Crystalline Solids & Structure
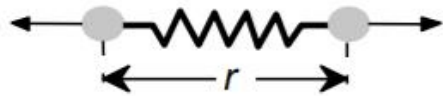
(Most content is from Callister & Rethwisch 8e)

Bonding Energy
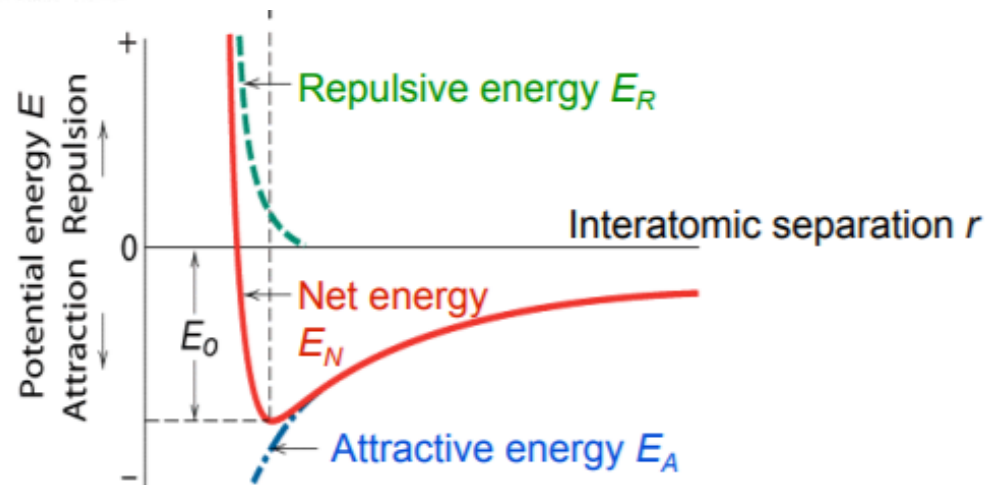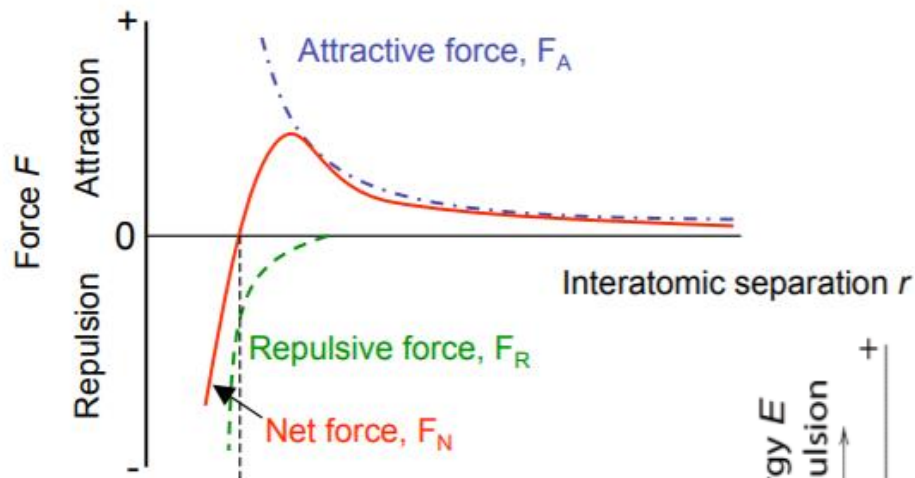
$$E = \int F\,dr$$

$$E_N = \int_{\infty}^{r} F_N\,dr = \int_{\infty}^{r} F_A\,dr + \int_{\infty}^{r} F_R\,dr$$
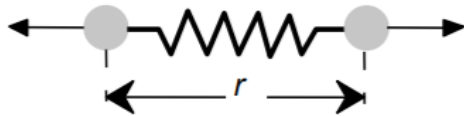
$$= E_A + E_R$$

- Attractive force, F_A
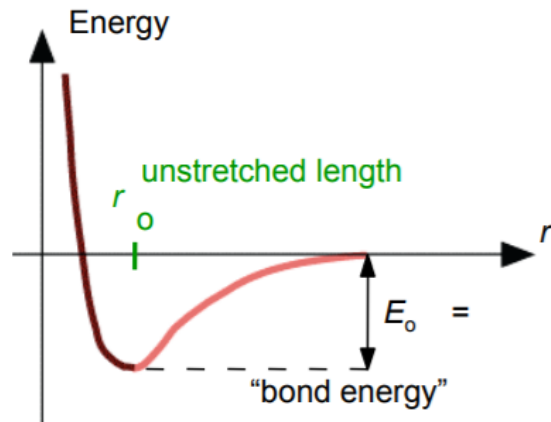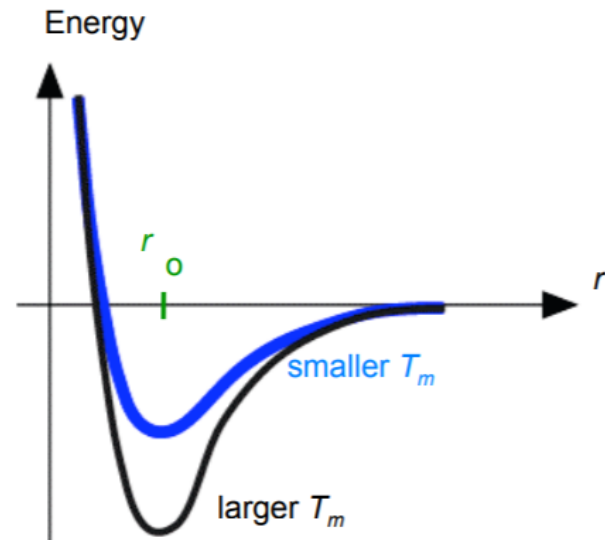- Repulsive force, F_R

Melting properties from bonding

- Bond length, r

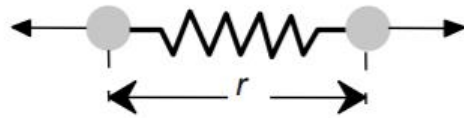

- Bond energy, E_o

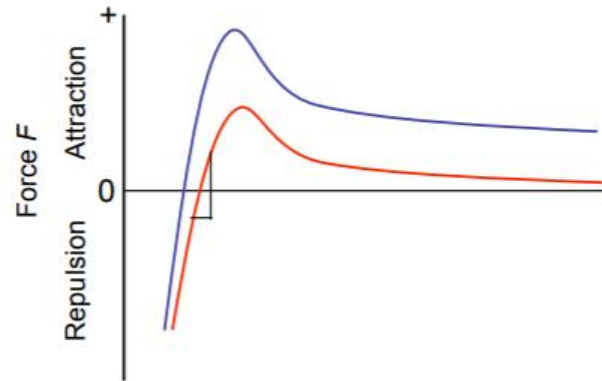- Melting Temperature, T_m

T_m is larger if E_o is larger.
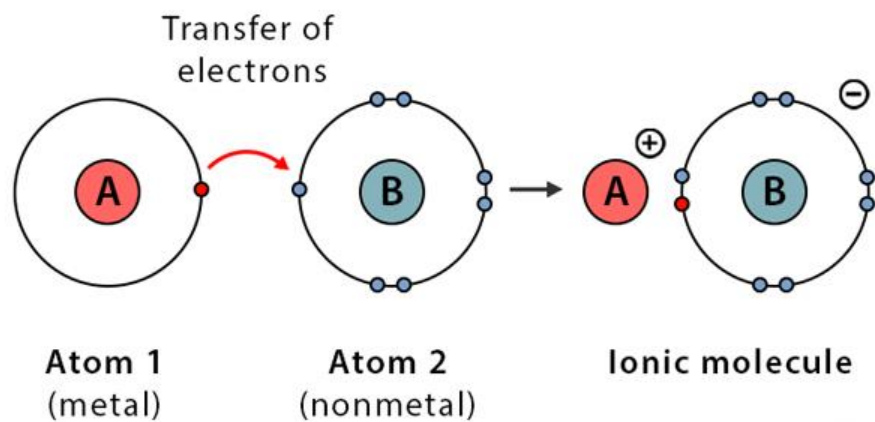
Stiffness properties from bonding

$$F = kx$$

Types of bonding

Ionic Bonding

- Occurs between + and - ions.

- Requires electron transfer.

- Large difference in electronegativity required.

Transfer of electrons

Atom 1 (metal)   Atom 2 (nonmetal)   Ionic molecule

ChemistryLearner.com

Covalent Bonding

•similar electronegativity ∴ share electrons
•bonds determined by valence – *s* & *p* orbitals dominate bonding

•Example: CH_4

C: has 4 valence e^-,
    needs 4 more

H: has 1 valence e^-,
    needs 1 more

Electronegativities
    are comparable.

CH_4

• shared electrons
from carbon atom

• shared electrons
from hydrogen
atoms
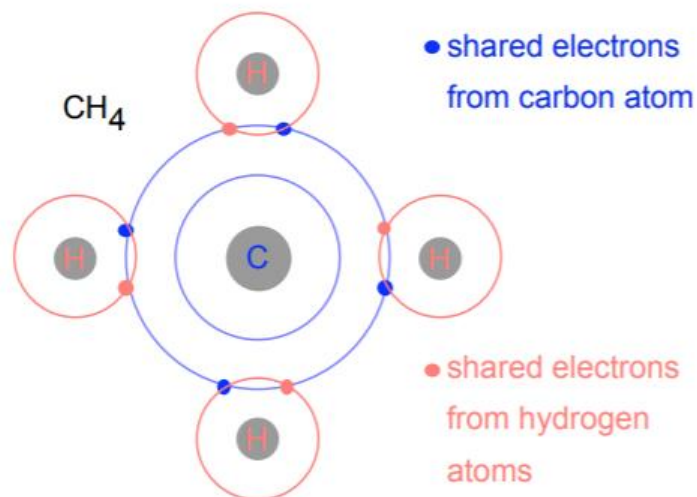
Metallic Bonding

- Ions in a sea of electrons
- Attraction between free electrons and metal ions

free electrons from outer
shells of metal atoms

metal ions
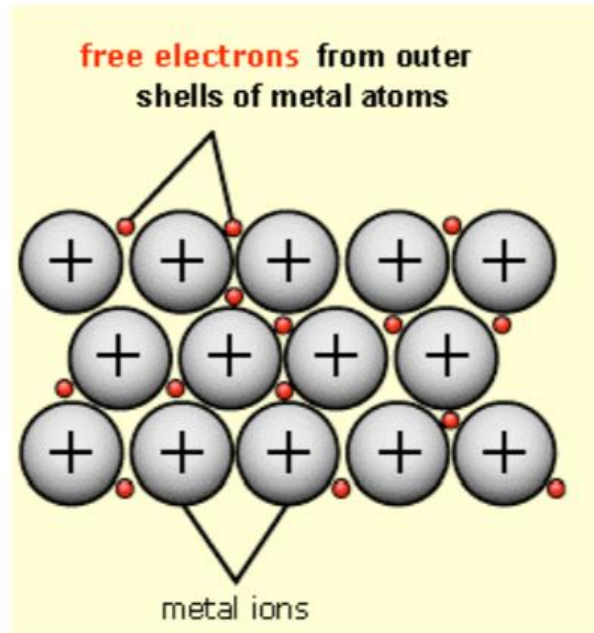
Energy and Packing

- Non dense, random packing

Energy

typical neighbor
bond length

typical neighbor
bond energy

r
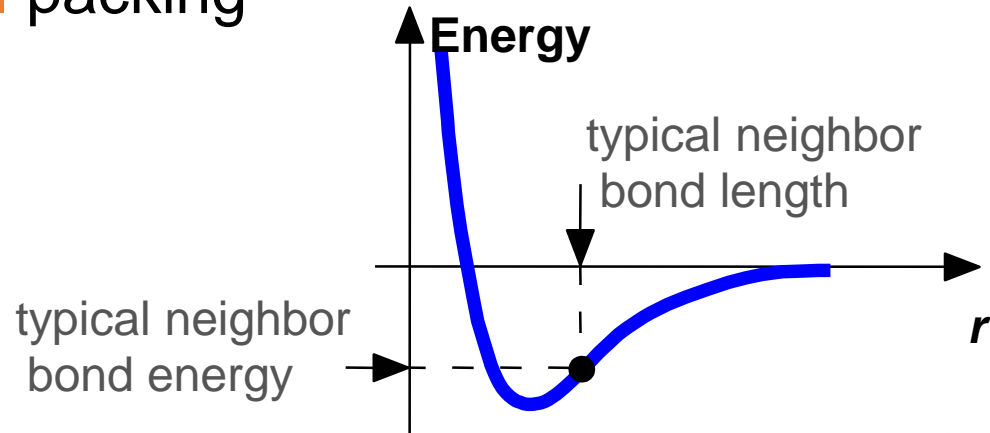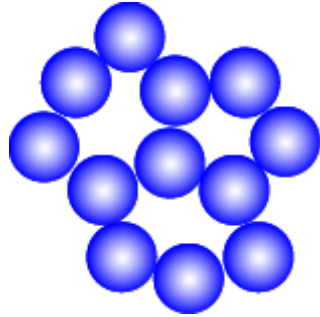
- Dense, ordered packing

Energy

typical neighbor
bond length

typical neighbor
bond energy

r
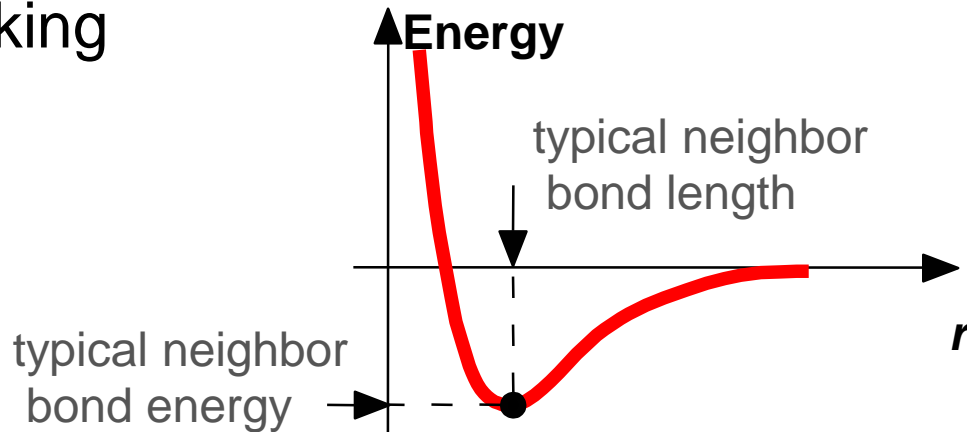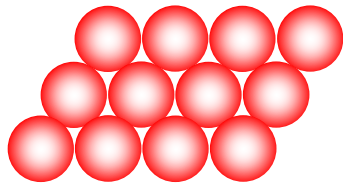
Dense, ordered packed structures tend to have lower energies.

