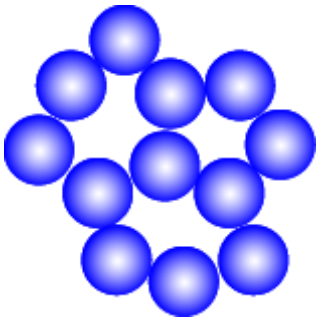
Chapter 3: Fundamentals of Crystallography

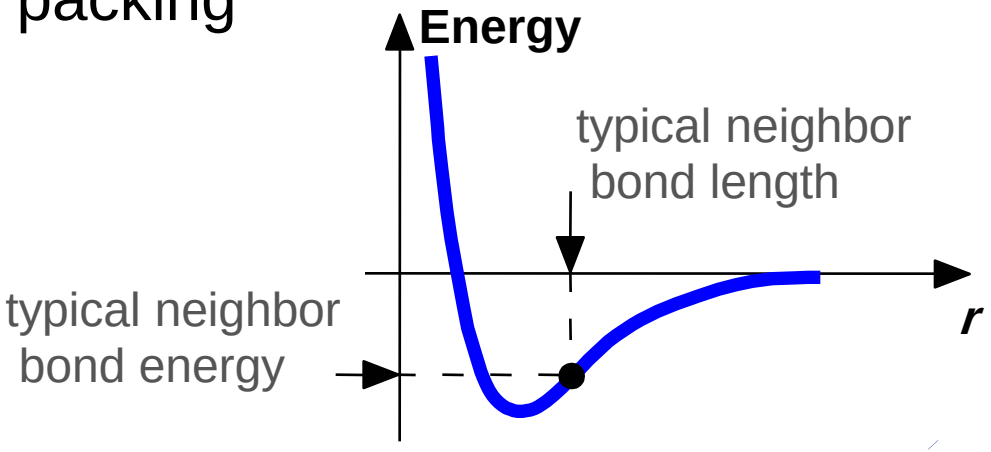
ISSUES TO ADDRESS...

- What is the difference in atomic arrangement between crystalline and noncrystalline solids?
- How are crystallographic directions and planes named?
- Under what circumstances does a material property vary with the measurement direction?

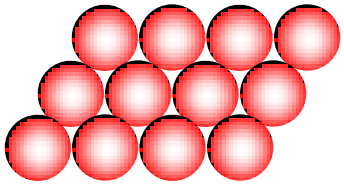
Energy and Packing

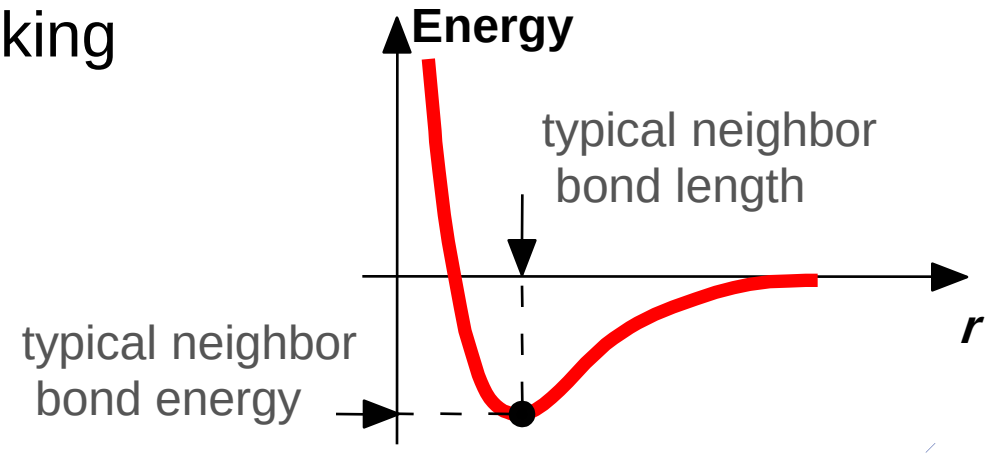
- Non dense, random packing





- Dense, ordered packing



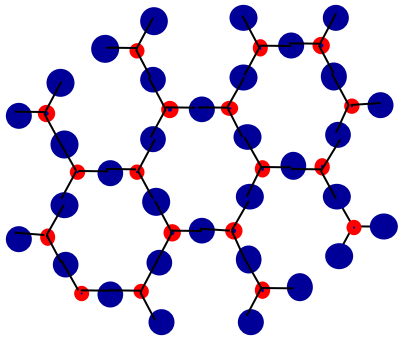


Dense, ordered packed structures tend to have lower energies.

Materials and Packing

Crystalline materials...

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



crystalline SiO_2

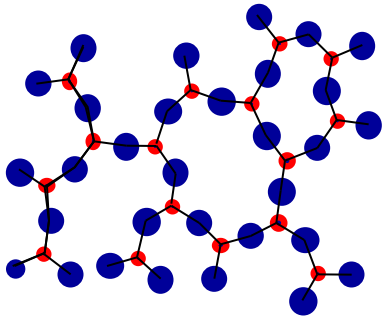
Adapted from Fig. 3.11(a), *Callister & Rethwisch 9e.*

• **Si** ● **Oxygen**

Noncrystalline materials...

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

"Amorphous" = Noncrystalline



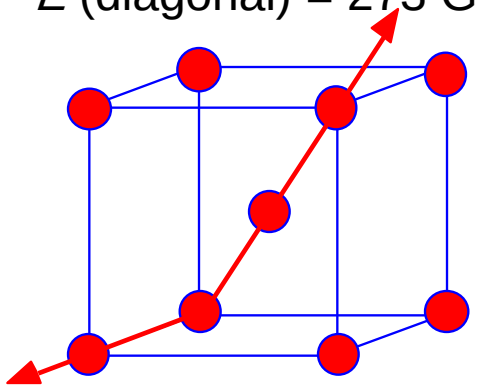
noncrystalline SiO_2

Adapted from Fig. 3.11(b), *Callister & Rethwisch 9e.*

Single vs Polycrystals

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

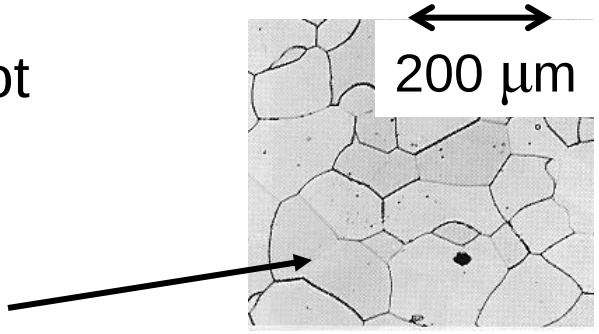
E (diagonal) = 273 GPa

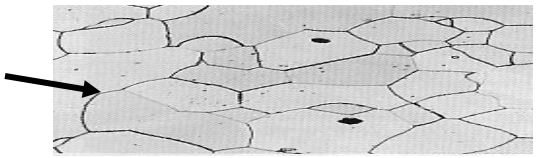


E (edge) = 125 GPa

Data from Table 3.3, *Callister & Rethwisch 9e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

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

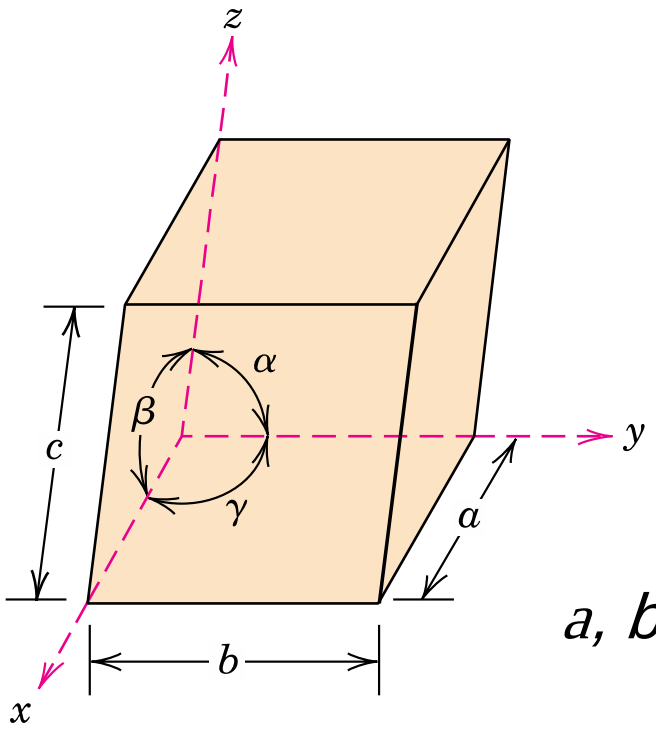




Adapted from Fig. 6.19(b), *Callister & Rethwisch 9e*. [Fig. 6.19(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

