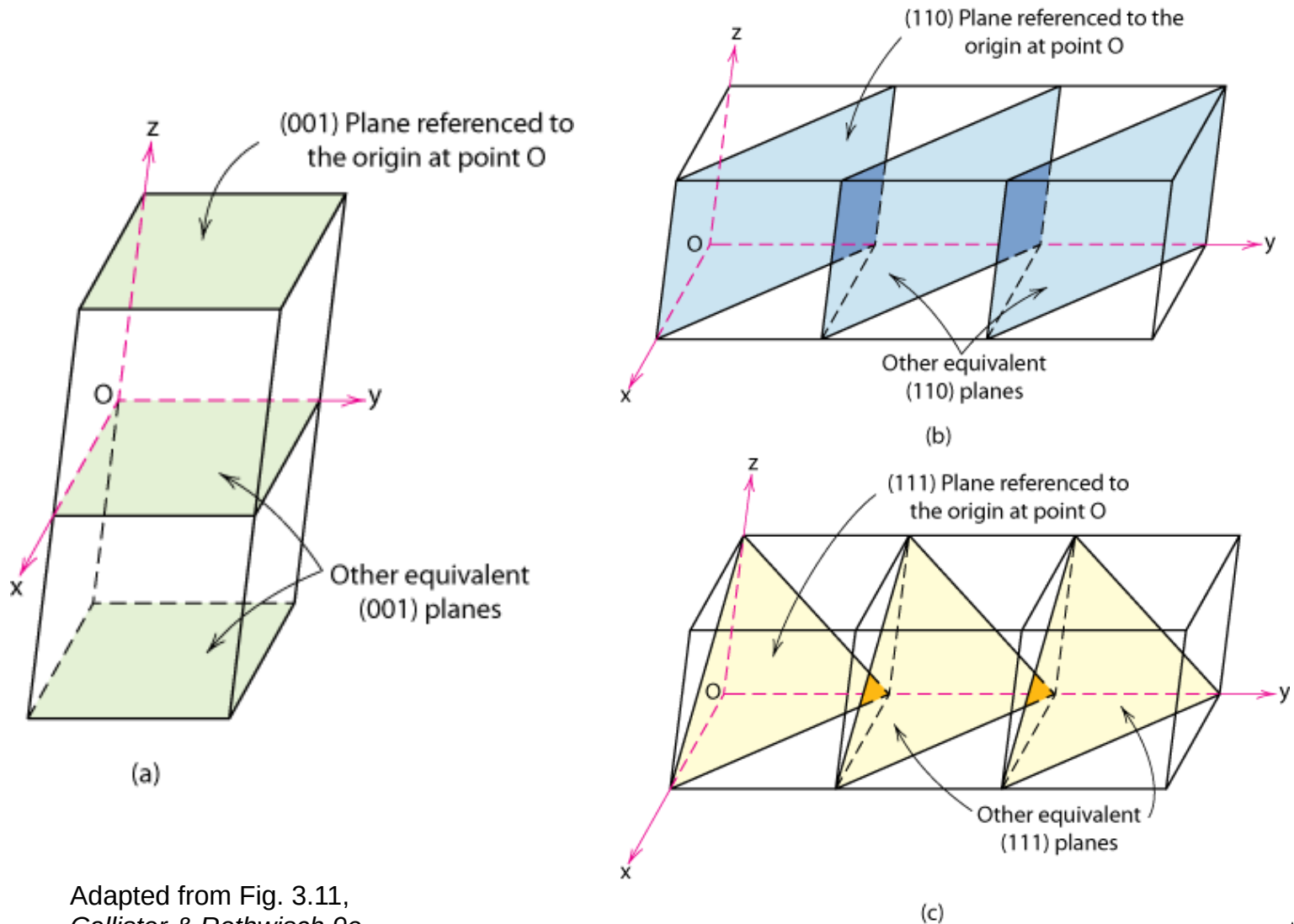
$$u = \frac{1}{3}[(2)(1) - (1)] = \frac{1}{3} \qquad v = \frac{1}{3}[(2)(1) - (1)] = \frac{1}{3}$$

$$t = -(\frac{1}{3} + \frac{1}{3}) = -\frac{2}{3} \qquad w = 0$$

6. Reduction & Brackets

1/3, 1/3, -2/3, 0   =>   1, 1, -2, 0   => $[11\bar{2}0]$

Crystallographic Planes

(001) Plane referenced to the origin at point O

Other equivalent (001) planes

(a)

