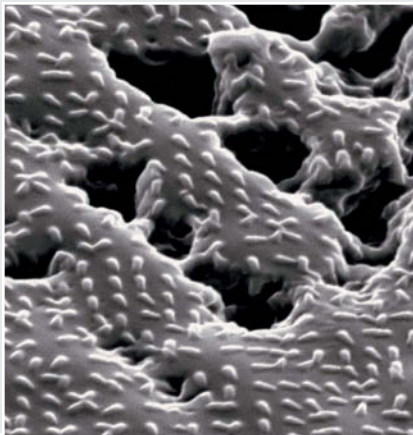


## Chapter 2 Atomic Structure and Interatomic Bonding

Courtesy Jeffrey Karp, Robert Langer and Alex Galakatos



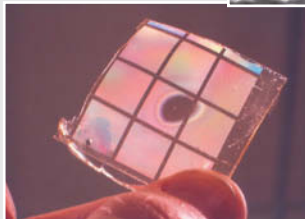
The photograph at the bottom of this page is of a gecko.

Geckos, harmless tropical lizards, are extremely fascinating and extraordinary animals. They have very sticky feet (one of which is shown in the third photograph) that cling to virtually any surface. This characteristic makes it possible for them to run rapidly up vertical walls and along the undersides of horizontal surfaces. In fact, a gecko can support its body mass with a single toe! The secret to this remarkable ability is the presence of an extremely large number of microscopically small hairs on each of their toe pads. When these hairs come in contact

with a surface, weak forces of attraction (i.e., van der Waals forces) are established between hair molecules and molecules on the surface. The fact that these hairs are so small and so numerous explains why the gecko grips surfaces so tightly. To release its grip, the gecko simply curls up its toes and peels the hairs away from the surface.

Using their knowledge of this mechanism of adhesion, scientists have developed several ultrastrong synthetic adhesives, one of which is an adhesive tape (shown in the second photograph) that is an especially promising tool for use in surgical procedures as a replacement for sutures and staples to close wounds and incisions. This material retains its adhesive nature in wet environments, is biodegradable, and does not release toxic substances as it dissolves during the healing process. Microscopic features of this adhesive tape are shown in the top photograph.

Courtesy Jeffrey Karp, Robert Langer and Alex Galakatos



Paul D. Stewart/Science Source



Barbara Peacock/Photodisc/Getty Images, Inc.



## WHY STUDY *Atomic Structure and Interatomic Bonding*?

An important reason to have an understanding of interatomic bonding in solids is that in some instances, the type of bond allows us to explain a material's properties. For example, consider carbon, which may exist as both graphite and diamond. Whereas graphite is relatively soft and has a "greasy" feel to it, diamond is the hardest known material. In addition, the electrical

properties of diamond and graphite are dissimilar: diamond is a poor conductor of electricity, but graphite is a reasonably good conductor. These disparities in properties are directly attributable to a type of interatomic bonding found in graphite that does not exist in diamond (see Section 3.9).

### Learning Objectives

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

1. Name the two atomic models cited, and note the differences between them.
2. Describe the important quantum-mechanical principle that relates to electron energies.
3. (a) Schematically plot attractive, repulsive, and net energies versus interatomic separation for two atoms or ions.  
(b) Note on this plot the equilibrium separation and the bonding energy.
4. (a) Briefly describe ionic, covalent, metallic, hydrogen, and van der Waals bonds.  
(b) Note which materials exhibit each of these bonding types.

## 2.1 INTRODUCTION

Some of the important properties of solid materials depend on geometric atomic arrangements and also the interactions that exist among constituent atoms or molecules. This chapter, by way of preparation for subsequent discussions, considers several fundamental and important concepts—namely, atomic structure, electron configurations in atoms and the periodic table, and the various types of primary and secondary interatomic bonds that hold together the atoms that compose a solid. These topics are reviewed briefly, under the assumption that some of the material is familiar to the reader.

## Atomic Structure

### 2.2 FUNDAMENTAL CONCEPTS

Each atom consists of a very small nucleus composed of protons and neutrons and is encircled by moving electrons.<sup>1</sup> Both electrons and protons are electrically charged, the charge magnitude being  $1.602 \times 10^{-19}$  C, which is negative in sign for electrons and positive for protons; neutrons are electrically neutral. Masses for these subatomic particles are extremely small; protons and neutrons have approximately the same mass,  $1.67 \times 10^{-27}$  kg, which is significantly larger than that of an electron,  $9.11 \times 10^{-31}$  kg.

Each chemical element is characterized by the number of protons in the nucleus, or the **atomic number (Z)**.<sup>2</sup> For an electrically neutral or complete atom, the atomic number also equals the number of electrons. This atomic number ranges in integral units from 1 for hydrogen to 92 for uranium, the highest of the naturally occurring elements.

The *atomic mass (A)* of a specific atom may be expressed as the sum of the masses of protons and neutrons within the nucleus. Although the number of protons is the same

<sup>1</sup>Protons, neutrons, and electrons are composed of other subatomic particles such as quarks, neutrinos, and bosons. However, this discussion is concerned only with protons, neutrons, and electrons.

<sup>2</sup>Terms appearing in **boldface** type are defined in the Glossary, which follows Appendix E.

**isotope****atomic weight****atomic mass unit  
(amu)**

for all atoms of a given element, the number of neutrons ( $N$ ) may be variable. Thus atoms of some elements have two or more different atomic masses, which are called **isotopes**. The **atomic weight** of an element corresponds to the weighted average of the atomic masses of the atom's naturally occurring isotopes.<sup>3</sup> The **atomic mass unit (amu)** may be used to compute atomic weight. A scale has been established whereby 1 amu is defined as  $\frac{1}{12}$  of the atomic mass of the most common isotope of carbon, carbon 12 ( $^{12}\text{C}$ ) ( $A = 12.00000$ ). Within this scheme, the masses of protons and neutrons are slightly greater than unity, and

$$A \cong Z + N \quad (2.1)$$

**mole**

The atomic weight of an element or the molecular weight of a compound may be specified on the basis of amu per atom (molecule) or mass per mole of material. In one **mole** of a substance, there are  $6.022 \times 10^{23}$  (Avogadro's number) atoms or molecules. These two atomic weight schemes are related through the following equation:

$$1 \text{ amu/atom (or molecule)} = 1 \text{ g/mol}$$

For example, the atomic weight of iron is 55.85 amu/atom, or 55.85 g/mol. Sometimes use of amu per atom or molecule is convenient; on other occasions, grams (or kilograms) per mole is preferred. The latter is used in this book.

### EXAMPLE PROBLEM 2.1

#### Average Atomic Weight Computation for Cerium

Cerium has four naturally occurring isotopes: 0.185% of  $^{136}\text{Ce}$ , with an atomic weight of 135.907 amu; 0.251% of  $^{138}\text{Ce}$ , with an atomic weight of 137.906 amu; 88.450% of  $^{140}\text{Ce}$ , with an atomic weight of 139.905 amu; and 11.114% of  $^{142}\text{Ce}$ , with an atomic weight of 141.909 amu. Calculate the average atomic weight of Ce.

#### Solution

The average atomic weight of a hypothetical element M,  $\bar{A}_M$ , is computed by adding fraction-of-occurrence—atomic weight products for all its isotopes; that is,

$$\bar{A}_M = \sum_i f_{iM} A_{iM} \quad (2.2)$$

In this expression,  $f_{iM}$  is the fraction-of-occurrence of isotope  $i$  for element M (i.e., the percentage-of-occurrence divided by 100), and  $A_{iM}$  is the atomic weight of the isotope.

For cerium, Equation 2.2 takes the form

$$\bar{A}_{\text{Ce}} = f_{^{136}\text{Ce}} A_{^{136}\text{Ce}} + f_{^{138}\text{Ce}} A_{^{138}\text{Ce}} + f_{^{140}\text{Ce}} A_{^{140}\text{Ce}} + f_{^{142}\text{Ce}} A_{^{142}\text{Ce}}$$

Incorporating values provided in the problem statement for the several parameters leads to

$$\begin{aligned} \bar{A}_{\text{Ce}} &= \left( \frac{0.185\%}{100} \right) (135.907 \text{ amu}) + \left( \frac{0.251\%}{100} \right) (137.906 \text{ amu}) + \left( \frac{88.450\%}{100} \right) (139.905 \text{ amu}) \\ &\quad + \left( \frac{11.114\%}{100} \right) (141.909 \text{ amu}) \\ &= (0.00185)(135.907 \text{ amu}) + (0.00251)(137.906 \text{ amu}) + (0.8845)(139.905 \text{ amu}) \\ &\quad + (0.11114)(141.909 \text{ amu}) \\ &= 140.115 \text{ amu} \end{aligned}$$

<sup>3</sup>The term *atomic mass* is really more accurate than *atomic weight* inasmuch as, in this context, we are dealing with masses and not weights. However, atomic weight is, by convention, the preferred terminology and is used throughout this book. The reader should note that it is *not* necessary to divide molecular weight by the gravitational constant.



**Concept Check 2.1** Why are the atomic weights of the elements generally not integers? Cite two reasons.

(The answer is available in *WileyPLUS*.)

## 2.3 ELECTRONS IN ATOMS

### Atomic Models

#### quantum mechanics

During the latter part of the nineteenth century it was realized that many phenomena involving electrons in solids could not be explained in terms of classical mechanics. What followed was the establishment of a set of principles and laws that govern systems of atomic and subatomic entities that came to be known as **quantum mechanics**. An understanding of the behavior of electrons in atoms and crystalline solids necessarily involves the discussion of quantum-mechanical concepts. However, a detailed exploration of these principles is beyond the scope of this text, and only a very superficial and simplified treatment is given.

#### Bohr atomic model

One early outgrowth of quantum mechanics was the simplified **Bohr atomic model**, in which electrons are assumed to revolve around the atomic nucleus in discrete orbitals, and the position of any particular electron is more or less well defined in terms of its orbital. This model of the atom is represented in Figure 2.1.

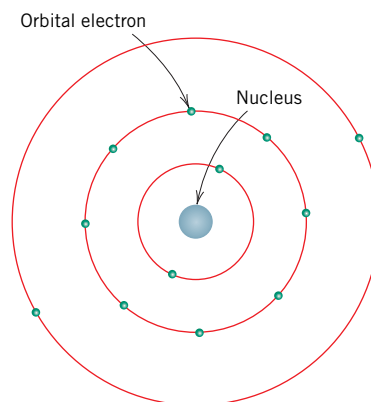
Another important quantum-mechanical principle stipulates that the energies of electrons are quantized; that is, electrons are permitted to have only specific values of energy. An electron may change energy, but in doing so, it must make a quantum jump either to an allowed higher energy (with absorption of energy) or to a lower energy (with emission of energy). Often, it is convenient to think of these allowed electron energies as being associated with *energy levels* or *states*. These states do not vary continuously with energy; that is, adjacent states are separated by finite energies. For example, allowed states for the Bohr hydrogen atom are represented in Figure 2.2a. These energies are taken to be negative, whereas the zero reference is the unbound or free electron. Of course, the single electron associated with the hydrogen atom fills only one of these states.

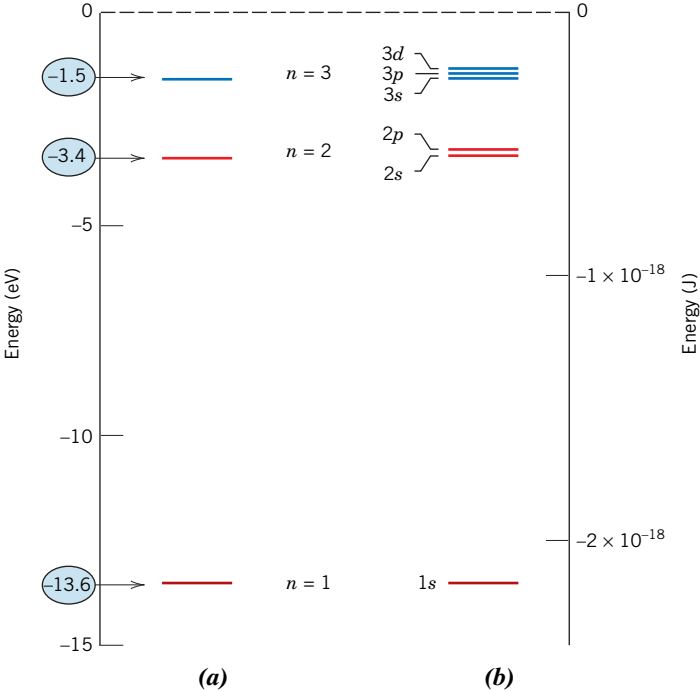
Thus, the Bohr model represents an early attempt to describe electrons in atoms, in terms of both position (electron orbitals) and energy (quantized energy levels).

#### wave-mechanical model

This Bohr model was eventually found to have some significant limitations because of its inability to explain several phenomena involving electrons. A resolution was reached with a **wave-mechanical model**, in which the electron is considered to exhibit both wave-like and particlelike characteristics. With this model, an electron is no longer treated as a particle moving in a discrete orbital; rather, position is considered to be the probability of an electron's being at various locations around the nucleus. In other words, position is described by a probability distribution or electron cloud. Figure 2.3 compares Bohr and

**Figure 2.1** Schematic representation of the Bohr atom.





**Figure 2.2** (a) The first three electron energy states for the Bohr hydrogen atom. (b) Electron energy states for the first three shells of the wave-mechanical hydrogen atom. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, Structure, p. 10. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

wave-mechanical models for the hydrogen atom. Both models are used throughout the course of this text; the choice depends on which model allows the simplest explanation.

Quantum Numbers

quantum number

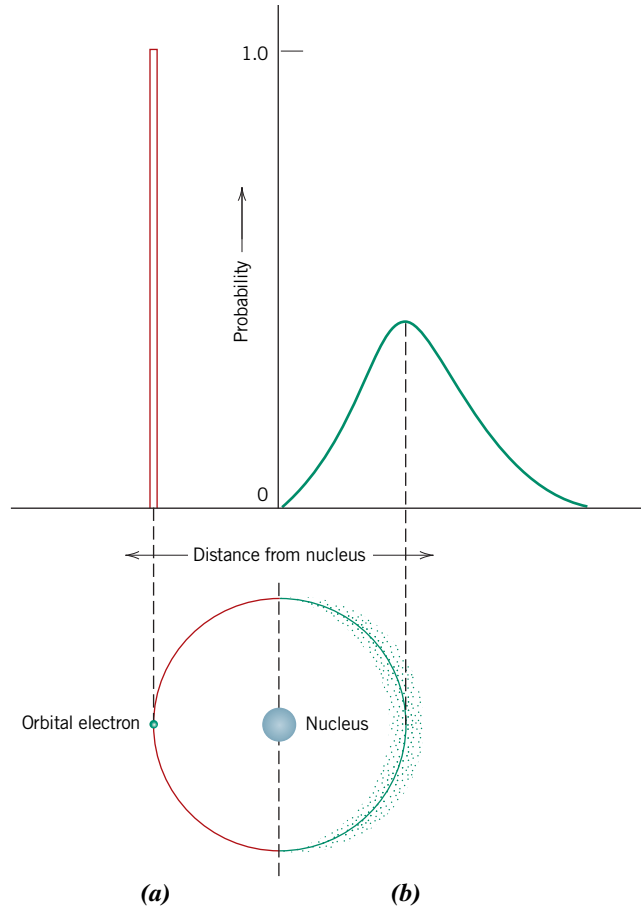
In wave mechanics, every electron in an atom is characterized by four parameters called **quantum numbers**. The size, shape, and spatial orientation of an electron’s probability density (or *orbital*) are specified by three of these quantum numbers. Furthermore, Bohr energy levels separate into electron subshells, and quantum numbers dictate the number of states within each subshell. Shells are specified by a *principal quantum number*  $n$ , which may take on integral values beginning with unity; sometimes these shells are designated by the letters *K*, *L*, *M*, *N*, *O*, and so on, which correspond, respectively, to  $n = 1, 2, 3, 4, 5, \dots$ , as indicated in Table 2.1. Note also that this quantum number,

**Table 2.1** Summary of the Relationships among the Quantum Numbers  $n$ ,  $l$ ,  $m_l$  and Numbers of Orbitals and Electrons

Value of $n$	Value of $l$	Values of $m_l$	Subshell	Number of Orbitals	Number of Electrons
1	0	0	1s	1	2
2	0	0	2s	1	2
	1	-1, 0, +1	2p	3	6
3	0	0	3s	1	2
	1	-1, 0, +1	3p	3	6
	2	-2, -1, 0, +1, +2	3d	5	10
4	0	0	4s	1	2
	1	-1, 0, +1	4p	3	6
	2	-2, -1, 0, +1, +2	4d	5	10
	3	-3, -2, -1, 0, +1, +2, +3	4f	7	14

**Source:** From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.

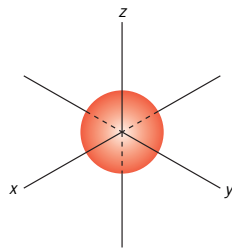
**Figure 2.3** Comparison of the (a) Bohr and (b) wave-mechanical atom models in terms of electron distribution. (Adapted from Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd edition, p. 4. Copyright © 1987 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



and it only, is also associated with the Bohr model. This quantum number is related to the size of an electron's orbital (or its average distance from the nucleus).

The second (or *azimuthal*) quantum number,  $l$ , designates the subshell. Values of  $l$  are restricted by the magnitude of  $n$  and can take on integer values that range from  $l = 0$  to  $l = (n - 1)$ . Each subshell is denoted by a lowercase letter—an  $s$ ,  $p$ ,  $d$ , or  $f$ —related to  $l$  values as follows:

<i>Value of <math>l</math></i>	<i>Letter Designation</i>
0	$s$
1	$p$
2	$d$
3	$f$

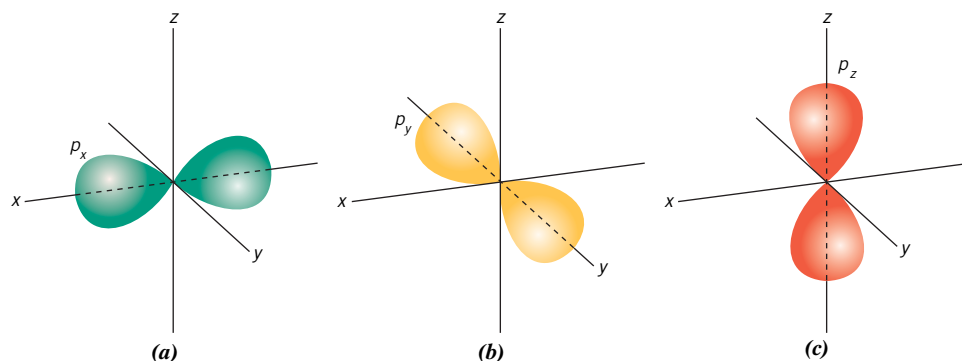


**Figure 2.4**  
Spherical shape of an  $s$  electron orbital.

Furthermore, electron orbital shapes depend on  $l$ . For example  $s$  orbitals are spherical and centered on the nucleus (Figure 2.4). There are three orbitals for a  $p$  subshell (as explained next); each has a nodal surface in the shape of a dumbbell (Figure 2.5). Axes for these three orbitals are mutually perpendicular to one another like those of an  $x$ - $y$ - $z$  coordinate system; thus, it is convenient to label these orbitals  $p_x$ ,  $p_y$ , and  $p_z$  (see Figure 2.5). Orbital configurations for  $d$  subshells are more complex and are not discussed here.

**Figure 2.5**

Orientations and shapes of (a)  $p_x$ , (b)  $p_y$ , and (c)  $p_z$  electron orbitals.

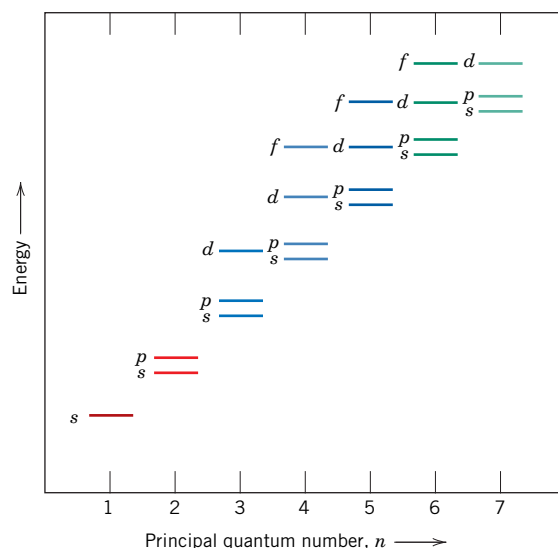


The number of electron orbitals for each subshell is determined by the third (or magnetic) quantum number,  $m_l$ ;  $m_l$  can take on integer values between  $-l$  and  $+l$ , including 0. When  $l = 0$ ,  $m_l$  can only have a value of 0 because  $+0$  and  $-0$  are the same. This corresponds to an  $s$  subshell, which can have only one orbital. Furthermore, for  $l = 1$ ,  $m_l$  can take on values of  $-1$ ,  $0$ , and  $+1$ , and three  $p$  orbitals are possible. Similarly, it can be shown that  $d$  subshells have five orbitals, and  $f$  subshells have seven. In the absence of an external magnetic field, all orbitals within each subshell are identical in energy. However, when a magnetic field is applied, these subshell states split, with each orbital assuming a slightly different energy. Table 2.1 presents a summary of the values and relationships among the  $n$ ,  $l$ , and  $m_l$  quantum numbers.

Associated with each electron is a *spin moment*, which must be oriented either up or down. Related to this spin moment is the fourth quantum number,  $m_s$ , for which two values are possible:  $+\frac{1}{2}$  (for spin up) and  $-\frac{1}{2}$  (for spin down).

Thus, the Bohr model was further refined by wave mechanics, in which the introduction of three new quantum numbers gives rise to electron subshells within each shell. A comparison of these two models on this basis is illustrated, for the hydrogen atom, in Figures 2.2a and 2.2b.

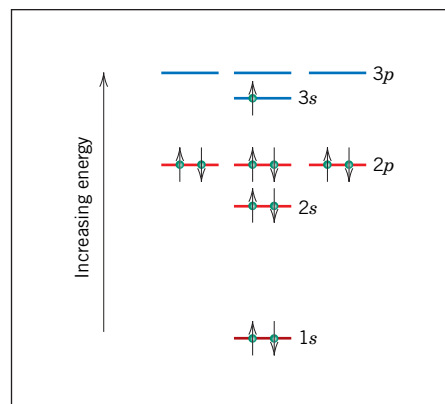
A complete energy level diagram for the various shells and subshells using the wave-mechanical model is shown in Figure 2.6. Several features of the diagram are

**Figure 2.6** Schematic representation of the relative energies of the electrons for the various shells and subshells.

(From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



**Figure 2.7** Schematic representation of the filled and lowest unfilled energy states for a sodium atom.



worth noting. First, the smaller the principal quantum number, the lower is the energy level; for example, the energy of a  $1s$  state is less than that of a  $2s$  state, which in turn is lower than that of the  $3s$ . Second, within each shell, the energy of a subshell level increases with the value of the  $l$  quantum number. For example, the energy of a  $3d$  state is greater than that of a  $3p$ , which is larger than that of a  $3s$ . Finally, there may be overlap in energy of a state in one shell with states in an adjacent shell, which is especially true of  $d$  and  $f$  states; for example, the energy of a  $3d$  state is generally greater than that of a  $4s$ .

## Electron Configurations

### electron state

### Pauli exclusion principle

The preceding discussion has dealt primarily with **electron states**—values of energy that are permitted for electrons. To determine the manner in which these states are filled with electrons, we use the **Pauli exclusion principle**, another quantum-mechanical concept, which stipulates that each electron state can hold no more than two electrons that must have opposite spins. Thus,  $s$ ,  $p$ ,  $d$ , and  $f$  subshells may each accommodate, respectively, a total of 2, 6, 10, and 14 electrons; the right column of Table 2.1 notes the maximum number of electrons that may occupy each orbital for the first four shells.

### ground state

### electron configuration

Of course, not all possible states in an atom are filled with electrons. For most atoms, the electrons fill up the lowest possible energy states in the electron shells and subshells, two electrons (having opposite spins) per state. The energy structure for a sodium atom is represented schematically in Figure 2.7. When all the electrons occupy the lowest possible energies in accord with the foregoing restrictions, an atom is said to be in its **ground state**. However, electron transitions to higher energy states are possible, as discussed in Chapters 12 and 19. The **electron configuration** or structure of an atom represents the manner in which these states are occupied. In the conventional notation, the number of electrons in each subshell is indicated by a superscript after the shell–subshell designation. For example, the electron configurations for hydrogen, helium, and sodium are, respectively,  $1s^1$ ,  $1s^2$ , and  $1s^2 2s^2 2p^6 3s^1$ . Electron configurations for some of the more common elements are listed in Table 2.2.

### valence electron

At this point, comments regarding these electron configurations are necessary. First, the **valence electrons** are those that occupy the outermost shell. These electrons are extremely important; as will be seen, they participate in the bonding between atoms to form atomic and molecular aggregates. Furthermore, many of the physical and chemical properties of solids are based on these valence electrons.

In addition, some atoms have what are termed *stable electron configurations*; that is, the states within the outermost or valence electron shell are completely filled. Normally this corresponds to the occupation of just the  $s$  and  $p$  states for the outermost shell by a total of eight electrons, as in neon, argon, and krypton; one exception is helium, which contains only two  $1s$  electrons. These elements (Ne, Ar, Kr, and He) are the inert, or



**Table 2.2**

Expected Electron Configurations for Some Common Elements<sup>a</sup>

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Electron Configuration</i>
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p^1$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
Gallium	Ga	31	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Arsenic	As	33	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
Selenium	Se	34	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
Bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
Krypton	Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

<sup>a</sup>When some elements covalently bond, they form *sp* hybrid bonds. This is especially true for C, Si, and Ge.

noble, gases, which are virtually unreactive chemically. Some atoms of the elements that have unfilled valence shells assume stable electron configurations by gaining or losing electrons to form charged ions or by sharing electrons with other atoms. This is the basis for some chemical reactions and also for atomic bonding in solids, as explained in Section 2.6.



**Concept Check 2.2** Give electron configurations for the  $\text{Fe}^{3+}$  and  $\text{S}^{2-}$  ions.

(The answer is available in *WileyPLUS*.)

## 2.4 THE PERIODIC TABLE

**periodic table**

All the elements have been classified according to electron configuration in the **periodic table** (Figure 2.8). Here, the elements are situated, with increasing atomic number, in seven horizontal rows called *periods*. The arrangement is such that all elements arrayed in a given column or group have similar valence electron structures, as well as chemical and physical properties. These properties change gradually, moving horizontally across each period and vertically down each column.

The elements positioned in Group 0, the rightmost group, are the *inert gases*, which have filled electron shells and stable electron configurations. Group VIIA and VIA elements are one and two electrons deficient, respectively, from having stable structures. The Group VIIA elements (F, Cl, Br, I, and At) are sometimes termed the *halogens*.

[illegible]

**Figure 2.8** The periodic table of the elements. The numbers in parentheses are the atomic weights of the most stable or common isotopes.

The alkali and the alkaline earth metals (Li, Na, K, Be, Mg, Ca, etc.) are labeled as Groups IA and IIA, having, respectively, one and two electrons in excess of stable structures. The elements in the three long periods, Groups IIIB through IIB, are termed the *transition metals*, which have partially filled *d* electron states and in some cases one or two electrons in the next-higher energy shell. Groups IIIA, IVA, and VA (B, Si, Ge, As, etc.) display characteristics that are intermediate between the metals and nonmetals by virtue of their valence electron structures.

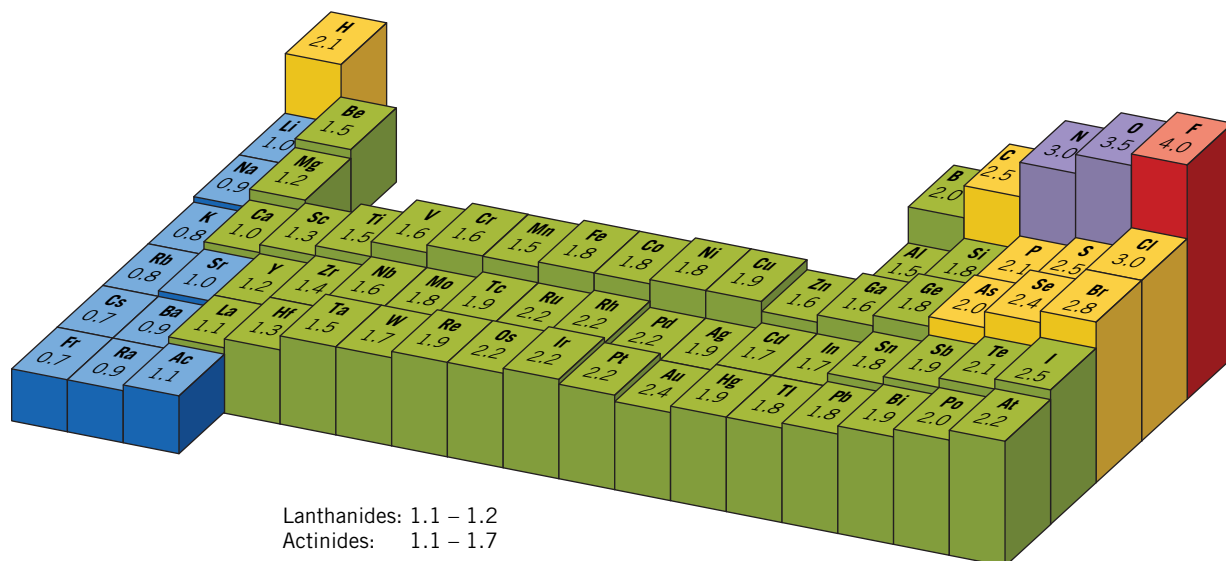
electropositive

electronegative

As may be noted from the periodic table, most of the elements really come under the metal classification. These are sometimes termed **electropositive** elements, indicating that they are capable of giving up their few valence electrons to become positively charged ions. Furthermore, the elements situated on the right side of the table are **electronegative**; that is, they readily accept electrons to form negatively charged ions, or sometimes they share electrons with other atoms. Figure 2.9 displays electronegativity values that have been assigned to the various elements arranged in the periodic table. As a general rule, electronegativity increases in moving from left to right and from bottom to top. Atoms are more likely to accept electrons if their outer shells are almost full and if they are less “shielded” from (i.e., closer to) the nucleus.

In addition to chemical behavior, physical properties of the elements also tend to vary systematically with position in the periodic table. For example, most metals that reside in the center of the table (Groups IIIB through IIB) are relatively good conductors of electricity and heat; nonmetals are typically electrical and thermal insulators. Mechanically, the metallic elements exhibit varying degrees of *ductility*—the ability to be plastically deformed without fracturing (e.g., the ability to be rolled into thin sheets). Most of the nonmetals are either gases or liquids, or in the solid state are brittle in nature. Furthermore, for the Group IVA elements [C (diamond), Si, Ge, Sn, and Pb], electrical conductivity increases as we move down this column. The Group VB metals (V, Nb, and Ta) have very high melting temperatures, which increase in going down this column.

It should be noted that there is not always this consistency in property variations within the periodic table. Physical properties change in a more or less regular manner; however, there are some rather abrupt changes when one moves across a period or down a group.



**Figure 2.9** The electronegativity values for the elements.

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# Atomic Bonding in Solids

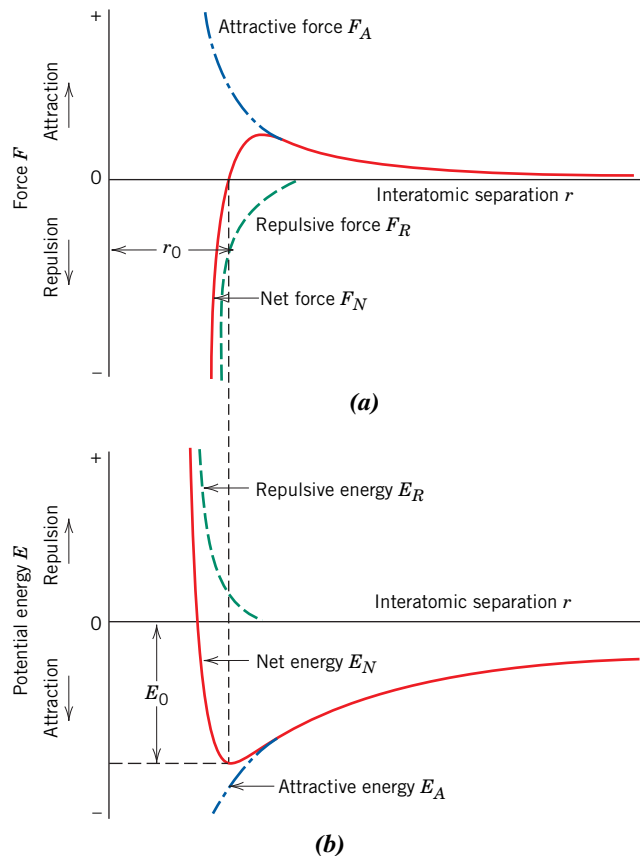
## 2.5 BONDING FORCES AND ENERGIES

An understanding of many of the physical properties of materials is enhanced by a knowledge of the interatomic forces that bind the atoms together. Perhaps the principles of atomic bonding are best illustrated by considering how two isolated atoms interact as they are brought close together from an infinite separation. At large distances, interactions are negligible because the atoms are too far apart to have an influence on each other; however, at small separation distances, each atom exerts forces on the others. These forces are of two types, attractive ( $F_A$ ) and repulsive ( $F_R$ ), and the magnitude of each depends on the separation or interatomic distance ( $r$ ); Figure 2.10a is a schematic plot of  $F_A$  and  $F_R$  versus  $r$ . The origin of an attractive force  $F_A$  depends on the particular type of bonding that exists between the two atoms, as discussed shortly. Repulsive forces arise from interactions between the negatively charged electron clouds for the two atoms and are important only at small values of  $r$  as the outer electron shells of the two atoms begin to overlap (Figure 2.10a).

The net force  $F_N$  between the two atoms is just the sum of both attractive and repulsive components; that is,

$$F_N = F_A + F_R \quad (2.3)$$

**Figure 2.10** (a) The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms. (b) The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms.



which is also a function of the interatomic separation, as also plotted in Figure 2.10a. When  $F_A$  and  $F_R$  are equal in magnitude but opposite in sign, there is no net force—that is,

$$F_A + F_R = 0 \quad (2.4)$$

and a state of equilibrium exists. The centers of the two atoms remain separated by the equilibrium spacing  $r_0$ , as indicated in Figure 2.10a. For many atoms,  $r_0$  is approximately 0.3 nm. Once in this position, any attempt to move the two atoms farther apart is counteracted by the attractive force, while pushing them closer together is resisted by the increasing repulsive force.

Sometimes it is more convenient to work with the potential energies between two atoms instead of forces. Mathematically, energy ( $E$ ) and force ( $F$ ) are related as

Force–potential  
energy relationship  
for two atoms

$$E = \int F dr \quad (2.5a)$$

And, for atomic systems,

$$E_N = \int_r^\infty F_N dr \quad (2.6)$$

$$= \int_r^\infty F_A dr + \int_r^\infty F_R dr \quad (2.7)$$

$$= E_A + E_R \quad (2.8a)$$

in which  $E_N$ ,  $E_A$ , and  $E_R$  are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms.<sup>4</sup>

bonding energy

Figure 2.10b plots attractive, repulsive, and net potential energies as a function of interatomic separation for two atoms. From Equation 2.8a, the net curve is the sum of the attractive and repulsive curves. The minimum in the net energy curve corresponds to the equilibrium spacing,  $r_0$ . Furthermore, the **bonding energy** for these two atoms,  $E_0$ , corresponds to the energy at this minimum point (also shown in Figure 2.10b); it represents the energy required to separate these two atoms to an infinite separation.

Although the preceding treatment deals with an ideal situation involving only two atoms, a similar yet more complex condition exists for solid materials because force and energy interactions among atoms must be considered. Nevertheless, a bonding energy, analogous to  $E_0$ , may be associated with each atom. The magnitude of this bonding energy and the shape of the energy-versus-interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding. Furthermore,

<sup>4</sup>Force in Equation 2.5a may also be expressed as

$$F = \frac{dE}{dr} \quad (2.5b)$$

Likewise, the force equivalent of Equation 2.8a is as follows:

$$F_N = F_A + F_R \quad (2.3)$$

$$= \frac{dE_A}{dr} + \frac{dE_R}{dr} \quad (2.8b)$$

a number of material properties depend on  $E_0$ , the curve shape, and bonding type. For example, materials having large bonding energies typically also have high melting temperatures; at room temperature, solid substances are formed for large bonding energies, whereas for small energies, the gaseous state is favored; liquids prevail when the energies are of intermediate magnitude. In addition, as discussed in Section 7.3, the mechanical stiffness (or modulus of elasticity) of a material is dependent on the shape of its force-versus-interatomic separation curve (Figure 7.7). The slope for a relatively stiff material at the  $r = r_0$  position on the curve will be quite steep; slopes are shallower for more flexible materials. Furthermore, how much a material expands upon heating or contracts upon cooling (i.e., its linear coefficient of thermal expansion) is related to the shape of its  $E$ -versus- $r$  curve (see Section 17.3). A deep and narrow “trough,” which typically occurs for materials having large bonding energies, normally correlates with a low coefficient of thermal expansion and relatively small dimensional alterations for changes in temperature.

### primary bond

Three different types of **primary** or chemical **bond** are found in solids—ionic, covalent, and metallic. For each type, the bonding necessarily involves the valence electrons; furthermore, the nature of the bond depends on the electron structures of the constituent atoms. In general, each of these three types of bonding arises from the tendency of the atoms to assume stable electron structures, like those of the inert gases, by completely filling the outermost electron shell.

Secondary or physical forces and energies are also found in many solid materials; they are weaker than the primary ones but nonetheless influence the physical properties of some materials. The sections that follow explain the several kinds of primary and secondary interatomic bonds.

## 2.6 PRIMARY INTERATOMIC BONDS

### Ionic Bonding

#### ionic bonding

**Ionic bonding** is perhaps the easiest to describe and visualize. It is always found in compounds composed of both metallic and nonmetallic elements, elements situated at the horizontal extremities of the periodic table. Atoms of a metallic element easily give up their valence electrons to the nonmetallic atoms. In the process, all the atoms acquire stable or inert gas configurations (i.e., completely filled orbital shells) and, in addition, an electrical charge—that is, they become ions. Sodium chloride (NaCl) is the classic ionic material. A sodium atom can assume the electron structure of neon (and a net single positive charge with a reduction in size) by a transfer of its one valence  $3s$  electron to a chlorine atom (Figure 2.11a). After such a transfer, the chlorine ion acquires a net negative charge, an electron configuration identical to that of argon; it is also larger than the chlorine atom. Ionic bonding is illustrated schematically in Figure 2.11b.

#### coulombic force

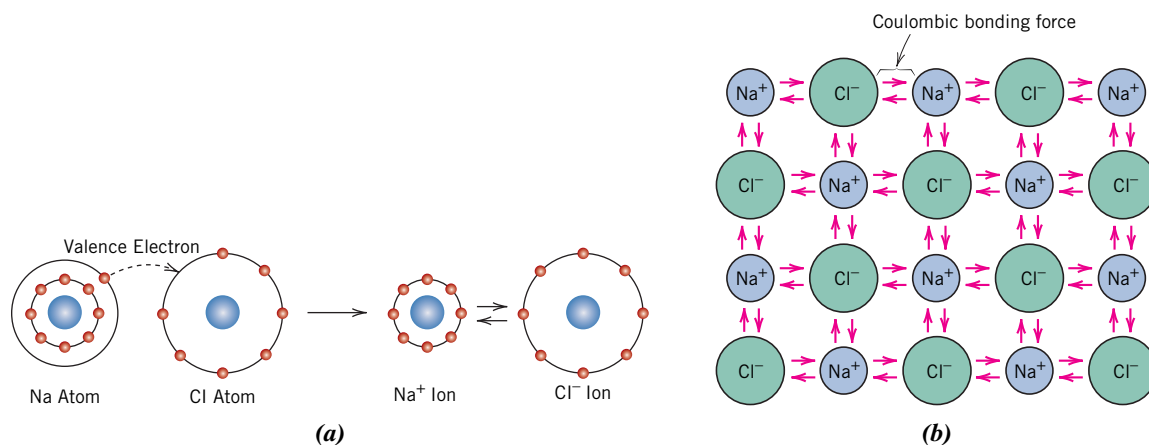
The attractive bonding forces are **coulombic**—that is, positive and negative ions, by virtue of their net electrical charge, attract one another. For two isolated ions, the attractive energy  $E_A$  is a function of the interatomic distance according to

Attractive energy—  
interatomic  
separation  
relationship

$$E_A = -\frac{A}{r} \quad (2.9)$$

Theoretically, the constant  $A$  is equal to

$$A = \frac{1}{4\pi\epsilon_0} (|Z_1|e)(|Z_2|e) \quad (2.10)$$



**Figure 2.11** Schematic representations of (a) the formation of Na<sup>+</sup> and Cl<sup>-</sup> ions and (b) ionic bonding in sodium chloride (NaCl).

Here  $\epsilon_0$  is the permittivity of a vacuum ( $8.85 \times 10^{-12}$  F/m),  $|Z_1|$  and  $|Z_2|$  are absolute values of the valences for the two ion types, and  $e$  is the electronic charge ( $1.602 \times 10^{-19}$  C). The value of  $A$  in Equation 2.9 assumes the bond between ions 1 and 2 is totally ionic (see Equation 2.16). Inasmuch as bonds in most of these materials are not 100% ionic, the value of  $A$  is normally determined from experimental data rather than computed using Equation 2.10.

An analogous equation for the repulsive energy is<sup>5</sup>

$$E_R = \frac{B}{r^n} \quad (2.11)$$

In this expression,  $B$  and  $n$  are constants whose values depend on the particular ionic system. The value of  $n$  is approximately 8.

Ionic bonding is termed *nondirectional*—that is, the magnitude of the bond is equal in all directions around an ion. It follows that for ionic materials to be stable, all positive ions must have as nearest neighbors negatively charged ions in a three-dimensional scheme, and vice versa. Some of the ion arrangements for these materials are discussed in Chapter 3.

Bonding energies, which generally range between 600 and 1500 kJ/mol, are relatively large, as reflected in high melting temperatures.<sup>6</sup> Table 2.3 contains bonding energies and melting temperatures for several ionic materials. Interatomic bonding is typified by ceramic materials, which are characteristically hard and brittle and, furthermore, electrically and thermally insulative. As discussed in subsequent chapters, these properties are a direct consequence of electron configurations and/or the nature of the ionic bond.

Repulsive energy—  
interatomic  
separation  
relationship

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What Is Ionic Bonding?

<sup>5</sup>In Equation 2.11, the value of the constant  $B$  is also fit using experimental data.

<sup>6</sup>Sometimes bonding energies are expressed per atom or per ion. Under these circumstances, the electron volt (eV) is a conveniently small unit of energy. It is, by definition, the energy imparted to an electron as it falls through an electric potential of one volt. The joule equivalent of the electron volt is as follows:  $1.602 \times 10^{-19}$  J = 1 eV.



**Table 2.3**  
Bonding Energies and  
Melting Temperatures  
for Various Substances

<i>Substance</i>	<i>Bonding Energy (kJ/mol)</i>	<i>Melting Temperature (°C)</i>
<b>Ionic</b>		
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF <sub>2</sub>	1548	1418
<b>Covalent</b>		
Cl <sub>2</sub>	121	−102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
<b>Metallic</b>		
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414
<b>van der Waals<sup>a</sup></b>		
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH <sub>4</sub>	18	−182
Cl <sub>2</sub>	31	−101
<b>Hydrogen<sup>a</sup></b>		
HF	29	−83
NH <sub>3</sub>	35	−78
H <sub>2</sub> O	51	0

<sup>a</sup>Values for van der Waals and hydrogen bonds are energies *between* molecules or atoms (*intermolecular*), not between atoms within a molecule (*intramolecular*).

## EXAMPLE PROBLEM 2.2

### Computation of Attractive and Repulsive Forces between Two Ions

The atomic radii of K<sup>+</sup> and Br<sup>−</sup> ions are 0.138 and 0.196 nm, respectively.

- Using Equations 2.9 and 2.10, calculate the force of attraction between these two ions at their equilibrium interionic separation (i.e., when the ions just touch one another).
- What is the force of repulsion at this same separation distance?

#### Solution

- From Equation 2.5b, the force of attraction between two ions is

$$F_A = \frac{dE_A}{dr}$$

Whereas, according to Equation 2.9,

$$E_A = -\frac{A}{r}$$

Now, taking the derivative of  $E_A$  with respect to  $r$  yields the following expression for the force of attraction  $F_A$ :

$$F_A = \frac{dE_A}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} = -\left(\frac{-A}{r^2}\right) = \frac{A}{r^2} \quad (2.12)$$

Now substitution into this equation the expression for  $A$  (Eq. 2.10) gives

$$F_A = \frac{1}{4\pi\epsilon_0 r^2} (|Z_1|e)(|Z_2|e) \quad (2.13)$$

Incorporation into this equation values for  $e$  and  $\epsilon_0$  leads to

$$\begin{aligned} F_A &= \frac{1}{4\pi(8.85 \times 10^{-12} \text{ F/m})(r^2)} [ |Z_1|(1.602 \times 10^{-19} \text{ C}) ][ |Z_2|(1.602 \times 10^{-19} \text{ C}) ] \\ &= \frac{(2.31 \times 10^{-28} \text{ N} \cdot \text{m}^2)(|Z_1|)(|Z_2|)}{r^2} \end{aligned} \quad (2.14)$$

For this problem,  $r$  is taken as the interionic separation  $r_0$  for KBr, which is equal to the sum of the  $\text{K}^+$  and  $\text{Br}^-$  ionic radii inasmuch as the ions touch one another—that is,

$$\begin{aligned} r_0 &= r_{\text{K}^+} + r_{\text{Br}^-} \\ &= 0.138 \text{ nm} + 0.196 \text{ nm} \\ &= 0.334 \text{ nm} \\ &= 0.334 \times 10^{-9} \text{ m} \end{aligned} \quad (2.15)$$

When we substitute this value for  $r$  into Equation 2.14, and taking ion 1 to be  $\text{K}^+$  and ion 2 as  $\text{Br}^-$  (i.e.,  $Z_1 = +1$  and  $Z_2 = -1$ ), then the force of attraction is equal to

$$F_A = \frac{(2.31 \times 10^{-28} \text{ N} \cdot \text{m}^2)(|+1|)(|-1|)}{(0.334 \times 10^{-9} \text{ m})^2} = 2.07 \times 10^{-9} \text{ N}$$

- (b) At the equilibrium separation distance the sum of attractive and repulsive forces is zero according to Equation 2.4. This means that

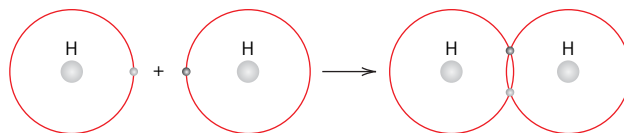
$$F_R = -F_A = -(2.07 \times 10^{-9} \text{ N}) = -2.07 \times 10^{-9} \text{ N}$$

## Covalent Bonding

### covalent bonding

A second bonding type, **covalent bonding**, is found in materials whose atoms have small differences in electronegativity—that is, that lie near one another in the periodic table. For these materials, stable electron configurations are assumed by the sharing of electrons between adjacent atoms. Two covalently bonded atoms will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms. Covalent bonding is schematically illustrated in Figure 2.12 for a molecule of hydrogen ( $\text{H}_2$ ). The hydrogen atom has a single  $1s$  electron. Each of the atoms can acquire a helium electron configuration (two  $1s$  valence electrons) when they share their single electron (right side of Figure 2.12). Furthermore, there is an overlapping of

**Figure 2.12** Schematic representation of covalent bonding in a molecule of hydrogen ( $\text{H}_2$ ).



electron orbitals in the region between the two bonding atoms. In addition, the covalent bond is *directional*—that is, it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.

Many nonmetallic elemental molecules (e.g.,  $\text{Cl}_2$ ,  $\text{F}_2$ ), as well as molecules containing dissimilar atoms, such as  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and  $\text{HF}$ , are covalently bonded.<sup>7</sup> Furthermore, this type of bonding is found in elemental solids such as diamond (carbon), silicon, and germanium and other solid compounds composed of elements that are located on the right side of the periodic table, such as gallium arsenide ( $\text{GaAs}$ ), indium antimonide ( $\text{InSb}$ ), and silicon carbide ( $\text{SiC}$ ).

Covalent bonds may be very strong, as in diamond, which is very hard and has a very high melting temperature,  $>3550^\circ\text{C}$  ( $6400^\circ\text{F}$ ), or they may be very weak, as with bismuth, which melts at about  $270^\circ\text{C}$  ( $518^\circ\text{F}$ ). Bonding energies and melting temperatures for a few covalently bonded materials are presented in Table 2.3. Inasmuch as electrons participating in covalent bonds are tightly bound to the bonding atoms, most covalently bonded materials are electrical insulators, or, in some cases, semiconductors. Mechanical behaviors of these materials vary widely: some are relatively strong, others are weak; some fail in a brittle manner, whereas others experience significant amounts of deformation before failure. It is difficult to predict the mechanical properties of covalently bonded materials on the basis of their bonding characteristics.

### Bond Hybridization in Carbon

Often associated with the covalent bonding of carbon (as well other nonmetallic substances) is the phenomenon of *hybridization*—the mixing (or combining) of two or more atomic orbitals with the result that more orbital overlap during bonding results. For example, consider the electron configuration of carbon:  $1s^2 2s^2 2p^2$ . Under some circumstances, one of the  $2s$  orbitals is promoted to the empty  $2p$  orbital (Figure 2.13a), which gives rise to a  $1s^2 2s^1 2p^3$  configuration (Figure 2.13b). Furthermore, the  $2s$  and  $2p$  orbitals can mix to produce four  $sp^3$  orbitals that are equivalent to one another, have parallel spins, and are capable of covalently bonding with other atoms. This orbital mixing is termed *hybridization*, which leads to the electron configuration shown in Figure 2.13c; here, each  $sp^3$  orbital contains one electron, and, therefore, is half-filled.

Bonding hybrid orbitals are directional in nature—that is, each extends to and overlaps the orbital of an adjacent bonding atom. Furthermore, for carbon, each of its four  $sp^3$  hybrid orbitals is directed symmetrically from a carbon atom to the vertex of a tetrahedron—a configuration represented schematically in Figure 2.14; the angle between each set of adjacent bonds is  $109.5^\circ$ .<sup>8</sup> The bonding of  $sp^3$  hybrid orbitals to the  $1s$  orbitals of four hydrogen atoms, as in a molecule of methane ( $\text{CH}_4$ ), is presented in Figure 2.15.

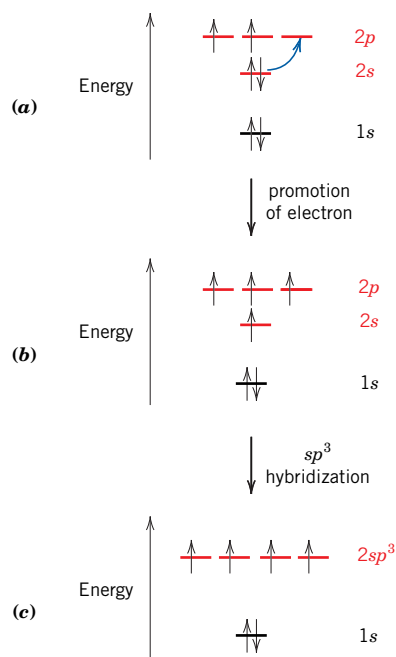
For diamond, its carbon atoms are bonded to one another with  $sp^3$  covalent hybrids—each atom is bonded to four other carbon atoms. The crystal structure for diamond is shown in Figure 3.17. Diamond's carbon–carbon bonds are extremely strong, which accounts for its high melting temperature and ultrahigh hardness (it is the hardest of all materials). Many polymeric materials are composed of long chains of carbon atoms that are also bonded together using  $sp^3$  tetrahedral bonds; these chains form a zigzag structure (Figure 4.1b) because of this  $109.5^\circ$  interbonding angle.

<sup>7</sup>For these substances, the *intramolecular* bonds (bonds between atoms in molecule) are covalent. As noted in the next section, other types of bonds can operate between molecules, which are termed *intermolecular*.

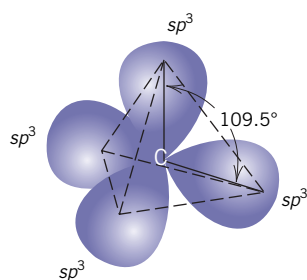
<sup>8</sup>Bonding of this type (to four other atoms) is sometimes termed *tetrahedral bonding*.

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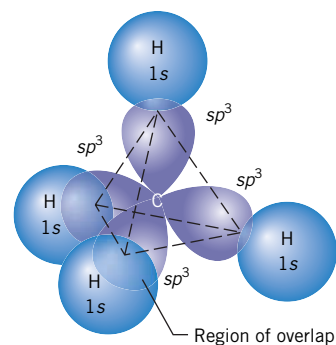
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What Is Covalent  
Bonding?



**Figure 2.13** Schematic diagram that shows the formation of  $sp^3$  hybrid orbitals in carbon. (a) Promotion of a 2s electron to a 2p state; (b) this promoted electron in a 2p state; (c) four  $2sp^3$  orbitals that form by mixing the single 2s orbital with the three 2p orbitals.



**Figure 2.14** Schematic diagram showing four  $sp^3$  hybrid orbitals that point to the corners of a tetrahedron; the angle between orbitals is  $109.5^\circ$ . (From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.)



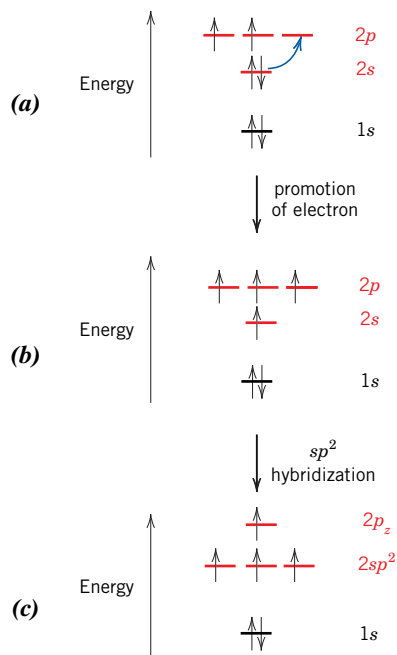
**Figure 2.15** Schematic diagram that shows bonding of carbon  $sp^3$  hybrid orbitals to the 1s orbitals of four hydrogen atoms in a molecule of methane ( $\text{CH}_4$ ). (From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.)

Other types of hybrid bonds are possible for carbon, as well as other substances. One of these is  $sp^2$ , in which an s orbital and two p orbitals are hybridized. To achieve this configuration, one 2s orbital mixes with two of the three 2p orbitals—the third p orbital remains unhybridized; this is shown in Figure 2.16. Here,  $2p_z$  denotes the unhybridized p orbital.<sup>9</sup> Three  $sp^2$  hybrids belong to each carbon atom, which lie in the same plane such that the angle between adjacent orbitals is  $120^\circ$  (Figure 2.17); lines drawn from one orbital to another form a triangle. Furthermore, the unhybridized  $2p_z$  orbital is oriented perpendicular to the plane containing the  $sp^2$  hybrids.

These  $sp^2$  bonds are found in graphite, another form of carbon, which has a structure and properties distinctly different from those of diamond (as discussed in Section 3.9). Graphite is composed of parallel layers of interconnecting hexagons. Hexagons form from planar  $sp^2$  triangles that bond to one another in the manner presented in Figure 2.18—a carbon atom is located at each vertex. In-plane  $sp^2$  bonds are strong; by way of contrast, weak interplanar bonding results from van der Waals forces that involve electrons originating from the unhybridized  $2p_z$  orbitals. The structure of graphite is shown in Figure 3.18.

<sup>9</sup>This  $2p_z$  orbital has the shape and orientation of the  $p_z$  shown in Figure 2.5c. In addition, the two p orbitals found in the  $sp^2$  hybrid correspond to the  $p_x$  and  $p_y$  orbitals of this same figure. Furthermore,  $p_x$ ,  $p_y$ , and  $p_z$  are the three orbitals of the  $sp^3$  hybrid.

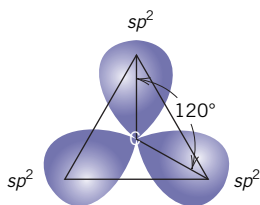
**Figure 2.16** Schematic diagram that shows the formation of  $sp^2$  hybrid orbitals in carbon. (a) Promotion of a  $2s$  electron to a  $2p$  state; (b) this promoted electron in a  $2p$  state; (c) three  $2sp^2$  orbitals that form by mixing the single  $2s$  orbital with two  $2p$  orbitals—the  $2p_z$  orbital remains unhybridized.



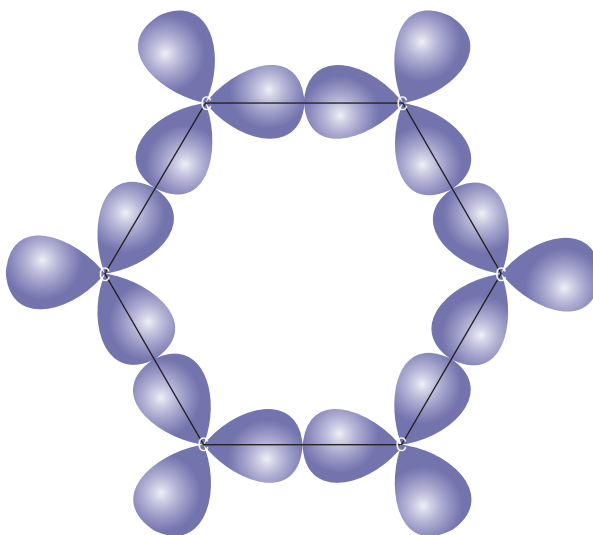
### metallic bonding

#### Metallic Bonding

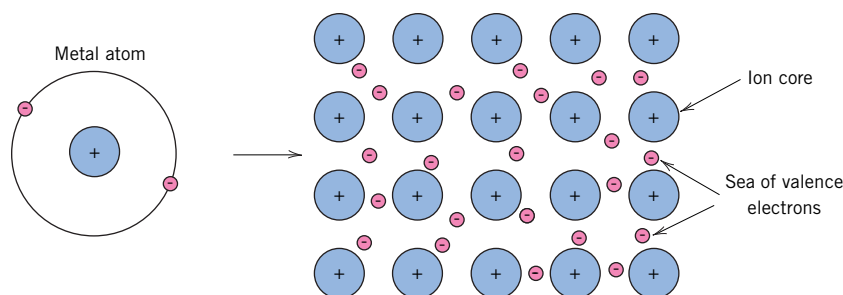
**Metallic bonding**, the final primary bonding type, is found in metals and their alloys. A relatively simple model has been proposed that very nearly approximates the bonding scheme. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal. They may be thought of as belonging to the metal as a whole, or forming a “sea of electrons” or an “electron cloud.” The remaining nonvalence electrons and atomic nuclei form what are called *ion cores*, which possess a net positive charge equal in magnitude to the total



**Figure 2.17** Schematic diagram showing three  $sp^2$  orbitals that are coplanar and point to the corners of a triangle; the angle between adjacent orbitals is  $120^\circ$ . (From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.)



**Figure 2.18** The formation of a hexagon by the bonding of six  $sp^2$  triangles to one another.



**Figure 2.19** Schematic illustration of metallic bonding.

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Bonding?

valence electron charge per atom. Figure 2.19 illustrates metallic bonding. The free electrons shield the positively charged ion cores from the mutually repulsive electrostatic forces that they would otherwise exert upon one another; consequently, the metallic bond is nondirectional in character. In addition, these free electrons act as a “glue” to hold the ion cores together. Bonding energies and melting temperatures for several metals are listed in Table 2.3. Bonding may be weak or strong; energies range from 62 kJ/mol for mercury to 850 kJ/mol for tungsten. Their respective melting temperatures are  $-39^{\circ}\text{C}$  and  $3414^{\circ}\text{C}$  ( $-39^{\circ}\text{F}$  and  $6177^{\circ}\text{F}$ ).

Metallic bonding is found in the periodic table for Group IA and IIA elements and, in fact, for all elemental metals.

Metals are good conductors of both electricity and heat as a consequence of their free electrons (see Sections 12.5, 12.6, and 17.4). Furthermore, in Section 8.5, we note that at room temperature, most metals and their alloys fail in a ductile manner—that is, fracture occurs after the materials have experienced significant degrees of permanent deformation. This behavior is explained in terms of deformation mechanism (Section 8.3), which is implicitly related to the characteristics of the metallic bond.



**Concept Check 2.3** Explain why covalently bonded materials are generally less dense than ionically or metallically bonded ones.

(The answer is available in *WileyPLUS*.)

## 2.7 SECONDARY BONDING OR VAN DER WAALS BONDING

**secondary bond**

**van der Waals bond**

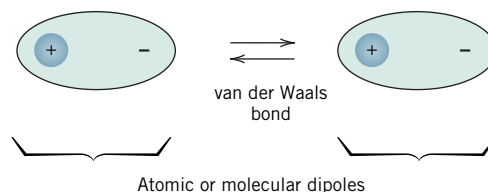
**dipole**

**hydrogen bonding**

**Secondary bonds**, or **van der Waals (physical) bonds**, are weak in comparison to the primary or chemical bonds; bonding energies range between about 4 and 30 kJ/mol. Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present. Secondary bonding is evidenced for the inert gases, which have stable electron structures. In addition, secondary (or *intermolecular*) bonds are possible between atoms or groups of atoms, which themselves are joined together by primary (or *intramolecular*) ionic or covalent bonds.

Secondary bonding forces arise from atomic or molecular **dipoles**. In essence, an electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule. The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one, as indicated in Figure 2.20. Dipole interactions occur between induced dipoles, between induced dipoles and polar molecules (which have permanent dipoles), and between polar molecules. **Hydrogen bonding**, a special type of secondary bonding, is found to exist

**Figure 2.20** Schematic illustration of van der Waals bonding between two dipoles.



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What Is a Dipole?

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**Bonding**  
What Is van der Waals Bonding?

between some molecules that have hydrogen as one of the constituents. These bonding mechanisms are discussed briefly next.

### Fluctuating Induced Dipole Bonds

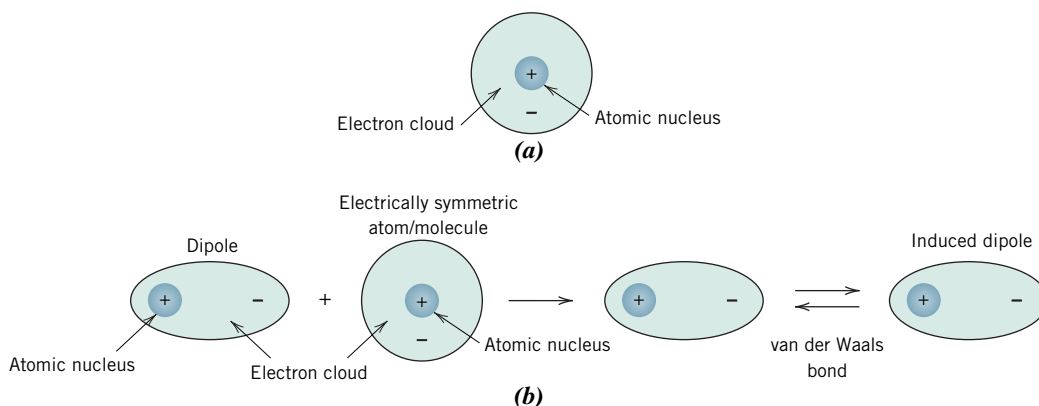
A dipole may be created or induced in an atom or molecule that is normally electrically symmetric—that is, the overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus, as shown in Figure 2.21a. All atoms experience constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles. One of these dipoles can in turn produce a displacement of the electron distribution of an adjacent molecule or atom, which induces the second one also to become a dipole that is then weakly attracted or bonded to the first (Figure 2.21b); this is one type of van der Waals bonding. These attractive forces, which are temporary and fluctuate with time, may exist between large numbers of atoms or molecules.

The liquefaction and, in some cases, the solidification of the inert gases and other electrically neutral and symmetric molecules such as  $\text{H}_2$  and  $\text{Cl}_2$  are realized because of this type of bonding. Melting and boiling temperatures are extremely low in materials for which induced dipole bonding predominates; of all possible intermolecular bonds, these are the weakest. Bonding energies and melting temperatures for argon, krypton, methane, and chlorine are also tabulated in Table 2.3.

### Polar Molecule–Induced Dipole Bonds

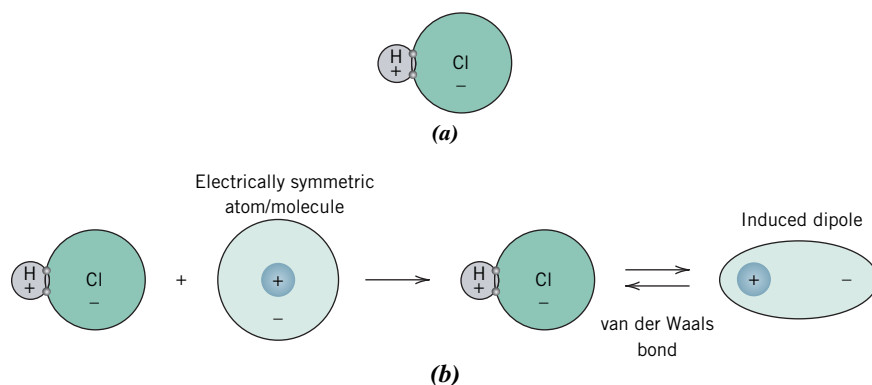
Permanent dipole moments exist in some molecules by virtue of an asymmetrical arrangement of positively and negatively charged regions; such molecules are termed **polar molecules**. Figure 2.22a shows a schematic representation of a hydrogen chloride molecule; a permanent dipole moment arises from net positive and negative charges that are respectively associated with the hydrogen and chlorine ends of the HCl molecule.

polar molecule



**Figure 2.21** Schematic representations of (a) an electrically symmetric atom and (b) how an electric dipole induces an electrically symmetric atom/molecule to become a dipole—also the van der Waals bond between the dipoles.





**Figure 2.22** Schematic representations of (a) a hydrogen chloride molecule (dipole) and (b) how an HCl molecule induces an electrically symmetric atom/molecule to become a dipole—also the van der Waals bond between these dipoles.

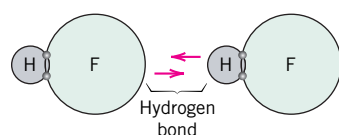
Polar molecules can also induce dipoles in adjacent nonpolar molecules, and a bond forms as a result of attractive forces between the two molecules; this bonding scheme is represented schematically in Figure 2.22b. Furthermore, the magnitude of this bond is greater than for fluctuating induced dipoles.

### Permanent Dipole Bonds

Coulombic forces also exist between adjacent polar molecules as in Figure 2.20. The associated bonding energies are significantly greater than for bonds involving induced dipoles.

The strongest secondary bonding type, the hydrogen bond, is a special case of polar molecule bonding. It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in H<sub>2</sub>O), or nitrogen (as in NH<sub>3</sub>). For each H—F, H—O, or H—N bond, the single hydrogen electron is shared with the other atom. Thus, the hydrogen end of the bond is essentially a positively charged bare proton unscreened by any electrons. This highly positively charged end of the molecule is capable of a strong attractive force with the negative end of an adjacent molecule, as demonstrated in Figure 2.23 for HF. In essence, this single proton forms a bridge between two negatively charged atoms. The magnitude of the hydrogen bond is generally greater than that of the other types of secondary bonds and may be as high as 51 kJ/mol, as shown in Table 2.3. Melting and boiling temperatures for hydrogen fluoride, ammonia, and water are abnormally high in light of their low molecular weights, as a consequence of hydrogen bonding.

In spite of the small energies associated with secondary bonds, they nevertheless are involved in a number of natural phenomena and many products that we use on a daily basis. Examples of physical phenomena include the solubility of one substance in another, surface tension and capillary action, vapor pressure, volatility, and viscosity. Common applications that make use of these phenomena include *adhesives*—van der Waals bonds form between two surfaces so that they adhere to one another (as discussed in the chapter opener for this chapter); *surfactants*—compounds that lower the surface tension of a liquid and are found in soaps, detergents, and foaming agents; *emulsifiers*—substances that, when added to two immiscible materials (usually liquids), allow particles of one material to be suspended in another (common emulsions include sunscreens, salad dressings, milk, and mayonnaise); and *desiccants*—materials that form hydrogen bonds with water molecules (and remove moisture from closed containers—e.g., small packets that are often found in cartons of packaged goods); and finally, the strengths, stiffnesses, and softening temperatures of polymers, to some degree, depend on secondary bonds that form between chain molecules.



**Figure 2.23** Schematic representation of hydrogen bonding in hydrogen fluoride (HF).

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What Are the Differences between Ionic, Covalent, Metallic, and van der Waals Types of Bonding?

## M A T E R I A L S   O F   I M P O R T A N C E

*Water (Its Volume Expansion upon Freezing)*

Upon freezing (i.e., transforming from a liquid to a solid upon cooling), most substances experience an increase in density (or, correspondingly, a decrease in volume). One exception is water, which exhibits the anomalous and familiar expansion upon freezing—approximately 9 volume percent expansion. This behavior may be explained on the basis of hydrogen bonding. Each  $\text{H}_2\text{O}$  molecule has two hydrogen atoms that can bond to oxygen atoms; in addition, its single O atom can bond to two hydrogen atoms of other  $\text{H}_2\text{O}$  molecules. Thus, for solid ice, each water molecule participates in four hydrogen bonds, as shown in the three-dimensional schematic of Figure 2.24a; here, hydrogen bonds are denoted by dashed lines, and each water molecule has 4 nearest-neighbor molecules. This is a

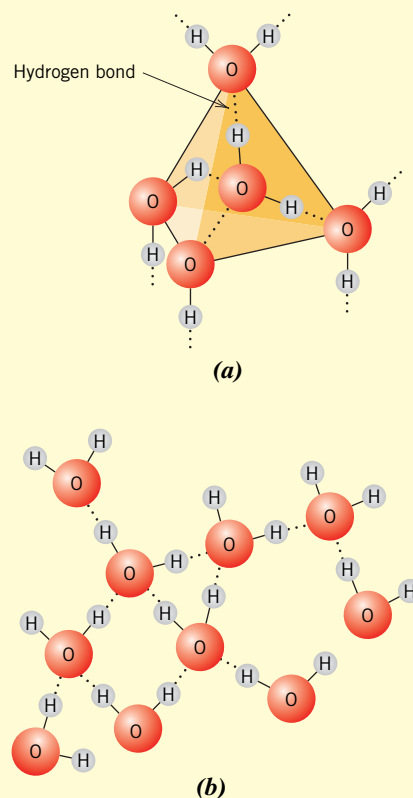
relatively open structure—that is, the molecules are not closely packed together—and as a result, the density is comparatively low. Upon melting, this structure is partially destroyed, such that the water molecules become more closely packed together (Figure 2.24b)—at room temperature, the average number of nearest-neighbor water molecules has increased to approximately 4.5; this leads to an increase in density.

Consequences of this anomalous freezing phenomenon are familiar; it explains why icebergs float; why, in cold climates, it is necessary to add antifreeze to an automobile's cooling system (to keep the engine block from cracking); and why freeze-thaw cycles break up the pavement in streets and cause potholes to form.



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A watering can that ruptured along a side panel—bottom panel seam. Water that was left in the can during a cold late-autumn night expanded as it froze and caused the rupture.



**Figure 2.24** The arrangement of water ( $\text{H}_2\text{O}$ ) molecules in (a) solid ice and (b) liquid water.

## 2.8 MIXED BONDING

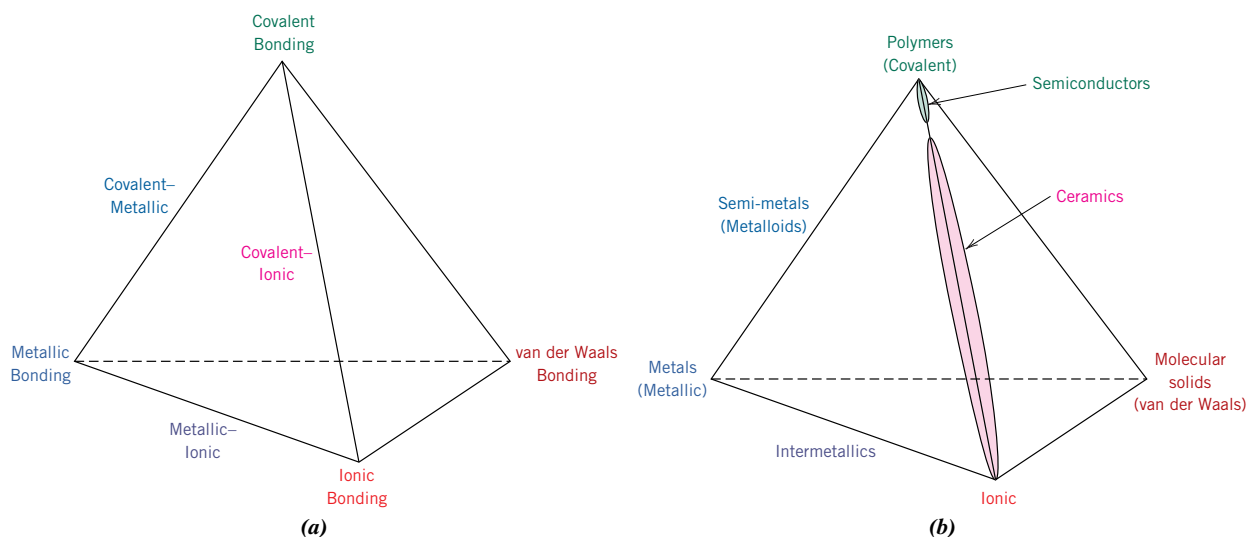
Sometimes it is illustrative to represent the four bonding types—ionic, covalent, metallic, and van der Waals—on what is called a *bonding tetrahedron*—a three-dimensional tetrahedron with one of these “extreme” types located at each vertex, as shown in Figure 2.25a. Furthermore, we should point out that for many real materials, the atomic bonds are mixtures of two or more of these extremes (i.e., *mixed bonds*). Three mixed-bond types—covalent–ionic, covalent–metallic, and metallic–ionic—are also included on edges of this tetrahedron; we now discuss each of them.

For mixed covalent–ionic bonds, there is some ionic character to most covalent bonds and some covalent character to ionic ones. As such, there is a continuum between these two extreme bond types. In Figure 2.25a, this type of bond is represented between the ionic and covalent bonding vertices. The degree of either bond type depends on the relative positions of the constituent atoms in the periodic table (see Figure 2.8) or the difference in their electronegativities (see Figure 2.9). The wider the separation (both horizontally—relative to Group IVA—and vertically) from the lower left to the upper right corner (i.e., the greater the difference in electronegativity), the more ionic is the bond. Conversely, the closer the atoms are together (i.e., the smaller the difference in electronegativity), the greater is the degree of covalency. Percent ionic character (%IC) of a bond between elements A and B (A being the most electronegative) may be approximated by the expression

$$\%IC = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100 \quad (2.16)$$

where  $X_A$  and  $X_B$  are the electronegativities for the respective elements.

Another type of mixed bond is found for some elements in Groups IIIA, IVA, and VA of the periodic table (viz., B, Si, Ge, As, Sb, Te, Po, and At). Interatomic bonds for these elements are mixtures of metallic and covalent, as noted on Figure 2.25a. These materials are called the *metalloids* or *semi-metals*, and their properties are intermediate between the metals and nonmetals. In addition, for Group IV elements, there is a gradual transition from covalent to metallic bonding as one moves vertically down this column—for example, bonding in carbon (diamond) is purely covalent, whereas for tin and lead, bonding is predominantly metallic.



**Figure 2.25** (a) Bonding tetrahedron: Each of the four extreme (or pure) bonding types is located at one corner of the tetrahedron; three mixed bonding types are included along tetrahedron edges. (b) Material-type tetrahedron: correlation of each material classification (metals, ceramics, polymers, etc.) with its type(s) of bonding.

Mixed metallic–ionic bonds are observed for compounds composed of two metals when there is a significant difference between their electronegativities. This means that some electron transfer is associated with the bond inasmuch as it has an ionic component. Furthermore, the larger this electronegativity difference, the greater the degree of ionicity. For example, there is little ionic character to the titanium–aluminum bond for the intermetallic compound  $\text{TiAl}_3$  because electronegativities of both Al and Ti are the same (1.5; see Figure 2.9). However, a much greater degree of ionic character is present for  $\text{AuCu}_3$ ; the electronegativity difference for copper and gold is 0.5.

### EXAMPLE PROBLEM 2.3

#### Calculation of the Percent Ionic Character for the C–H Bond

Compute the percent ionic character (%IC) of the interatomic bond that forms between carbon and hydrogen.

#### Solution

The %IC of a bond between two atoms/ions, A and B (A being the more electronegative), is a function of their electronegativities  $X_A$  and  $X_B$ , according to Equation 2.16. The electronegativities for C and H (see Figure 2.9) are  $X_C = 2.5$  and  $X_H = 2.1$ . Therefore, the %IC is

$$\begin{aligned}\% \text{IC} &= \{1 - \exp[-(0.25)(X_C - X_H)^2]\} \times 100 \\ &= \{1 - \exp[-(0.25)(2.5 - 2.1)^2]\} \times 100 \\ &= 3.9\%\end{aligned}$$

Thus the C–H atomic bond is primarily covalent (96.1%).

## 2.9 MOLECULES

Many common molecules are composed of groups of atoms bound together by strong covalent bonds, including elemental diatomic molecules ( $\text{F}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ , etc.), as well as a host of compounds ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{HNO}_3$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_4$ , etc.). In the condensed liquid and solid states, bonds between molecules are weak secondary ones. Consequently, molecular materials have relatively low melting and boiling temperatures. Most materials that have small molecules composed of a few atoms are gases at ordinary, or ambient, temperatures and pressures. However, many modern polymers, being molecular materials composed of extremely large molecules, exist as solids; some of their properties are strongly dependent on the presence of van der Waals and hydrogen secondary bonds.

## 2.10 BONDING TYPE-MATERIAL CLASSIFICATION CORRELATIONS

In previous discussions of this chapter, some correlations have been drawn between bonding type and material classification—namely, ionic bonding (ceramics), covalent bonding (polymers), metallic bonding (metals), and van der Waals bonding (molecular solids). We summarized these correlations in the material-type tetrahedron shown in Figure 2.25*b*—the bonding tetrahedron of Figure 2.25*a*, on which is superimposed the bonding location/region typified by each of the four material classes.<sup>10</sup> Also included

<sup>10</sup>Although most atoms in polymer molecules are covalently bonded, some van der Waals bonding is normally present. We chose not to include van der Waals bonds for polymers because they (van der Waals) are *intermolecular* (i.e., between molecules) as opposed to *intramolecular* (within molecules) and not the principal bonding type.

are those materials having mixed bonding: intermetallics and semi-metals. Mixed ionic-covalent bonding for ceramics is also noted. Furthermore, the predominant bonding type for semiconducting materials is covalent, with the possibility of an ionic contribution.

## SUMMARY

### Electrons in Atoms

- The two atomic models are Bohr and wave mechanical. Whereas the Bohr model assumes electrons to be particles orbiting the nucleus in discrete paths, in wave mechanics we consider them to be wavelike and treat electron position in terms of a probability distribution.
- The energies of electrons are *quantized*—that is, only specific values of energy are allowed.
- The four electron quantum numbers are  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ . They specify, respectively, electron orbital size, orbital shape, number of electron orbitals, and spin moment.
- According to the Pauli exclusion principle, each electron state can accommodate no more than two electrons, which must have opposite spins.

### The Periodic Table

- Elements in each of the columns (or groups) of the periodic table have distinctive electron configurations. For example:  
     Group 0 elements (the inert gases) have filled electron shells.  
     Group IA elements (the alkali metals) have one electron greater than a filled electron shell.

### Bonding Forces and Energies

- *Bonding force* and *bonding energy* are related to one another according to Equations 2.5a and 2.5b.
- Attractive, repulsive, and net energies for two atoms or ions depend on interatomic separation per the schematic plot of Figure 2.10b.
- From a plot of interatomic separation versus force for two atoms/ions, the equilibrium separation corresponds to the value at zero force.
- From a plot of interatomic separation versus potential energy for two atoms/ions, the bonding energy corresponds to the energy value at the minimum of the curve.

### Primary Interatomic Bonds

- For ionic bonds, electrically charged ions are formed by the transference of valence electrons from one atom type to another.
- The attractive force between two isolated ions that have opposite charges may be computed using Equation 2.13.
- There is a sharing of valence electrons between adjacent atoms when bonding is covalent.
- Electron orbitals for some covalent bonds may overlap or hybridize. Hybridization of  $s$  and  $p$  orbitals to form  $sp^3$  and  $sp^2$  orbitals in carbon was discussed. Configurations of these hybrid orbitals were also noted.
- With metallic bonding, the valence electrons form a “sea of electrons” that is uniformly dispersed around the metal ion cores and acts as a form of glue for them.

### Secondary Bonding or van der Waals Bonding

- Relatively weak van der Waals bonds result from attractive forces between electric dipoles, which may be induced or permanent.
- For hydrogen bonding, highly polar molecules form when hydrogen covalently bonds to a nonmetallic element such as fluorine.

**Mixed Bonding**

- In addition to van der Waals bonding and the three primary bonding types, covalent–ionic, covalent–metallic, and metallic–ionic mixed bonds exist.
- The percent ionic character (%IC) of a bond between two elements (A and B) depends on their electronegativities ( $X$ 's) according to Equation 2.16.

**Bonding Type–Material Classification Correlations**

- Correlations between bonding type and material class were noted:  
 Polymers—covalent  
 Metals—metallic  
 Ceramics—ionic/mixed ionic–covalent  
 Molecular solids—van der Waals  
 Semi-metals—mixed covalent–metallic  
 Intermetallics—mixed metallic–ionic

**Equation Summary**

Equation Number	Equation	Solving For	Page Number
2.5a	$E = \int F dr$	Potential energy between two atoms	29
2.5b	$F = \frac{dE}{dr}$	Force between two atoms	29
2.9	$E_A = -\frac{A}{r}$	Attractive energy between two atoms	30
2.11	$E_R = \frac{B}{r^n}$	Repulsive energy between two atoms	31
2.13	$F_A = \frac{1}{4\pi\epsilon_0 r^2} ( Z_1 e)( Z_2 e)$	Force of attraction between two isolated ions	33
2.16	$\%IC = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100$	Percent ionic character	41

**List of Symbols**

Symbol	Meaning
$A, B, n$	Material constants
$E$	Potential energy between two atoms/ions
$E_A$	Attractive energy between two atoms/ions
$E_R$	Repulsive energy between two atoms/ions
$e$	Electronic charge
$\epsilon_0$	Permittivity of a vacuum
$F$	Force between two atoms/ions
$r$	Separation distance between two atoms/ions
$X_A$	Electronegativity value of the more electronegative element for compound BA
$X_B$	Electronegativity value of the more electropositive element for compound BA
$Z_1, Z_2$	Valence values for ions 1 and 2

## Important Terms and Concepts

atomic mass unit (amu)	electron state	periodic table
atomic number ( $Z$ )	electropositive	polar molecule
atomic weight ( $A$ )	ground state	primary bond
Bohr atomic model	hydrogen bond	quantum mechanics
bonding energy	ionic bond	quantum number
coulombic force	isotope	secondary bond
covalent bond	metallic bond	valence electron
dipole (electric)	mole	van der Waals bond
electron configuration	Pauli exclusion principle	wave-mechanical model
electronegative		

## REFERENCES

Most of the material in this chapter is covered in college-level chemistry textbooks. Two are listed here as references.  
 Ebbing, D. D., S. D. Gammon, and R. O. Ragsdale, *Essentials of General Chemistry*, 2nd edition, Cengage Learning, Boston, MA, 2006.

Jespersen, N. D., and A. Hyslop, *Chemistry: The Molecular Nature of Matter*, 7th edition, Wiley, Hoboken, NJ, 2014.

## QUESTIONS AND PROBLEMS

### Fundamental Concepts

#### Electrons in Atoms

- 2.1 Cite the difference between *atomic mass* and *atomic weight*.
- 2.2 Silicon has three naturally occurring isotopes: 92.23% of  $^{28}\text{Si}$ , with an atomic weight of 27.9769 amu; 4.68% of  $^{29}\text{Si}$ , with an atomic weight of 28.9765 amu; and 3.09% of  $^{30}\text{Si}$ , with an atomic weight of 29.9738 amu. On the basis of these data, confirm that the average atomic weight of Si is 28.0854 amu.
- 2.3 Zinc has five naturally occurring isotopes: 48.63% of  $^{64}\text{Zn}$ , with an atomic weight of 63.929 amu; 27.90% of  $^{66}\text{Zn}$ , with an atomic weight of 65.926 amu; 4.10% of  $^{67}\text{Zn}$ , with an atomic weight of 66.927 amu; 18.75% of  $^{68}\text{Zn}$ , with an atomic weight of 67.925 amu; and 0.62% of  $^{70}\text{Zn}$ , with an atomic weight of 69.925 amu. Calculate the average atomic weight of Zn.
- 2.4 Indium has two naturally occurring isotopes:  $^{113}\text{In}$ , with an atomic weight of 112.904 amu, and  $^{115}\text{In}$ , with an atomic weight of 114.904 amu. If the average atomic weight for In is 114.818 amu, calculate the fraction-of-occurrences of these two isotopes.
- 2.5 (a) How many grams are there in one amu of a material?  
 (b) Mole, in the context of this book, is taken in units of gram-mole. On this basis, how many atoms are there in a pound-mole of a substance?
- 2.6 (a) Cite two important quantum-mechanical concepts associated with the Bohr model of the atom.  
 (b) Cite two important additional refinements that resulted from the wave-mechanical atomic model.
- 2.7 Relative to electrons and electron states, what does each of the four quantum numbers specify?
- 2.8 For the  $K$  shell, the four quantum numbers for each of the two electrons in the  $1s$  state, in the order of  $nlm, m_s$ , are  $100\frac{1}{2}$  and  $100(-\frac{1}{2})$ . Write the four quantum numbers for all of the electrons in the  $L$  and  $M$  shells, and note which correspond to the  $s$ ,  $p$ , and  $d$  subshells.
- 2.9 Give the electron configurations for the following ions:  $\text{P}^{5+}$ ,  $\text{P}^{3-}$ ,  $\text{Sn}^{4+}$ ,  $\text{Se}^{2-}$ ,  $\text{I}^-$ , and  $\text{Ni}^{2+}$ .
- 2.10 Potassium iodide (KI) exhibits predominantly ionic bonding. The  $\text{K}^+$  and  $\text{I}^-$  ions have electron structures that are identical to which two inert gases?

*Note:* In each chapter, most of the terms listed in the Important Terms and Concepts section are defined in the Glossary, which follows Appendix E. The other terms are important enough to warrant treatment in a full section of the text and can be found in the Contents or the Index.



## The Periodic Table

**2.11** With regard to electron configuration, what do all the elements in Group IIA of the periodic table have in common?

**2.12** To what group in the periodic table would an element with atomic number 112 belong?

**2.13** Without consulting Figure 2.8 or Table 2.2, determine whether each of the following electron configurations is an inert gas, a halogen, an alkali metal, an alkaline earth metal, or a transition metal. Justify your choices.

(a)  $1s^2 2s^2 2p^6 3s^2 3p^5$

(b)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

(c)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

(d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(e)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$

(f)  $1s^2 2s^2 2p^6 3s^2$

**2.14 (a)** What electron subshell is being filled for the rare earth series of elements on the periodic table?

**(b)** What electron subshell is being filled for the actinide series?

## Bonding Forces and Energies

**2.15** Calculate the force of attraction between a  $\text{Ca}^{2+}$  and an  $\text{O}^{2-}$  ion whose centers are separated by a distance of 1.25 nm.

**2.16** The atomic radii of  $\text{Mg}^{2+}$  and  $\text{F}^-$  ions are 0.072 and 0.133 nm, respectively.

**(a)** Calculate the force of attraction between these two ions at their equilibrium interionic separation (i.e., when the ions just touch one another).

**(b)** What is the force of repulsion at this same separation distance?

**2.17** The force of attraction between a divalent cation and a divalent anion is  $1.67 \times 10^{-8}$  N. If the ionic radius of the cation is 0.080 nm, what is the anion radius?

**2.18** The net potential energy between two adjacent ions,  $E_N$ , may be represented by the sum of Equations 2.9 and 2.11; that is,

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \quad (2.17)$$

Calculate the bonding energy  $E_0$  in terms of the parameters  $A$ ,  $B$ , and  $n$  using the following procedure:

**1.** Differentiate  $E_N$  with respect to  $r$ , and then set the resulting expression equal to zero, because the curve of  $E_N$  versus  $r$  is a minimum at  $E_0$ .

**2.** Solve for  $r$  in terms of  $A$ ,  $B$ , and  $n$ , which yields  $r_0$ , the equilibrium interionic spacing.

**3.** Determine the expression for  $E_0$  by substituting  $r_0$  into Equation 2.17.

**2.19** For an  $\text{Na}^+ - \text{Cl}^-$  ion pair, attractive and repulsive energies  $E_A$  and  $E_R$ , respectively, depend on the distance between the ions  $r$ , according to

$$E_A = -\frac{1.436}{r}$$

$$E_R = \frac{7.32 \times 10^{-6}}{r^8}$$

For these expressions, energies are expressed in electron volts per  $\text{Na}^+ - \text{Cl}^-$  pair, and  $r$  is the distance in nanometers. The net energy  $E_N$  is just the sum of the preceding two expressions.

**(a)** Superimpose on a single plot  $E_N$ ,  $E_R$ , and  $E_A$  versus  $r$  up to 1.0 nm.

**(b)** On the basis of this plot, determine (i) the equilibrium spacing  $r_0$  between the  $\text{Na}^+$  and  $\text{Cl}^-$  ions, and (ii) the magnitude of the bonding energy  $E_0$  between the two ions.

**(c)** Mathematically determine the  $r_0$  and  $E_0$  values using the solutions to Problem 2.18, and compare these with the graphical results from part (b).

**2.20** Consider a hypothetical  $\text{X}^+ - \text{Y}^-$  ion pair for which the equilibrium interionic spacing and bonding energy values are 0.38 nm and  $-5.37$  eV, respectively. If it is known that  $n$  in Equation 2.17 has a value of 8, using the results of Problem 2.18, determine explicit expressions for attractive and repulsive energies  $E_A$  and  $E_R$  of Equations 2.9 and 2.11.

**2.21** The net potential energy  $E_N$  between two adjacent ions is sometimes represented by the expression

$$E_N = -\frac{C}{r} + D \exp\left(-\frac{r}{\rho}\right) \quad (2.18)$$

in which  $r$  is the interionic separation and  $C$ ,  $D$ , and  $\rho$  are constants whose values depend on the specific material.

**(a)** Derive an expression for the bonding energy  $E_0$  in terms of the equilibrium interionic separation  $r_0$  and the constants  $D$  and  $\rho$  using the following procedure:

**(i)** Differentiate  $E_N$  with respect to  $r$ , and set the resulting expression equal to zero.

- (ii) Solve for  $C$  in terms of  $D$ ,  $\rho$ , and  $r_0$ .
- (iii) Determine the expression for  $E_0$  by substitution for  $C$  in Equation 2.18.
- (b) Derive another expression for  $E_0$  in terms of  $r_0$ ,  $C$ , and  $\rho$  using a procedure analogous to the one outlined in part (a).

### Primary Interatomic Bonds

- 2.22 (a)** Briefly cite the main differences among ionic, covalent, and metallic bonding.
- (b)** State the Pauli exclusion principle.
- 2.23** Make a plot of bonding energy versus melting temperature for the metals listed in Table 2.3. Using this plot, approximate the bonding energy for molybdenum, which has a melting temperature of 2617°C.

### Secondary Bonding or van der Waals Bonding

- 2.24** Explain why hydrogen fluoride (HF) has a higher boiling temperature than hydrogen chloride (HCl) (19.4°C vs. -85°C), even though HF has a lower molecular weight.

### Mixed Bonding

- 2.25** Compute the %IC of the interatomic bond for each of the following compounds: MgO, GaP, CsF, CdS, and FeO.
- 2.26 (a)** Calculate the %IC of the interatomic bonds for the intermetallic compound  $\text{Al}_6\text{Mn}$ .
- (b)** On the basis of this result, what type of interatomic bonding would you expect to be found in  $\text{Al}_6\text{Mn}$ ?

### Bonding Type–Material Classification Correlations

- 2.27** What type(s) of bonding would be expected for each of the following materials: solid xenon, calcium fluoride ( $\text{CaF}_2$ ), bronze, cadmium telluride ( $\text{CdTe}$ ), rubber, and tungsten?

### Spreadsheet Problems

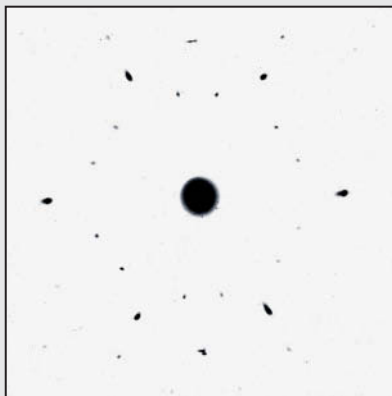
- 2.1SS** Generate a spreadsheet that allows the user to input values of  $A$ ,  $B$ , and  $n$  (Equation 2.17) and then does the following:
  - (a)** Plots on a graph of potential energy versus interatomic separation for two atoms/ions, curves for attractive ( $E_A$ ), repulsive ( $E_R$ ), and net ( $E_N$ ) energies.
  - (b)** Determines the equilibrium spacing ( $r_0$ ) and the bonding energy ( $E_0$ ).
- 2.2SS** Generate a spreadsheet that computes the %IC of a bond between atoms of two elements, once the user has input values for the elements' electronegativities.

## FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

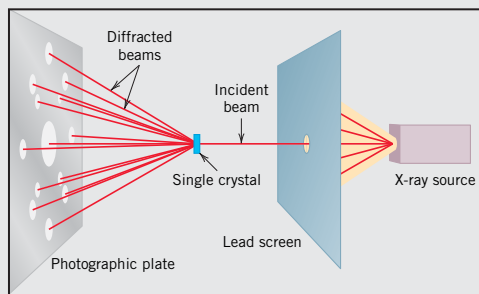
- 2.1FE** Which of the following electron configurations is for an inert gas?
  - (A)  $1s^2 2s^2 2p^6 3s^2 3p^6$
  - (B)  $1s^2 2s^2 2p^6 3s^2$
  - (C)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
  - (D)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
- 2.2FE** What type(s) of bonding would be expected for brass (a copper–zinc alloy)?
  - (A) Ionic bonding
  - (B) Metallic bonding
  - (C) Covalent bonding with some van der Waals bonding
  - (D) van der Waals bonding
- 2.3FE** What type(s) of bonding would be expected for rubber?
  - (A) Ionic bonding
  - (B) Metallic bonding
  - (C) Covalent bonding with some van der Waals bonding
  - (D) van der Waals bonding

# Chapter 3 Structures of Metals and Ceramics

Courtesy of J. G. Byrne

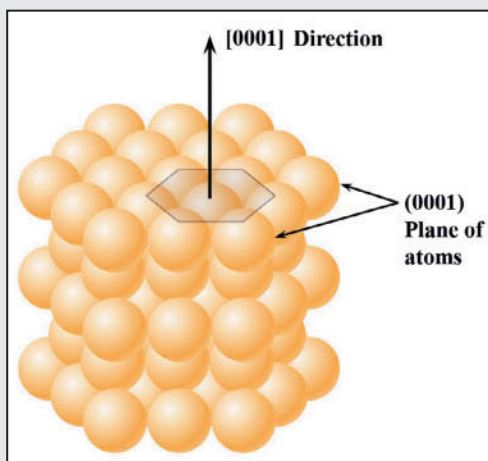


(a)

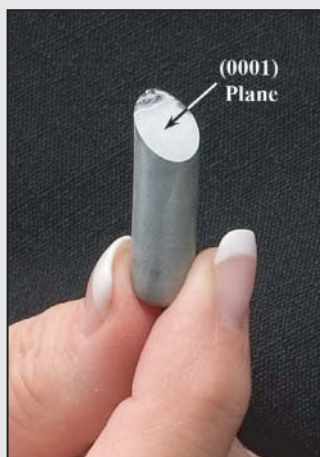


(b)

(a) X-ray diffraction photograph [or Laue photograph (Section 3.20)] for a single crystal of magnesium. (b) Schematic diagram illustrating how the spots (i.e., the diffraction pattern) in (a) are produced. The lead screen blocks out all beams generated from the x-ray source, except for a narrow beam traveling in a single direction. This incident beam is diffracted by individual crystallographic planes in the single crystal (having different orientations), which gives rise to the various diffracted beams that impinge on the photographic plate. Intersections of these beams with the plate appear as spots when the film is developed. The large spot in the center of (a) is from the incident beam, which is parallel to a  $[0001]$  crystallographic direction. It should be noted that the hexagonal symmetry of magnesium's hexagonal close-packed crystal structure



(c)



(d)

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[shown in (c)] is indicated by the diffraction spot pattern that was generated.

(d) Photograph of a single crystal of magnesium that was cleaved (or split) along a  $(0001)$  plane—the flat surface is a  $(0001)$  plane. Also, the direction perpendicular to this plane is a  $[0001]$  direction.

(e) Photograph of a mag wheel—a light-weight automobile wheel made of magnesium.

iStockphoto



(e)

[Figure (b) from J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Copyright © 2004 by John Wiley & Sons, Hoboken, NJ. Reprinted by permission of John Wiley & Sons, Inc.]

## WHY STUDY *Structures of Metals and Ceramics*?

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 8.5).

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. Sketch/describe unit cells for sodium chloride, cesium chloride, zinc blende, diamond cubic, fluorite, and perovskite crystal structures. Do likewise for the atomic structures of graphite and a silica glass.
6. Given the chemical formula for a ceramic compound and the ionic radii of its component ions, predict the crystal structure.
7. Given three direction index integers, sketch the direction corresponding to these indices within a unit cell.
8. Specify the Miller indices for a plane that has been drawn within a unit cell.
9. Describe how face-centered cubic and hexagonal close-packed crystal structures may be generated by the stacking of close-packed planes of atoms. Do the same for the sodium chloride crystal structure in terms of close-packed planes of anions.
10. Distinguish between single crystals and polycrystalline materials.
11. 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 structures 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. Crystal structures found in both metals and ceramics are then detailed, along with the scheme by which crystallographic points, directions, and planes are expressed. Single crystals, polycrystalline materials, and noncrystalline materials are considered. Another section of this chapter briefly describes how crystal structures are determined experimentally using x-ray diffraction techniques.

## Crystal Structures

### 3.2 FUNDAMENTAL CONCEPTS

#### crystalline

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 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.

### crystal structure

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 and ceramic crystal structures. The next chapter is devoted to structures of polymers.

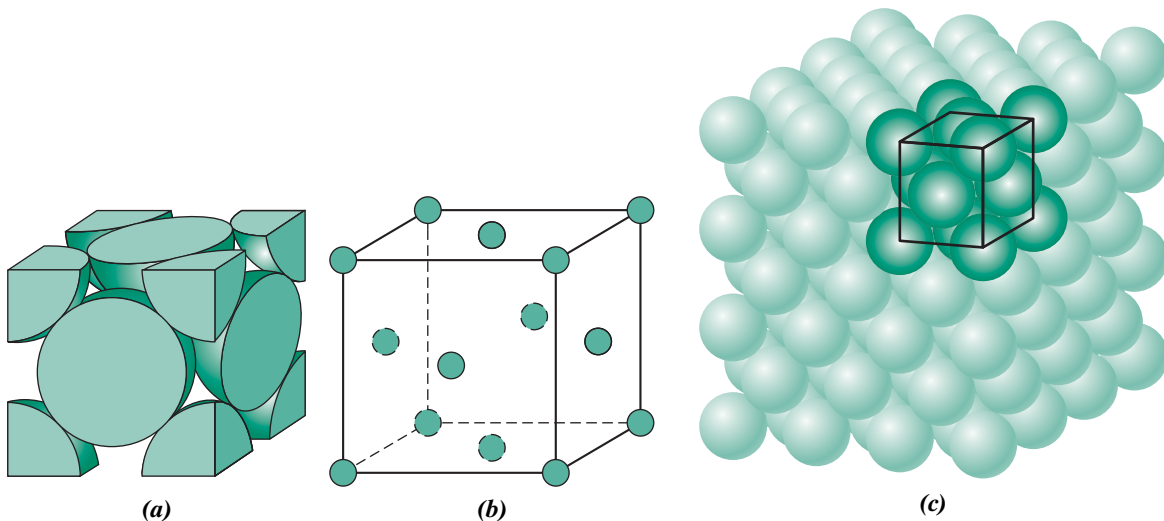
### lattice

When crystalline structures are described, 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 3.1c. 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

### unit cell

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 repeating entities called **unit cells**. Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn



**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.]

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 minimal 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, when we use 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

face-centered cubic  
(FCC)



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Crystal Systems and  
Unit Cells for Metals

Unit cell edge length  
for face-centered  
cubic

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 on 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 in Example Problem 3.1.

**Table 3.1**  
Atomic Radii and  
Crystal Structures for  
16 Metals

<i>Metal</i>	<i>Crystal Structure<sup>a</sup></i>	<i>Atomic Radius<sup>b</sup> (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 ( $\alpha$ )	HCP	0.1445
Iron ( $\alpha$ )	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

<sup>a</sup>FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

<sup>b</sup>A nanometer (nm) equals  $10^{-9}$  m; to convert from nanometers to angstrom units ( $\text{\AA}$ ), multiply the nanometer value by 10.



On occasion, we need to determine the number of atoms associated with each unit cell. Depending on an atom's location, it may be considered to be shared with adjacent unit cells—that is, only some fraction of the atom is assigned to a specific cell. For example, for cubic unit cells, an atom completely within the interior “belongs” to that unit cell, one at a cell face is shared with one other cell, and an atom residing at a corner is shared among eight. The number of atoms per unit cell,  $N$ , can be computed using the following formula:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \quad (3.2)$$

where

$N_i$  = the number of interior atoms

$N_f$  = the number of face atoms

$N_c$  = the number of corner atoms

### WileyPLUS

#### Tutorial Video:

FCC Unit Cell  
Calculations

For the FCC crystal structure, there are eight corner atoms ( $N_c = 8$ ), six face atoms ( $N_f = 6$ ), and no interior atoms ( $N_i = 0$ ). Thus, from Equation 3.2,

$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$

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 is composed of the volume of the cube that 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 does not alter the cell structure.

coordination number  
atomic packing  
factor (APF)

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 (not shown).

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,

Definition of atomic  
packing factor

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} \quad (3.3)$$

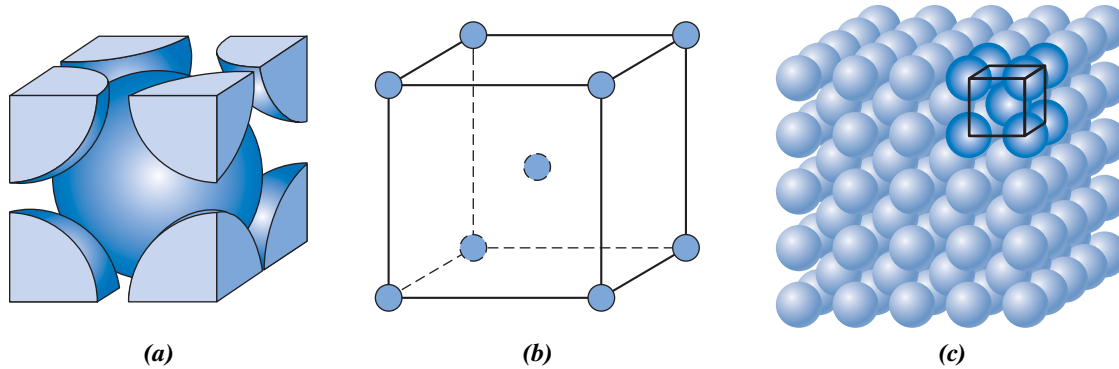
For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter. Computation of this APF is also included as an example problem. Metals typically have relatively large atomic packing factors to maximize the shielding provided by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

## The Body-Centered Cubic Crystal Structure

body-centered cubic  
(BCC)

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





**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.]

and corner atoms touch one another along cube diagonals, and unit cell length  $a$  and atomic radius  $R$  are related through

$$a = \frac{4R}{\sqrt{3}} \quad (3.4)$$

Unit cell edge length  
for body-centered  
cubic



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

Each BCC unit cell has eight corner atoms and a single center atom, which is wholly contained within its cell; therefore, from Equation 3.2, the number of atoms per BCC unit cell is

$$\begin{aligned} N &= N_i + \frac{N_f}{2} + \frac{N_c}{8} \\ &= 1 + 0 + \frac{8}{8} = 2 \end{aligned}$$

**WileyPLUS**

**Tutorial Video:**  
BCC Unit Cell  
Calculations

The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms. Because the coordination number is less for BCC than for FCC, the atomic packing factor is also lower for BCC—0.68 versus 0.74.

It is also possible to have a unit cell that consists of atoms situated only at the corners of a cube. This is called the *simple cubic (SC) crystal structure*; hard-sphere and reduced-sphere models are shown, respectively, in Figures 3.3a and 3.3b. None of the metallic elements have this crystal structure because of its relatively low atomic packing factor (see Concept Check 3.1). The only simple-cubic element is polonium, which is considered to be a metalloid (or semi-metal).

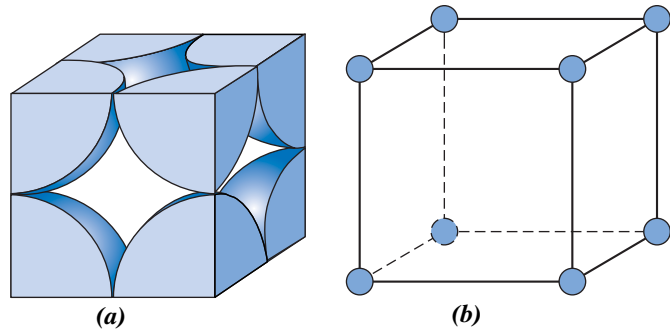
### The Hexagonal Close-Packed Crystal Structure

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 3.4a 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 3.4b.<sup>1</sup> The top and bottom

hexagonal close-  
packed (HCP)

<sup>1</sup>Alternatively, the unit cell for HCP may be specified in terms of the parallelepiped defined by the atoms labeled A through H in Figure 3.4a. Thus, the atom denoted J lies within the unit cell interior.

**Figure 3.3** For the simple cubic crystal structure, (a) a hard-sphere unit cell, and (b) a reduced-sphere unit cell.



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Crystal Systems and  
Unit Cells for Metals

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.

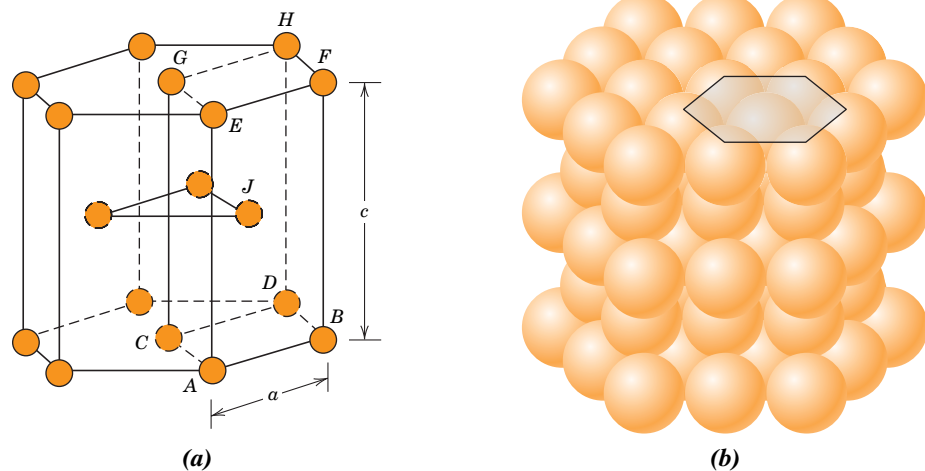
In order to compute the number of atoms per unit cell for the HCP crystal structure, Equation 3.2 is modified to read as follows:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6} \quad (3.5)$$

That is, one-sixth of each corner atom is assigned to a unit cell (instead of 8 as with the cubic structure). Because for HCP there are 6 corner atoms in each of the top and bottom faces (for a total of 12 corner atoms), 2 face center atoms (one from each of the top and bottom faces), and 3 midplane interior atoms, the value of  $N$  for HCP is found, using Equation 3.5, to be

$$N = 3 + \frac{2}{2} + \frac{12}{6} = 6$$

Thus, 6 atoms are assigned to each unit cell.



**Figure 3.4** 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.]

If  $a$  and  $c$  represent, respectively, the short and long unit cell dimensions of Figure 3.4a, 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.

### EXAMPLE PROBLEM 3.1

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#### Determination of FCC Unit Cell Volume

Tutorial Video

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  $4R$ . Because 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,

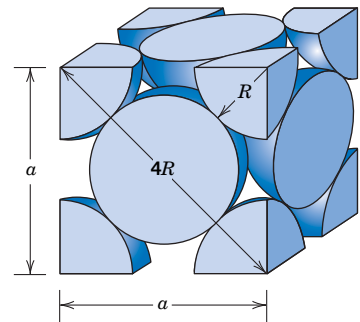
$$a^2 + a^2 = (4R)^2$$

or, solving for  $a$ ,

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

The FCC unit cell volume  $V_C$  may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \quad (3.6)$$



### EXAMPLE PROBLEM 3.2

WileyPLUS

#### Computation of the Atomic Packing Factor for FCC

Tutorial Video

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 atom 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 because there are four atoms per FCC unit cell, the total FCC atom (or 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

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

**Concept Check 3.1**

- (a) What is the coordination number for the simple-cubic crystal structure?  
 (b) Calculate the atomic packing factor for simple cubic.

(The answer is available in *WileyPLUS*.)

**EXAMPLE PROBLEM 3.3****Determination of HCP Unit Cell Volume**

- (a) Calculate the volume of an HCP unit cell in terms of its  $a$  and  $c$  lattice parameters.  
 (b) Now provide an expression for this volume in terms of the atomic radius,  $R$ , and the  $c$  lattice parameter.

**Solution**

- (a) We use the adjacent reduced-sphere HCP unit cell to solve this problem.

Now, the unit cell volume is just the product of the base area times the cell height,  $c$ . This base area is just three times the area of the parallelepiped  $ACDE$  shown below. (This  $ACDE$  parallelepiped is also labeled in the above unit cell.)

The area of  $ACDE$  is just the length of  $\overline{CD}$  times the height  $\overline{BC}$ . But  $\overline{CD}$  is just  $a$ , and  $\overline{BC}$  is equal to

$$\overline{BC} = a \cos(30^\circ) = \frac{a\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(a)\left(\frac{a\sqrt{3}}{2}\right) = \frac{3a^2\sqrt{3}}{2}$$

Again, the unit cell volume  $V_C$  is just the product of the AREA and  $c$ ; thus,

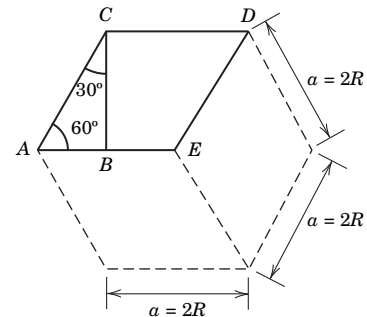
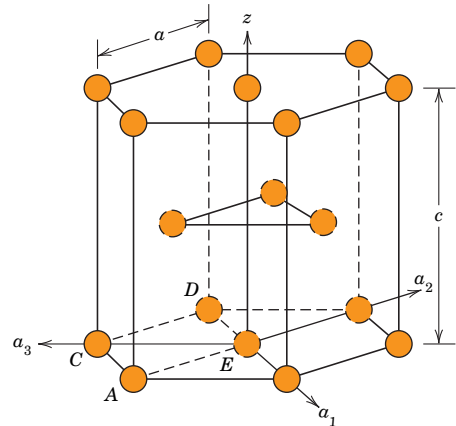
$$\begin{aligned} V_C &= \text{AREA}(c) \\ &= \left(\frac{3a^2\sqrt{3}}{2}\right)(c) \\ &= \frac{3a^2c\sqrt{3}}{2} \end{aligned} \quad (3.7a)$$

- (b) For this portion of the problem, all we need do is realize that the lattice parameter  $a$  is related to the atomic radius  $R$  as

$$a = 2R$$

Now making this substitution for  $a$  in Equation 3.7a gives

$$\begin{aligned} V_C &= \frac{3(2R)^2c\sqrt{3}}{2} \\ &= 6R^2c\sqrt{3} \end{aligned} \quad (3.7b)$$



### 3.5 DENSITY COMPUTATIONS—METALS

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

Theoretical density  
for metals

$$\rho = \frac{nA}{V_C N_A} \quad (3.8)$$

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 ( $6.022 \times 10^{23}$  atoms/mol)

#### EXAMPLE PROBLEM 3.4

##### Theoretical Density Computation for Copper

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

##### Solution

Equation 3.8 is employed in the solution of this problem. Because the crystal structure is FCC,  $n$ , the number of atoms per unit cell, is 4. Furthermore, the atomic weight  $A_{\text{Cu}}$  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 3.8 yields

$$\begin{aligned} \rho &= \frac{nA_{\text{Cu}}}{V_C N_A} = \frac{nA_{\text{Cu}}}{(16R^3\sqrt{2})N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.022 \times 10^{23} \text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3 \end{aligned}$$

The literature value for the density of copper is  $8.94 \text{ g/cm}^3$ , which is in very close agreement with the foregoing result.

### 3.6 CERAMIC CRYSTAL STRUCTURES

Because ceramics are composed of at least two elements and often more, their crystal structures are generally more complex than those of metals. The atomic bonding in these materials ranges from purely ionic to totally covalent; many ceramics exhibit a combination of these two bonding types, the degree of ionic character being dependent on the electronegativities of the atoms. Table 3.2 presents the percent ionic character for several common ceramic materials; these values were determined using Equation 2.16 and the electronegativities in Figure 2.9.

For those ceramic materials for which the atomic bonding is predominantly ionic, the crystal structures may be thought of as being composed of electrically charged ions instead of atoms. The metallic ions, or **cations**, are positively charged because they have given up their valence electrons to the nonmetallic ions, or **anions**, which are negatively charged. Two characteristics of the component ions in crystalline ceramic materials influence the crystal structure: the magnitude of the electrical charge on each of the component ions, and the relative sizes of the cations and anions. With regard to the first characteristic,

cation  
anion

**Table 3.2**

Percent Ionic Character of the Interatomic Bonds for Several Ceramic Materials

<i>Material</i>	<i>Percent Ionic Character</i>
CaF <sub>2</sub>	89
MgO	73
NaCl	67
Al <sub>2</sub> O <sub>3</sub>	63
SiO <sub>2</sub>	51
Si <sub>3</sub> N <sub>4</sub>	30
ZnS	18
SiC	12

the crystal must be electrically neutral; that is, all the cation positive charges must be balanced by an equal number of anion negative charges. The chemical formula of a compound indicates the ratio of cations to anions, or the composition that achieves this charge balance. For example, in calcium fluoride, each calcium ion has a +2 charge ( $\text{Ca}^{2+}$ ), and associated with each fluorine ion is a single negative charge ( $\text{F}^-$ ). Thus, there must be twice as many  $\text{F}^-$  as  $\text{Ca}^{2+}$  ions, which is reflected in the chemical formula  $\text{CaF}_2$ .

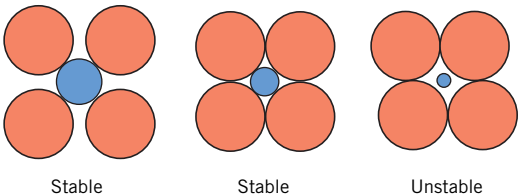
The second criterion involves the sizes or ionic radii of the cations and anions,  $r_C$  and  $r_A$ , respectively. Because the metallic elements give up electrons when ionized, cations are ordinarily smaller than anions, and, consequently, the ratio  $r_C/r_A$  is less than unity. Each cation prefers to have as many nearest-neighbor anions as possible. The anions also desire a maximum number of cation nearest neighbors.

Stable ceramic crystal structures form when those anions surrounding a cation are all in contact with that cation, as illustrated in Figure 3.5. The coordination number (i.e., number of anion nearest neighbors for a cation) is related to the cation–anion radius ratio. For a specific coordination number, there is a critical or minimum  $r_C/r_A$  ratio for which this cation–anion contact is established (Figure 3.5); this ratio may be determined from pure geometrical considerations (see Example Problem 3.5).

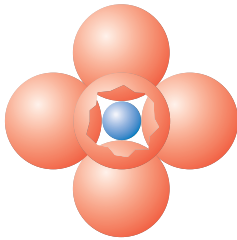
The coordination numbers and nearest-neighbor geometries for various  $r_C/r_A$  ratios are presented in Table 3.3. For  $r_C/r_A$  ratios less than 0.155, the very small cation is bonded to two anions in a linear manner. If  $r_C/r_A$  has a value between 0.155 and 0.225, the coordination number for the cation is 3. This means each cation is surrounded by three anions in the form of a planar equilateral triangle, with the cation located in the center. The coordination number is 4 for  $r_C/r_A$  between 0.225 and 0.414; the cation is located at the center of a tetrahedron, with anions at each of the four corners. For  $r_C/r_A$  between 0.414 and 0.732, the cation may be thought of as being situated at the center of an octahedron surrounded by six anions, one at each corner, as also shown in the table. The coordination number is 8 for  $r_C/r_A$  between 0.732 and 1.0, with anions at all corners of a cube and a cation positioned at the center. For a radius ratio greater than unity, the coordination number is 12. The most common coordination numbers for ceramic materials are 4, 6, and 8. Table 3.4 gives the ionic radii for several anions and cations that are common in ceramic materials.

The relationships between coordination number and cation–anion radius ratios (as noted in Table 3.3) are based on geometrical considerations and assuming “hard-sphere” ions; therefore, these relationships are only approximate, and there are exceptions.

**Figure 3.5** Stable and unstable anion–cation coordination configurations. Red circles represent anions; blue circles denote cations.



**Table 3.3**  
Coordination  
Numbers and  
Geometries for  
Various Cation–Anion  
Radius Ratios ( $r_C/r_A$ )

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	$<0.155$	
3	$0.155\text{--}0.225$	
4	$0.225\text{--}0.414$	
6	$0.414\text{--}0.732$	
8	$0.732\text{--}1.0$	

**Source:** W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

For example, some ceramic compounds with  $r_C/r_A$  ratios greater than 0.414 in which the bonding is highly covalent (and directional) have a coordination number of 4 (instead of 6).

The size of an ion depends on several factors. One of these is coordination number: ionic radius tends to increase as the number of nearest-neighbor ions of opposite charge increases. Ionic radii given in Table 3.4 are for a coordination number of 6. Therefore, the radius is greater for a coordination number of 8 and less when the coordination number is 4.

In addition, the charge on an ion will influence its radius. For example, from Table 3.4, the radii for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are 0.077 and 0.069 nm, respectively, which values may be contrasted to the radius of an iron atom—0.124 nm. When an electron is removed from an atom or ion, the remaining valence electrons become more tightly bound to the nucleus, which results in a decrease in ionic radius. Conversely, ionic size increases when electrons are added to an atom or ion.

**Table 3.4**

Ionic Radii for Several  
Cations and Anions  
for a Coordination  
Number of 6

Cation	Ionic Radius (nm)	Anion	Ionic Radius (nm)
Al <sup>3+</sup>	0.053	Br <sup>-</sup>	0.196
Ba <sup>2+</sup>	0.136	Cl <sup>-</sup>	0.181
Ca <sup>2+</sup>	0.100	F <sup>-</sup>	0.133
Cs <sup>+</sup>	0.170	I <sup>-</sup>	0.220
Fe <sup>2+</sup>	0.077	O <sup>2-</sup>	0.140
Fe <sup>3+</sup>	0.069	S <sup>2-</sup>	0.184
K <sup>+</sup>	0.138		
Mg <sup>2+</sup>	0.072		
Mn <sup>2+</sup>	0.067		
Na <sup>+</sup>	0.102		
Ni <sup>2+</sup>	0.069		
Si <sup>4+</sup>	0.040		
Ti <sup>4+</sup>	0.061		

**EXAMPLE PROBLEM 3.5**

**Computation of Minimum Cation-to-Anion Radius Ratio for a Coordination Number of 3**

Show that the minimum cation-to-anion radius ratio for the coordination number 3 is 0.155.

**Solution**

For this coordination, the small cation is surrounded by three anions to form an equilateral triangle as shown here, triangle  $ABC$ ; the centers of all four ions are coplanar.

This boils down to a relatively simple plane trigonometry problem. Consideration of the right triangle  $APO$  makes it clear that the side lengths are related to the anion and cation radii  $r_A$  and  $r_C$  as

$$\overline{AP} = r_A$$

and

$$\overline{AO} = r_A + r_C$$

Furthermore, the side length ratio  $\overline{AP}/\overline{AO}$  is a function of the angle  $\alpha$  as

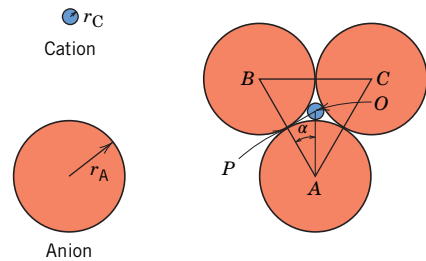
$$\frac{\overline{AP}}{\overline{AO}} = \cos \alpha$$

The magnitude of  $\alpha$  is  $30^\circ$  because line  $\overline{AO}$  bisects the  $60^\circ$  angle  $BAC$ . Thus,

$$\frac{\overline{AP}}{\overline{AO}} = \frac{r_A}{r_A + r_C} = \cos 30^\circ = \frac{\sqrt{3}}{2}$$

Solving for the cation–anion radius ratio, we have

$$\frac{r_C}{r_A} = \frac{1 - \sqrt{3}/2}{\sqrt{3}/2} = 0.155$$





## AX-Type Crystal Structures

Some of the common ceramic materials are those in which there are equal numbers of cations and anions. These are often referred to as AX compounds, where A denotes the cation and X the anion. There are several different crystal structures for AX compounds; each is typically named after a common material that assumes the particular structure.

### Rock Salt Structure



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Perhaps the most common AX crystal structure is the *sodium chloride* (NaCl), or *rock salt*, type. The coordination number for both cations and anions is 6, and therefore the cation–anion radius ratio is between approximately 0.414 and 0.732. A unit cell for this crystal structure (Figure 3.6) is generated from an FCC arrangement of anions with one cation situated at the cube center and one at the center of each of the 12 cube edges. An equivalent crystal structure results from a face-centered arrangement of cations. Thus, the rock salt crystal structure may be thought of as two interpenetrating FCC lattices—one composed of the cations, the other of anions. Some common ceramic materials that form with this crystal structure are NaCl, MgO, MnS, LiF, and FeO.

### Cesium Chloride Structure



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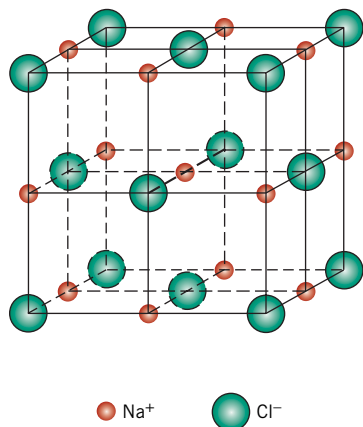
Figure 3.7 shows a unit cell for the *cesium chloride* (CsCl) crystal structure; the coordination number is 8 for both ion types. The anions are located at each of the corners of a cube, whereas the cube center is a single cation. Interchange of anions with cations, and vice versa, produces the same crystal structure. This is *not* a BCC crystal structure because ions of two different kinds are involved.

### Zinc Blende Structure

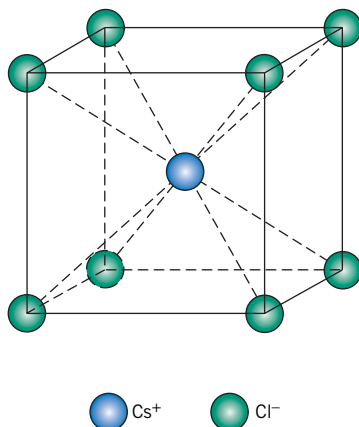


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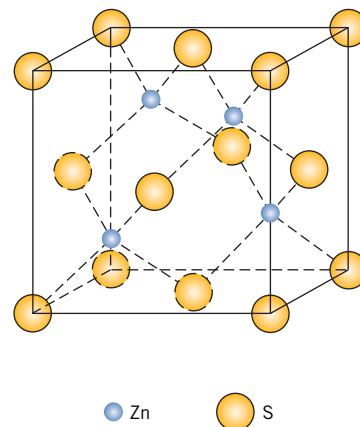
A third AX structure is one in which the coordination number is 4; that is, all ions are tetrahedrally coordinated. This is called the *zinc blende*, or *sphalerite*, structure, after the mineralogical term for zinc sulfide (ZnS). A unit cell is presented in Figure 3.8; all corner and face positions of the cubic cell are occupied by S atoms, whereas the Zn atoms fill interior tetrahedral positions. An equivalent structure results if Zn and S atom positions are reversed. Thus, each Zn atom is bonded to four S atoms, and vice versa.



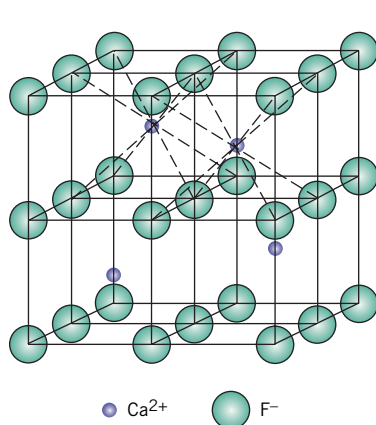
**Figure 3.6** A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.



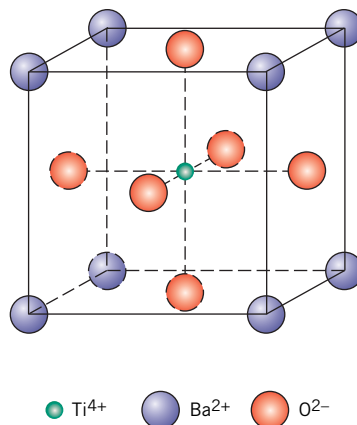
**Figure 3.7** A unit cell for the cesium chloride (CsCl) crystal structure.



**Figure 3.8** A unit cell for the zinc blende (ZnS) crystal structure.



**Figure 3.9** A unit cell for the fluorite ( $\text{CaF}_2$ ) crystal structure.



**Figure 3.10** A unit cell for the perovskite crystal structure.

Most often the atomic bonding is highly covalent in compounds exhibiting this crystal structure (Table 3.2), which include  $\text{ZnS}$ ,  $\text{ZnTe}$ , and  $\text{SiC}$ .

### $A_mX_p$ -Type Crystal Structures



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If the charges on the cations and anions are not the same, a compound can exist with the chemical formula  $A_mX_p$ , where  $m$  and/or  $p \neq 1$ . An example is  $\text{AX}_2$ , for which a common crystal structure is found in *fluorite* ( $\text{CaF}_2$ ). The ionic radius ratio  $r_C/r_A$  for  $\text{CaF}_2$  is about 0.8, which, according to Table 3.3, gives a coordination number of 8. Calcium ions are positioned at the centers of cubes, with fluorine ions at the corners. The chemical formula shows that there are only half as many  $\text{Ca}^{2+}$  ions as  $\text{F}^-$  ions, and therefore the crystal structure is similar to  $\text{CsCl}$  (Figure 3.7), except that only half the center cube positions are occupied by  $\text{Ca}^{2+}$  ions. One unit cell consists of eight cubes, as indicated in Figure 3.9. Other compounds with this crystal structure include  $\text{ZrO}_2$  (cubic),  $\text{UO}_2$ ,  $\text{PuO}_2$ , and  $\text{ThO}_2$ .

### $A_mB_nX_p$ -Type Crystal Structures



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It is also possible for ceramic compounds to have more than one type of cation; for two types of cations (represented by A and B), their chemical formula may be designated as  $A_mB_nX_p$ . Barium titanate ( $\text{BaTiO}_3$ ), having both  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  cations, falls into this classification. This material has a *perovskite crystal structure* and rather interesting electromechanical properties to be discussed later. At temperatures above  $120^\circ\text{C}$  ( $248^\circ\text{F}$ ), the crystal structure is cubic. A unit cell of this structure is shown in Figure 3.10;  $\text{Ba}^{2+}$  ions are situated at all eight corners of the cube, and a single  $\text{Ti}^{4+}$  is at the cube center, with  $\text{O}^{2-}$  ions located at the center of each of the six faces.

Table 3.5 summarizes the rock salt, cesium chloride, zinc blende, fluorite, and perovskite crystal structures in terms of cation–anion ratios and coordination numbers and gives examples for each. Of course, many other ceramic crystal structures are possible.

## EXAMPLE PROBLEM 3.6

### Ceramic Crystal Structure Prediction

On the basis of ionic radii (Table 3.4), what crystal structure do you predict for  $\text{FeO}$ ?

**Table 3.5** Summary of Some Common Ceramic Crystal Structures

Structure Name	Structure Type	Anion Packing	Coordination Number		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX <sub>2</sub>	Simple cubic	8	4	CaF <sub>2</sub> , UO <sub>2</sub> , ThO <sub>2</sub>
Perovskite	ABX <sub>3</sub>	FCC	12 (A) 6 (B)	6	BaTiO <sub>3</sub> , SrZrO <sub>3</sub> , SrSnO <sub>3</sub>
Spinel	AB <sub>2</sub> X <sub>4</sub>	FCC	4 (A) 6 (B)	4	MgAl <sub>2</sub> O <sub>4</sub> , FeAl <sub>2</sub> O <sub>4</sub>

**Source:** W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

### Solution

First, note that FeO is an AX-type compound. Next, determine the cation–anion radius ratio, which from Table 3.4 is

$$\frac{r_{\text{Fe}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.077 \text{ nm}}{0.140 \text{ nm}} = 0.550$$

This value lies between 0.414 and 0.732, and, therefore, from Table 3.3 the coordination number for the Fe<sup>2+</sup> ion is 6; this is also the coordination number of O<sup>2−</sup> because there are equal numbers of cations and anions. The predicted crystal structure is rock salt, which is the AX crystal structure having a coordination number of 6, as given in Table 3.5.



**Concept Check 3.2** Table 3.4 gives the ionic radii for K<sup>+</sup> and O<sup>2−</sup> as 0.138 and 0.140 nm, respectively.

- What is the coordination number for each O<sup>2−</sup> ion?
- Briefly describe the resulting crystal structure for K<sub>2</sub>O.
- Explain why this is called the *antifluorite structure*.

(The answer is available in *WileyPLUS*.)

## 3.7 DENSITY COMPUTATIONS—CERAMICS

It is possible to compute the theoretical density of a crystalline ceramic material from unit cell data in a manner similar to that described in Section 3.5 for metals. In this case the density  $\rho$  may be determined using a modified form of Equation 3.8, as follows:

Theoretical density  
for ceramic materials

$$\rho = \frac{n'(\sum A_C + \sum A_A)}{V_C N_A} \quad (3.9)$$

where

$n'$  = the number of formula units within the unit cell<sup>2</sup>

$\Sigma A_C$  = the sum of the atomic weights of all cations in the formula unit

$\Sigma A_A$  = the sum of the atomic weights of all anions in the formula unit

$V_C$  = the unit cell volume

$N_A$  = Avogadro's number,  $6.022 \times 10^{23}$  formula units/mol

### EXAMPLE PROBLEM 3.7

#### Theoretical Density Calculation for Sodium Chloride

On the basis of the crystal structure, compute the theoretical density for sodium chloride. How does this compare with its measured density?

#### Solution

The theoretical density may be determined using Equation 3.9, where  $n'$ , the number of NaCl units per unit cell, is 4 because both sodium and chloride ions form FCC lattices. Furthermore,

$$\Sigma A_C = A_{\text{Na}} = 22.99 \text{ g/mol}$$

$$\Sigma A_A = A_{\text{Cl}} = 35.45 \text{ g/mol}$$

Because the unit cell is cubic,  $V_C = a^3$ ,  $a$  being the unit cell edge length. For the face of the cubic unit cell shown in the accompanying figure,

$$a = 2r_{\text{Na}^+} + 2r_{\text{Cl}^-}$$

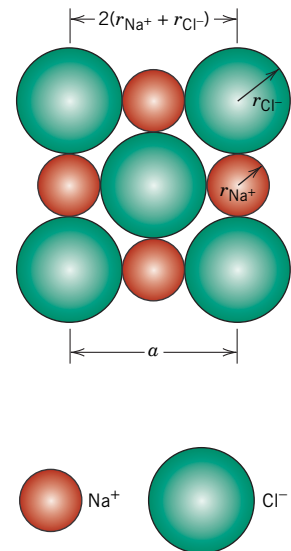
$r_{\text{Na}^+}$  and  $r_{\text{Cl}^-}$  being the sodium and chlorine ionic radii, respectively, given in Table 3.4 as 0.102 and 0.181 nm. Thus,

$$V_C = a^3 = (2r_{\text{Na}^+} + 2r_{\text{Cl}^-})^3$$

Finally,

$$\begin{aligned} \rho &= \frac{n'(A_{\text{Na}} + A_{\text{Cl}})}{(2r_{\text{Na}^+} + 2r_{\text{Cl}^-})^3 N_A} \\ &= \frac{4(22.99 + 35.45)}{[2(0.102 \times 10^{-7}) + 2(0.181 \times 10^{-7})]^3 (6.022 \times 10^{23})} \\ &= 2.14 \text{ g/cm}^3 \end{aligned}$$

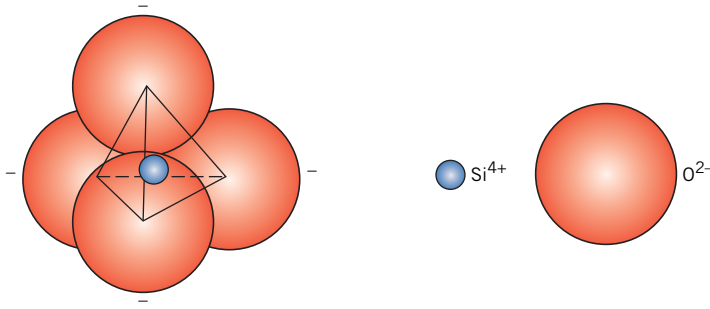
This result compares very favorably with the experimental value of 2.16 g/cm<sup>3</sup>.



## 3.8 SILICATE CERAMICS

*Silicates* are materials composed primarily of silicon and oxygen, the two most abundant elements in Earth's crust; consequently, the bulk of soils, rocks, clays, and sand come under the silicate classification. Rather than characterizing the crystal structures of these

<sup>2</sup>By *formula unit* we mean all the ions that are included in the chemical formula unit. For example, for BaTiO<sub>3</sub>, a formula unit consists of one barium ion, one titanium ion, and three oxygen ions.



**Figure 3.11** A silicon–oxygen ( $\text{SiO}_4^{4-}$ ) tetrahedron.

materials in terms of unit cells, it is more convenient to use various arrangements of an  $\text{SiO}_4^{4-}$  tetrahedron (Figure 3.11). Each atom of silicon is bonded to four oxygen atoms, which are situated at the corners of the tetrahedron; the silicon atom is positioned at the center. Because this is the basic unit of the silicates, it is often treated as a negatively charged entity.

Often the silicates are not considered to be ionic because there is a significant covalent character to the interatomic Si–O bonds (Table 3.2), which are directional and relatively strong. Regardless of the character of the Si–O bond, a  $-4$  charge is associated with every  $\text{SiO}_4^{4-}$  tetrahedron because each of the four oxygen atoms requires an extra electron to achieve a stable electronic structure. Various silicate structures arise from the different ways in which the  $\text{SiO}_4^{4-}$  units can be combined into one-, two-, and three-dimensional arrangements.

### Silica

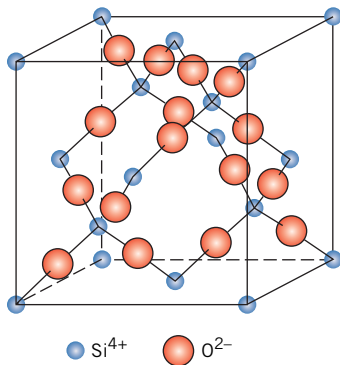
Chemically, the most simple silicate material is silicon dioxide, or silica ( $\text{SiO}_2$ ). Structurally, it is a three-dimensional network that is generated when the corner oxygen atoms in each tetrahedron are shared by adjacent tetrahedra. Thus, the material is electrically neutral, and all atoms have stable electronic structures. Under these circumstances the ratio of Si to O atoms is 1:2, as indicated by the chemical formula.

If these tetrahedra are arrayed in a regular and ordered manner, a crystalline structure is formed. There are three primary polymorphic crystalline forms of silica: quartz, cristobalite (Figure 3.12), and tridymite. Their structures are relatively complicated and comparatively open—that is, the atoms are not closely packed together. As a consequence, these crystalline silicas have relatively low densities; for example, at room temperature, quartz has a density of only  $2.65 \text{ g/cm}^3$ . The strength of the Si–O interatomic bonds is reflected in its relatively high melting temperature,  $1710^\circ\text{C}$  ( $3110^\circ\text{F}$ ).

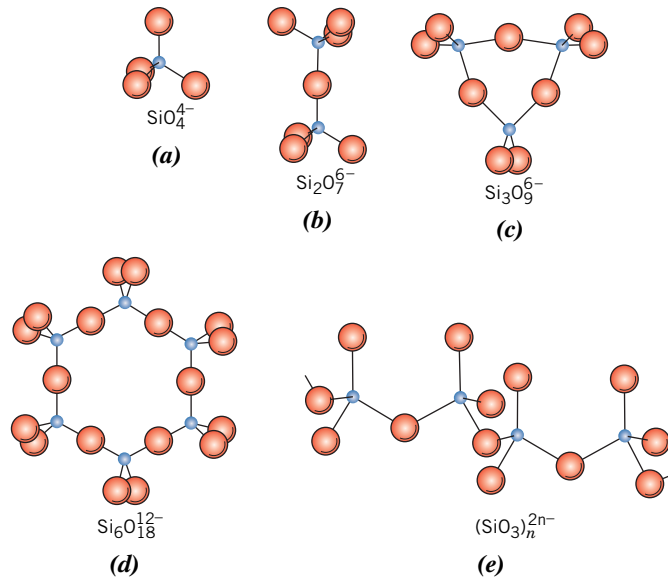
Silica can also be made to exist as a noncrystalline solid or glass; its structure is discussed in Section 3.21.

### The Silicates

For the various silicate minerals, one, two, or three of the corner oxygen atoms of the  $\text{SiO}_4^{4-}$  tetrahedra are shared by other tetrahedra to form some rather complex structures. Some of these, represented in Figure 3.13, have formulas  $\text{SiO}_4^{4-}$ ,  $\text{Si}_2\text{O}_7^{6-}$ ,  $\text{Si}_3\text{O}_9^{6-}$ , and so on; single-chain structures are also possible, as in Figure 3.13e. Positively charged cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  serve two roles: First, they compensate the negative charges from the  $\text{SiO}_4^{4-}$  units so that charge neutrality is achieved; second, these cations ionically bond the  $\text{SiO}_4^{4-}$  tetrahedra together.



**Figure 3.12** The arrangement of silicon and oxygen atoms in a unit cell of cristobalite, a polymorph of  $\text{SiO}_2$ .



**Figure 3.13** Five silicate ion structures formed from  $\text{SiO}_4^{4-}$  tetrahedra.

### Simple Silicates

Of these silicates, the most structurally simple ones involve isolated tetrahedra (Figure 3.13a). For example, forsterite ( $\text{Mg}_2\text{SiO}_4$ ) has the equivalent of two  $\text{Mg}^{2+}$  ions associated with each tetrahedron in such a way that every  $\text{Mg}^{2+}$  ion has six oxygen nearest neighbors.

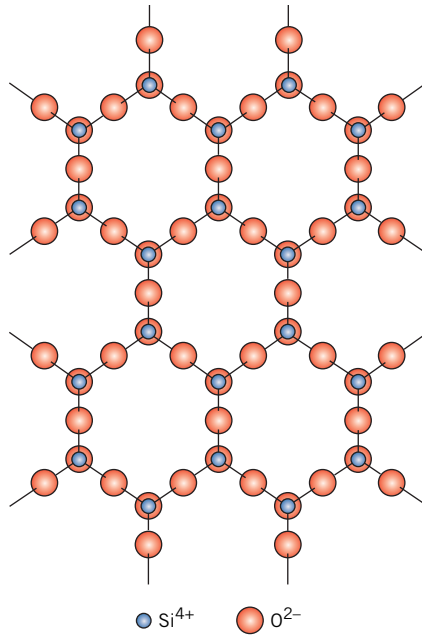
The  $\text{Si}_2\text{O}_7^{6-}$  ion is formed when two tetrahedra share a common oxygen atom (Figure 3.13b). Akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) is a mineral having the equivalent of two  $\text{Ca}^{2+}$  ions and one  $\text{Mg}^{2+}$  ion bonded to each  $\text{Si}_2\text{O}_7^{6-}$  unit.

### Layered Silicates

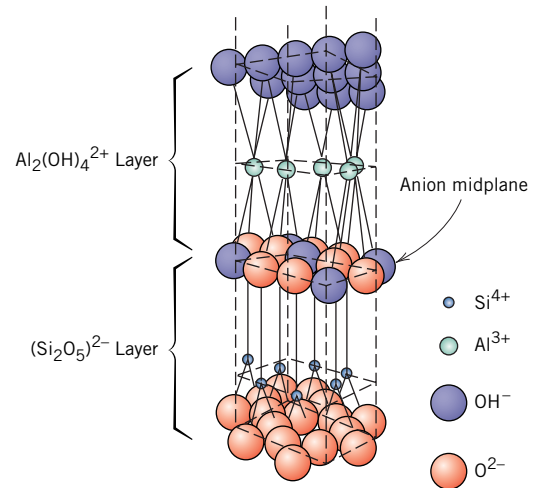
A two-dimensional sheet or layered structure can also be produced by the sharing of three oxygen ions in each of the tetrahedra (Figure 3.14); for this structure, the repeating unit formula may be represented by  $(\text{Si}_2\text{O}_5)^{2-}$ . The net negative charge is associated with the unbonded oxygen atoms projecting out of the plane of the page. Electroneutrality is ordinarily established by a second planar sheet structure having an excess of cations, which bond to these unbonded oxygen atoms from the  $\text{Si}_2\text{O}_5$  sheet. Such materials are called the sheet or layered silicates, and their basic structure is characteristic of the clays and other minerals.

One of the most common clay minerals, kaolinite, has a relatively simple two-layer silicate sheet structure. Kaolinite clay has the formula  $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$  in which the silica tetrahedral layer, represented by  $(\text{Si}_2\text{O}_5)^{2-}$ , is made electrically neutral by an adjacent  $\text{Al}_2(\text{OH})_4^{2+}$  layer. A single sheet of this structure is shown in Figure 3.15, which is exploded in the vertical direction to provide a better perspective on the ion positions; the two distinct layers are indicated in the figure. The midplane of anions consists of  $\text{O}^{2-}$  ions from the  $(\text{Si}_2\text{O}_5)^{2-}$  layer, as well as  $\text{OH}^-$  ions that are a part of the  $\text{Al}_2(\text{OH})_4^{2+}$  layer. Whereas the bonding within this two-layered sheet is strong and intermediate ionic-covalent, adjacent sheets are only loosely bound to one another by weak van der Waals forces.

A crystal of kaolinite is made of a series of these double layers or sheets stacked parallel to each other to form small flat plates that are typically less than  $1\text{ }\mu\text{m}$  in diameter and nearly hexagonal. Figure 3.16 is an electron micrograph of kaolinite crystals



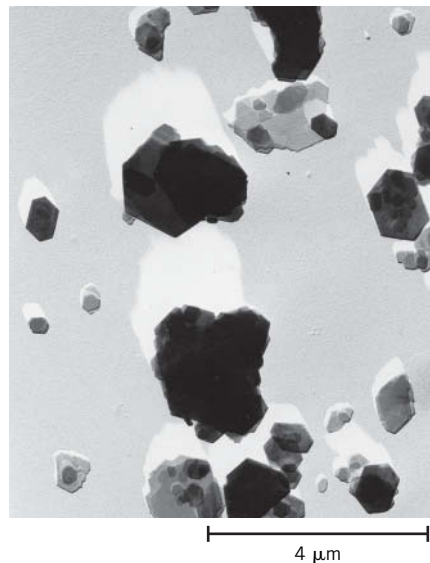
**Figure 3.14** Schematic representation of the two-dimensional silicate sheet structure having a repeat unit formula of  $(\text{Si}_2\text{O}_5)^{2-}$ .



**Figure 3.15** The structure of kaolinite clay. (Adapted from W. E. Hauth, "Crystal Chemistry of Ceramics," *American Ceramic Society Bulletin*, Vol. 30, No. 4, 1951, p. 140.)

at a high magnification, showing the hexagonal crystal plates, some of which are piled one on top of the other.

These silicate sheet structures are not confined to the clays; other minerals also in this group are talc  $[\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2]$  and the micas [e.g., muscovite,  $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ], which are important ceramic raw materials. As might be deduced from the chemical formulas, the structures for some silicates are among the most complex of all the inorganic materials.



**Figure 3.16** Electron micrograph of kaolinite crystals. They are in the form of hexagonal plates, some of which are stacked on top of one another. 7,500 $\times$ . (Photograph courtesy of Georgia Kaolin Co., Inc.)



### 3.9 CARBON

Although not one of the most frequently occurring elements found on Earth, carbon affects our lives in diverse and interesting ways. It exists in the elemental state in nature, and solid carbon has been used by all civilizations since prehistoric times. In today's world, the unique properties (and property combinations) of the several forms of carbon make it extremely important in many commercial sectors, including some cutting-edge technologies.

Carbon exists in two allotropic forms—diamond and graphite—as well as in the amorphous state. The carbon group of materials does not fall within any of the traditional metal, ceramic, or polymer classification schemes. However, we choose to discuss them in this chapter because graphite is sometimes classified as a ceramic. This treatment of the carbons focuses primarily on the structures of diamond and graphite. Discussions on the properties and applications (both current and potential) of diamond and graphite as well as the nanocarbons (i.e., fullerenes, carbon nanotubes, and graphene) are presented in Section 13.10 and 13.11.

#### Diamond



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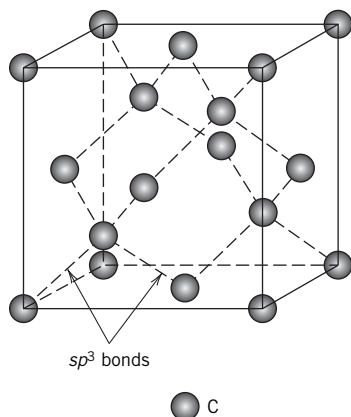
Diamond is a metastable carbon polymorph at room temperature and atmospheric pressure. Its crystal structure is a variant of the zinc blende structure (Figure 3.8) in which carbon atoms occupy all position (both Zn and S); the unit cell for diamond is shown in Figure 3.17. Each carbon atom has undergone  $sp^3$  hybridization so that it bonds (tetrahedrally) to four other carbons; these are extremely strong covalent bonds discussed in Section 2.6 (and represented in Figure 2.14). The crystal structure of diamond is appropriately called the *diamond cubic* crystal structure, which is also found for other Group IVA elements in the periodic table [e.g., germanium, silicon, and gray tin below  $13^\circ\text{C}$  ( $55^\circ\text{F}$ )].

#### Graphite

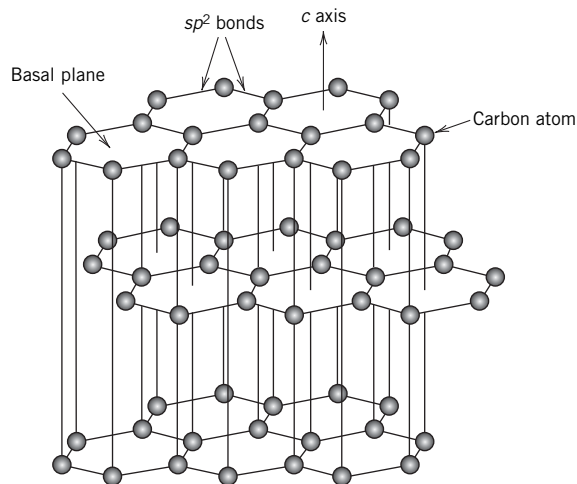


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Another polymorph of carbon, graphite, has a crystal structure (Figure 3.18) distinctly different from that of diamond; furthermore, it is a stable polymorph at ambient temperature and pressure. For the graphite structure, carbon atoms are located at corners of interlocking regular hexagons that lie in parallel (basal) planes. Within these planes



**Figure 3.17** A unit cell for the diamond cubic crystal structure.



**Figure 3.18** The structure of graphite.



(layers or sheets),  $sp^2$  hybrid orbitals bond each carbon atom to three other adjacent and coplanar carbon atoms; these bonds are strong covalent ones.<sup>3</sup> This hexagonal configuration assumed by  $sp^2$  bonded carbon atoms is represented in Figure 2.18. Furthermore, each atom's fourth bonding electron is *delocalized* (i.e., does not belong to a specific atom or bond). Rather, its orbital becomes part of a molecular orbital that extends over adjacent atoms and resides between layers. Furthermore, interlayer bonds are directed perpendicular to these planes (i.e., in the  $c$  direction noted in Figure 3.18) and are of the weak van der Waals type.

### 3.10 POLYMORPHISM AND ALLOTROPY

polymorphism

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**. The prevailing crystal structure depends on both the temperature and the external pressure. One familiar example is found in carbon, as discussed in the previous section: 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.

### 3.11 CRYSTAL SYSTEMS



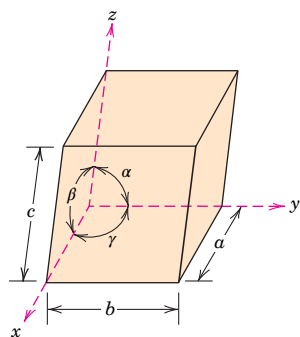
**WileyPLUS: VMSE**  
Crystal Systems and  
Unit Cells for Metals

lattice parameters

crystal system

Because 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 3.19. 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 3.19 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  $\alpha$ ,  $\beta$ , and  $\gamma$ , each of which represents a distinct **crystal system**. These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral (also called trigonal),





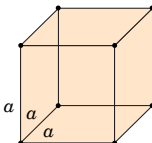

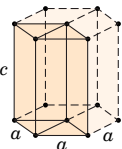

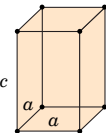

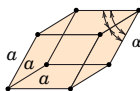

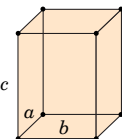

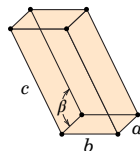

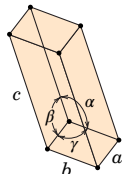
**Figure 3.19** A unit cell with  $x$ ,  $y$ , and  $z$  coordinate axes, showing axial lengths ( $a$ ,  $b$ , and  $c$ ) and interaxial angles ( $\alpha$ ,  $\beta$ , and  $\gamma$ ).

<sup>3</sup>A single layer of this  $sp^2$  bonded graphite is called “graphene.” Graphene is one of the nanocarbon materials, discussed in Section 13.11.

monoclinic, and triclinic. The lattice parameter relationships and unit cell sketches for each are represented in Table 3.6. The cubic system, for which  $a = b = c$  and  $\alpha = \beta = \gamma = 90^\circ$ , has the greatest degree of symmetry. The least symmetry is displayed by the triclinic system because  $a \neq b \neq c$  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 the hexagonal system. The conventional hexagonal unit cell really consists of three parallelepipeds situated as shown in Table 3.6.

**Table 3.6** Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

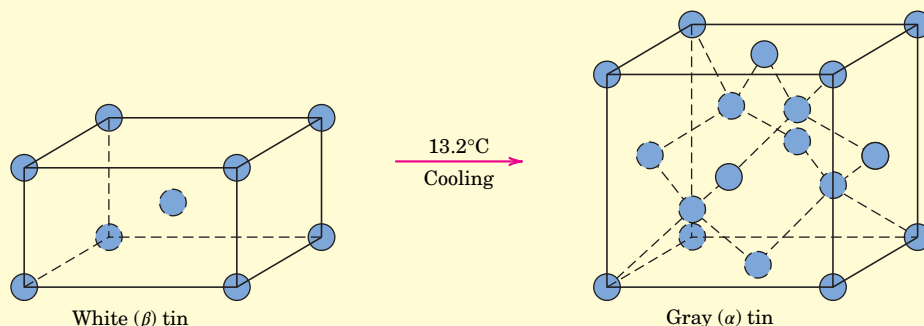
	<i>Crystal System</i>	<i>Axial Relationships</i>	<i>Interaxial Angles</i>	<i>Unit Cell Geometry</i>
 <b>WileyPLUS: VMSE</b> Crystal Systems and Unit Cells for Metals	 Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
	 Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
	 Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
	 Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
	 Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
	 Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
	 Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

## M A T E R I A L   O F   I M P O R T A N C E

*Tin (Its Allotropic Transformation)*

Another common metal that experiences an allotropic change is tin. White (or  $\beta$ ) tin, having a body-centered tetragonal crystal structure at room temperature, transforms, at 13.2°C (55.8°F), to gray

(or  $\alpha$ ) tin, which has a crystal structure similar to that of diamond (i.e., the diamond cubic crystal structure); this transformation is represented schematically as follows:



The rate at which this change takes place is extremely slow; however, the lower the temperature (below 13.2°C), the faster the rate. Accompanying this white-to-gray tin transformation is an increase in volume (27%), and, accordingly, a decrease in density (from 7.30 g/cm<sup>3</sup> to 5.77 g/cm<sup>3</sup>). Consequently, this volume expansion results in the disintegration of the white tin metal into a coarse powder of the gray allotrope. For normal subambient temperatures, there is no need to worry about this disintegration process for tin products because of the very slow rate at which the transformation occurs.

This white-to-gray tin transition produced some rather dramatic results in 1850 in Russia. The winter that year was particularly cold, and record low temperatures persisted for extended periods of time. The uniforms of some Russian soldiers had tin buttons, many of which crumbled because of these extreme cold conditions, as did also many of the tin church organ pipes. This problem came to be known as the *tin disease*.



Specimen of white tin (left). Another specimen disintegrated upon transforming to gray tin (right) after it was cooled to and held at a temperature below 13.2°C for an extended period of time.

(Photograph courtesy of Professor Bill Plumbridge, Department of Materials Engineering, The Open University, Milton Keynes, England.)



**Concept Check 3.3** What is the difference between crystal structure and crystal system?  
(The answer is available in *WileyPLUS*.)

## Crystallographic Points, Directions, and Planes

When dealing with crystalline materials, it often becomes necessary to specify a particular point within a unit cell, a crystallographic direction, or some crystallographic plane of atoms. Labeling conventions have been established in which three numbers or indices are used to designate point locations, directions, and planes. The basis for determining index values is the unit cell, with a right-handed coordinate system consisting of three ( $x$ ,  $y$ , and  $z$ ) axes situated at one of the corners and coinciding with the unit cell edges, as shown in Figure 3.19. For some crystal systems—namely, hexagonal, rhombohedral, monoclinic, and triclinic—the three axes are *not* mutually perpendicular as in the familiar Cartesian coordinate scheme.

### 3.12 POINT COORDINATES

Sometimes it is necessary to specify a lattice position within a unit cell. This is possible using three *point coordinate indices*:  $q$ ,  $r$ , and  $s$ . These indices are fractional multiples of  $a$ ,  $b$ , and  $c$  unit cell edge lengths—that is,  $q$  is some fractional length of  $a$  along the  $x$  axis,  $r$  is some fractional length of  $b$  along the  $y$  axis, and similarly for  $s$ ; or

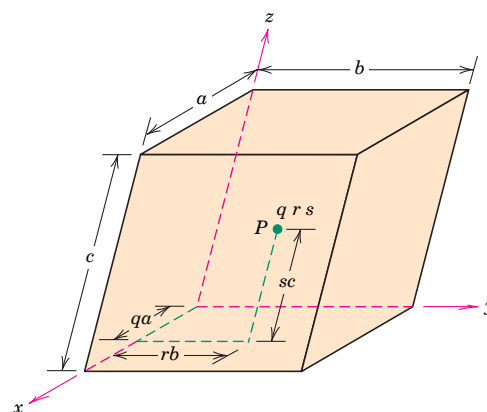
$$qa = \text{lattice position referenced to the } x \text{ axis} \quad (3.10a)$$

$$rb = \text{lattice position referenced to the } y \text{ axis} \quad (3.10b)$$

$$sc = \text{lattice position referenced to the } z \text{ axis} \quad (3.10c)$$

To illustrate, consider the unit cell in Figure 3.20, the  $x$ - $y$ - $z$  coordinate system with its origin located at a unit cell corner, and the lattice site located at point  $P$ . Note how the location of  $P$  is related to the products of its  $q$ ,  $r$ , and  $s$  coordinate indices and the unit cell edge lengths.<sup>4</sup>

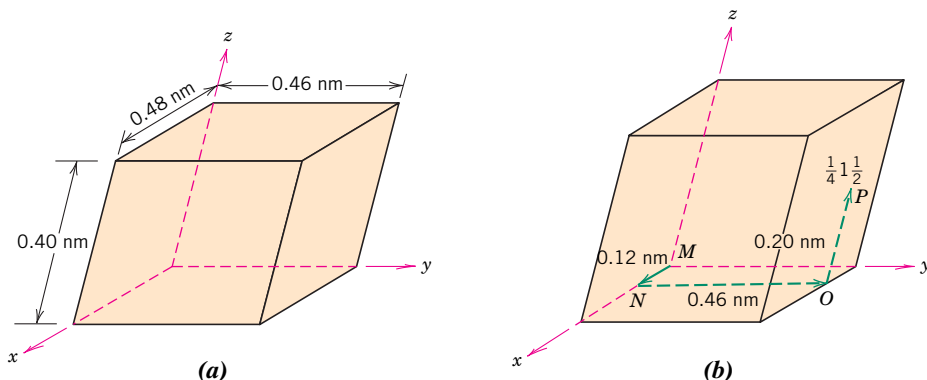
**Figure 3.20** The manner in which the  $q$ ,  $r$ , and  $s$  coordinates at point  $P$  within the unit cell are determined. The  $q$  coordinate (which is a fraction) corresponds to the distance  $qa$  along the  $x$  axis, where  $a$  is the unit cell edge length. The respective  $r$  and  $s$  coordinates for the  $y$  and  $z$  axes are determined similarly.



<sup>4</sup>We have chosen not to separate the  $q$ ,  $r$ , and  $s$  indices by commas or any other punctuation marks (which is the normal convention).

**EXAMPLE PROBLEM 3.8****Location of Point Having Specified Coordinates**

For the unit cell shown in the accompanying sketch (a), locate the point having coordinates  $\frac{1}{4} 1 \frac{1}{2}$ .

**Solution**

From sketch (a), edge lengths for this unit cell are as follows:  $a = 0.48$  nm,  $b = 0.46$  nm, and  $c = 0.40$  nm. Furthermore, in light of the preceding discussion, the three point coordinate indices are  $q = \frac{1}{4}$ ,  $r = 1$ , and  $s = \frac{1}{2}$ . We use Equations 3.10a through 3.10c to determine lattice positions for this point as follows:

$$\begin{aligned} \text{lattice position referenced to the } x \text{ axis} &= qa \\ &= \left(\frac{1}{4}\right)a = \frac{1}{4}(0.48 \text{ nm}) = 0.12 \text{ nm} \end{aligned}$$

$$\begin{aligned} \text{lattice position referenced to the } y \text{ axis} &= rb \\ &= (1)b = (1)(0.46 \text{ nm}) = 0.46 \text{ nm} \end{aligned}$$

$$\begin{aligned} \text{lattice position referenced to the } z \text{ axis} &= sc \\ &= \left(\frac{1}{2}\right)c = \left(\frac{1}{2}\right)(0.40 \text{ nm}) = 0.20 \text{ nm} \end{aligned}$$

To locate the point having these coordinates within the unit cell, first use the  $x$  lattice position and move from the origin (point  $M$ ) 0.12 nm units along the  $x$  axis (to point  $N$ ), as shown in (b). Similarly, using the  $y$  lattice position, proceed 0.46 nm parallel to the  $y$  axis, from point  $N$  to point  $O$ . Finally, move from this position 0.20 nm units parallel to the  $z$  axis to point  $P$  (per the  $z$  lattice position), as noted again in (b). Thus, point  $P$  corresponds to the  $\frac{1}{4} 1 \frac{1}{2}$  point coordinates.

**EXAMPLE PROBLEM 3.9****Specification of Point Coordinate Indices**

Specify coordinate indices for all numbered points of the unit cell in the illustration on the next page.

**Solution**

For this unit cell, coordinate points are located at all eight corners with a single point at the center position.

Point 1 is located at the origin of the coordinate system, and, therefore, its lattice position indices referenced to the  $x$ ,  $y$ , and  $z$  axes are  $0a$ ,  $0b$ , and  $0c$ , respectively. And from Equations 3.10a through 3.10c,

lattice position referenced to the  $x$  axis =  $0a = qa$

lattice position referenced to the  $y$  axis =  $0b = rb$

lattice position referenced to the  $z$  axis =  $0c = sc$

Solving the above three expressions for values of the  $q$ ,  $r$ , and  $s$  indices leads to

$$q = \frac{0a}{a} = 0$$

$$r = \frac{0b}{b} = 0$$

$$s = \frac{0c}{c} = 0$$

Therefore this is the  $000$  point.

Because point number 2, lies one unit cell edge length along the  $x$  axis, its lattice position indices referenced to the  $x$ ,  $y$ , and  $z$  axes are  $a$ ,  $0b$ , and  $0c$ , and

lattice position index referenced to the  $x$  axis =  $a = qa$

lattice position index referenced to the  $y$  axis =  $0b = rb$

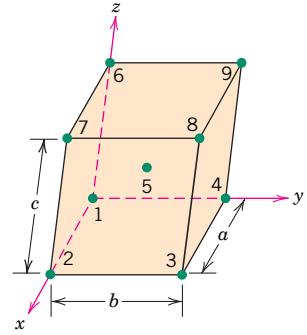
lattice position index referenced to the  $z$  axis =  $0c = sc$

Thus we determine values for the  $q$ ,  $r$ , and  $s$  indices as follows:

$$q = 1 \quad r = 0 \quad s = 0$$

Hence, point 2 is  $100$ .

This same procedure is carried out for the remaining seven points in the unit cell. Point indices for all nine points are listed in the following table.



<b>Point Number</b>	<b><math>q</math></b>	<b><math>r</math></b>	<b><math>s</math></b>
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1

### 3.13 CRYSTALLOGRAPHIC DIRECTIONS



**WileyPLUS: VMSE**

Crystallographic  
Directions

**WileyPLUS**

**Tutorial Video:**

Crystallographic Planes  
and Directions

A *crystallographic direction* is defined as a line directed between two points, or a *vector*. The following steps are used to determine the three directional indices:

1. A right-handed  $x$ - $y$ - $z$  coordinate system is first constructed. As a matter of convenience, its origin may be located at a unit cell corner.
2. The coordinates of two points that lie on the direction vector (referenced to the coordinate system) are determined—for example, for the vector tail, point 1:  $x_1$ ,  $y_1$ , and  $z_1$ ; whereas for the vector head, point 2:  $x_2$ ,  $y_2$ , and  $z_2$ .
3. Tail point coordinates are subtracted from head point components—that is,  $x_2 - x_1$ ,  $y_2 - y_1$ , and  $z_2 - z_1$ .
4. These coordinate differences are then normalized in terms of (i.e., divided by) their respective  $a$ ,  $b$ , and  $c$  lattice parameters—that is,

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

which yields a set of three numbers.

5. If necessary, these three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
6. The three resulting indices, not separated by commas, are enclosed in square brackets, thus:  $[uvw]$ . The  $u$ ,  $v$ , and  $w$  integers correspond to the normalized coordinate differences referenced to the  $x$ ,  $y$ , and  $z$  axes, respectively.

In summary, the  $u$ ,  $v$ , and  $w$  indices may be determined using the following equations:

$$u = n \left( \frac{x_2 - x_1}{a} \right) \quad (3.11a)$$

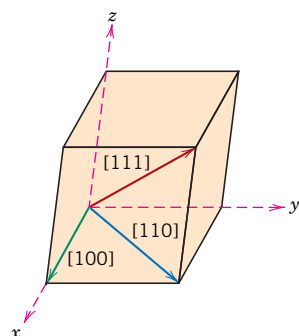
$$v = n \left( \frac{y_2 - y_1}{b} \right) \quad (3.11b)$$

$$w = n \left( \frac{z_2 - z_1}{c} \right) \quad (3.11c)$$

In these expressions,  $n$  is the factor that may be required to reduce  $u$ ,  $v$ , and  $w$  to integers.

For each of the three axes, there are both positive and negative coordinates. Thus, negative indices are also possible, which are represented by a bar over the appropriate index. For example, the  $[\bar{1}11]$  direction has a component in the  $-y$  direction. Also, changing the signs of all indices produces an antiparallel direction; that is,  $[\bar{1}\bar{1}\bar{1}]$  is directly opposite to  $[111]$ . If more than one direction (or plane) is to be specified for a particular crystal structure, it is imperative for maintaining consistency that a positive–negative convention, once established, not be changed.

The  $[100]$ ,  $[110]$ , and  $[111]$  directions are common ones; they are drawn in the unit cell shown in Figure 3.21.



**Figure 3.21** The  $[100]$ ,  $[110]$ , and  $[111]$  directions within a unit cell.

**EXAMPLE PROBLEM 3.10****Determination of Directional Indices**

Determine the indices for the direction shown in the accompanying figure.

**Solution**

It is first necessary to take note of the vector tail and head coordinates. From the illustration, tail coordinates are as follows:

$$x_1 = a \quad y_1 = 0b \quad z_1 = 0c$$

For the head coordinates,

$$x_2 = 0a \quad y_2 = b \quad z_2 = c/2$$

Now taking point coordinate differences,

$$x_2 - x_1 = 0a - a = -a$$

$$y_2 - y_1 = b - 0b = b$$

$$z_2 - z_1 = c/2 - 0c = c/2$$

It is now possible to use Equations 3.11a through 3.11c to compute values of  $u$ ,  $v$ , and  $w$ . However, because the  $z_2 - z_1$  difference is a fraction (i.e.,  $c/2$ ), we anticipate that in order to have integer values for the three indices, it is necessary to assign  $n$  a value of 2. Thus,

$$u = n \left( \frac{x_2 - x_1}{a} \right) = 2 \left( \frac{-a}{a} \right) = -2$$

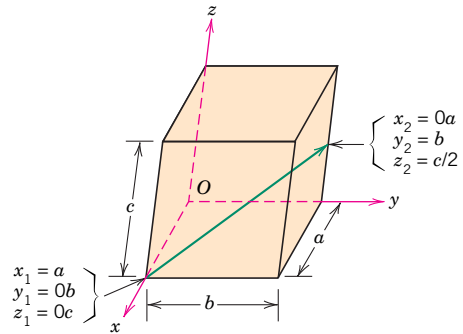
$$v = n \left( \frac{y_2 - y_1}{b} \right) = 2 \left( \frac{b}{b} \right) = 2$$

$$w = n \left( \frac{z_2 - z_1}{c} \right) = 2 \left( \frac{c/2}{c} \right) = 1$$

And, finally enclosure of the  $-2$ ,  $2$ , and  $1$  indices in brackets leads to  $[\bar{2}21]$  as the direction designation.<sup>5</sup>

This procedure is summarized as follows:

	$x$	$y$	$z$
Head coordinates ( $x_2, y_2, z_2$ )	$0a$	$b$	$c/2$
Tail coordinates ( $x_1, y_1, z_1$ )	$a$	$0b$	$0c$
Coordinate differences	$-a$	$b$	$c/2$
Calculated values of $u$ , $v$ , and $w$	$u = -2$	$v = 2$	$w = 1$
Enclosure	$[\bar{2}21]$		



<sup>5</sup>If these  $u$ ,  $v$ , and  $w$  values are not integers, it is necessary to choose another value for  $n$ .



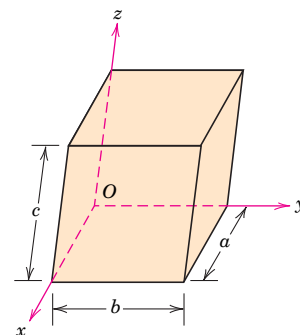
**EXAMPLE PROBLEM 3.11****Construction of a Specified Crystallographic Direction**

Within the following unit cell draw a  $[1\bar{1}0]$  direction with its tail located at the origin of the coordinate system, point  $O$ .

**Solution**

This problem is solved by reversing the procedure of the preceding example. For this  $[1\bar{1}0]$  direction,

$$\begin{aligned}u &= 1 \\v &= -1 \\w &= 0\end{aligned}$$



Because the tail of the direction vector is positioned at the origin, its coordinates are as follows:

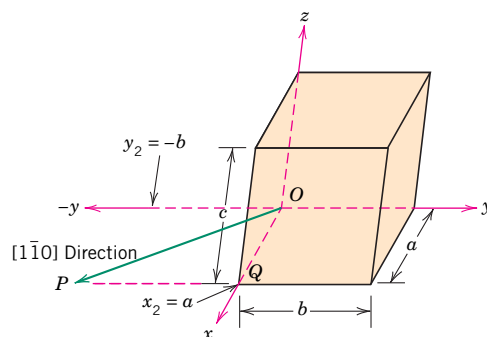
$$\begin{aligned}x_1 &= 0a \\y_1 &= 0b \\z_1 &= 0c\end{aligned}$$

We now want to solve for the coordinates of the vector head—that is,  $x_2$ ,  $y_2$ , and  $z_2$ . This is possible using rearranged forms of Equations 3.11a through 3.11c and incorporating the above values for the three direction indices ( $u$ ,  $v$ , and  $w$ ) and vector tail coordinates. Taking the value of  $n$  to be 1 because the three direction indices are all integers leads to

$$\begin{aligned}x_2 &= ua + x_1 = (1)(a) + 0a = a \\y_2 &= vb + y_1 = (-1)(b) + 0b = -b \\z_2 &= wc + z_1 = (0)(c) + 0c = 0c\end{aligned}$$

The construction process for this direction vector is shown in the following figure.

Because the tail of the vector is positioned at the origin, we start at the point labeled  $O$  and then move in a stepwise manner to locate the vector head. Because the  $x$  head coordinate ( $x_2$ ) is  $a$ , we proceed from point  $O$ ,  $a$  units along the  $x$  axis to point  $Q$ . From point  $Q$ , we move  $b$  units parallel to the  $-y$  axis to point  $P$ , because the  $y$  head coordinate ( $y_2$ ) is  $-b$ . There is no  $z$  component to the vector inasmuch as the  $z$  head coordinate ( $z_2$ ) is  $0c$ . Finally, the vector corresponding to this  $[1\bar{1}0]$  direction is constructed by drawing a line from point  $O$  to point  $P$ , as noted in the illustration.



For some crystal structures, several nonparallel directions with different indices are *crystallographically equivalent*, meaning that the spacing of atoms along each direction is the same. For example, in cubic crystals, all the directions represented by the following indices are equivalent:  $[100]$ ,  $[\bar{1}00]$ ,  $[010]$ ,  $[0\bar{1}0]$ ,  $[001]$ , and  $[00\bar{1}]$ . As a convenience, equivalent directions are grouped together into a *family*, which is enclosed in

angle brackets, thus:  $\langle 100 \rangle$ . Furthermore, directions in cubic crystals having the same indices without regard to order or sign—for example,  $[123]$  and  $[\bar{2}1\bar{3}]$ —are equivalent. This is, in general, not true for other crystal systems. For example, for crystals of tetragonal symmetry, the  $[100]$  and  $[010]$  directions are equivalent, whereas the  $[100]$  and  $[001]$  are not.

### Directions in Hexagonal Crystals

A problem arises for crystals having hexagonal symmetry in that some equivalent crystallographic directions do not have the same set of indices. This situation is addressed using a four-axis, or *Miller–Bravais*, coordinate system, which is shown in Figure 3.22a. The three  $a_1$ ,  $a_2$ , and  $a_3$  axes are all contained within a single plane (called the *basal plane*) and are at  $120^\circ$  angles to one another. The  $z$  axis is perpendicular to this basal plane. Directional indices, which are obtained as described earlier, are denoted by four indices, as  $[uvw]$ ; by convention, the  $u$ ,  $v$ , and  $t$  relate to vector coordinate differences referenced to the respective  $a_1$ ,  $a_2$ , and  $a_3$  axes in the basal plane; the fourth index pertains to the  $z$  axis.

Conversion from the three-index system (using the  $a_1$ – $a_2$ – $z$  coordinate axes of Figure 3.22b) to the four-index system as

$$[UVW] \rightarrow [uvw]$$

is accomplished using the following formulas<sup>6</sup>:

$$u = \frac{1}{3}(2U - V) \quad (3.12a)$$

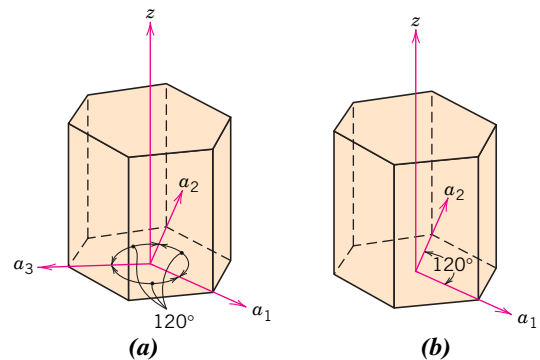
$$v = \frac{1}{3}(2V - U) \quad (3.12b)$$

$$t = -(u + v) \quad (3.12c)$$

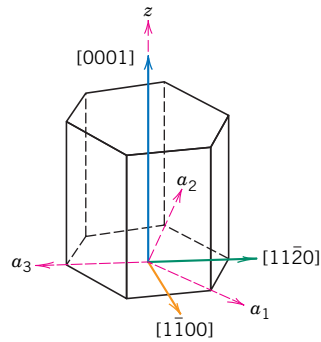
$$w = W \quad (3.12d)$$

Here, uppercase  $U$ ,  $V$ , and  $W$  indices are associated with the three-index scheme (instead of  $u$ ,  $v$ , and  $w$  as previously), whereas lowercase  $u$ ,  $v$ ,  $t$ , and  $w$  correlate with the Miller–Bravais four-index system. For example, using these equations, the  $[010]$  direction becomes  $[\bar{1}2\bar{1}0]$ ; furthermore,  $[\bar{1}2\bar{1}0]$  is also equivalent to the following:  $[1210]$ ,  $[\bar{1}210]$ ,  $[\bar{1}210]$ .

**Figure 3.22** Coordinate axis systems for a hexagonal unit cell: (a) four-axis Miller–Bravais; (b) three-axis.



<sup>6</sup>Reduction to the lowest set of integers may be necessary, as discussed earlier.



**Figure 3.23** For the hexagonal crystal system, the  $[0001]$ ,  $[1\bar{1}00]$ , and  $[11\bar{2}0]$  directions.

Several directions have been drawn in the hexagonal unit cell of Figure 3.23.

Determination of directional indices is carried out using a procedure similar to the one used for other crystal systems—by the subtraction of vector tail point coordinates from head point coordinates. To simplify the demonstration of this procedure, we first determine the  $U$ ,  $V$ , and  $W$  indices using the three-axis  $a_1$ – $a_2$ – $z$  coordinate system of Figure 3.22b and then convert to the  $u$ ,  $v$ ,  $t$ , and  $w$  indices using Equations 3.12a–3.12d.

The designation scheme for the three sets of head and tail coordinates is as follows:

<i>Axis</i>	<i>Head Coordinate</i>	<i>Tail Coordinate</i>
$a_1$	$a_1''$	$a_1'$
$a_2$	$a_2''$	$a_2'$
$z$	$z''$	$z'$

Using this scheme, the  $U$ ,  $V$ , and  $W$  hexagonal index equivalents of Equations 3.11a through 3.11c are as follows:

$$U = n \left( \frac{a_1'' - a_1'}{a} \right) \quad (3.13a)$$

$$V = n \left( \frac{a_2'' - a_2'}{a} \right) \quad (3.13b)$$

$$W = n \left( \frac{z'' - z'}{c} \right) \quad (3.13c)$$

In these expressions, the parameter  $n$  is included to facilitate, if necessary, reduction of the  $U$ ,  $V$ , and  $W$  to integer values.

### EXAMPLE PROBLEM 3.12

#### Determination of Directional Indices for a Hexagonal Unit Cell

For the direction shown in the accompanying figure, do the following:

- Determine the directional indices referenced to the three-axis coordinate system of Figure 3.22b.
- Convert these indices into an index set referenced to the four-axis scheme (Figure 3.22a).

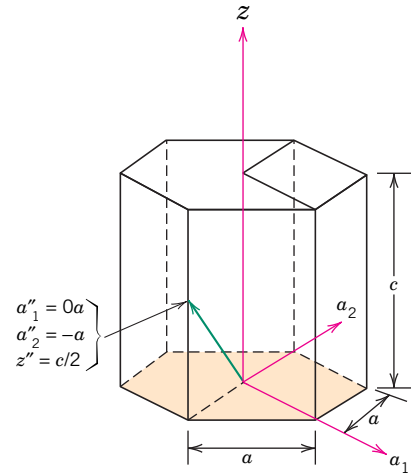
**Solution**

The first thing we need to do is determine  $U$ ,  $V$ , and  $W$  indices for the vector referenced to the three-axis scheme represented in the sketch; this is possible using Equations 3.13a through 3.13c. Because the vector passes through the origin,  $a'_1 = a'_2 = 0a$  and  $z' = 0c$ . Furthermore, from the sketch, coordinates for the vector head are as follows:

$$a''_1 = 0a$$

$$a''_2 = -a$$

$$z'' = \frac{c}{2}$$



Because the denominator in  $z''$  is 2, we assume that  $n = 2$ . Therefore,

$$U = n \left( \frac{a''_1 - a'_1}{a} \right) = 2 \left( \frac{0a - 0a}{a} \right) = 0$$

$$V = n \left( \frac{a''_2 - a'_2}{a} \right) = 2 \left( \frac{-a - 0a}{a} \right) = -2$$

$$W = n \left( \frac{z'' - z'}{c} \right) = 2 \left( \frac{c/2 - 0c}{c} \right) = 1$$

This direction is represented by enclosing the above indices in brackets—namely,  $[0\bar{2}1]$ .

(b) To convert these indices into an index set referenced to the four-axis scheme requires the use of Equations 3.12a–3.12d. For this  $[0\bar{2}1]$  direction

$$U = 0 \quad V = -2 \quad W = 1$$

and

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}[(2)(0) - (-2)] = \frac{2}{3}$$

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}[(2)(-2) - 0] = -\frac{4}{3}$$

$$t = -(u + v) = -\left(\frac{2}{3} - \frac{4}{3}\right) = \frac{2}{3}$$

$$w = W = 1$$

Multiplication of the preceding indices by 3 reduces them to the lowest set, which yields values for  $u$ ,  $v$ ,  $t$ , and  $w$  of 2,  $-4$ , 2, and 3, respectively. Hence, the direction vector shown in the figure is  $[2\bar{4}23]$ .

The procedure used to plot direction vectors in crystals having hexagonal symmetry given their sets of indices is relatively complicated; therefore, we have elected to omit a description of this procedure.

## 3.14 CRYSTALLOGRAPHIC PLANES



**WileyPLUS: VMSE**  
Crystallographic  
Planes

### Miller indices

The orientations of planes for a crystal structure are represented in a similar manner. Again, the unit cell is the basis, with the three-axis coordinate system as represented in Figure 3.19. In all but the hexagonal crystal system, crystallographic planes are specified by three **Miller indices** as  $(hkl)$ . Any two planes parallel to each other are equivalent and have identical indices. The procedure used to determine 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.<sup>7</sup>
2. At this point, the crystallographic plane either intersects or parallels each of the three axes. The coordinate for the intersection of the crystallographic plane with each of the axes is determined (referenced to the origin of the coordinate system). These intercepts for the  $x$ ,  $y$ , and  $z$  axes will be designed by  $A$ ,  $B$ , and  $C$ , respectively.
3. The reciprocals of these numbers are taken. A plane that parallels an axis is considered to have an infinite intercept and therefore a zero index.
4. The reciprocals of the intercepts are then normalized in terms of (i.e., multiplied by) their respective  $a$ ,  $b$ , and  $c$  lattice parameters. That is,

$$\frac{a}{A} \quad \frac{b}{B} \quad \frac{c}{C}$$

5. If necessary, these three numbers are changed to the set of smallest integers by multiplication or by division by a common factor.<sup>8</sup>
6. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus:  $(hkl)$ . The  $h$ ,  $k$ , and  $l$  integers correspond to the normalized intercept reciprocals referenced to the  $x$ ,  $y$ , and  $z$  axes, respectively.

In summary, the  $h$ ,  $k$ , and  $l$  indices may be determined using the following equations:

$$h = \frac{na}{A} \quad (3.14a)$$

$$k = \frac{nb}{B} \quad (3.14b)$$

$$l = \frac{nc}{C} \quad (3.14c)$$

In these expressions,  $n$  is the factor that may be required to reduce  $h$ ,  $k$ , and  $l$  to integers.

An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index. Furthermore, reversing the directions of all indices specifies another plane parallel to, on the opposite side of, and equidistant from the origin. Several low-index planes are represented in Figure 3.24.

<sup>7</sup>When selecting a new origin, the following procedure is suggested:

If the crystallographic plane that intersects the origin lies in one of the unit cell faces, move the origin one unit cell distance parallel to the axis that intersects this plane.

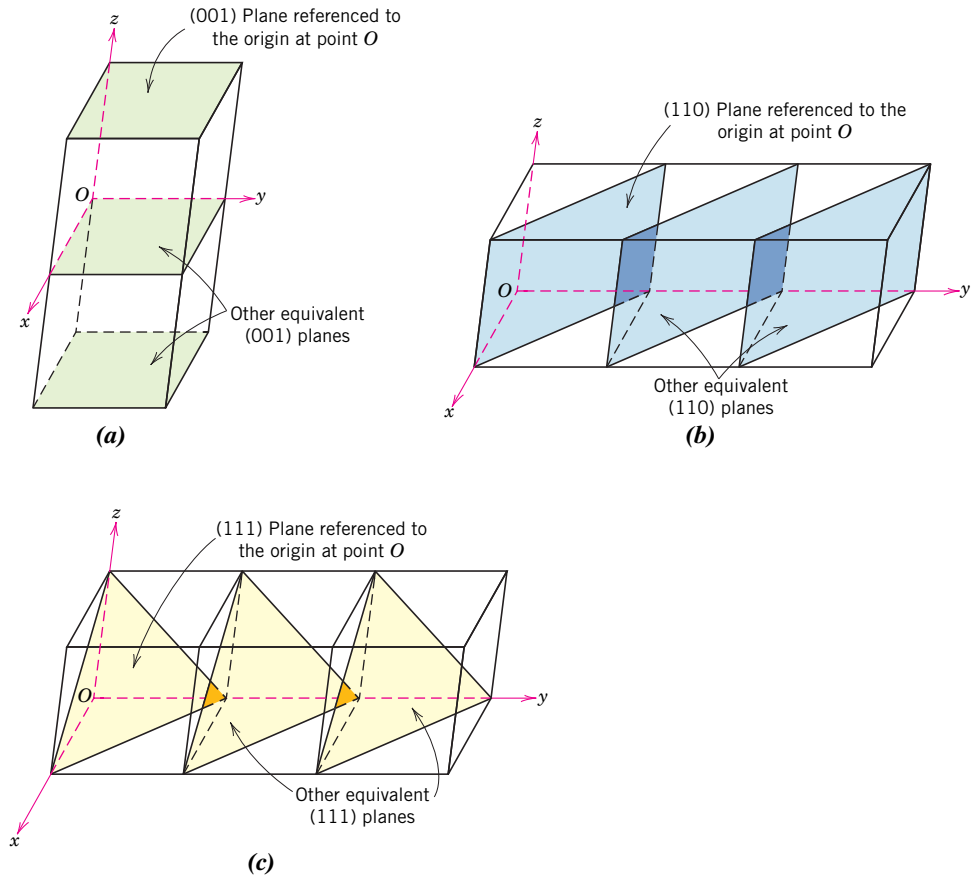
If the crystallographic plane that intersects the origin passes through one of the unit cell axes, move the origin one unit cell distance parallel to either of the two other axes.

For all other cases, move the origin one unit cell distance parallel to any of the three unit cell axes.

<sup>8</sup>On occasion, index reduction is not carried out (e.g., for x-ray diffraction studies described in Section 3.20); for example,  $(002)$  is not reduced to  $(001)$ . In addition, for ceramic materials, the ionic arrangement for a reduced-index plane may be different from that for a nonreduced one.

**Figure 3.24**

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

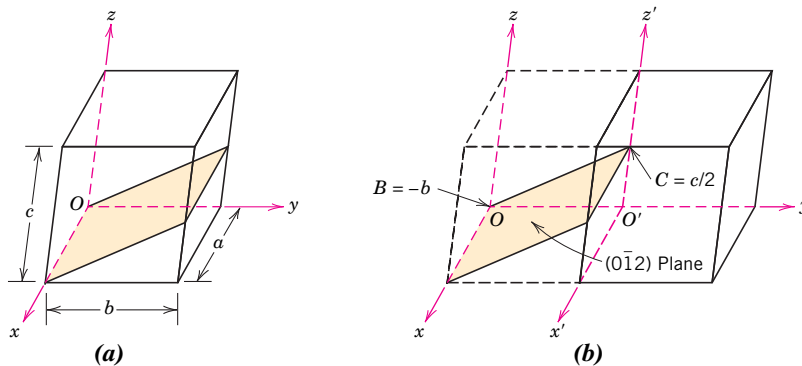


One interesting and unique characteristic of cubic crystals is that planes and directions having the same indices are perpendicular to one another; however, for other crystal systems there are no simple geometrical relationships between planes and directions having the same indices.

### EXAMPLE PROBLEM 3.13

#### Determination of Planar (Miller) Indices

Determine the Miller indices for the plane shown in the accompanying sketch (a).



**Solution**

Because the plane passes through the selected origin  $O$ , a new origin must be chosen at the corner of an adjacent unit cell. In choosing this new unit cell, we move one unit-cell distance parallel to the  $y$ -axis, as shown in sketch (b). Thus  $x'$ - $y$ - $z'$  is the new coordinate axis system having its origin located at  $O'$ . Because this plane is parallel to the  $x'$  axis its intercept is  $\infty a$ —that is,  $A = \infty a$ . Furthermore, from illustration (b), intersections with the  $y$  and  $z'$  axes are as follows:

$$B = -b \quad C = c/2$$

It is now possible to use Equations 3.14a–3.14c to determine values of  $h$ ,  $k$ , and  $l$ . At this point, let us choose a value of 1 for  $n$ . Thus,

$$h = \frac{na}{A} = \frac{1a}{\infty a} = 0$$

$$k = \frac{nb}{B} = \frac{1b}{-b} = -1$$

$$l = \frac{nc}{C} = \frac{1c}{c/2} = 2$$

And finally, enclosure of the 0,  $-1$ , and 2 indices in parentheses leads to  $(0\bar{1}2)$  as the designation for this direction.<sup>9</sup>

This procedure is summarized as follows:

	$x$	$y$	$z$
Intercepts ( $A, B, C$ )	$\infty a$	$-b$	$c/2$
Calculated values of $h, k$ , and $l$ (Equations 3.14a–3.14c)	$h = 0$	$k = -1$	$l = 2$
Enclosure	$(0\bar{1}2)$		

**EXAMPLE PROBLEM 3.14****Construction of a Specified Crystallographic Plane**

Construct a  $(101)$  plane within the following unit cell.

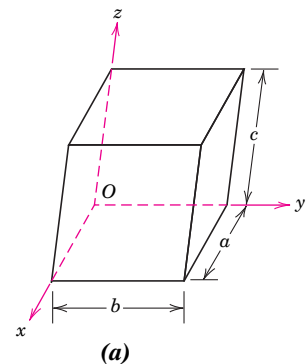
**Solution**

To solve this problem, carry out the procedure used in the preceding example in reverse order. For this  $(101)$  direction,

$$h = 1$$

$$k = 0$$

$$l = 1$$



<sup>9</sup>If  $h$ ,  $k$ , and  $l$  are not integers, it is necessary to choose another value for  $n$ .



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Using these  $h$ ,  $k$ , and  $l$  indices, we want to solve for the values of  $A$ ,  $B$ , and  $C$  using rearranged forms of Equations 3.14a–3.14c. Taking the value of  $n$  to be 1—because these three Miller indices are all integers—leads to the following:

$$A = \frac{na}{h} = \frac{(1)(a)}{1} = a$$

$$B = \frac{nb}{k} = \frac{(1)(b)}{0} = \infty b$$

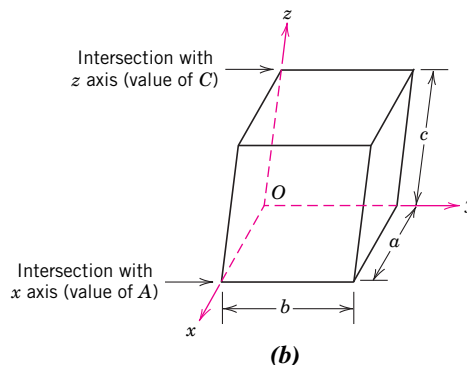
$$C = \frac{nc}{l} = \frac{(1)(c)}{1} = c$$

Thus, this (101) plane intersects the  $x$  axis at  $a$  (because  $A = a$ ), it parallels the  $y$  axis (because  $B = \infty b$ ), and intersects the  $z$  axis at  $c$ . On the unit cell shown in (b) are noted the locations of the intersections for this plane.

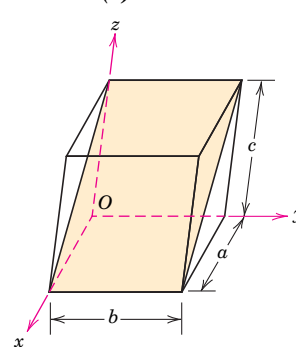
The only plane that parallels the  $y$  axis and intersects the  $x$  and  $z$  axes at axial  $a$  and  $c$  coordinates, respectively, is shown in (c).

Note that the representation of a crystallographic plane referenced to a unit cell is by lines drawn to indicate intersections of this plane with unit cell faces (or extensions of these faces). The following guides are helpful with representing crystallographic planes:

- If two of the  $h$ ,  $k$ , and  $l$  indices are zeros [as with (100)], the plane will parallel one of the unit cell faces (per Figure 3.24a).
- If one of the indices is a zero [as with (110)], the plane will be a parallelogram, having two sides that coincide with opposing unit cell edges (or edges of adjacent unit cells) (per Figure 3.24b).
- If none of the indices is zero [as with (111)], all intersections will pass through unit cell faces (per Figure 3.24c).



(b)



(c)

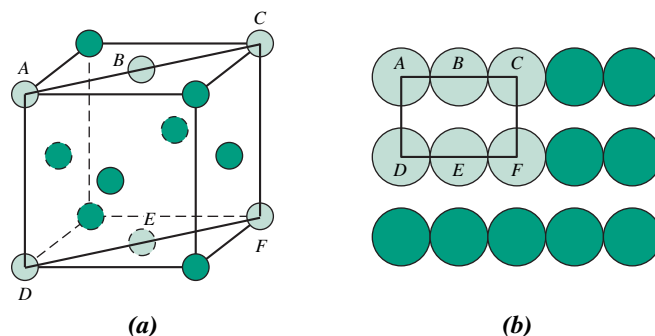
## Atomic Arrangements



WileyPLUS: VMSE  
Planar Atomic  
Arrangements

The atomic arrangement for a crystallographic plane, which is often of interest, depends on the crystal structure. The (110) atomic planes for FCC and BCC crystal structures are represented in Figures 3.25 and 3.26, respectively. Reduced-sphere unit cells are also included. Note that the atomic packing is different for each case. The circles represent atoms lying in the crystallographic planes as would be obtained from a slice taken through the centers of the full-size hard spheres.

A “family” of planes contains all planes that are *crystallographically equivalent*—that is, having the same atomic packing; a family is designated by indices enclosed in braces—such as {100}. For example, in cubic crystals the (111),  $(\bar{1}\bar{1}\bar{1})$ ,  $(\bar{1}11)$ ,  $(1\bar{1}\bar{1})$ ,  $(11\bar{1})$ ,  $(\bar{1}1\bar{1})$ , and  $(\bar{1}\bar{1}1)$  planes all belong to the {111} family. However, for



**Figure 3.25** (a) Reduced-sphere FCC unit cell with the (110) plane. (b) Atomic packing of an FCC (110) plane. Corresponding atom positions from (a) are indicated.

tetragonal crystal structures, the  $\{100\}$  family contains only the (100),  $(\bar{1}00)$ , (010) and  $(0\bar{1}0)$  planes because the (001) and  $(00\bar{1})$  planes are not crystallographically equivalent. Also, in the cubic system only, planes having the same indices, irrespective of order and sign, are equivalent. For example, both (123) and  $(3\bar{1}2)$  belong to the  $\{123\}$  family.

### Hexagonal Crystals

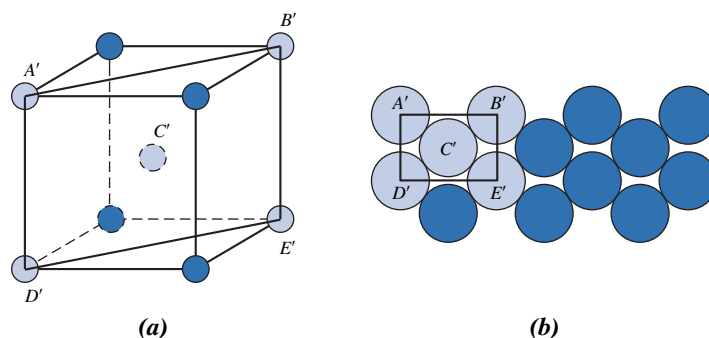
For crystals having hexagonal symmetry, it is desirable that equivalent planes have the same indices; as with directions, this is accomplished by the Miller–Bravais system shown in Figure 3.22a. This convention leads to the four-index  $(hkil)$  scheme, which is favored in most instances because it more clearly identifies the orientation of a plane in a hexagonal crystal. There is some redundancy in that  $i$  is determined by the sum of  $h$  and  $k$  through

$$i = -(h + k) \quad (3.15)$$

Otherwise, the three  $h$ ,  $k$ , and  $l$  indices are identical for both indexing systems.

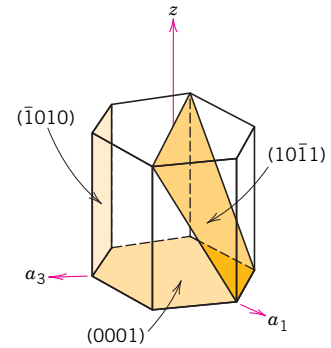
We determine these indices in a manner analogous to that used for other crystal systems as described previously—that is, taking normalized reciprocals of axial intercepts, as described in the following example problem.

Figure 3.27 presents several of the common planes that are found for crystals having hexagonal symmetry.



**Figure 3.26** (a) Reduced-sphere BCC unit cell with the (110) plane. (b) Atomic packing of a BCC (110) plane. Corresponding atom positions from (a) are indicated.

**Figure 3.27** For the hexagonal crystal system, the (0001), (10 $\bar{1}$ 1), and ( $\bar{1}$ 010) planes.



### EXAMPLE PROBLEM 3.15

#### Determination of the Miller–Bravais Indices for a Plane within a Hexagonal Unit Cell

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

##### Solution

These indices may be determined in the same manner that was used for the  $x$ - $y$ - $z$  coordinate situation and described in Example Problem 3.13. However, in this case the  $a_1$ ,  $a_2$ , and  $z$  axes are used and correlate, respectively, with the  $x$ ,  $y$ , and  $z$  axes of the previous discussion. If we again take  $A$ ,  $B$ , and  $C$  to represent intercepts on the respective  $a_1$ ,  $a_2$ , and  $z$  axes, normalized intercept reciprocals may be written as

$$\frac{a}{A} \quad \frac{a}{B} \quad \frac{c}{C}$$

Now, because the three intercepts noted on the above unit cell are

$$A = a \quad B = -a \quad C = c$$

values of  $h$ ,  $k$ , and  $l$ , may be determined using Equations 3.14a–3.14c, as follows (assuming  $n = 1$ ):

$$h = \frac{na}{A} = \frac{(1)(a)}{a} = 1$$

$$k = \frac{na}{B} = \frac{(1)(a)}{-a} = -1$$

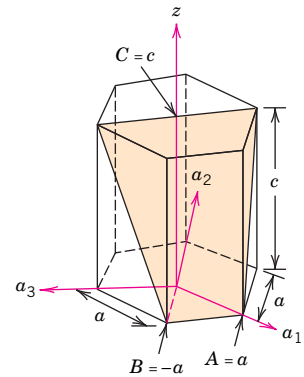
$$l = \frac{nc}{C} = \frac{(1)(c)}{c} = 1$$

And, finally, the value of  $i$  is found using Equation 3.15, as follows:

$$i = -(h + k) = -[1 + (-1)] = 0$$

Therefore, the  $(hkil)$  indices are  $(1\bar{1}01)$ .

Notice that the third index is zero (i.e., its reciprocal =  $\infty$ ), which means this plane parallels the  $a_3$  axis. Inspection of the preceding figure shows that this is indeed the case.



This concludes our discussion on crystallographic points, directions, and planes. A review and summary of these topics is found in Table 3.7.

**Table 3.7** Summary of Equations Used to Determine Crystallographic Point, Direction, and Planar Indices

Coordinate Type	Index Symbols	Representative Equation <sup>a</sup>	Equation Symbols
Point	$q\ r\ s$	$qa$ = lattice position referenced to $x$ axis	—
Direction			
Non-hexagonal	$[uvw]$	$u = n \left( \frac{x_2 - x_1}{a} \right)$	$x_1$ = tail coordinate— $x$ axis $x_2$ = head coordinate— $x$ axis
Hexagonal	$[UVW]$	$U = n \left( \frac{a_1'' - a_1'}{a} \right)$	$a_1'$ = tail coordinate— $a_1$ axis $a_1''$ = head coordinate— $a_1$ axis
	$[uvtw]$	$u = \frac{1}{3}(2U - V)$	—
Plane			
Non-hexagonal	$(hkl)$	$h = \frac{na}{A}$	$A$ = plane intercept— $x$ axis
Hexagonal	$(hkil)$	$i = -(h + k)$	—

<sup>a</sup>In these equations  $a$  and  $n$  denote, respectively, the  $x$ -axis lattice parameter, and a reduction-to-integer parameter.

### 3.15 LINEAR AND PLANAR DENSITIES

The two previous sections discussed the equivalency of nonparallel crystallographic directions and planes. Directional equivalency is related to *linear density* in the sense that, for a particular material, equivalent directions have identical linear densities. The corresponding parameter for crystallographic planes is *planar density*, and planes having the same planar density values are also equivalent.

*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,

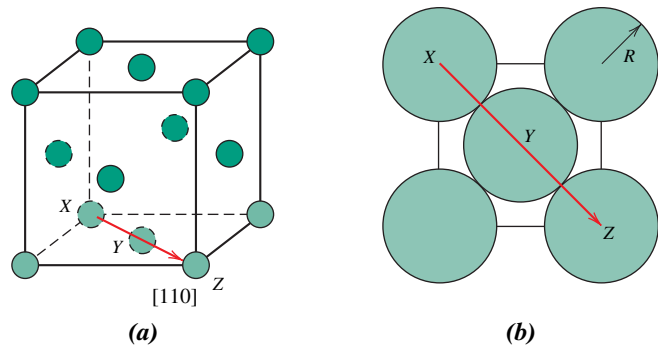
$$\text{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}} \quad (3.16)$$

The units of linear density are reciprocal length (e.g.,  $\text{nm}^{-1}$ ,  $\text{m}^{-1}$ ).

For example, let us determine the linear density of the  $[110]$  direction for the FCC crystal structure. An FCC unit cell (reduced sphere) and the  $[110]$  direction therein are shown in Figure 3.28a. Represented in Figure 3.28b are five atoms that lie on the bottom face of this unit cell; here the  $[110]$  direction vector passes from the center of atom  $X$ , through atom  $Y$ , and finally to the center of atom  $Z$ . With regard to the numbers of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells (as discussed in Section 3.4 relative to atomic packing factor computations). Each of the  $X$  and  $Z$  corner atoms is also shared with one other adjacent unit cell along this  $[110]$  direction (i.e., one-half of each of these atoms belongs to the unit cell being considered), whereas atom  $Y$  lies entirely within the unit cell. Thus, there is an equivalence of two atoms along the  $[110]$  direction vector in the unit cell. Now, the direction vector length is equal to  $4R$  (Figure 3.28b); thus, from Equation 3.16, the  $[110]$  linear density for FCC is

$$\text{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R} \quad (3.17)$$

**Figure 3.28** (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.



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

$$\text{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}} \quad (3.18)$$

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

For example, consider the section of a  $(110)$  plane within an FCC unit cell as represented in Figures 3.25a and 3.25b. Although six atoms have centers that lie on this plane (Figure 3.25b), only one-quarter of each of atoms A, C, D, and F and one-half of atoms B and E, for a total equivalence of just 2 atoms, are on that plane. Furthermore, the area of this rectangular section is equal to the product of its length and width. From Figure 3.25b, the length (horizontal dimension) is equal to  $4R$ , whereas the width (vertical dimension) is equal to  $2R\sqrt{2}$  because it corresponds to the FCC unit cell edge length (Equation 3.1). Thus, the area of this planar region is  $(4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$ , and the planar density is determined as follows:

$$\text{PD}_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}} \quad (3.19)$$

Linear and planar densities are important considerations relative to the process of slip—that is, the mechanism by which metals plastically deform (Section 8.5). Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing.

### 3.16 CLOSE-PACKED CRYSTAL STRUCTURES

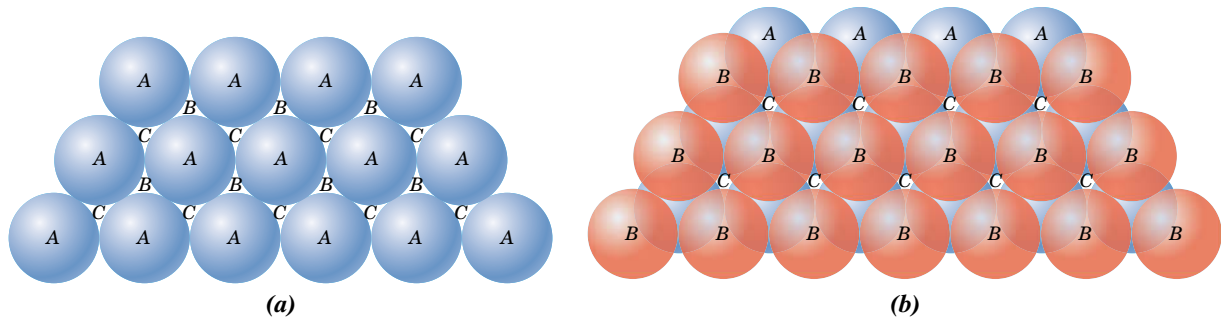
#### Metals



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Close-Packed  
Structures (Metals)

You may remember from the discussion on metallic crystal structures (Section 3.4) that both face-centered cubic and hexagonal close-packed crystal structures have atomic packing factors of 0.74, which is the most efficient packing of equal-size spheres or atoms. In addition to unit cell representations, these two crystal structures may be described in terms of close-packed planes of atoms (i.e., planes having a maximum atom or sphere-packing density); a portion of one such plane is illustrated in Figure 3.29a. Both crystal structures may be generated by the stacking of these close-packed planes on top of one another; the difference between the two structures lies in the stacking sequence.

Let the centers of all the atoms in one close-packed plane be labeled A. Associated with this plane are two sets of equivalent triangular depressions formed by three



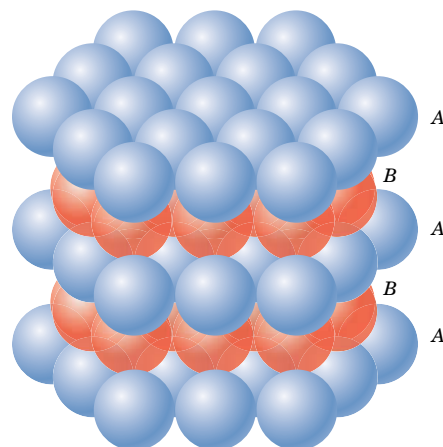
**Figure 3.29** (a) A portion of a close-packed plane of atoms; A, B, and C positions are indicated. (b) The AB stacking sequence for close-packed atomic planes.

(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.)

adjacent atoms, into which the next close-packed plane of atoms may rest. Those having the triangle vertex pointing up are arbitrarily designated as B positions, whereas the remaining depressions are those with the down vertices, which are marked C in Figure 3.29b.

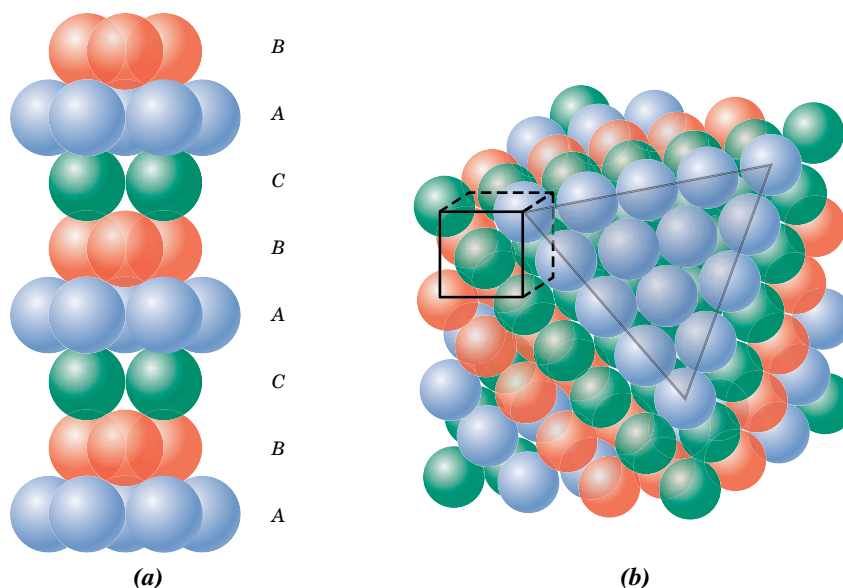
A second close-packed plane may be positioned with the centers of its atoms over either B or C sites; at this point both are equivalent. Suppose that the B positions are arbitrarily chosen; the stacking sequence is termed AB, which is illustrated in Figure 3.29b. The real distinction between FCC and HCP lies in where the third close-packed layer is positioned. For HCP, the centers of this layer are aligned directly above the original A positions. This stacking sequence,  $ABABAB \dots$ , is repeated over and over. Of course, the  $ACACAC \dots$  arrangement would be equivalent. These close-packed planes for HCP are (0001)-type planes, and the correspondence between this and the unit cell representation is shown in Figure 3.30.

For the face-centered crystal structure, the centers of the third plane are situated over the C sites of the first plane (Figure 3.31a). This yields an  $ABCABCABC \dots$  stacking sequence; that is, the atomic alignment repeats every third plane. It is more difficult to correlate the stacking of close-packed planes to the FCC unit cell. However,



**Figure 3.30** Close-packed plane stacking sequence for the hexagonal close-packed structure.

(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 3.31** (a) Close-packed stacking sequence for the face-centered cubic structure. (b) A corner has been removed to show the relation between the stacking of close-packed planes of atoms and the FCC crystal structure (i.e., the unit cell that has been outlined in the front and upper left-hand corner of the assemblage of spheres); 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.]

this relationship is demonstrated in Figure 3.31b. These planes are of the (111) type; an FCC unit cell is outlined on the upper left-hand front face of Figure 3.31b to provide perspective. The significance of these FCC and HCP close-packed structures will become apparent in Chapter 8.

## Ceramics



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tetrahedral position

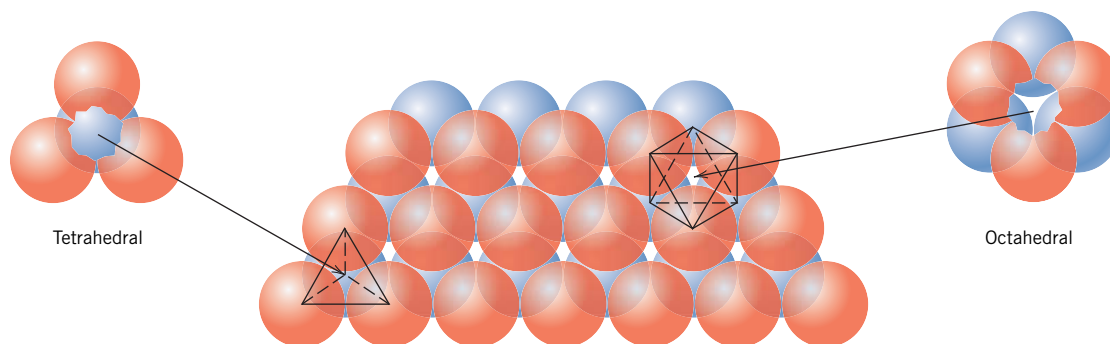
octahedral position

A number of ceramic crystal structures may also be considered in terms of close-packed planes of ions (as opposed to *atoms* for metals). Ordinarily, the close-packed planes are composed of the large anions. As these planes are stacked atop each other, small interstitial sites are created between them in which the cations may reside.

These interstitial positions exist in two different types, as illustrated in Figure 3.32. Four atoms (three in one plane and a single one in the adjacent plane) surround one type; this is termed a **tetrahedral position** because straight lines drawn from the centers of the surrounding spheres form a four-sided tetrahedron. The other site type in Figure 3.32 involves six ion spheres, three in each of the two planes. Because an octahedron is produced by joining these six sphere centers, this site is called an **octahedral position**. Thus, the coordination numbers for cations filling tetrahedral and octahedral positions are 4 and 6, respectively. Furthermore, for each of these anion spheres, one octahedral and two tetrahedral positions will exist.

Ceramic crystal structures of this type depend on two factors: (1) the stacking of the close-packed anion layers (both FCC and HCP arrangements are possible, which correspond to *ABCABC* . . . and *ABABAB* . . . sequences, respectively), and (2) the manner in which the interstitial sites are filled with cations. For example, consider the rock salt crystal structure discussed earlier. The unit cell has cubic symmetry, and each cation





**Figure 3.32** The stacking of one plane of close-packed (orange) spheres (anions) on top of another (blue spheres); the geometries of tetrahedral and octahedral positions between the planes are noted.

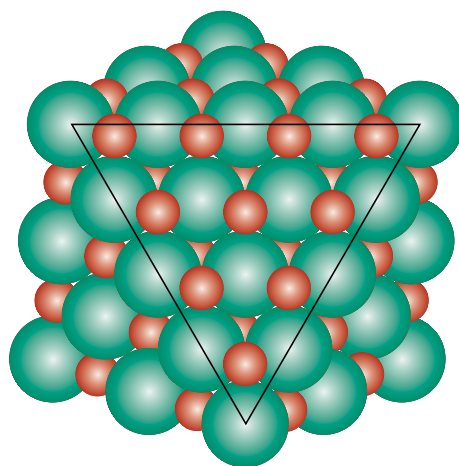
(From W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

( $\text{Na}^+$  ion) has six  $\text{Cl}^-$  ion nearest neighbors, as may be verified from Figure 3.6. That is, the  $\text{Na}^+$  ion at the center has as nearest neighbors the six  $\text{Cl}^-$  ions that reside at the centers of each of the cube faces. The crystal structure, having cubic symmetry, may be considered in terms of an FCC array of close-packed planes of anions, and all planes are of the  $\{111\}$  type. The cations reside in octahedral positions because they have as nearest neighbors six anions. Furthermore, all octahedral positions are filled because there is a single octahedral site per anion, and the ratio of anions to cations is 1:1. For this crystal structure, the relationship between the unit cell and close-packed anion plane stacking schemes is illustrated in Figure 3.33.



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Other, but not all, ceramic crystal structures may be treated in a similar manner; included are the zinc blende and perovskite structures. The *spinel structure* is one of the  $A_mB_nX_p$  types, which is found for magnesium aluminate, or spinel ( $\text{MgAl}_2\text{O}_4$ ). With this structure, the  $\text{O}^{2-}$  ions form an FCC lattice, whereas  $\text{Mg}^{2+}$  ions fill tetrahedral sites and  $\text{Al}^{3+}$  ions reside in octahedral positions. Magnetic ceramics, or ferrites, have a crystal structure that is a slight variant of this spinel structure, and the magnetic characteristics are affected by the occupancy of tetrahedral and octahedral positions (see Section 18.5).



**Figure 3.33** A section of the rock salt crystal structure from which a corner has been removed. The exposed plane of anions (green spheres inside the triangle) is a  $\{111\}$ -type plane; the cations (red spheres) occupy the interstitial octahedral positions.



**Figure 3.34** Photograph of a garnet single crystal found in Tongbei, Fujian Province, China. (Photograph courtesy of Irocks.com, Megan Foreman photo.)



## Crystalline and Noncrystalline Materials

### 3.17 SINGLE CRYSTALS

#### single crystal

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal**. All unit cells interlock in the same way and have the same orientation. Single crystals exist in nature, but they can also be produced artificially. They are ordinarily difficult to grow because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal assumes a regular geometric shape having flat faces, as with some of the gemstones; the shape is indicative of the crystal structure. A garnet single crystal is shown in Figure 3.34. Single crystals are extremely important in many modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

### 3.18 POLYCRYSTALLINE MATERIALS

#### grain

#### polycrystalline

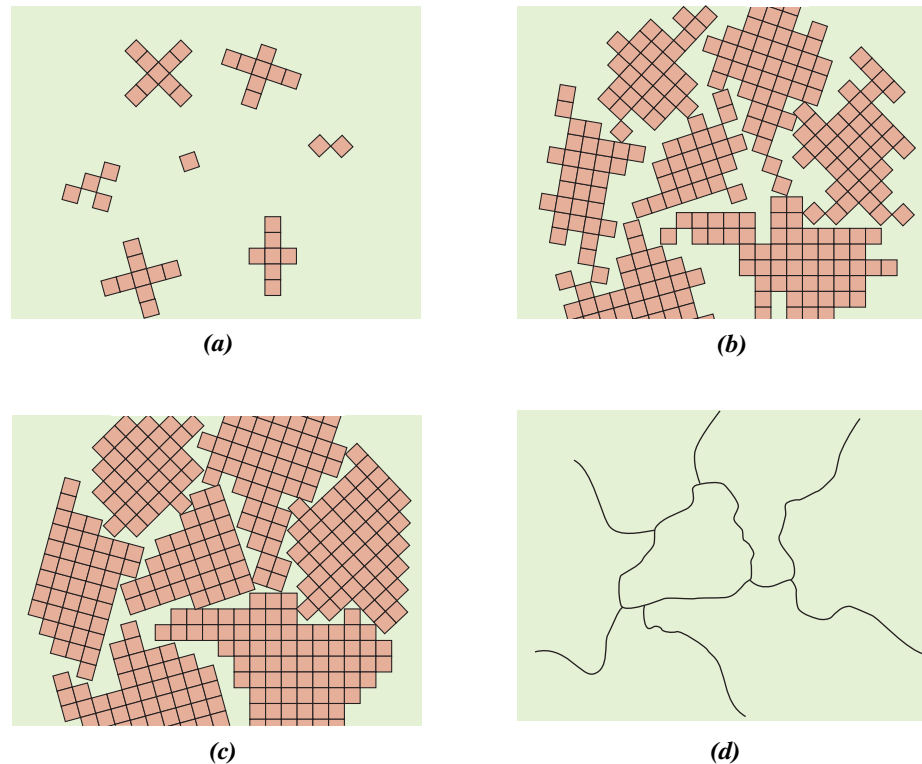
Most crystalline solids are composed of a collection of many small crystals or **grains**; such materials are termed **polycrystalline**. Various stages in the solidification of a polycrystalline specimen are represented schematically in Figure 3.35. Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. As indicated in Figure 3.35, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary**, is discussed in more detail in Section 5.8.

#### grain boundary

### 3.19 ANISOTROPY

#### anisotropy

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed **anisotropy**, and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of



**Figure 3.35** 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.)

### isotropic

measurement are **isotropic**. The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic. The modulus of elasticity values at  $[100]$ ,  $[110]$ , and  $[111]$  orientations for several metals are presented in Table 3.8.

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random. Under these circumstances, even though each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically.

**Table 3.8**

Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

Metal	Modulus of Elasticity (GPa)		
	$[100]$	$[110]$	$[111]$
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.

Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a “texture.”

The magnetic properties of some iron alloys used in transformer cores are anisotropic—that is, grains (or single crystals) magnetize in a  $\langle 100 \rangle$ -type direction more easily than in any other crystallographic direction. Energy losses in transformer cores are minimized by utilizing polycrystalline sheets of these alloys into which have been introduced a *magnetic texture*: most of the grains in each sheet have a  $\langle 100 \rangle$ -type crystallographic direction that is aligned (or almost aligned) in the same direction, which is oriented parallel to the direction of the applied magnetic field. Magnetic textures for iron alloys are discussed in detail in the Material of Importance box in Chapter 18 following Section 18.9.

## 3.20 X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Historically, much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials. We now give a brief overview of the diffraction phenomenon and how, using x-rays, atomic interplanar distances and crystal structures are deduced.

### The Diffraction Phenomenon

*Diffraction* occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave and (2) have spacings that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.

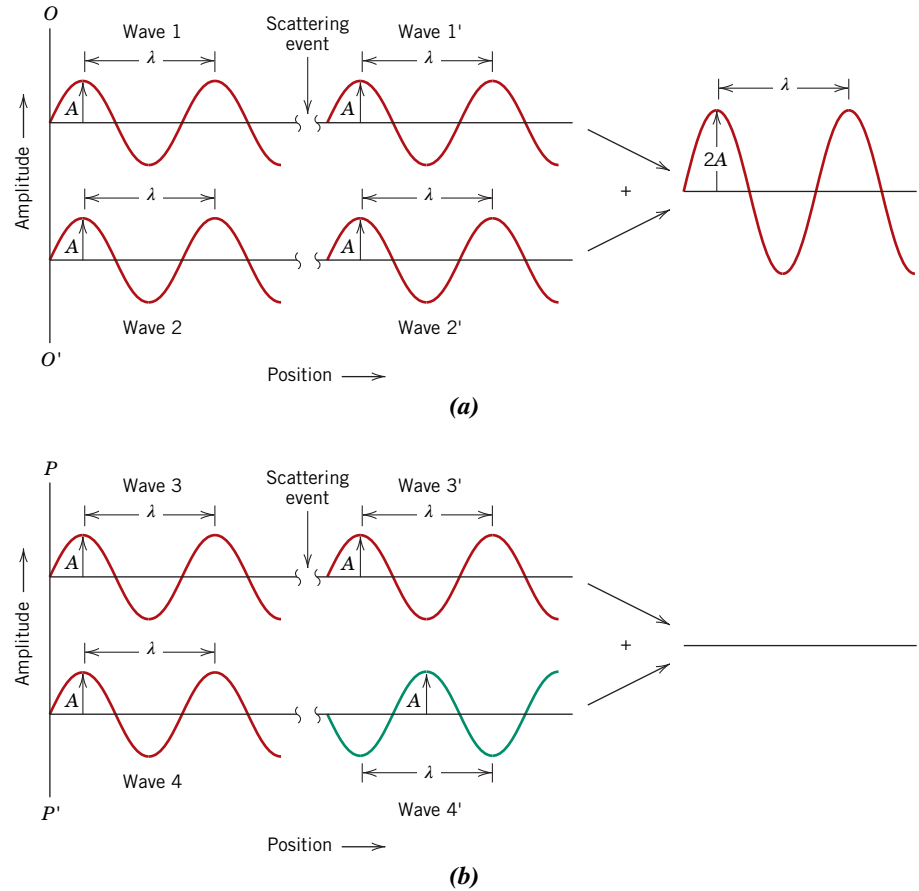
Consider waves 1 and 2 in Figure 3.36a, which have the same wavelength ( $\lambda$ ) and are in phase at point  $O-O'$ . Now let us suppose that both waves are scattered in such a way that they traverse different paths. The phase relationship between the scattered waves, which depend upon the difference in path length, is important. One possibility results when this path length difference is an integral number of wavelengths. As noted in Figure 3.36a, these scattered waves (now labeled 1' and 2') are still in phase. They are said to mutually reinforce (or constructively interfere with) one another; when amplitudes are added, the wave shown on the right side of the figure results. This is a manifestation of **diffraction**, and we refer to a *diffracted beam* as one composed of a large number of scattered waves that mutually reinforce one another.

Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is that demonstrated in Figure 3.36b, in which the path length difference after scattering is some integral number of *half*-wavelengths. The scattered waves are out of phase—that is, corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the resultant wave has zero amplitude), as indicated on the right side of the figure. Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

### X-Ray Diffraction and Bragg's Law

X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids. When a beam of x-rays impinges on a solid material, a portion of this beam is scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

diffraction



**Figure 3.36** (a) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength  $\lambda$  and remain in phase after a scattering event (waves 1' and 2') constructively interfere with one another. The amplitudes of the scattered waves add together in the resultant wave. (b) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3' and 4') destructively interfere with one another. The amplitudes of the two scattered waves cancel one another.

Consider the two parallel planes of atoms  $A-A'$  and  $B-B'$  in Figure 3.37, which have the same  $h$ ,  $k$ , and  $l$  Miller indices and are separated by the interplanar spacing  $d_{hkl}$ . Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength  $\lambda$  is incident on these two planes at an angle  $\theta$ . Two rays in this beam, labeled 1 and 2, are scattered by atoms  $P$  and  $Q$ . Constructive interference of the scattered rays 1' and 2' occurs also at an angle  $\theta$  to the planes if the path length difference between 1– $P$ –1' and 2– $Q$ –2' (i.e.,  $\overline{SQ} + \overline{QT}$ ) is equal to a whole number,  $n$ , of wavelengths. That is, the condition for diffraction is

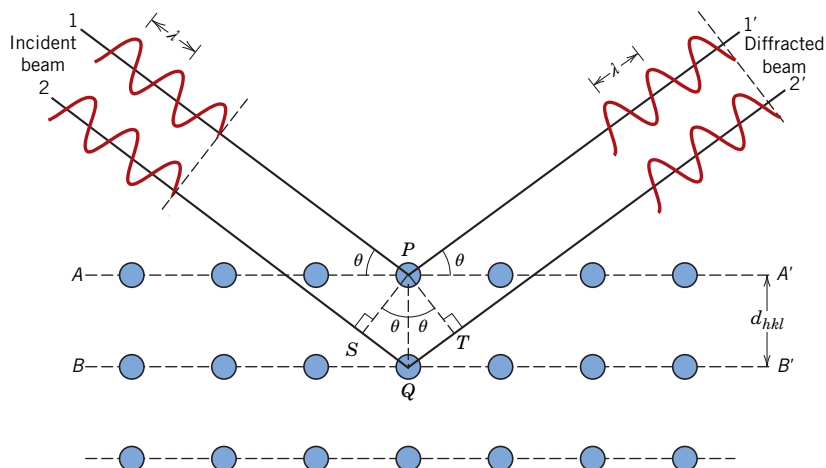
$$n\lambda = \overline{SQ} + \overline{QT} \quad (3.20)$$

Bragg's law—  
relationship among  
x-ray wavelength,  
interatomic spacing,  
and angle of  
diffraction for  
constructive  
interference

or

$$\begin{aligned} n\lambda &= d_{hkl} \sin \theta + d_{hkl} \sin \theta \\ &= 2d_{hkl} \sin \theta \end{aligned} \quad (3.21)$$

**Figure 3.37** Diffraction of x-rays by planes of atoms ( $A-A'$  and  $B-B'$ ).



### Bragg's law

Equation 3.21 is known as **Bragg's law**;  $n$  is the order of reflection, which may be any integer (1, 2, 3, ...) consistent with  $\sin \theta$  not exceeding unity. Thus, we have a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg's law is not satisfied, then the interference will be nonconstructive so as to yield a very low-intensity diffracted beam.

The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing  $d_{hkl}$ ) is a function of the Miller indices ( $h$ ,  $k$ , and  $l$ ) as well as the lattice parameter(s). For example, for crystal structures that have cubic symmetry,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.22)$$

Interplanar separation for a plane having indices  $h$ ,  $k$ , and  $l$

in which  $a$  is the lattice parameter (unit cell edge length). Relationships similar to Equation 3.22, but more complex, exist for the other six crystal systems noted in Table 3.6.

Bragg's law, Equation 3.21, is a necessary but not sufficient condition for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams that, according to Equation 3.21, should be present. Specific sets of crystallographic planes that do not give rise to diffracted beams depend on crystal structure. For the BCC crystal structure,  $h + k + l$  must be even if diffraction is to occur, whereas for FCC,  $h$ ,  $k$ , and  $l$  must all be either odd or even; diffracted beams for all sets of crystallographic planes are present for the simple cubic crystal structure (Figure 3.3). These restrictions, called *reflection rules*, are summarized in Table 3.9.<sup>10</sup>



**Concept Check 3.4** For cubic crystals, as values of the planar indices  $h$ ,  $k$ , and  $l$  increase, does the distance between adjacent and parallel planes (i.e., the interplanar spacing) increase or decrease? Why?

(The answer is available in WileyPLUS.)

<sup>10</sup>Zero is considered to be an even integer.

**Table 3.9**

X-Ray Diffraction  
Reflection Rules and  
Reflection Indices  
for Body-Centered  
Cubic, Face-Centered  
Cubic, and Simple  
Cubic Crystal  
Structures

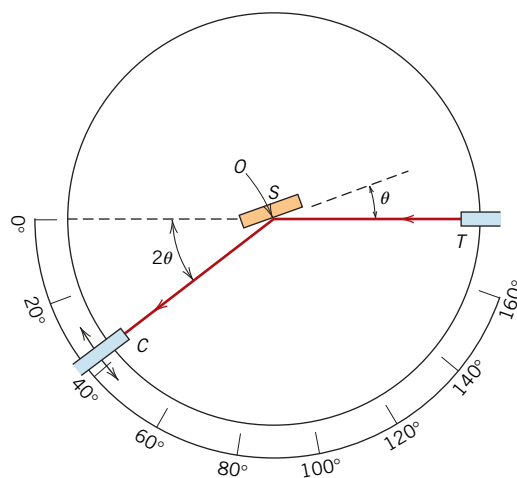
<i>Crystal Structure</i>	<i>Reflections Present</i>	<i>Reflection Indices for First Six Planes</i>
BCC	$(h + k + l)$ even	110, 200, 211, 220, 310, 222
FCC	$h, k,$ and $l$ either all odd or all even	111, 200, 220, 311, 222, 400
Simple cubic	All	100, 110, 111, 200, 210, 211

### Diffraction Techniques

One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation. Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

The *diffractometer* is an apparatus used to determine the angles at which diffraction occurs for powdered specimens; its features are represented schematically in Figure 3.38. A specimen  $S$  in the form of a flat plate is supported so that rotations about the axis labeled  $O$  are possible; this axis is perpendicular to the plane of the page. The monochromatic x-ray beam is generated at point  $T$ , and the intensities of diffracted beams are detected with a counter labeled  $C$  in the figure. The specimen, x-ray source, and counter are coplanar.

The counter is mounted on a movable carriage that may also be rotated about the  $O$  axis; its angular position in terms of  $2\theta$  is marked on a graduated scale.<sup>11</sup> Carriage and specimen are mechanically coupled such that a rotation of the specimen through  $\theta$  is accompanied by a  $2\theta$  rotation of the counter; this ensures that the incident and reflection angles are maintained equal to one another (Figure 3.38). Collimators are incorporated

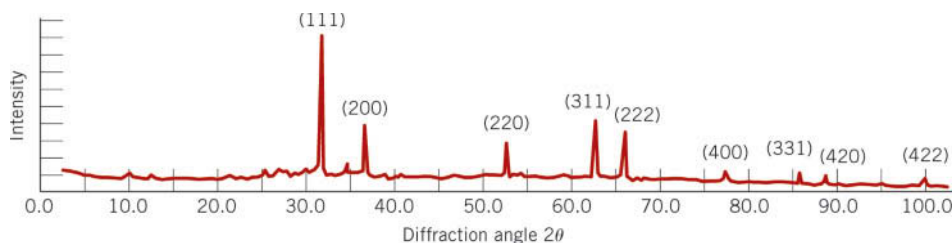


**Figure 3.38** Schematic diagram of an x-ray diffractometer;  $T$  = x-ray source,  $S$  = specimen,  $C$  = detector, and  $O$  = the axis around which the specimen and detector rotate.

<sup>11</sup>Note that the symbol  $\theta$  has been used in two different contexts for this discussion. Here,  $\theta$  represents the angular locations of both x-ray source and counter relative to the specimen surface. Previously (e.g., Equation 3.21), it denoted the angle at which the Bragg criterion for diffraction is satisfied.

**Figure 3.39**

Diffraction pattern for powdered lead.



within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam.

As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of  $2\theta$ ;  $2\theta$  is termed the *diffraction angle*, which is measured experimentally. Figure 3.39 shows a diffraction pattern for a powdered specimen of lead. The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes. These peaks are plane-indexed in the figure.

Other powder techniques have been devised in which diffracted beam intensity and position are recorded on a photographic film instead of being measured by a counter.

One of the primary uses of x-ray diffractometry is for the determination of crystal structure. The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks, whereas the arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

X-rays, as well as electron and neutron beams, are also used in other types of material investigations. For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs. The chapter-opening photograph (*a*) was generated using an incident x-ray beam that was directed on a magnesium crystal; each spot (with the exception of the darkest one near the center) resulted from an x-ray beam that was diffracted by a specific set of crystallographic planes. Other uses of x-rays include qualitative and quantitative chemical identifications and the determination of residual stresses and crystal size.

### EXAMPLE PROBLEM 3.16

#### Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute (a) the interplanar spacing and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

#### Solution

- (a) The value of the interplanar spacing  $d_{hkl}$  is determined using Equation 3.22 with  $a = 0.2866$  nm and  $h = 2$ ,  $k = 2$ , and  $l = 0$  because we are considering the (220) planes. Therefore,

$$\begin{aligned} d_{hkl} &= \frac{a}{\sqrt{h^2 + k^2 + l^2}} \\ &= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm} \end{aligned}$$

- (b) The value of  $\theta$  may now be computed using Equation 3.21, with  $n = 1$  because this is a first-order reflection:

$$\sin \theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790 \text{ nm})}{(2)(0.1013 \text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13^\circ$$

The diffraction angle is  $2\theta$ , or

$$2\theta = (2)(62.13^\circ) = 124.26^\circ$$

### EXAMPLE PROBLEM 3.17

#### Interplanar Spacing and Lattice Parameter Computations for Lead

Figure 3.39 shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also, determine the lattice parameter of Pb for each of the peaks. For all peaks, assume the order of diffraction is 1.

#### Solution

For each peak, in order to compute the interplanar spacing and the lattice parameter we must employ Equations 3.21 and 3.22, respectively. The first peak of Figure 3.39, which results from diffraction by the (111) set of planes, occurs at  $2\theta = 31.3^\circ$ ; the corresponding interplanar spacing for this set of planes, using Equation 3.21, is equal to

$$d_{111} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2) \left[ \sin \left( \frac{31.3^\circ}{2} \right) \right]} = 0.2858 \text{ nm}$$

And, from Equation 3.22, the lattice parameter  $a$  is determined as

$$\begin{aligned} a &= d_{hkl} \sqrt{h^2 + k^2 + l^2} \\ &= d_{111} \sqrt{(1)^2 + (1)^2 + (1)^2} \\ &= (0.2858 \text{ nm}) \sqrt{3} = 0.4950 \text{ nm} \end{aligned}$$

Similar computations are made for the next four peaks; the results are tabulated below:

Peak Index	$2\theta$	$d_{hkl}(\text{nm})$	$a(\text{nm})$
200	36.6	0.2455	0.4910
220	52.6	0.1740	0.4921
311	62.5	0.1486	0.4929
222	65.5	0.1425	0.4936

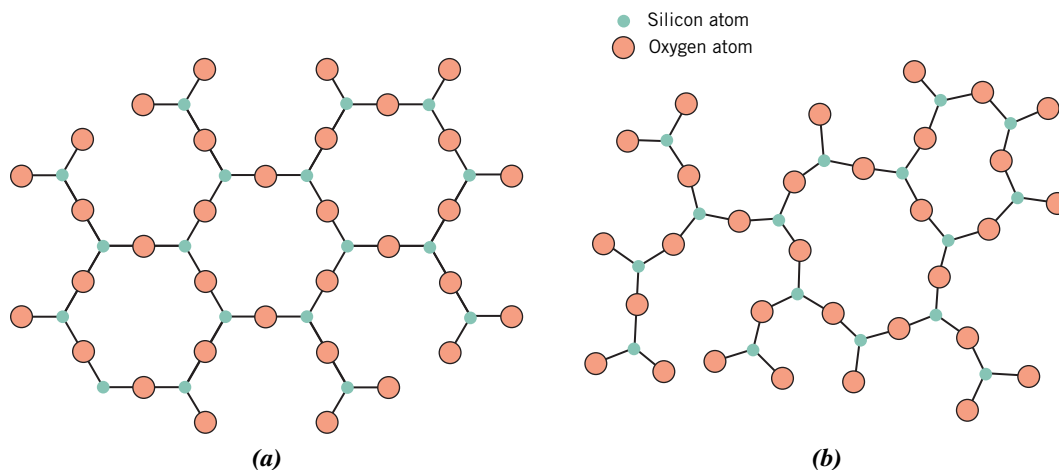
## 3.21 NONCRYSTALLINE SOLIDS

### noncrystalline

### amorphous

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally “without form”) or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.





**Figure 3.40** Two-dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide ( $\text{SiO}_2$ ), which may exist in both states. Figures 3.40a and 3.40b present two-dimensional schematic diagrams for both structures of  $\text{SiO}_2$ , in which the  $\text{SiO}_4^{4-}$  tetrahedron is the basic unit (Figure 3.11). Even though each silicon ion bonds to three oxygen ions for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or an amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Furthermore, rapidly cooling through the freezing temperature favors the formation of a noncrystalline solid because little time is allowed for the ordering process.

Metals normally form crystalline solids, but some ceramic materials are crystalline, whereas others—the inorganic glasses—are amorphous. Polymers may be completely noncrystalline or semicrystalline consisting of varying degrees of crystallinity. More about the structure and properties of amorphous materials is discussed below and in subsequent chapters.

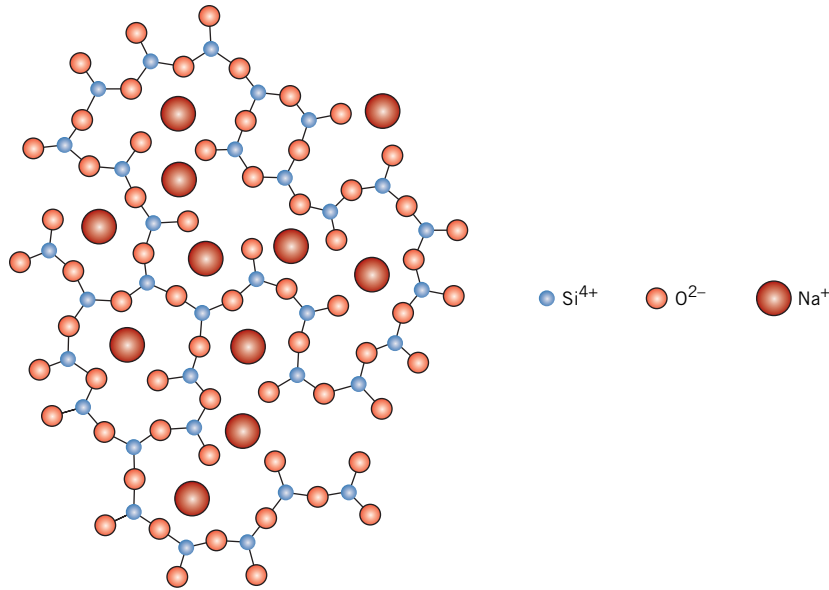


**Concept Check 3.5** Do noncrystalline materials display the phenomenon of allotropy (or polymorphism)? Why or why not?

**Concept Check 3.6** Do noncrystalline materials have grain boundaries? Why or why not? (The answers are available in *WileyPLUS*.)

### Silica Glasses

Silicon dioxide (or silica,  $\text{SiO}_2$ ) in the noncrystalline state is called *fused silica*, or *vitreous silica*; again, a schematic representation of its structure is shown in Figure 3.40b. Other



**Figure 3.41** Schematic representation of ion positions in a sodium-silicate glass.

oxides (e.g.,  $\text{B}_2\text{O}_3$  and  $\text{GeO}_2$ ) may also form glassy structures (and polyhedral oxide structures similar to that shown in Figure 3.13); these materials, as well as  $\text{SiO}_2$ , are termed *network formers*.

The common inorganic glasses that are used for containers, windows, and so on are silica glasses to which have been added other oxides such as  $\text{CaO}$  and  $\text{Na}_2\text{O}$ . These oxides do not form polyhedral networks. Rather, their cations are incorporated within and modify the  $\text{SiO}_4^{4-}$  network; for this reason, these oxide additives are termed *network modifiers*. For example, Figure 3.41 is a schematic representation of the structure of a sodium-silicate glass. Still other oxides, such as  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , although not network formers, substitute for silicon and become part of and stabilize the network; these are called *intermediates*. From a practical perspective, the addition of these modifiers and intermediates lowers the melting point and viscosity of a glass and makes it easier to form at lower temperatures (Section 14.7).

## SUMMARY

### Fundamental Concepts

- Atoms in crystalline solids are positioned in orderly and repeated patterns that are in contrast to the random and disordered atomic distribution found in noncrystalline or amorphous materials.

### Unit Cells

- Crystal structures are specified in terms of parallelepiped unit cells, which are characterized by geometry and atom positions within.

### Metallic Crystal Structures

- Most common metals exist in at least one of three relatively simple crystal structures: Face-centered cubic (FCC), which has a cubic unit cell (Figure 3.1). Body-centered cubic (BCC), which also has a cubic unit cell (Figure 3.2). Hexagonal close-packed, which has a unit cell of hexagonal symmetry (Figure 3.4a).
- Unit cell edge length ( $a$ ) and atomic radius ( $R$ ) are related according to Equation 3.1 for face-centered cubic, and Equation 3.4 for body-centered cubic.

- Two features of a crystal structure are
    - Coordination number—the number of nearest-neighbor atoms, and
    - Atomic packing factor—the fraction of solid-sphere volume in the unit cell.
- Density Computations—Metals**
- The theoretical density of a metal ( $\rho$ ) is a function of the number of equivalent atoms per unit cell, the atomic weight, the unit cell volume, and Avogadro's number (Equation 3.8).
- Ceramic Crystal Structures**
- Interatomic bonding in ceramics ranges from purely ionic to totally covalent.
  - For predominantly ionic bonding:
    - Metallic cations are positively charged, whereas nonmetallic ions have negative charges.
    - Crystal structure is determined by (1) the charge magnitude on each ion and (2) the radius of each type of ion.
  - Many of the simpler crystal structures are described in terms of unit cells:
    - Rock salt (Figure 3.6)
    - Cesium chloride (Figure 3.7)
    - Zinc blende (Figure 3.8)
    - Fluorite (Figure 3.9)
    - Perovskite (Figure 3.10)
- Density Computations—Ceramics**
- The theoretical density of a ceramic material can be computed using Equation 3.9.
- Silicate Ceramics**
- For the silicates, structure is more conveniently represented in terms of interconnecting  $\text{SiO}_4^{4-}$  tetrahedra (Figure 3.11). Relatively complex structures may result when other cations (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) and anions (e.g.,  $\text{OH}^-$ ) are added.
  - Silicate ceramics include the following:
    - Crystalline silica ( $\text{SiO}_2$ ) (as cristobalite, Figure 3.12)
    - Layered silicates (Figures 3.14 and 3.15)
    - Noncrystalline silica glasses (Figure 3.41)
- Carbon**
- Carbon (sometimes also considered a ceramic) can exist in several polymorphic forms, to include
    - Diamond (Figure 3.17)
    - Graphite (Figure 3.18)
- Polymorphism and Allotropy**
- *Polymorphism* occurs when a specific material can have more than one crystal structure. *Allotropy* is polymorphism for elemental solids.
- Crystal Systems**
- The concept of a crystal system is used to classify crystal structures on the basis of unit cell geometry—that is, unit cell edge lengths and interaxial angles. There are seven crystal systems: cubic, tetragonal, hexagonal, orthorhombic, rhombohedral (trigonal), monoclinic, and triclinic.
- Point Coordinates**
- Crystallographic points, directions, and planes are specified in terms of indexing schemes. The basis for the determination of each index is a coordinate axis system defined by the unit cell for the particular crystal structure.
    - The location of a point within a unit cell is specified using coordinates that are fractional multiples of the cell edge lengths (Equations 3.10a–3.10c).
    - Directional indices are computed in terms of differences between vector head and tail coordinates (Equations 3.11a–3.11c).
    - Planar (or Miller) indices are determined from the reciprocals of axial intercepts (Equations 3.14a–3.14c).
- Crystallographic Directions**
- Crystallographic Planes**

- For hexagonal unit cells, a four-index scheme for both directions and planes is found to be more convenient. Directions may be determined using Equations 3.12a–3.12d and 3.13a–3.13c.
- Linear and Planar Densities**
- Crystallographic directional and planar equivalencies are related to atomic linear and planar densities, respectively.
    - Linear density* (for a specific crystallographic direction) is defined as the number of atoms per unit length whose centers lie on the vector for this direction (Equation 3.16).
    - Planar density* (for a specific crystallographic plane) is taken as the number of atoms per unit area that are centered on the particular plane (Equation 3.18).
  - For a given crystal structure, planes having identical atomic packing yet different Miller indices belong to the same family.
- Close-Packed Crystal Structures**
- Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes of atoms on top of one another. With this scheme *A*, *B*, and *C* denote possible atom positions on a close-packed plane.
    - The stacking sequence for HCP is *ABABAB*. . . .
    - The stacking sequence for FCC is *ABCABCABC*. . . .
  - Close-packed planes for FCC and HCP are {111} and {0001}, respectively.
  - Some ceramic crystal structures can be generated from the stacking of close-packed planes of anions; cations fill interstitial tetrahedral and/or octahedral positions that exist between adjacent planes.
- Single Crystals**
- Polycrystalline Materials**
- *Single crystals* are materials in which the atomic order extends uninterrupted over the entirety of the specimen; under some circumstances, single crystals may have flat faces and regular geometric shapes.
  - The vast majority of crystalline solids, however, are *polycrystalline*, being composed of many small crystals or grains having different crystallographic orientations.
  - A *grain boundary* is the boundary region separating two grains where there is some atomic mismatch.
- Anisotropy**
- *Anisotropy* is the directionality dependence of properties. For isotropic materials, properties are independent of the direction of measurement.
- X-Ray Diffraction: Determination of Crystal Structures**
- *X-ray diffractometry* is used for crystal structure and interplanar spacing determinations. A beam of x-rays directed on a crystalline material may experience diffraction (constructive interference) as a result of its interaction with a series of parallel atomic planes.
  - Bragg's law specifies the condition for diffraction of x-rays—Equation 3.21.
- Noncrystalline Solids**
- Noncrystalline solid materials lack a systematic and regular arrangement of atoms or ions over relatively large distances (on an atomic scale). Sometimes the term *amorphous* is also used to describe these materials.

## Equation Summary

Equation Number	Equation	Solving For	Page Number
3.1	$a = 2R\sqrt{2}$	Unit cell edge length, FCC	51
3.3	$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$	Atomic packing factor	52

(continued)

Equation Number	Equation	Solving For	Page Number
3.4	$a = \frac{4R}{\sqrt{3}}$	Unit cell edge length, BCC	53
3.8	$\rho = \frac{nA}{V_C N_A}$	Theoretical density of a metal	57
3.9	$\rho = \frac{n'(\sum A_C + \sum A_A)}{V_C N_A}$	Theoretical density of a ceramic material	63
3.10a	$q = \frac{\text{lattice position referenced to the } x \text{ axis}}{a}$	Point coordinate referenced to $x$ axis	72
3.11a	$u = n\left(\frac{x_2 - x_1}{a}\right)$	Direction index referenced to $x$ axis	75
3.12a	$u = \frac{1}{3}(2U - V)$	Direction index conversion to hexagonal	78
3.13a	$U = n\left(\frac{a_1'' - a_1'}{a}\right)$	Hexagonal direction index referenced to $a_1$ axis (three-axis scheme)	79
3.14a	$h = \frac{na}{A}$	Planar (Miller) index referenced to $x$ axis	81
3.16	$LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$	Linear density	87
3.18	$PD = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$	Planar density	88
3.21	$n\lambda = 2d_{hkl}\sin\theta$	Bragg's law; wavelength–interplanar spacing–angle of diffracted beam	95
3.22	$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$	Interplanar spacing for crystals having cubic symmetry	96

### List of Symbols

Symbol	Meaning
$a$	Unit cell edge length for cubic structures; unit cell $x$ -axial length
$a_1'$	Vector tail coordinate, hexagonal
$a_1''$	Vector head coordinate, hexagonal
$A$	Atomic weight
$A$	Planar intercept on $x$ axis
$\sum A_A$	Sum of the atomic weights of all anions in formula unit
$\sum A_C$	Sum of the atomic weights of all cations in formula unit
$d_{hkl}$	Interplanar spacing for crystallographic planes having indices $h$ , $k$ , and $l$
$n$	Order of reflection for x-ray diffraction
$n$	Number of atoms associated with a unit cell

(continued)

Symbol	Meaning
$n$	Normalization factor—reduction of directional/planar indices to integers
$n'$	Number of formula units in a unit cell
$N_A$	Avogadro's number ( $6.022 \times 10^{23}$ atoms/mol)
$R$	Atomic radius
$V_C$	Unit cell volume
$x_1$	Vector tail coordinate
$x_2$	Vector head coordinate
$\lambda$	X-ray wavelength
$\rho$	Density; theoretical density

## Important Terms and Concepts

allotropy	crystal system	Miller indices
amorphous	crystalline	noncrystalline
anion	diffraction	octahedral position
anisotropy	face-centered cubic (FCC)	polycrystalline
atomic packing factor (APF)	grain	polymorphism
body-centered cubic (BCC)	grain boundary	single crystal
Bragg's law	hexagonal close-packed (HCP)	tetrahedral position
cation	isotropic	unit cell
coordination number	lattice	
crystal structure	lattice parameters	

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## QUESTIONS AND PROBLEMS

### Fundamental Concepts

- 3.1 What is the difference between *atomic structure* and *crystal structure*?

### Unit Cells

#### Metallic Crystal Structures

- 3.2 If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters.

- 3.3** Show for the body-centered cubic crystal structure that the unit cell edge length  $a$  and the atomic radius  $R$  are related through  $a = 4R/\sqrt{3}$ .
- 3.4** For the HCP crystal structure, show that the ideal  $c/a$  ratio is 1.633.
- 3.5** Show that the atomic packing factor for BCC is 0.68.
- 3.6** Show that the atomic packing factor for HCP is 0.74.

### Density Computations—Metals

- 3.7** Molybdenum (Mo) has a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover of the book.
- 3.8** Strontium (Sr) has an FCC crystal structure, an atomic radius of 0.215 nm, and an atomic weight of 87.62 g/mol. Calculate the theoretical density for Sr.
- 3.9** Calculate the radius of a palladium (Pd) atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm<sup>3</sup>, and an atomic weight of 106.4 g/mol.
- 3.10** Calculate the radius of a tantalum (Ta) atom, given that Ta has a BCC crystal structure, a density of 16.6 g/cm<sup>3</sup>, and an atomic weight of 180.9 g/mol.
- 3.11** A hypothetical metal has the simple cubic crystal structure shown in Figure 3.3. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density.
- 3.12** Titanium (Ti) has an HCP crystal structure and a density of 4.51 g/cm<sup>3</sup>.
- (a) What is the volume of its unit cell in cubic meters?
- (b) If the  $c/a$  ratio is 1.58, compute the values of  $c$  and  $a$ .
- 3.13** Magnesium (Mg) has an HCP crystal structure and a density of 1.74 g/cm<sup>3</sup>.
- (a) What is the volume of its unit cell in cubic centimeters?
- (b) If the  $c/a$  ratio is 1.624, compute the values of  $c$  and  $a$ .
- 3.14** Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover of the book, compute the theoretical densities of aluminum (Al), nickel (Ni), magnesium (Mg), and tungsten (W), and then compare these values with the measured densities listed

in this same table. The  $c/a$  ratio for magnesium is 1.624.

- 3.15** Niobium (Nb) has an atomic radius of 0.1430 nm and a density of 8.57 g/cm<sup>3</sup>. Determine whether it has an FCC or a BCC crystal structure.
- 3.16** The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each, determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.

<i>Alloy</i>	<i>Atomic Weight (g/mol)</i>	<i>Density (g/cm<sup>3</sup>)</i>	<i>Atomic Radius (nm)</i>
A	43.1	6.40	0.122
B	184.4	12.30	0.146
C	91.6	9.60	0.137

- 3.17** The unit cell for uranium (U) has orthorhombic symmetry, with  $a$ ,  $b$ , and  $c$  lattice parameters of 0.286, 0.587, and 0.495 nm, respectively. If its density, atomic weight, and atomic radius are 19.05 g/cm<sup>3</sup>, 238.03 g/mol, and 0.1385 nm, respectively, compute the atomic packing factor.
- 3.18** Indium (In) has a tetragonal unit cell for which the  $a$  and  $c$  lattice parameters are 0.459 and 0.495 nm, respectively.
- (a) If the atomic packing factor and atomic radius are 0.693 and 0.1625 nm, respectively, determine the number of atoms in each unit cell.
- (b) The atomic weight of In is 114.82 g/mol; compute its theoretical density.
- 3.19** Beryllium (Be) has an HCP unit cell for which the ratio of the lattice parameters  $c/a$  is 1.568. If the radius of the Be atom is 0.1143 nm, (a) determine the unit cell volume, and (b) calculate the theoretical density of Be and compare it with the literature value.
- 3.20** Magnesium (Mg) has an HCP crystal structure, a  $c/a$  ratio of 1.624, and a density of 1.74 g/cm<sup>3</sup>. Compute the atomic radius for Mg.
- 3.21** Cobalt (Co) has an HCP crystal structure, an atomic radius of 0.1253 nm, and a  $c/a$  ratio of 1.623. Compute the volume of the unit cell for Co.

### Ceramic Crystal Structures

- 3.22** For a ceramic compound, what are the two characteristics of the component ions that determine the crystal structure?
- 3.23** Show that the minimum cation-to-anion radius ratio for a coordination number of 4 is 0.225.



- 3.24** Show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414. (*Hint:* Use the NaCl crystal structure in Figure 3.6, and assume that anions and cations are just touching along cube edges and across face diagonals.)
- 3.25** Demonstrate that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732.
- 3.26** On the basis of ionic charge and ionic radii given in Table 3.4, predict crystal structures for the following materials:
- (a) CaO
  - (b) MnS
  - (c) KBr
  - (d) CsBr
- Justify your selections.
- 3.27** Which of the cations in Table 3.4 would you predict to form fluorides having the cesium chloride crystal structure? Justify your choices.
- (b) The measured density is  $3.99 \text{ g/cm}^3$ . How do you explain the slight discrepancy between your calculated value and the measured value?
- 3.35** From the data in Table 3.4, compute the theoretical density of  $\text{CaF}_2$ , which has the fluorite structure.
- 3.36** A hypothetical AX type of ceramic material is known to have a density of  $2.10 \text{ g/cm}^3$  and a unit cell of cubic symmetry with a cell edge length of  $0.57 \text{ nm}$ . The atomic weights of the A and X elements are  $28.5$  and  $30.0 \text{ g/mol}$ , respectively. On the basis of this information, which of the following crystal structures is (are) possible for this material: sodium chloride, cesium chloride, or zinc blende? Justify your choice(s).
- 3.37** The unit cell for  $\text{Fe}_3\text{O}_4$  ( $\text{FeO}\text{--}\text{Fe}_2\text{O}_3$ ) has cubic symmetry with a unit cell edge length of  $0.839 \text{ nm}$ . If the density of this material is  $5.24 \text{ g/cm}^3$ , compute its atomic packing factor. For this computation, you will need to use the ionic radii listed in Table 3.4.

#### Density Computations—Ceramics

- 3.28** Compute the atomic packing factor for the rock salt crystal structure in which  $r_C/r_A = 0.414$ .
- 3.29** The unit cell for  $\text{Al}_2\text{O}_3$  has hexagonal symmetry with lattice parameters  $a = 0.4759 \text{ nm}$  and  $c = 1.2989 \text{ nm}$ . If the density of this material is  $3.99 \text{ g/cm}^3$ , calculate its atomic packing factor. For this computation, use ionic radii listed in Table 3.4.
- 3.30** Compute the atomic packing factor for cesium chloride using the ionic radii in Table 3.4 and assuming that the ions touch along the cube diagonals.
- 3.31** Calculate the theoretical density of NiO, given that it has the rock salt crystal structure.
- 3.32** Iron oxide ( $\text{FeO}$ ) has the rock salt crystal structure and a density of  $5.70 \text{ g/cm}^3$ .
- (a) Determine the unit cell edge length.
  - (b) How does this result compare with the edge length as determined from the radii in Table 3.4, assuming that the  $\text{Fe}^{2+}$  and  $\text{O}^{2-}$  ions just touch each other along the edges?
- 3.33** One crystalline form of silica ( $\text{SiO}_2$ ) has a cubic unit cell, and from x-ray diffraction data it is known that the cell edge length is  $0.700 \text{ nm}$ . If the measured density is  $2.32 \text{ g/cm}^3$ , how many  $\text{Si}^{4+}$  and  $\text{O}^{2-}$  ions are there per unit cell?
- 3.34** (a) Using the ionic radii in Table 3.4, compute the theoretical density of CsCl. (*Hint:* Use a modification of the result of Problem 3.3.)

#### Silicate Ceramics

- 3.38** In terms of bonding, explain why silicate materials have relatively low densities.
- 3.39** Determine the angle between covalent bonds in an  $\text{SiO}_4^{4-}$  tetrahedron.

#### Carbon

- 3.40** Compute the theoretical density of diamond, given that the C—C distance and bond angle are  $0.154 \text{ nm}$  and  $109.5^\circ$ , respectively. How does this value compare with the measured density?
- 3.41** Compute the theoretical density of ZnS, given that the Zn—S distance and bond angle are  $0.234 \text{ nm}$  and  $109.5^\circ$ , respectively. How does this value compare with the measured density?
- 3.42** Compute the atomic packing factor for the diamond cubic crystal structure (Figure 3.17). Assume that bonding atoms touch one another, that the angle between adjacent bonds is  $109.5^\circ$ , and that each atom internal to the unit cell is positioned  $a/4$  of the distance away from the two nearest cell faces ( $a$  is the unit cell edge length).

#### Polymorphism and Allotropy

- 3.43** Iron (Fe) undergoes an allotropic transformation at  $912^\circ\text{C}$ : upon heating from a BCC ( $\alpha$  phase) to an FCC ( $\gamma$  phase). Accompanying this transformation is a change in the atomic radius of Fe—from  $R_{\text{BCC}} = 0.12584 \text{ nm}$  to  $R_{\text{FCC}} = 0.12894 \text{ nm}$ —and, in addition, a change in density (and volume). Compute

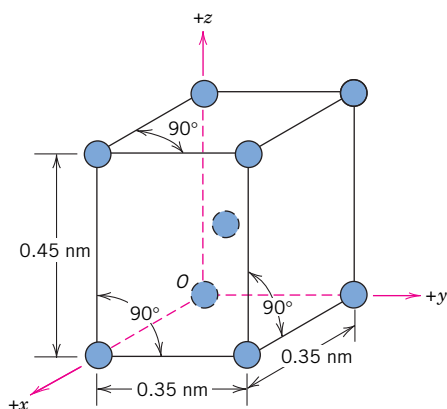


the percentage volume change associated with this reaction. Does the volume increase or decrease?

### Crystal Systems

**3.44** The accompanying figure shows a unit cell for a hypothetical metal.

- To which crystal system does this unit cell belong?
- What would this crystal structure be called?
- Calculate the density of the material, given that its atomic weight is 141 g/mol.



**3.45** Sketch a unit cell for the face-centered orthorhombic crystal structure.

### Point Coordinates

- List the point coordinates for all atoms that are associated with the FCC unit cell (Figure 3.1).
- List the point coordinates of both the sodium (Na) and chlorine (Cl) ions for a unit cell of the sodium chloride (NaCl) crystal structure (Figure 3.6).
- List the point coordinates of both the zinc (Zn) and sulfur (S) atoms for a unit cell of the zinc blende (ZnS) crystal structure (Figure 3.8).
- Sketch a tetragonal unit cell, and within that cell indicate locations of the  $1\frac{1}{2}\frac{1}{2}$  and  $\frac{1}{2}\frac{1}{4}\frac{1}{2}$  point coordinates.
- Sketch an orthorhombic unit cell, and within that cell indicate locations of the  $0\frac{1}{2}1$  and  $\frac{1}{3}\frac{1}{4}\frac{1}{4}$  point coordinates.

**3.51** Using the Molecule Definition Utility found in the “Metallic Crystal Structures and Crystallography” and “Ceramic Crystal Structures” modules of VMSE located in WileyPLUS, generate (and print out) a three-dimensional unit cell for  $\beta$  tin (Sn), given the following: (1) the unit cell is tetragonal with  $a = 0.583$  nm and  $c = 0.318$  nm,

and (2) Sn atoms are located at the following point coordinates:

0 0 0	0 1 1
1 0 0	$\frac{1}{2} 0 \frac{3}{4}$
1 1 0	$\frac{1}{2} 1 \frac{3}{4}$
0 1 0	$1 \frac{1}{2} \frac{1}{4}$
0 0 1	$0 \frac{1}{2} \frac{1}{4}$
1 0 1	$\frac{1}{2} \frac{1}{2} \frac{1}{2}$
1 1 1	

**3.52** Using the Molecule Definition Utility found in both “Metallic Crystal Structures and Crystallography” and “Ceramic Crystal Structures” modules of VMSE, located in WileyPLUS, generate (and print out) a three-dimensional unit cell for lead oxide, PbO, given the following: (1) The unit cell is tetragonal with  $a = 0.397$  nm and  $c = 0.502$  nm, (2) oxygen atoms are located at the following point coordinates:

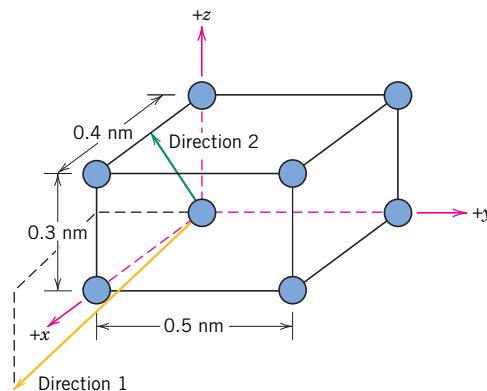
0 0 0	0 0 1
1 0 0	1 0 1
0 1 0	0 1 1
$\frac{1}{2} \frac{1}{2} 0$	$\frac{1}{2} \frac{1}{2} 1$

and (3) Pb atoms are located at the following point coordinates:

$\frac{1}{2} 0 0.763$	$0 \frac{1}{2} 0.237$
$\frac{1}{2} 1 0.763$	$1 \frac{1}{2} 0.237$

### Crystallographic Directions

- Draw an orthorhombic unit cell, and within that cell, a  $[2\bar{1}1]$  direction.
- Sketch a monoclinic unit cell, and within that cell, a  $[\bar{1}01]$  direction.
- What are the indices for the directions indicated by the two vectors in the following sketch?

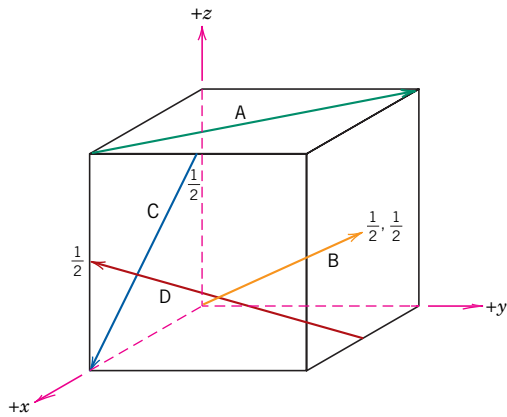


**3.56** Within a cubic unit cell, sketch the following directions:

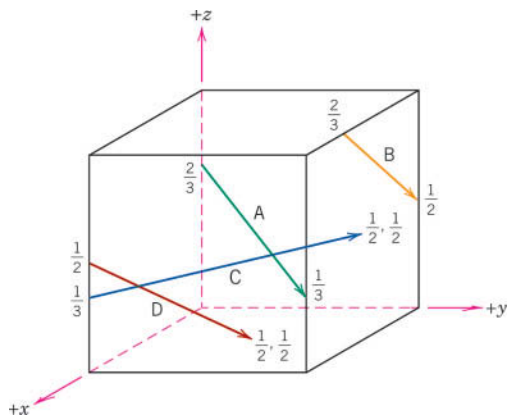


- (a)  $[101]$  (e)  $[\bar{1}\bar{1}\bar{1}]$   
 (b)  $[211]$  (f)  $[\bar{2}12]$   
 (c)  $[10\bar{2}]$  (g)  $[3\bar{1}2]$   
 (d)  $[3\bar{1}3]$  (h)  $[301]$

**3.57** Determine the indices for the directions shown in the following cubic unit cell:



**3.58** Determine the indices for the directions shown in the following cubic unit cell:



**3.59 (a)** What are the direction indices for a vector that passes from point  $\frac{1}{4}0\frac{1}{2}$  to point  $\frac{3}{4}\frac{1}{2}\frac{1}{2}$  in a cubic unit cell?

(b) Repeat part (a) for a monoclinic unit cell.

**3.60 (a)** What are the direction indices for a vector that passes from point  $\frac{1}{3}\frac{1}{2}0$  to point  $\frac{2}{3}\frac{3}{4}\frac{1}{2}$  in a tetragonal unit cell?

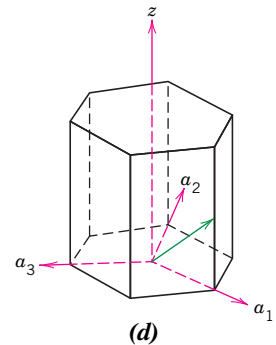
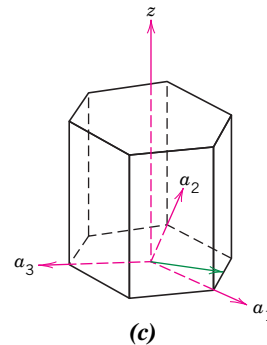
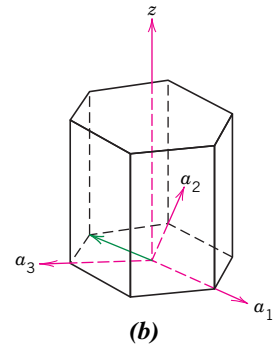
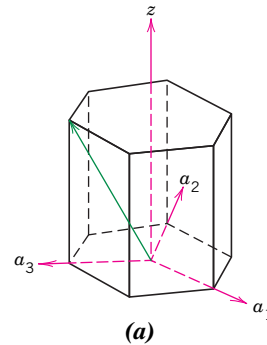
(b) Repeat part (a) for a rhombohedral unit cell.

**3.61** For tetragonal crystals, cite the indices of directions that are equivalent to each of the following directions:

- (a)  $[011]$   
 (b)  $[100]$

**3.62** Convert the  $[110]$  and  $[00\bar{1}]$  directions into the four-index Miller–Bravais scheme for hexagonal unit cells.

**3.63** Determine the indices for the directions shown in the following hexagonal unit cells:



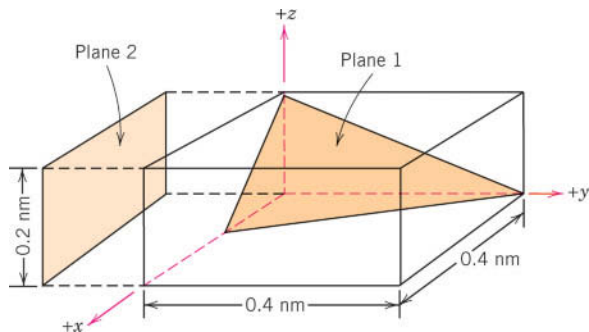
**3.64** Using Equations 3.12a–3.12d, derive expressions for each of the three  $U$ ,  $V$ , and  $W$  indices in terms of the four  $u$ ,  $v$ ,  $t$ , and  $w$  indices.

### Crystallographic Planes

**3.65 (a)** Draw an orthorhombic unit cell, and within that cell, a  $(02\bar{1})$  plane.

(b) Draw a monoclinic unit cell, and within that cell, a  $(200)$  plane.

**3.66** What are the indices for the two planes drawn in the following sketch?

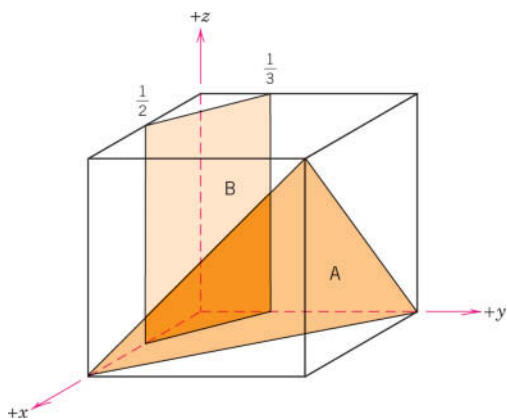


**3.67** Sketch within a cubic unit cell the following planes:

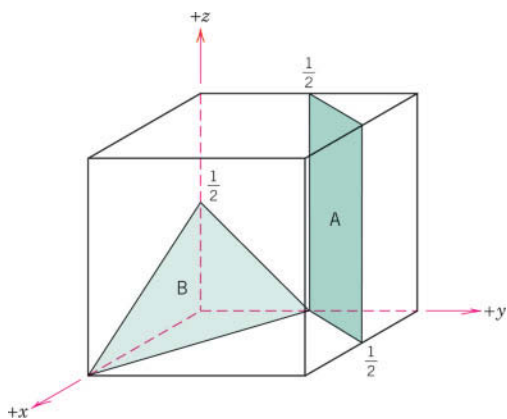


- (a)  $(10\bar{1})$     (e)  $(\bar{1}\bar{1}\bar{1})$   
 (b)  $(2\bar{1}\bar{1})$     (f)  $(\bar{2}12)$   
 (c)  $(012)$     (g)  $(3\bar{1}2)$   
 (d)  $(3\bar{1}3)$     (h)  $(301)$

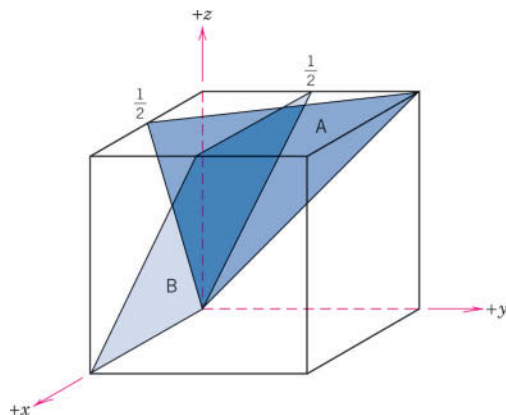
**3.68** Determine the Miller indices for the planes shown in the following unit cell:



**3.69** Determine the Miller indices for the planes shown in the following unit cell:



**3.70** Determine the Miller indices for the planes shown in the following unit cell:



**3.71** Cite the indices of the direction that results from the intersection of each of the following pairs of planes within a cubic crystal:

- (a) The  $(110)$  and  $(111)$  planes  
 (b) The  $(110)$  and  $(\bar{1}\bar{1}0)$  planes  
 (c) The  $(11\bar{1})$  and  $(001)$  planes.

**3.72** Sketch the atomic packing of the following:

- (a) The  $(100)$  plane for the FCC crystal structure  
 (b) The  $(111)$  plane for the BCC crystal structure (similar to Figures 3.25b and 3.26b).

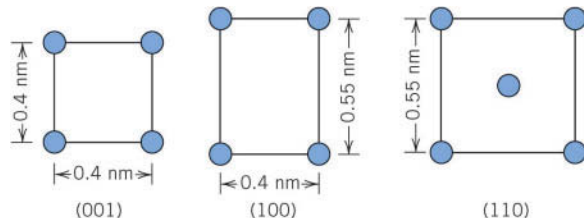
**3.73** For each of the following crystal structures, represent the indicated plane in the manner of Figures 3.25b and 3.26b, showing both anions and cations:

- (a)  $(100)$  plane for the cesium chloride crystal structure  
 (b)  $(200)$  plane for the cesium chloride crystal structure  
 (c)  $(111)$  plane for the diamond cubic crystal structure  
 (d)  $(110)$  plane for the fluorite crystal structure

**3.74** Consider the reduced-sphere unit cell shown in Problem 3.44, having an origin of the coordinate system positioned at the atom labeled O. For the following sets of planes, determine which are equivalent:

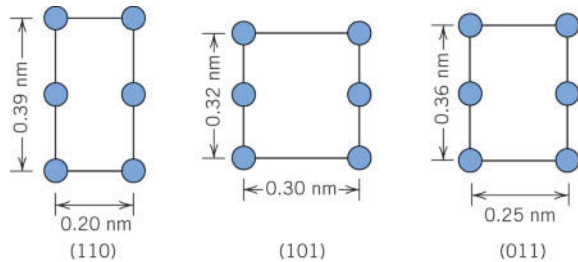
- (a)  $(100)$ ,  $(0\bar{1}0)$ , and  $(001)$   
 (b)  $(110)$ ,  $(101)$ ,  $(011)$ , and  $(\bar{1}01)$   
 (c)  $(111)$ ,  $(\bar{1}\bar{1}\bar{1})$ ,  $(1\bar{1}\bar{1})$ , and  $(\bar{1}\bar{1}1)$

**3.75** The accompanying figure shows three different crystallographic planes for a unit cell of a hypothetical metal. The circles represent atoms:



- (a) To what crystal system does the unit cell belong?  
 (b) What would this crystal structure be called?

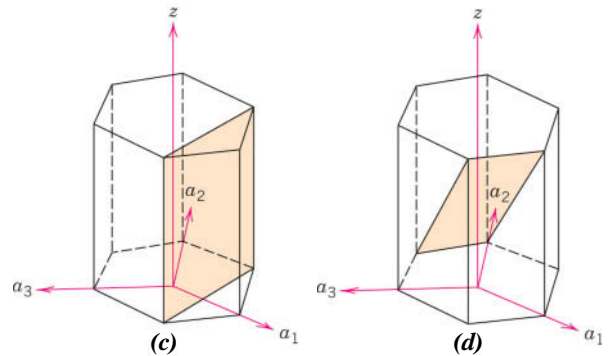
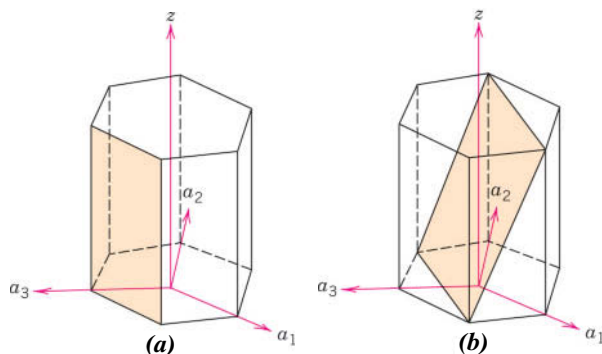
**3.76** The accompanying figure shows three different crystallographic planes for a unit cell of some hypothetical metal. The circles represent atoms:



- (a) To what crystal system does the unit cell belong?  
 (b) What would this crystal structure be called?  
 (c) If the density of this metal is  $18.91 \text{ g/cm}^3$ , determine its atomic weight.

**3.77** Convert the (111) and  $(0\bar{1}2)$  planes into the four-index Miller–Bravais scheme for hexagonal unit cells.

**3.78** Determine the indices for the planes shown in the following hexagonal unit cells:



**3.79** Sketch the  $(01\bar{1}1)$  and  $(2\bar{1}\bar{1}0)$  planes in a hexagonal unit cell.

### Linear and Planar Densities

**3.80 (a)** Derive linear density expressions for FCC  $[100]$  and  $[111]$  directions in terms of the atomic radius  $R$ .

(b) Compute and compare linear density values for these same two directions for copper (Cu).

**3.81 (a)** Derive linear density expressions for BCC  $[110]$  and  $[111]$  directions in terms of the atomic radius  $R$ .

(b) Compute and compare linear density values for these same two directions for iron (Fe).

**3.82 (a)** Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius  $R$ .

(b) Compute and compare planar density values for these same two planes for aluminum (Al).

**3.83 (a)** Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius  $R$ .

(b) Compute and compare planar density values for these same two planes for molybdenum (Mo).

**3.84 (a)** Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius  $R$ .

(b) Compute the planar density value for this same plane for titanium (Ti).

### Close-Packed Structures

**3.85** The zinc blende crystal structure is one that may be generated from close-packed planes of anions.

(a) Will the stacking sequence for this structure be FCC or HCP? Why?

- (b) Will cations fill tetrahedral or octahedral positions? Why?
- (c) What fraction of the positions will be occupied?
- 3.86** The corundum crystal structure, found for  $\text{Al}_2\text{O}_3$ , consists of an HCP arrangement of  $\text{O}^{2-}$  ions; the  $\text{Al}^{3+}$  ions occupy octahedral positions.
- (a) What fraction of the available octahedral positions are filled with  $\text{Al}^{3+}$  ions?
- (b) Sketch two close-packed  $\text{O}^{2-}$  planes stacked in an  $AB$  sequence, and note octahedral positions that will be filled with the  $\text{Al}^{3+}$  ions.
- 3.87** Beryllium oxide ( $\text{BeO}$ ) may form a crystal structure that consists of an HCP arrangement of  $\text{O}^{2-}$  ions. If the ionic radius of  $\text{Be}^{2+}$  is 0.035 nm, then
- (a) Which type of interstitial site will the  $\text{Be}^{2+}$  ions occupy?
- (b) What fraction of these available interstitial sites will be occupied by  $\text{Be}^{2+}$  ions?
- 3.88** Iron titanate,  $\text{FeTiO}_3$ , forms in the ilmenite crystal structure that consists of an HCP arrangement of  $\text{O}^{2-}$  ions.
- (a) Which type of interstitial site will the  $\text{Fe}^{2+}$  ions occupy? Why?
- (b) Which type of interstitial site will the  $\text{Ti}^{4+}$  ions occupy? Why?
- (c) What fraction of the total tetrahedral sites will be occupied?
- (d) What fraction of the total octahedral sites will be occupied?
- 3.92** Using the data for  $\alpha$ -iron in Table 3.1, compute the interplanar spacings for the (111) and (211) sets of planes.
- 3.93** Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium (Cr) when monochromatic radiation of wavelength 0.0711 nm is used.
- 3.94** Determine the expected diffraction angle for the first-order reflection from the (111) set of planes for FCC nickel (Ni) when monochromatic radiation of wavelength 0.1937 nm is used.
- 3.95** The metal rhodium (Rh) has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at  $36.12^\circ$  (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute the following:
- (a) The interplanar spacing for this set of planes
- (b) The atomic radius for a Rh atom
- 3.96** The metal niobium (Nb) has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at  $75.99^\circ$  (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute the following:
- (a) The interplanar spacing for this set of planes
- (b) The atomic radius for the Nb atom.
- 3.97** For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of  $44.53^\circ$  for FCC nickel (Ni) when monochromatic radiation having a wavelength of 0.1542 nm is used?
- 3.98** For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of  $136.15^\circ$  for BCC tantalum (Ta) when monochromatic radiation having a wavelength of 0.1937 nm is used?
- 3.99** Figure 3.42 shows the first five peaks of the x-ray diffraction pattern for tungsten (W), which has a BCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.
- (a) Index (i.e., give  $h$ ,  $k$ , and  $l$  indices) each of these peaks.
- (b) Determine the interplanar spacing for each of the peaks.
- (c) For each peak, determine the atomic radius for W, and compare these with the value presented in Table 3.1.

### Polycrystalline Materials

- 3.89** Explain why the properties of polycrystalline materials are most often isotropic.

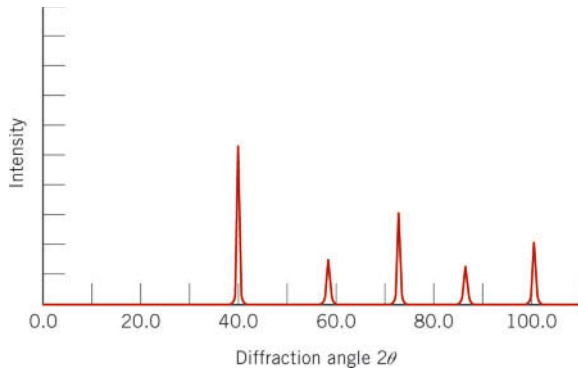
### X-Ray Diffraction: Determination of Crystal Structures

- 3.90** The interplanar spacing  $d_{hkl}$  for planes in a unit cell having orthorhombic geometry is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where  $a$ ,  $b$ , and  $c$  are the lattice parameters.

- (a) To what equation does this expression reduce for crystals having cubic symmetry?
- (b) For crystals having tetragonal symmetry?
- 3.91** Using the data for aluminum in Table 3.1, compute the interplanar spacing for the (110) set of planes.



**Figure 3.42** Diffraction pattern for powdered tungsten.

**3.100** The following table lists diffraction angles for the first four peaks (first-order) of the x-ray diffraction pattern for platinum (Pt), which has an FCC crystal structure; monochromatic x-radiation having a wavelength of 0.0711 nm was used.

Plane Indices	Diffraction Angle ( $2\theta$ )
(111)	18.06°
(200)	20.88°
(220)	26.66°
(311)	31.37°

(a) Determine the interplanar spacing for each of the peaks.

(b) For each peak, determine the atomic radius for Pt, and compare these with the value presented in Table 3.1.

**3.101** The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.1397 nm was used.

(a) Determine whether this metal's crystal structure is FCC, BCC, or neither FCC or BCC, and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	Diffraction Angle ( $2\theta$ )
1	34.51°
2	40.06°
3	57.95°

**3.102** The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.0711 nm was used.

(a) Determine whether this metal's crystal structure is FCC, BCC, or neither FCC or BCC, and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	Diffraction Angle ( $2\theta$ )
1	18.27°
2	25.96°
3	31.92°

### Noncrystalline Solids

**3.103** Would you expect a material in which the atomic bonding is predominantly ionic to be more likely or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)

### Spreadsheet Problem

**3.1SS** For an x-ray diffraction pattern (having all peaks plane-indexed) of a metal that has a unit cell of cubic symmetry, generate a spreadsheet that allows the user to input the x-ray wavelength, and then determine, for each plane, the following:

(a)  $d_{hkl}$

(b) The lattice parameter,  $a$

### FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

**3.1FE** A hypothetical metal has the BCC crystal structure, a density of  $7.24 \text{ g/cm}^3$ , and an atomic weight of  $48.9 \text{ g/mol}$ . The atomic radius of this metal is

- (A)  $0.122 \text{ nm}$             (C)  $0.0997 \text{ nm}$   
(B)  $1.22 \text{ nm}$             (D)  $0.154 \text{ nm}$

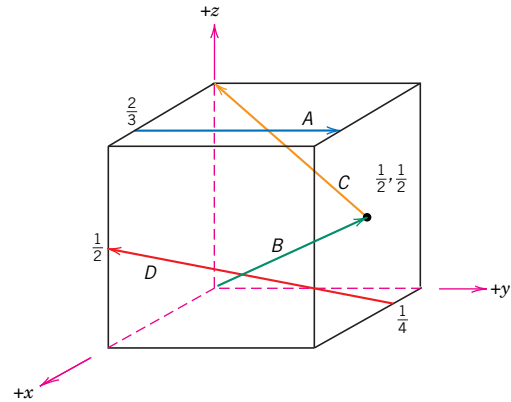
**3.2FE** Which of the following are the most common coordination numbers for ceramic materials?

- (A) 2 and 3            (C) 6, 8, and 12  
(B) 6 and 12            (D) 4, 6, and 8

**3.3FE** An AX ceramic compound has the rock salt crystal structure. If the radii of the A and X ions are  $0.137$  and  $0.241 \text{ nm}$ , respectively, and the respective atomic weights are  $22.7$  and  $91.4 \text{ g/mol}$ , what is the density (in  $\text{g/cm}^3$ ) of this material?

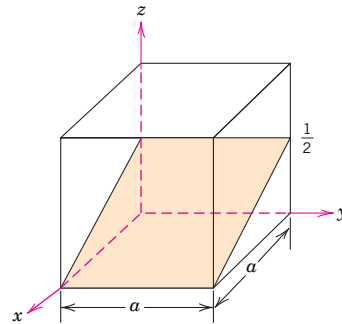
- (A)  $0.438 \text{ g/cm}^3$             (C)  $1.75 \text{ g/cm}^3$   
(B)  $0.571 \text{ g/cm}^3$             (D)  $3.50 \text{ g/cm}^3$

**3.4FE** In the following unit cell, which vector represents the  $[121]$  direction?



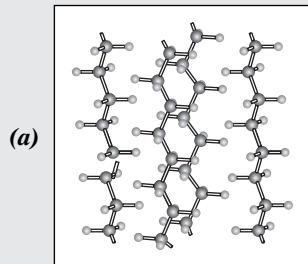
**3.5FE** What are the Miller indices for the plane shown in the following cubic unit cell?

- (A)  $(201)$             (C)  $(10\frac{1}{2})$   
(B)  $(1\infty\frac{1}{2})$             (D)  $(102)$

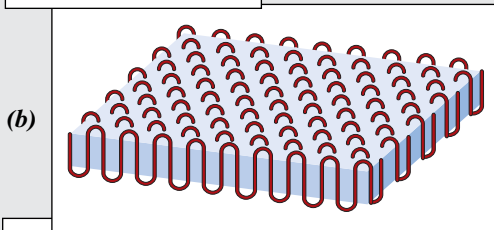




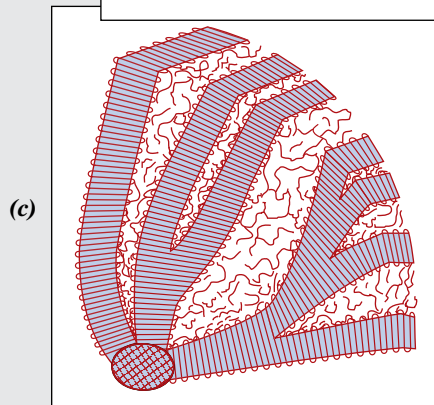
# Chapter 4 Polymer Structures



(a) Schematic representation of the arrangement of molecular chains for a crystalline region of polyethylene. Black and gray balls represent, respectively, carbon and hydrogen atoms.

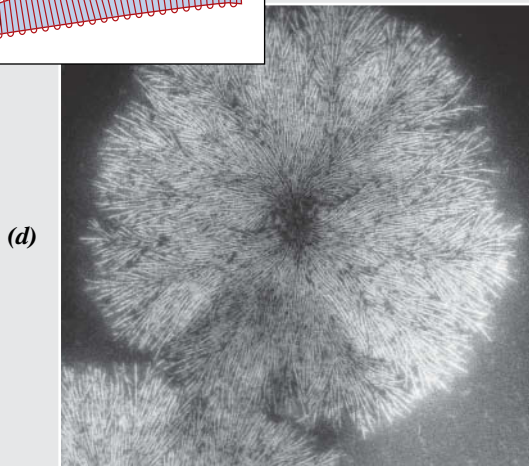


(b) Schematic diagram of a polymer chain-folded crystallite—a plate-shaped crystalline region in which the molecular chains (red lines/curves) fold back and forth on themselves; these folds occur at the crystallite faces.



(c) Structure of a spherulite found in some semicrystalline polymers (schematic). Chain-folded crystallites radiate outward from a common center. Separating and connecting these crystallites are regions of amorphous material, wherein the molecular chains (red curves) assume misaligned and disordered configurations.

(d) Transmission electron micrograph showing the spherulite structure. Chain-folded lamellar crystallites (white lines) approximately 10 nm thick extend in radial directions from the center. 15,000 $\times$ .



(e) A polyethylene produce bag containing some fruit.



Glow Images

(e)

[Photograph of Figure (d) supplied by P. J. Phillips. First published in R. Bartnikas and R. M. Eichhorn, *Engineering Dielectrics*, Vol. IIA, *Electrical Properties of Solid Insulating Materials: Molecular Structure and Electrical Behavior*, 1983. Copyright ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.]



## WHY STUDY *Polymer Structures*?

A relatively large number of chemical and structural characteristics affect the properties and behaviors of polymeric materials. Some of these influences are as follows:

1. Degree of crystallinity of semicrystalline polymers—on density, stiffness, strength, and ductility (Sections 4.11 and 8.18).
2. Degree of crosslinking—on the stiffness of rubber-like materials (Section 8.19).
3. Polymer chemistry—on melting and glass-transition temperatures (Section 11.17).

### Learning Objectives

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

1. Describe a typical polymer molecule in terms of its chain structure and, in addition, how the molecule may be generated from repeat units.
2. Draw repeat units for polyethylene, poly(vinyl chloride), polytetrafluoroethylene, polypropylene, and polystyrene.
3. Calculate number-average and weight-average molecular weights and degree of polymerization for a specified polymer.
4. Name and briefly describe:
  - (a) the four general types of polymer molecular structures,
  - (b) the three types of stereoisomers,
  - (c) the two kinds of geometric isomers, and
  - (d) the four types of copolymers.
5. Cite the differences in behavior and molecular structure for thermoplastic and thermosetting polymers.
6. Briefly describe the crystalline state in polymeric materials.
7. Briefly describe/diagram the spherulitic structure for a semicrystalline polymer.

## 4.1 INTRODUCTION

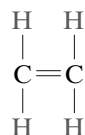
Naturally occurring polymers—those derived from plants and animals—have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers, such as proteins, enzymes, starches, and cellulose, are important in biological and physiological processes in plants and animals. Modern scientific research tools have made possible the determination of the molecular structures of this group of materials and the development of numerous polymers that are synthesized from small organic molecules. Many of our useful plastics, rubbers, and fiber materials are synthetic polymers. In fact, since the conclusion of World War II, the field of materials has been virtually revolutionized by the advent of synthetic polymers. The synthetics can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts. In some applications, metal and wood parts have been replaced by plastics, which have satisfactory properties and can be produced at a lower cost.

As with metals and ceramics, the properties of polymers are intricately related to the structural elements of the material. This chapter explores molecular and crystal structures of polymers; Chapter 8 discusses the relationships between structure and some of the mechanical properties.

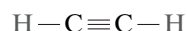
## 4.2 HYDROCARBON MOLECULES

Because most polymers are organic in origin, we briefly review some of the basic concepts relating to the structure of their molecules. First, many organic materials are *hydrocarbons*—that is, they are composed of hydrogen and carbon. Furthermore, the intramolecular bonds are covalent. Each carbon atom has four electrons that may

participate in covalent bonding, whereas every hydrogen atom has only one bonding electron. A single covalent bond exists when each of the two bonding atoms contributes one electron, as represented schematically in Figure 2.12 for a molecule of hydrogen ( $\text{H}_2$ ). Double and triple bonds between two carbon atoms involve the sharing of two and three pairs of electrons, respectively.<sup>1</sup> For example, in ethylene, which has the chemical formula  $\text{C}_2\text{H}_4$ , the two carbon atoms are doubly bonded together, and each is also singly bonded to two hydrogen atoms, as represented by the structural formula



where — and = denote single and double covalent bonds, respectively. An example of a triple bond is found in acetylene,  $\text{C}_2\text{H}_2$ :



**unsaturated**

Molecules that have double and triple covalent bonds are termed **unsaturated**—that is, each carbon atom is not bonded to the maximum (four) other atoms. Therefore, it is possible for another atom or group of atoms to become attached to the original molecule. Furthermore, for a **saturated** hydrocarbon, all bonds are single ones, and no new atoms may be joined without the removal of others that are already bonded.

**saturated**

Some of the simple hydrocarbons belong to the paraffin family; the chainlike paraffin molecules include methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), and butane ( $\text{C}_4\text{H}_{10}$ ). Compositions and molecular structures for paraffin molecules are contained in Table 4.1. The covalent bonds in each molecule are strong, but only weak van der Waals bonds exist between molecules, and thus these hydrocarbons have relatively low melting and boiling points. However, boiling temperatures rise with increasing molecular weight (Table 4.1).

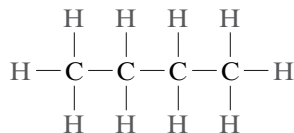
**Table 4.1**  
Compositions and  
Molecular Structures  
for Some Paraffin  
Compounds:  $\text{C}_n\text{H}_{2n+2}$

Name	Composition	Structure	Boiling Point ( $^{\circ}\text{C}$ )
Methane	$\text{CH}_4$	$\begin{array}{c} \text{H} \\   \\ \text{H} - \text{C} - \text{H} \\   \\ \text{H} \end{array}$	−164
Ethane	$\text{C}_2\text{H}_6$	$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H} - \text{C} & - \text{C} - \text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	−88.6
Propane	$\text{C}_3\text{H}_8$	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H} - \text{C} & - \text{C} - & \text{C} - \text{H} \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array}$	−42.1
Butane	$\text{C}_4\text{H}_{10}$		−0.5
Pentane	$\text{C}_5\text{H}_{12}$		36.1
Hexane	$\text{C}_6\text{H}_{14}$		69.0

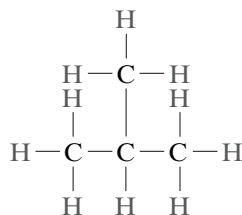
<sup>1</sup>In the hybrid bonding scheme for carbon (Section 2.6), a carbon atom forms  $sp^3$  hybrid orbitals when all its bonds are single ones; a carbon atom with a double bond has  $sp^2$  hybrid orbitals; and a carbon atom with a triple bond has  $sp$  hybridization.

**isomerism**

Hydrocarbon compounds with the same composition may have different atomic arrangements, a phenomenon termed **isomerism**. For example, there are two isomers for butane; normal butane has the structure

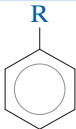
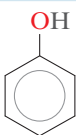


whereas a molecule of isobutane is represented as follows:

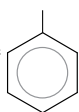


Some of the physical properties of hydrocarbons depend on the isomeric state; for example, the boiling temperatures for normal butane and isobutane are  $-0.5^{\circ}\text{C}$  and  $-12.3^{\circ}\text{C}$  ( $31.1^{\circ}\text{F}$  and  $9.9^{\circ}\text{F}$ ), respectively.

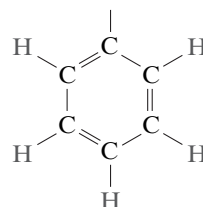
**Table 4.2**  
Some Common  
Hydrocarbon Groups

<i>Family</i>	<i>Characteristic Unit</i>		<i>Representative Compound</i>
Alcohols	$\text{R}-\text{OH}$	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{OH} \\    \\  \text{H}  \end{array}  $	Methyl alcohol
Ethers	$\text{R}-\text{O}-\text{R}'$	$  \begin{array}{ccc}  \text{H} & & \text{H} \\    & &   \\  \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\    & &   \\  \text{H} & & \text{H}  \end{array}  $	Dimethyl ether
Acids	$  \begin{array}{c}  \text{OH} \\    \\  \text{R}-\text{C} \\     \\  \text{O}  \end{array}  $	$  \begin{array}{ccc}  \text{H} & & \text{OH} \\    & &   \\  \text{H}-\text{C}-\text{C} \\    & &    \\  \text{H} & & \text{O}  \end{array}  $	Acetic acid
Aldehydes	$  \begin{array}{c}  \text{R} \\    \\  \text{C}=\text{O} \\    \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \text{H} \\    \\  \text{C}=\text{O} \\    \\  \text{H}  \end{array}  $	Formaldehyde
Aromatic hydrocarbons <sup>a</sup>			Phenol

<sup>a</sup>The simplified structure



denotes a phenyl group,



There are numerous other organic groups, many of which are involved in polymer structures. Several of the more common groups are presented in Table 4.2, where R and R' represent organic groups such as CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, and C<sub>6</sub>H<sub>5</sub> (methyl, ethyl, and phenyl).



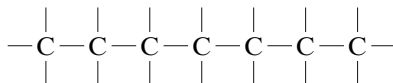
**Concept Check 4.1** Differentiate between polymorphism (see Chapter 3) and isomerism.

(The answer is available in *WileyPLUS*.)

### 4.3 POLYMER MOLECULES

#### macromolecule

The molecules in polymers are gigantic in comparison to the hydrocarbon molecules already discussed; because of their size they are often referred to as **macromolecules**. Within each molecule, the atoms are bound together by covalent interatomic bonds. For carbon-chain polymers, the backbone of each chain is a string of carbon atoms. Many times each carbon atom singly bonds to two adjacent carbons atoms on either side, represented schematically in two dimensions as follows:



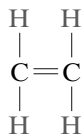
Each of the two remaining valence electrons for every carbon atom may be involved in side bonding with atoms or radicals that are positioned adjacent to the chain. Of course, both chain and side double bonds are also possible.

#### repeat unit monomer

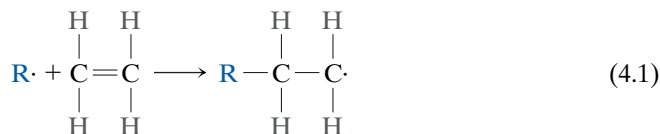
These long molecules are composed of structural entities called **repeat units**, which are successively repeated along the chain.<sup>2</sup> The term **monomer** refers to the small molecule from which a polymer is synthesized. Hence, *monomer* and *repeat unit* mean different things, but sometimes the term *monomer* or *monomer unit* is used instead of the more proper term *repeat unit*.

### 4.4 THE CHEMISTRY OF POLYMER MOLECULES

Consider again the hydrocarbon ethylene (C<sub>2</sub>H<sub>4</sub>), which is a gas at ambient temperature and pressure and has the following molecular structure:



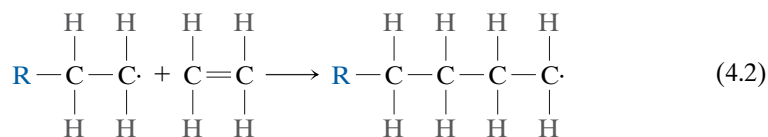
If the ethylene gas is reacted under appropriate conditions, it will transform to polyethylene (PE), which is a solid polymeric material. This process begins when an active center is formed by the reaction between an initiator or catalyst species (R·) and the ethylene monomer, as follows:



#### polymer

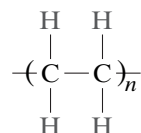
<sup>2</sup>A repeat unit is also sometimes called a mer. *Mer* originates from the Greek word *meros*, which means “part”; the term **polymer** was coined to mean “many mers.”

The polymer chain then forms by the sequential addition of monomer units to this actively growing chain molecule. The active site, or unpaired electron (denoted by  $\cdot$ ), is transferred to each successive end monomer as it is linked to the chain. This may be represented schematically as follows:

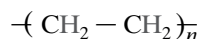


**WileyPLUS: VMSE**  
Repeat Unit Structures

The final result, after the addition of many ethylene monomer units, is the polyethylene molecule.<sup>3</sup> A portion of one such molecule and the polyethylene repeat unit are shown in Figure 4.1a. This polyethylene chain structure can also be represented as



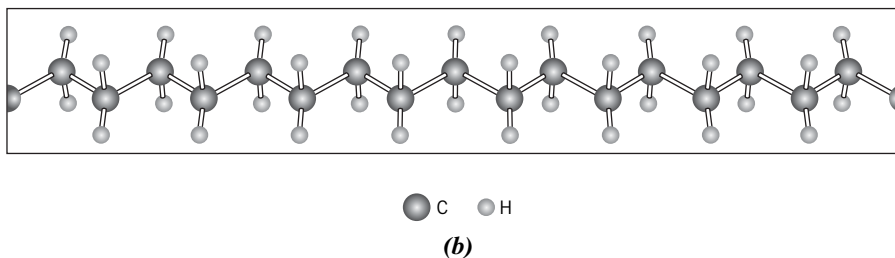
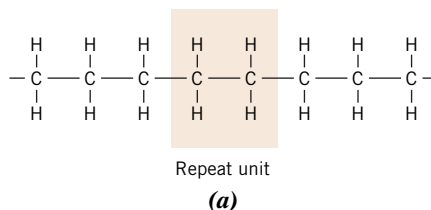
or alternatively as



Here, the repeat units are enclosed in parentheses, and the subscript  $n$  indicates the number of times it repeats.<sup>4</sup>

The representation in Figure 4.1a is not strictly correct, in that the angle between the singly bonded carbon atoms is not  $180^\circ$  as shown, but rather is close to  $109^\circ$ . A more accurate three-dimensional model is one in which the carbon atoms form a zigzag pattern (Figure 4.1b), the C—C bond length being 0.154 nm. In this discussion, depiction of polymer molecules is frequently simplified using the linear chain model shown in Figure 4.1a.

**Figure 4.1** For polyethylene, (a) a schematic representation of repeat unit and chain structures, and (b) a perspective of the molecule, indicating the zigzag backbone structure.



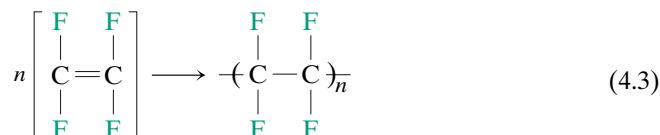
<sup>3</sup>A more detailed discussion of polymerization reactions, including both addition and condensation mechanisms, is given in Section 14.11.

<sup>4</sup>Chain ends/end groups (i.e., the Rs in Equation 4.2) are not normally represented in chain structures.



**WileyPLUS: VMSE**  
Repeat Unit Structures

Of course polymer structures having other chemistries are possible. For example, the tetrafluoroethylene monomer,  $\text{CF}_2=\text{CF}_2$ , can polymerize to form *polytetrafluoroethylene* (PTFE) as follows:

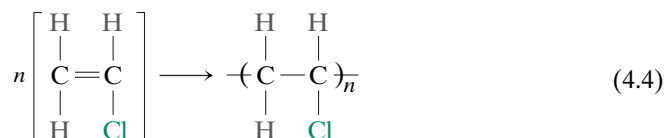


Polytetrafluoroethylene (trade name Teflon) belongs to a family of polymers called the *fluorocarbons*.



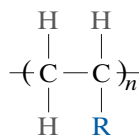
**WileyPLUS: VMSE**  
Repeat Unit Structures

The vinyl chloride monomer ( $\text{CH}_2=\text{CHCl}$ ) is a slight variant of that for ethylene, in which one of the four H atoms is replaced with a Cl atom. Its polymerization is represented as



and leads to *poly(vinyl chloride)* (PVC), another common polymer.

Some polymers may be represented using the following generalized form:



**WileyPLUS: VMSE**  
Repeat Unit Structures

where the **R** depicts either an atom [i.e., H or Cl, for polyethylene or poly(vinyl chloride), respectively] or an organic group such as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{C}_6\text{H}_5$  (methyl, ethyl, and phenyl). For example, when R represents a  $\text{CH}_3$  group, the polymer is *polypropylene* (PP). Poly(vinyl chloride) and polypropylene chain structures are also represented in Figure 4.2. Table 4.3 lists repeat units for some of the more common polymers; as may be noted, some of them—for example, nylon, polyester, and polycarbonate—are relatively complex. Repeat units for a large number of relatively common polymers are given in Appendix D.

When all of the repeating units along a chain are of the same type, the resulting polymer is called a **homopolymer**. Chains may be composed of two or more different repeat units, in what are termed **copolymers** (see Section 4.10).

The monomers discussed thus far have an active bond that may react to form two covalent bonds with other monomers forming a two-dimensional chainlike molecular structure, as indicated earlier for ethylene. Such a monomer is termed **bifunctional**. In general, the **functionality** is the number of bonds that a given monomer can form. For example, monomers such as phenol-formaldehyde (Table 4.3) are **trifunctional**: they have three active bonds, from which a three-dimensional molecular network structure results.

**homopolymer**

**copolymer**

**bifunctional**

**functionality**

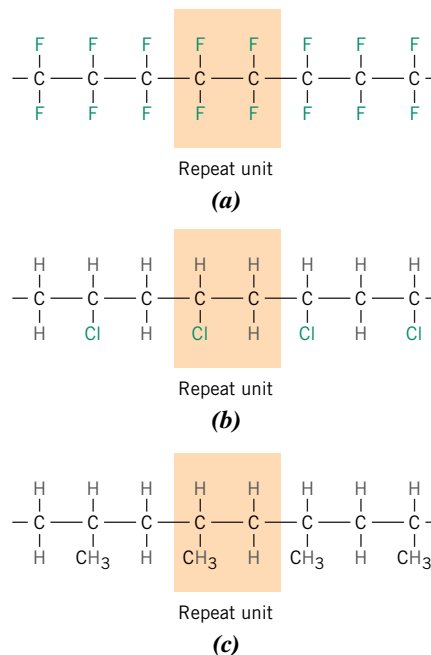
**trifunctional**








**Concept Check 4.2** On the basis of the structures presented in the previous section, sketch the repeat unit structure for poly(vinyl fluoride).

(The answer is available in *WileyPLUS*.)

**Figure 4.2** Repeat unit and chain structures for (a) polytetrafluoroethylene, (b) poly(vinyl chloride), and (c) polypropylene.









**Table 4.3** Repeat Units for 10 of the More Common Polymeric Materials

Polymer	Repeat Unit
 Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
 Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array}$
 Polytetrafluoroethylene (PTFE)	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{F} \end{array}$
 Polypropylene (PP)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array}$
 Polystyrene (PS)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$

(continued)

**WileyPLUS: VMSE**  
Repeat Unit Structures

**Table 4.3** (Continued)

Polymer	Repeat Unit
 Poly(methyl methacrylate) (PMMA)	$  \begin{array}{c}  \text{H} \quad \text{CH}_3 \\    \quad   \\  -\text{C}-\text{C}- \\    \quad   \\  \text{H} \quad \text{C}=\text{O} \\    \\  \text{O} \\    \\  \text{CH}_3  \end{array}  $
 Phenol-formaldehyde (Bakelite)	$  \begin{array}{c}  \text{OH} \\    \\  -\text{CH}_2-\text{C}_6\text{H}_2-\text{CH}_2- \\    \\  \text{CH}_2-  \end{array}  $
 Poly(hexamethylene adipamide) (nylon 6,6)	$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \quad \text{O} \\    \quad    \quad   \quad    \\  -\text{N}-\left[ \text{C}-\text{C} \right]_6-\text{N}-\text{C}-\left[ \text{C}-\text{C} \right]_4-\text{C}- \\    \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $
 Poly(ethylene terephthalate) (PET, a polyester)	$  \begin{array}{c}  \text{O} \quad \text{O} \quad \text{H} \quad \text{H} \\     \quad    \quad   \quad   \\  -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{C}-\text{C}-\text{O}- \\  \quad \quad \quad \quad   \quad   \\  \quad \quad \quad \quad \text{H} \quad \text{H}  \end{array}  $
 Polycarbonate (PC)	$  \begin{array}{c}  \text{O} \quad \text{CH}_3 \quad \text{O} \quad \text{O} \\    \quad   \quad   \quad    \\  -\text{O}-\text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{C}- \\  \quad \quad \quad   \quad   \\  \quad \quad \quad \text{CH}_3 \quad \text{CH}_3  \end{array}  $
<sup>a</sup> The  symbol in the backbone chain denotes an aromatic ring as $  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  -\text{C}=\text{C}- \\    \quad   \\  -\text{C}=\text{C}- \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	

## 4.5 MOLECULAR WEIGHT

Extremely large molecular weights<sup>5</sup> are observed in polymers with very long chains. During the polymerization process not all polymer chains will grow to the same length; this results in a distribution of chain lengths or molecular weights. Ordinarily, an average molecular weight is specified, which may be determined by the measurement of various physical properties such as viscosity and osmotic pressure.

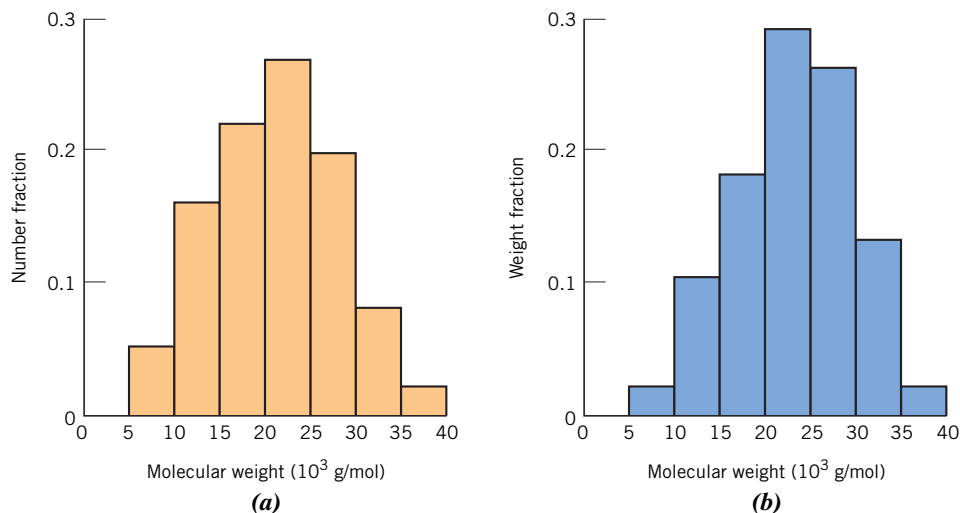
There are several ways of defining average molecular weight. The number-average molecular weight  $\bar{M}_n$  is obtained by dividing the chains into a series of size ranges and

<sup>5</sup>Molecular mass, molar mass, and relative molecular mass are sometimes used and are really more appropriate terms than molecular weight in the context of the present discussion—in fact, we are dealing with masses and not weights. However, molecular weight is most commonly found in the polymer literature and thus is used throughout this book.



**Figure 4.3**

Hypothetical polymer molecule size distributions on the basis of (a) number and (b) weight fractions of molecules.



then determining the number fraction of chains within each size range (Figure 4.3a). The number-average molecular weight is expressed as

Number-average  
molecular weight

$$\bar{M}_n = \sum x_i M_i \quad (4.5a)$$

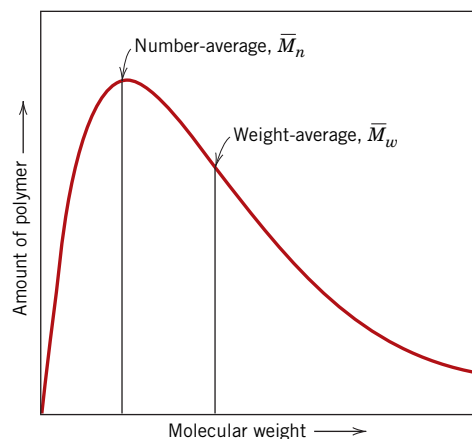
where  $M_i$  represents the mean (middle) molecular weight of size range  $i$ , and  $x_i$  is the fraction of the total number of chains within the corresponding size range.

A weight-average molecular weight  $\bar{M}_w$  is based on the weight fraction of molecules within the various size ranges (Figure 4.3b). It is calculated according to

Weight-average  
molecular weight

$$\bar{M}_w = \sum w_i M_i \quad (4.5b)$$

where, again,  $M_i$  is the mean molecular weight within a size range, whereas  $w_i$  denotes the weight fraction of molecules within the same size interval. Computations for both number-average and weight-average molecular weights are carried out in Example Problem 4.1. A typical molecular weight distribution along with these molecular weight averages is shown in Figure 4.4.

**Figure 4.4** Distribution of molecular weights for a typical polymer.

### degree of polymerization

Degree of polymerization—dependence on number-average and repeat unit molecular weights

An alternative way of expressing average chain size of a polymer is as the **degree of polymerization**,  $DP$ , which represents the average number of repeat units in a chain.  $DP$  is related to the number-average molecular weight  $\bar{M}_n$  by the equation

$$DP = \frac{\bar{M}_n}{m} \quad (4.6)$$

where  $m$  is the repeat unit molecular weight.

## EXAMPLE PROBLEM 4.1

### Computations of Average Molecular Weights and Degree of Polymerization

Assume that the molecular weight distributions shown in Figure 4.3 are for poly(vinyl chloride). For this material, compute **(a)** the number-average molecular weight, **(b)** the degree of polymerization, and **(c)** the weight-average molecular weight.

#### Solution

- (a)** The data necessary for this computation, as taken from Figure 4.3a, are presented in Table 4.4a. According to Equation 4.5a, summation of all the  $x_i M_i$  products (from the right-hand column) yields the number-average molecular weight, which in this case is 21,150 g/mol.
- (b)** To determine the degree of polymerization (Equation 4.6), it is first necessary to compute the repeat unit molecular weight. For PVC, each repeat unit consists of two carbon atoms, three hydrogen atoms, and a single chlorine atom (Table 4.3). Furthermore, the atomic weights of C, H, and Cl are, respectively, 12.01, 1.01, and 35.45 g/mol. Thus, for PVC,

$$\begin{aligned} m &= 2(12.01 \text{ g/mol}) + 3(1.01 \text{ g/mol}) + 35.45 \text{ g/mol} \\ &= 62.50 \text{ g/mol} \end{aligned}$$

and

$$DP = \frac{\bar{M}_n}{m} = \frac{21,150 \text{ g/mol}}{62.50 \text{ g/mol}} = 338$$

**Table 4.4a** Data Used for Number-Average Molecular Weight Computations in Example Problem 4.1

Molecular Weight Range (g/mol)	Mean $M_i$ (g/mol)	$x_i$	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\bar{M}_n = 21,150$

- (c) Table 4.4b shows the data for the weight-average molecular weight, as taken from Figure 4.3b. The  $w_i M_i$  products for the size intervals are tabulated in the right-hand column. The sum of these products (Equation 4.5b) yields a value of 23,200 g/mol for  $\overline{M}_w$ .

**Table 4.4b** Data Used for Weight-Average Molecular Weight Computations in Example Problem 4.1

Molecular Weight Range (g/mol)	Mean $M_i$ (g/mol)	$w_i$	$w_i M_i$
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750
			$\overline{M}_w = 23,200$

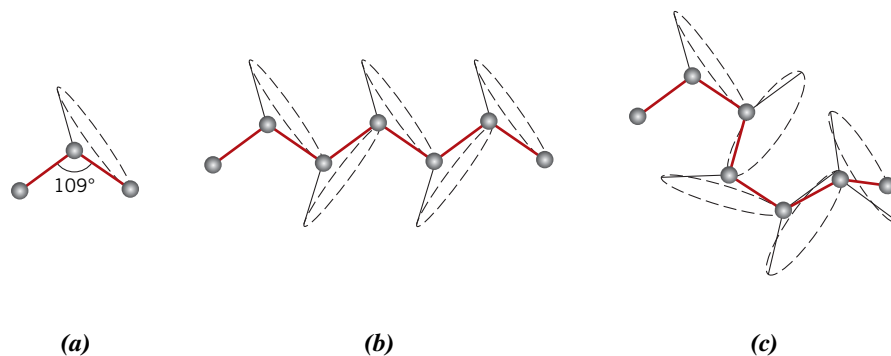
Many polymer properties are affected by the length of the polymer chains. For example, the melting or softening temperature increases with increasing molecular weight (for  $\overline{M}$  up to about 100,000 g/mol). At room temperature, polymers with very short chains (having molecular weights on the order of 100 g/mol) will generally exist as liquids. Those with molecular weights of approximately 1000 g/mol are waxy solids (such as paraffin wax) and soft resins. Solid polymers (sometimes termed *high polymers*), which are of prime interest here, commonly have molecular weights ranging between 10,000 and several million g/mol. Thus, the same polymer material can have quite different properties if it is produced with a different molecular weight. Other properties that depend on molecular weight include elastic modulus and strength (see Chapter 8).

## 4.6 MOLECULAR SHAPE

Previously, polymer molecules have been shown as linear chains, neglecting the zigzag arrangement of the backbone atoms (Figure 4.1b). Single-chain bonds are capable of rotating and bending in three dimensions. Consider the chain atoms in Figure 4.5a; a third carbon atom may lie at any point on the cone of revolution and still subtend about a  $109^\circ$  angle with the bond between the other two atoms. A straight chain segment results when successive chain atoms are positioned as in Figure 4.5b. However, chain bending and twisting are possible when there is a rotation of the chain atoms into other positions, as illustrated in Figure 4.5c.<sup>6</sup> Thus, a single chain molecule composed of many chain atoms might assume a shape similar to that represented schematically in Figure 4.6, having a multitude of bends, twists, and kinks.<sup>7</sup> Also indicated in this figure

<sup>6</sup>For some polymers, rotation of carbon backbone atoms within the cone may be hindered by bulky side group elements on neighboring chain atoms.

<sup>7</sup>The term *conformation* is often used in reference to the physical outline of a molecule, or molecular shape, that can be altered only by rotation of chain atoms about single bonds.

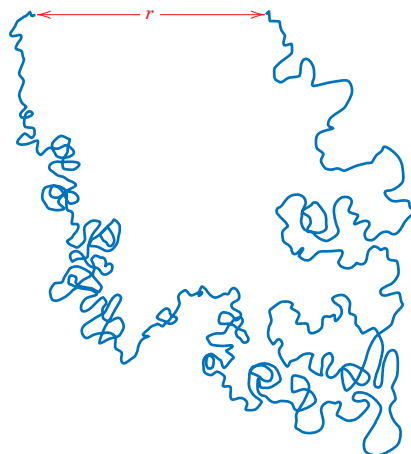


**Figure 4.5** Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (gray circles). For (a), the rightmost atom may lie anywhere on the dashed circle and still subtend a  $109^\circ$  angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (b) and (c), respectively.

is the end-to-end distance of the polymer chain  $r$ ; this distance is much smaller than the total chain length.

Polymers consist of large numbers of molecular chains, each of which may bend, coil, and kink in the manner of Figure 4.6. This leads to extensive intertwining and entanglement of neighboring chain molecules, a situation similar to what is seen in a heavily tangled fishing line. These random coils and molecular entanglements are responsible for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials.

Some of the mechanical and thermal characteristics of polymers are a function of the ability of chain segments to experience rotation in response to applied stresses or thermal vibrations. Rotational flexibility is dependent on repeat unit structure and chemistry. For example, the region of a chain segment that has a double bond ( $C=C$ ) is rotationally rigid. Also, introduction of a bulky or large side group of atoms restricts rotational movement. For example, polystyrene molecules, which have a phenyl side group (Table 4.3), are more resistant to rotational motion than are polyethylene chains.



**Figure 4.6** Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations.

## 4.7 MOLECULAR STRUCTURE

The physical characteristics of a polymer depend not only on its molecular weight and shape, but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network, in addition to various isomeric configurations.

### Linear Polymers

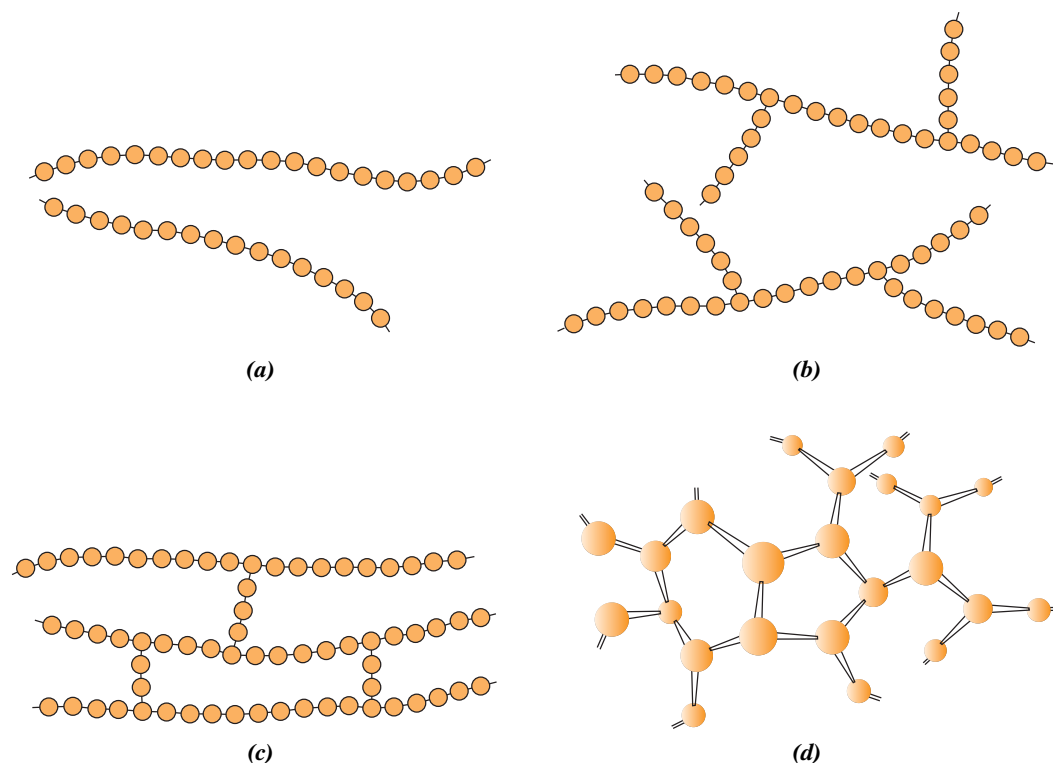
#### linear polymer

**Linear polymers** are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of “spaghetti,” as represented schematically in Figure 4.7a, where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

### Branched Polymers

#### branched polymer

Polymers may be synthesized in which side-branch chains are connected to the main ones, as indicated schematically in Figure 4.7b; these are fittingly called **branched polymers**. The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density. Polymers that form linear structures may also be branched. For example, high-density polyethylene (HDPE) is primarily a linear polymer, whereas low-density polyethylene (LDPE) contains short-chain branches.



**Figure 4.7** Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles designate individual repeat units.

**crosslinked polymer****Crosslinked Polymers**

In **crosslinked polymers**, adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure 4.7c. The process of crosslinking is achieved either during synthesis or by a nonreversible chemical reaction. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization, a process described in Section 8.19.

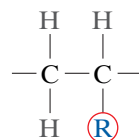
**network polymer****Network Polymers**

Multifunctional monomers forming three or more active covalent bonds make three-dimensional networks (Figure 4.7d) and are termed **network polymers**. Actually, a polymer that is highly crosslinked may also be classified as a network polymer. These materials have distinctive mechanical and thermal properties; the epoxies, polyurethanes, and phenol-formaldehyde belong to this group.

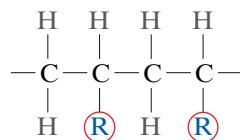
Polymers are not usually of only one distinctive structural type. For example, a predominantly linear polymer may have limited branching and crosslinking.

**4.8 MOLECULAR CONFIGURATIONS**

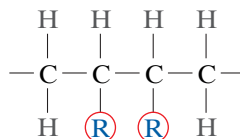
For polymers having more than one side atom or group of atoms bonded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties. Consider the repeat unit



in which R represents an atom or side group other than hydrogen (e.g., Cl, CH<sub>3</sub>). One arrangement is possible when the R side groups of successive repeat units are bound to alternate carbon atoms as follows:



This is designated as a head-to-tail configuration.<sup>8</sup> Its complement, the head-to-head configuration, occurs when R groups are bound to adjacent chain atoms:



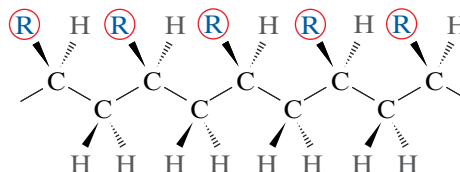
In most polymers, the head-to-tail configuration predominates; often a polar repulsion occurs between R groups for the head-to-head configuration.

Isomerism (Section 4.2) is also found in polymer molecules, wherein different atomic configurations are possible for the same composition. Two isomeric subclasses—stereoisomerism and geometric isomerism—are topics of discussion in the succeeding sections.

<sup>8</sup>The term *configuration* is used in reference to arrangements of units along the axis of the chain, or atom positions that are not alterable except by the breaking and then re-forming of primary bonds.

**Stereoisomerism****stereoisomerism****WileyPLUS: VMSE**Stereo and  
Geometric Isomers

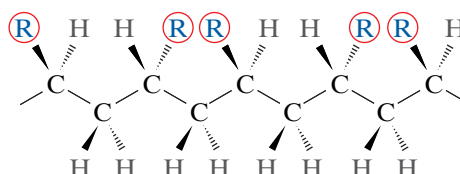
**Stereoisomerism** denotes the situation in which atoms are linked together in the same order (head to tail) but differ in their spatial arrangement. For one stereoisomer, all of the R groups are situated on the same side of the chain as follows:

**isotactic  
configuration**

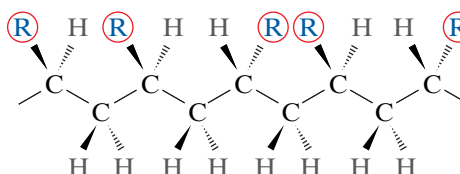
This is called an **isotactic configuration**. This diagram shows the zigzag pattern of the carbon chain atoms. Furthermore, representation of the structural geometry in three dimensions is important, as indicated by the wedge-shaped bonds; solid wedges represent bonds that project out of the plane of the page, and dashed ones represent bonds that project into the page.<sup>9</sup>

**syndiotactic  
configuration**

In a **syndiotactic configuration**, the R groups alternate sides of the chain:<sup>10</sup>

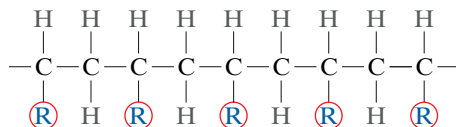
**WileyPLUS: VMSE**Stereo and  
Geometric Isomers

and for random positioning

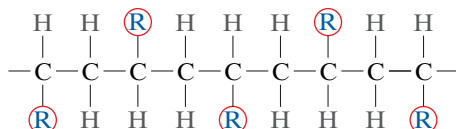
**WileyPLUS: VMSE**Stereo and  
Geometric Isomers**atactic configuration**

the term **atactic configuration** is used.<sup>11</sup>

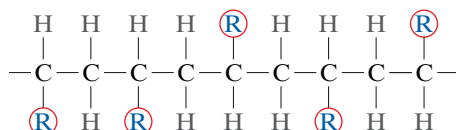
<sup>9</sup>The isotactic configuration is sometimes represented using the following linear (i.e., nonzigzag) and two-dimensional schematic:



<sup>10</sup>The linear and two-dimensional schematic for the syndiotactic configuration is represented as



<sup>11</sup>For the atactic configuration the linear and two-dimensional schematic is



Conversion from one stereoisomer to another (e.g., isotactic to syndiotactic) is not possible by a simple rotation about single-chain bonds. These bonds must first be severed; then, after the appropriate rotation, they are re-formed into the new configuration.

In reality, a specific polymer does not exhibit just one of these configurations; the predominant form depends on the method of synthesis.

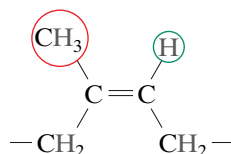
### Geometric Isomerism

Other important chain configurations, or geometric isomers, are possible within repeat units having a double bond between chain carbon atoms. Bonded to each of the carbon atoms participating in the double bond is a side group, which may be situated on one side of the chain or its opposite. Consider the isoprene repeat unit having the structure



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Stereo and  
Geometric Isomers



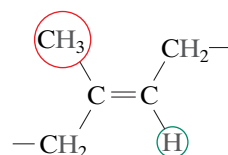
cis (structure)

in which the  $\text{CH}_3$  group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, *cis*-polyisoprene, is natural rubber. For the alternative isomer



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Stereo and  
Geometric Isomers

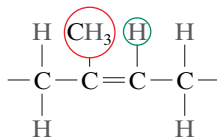


trans (structure)

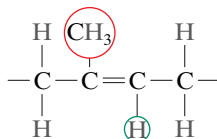
the **trans** structure, the  $\text{CH}_3$  and H reside on opposite sides of the double bond.<sup>12</sup> *Trans*-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from those of natural rubber as a result of this configurational alteration. Conversion of trans to cis, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

To summarize the preceding sections: Polymer molecules may be characterized in terms of their size, shape, and structure. Molecular size is specified in terms

<sup>12</sup>For *cis*-polyisoprene the linear chain representation is as follows:



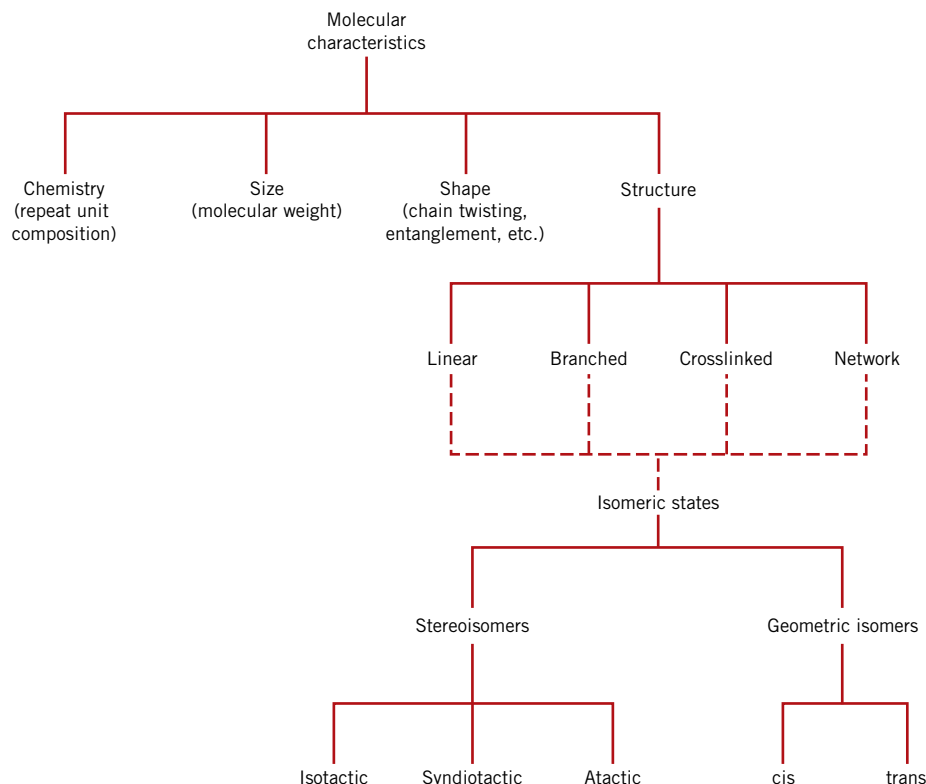
whereas the linear schematic for the trans structure is





**Figure 4.8**

Classification scheme for the characteristics of polymer molecules.



of molecular weight (or degree of polymerization). Molecular shape relates to the degree of chain twisting, coiling, and bending. Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked, and network structures are all possible, in addition to several isomeric configurations (isotactic, syndiotactic, atactic, cis, and trans). These molecular characteristics are presented in the taxonomic chart shown in Figure 4.8. Note that some of the structural elements are not mutually exclusive, and it may be necessary to specify molecular structure in terms of more than one. For example, a linear polymer may also be isotactic.



**Concept Check 4.3** What is the difference between *configuration* and *conformation* in relation to polymer chains?

(The answer is available in *WileyPLUS*.)

## 4.9 THERMOPLASTIC AND THERMOSETTING POLYMERS

**thermoplastic polymer**

**thermosetting polymer**

The response of a polymer to mechanical forces at elevated temperatures is related to its dominant molecular structure. In fact, one classification scheme for these materials is according to behavior with rising temperature. *Thermoplastics* (or **thermoplastic polymers**) and *thermosets* (or **thermosetting polymers**) are the two subdivisions.

Thermoplastics soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated. On a molecular level, as the temperature is raised, secondary bonding forces are diminished (by increased molecular motion) so that the relative movement of adjacent chains is facilitated when a stress is applied. Irreversible degradation results when a molten thermoplastic polymer is raised to too high a temperature. In addition, thermoplastics are relatively soft. Most linear polymers and those having some branched structures with flexible chains are thermoplastic. These materials are normally fabricated by the simultaneous application of heat and pressure (see Section 14.13). Examples of common thermoplastic polymers include polyethylene, polystyrene, poly(ethylene terephthalate), and poly(vinyl chloride).

Thermosetting polymers are network polymers. They become permanently hard during their formation and do not soften upon heating. Network polymers have covalent crosslinks between adjacent molecular chains. During heat treatments, these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures. Thus, the materials do not soften when heated. Crosslinking is usually extensive, in that 10% to 50% of the chain repeat units are crosslinked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, phenolics, and some polyester resins, are thermosetting.



**Concept Check 4.4** Some polymers (such as the polyesters) may be either thermoplastic or thermosetting. Suggest one reason for this.

(The answer is available in *WileyPLUS*.)

## 4.10 COPOLYMERS

Polymer chemists and scientists are continually searching for new materials that can be easily and economically synthesized and fabricated with improved properties or better property combinations than are offered by the homopolymers previously discussed. One group of these materials are the copolymers.

Consider a copolymer that is composed of two repeat units as represented by ● and ● in Figure 4.9. Depending on the polymerization process and the relative fractions of these repeat unit types, different sequencing arrangements along the polymer chains are possible. For one, as depicted in Figure 4.9a, the two different units are randomly dispersed along the chain in what is termed a **random copolymer**. For an **alternating copolymer**, as the name suggests, the two repeat units alternate chain positions, as illustrated in Figure 4.9b. A **block copolymer** is one in which identical repeat units are clustered in blocks along the chain (Figure 4.9c). Finally, homopolymer side branches of one type may be grafted to homopolymer main chains that are composed of a different repeat unit; such a material is termed a **graft copolymer** (Figure 4.9d).

When calculating the degree of polymerization for a copolymer, the value  $m$  in Equation 4.6 is replaced with the average value  $\bar{m}$  determined from

$$\bar{m} = \sum f_j m_j \quad (4.7)$$

In this expression,  $f_j$  and  $m_j$  are, respectively, the mole fraction and molecular weight of repeat unit  $j$  in the polymer chain.

random copolymer

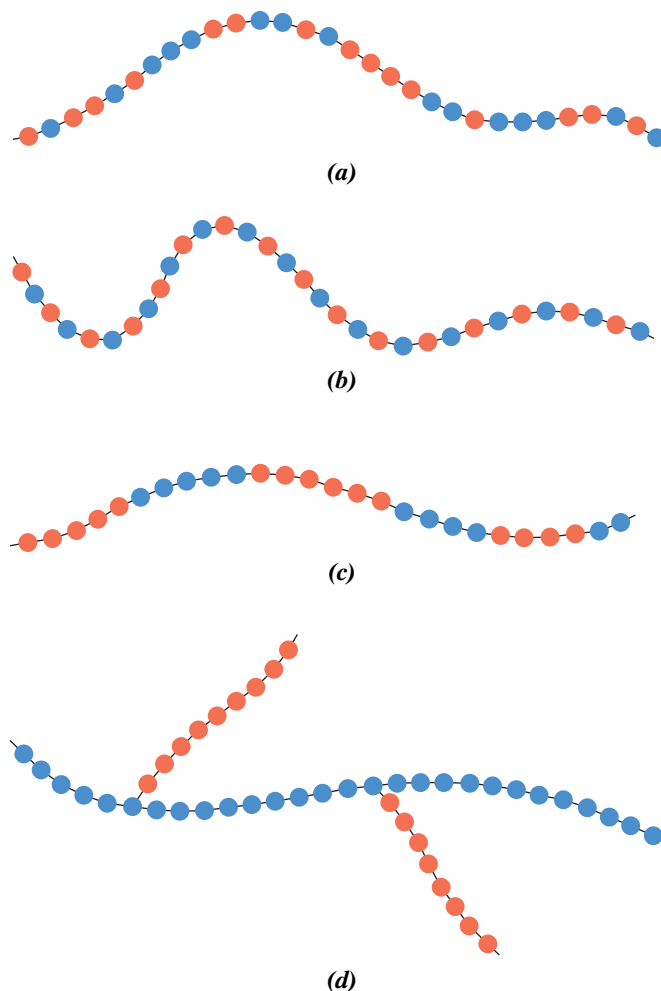
alternating  
copolymer

block copolymer

graft copolymer

Average repeat unit  
molecular weight for  
a copolymer

**Figure 4.9** Schematic representations of (a) random, (b) alternating, (c) block, and (d) graft copolymers. The two different repeat unit types are designated by blue and red circles.










Synthetic rubbers, discussed in Section 13.13, are often copolymers; chemical repeat units that are employed in some of these rubbers are shown in Table 4.5. Styrene–butadiene rubber (SBR) is a common random copolymer from which automobile tires are made. Nitrile rubber (NBR) is another random copolymer composed of acrylonitrile and butadiene. It is also highly elastic and, in addition, resistant to swelling in organic solvents; gasoline hoses are made of NBR. Impact-modified polystyrene is a block copolymer that consists of alternating blocks of styrene and butadiene. The rubbery isoprene blocks act to slow cracks propagating through the material.

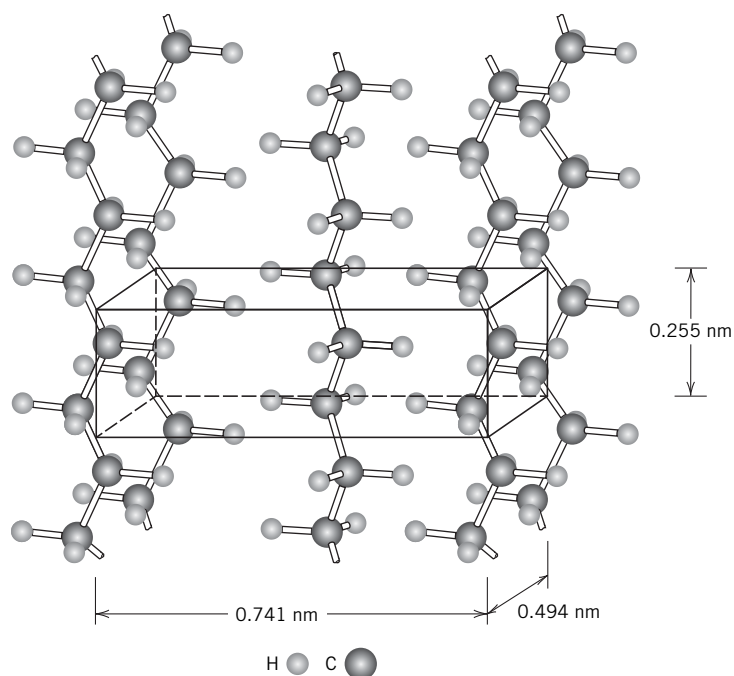
## 4.11 POLYMER CRYSTALLINITY

### polymer crystallinity

The crystalline state may exist in polymeric materials. However, because it involves molecules instead of just atoms or ions, as with metals and ceramics, the atomic arrangements will be more complex for polymers. We think of **polymer crystallinity** as the packing of molecular chains to produce an ordered atomic array. Crystal structures may be specified in terms of unit cells, which are often quite complex. For example, Figure 4.10 shows the unit cell for polyethylene and its relationship to the molecular chain structure; this unit cell has orthorhombic geometry (Table 3.6). Of course, the chain molecules also extend beyond the unit cell shown in the figure.

**Table 4.5** Chemical Repeat Units That Are Employed in Copolymer Rubbers

Repeat Unit Name	Repeat Unit Structure	Repeat Unit Name	Repeat Unit Structure
 <b>VMSE</b> Repeat Units for Rubbers	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}\equiv\text{N} \end{array}$		$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$
	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$		$\begin{array}{c} \text{H} \quad \text{CH}_3 \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array}$
	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$		$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array}$
	$\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$		

**Figure 4.10** Arrangement of molecular chains in a unit cell for polyethylene.

Molecular substances having small molecules (e.g., water and methane) are normally either totally crystalline (as solids) or totally amorphous (as liquids). As a consequence of their size and often complexity, polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material. Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common, because twisting, kinking, and coiling of the chains prevent the strict ordering of every segment of every chain. Other structural effects are also influential in determining the extent of crystallinity, as discussed shortly.

The degree of crystallinity may range from completely amorphous to almost entirely (up to about 95%) crystalline; in contrast, metal specimens are almost always entirely crystalline, whereas many ceramics are either totally crystalline or totally noncrystalline. Semicrystalline polymers are, in a sense, analogous to two-phase metal alloys, discussed in subsequent chapters.

The density of a crystalline polymer will be greater than an amorphous one of the same material and molecular weight because the chains are more closely packed together for the crystalline structure. The degree of crystallinity by weight may be determined from accurate density measurements, according to

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \quad (4.8)$$

where  $\rho_s$  is the density of a specimen for which the percent crystallinity is to be determined,  $\rho_a$  is the density of the totally amorphous polymer, and  $\rho_c$  is the density of the perfectly crystalline polymer. The values of  $\rho_a$  and  $\rho_c$  must be measured by other experimental means.

The degree of crystallinity of a polymer depends on the rate of cooling during solidification as well as on the chain configuration. During crystallization upon cooling through the melting temperature, the chains, which are highly random and entangled in the viscous liquid, must assume an ordered configuration. For this to occur, sufficient time must be allowed for the chains to move and align themselves.

The molecular chemistry as well as chain configuration also influence the ability of a polymer to crystallize. Crystallization is not favored in polymers that are composed of chemically complex repeat units (e.g., polyisoprene). However, crystallization is not easily prevented in chemically simple polymers such as polyethylene and polytetrafluoroethylene, even for very rapid cooling rates.

For linear polymers, crystallization is easily accomplished because there are few restrictions to prevent chain alignment. Any side branches interfere with crystallization, such that branched polymers never are highly crystalline; in fact, excessive branching may prevent any crystallization whatsoever. Most network and crosslinked polymers are almost totally amorphous because the crosslinks prevent the polymer chains from rearranging and aligning into a crystalline structure. A few crosslinked polymers are partially crystalline. With regard to the stereoisomers, atactic polymers are difficult to crystallize; however, isotactic and syndiotactic polymers crystallize much more easily because the regularity of the geometry of the side groups facilitates the process of fitting together adjacent chains. Also, the bulkier or larger the side-bonded groups of atoms, the less is the tendency for crystallization.

For copolymers, as a general rule, the more irregular and random the repeat unit arrangements, the greater is the tendency for the development of noncrystallinity. For alternating and block copolymers there is some likelihood of crystallization. However, random and graft copolymers are normally amorphous.

To some extent, the physical properties of polymeric materials are influenced by the degree of crystallinity. Crystalline polymers are usually stronger and more resistant to dissolution and softening by heat. Some of these properties are discussed in subsequent chapters.

Percent crystallinity (semicrystalline polymer) — dependence on specimen density, and densities of totally crystalline and totally amorphous materials



**Concept Check 4.5** (a) Compare the crystalline state in metals and polymers. (b) Compare the noncrystalline state as it applies to polymers and ceramic glasses.

(The answer is available in *WileyPLUS*.)

## EXAMPLE PROBLEM 4.2

### Computations of the Density and Percent Crystallinity of Polyethylene

- (a) Compute the density of totally crystalline polyethylene. The orthorhombic unit cell for polyethylene is shown in Figure 4.10; also, the equivalent of two ethylene repeat units is contained within each unit cell.
- (b) Using the answer to part (a), calculate the percent crystallinity of a branched polyethylene that has a density of  $0.925 \text{ g/cm}^3$ . The density for the totally amorphous material is  $0.870 \text{ g/cm}^3$ .

#### Solution

- (a) Equation 3.8, used in Chapter 3 to determine densities for metals, also applies to polymeric materials and is used to solve this problem. It takes the same form, namely

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

where  $n$  represents the number of repeat units within the unit cell (for polyethylene  $n = 2$ ) and  $A$  is the repeat unit molecular weight, which for polyethylene is

$$\begin{aligned} A &= 2(A_C) + 4(A_H) \\ &= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol} \end{aligned}$$

Also,  $V_C$  is the unit cell volume, which is just the product of the three unit cell edge lengths in Figure 4.10; or

$$\begin{aligned} V_C &= (0.741 \text{ nm})(0.494 \text{ nm})(0.255 \text{ nm}) \\ &= (7.41 \times 10^{-8} \text{ cm})(4.94 \times 10^{-8} \text{ cm})(2.55 \times 10^{-8} \text{ cm}) \\ &= 9.33 \times 10^{-23} \text{ cm}^3/\text{unit cell} \end{aligned}$$

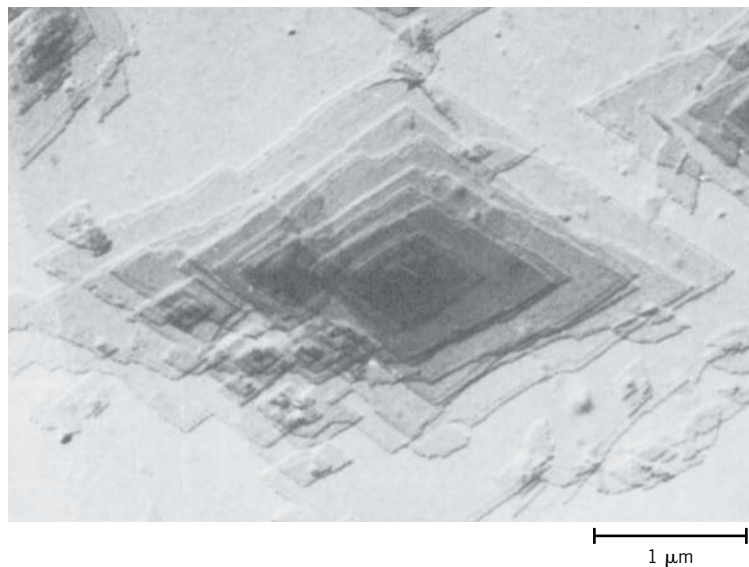
Now, substitution into Equation 3.8 of this value, values for  $n$  and  $A$  cited previously, and the value of  $N_A$  leads to

$$\begin{aligned} \rho &= \frac{nA}{V_C N_A} \\ &= \frac{(2 \text{ repeat units/unit cell})(28.05 \text{ g/mol})}{(9.33 \times 10^{-23} \text{ cm}^3/\text{unit cell})(6.022 \times 10^{23} \text{ repeat units/mol})} \\ &= 0.998 \text{ g/cm}^3 \end{aligned}$$

- (b) We now use Equation 4.8 to calculate the percent crystallinity of the branched polyethylene with  $\rho_c = 0.998 \text{ g/cm}^3$ ,  $\rho_a = 0.870 \text{ g/cm}^3$ , and  $\rho_s = 0.925 \text{ g/cm}^3$ . Thus,

$$\begin{aligned} \% \text{ crystallinity} &= \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100 \\ &= \frac{0.998 \text{ g/cm}^3 (0.925 \text{ g/cm}^3 - 0.870 \text{ g/cm}^3)}{0.925 \text{ g/cm}^3 (0.998 \text{ g/cm}^3 - 0.870 \text{ g/cm}^3)} \times 100 \\ &= 46.4\% \end{aligned}$$

**Figure 4.11** Electron micrograph of a polyethylene single crystal. 20,000 $\times$ . [From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Editors), *Growth and Perfection of Crystals*. General Electric Company and John Wiley & Sons, Inc., 1958, p. 498.]



## 4.12 POLYMER CRYSTALS

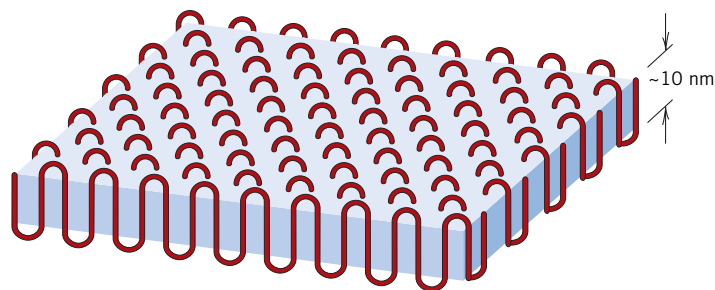
### crystallite

It has been proposed that a semicrystalline polymer consists of small crystalline regions (**crystallites**), each having a precise alignment, which are interspersed with amorphous regions composed of randomly oriented molecules. The structure of the crystalline regions may be deduced by examination of polymer single crystals, which may be grown from dilute solutions. These crystals are regularly shaped, thin platelets (or *lamellae*) approximately 10 to 20 nm thick and on the order of 10  $\mu\text{m}$  long. Frequently, these platelets form a multilayered structure like that shown in the electron micrograph of a single crystal of polyethylene in Figure 4.11. The molecular chains within each platelet fold back and forth on themselves, with folds occurring at the faces; this structure, aptly termed the **chain-folded model**, is illustrated schematically in Figure 4.12. Each platelet consists of a number of molecules; however, the average chain length is much greater than the thickness of the platelet.

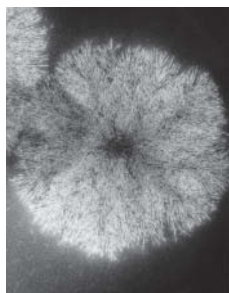
### chain-folded model

### spherulite

Many bulk polymers that are crystallized from a melt are semicrystalline and form a **spherulite** structure. As implied by the name, each spherulite may grow to be roughly spherical in shape; one of them, as found in natural rubber, is shown in the transmission



**Figure 4.12** The chain-folded structure for a plate-shaped polymer crystallite.

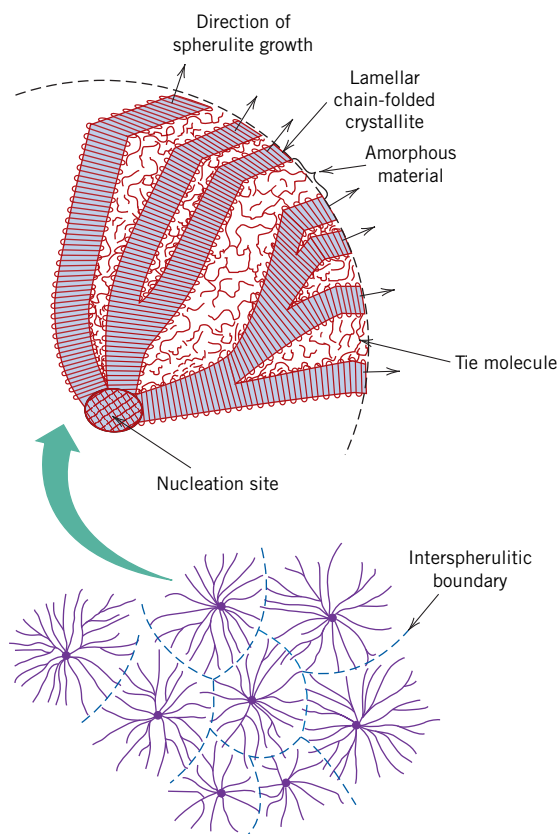


Transmission electron micrograph showing the spherulite structure in a natural rubber specimen.

electron micrograph in chapter-opening photograph (*d*) for this chapter and in the photograph that appears in the adjacent left margin. The spherulite consists of an aggregate of ribbon-like chain-folded crystallites (lamellae) approximately 10 nm thick that radiate outward from a single nucleation site in the center. In this electron micrograph, these lamellae appear as thin white lines. The detailed structure of a spherulite is illustrated schematically in Figure 4.13. Shown here are the individual chain-folded lamellar crystals that are separated by amorphous material. Tie-chain molecules that act as connecting links between adjacent lamellae pass through these amorphous regions.

As the crystallization of a spherulitic structure nears completion, the extremities of adjacent spherulites begin to impinge on one another, forming more-or-less planar boundaries; prior to this time, they maintain their spherical shape. These boundaries are evident in Figure 4.14, which is a photomicrograph of polyethylene using cross-polarized light. A characteristic Maltese cross pattern appears within each spherulite. The bands or rings in the spherulite image result from twisting of the lamellar crystals as they extend like ribbons from the center.

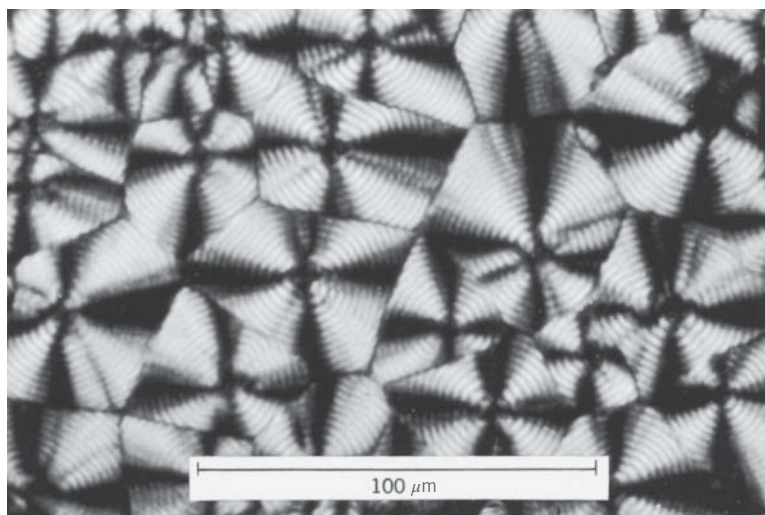
Spherulites are considered to be the polymer analogue of grains in polycrystalline metals and ceramics. However, as discussed earlier, each spherulite is really composed of many different lamellar crystals and, in addition, some amorphous material. Polyethylene, polypropylene, poly(vinyl chloride), polytetrafluoroethylene, and nylon form a spherulitic structure when they crystallize from a melt.



**Figure 4.13** Schematic representation of the detailed structure of a spherulite.



**Figure 4.14** A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of polyethylene. Linear boundaries form between adjacent spherulites, and within each spherulite appears a Maltese cross. 525 $\times$ .



Courtesy F. P. Price, General Electric Company

## SUMMARY

### Polymer Molecules

- Most polymeric materials are composed of very large molecular chains with side groups of various atoms (O, Cl, etc.) or organic groups such as methyl, ethyl, or phenyl groups.
- These macromolecules are composed of repeat units—smaller structural entities—which are repeated along the chain.

### The Chemistry of Polymer Molecules

- Repeat units for some of the chemically simple polymers [polyethylene, polytetrafluoroethylene, poly(vinyl chloride), polypropylene, etc.] are presented in Table 4.3.
- A *homopolymer* is one for which all of the repeat units are the same type. The chains for copolymers are composed of two or more kinds of repeat units.
- Repeat units are classified according to the number of active bonds (i.e., functionality):  
     For bifunctional monomers, a two-dimensional chainlike structure results from a monomer that has two active bonds.  
     Trifunctional monomers have three active bonds, from which three-dimensional network structures form.

### Molecular Weight

- Molecular weights for high polymers may be in excess of a million. Because all molecules are not of the same size, there is a distribution of molecular weights.
- Molecular weight is often expressed in terms of number and weight averages; values for these parameters may be determined using Equations 4.5a and 4.5b, respectively.
- Chain length may also be specified by degree of polymerization—the number of repeat units per average molecule (Equation 4.6).

### Molecular Shape

- Molecular entanglements occur when the chains assume twisted, coiled, and kinked shapes or contours as a consequence of chain bond rotations.
- Rotational flexibility is diminished when double chain bonds are present and also when bulky side groups are part of the repeat unit.

### Molecular Structure

- Four different polymer molecular chain structures are possible: linear (Figure 4.7a), branched (Figure 4.7b), crosslinked (Figure 4.7c), and network (Figure 4.7d).

**Molecular Configurations**

- For repeat units that have more than one side atom or groups of atoms bonded to the main chain:  
Head-to-head and head-to-tail configurations are possible.  
Differences in spatial arrangements of these side atoms or groups of atoms lead to isotactic, syndiotactic, and atactic stereoisomers.
- When a repeat unit contains a double chain bond, both cis and trans geometric isomers are possible.

**Thermoplastic and Thermosetting Polymers**

- With regard to behavior at elevated temperatures, polymers are classified as either thermoplastic or thermosetting.  
*Thermoplastic* polymers have linear and branched structures; they soften when heated and harden when cooled.  
In contrast, *thermosetting* polymers, once they have hardened, will not soften upon heating; their structures are crosslinked and network.

**Copolymers**

- The copolymers include random (Figure 4.9a), alternating (Figure 4.9b), block (Figure 4.9c), and graft (Figure 4.9d) types.
- Repeat units that are employed in copolymer rubber materials are presented in Table 4.5.

**Polymer Crystallinity**

- When the molecular chains are aligned and packed in an ordered atomic arrangement, the condition of crystallinity is said to exist.
- Amorphous polymers are also possible wherein the chains are misaligned and disordered.
- In addition to being entirely amorphous, polymers may also exhibit varying degrees of crystallinity; that is, crystalline regions are interdispersed within amorphous areas.
- Crystallinity is facilitated for polymers that are chemically simple and that have regular and symmetrical chain structures.
- The percent crystallinity of a semicrystalline polymer is dependent on its density, as well as the densities of the totally crystalline and totally amorphous materials, according to Equation 4.8.

**Polymer Crystals**

- Crystalline regions (or crystallites) are plate-shape and have a chain-folded structure (Figure 4.12)—chains within the platelet are aligned and fold back and forth on themselves, with folds occurring at the faces.
- Many semicrystalline polymers form spherulites; each spherulite consists of a collection of ribbon-like chain-folded lamellar crystallites that radiate outward from its center.

**Equation Summary**

Equation Number	Equation	Solving For	Page Number
4.5a	$\overline{M}_n = \sum x_i M_i$	Number-average molecular weight	124
4.5b	$\overline{M}_w = \sum w_i M_i$	Weight-average molecular weight	124
4.6	$DP = \frac{\overline{M}_n}{m}$	Degree of polymerization	125
4.7	$\overline{m} = \sum f_j m_j$	For a copolymer, average repeat unit molecular weight	133
4.8	$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$	Percent crystallinity, by weight	136

## List of Symbols

Symbol	Meaning
$f_j$	Mole fraction of repeat unit $j$ in a copolymer chain
$m$	Repeat unit molecular weight
$M_i$	Mean molecular weight within the size range $i$
$m_j$	Molecular weight of repeat unit $j$ in a copolymer chain
$x_i$	Fraction of the total number of molecular chains that lie within the size range $i$
$w_i$	Weight fraction of molecules that lie within the size range $i$
$\rho_a$	Density of a totally amorphous polymer
$\rho_c$	Density of a completely crystalline polymer
$\rho_s$	Density of polymer specimen for which percent crystallinity is to be determined

## Important Terms and Concepts

alternating copolymer	functionality	polymer
atactic configuration	graft copolymer	random copolymer
bifunctional	homopolymer	repeat unit
block copolymer	isomerism	saturated
branched polymer	isotactic configuration	spherulite
chain-folded model	linear polymer	stereoisomerism
cis (structure)	macromolecule	syndiotactic configuration
copolymer	molecular chemistry	thermoplastic polymer
crosslinked polymer	molecular structure	thermosetting polymer
crystallinity (polymer)	molecular weight	trans (structure)
crystallite	monomer	trifunctional
degree of polymerization	network polymer	unsaturated

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## QUESTIONS AND PROBLEMS

### Hydrocarbon Molecules

### Polymer Molecules

### The Chemistry of Polymer Molecules

**4.1** On the basis of the structures presented in this chapter, sketch repeat unit structures for the following polymers:

- (a) polychlorotrifluoroethylene
- (b) poly(vinyl alcohol).

### Molecular Weight

**4.2** Compute repeat unit molecular weights for the following:

- (a) polytetrafluoroethylene
- (b) poly(methyl methacrylate)
- (c) nylon 6,6
- (d) poly(ethylene terephthalate).

**4.3** The number-average molecular weight of a polystyrene is 500,000 g/mol. Compute the degree of polymerization.

**4.4 (a)** Compute the repeat unit molecular weight of polypropylene.

**(b)** Compute the number-average molecular weight for a polypropylene for which the degree of polymerization is 15,000.

**4.5** The following table lists molecular weight data for a polytetrafluoroethylene material. Compute the following:

- (a) the number-average molecular weight,
- (b) the weight-average molecular weight, and
- (c) the degree of polymerization.

<b>Molecular Weight Range (g/mol)</b>	<b><math>x_i</math></b>	<b><math>w_i</math></b>
10,000–20,000	0.03	0.01
20,000–30,000	0.09	0.04
30,000–40,000	0.15	0.11
40,000–50,000	0.25	0.23
50,000–60,000	0.22	0.24
60,000–70,000	0.14	0.18
70,000–80,000	0.08	0.12
80,000–90,000	0.04	0.07

**4.6** Molecular weight data for some polymer are tabulated here. Compute the following:

- (a) the number-average molecular weight

**(b)** the weight-average molecular weight.

**(c)** If it is known that this material's degree of polymerization is 477, which one of the polymers listed in Table 4.3 is this polymer? Why?

<b>Molecular Weight Range (g/mol)</b>	<b><math>x_i</math></b>	<b><math>w_i</math></b>
8,000–20,000	0.05	0.02
20,000–32,000	0.15	0.08
32,000–44,000	0.21	0.17
44,000–56,000	0.28	0.29
56,000–68,000	0.18	0.23
68,000–80,000	0.10	0.16
80,000–92,000	0.03	0.05

**4.7** Is it possible to have a poly(vinyl chloride) homopolymer with the following molecular weight data, and a degree of polymerization of 1120? Why or why not?

<b>Molecular Weight Range (g/mol)</b>	<b><math>w_i</math></b>	<b><math>x_i</math></b>
8,000–20,000	0.02	0.05
20,000–32,000	0.08	0.15
32,000–44,000	0.17	0.21
44,000–56,000	0.29	0.28
56,000–68,000	0.23	0.18
68,000–80,000	0.16	0.10
80,000–92,000	0.05	0.03

**4.8** High-density polyethylene may be chlorinated by inducing the random substitution of chlorine atoms for hydrogen.

**(a)** Determine the concentration of Cl (in wt%) that must be added if this substitution occurs for 8% of all the original hydrogen atoms.

**(b)** In what ways does this chlorinated polyethylene differ from poly(vinyl chloride)?

### Molecular Shape

**4.9** For a linear, freely rotating polymer molecule, the total chain length  $L$  depends on the bond length between chain atoms  $d$ , the total number of bonds in the molecule  $N$ , and the angle between adjacent backbone chain atoms  $\theta$ , as follows:

$$L = Nd \sin\left(\frac{\theta}{2}\right) \quad (4.9)$$

Furthermore, the average end-to-end distance for a series of polymer molecules  $r$  in Figure 4.6 is equal to

$$r = d\sqrt{N} \quad (4.10)$$

A linear polyethylene has a number-average molecular weight of 300,000 g/mol; compute average values of  $L$  and  $r$  for this material.

- 4.10** Using the definitions for total chain molecule length  $L$  (Equation 4.9) and average chain end-to-end distance  $r$  (Equation 4.10), determine the following for a linear polytetrafluoroethylene:

- (a) the number-average molecular weight for  $L = 2000$  nm
- (b) the number-average molecular weight for  $r = 15$  nm

### Molecular Configurations

- 4.11** Sketch portions of a linear polypropylene molecule that are (a) syndiotactic, (b) atactic, and (c) isotactic. Use two-dimensional schematics per footnote 9 of this chapter.
- 4.12** Sketch cis and trans structures for (a) polybutadiene and (b) polychloroprene. Use two-dimensional schematics per footnote 12 of this chapter.

### Thermoplastic and Thermosetting Polymers

- 4.13** Compare thermoplastic and thermosetting polymers (a) on the basis of mechanical characteristics upon heating and (b) according to possible molecular structures.
- 4.14** (a) Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?
- (b) Is it possible to grind up and reuse polypropylene? Why or why not?

### Copolymers

- 4.15** Sketch the repeat structure for each of the following alternating copolymers: (a) poly(ethylene-propylene), (b) poly(butadiene-styrene), and (c) poly(isobutylene-isoprene).
- 4.16** The number-average molecular weight of a poly(acrylonitrile-butadiene) alternating copolymer is 1,000,000 g/mol; determine the average number of acrylonitrile and butadiene repeat units per molecule.
- 4.17** Calculate the number-average molecular weight of a random poly(isobutylene-isoprene) copolymer in which the fraction of isobutylene repeat units is 0.25; assume that this concentration corresponds to a degree of polymerization of 1500.

- 4.18** An alternating copolymer is known to have a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210. If one of the repeat units is ethylene, which of styrene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?

- 4.19** (a) Determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640.

(b) Which type(s) of copolymer(s) will this copolymer be, considering the following possibilities: random, alternating, graft, and block? Why?

- 4.20** Crosslinked copolymers consisting of 35 wt% ethylene and 65 wt% propylene may have elastic properties similar to those for natural rubber. For a copolymer of this composition, determine the fraction of both repeat unit types.

- 4.21** A random poly(styrene-butadiene) copolymer has a number-average molecular weight of 350,000 g/mol and a degree of polymerization of 5000. Compute the fraction of styrene and butadiene repeat units in this copolymer.

### Polymer Crystallinity

- 4.22** Explain briefly why the tendency of a polymer to crystallize decreases with increasing molecular weight.

- 4.23** For each of the following pairs of polymers, do the following: (1) State whether it is possible to determine whether one polymer is more likely to crystallize than the other; (2) if it is possible, note which is the more likely and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.

(a) Linear and atactic poly(vinyl chloride); linear and isotactic polypropylene

(b) Linear and syndiotactic polypropylene; crosslinked *cis*-polyisoprene

(c) Network phenol-formaldehyde; linear and isotactic polystyrene

(d) Block poly(acrylonitrile-isoprene) copolymer; graft poly(chloroprene-isobutylene) copolymer

- 4.24** The density of totally crystalline nylon 6,6 at room temperature is 1.213 g/cm<sup>3</sup>. Also, at room temperature the unit cell for this material is triclinic with the following lattice parameters:

$$\begin{aligned} a &= 0.497 \text{ nm} & \alpha &= 48.4^\circ \\ b &= 0.547 \text{ nm} & \beta &= 76.6^\circ \\ c &= 1.729 \text{ nm} & \gamma &= 62.5^\circ \end{aligned}$$

If the volume of a triclinic unit cell, is a function of these lattice parameters as

$$V_{\text{tri}} = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

determine the number of repeat units per unit cell.

- 4.25** The density and associated percent crystallinity for two poly(ethylene terephthalate) materials are as follows:

$\rho$ (g/cm <sup>3</sup> )	Crystallinity (%)
1.408	74.3
1.343	31.2

(a) Compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate).

(b) Determine the percent crystallinity of a specimen having a density of 1.382 g/cm<sup>3</sup>.

- 4.26** The density and associated percent crystallinity for two polypropylene materials are as follows:

$\rho$ (g/cm <sup>3</sup> )	Crystallinity (%)
0.904	62.8
0.895	54.4

(a) Compute the densities of totally crystalline and totally amorphous polypropylene.

(b) Determine the density of a specimen having 74.6% crystallinity.

### Spreadsheet Problem

- 4.1SS** For a specific polymer, given at least two density values and their corresponding percent crystallinity values, develop a spreadsheet that allows the user to determine the following:

- (a) the density of the totally crystalline polymer
- (b) the density of the totally amorphous polymer
- (c) the percent crystallinity of a specified density
- (d) the density for a specified percent crystallinity.

## FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

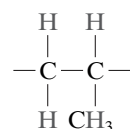
- 4.1FE** What type(s) of bonds is (are) found between atoms within hydrocarbon molecules?

- (A) Ionic bonds
- (B) Covalent bonds
- (C) van der Waals bonds
- (D) Metallic bonds

- 4.2FE** How do the densities compare for crystalline and amorphous polymers of the same material that have identical molecular weights?

- (A) Density of crystalline polymer < density of amorphous polymer
- (B) Density of crystalline polymer = density of amorphous polymer
- (C) Density of crystalline polymer > density of amorphous polymer

- 4.3FE** What is the name of the polymer represented by the following repeat unit?



- (A) Poly(methyl methacrylate)
- (B) Polyethylene
- (C) Polypropylene
- (D) Polystyrene