Crystal Systems

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



7 crystal systems

14 crystal lattices

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

Polymorphism

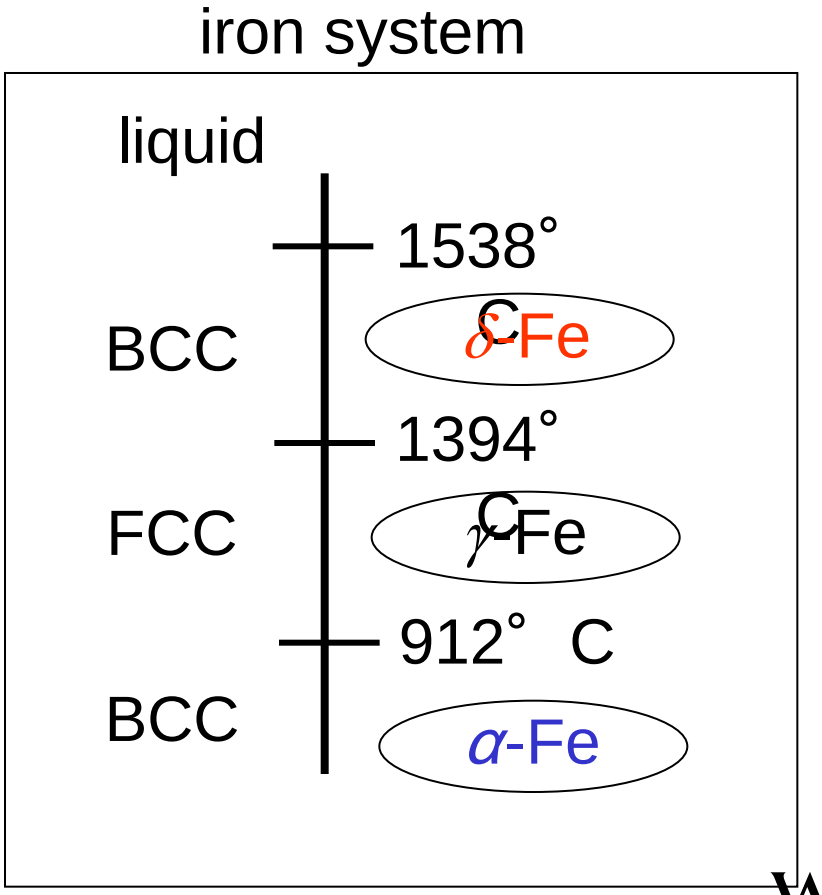
- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

titanium

α, β-Ti

carbon

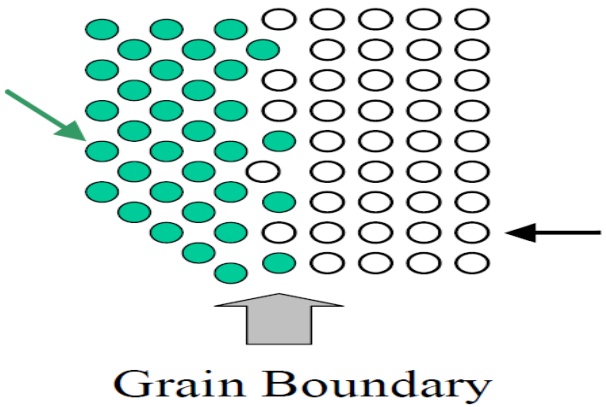
diamond, graphite

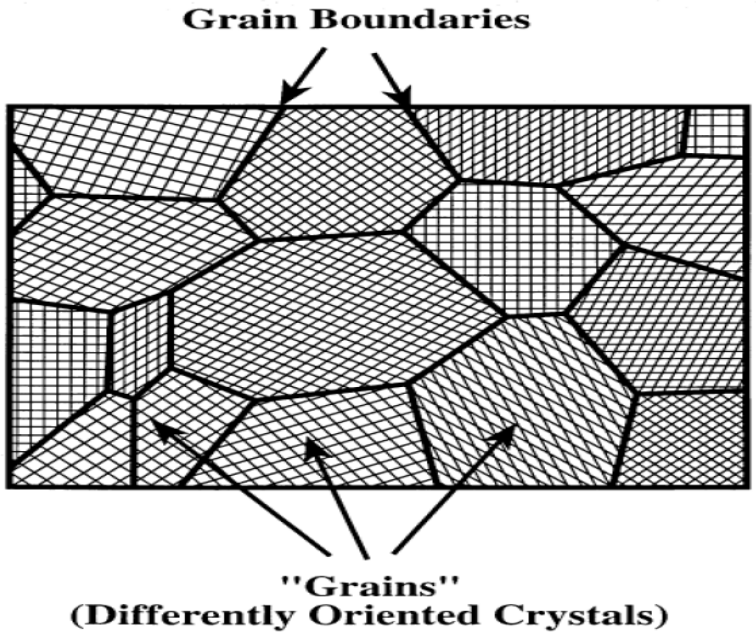


Single Crystals and Polycrystalline Materials

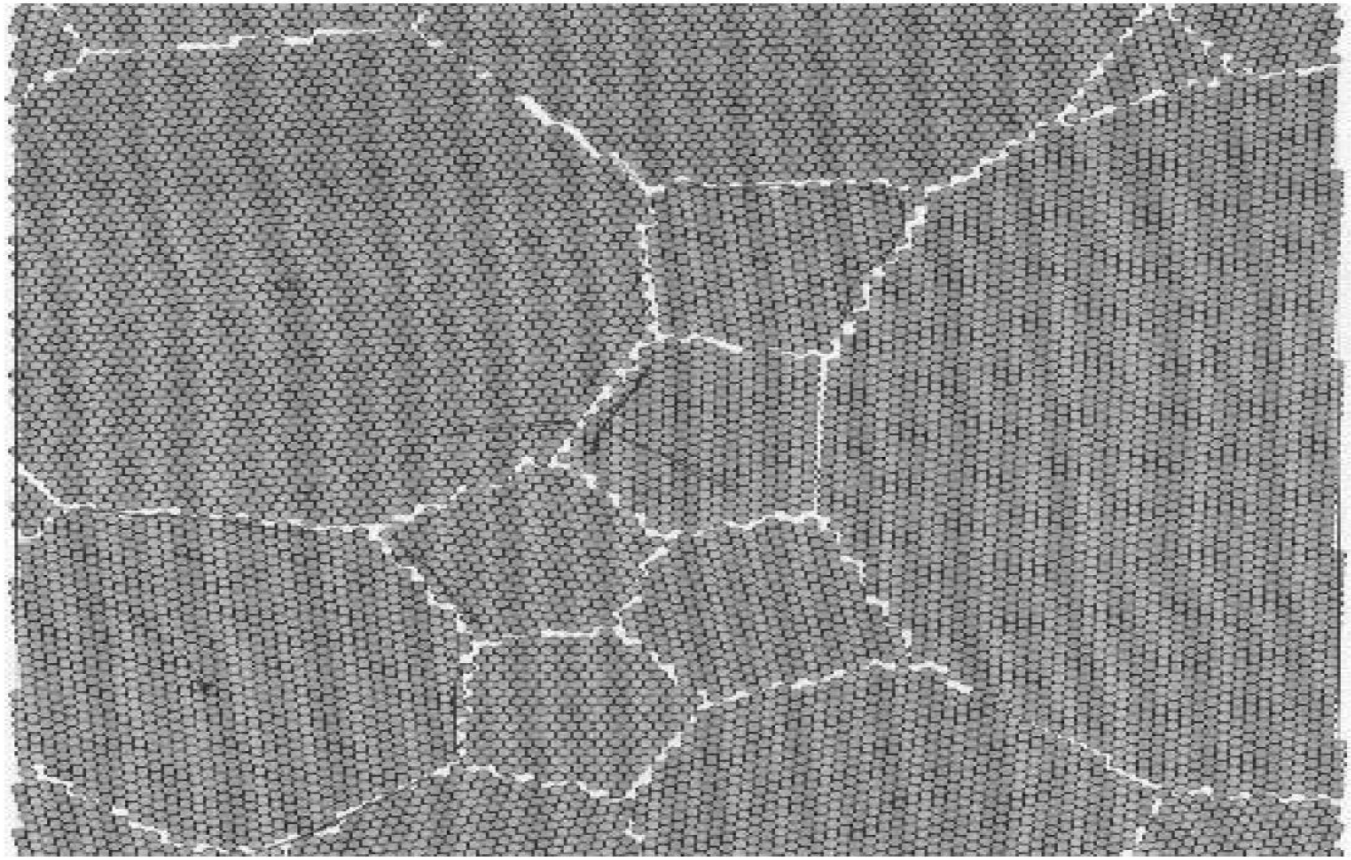
Single crystal: atoms are in a repeating or periodic array over the entire extent of the material

Polycrystalline material: comprised of many small crystals or **grains.** The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.



