

**Should we not suppose  
that in the formation  
of a crystal, the particles  
are not only established  
in rows and columns set  
in regular figures, but  
also by means of some  
polar property have  
turned identical sides  
in identical directions?**

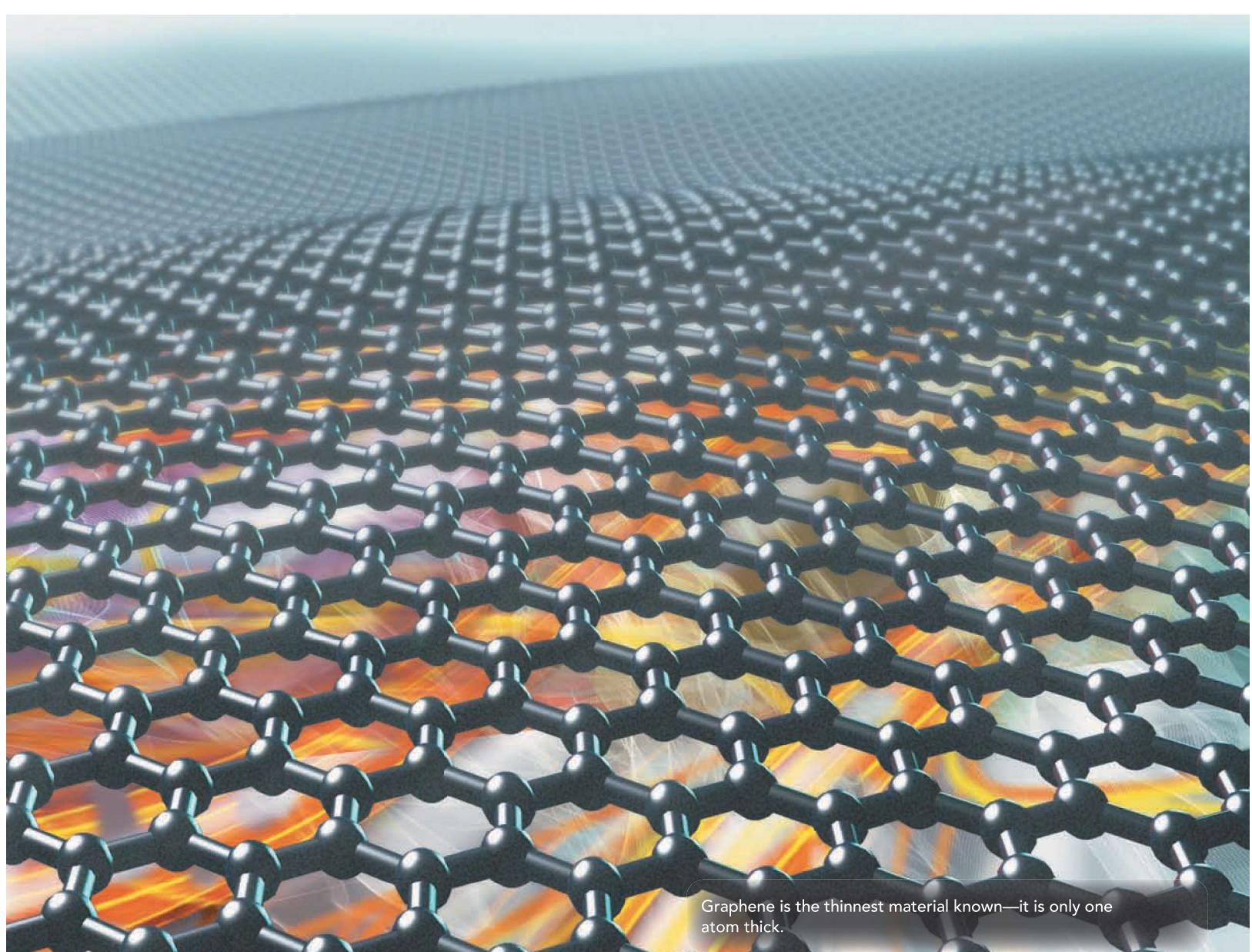
—ISAAC NEWTON (1642–1727)

CHAPTER

# 13

## Solids and Modern Materials

In this chapter, we focus on the solid state of matter. We first examine the structures of solids, keeping in mind that these structures determine the properties of solids. For example, the repeating hexagonal pattern of water molecules in crystalline ice determines the hexagonal shape of a snowflake, and the repeating cubic pattern of sodium and chloride ions in sodium chloride determines the cubic shape of salt grains. We then turn our attention to the study and development of solids with unique and useful properties, a field known as *materials science*. The ceramics that compose your coffee cups, the semiconductors in your electronic devices, and the plastics that are most likely all around you even at this moment are materials developed to have specific properties that serve specific purposes. In this chapter, we take a brief look at each of these kinds of materials.



Graphene is the thinnest material known—it is only one atom thick.

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### 13.1 Friday Night Experiments: The Discovery of Graphene

In 2010, Andre Geim (1958–) and Konstantin Novoselov (1974–) were awarded the Nobel Prize in Physics for the discovery of a new material—**graphene**. Graphene is the thinnest known material (only one atom thick); it is also the strongest. It conducts heat and electricity, it is transparent, and it is completely impermeable to all substances, including helium. Although its many possible applications are yet to be realized, graphene may one day be used to make faster computers, foldable touchscreens, ultrathin

light panels, and super-strong plastics to construct satellites, airplanes, ships, and cars. And how did these scientists discover this wonder material? Through *Friday night experiments*.

Most successful modern scientists work in a narrow field of study, chipping away at a problem about which they have become experts. Andre Geim also worked this way—but not all of the time. Geim often ventured into what he calls *lateral ideas*, which were explorations into fields far from his immediate area of expertise. Over a 15-year period, he explored about two dozen such ideas. These explorations became known as *Friday night experiments* (even though they took much longer than just one night). Most of Geim's Friday night experiments were complete failures, but some succeeded. For example, in one Friday night experiment, Geim was able to suspend an entire frog in a magnetic field. In another, he developed a new kind of tape based on mimicking the toes of a gecko. However, his most successful Friday night experiment was the discovery of graphene.

In 2002, Geim assigned his brand-new graduate student a Friday night experiment as a way to give the student time to get acquainted with the laboratory. His assignment was to make films of graphite “as thin as possible.” The graduate student tackled the task by attempting to polish a tablet of graphite down to almost nothingness. In spite of his best efforts, the thinnest sheet he could attain by this method was still pretty thick (about 10  $\mu\text{m}$ ).

In a breakthrough moment, a colleague brought Geim a piece of scotch tape that had been adhered to a graphite surface and then removed. The tape had remnants of graphite stuck to it. When Geim examined the graphite flakes under a microscope, he realized that these flakes were much thinner than those his graduate student was able to produce through polishing. In fact, some of the flakes were just one layer thick! Over the next several months, Geim and his colleagues were able to isolate these flakes and measure some of their properties. In 2004, Geim and his colleagues published their results—the discovery of atomically thin carbon—in *Nature*. In 2010, Geim and his closest collaborator on the project, Konstantin Novoselov, were awarded the Nobel Prize in Physics for “ground-breaking experiments regarding the two-dimensional material graphene.”

Graphene has been right under our noses for some time. Every time you write with a pencil, layers of graphite flake onto the paper, leaving the familiar gray trail. That trail undoubtedly also contains flakes of graphene—too small to see. Geim and Novoselov were able to see what others had missed and as a result discovered a new wonder material. These kinds of discoveries often have huge impacts on society—although it may take decades to realize and refine their applications.

In this chapter, we look into the world of solids and materials and see how they permanently changed societies, just as graphene may someday change our present society. For example, the discovery of cement led to a revolution in building, the discovery of porcelain led to a revolution in dishware, and the discovery of semiconducting materials made possible the computer and Internet revolution which is still unfolding today. The development of new materials continues to be an active and growing area of research. We begin by examining a technique to determine the structure of solids.



▲ The hexagonal shape of a snowflake derives from the hexagonal arrangement of water molecules in crystalline ice.

## 13.2 X-Ray Crystallography

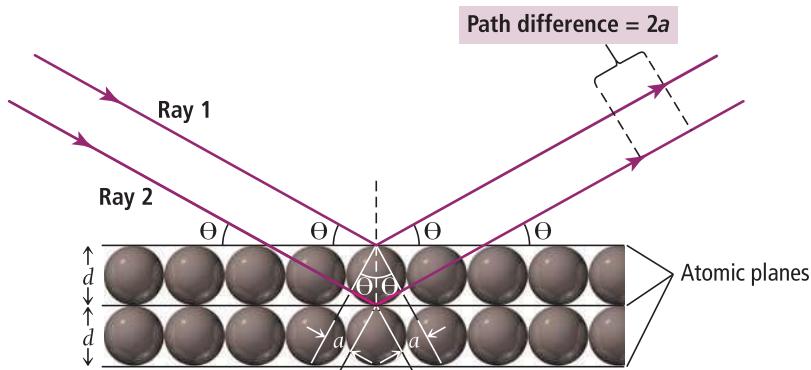
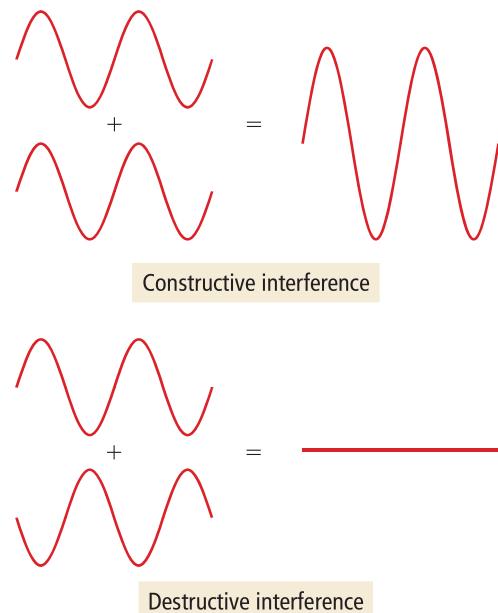
In Section 12.2, we discussed the differences between solids, liquids, and gases. Recall that solids can be *crystalline* (composed of atoms or molecules arranged in structures with long-range order) or *amorphous* (composed of atoms or molecules with no long-range order). If you have ever visited the mineral section of a natural history museum and seen crystals with smooth faces and well-defined angles, or if you have carefully observed the hexagonal shapes of snowflakes, you have witnessed some of the effects of the underlying long-range order in crystalline solids. The beautiful geometric shapes that are visible on the macroscopic scale are the result of specific structural patterns on the molecular and atomic scales. But how do we study these patterns? How do we look into the atomic and molecular world to determine the arrangement of the atoms and measure the distances between them? In this section, we examine **X-ray diffraction**, a powerful laboratory technique that enables us to do exactly that.