Materials and Packing

Crystalline materials...
- atoms pack in periodic, 3D arrays
- typical of: -metals
              -many ceramics
              -some polymers
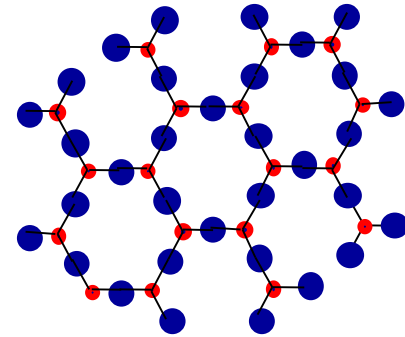
crystalline SiO2
Adapted from Fig. 3.23(a),
Callister & Rethwisch 8e.

•**Si**   ●**Oxygen**

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

"Amorphous" = Noncrystalline

noncrystalline SiO2
Adapted from Fig. 3.23(b),
Callister & Rethwisch 8e.

- Bond energies are different.
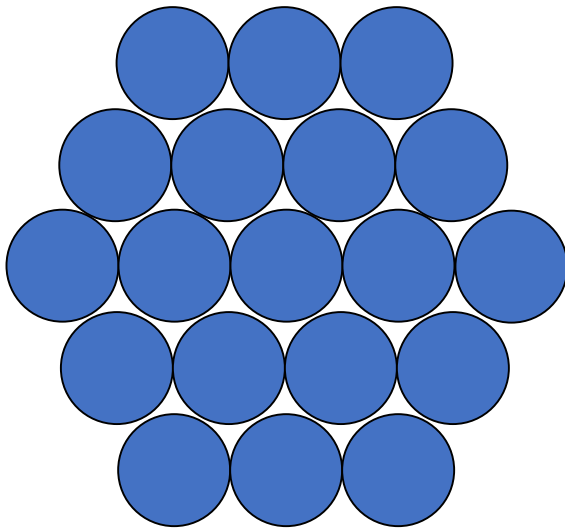
vs.
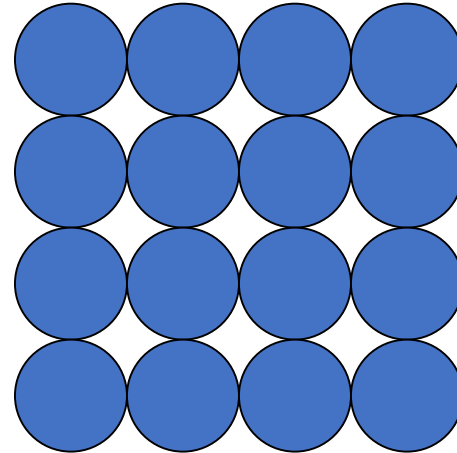
Metallic Crystal Structures

Metallic Crystal Structures

- Tend to be densely packed.

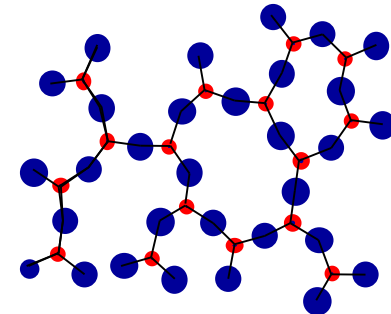- Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - Electron cloud shields cores from each other

Unit Cell

The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, the small repeat entities called **unit cells.**
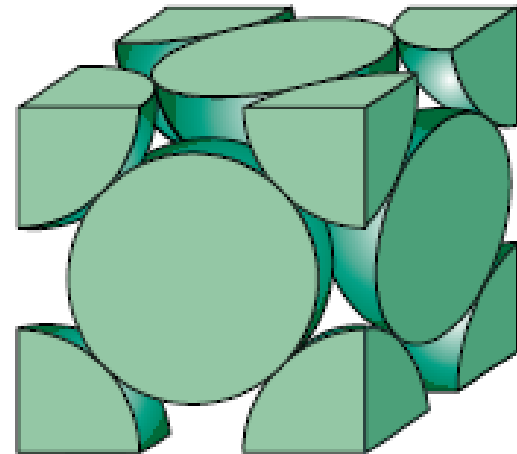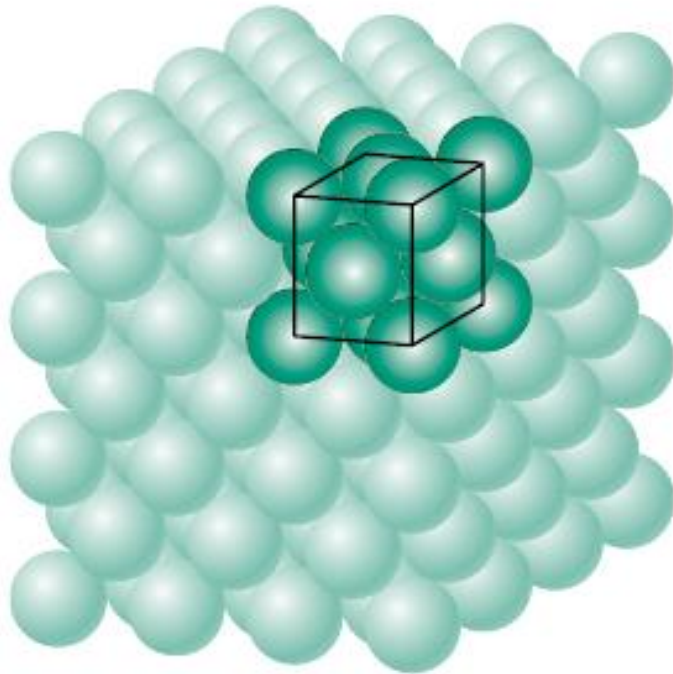
Density of the unit cell is = density of the whole specimen

Atomic Packing Factor (APF)

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

*assume hard spheres
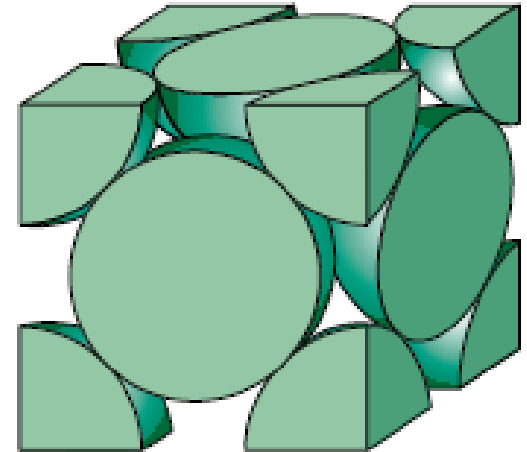
Density of the unit cell is = density of the whole specimen

Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.
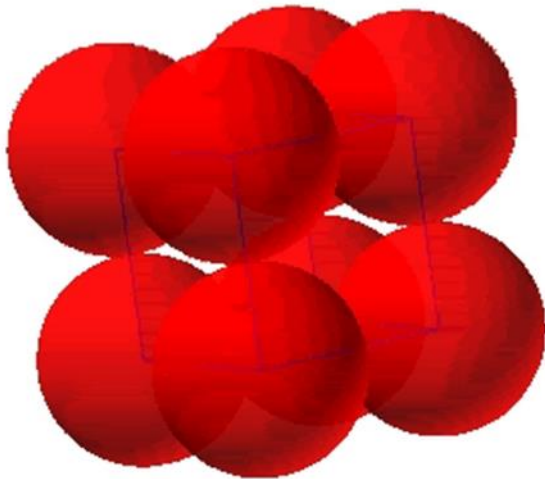
- Coordination # = 6
  (# nearest neighbors)
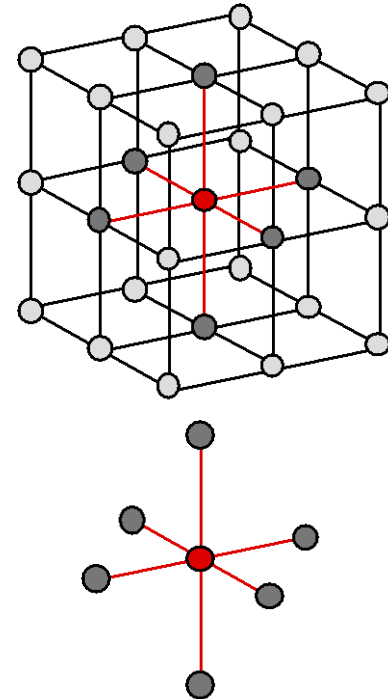
APF of Simple Cubic
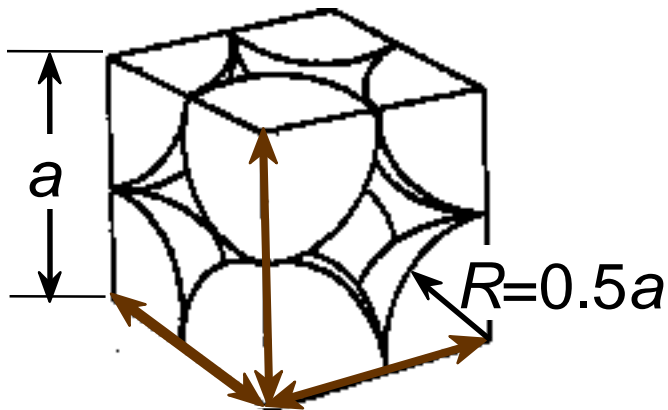
$$APF = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

$R = 0.5a$

a

close-packed directions

contains 8 x 1/8 =
 1 atom/unit cell

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

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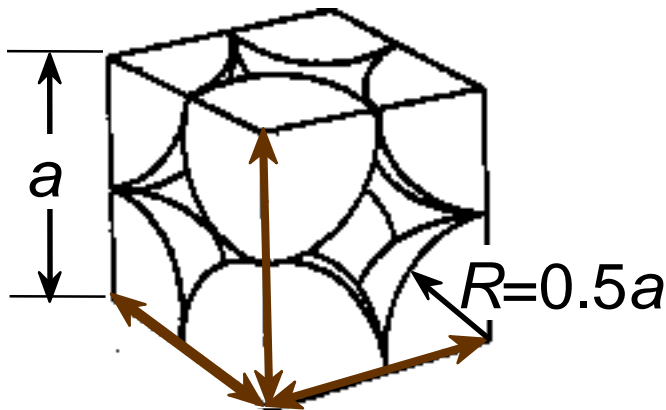
$$APF = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

a

$R = 0.5a$

close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

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

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

• APF for a simple cubic structure = 0.52

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

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

Atomic Packing Factor: BCC

$\sqrt{3}\,a$

a

$\sqrt{2}\,a$

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

R

a

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

atoms / unit cell $\rightarrow$ 2

volume / atom $\rightarrow \frac{4}{3}\pi(\sqrt{3}a/4)^3$
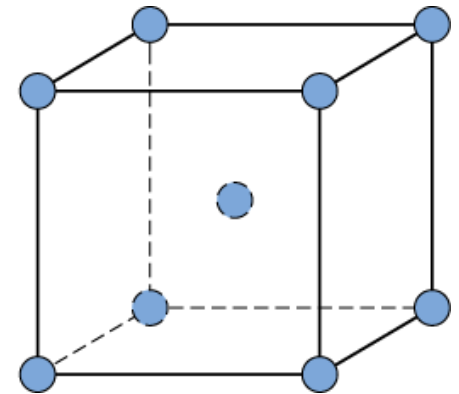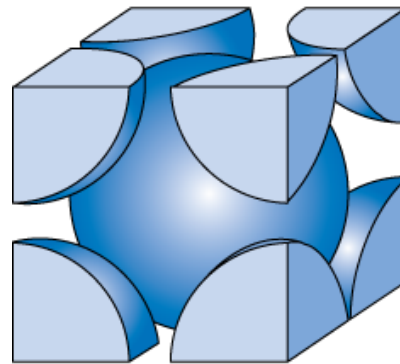
volume / unit cell $\rightarrow a^3$

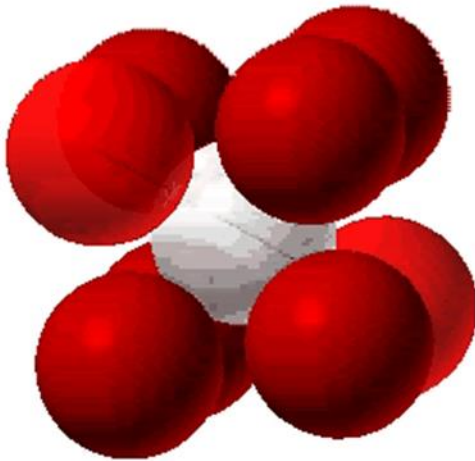- APF for a body-centered cubic structure = 0.68

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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.