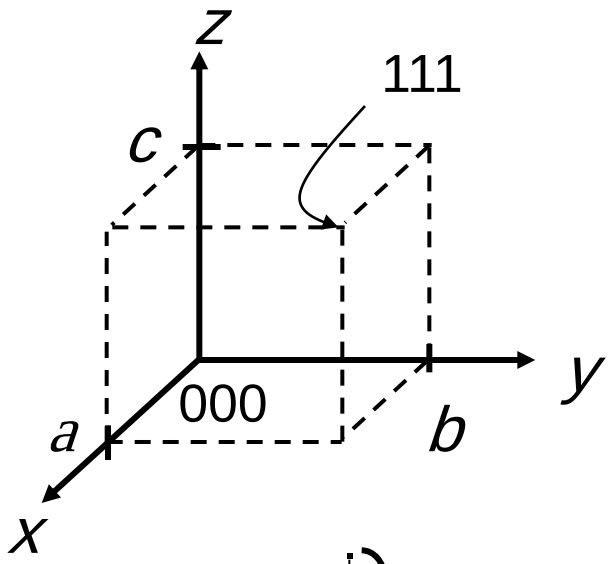


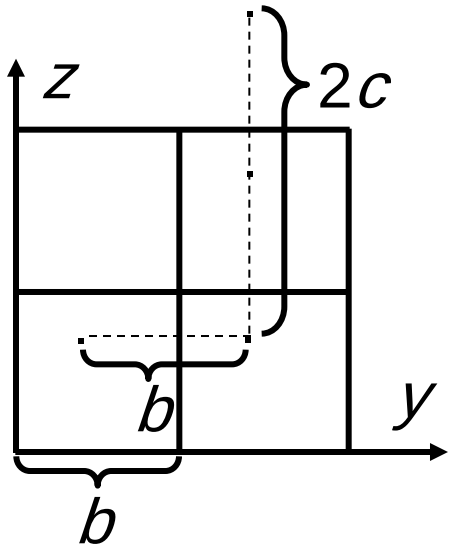
Polycrystalline Materials



Atomistic model of a nanocrystalline solid by Mo Li, JHU

Point Coordinates





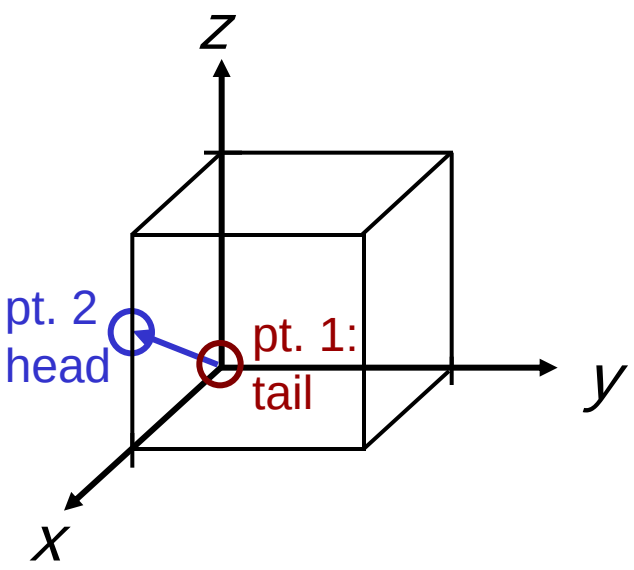
Point coordinates for unit cell center are

a/2, *b*/2, *c*/2 ½ ½ ½

Point coordinates for unit cell corner are 111

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

Crystallographic Directions



Algorithm

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

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

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

$$[uvw]$$

ex:

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

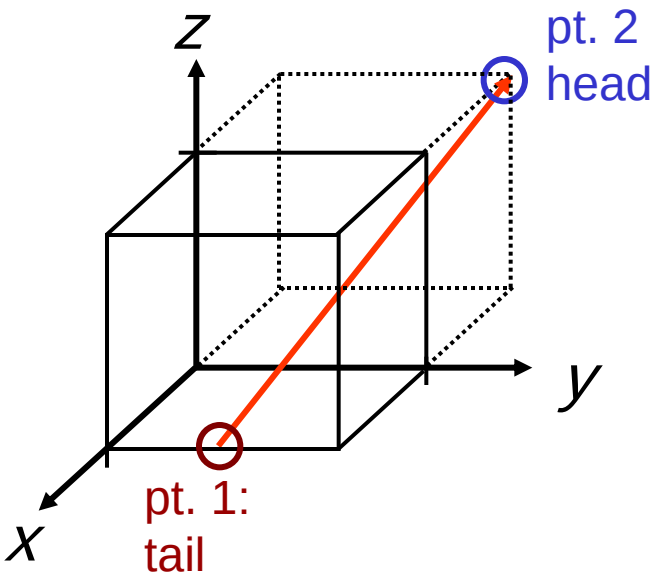
pt. 2 $x_2 = a$, $y_2 = 0$, $z_2 = c/2$

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

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

=> [201]

Crystallographic Directions



Example 2:

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

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

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

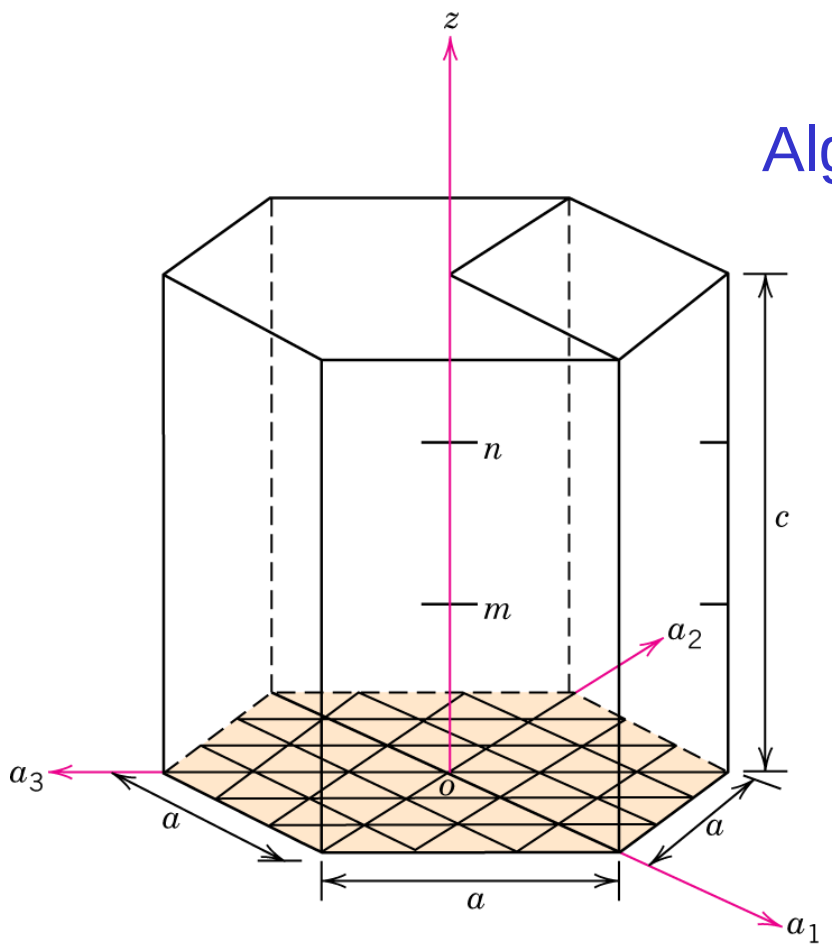
=> -2, 1/2, 1

Multiplying by 2 to eliminate the fraction

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

families of directions <*uvw*>

Drawing HCP Crystallographic Directions (i)

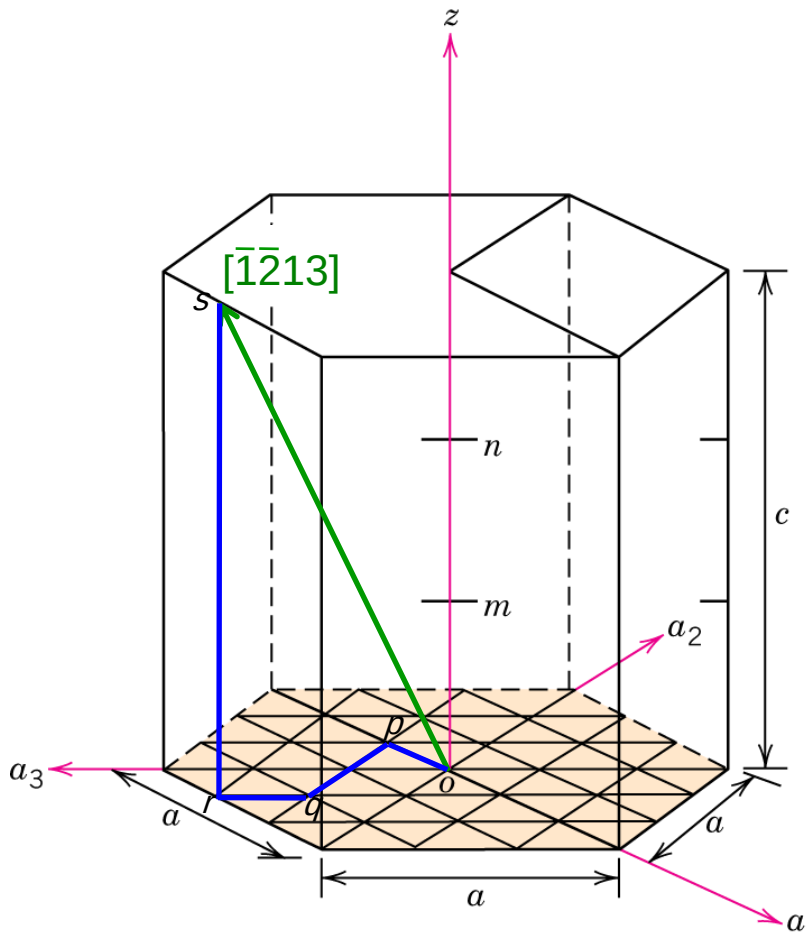


Algorithm (Miller-Bravais coordinates)