In Section 8.2, we saw that electromagnetic waves (light waves) interact with each other in a characteristic way called *interference*: they can cancel each other out or reinforce each other, depending on the alignment of their crests and troughs. *Constructive interference* occurs when two waves interact with their crests and troughs in alignment. *Destructive interference* occurs when two waves interact with the crests of one aligning with the troughs of the other. Recall also that when light encounters two slits separated by a distance comparable to the wavelength of the light, constructive and destructive interference produces a characteristic *interference pattern*, consisting of alternating bright and dark lines.

Atomic planes within crystals are separated by about  $10^2$  pm. As a result, light of similar wavelength (which happens to fall in the X-ray region of the electromagnetic spectrum) forms interference patterns or *diffraction patterns* when it interacts with those atoms. The exact pattern of diffraction reveals the spacing between planes of atoms.

Consider two planes of atoms within a crystalline lattice separated by a distance  $d$ , as illustrated in Figure 13.1▼. If two rays of light with wavelength  $\lambda$  that are initially in phase (that is, the crests of one wave are aligned with the crests of the other) diffract from the two planes, the diffracted rays may interfere with each other constructively or destructively, depending on the difference between the path lengths traveled by each ray. If the difference between the two path lengths ( $2a$ ) is an integral number ( $n$ ) of wavelengths, then the interference is constructive:

$$n\lambda = 2a \quad (\text{criterion for constructive interference}) \quad [13.1]$$



**◀ FIGURE 13.1 Diffraction from a Crystal** When X-rays strike parallel planes of atoms in a crystal, constructive interference occurs if the difference in path length between beams reflected from adjacent planes is an integral number of wavelengths.

Using trigonometry, we can determine that constructive interference occurs when the angle of reflection ( $\theta$ ) is related to the distance  $a$  and the separation between layers ( $d$ ) by the following relation:

$$\sin \theta = \frac{a}{d} \quad [13.2]$$

Rearranging, we get:

$$a = d \sin \theta \quad [13.3]$$

By substituting Equation 13.3 into Equation 13.1, we arrive at the following important relationship:

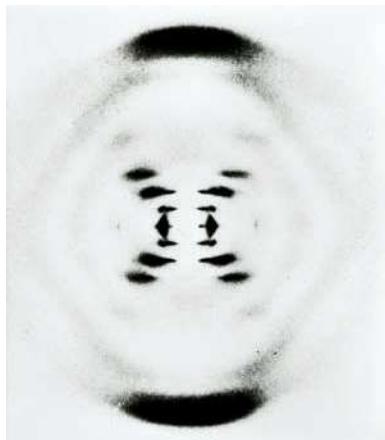
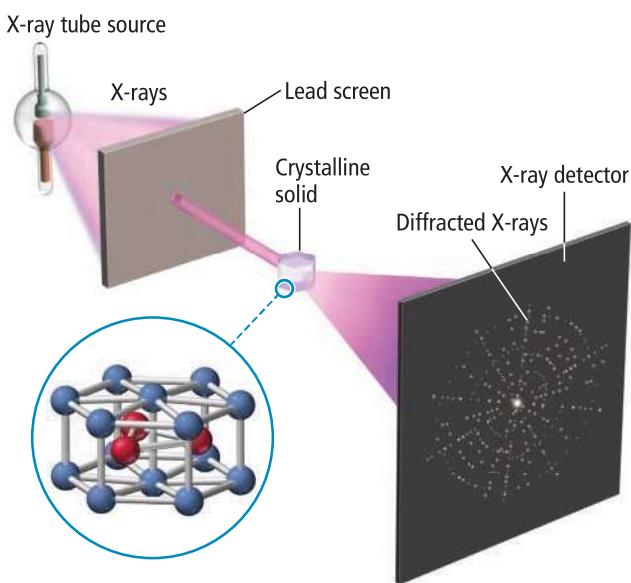
$$n\lambda = 2d \sin \theta \quad \text{Bragg's law}$$

This equation is *Bragg's law*. For a given wavelength of light incident on atoms arranged in layers, we can measure the angle that produces constructive interference (which appears as a bright spot on the X-ray diffraction pattern) and then calculate  $d$ , the distance between the atomic layers:

$$d = \frac{n\lambda}{2 \sin \theta} \quad [13.4]$$

**► FIGURE 13.2 X-Ray Diffraction Analysis**

In X-ray crystallography, an X-ray beam is passed through a sample, which is rotated to allow diffraction from different crystalline planes. The resulting patterns, representing constructive interference from various planes, are analyzed to determine crystalline structure.



In a modern X-ray diffractometer (Figure 13.2▲), a computer collects and analyzes the diffraction pattern from a crystal. By rotating the crystal and collecting the resulting diffraction patterns at different angles, the distances between various crystalline planes can be measured, eventually yielding the entire crystalline structure. This process is **X-ray crystallography**.

Researchers use X-ray crystallography to determine not only the structures of simple atomic lattices, but also the structures of proteins, DNA, and other biologically important molecules. For example, the famous X-ray diffraction photograph shown in the margin, obtained by Rosalind Franklin (1920–1958) and Maurice Wilkins (1916–2004), helped Watson and Crick determine the double-helical structure of DNA. Recall from Section 10.1 that researchers also used X-ray diffraction to determine the structure of HIV protease, a protein critical to the reproduction of HIV and the development of AIDS. Knowledge of that structure was then employed to design drug molecules to inhibit the action of HIV protease and halt the advance of the disease.

### EXAMPLE 13.1 Using Bragg's Law

When an X-ray beam of  $\lambda = 154 \text{ pm}$  is incident on the surface of an iron crystal, it produces a maximum diffraction at an angle of  $\theta = 32.6^\circ$ . Assuming  $n = 1$ , calculate the separation between layers of iron atoms in the crystal.

#### SOLUTION

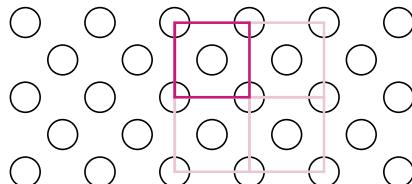
To solve this problem, use Bragg's law in the form given by Equation 13.4. The distance,  $d$ , is the separation between layers in the crystal.

$$\begin{aligned} d &= \frac{n\lambda}{2 \sin \theta} \\ &= \frac{154 \text{ pm}}{2 \sin(32.6^\circ)} \\ &= 143 \text{ pm} \end{aligned}$$

**FOR PRACTICE 13.1** The spacing between layers of molybdenum atoms is 157 pm. Calculate the angle at which 154-pm X-rays produce a maximum reflection for  $n = 1$ .

## 13.3 Unit Cells and Basic Structures

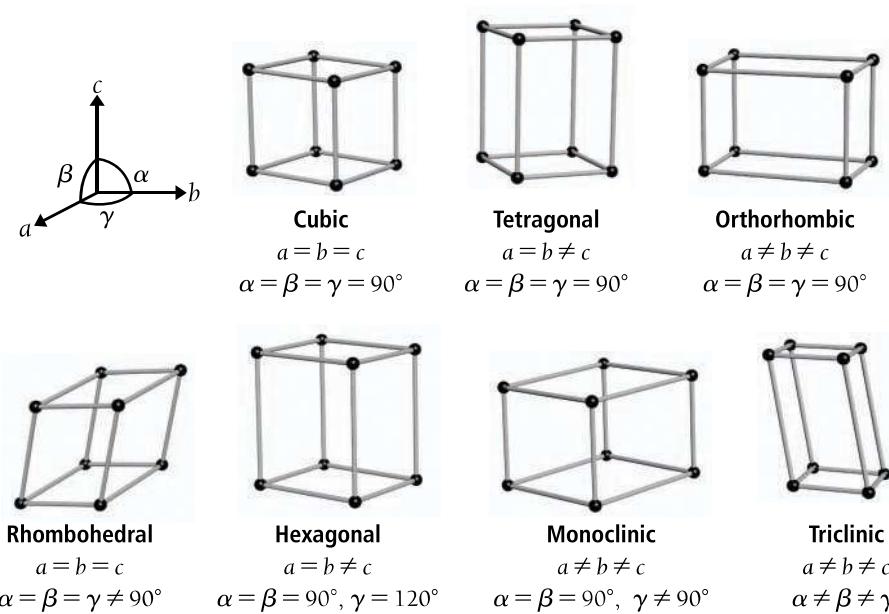
X-ray crystallography allows us to determine the regular arrangements of atoms within a crystalline solid. This arrangement is called the **crystalline lattice**. The crystalline lattice of any solid is nature's way of aggregating the particles to minimize their energy. We represent the crystalline lattice with a small collection of atoms, ions, or molecules called the **unit cell**. When the unit cell is repeated over and over—like the tiles of a floor or the pattern in a wallpaper design, but in three dimensions—the entire lattice is reproduced. For example, consider the two-dimensional crystalline lattice shown here:



The unit cell for this lattice is the dark-colored square. Each circle represents an atom, ion, or molecule. Repeating the pattern in the square throughout the two-dimensional space generates the entire lattice.

### Cubic Unit Cells

Many different unit cells exist, and we often classify unit cells by their symmetry. Figure 13.3▼ shows the different fundamental types of unit cells. In this book, we focus primarily on *cubic unit cells* (although we look at one hexagonal unit cell). Cubic unit cells are characterized by equal edge lengths and 90° angles at their corners. Figure 13.4► lists three cubic unit cells—simple cubic, body-centered cubic, and face-centered cubic—along with some of their basic characteristics. The two colors in the images in this table make it easier to visualize the different positions of the atoms; the colors *do not* represent different kinds of atoms. For these unit cells, *each atom in any one structure is identical to the other atoms in that structure*.

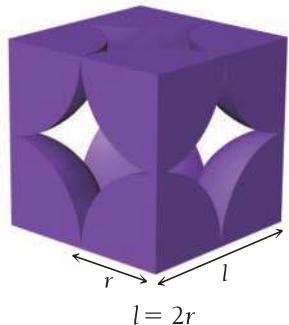


▲ FIGURE 13.3 The Seven Fundamental Types of Unit Cells In this book, we focus on cubic unit cells.

