Chapter-3

- ***MSE-201-R***

- ***Prof. Dr. Altan Türkeli***

The Structure of Crystalline Solids

FUNDAMENTAL CONCEPTS

- Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another.
- A **crystalline material is one in which** the atoms are situated in a repeating or periodic array over large atomic distances; that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern

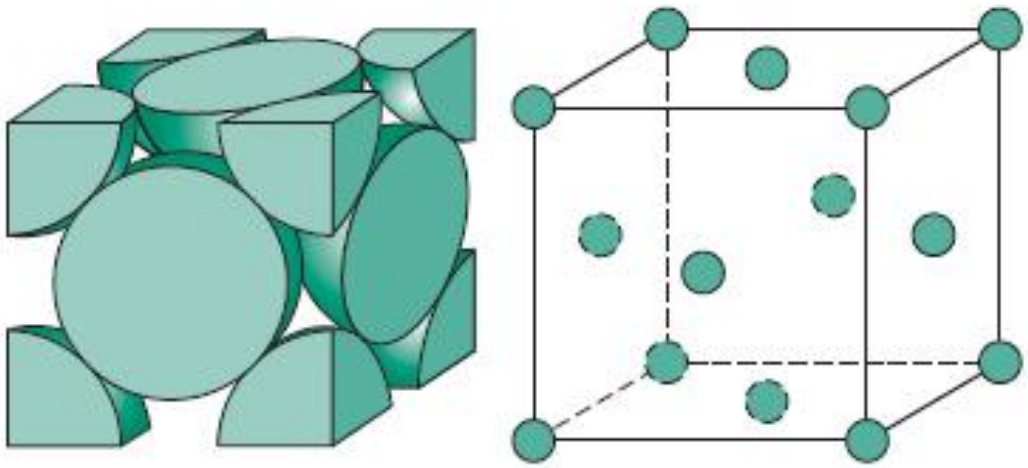
- All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these *noncrystalline* or *amorphous materials are discussed briefly at the end of this chapter*

UNIT CELLS

- The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern.Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells.**

- When describing crystalline structures, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the *atomic hard sphere model in which spheres representing nearest-neighbor atoms touch one another.*

- An example of the hard sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure 3.1*c.*
- *In this particular case* all the atoms are identical. Sometimes the term **lattice is used in the context of crystal** structures; in this sense “lattice” means a three-dimensional array of points coinciding with atom positions (or sphere centers).



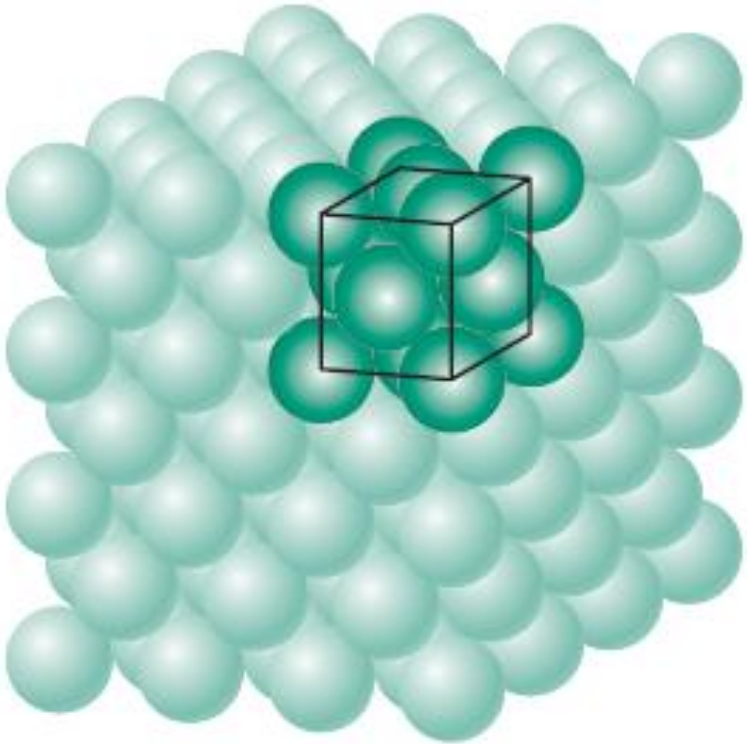


Figure 3.1 For the face-centered cubic crystal structure, (*a*) a hard sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms. [Figure (*c*) adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I,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

METALLIC CRYSTAL STRUCTURES

- **The Face-Centered Cubic Crystal Structure**
- The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces.
- It is aptly called the **face-centered cubic (FCC) crystal structure. Some of the familiar metals having** this crystal structure are copper, aluminum, silver, and gold

- Figure 3.1*a shows a hard sphere model for the FCC unit cell.*
- The spheres or ion cores touch one another across a face diagonal; the cube edge length *a and the atomic radius R are related through*

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

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.

- Two other important characteristics of a crystal structure are the **coordination number and the atomic packing factor (APF).**

- **For metals, each atom has the same** number of nearest-neighbor or touching atoms, which is the coordination number.

- For face-centered cubics, the coordination number is 12.

- The APF is the sum of the sphere volumes of all atoms within a unit cell (assuming the atomic hard sphere model) divided by the unit cell volume—that is

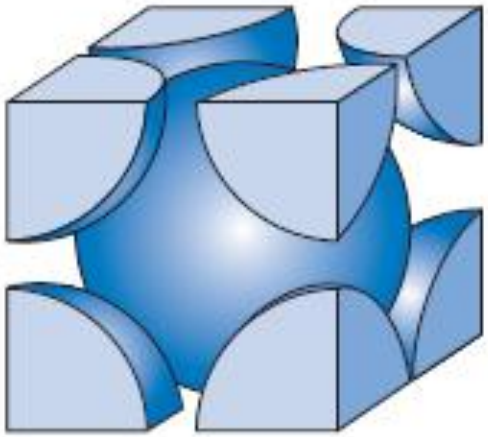
$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

- For the FCC structure, the atomic packing factor is 0.74, which is the maximum
- packing possible for spheres all having the same diameter.

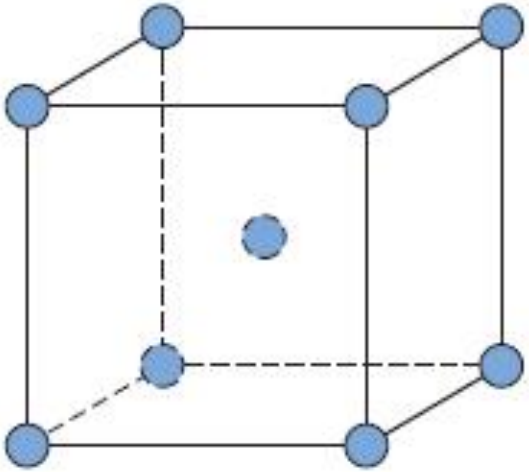
The Body-Centered Cubic Crystal Structure

- Figures 3.2*a and 3.2b are diagrams* of BCC unit cells with the atoms represented by hard sphere and reduced-sphere models, respectively. Center and corner atoms touch one another along cube diagonals, and unit cell length *a and atomic radius R are related through*

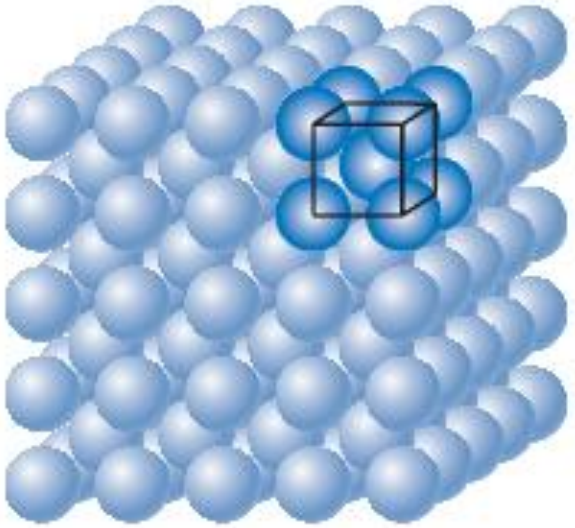
$$a = \frac{4R}{\sqrt{3}}$$



(a)



(b)



(c)

The Simple (primitive) Cubic Crystal Structure

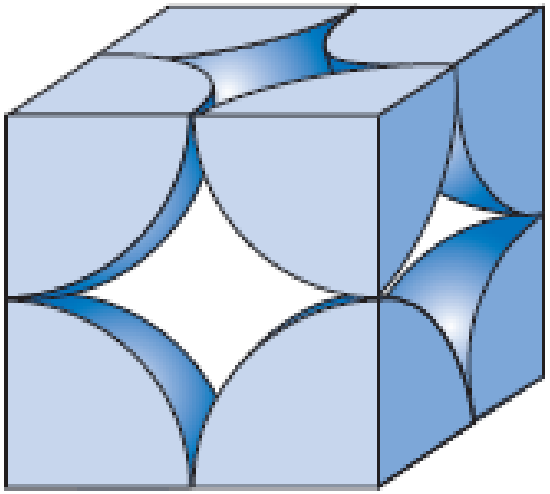


Figure 3.23 Hard-sphere unit cell representation of the simple cubic crystal structure.

The Hexagonal Close-Packed Crystal Structure

- Figure 3.3*a shows* a reduced-sphere unit cell for this structure, which is termed **hexagonal closepacked (HCP).**
- The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes.

- The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 midplane interior atoms

- If *a and c* represent, respectively, the short and long unit cell dimensions of Figure 3.3*a, the c/a ratio should be 1.633; however, for some HCP metals this ratio deviates from*the ideal value.

- The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively

DENSITY COMPUTATIONS

A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density ρ through the relationship

$$\rho = \frac{nA}{V_C N_A} \tag{3.5}$$

where

n = number of atoms associated with each unit cell

A = atomic weight

V_C = volume of the unit cell

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

POLYMORPHISM AND ALLOTROPY

- Some metals, as well as nonmetals, may have more than one crystal structure, a phenomenon known as **polymorphism. When found in elemental solids, the condition** is often termed **allotropy.**
- Pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912 C Most often a modification of the density and other physical properties accompanies a polymorphic transformation.

CRYSTAL SYSTEMS

- The unit cell geometry is completely defined in terms of six parameters: the three edge lengths *a, b, and c, and the three interaxial angles , , and .*
- *These* are indicated in Figure 3.4, and are sometimes termed the **lattice parameters of a** crystal structure.

On this basis there are seven different possible combinations of a, b, and c, and α, β, and γ, each of which represents a distinct **crystal system.** These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral,[2] monoclinic, and triclinic. The lattice parameter relationships and unit cell sketches for each are represented in Table 3.2. The cubic system, for which $a = b = c$ and $\alpha = \beta = \gamma = 90°$, has the greatest degree of symmetry. Least symmetry is displayed by the triclinic system, since $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$.

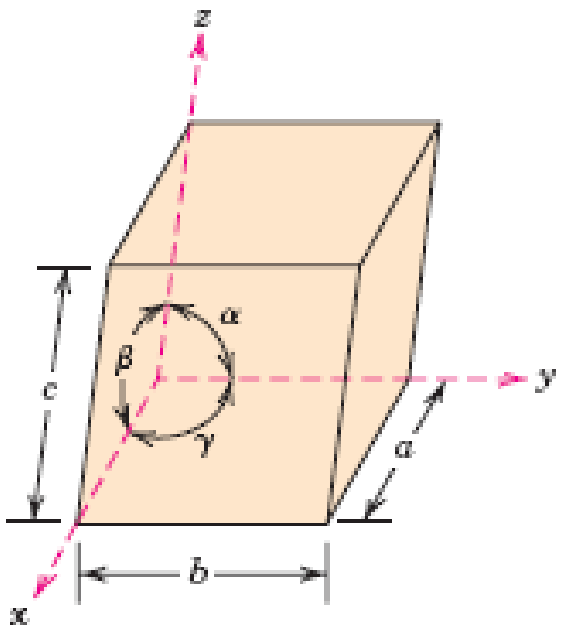
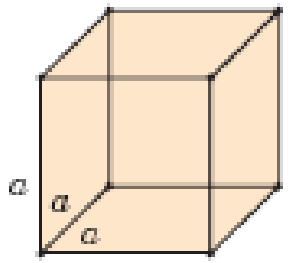
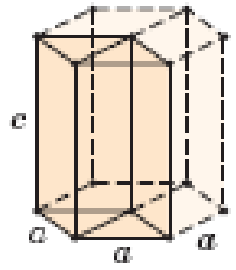
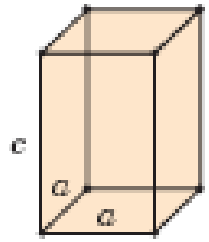
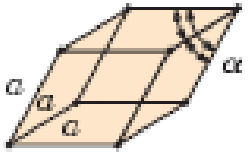
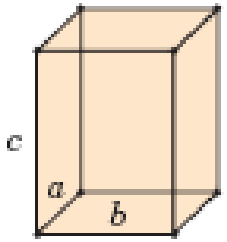
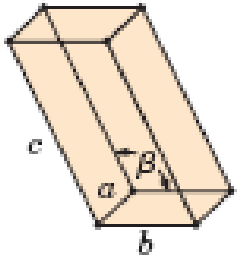
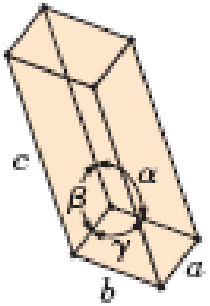


Figure 3.4 A unit cell with x, y, and z coordinate axes, showing axial lengths (a, b, and c) and interaxial angles (α, β, and γ).

Table 3.2 **Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems**

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 (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Crystallographic Points, Directions, and Planes

POINT COORDINATES

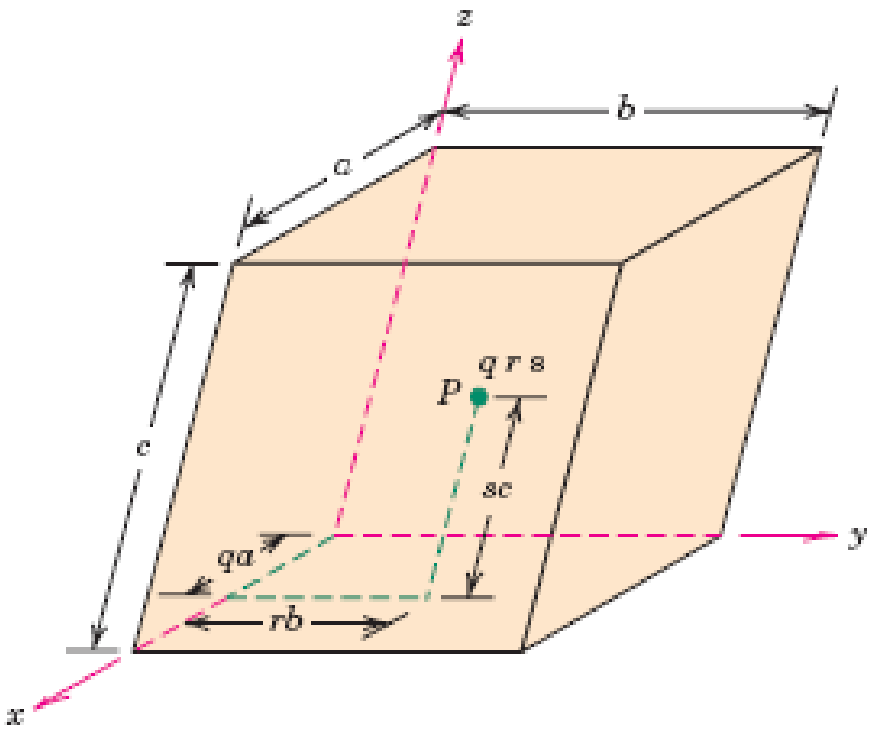
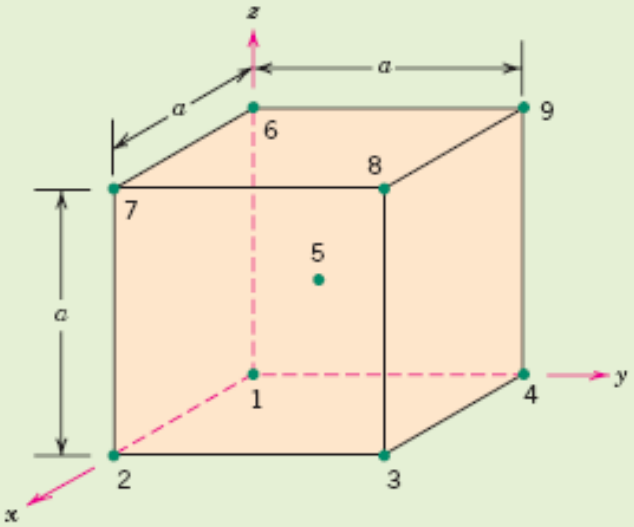


Figure 3.5 The manner in which the q, r, and s coordinates at point P within the unit cell are determined. The q coordinate (which is a fraction) corresponds to the distance qa along the x axis, where a is the unit cell edge length. The respective r and s coordinates for the y and z axes are determined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

- The position of any point located within a unit cell may be specified in terms of its coordinates as fractional multiples of the unit cell edge lengths (i.e., in terms of *a, b, and c).*

- *To illustrate, consider the unit cell and the point P situated therein as shown* in Figure 3.5

- We specify the position of *P in terms of the generalized coordinates q, r, and s where q is some fractional length of a along the x axis, r is some fractional* length of *b along the y axis, and similarly for s.*
- *Thus, the position of P is designated* using coordinates *q r s with values that are less than or equal to unity.*
- *Furthermore,* we have chosen not to separate these coordinates by commas or any other punctuation marks (which is the normal convention).



Point coordinates for position number 1 are 0 0 0; this position is located at the origin of the coordinate system, and, as such, the fractional unit cell edge lengths along the x, y, and z axes are, respectively, $0a$, $0a$, and $0a$. Furthermore, for position number 2, since it lies one unit cell edge length along the x axis, its fractional edge lengths are a, $0a$, and $0a$, respectively, which yield point coordinates of 1 0 0. The following table presents fractional unit cell lengths along the x, y, and z axes, and their corresponding point coordinates for each of the nine points in the above figure.

Point Number	*Fractional Lengths*			*Point Coordinates*
	x axis	*y axis*	*z axis*	
1	0	0	0	0 0 0
2	1	0	0	1 0 0
3	1	1	0	1 1 0
4	0	1	0	0 1 0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
6	0	0	1	0 0 1
7	1	0	1	1 0 1
8	1	1	1	1 1 1
9	0	1	1	0 1 1

CRYSTALLOGRAPHIC DIRECTIONS

- A crystallographic direction is defined as a line between two points, or a vector. The following steps are utilized in the determination of the three directional indices:
- **1. A vector of convenient length is positioned such that it passes through the** origin of the coordinate system. Any vector may be translated throughout the crystal lattice without alteration, if parallelism is maintained.
- **2. The length of the vector projection on each of the three axes is determined;** *these are measured in terms of the unit cell dimensions a, b, and c.*

- **3. These three numbers are multiplied or divided by a common factor to reduce** them to the smallest integer values.
- **4. The three indices, not separated by commas, are enclosed in square brackets,** thus: [*uvw]. The u, v, and w integers correspond to the reduced projections* along the *x, y, and z axes, respectively.*

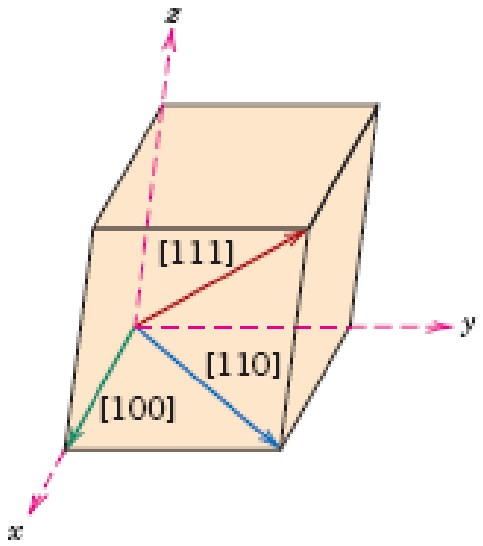


Figure 3.6 The [100], [110], and [111] directions within a unit cell.

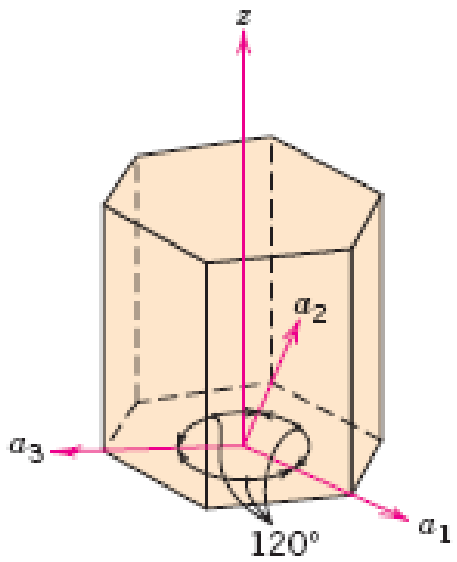


Figure 3.7 Coordinate axis system for a hexagonal unit cell (Miller–Bravais scheme).

Conversion from the three-index system to the four-index system,

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

is accomplished by the following formulas:

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

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

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

$$w = w'$$

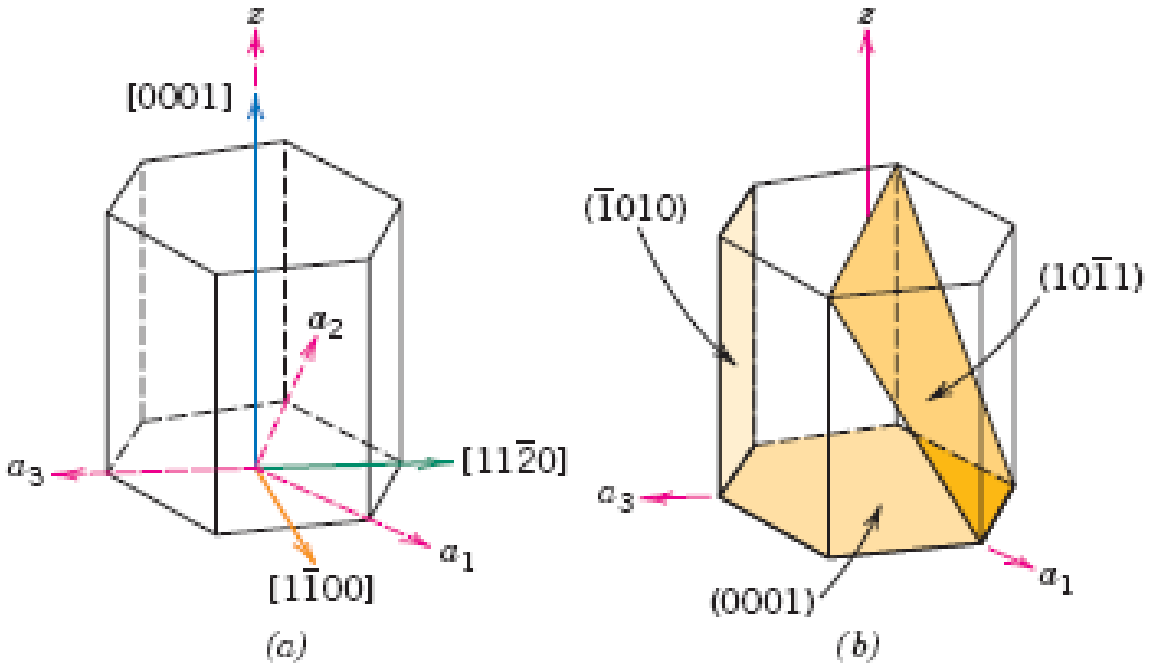


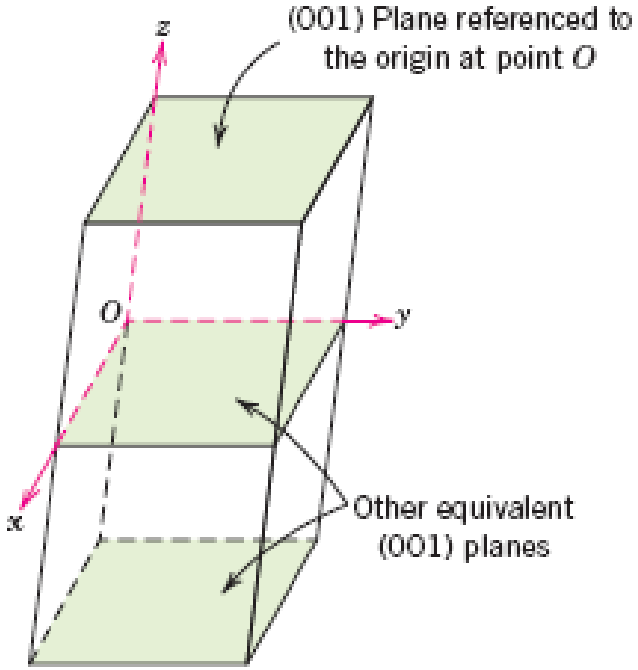
Figure 3.8 For the hexagonal crystal system, (*a*) [0001], [1$\bar{1}$00], and [11$\bar{2}$0] directions, and (*b*) the (0001), (10$\bar{1}$1), and ($\bar{1}$010) planes.

CRYSTALLOGRAPHIC PLANES

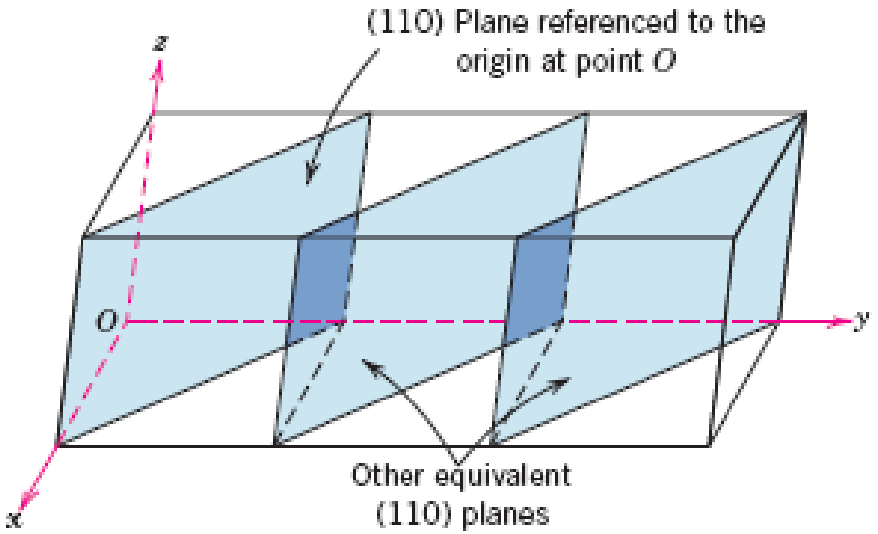
- The procedure employed in determination of the *h, k, and l index numbers is as follows:*

- **1. If the plane passes through the selected origin, either another parallel plane** must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.
- **2. At this point the crystallographic plane either intersects or parallels each of** the three axes; the length of the planar intercept for each axis is determined in terms of the lattice parameters *a, b, and c.*

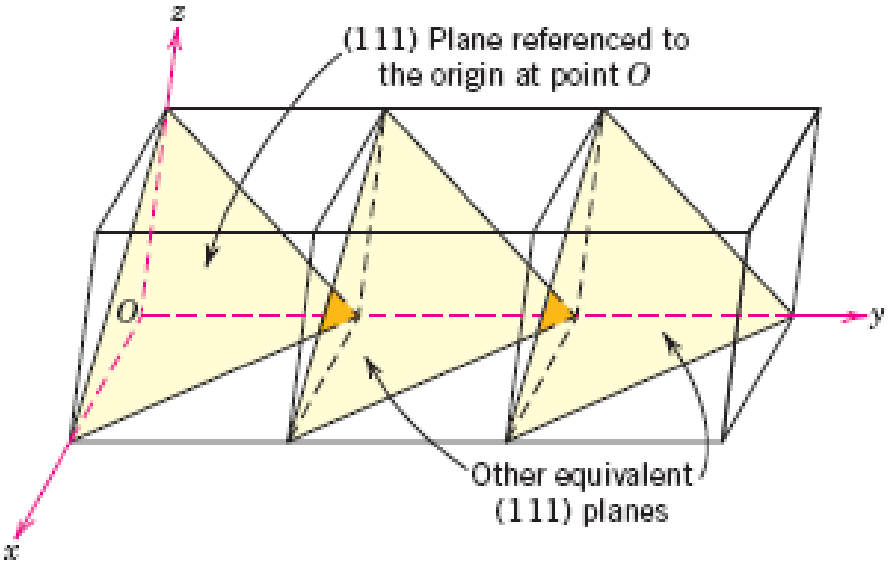
- **3. The reciprocals of these numbers are taken. A plane that parallels an axis** may be considered to have an infinite intercept, and, therefore, a zero index.
- **4. If necessary, these three numbers are changed to the set of smallest integers** by multiplication or division by a common factor.3
- **5. Finally, the integer indices, not separated by commas, are enclosed within** parentheses, thus: (*hkl).*


z
(001) Plane referenced to
the origin at point O
O
y
x
Other equivalent
(001) planes

(a)


z
(110) Plane referenced to the
origin at point O
O
y
x
Other equivalent
(110) planes

(b)


z
(111) Plane referenced to
the origin at point O
O
y
x
Other equivalent
(111) planes

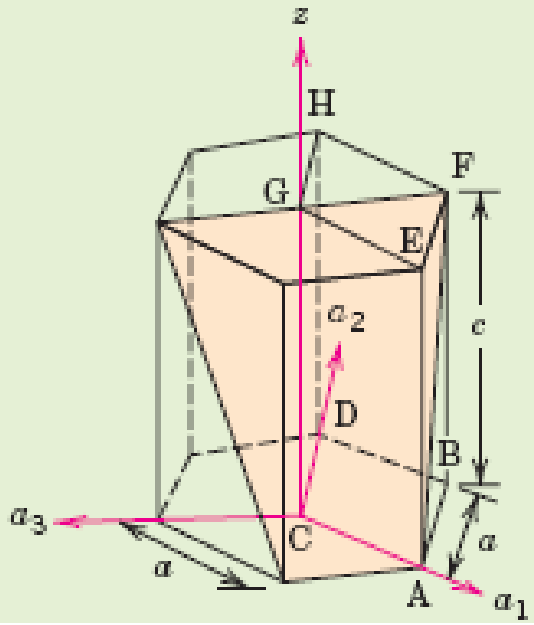
- A “family” of planes contains all those planes that are crystallographically equivalent.

- A family is designated by indices that are enclosed in braces—such as {100}.

Hexagonal Crystals

$$i = -(h + k)$$

Determine the Miller–Bravais indices for the plane shown in the hexagonal unit cell.



LINEAR AND PLANAR DENSITIES

Linear density (LD) is defined as the number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction; that is,

$$\text{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}} \tag{3.8}$$

Of course, the units of linear density are reciprocal length (e.g., nm^{-1}, m^{-1}).

$$\text{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

In an analogous manner, planar density (PD) is taken as the number of atoms per unit area that are centered on a particular crystallographic plane, or

$$\text{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}} \tag{3.10}$$

The units for planar density are reciprocal area (e.g., nm^{-2}, m^{-2}).

$$\text{PD}_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}}$$

CLOSE-PACKED CRYSTAL STRUCTURES

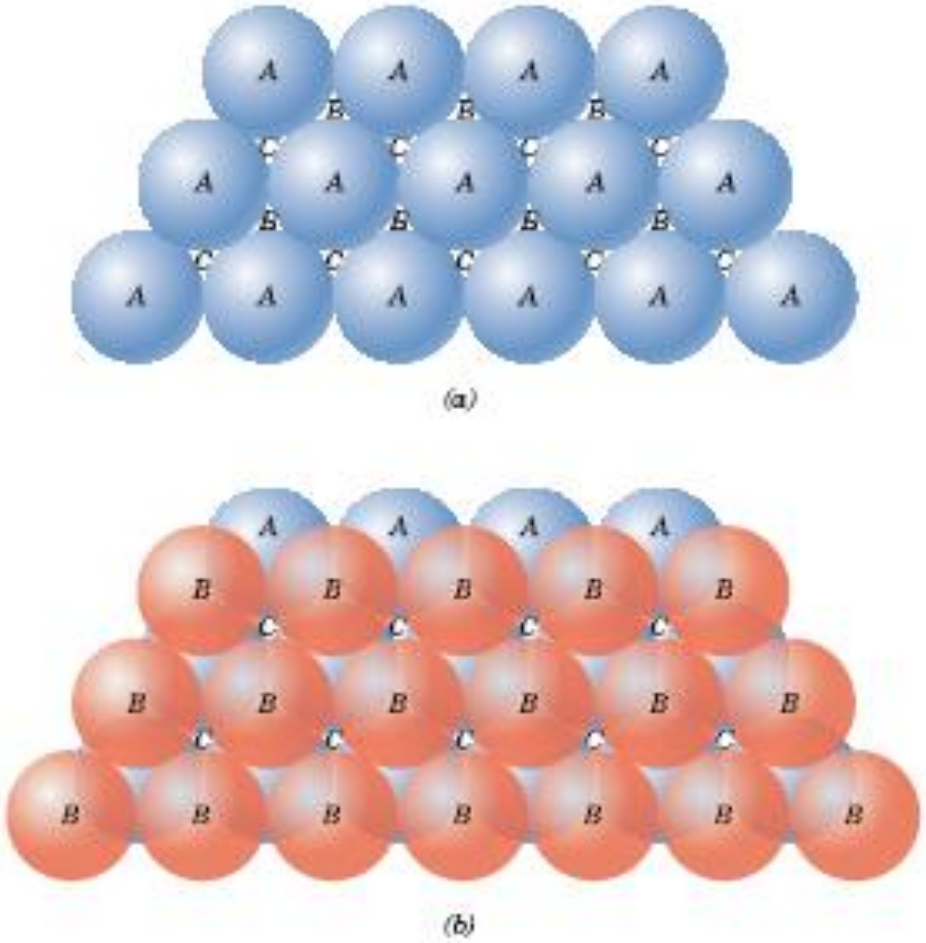


Figure 3.13 (*a*) A portion of a close-packed plane of atoms; *A*, *B*, and *C* positions are indicated. (*b*) The *AB* stacking sequence for close-packed atomic planes. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 50. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

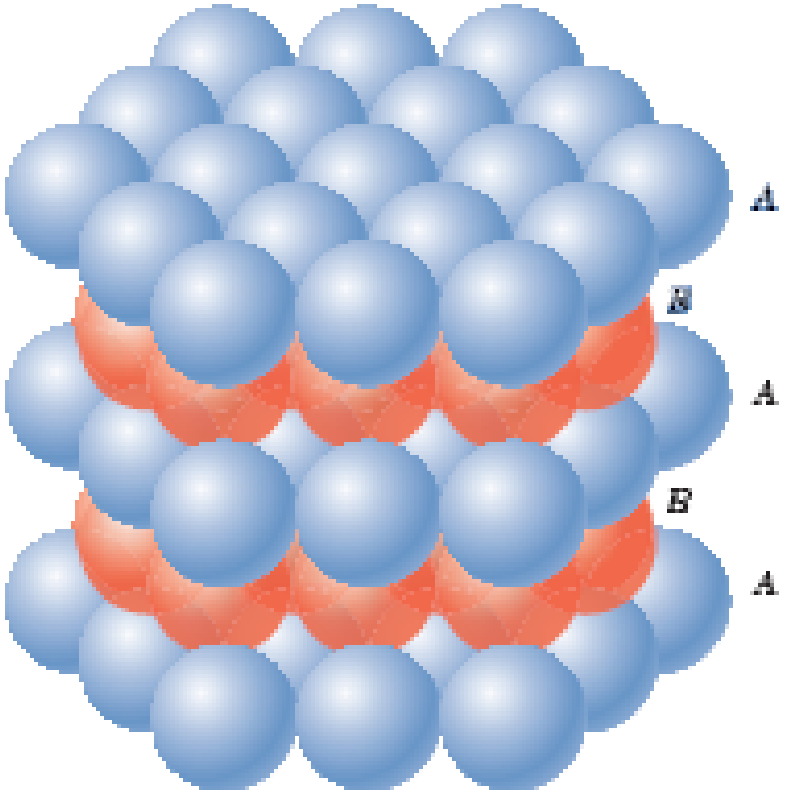


Figure 3.14 Close-packed plane stacking sequence for hexagonal close-packed. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

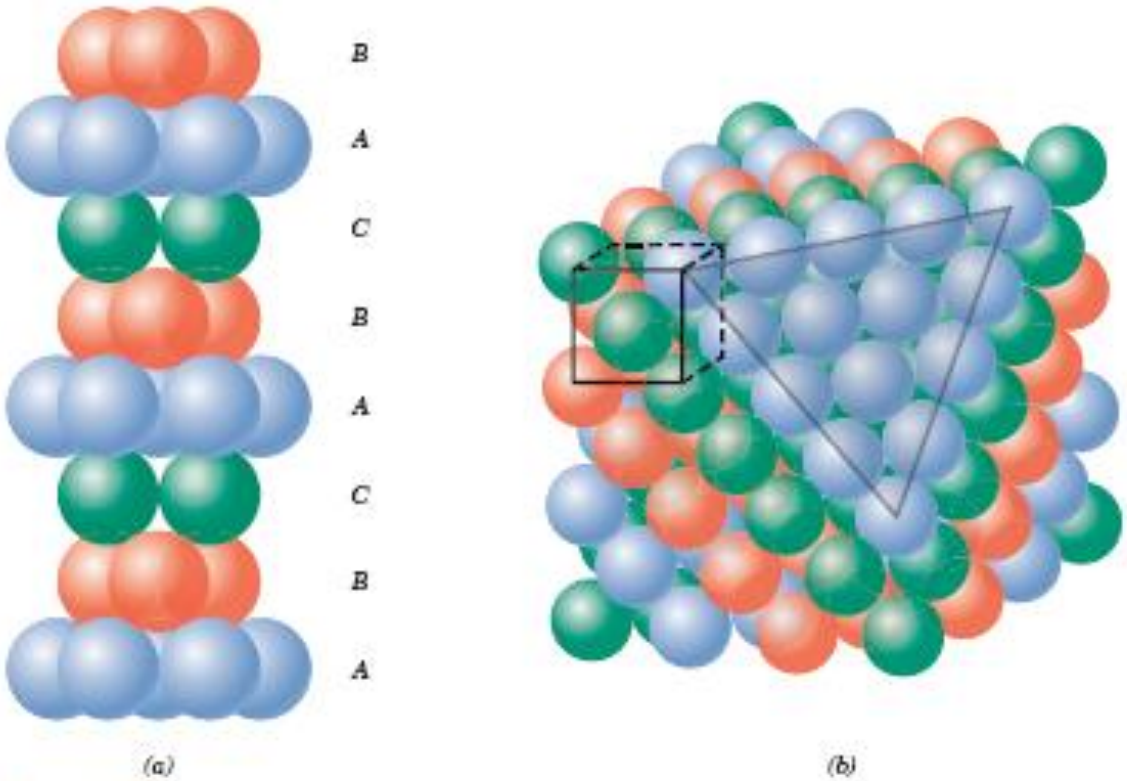


Figure 3.15 (*a*) Close-packed stacking sequence for face-centered cubic. (*b*) A corner has been removed to show the relation between the stacking of close-packed planes of atoms and the FCC crystal structure; the heavy triangle outlines a (111) plane. [Figure (*b*) from W. G. Moffatt, G. W. Pearsall, 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.]

Cryst alline and Noncryst alline Materials

Figure 3.16
Photograph of a garnet single crystal that was found in Tongbei, Fujian Province, China. (Photograph courtesy of Irocks.com, Megan Foreman photo.)

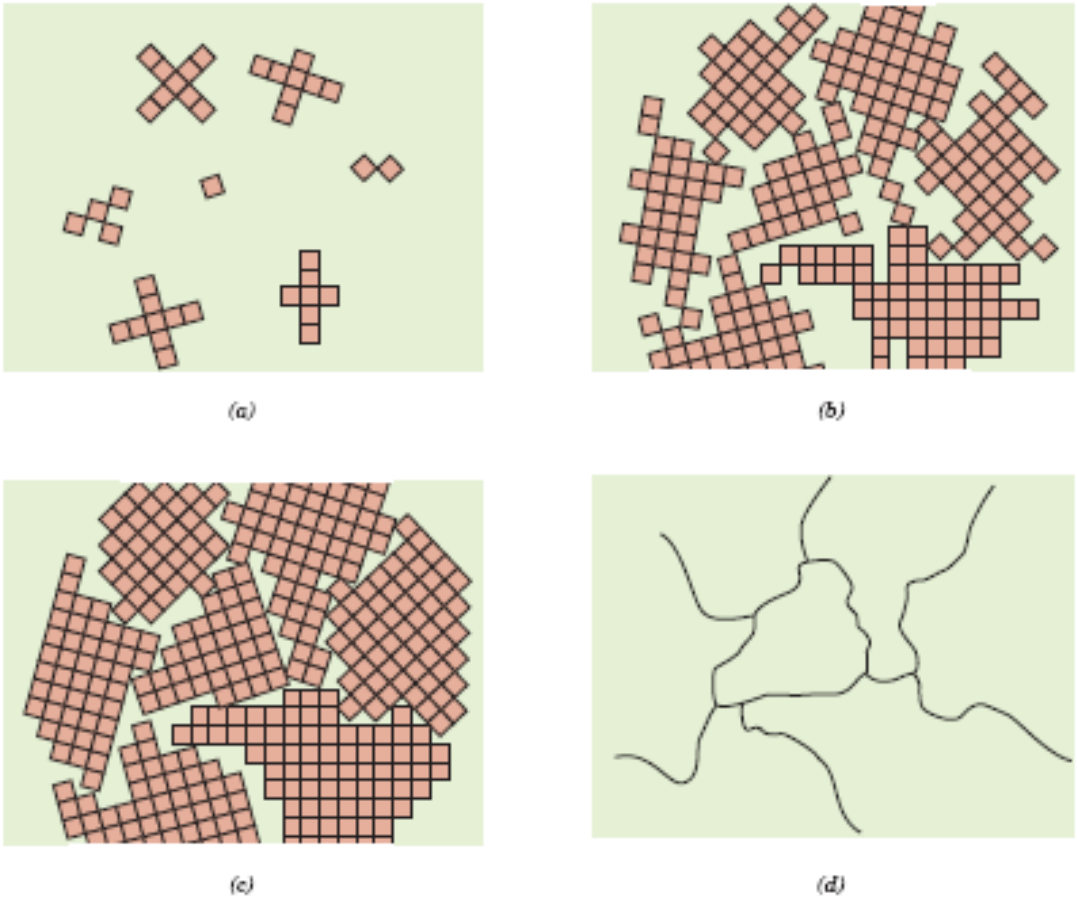


Figure 3.17 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion 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.)

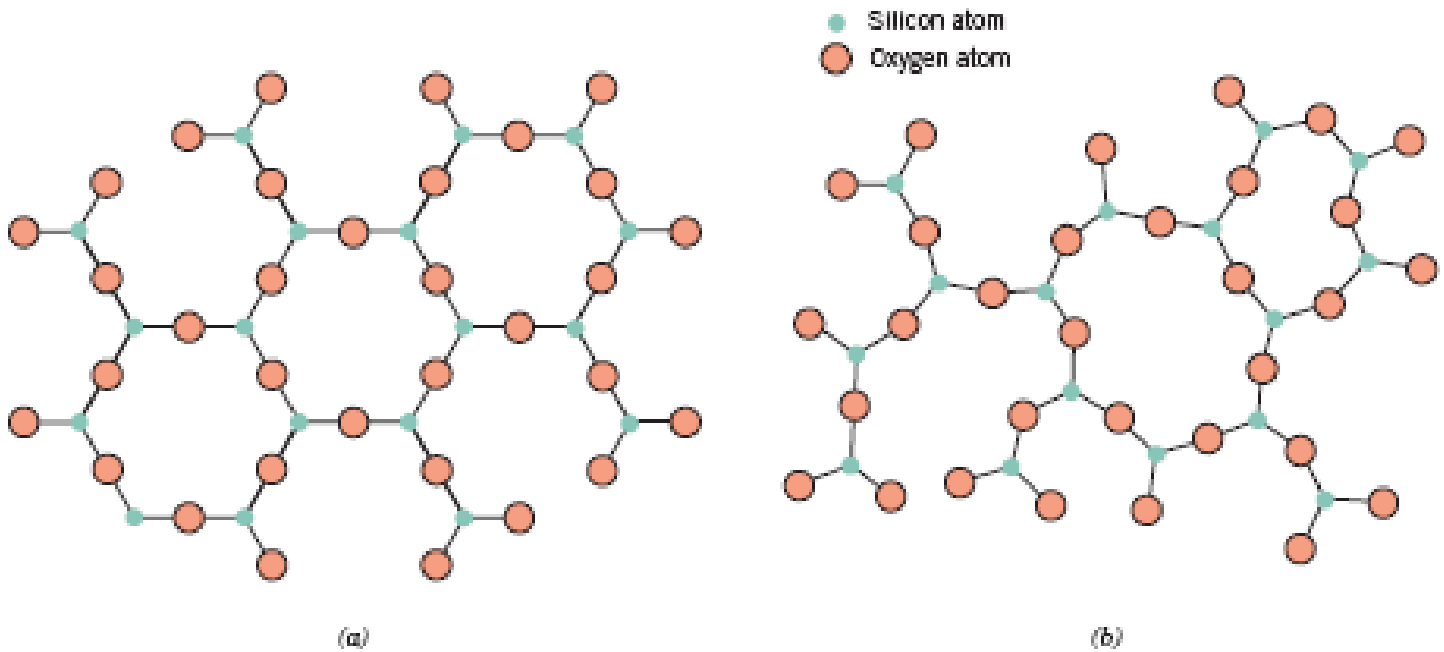


Figure 3.22 Two-dimensional schemes of the structure of (*a*) crystalline silicon dioxide and (*b*) noncrystalline silicon dioxide.

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.