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

Drawing HCP Crystallographic Directions (ii)

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



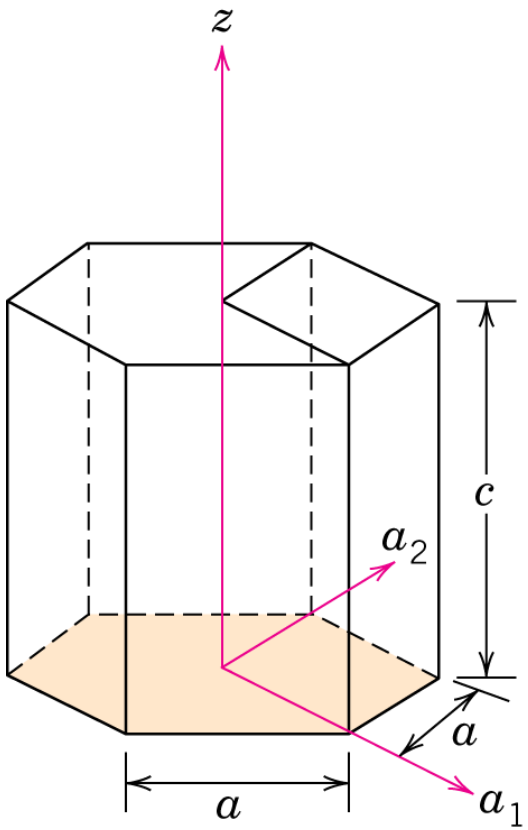
Algorithm

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

4. Construct Vector
   - start at point *o*
   - proceed $-a/3$ units along a_1 axis to point *p*
   - $-2a/3$ units parallel to a_2 axis to point *q*
   - $a/3$ units parallel to a_3 axis to point *r*
   - *c* units parallel to *z* axis to point *s*

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

Determination of HCP Crystallographic Directions (ii)



Algorithm

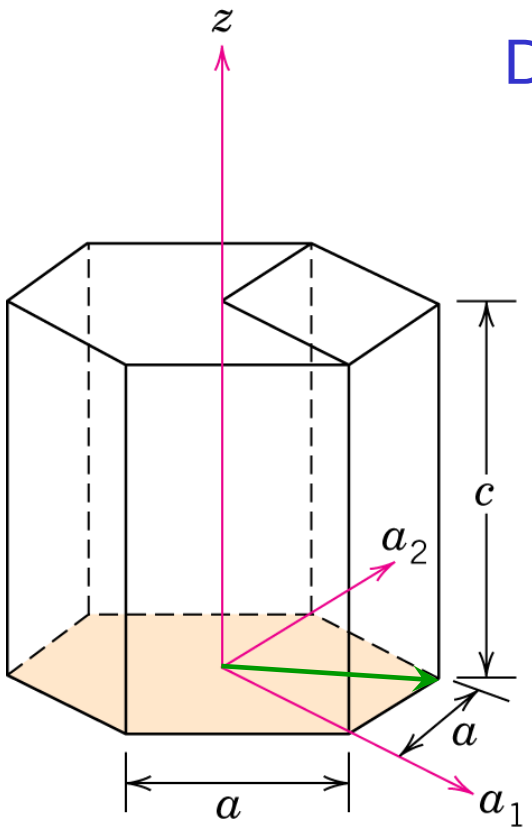
1. Determine coordinates of vector tail, pt. 1: x_1, y_1, & z_1; and vector head, pt. 2: x_2, y_2, & z_2. in terms of three axis (a_1, a_2, and z)
2. Tail point coordinates subtracted from head point coordinates and normalized by unit cell dimensions a and c
3. Adjust to smallest integer values
4. Enclose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

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

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

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

Determination of HCP Crystallographic Directions (ii)



Determine indices for green vector

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

5. Convert to 4-axis parameters

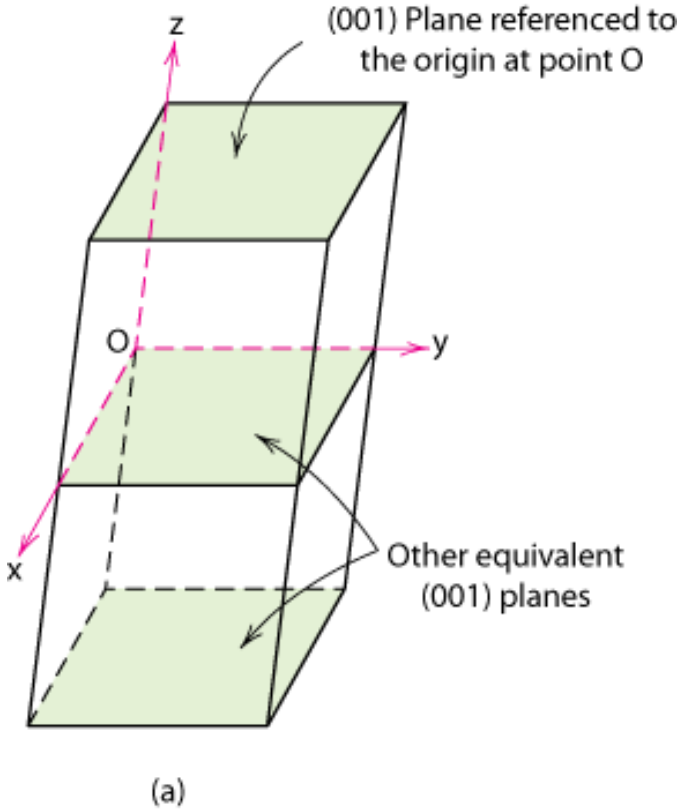
$$u = \frac{1}{3}[(2)(1) - (1)] = \frac{1}{3} \qquad v = \frac{1}{3}[(2)(1) - (1)] = \frac{1}{3}$$

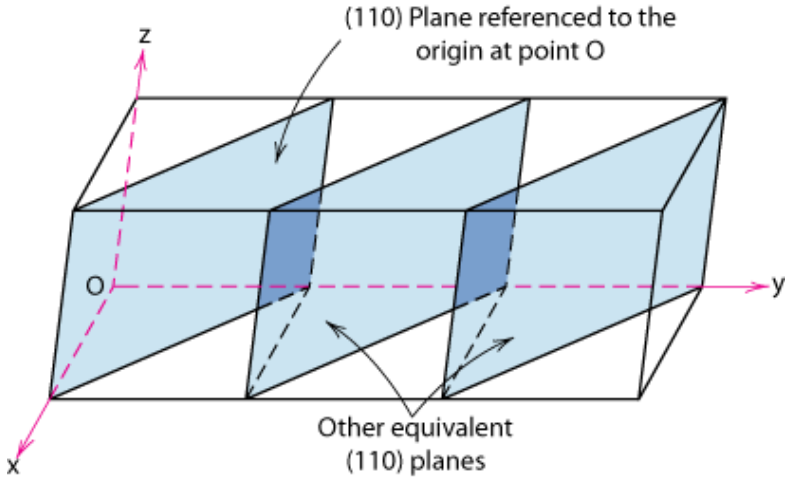
$$t = -(\frac{1}{3} + \frac{1}{3}) = -\frac{2}{3} \qquad w = 0$$

