Chapter 3 and Chapter 4:
The Structure of Crystalline Solids

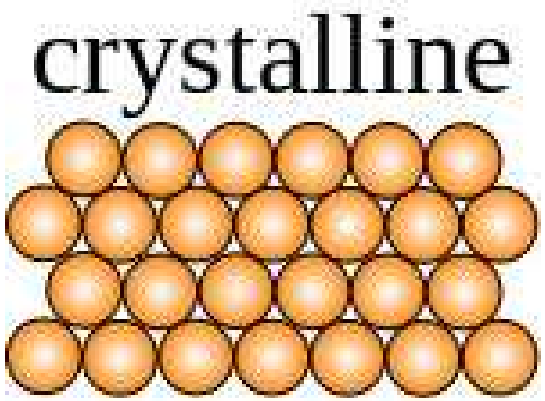
ISSUES TO ADDRESS...

- How do atoms assemble into solid structures? (for now, focus on metals)
- How does the **density** of a material depend on its structure?
- When do material **properties** vary with the sample (i.e., part) orientation?

Materials and Packing

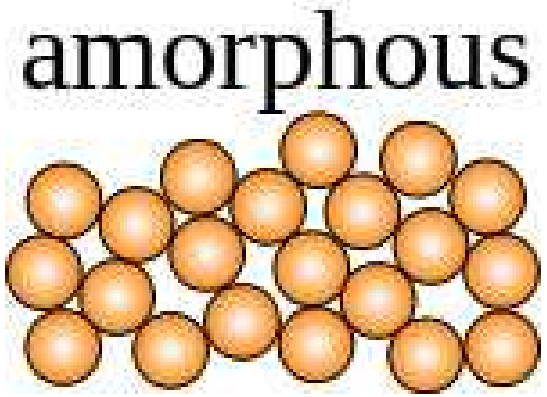
Crystalline materials...

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



Noncrystalline materials...

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



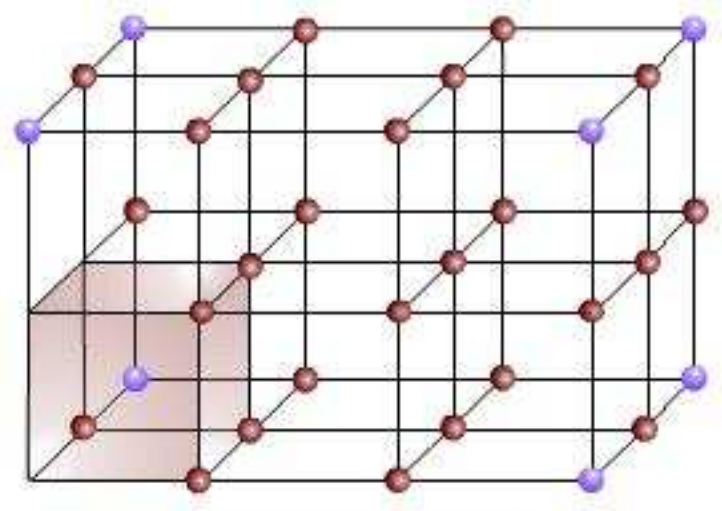
"Amorphous" = Noncrystalline

http://www.medgadget.com/2012/09/levitating-drugs-may-improve-efficacy.html

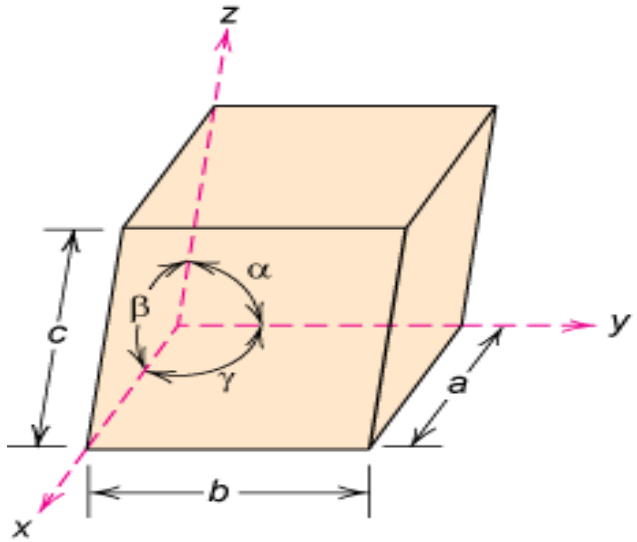
Crystal Systems

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

Lattice: a three-dimensional array of points coinciding with atom positions.



Representation of space lattice and unit cell



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

http://criticalpoint.altervista.org/chimica-generale/6/cellaunitaria.html

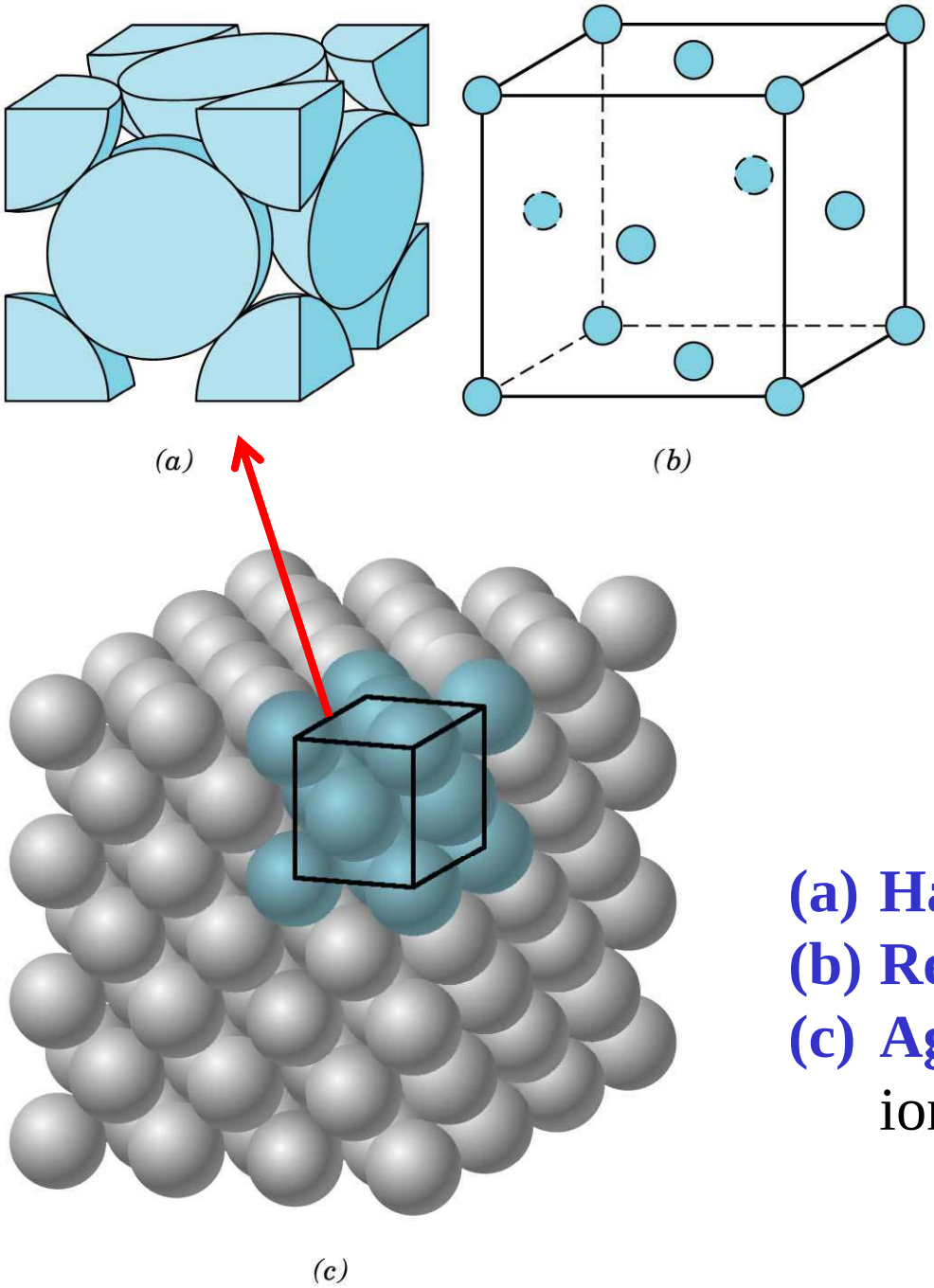


FIGURE 3.1 For the face-centered cubic crystal structure: (*a*) a hard sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms. (Figure *c* adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

(a) Hard sphere unit cell model
(b) Reduced-sphere unit cell
(c) Aggregate of many atoms, ions, or molecules.