### WATCH NOW!

**KEY CONCEPT VIDEO 13.3**  
Unit Cells: Simple Cubic, Body-Centered Cubic, and Face-Centered Cubic

Cubic Cell Name	Atoms per Unit Cell	Structure	Coordination Number	Edge Length in terms of $r$	Packing Efficiency (fraction of volume occupied)
Simple Cubic	1		6	$2r$	52%
Body-Centered Cubic	2		8	$\frac{4r}{\sqrt{3}}$	68%
Face-Centered Cubic	4		12	$2\sqrt{2}r$	74%

**Simple cubic**

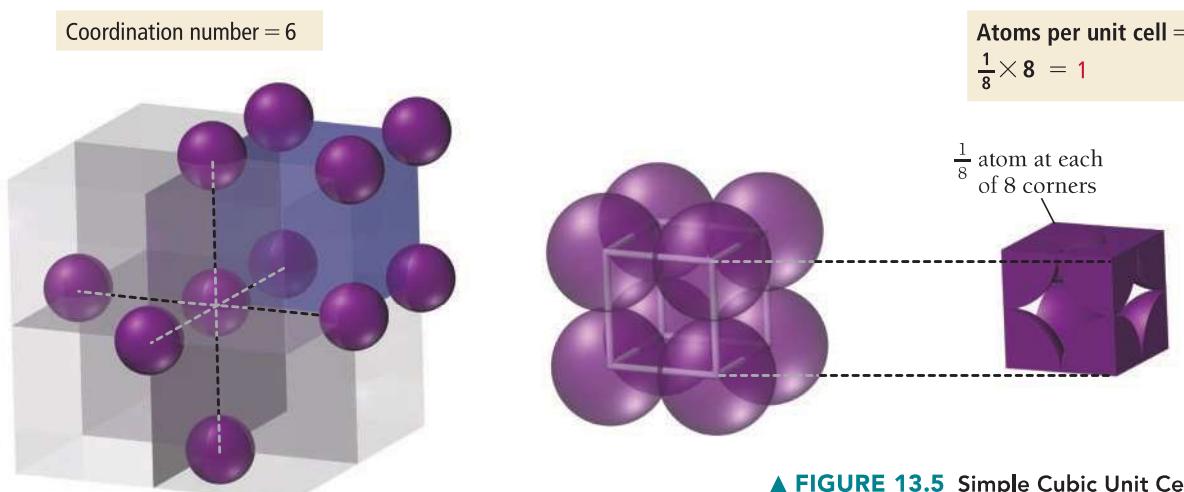
▲ In the simple cubic lattice, the atoms touch along each edge so that the edge length is  $2r$ .

**▲ FIGURE 13.4 Cubic Crystalline Lattices** The different colors used for the atoms in this figure are for clarity only. All atoms within each structure are identical. Unit cells, such as the cubic ones shown here, are customarily portrayed with “whole” atoms, even though only a part of the whole atom may actually be in the unit cell.

The **simple cubic** unit cell (Figure 13.5▼) consists of a cube with one atom at each corner. As we can see in the figure at the left, the atoms touch along each edge of the cube, so the edge length is twice the radius of the atoms ( $l = 2r$ ).

Even though it may seem like the unit cell contains eight atoms, it actually contains only one as close examination makes evident. Each corner atom is shared by eight other unit cells. In other words, any one unit cell actually contains only one-eighth of each of the eight atoms at its corners, for a total of only one atom per unit cell.

### Simple Cubic Unit Cell

**▲ FIGURE 13.5 Simple Cubic Unit Cell**

A characteristic feature of any unit cell is the **coordination number**, the number of atoms with which each atom is in *direct contact*. The coordination number is the number of atoms with which a particular atom can strongly interact. The simple cubic unit cell has a coordination number of 6; any one atom touches only six others, as you can see in Figure 13.5. A quantity closely related to the coordination number is the **packing efficiency**, the percentage of the volume of the unit cell occupied by the spheres. The higher the coordination number is, the greater the packing efficiency is. The simple cubic unit cell has a packing efficiency of 52%—it contains a lot of empty space.

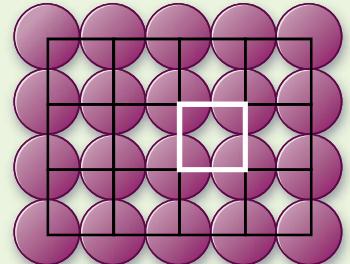
### EXAMPLE 13.2 Calculating the Packing Efficiency of a Unit Cell

Calculate the packing efficiency of the simple cubic unit cell.

#### SOLUTION

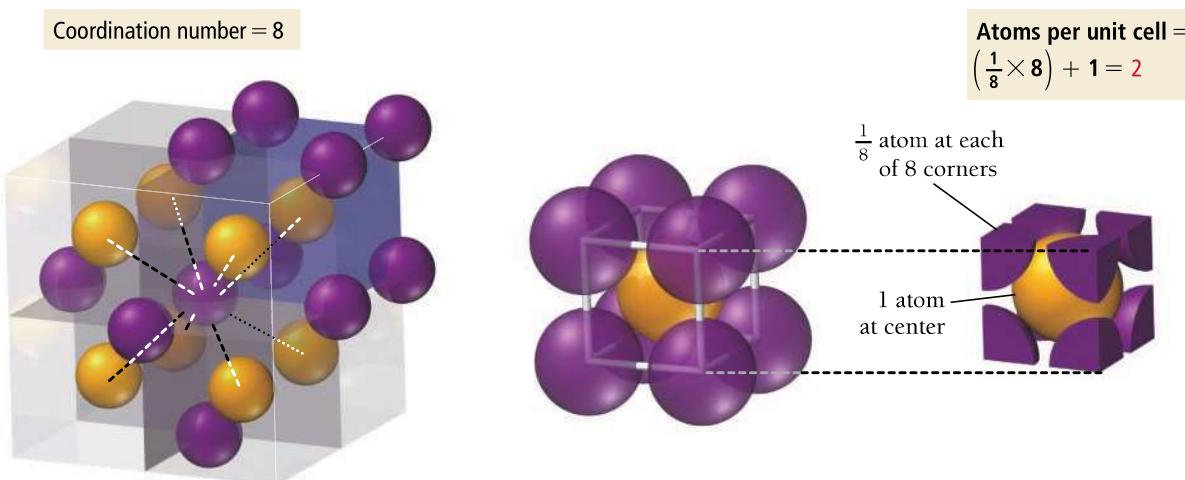
The packing efficiency is defined as the ratio of the volume of the unit cell occupied by atoms to the volume of the unit cell itself, all multiplied by 100%.	$\text{Packing Efficiency} = \frac{V_{\text{atom}}}{V_{\text{unit cell}}} \times 100\%$
First, determine the volume occupied by atoms. Each unit cell contains one atom, so the volume of the unit cell occupied by atoms is simply the volume of one atom.	$V_{\text{atom}} = \frac{4}{3}\pi r^3$
Next, calculate the volume of the cube in terms of the radius of the atom. The volume of a cube is its edge length cubed, and the edge length of the simple cubic unit cell is $2r$ .	$\begin{aligned} V_{\text{unit cell}} &= l^3 \\ &= (2r)^3 \\ &= 8r^3 \end{aligned}$
Calculate the packing efficiency by dividing the volume of the atom by the volume of the unit cell and multiplying by 100%.	$\begin{aligned} \text{Packing Efficiency} &= \frac{V_{\text{atom}}}{V_{\text{unit cell}}} \times 100\% \\ &= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\% \\ &= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100\% \\ &= \frac{4}{24}\pi \times 100\% = 52.36\% \end{aligned}$

**FOR PRACTICE 13.2** Calculate the packing efficiency of the two-dimensional lattice shown here:



The **body-centered cubic** unit cell (Figure 13.6►) consists of a cube with one atom at each corner and one atom (of the same kind) in the very center of the cube. Note that in the body-centered unit cell, the atoms *do not* touch along each edge of the cube, but instead touch along the diagonal line that runs from one corner, through the

### Body-Centered Cubic Unit Cell

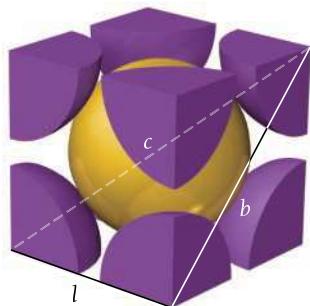


**▲ FIGURE 13.6 Body-Centered Cubic Crystal Structure** The different colors used for the atoms in this figure are for clarity only. All atoms within the structure are identical.

In the body-centered cubic lattice, the atoms touch only along the cube diagonal. The edge length is  $4r/\sqrt{3}$ .

middle of the cube, to the opposite corner. The edge length in terms of the atomic radius is therefore  $l = 4r/\sqrt{3}$  as shown here:

Body-centered cubic



$$\begin{aligned}c^2 &= b^2 + l^2 & b^2 &= l^2 + l^2 \\c &= 4r & b^2 &= 2l^2 \\(4r)^2 &= 2l^2 + l^2 & (4r)^2 &= 3l^2 \\(4r)^2 &= 3l^2 & l^2 &= \frac{(4r)^2}{3} \\l^2 &= \frac{(4r)^2}{3} & l &= \frac{4r}{\sqrt{3}} \\l &= \frac{4r}{\sqrt{3}}\end{aligned}$$

The body-centered unit cell contains two atoms per unit cell because the center atom is not shared with any other neighboring cells. The coordination number of the body-centered cubic unit cell is 8, which we can see by examining the atom in the very center of the cube, which touches eight atoms at the corners. The packing efficiency for the body-centered unit cell is 68%, significantly higher than for the simple cubic unit cell. Each atom in this structure strongly interacts with more atoms than each atom in the simple cubic unit cell.

ANSWER NOW!



### 13.1 Cc

Conceptual Connection

**EDGE LENGTH AND ATOMIC RADIUS** A body-centered cubic unit cell has an edge length of 588 pm. What is the radius of the atoms composing the unit cell?

- (a) 588 pm      (b) 294 pm      (c) 255 pm      (d) 208 pm

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 13.3

### EXAMPLE 13.3 Relating Unit Cell Volume, Edge Length, and Atomic Radius

A body-centered cubic unit cell has a volume of  $4.32 \times 10^{-23} \text{ cm}^3$ . Find the radius of the atom in pm.

**SORT** You are given the volume of a unit cell and asked to find the radius of the atom.

**GIVEN:**  $V = 4.32 \times 10^{-23} \text{ cm}^3$

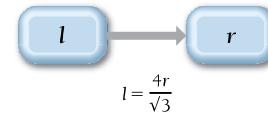
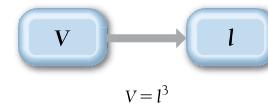
**FIND:**  $r$  (in pm)



**STRATEGIZE** Use the given volume to find the edge length of the unit cell.

Then use the edge length to determine the radius of the atom.