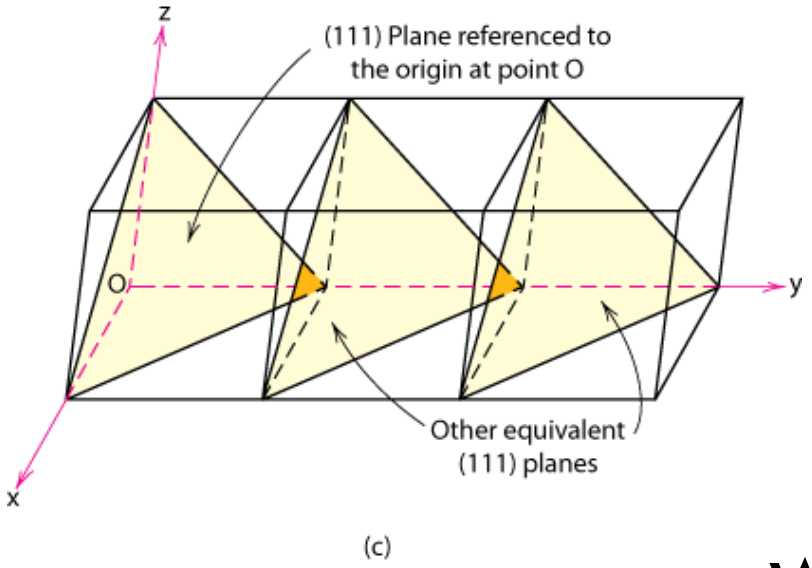
6. Reduction & Brackets

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

Crystallographic Planes







Adapted from Fig. 3.7, *Callister & Rethwisch 9e.*

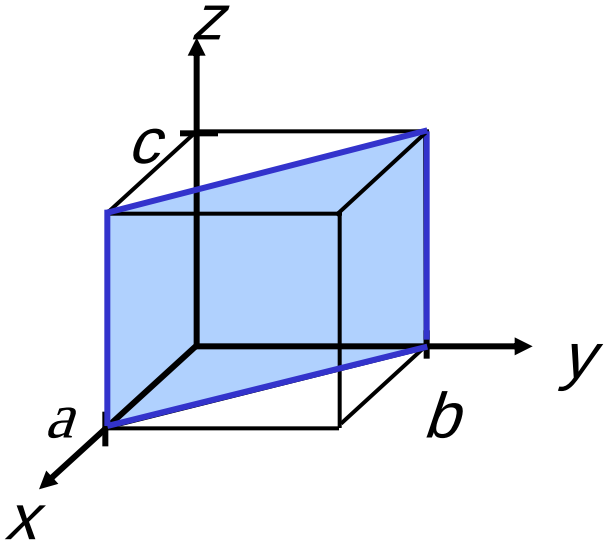
Crystallographic Planes

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

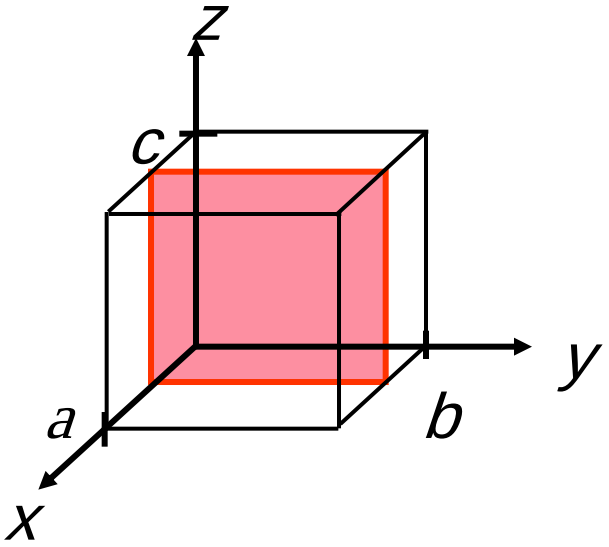
- Algorithm
  1. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
  2. Take reciprocals of intercepts
  3. Reduce to smallest integer values
  4. Enclose in parentheses, no commas i.e., (*hkl*)

Crystallographic Planes

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

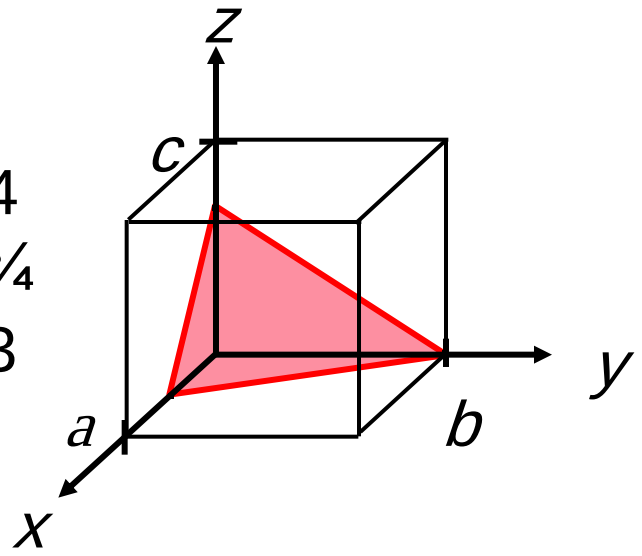


example		*a*	*b*	*c*
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		



Crystallographic Planes

example	*a*	*b*	*c*
1. Intercepts	1/2	1	3/4
2. Reciprocals	1/½	1/1	1/¾
	2	1	4/3
3. Reduction	6	3	4
4. Miller Indices	(634)		



Family of Planes $\{hkl\}$

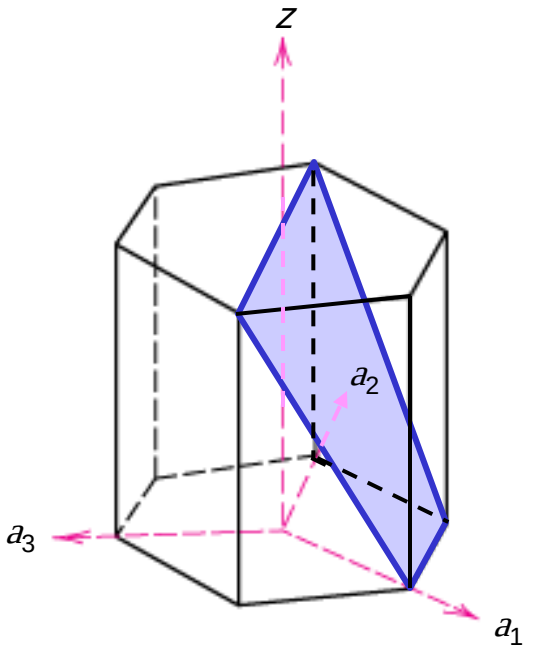
Ex: {100} = (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$

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,
Callister & Rethwisch 9e.

Crystallographic Planes

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

a) Draw (100) and (111) crystallographic planes for Fe.

b) Calculate the planar density for each of these planes.

Summary

- Atoms may assemble into crystalline or amorphous structures.
- 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.
- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.

Chapter 4: The Structure of Crystalline Solids

ISSUES TO ADDRESS...

- What are common crystal structures for metals and ceramics?
- What features of a metal's/ceramic's atomic structure determine its density?
- How do the crystal structures of ceramic materials differ from those for metals?

Metallic Crystal Structures

- Metals are usually (poly)crystalline; although formation of amorphous metals is possible by rapid cooling

- As we learned in Chapter 2, the atomic bonding in metals is non-directional $\Rightarrow$ no restriction on numbers or positions of nearest-neighbor atoms $\Rightarrow$ large number of nearest neighbors and dense atomic packing

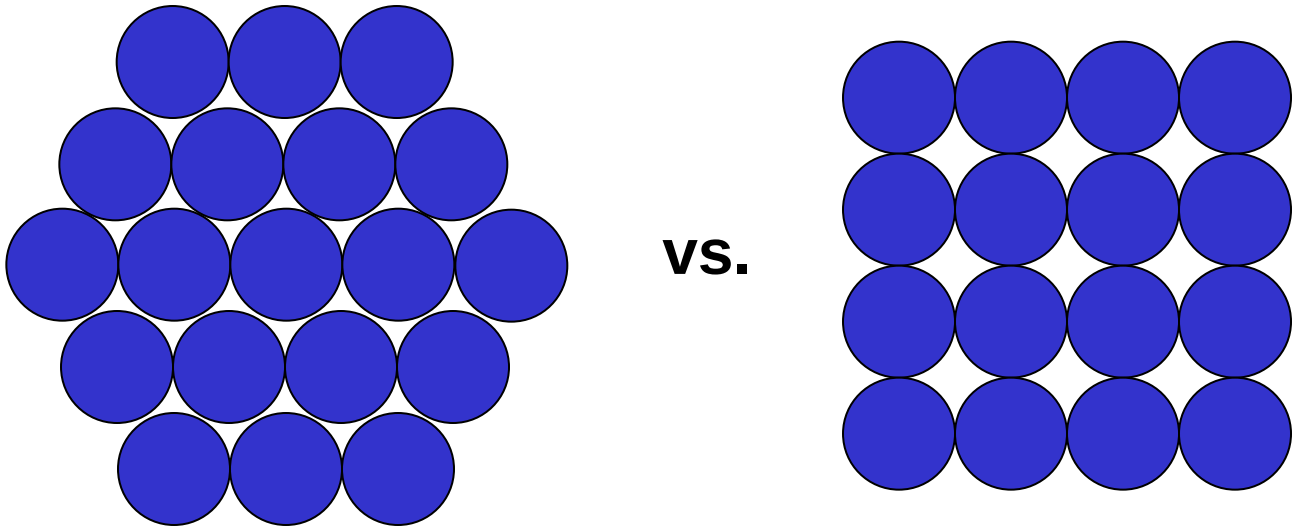
- **Atom (hard sphere) radius, R,** defined by ion core radius - typically 0.1 - 0.2 nm

- The most common types of unit cells are the faced-centered cubic (FCC), the body-centered cubic (FCC) and the hexagonal close-packed (HCP).