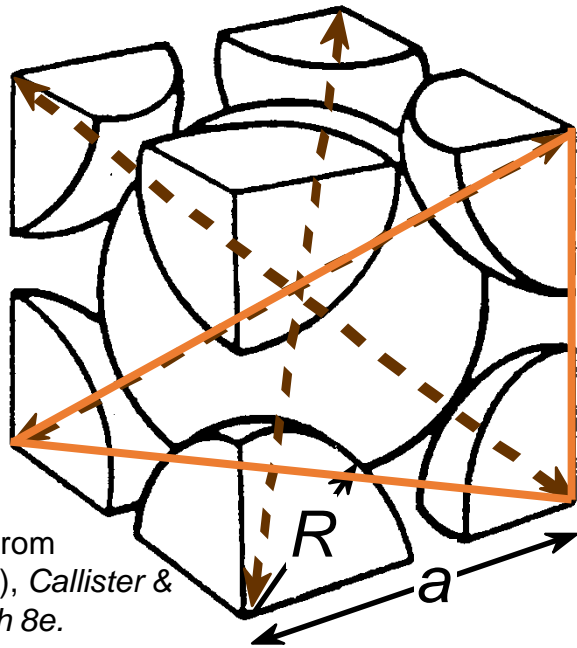ex: Al, Cu, Au, Pb, Ni, Pt, Ag, Fe(γ)

- Coordination # = 12
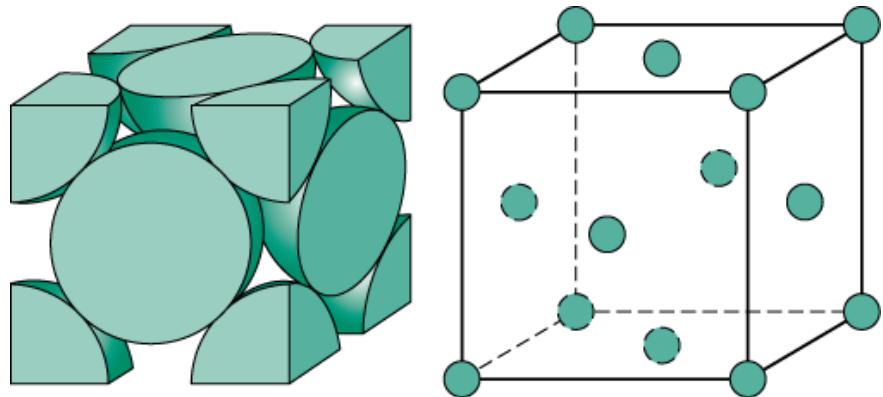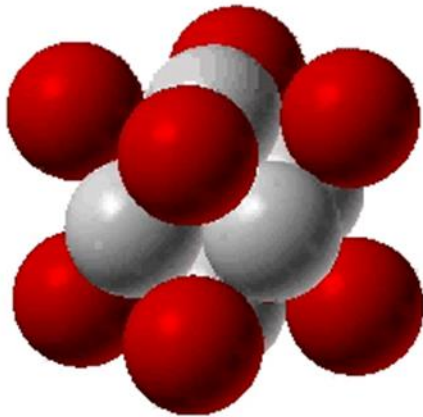
Adapted from Fig. 3.1, *Callister & Rethwisch 8e.*

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

Atomic Packing Factor: FCC

Close-packed directions:

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

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

$\sqrt{2}\,a$

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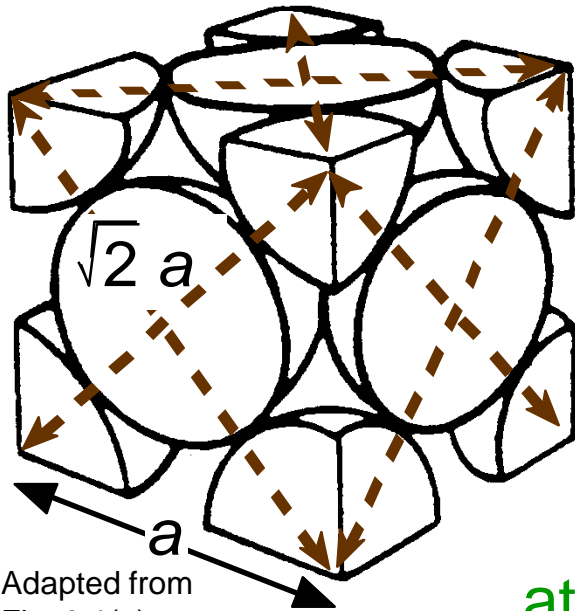
Adapted from Fig. 3.1(a), *Callister & Rethwisch 8e.*

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

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

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

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

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

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Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence

- 3D Projection

A sites

B sites

A sites

Adapted from Fig. 3.3(a),
Callister & Rethwisch 8e.
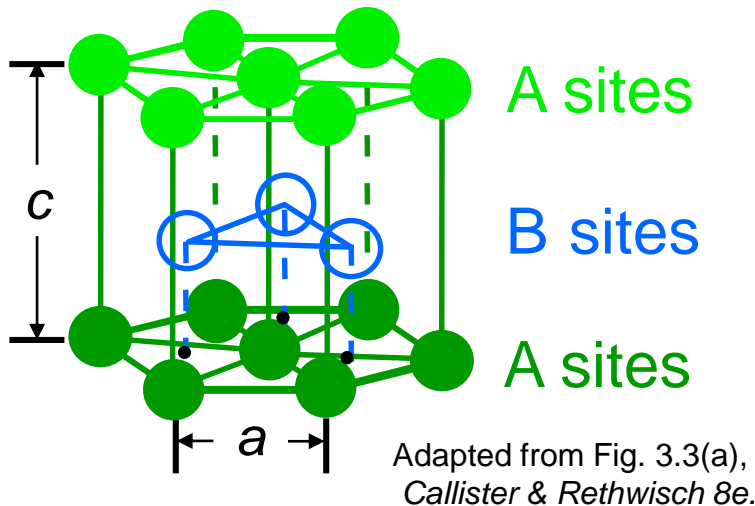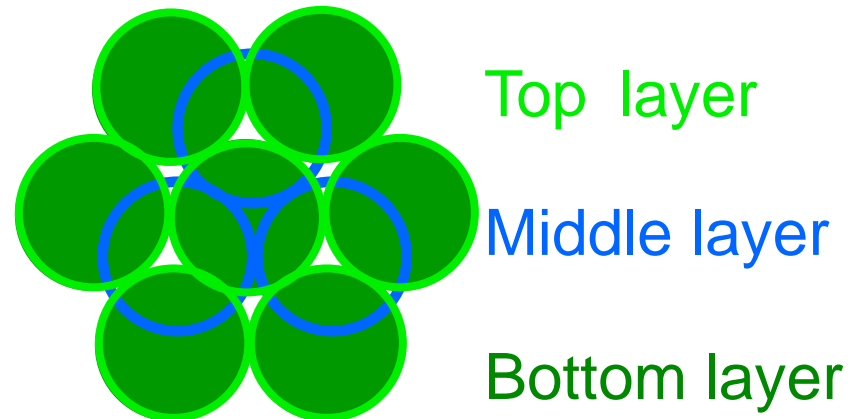
- Coordination # = 12

- APF = 0.74

- c/a = 1.633

- 2D Projection

Top layer

Middle layer

Bottom layer

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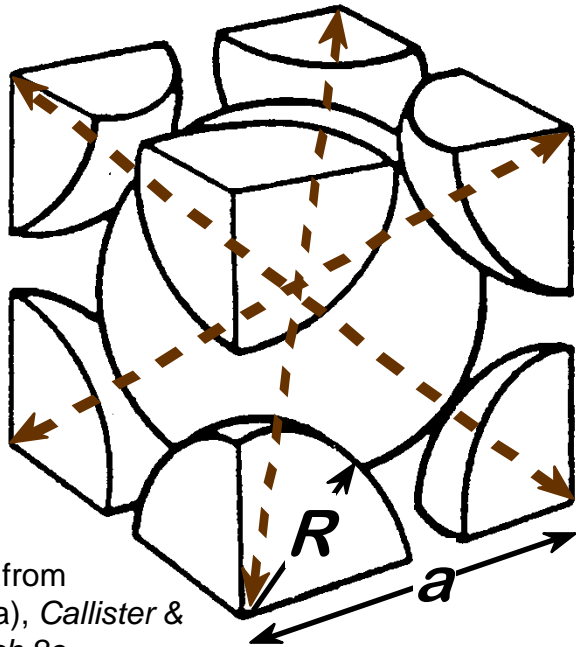
Adapted from Fig. 3.2(a), *Callister & Rethwisch 8e.*

- Ex: Cr (BCC)

A = 52.00 g/mol

R = 0.125 nm

n = 2 atoms/unit cell

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

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

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

ρ_{actual} = 7.19 g/cm^3

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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 — 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

$\rho\ (g/cm^3)$

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.*

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Polymorphism/Allotropes

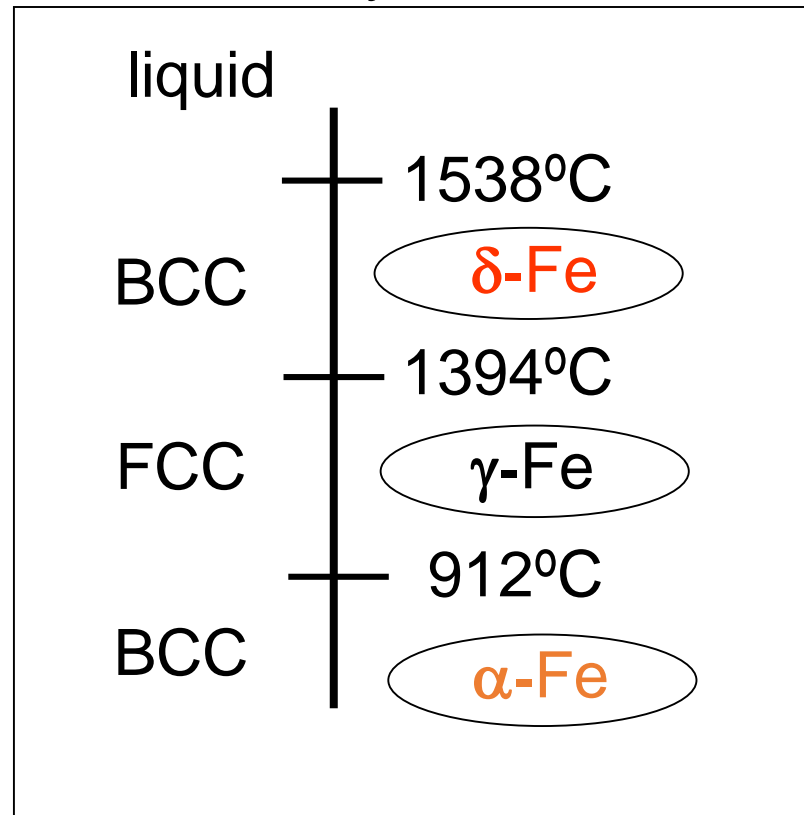- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

titanium

α, β-Ti

carbon

diamond, graphite

iron system

liquid

BCC   δ-Fe
1538ºC

1394ºC
FCC   γ-Fe

912ºC
BCC   α-Fe

Single Crystal:

- If the regular atomic arrangement spans through the entirety of the specimen, it is a single crystal material.

- There are several naturally available single crystal materials such as the one shown here. It is a garnet single crystal – stone containing silicate mineral.

- Apart from the naturally available materials, artificially one can grow single crystals by maintaining stringent ambient conditions.

- Single crystal materials have applications in electronic microcircuits and other semiconductors.
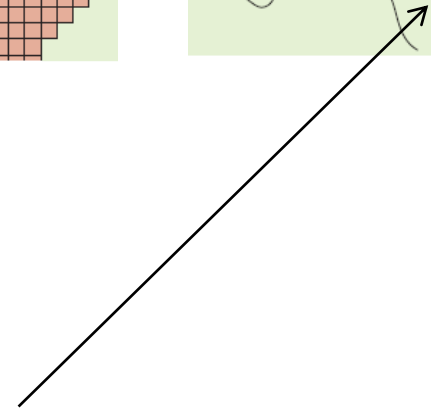
What are the practical difficulties that you expect in growing a single crystal?

Poly–crystalline Material:
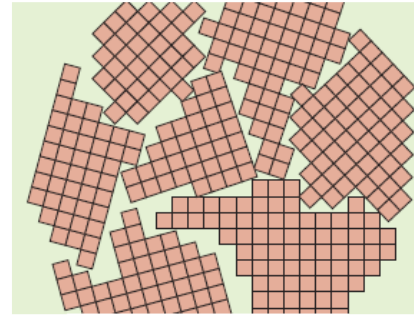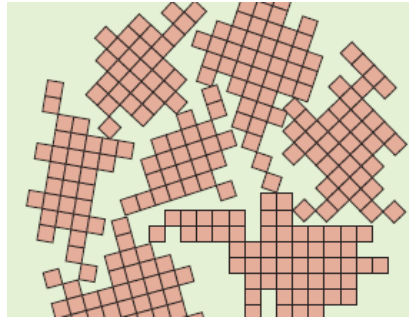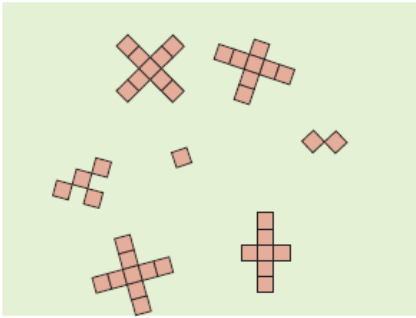
Solidification Process

There exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary,** dark lines are the grain boundaries.