### CONCEPTUAL PLAN



### RELATIONSHIPS USED:

$$V = l^3 \text{ (Volume of a cube)}$$

$$l = \frac{4r}{\sqrt{3}} \text{ (Edge length of body-centered cubic unit cell)}$$

### SOLVE

Solve the equation for the volume of a cube for  $l$  and substitute in the given value for  $V$  to find  $l$ .

Solve the equation for the edge length of a body-centered cubic unit cell for  $r$  and substitute in the value of  $l$  (from the previous step) to find  $r$ .

Convert  $r$  from cm to m and then to pm.

### SOLUTION

$$V = l^3$$

$$l = \sqrt[3]{V} = \sqrt[3]{4.32 \times 10^{-23} \text{ cm}^3} = 3.5088 \times 10^{-8} \text{ cm}$$

$$l = \frac{4r}{\sqrt{3}}$$

$$r = \frac{\sqrt{3}l}{4} = \frac{\sqrt{3}(3.5088 \times 10^{-8} \text{ cm})}{4} = 1.5193 \times 10^{-8} \text{ cm}$$

$$1.5193 \times 10^{-8} \text{ cm} \times \frac{0.01 \text{ m}}{1 \text{ cm}} \times \frac{1 \text{ pm}}{10^{-12} \text{ m}} = 152 \text{ pm}$$

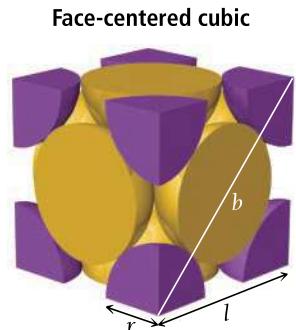
**CHECK** The units of the answer (pm) are correct. The magnitude is reasonable because atomic radii range roughly from 50 to 200 pm.

**FOR PRACTICE 13.3** An atom has radius of 138 pm and crystallizes in the body-centered cubic unit cell. What is the volume of the unit cell in  $\text{cm}^3$ ?

► In the face-centered cubic lattice, the atoms touch along a face diagonal. The edge length is  $2\sqrt{2}r$ .

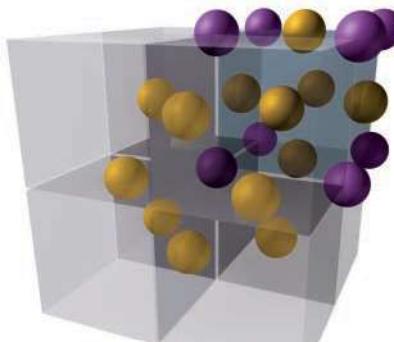
The **face-centered cubic** unit cell (Figure 13.7▼) is a cube with one atom at each corner and one atom (of the same kind) in the center of each cube face. Note that in the face-centered unit cell (like the body-centered unit cell), the atoms *do not* touch along each edge of the cube. Instead, the atoms touch *along the face diagonal*. The edge length in terms of the atomic radius is therefore  $l = 2\sqrt{2}r$ , as shown here.

$$\begin{aligned} b^2 &= l^2 + l^2 = 2l^2 \\ b &= 4r \\ (4r)^2 &= 2l^2 \\ l^2 &= \frac{(4r)^2}{2} \\ l &= \frac{4r}{\sqrt{2}} \\ &= 2\sqrt{2}r \end{aligned}$$

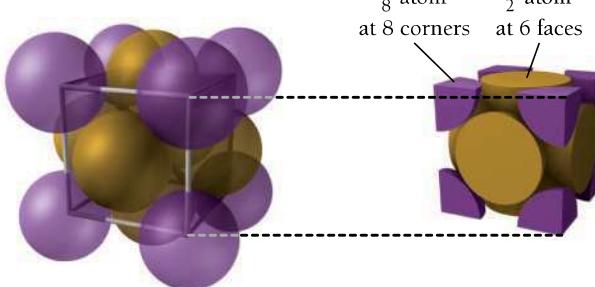


### Face-Centered Cubic Unit Cell

Coordination number = 12



$$\text{Atoms/unit} = \left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 4$$



◀ **FIGURE 13.7**  
**Face-Centred Cubic Crystal Structure** The different colors used on the atoms in this figure are for clarity only. All atoms within the structure are identical.

The face-centered unit cell contains four atoms per unit cell because the center atoms on each of the six faces are shared between two unit cells. There are  $\frac{1}{2} \times 6 = 3$  face-centered atoms plus  $\frac{1}{8} \times 8 = 1$  corner atom, for a total of four atoms per unit cell. The coordination number of the face-centered cubic unit cell is 12, and its packing efficiency is 74%. In this structure, any one atom strongly interacts with more atoms than the atoms in either the simple cubic unit cell or the body-centered cubic unit cell.

## WATCH NOW!

## INTERACTIVE WORKED EXAMPLE 13.4

**EXAMPLE 13.4** Relating Density to Crystal Structure

Aluminum crystallizes with a face-centered cubic unit cell. The radius of an aluminum atom is 143 pm. Calculate the density of solid crystalline aluminum in g/cm<sup>3</sup>.



**SORT** You are given the radius of an aluminum atom and its crystal structure. You are asked to find the density of solid aluminum.

**STRATEGIZE** The conceptual plan is based on the definition of density.

Since the unit cell has the physical properties of the entire crystal, you can find the mass and volume of the unit cell and use these to calculate its density.

**SOLVE** Begin by finding the mass of the unit cell. Determine the mass of an aluminum atom from its molar mass. Because the face-centered cubic unit cell contains four atoms per unit cell, multiply the mass of aluminum by 4 to get the mass of a unit cell.

Next, calculate the edge length ( $l$ ) of the unit cell (in m) from the atomic radius of aluminum. For the face-centered cubic structure,  $l = 2\sqrt{2}r$ .

Calculate the volume of the unit cell (in cm) by converting the edge length to cm and cubing the edge length. (Use centimeters because you want to report the density in units of g/cm<sup>3</sup>.)

Finally, calculate the density by dividing the mass of the unit cell by the volume of the unit cell.

**GIVEN:**  $r = 143$  pm, face-centered cubic

**FIND:**  $d$

**CONCEPTUAL PLAN**

$$d = m/V$$

$m$  = mass of unit cell

= number of atoms in unit cell  $\times$  mass of each atom

$V$  = volume of unit cell

$$= (\text{edge length})^3$$

**SOLUTION**

$$m(\text{Al atom}) = 26.98 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \\ = 4.480 \times 10^{-23} \text{ g/atom}$$

$$m(\text{unit cell}) = 4 \text{ atoms} (4.480 \times 10^{-23} \text{ g/atom}) \\ = 1.792 \times 10^{-22} \text{ g}$$

$$l = 2\sqrt{2}r \\ = 2\sqrt{2}(143 \text{ pm}) \\ = 2\sqrt{2}(143 \times 10^{-12} \text{ m}) \\ = 4.045 \times 10^{-10} \text{ m}$$

$$V = l^3 \\ = \left( 4.045 \times 10^{-10} \text{ m} \times \frac{1 \text{ cm}}{10^{-2} \text{ m}} \right)^3 \\ = 6.618 \times 10^{-23} \text{ cm}^3$$

$$d = \frac{m}{V} = \frac{1.792 \times 10^{-22} \text{ g}}{6.618 \times 10^{-23} \text{ cm}^3} \\ = 2.71 \text{ g/cm}^3$$

**CHECK** The units of the answer are correct. The magnitude of the answer is reasonable because the density is greater than 1 g/cm<sup>3</sup> (as you would expect for metals), but still not too high (because aluminum is a low-density metal).

**FOR PRACTICE 13.4** Chromium crystallizes with a body-centered cubic unit cell. The radius of a chromium atom is 125 pm. Calculate the density of solid crystalline chromium in g/cm<sup>3</sup>.

## ANSWER NOW!


**13.2**  
**Cc**  
 Conceptual Connection

**CUBIC STRUCTURES** How many atoms are in the unit cell in the face-centered cubic structure?

(a) 1

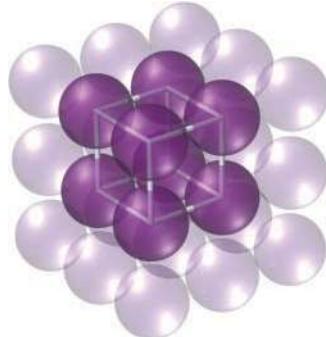
(b) 2

(c) 4

(d) 14

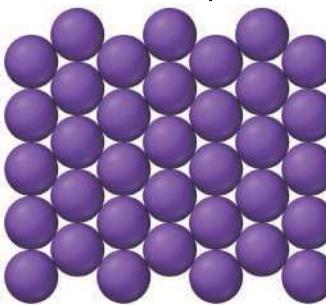
## Closest-Packed Structures

Another way to envision crystal structures, especially useful for metals, in which bonds are not usually directional, is to think of the atoms as stacking in layers, much as fruit is stacked at the grocery store. For example, we can envision the simple cubic structure as one layer of atoms arranged in a square pattern, with the next layer stacking directly over the first, so that the atoms in one layer align exactly on top of the atoms in the layer beneath it, as shown here:

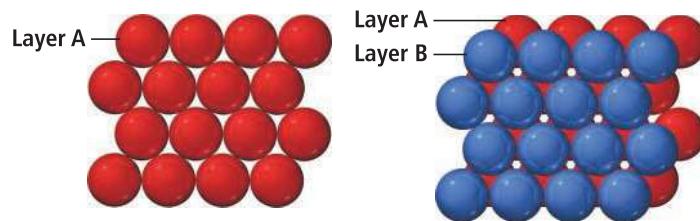


As we saw previously, this crystal structure has a great deal of empty space—only 52% of the volume is occupied by the spheres, and the coordination number is 6.