(110) Plane referenced to the origin at point O

Other equivalent (110) planes

(b)

(111) Plane referenced to the origin at point O

Other equivalent (111) planes

(c)

Adapted from Fig. 3.11,
Callister & Rethwisch 9e.
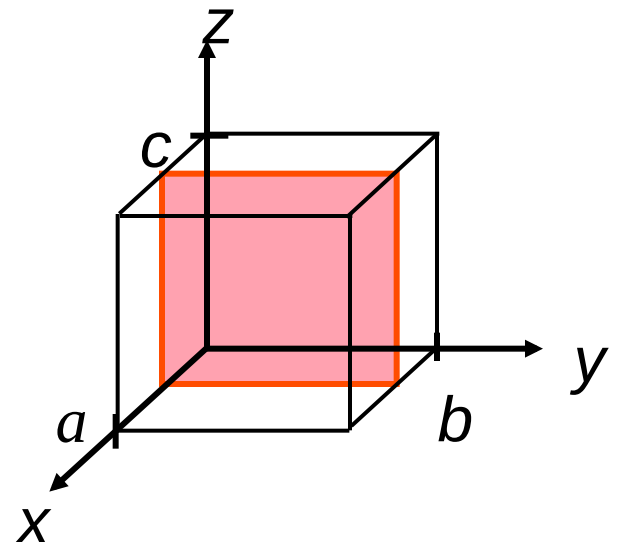
Crystallographic Planes

- 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

example		*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)		
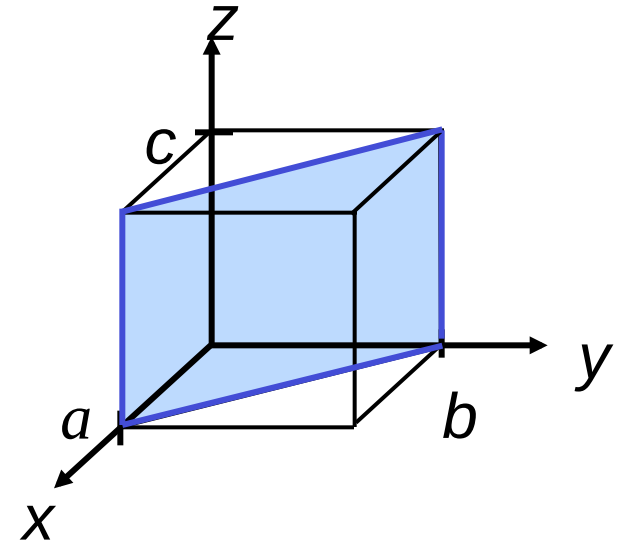
example		*a*	*b*	*c*
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		

Crystallographic Planes

example		a	b	c
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		
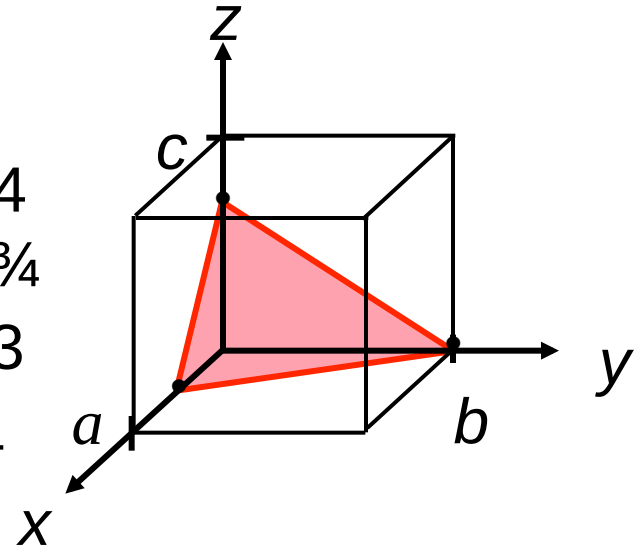
Family of Planes   {hkl}