Anisotropy:

- Directional dependency of a property is called **<u>Anisotropy</u>**.

- A material which is **magnetically anisotropic need NOT** have **mechanical anisotropy**.

- When there is no directional dependence of a property, then we call the material to be isotropic.

- A polycrystalline material can be isotropic if there are a large number of crystals or grains, each with random orientation. Thus, although an individual grain may be anisotropic, a collection of such grains with random orientations can behave isotropic.

Metal	*Modulus of Elasticity (GPa)*		
	[100]	*[110]*	*[111]*
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Single vs Polycrystals

- ## Single Crystals

  -Properties vary with direction: anisotropic.

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

E (diagonal) = 273 GPa
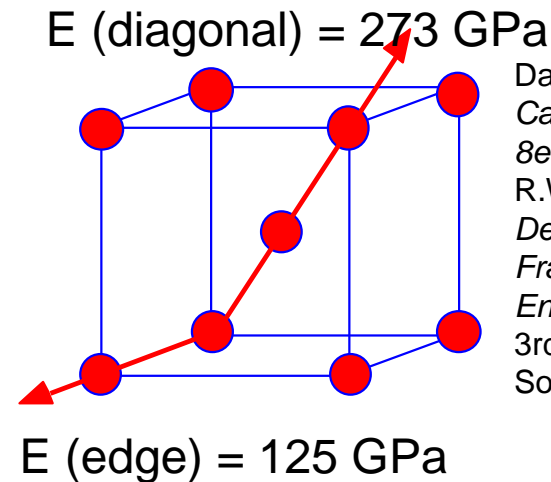
Data from Table 3.3, *Callister & Rethwisch 8e.* (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

E (edge) = 125 GPa

- ## Polycrystals

  -Properties may/may not vary with direction.

  -If grains are randomly oriented: isotropic.

  ($E_{poly\ iron}$ = 210 GPa)

  -If grains are textured, anisotropic.

200 μm
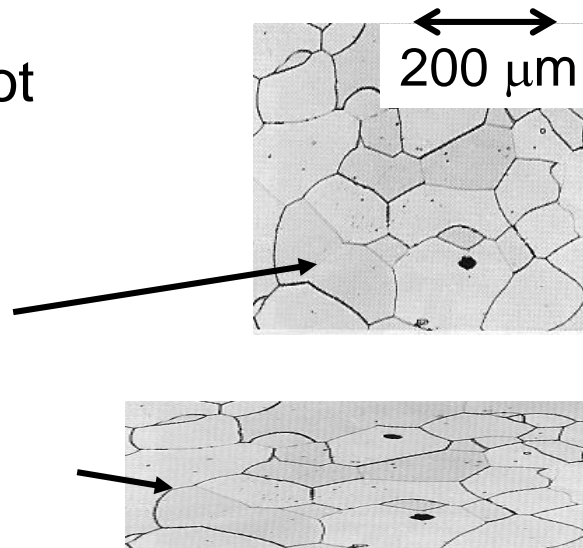
Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e.* (Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Crystal Systems

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

Fig. 3.4, *Callister & Rethwisch 8e.*
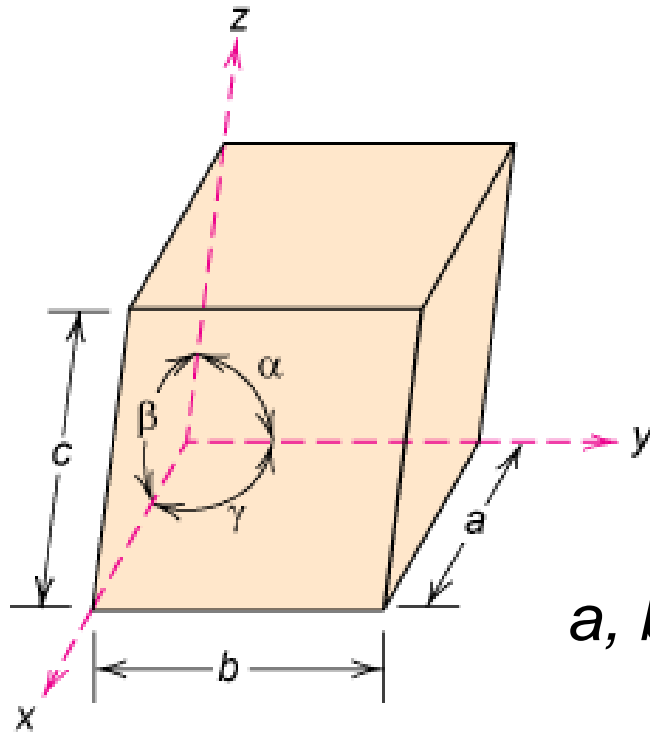
7 crystal systems

14 crystal lattices

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

https://en.wikipedia.org/wiki/Crystal_system

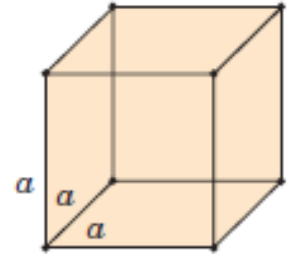# Crystal Systems – Based on Unit Cell Geometry

- Based on Unit Cell Geometry there are *SEVEN* crystal systems.

Cubic $\qquad a = b = c \qquad \alpha = \beta = \gamma = 90°$
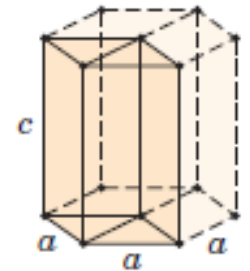

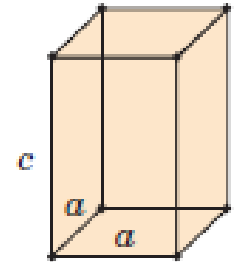Hexagonal $\qquad a = b \neq c \qquad \alpha = \beta = 90°, \gamma = 120°$

Crystal Systems – Based on Unit Cell Geometry

- Based on Unit Cell Geometry there are *SEVEN* crystal systems.
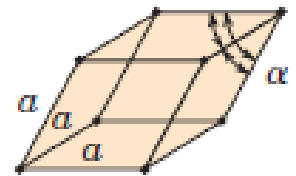
Tetragonal $\qquad$ $a = b \neq c$ $\qquad$ $\alpha = \beta = \gamma = 90°$

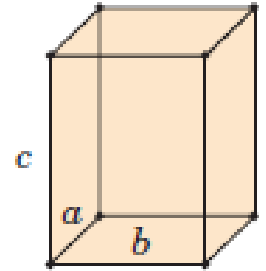Rhombohedral (Trigonal) $\qquad$ $a = b = c$ $\qquad$ $\alpha = \beta = \gamma \neq 90°$

Crystal Systems – Based on Unit Cell Geometry

- Based on Unit Cell Geometry there are *SEVEN* crystal systems.

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

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

Crystal Systems – Based on Unit Cell Geometry

- Based on Unit Cell Geometry there are *SEVEN* crystal systems.
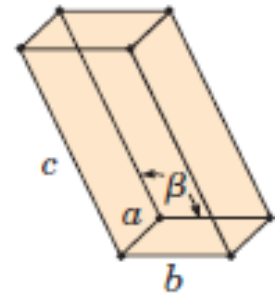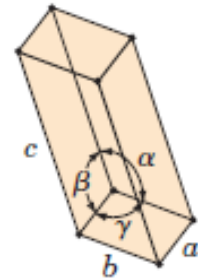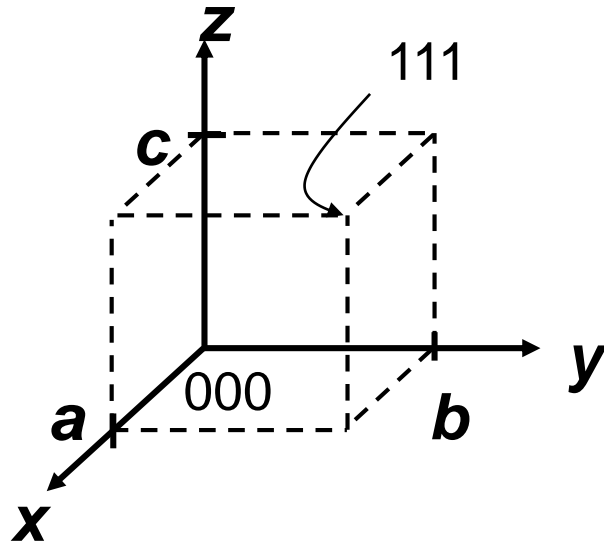
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$

Point Coordinates

Lattice position co-ordinate (P_x, P_y, P_z) for unit cell center are

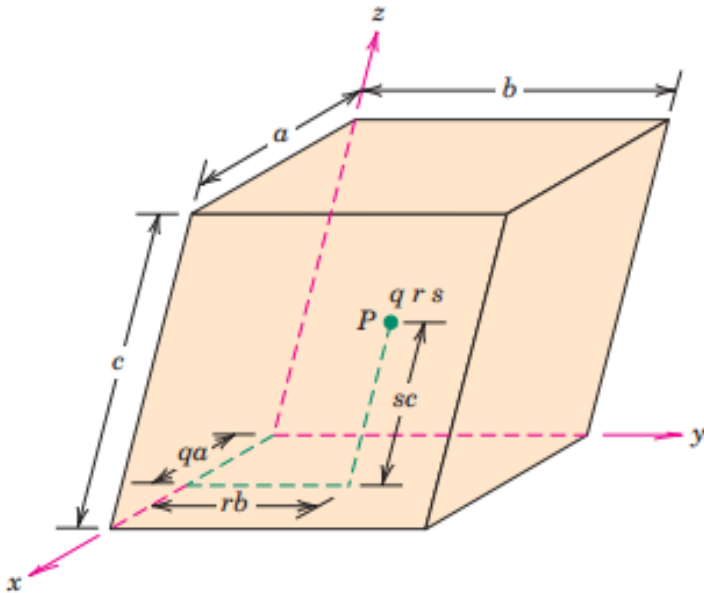$a/2$, $b/2$, $c/2$

The *indices (q r s)* are

½ ½ ½

position co-ordinate for unit cell corner are 111

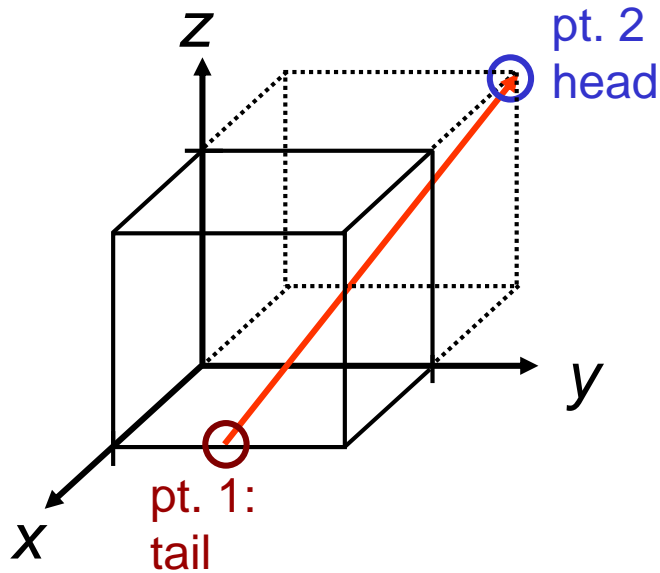*indices*: fractional multiples of a, b, c

$P_x = qa$

$P_y = rb$

$P_z = sc$

Crystallographic Directions

Line directed between two points

Example:

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

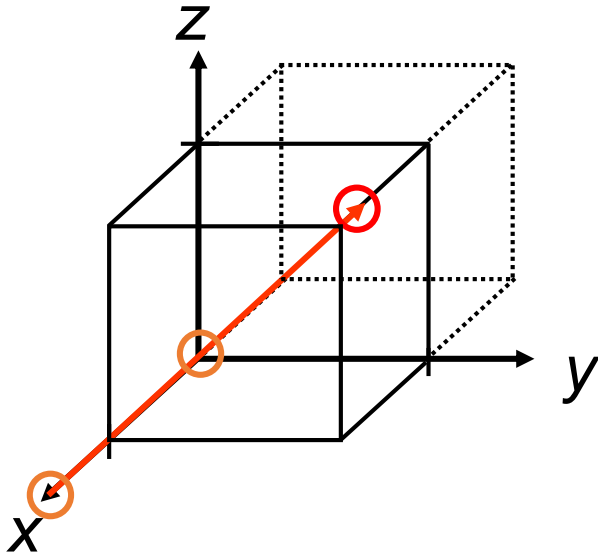pt. 2 $x_2 = -a$, $y_2 = b$, $z_2 = c$

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

=>   -2, 1/2, 1

Multiplying by 2 to eliminate the fraction

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

Crystallographic Directions

z

y

x

Crystallographically equivalent

1. several non-parallel directions with different indices have same spacing of atoms.
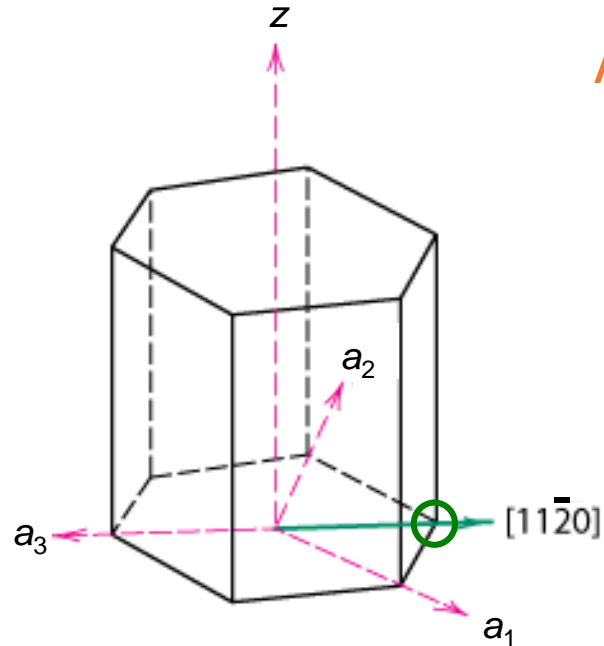
Ex. [100], [100], [010], [010], [001], and [001] in a cubic crystal.