Crystal Systems

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

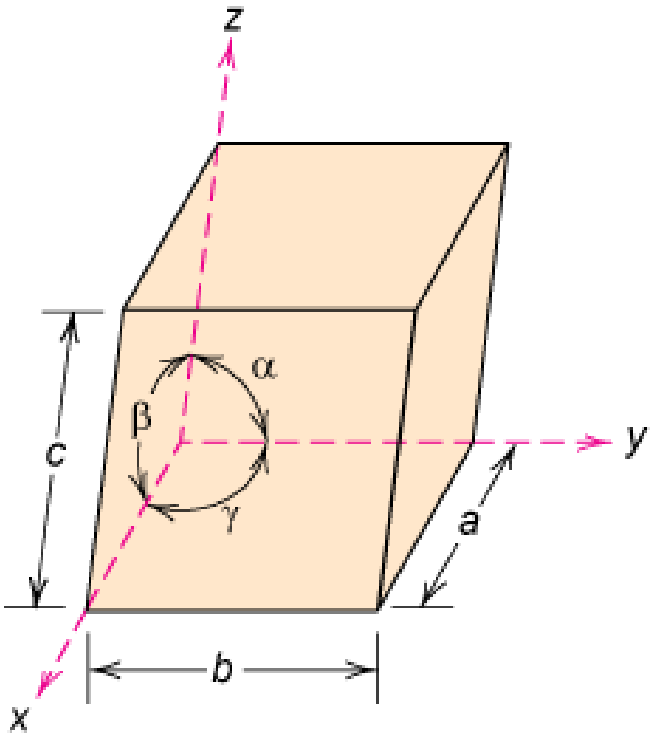


Fig. 3.4, *Callister 7e.*

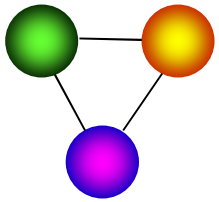
7 crystal systems

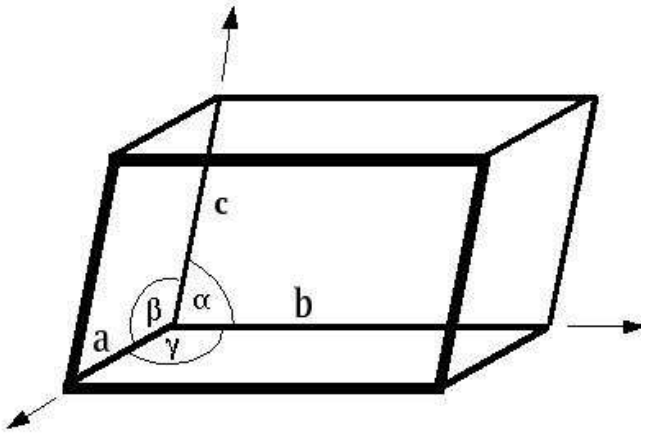
14 crystal lattices

三軸長度(a、b、c，常以A^{o}為單位)與三軸夾角(α、β、γ)。

Crystal Systems

Lattice parameter relationship and Seven crystal system

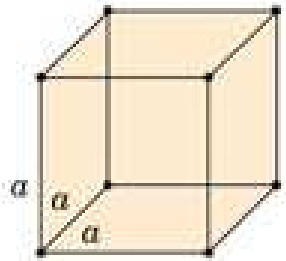




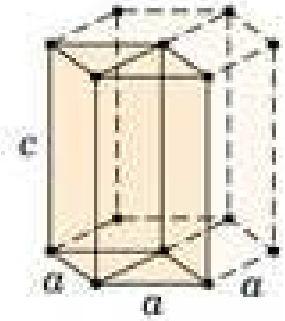
System	Axes
Triclinic (三斜晶系)	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^o$
Monoclinic (單斜晶系)	$a \neq b \neq c$, $\alpha = \beta = 90^o \neq \gamma$
Orthrhombic (正交晶系)	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$
Trigonal (菱方晶系)	$a = b = c$, $\alpha = \beta = \gamma \neq 90^o$
Tetragonal (正方晶系)	$a = b \neq c$, $\alpha = \beta = \gamma = 90^o$
Hexagonal (六方晶系)	$a = b \neq c$, $\alpha = \beta = 90^o$ $\gamma = 120^o$
Cubic (立方晶系)	$a = b = c$, $\alpha = \beta = \gamma = 90^o$

http://xray0.princeton.edu/~phil/Facility/Guides/XrayDataCollection.html

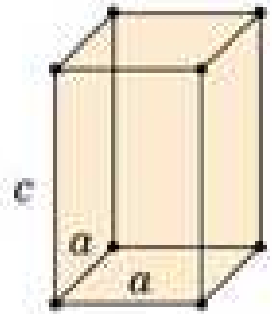
Crystal Systems



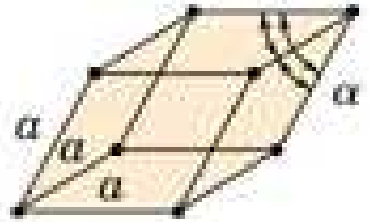
Cubic
(立方)



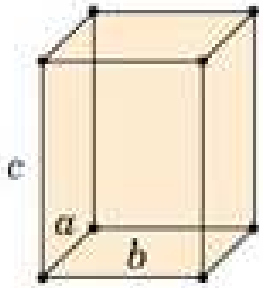
Hexagonal
(六方)



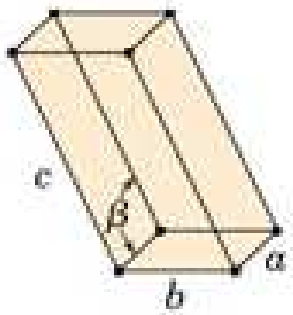
Tetragonal
(正方)



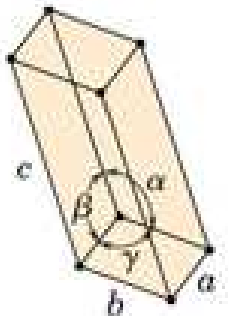
Rhombohedral
/ Trigonal
(斜方六面体)



Orthorhombic (斜方)



Monoclinic (單斜)



Triclinic (三斜)

Seven Crystal Systems

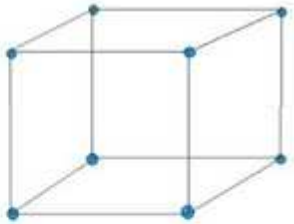
Crystal Systems and Bravais Lattices

Seven crystal systems are each described by the shape of the unit cell which can be translated to fill space.

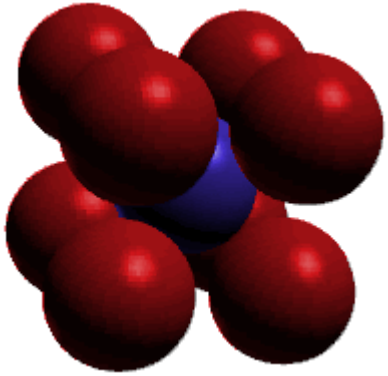
Bravais lattices -- fourteen simple and complex lattices within the seven crystal systems.

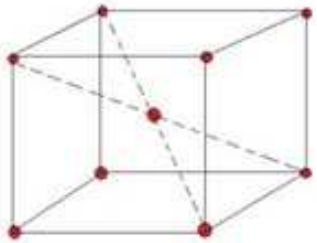
The complex lattices have atoms centered either in the center of a "primitive" unit cell or in the center of two/or more of the unit cell faces.

Cubic Bravais Lattices

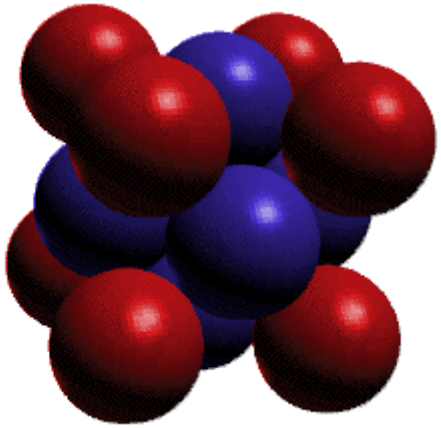


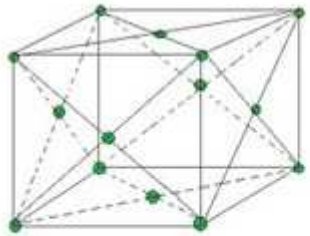
Primitive cube (P)



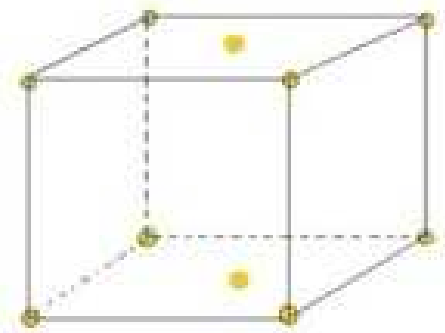


Body centered cube (I)





Face centered cube (F)



Base centered Orthorhombic (C)

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Diffraction/Powder_X-ray_Diffraction1

Bravais Lattices

Crystal System	No.	Unit Cell	Coordinate Description
Triclinic	1	Primitive(P)	$\mathbf{a} \neq \mathbf{b} \neq \mathbf{c}$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	Primitive(P)	$\mathbf{a} \neq \mathbf{b} \neq \mathbf{c}$ $\alpha = \beta = 90^\circ \neq \gamma$
	3	Base Centered(C)	
Orthorhombic	4	Primitive(P)	$\mathbf{a} \neq \mathbf{b} \neq \mathbf{c}$ $\alpha = \beta = \gamma = 90^\circ$
	5	Base Centered(C)	
	6	Body Centered(I)	
	7	Face Centered(F)	
Tetragonal	8	Primitive(P)	$\mathbf{a} = \mathbf{b} \neq \mathbf{c}$ $\alpha = \beta = \gamma = 90^\circ$
	9	Body Centered(I)	
Rhombohedral (Trigonal)	10	Primitive(P)	$\mathbf{a} = \mathbf{b} = \mathbf{c}$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	11	Primitive(P)	$\mathbf{a} = \mathbf{b} \neq \mathbf{c}$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Cubic	12	Primitive(P)	$\mathbf{a} = \mathbf{b} = \mathbf{c}$ $\alpha = \beta = \gamma = 90^\circ$
	13	Body Centered(I)	
	14	Face Centered(F)	

Metallic Crystal Structures

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

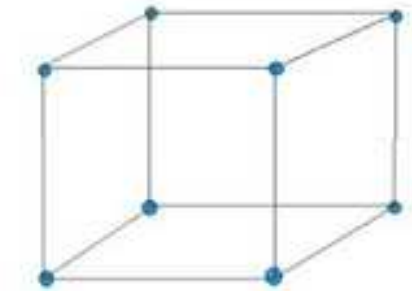
We will examine three such structures...