Ex: {100} = (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$)
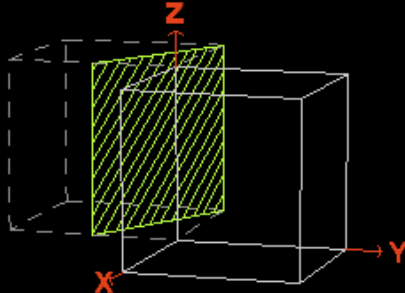
VMSE Screenshot – Crystallographic Planes

Additional practice on indexing crystallographic planes

Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

example		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 $(10\bar{1}1)$
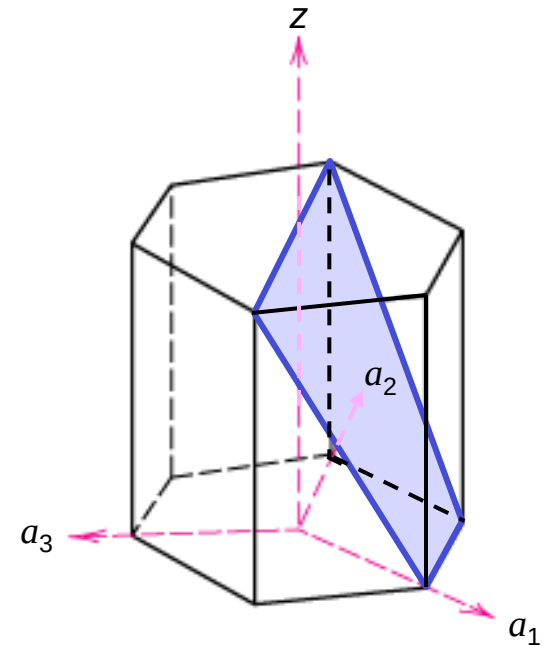
Adapted from Fig. 3.14,
Callister & Rethwisch 9e.

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°C iron has the BCC structure.
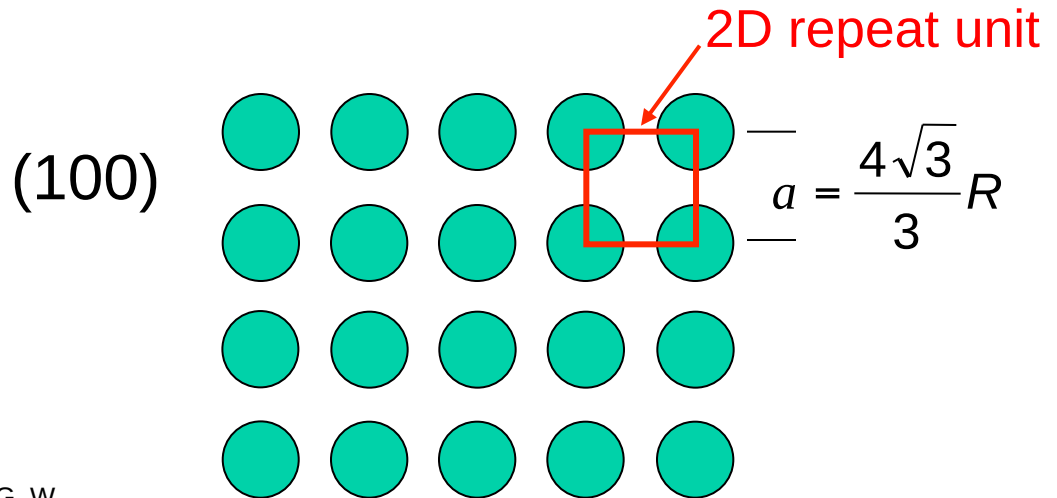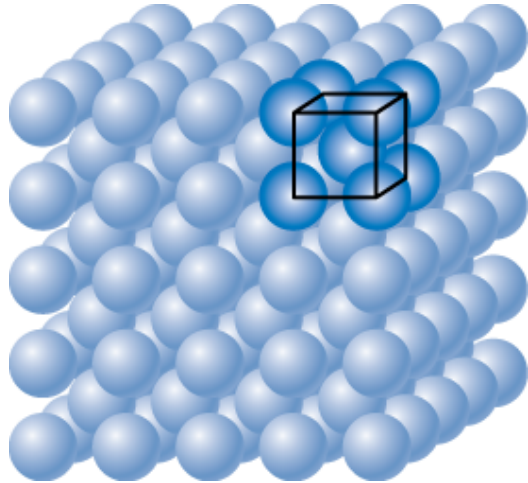

