Al-Karkh University for Science

College of Remote Sensing and Geophysics

Geophysics Department

An Introduction to Crystallography

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Text Books

1- الصائغ، عبد الهادي، والكفيشي، فيصل، والجبوري، زكي. 1989. علم البلورات. بيت الحكمة- جامعة بغداد. 352 صفحة.

2- Waler Borchardt- Ott. 2011.Crystallography, An Introduction. Third Edithion. Springer. 355 p.

3- Carl W. Correns, 1969. Introduction to Mineralogy, Crystallography and Petrology Second Edition, Springer-Verlag Berlin Heidelberg.

Lecture- 1
Introduction to Crystallography

CRYSTALLOGRAPHY:

meaning the study of crystalline solids, external shape, and internal structure.

It is divided into 3 sections: geometrical, physical, and chemical.

Definition of Crystal: A crystal is:

1.Solid and Homogeneous body.

2. bounded by flat faces.

3.Has internal atomic structure.

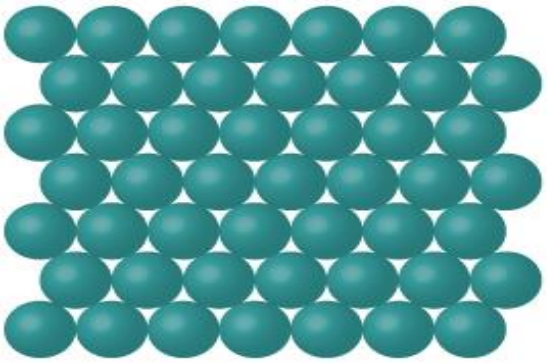
4.It has a specific chemical compound.

5.It is formed under suitable conditions, from liquid or gas to the solid.

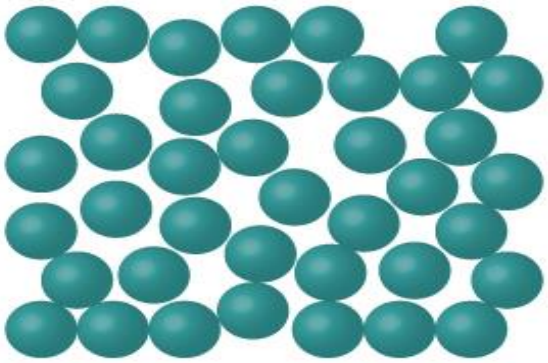
Classification of substances: Crystalline & Amorphous:

Crystalline Substances: : 1- Solid, 2- Anisotropy & Isotropy, 3- It has flat faces on external surfaces, 4- It has Internal atomic structure, and 5- Symmetry space lattice skeleton.

Amorphous substances: (in Greek amorphous means “formless”) 1. Do not have overall regular internal structure. 2. They are isotropic. 3.Their constituent particles are arranged randomly.4.Have no symmetry.5.Cannot be bounded by flat faces.Examples of amorphous substances are: glass, plastics. Glue, resin, and solid colloids (gels).



Crystalline



Amorphous

Classification of crystals according to the degree of crystallization: Euhedral crystals, Subhedral crystals and Anhedral crystals.

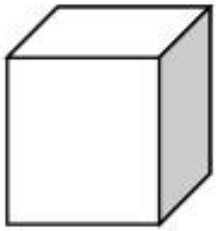
External characteristices of crystals:

Crystal faces, Edge, Solid angle, Interfacial angle, Crystal form and Crystal habit.

Crystal faces: The crystal is bounded by flat plane surfaces. These surfaces represent the internal arrangement of atoms. Faces are two kinds, like and unlike.

Classification of crystals

- Classification of crystals according to the degree of crystallization
  - Euhedral crystals
  - Subhedral crystals
  - Anhedral crystals



Euhedral Crystal

Subhedral Crystal

Anhedral Crystal

fppt.com

Edge: formed by the intersection of any two adjacent faces.

Solid Angles: formed by intersection of three or more faces.

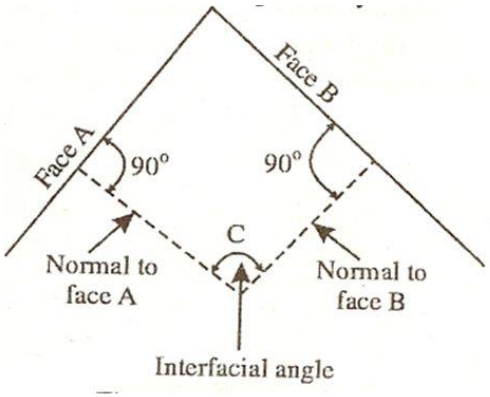
Interfacial angle: the angle between two lines that are perpendicular to the faces.

Such lines are called the poles to the crystal face.

this angle measured by a device called a contact goniometer.

Interfacial angle & Goniometer

CRYSTAL



Lecture- 2

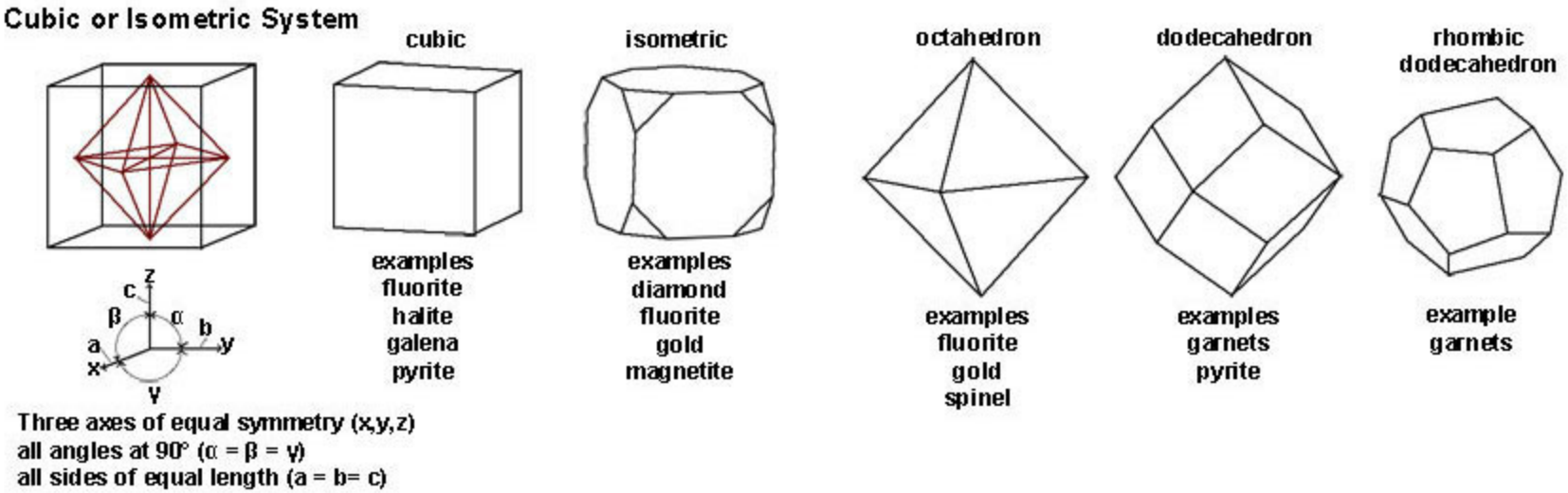
Crystal forms:

A number of faces which have the same relation with the crystallographic axes.

A crystal made up entirely of like faces is termed a simple form.

A crystal which consists of two or more simple forms is called combination.

Crystal form



Nicholas Steno (1669):

A Danish physician and natural scientist, found that, the angles between similar crystal faces remain constant regardless of the size or the shape of the crystal when measured at the same temperature.

Like other laws of physics and chemistry, we just can't get away from it.

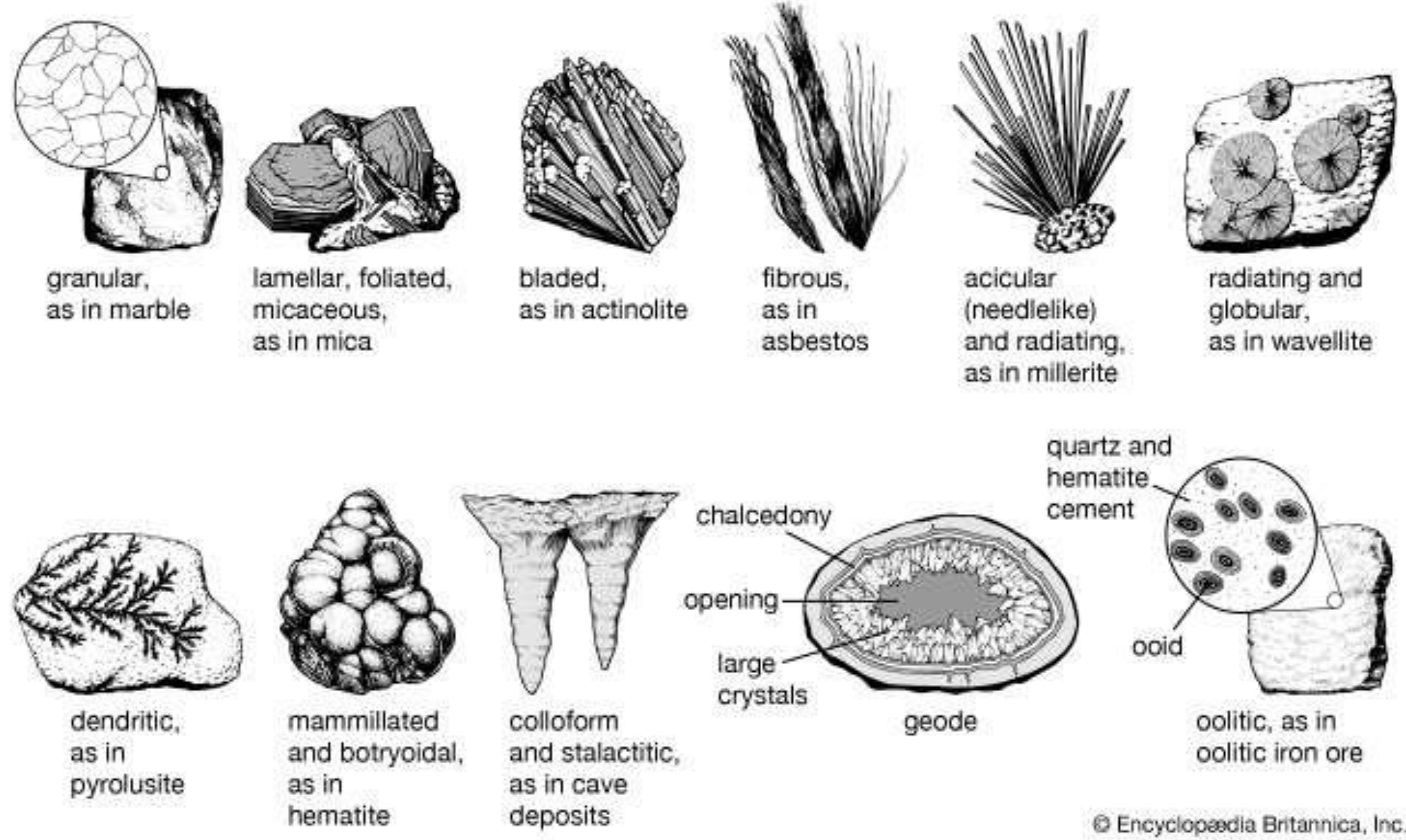
So whether the crystal grew under ideal conditions or not, if you compare the angles between corresponding faces on various crystals of the same mineral, the angle remains the same Steno's law is called the (consistency of interfacial angles).

Crystal Habit: the general external shape of a crystal.

(Tabular habit, Platy habit, Prismatic habit, Acicular habit, Bladed habit)

Crystal Habit

Common crystal aggregations and habits



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Crystal Systems

Crystallographic axes are used to subdivide minerals into systems:

1-Cubic (isometric): 3 axes (a1, a2, a3) are equal and at right angles to each other.

2- Tetragonal: 3 axes, all at right angles, two are equal in length (a & b) and (c) is shorter or longer.

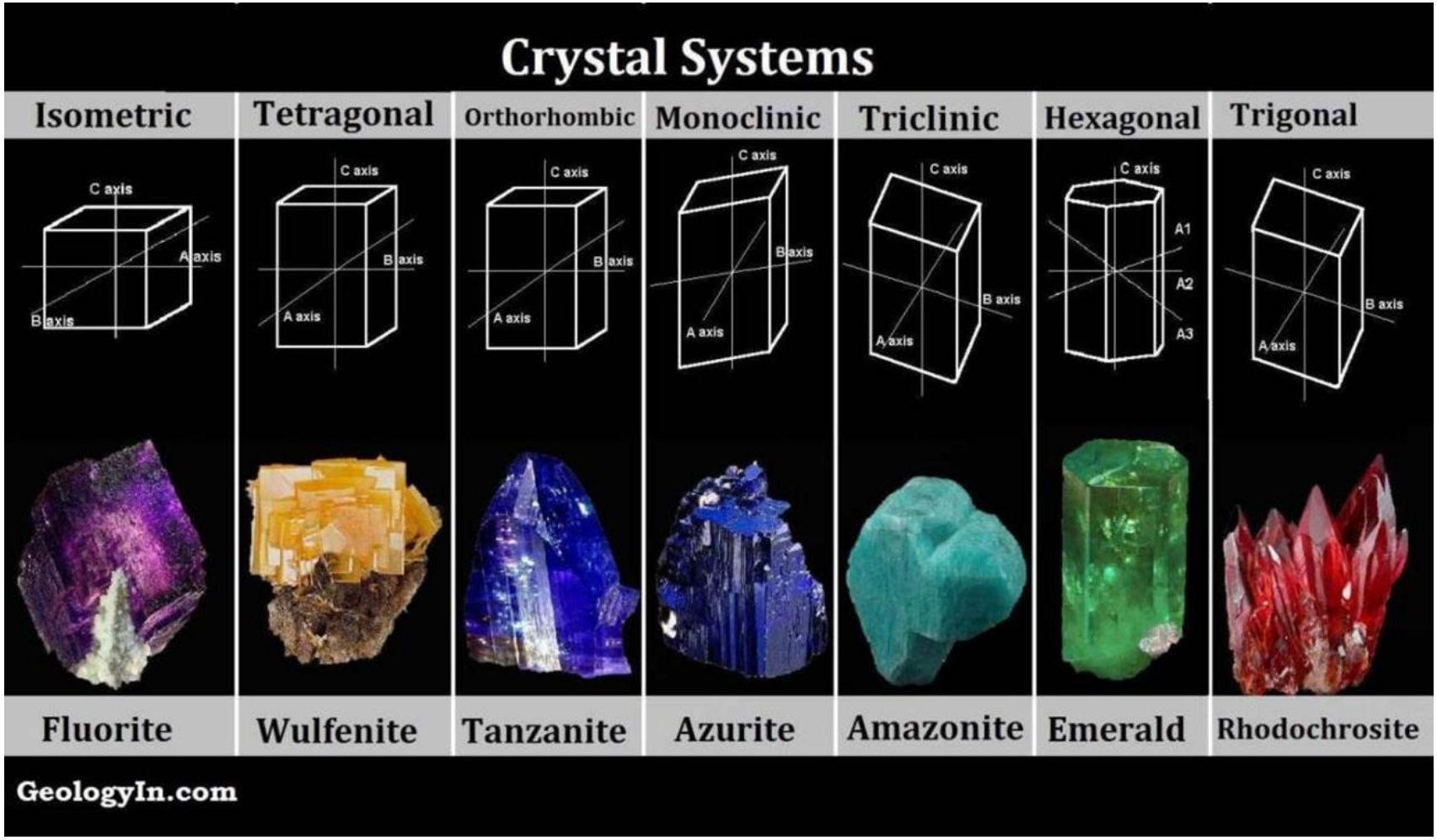
3- Orthorhombic: 3 different lengths axes, all at right angles.

4- Hexagonal: 4 axes,Three in the same plane and intersect at 120°. 3 axes (a1,a2, a3) equal in length. Forth axis © may be longer or shorter.

5- Monoclinic: 3 axes,unequal in length, which (a and c) intersect at oblique angle (not 90 degrees), axis (b) is perpendicular to the other two axes.

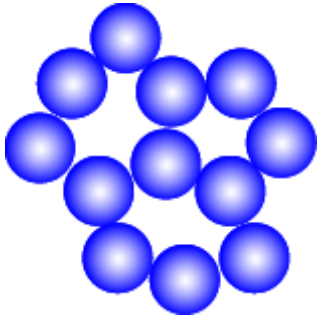
6- Triclinic: 3 axes are unequal in length and intersect at three different angles.

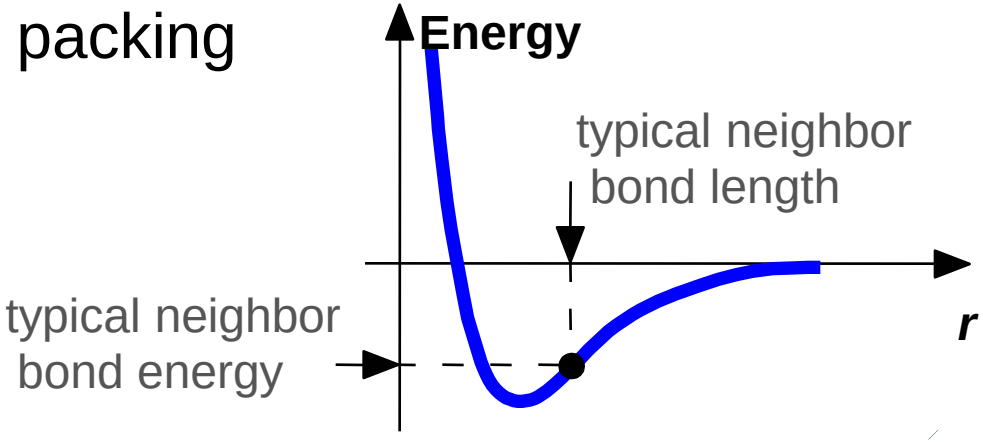
Crystal System



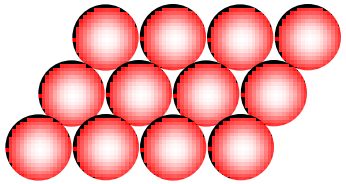
Energy and Packing

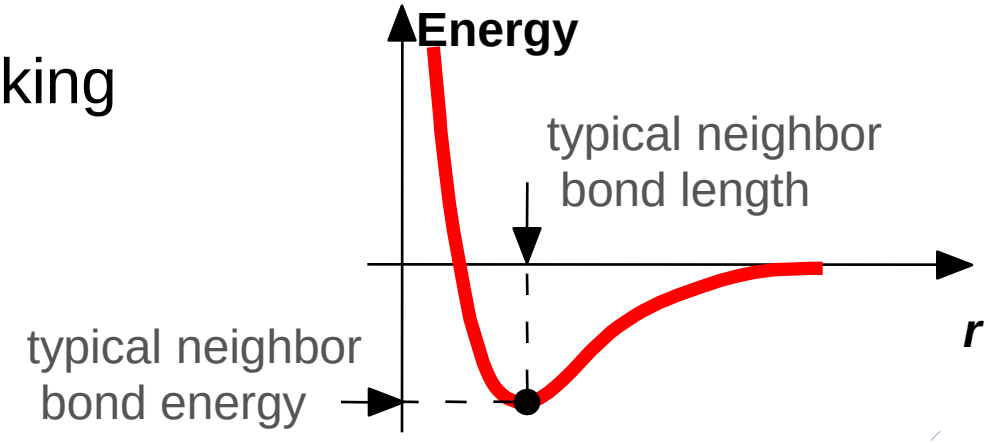
- Non dense, random packing





- Dense, ordered packing





Dense, ordered packed structures tend to have lower energies & thus are more stable.

CRYSTAL STRUCTURES

Crystal Structure

Means: ***PERIODIC ARRANGEMENT OF ATOMS/IONS OVER LARGE ATOMIC DISTANCES***

→Leads to structure displaying
LONG-RANGE ORDER that is
Measurable and Quantifiable

All metals, many ceramics, and some polymers exhibit this "High Bond Energy" and a More Closely Packed Structure

Materials Lacking Long range order

Amorphous Materials

These less densely packed lower bond energy "structures" can be found in Metals are observed in Ceramic GLASS and many "plastics"

Crystal Systems – Some Definitional information

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

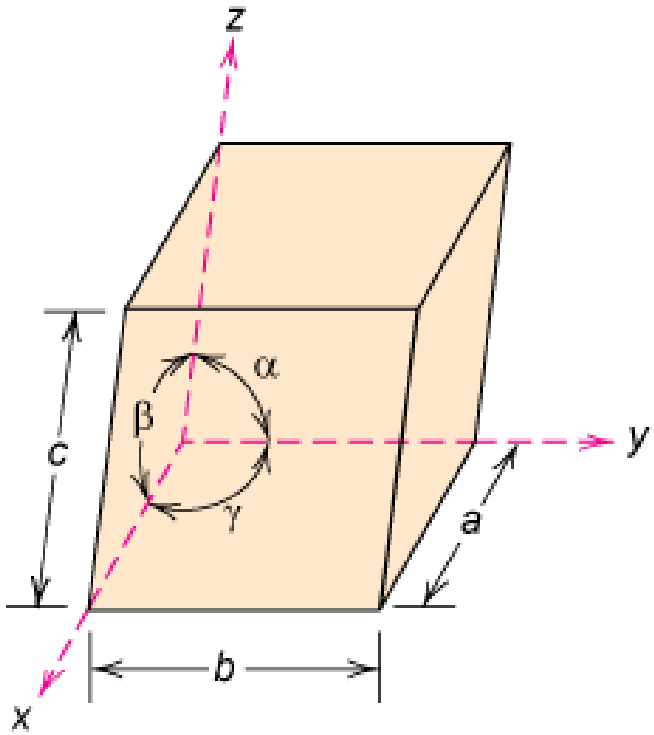


Fig. 3.4, *Callister 7e.*

7 crystal **systems of varying symmetry are known**

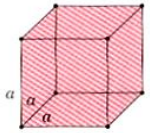
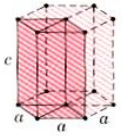
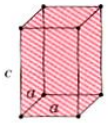
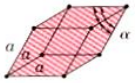
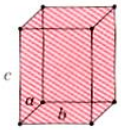
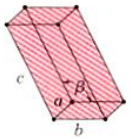
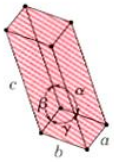
These systems are built by changing the lattice parameters:

a, b, and *c* are the edge lengths

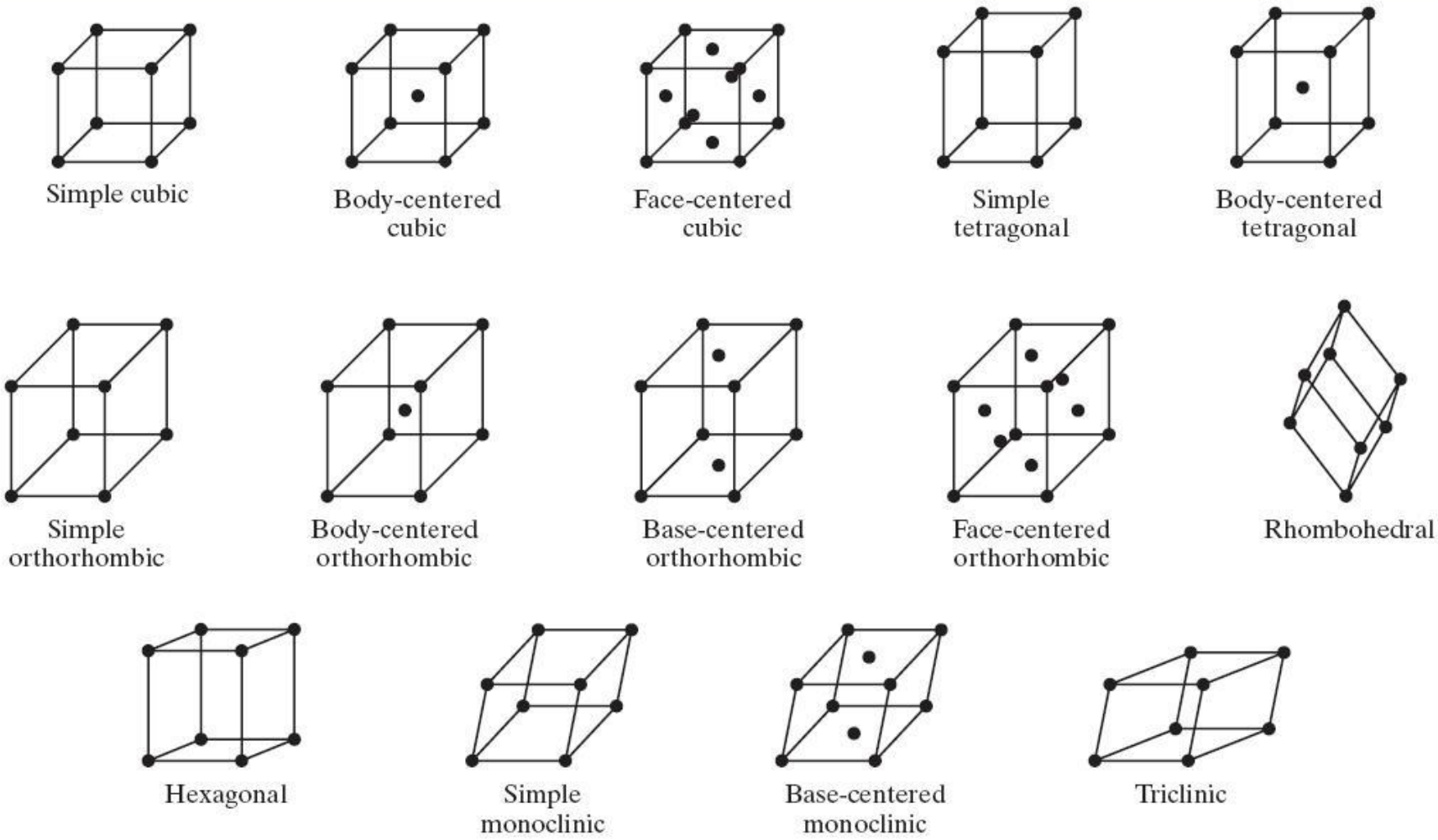
α, β, and γ are interaxial angles

Crystal Systems

Crystal structures are divided into groups according to unit cell geometry (symmetry).

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

The 14 Crystal (Bravais) Lattices



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 (those of engineering importance) called: FCC, BCC and HCP – with a nod to Simple Cubic

Crystal Structure of Metals – of engineering interest

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

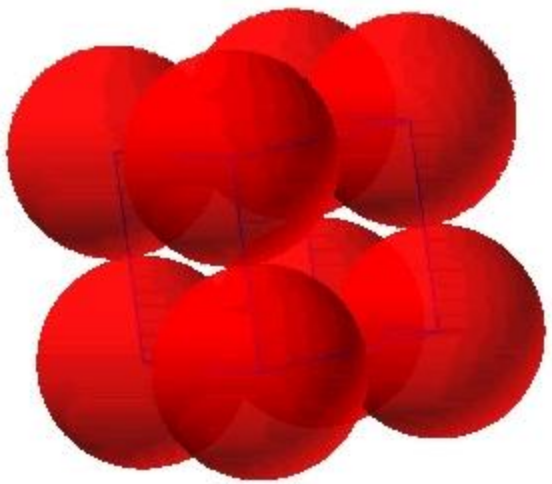
Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	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

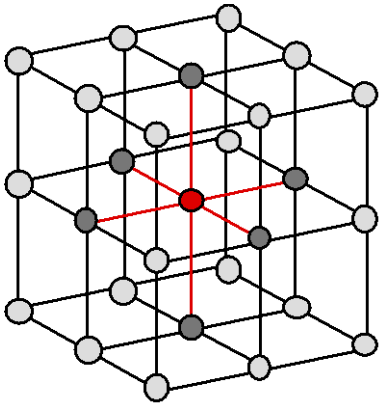
[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

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

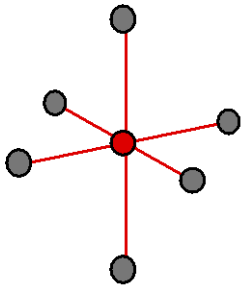
Simple Cubic Structure (SC)

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





- Coordination No. = 6 (# nearest neighbors) for each atom as seen



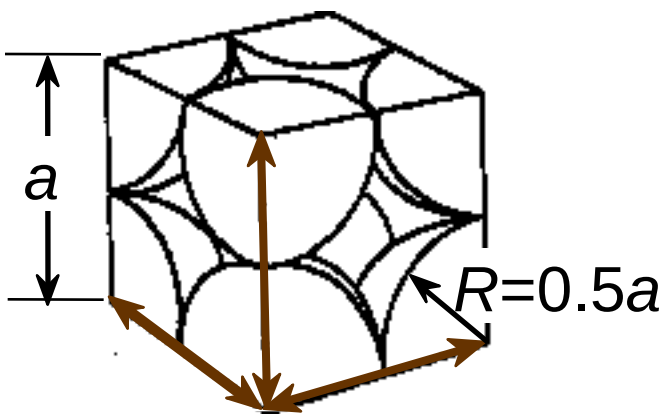
(Courtesy P.M. Anderson)

Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

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

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

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

Here: $a = R_{at} * 2$

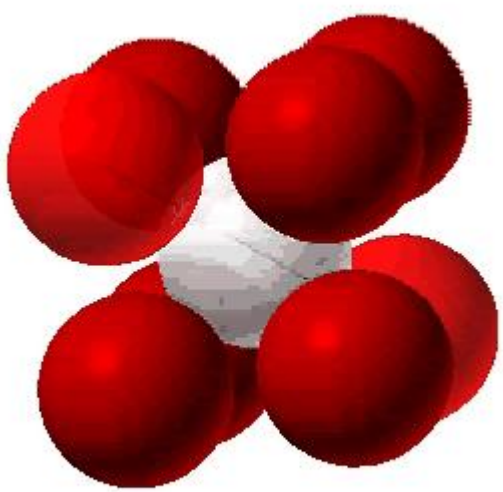
Where R_{at} is the 'handbook' atomic radius

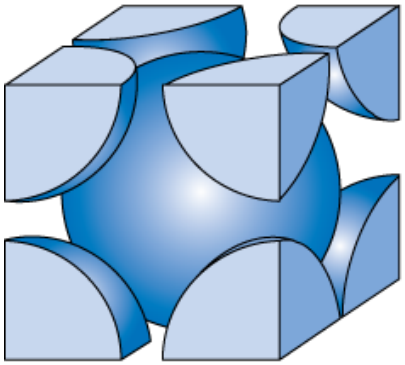
Body Centered Cubic Structure (BCC)

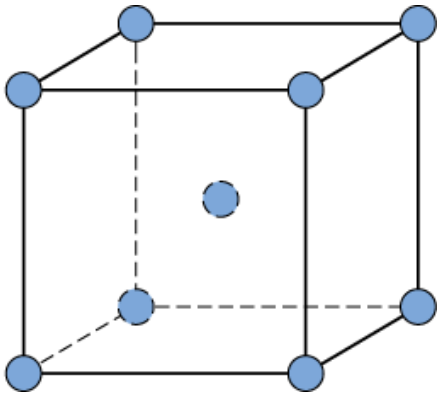
- Atoms touch each other along *cube diagonals within a unit cell*.

--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

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







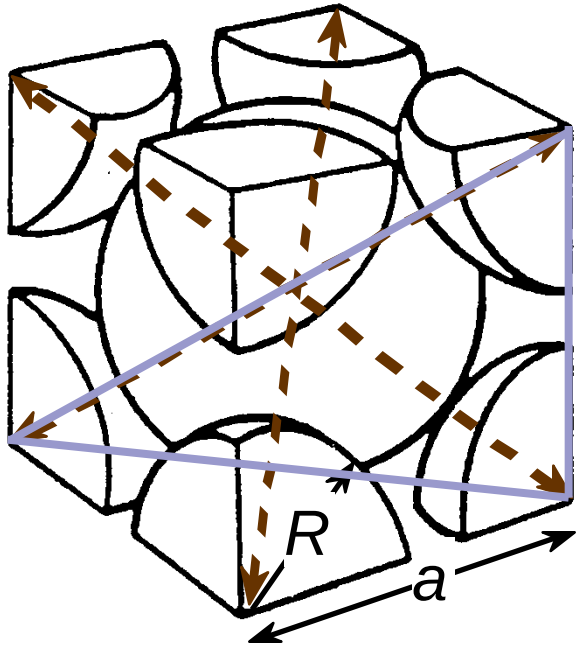
Adapted from Fig. 3.2, *Callister 7e.*

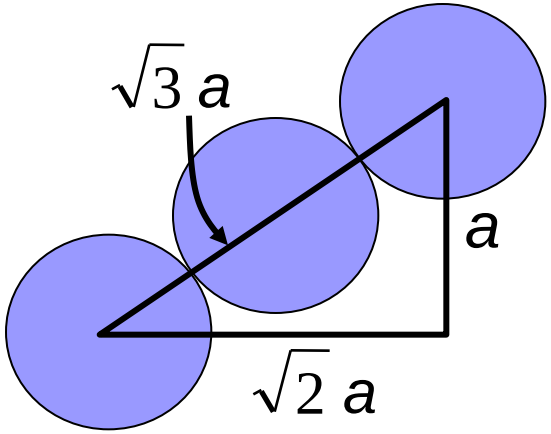
- Coordination # = 8

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

(Courtesy P.M. Anderson)

Atomic Packing Factor: BCC





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

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

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

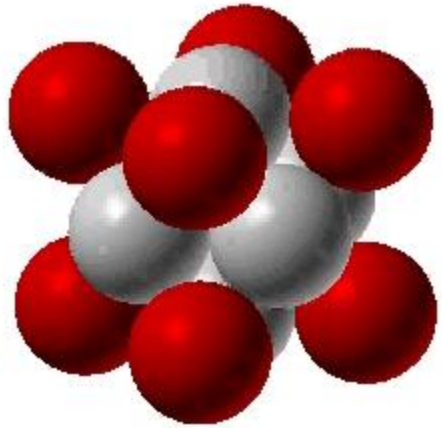
- APF for a body-centered cubic structure = 0.68

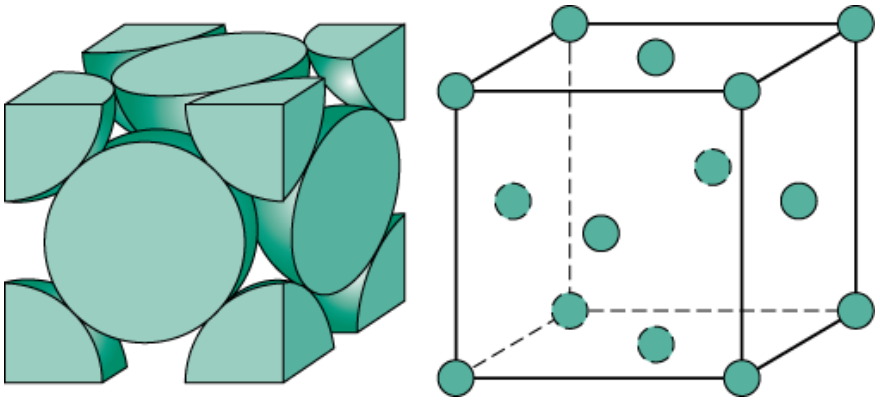
Face Centered Cubic Structure (FCC)

- 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





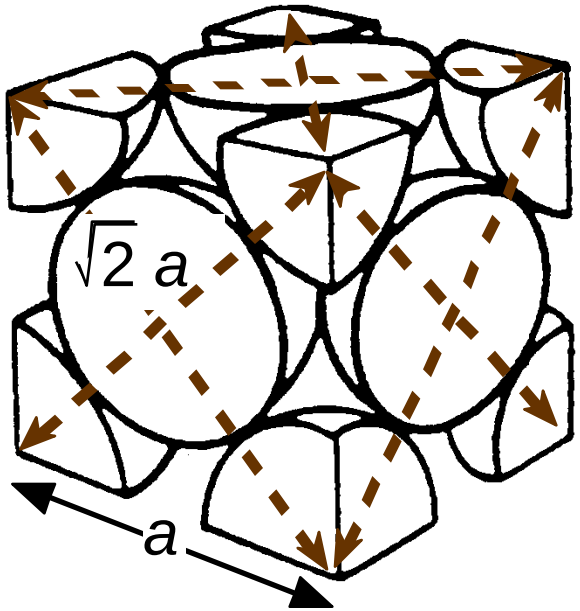
Adapted from Fig. 3.1, *Callister 7e.*

4 atoms/unit cell: (6 face x ½) + (8 corners x 1/8)

(Courtesy P.M. Anderson)

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74



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

The maximum achievable APF!

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

(a = 2√2*R)

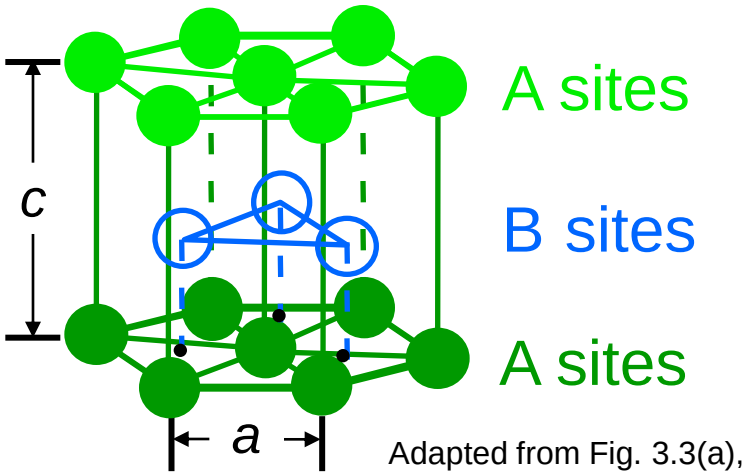
Unit cell contains:
6 x 1/2 + 8 x 1/8
= 4 atoms/unit cell

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

Hexagonal Close-Packed Structure (HCP)

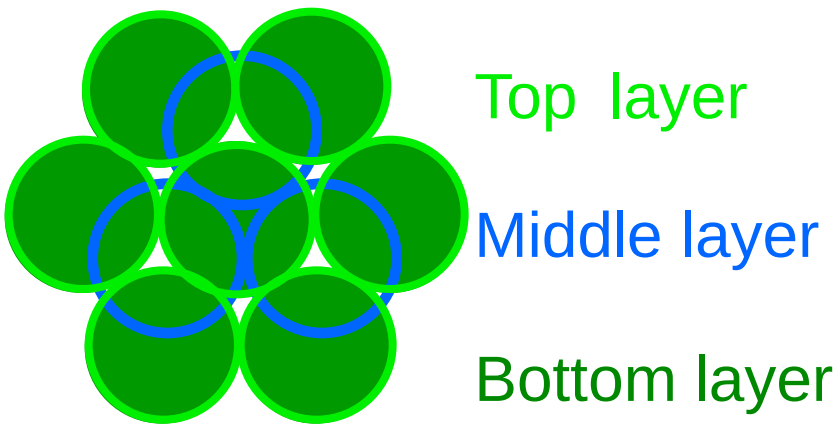
ex: Cd, Mg, Ti, Zn

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), *Callister 7e.*

- 2D Projection



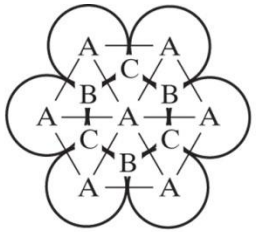
- Coordination # = 12

6 atoms/unit cell

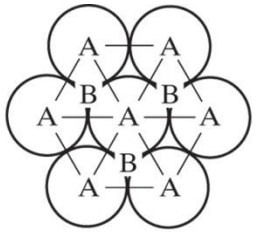
- APF = 0.74

- *c*/*a* = 1.633 *(ideal)*

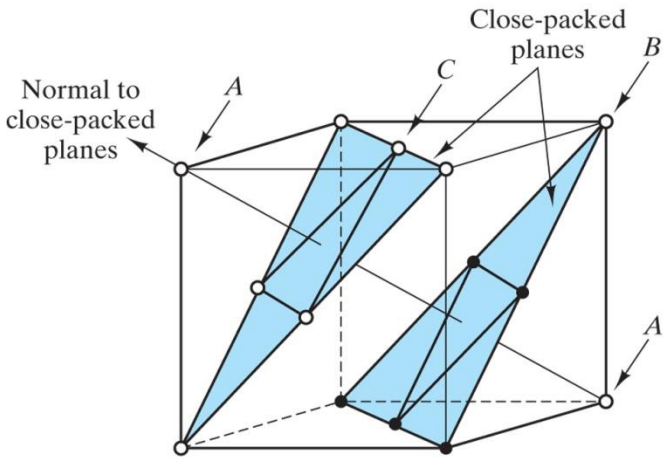
We find that both FCC & HCP are highest density packing schemes (APF = .74) – this illustration shows their differences as the closest packed planes are “built-up”



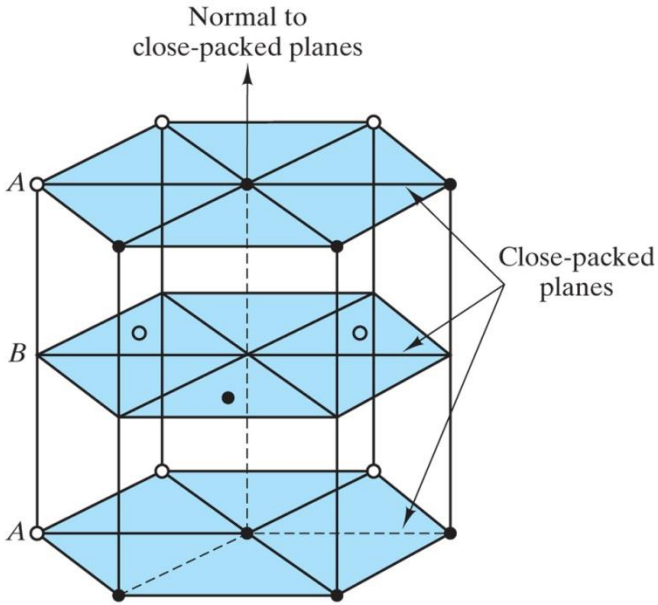
(a) Stacking of close-packed planes



(b) Stacking of close-packed planes



(c) Face-centered cubic



(d) Hexagonal close packed

Theoretical Density, ρ

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

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

where n = number of atoms/unit cell

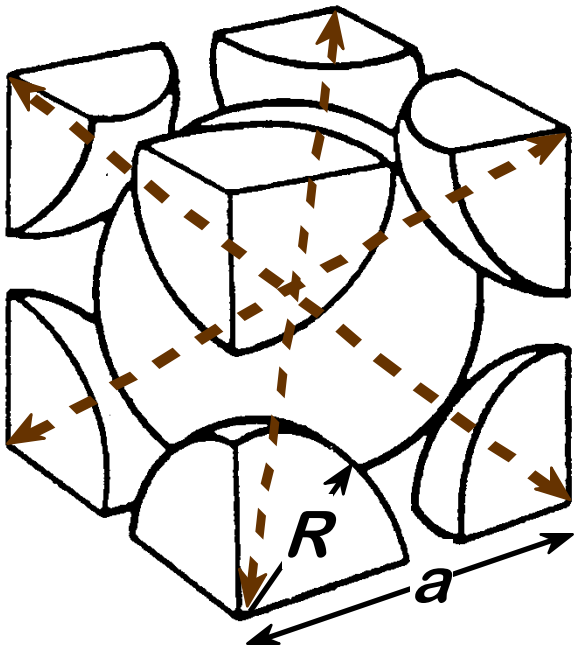
A = atomic weight

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

N_A = Avogadro's number

= 6.023×10^{23} atoms/mol

Theoretical Density, ρ



- Ex: Cr (BCC)

  A = 52.00 g/mol

  R = 0.125 nm

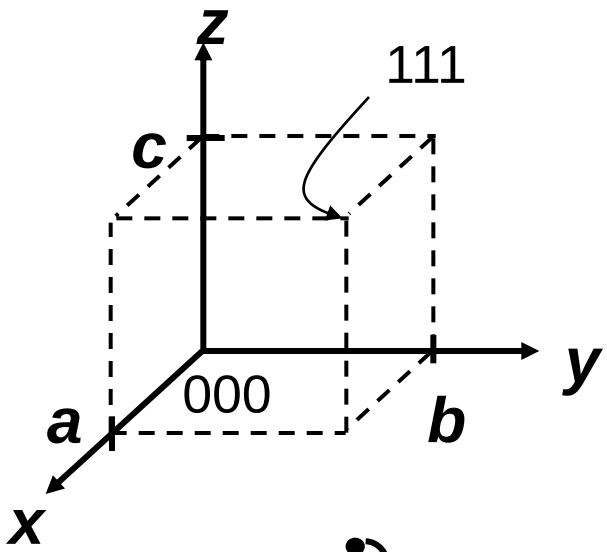
  n = 2

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

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

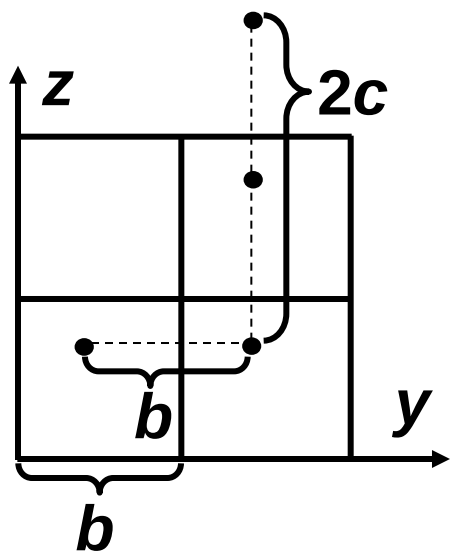
$\rho_{theoretical}$	= 7.18 g/cm^3
ρ_{actual}	= 7.19 g/cm^3

Locations in Lattices: Point Coordinates



Point coordinates for unit cell center are

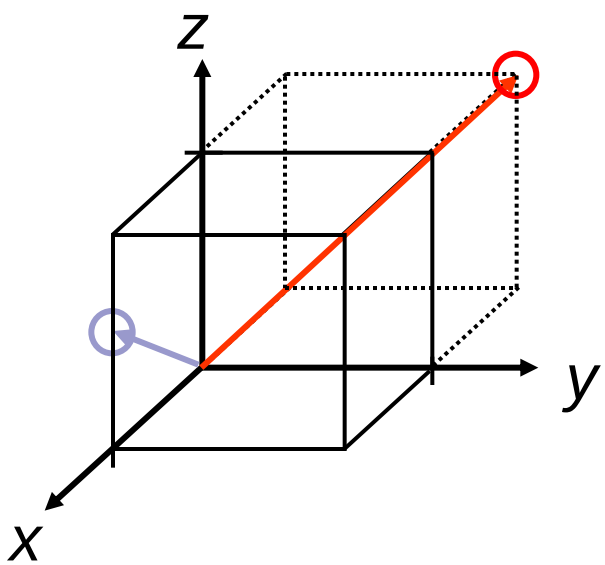
a/2, *b*/2, *c*/2 ½ ½ ½



Point coordinates for unit cell (body diagonal) corner are 111

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

Crystallographic Directions



Algorithm

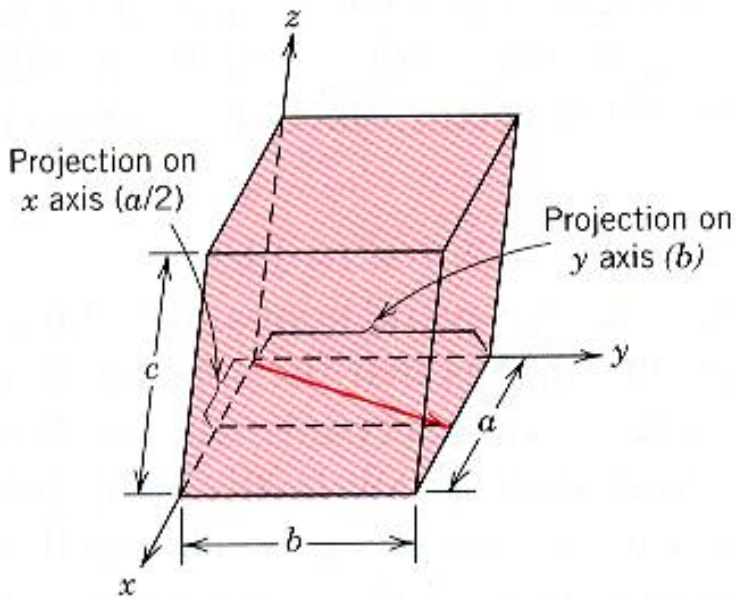
1. Vector is repositioned (if necessary) to ***pass through the Unit Cell origin***.
2. Read off line projections (to principal axes of U.C.) in terms of unit cell dimensions *a*, *b*, and *c*
3. Adjust to smallest **integer values**
4. Enclose in square brackets, *no commas*

[*uvw*]

ex: 1, 0, ½ => 2, 0, 1 => [201]

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

families of directions <*uvw*>



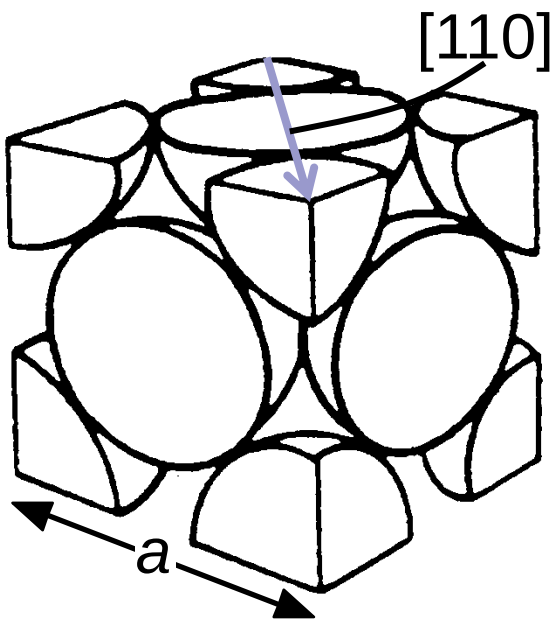
What is this ***Direction ?????***

	x	y	z
Projections:	a/2	b	0c
Projections in terms of a,b and c:	1/2	1	0
Reduction:	1	2	0

Enclosure [brackets] **[120]**

Linear Density – considers equivalance and is important in Slip

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



ex: linear density of Al in [110] direction

a = 0.405 nm

atoms

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

length

atoms **CENTERED** on the direction of interest!

Length is of the **direction** of interest **within** the Unit Cell

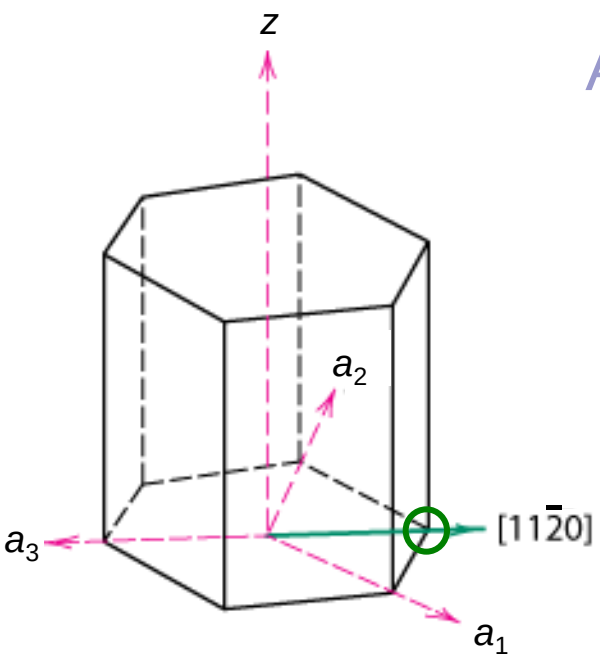
Determining Angles Between Crystallographic Direction:

$$\theta = Cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\bullet\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

Where u_i's , v_i's & w_i's are the "Miller Indices" of the directions in question

– also (for information) If a direction has the same Miller Indices as a plane, it is NORMAL to that plane

HCP Crystallographic Directions



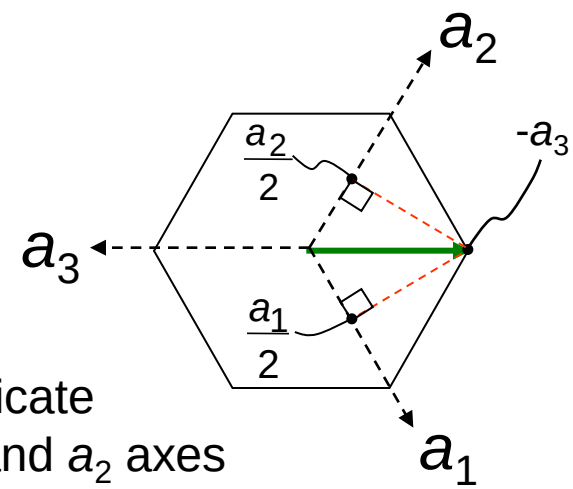
Adapted from Fig. 3.8(a), *Callister 7e.*

Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a_1, a_2, a_3, or c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

[*uvtw*]

ex: ½, ½, -1, 0 => $[11\bar{2}0]$



dashed red lines indicate projections onto a_1 and a_2 axes

HCP Crystallographic Directions

- Hexagonal Crystals
  - 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., *u'v'w'*) in the '3 space' Bravais lattice as follows.

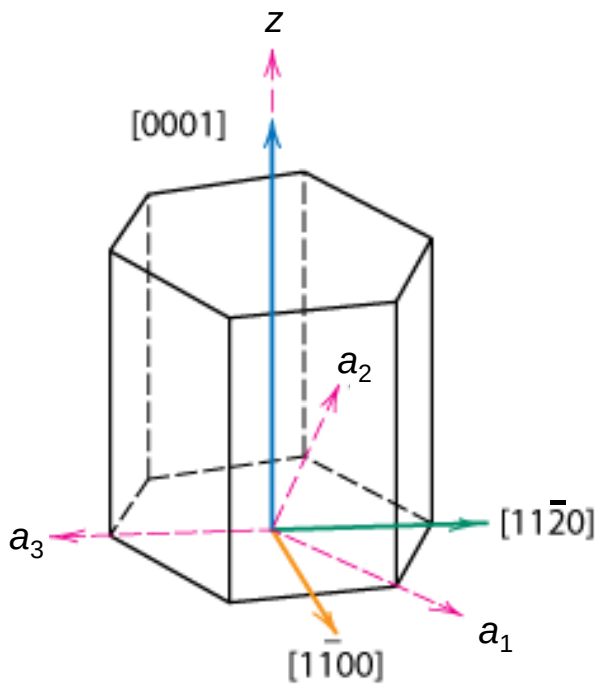


Fig. 3.8(a), *Callister 7e.*

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

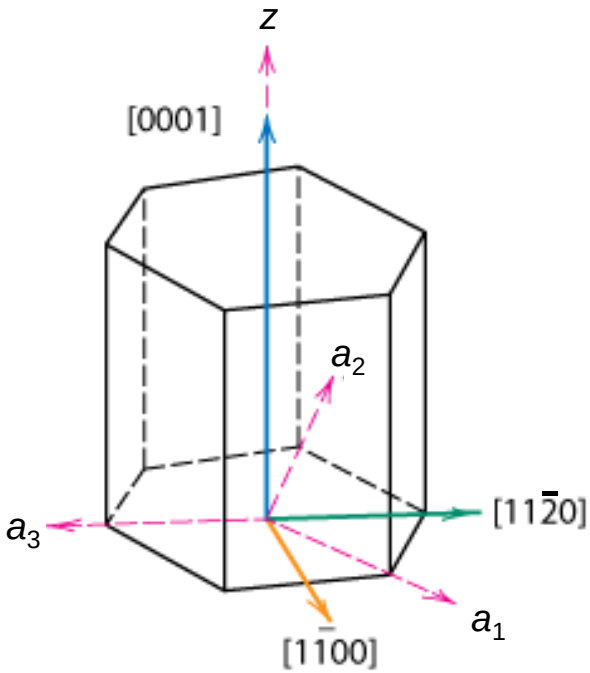
$$u = \frac{1}{3}(2u' - v')$$

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

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

$$w = w'$$

Computing HCP Miller- Bravais Directional Indices (an alternative way):



We confine ourselves to the bravais parallelopiped in the hexagon: a_1-a_2-Z and determine: (u',v'w')

Here: [1 1 0] - so now apply the models to create M-B Indices

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

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

$$t = -(u+v) = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3} \rightarrow -2$$

$$w = w' = 0$$

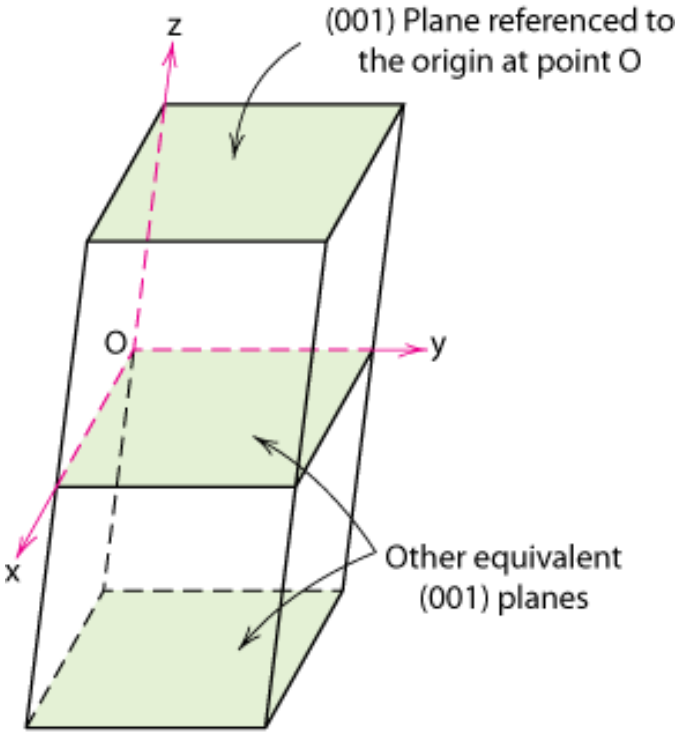
M-B Indices: $[11\bar{2}0]$

Defining Crystallographic Planes

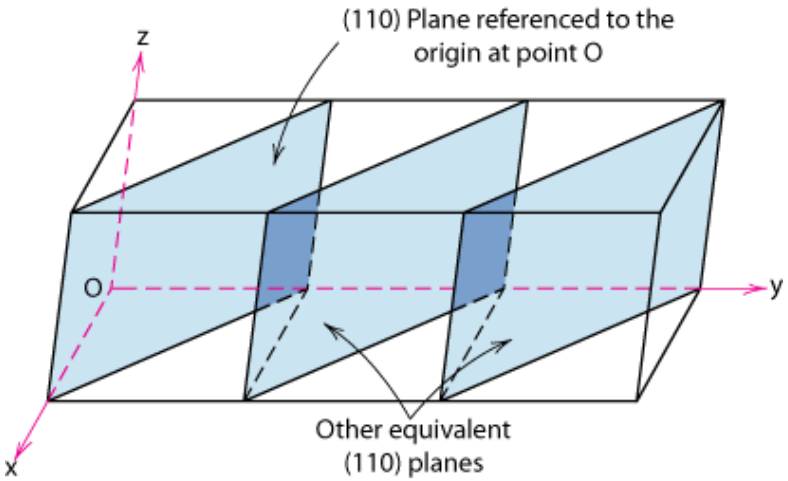
- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

- Algorithm (in cubic lattices this is direct)
  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*) $\rightarrow$ families {hkl}

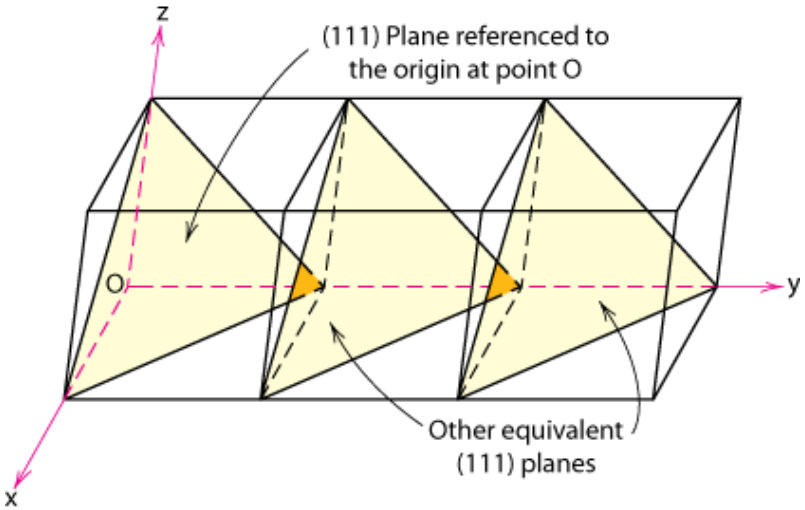
Crystallographic Planes -- families



(a)



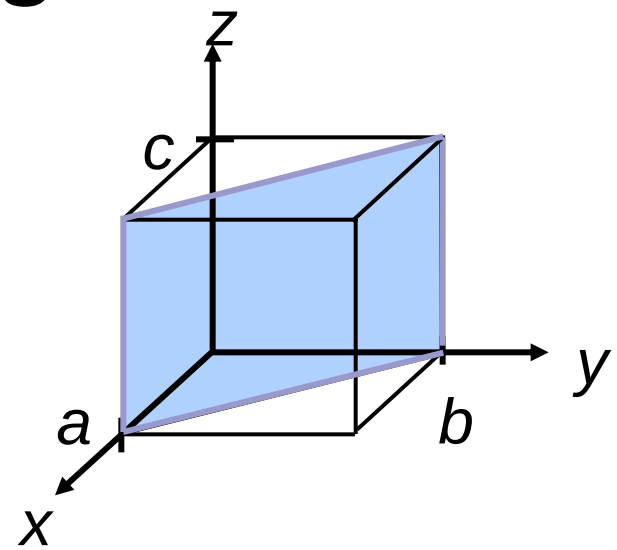
(b)



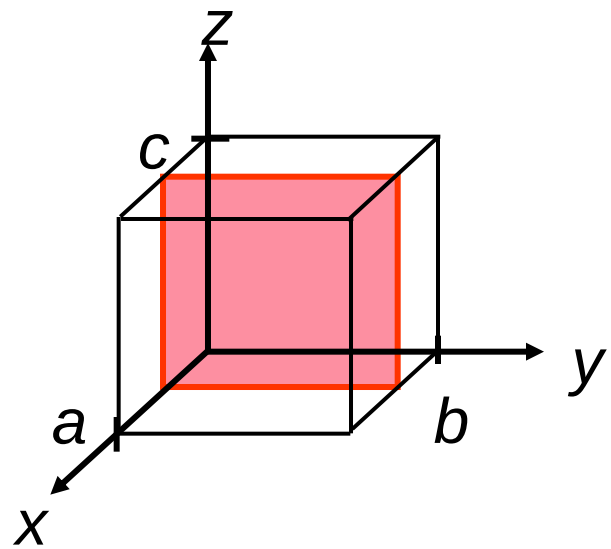
(c)

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)		

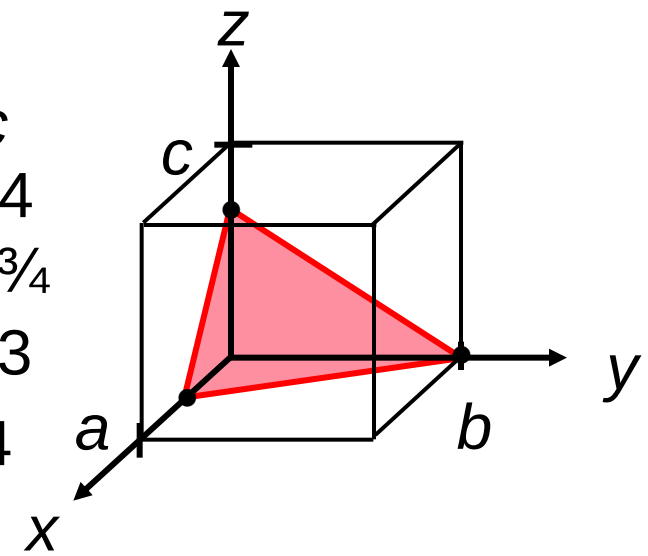


example		*a*	*b*	*c*
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		



Crystallographic Planes

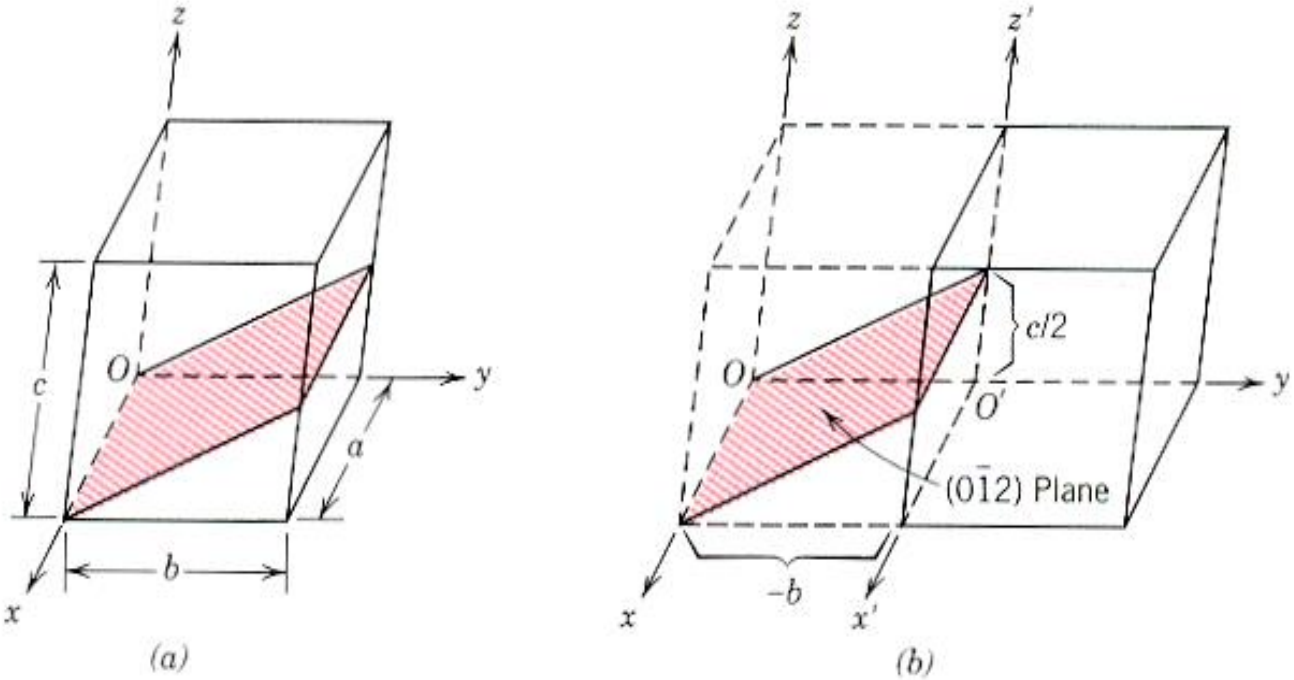
example		*a*	*b*	*c*
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		



Family of Planes {*hkl*}

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

Determine the Miller indices for the plane shown in the sketch



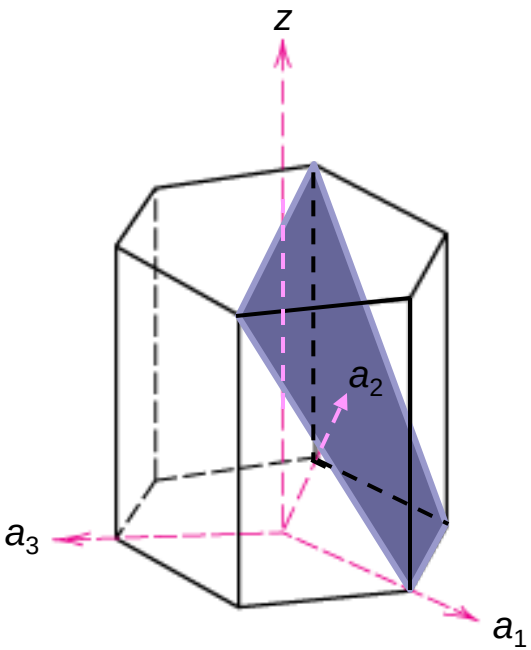
	x	y	z
Intercepts	∝a	-b	c/2
Intercept in terms of lattice parameters	∝	-1	1/2
Reciprocals	0	-1	2
Reductions		N/A	
Enclosure		$(0\bar{1}2)$	

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 $(10\bar{1}1)$



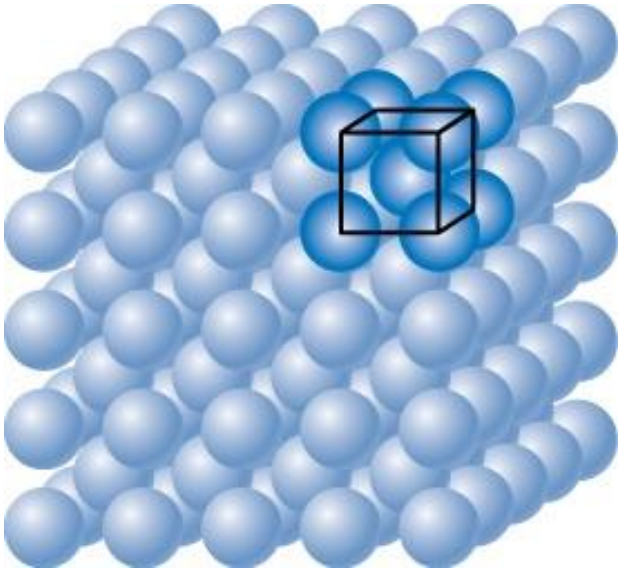
Adapted from Fig. 3.8(a), *Callister 7e.*

Crystallographic Planes

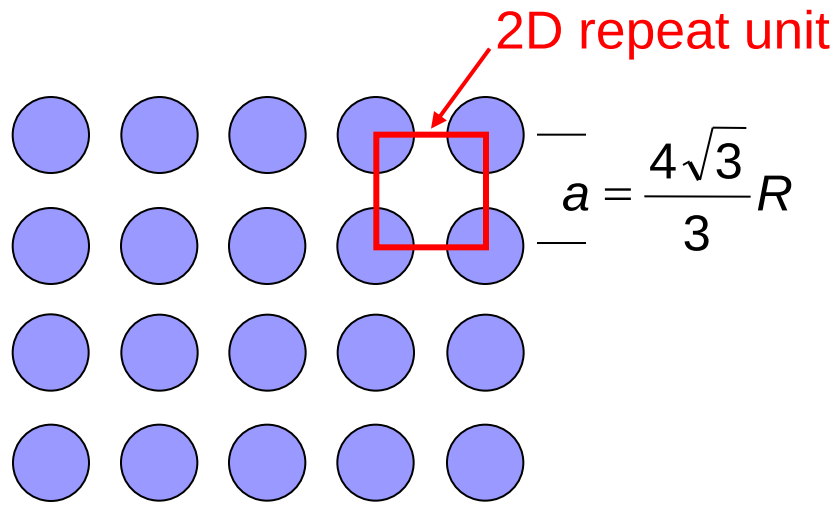
- We want to examine the atomic packing of crystallographic planes – those with the same packing are equivalent and part of families
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
  a) Draw (100) and (111) crystallographic planes for Fe.
  b) Calculate the planar density for each of these planes.

Planar Density of (100) Iron

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



(100)



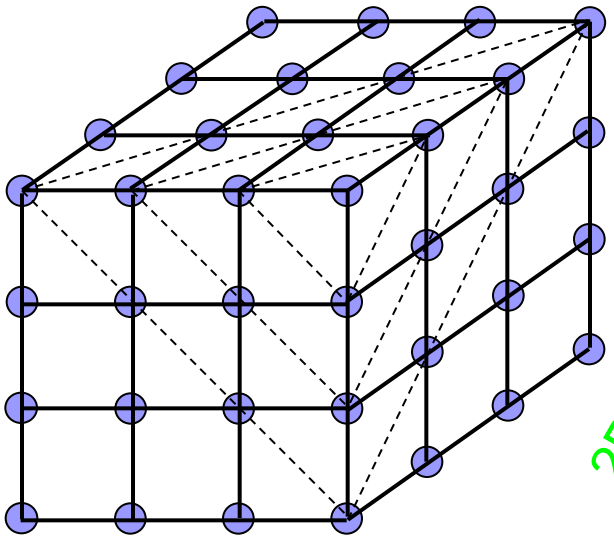
Radius of iron R = 0.1241 nm

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

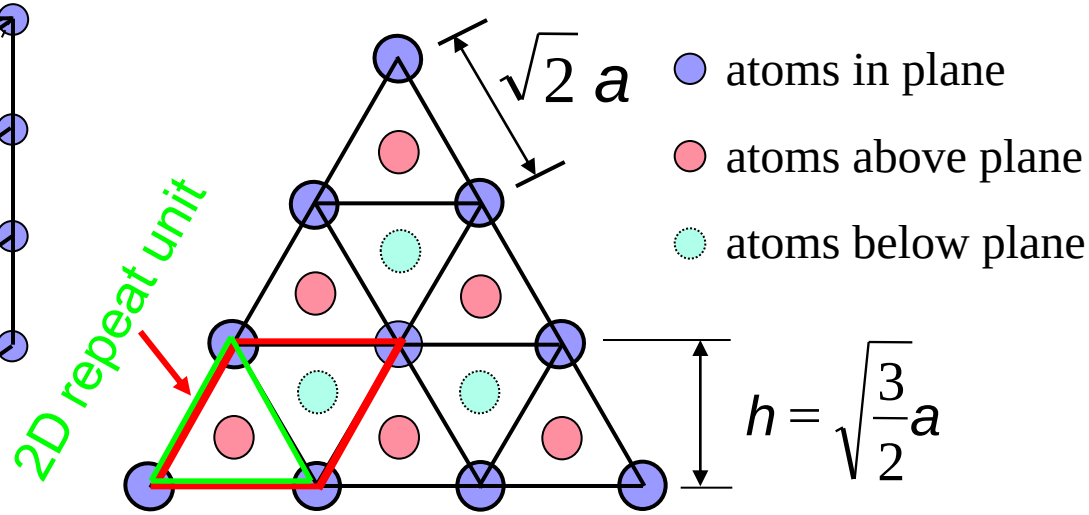
Atoms: wholly contained and centered in/on plane within U.C., area of plane in U.C.

Planar Density of (111) Iron

Solution (cont): (111) plane



1/2 atom centered on plane/ unit cell



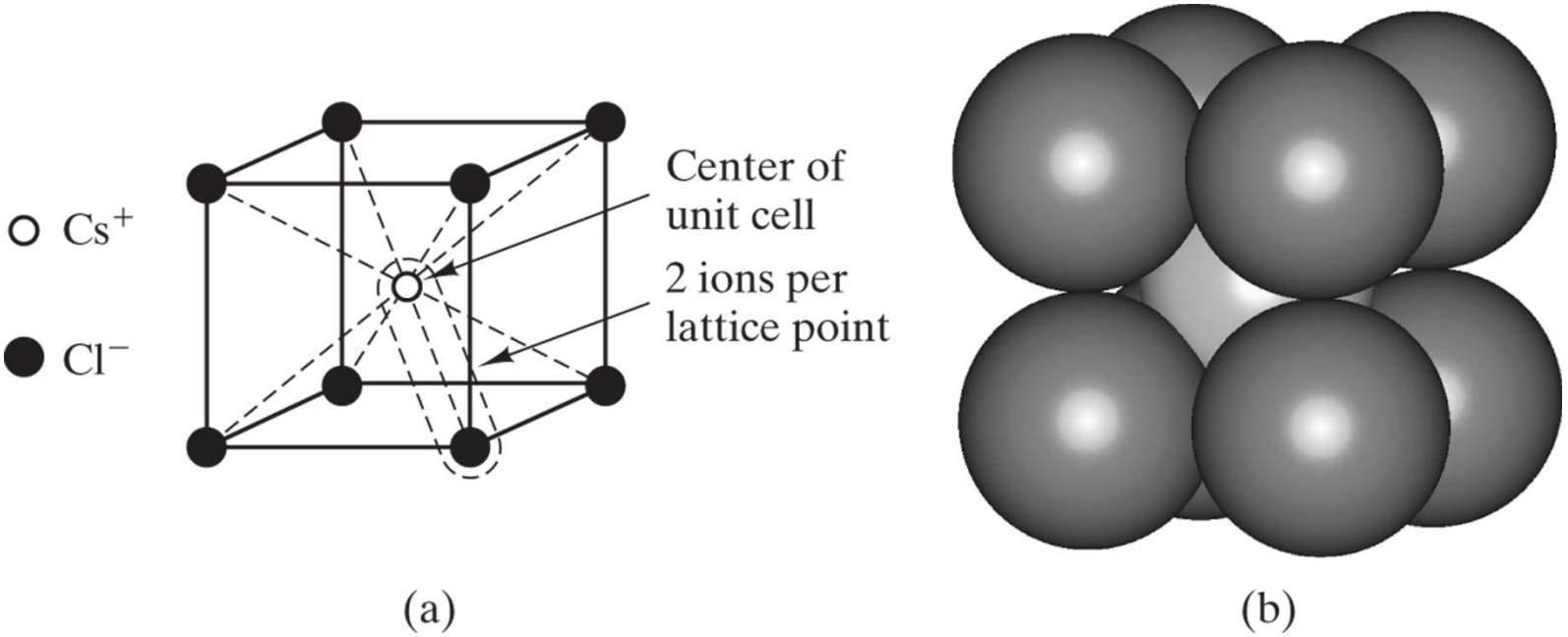
Area 2D Unit: ½ hb = ½*[(√3/2)a][(√2)a]=1/2(√3)a^2=8R^2/(√3)

$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{3*1/6}{\dfrac{8R^2}{\sqrt{3}}} = 7.0\,\frac{\text{atoms}}{\text{nm}^2} = \boxed{0.70 \times 10^{19}\ \frac{\text{atoms}}{\text{m}^2}}$$

Adding Ionic Complexities

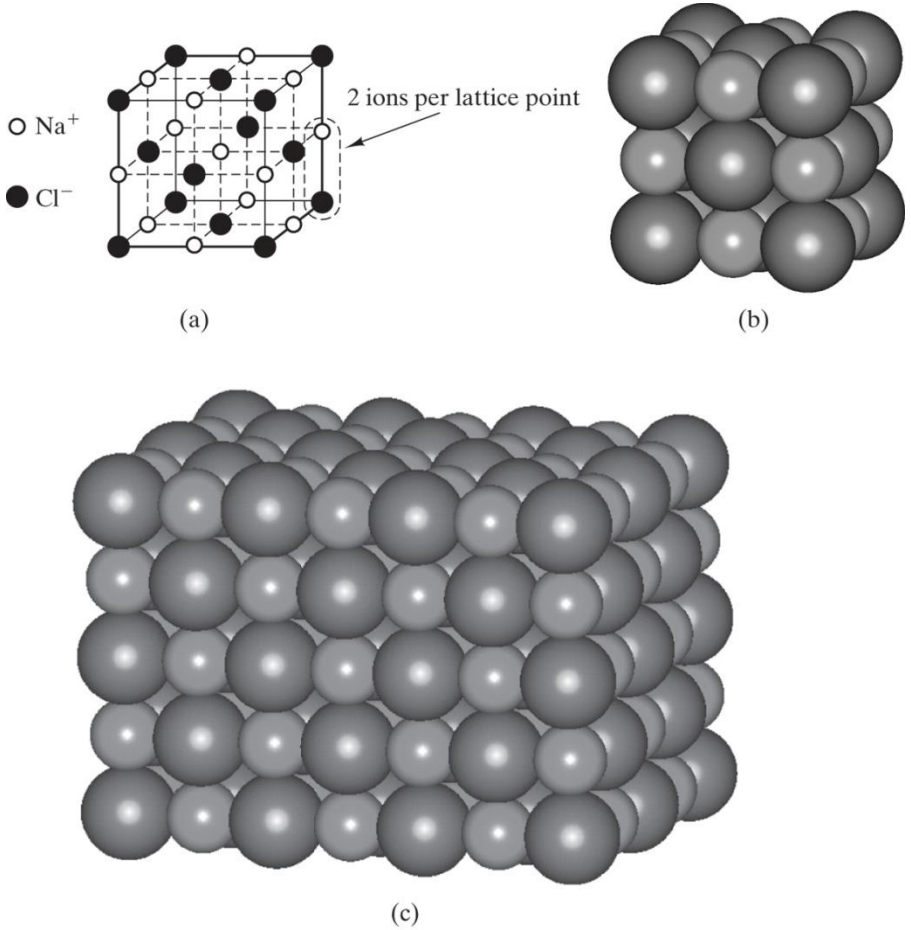
LOOKING AT THE CERAMIC UNIT CELLS (CH 12)

Cesium chloride (CsCl) unit cell showing (a) ion positions and the two ions per lattice point and (b) full-size ions. Note that the Cs^+−Cl^- pair associated with a given lattice point is not a molecule because the ionic bonding is nondirectional and because a given Cs^+ is equally bonded to eight adjacent Cl^-, and vice versa. [Part (b) courtesy of Accelrys, Inc.]



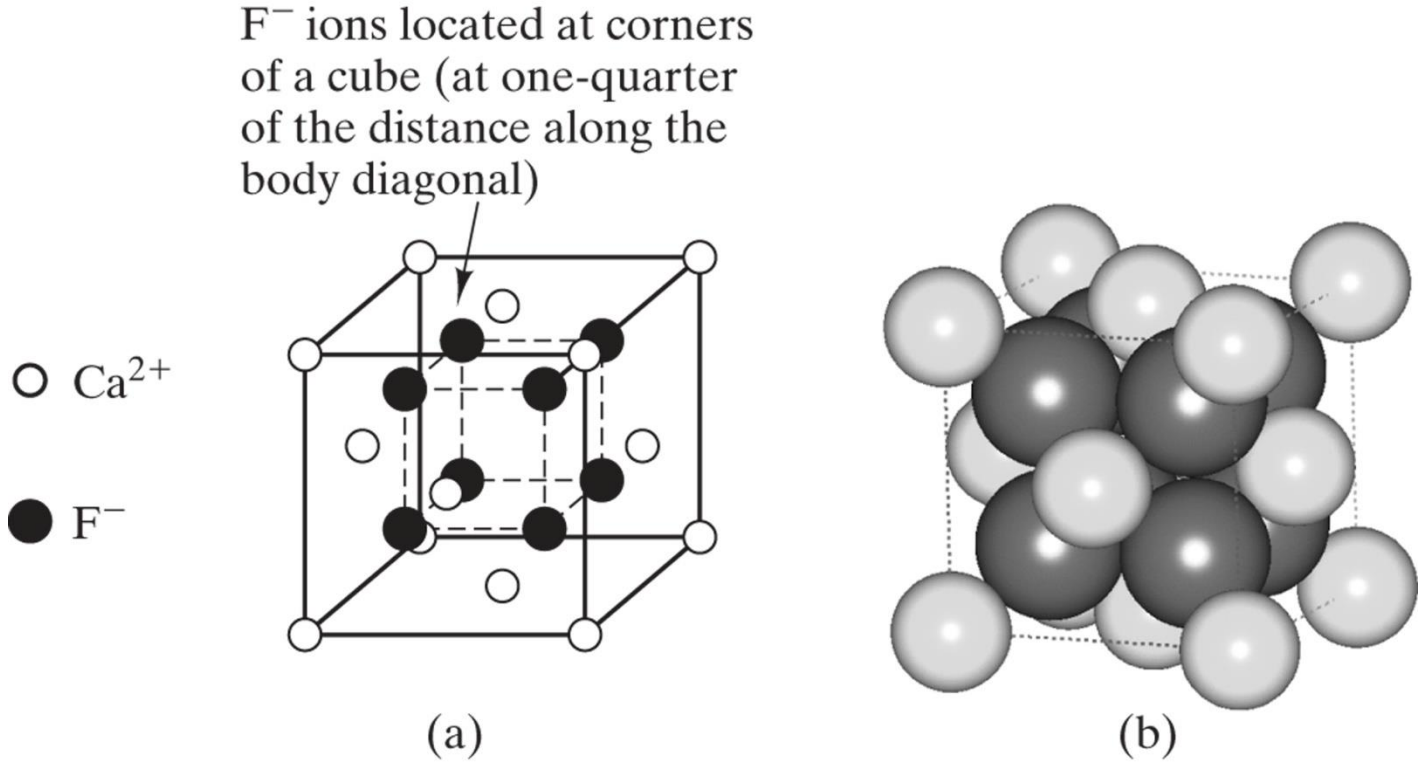
Structure: CsCl type
Bravais lattice: simple cubic
Ions/unit cell: $1Cs^+ + 1Cl^-$

Sodium chloride (NaCl) structure showing (a) ion positions in a unit cell, (b) full-size ions, and (c) many adjacent unit cells. [Parts (b) and (c) courtesy of Accelrys, Inc.]



Structure: NaCl type
Bravais lattice: fcc
Ions/unit cell: $4Na^+ + 4Cl^-$
Typical ceramics: MgO, CaO, FeO, and NiO

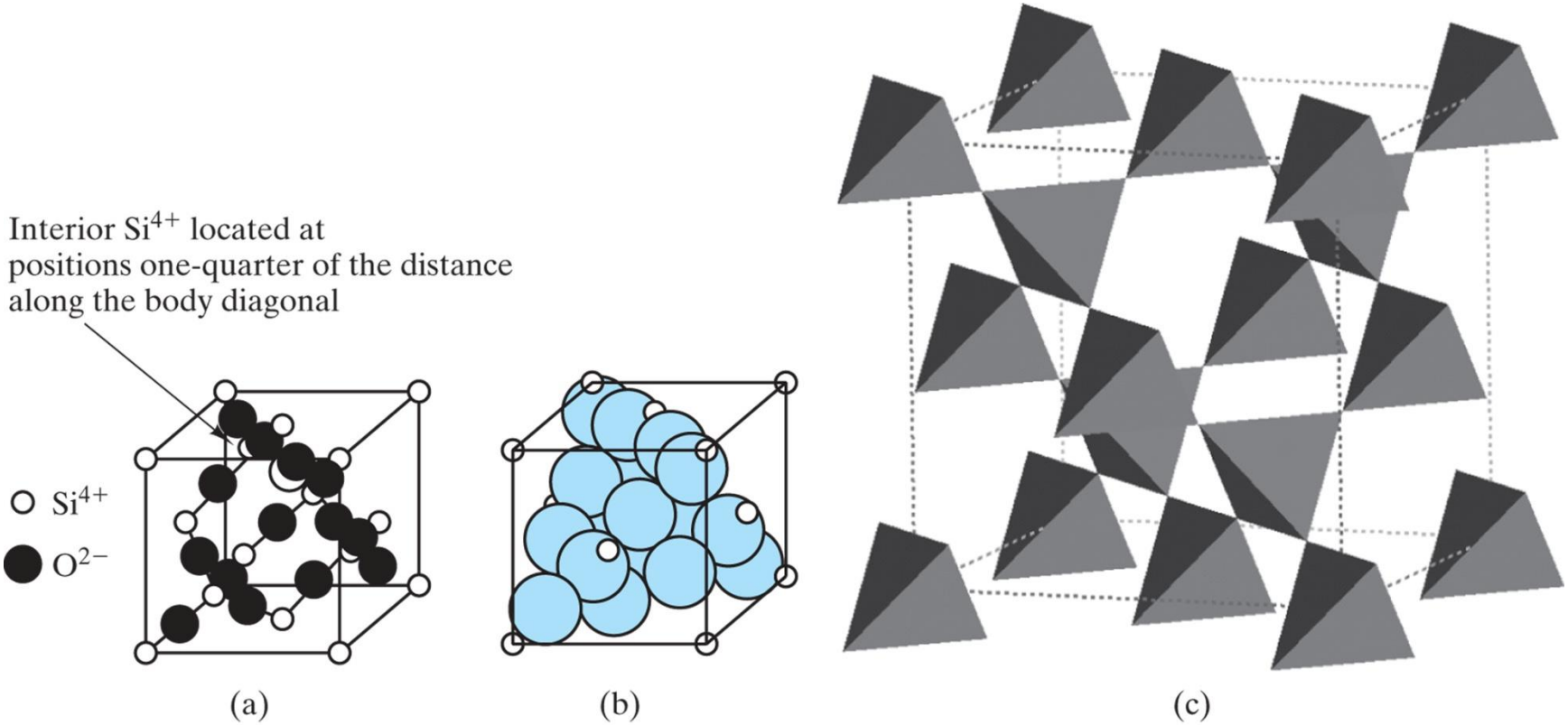
Fluorite (CaF_2) unit cell showing (a) ion positions and (b) full-size ions. [Part (b) courtesy of Accelrys, Inc.]



Structure: fluorite (CaF_2) type
Bravais lattice: fcc
Ions/unit cell: $4Ca^{2+} + 8F^-$
Typical ceramics: UO_2, ThO_2, and TeO_2

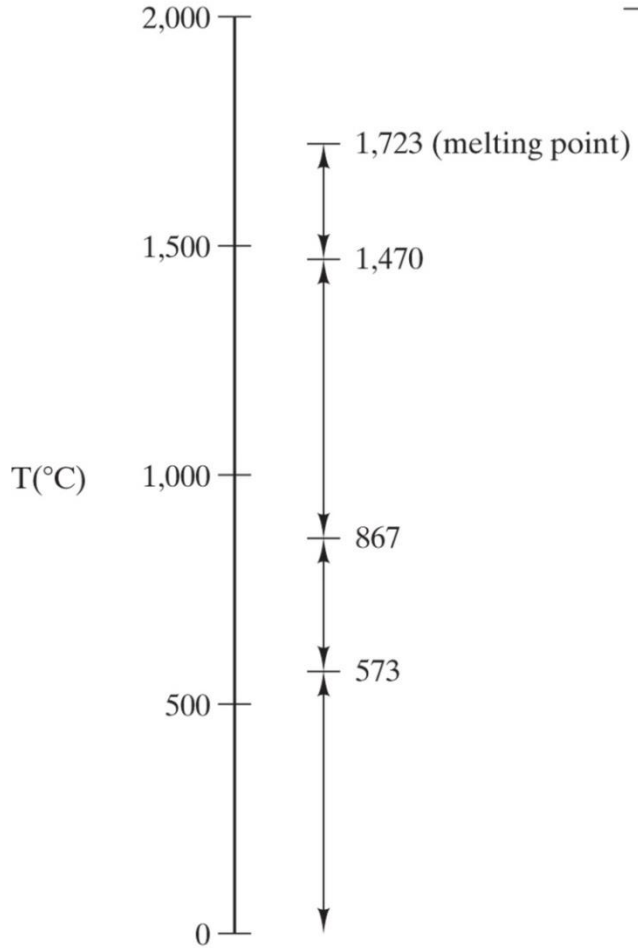
SiO_4^{4-}

The cristobalite (SiO_2) unit cell showing (a) ion positions, (b) full-size ions, and (c) the connectivity of SiO_4^{4-} tetrahedra. In the schematic, each tetrahedron has a Si^{4+} at its center. In addition, an O^{2-} would be at each corner of each tetrahedron and is shared with an adjacent tetrahedron. [Part (c) courtesy of Accelrys, Inc.]



Structure: cristobalite (SiO_2) type
Bravais lattice: fcc
Ions/unit cell: $8Si^{4+} + 16O^{2-}$

Many crystallographic forms of SiO_2 are stable as they are heated from room temperature to melting temperature. Each form represents a different way to connect adjacent SiO_4^{4-} tetrahedra.



Crystallographic form	Bravais lattice
High cristobalite (shown in Figure 3.11)	fcc
High tridymite	Hexagonal
High quartz	Hexagonal
Low quartz	Hexagonal

Polymorphism: Also in Metals

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

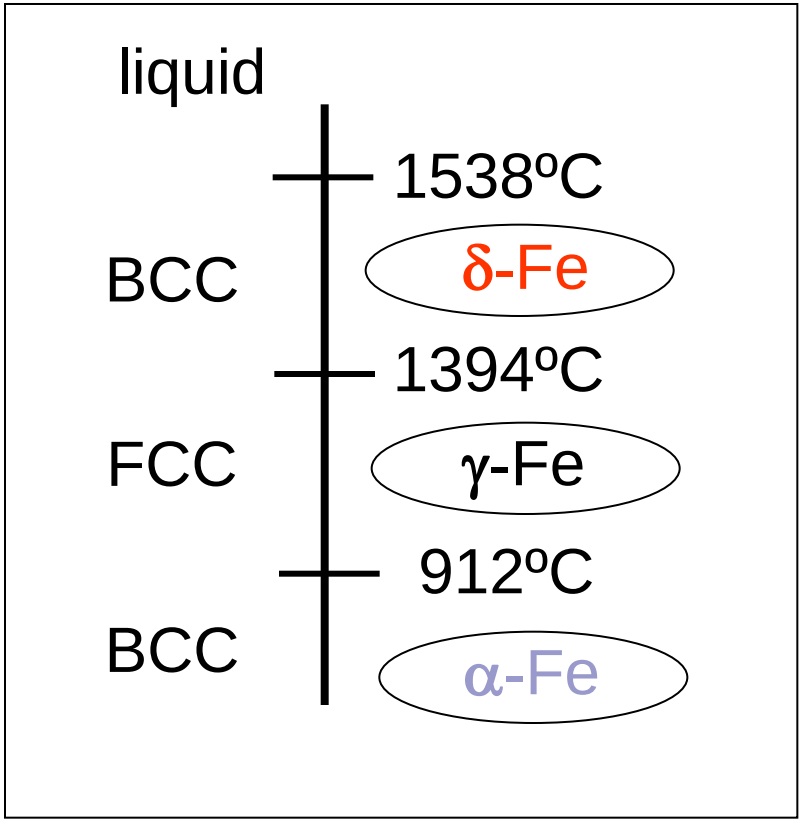
titanium

α (HCP), β(BCC)-Ti

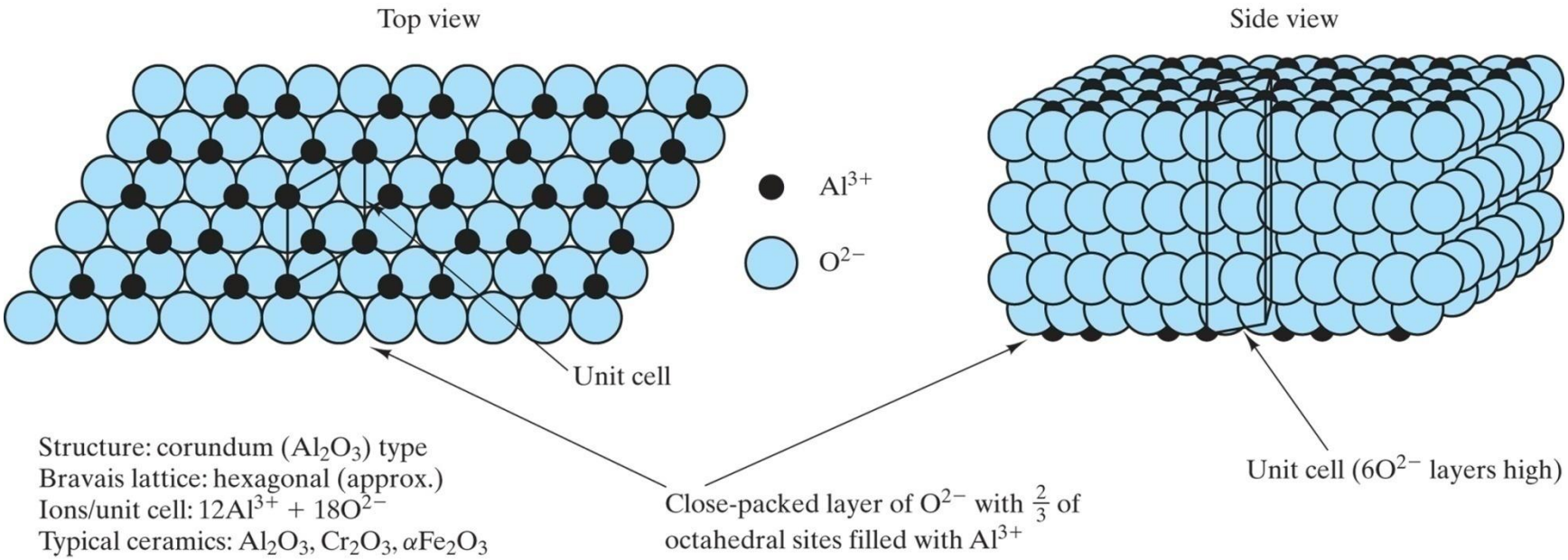
carbon:

diamond, graphite

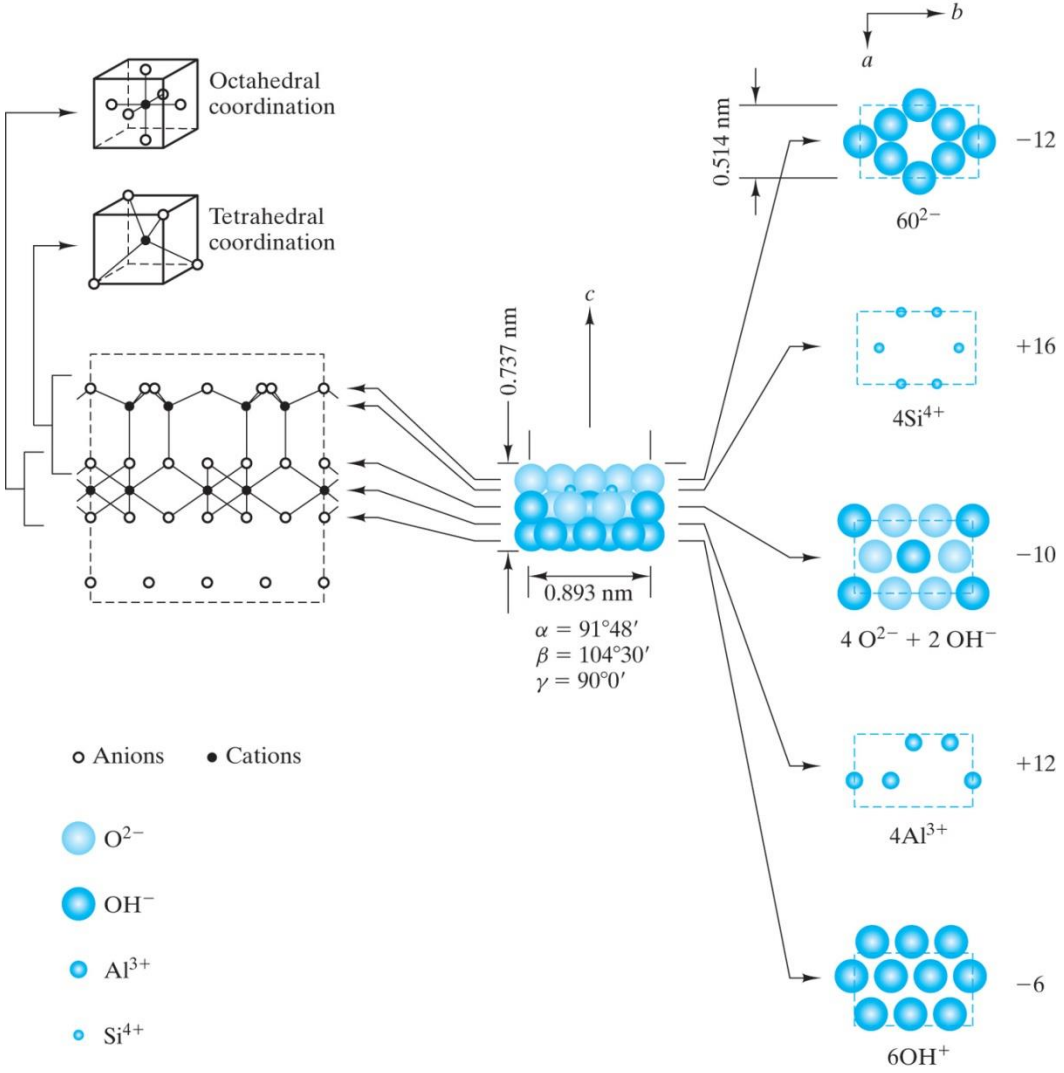
iron system:



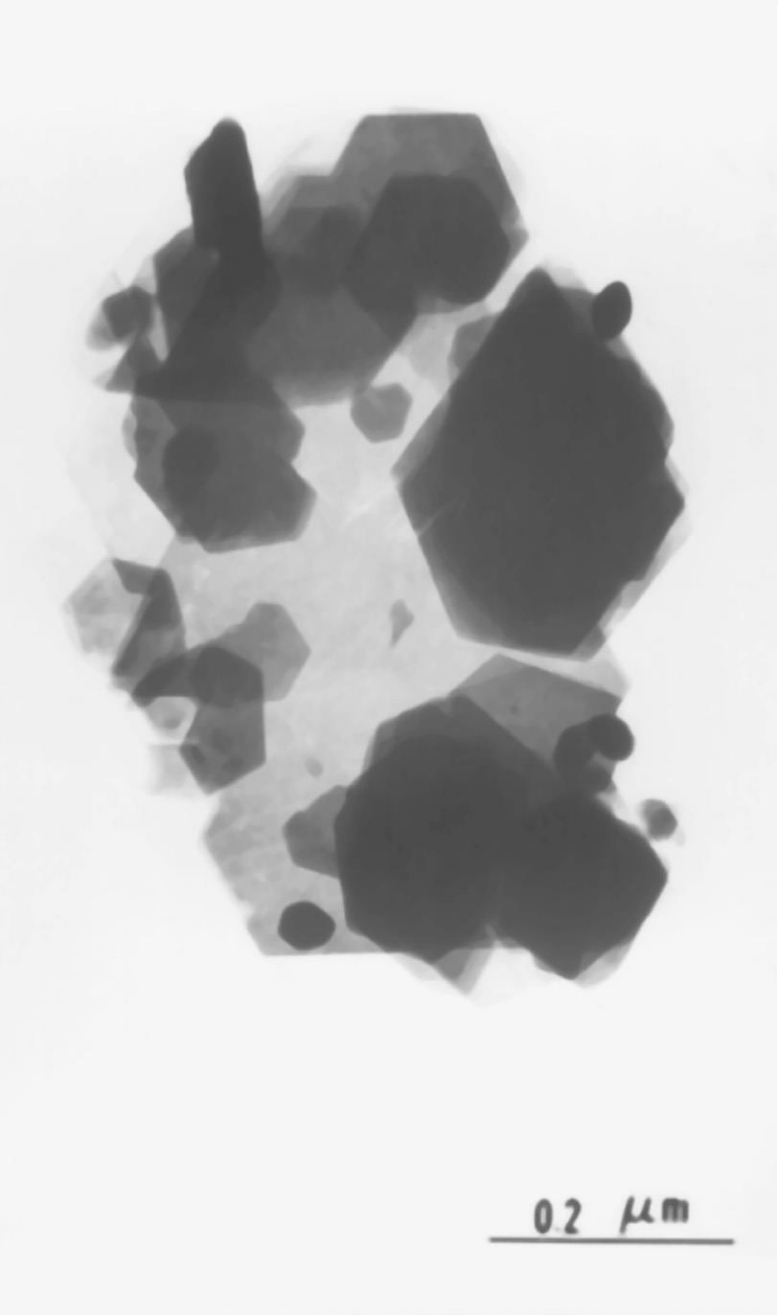
The corundum (Al_2O_3) unit cell is shown superimposed on the repeated stacking of layers of close-packed O^{2-} ions. The Al^{3+} ions fill two-thirds of the small (octahedral) interstices between adjacent layers.



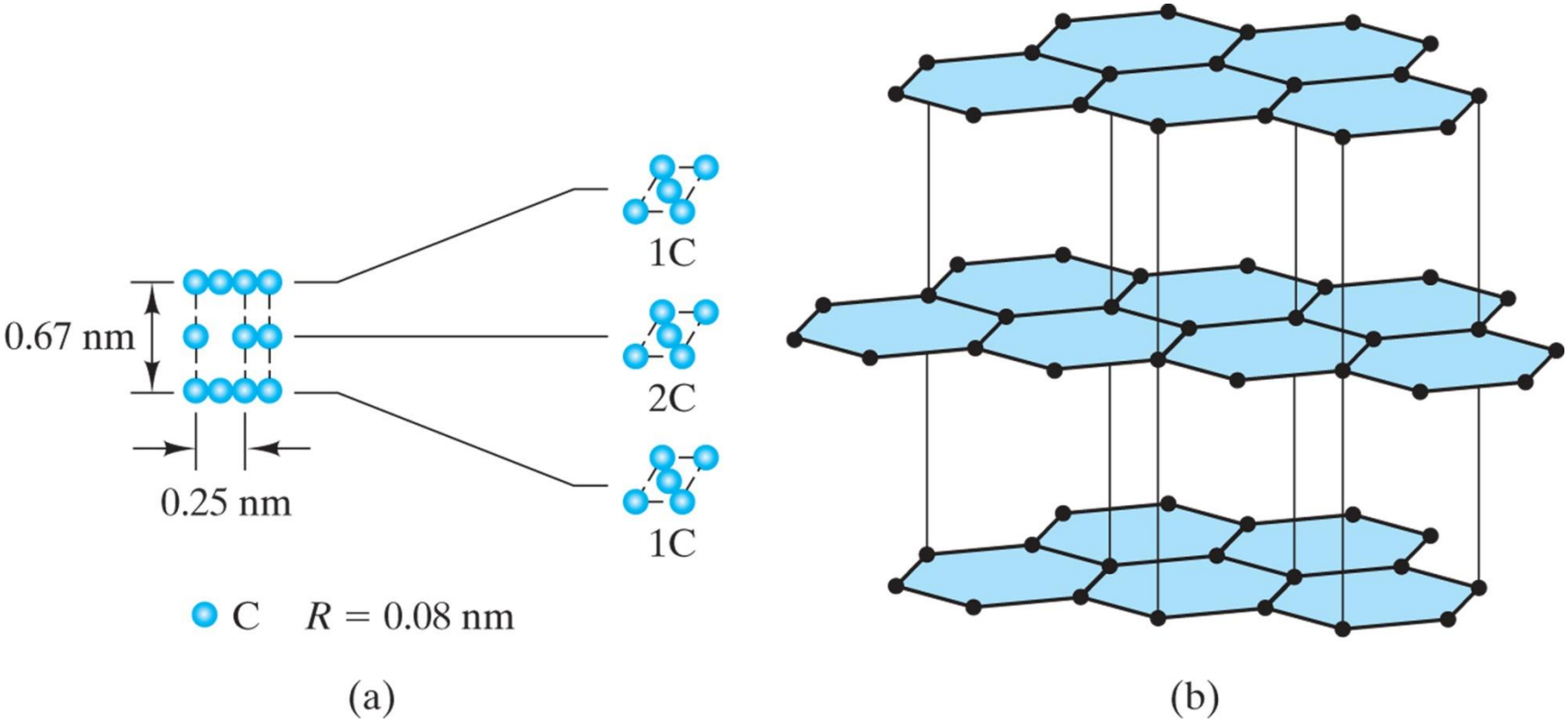
Exploded view of the kaolinite unit cell, $2(OH)_4Al_2Si_2O_5$. (From F. H. Norton, Elements of Ceramics*, 2nd ed., Addison-Wesley Publishing Co., Inc., Reading, MA, 1974.)*



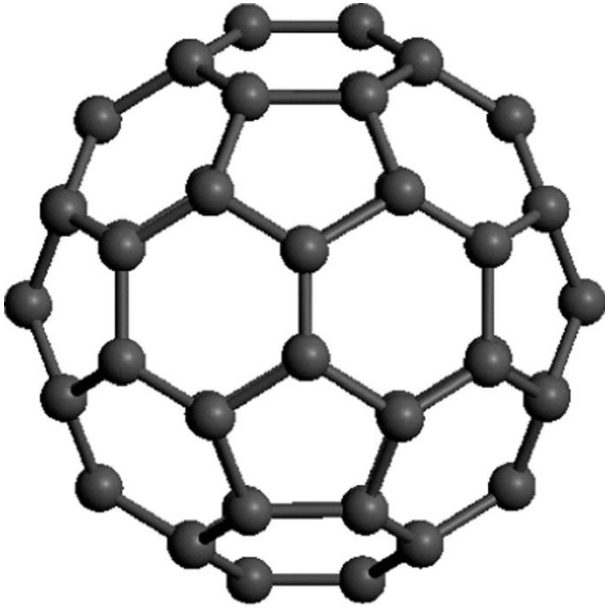
Transmission electron micrograph of the structure of clay platelets. This microscopic-scale structure is a manifestation of the layered crystal structure shown in the previous slide. (Courtesy of I. A. Aksay.)