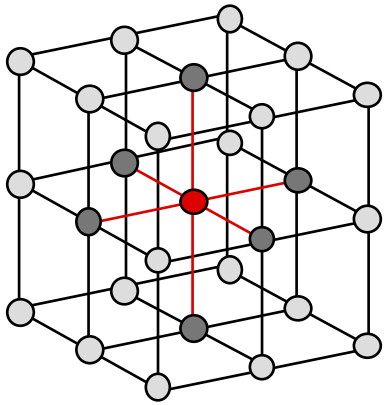
FCC, BCC and HCP in Cubic system

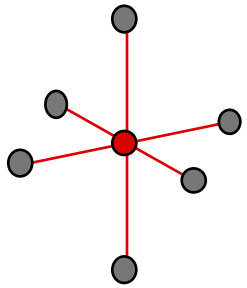
Simple Cubic Structure (SC)

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

- **Coordination #** = 6
  (# nearest neighbors)





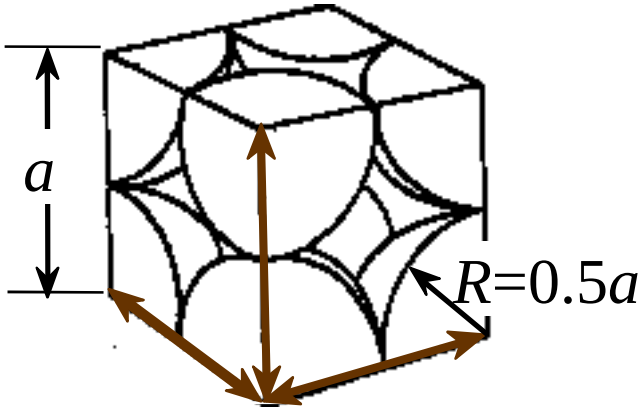


(Courtesy P.M. Anderson)

Atomic Packing Factor (APF)

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

*assume hard spheres



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.23, *Callister 7e.*

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

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

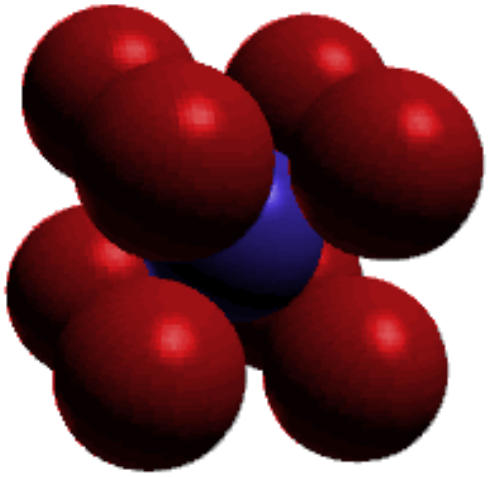
- **APF for a simple cubic structure = 52%**

Body Centered Cubic Structure (BCC)

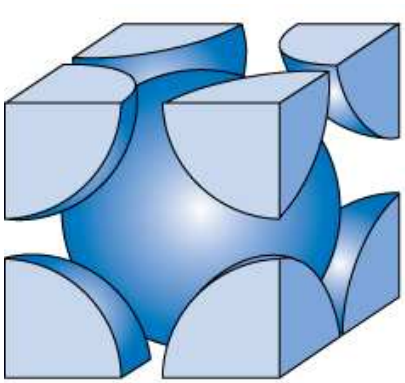
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

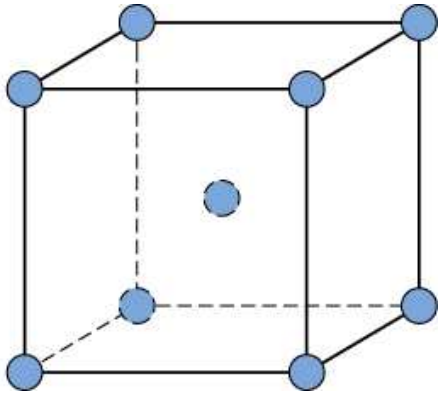
ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8



(Courtesy P.M. Anderson)

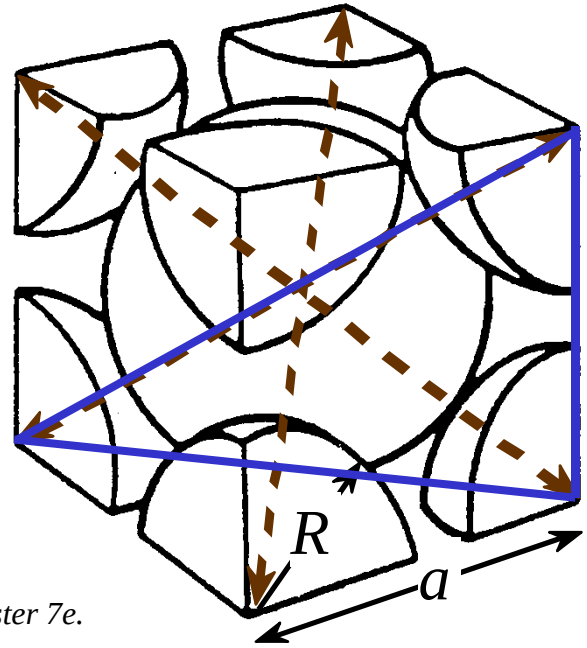




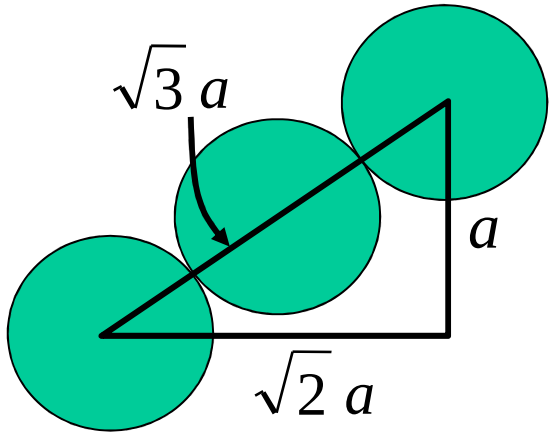
Adapted from Fig. 3.2, *Callister 7e.*

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

Atomic Packing Factor: BCC



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



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

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

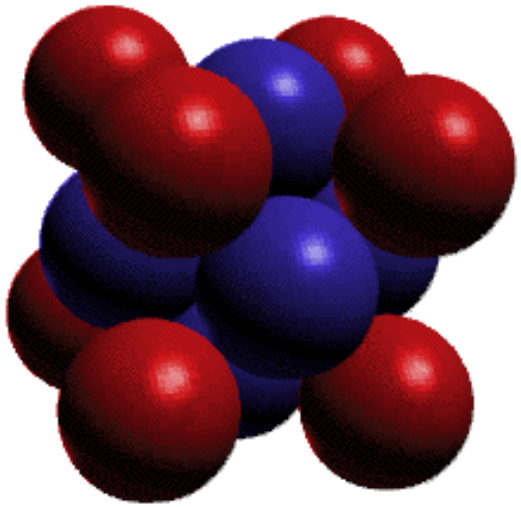
- **APF for a body-centered cubic structure = 68%**

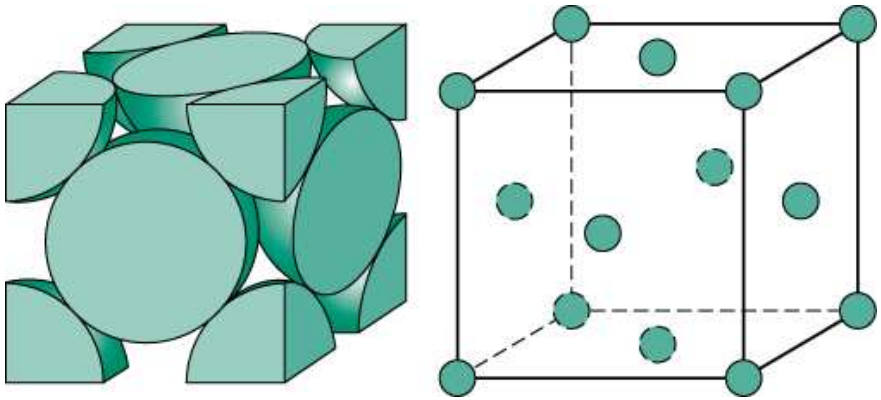
Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

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

- Coordination # = 12



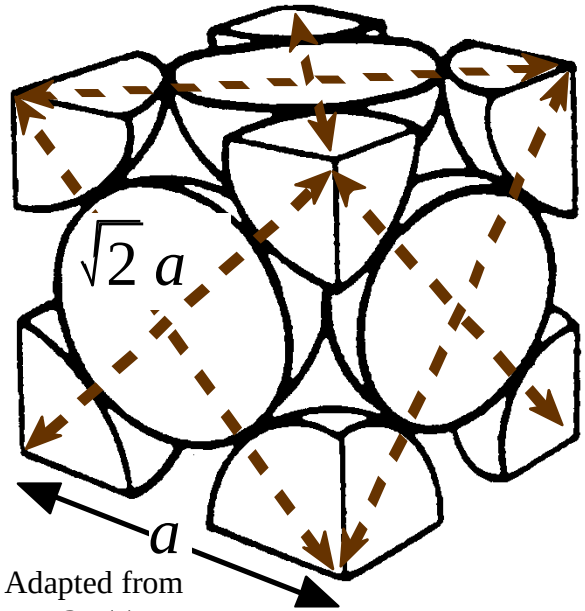


Adapted from Fig. 3.1, *Callister 7e.*

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

(Courtesy P.M. Anderson)

Atomic Packing Factor: FCC



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

maximum achievable APF

Close-packed directions:

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

Unit cell contains:

6 x 1/2 + 8 x 1/8

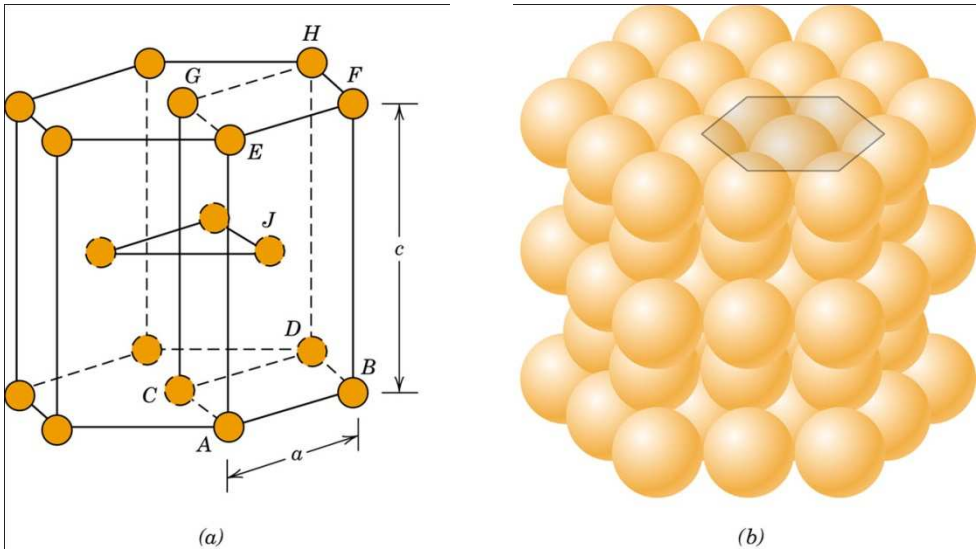
= 4 atoms/unit cell

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

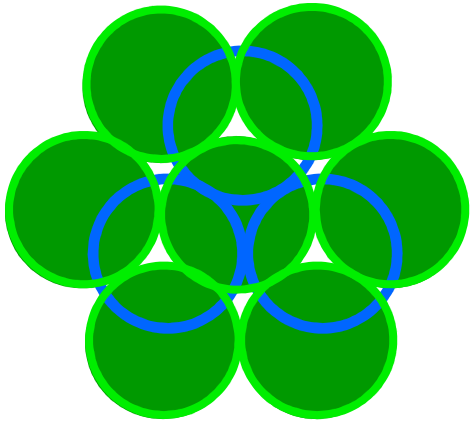
- **APF for a face-centered cubic structure = 74%**

Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence



- 2D Projection



Top layer (A) Middle layer (B)

Bottom layer(A)

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

6 atoms/unit cell $= 12 \cdot \frac{1}{6} + 2 \cdot \frac{1}{2} + 3$

ex: Cd, Mg, Ti, Zn

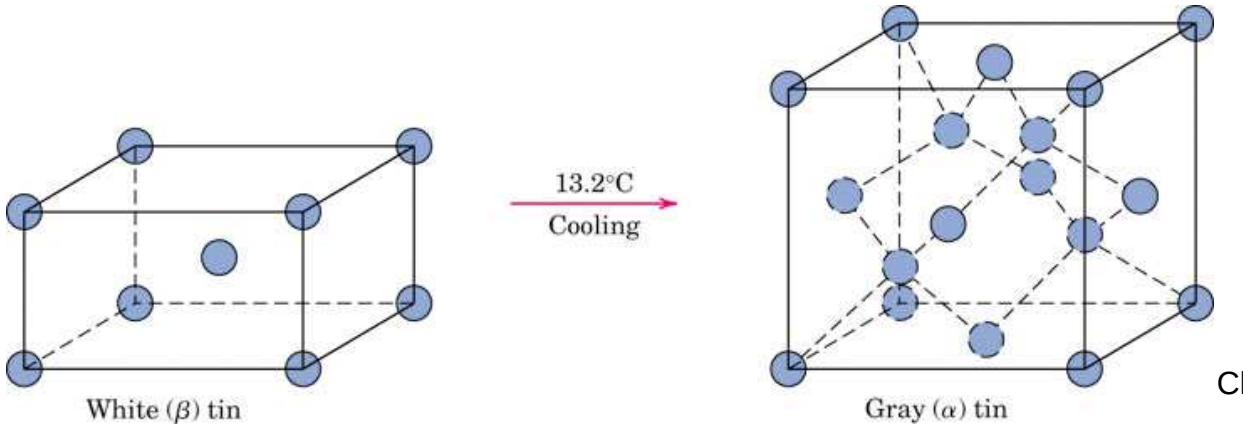
Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

t01_03_pg41


13.2°C
Cooling
White (β) tin
Gray (α) tin

Theoretical Density, r

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

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

where n = number of atoms/unit cell

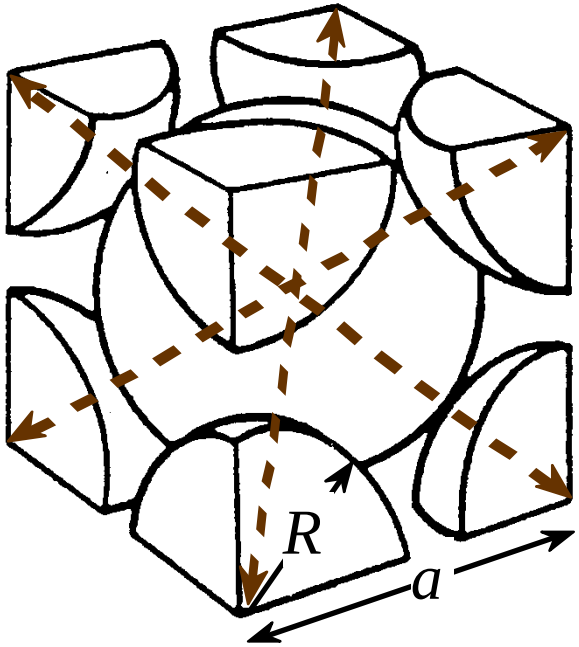
A = atomic weight

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

N_A = Avogadro's number

= 6.023×10^{23} atoms/mol

Theoretical Density, r



- Ex: Cr (BCC)

  A = 52.00 g/mol

  R = 0.125 nm

  n = 2

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

$$\rho = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{g}}{\text{mol}} \cdot \frac{\text{volume}}{\text{unit cell}} \cdot \frac{\text{atoms}}{\text{mol}}$$

$$\rho = \frac{2 \quad 52.00}{a^3 \quad 6.023 \times 10^{23}}$$

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

Densities of Material Classes

In general

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

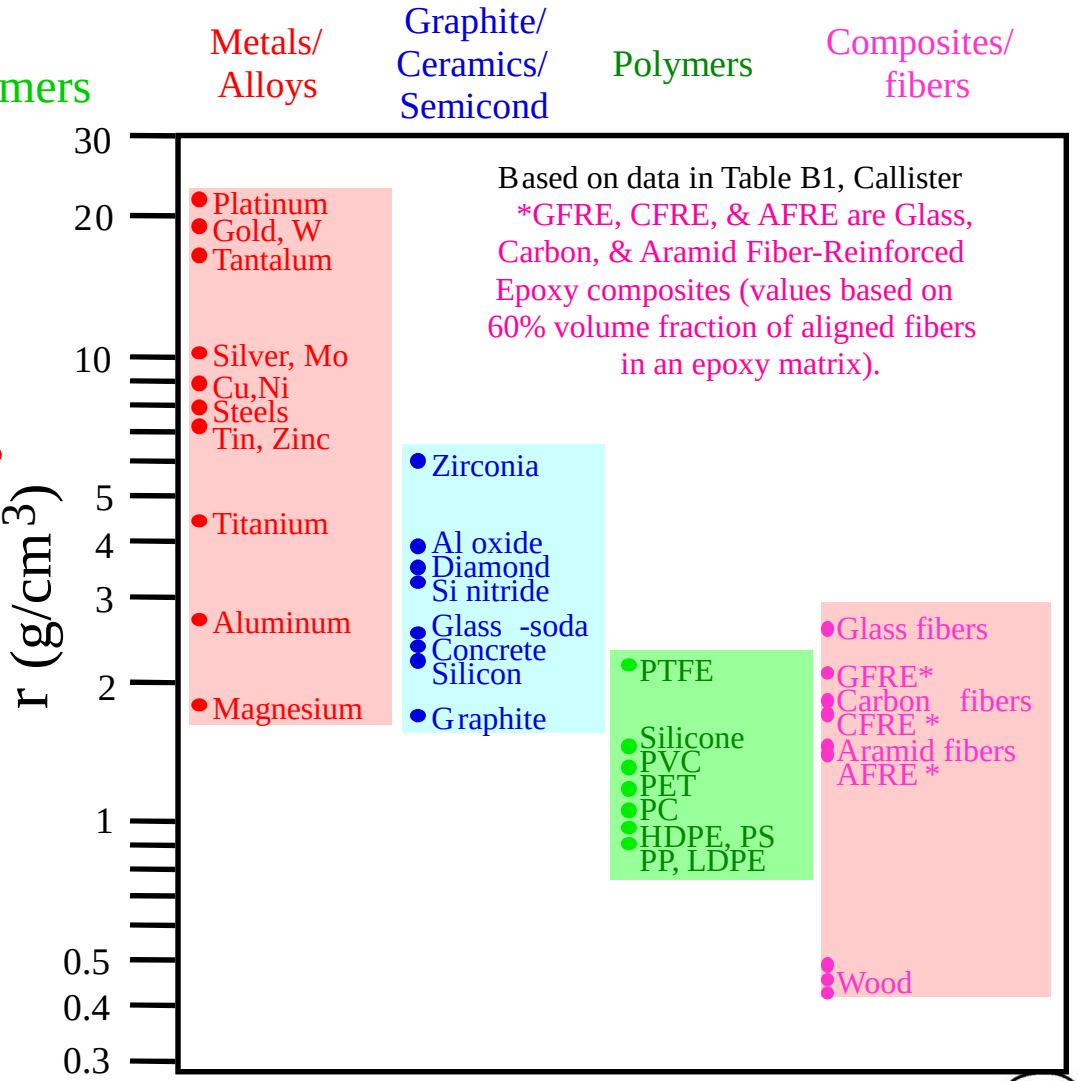
Why?

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

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

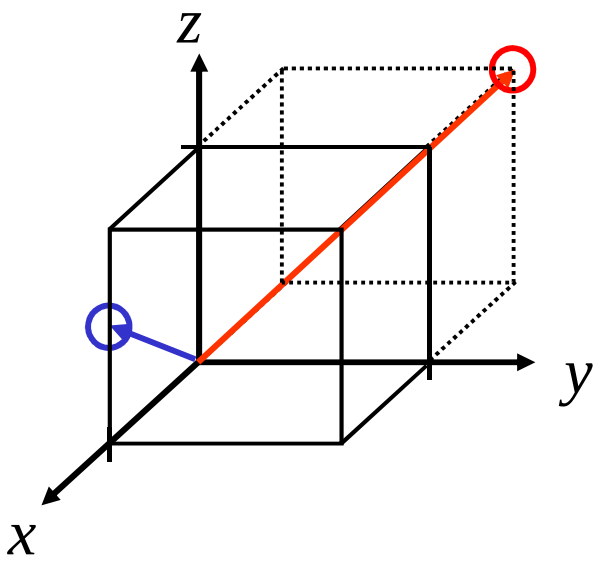
Polymers have...
- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...
- intermediate values



Data from Table B1, *Callister 7e.*

Crystallographic Directions



Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions *a*, *b*, and *c*
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

[*uvw*]

ex: 1, 0, ½ => 2, 0, 1 => [201]

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

Crystallographic Directions

- Families of directions ***<uvw>***

→ several nonparallel directions with different indices are crystallographically equivalent。

→ the spacing of atoms along each direction is the same.

ex：<110> = [110] ，$[\bar{1}10]$ ，$[1\bar{1}0]$ ，$[\bar{1}\bar{1}0]$ ，[101] ，

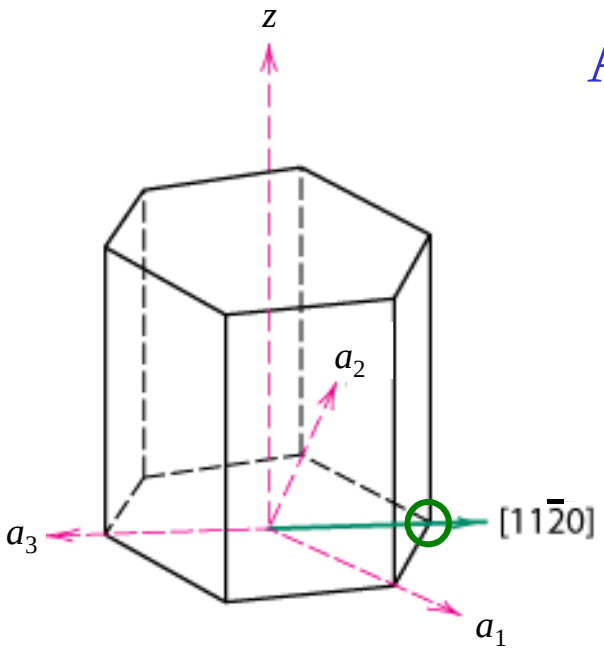
$[\bar{1}01]$ ，$[10\bar{1}]$ ，$[\bar{1}0\bar{1}]$ ，[011] ，$[01\bar{1}]$ ，

$[0\bar{1}\bar{1}]$ ，$[0\bar{1}\bar{1}]$ 。(in cubic system)

- For Tetragonal system →

<100>= [100], [010] and [001] ??

HCP Crystallographic Directions

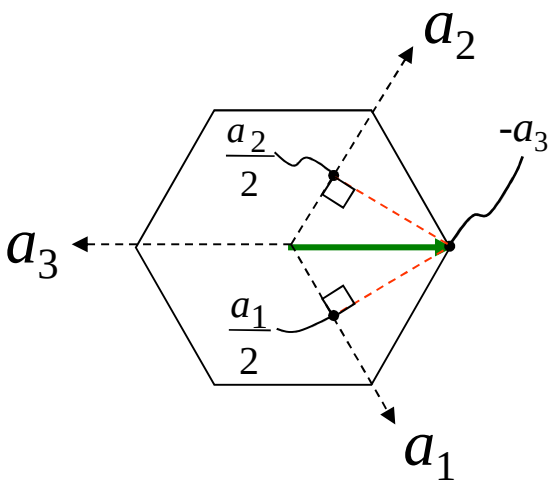


Adapted from Fig. 3.8(a), *Callister 7e.*

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

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

ex: ½, ½, -1, 0 => $[11\bar{2}0]$



dashed red lines indicate projections onto a_1 and a_2 axes

HCP Crystallographic Directions

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

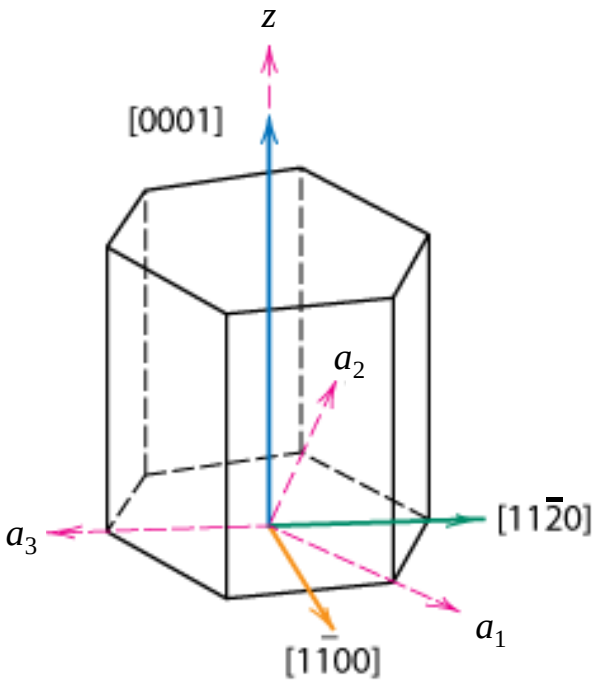


Fig. 3.8(a), *Callister 7e.*

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

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

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

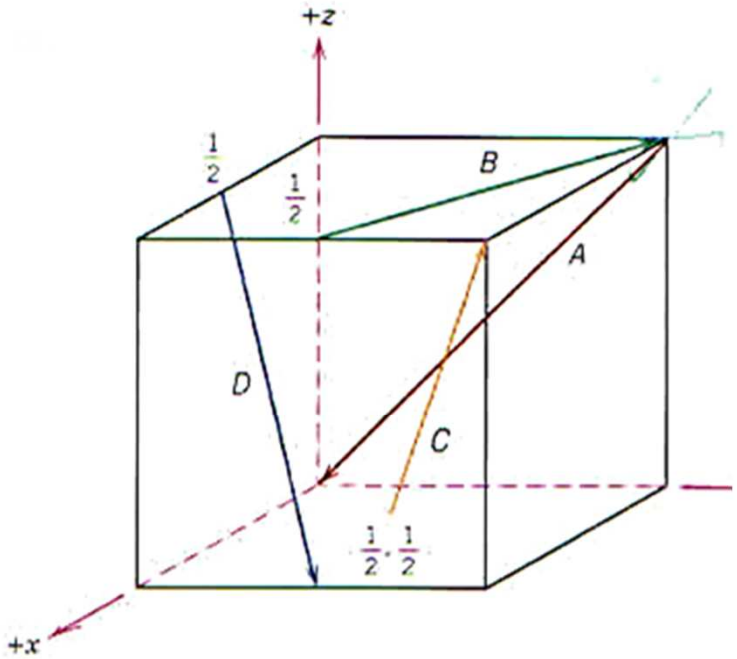
$$t = -(u + v)$$

$$w = w'$$

Crystallographic Directions

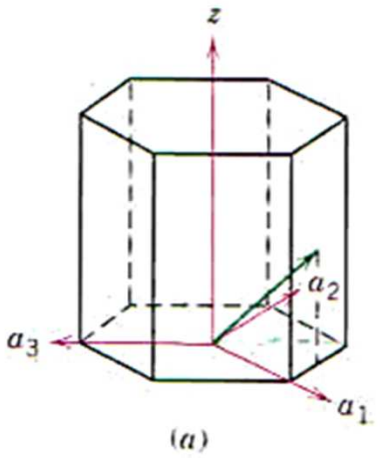
- Example ： 3.31

3.31 Determine the indices for the direction shown in the following cubic unit cell:

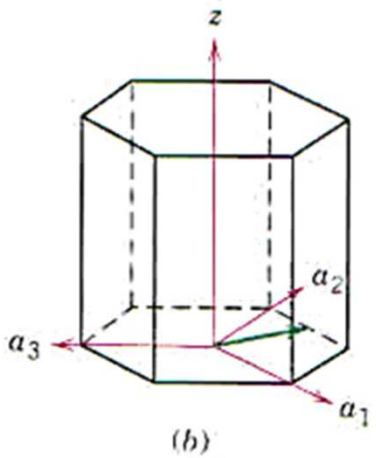


- Example ： 3.35

3.35 Determine indices for the directions shown in the following hexagonal unit cells:



(a)



(b)

Crystallographic Planes

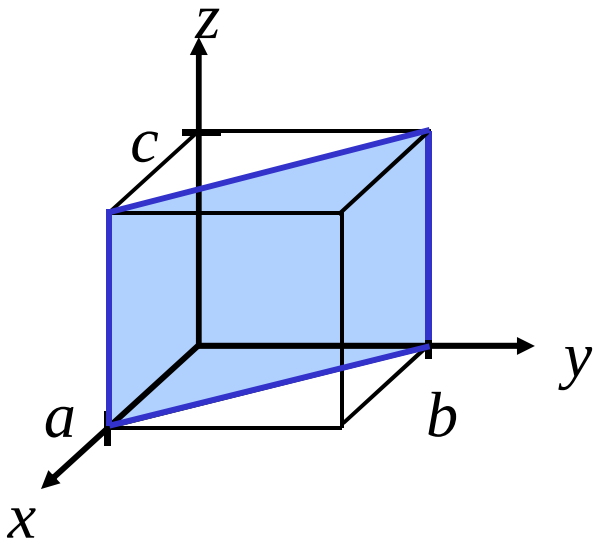
- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

- 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

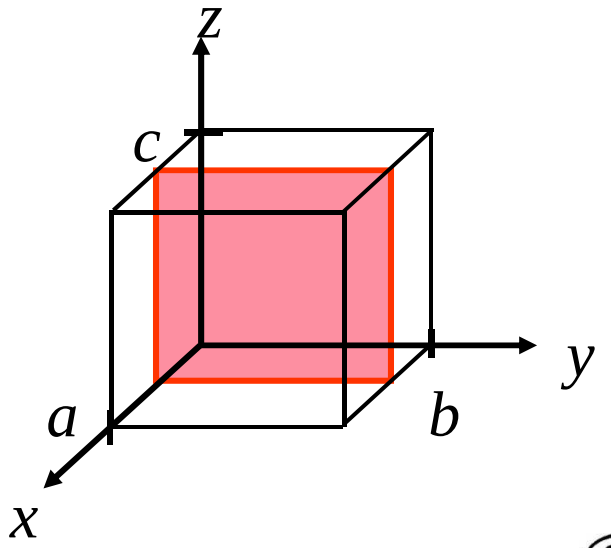
Example 1 :

		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 2 :

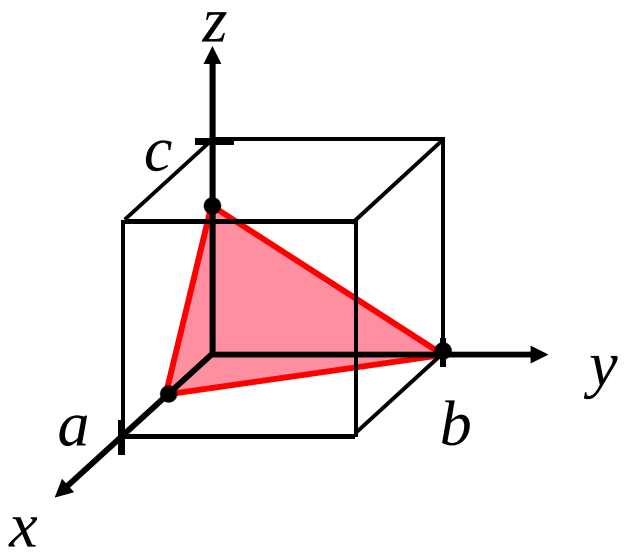
		a	*b*	*c*
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	1	0	0
4.	Miller Indices	(100)		



Crystallographic Planes

Example 3：

		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)		



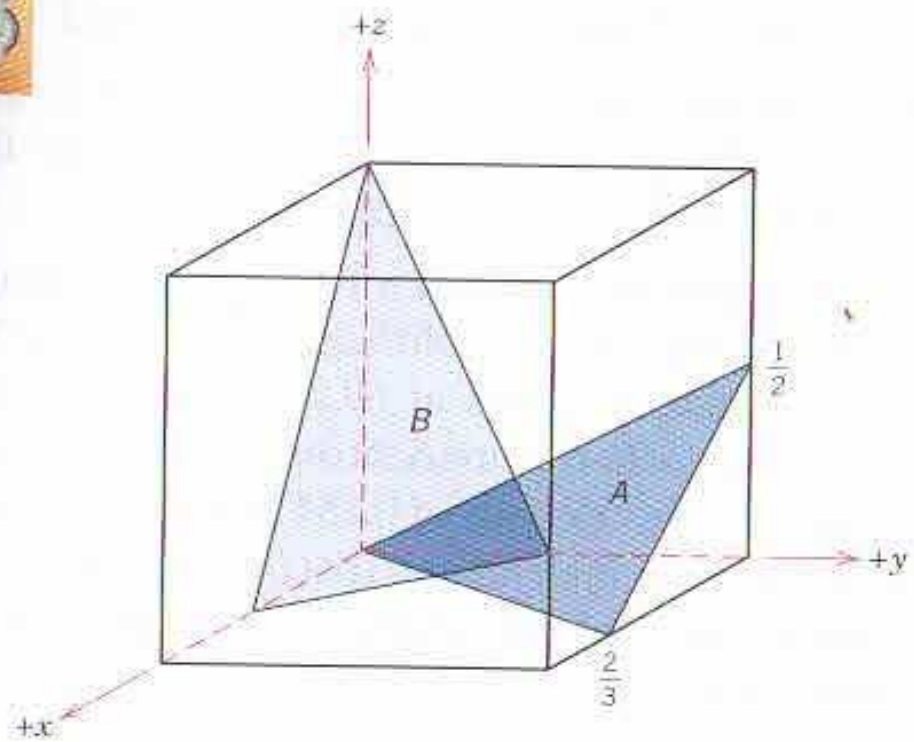
Family of Planes $\{hkl\}$

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

Crystallographic Planes

- Example 3.43

3.43 Determine the Miller indices for the planes shown in the following unit cell:

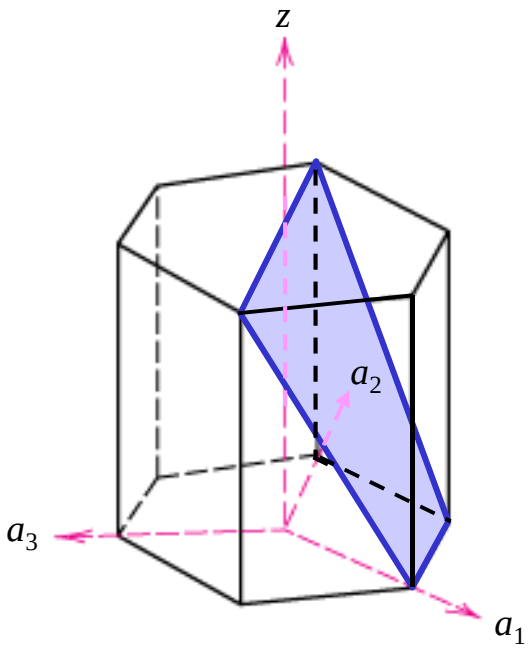


Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

Example 4:

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

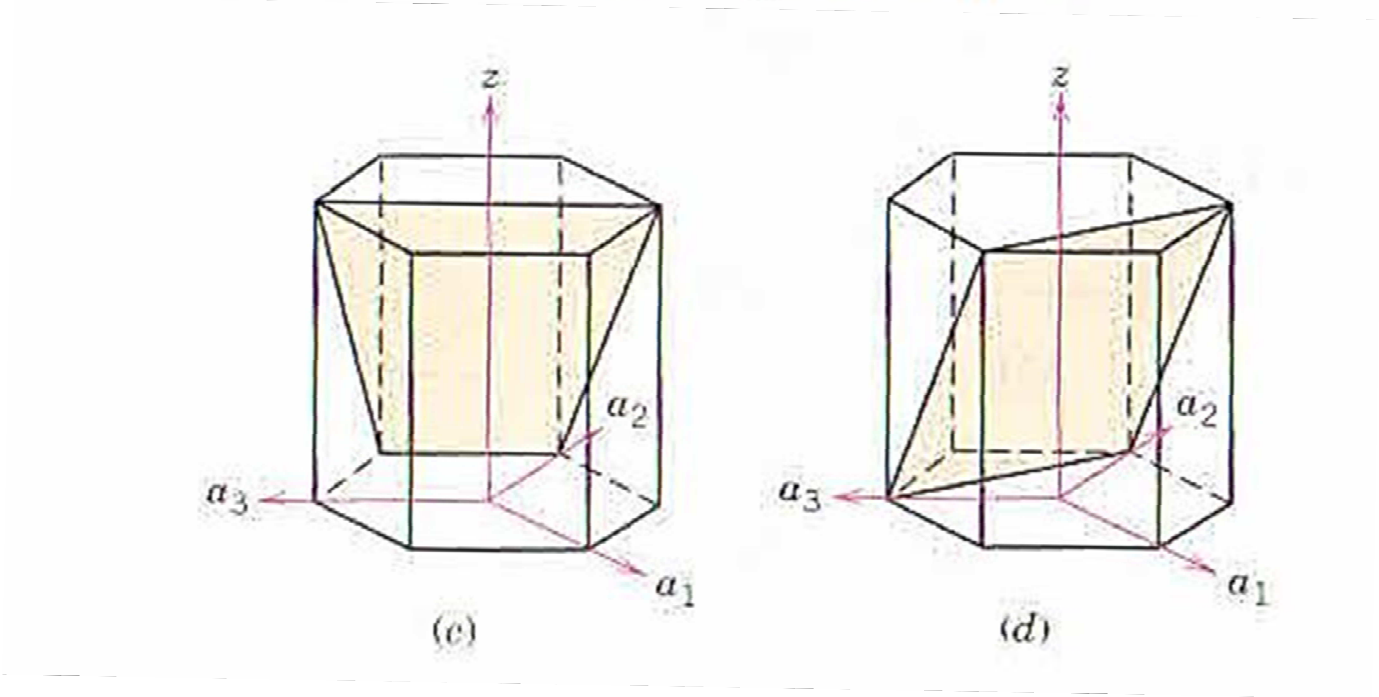


Adapted from Fig. 3.8(a), *Callister 7e.*

Crystallographic Planes (HCP)

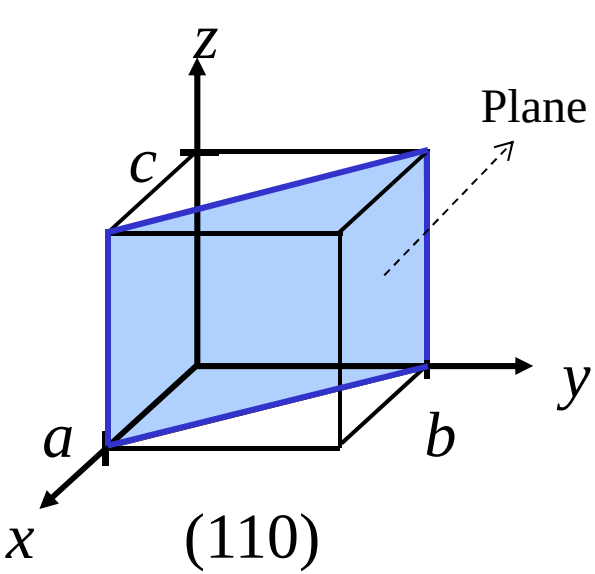
- Example 3.50

3.50 Determine the indices for the planes shown in the following hexagonal unit cells:

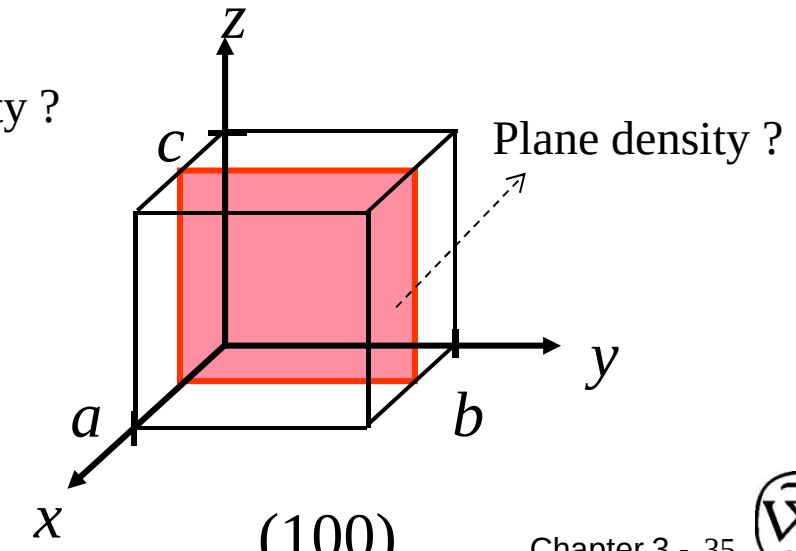


Crystallographic Planes

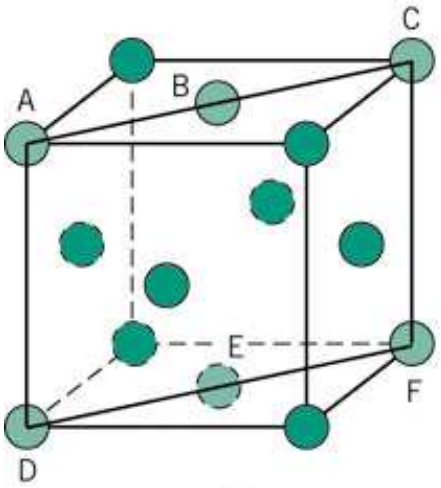
- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.



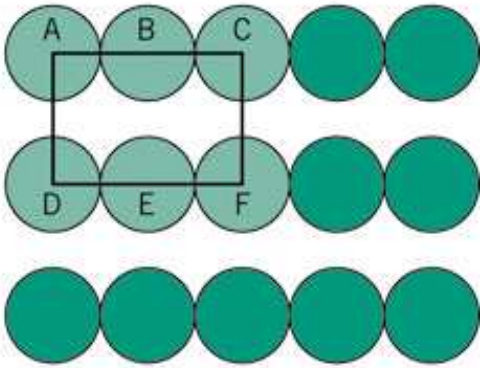
(110)



(100)

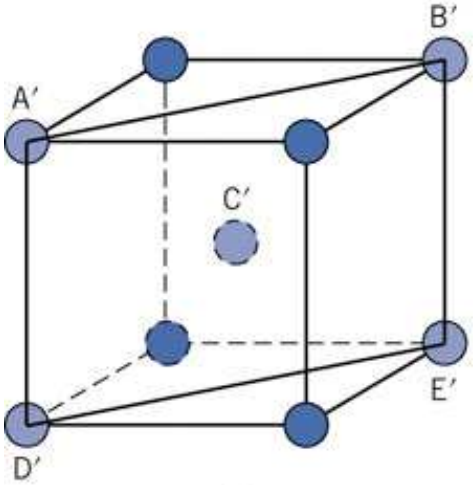


(a)

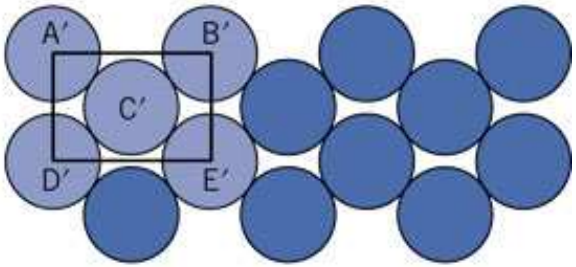


(b)

FCC (110) Plane



(a)



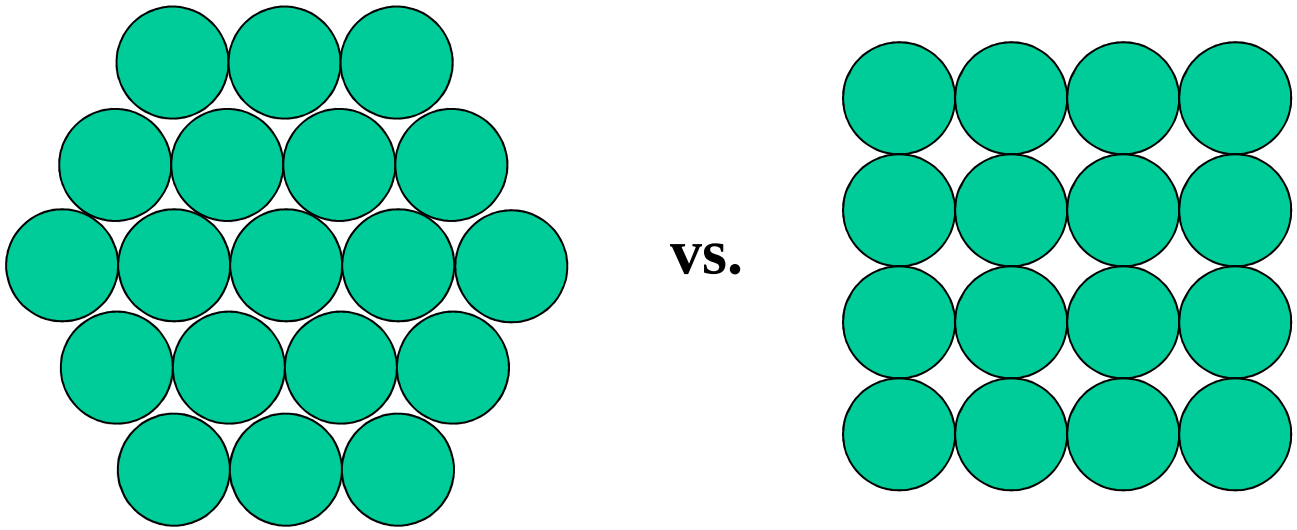
(b)

BCC (110) Plane

Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

2-dimensions

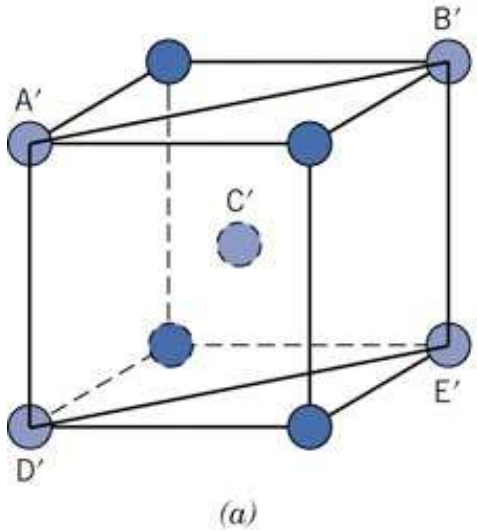


vs.

Now stack these 2-D layers to make 3-D structures

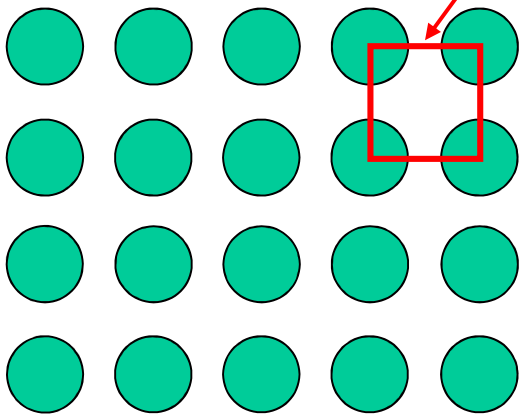
Planar Density of (100) Iron

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



(a)

(100)

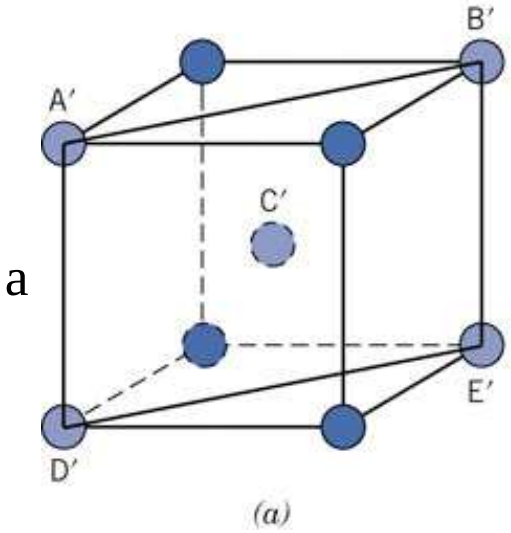


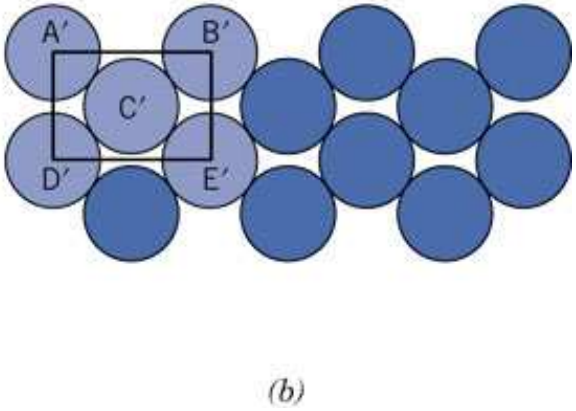
$a = \frac{4\sqrt{3}}{3}R$

Radius of iron R = 0.1241 nm

$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{a^2} = \frac{\pi\left(\frac{\sqrt{3}a}{4}\right)^2}{a^2} = \mathbf{59\ \%}$$

Planar Density of BCC(110)





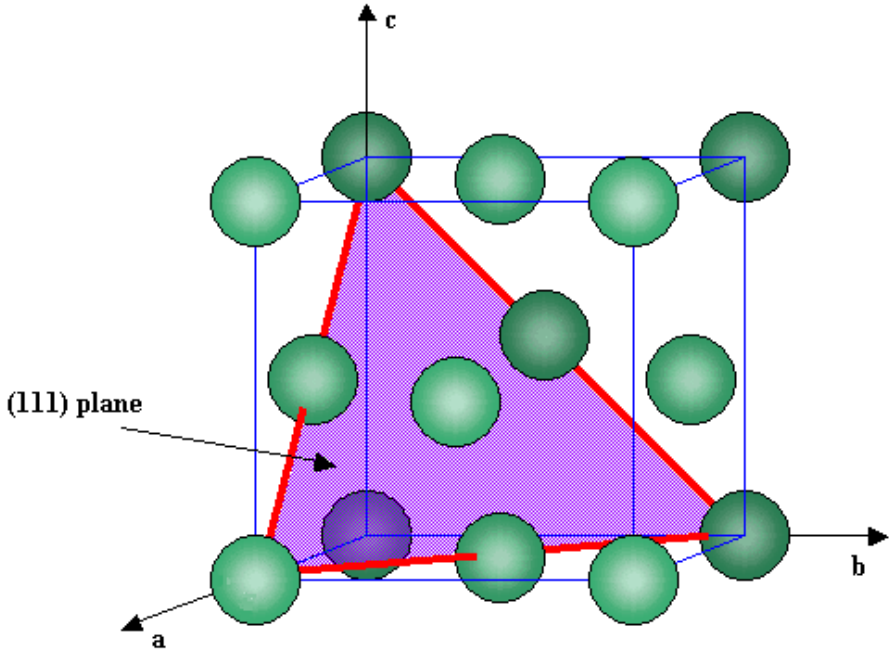
BCC (110) Plane

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

$$\text{Planar Density} = \frac{\text{atoms}}{\text{2D repeat unit}} = \frac{\text{area}}{\text{2D repeat unit}}$$

$$= \frac{2}{\sqrt{2}a^2} = \frac{2 \times \pi \left(\frac{\sqrt{3}a}{4} \right)^2}{\sqrt{2}a^2} = \mathbf{83\ \%}$$