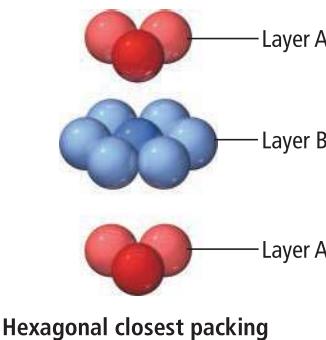
More space-efficient packing can be achieved by aligning neighboring rows of atoms in a pattern, with one row offset from the next by one-half a sphere, as shown here:



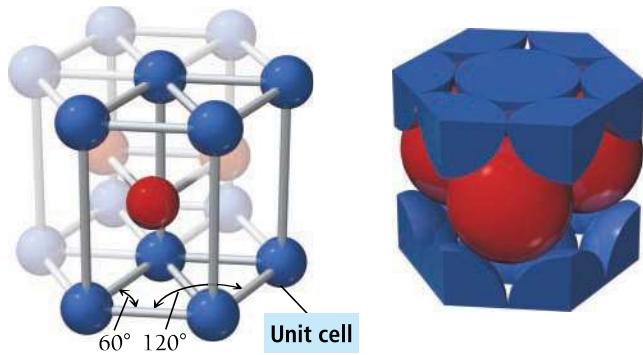
In this way, the atoms pack more closely to each other in any one layer. We can further increase the packing efficiency by placing the next layer *not directly on top of the first*, but again offset so that any one atom actually sits in the indentation formed by three atoms in the layer beneath it, as shown here:



This kind of packing leads to two different crystal structures called *closest-packed structures*, both of which have a packing efficiency of 74% and a coordination number of 12. In the first of these two closest-packed structures—called **hexagonal closest packing**—the third layer of atoms aligns exactly on top of the first, as shown here:



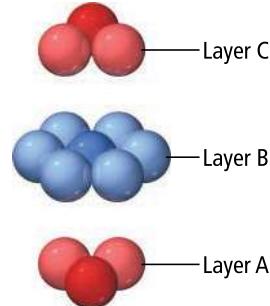
## Hexagonal Closest Packing



**▲ FIGURE 13.8** Hexagonal Closest-Packing Crystal Structure The unit cell is shown at left (unfaded part).

The pattern from one layer to the next is ABAB, with the third layer aligning exactly above the first. Notice that the central atom in layer B of this structure is touching six atoms in its own layer, three atoms in the layer above it, and three atoms in the layer below, for a coordination number of 12. The unit cell for this crystal structure is not a cubic unit cell, but a hexagonal one, shown in Figure 13.8◀.

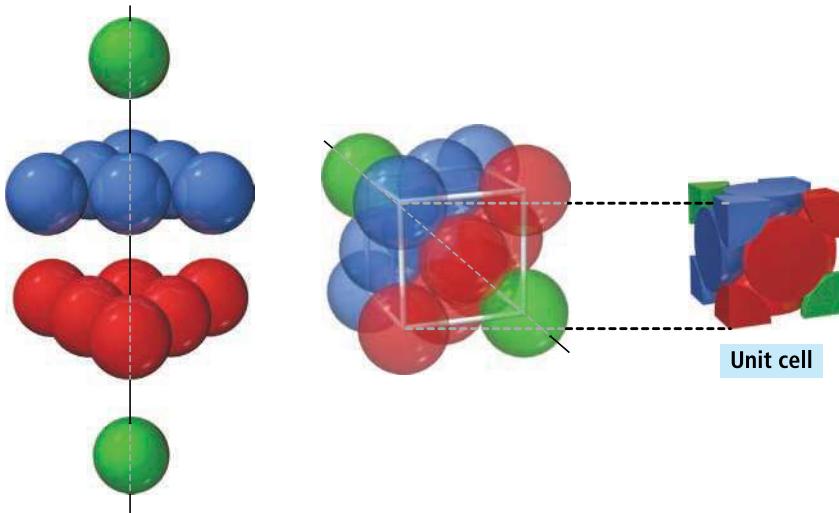
In the second of the two closest-packed structures—called **cubic closest packing**—the third layer of atoms is offset from the first, as shown here:



**Cubic closest packing**

The pattern from one layer to the next is ABCABC, with every fourth layer aligning with the first. Although not simple to visualize, the unit cell for cubic closest packing is the face-centered cubic unit cell, shown in Figure 13.9▼. The cubic closest-packed structure is identical to the face-centered cubic unit cell structure.

## Cubic Closest Packed = Face-Centred Cubic

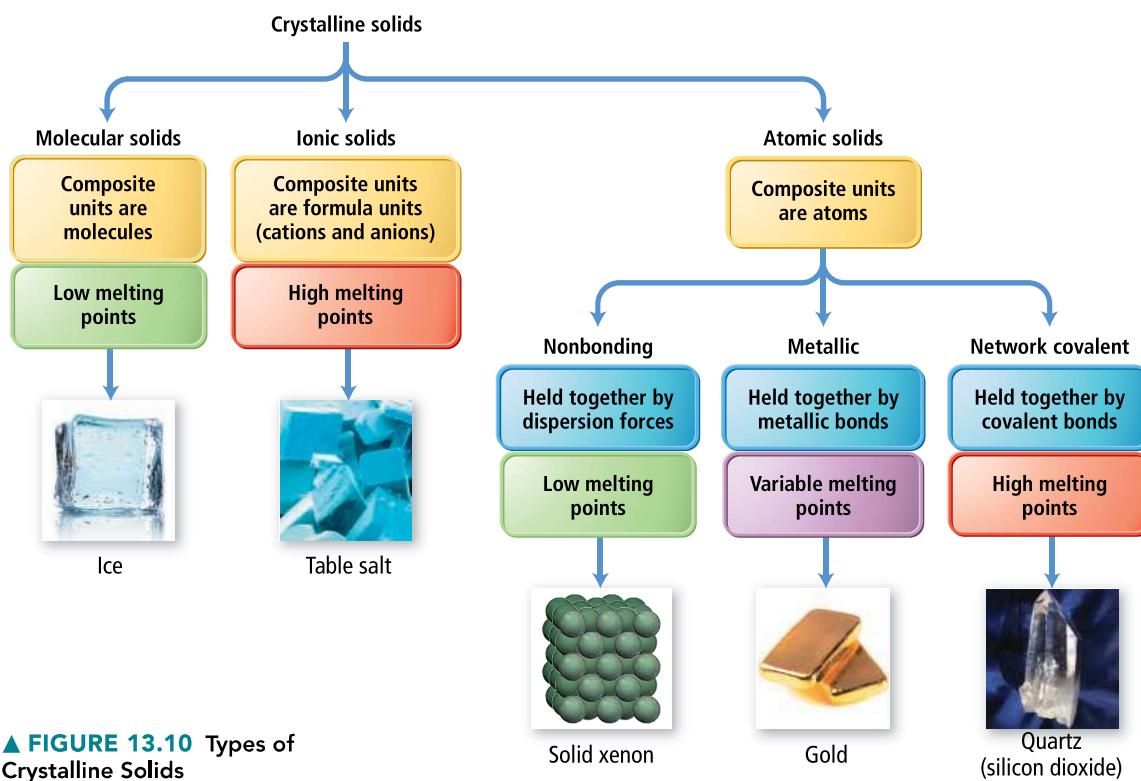


**► FIGURE 13.9** Cubic Closest-Packing Crystal Structure The unit cell of the cubic closest-packed structure is a face-centered cubic.

### 13.4

## The Fundamental Types of Crystalline Solids

We examined some of the basic *structures* of crystalline solids in Section 13.3. In this section, we turn to the different *types* of crystalline solids. We can classify crystalline solids into three categories—molecular, ionic, and atomic—based on the individual particles that compose the solid. Atomic solids can themselves be classified into three categories—nonbonded, metallic, and network covalent—depending on the types of interactions between atoms within the solid. Figure 13.10▶ shows the different categories of crystalline solids.



▲ FIGURE 13.10 Types of Crystalline Solids

## Molecular Solids

**Molecular solids** are solids in which the composite particles are *molecules*. The unit cells in a crystalline molecular solid are therefore occupied by molecules. Ice (solid H<sub>2</sub>O) and dry ice (solid CO<sub>2</sub>) are examples of molecular solids. Molecular solids are held together by the kinds of intermolecular forces—dispersion forces, dipole–dipole forces, and hydrogen bonding—discussed in Chapter 12. Although molecular solids as a whole tend to have low to moderately low melting points, their specific properties depend on the types of intermolecular forces between the molecules as well as the structure of the molecule and the crystal structure of the solid. For example, benzene and toluene have similar molar masses and similar intermolecular forces (dispersion forces):

Compound	Structure	Molar Mass	Type of Intermolecular Force	Melting Point of Solid
Benzene (C <sub>6</sub> H <sub>6</sub> )		78.11 g/mol	Dispersion	5.5 °C
Toluene (C <sub>7</sub> H <sub>8</sub> )		92.14 g/mol	Dispersion	-95.5 °C

Polymorphism can exist in any crystalline material, not just molecular solids.

However, the extra  $-\text{CH}_3$  group on toluene prevents the molecules from packing as efficiently in the crystal as they do in benzene. The result is that, even though toluene has a higher molar mass than benzene, it has a much a lower melting point.

Some molecular solids crystallize in different structures called **polymorphs**. The different crystal structures can have different properties, including different melting points and solubilities (see *Chemistry in Your Day: Chocolate, An Edible Material*). Polymorphism is important in pharmaceuticals because different forms of a drug can have different physiological activities. For example, ritonavir was among the first drugs found to be effective in treating HIV and AIDS. When it was first discovered and approved for use, only one polymorph was known. However, soon after its widespread use, a second polymorph was discovered. This second polymorph was more stable, less water-soluble, and much less physiologically active. Even worse, small amounts of this second polymorph in a sample could convert the active polymorph into the less active one. The drug manufacturer had to halt production of ritonavir until researchers solved the problem by switching from a capsule form to a refrigerated gelcap form and later to a stable tablet form.

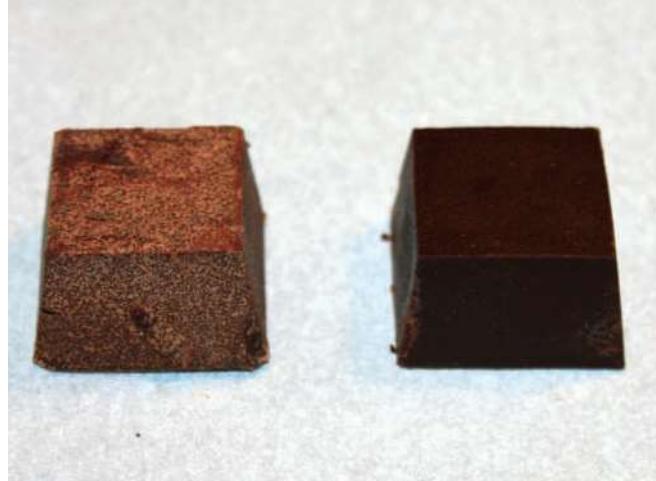


## CHEMISTRY IN YOUR DAY

### Chocolate, An Edible Material

**C**hocolate is an edible and delicious material designed to please your senses. Good chocolate has a smooth and shiny surface, snaps when you break it, and melts in your mouth, releasing its delicious combination of flavors and texture. Like all materials, chocolate's properties depend on its structure. The main structural ingredient in chocolate is cocoa butter, a triglyceride. We examine triglycerides more carefully in Chapter 23, but for now, just know that triglycerides are long organic molecules, which means that chocolate is a crystalline molecular solid. Many crystalline molecular solids only have one crystalline structure; however, some (including cocoa butter) have several possible crystalline structures called polymorphs, each with different properties. Cocoa butter has six possible polymorphs, often called Types I–VI, as shown in Table 13.1. For reference, body temperature is 37 °C.