2. Equivalent directions are grouped in a family.

3. directions in cubic crystals having the same indices without regard to order or sign—for example, [123] and [213]—are equivalent

families of directions *<uvw>*

HCP Crystallographic Directions: 4 parameter Miller-Bravais lattice coordinates
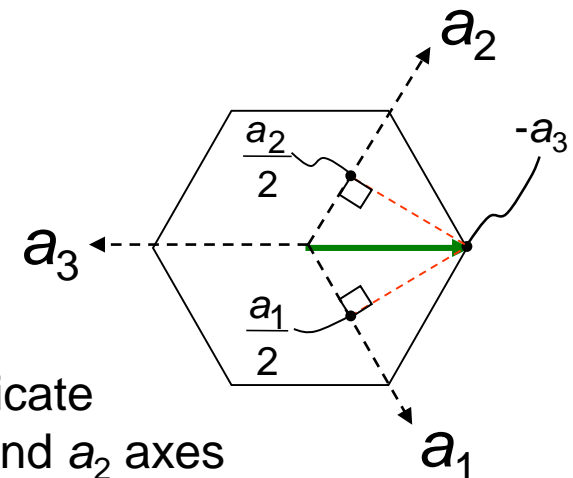

Adapted from Fig. 3.8(a),
Callister & Rethwisch 8e.

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
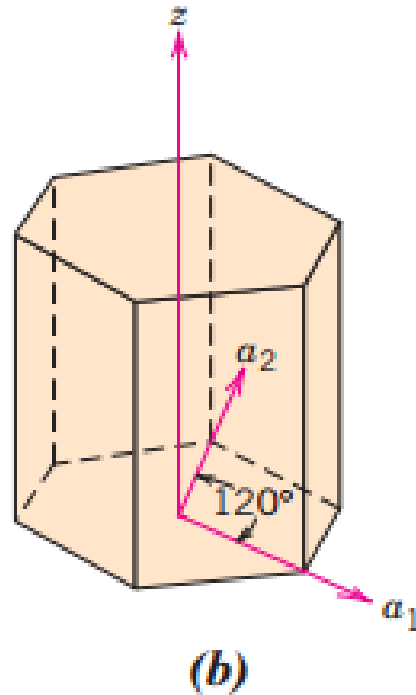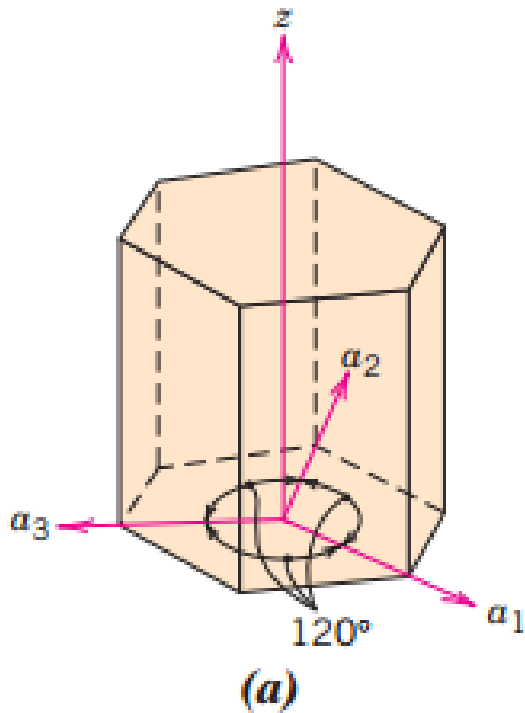4. Enclose in square brackets, no commas

$$[uvtw]$$

ex: ½, ½, -1, 0   => $[11\bar{2}0]$

dashed red lines indicate projections onto a_1 and a_2 axes

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Hexagonal Crystals

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

(a)

(b)

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

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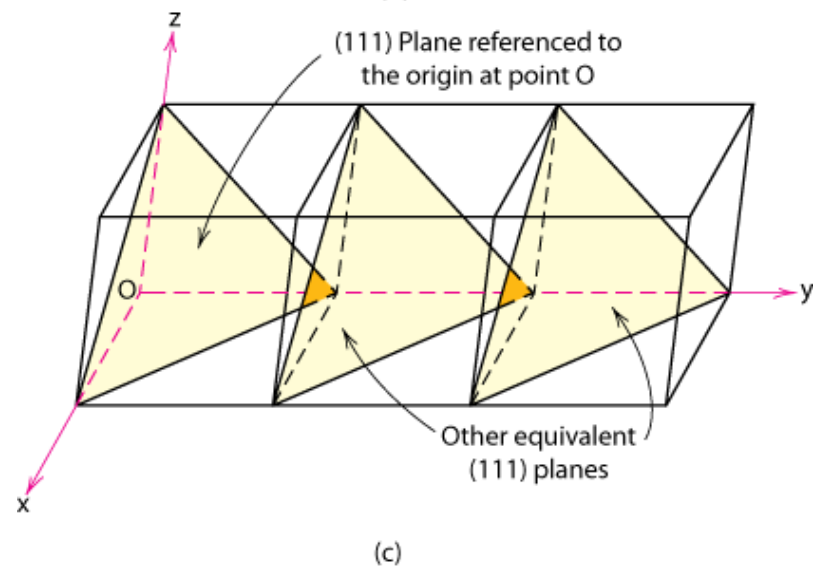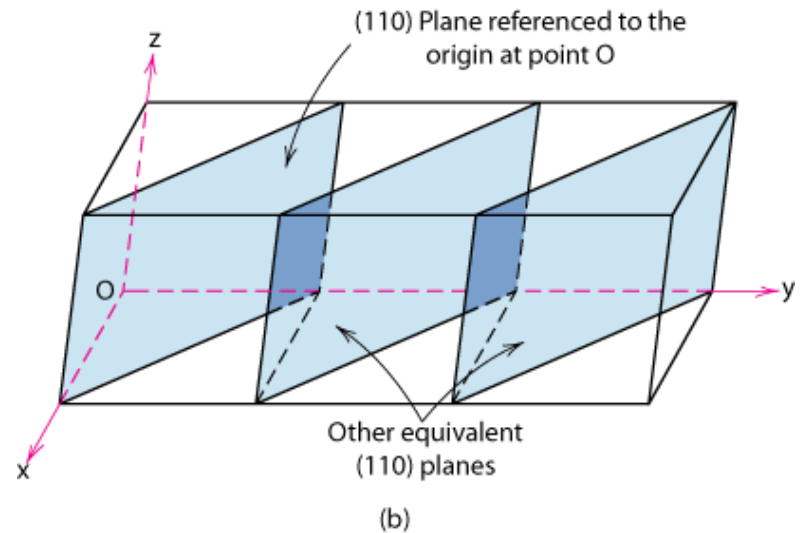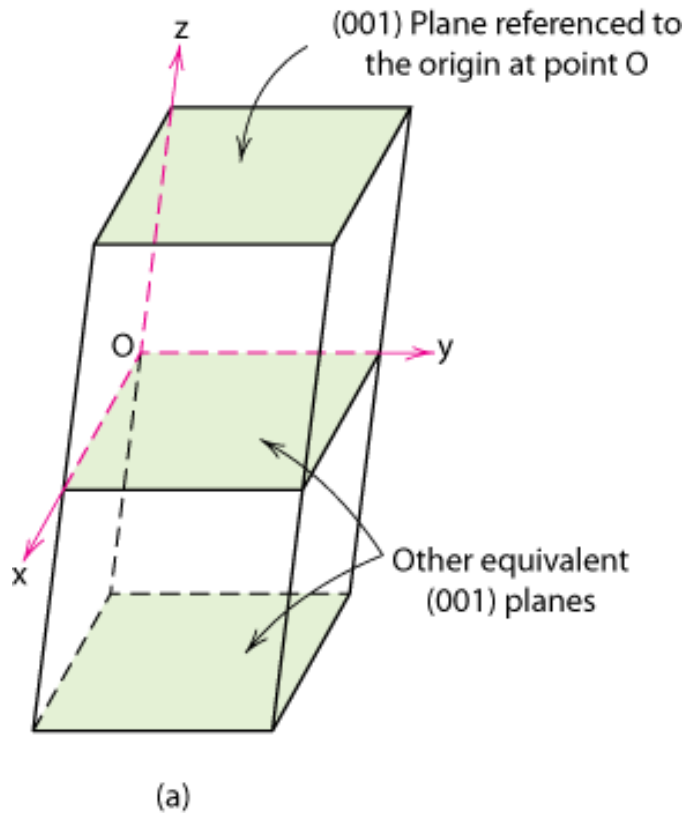
$$v = \frac{1}{3}(2v' - u')$$

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

$$w = w'$$

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. Designate intercepts for the x, y, and z axes as A, B, and C, respectively.
  2. Take reciprocals of intercepts.
  3. Multiply by their respective lattice parameters, a, b, and c.
  3. Reduce to smallest integer values.
  4. Enclose in parentheses, no commas i.e., (*hkl*)

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)

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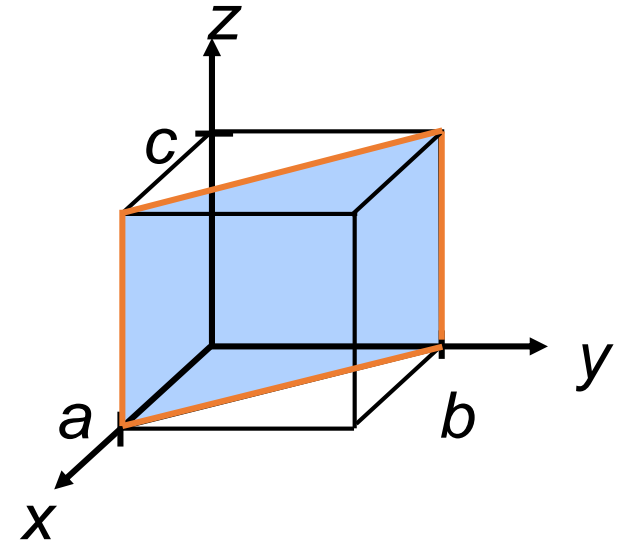
example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		

z
c
a
y
b
x

z
c
a
y
b
x
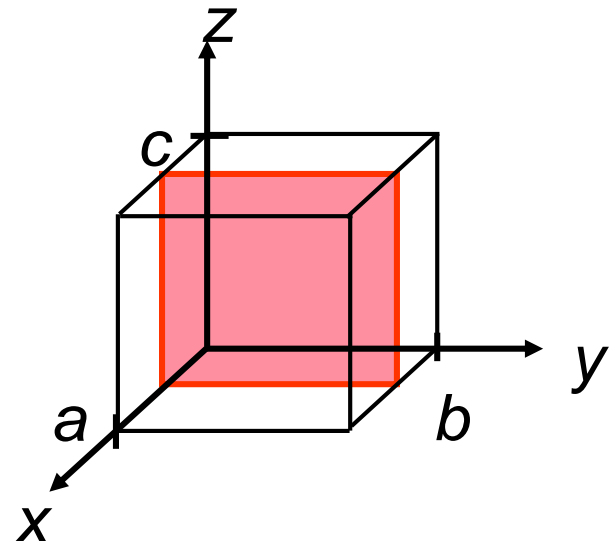
Crystallographic Planes

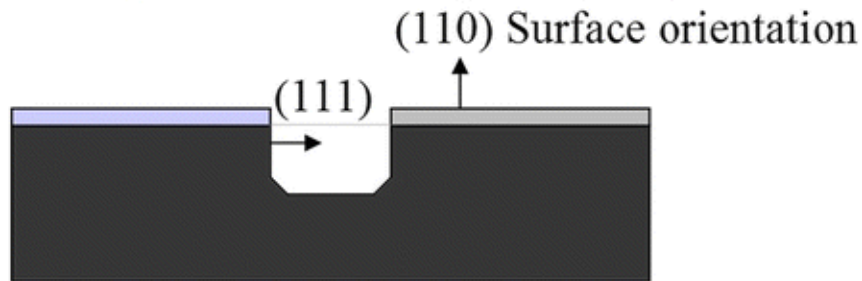| example		a	b	c
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		
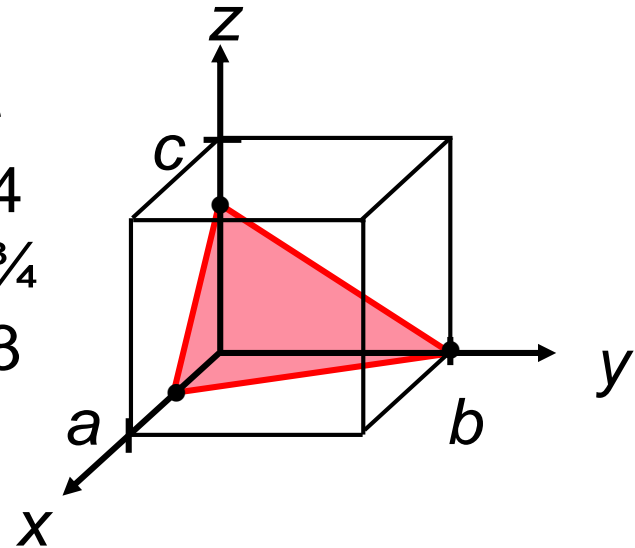
Family of Planes   {hkl}