Planar Density of FCC(111)



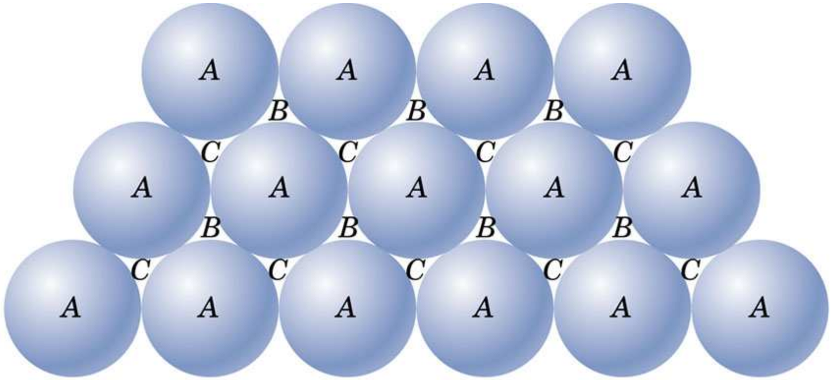
FCC (111) Plane

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

Planar Density = $\dfrac{\left(\frac{1}{6}\times 3+\frac{1}{2}\times 3\right)\times \pi r^2}{\frac{1}{2}\times\sqrt{2}a\times\frac{\sqrt{6}}{2}a} = \dfrac{2\times\pi\left(\frac{\sqrt{2}a}{4}\right)^2}{\frac{\sqrt{3}}{2}a^2} =$ **91 %**

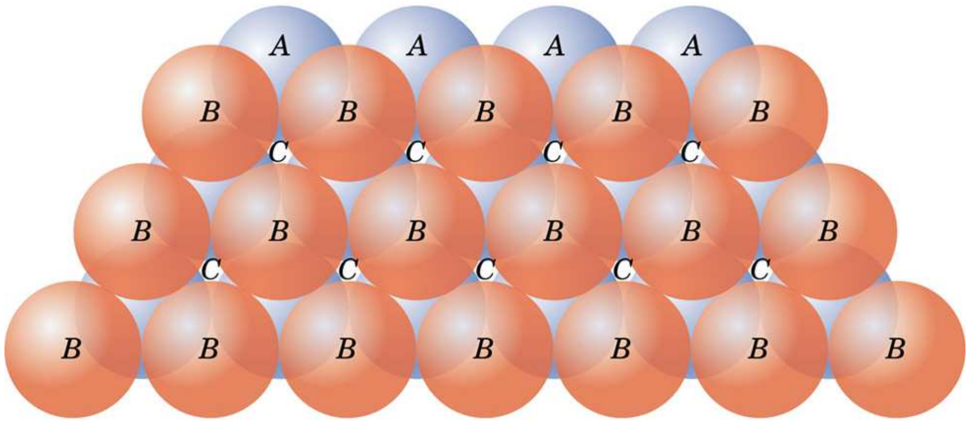
http://www.chm.bris.ac.uk/webprojects2003/cook/millerindices.htm

FCC Stacking Sequence - First layer

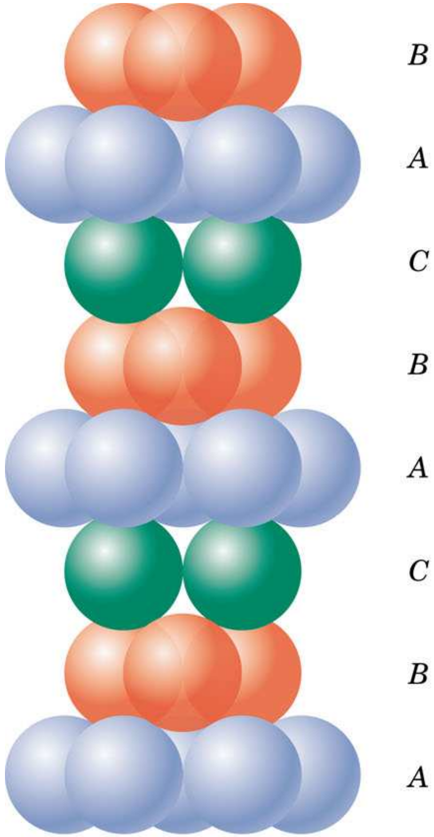


(a)

FCC Stacking Sequence - 2^{nd} layer



(b)

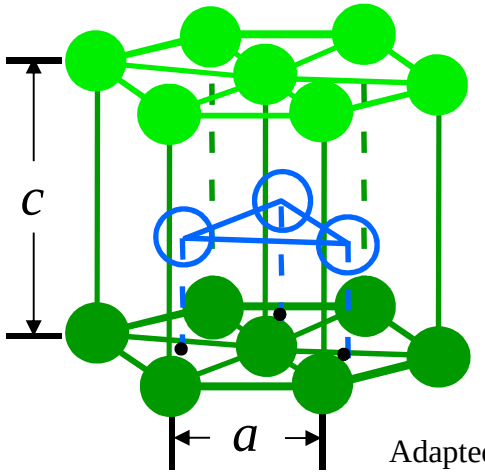


(a)

- ABCABC...
  ABCABC…
  Stacking Sequence

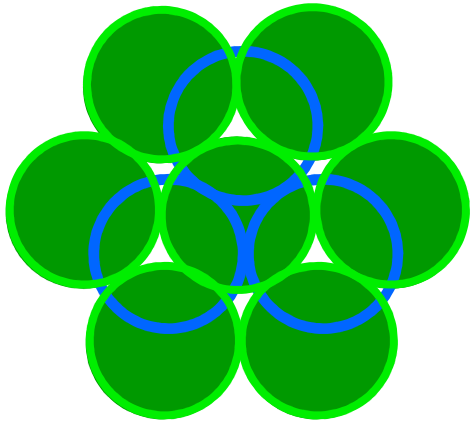
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), *Callister & Rethwisch 8e.*

- 2D Projection



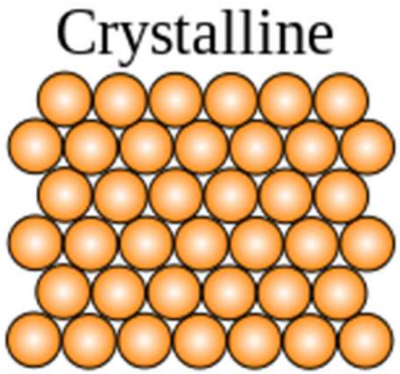
- Coordination # = 12
- APF = 0.74
- c/a = 1.633

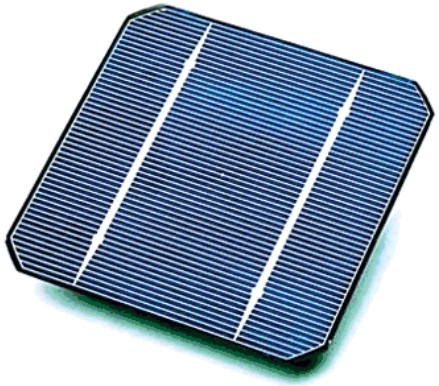
6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

Single Crystals

- For a crystalline solid.
- Periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption.
- Difficult to grow (environment must be carefully controlled)





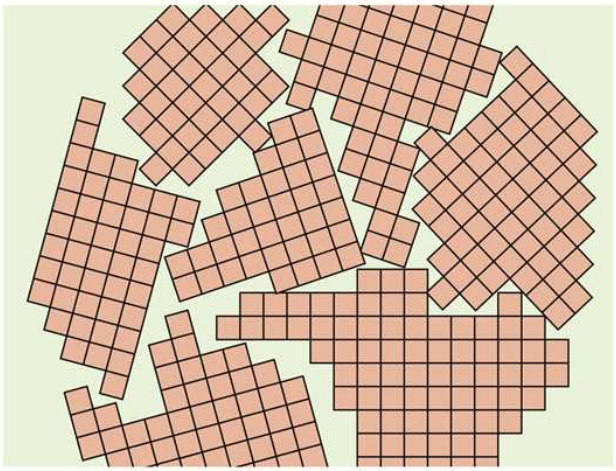
http://en.wikipedia.org/wiki/Crystal

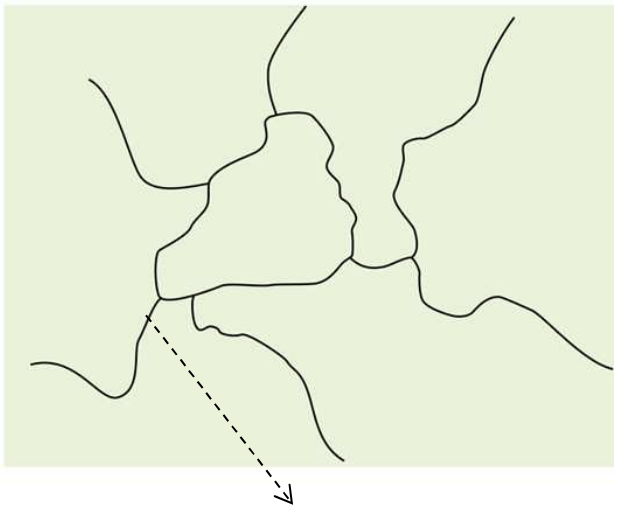
http://www.hope.com.tw/art/print.asp?O=HJQBN6CV8H8AR-STDF

Polycrystals

- Most engineering materials are polycrystals.
- Several crystals or grains
- The boundary between the grains is the grain boundary

  → the orientation of the crystal changes





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.