2D repeat unit

(100)

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

Fig. 3.2(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

$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}} \rightarrow 1}{\underset{\text{2D repeat unit}}{\underbrace{\text{area}}} \rightarrow a^2} = \frac{1}{\left(\dfrac{4\sqrt{3}}{3}R\right)^2} = 12.1\frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19}\frac{\text{atoms}}{\text{m}^2}$$
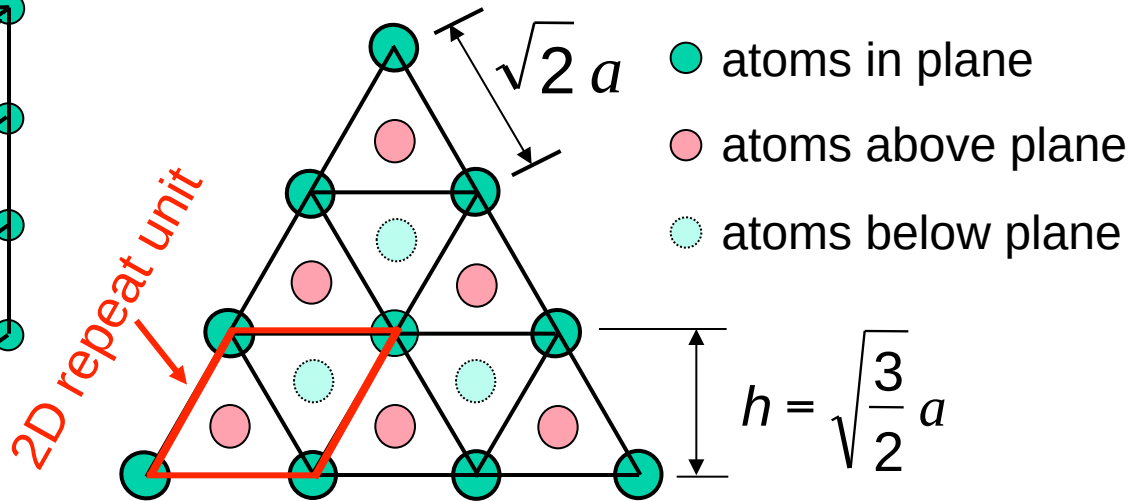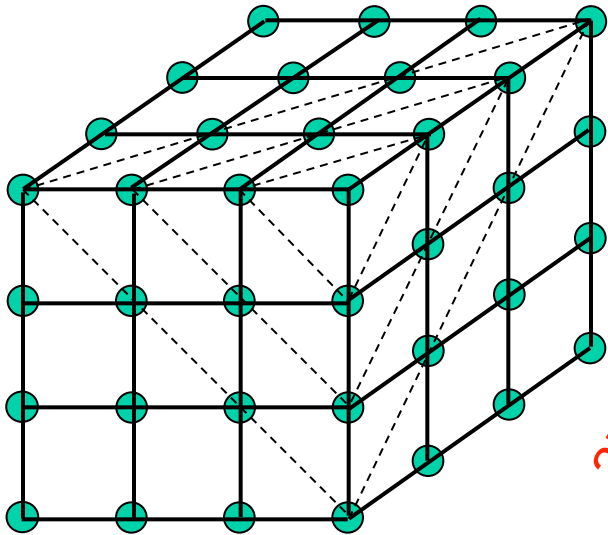
Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell

$\sqrt{2}\,a$

● atoms in plane
● atoms above plane
○ atoms below plane

2D repeat unit

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

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

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

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

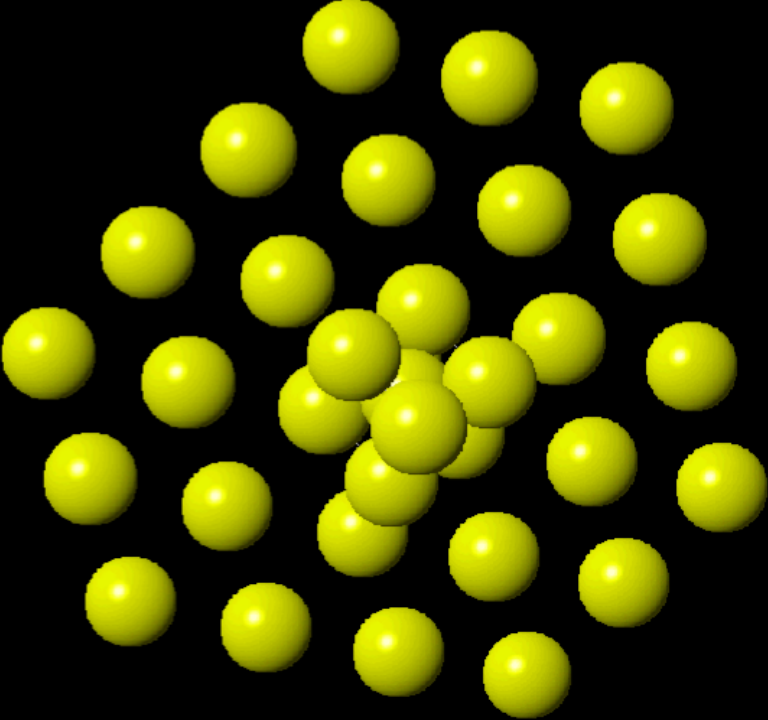# VMSE Screenshot – Atomic Packing – (111) Plane for BCC

X-Ray Diffraction

Electromagnetic Spectrum

Frequency (Hz)

1 Hz	1 kHz	1 MHz					
1.0	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

Long Radio Waves

FM,TV

Infrared   Ultraviolet

Microwaves   Visible Light

AM   Short Radio Waves

Gamma Rays

X-Rays

10^9 10^6 10^3 1.0 10^{-3} 10^{-6} 10^{-9} 10^{-12} 10^{-15}

1 km   1 m   1 μm   1 nm
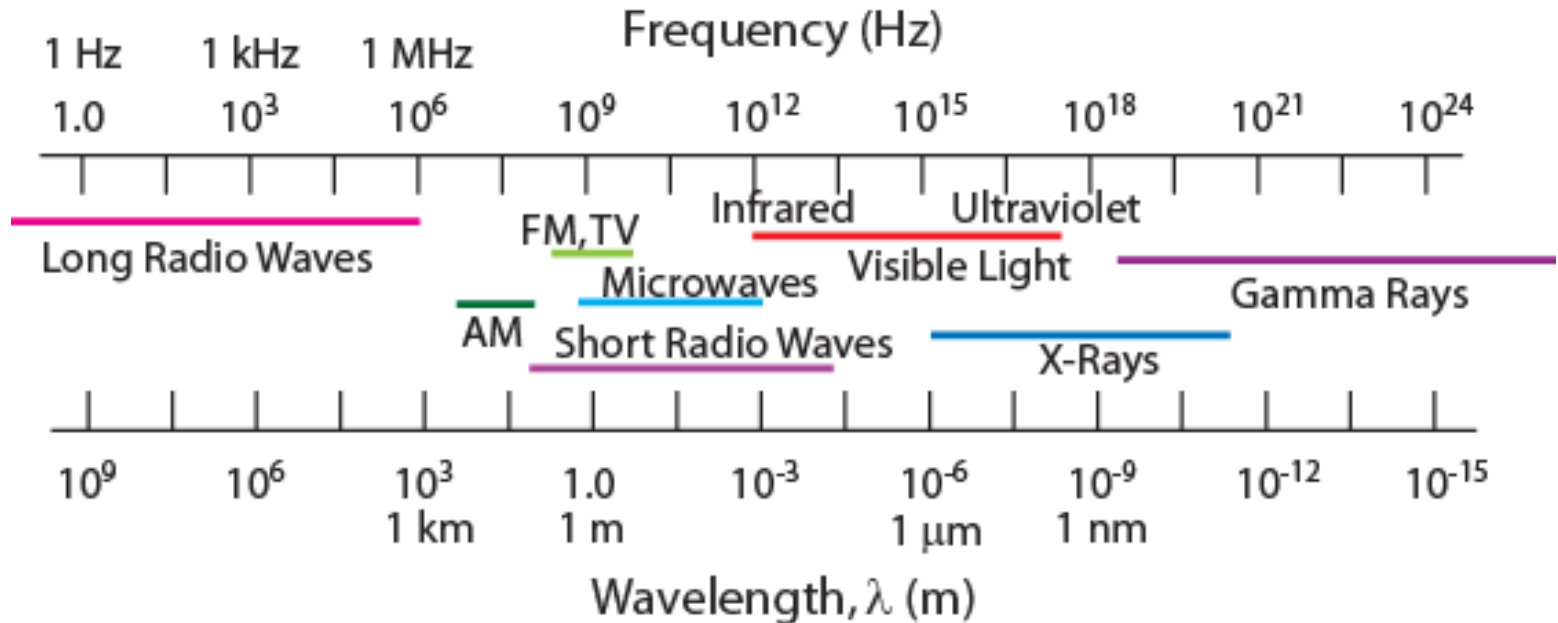
Wavelength, λ (m)