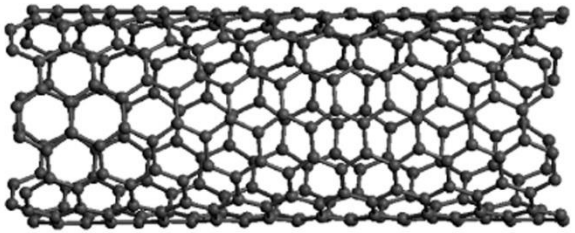
(a) An exploded view of the graphite (C) unit cell. (From F. H. Norton, Elements of Ceramics, *2nd ed., Addison-Wesley Publishing Co., Inc., Reading, MA, 1974.) (b) A schematic of the nature of graphite's layered structure. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann,* Introduction to Ceramics, *2nd ed., John Wiley & Sons, Inc., NY, 1976.)*



(a) C_{60} molecule, or buckyball. (b) Cylindrical array of hexagonal rings of carbon atoms, or buckytube. (Courtesy of Accelrys, Inc.)

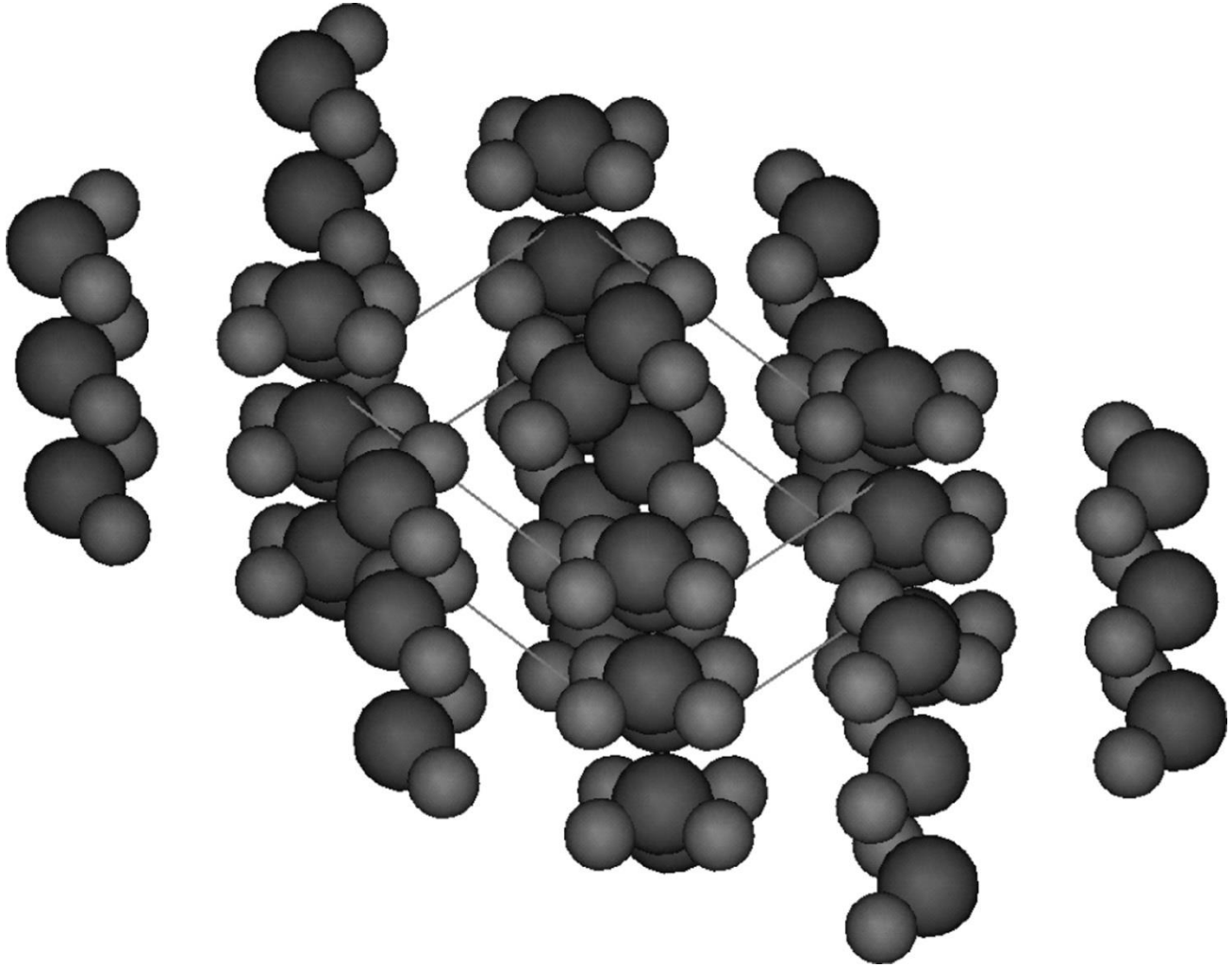


(a)

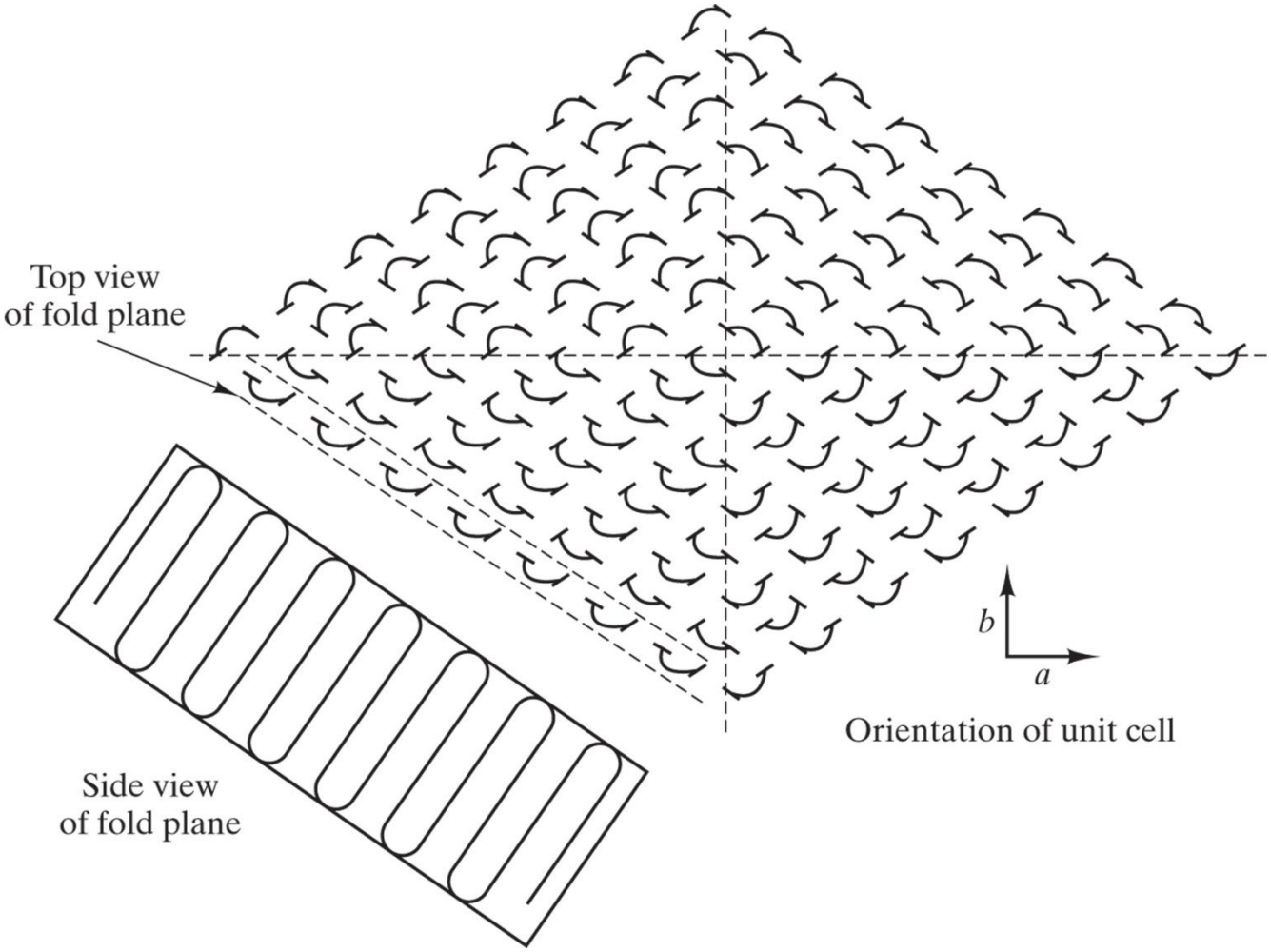


(b)

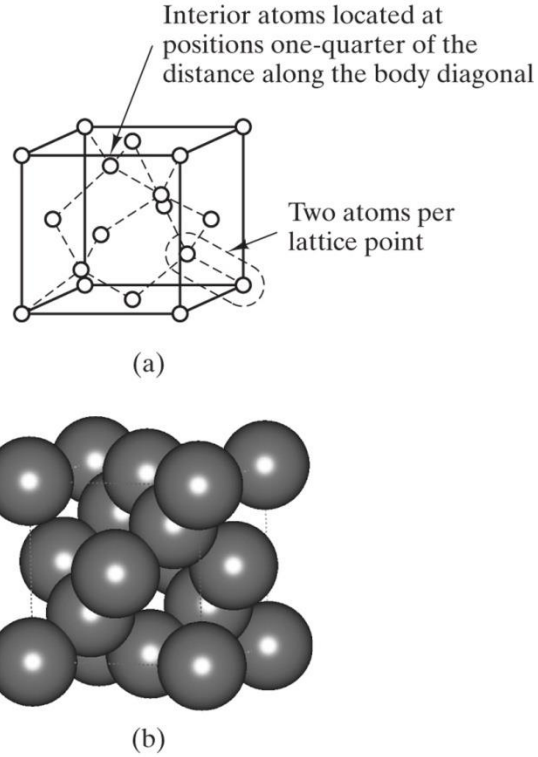
Arrangement of polymeric chains in the unit cell of polyethylene. The dark spheres are carbon atoms, and the light spheres are hydrogen atoms. The unit-cell dimensions are 0.255 nm × 0.494 nm × 0.741 nm. (Courtesy of Accelrys, Inc.)



Weaving-like pattern of folded polymeric chains that occurs in thin crystal platelets of polyethylene. (From D. J. Williams, Polymer Science and Engineering*, Prentice Hall, Inc., Englewood Cliffs, NJ, 1971.)*

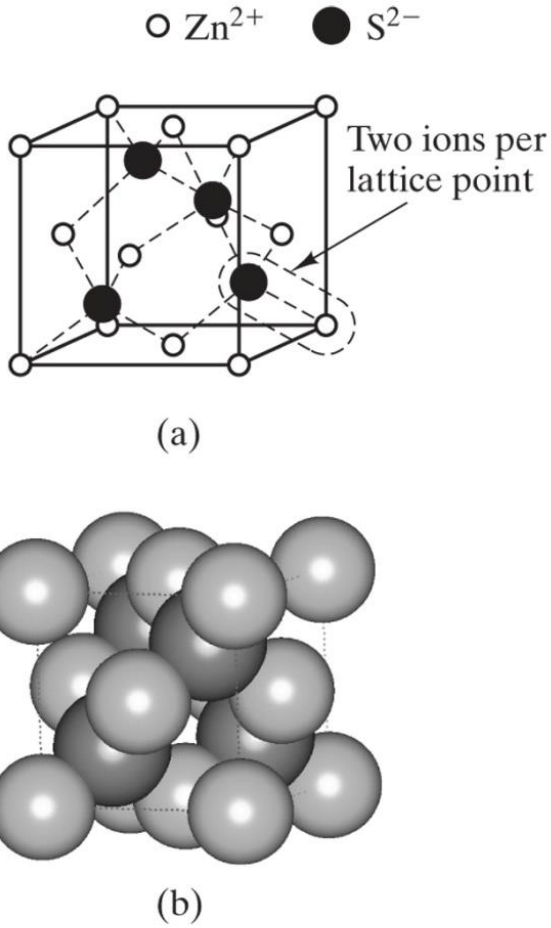


Diamond cubic unit cell showing (a) atom positions. There are two atoms per lattice point (note the outlined example). Each atom is tetrahedrally coordinated. (b) The actual packing of full-size atoms associated with the unit cell. [Part (b) courtesy of Accelrys, Inc.]



Structure: diamond cubic
Bravais lattice: fcc
Atoms/unit cell: $4 + 6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 8$
Typical semiconductors: Si, Ge, and gray Sn

Zinc blende (ZnS) unit cell showing (a) ion positions. There are two ions per lattice point (note the outlined example). Compare this structure with the diamond cubic structure (Figure 3.20a). (b) The actual packing of full-size ions associated with the unit cell. [Part (b) courtesy of Accelrys, Inc.]



Structure: Zinc blende (ZnS) type
Bravais lattice: fcc
Ions/unit cell: $4Zn^{2+} + 4S^{2-}$
Typical semiconductors:
GaAs, AlP, InSb (III–V compounds),
ZnS, ZnSe, CdS, HgTe (II–VI compounds)

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...

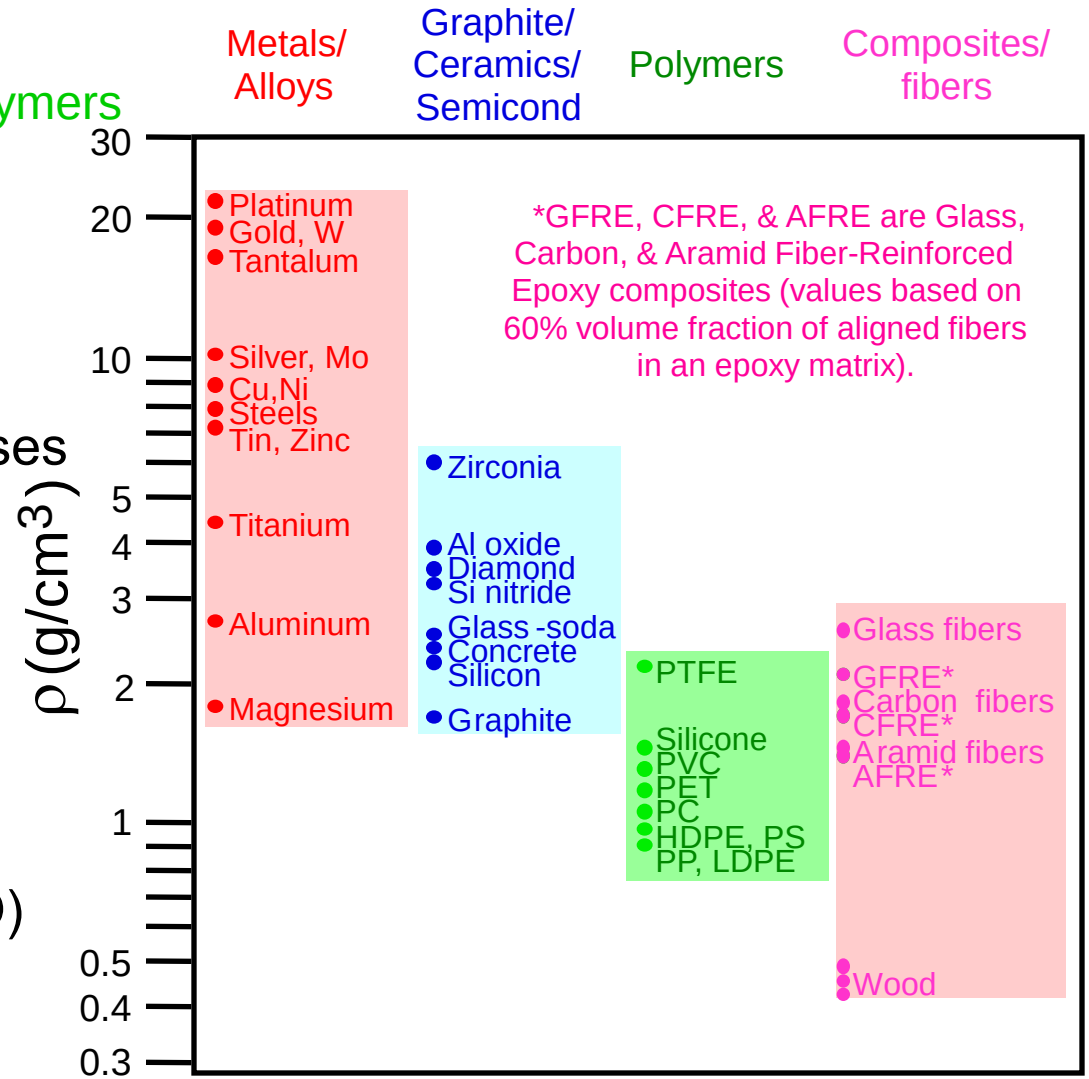
- less dense packing
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values

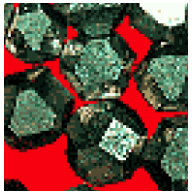


Data from Table B1, *Callister 7e.*

Crystals as Building Blocks

- *Some* engineering applications require single crystals:

--diamond single crystals for abrasives



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

--turbine blades

Fig. 8.33(c), *Callister 7e.* (Fig. 8.33(c) courtesy of Pratt and Whitney).

- Properties of crystalline materials often related to crystal structure.

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

(Courtesy P.M. Anderson)

Polycrystals

- *Most* engineering materials are polycrystals.

Anisotropic

Adapted from Fig. K, color inset pages of *Callister 5e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

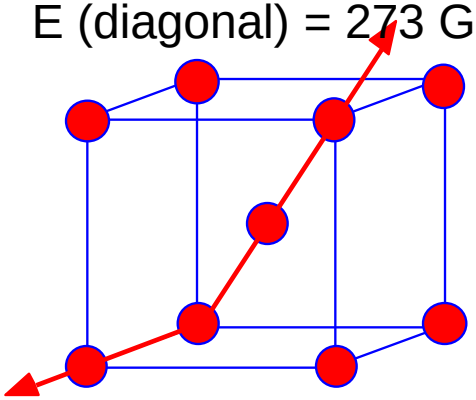
Isotropic

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

Single vs Polycrystals

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

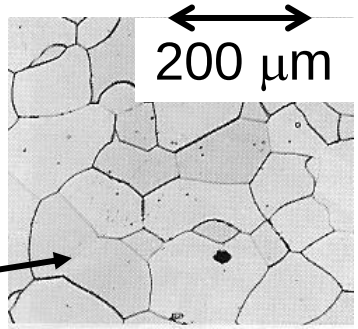
E (diagonal) = 273 GPa

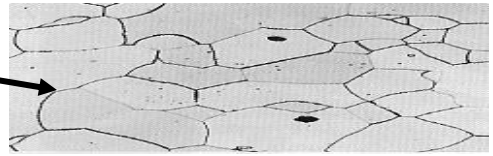


E (edge) = 125 GPa

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.
    ($E_{poly\ iron}$ = 210 GPa)
  - -If grains are textured, anisotropic.





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].

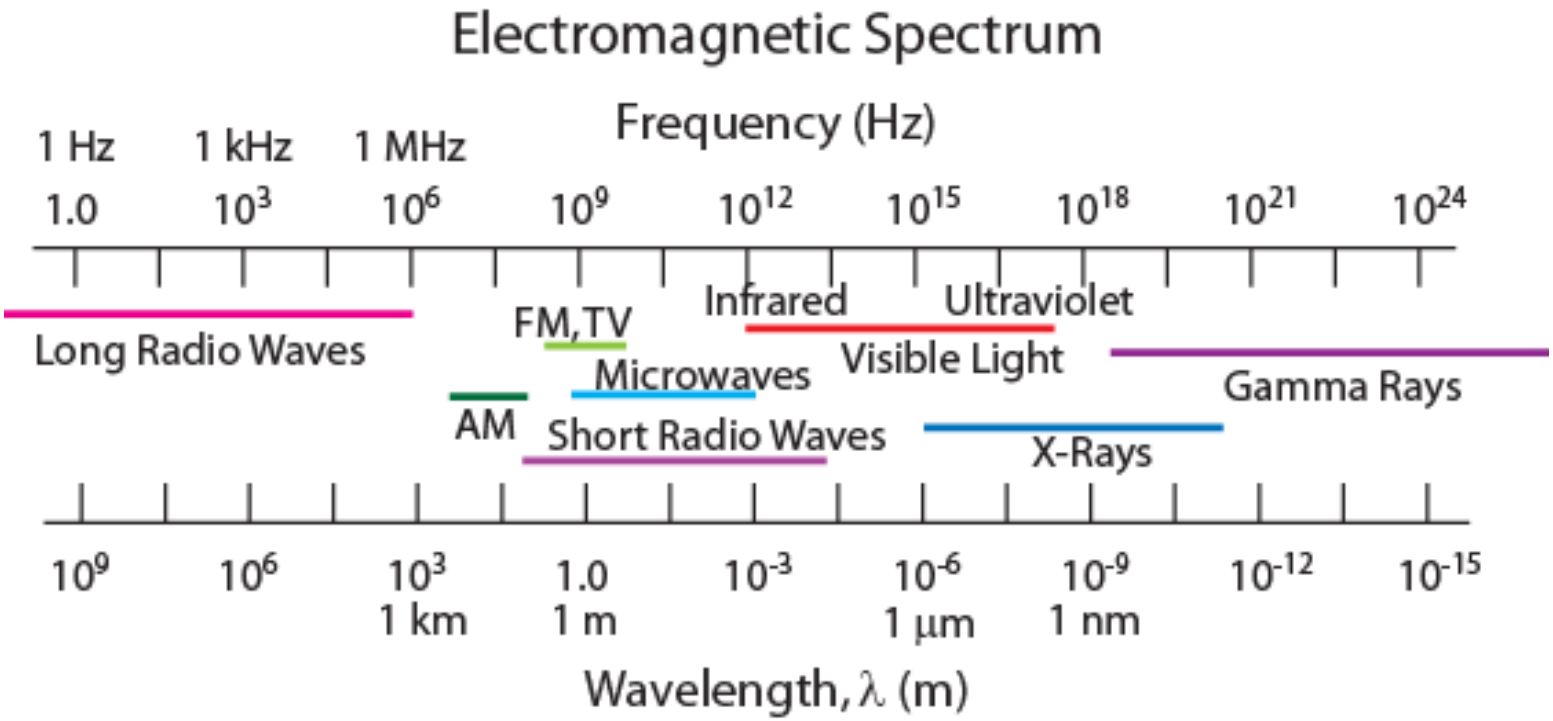
Effects of Anisotropy:

Table 3.3 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

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

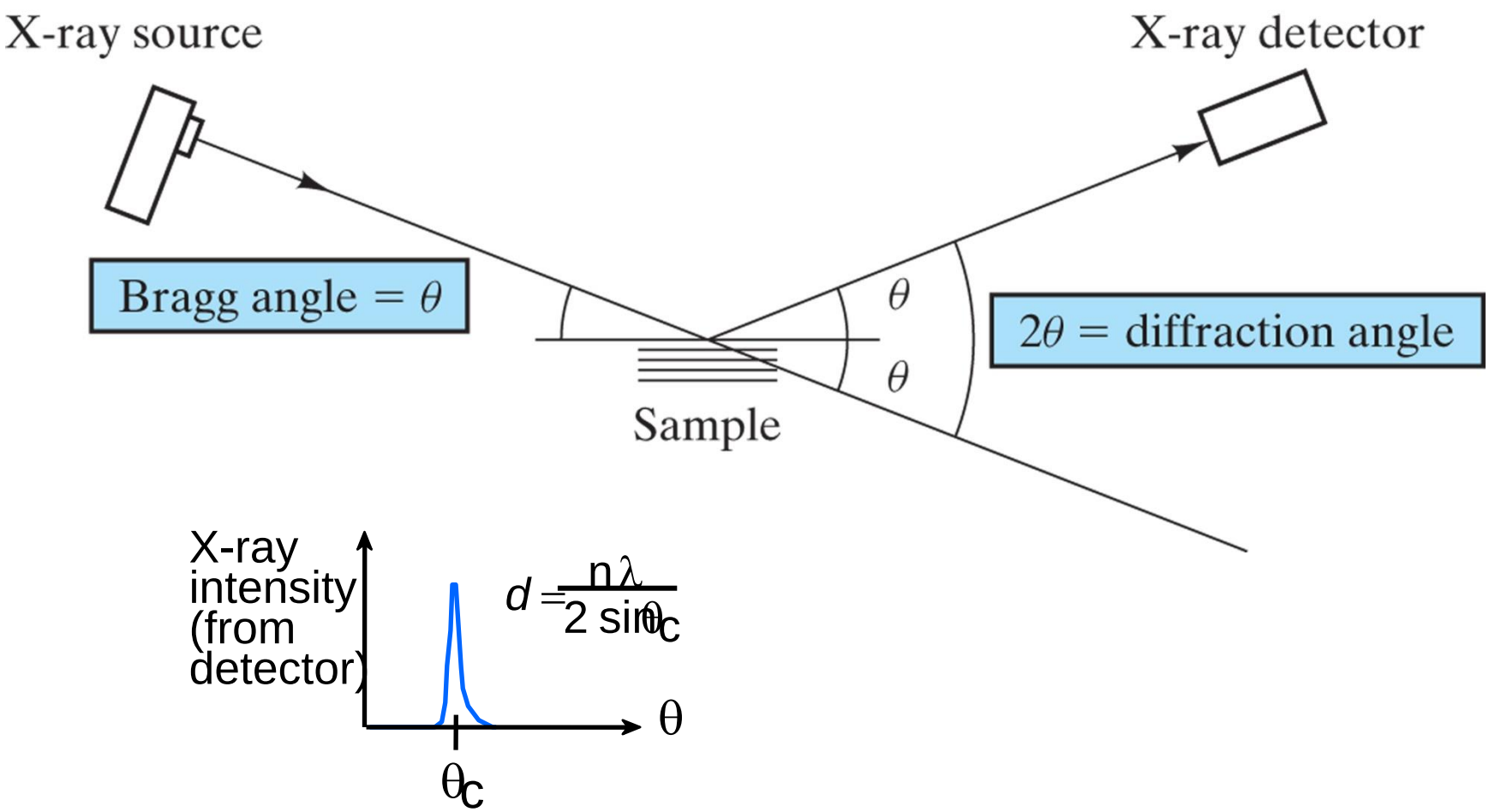
Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials,* 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

X-Ray Diffraction



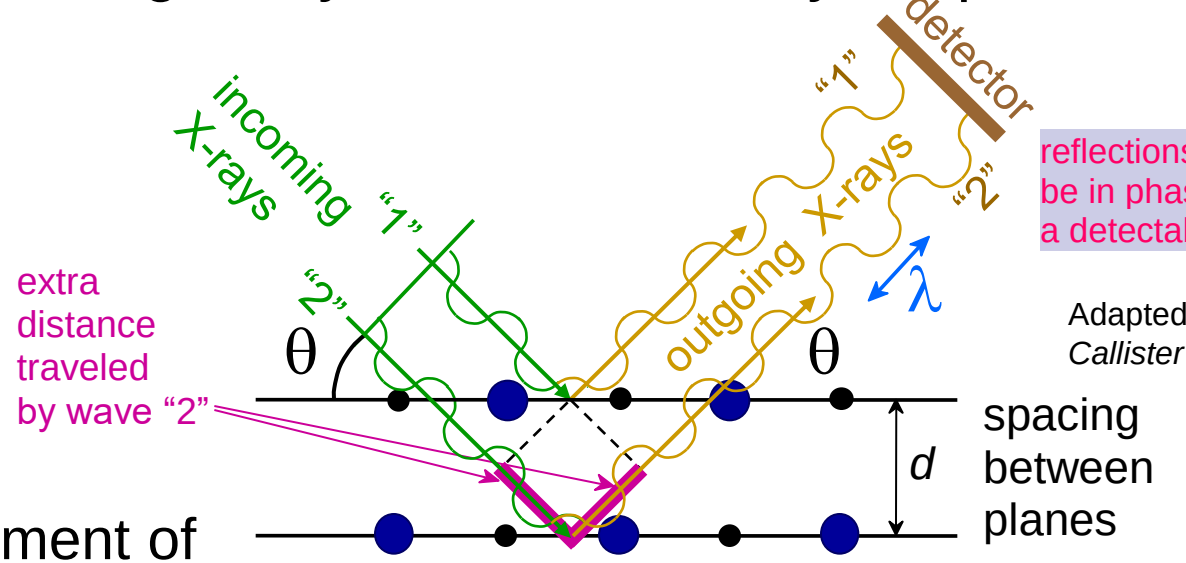
- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

Figure 3.32 *Relationship of the Bragg angle (θ) and the experimentally measured diffraction angle (2θ).*



X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.

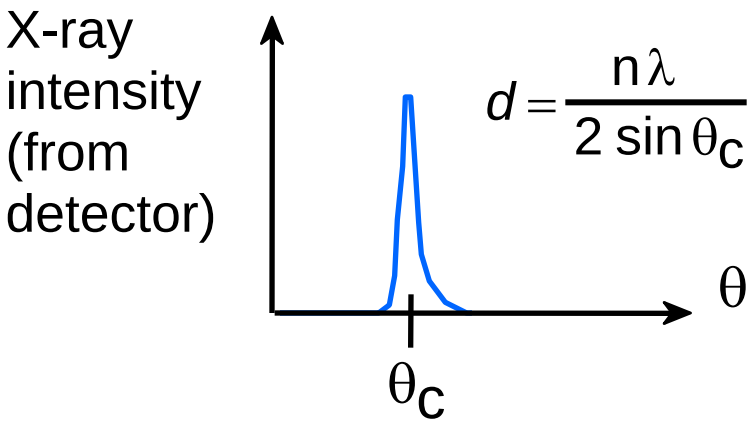


reflections must be in phase for a detectable signal!

Adapted from Fig. 3.19, *Callister 7e*.

spacing between planes

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



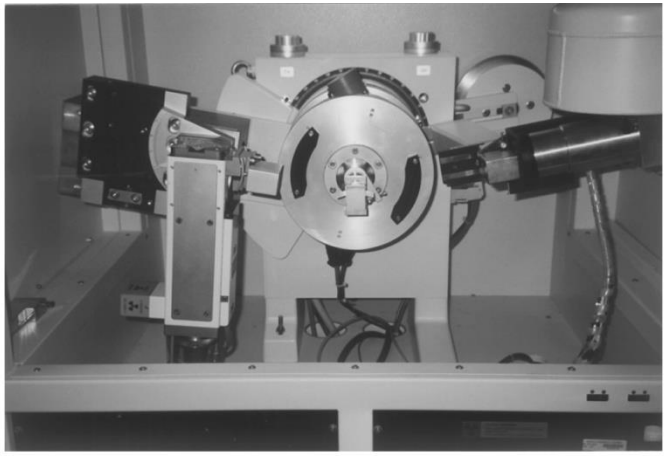
$$d = \frac{n\lambda}{2\sin\theta_c}$$

For Cubic Crystals:

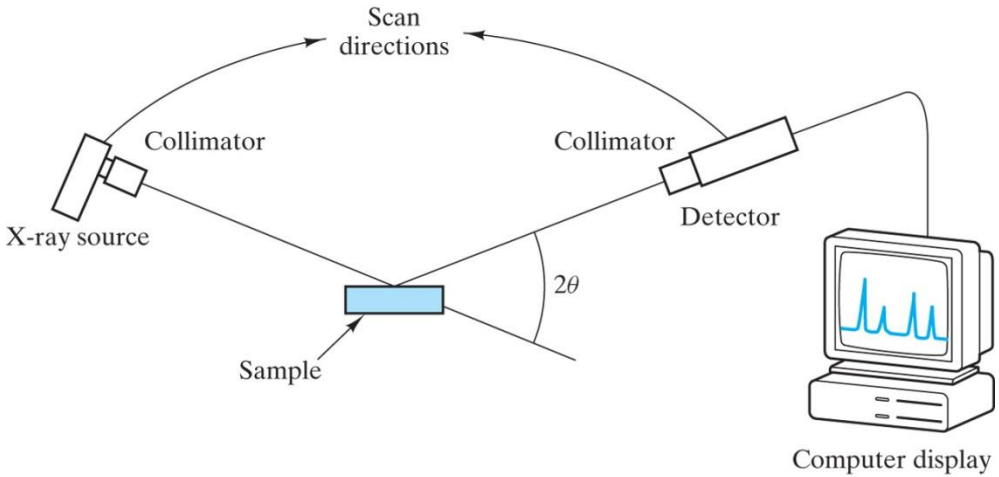
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

h, k, l are Miller Indices

Figure 3.34 *(a) An x-ray diffractometer. (Courtesy of Scintag, Inc.) (b) A schematic of the experiment.*

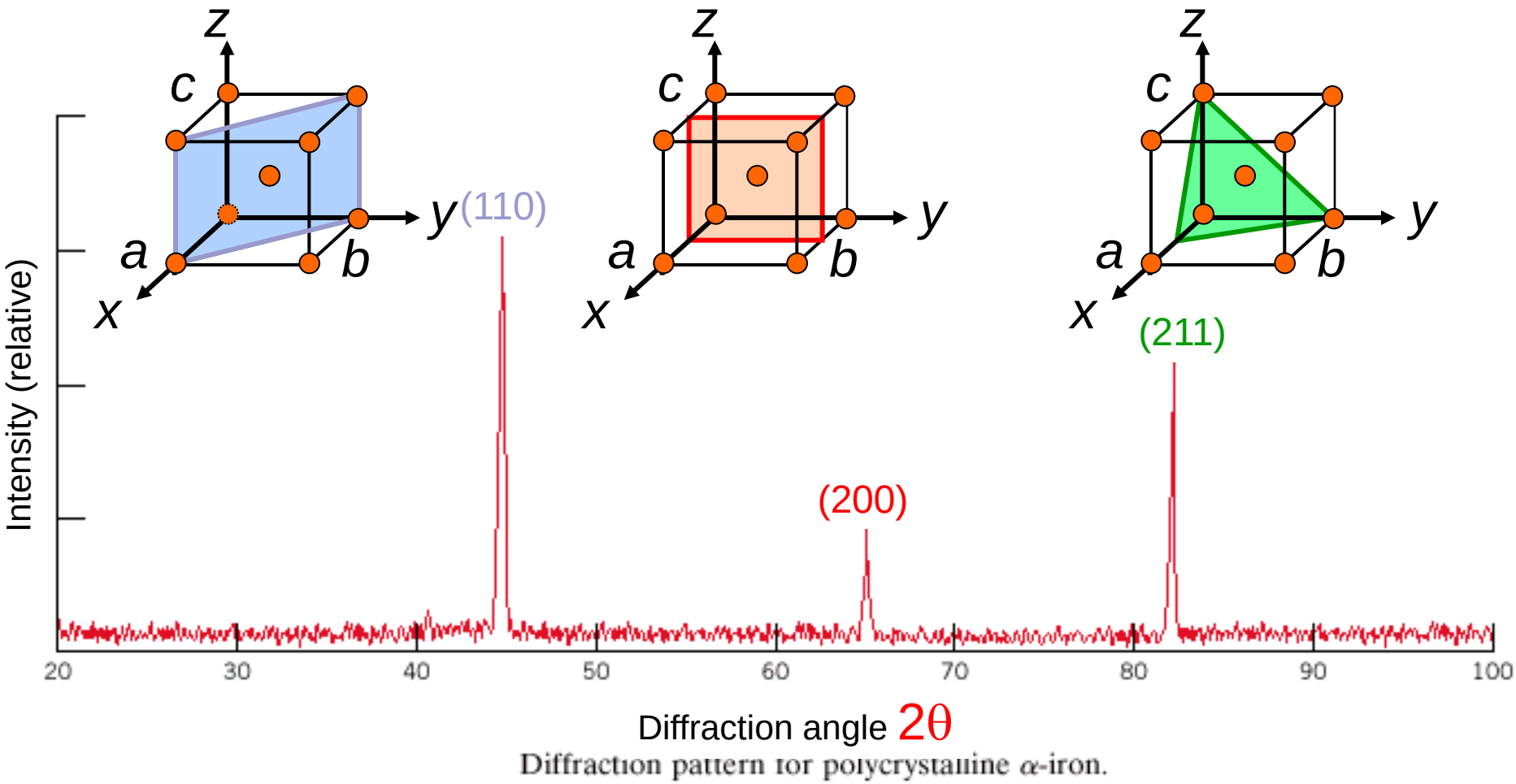


(a)



(b)

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.20, *Callister 5e.*

Diffraction in Cubic Crystals:

TABLE 3.4

Reflection Rules of X-Ray Diffraction for the Common Metal Structures

Crystal structure	Diffraction does not occur when	Diffraction occurs when
Body-centered cubic (bcc)	$h + k + l =$ odd number	$h + k + l =$ even number
Face-centered cubic (fcc)	h, k, l mixed (i.e., both even and odd numbers)	h, k, l unmixed (i.e., are all even numbers or all are odd numbers)
Hexagonal close packed (hcp)	$(h + 2k) = 3n, l$ odd (n is an integer)	All other cases

SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.