The most desirable crystalline form of cocoa butter in chocolate is Type V. Types I and II are soft and crumbly and show noticeable blooming. *Blooming* is the white residue that forms on the outside of chocolate. If you have ever let a chocolate bar melt and then re-solidify, you have probably noticed this undesirable residue. Types III and IV are firmer, but they don't have a sharp snap when you break or bite into them. Type V is firm, displays a sharp snap, has a smooth and shiny surface, and tends to melt in your mouth rather than your hand. For this reason, chocolatiers aim for this crystal structure. However, this structure is not easy to achieve. If you simply melt chocolate and let it re-solidify, you get a mix of Types I–V with all of their



▲ The white residue on the surface of the chocolate bon bon on the left is called bloom. The chocolate bon bon on the right has a smooth, shiny surface, characteristic of Type V cocoa butter.

undesirable qualities. Chocolatiers "temper" their chocolate in their quest for primarily Type V characteristics.

Tempering chocolate requires a specific and carefully controlled heating and cooling sequence (Figure 13.11►).

TABLE 13.1 ■ Crystalline Forms of Cocoa Butter

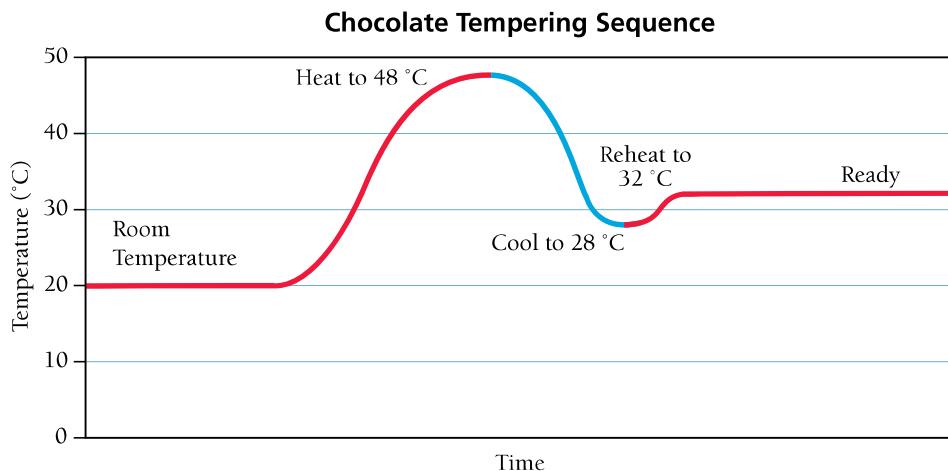
Crystalline Structure Type (Polymorph)	Melting Point (°C)	Description	Increasing Density and Stability
I	17.3	Soft, crumbly, noticeable blooming, melts in the hand.	
II	23.3	Soft, crumbly, noticeable blooming, melts in the hand.	
III	25.5	Firm, poor snap, some blooming, melts in the hand.	
IV	27.3	Firm, poor snap, some blooming, melts in the hand.	
V	33.8	Firm, good snap, smooth and shiny surface, melts in the mouth, most desirable.	
VI	36.3	Hard, some blooming, cannot be formed from melt, takes several months to form.	

First, chocolatiers heat the chocolate to melt it. Then they allow it to cool slowly. The slow cooling favors the formation of Type V crystals; however, the other types form as well. The final step is to reheat the chocolate to a temperature just below the melting point of the Type V crystals. This step melts all of the Type I–IV crystals, leaving only the Type V crystals to act as “seed crystals.”\* A seed

crystal is a crystal upon which more of the crystal can grow. Seed crystals have the effect of imposing their own structure on the growing crystalline solid. When the properly tempered chocolate cools, the Type V seed crystals cause the majority of the chocolate to crystallize in the Type V structure, resulting in silky smooth, melt-in-your-mouth, chocolate.

**► FIGURE 13.11 Chocolate Tempering** In order to temper chocolate, chocolate makers heat it carefully. After the tempering sequence is completed, the chocolate can be poured into molds or used as coatings. When the tempered chocolate cools, it is primarily Type V and has a shiny smooth surface.

\*Sometimes solid bits of tempered chocolate are added at this point to act as additional seed crystals.



## Ionic Solids

The composite particles of **ionic solids** are ions. Table salt ( $\text{NaCl}$ ) and calcium fluoride ( $\text{CaF}_2$ ) are examples of ionic solids. The forces holding ionic solids together are strong coulombic forces (or ionic bonds), and because these forces are much stronger than intermolecular forces, ionic solids tend to have much higher melting points than molecular solids. For example, sodium chloride melts at  $801\text{ }^\circ\text{C}$ , while carbon disulfide ( $\text{CS}_2$ )—a molecular solid with a higher molar mass—melts at  $-110\text{ }^\circ\text{C}$ . We examine the structure of ionic solids in more detail in Section 13.5.

## Atomic Solids

In **atomic solids** the composite particles are individual atoms. Solid xenon ( $\text{Xe}$ ), iron ( $\text{Fe}$ ), and silicon dioxide ( $\text{SiO}_2$ ) are examples of atomic solids. We classify atomic solids into three categories—*nonbonding atomic solids*, *metallic atomic solids*, and *network covalent atomic solids*—with each type held together by a different kind of force.

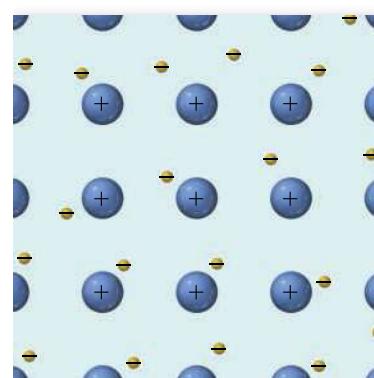
### Nonbonding Atomic Solids

**Nonbonding atomic solids** are held together by relatively weak dispersion forces. In order to maximize these interactions, nonbonding atomic solids form closest-packed structures, maximizing their coordination numbers and minimizing the distance between composite units. Nonbonding atomic solids have very low melting points that increase uniformly with molar mass. The only nonbonding atomic solids are noble gases in their solid form. Argon, for example, has a melting point of  $-189\text{ }^\circ\text{C}$ , and xenon has a melting point of  $-112\text{ }^\circ\text{C}$ .

### Metallic Atomic Solids

**Metallic atomic solids**, such as iron or gold, are held together by *metallic bonds*, which in the simplest model are represented by the interaction of metal cations with the sea of electrons that surrounds them, as described in Section 10.11 (Figure 13.12►).

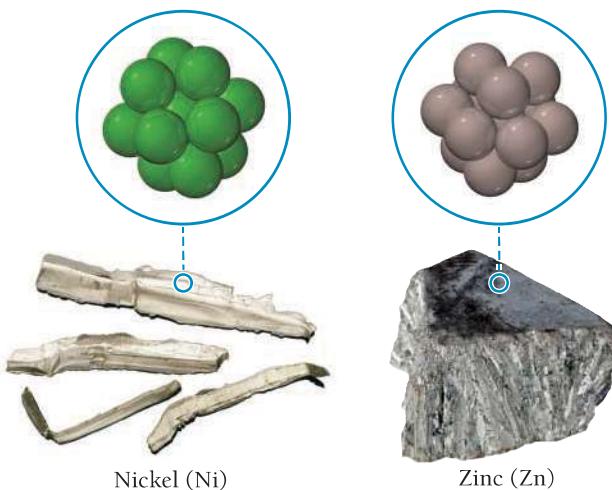
Because metallic bonds are not directional, many metals tend to form closest-packed crystal structures. For example, nickel crystallizes in the cubic closest-packed structure, and zinc crystallizes in the hexagonal closest-packed structure (Figure 13.13►). Metallic bonds have varying strengths. Some metals, such as mercury, have melting points below room temperature, whereas other metals, such as iron, have relatively high melting points (iron melts at  $1538\text{ }^\circ\text{C}$ ).



**► FIGURE 13.12 The Electron Sea Model** In the electron sea model for metals, the metal cations exist in a “sea” of electrons.

**► FIGURE 13.13 Closest-Packed Crystal Structures in Metals**

Nickel crystallizes in the cubic closest-packed structure. Zinc crystallizes in the hexagonal closest-packed structure.

**Network Covalent Solids**

Covalent bonds hold together **network covalent atomic solids**, such as diamond, graphite, and silicon dioxide. The crystal structures of these solids are more restricted by the geometrical constraints of the covalent bonds (which tend to be more directional than intermolecular forces, ionic bonds, or metallic bonds), so they *do not* tend to form closest-packed structures. Network covalent atomic solids have very high melting points because the crystalline solid is held together by covalent bonds. We examine some examples of this class of solids in Section 13.6.

**EXAMPLE 13.5 Classifying Crystalline Solids**

Classify each crystalline solid as molecular, ionic, or atomic.

- (a) Au(s)      (b) CH<sub>3</sub>CH<sub>2</sub>OH(s)      (c) CaF<sub>2</sub>(s)

**SOLUTION**

- (a) Gold (Au) is a metal and is therefore an atomic solid.  
 (b) Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) is a molecular compound. Solid ethanol is therefore a molecular solid.  
 (c) Calcium fluoride (CaF<sub>2</sub>) is an ionic compound, so it is an ionic solid.

**FOR PRACTICE 13.5** What type of atomic solid is Au(s)?

ANSWER NOW!



**13.3**  
**Cc**  
Conceptual Connection

**CRYSTALLINE SOLID TYPES AND MELTING POINTS**

Which solid would you expect to have the highest melting point?

- (a) MgO(s)      (b) I<sub>2</sub>(s)      (c) Kr(s)

**13.5 The Structures of Ionic Solids**

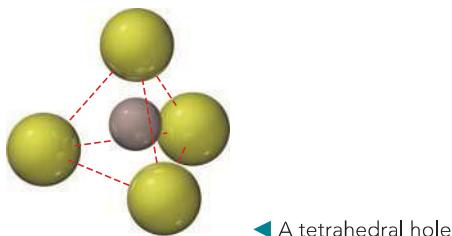
Many ionic solids have crystalline structures that are closely related to the unit cells that we examined in Section 13.3. However, because ionic compounds necessarily contain both cations and anions, their structures must accommodate the two different types of ions. In an ionic solid, the cations and anions attract one another. The coordination number of the unit cell represents the number of close cation–anion interactions.