- 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.

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X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.

incoming X-rays

"1"

"2"

θ

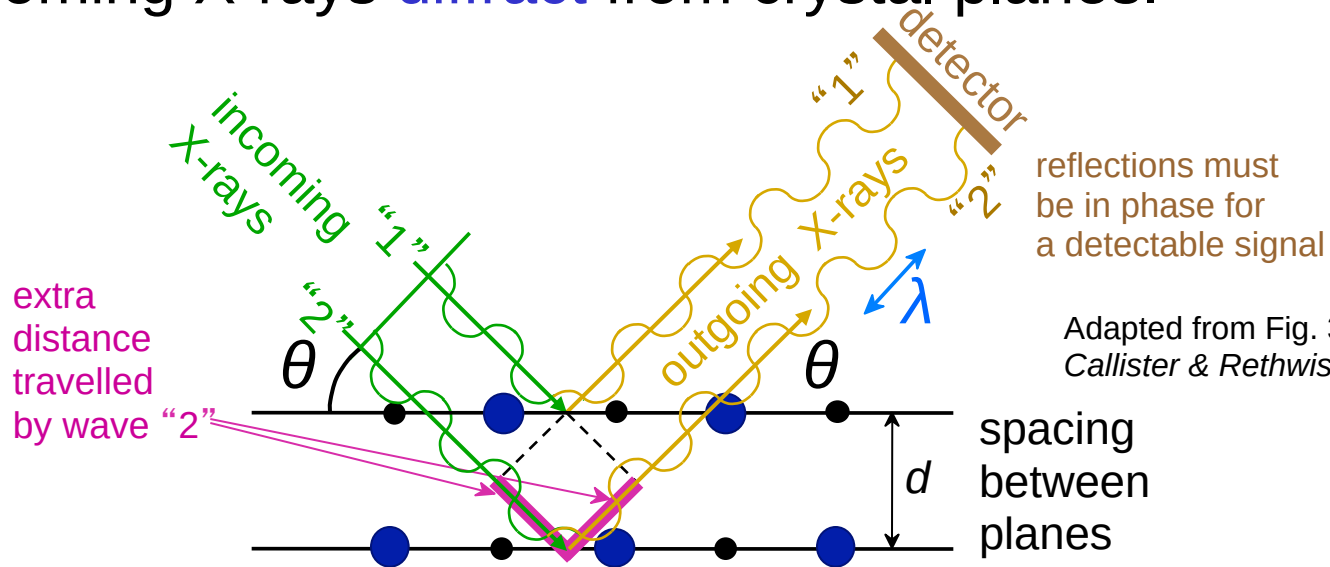extra distance travelled by wave "2"

detector

"1"

"2"

outgoing X-rays

λ

reflections must be in phase for a detectable signal

Adapted from Fig. 3.22, *Callister & Rethwisch 9e*.