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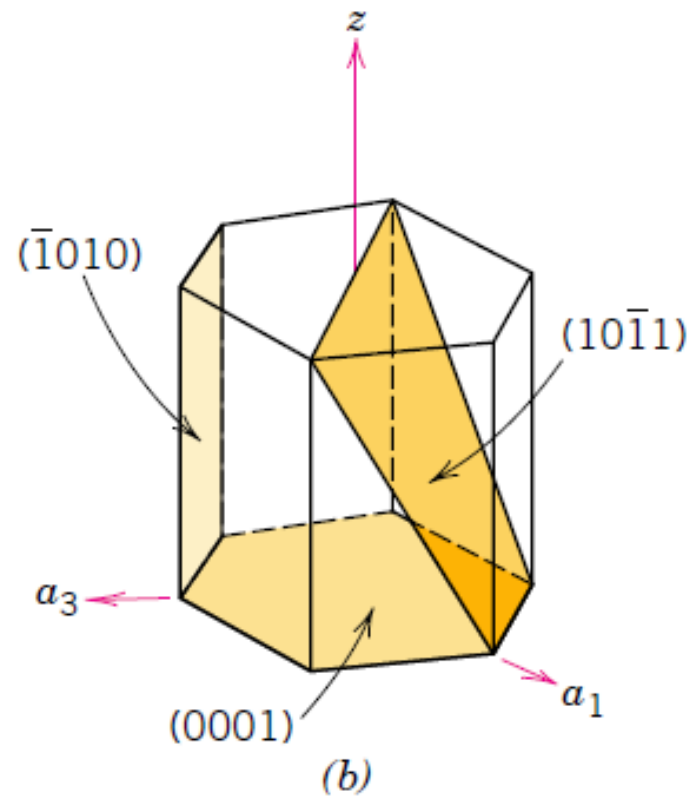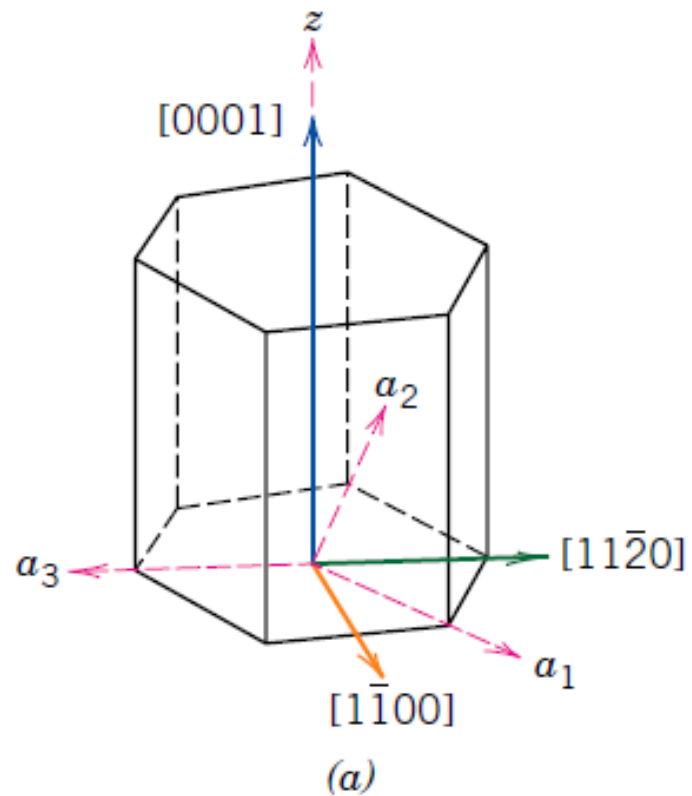
Anisotropic etching of Silicon

Anisotropic wet etching on (100) silicon

Anisotropic wet etching on (110) silicon

Orientation	KOH (34 wt.%, 70.9°C)
	Etching Rate (um/min)
100	0.629
110	1.292
210	1.237
211	0.983
221	0.586
310	1.079
311	1.065
320	1.285
331	0.845
530	1.273
540	1.283
111	0.009

Explain this

(a)

(b)

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 $(10\bar{1}1)$
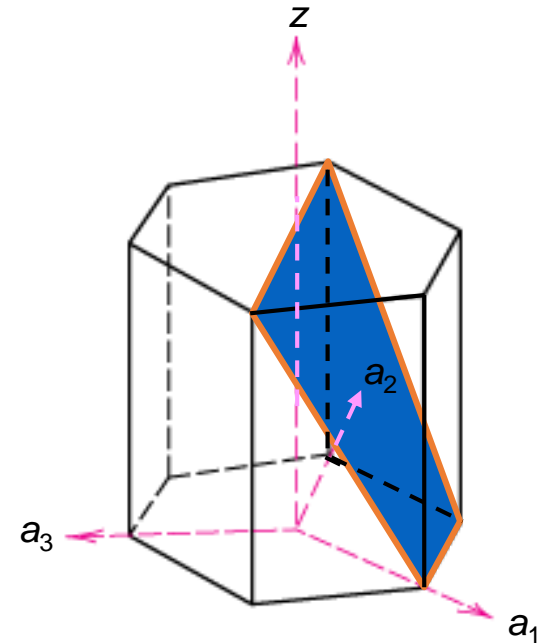
Adapted from Fig. 3.8(b),
Callister & Rethwisch 8e.

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

[110]

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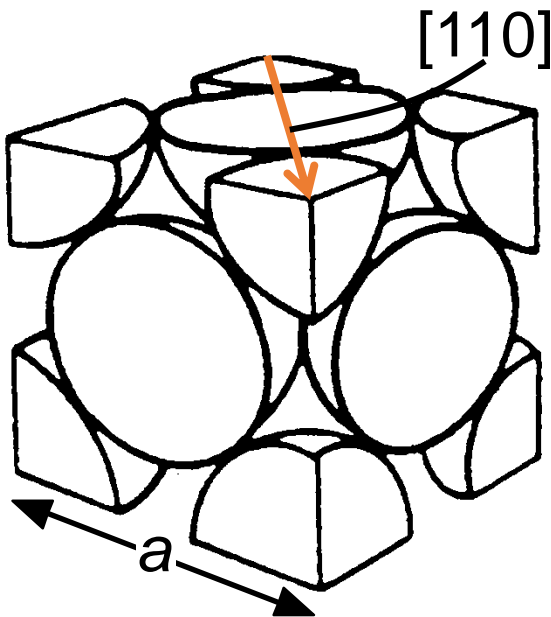
ex: linear density of Al in [110] direction

$a = 0.405$ nm
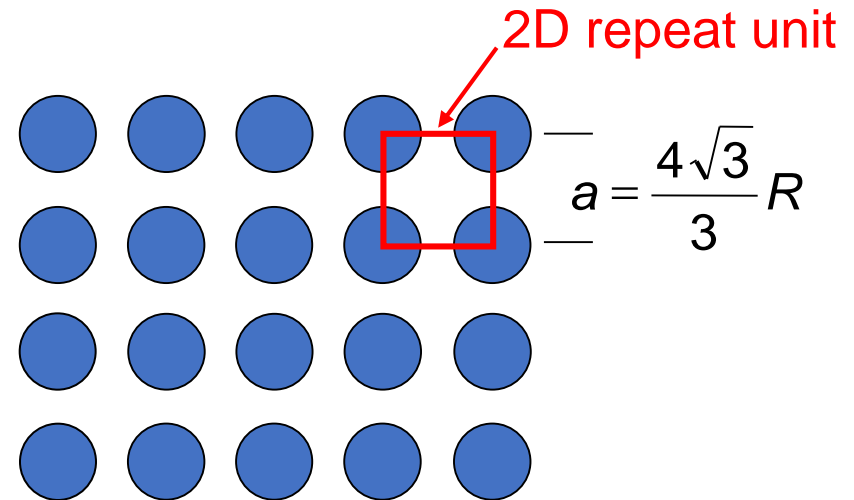
atoms

length

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

Planar Density of (100) Iron

Solution: At T < 912ºC iron has the BCC structure.
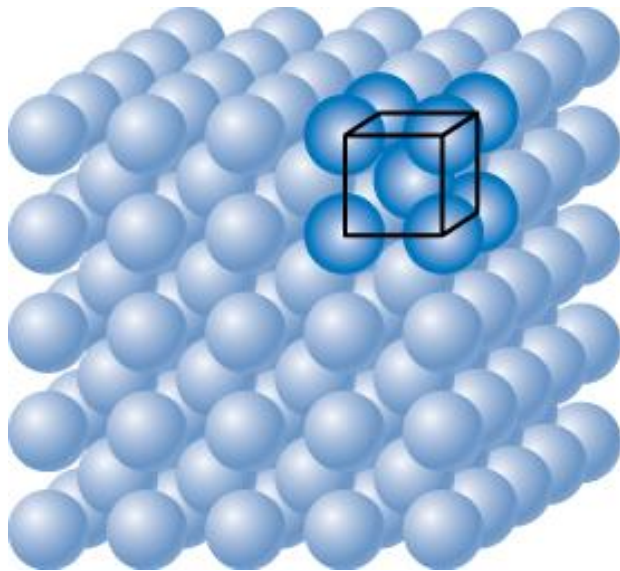
Adapted from Fig. 3.2(c), *Callister & Rethwisch 8e.*
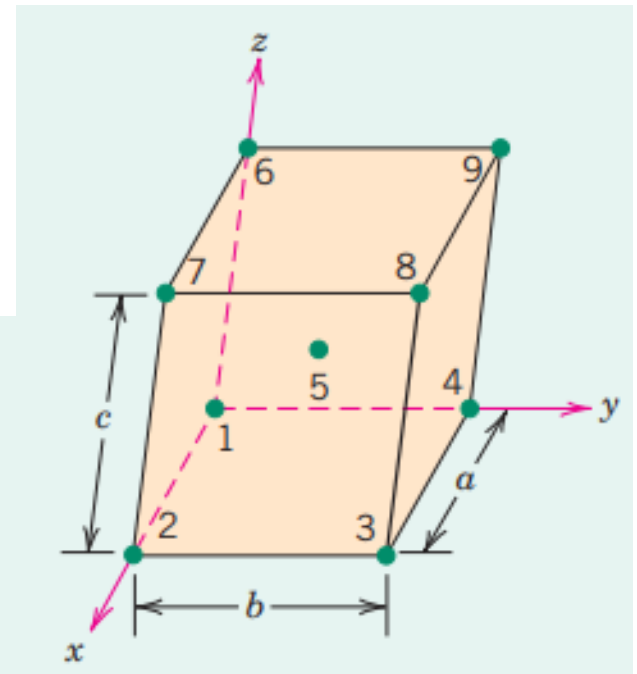
2D repeat unit
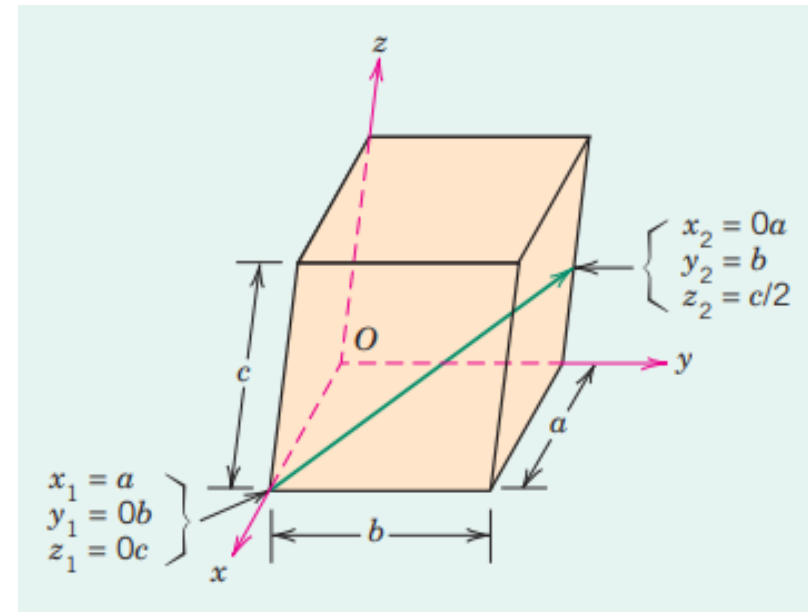
(100)

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

Radius of iron $R = 0.1241$ nm

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

1. Specify indices for all numbered points of the unit cell in the illustration

Point Number	q	r	s
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1

2. Determine the indices for the direction shown in the accompanying figure.

	x	y	z
Head coordinates $(x_2, y_2, z_2,)$	$0a$	b	$c/2$
Tail coordinates $(x_1, y_1, z_1,)$	a	$0b$	$0c$
Coordinate differences	$-a$	b	$c/2$
Calculated values of u, v, and w	$u = -2$	$v = 2$	$w = 1$
Enclosure		$[\bar{2}21]$	

3. Within a unit cell draw a [1-10] direction

1. Assume tail to be at origin
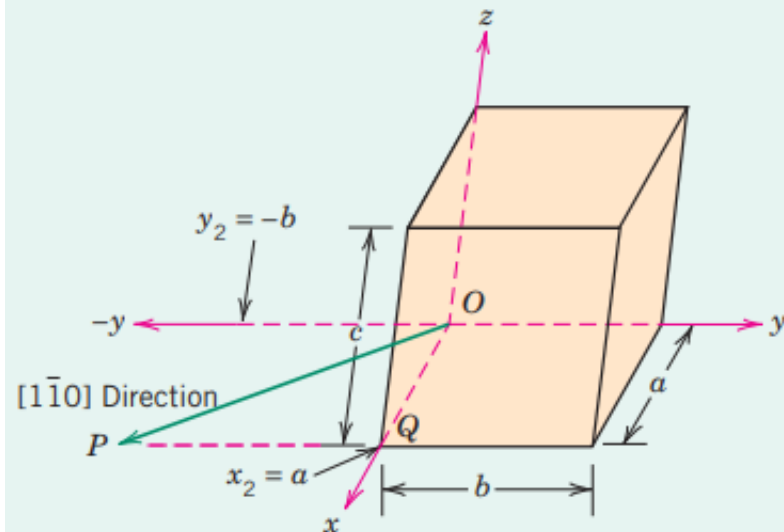
$$x_1 = 0a$$

$$y_1 = 0b$$

$$z_1 = 0c$$

2. Solve for coordinates of head
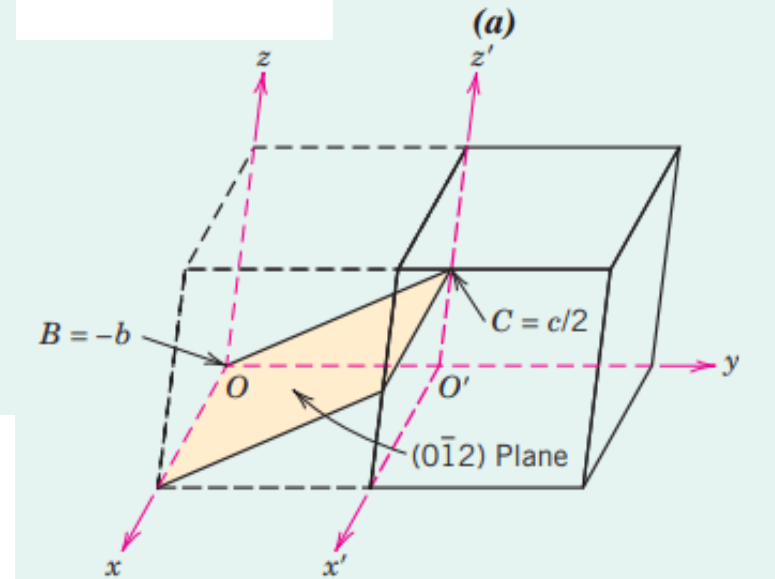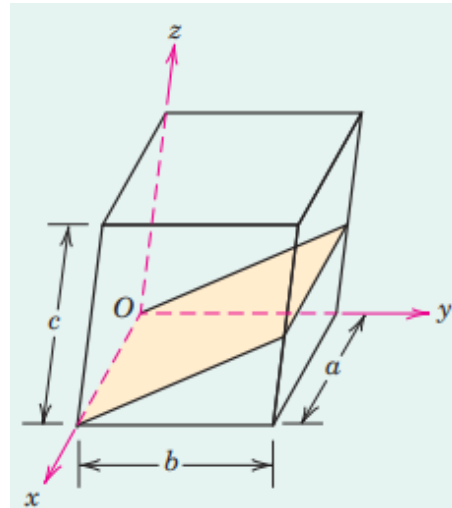
$$x_2 = ua + x_1 = (1)(a) + 0a = a$$

$$y_2 = vb + y_1 = (-1)(b) + 0b = -b$$

$$z_2 = wc + z_1 = (0)(c) + 0c = 0c$$

4. Determine the Miller indices for the plane shown in the accompanying sketch

Because the plane passes through the selected origin O, a new origin must be chosen at the corner of an adjacent unit cell.
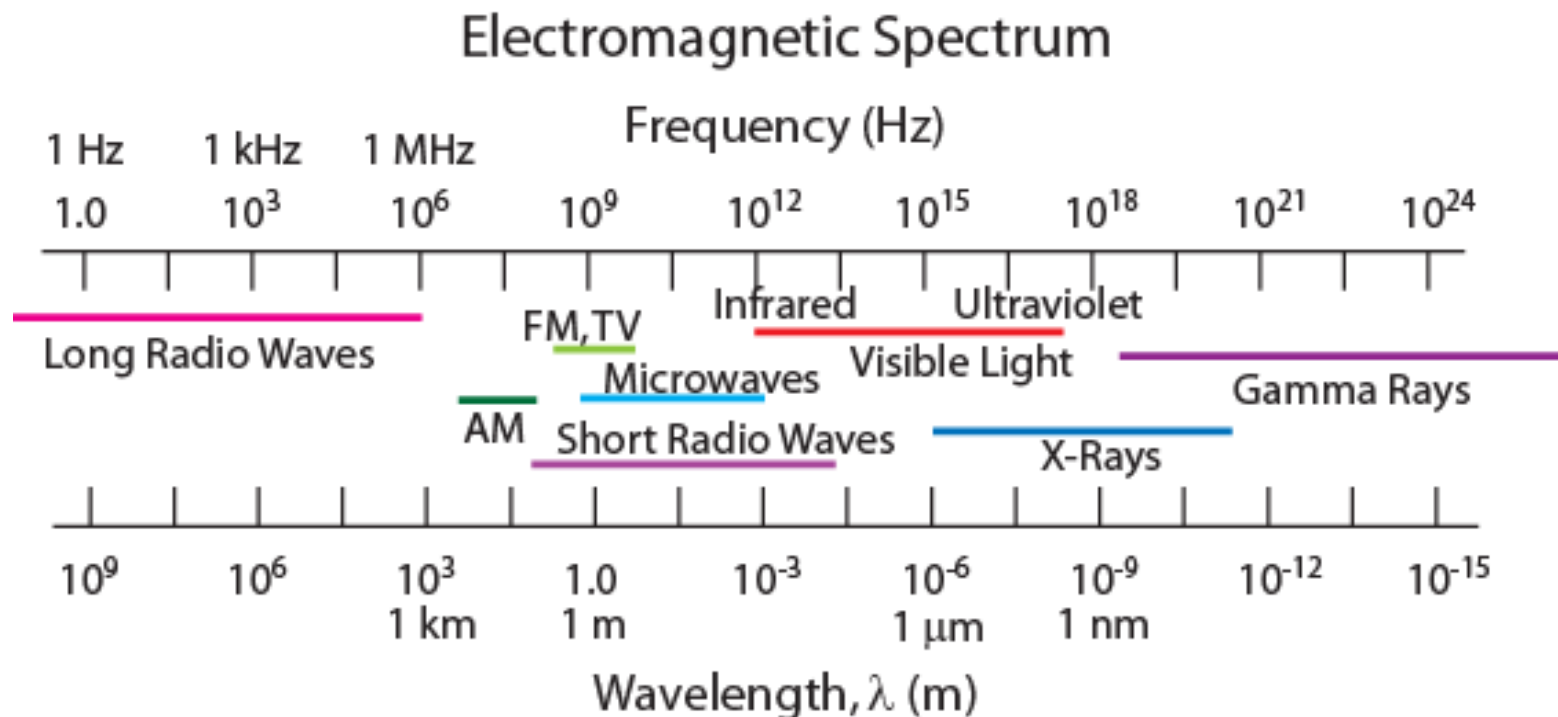

(a)

	x	y	z
Intercepts (A, B, C)	∞a	$-b$	$c/2$
Calculated values of h, k, and l (Equations 3.13a–3.13c)	$h = 0$	$k = -1$	$l = 2$
Enclosure		$(0\bar{1}2)$	

5. Construct a (101) plane within a unit cell.
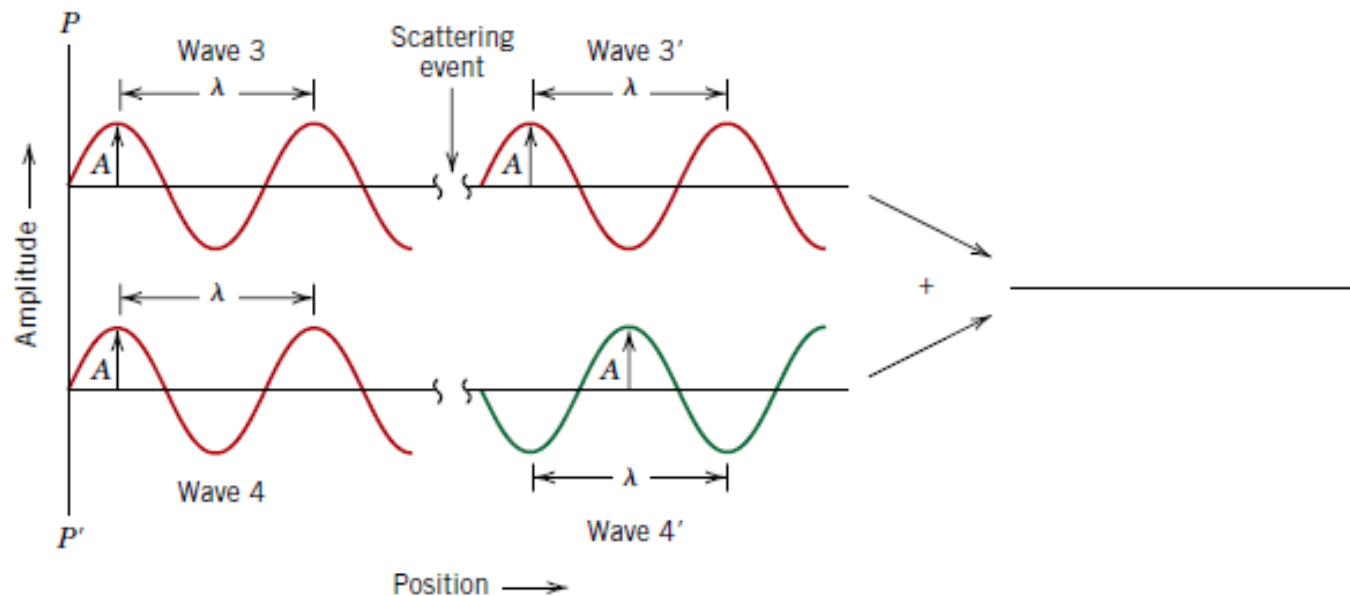
X-Ray Diffraction

Electromagnetic Spectrum
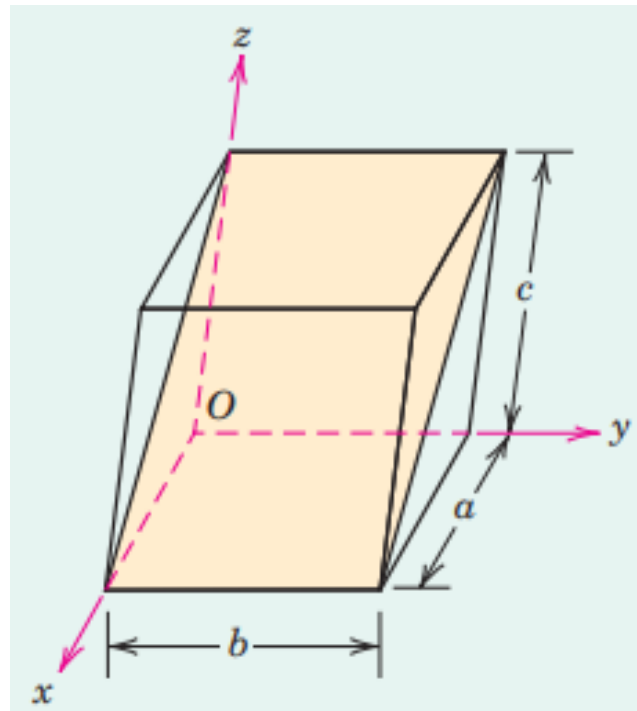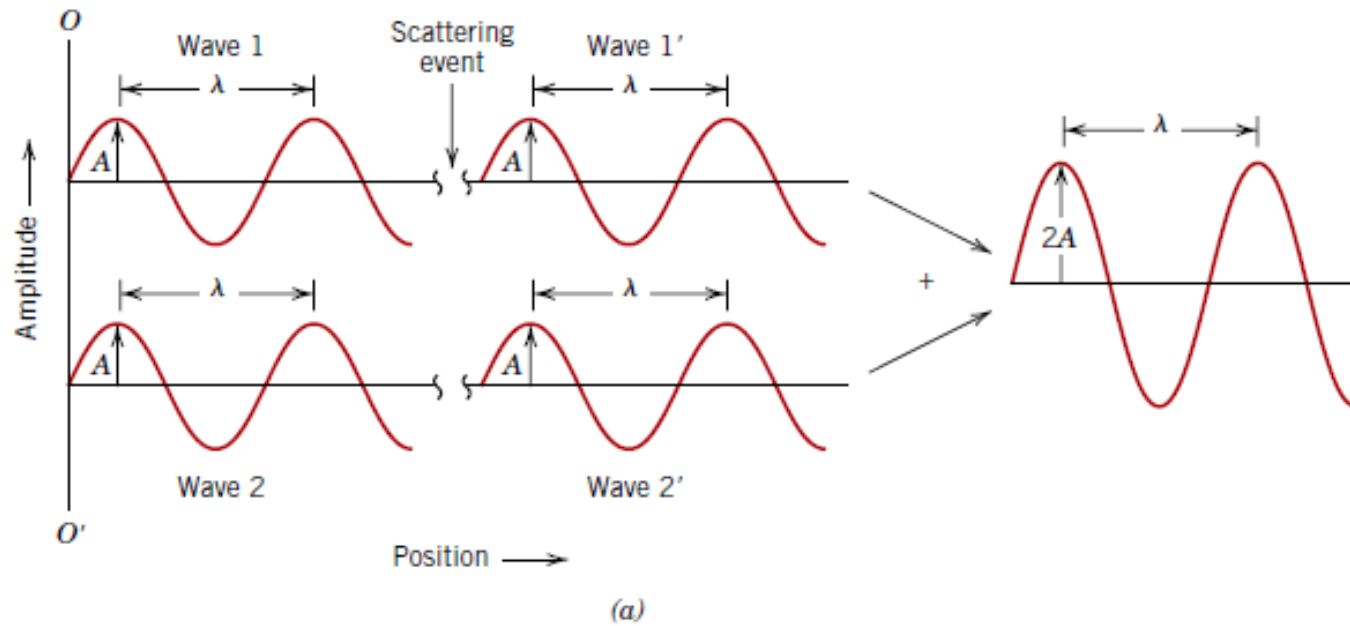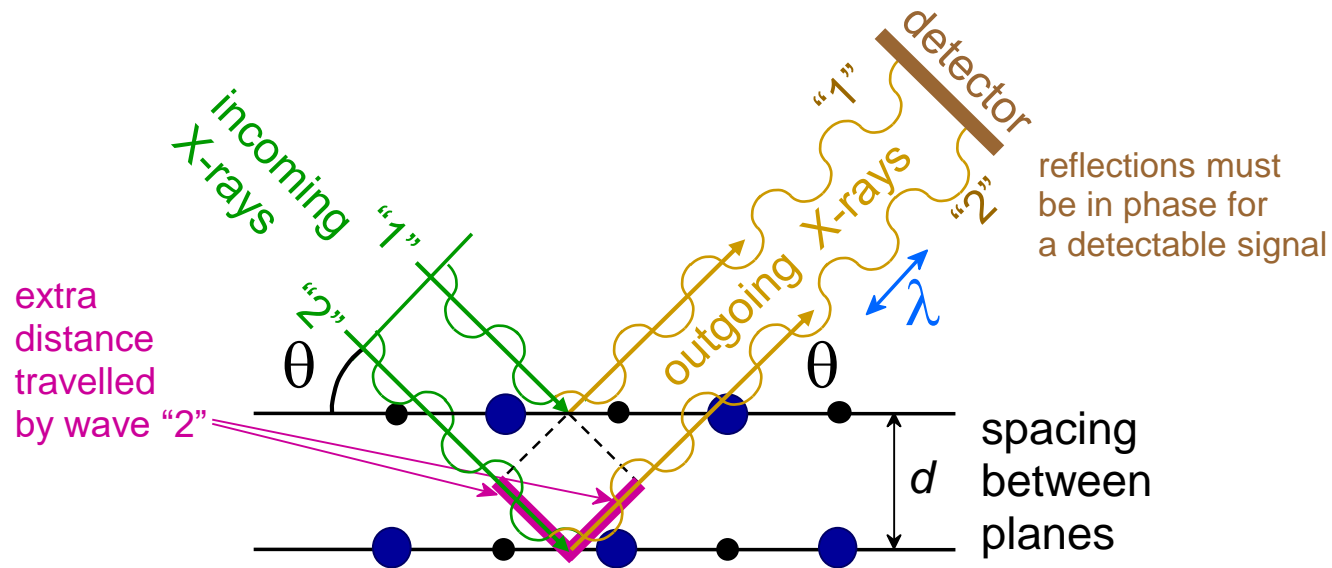

- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

Constructive and Destructive Interference

X-Rays to Determine Crystal Structure

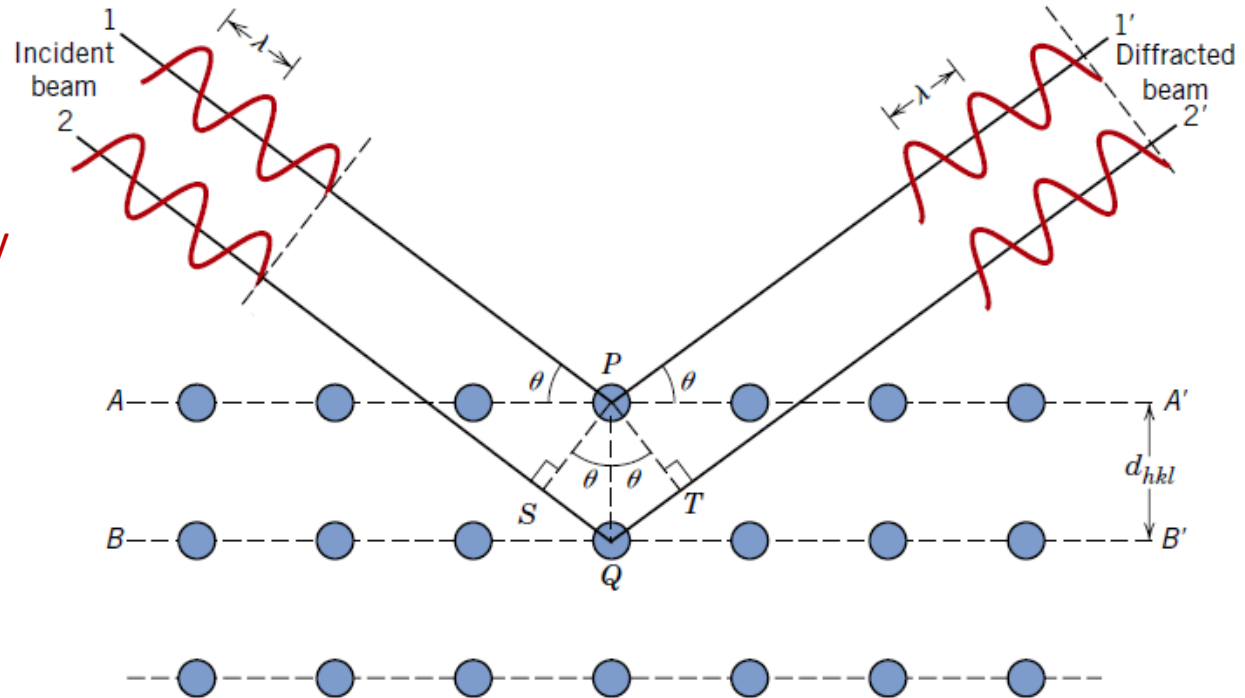- Incoming X-rays diffract from crystal planes.

Condition for the diffraction to occur: the difference in the lengths of the path travelled by the two beams must be an integral multiple of the wavelength.

i.e., $n\lambda = \overline{SQ} + \overline{QT}$

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

Bragg's Law
Assumption - atoms are only in the corners
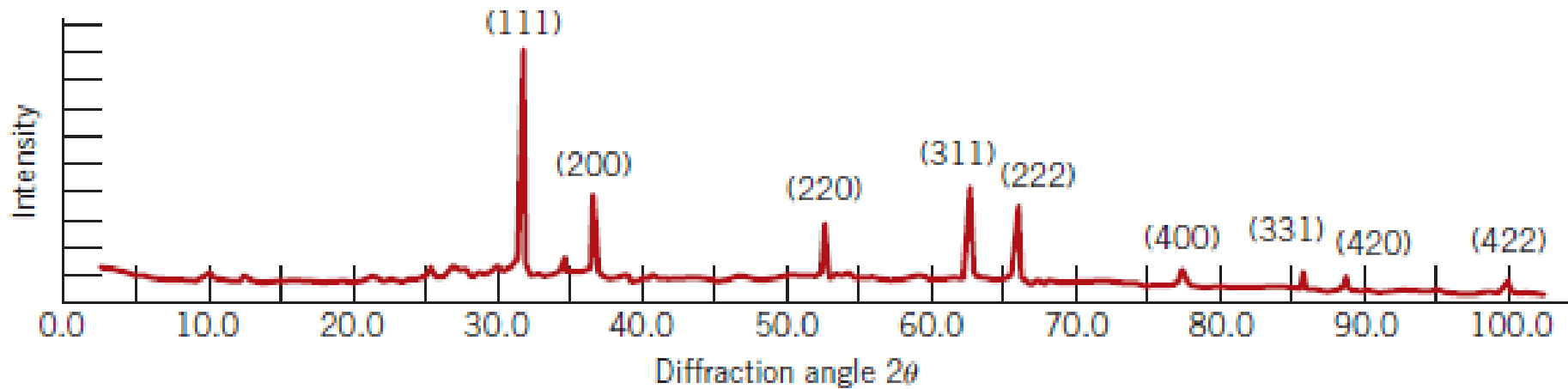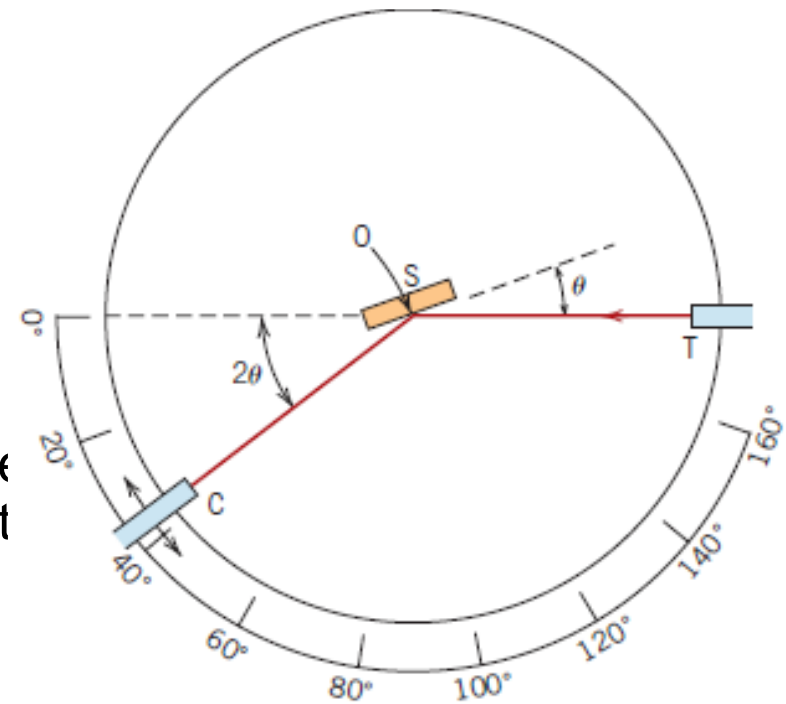
$\bullet\; d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

The above condition is *necessary*, but *not sufficient*.

- For BCC, $h + k + l$ must be even.

- For FCC, h, k, l all must be either odd or even.

X-ray diffractometer

- *T* x-ray source,
- *S* specimen,
- *C* detector, and
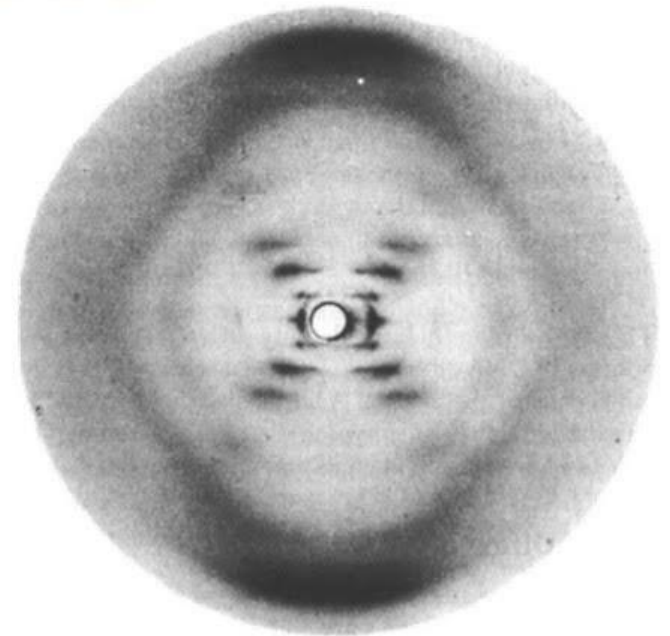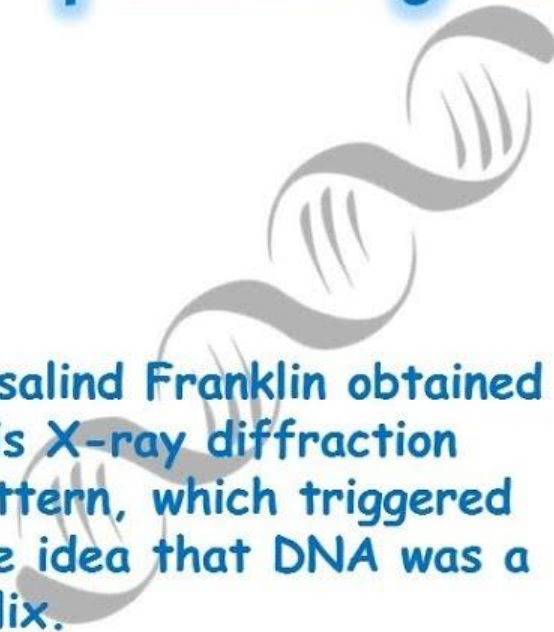- *O* the axis around which the specimen and detector rotat

A typical plot of Intensity Vs Diffraction Angle

Rosalind Franklin's X-ray diffraction pattern of DNA

Rosalind Franklin obtained this X-ray diffraction pattern, which triggered the idea that DNA was a helix.

Biotech Review

Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute (a) the interplanar spacing and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Interplanar spacing

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

$$= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm}$$

Compute theta

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790\,\text{nm})}{(2)(0.1013\,\text{nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13°$$

Compute diffraction angle, 2theta

$$2\theta = (2)(62.13°) = 124.26°$$