Because these interactions lower potential energy, the crystal structure of a particular ionic compound is the structure that maximizes the coordination number while accommodating both charge neutrality (each unit cell must be charge neutral) and the different sizes of the cations and anions that compose the particular compound. In general, the more similar the radii of the cation and the anion, the higher the coordination number.

Cesium chloride (CsCl) is a good example of an ionic compound with cations and anions of similar size (Cs<sup>+</sup> radius = 167 pm; Cl<sup>-</sup> radius = 181 pm). In the cesium chloride structure, the chloride ions occupy the lattice sites of a simple cubic cell, and one cesium ion lies in the very center of the cell, as shown in Figure 13.14▶. (Note that in this and subsequent figures of ionic crystal structures, the different colored spheres represent different ions.) The coordination number for cesium chloride is 8, meaning that each cesium ion is in direct contact with eight chloride ions (and vice versa). The cesium chloride unit cell contains one chloride anion ( $8 \times \frac{1}{8} = 1$ ) and one cesium cation for a ratio of Cs to Cl of 1:1, as the formula for the compound indicates. (Note that complete chloride ions are shown in Figure 13.14, even though only  $\frac{1}{8}$  of each ion is in the unit cell.) Calcium sulfide (CaS) has the same structure as cesium chloride.

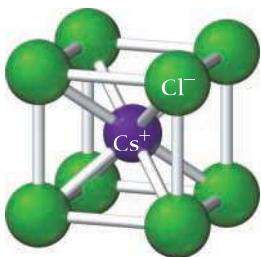
Sodium chloride is an example of an ionic compound with different ion sizes: Na<sup>+</sup> (radius = 97 pm) and Cl<sup>-</sup> (radius = 181 pm). The crystal structure must accommodate the disproportionate sizes. If ion size were the only consideration, the larger chloride anion could theoretically fit many of the smaller sodium cations around it, but charge neutrality requires that each sodium cation be surrounded by an equal number of chloride anions. Therefore, the coordination number is limited by the number of chloride anions that can fit around the relatively small sodium cation. The structure that minimizes the energy is shown in Figure 13.15▶ and has a coordination number of 6 (each chloride anion is surrounded by six sodium cations and vice versa). We can visualize this structure, called the *rock salt* structure, as chloride anions occupying the lattice sites of a face-centered cubic structure with the smaller sodium cations occupying the holes between the anions. (Alternatively, we can visualize this structure as the *sodium cations* occupying the lattice sites of a face-centered cubic structure with the *larger chloride anions* occupying the spaces between the cations.) Each unit cell contains four chloride anions [ $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ ] and four sodium cations [ $(12 \times \frac{1}{4}) + 1 = 4$ ], resulting in a ratio of 1:1, as the formula of the compound specifies. Other compounds exhibiting the sodium chloride structure include LiF, KCl, KBr, AgCl, MgO, and CaO.

When there is a greater disproportion between the sizes of the cations and anions in a compound, a coordination number of even 6 is physically impossible. For example, in ZnS (Zn<sup>2+</sup> radius = 74 pm; S<sup>2-</sup> radius = 184 pm) the crystal structure, shown in Figure 13.16▶, has a coordination number of only 4. We can visualize this structure, called the *zinc blende* structure, as sulfide anions occupying the lattice sites of a face-centered cubic structure, with the smaller zinc cations occupying four of the eight tetrahedral holes located directly beneath each corner atom. A tetrahedral hole is the empty space that lies in the center of a tetrahedral arrangement of four atoms, as shown in the accompanying figure. Each unit cell contains four sulfide anions [ $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ ] and four zinc cations (each of the four zinc cations is completely contained within the unit cell), resulting in a ratio of 1:1, just as the formula of the compound indicates. Other compounds that exhibit the zinc blende structure include CuCl, AgI, and CdS.



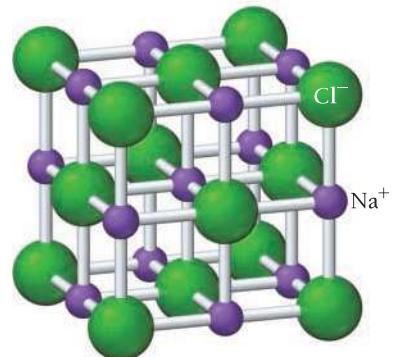
When the ratio of cations to anions is not 1:1, the crystal structure must accommodate the unequal number of cations and anions. Many compounds that contain a cation-to-anion ratio of 1:2 adopt the *fluorite* (CaF<sub>2</sub>) structure shown in Figure 13.17▶. We can visualize this structure as calcium cations occupying the lattice sites of a face-centered

Cesium chloride (CsCl)



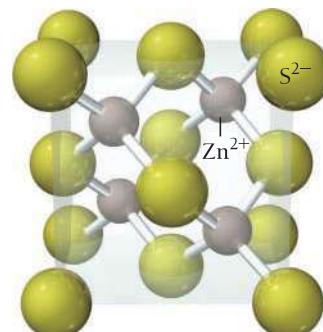
▲ FIGURE 13.14 Cesium Chloride Unit Cell The different colored spheres in this figure represent the different ions in the compound.

Sodium chloride (NaCl)

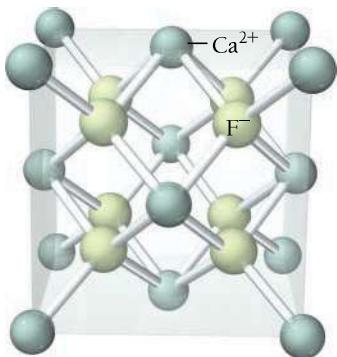


▲ FIGURE 13.15 Sodium Chloride Unit Cell The different colored spheres in this figure represent the different ions in the compound.

Zinc blende (ZnS)



▲ FIGURE 13.16 Zinc Sulfide (Zinc Blende) Unit Cell The different colored spheres in this figure represent the different ions in the compound.

Calcium fluoride ( $\text{CaF}_2$ )

cubic structure with the larger fluoride anions occupying all eight of the tetrahedral holes located directly beneath each corner atom. Each unit cell contains four calcium cations [ $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ ] and eight fluoride anions (each of the eight fluoride anions is completely contained within the unit cell), resulting in a cation-to-anion ratio of 1:2, just as in the formula of the compound. Other compounds exhibiting the fluorite structure include  $\text{PbF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaCl}_2$ . Compounds with a cation-to-anion ratio of 2:1 often exhibit the *antifluorite structure*, in which the anions occupy the lattice sites of a face-centered cubic structure and the cations occupy the tetrahedral holes beneath each corner atom.

◀ FIGURE 13.17 Calcium Fluoride (or Fluorite) Unit Cell The different colored spheres in this figure represent the different ions in the compound.

ANSWER NOW!

## 13.4 Cc Conceptual Connection



### IONIC CRYSTALLINE SOLID UNIT CELLS

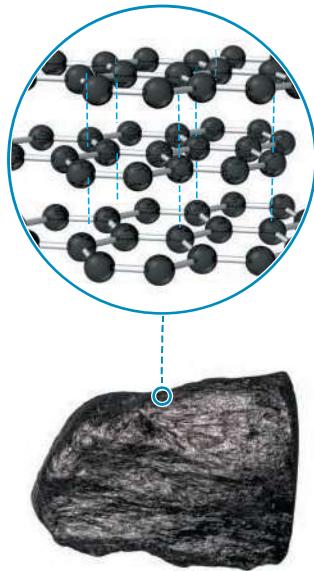
Which compound is most likely to crystallize in the zinc blende structure?

- (a)  $\text{RbCl}$  ( $\text{Rb}^+$  radius = 148 pm;  $\text{Cl}^-$  radius = 181 pm)
- (b)  $\text{MgCl}_2$  ( $\text{Mg}^{2+}$  radius = 65 pm;  $\text{Cl}^-$  radius = 181 pm)
- (c)  $\text{CuI}$  ( $\text{Cu}^+$  radius = 96 pm;  $\text{I}^-$  radius = 216 pm)

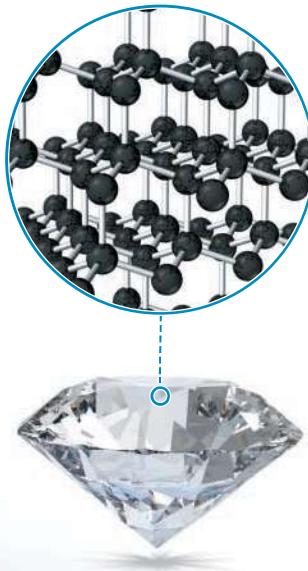
## 13.6

### Network Covalent Atomic Solids: Carbon and Silicates

As we saw in Section 13.4, network covalent atomic solids are composed of atoms held together by covalent bonds. Because the covalent bonds have to be broken for the solid to melt, network covalent atomic solids have some of the highest melting points of all substances. In this section, we examine two different families of network covalent atomic solids: carbon and silicates.



(a) Graphite



(b) Diamond

### Carbon

Elemental carbon exists in several different forms (or allotropes) including graphene, which we discussed in Section 13.1. Two well-known naturally occurring crystalline forms of carbon are **graphite** and **diamond**. Graphite's structure, shown in Figure 13.18(a)◀, consists of flat sheets of carbon atoms covalently bonded together as interconnected hexagonal rings. The bond length between carbon atoms *within a sheet* is 142 pm. However, the forces *between* sheets are much different. There are no covalent bonds between sheets, only relatively weak dispersion forces, and the separation between sheets is 341 pm. Consequently, the sheets slide past each other with relative ease, which explains the slippery feel of graphite and its extensive use as a lubricant. The electrons in the extended pi bonding network within a sheet make graphite a good electrical conductor in the direction of the plane of the sheets. Because of its relative stability and electrical properties, graphite is used for electrodes in electrochemical applications and for heating elements in furnaces.

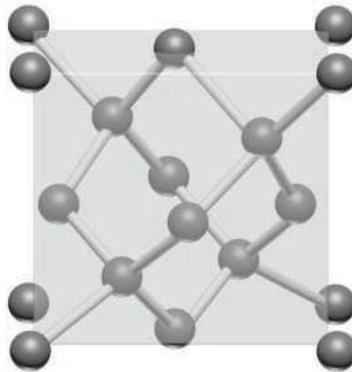
The density of graphite is  $2.2 \text{ g/cm}^3$ . Under high pressure, the carbon atoms in graphite rearrange to form diamond, which has a higher density of  $3.5 \text{ g/cm}^3$ .