θ

d spacing between planes

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

X-ray intensity (from detector)

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

θ

θ_c
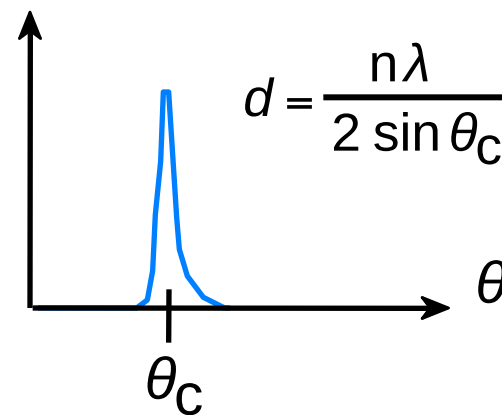
X-Ray Diffraction Pattern
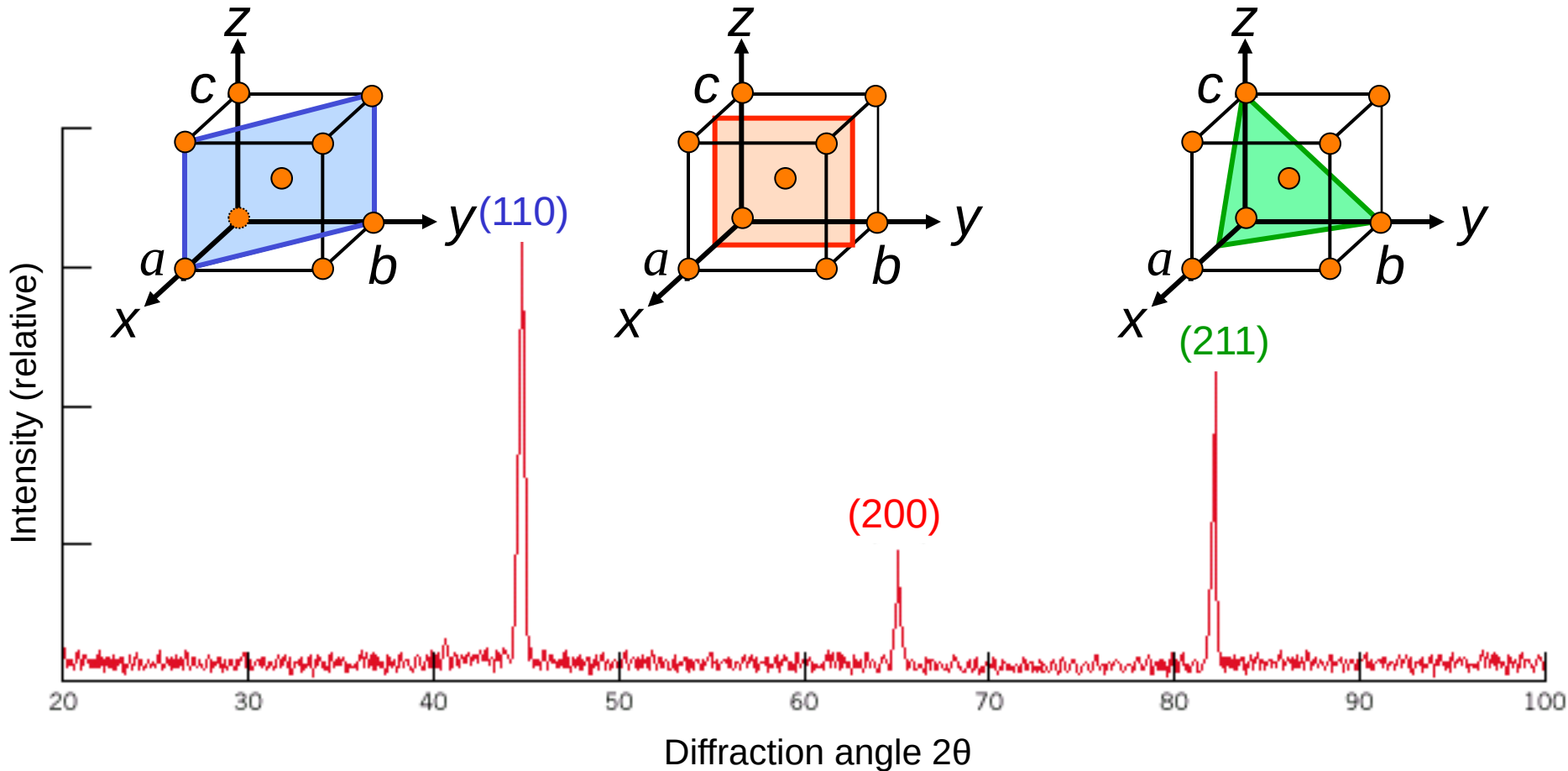
Diffraction pattern for polycrystalline α-iron (BCC)

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

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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: