STRUCTURE OF SOLIDS

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STRUCTURE OF SOLIDS

ISSUES TO ADDRESS...

- How do atoms assemble into solid structures?
- How does the density of a material depend on its structure?
- When do material properties vary with the sample orientation?

POLYCRYSTALLINE MATERIALS

- "Nuclei" form during solidification, each of which grows into crystals

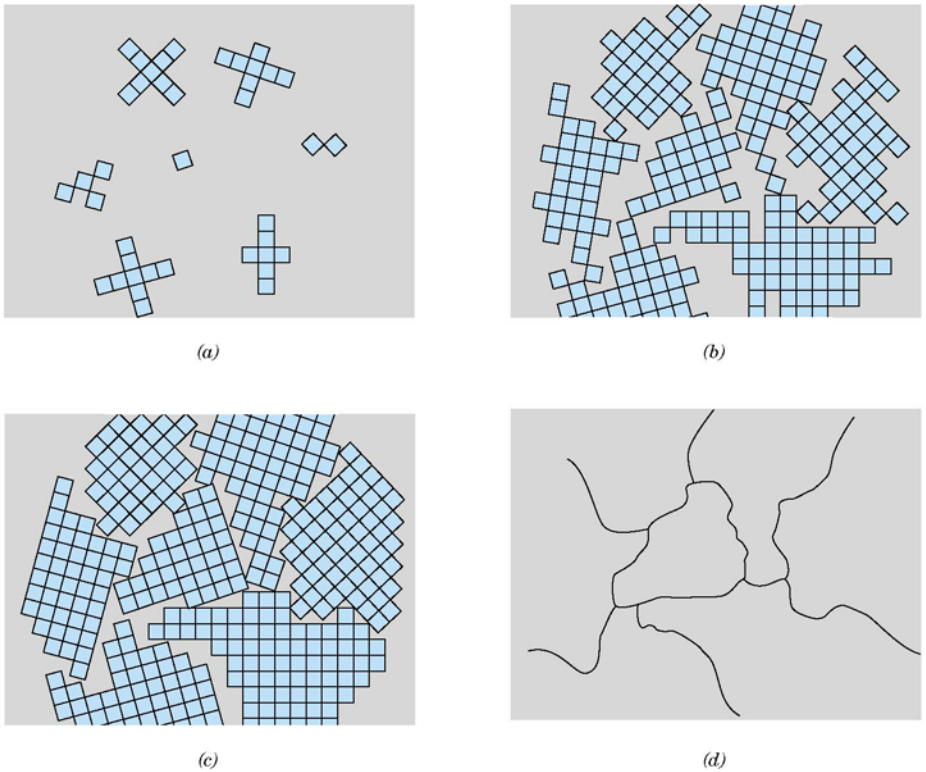
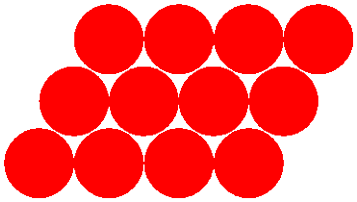
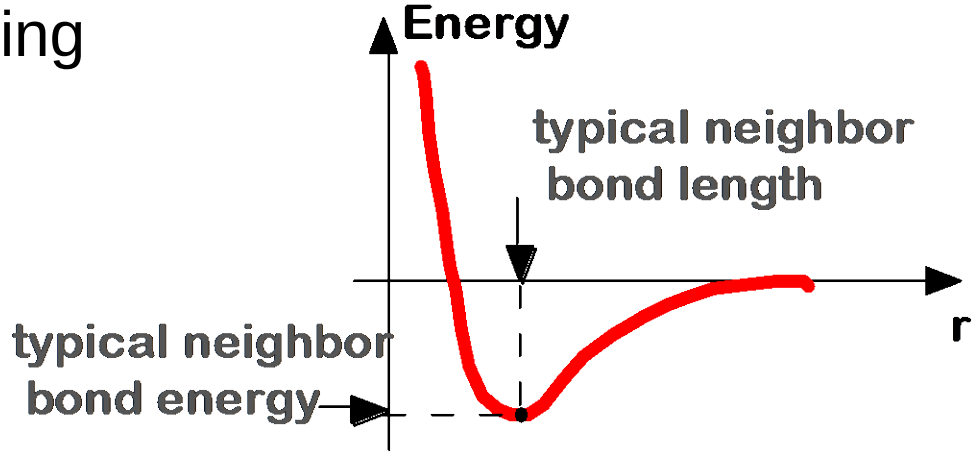


FIGURE 3.17 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy,* 2nd edition, Constable & Company Ltd., London, 1915.)

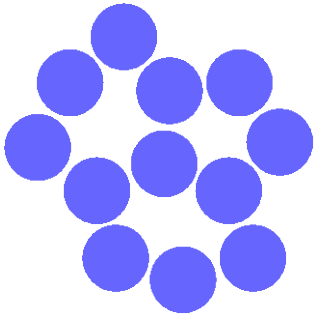
ENERGY AND PACKING

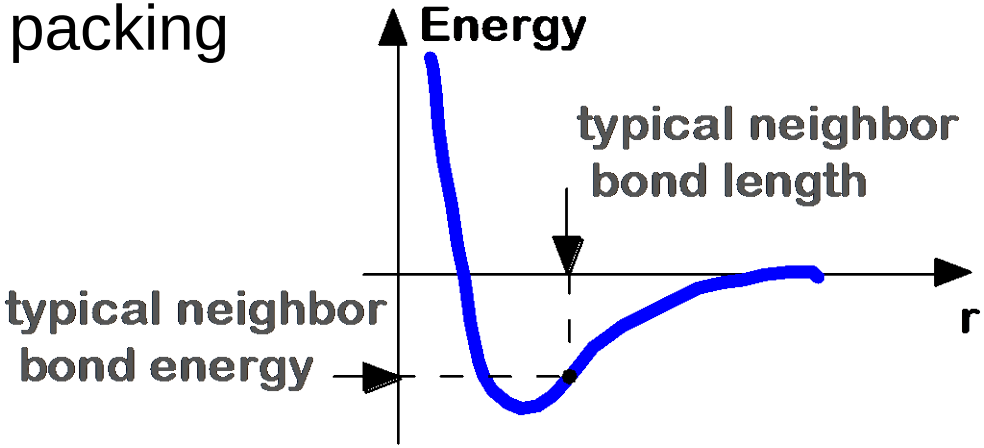
- Dense, regular packing





- Non dense, random packing





Dense, regular-packed structures tend to have lower energy

SOME DEFINITIONS ...

- Lattice: 3D array of regularly spaced points
- Crystalline material: atoms situated in a repeating 3D periodic array over large atomic distances
- Amorphous material: material with no such order
- Hard sphere representation: atoms denoted by hard, touching spheres
- Reduced sphere representation
- Unit cell: basic building block unit (such as a flooring tile) that repeats in space to create the crystal structure; it is usually a parallelepiped or prizm

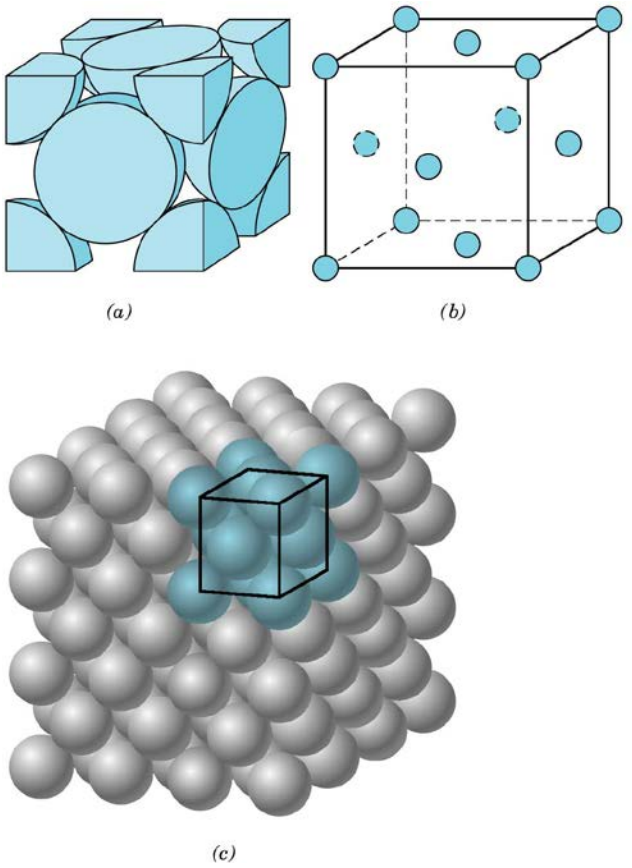


FIGURE 3.1 For the face-centered cubic crystal structure: (*a*) a hard sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms. (Figure *c* adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*,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

METALLIC CRYSTALS

- tend to be densely packed.
- have several reasons for dense packing:

  -Typically, made of heavy element.
  -Metallic bonding is not directional; i.e., no restrictions as to the number and position of nearest-neighbor atoms
  -Nearest neighbor distances tend to be small in order to lower bond energy.

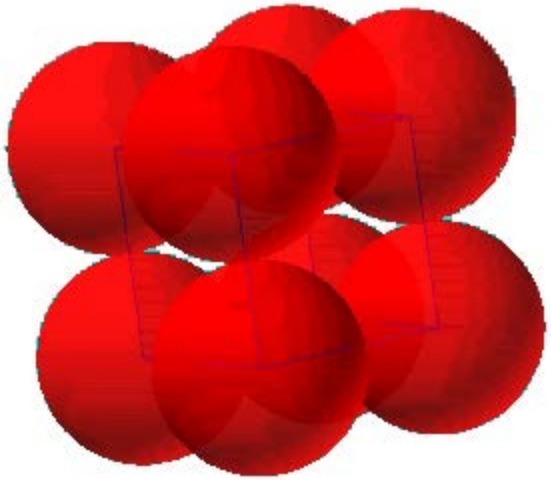
- have the simplest crystal structures.

We will look at four such structures...

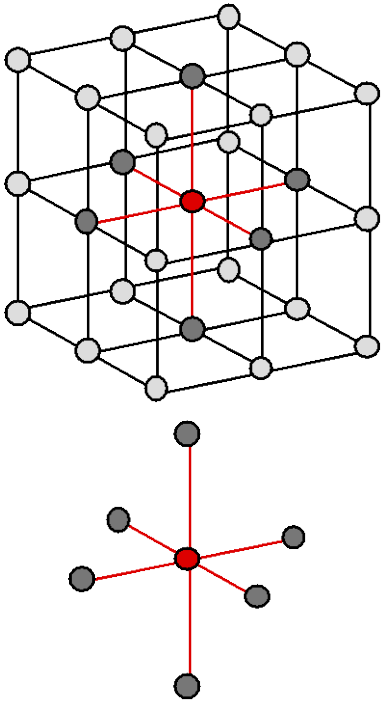
SIMPLE CUBIC STRUCTURE (SC)

- Cubic unit cell is 3D repeat unit
- Rare (only Po has this structure)
- Close-packed directions (directions along which atoms touch each other) are cube edges.

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



(Courtesy P.M. Anderson)



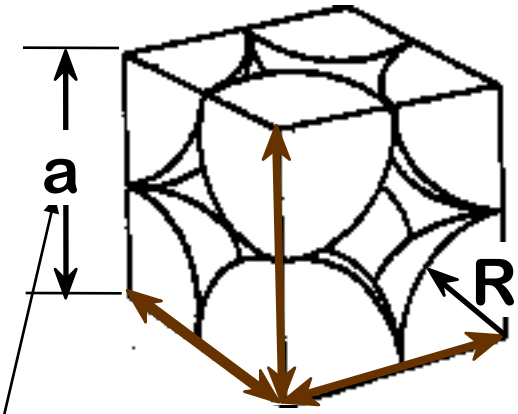
ATOMIC PACKING FACTOR

- Fill a box with hard spheres
  - Packing factor = total volume of spheres in box / volume of box
  - Question: what is the maximum packing factor you can expect?
- In crystalline materials:
  - Atomic packing factor = total volume of atoms in unit cell / volume of unit cell
  - (as unit cell repeats in space)

ATOMIC PACKING FACTOR

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

*assume hard spheres



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.19, *Callister 6e.*

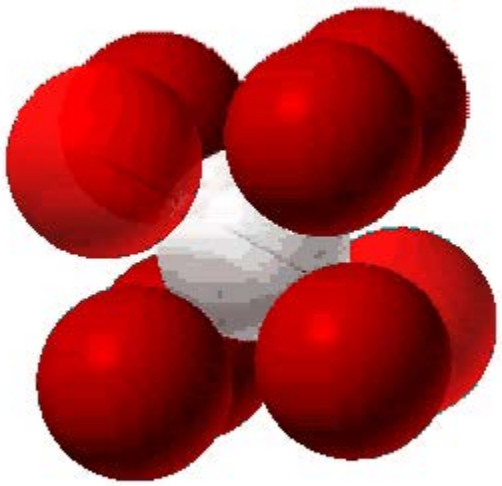
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}}$$

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

Lattice constant

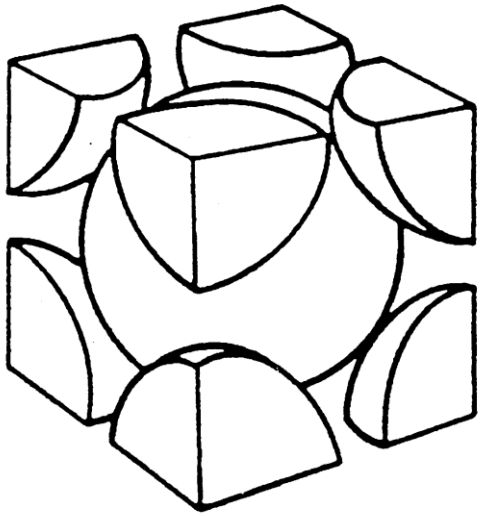
- APF for a simple cubic structure = 0.52

BODY CENTERED CUBIC STRUCTURE (BCC)



(Courtesy P.M. Anderson)

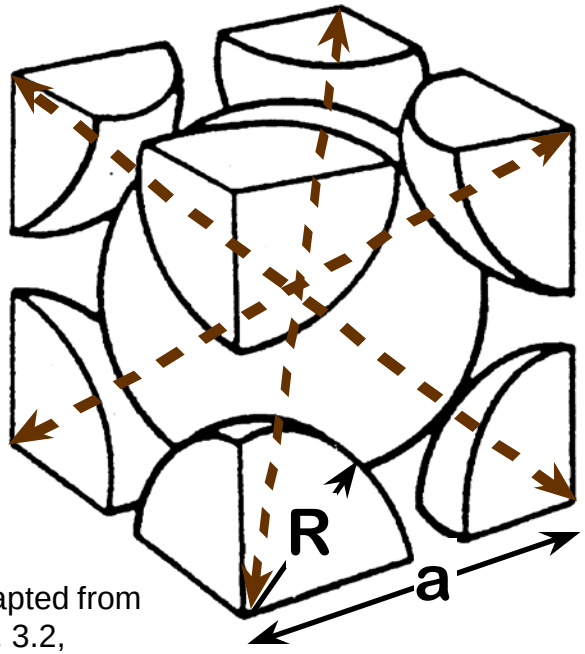
- Coordination # = 8



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

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

ATOMIC PACKING FACTOR: BCC



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

Close-packed directions:

length = 4R

$= \sqrt{3}\, a$

Unit cell contains:

1 + 8 x 1/8

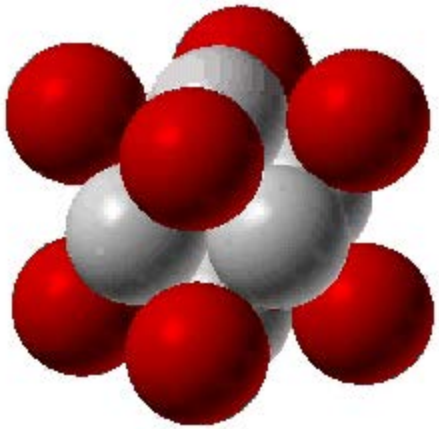
= 2 atoms/unit cell

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

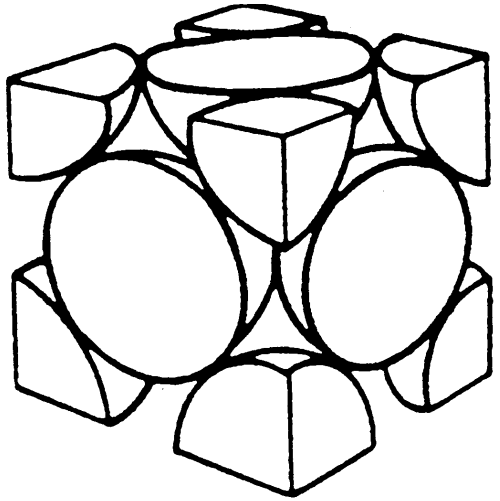
- APF for a body-centered cubic structure = $\pi\sqrt{3}/8 = 0.68$

FACE CENTERED CUBIC STRUCTURE (FCC)

- Coordination # = 12



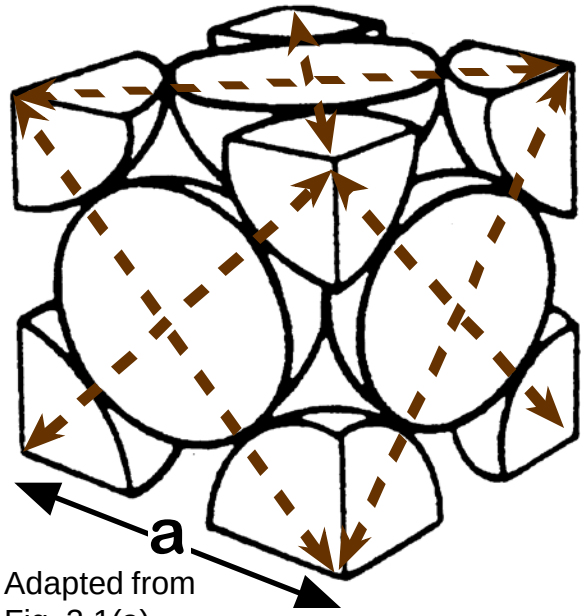
(Courtesy P.M. Anderson)



Adapted from Fig. 3.1(a), *Callister 6e.*

- Close packed directions are face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ATOMIC PACKING FACTOR: FCC



Adapted from Fig. 3.1(a), *Callister 6e.*

Close-packed directions:

length = 4R

$= \sqrt{2}\, a$

Unit cell contains:

6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

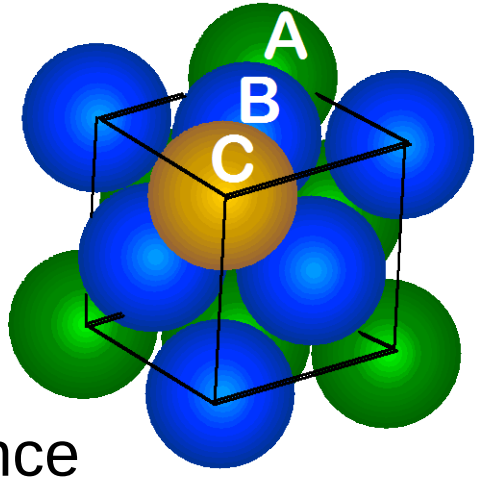
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

- APF for a body-centered cubic structure = $\pi/(3\sqrt{2}) = 0.74$

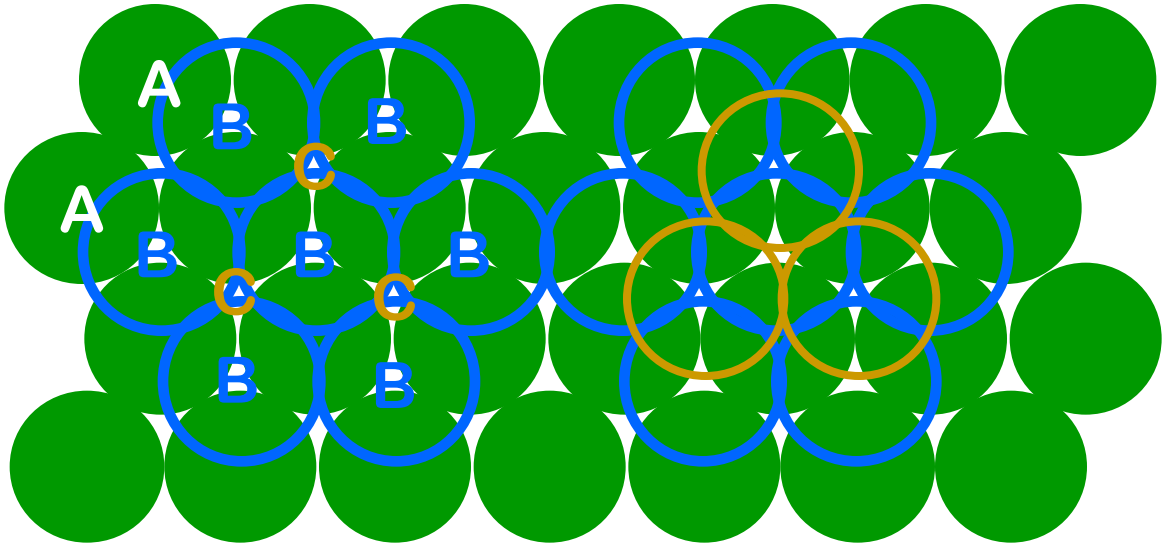
(best possible packing of identical spheres)

FCC STACKING SEQUENCE

- FCC Unit Cell



- ABCABC... Stacking Sequence
- 2D Projection



HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

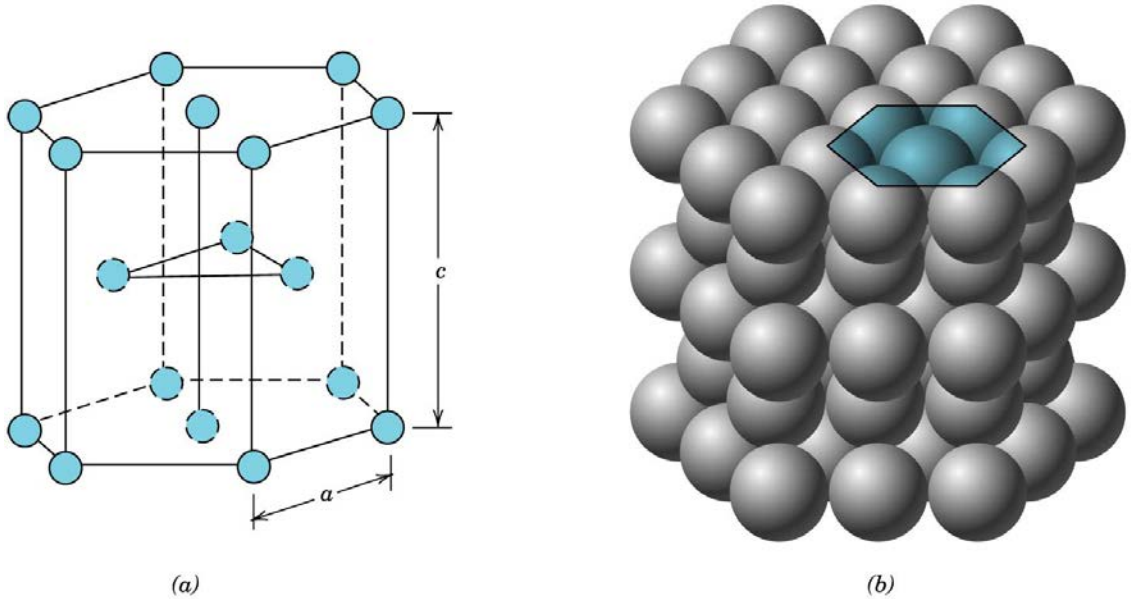


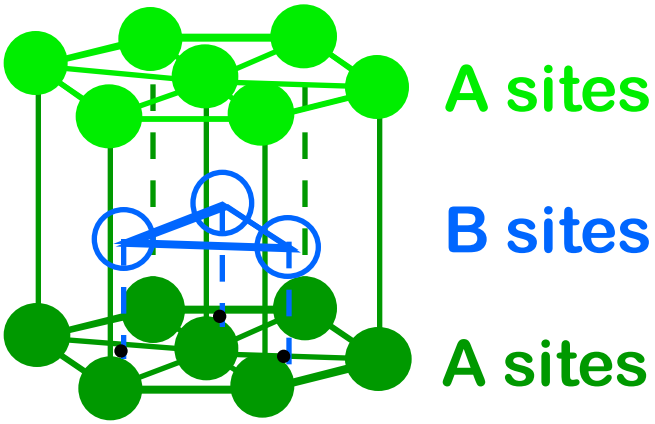
FIGURE 3.3 For the hexagonal close-packed crystal structure, (*a*) a reduced-sphere unit cell (*a* and *c* represent the short and long edge lengths, respectively), and (*b*) an aggregate of many atoms. (Figure *b* from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Ideally, c/a = 1.633 for close packing

However, in most metals, c/a ratio deviates from this value

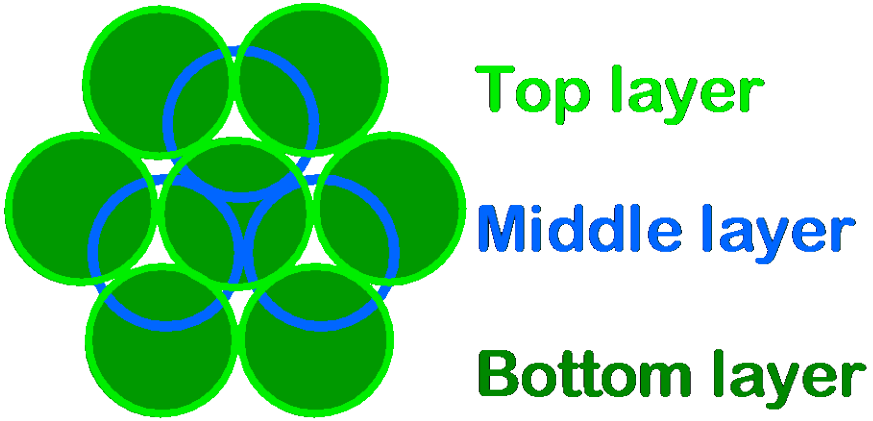
HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

- ABAB... Stacking Sequence
- 3D Projection



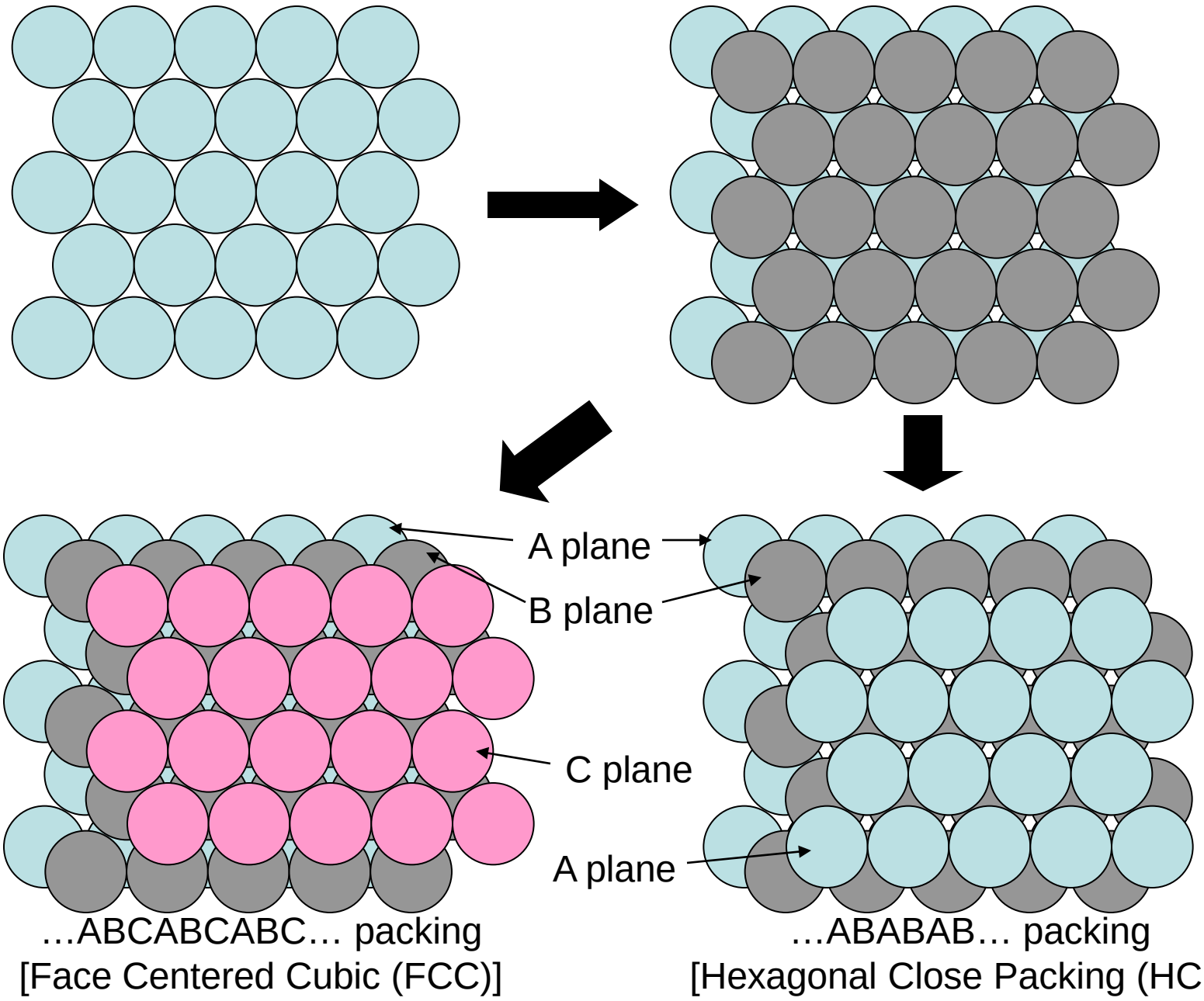
Adapted from Fig. 3.3, *Callister 6e.*

- 2D Projection



- Coordination # = 12
- APF = 0.74, for ideal c/a ratio of 1.633

Close packed crystals



COMPARISON OF CRYSTAL STRUCTURES

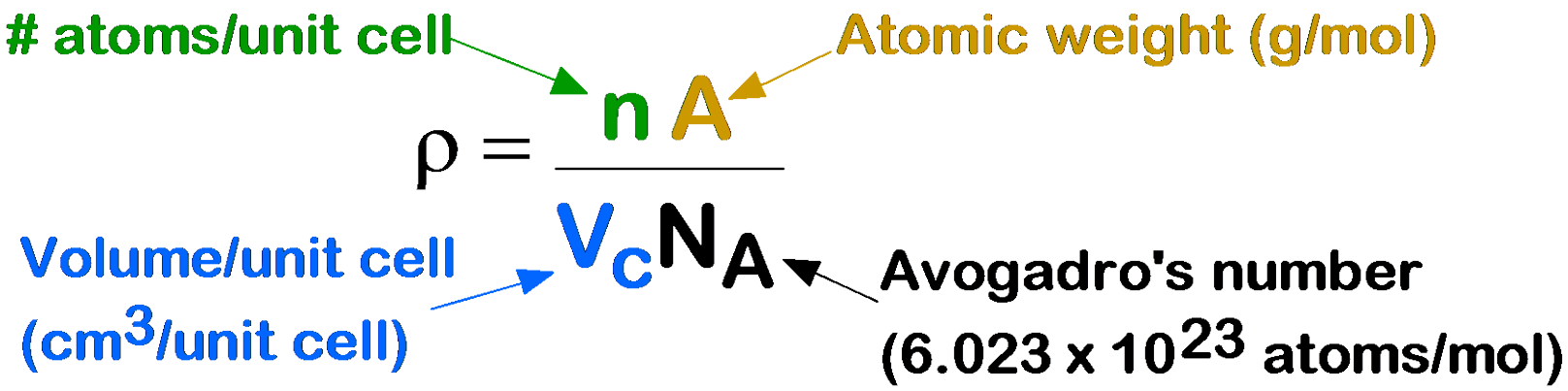
Crystal structure	coordination #	packing factor	close packed directions
• Simple Cubic (SC)	6	0.52	cube edges
• Body Centered Cubic (BCC)	8	0.68	body diagonal
• Face Centered Cubic (FCC)	12	0.74	face diagonal
• Hexagonal Close Pack (HCP)	12	0.74	hexagonal side

THEORETICAL DENSITY, ρ

Density = mass/volume

mass = number of atoms per unit cell * mass of each atom

mass of each atom = atomic weight/avogadro's number

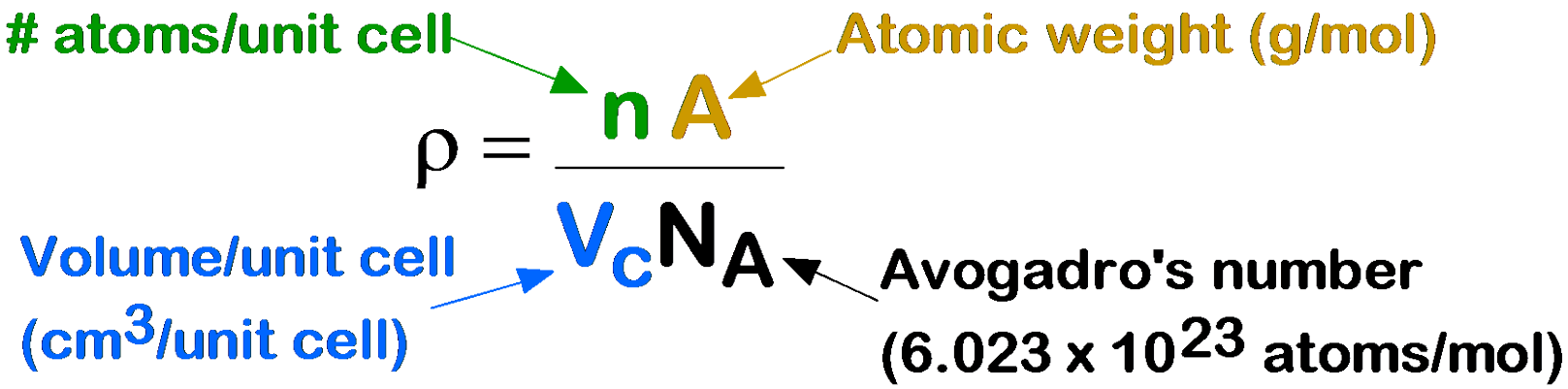


Characteristics of Selected Elements at 20C

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

Adapted from Table, "Characteristics of Selected Elements", inside front cover, *Callister 6e.*

THEORETICAL DENSITY, ρ



Example: Copper

Data from Table inside front cover of Callister (see previous slide):

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius R = 0.128 nm (1 nm = 10^{-7}cm)

$V_C = a^3$; For FCC, $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23} cm^3$

Result: theoretical $\rho_{Cu} = 8.89$ g/cm^3

Compare to actual: $\rho_{Cu} = 8.94$ g/cm^3

DENSITIES OF MATERIAL CLASSES

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

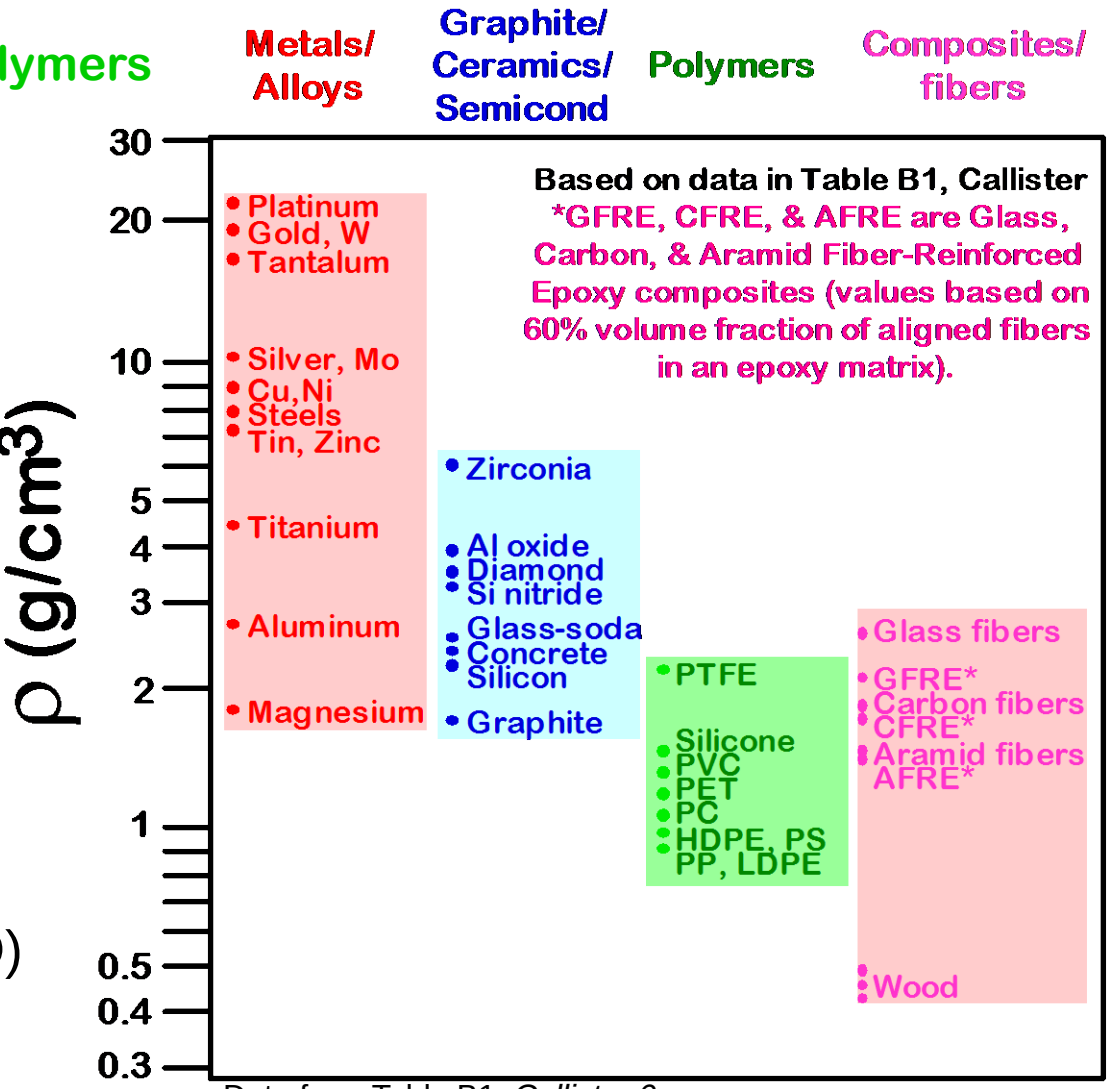
Why?

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

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

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

Composites have...
- intermediate values



Data from Table B1, *Callister 6e.*

CRYSTAL SYSTEMS

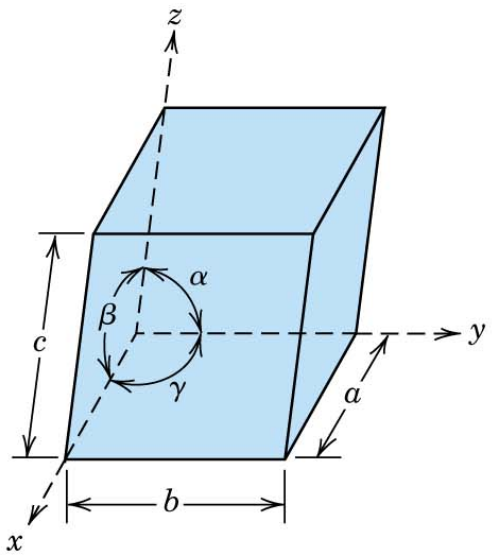
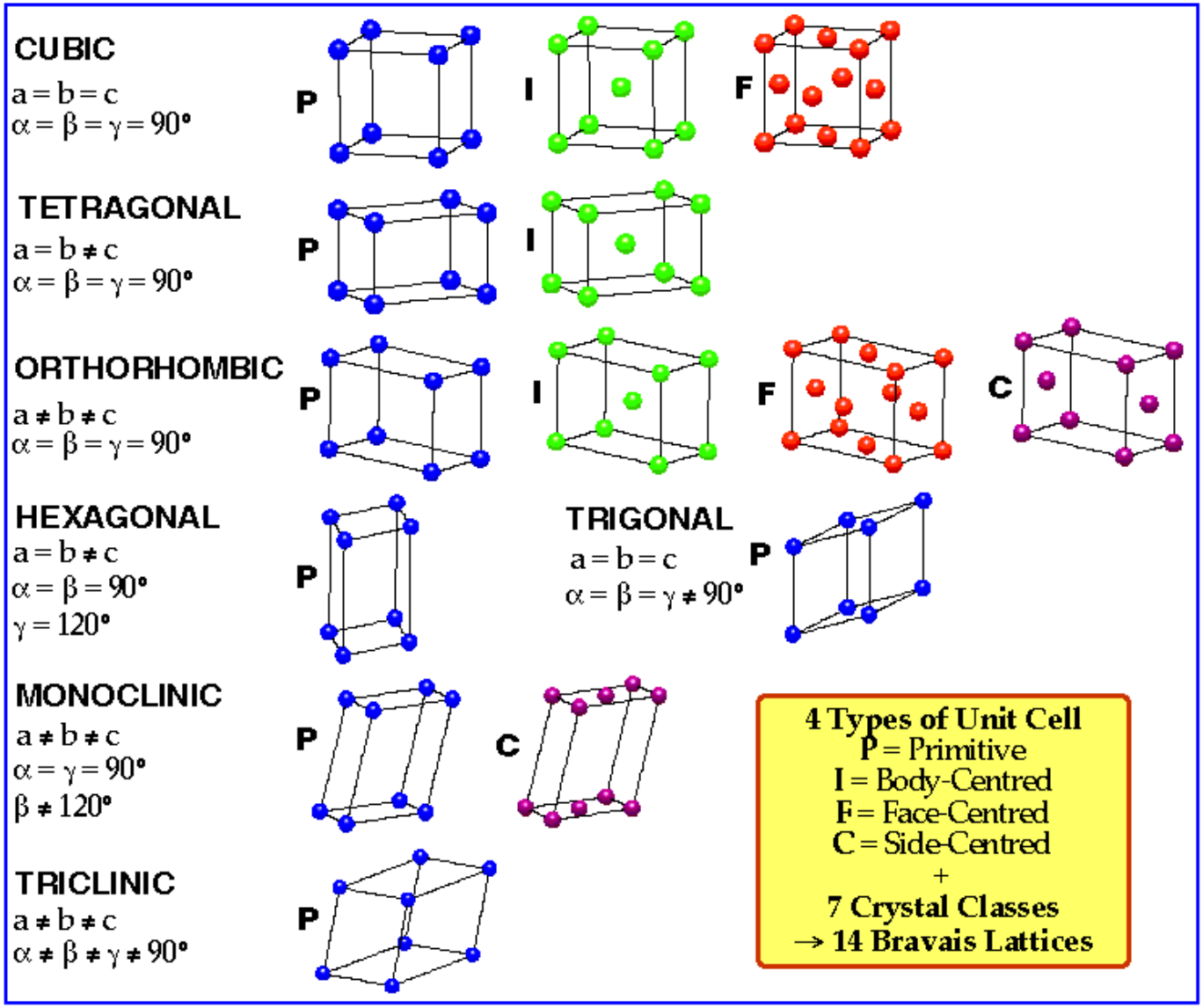


FIGURE 3.4 A unit cell with x, y, and z coordinate axes, showing axial lengths (a, b, and c) and interaxial angles (α, β, and γ).

- Based on shape of unit cell ignoring actual atomic locations
- Unit cell = 3-dimensional unit that repeats in space
- Unit cell geometry completely specified by *a, b, c* & α, β, γ ***(lattice parameters** or **lattice constants**)*
- Seven possible combinations of *a, b, c* & α, β, γ, resulting in seven crystal systems

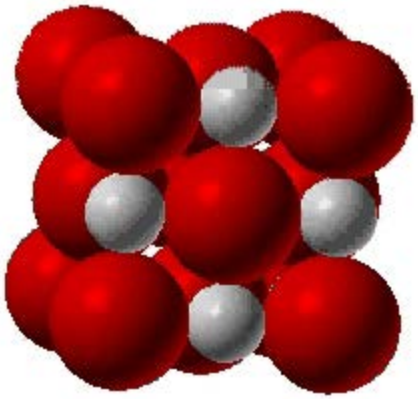
CRYSTAL SYSTEMS



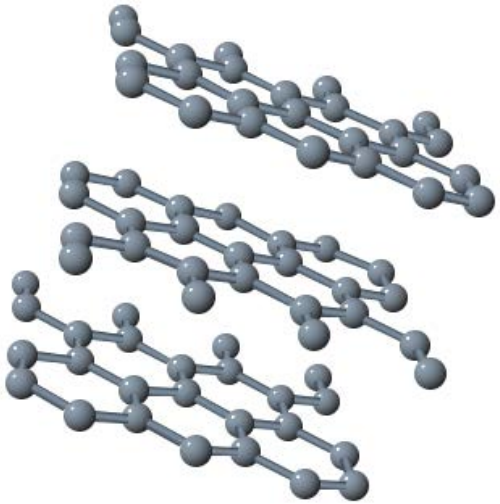
STRUCTURE OF OTHER SYSTEMS

- Structure of NaCl

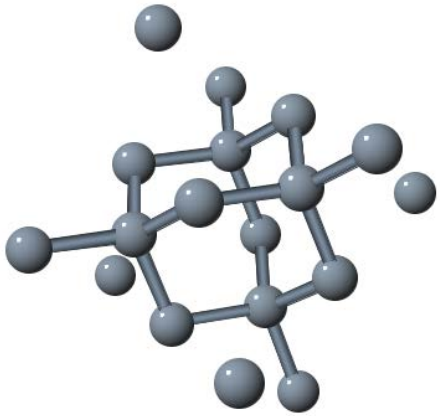
(Courtesy P.M. Anderson)



- Structure of Carbon



Graphite



Diamond

CRYSTAL STRUCTURES

- Plenty of crystal structures available at: http://cst-www.nrl.navy.mil/lattice/

- Polymorphism
  - Same compound occurring in more than one crystal structure

- Allotropy
  - Polymorphism in elemental solids (e.g., carbon)

CRYSTALLOGRAPHIC POINTS, DIRECTIONS & PLANES

- In crystalline materials, often necessary to specify points, directions and planes within unit cell and in crystal lattice
- Three numbers (or indices) used to designate points, directions (lines) or planes, based on basic geometric notions
- The three indices are determined by placing the origin at one of the corners of the unit cell, and the coordinate axes along the unit cell edges

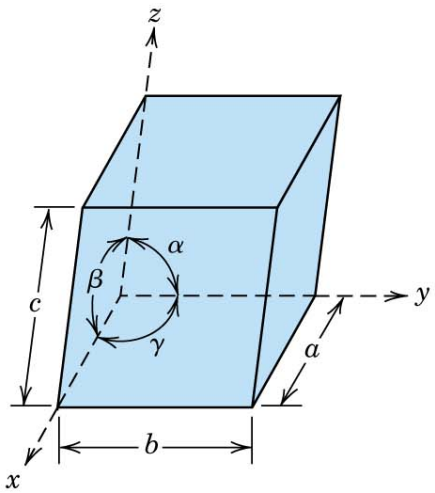


FIGURE 3.4 A unit cell with x, y, and z coordinate axes, showing axial lengths (a, b, and c) and interaxial angles (α, β, and γ).

POINT COORDINATES

- Any point within a unit cell specified as fractional multiples of the unit cell edge lengths
- Position P specified as *q r s*; convention: coordinates not separated by commas or punctuation marks

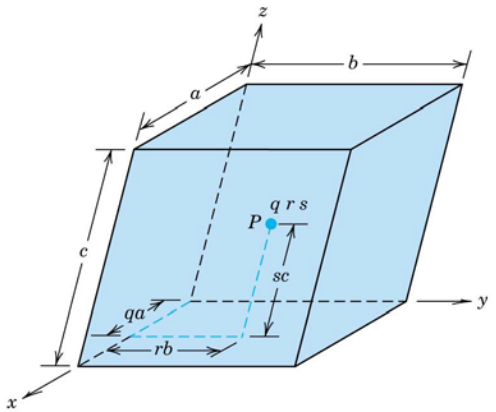
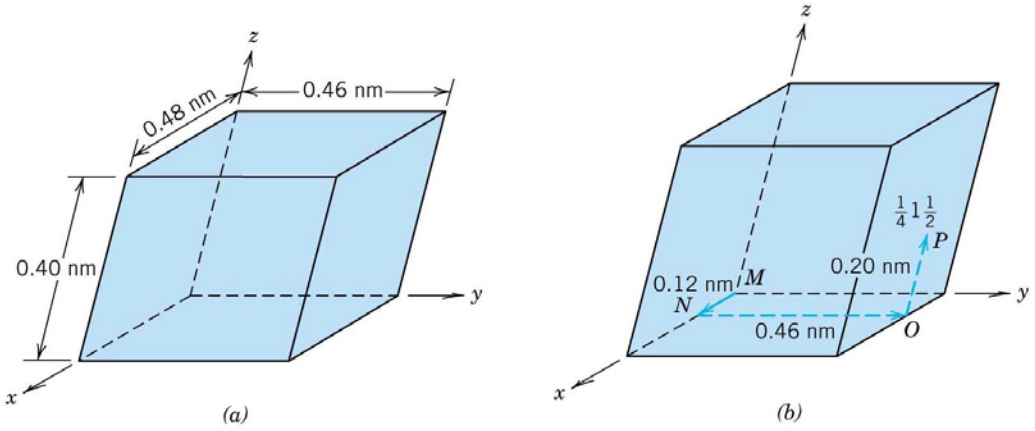


FIGURE 3.5 The manner in which the q, r, and s coordinates at point P within the unit cell are determined. The q coordinate (which is a fraction) corresponds to the distance qa along the x axis, where a is the unit cell edge length. The respective r and s coordinates for the y and z axes are determined similarly.

EXAMPLE: POINT COORDINATES

- Locate the point (1/4 1 ½)



- Specify point coordinates for all atom positions for a BCC unit cell
  - Answer: 0 0 0, 1 0 0, 1 1 0, 0 1 0, ½ ½ ½, 0 0 1, 1 0 1, 1 1 1, 0 1 1

CRYSTALLOGRAPHIC DIRECTIONS

- Defined as line between two points: a vector
- Steps for finding the 3 indices denoting a direction
  - Determine the point positions of a beginning point (X1 Y1 Z1) and a ending point (X2 Y2 Z2) for direction, in terms of unit cell edges
  - Calculate difference between ending and starting point
  - Multiply the differences by a common constant to convert them to the smallest possible integers u, v, w
  - The three indices are not separated by commas and are enclosed in square brackets: [uvw]
  - If any of the indices is negative, a bar is placed in top of that index

COMMON DIRECTIONS

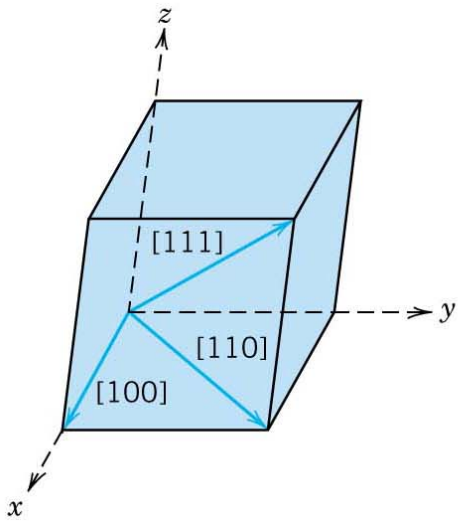
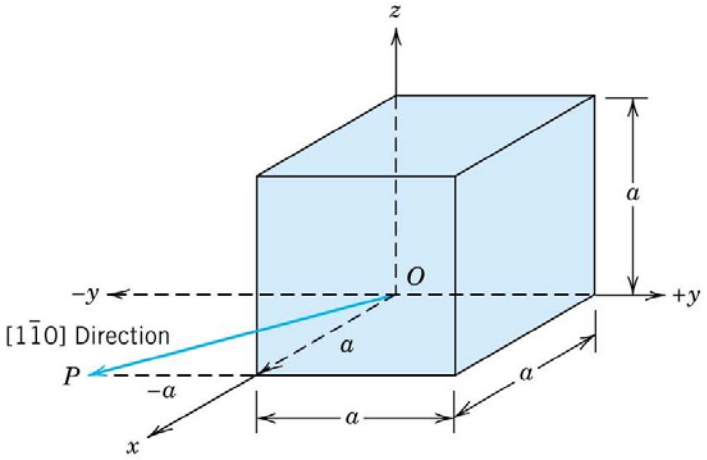


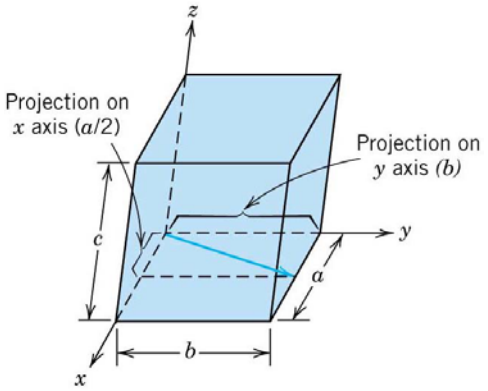
FIGURE 3.6 The [100], [110], and [111] directions within a unit cell.

EXAMPLES: DIRECTIONS

- Draw a [1,-1,0] direction within a cubic unit cell

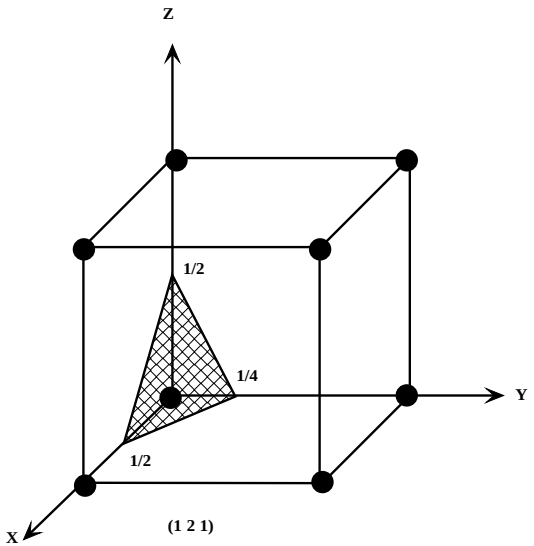


- Determine the indices for this direction
  - Answer: [120]

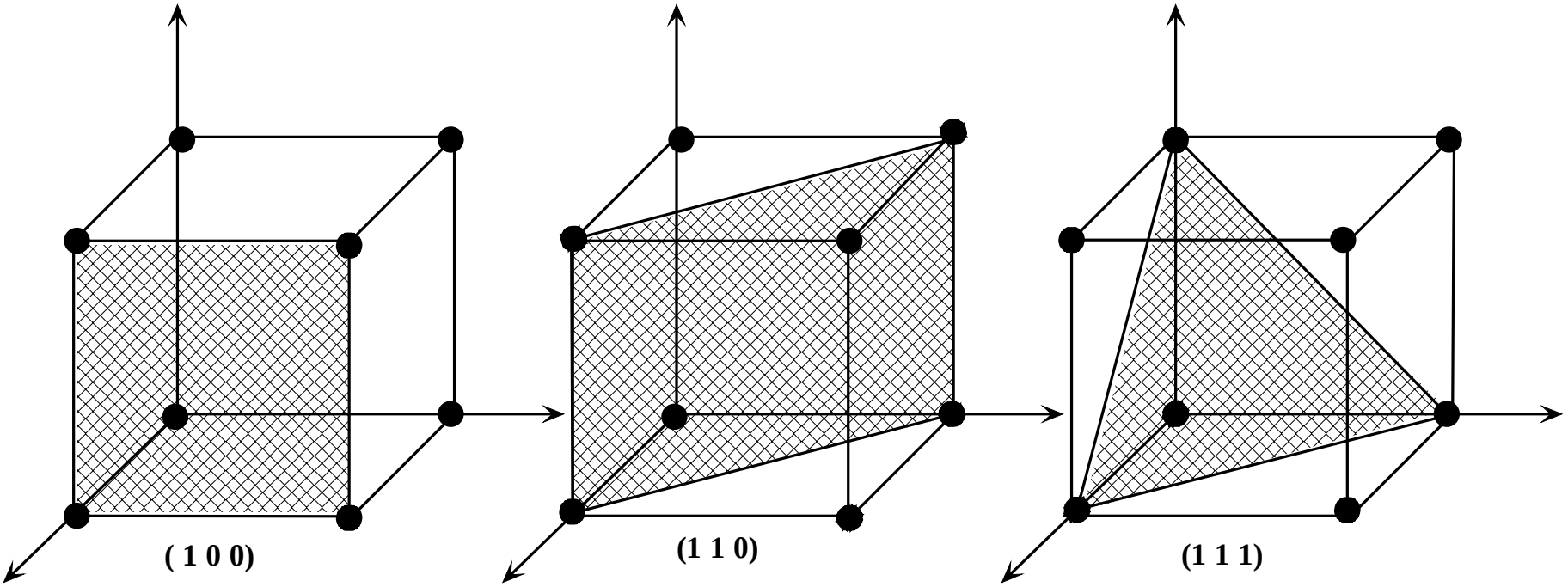


CRYSTALLOGRAPHIC PLANES

- Crystallographic planes specified by 3 **Miller indices** as (hkl)
- Procedure for determining h,k and l:
  - If plane passes through origin, translate plane or choose new origin
  - Determine intercepts of planes on each of the axes in terms of unit cell edge lengths (lattice parameters). Note: if plane has no intercept to an axis (i.e., it is parallel to that axis), intercept is infinity (½ ¼ ½)
  - Determine reciprocal of the three intercepts (2 4 2)
  - If necessary, multiply these three numbers by a common factor which converts all the reciprocals to small integers (1 2 1)
  - The three indices are not separated by commas and are enclosed in curved brackets: (hkl) (121)
  - If any of the indices is negative, a bar is placed in top of that index



THREE IMPORTANT CRYSTAL PLANES



THREE IMPORTANT CRYSTAL PLANES

- Parallel planes are equivalent

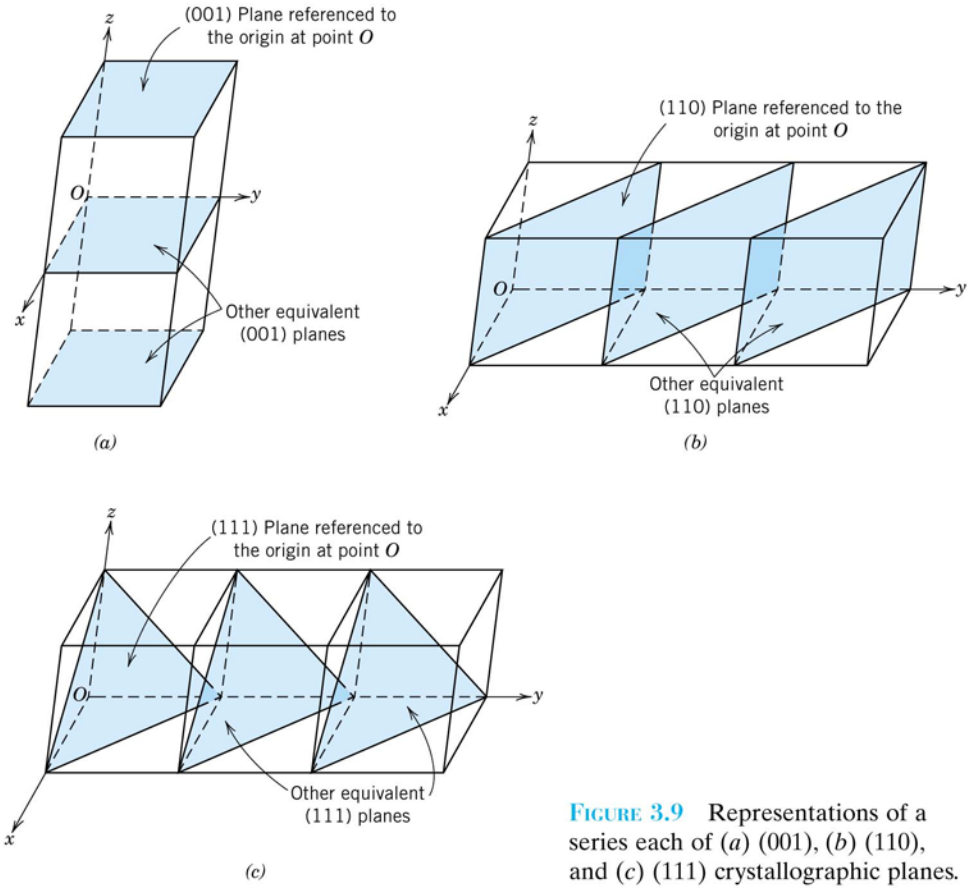
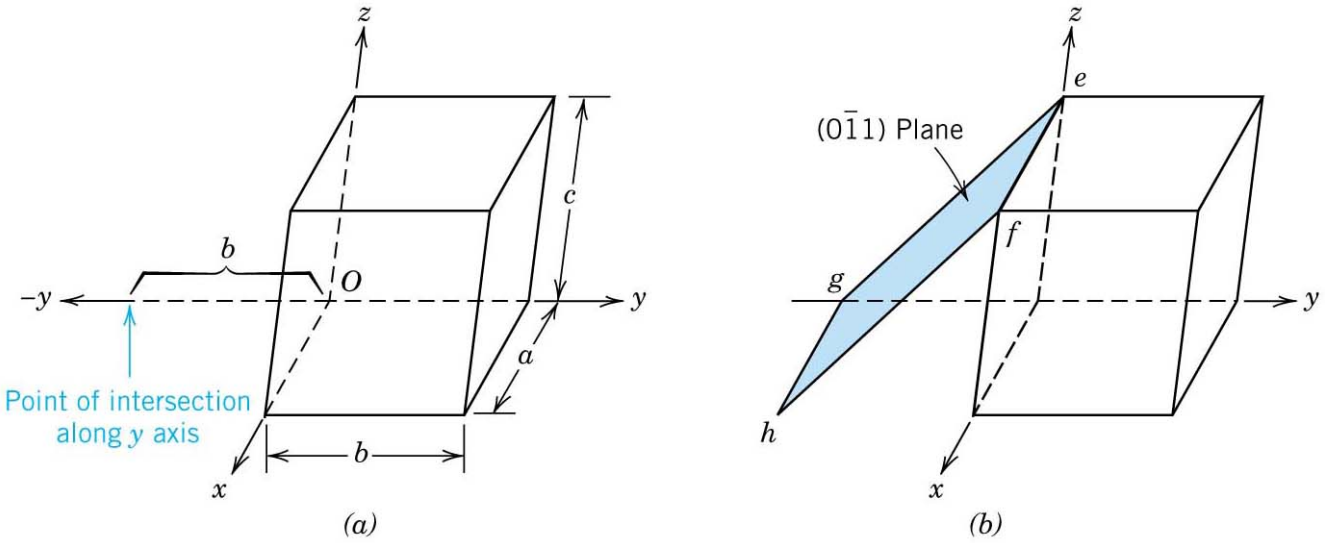


FIGURE 3.9 Representations of a series each of (*a*) (001), (*b*) (110), and (*c*) (111) crystallographic planes.

EXAMPLE: CRYSTAL PLANES

- Construct a (0,-1,1) plane



FCC & BCC CRYSTAL PLANES

- Consider (110) plane

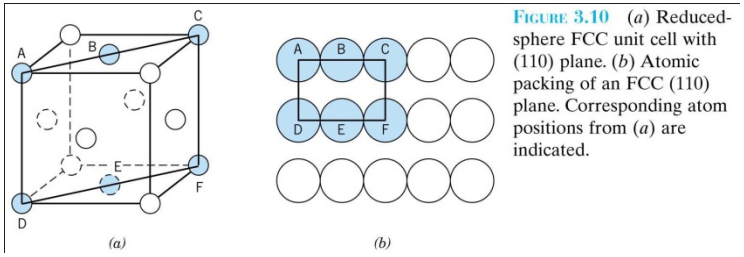


FIGURE 3.10 (*a*) Reduced-sphere FCC unit cell with (110) plane. (*b*) Atomic packing of an FCC (110) plane. Corresponding atom positions from (*a*) are indicated.

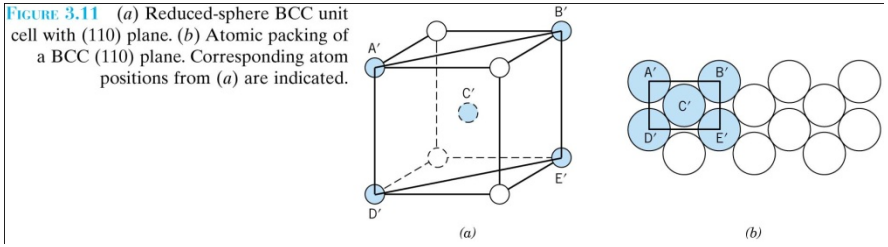


FIGURE 3.11 (*a*) Reduced-sphere BCC unit cell with (110) plane. (*b*) Atomic packing of a BCC (110) plane. Corresponding atom positions from (*a*) are indicated.

- Atomic packing different in the two cases
- Family of planes: all planes that are crystallographically equivalent—that is having the same atomic packing, indicated as {hkl}
  - For example, {100} includes (100), (010), (001) planes
  - {110} includes (110), (101), (011), etc.

LINEAR & PLANAR DENSITIES

- Linear density (LD) = number of atoms centered on a direction vector / length of direction vector
  - LD (110) = 2 atoms/(4R) = 1/(2R)
- Planar density (PD) = number of atoms centered on a plane / area of plane
  - PD (110) = 2 atoms / [(4R)(2R√2)] = 2 atoms / ($8R^2\sqrt{2}$) = $1/(4R^2\sqrt{2})$
- LD and PD are important considerations during deformation and “slip”; planes tend to slip or slide along planes with high PD along directions with high LD

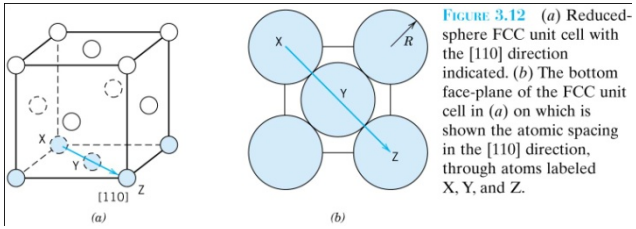


FIGURE 3.12 (*a*) Reduced-sphere FCC unit cell with the [110] direction indicated. (*b*) The bottom face-plane of the FCC unit cell in (*a*) on which is shown the atomic spacing in the [110] direction, through atoms labeled X, Y, and Z.

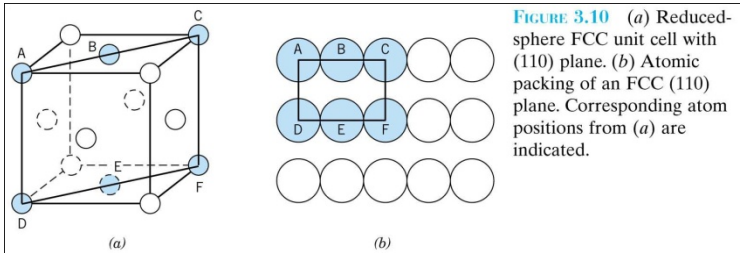


FIGURE 3.10 (*a*) Reduced-sphere FCC unit cell with (110) plane. (*b*) Atomic packing of an FCC (110) plane. Corresponding atom positions from (*a*) are indicated.

CRYSTALS AS BUILDING BLOCKS

- Single crystal: when the periodic and repeated arrangement of atoms is perfect and extends throughout the entirety of the specimen
- *Some* engineering applications require single crystals:

--diamond single crystals for abrasives

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

--turbine blades

Fig. 8.30(c), *Callister 6e.* (Fig. 8.30(c) courtesy of Pratt and Whitney).

- Crystal properties reveal features of atomic structure.

--Ex: Certain crystal planes in quartz fracture more easily than others.

(Courtesy P.M. Anderson)

POLYCRYSTALLINE MATERIALS

- "Nuclei" form during solidification, each of which grows into crystals

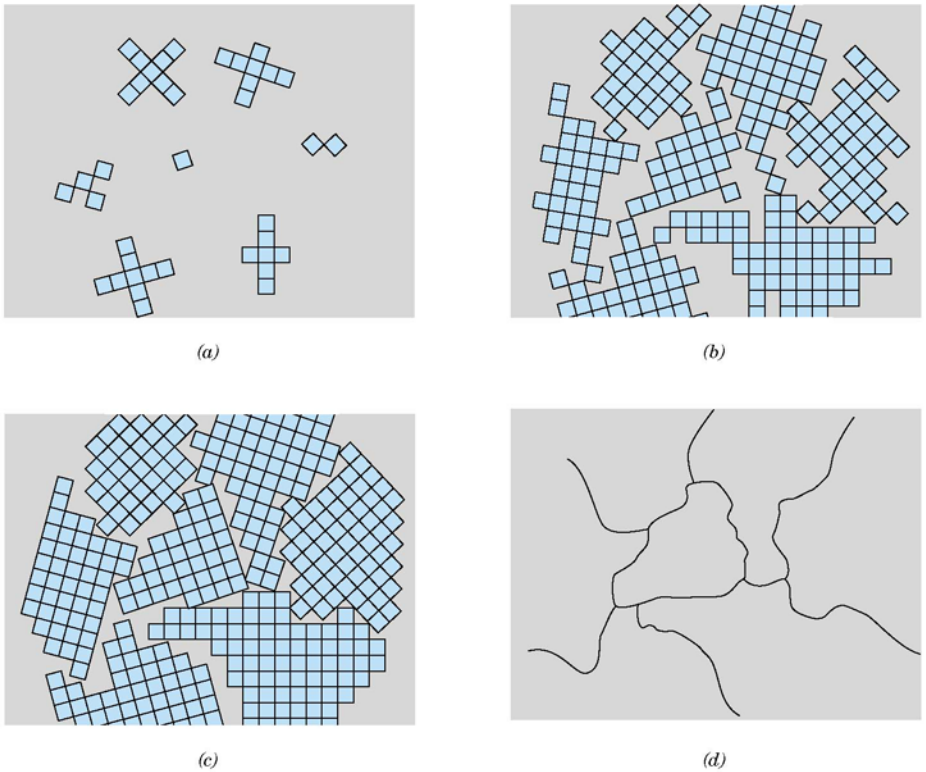


FIGURE 3.17 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy,* 2nd edition, Constable & Company Ltd., London, 1915.)

POLYCRYSTALS

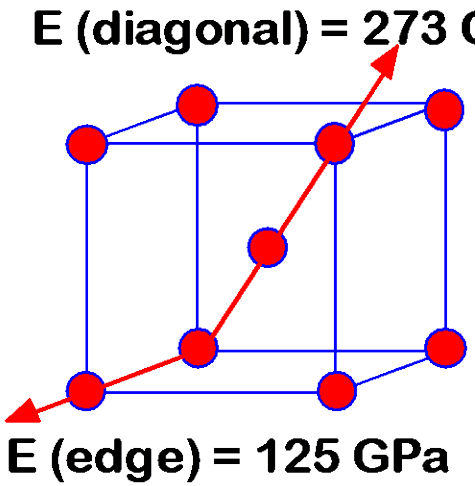
- *Most* engineering materials are polycrystals.

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

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

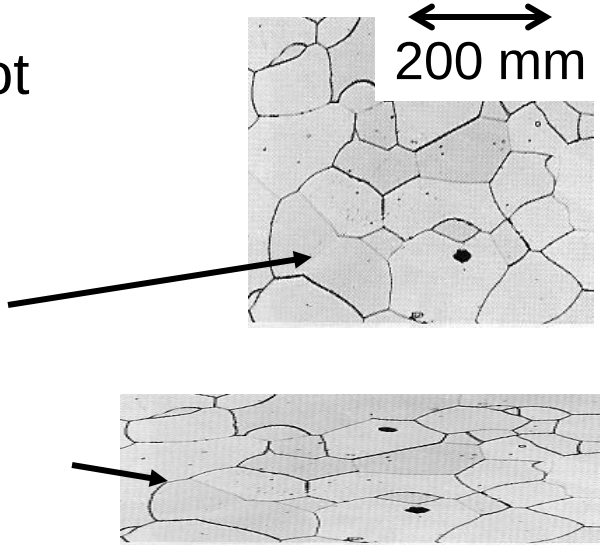
SINGLE VS POLYCRYSTALS

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



Data from Table 3.3, *Callister 6e*. (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.

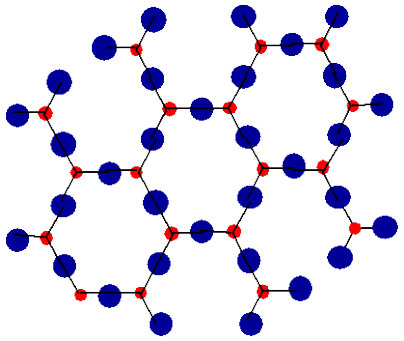


Adapted from Fig. 4.12(b), *Callister 6e*. (Fig. 4.12(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

AMORPHOUS MATERIALS

Crystalline materials...

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



crystalline SiO_2

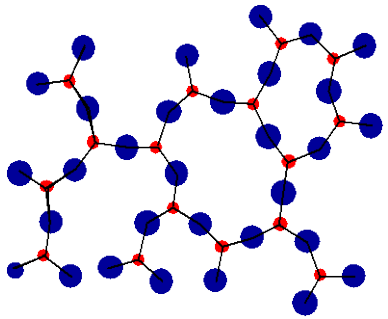
Adapted from Fig. 3.18(a), *Callister 6e.*

• Si • Oxygen

Noncrystalline materials...

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

"Amorphous" = Noncrystalline

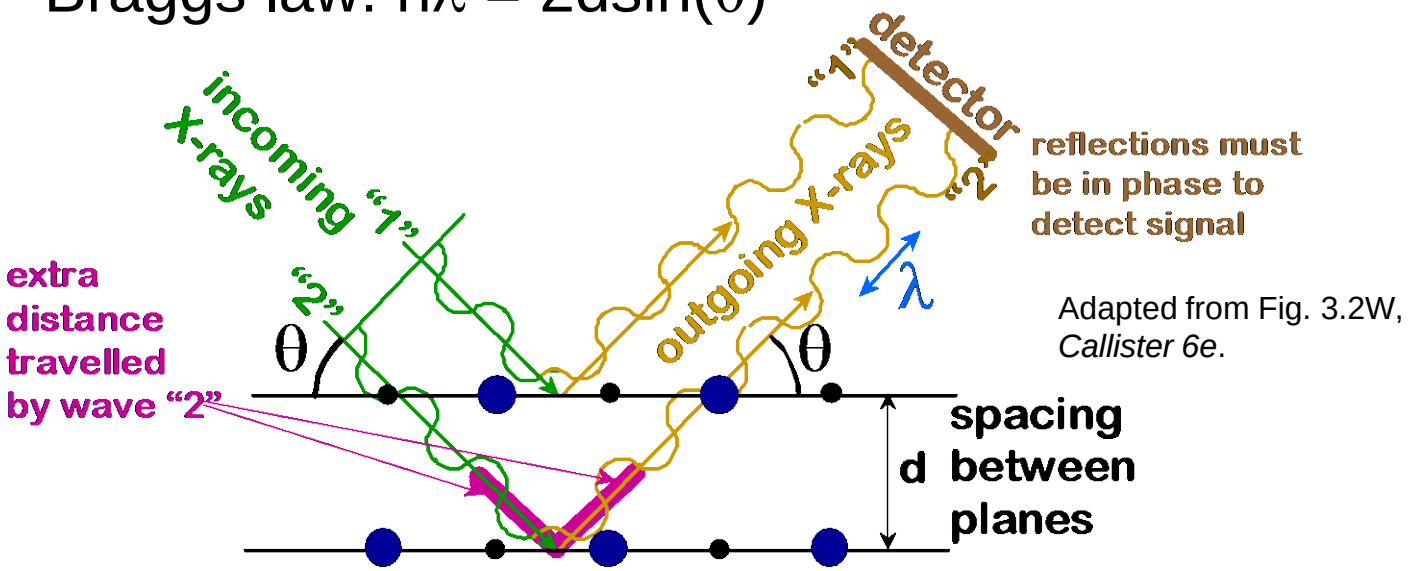


noncrystalline SiO_2

Adapted from Fig. 3.18(b), *Callister 6e.*

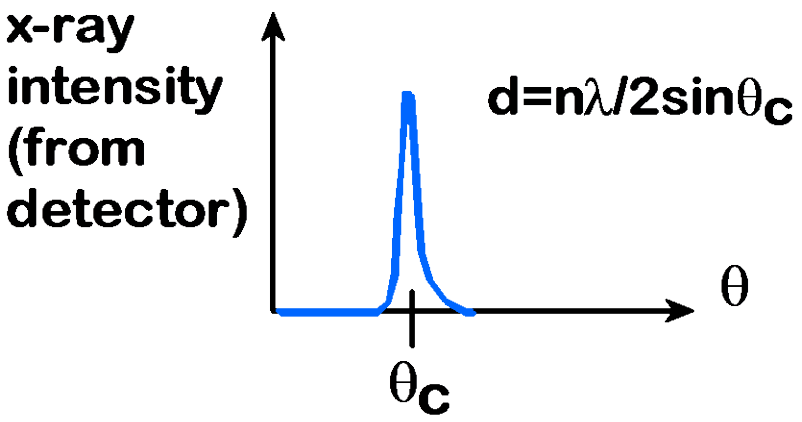
X-RAYS TO CONFIRM CRYSTAL STRUCTURE

- Incoming X-rays diffract from crystal planes, following Braggs law: $n\lambda = 2d\sin(\theta)$



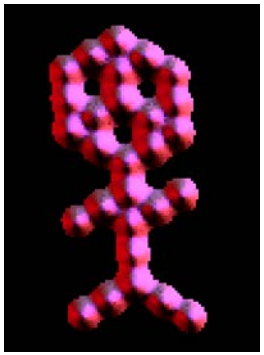
Adapted from Fig. 3.2W, *Callister 6e*.

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

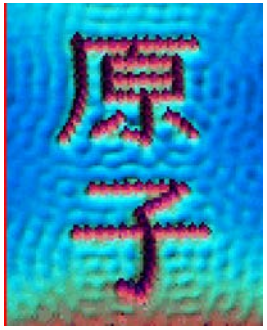


SCANNING TUNNELING MICROSCOPY

- Atoms can be arranged and imaged!



Carbon monoxide molecules arranged on a platinum (111) surface.



Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

Photos produced from the work of C.P. Lutz, Zeppenfeld, and D.M. Eigler. Reprinted with permission from International Business Machines Corporation, copyright 1995.

SUMMARY

- Atoms may assemble into crystalline, polycrystalline or amorphous structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.