Chapter 3

Structures of Metals and Ceramics

Chapter 3

Introduction to Crystal Structure

Issues to Address...

- How do atoms assemble into solid structures?

- How do the structures of ceramic materials differ from those of metals?

- How does the density of a material depend on its structure?

- When do material properties vary with the sample (i.e., part) orientation?

- What is Lattice, Unit Cell?

- What is Metallic Structures (SC, BCC, FCC, HCP)?

- Ionic Crystals

- Miller-Bravais Indices

- Seven Crystal System

- X-ray diffraction

Metallic Crystals

- Tend to be densely packed.

- Have several 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.

- Have the simplest crystal structures.

    We will look at three such structures...

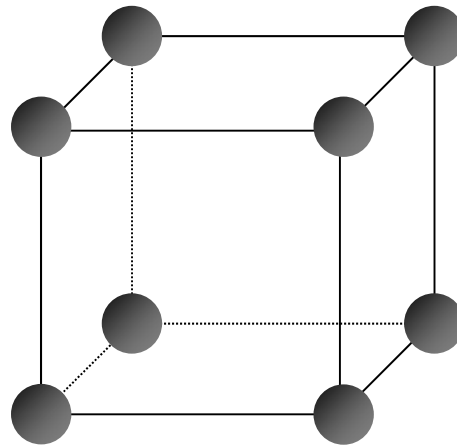**Lattice**   Three dimensional array of points coinciding with atom positions (lattice points).

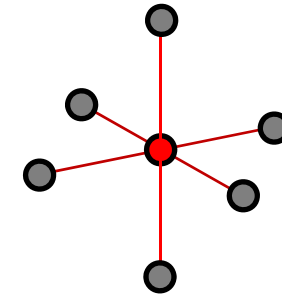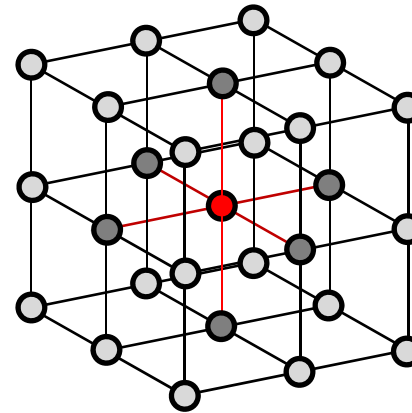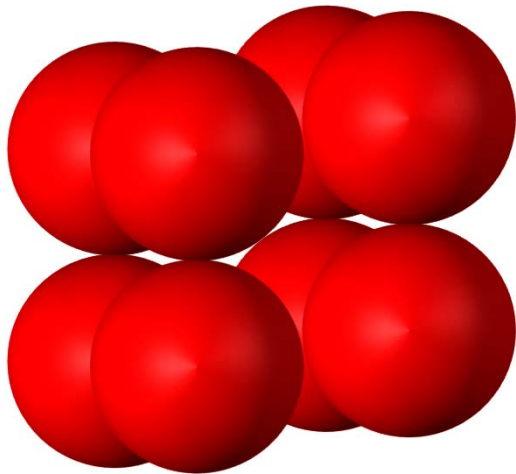**Lattice point**   Positions in the structure which are identical.

Unit cell   **Smallest** and **convenient** repeat unit in the lattice.

- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.
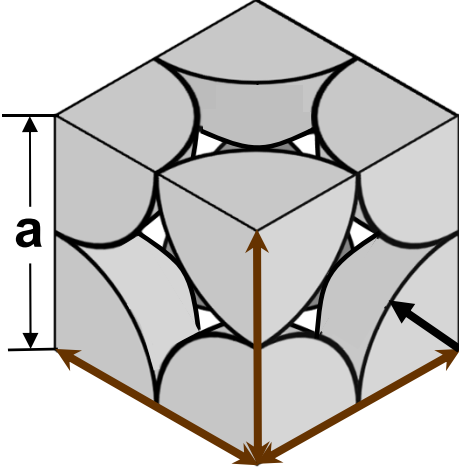
- Coordination # = 6
(# nearest neighbors)

1 atoms/unit cell: 8 corners x 1/8

Atomic Packing Factor

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

*assume hard spheres

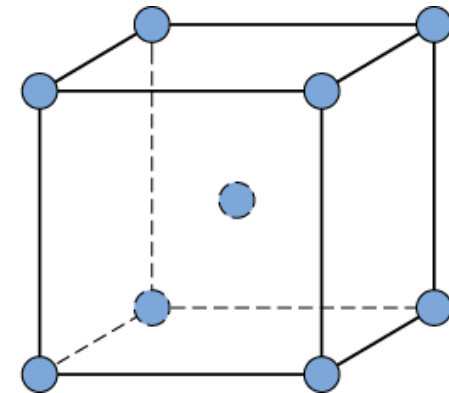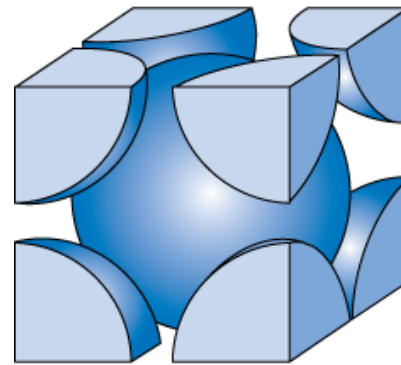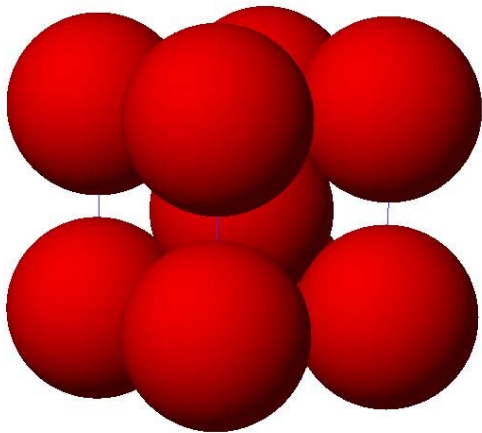- APF for a simple cubic structure = 0.52

close-packed directions

R = 0.5a

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

atoms / unit cell

volume / atom

volume / unit cell

Body Centered Cubic (BCC) Structure

- Atoms touch each other along cube diagonals.
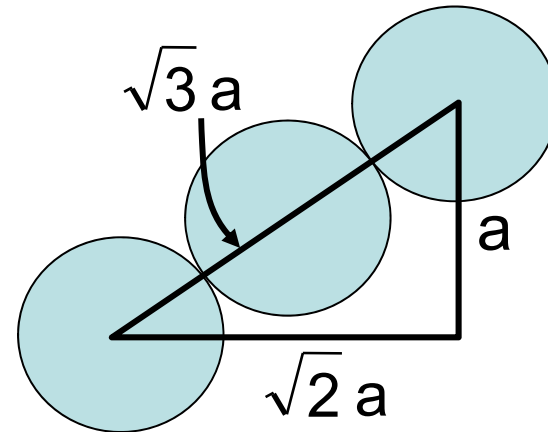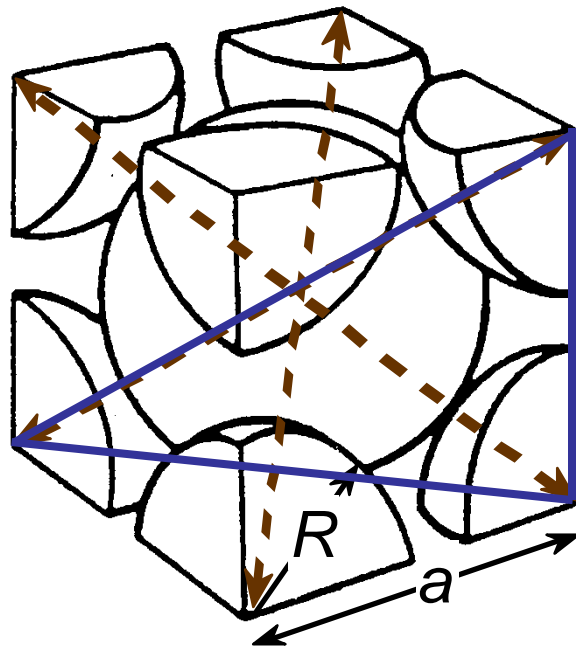
ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8

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

- APF for a body-centered cubic structure = 0.68

$\sqrt{3}\,a$

a

$\sqrt{2}\,a$

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

$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \to 2 \cdot \dfrac{4}{3}\pi \left(\dfrac{\sqrt{3}}{4}a\right)^3 \leftarrow \dfrac{\text{volume}}{\text{atom}}}{a^3 \leftarrow \dfrac{\text{volume}}{\text{unit cell}}}$$

Face Centered Cubic (FCC) Structure

• Atoms touch each other along face diagonals.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

• Coordination # = 12
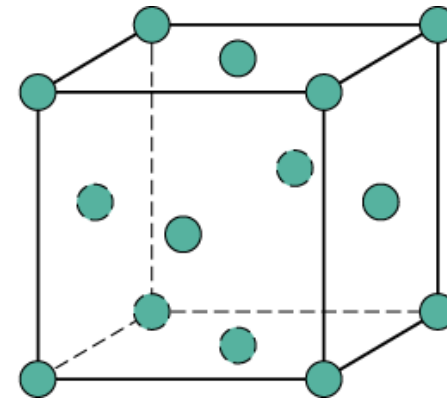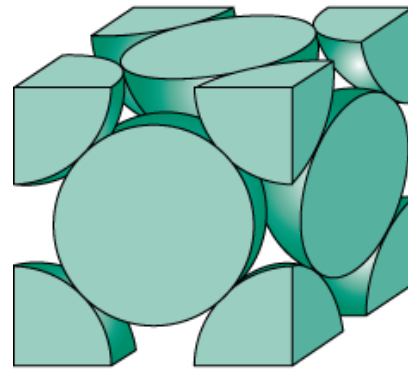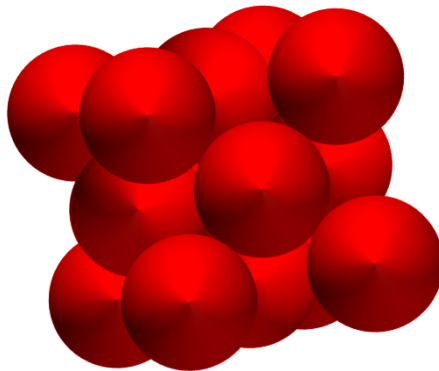
4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8
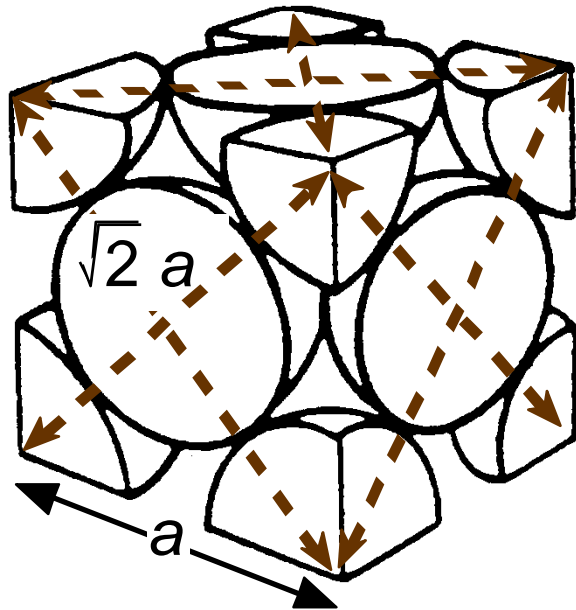
- APF for a face-centered cubic structure = 0.74
  maximum achievable APF

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

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

$$\frac{\text{atoms}}{\text{unit cell}} \quad \to \quad 4 \; \frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3 \quad \leftarrow \quad \frac{\text{volume}}{\text{atom}}$$

$$\text{APF} = \frac{}{a^3} \quad \leftarrow \quad \frac{\text{volume}}{\text{unit cell}}$$
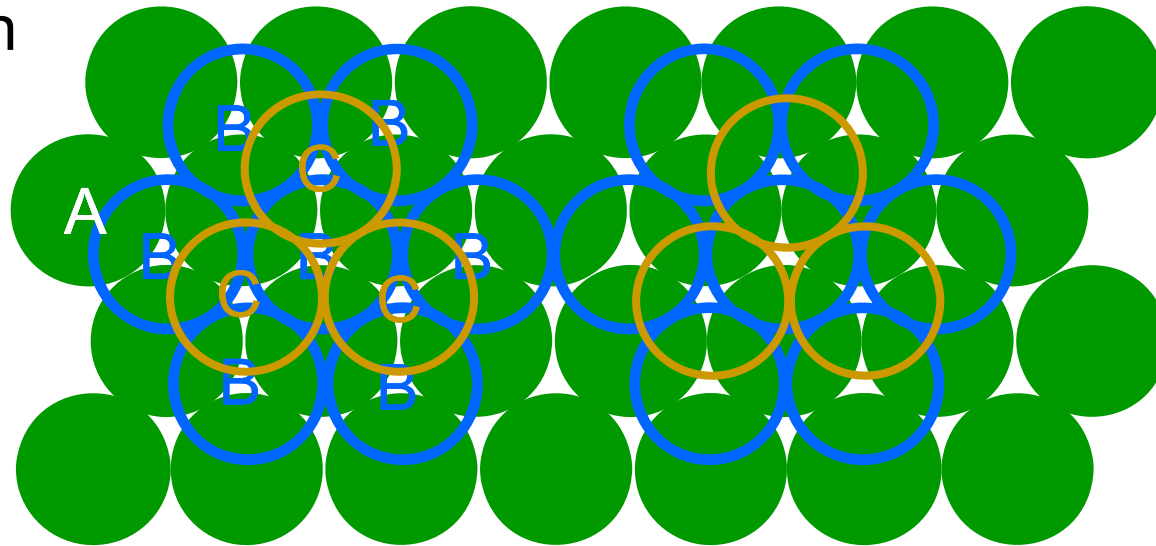
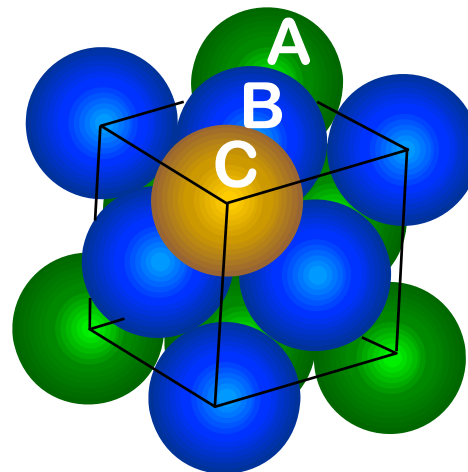# FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

  A sites
  B sites
  C sites

- FCC Unit Cell

Hexagonal Close-Packed (HCP) Structure

- ABAB... Stacking Sequence

- 3D Projection

A sites

B sites

A sites

- 2D Projection

Top layer

Middle layer

Bottom layer
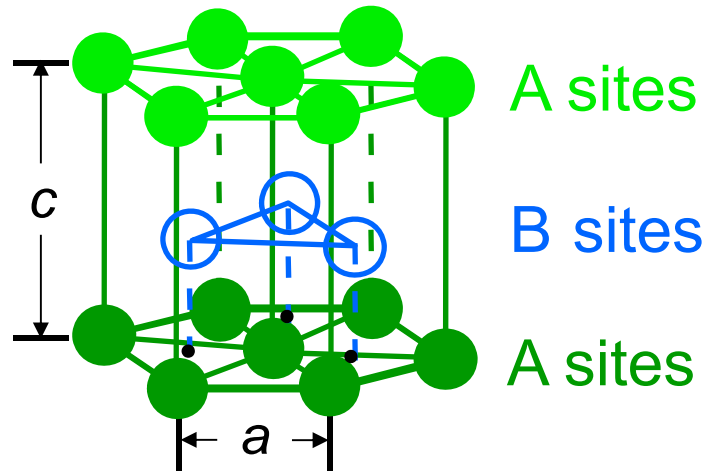
- Coordination # = 12

- APF = 0.74

- c/a = 1.633
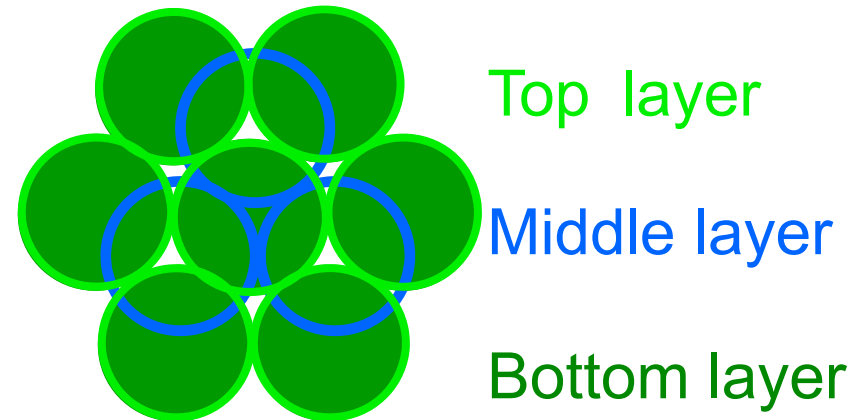
6 atoms/unit cell

ex: Cd, Mg, Ti, Zn
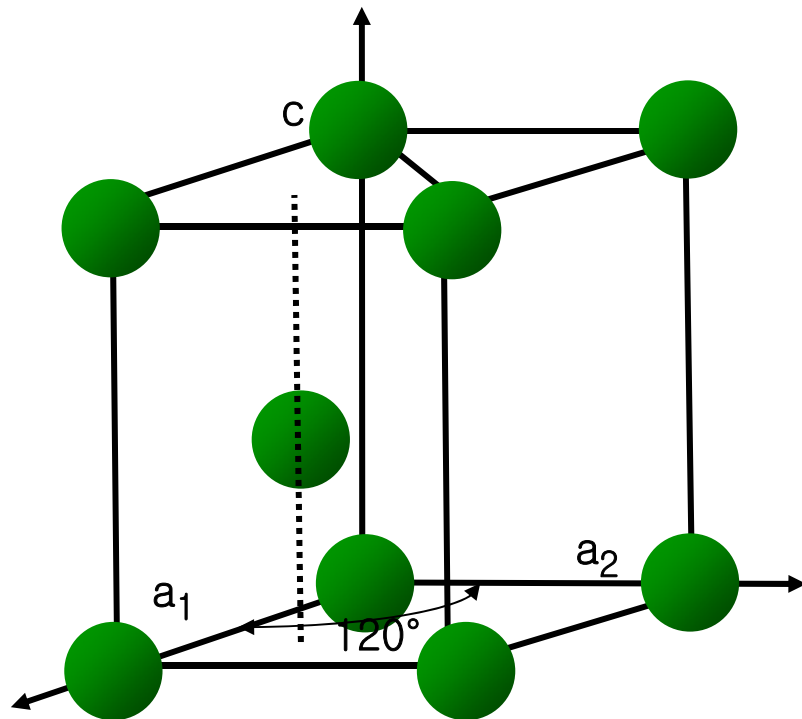
$$\frac{c}{a} = \frac{2 \times \sqrt{\frac{8}{3}} \ R}{2 \ R} = 1.633$$

$$APF_{HCP} = \frac{\frac{4}{3} \pi r^3 \times 2}{8\sqrt{2} \ R^3} = 74\%$$

Number of nearest atoms = 12

Density = ρ = $\dfrac{\text{Mass of Atoms in UnitCell}}{\text{Total Volume of UnitCell}}$

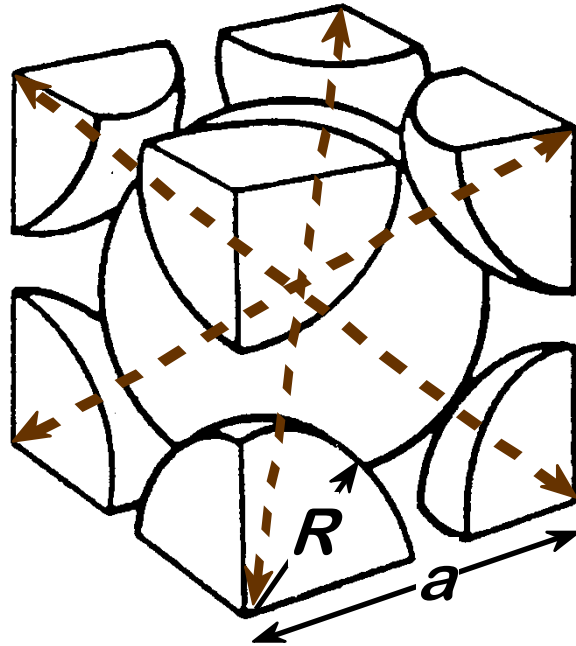$$\rho = \frac{n\,A}{V_C\,N_A}$$

where

n = number of atoms/unit cell

A = atomic weight

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

N_A = Avogadro's number
= 6.023×10^{23} atoms/mol

- Ex: Cr (BCC)

A = 52.00 g/mol

R = 0.125 nm

n = 2

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

$$\rho = \frac{\overset{\text{atoms/unit cell}}{2} \times \overset{\text{g/mol}}{52.00}}{\underset{\text{volume/unit cell}}{a^3} \times \underset{\text{atoms/mol}}{6.023 \times 10^{23}}}$$

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

ρ_{actual} = 7.19 g/cm^3

Comparing X-ray density with bulk density

can check if there are vacant atom sites or

extra atoms (interstitials).

Characteristics of Selected Elements at 20°C

Element	Symbol	At. Weight (amu)	Density (g/cm^3)	Crystal Structure	Atomic radius (nm)
Aluminum	Al	26.98	2.71	FCC	0.143
Argon	Ar	39.95	------	------	------
Barium	Ba	137.33	3.5	BCC	0.217
Beryllium	Be	9.012	1.85	HCP	0.114
Boron	B	10.81	2.34	Rhomb	------
Bromine	Br	79.90	------	------	------
Cadmium	Cd	112.41	8.65	HCP	0.149
Calcium	Ca	40.08	1.55	FCC	0.197
Carbon	C	12.011	2.25	Hex	0.071
Cesium	Cs	132.91	1.87	BCC	0.265
Chlorine	Cl	35.45	------	------	------
Chromium	Cr	52.00	7.19	BCC	0.125
Cobalt	Co	58.93	8.9	HCP	0.125
Copper	Cu	63.55	8.94	FCC	0.128
Flourine	F	19.00	------	------	------
Gallium	Ga	69.72	5.90	Ortho.	0.122
Germanium	Ge	72.59	5.32	Dia. cubic	0.122
Gold	Au	196.97	19.32	FCC	0.144
Helium	He	4.003	------	------	------
Hydrogen	H	1.008	------	------	------

Densities of Material Classes

ρ**metals** ? ρ**ceramics** ? ρ**polymers**

Why?

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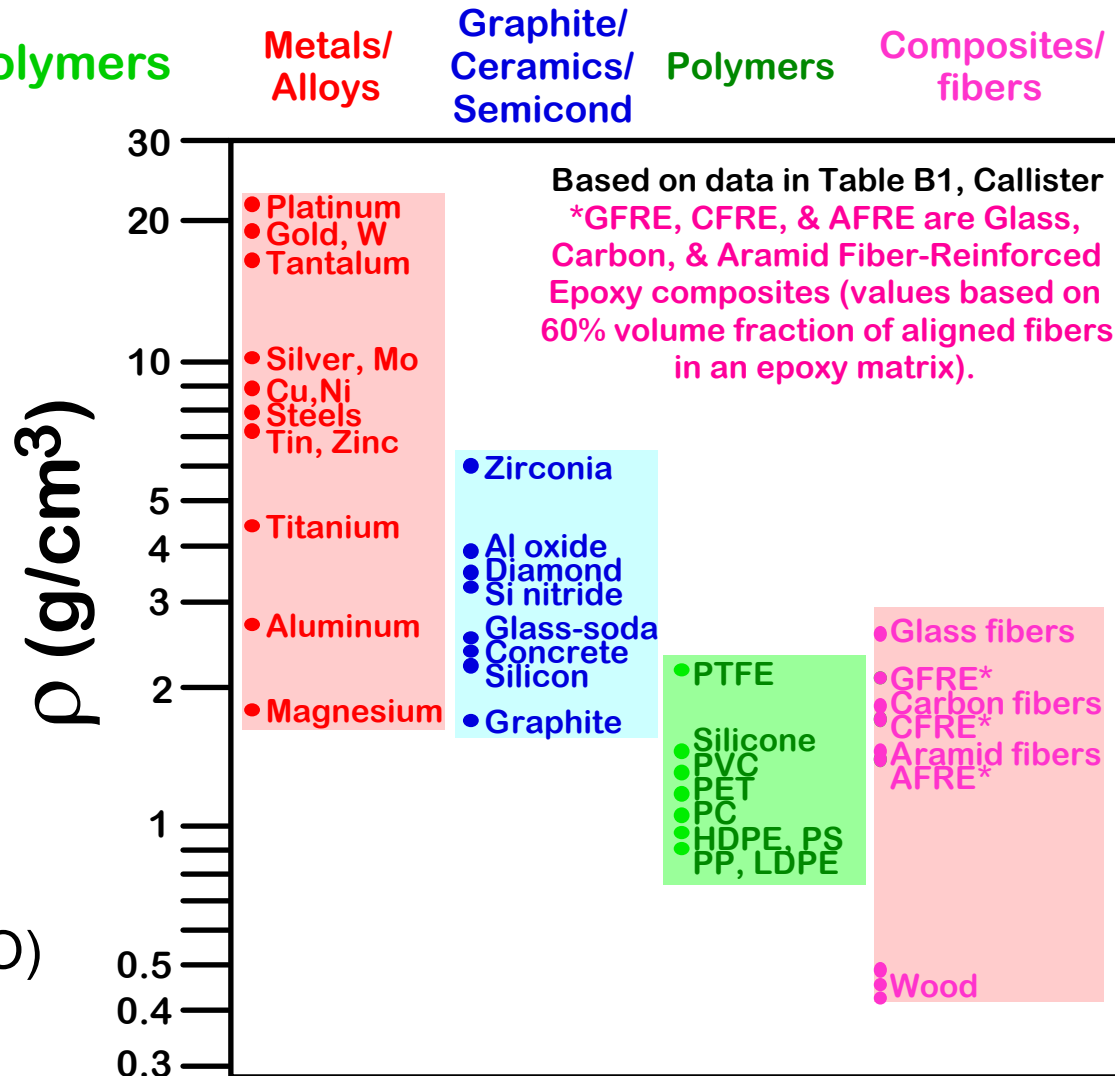 (metallic bonding)
- large atomic mass

Ceramics have...
- less dense packing
  (covalent bonding)
- often lighter elements

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

Composites have...
- intermediate values

Metals/ Alloys

Graphite/ Ceramics/ Semicond

Polymers

Composites/ fibers

ρ (g/cm^3)

30
20
10
5
4
3
2
1
0.5
0.4
0.3

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).

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

- Zirconia
- Al oxide
- Diamond
- Si nitride
- Glass-soda
- Concrete
- Silicon
- Graphite

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

- Glass fibers
- GFRE*
- Carbon fibers
- CFRE*
- Aramid fibers
- AFRE*
- Wood

Data from Table B1, *Callister 6e.*

Ceramic Bonding

- Bonding:
  --Mostly ionic, some covalent.
  --% ionic character increases with difference in electronegativity.

- Large vs small ionic bond character:

CaF$_2$: large

SiC : small

Figure 2.7
© John Wiley & Sons, Inc. All rights reserved.

Ionic Bonding & Structure

- **Charge Neutrality**:
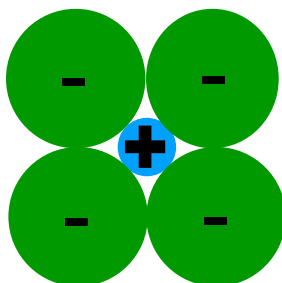 --Net charge in the structure should be zero.

CaF_2: ● Ca^{2+} cation **+** ● ● F^- anions, F^-
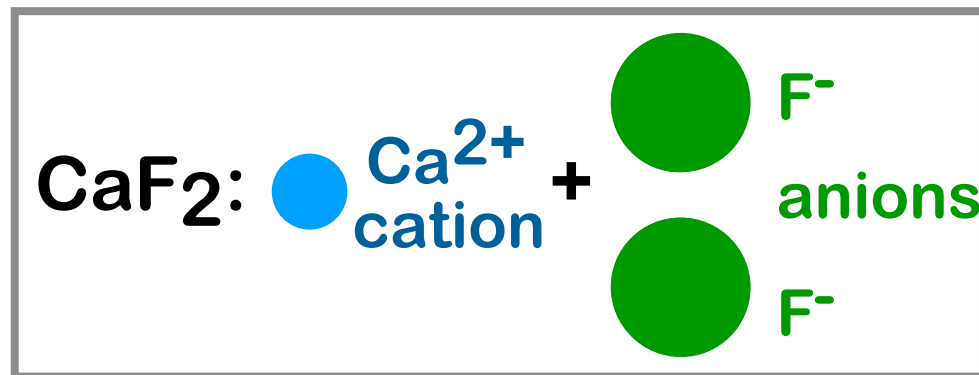
--General form: $A_m X_p$

m, p determined by charge neutrality

- **Stable structures**:
  --maximize the # of nearest oppositely charged neighbors.
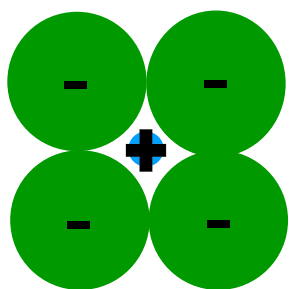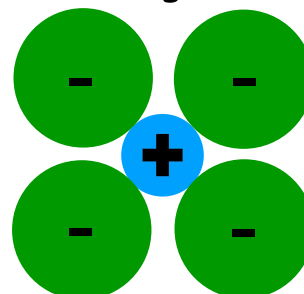
Unstable   **Stable**   **Stable**

Figure 3.4
© John Wiley & Sons, Inc. All rights reserved.

Coordination No. and Ionic Radii

- Coordination # increases with $\dfrac{r_{cation}}{r_{anion}}$

  Issue: How many anions can you arrange around a cation?

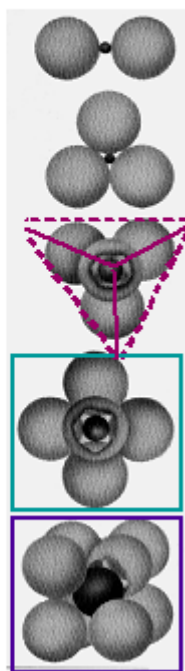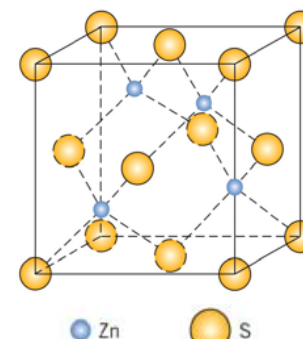| $\dfrac{r_{cation}}{r_{anion}}$	Coord #
< .155	2
.155-.225	3
.225-.414	4
.414-.732	6
.732-1.0	8

Figure 3.7
Zn   S
© John Wiley & Sons, Inc. All rights reserved.
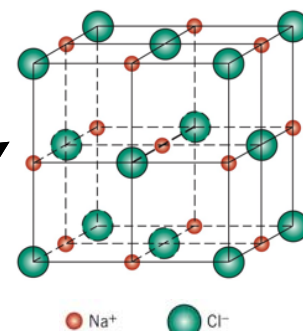
Figure 3.5
Na+   Cl–
© John Wiley & Sons, Inc. All rights reserved.
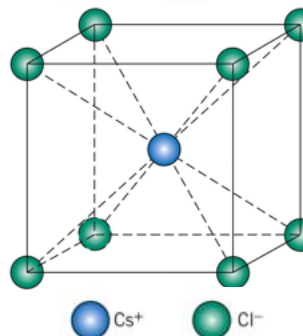
Figure 3.6
Cs+   Cl–
© John Wiley & Sons, Inc. All rights reserved.

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100

Anion	
O^{2-}	0.140
Cl^-	0.181
F^-	0.133

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140}$$

$$= 0.550$$

based on this ratio,
--coord # = 6
--structure = NaCl

- Compounds: Often have similar close-packed structures.

- Structure of NaCl

- Close-packed directions
  --along cube edges.
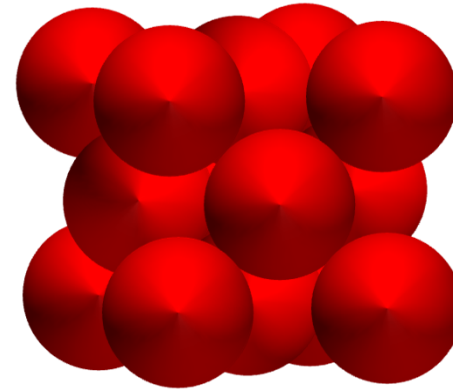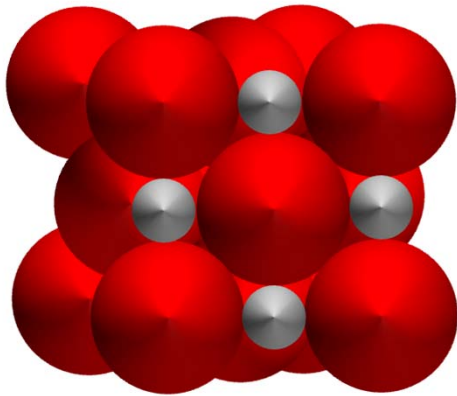
A_mX_p Structures

- Consider CaF_2 : $\dfrac{r_{cation}}{r_{anion}} = \dfrac{0.100}{0.133} \approx 0.8$

- Based on this ratio, coord # = 8 and structure = CsCl.
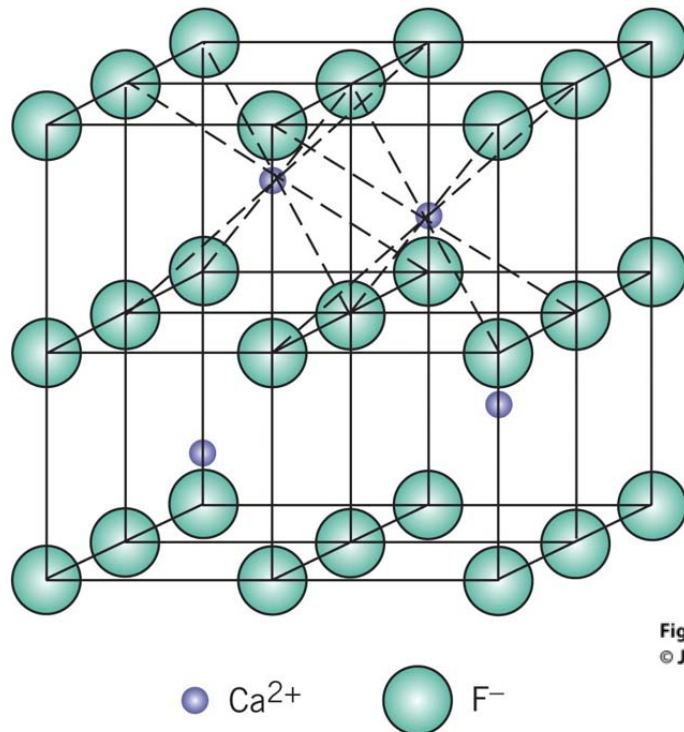- Result: CsCl structure w/only half the cation sites occupied.

- Only half the cation sites are occupied since #Ca^{2+} ions = 1/2 # F^- ions.

Figure 3.8
© John Wiley & Sons, Inc. All rights reserved.

○ Ca^{2+} ● F^-
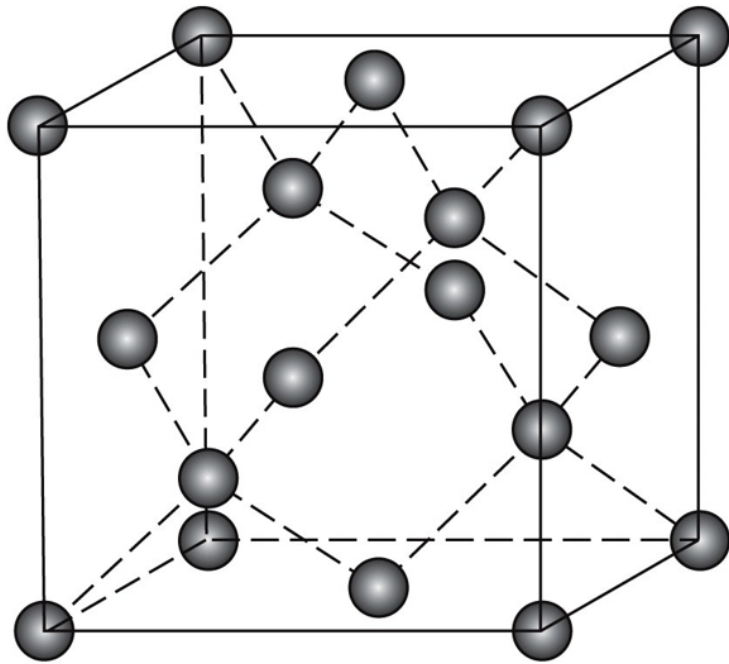
Figure 3.16
© John Wiley & Sons, Inc. All rights reserved.

C
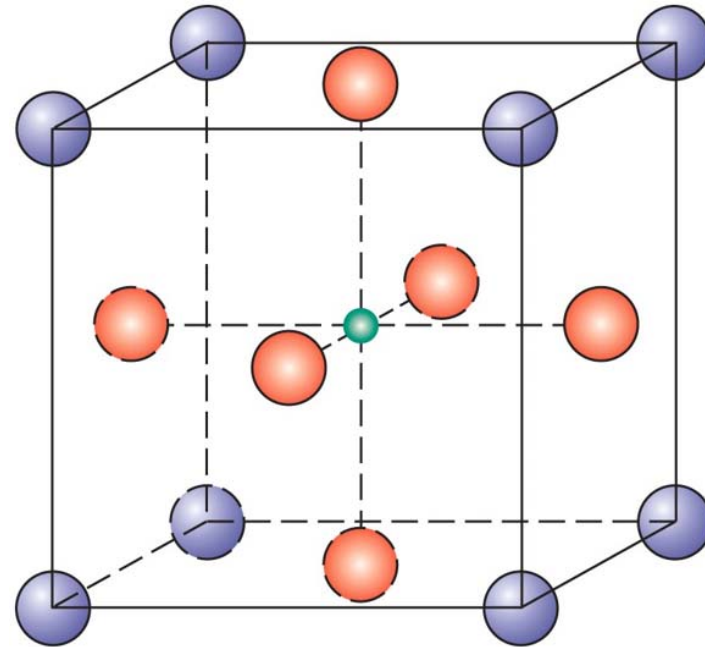
Figure 3.9
© John Wiley & Sons, Inc. All rights reserved.

Ti^{4+} Ba^{2+} O^{2-}

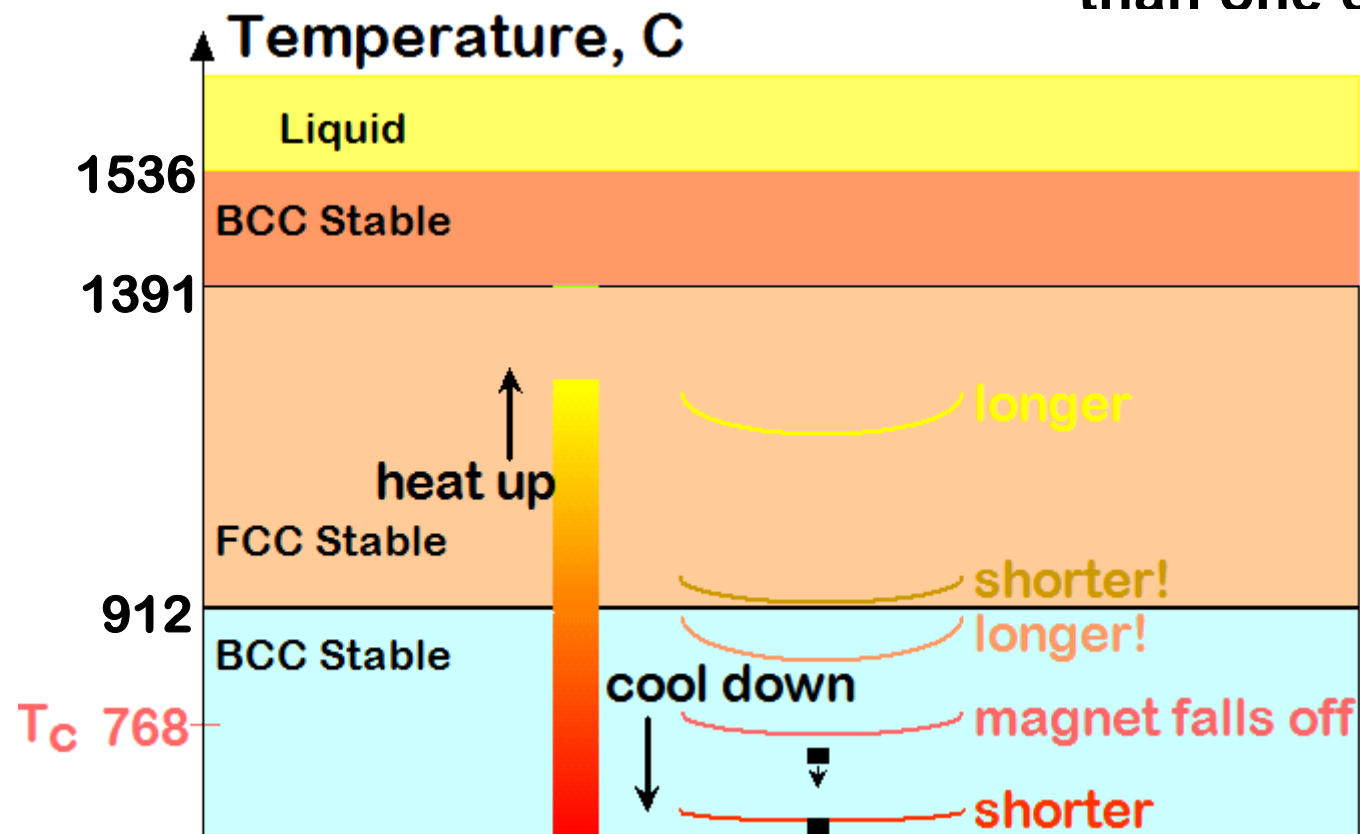**Diamond structure**   **Perovskite structure**

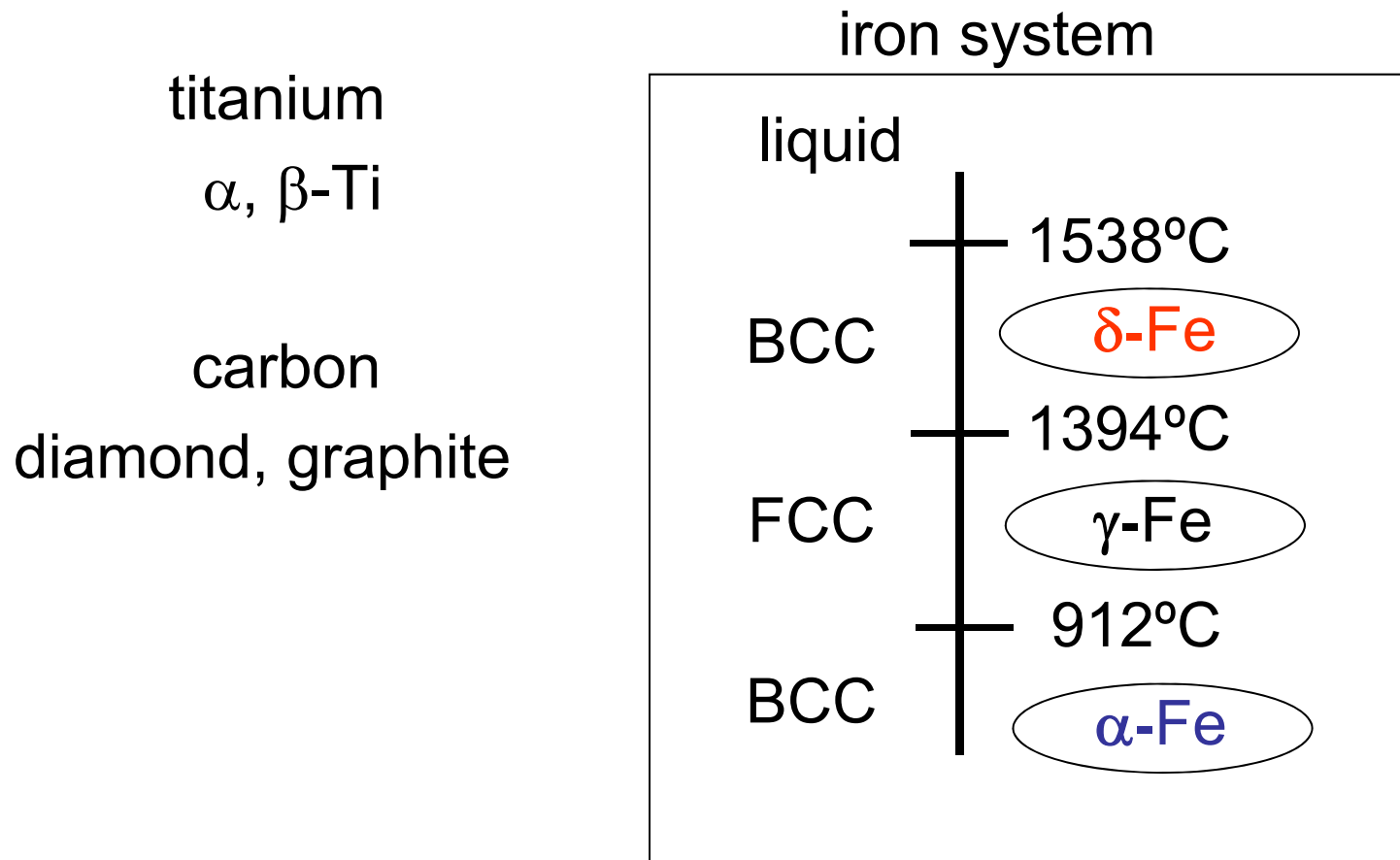# Heating and Cooling of an Iron Wire

α-Fe (BCC)   912℃   γ -Fe (FCC)

- Demonstrates "polymorphism" ← The same atoms can have more than one crystal

Polymorphism

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

titanium

α, β-Ti

carbon

diamond, graphite

iron system

liquid

1538ºC

BCC δ-Fe

1394ºC

FCC γ-Fe

912ºC

BCC α-Fe

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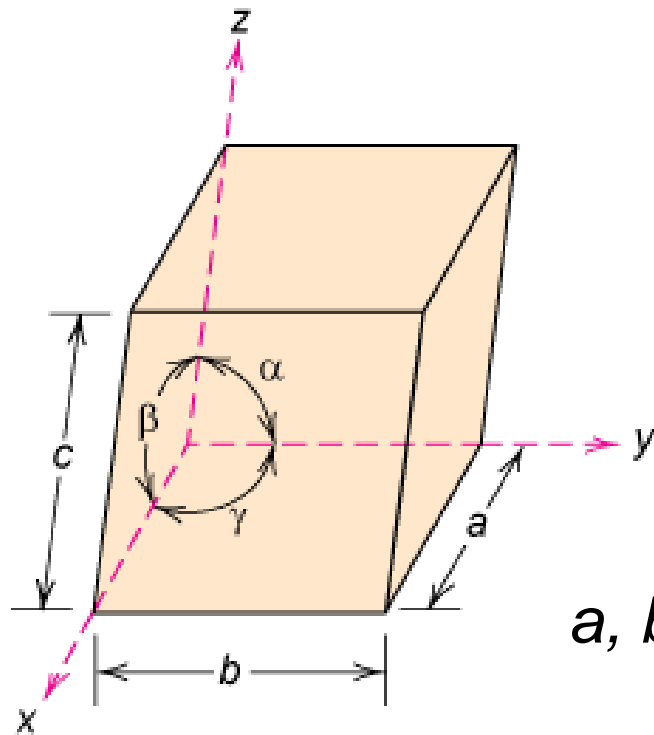
7 crystal systems

14 crystal lattices

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

Figure 3.20
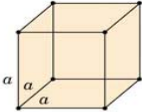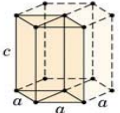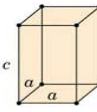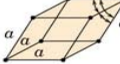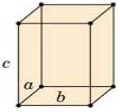© John Wiley & Sons, Inc. All rights reserved.
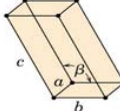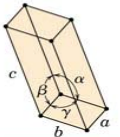
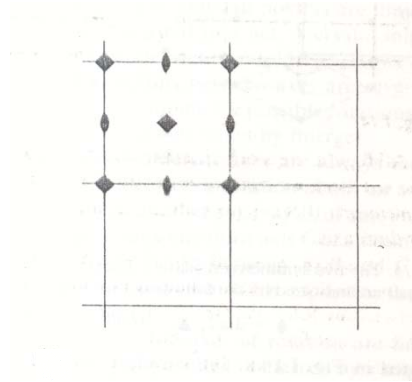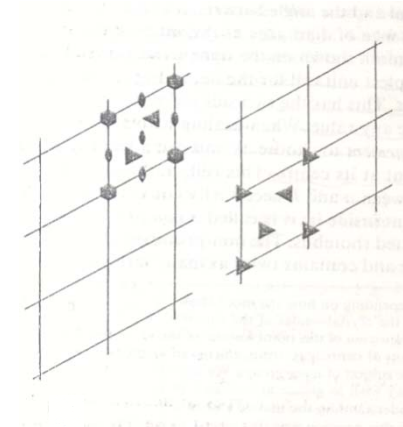| Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry	
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$		(P, B, F)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$		(P)
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$		(P, B)
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$		(P)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$		(P, B, F, B)
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$		(P, B)
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$		(P)

Table 3.6

Five Symmetrical Plane Lattices
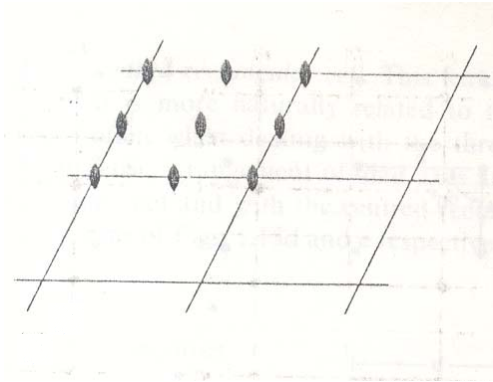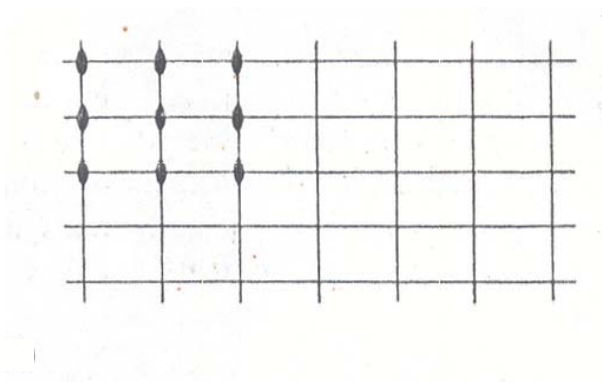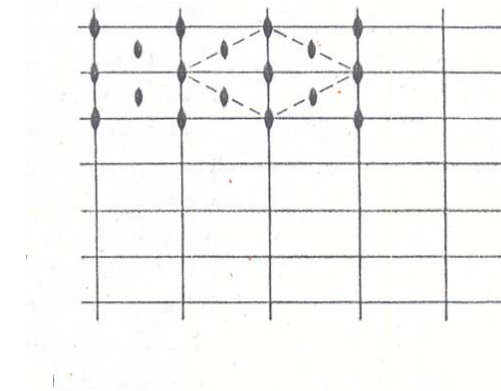

(a) Parallelogram

(b) Square

(c) Rhombus

(d) Rectangle

(e) Diamond

Seven Crystal Systems

Seven crystal systems : based on crystal symmetry

Cubic	-	four 3 fold mutually at 70°
Hexagonal	-	one 6 fold
Trigonal	-	one 3 fold (pulled out cubic along diagonal of cubic)
Tetragonal	-	one 4 fold (pulled out cubic along one edge)
Orthorhombic	-	three mutually perpendicular 2 fold
Monoclinic	-	one 2 fold
Triclinic	-	none

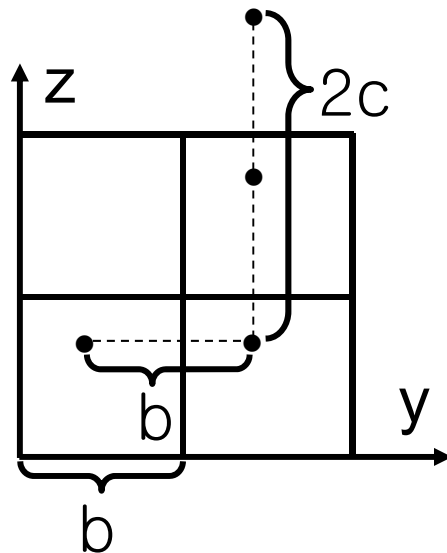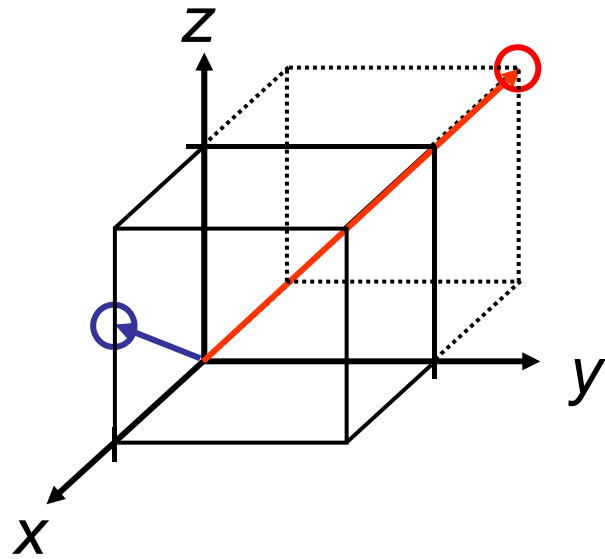# Point Coordinates
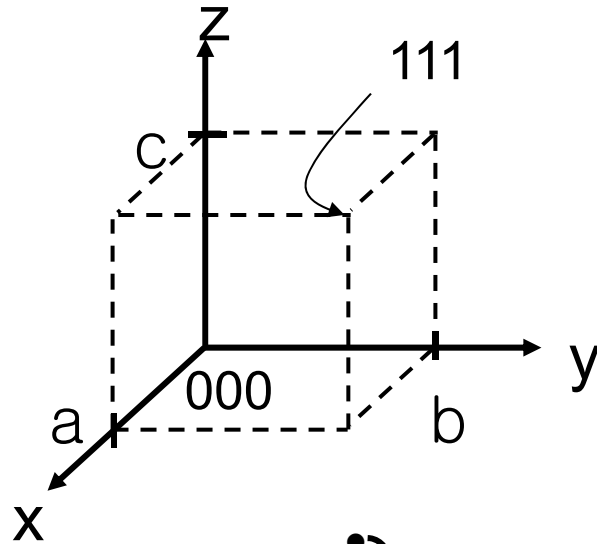
Point coordinates for unit cell center are

$$a/2, b/2, c/2 \qquad ½ ½ ½$$

Point coordinates for unit cell corner are 111

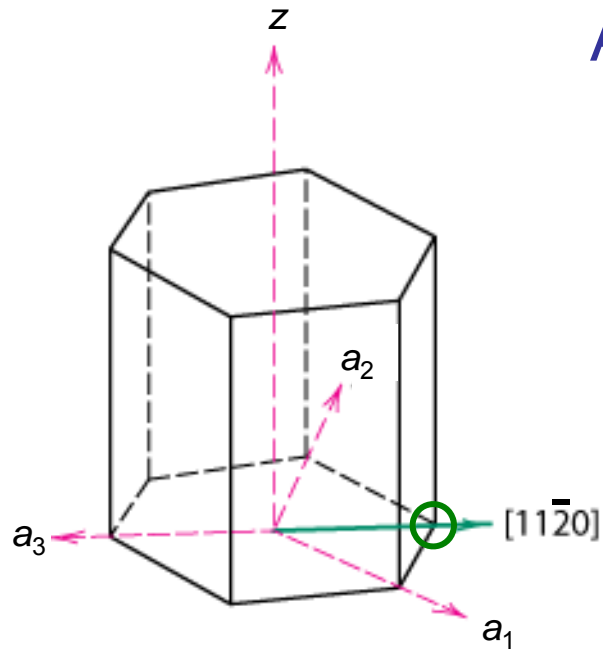Translation: integer multiple of lattice constants → identical position in another unit cell

Algorithm

1. Vector repositioned (if necessary) to pass through origin.

2. Read off projections in terms of unit cell dimensions a, b, and c.

3. Adjust to smallest integer values.

4. Enclose in square brackets, no commas [uvw].

ex: 1, 0, ½ => 2, 0, 1 => [201]

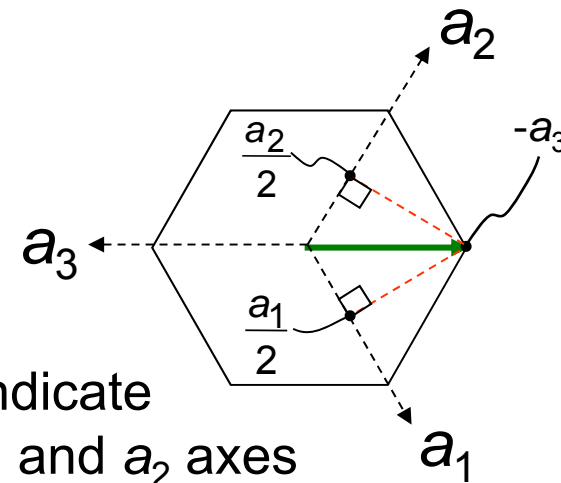-1, 1, 1 => [$\bar{1}$11]   where overbar represents a negative index

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 $[uvtw]$

$[11\bar{2}0]$

ex: ½, ½, -1, 0   => $[11\bar{2}0]$

dashed red lines indicate projections onto a_1 and a_2 axes

For hexagonal system (uvtw),   t = −(u+v)

Conversion from the three-index system to four-index system
[u´v´w´] → [uvtw]

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

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

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

$$w = nw'$$

Direction [uvw], Family of directions <uvw>
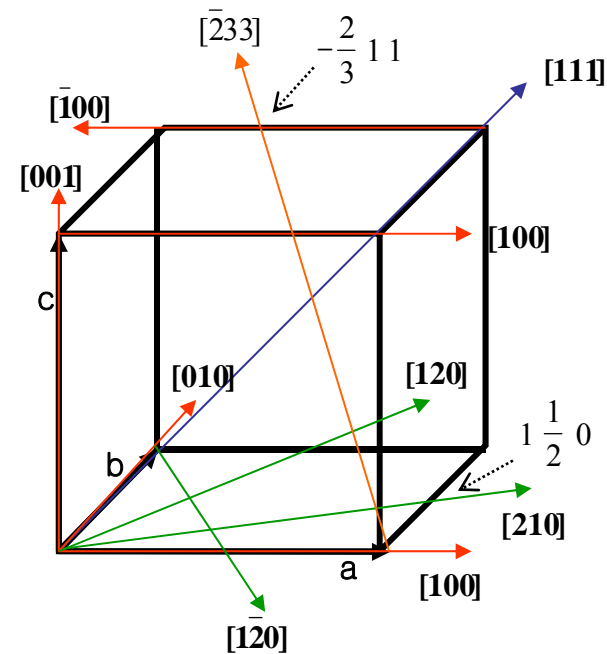
Example < 110 >

$[1\bar{1}0][10\bar{1}][01\bar{1}][\bar{1}10][1\bar{1}0][\bar{1}01]$

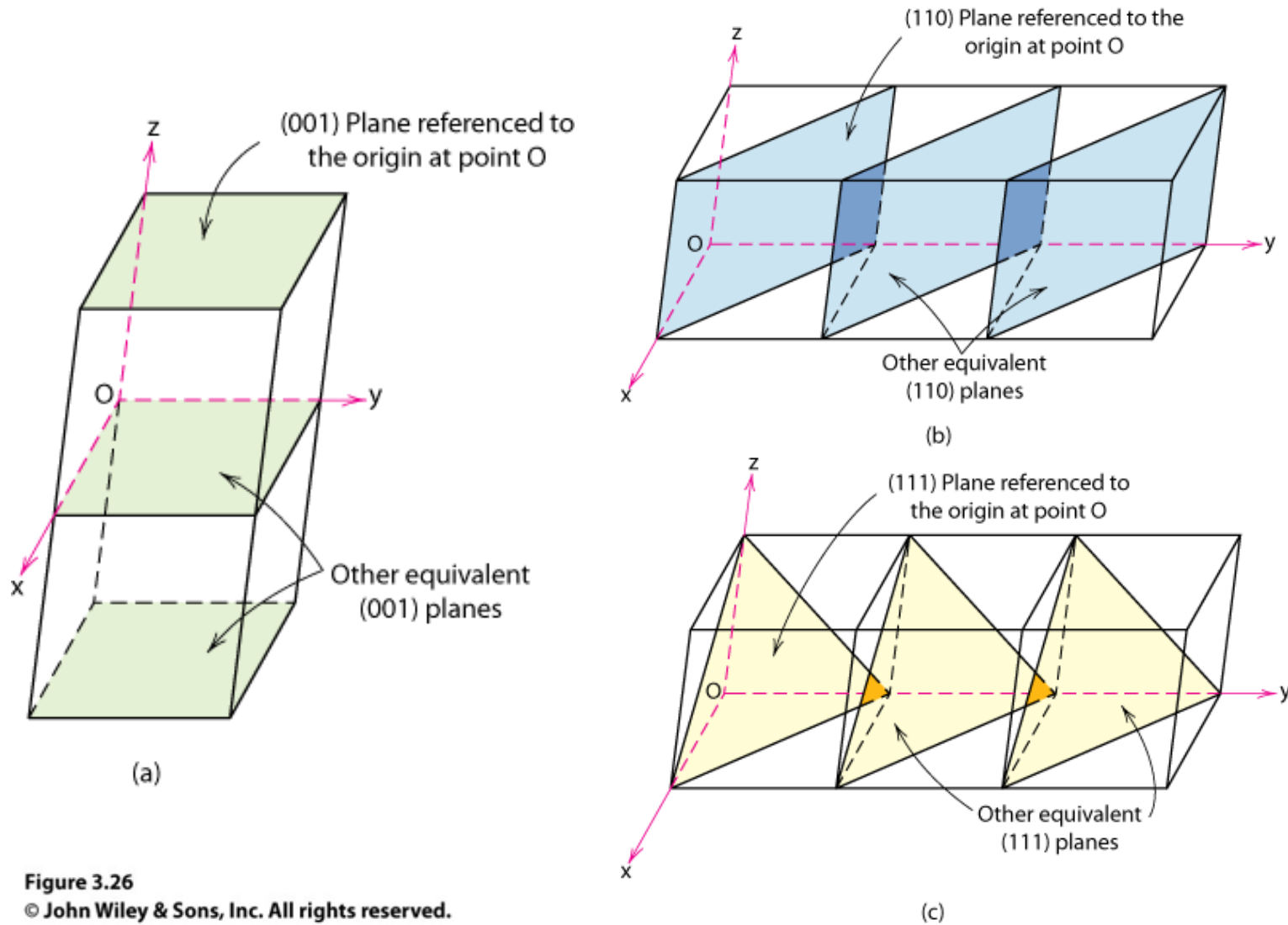$[10\bar{1}][0\bar{1}1][01\bar{1}][0\bar{1}\bar{1}][\bar{1}\bar{1}0][\bar{1}0\bar{1}]$

<110> : Face diagonal

<111> : Cube diagonal

<100> : Cube edge

(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)

Figure 3.26

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)		
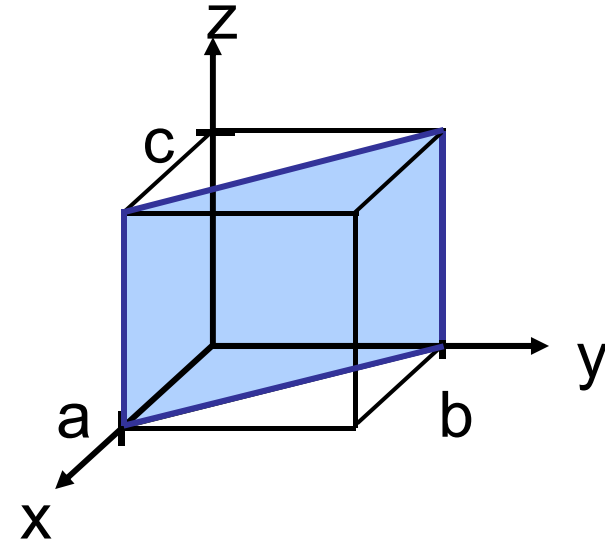
example

		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/ ∞	1/ ∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(200)		
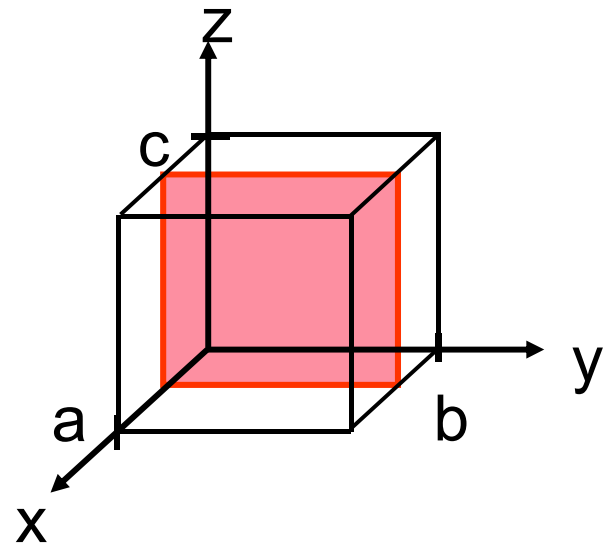
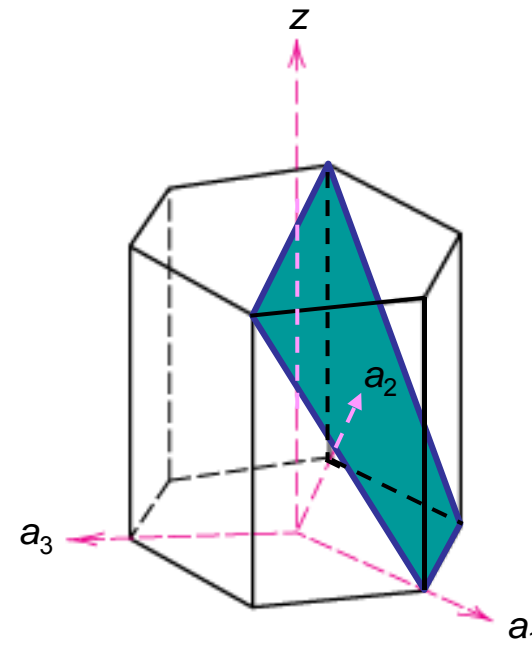|	example	a	b	c
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		
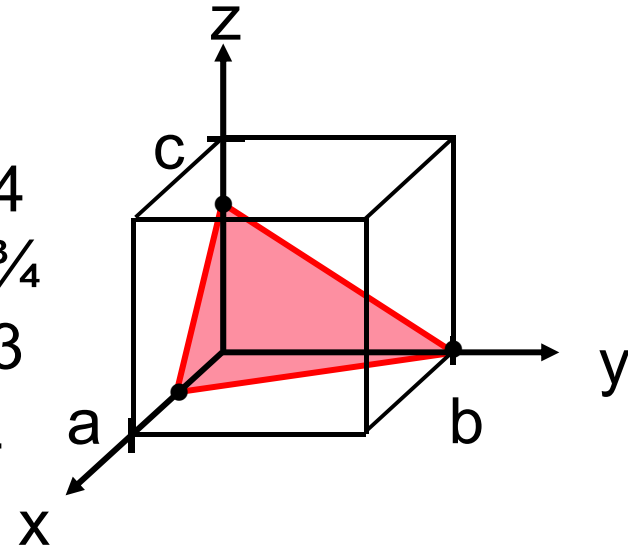
Family of Planes   {hkl}

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

- 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	1
	1	0	-1	1
3. Reduction	1	0	-1	1

4. Miller-Bravais Indices $(10\bar{1}1)$

Crystallographic Directions and Planes

In cubic system, planes are perpendicular to direction.

It does not apply for other systems.

For cubic system,

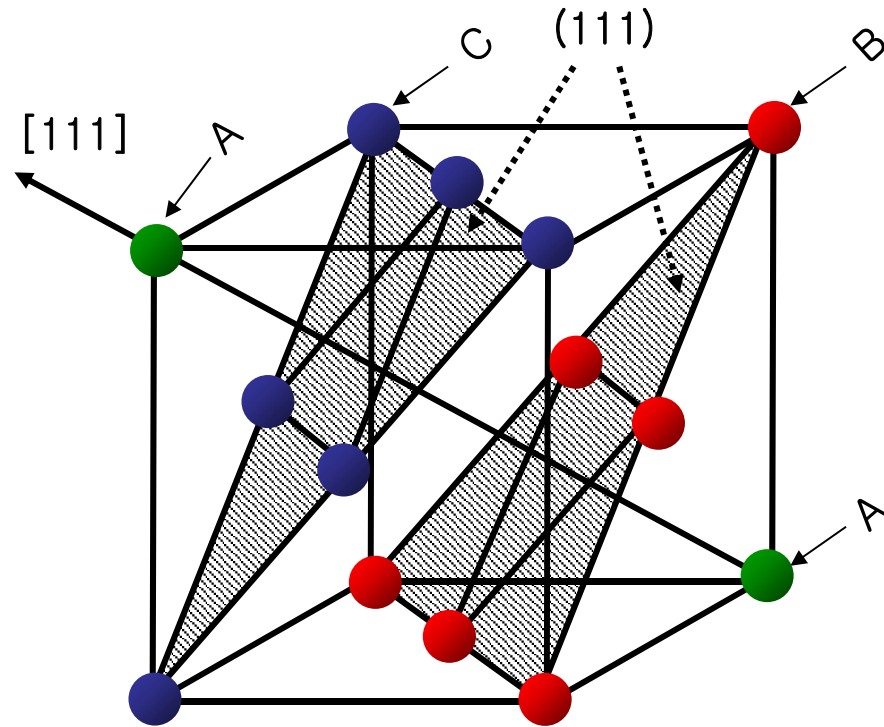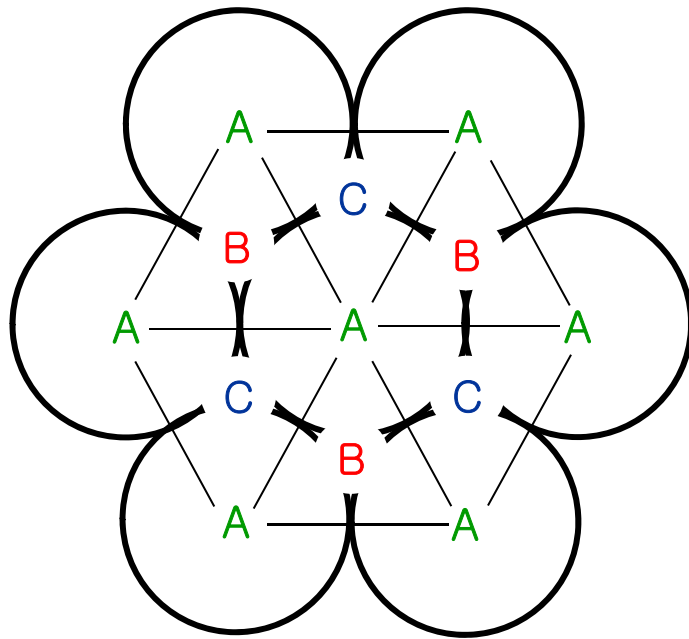$$\cos \theta = \frac{A \times B}{|A|\ |B|}$$

For example,

(111), (100)

$$\cos \theta = \frac{1 \times 1 + 1 \times 0 + 1 \times 0}{\sqrt{1^2 + 1^2 + 1^2} \cdot \sqrt{1^2 + 0^2 + 0^2}}$$

$$= \frac{1}{\sqrt{3}}$$

$$\therefore \theta = 54.74°$$

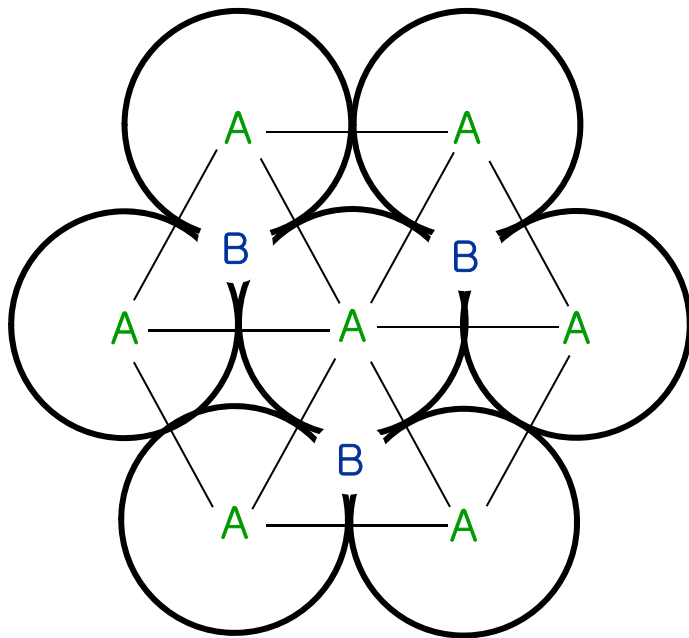cf) directions included in a plane
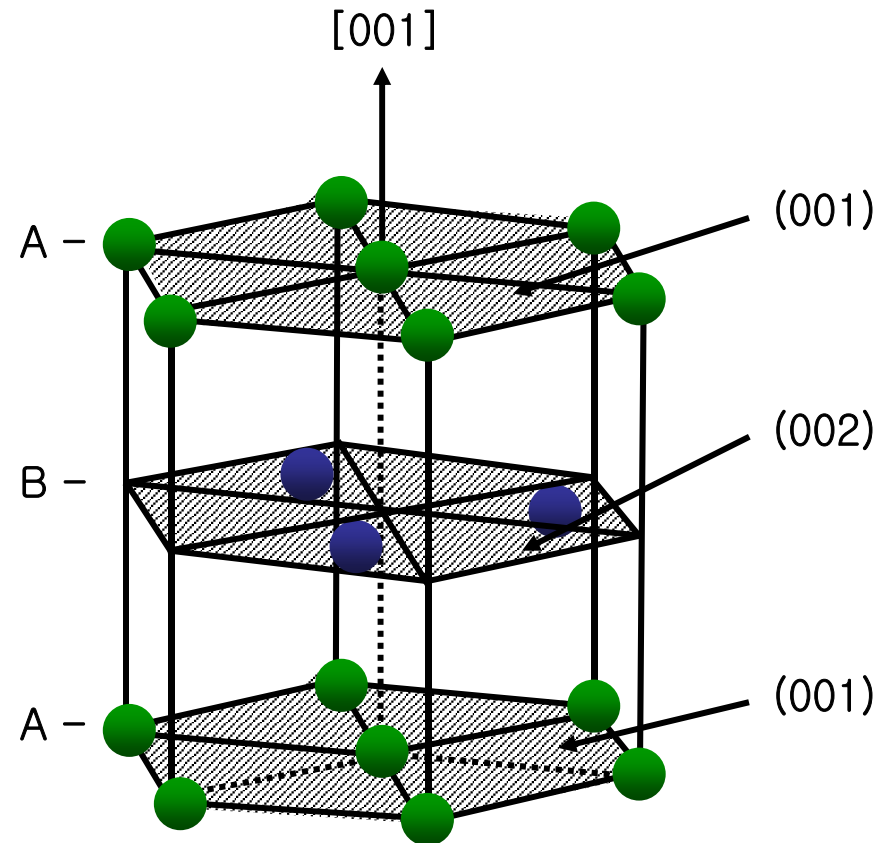
Close Packed Structure - FCC

FCC : ABCABCABC……

Stacking of (111) Planes

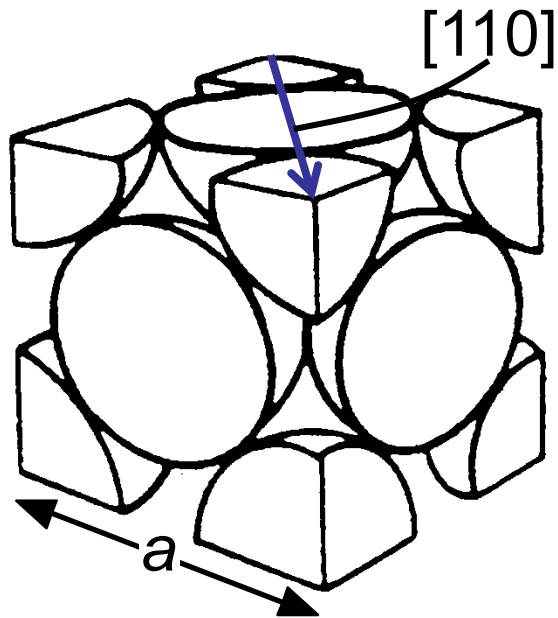HCP : ABABABAB……

[001]

A —

B —

A —

(001)

(002)

(001)

Stacking of (002) planes

Linear Density

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

[110]

Ex) Linear density of Al in [110] direction

a = 0.405 nm

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

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.

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

2D repeat unit

(100)

$$a = \frac{4\sqrt{3}}{3}R$$
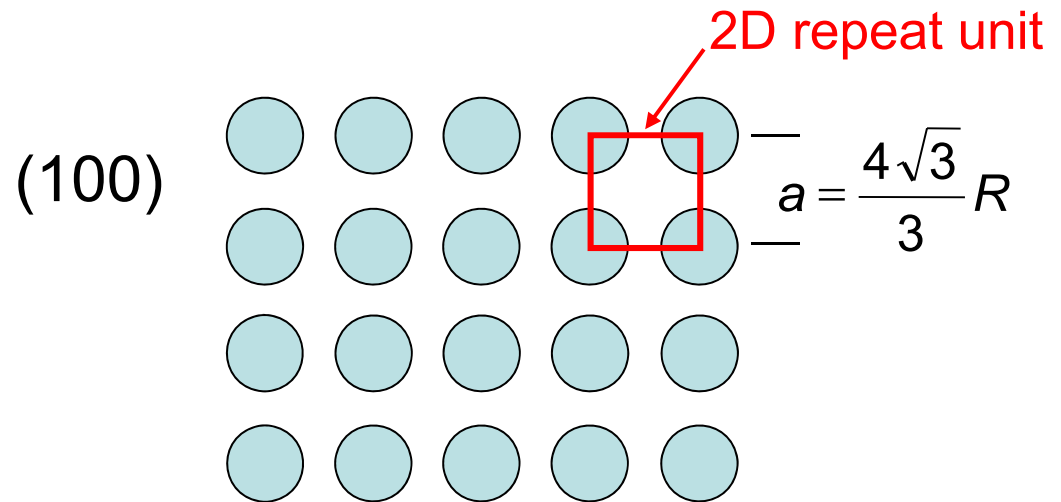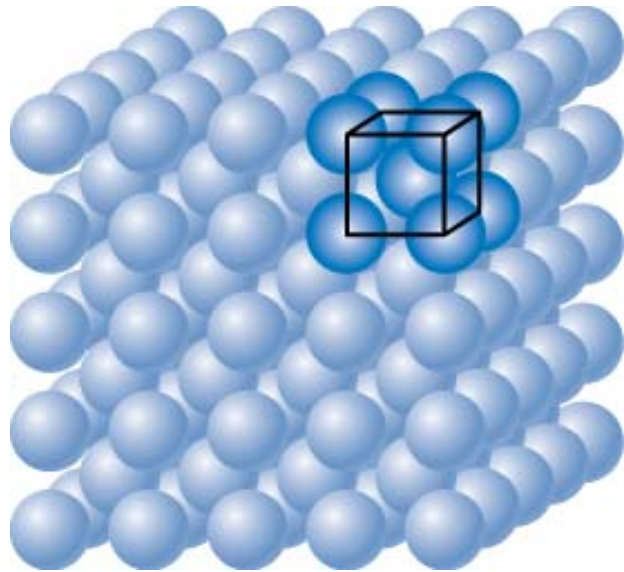
Figure 3.2

Radius of iron $R = 0.1241$ nm

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

Planar Density of (111) Iron

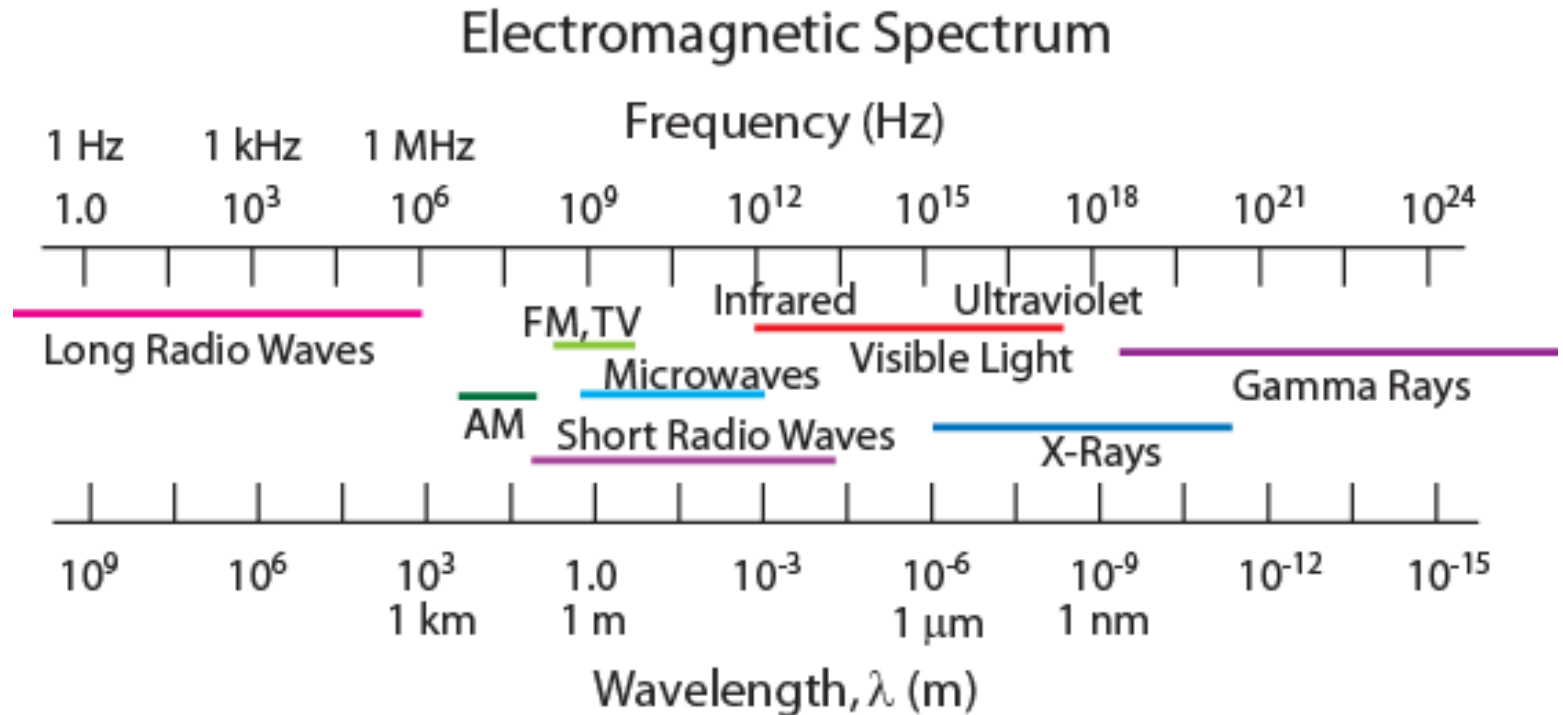**Solution (cont): (111) plane**

1 atom in plane/ unit surface cell

$\sqrt{2}\,a$ ○ atoms in plane

● atoms above plane

○ atoms below plane

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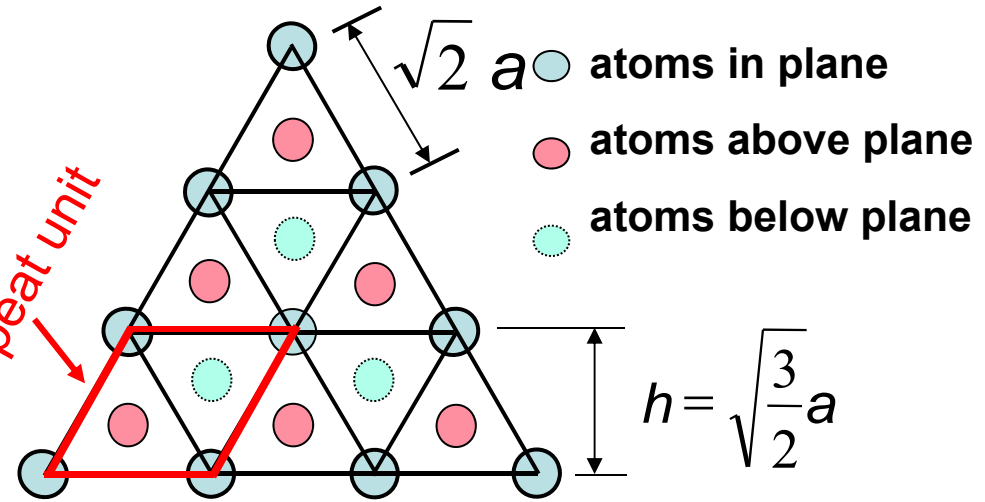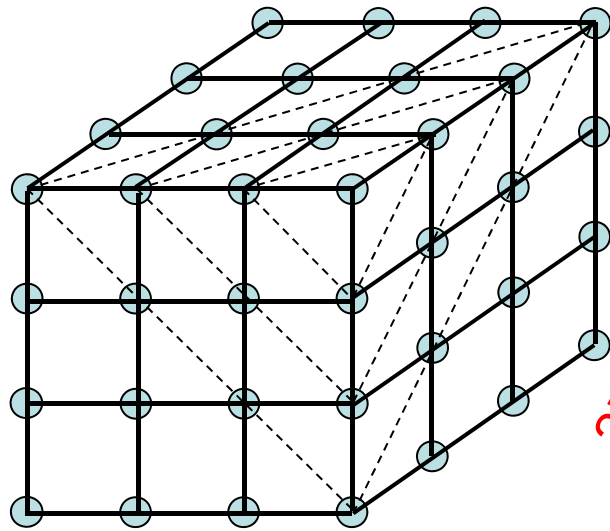
$$\text{area} = \sqrt{2}\,ah = \sqrt{3}\,a^2 = \sqrt{3}\left(\dfrac{4\sqrt{3}}{3}R\right)^2 = \dfrac{16\sqrt{3}}{3}R^2$$

$$\text{Planar Density} = \dfrac{\dfrac{\text{atoms}}{\text{2D repeat unit}} \;\; 1}{\dfrac{\text{area}}{\text{2D repeat unit}} \;\; \dfrac{16\sqrt{3}}{3}R^2} = 7.0\dfrac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19}\,\dfrac{\text{atoms}}{\text{m}^2}$$
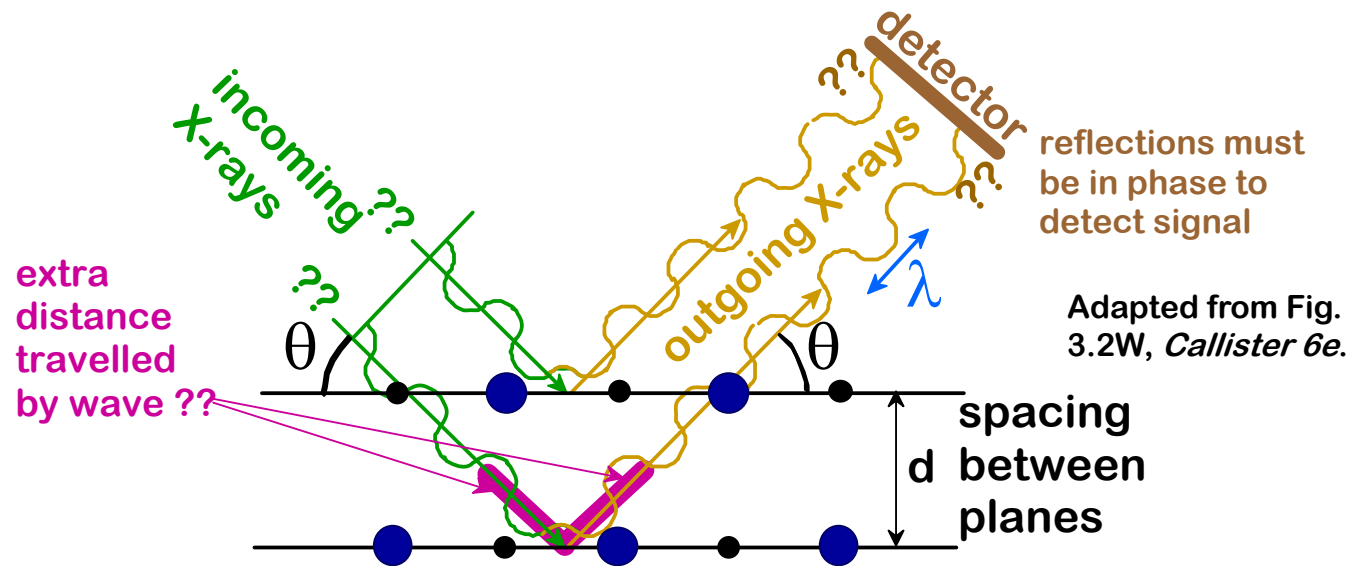
X-Ray Diffraction

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 Confirm Crystal Structure

- Incoming X-rays diffract from crystal planes.

incoming X-rays ??

??

θ

extra distance travelled by wave ??

detector ??

outgoing X-rays ??

λ

reflections must be in phase to detect signal

θ

Adapted from Fig. 3.2W, *Callister 6e*.

d spacing between planes

- Measurement of: Critical angles, q_c, for X-rays provide atomic spacing, d.

x-ray intensity (from detector)

$d = n\lambda / 2\sin\theta_c$

θ

θ_c
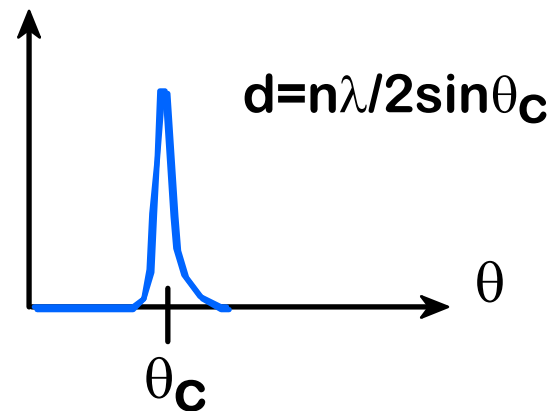
Crystalline and Noncrystalline Materials

X-ray diffraction

: advantages in X-rays for crystal structure analysis

wavelength 0.1~10 Å which is comparable to crystal lattice
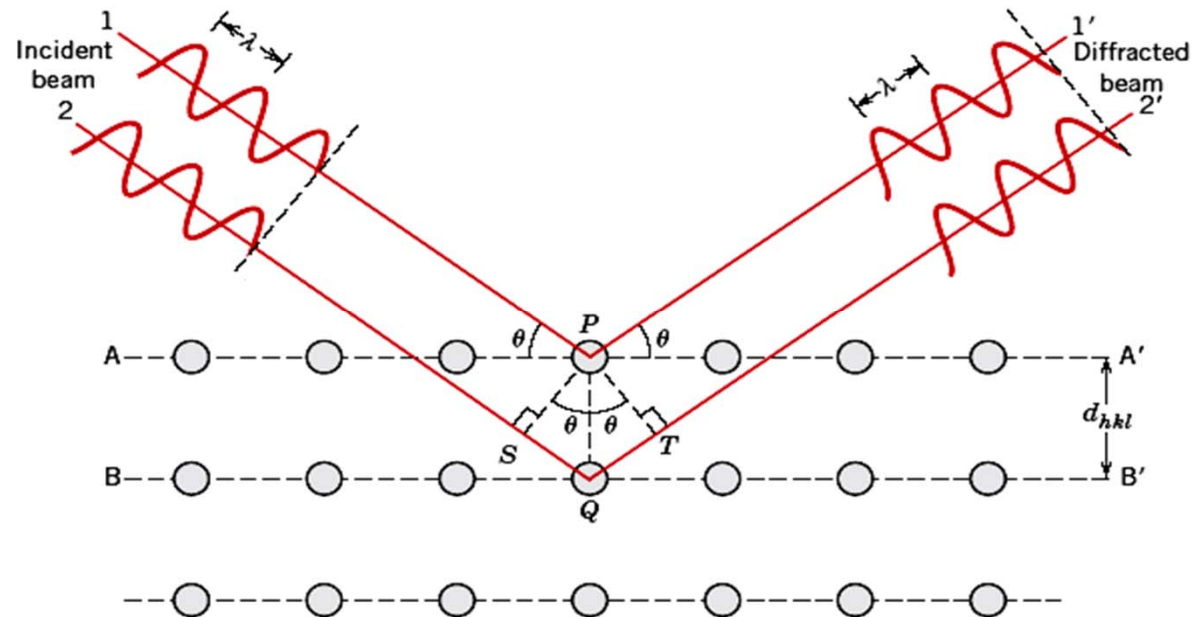
Bragg's law : $\lambda = 2d \sin\theta$

Figure 3.38

Uses monochromic X-ray $Cu_{K\alpha}$ (1.5418 Å)

Cubic system $d_{hkl} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

θ : variable, a : lattice constant
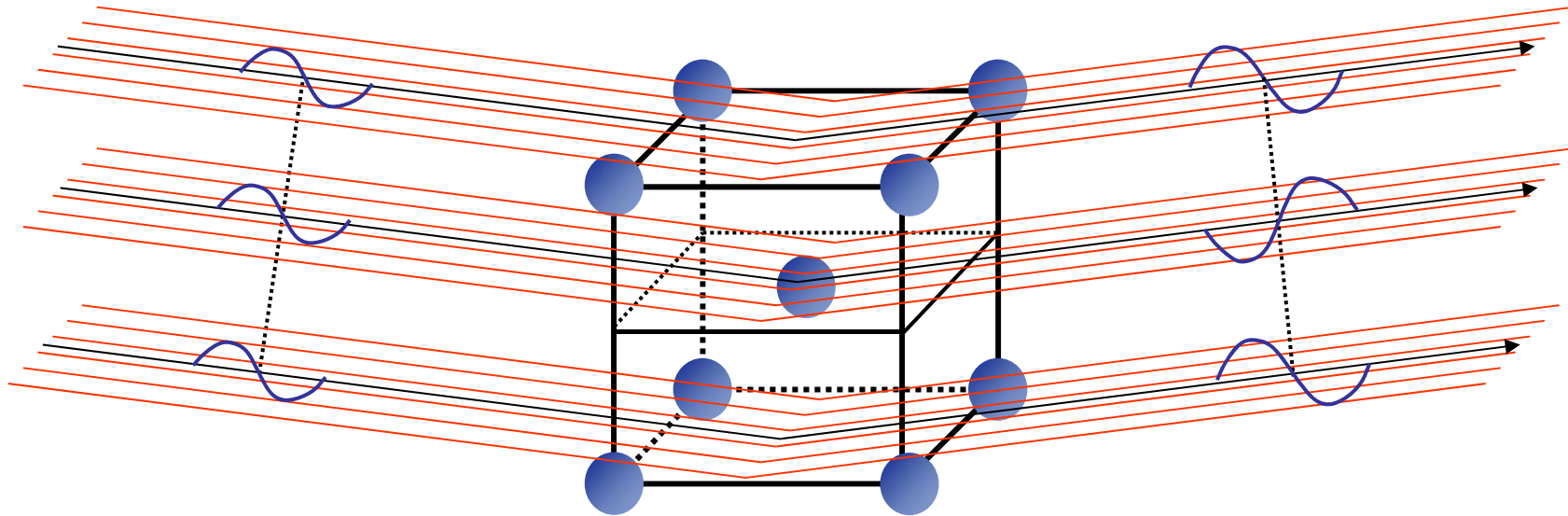
Simple Cubic
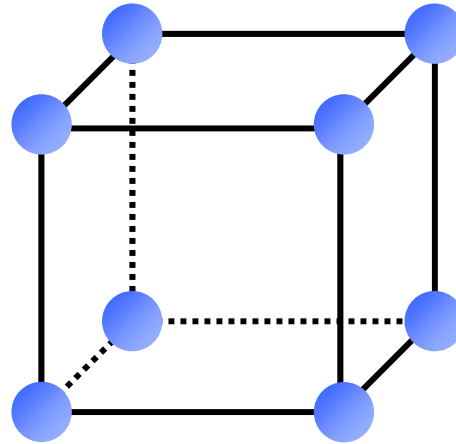
all {hkl}

{100} {110} {111} {200} {210} {211} {220} {221}

$h^2 + k^2 + l^2 = $ 1, 2, 3, 4, 5, 6, 8, 9

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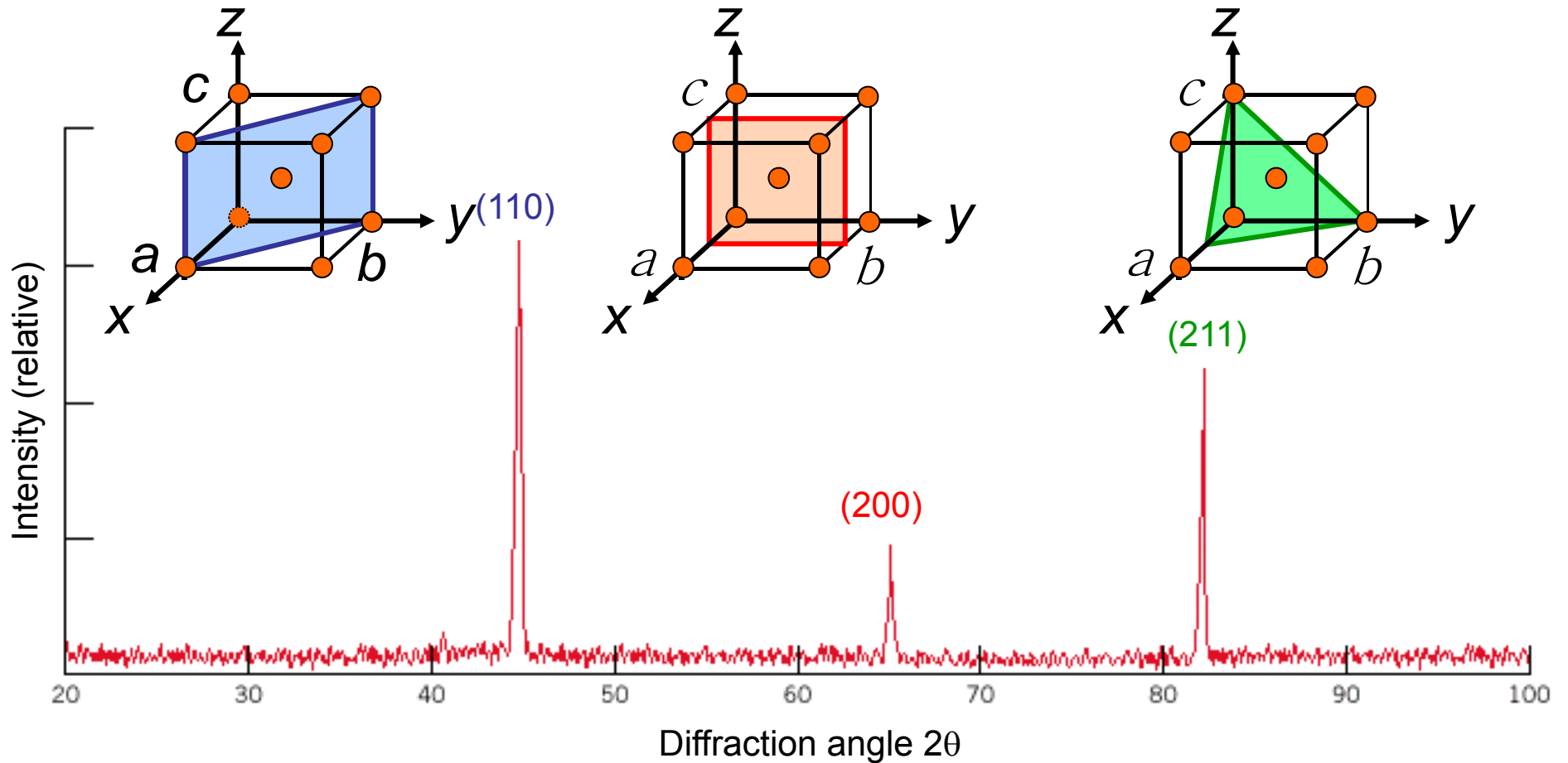
Diffraction pattern for polycrystalline α-iron (BCC)
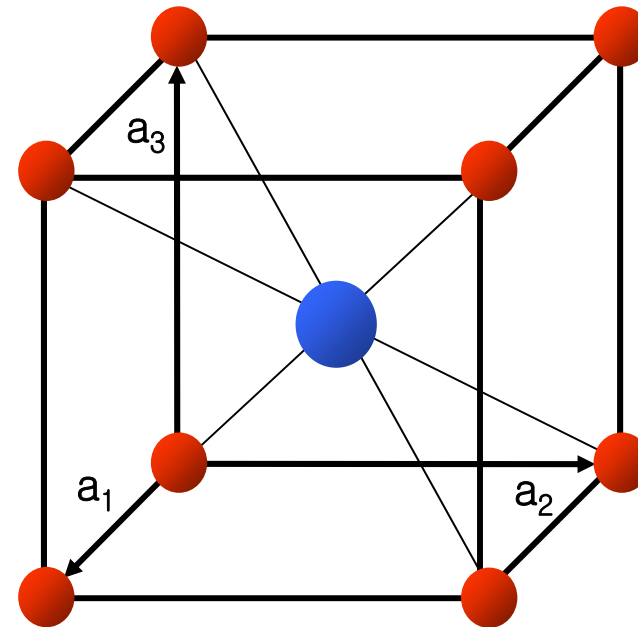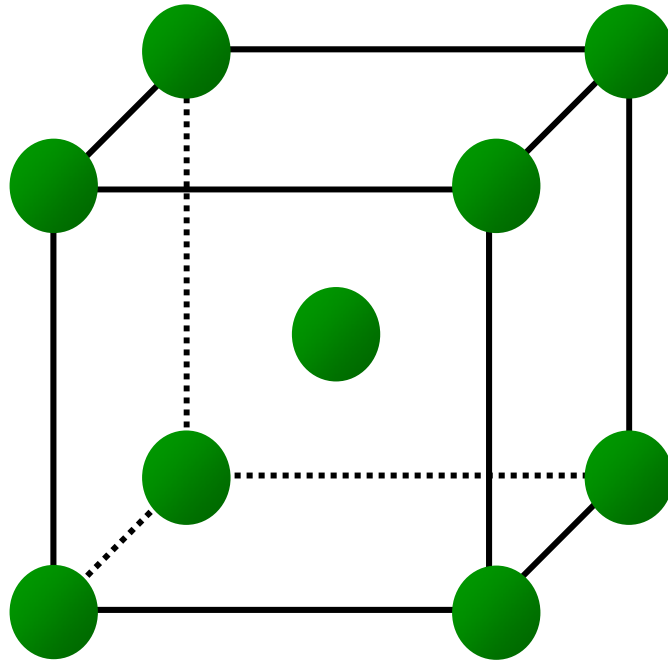
Importance of X-Ray Diffraction