Metallic Crystal Structures

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

2-dimensions



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

Metallic Crystal Structures

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

We will examine three such structures...

Simple Cubic Structure (SC)

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

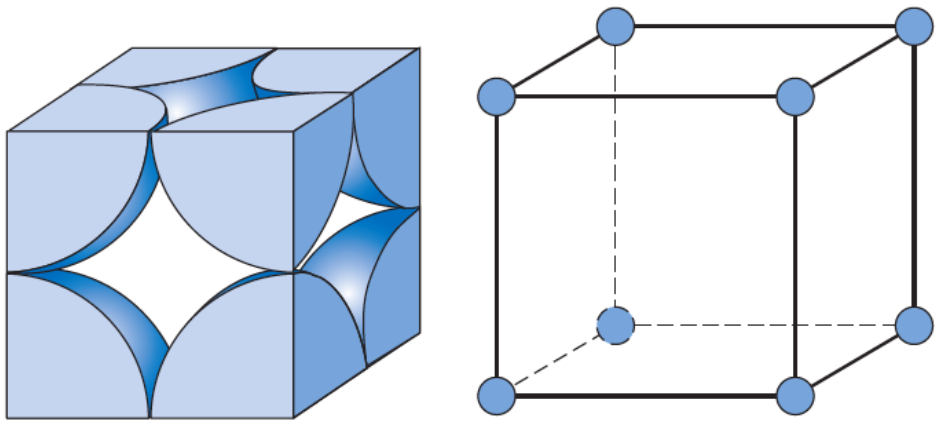
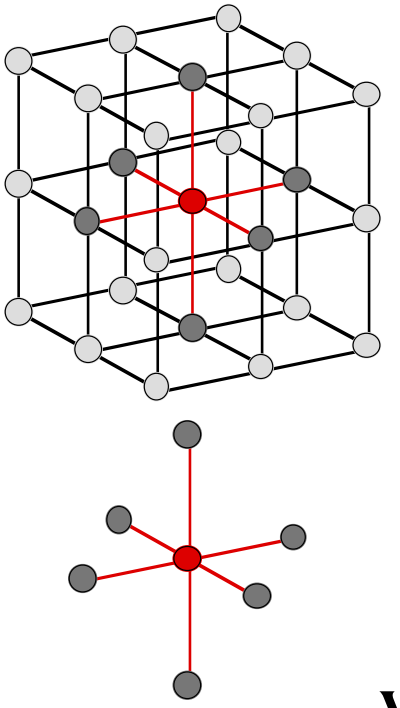


Fig. 4.2, *Callister & Rethwisch 9e.*

- Coordination # = 6
  (# nearest neighbors)

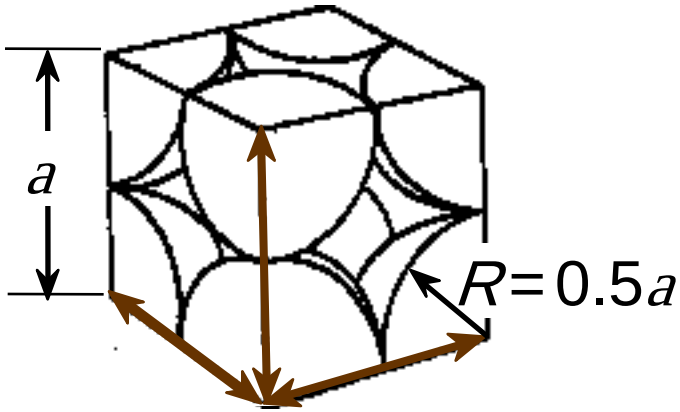


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

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

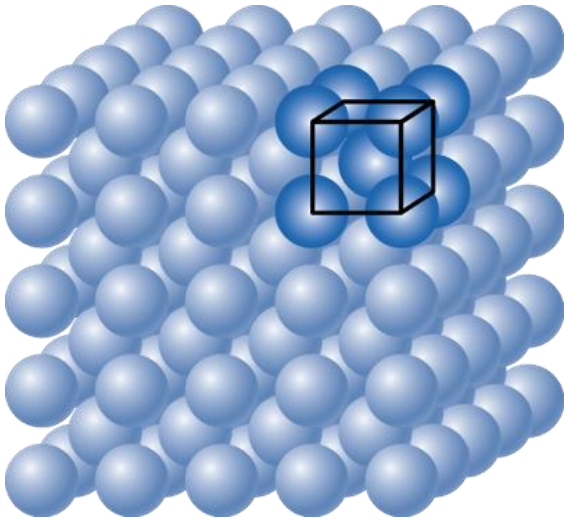
Adapted from Fig. 4.2 (a), *Callister & Rethwisch 9e.*

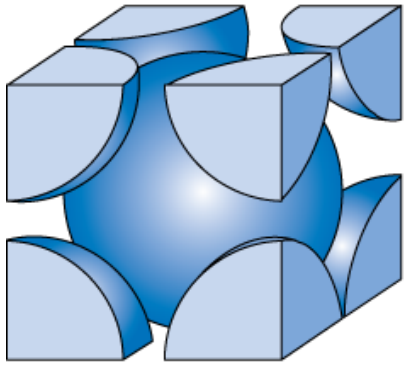
Body Centered Cubic Structure (BCC)

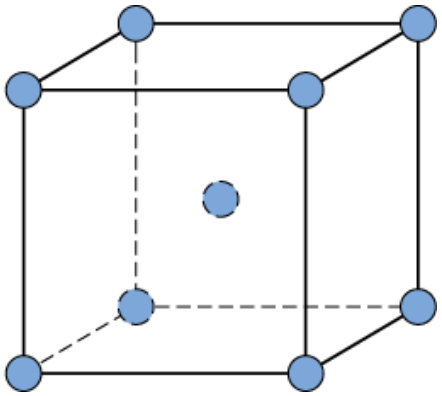
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

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

- Coordination # = 8





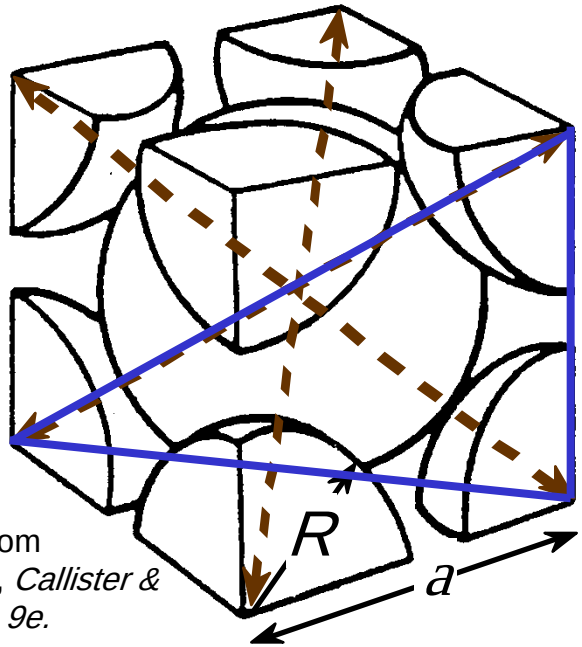


Adapted from Fig. 4.1,
Callister & Rethwisch 9e.

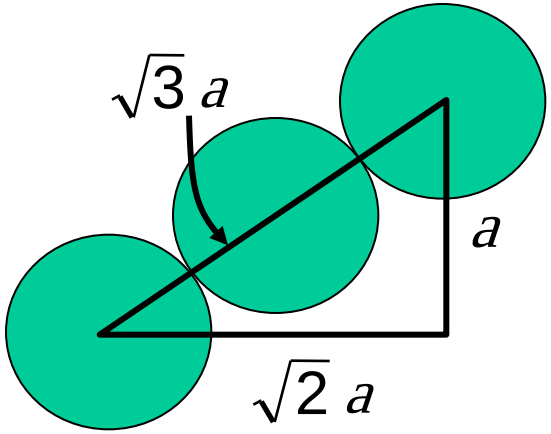
2 atoms/unit cell: 1 center + 8 corners x 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Adapted from Fig. 4.1(a), *Callister & Rethwisch 9e.*



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

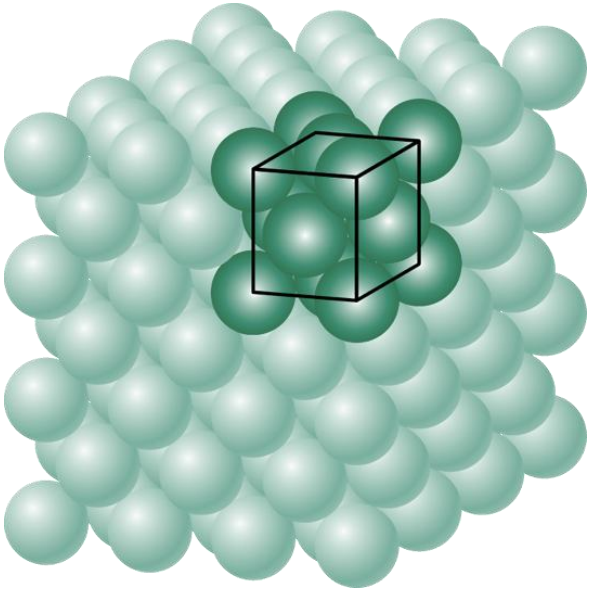
$$APF = \frac{\left(\frac{\text{atoms}}{\text{unit cell}}\right)\left(\frac{\text{volume}}{\text{atom}}\right)}{\left(\frac{\text{volume}}{\text{unit cell}}\right)} = \frac{2\left(\frac{4}{3}\pi(\sqrt{3}a/4)^3\right)}{a^3}$$

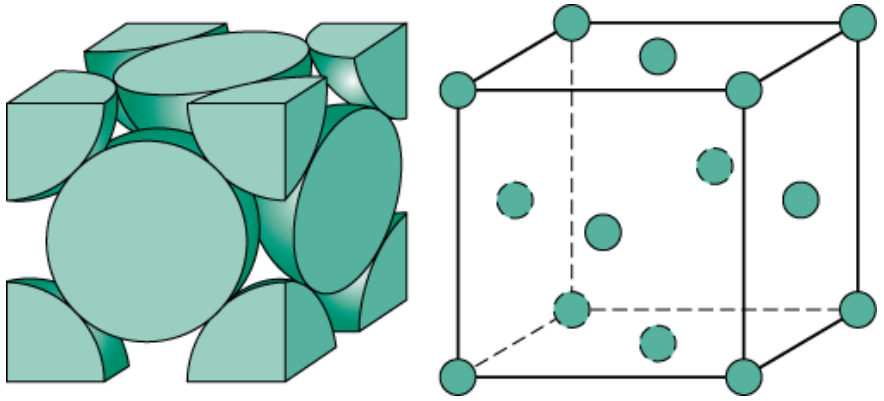
Face Centered Cubic Structure (FCC)

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

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

- Coordination # = 12



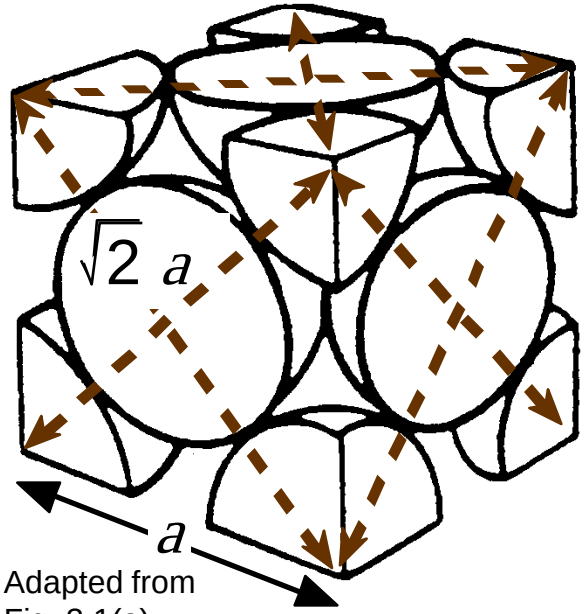


Adapted from Fig. 3.1, *Callister & Rethwisch 9e.*

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

Atomic Packing Factor: FCC

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



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

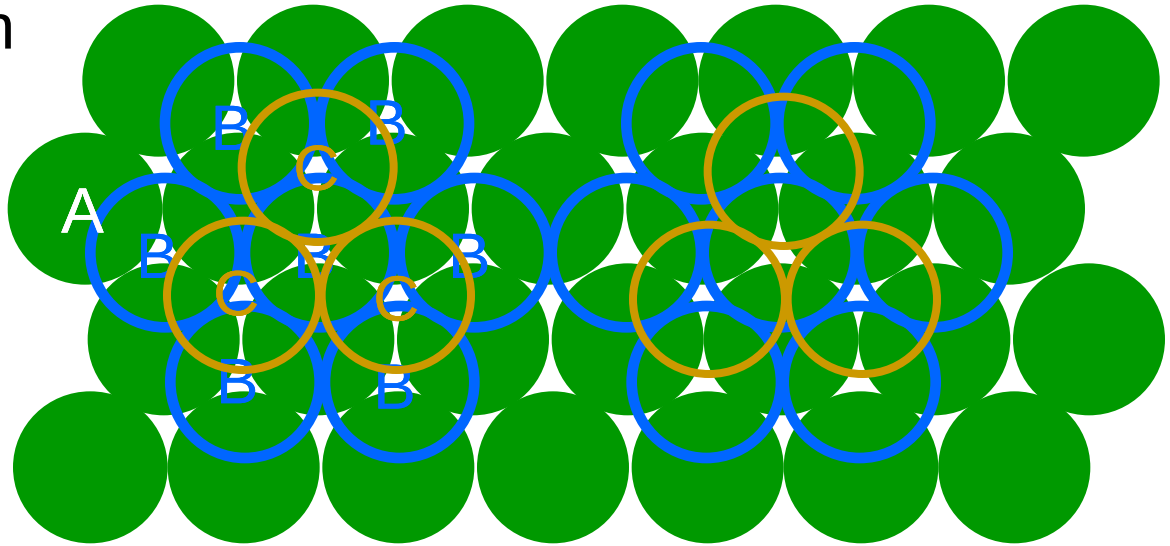
Close-packed directions:
length = $4R = \sqrt{2}\,a$

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

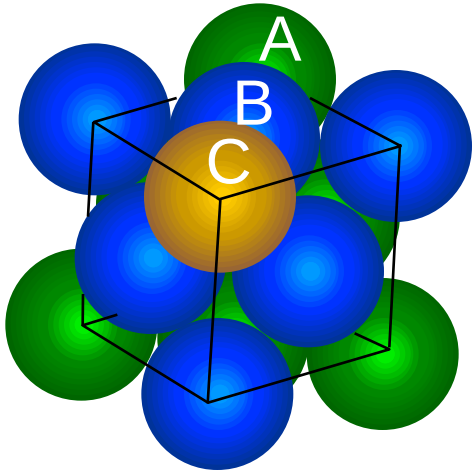
$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \cdot \dfrac{\text{volume}}{\text{atom}}}{\dfrac{\text{volume}}{\text{unit cell}}} = \frac{4\left(\frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3\right)}{a^3}$$

FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

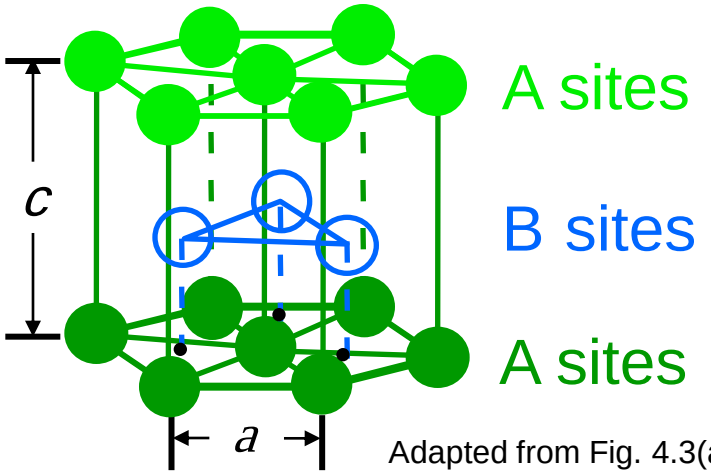


- FCC Unit Cell



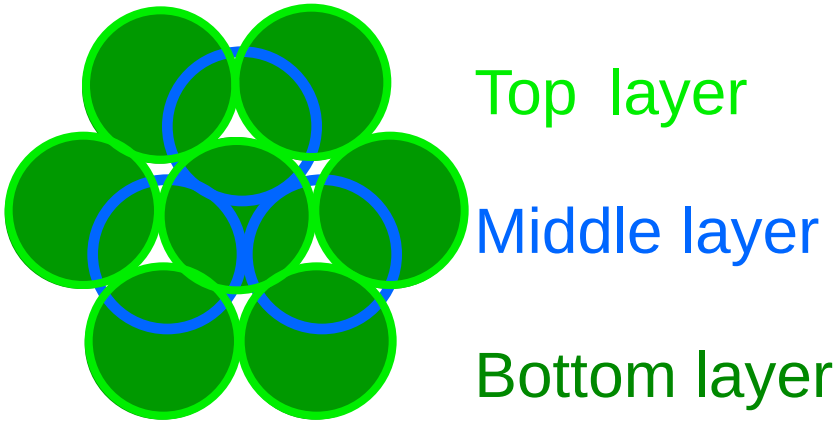
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 4.3(a), *Callister & Rethwisch 9e.*

