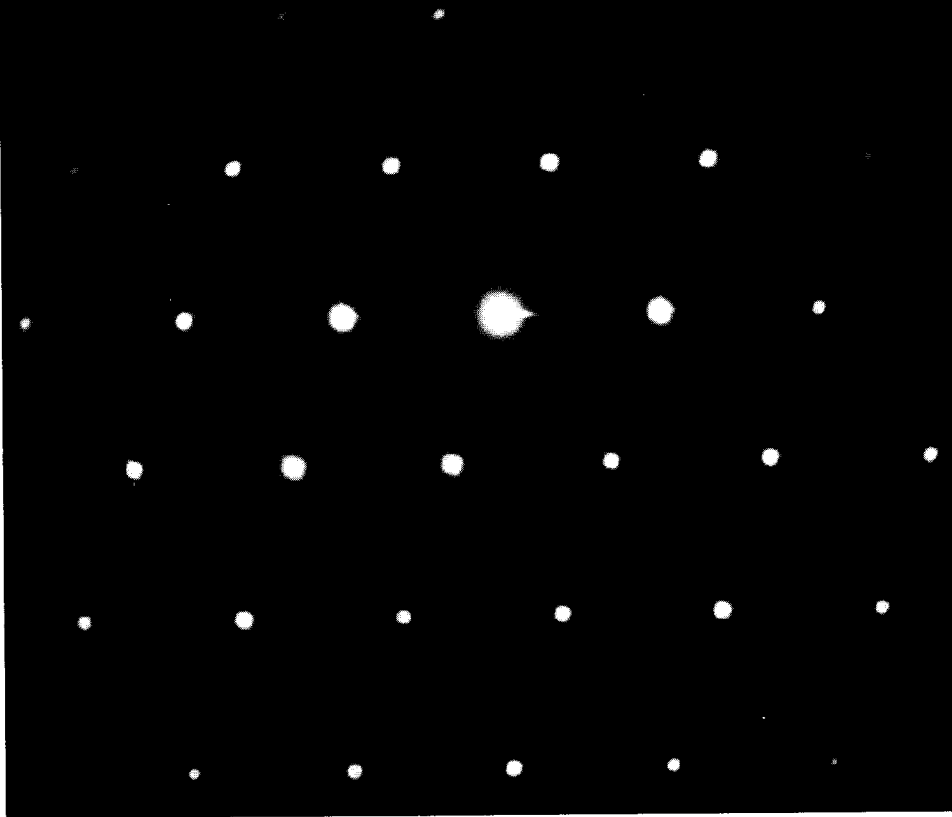


Chapter 3 / The Structure of Crystalline Solids



High velocity electron beams that are produced when electrons are accelerated across large voltages become wavelike in character. Their wavelengths are shorter than interatomic spacings, and thus these beams may be diffracted by atomic planes in crystalline materials, in the same manner as x-rays experience diffraction.

This photograph shows a diffraction pattern produced for a single crystal of gallium arsenide using a transmission electron microscope. The brightest spot near the center is produced by the incident electron beam, which is parallel to a $\langle 110 \rangle$ crystallographic direction. Each of the other white spots results from an electron beam that is diffracted by a specific set of crystallographic planes. (Photograph courtesy of Dr. Raghaw S. Rai, Motorola, Inc., Austin, Texas.)

Why Study the *Structure of Crystalline Solids*?

The properties of some materials are directly related to their crystal structures. For example, pure and undeformed magnesium and beryllium, having one crystal structure, are much more brittle (i.e., fracture at lower degrees of deformation) than are pure and undeformed metals such as gold and silver that have yet another crystal structure (see Section 7.4).

Furthermore, significant property differences exist between crystalline and noncrystalline materials having the same composition. For example, noncrystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semicrystalline) form tend to be opaque or, at best, translucent.

Learning Objectives

After studying this chapter you should be able to do the following:

1. Describe the difference in atomic/molecular structure between crystalline and noncrystalline materials.
 2. Draw unit cells for face-centered cubic, body-centered cubic, and hexagonal close-packed crystal structures.
 3. Derive the relationships between unit cell edge length and atomic radius for face-centered cubic and body-centered cubic crystal structures.
 4. Compute the densities for metals having face-centered cubic and body-centered cubic crystal structures given their unit cell dimensions.
 5. Given three direction index integers, sketch the direction corresponding to these indices within a unit cell.
 6. Specify the Miller indices for a plane that has been drawn within a unit cell.
 7. Describe how face-centered cubic and hexagonal close-packed crystal structures may be generated by the stacking of close-packed planes of atoms.
 8. Distinguish between single crystals and polycrystalline materials.
 9. Define *isotropy* and *anisotropy* with respect to material properties.
-

3.1 INTRODUCTION

Chapter 2 was concerned primarily with the various types of atomic bonding, which are determined by the electron structure of the individual atoms. The present discussion is devoted to the next level of the structure of materials, specifically, to some of the arrangements that may be assumed by atoms in the solid state. Within this framework, concepts of crystallinity and noncrystallinity are introduced. For crystalline solids the notion of crystal structure is presented, specified in terms of a unit cell. The three common crystal structures found in metals are then detailed, along with the scheme by which crystallographic directions and planes are expressed. Single crystals, polycrystalline, and noncrystalline materials are considered.

CRYSTAL STRUCTURES

3.2 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, in which each atom is bonded to its nearest-neighbor atoms. 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.

Some of the properties of crystalline solids depend on the **crystal structure** of the material, the manner in which atoms, ions, or molecules are spatially arranged. There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals, to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials. The present discussion deals with several common metallic crystal structures. Chapters 13 and 15 are devoted to crystal structures for ceramics and polymers, respectively.

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.

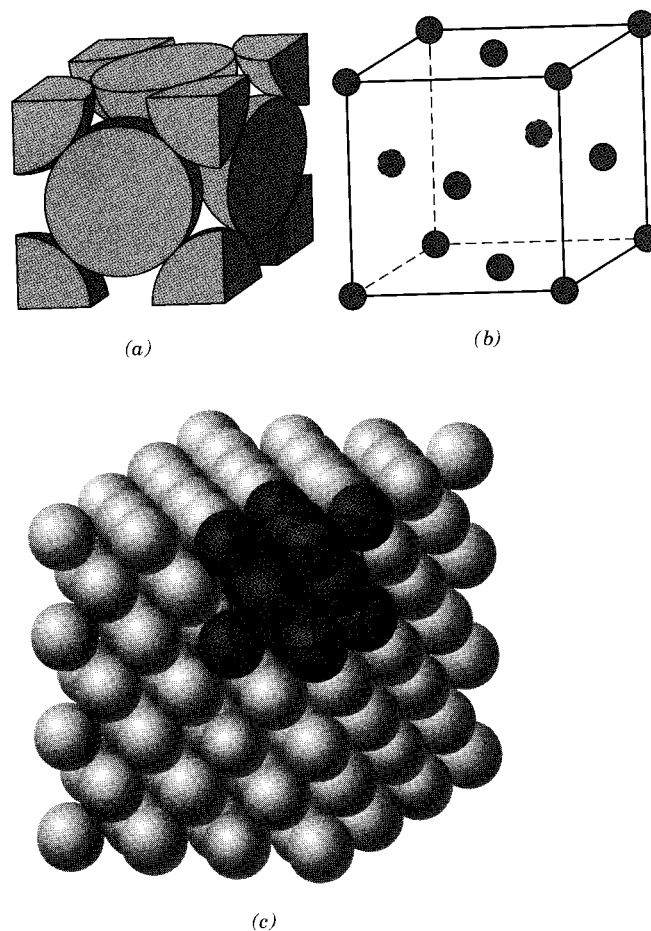


FIGURE 3.1 For the face-centered cubic crystal structure: (a) a hard sphere unit cell, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Figure c adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, Structure, p. 51. Copyright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

An example of the hard sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure 3.1c. 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).

3.3 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**. Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn within the aggregate of spheres (Figure 3.1c), which in this case happens to be a cube. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within. Convenience usually dictates that parallelepiped corners coincide with centers of the hard sphere atoms. Furthermore, more than a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the highest level of geometrical symmetry.

3.4 METALLIC CRYSTAL STRUCTURES

The atomic bonding in this group of materials is metallic, and thus nondirectional in nature. Consequently, there are no restrictions as to the number and position of nearest-neighbor atoms; this leads to relatively large numbers of nearest neighbors and dense atomic packings for most metallic crystal structures. Also, for metals, using the hard sphere model for the crystal structure, each sphere represents an ion core. Table 3.1 presents the atomic radii for a number of metals. Three relatively simple crystal structures are found for most of the common metals: face-centered cubic, body-centered cubic, and hexagonal close-packed.



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 (see also Table 3.1). Figure 3.1a shows a hard sphere model for the FCC unit cell, whereas in Figure 3.1b the atom centers are represented by small circles to provide a better perspective of atom positions. The aggregate of atoms in Figure 3.1c represents a section of crystal consisting of many FCC unit cells. These spheres or ion cores touch one another across a face diagonal; the cube edge length a and the atomic radius R are related through

$$a = 2R\sqrt{2} \quad (3.1)$$

This result is obtained as an example problem.

For the FCC crystal structure, each corner atom is shared among eight unit cells, whereas a face-centered atom belongs to only two. Therefore, one eighth of each of the eight corner atoms and one half of each of the six face atoms, or a total of four whole atoms, may be assigned to a given unit cell. This is depicted in Figure 3.1a, where only sphere portions are represented within the confines of the cube. The cell comprises the volume of the cube, which is generated from the centers of the corner atoms as shown in the figure.

Corner and face positions are really equivalent; that is, translation of the cube corner from an original corner atom to the center of a face atom will not alter the cell structure.

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
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 (\AA), multiply the nanometer value by 10.

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Copper	FCC	0.1278	Tantalum	BCC	0.1430
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^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 (\AA), 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. This may be confirmed by examination of Figure 3.1a; the front face atom has four corner nearest-neighbor atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front, which is not shown.

The APF is the fraction of solid sphere volume in a unit cell, assuming the atomic hard sphere model, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} \quad (3.2)$$

For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter. Computation of this APF is also included as an example problem. Metals typically have relatively large atomic packing factors to maximize the shielding provided by the free electron cloud.



THE BODY-CENTERED CUBIC CRYSTAL STRUCTURE

Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a **body-centered cubic (BCC)** crystal structure. A collection of spheres depicting this crystal structure is shown in Figure 3.2c, whereas Figures 3.2a 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

$$a = \frac{4R}{\sqrt{3}} \quad (3.3)$$

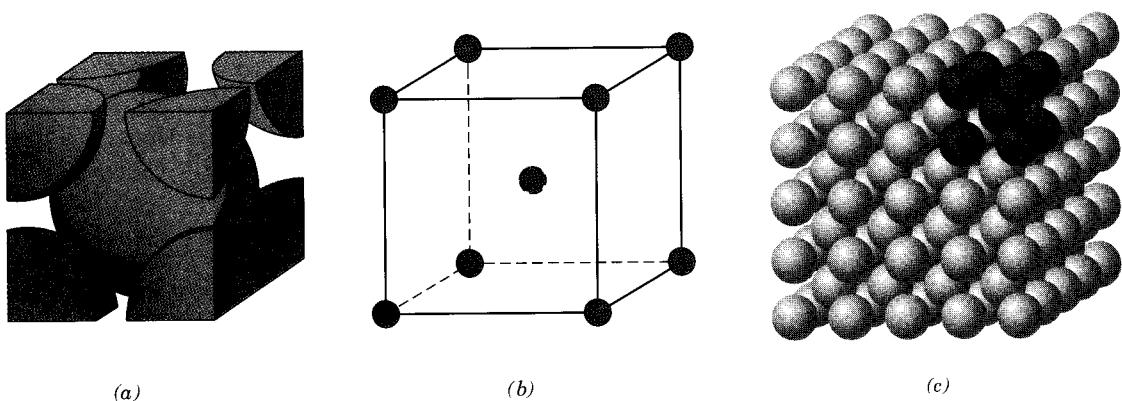


FIGURE 3.2 For the body-centered cubic crystal structure, (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Figure (c) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Chromium, iron, tungsten, as well as several other metals listed in Table 3.1 exhibit a BCC structure.

Two atoms are associated with each BCC unit cell: the equivalent of one atom from the eight corners, each of which is shared among eight unit cells, and the single center atom, which is wholly contained within its cell. In addition, corner and center atom positions are equivalent. The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms. Since the coordination number is less for BCC than FCC, so also is the atomic packing factor for BCC lower—0.68 versus 0.74.



THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal. Figure 3.3a shows a reduced-sphere unit cell for this structure, which is termed **hexagonal close-packed (HCP)**; an assemblage of several HCP unit cells is presented in Figure 3.3b. 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 the 3 midplane interior atoms. If a and c represent, respectively, the short and long unit cell dimensions of Figure 3.3a, 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. The HCP metals include cadmium, magnesium, titanium, and zinc; some of these are listed in Table 3.1.

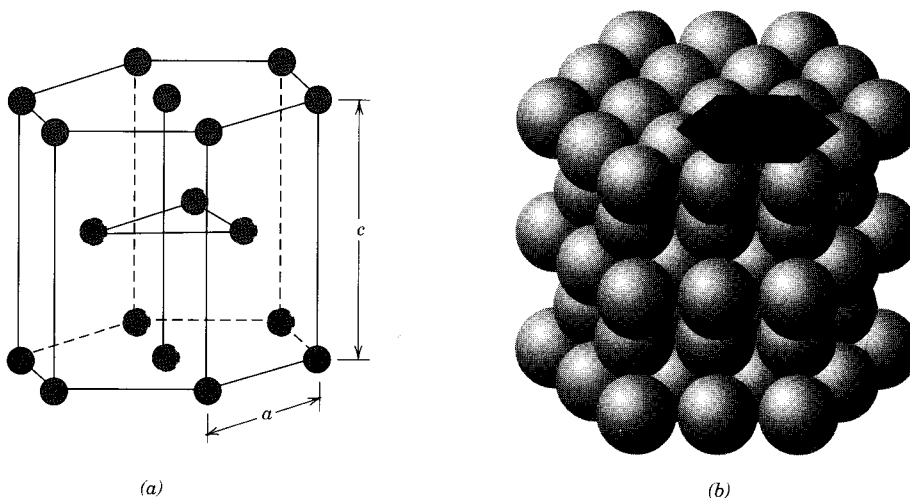


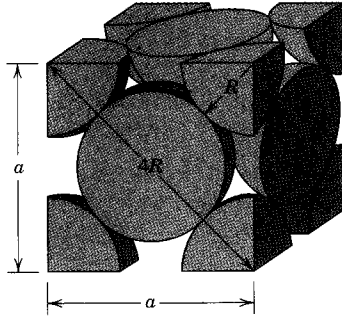
FIGURE 3.3 For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms. (Figure (b) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*,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

EXAMPLE PROBLEM 3.1

Calculate the volume of an FCC unit cell in terms of the atomic radius R .

SOLUTION

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Since the unit cell is a cube, its volume is a^3 , where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2$$

or, solving for a ,

$$a = 2R\sqrt{2} \quad (3.1)$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \quad (3.4)$$

EXAMPLE PROBLEM 3.2

Show that the atomic packing factor for the FCC crystal structure is 0.74.

SOLUTION

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{total sphere volume}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total sphere and unit cell volumes may be calculated in terms of the atomic radius R . The volume for a sphere is $\frac{4}{3}\pi R^3$, and since there are four atoms per FCC unit cell, the total FCC sphere volume is

$$V_S = (4) \frac{4}{3} \pi R^3 = \frac{16}{3} \pi R^3$$

From Example Problem 3.1, the total unit cell volume is

$$V_C = 16R^3\sqrt{2}$$

Therefore, the atomic packing factor is

$$\text{APF} = \frac{V_S}{V_C} = \frac{(\frac{16}{3})\pi R^3}{16R^3\sqrt{2}} = 0.74$$

3.5 DENSITY COMPUTATIONS

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

$$\rho = \frac{nA}{V_C N_A} \quad (3.5)$$

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)

EXAMPLE PROBLEM 3.3

Copper has an atomic radius of 0.128 nm (1.28 Å), an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its density and compare the answer with its measured density.

SOLUTION

Equation 3.5 is employed in the solution of this problem. Since the crystal structure is FCC, n , the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R , the atomic radius, is 0.128 nm.

Substitution for the various parameters into Equation 3.5 yields

$$\begin{aligned} \rho &= \frac{nA_{\text{Cu}}}{V_C N_A} = \frac{nA_{\text{Cu}}}{(16R^3\sqrt{2})N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.023 \times 10^{23} \text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3 \end{aligned}$$

The literature value for the density of copper is 8.94 g/cm³, which is in very close agreement with the foregoing result.

3.6 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 condi-

tion is often termed **allotropy**. The prevailing crystal structure depends on both the temperature and the external pressure. One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures. Also, pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912°C (1674°F). Most often a modification of the density and other physical properties accompanies a polymorphic transformation.

3.7 CRYSTAL SYSTEMS



Since there are many different possible crystal structures, it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic arrangements. One such scheme is based on the unit cell geometry, that is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell. Within this framework, an x, y, z coordinate system is established with its origin at one of the unit cell corners; each of the $x, y,$ and z axes coincides with one of the three parallelepiped edges that extend from this corner, as illustrated in Figure 3.4. 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 $\alpha, \beta,$ and $\gamma.$ These are indicated in Figure 3.4, and are sometimes termed the **lattice parameters** of a crystal structure.

On this basis there are found crystals having seven different possible combinations of $a, b,$ and $c,$ and $\alpha, \beta,$ and $\gamma,$ each of which represents a distinct **crystal system**. These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral, 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 $\alpha = \beta = \gamma = 90^\circ,$ has the greatest degree of symmetry. Least symmetry is displayed by the triclinic system, since $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma.$

From the discussion of metallic crystal structures, it should be apparent that both FCC and BCC structures belong to the cubic crystal system, whereas HCP falls within hexagonal. The conventional hexagonal unit cell really consists of three parallelepipeds situated as shown in Table 3.2.

It is important to note that many of the principles and concepts addressed in previous discussions in this chapter also apply to crystalline ceramic and polymeric systems (Chapters 13 and 15). For example, crystal structures are

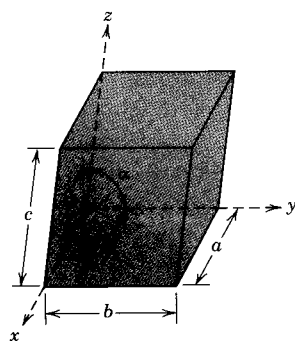


FIGURE 3.4 A unit cell with $x, y,$ and z coordinate axes, showing axial lengths ($a, b,$ and c) and interaxial angles ($\alpha, \beta,$ and γ).