difference in CsCl and BCC : (100) peak exists but weak
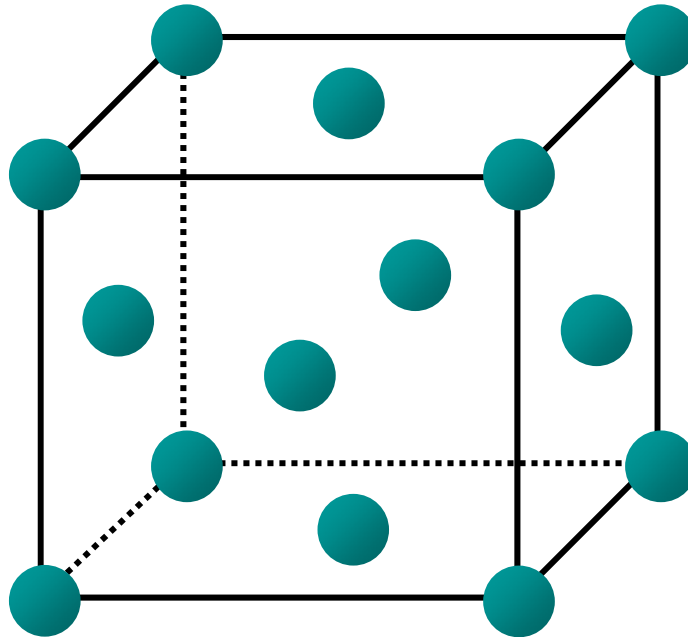

a_1　a_2　a_3

Cs$^+$　Cl$^-$

FCC

hkl all even or all odd (unmixed indices)

{111} {200} {220} {311} {222} {400} {331}

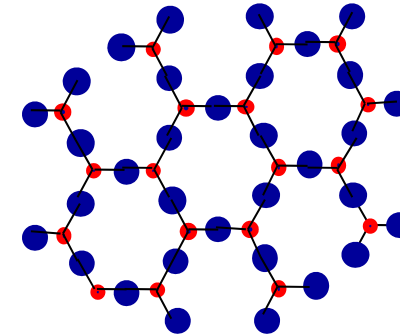$h^2 + k^2 + l^2$ =   3,   4,   8,   11,   12,   16,   19

Further Thinking !

1. X-Ray System
2. How can we get single λ ?
3. Diffraction Order
4. SC vs BCC
5. Alloying Effect
6. Why Powder ?
7. Lattice Parameter Measurement
8. Peak Separation (Phase Transformation)

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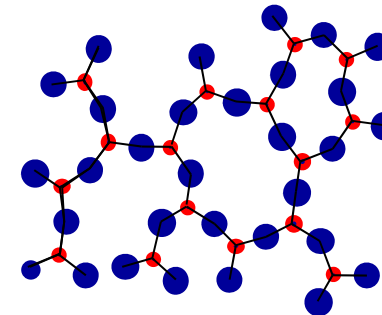   -some polymers

- long range order

crystalline SiO_2

• Si   **• Oxygen**

Noncrystalline materials...

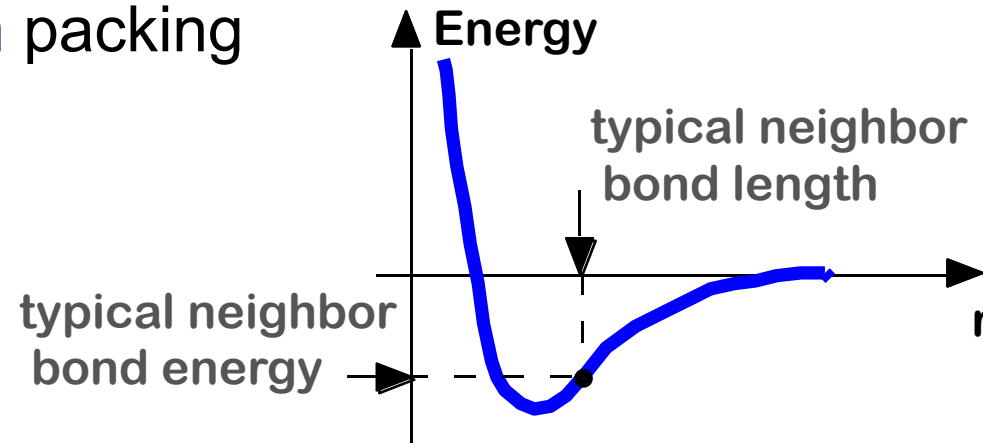- atoms have no periodic packing
- occurs for: -complex structures
                -rapid cooling

"Amorphous" = Noncrystalline

- short range order
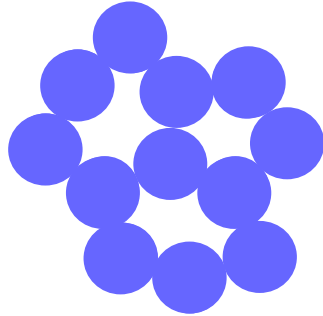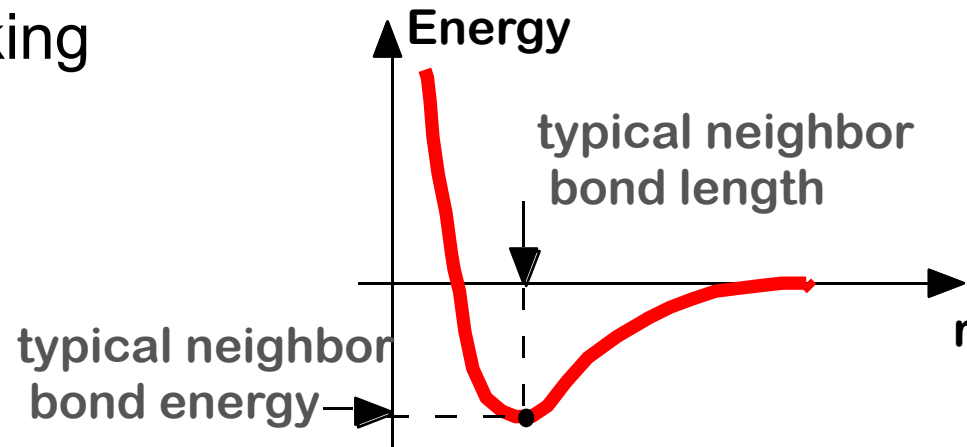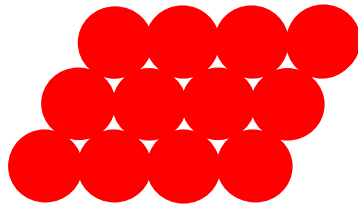

noncrystalline SiO_2

Noncrystalline Solids

- Basic Unit:

SiO_4^{4-} tetrahedron

Si^{4+}

O^{2-}
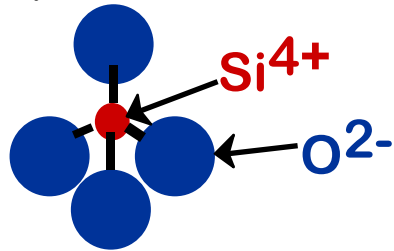
- Quartz is crystalline SiO_2:

- Glass is amorphous
- Amorphous structure occurs by adding impurities (Na^+, Mg^{2+}, Ca^{2+}, Al^{3+})
- Impurities: interfere with formation of crystalline structure.

Na^+

Si^{4+}

O^{2-}

(soda glass)
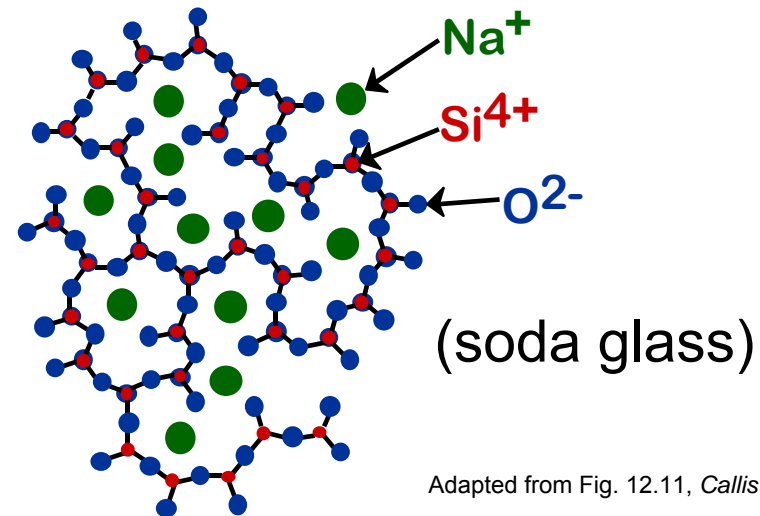
Adapted from Fig. 12.11, *Callister, 6e*.

Polycrstals

- Most engineering materials are polycrystals.

1 mm

Adapted from Fig. K, color inset
pages of Callister 6e.
(Fig. K is courtesy of Paul E.
Danielson, Teledyne Wah Chang
Albany)

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

Crystalline and Noncrystalline Materials

(1) Polycrystal

grain boundary

single grain
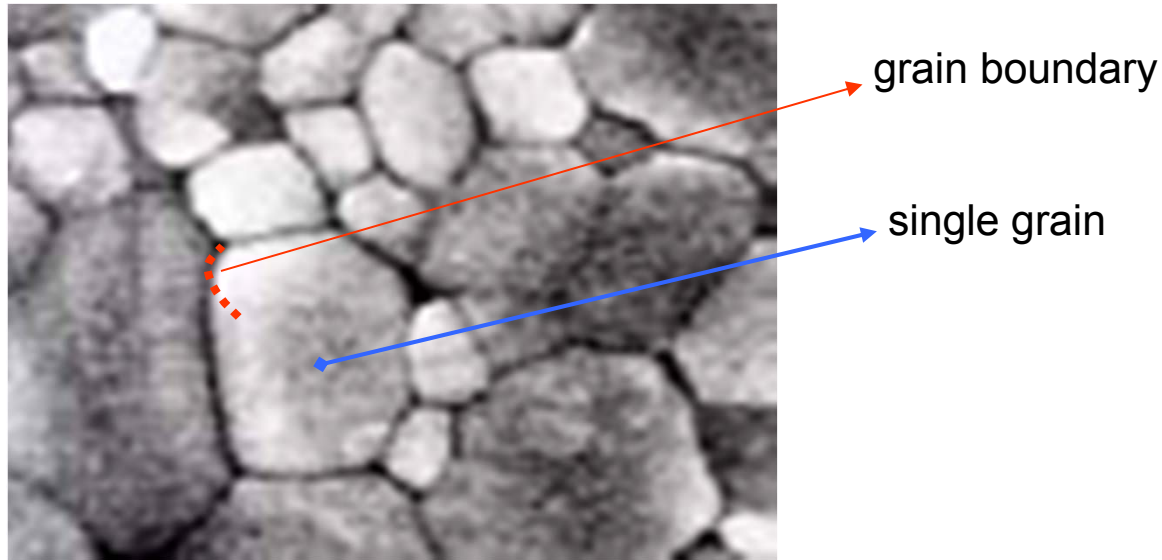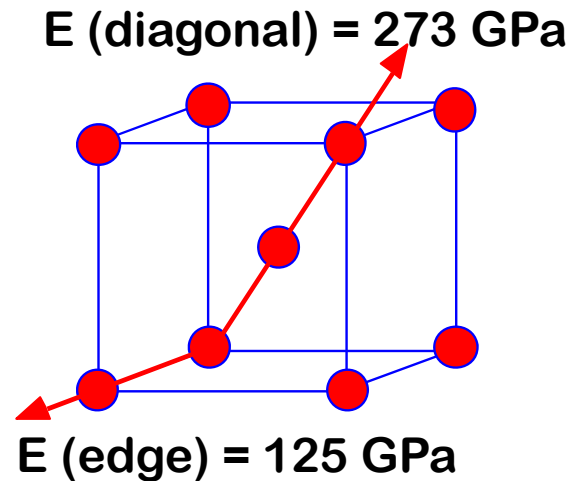
(2) Anisotropy

direction of properties

function of symmetry

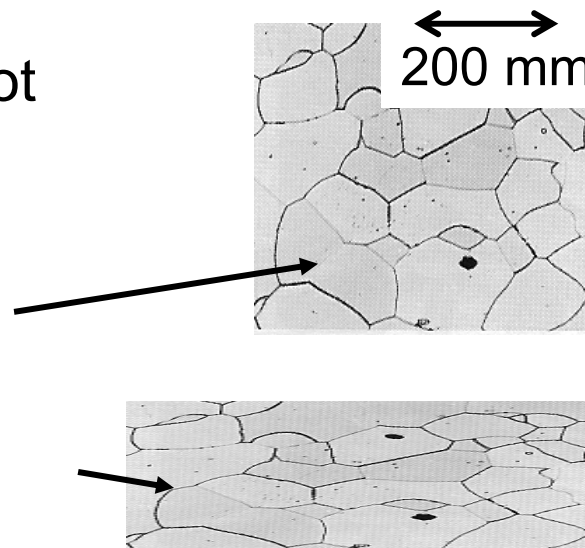amorphous material → isotropic

Single VS Polycrystals

- ## Single Crystals

  -Properties vary with
  direction: anisotropic.

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

- ## Polycrystals

  -Properties may/may not
  vary with direction.
  -If grains are randomly
  oriented: isotropic.
  ($E_{poly\ iron}$ = 210 GPa)
  -If grains are textured,
  anisotropic.

E (diagonal) = 273 GPa

E (edge) = 125 GPa

200 mm

Summary

- Atoms may assemble into crystalline or amorphous 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).

- Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.