- 2D Projection



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

Theoretical Density, ρ

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

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

where n = number of atoms/unit cell

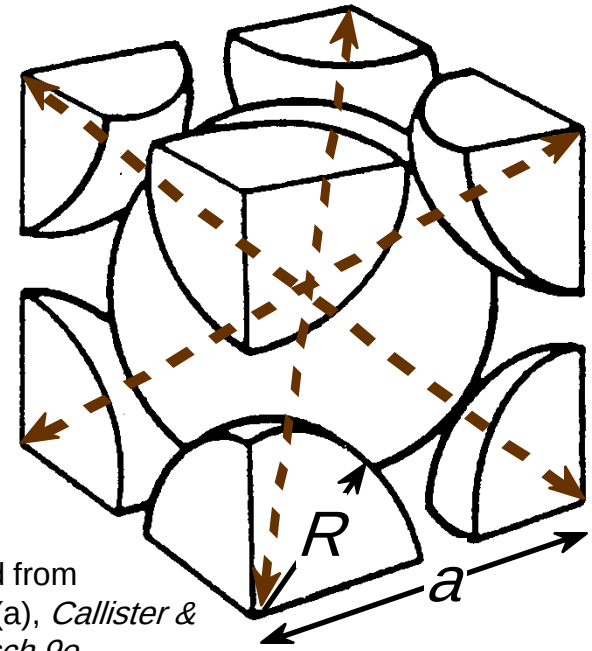
A = atomic weight

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

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol

Theoretical Density, ρ



Adapted from Fig. 4.1(a), *Callister & Rethwisch 9e.*

- Ex: Cr (BCC)

  A = 52.00 g/mol

  R = 0.125 nm

  n = 2 atoms/unit cell

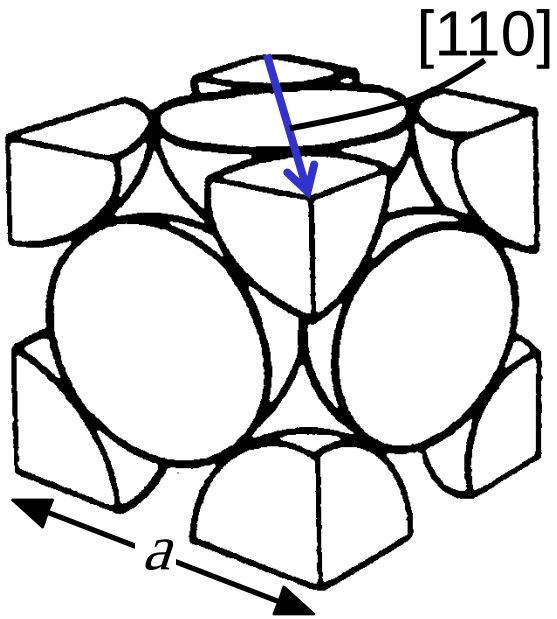
$a = 4R/\sqrt{3} = 0.2887$ nm

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

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

Linear Density

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



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

ex: linear density of Al in [110] direction

$a = 0.405$ nm

atoms → 2

length → $\sqrt{2}a$

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

Planar Density of (100) Iron

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

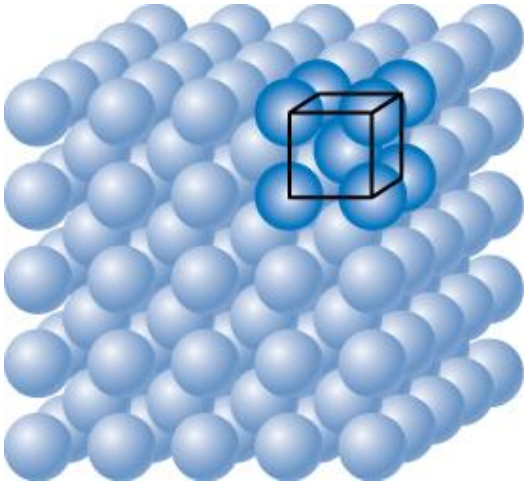
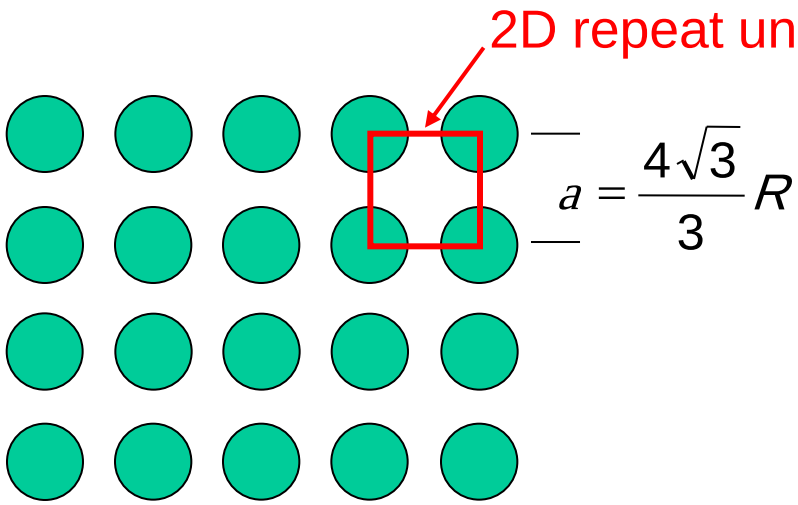


Fig. 4.2(c), *Callister & Rethwisch 9e* [from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

(100)

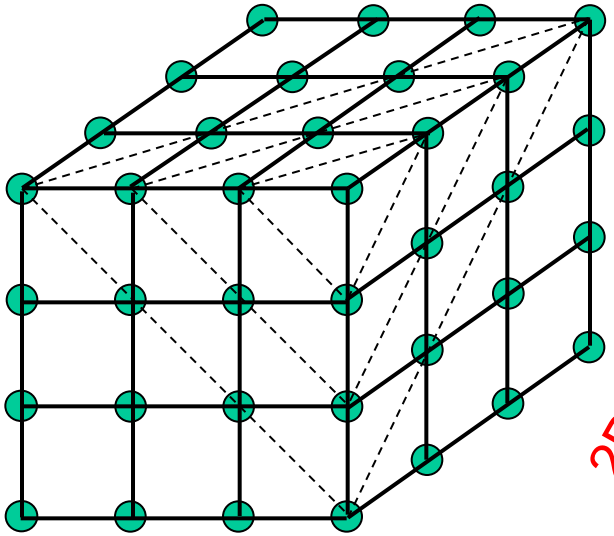


Radius of iron $R = 0.1241$ nm

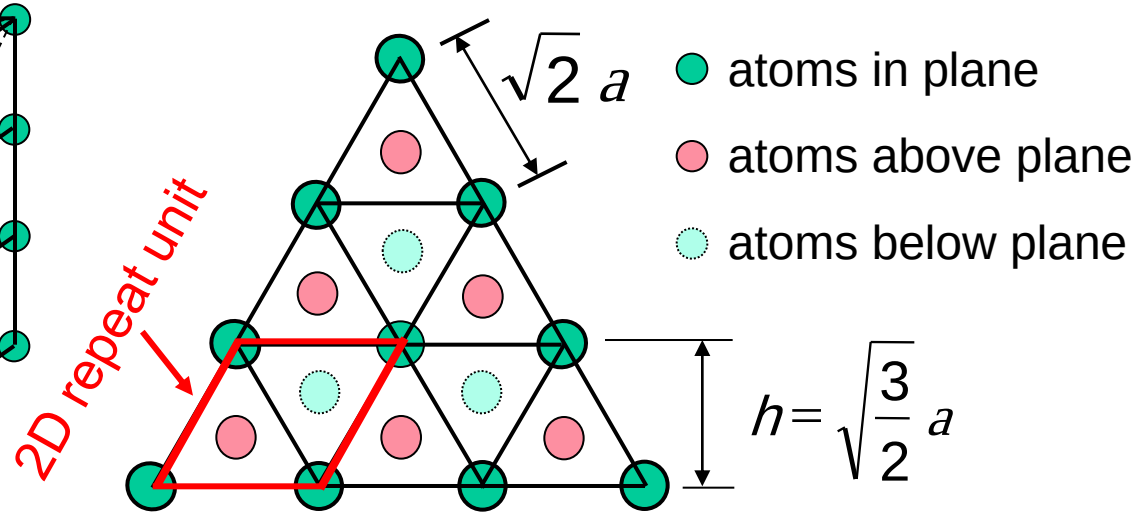
$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3} R\right)^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

Planar Density of (111) Iron

Solution (cont): (111) plane



1 atom in plane/ unit surface cell



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

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

Summary

- 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).
- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.