▲ FIGURE 13.18 Network Covalent Atomic Solids (a) In graphite, carbon atoms are arranged in sheets. Within each sheet, the atoms are covalently bonded to one another by a network of sigma and pi bonds. Neighboring sheets are held together by dispersion forces. (b) In diamond, each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry.

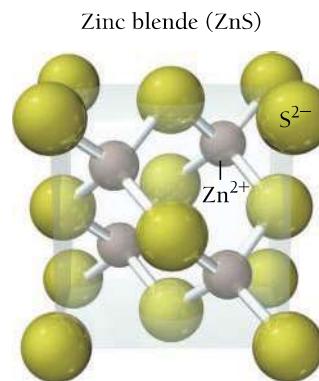
Diamond forms naturally when carbon is exposed to high pressures deep underground. Through movements in Earth's crust, diamond rises toward the surface. Most diamond is found in Africa, mainly in the Congo region and in South Africa. The first synthetic diamonds were produced in the 1940s, using pressures of 50,000 atm and a temperature of 1600 °C. The unit cell for diamond is shown here:

You can imagine the unit cell for diamond as a face-centered cubic structure with an additional carbon atom in half of the eight tetrahedral holes located directly beneath each corner atom. Notice the similarity between the diamond unit cell and the zinc blende unit cell that we discussed in Section 13.5. Notice also that each carbon atom is covalently bonded to four other carbon atoms at the corners of a tetrahedron. This structure extends throughout the entire crystal, so that a diamond crystal can be thought of as a giant molecule, held together by these covalent bonds.

Because covalent bonds are very strong, diamond has a very high melting point (it is estimated to melt at about 3800 °C). The electrons in diamond are confined to the covalent bonds and are not free to flow. Therefore, diamond does not conduct electricity. Diamond is very hard and is an excellent conductor of heat. Consequently, the largest use of diamonds is for abrasives and cutting tools. Small diamonds are used at the cutting edge of tools, making the edges much harder and giving them a longer life. Natural diamonds are valued as gems for their brilliance and relative inertness.



▲ Diamond unit cell



▲ Zinc blende unit cell

**PHASE CHANGES AND PRESSURE** High pressure favors the formation of diamond from graphite. What can you conclude about the relative densities of the two substances?

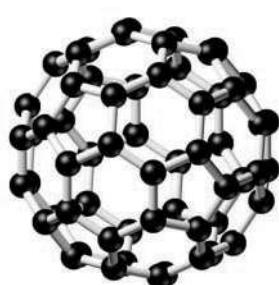
- (a) Diamond is denser than graphite.
- (b) Graphite is denser than diamond.
- (c) Nothing can be determined about the relative densities of the two substances without more information.

13.5  
**Cc**  
Conceptual Connection

ANSWER NOW!



In the 1980s, researchers discovered a new form of carbon when they aimed a powerful laser at a graphite surface. This new form of carbon occurs as soccer-ball-shaped clusters of 60 carbon atoms ( $C_{60}$ ). The atoms form five- and six-membered carbon rings wrapped into a 20-sided icosahedral structure (Figure 13.19▼). The compound was named *buckminsterfullerene*, honoring R. Buckminster Fuller (1895–1983), a twentieth-century engineer and architect who advocated the construction of buildings using a structurally strong geodesic dome shape that he patented.



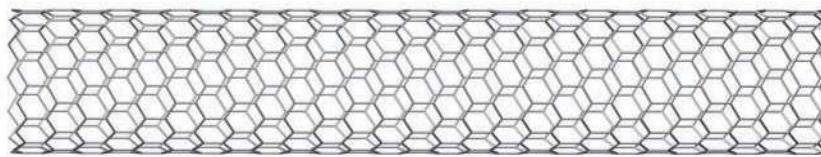
$C_{60}$



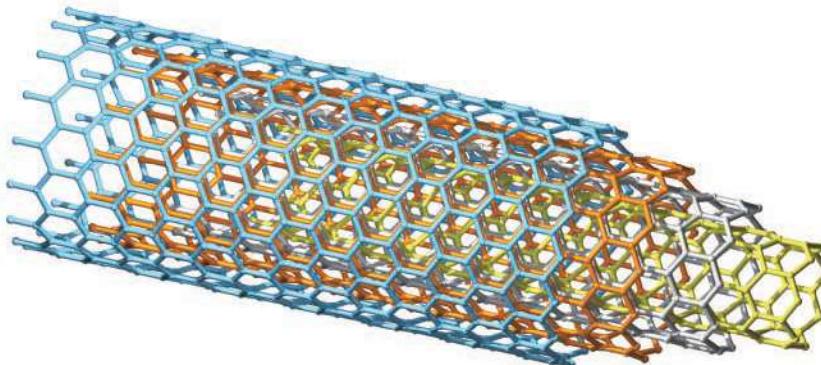
◀ FIGURE 13.19  $C_{60}$  and a Geodesic Dome The  $C_{60}$  structure resembles Buckminster Fuller's geodesic dome.

Researchers have since identified carbon clusters similar to C<sub>60</sub> containing from 36 to over 100 carbon atoms. As a class, these carbon clusters are called **fullerenes** and nicknamed *buckyballs*. At room temperature, fullerenes are black solids similar to graphite—the individual clusters are held to one another by dispersion forces. Fullerenes are somewhat soluble in nonpolar solvents, and the different fullerenes form solutions of different colors.

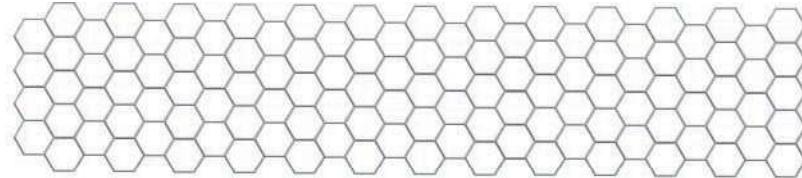
Researchers have also synthesized long carbon structures called **nanotubes**, which consist of sheets of interconnected C<sub>6</sub> rings that assume the shape of a cylinder (like a roll of chicken wire). The first nanotubes discovered consisted of tubes with double walls of C<sub>6</sub> rings with closed ends. The ends of the tubes can be opened when they are heated under the proper conditions. Today, two general types of nanotubes can be produced: (1) *single-walled nanotubes (SWNT)* that have one layer of interconnected C<sub>6</sub> rings forming the walls and (2) *multiwalled nanotubes (MWNT)* that have concentric layers of interconnected C<sub>6</sub> rings forming the walls. In addition, researchers have been able to form *nanoribbons* by slicing open nanotubes. As we discussed in Section 13.1, carbon can also form graphene, long, extended sheets of carbon atoms just one atom thick. These carbon structures are all shown in Figure 13.20▼.



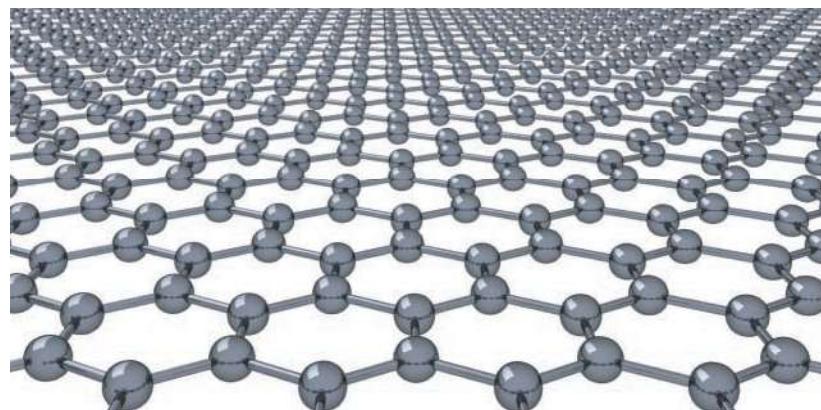
(a) Single-walled nanotube (SWNT)



(b) Multiwalled nanotube (MWNT)



(c) Graphene nanoribbon



(d) Graphene sheet

► **FIGURE 13.20** Carbon structures include (a) a single-walled nanotube; (b) a multiwalled nanotube; (c) a graphene nanoribbon; (d) a graphene sheet.

Nanotubes are 100 times stronger than steel and only  $\frac{1}{16}$  as dense. Consequently, we use carbon nanotubes commercially for lightweight applications that require strength, such as golf clubs and bicycle frames. When the nanotubes are lined up parallel to one another, a bundle of the tubes forms a “wire” with very low electrical resistance. These tiny wires raise the possibility of making incredibly small electronic devices.

## Silicates

The **silicates** (extended arrays of silicon and oxygen) are the most common network covalent atomic solids. Geologists estimate that 90% of Earth’s crust is composed of silicates. Silicon and oxygen form a network covalent structure in which a silicon atom bonds to four oxygen atoms, assuming a tetrahedral shape with the silicon atom in the middle and the four oxygen atoms at the corners of the tetrahedron (Figure 13.21►).

In this structure, the silicon atom bonds to each oxygen atom with a single covalent sigma bond. In contrast to carbon, which often bonds to oxygen with a double bond (one sigma and one pi bond), silicon typically forms only a single bond with oxygen because the silicon atom is too large to allow substantial overlap between the *p*-orbitals on the two atoms. The silicon atom in this structure, by bonding to four oxygen atoms, obtains a complete octet. However, each oxygen atom is one electron short of an octet. Therefore, each O atom forms a second covalent bond to a different Si atom, resulting in the three-dimensional structure of **quartz**. Quartz has a formula unit of  $\text{SiO}_2$  and is generally called **silica**. In silica, each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom acts as a bridge connecting the corners of two tetrahedrons (Figure 13.22►). See Section 24.3 for a more extended discussion of silicate structures.

## 13.7

## Ceramics, Cement, and Glass

The silicate structures we examined in Section 13.6 are common in ceramics, cement, and glass. These substances are used in buildings, electrical devices, pottery, and kitchenware. If you look around wherever you are sitting at this moment, you are likely to see examples of these materials. In this section of the chapter, we examine each of these amazing classes of materials individually.

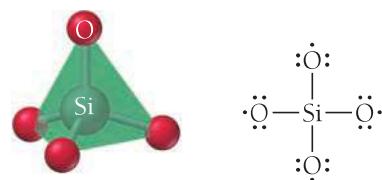
### Ceramics

**Ceramics** are traditionally defined as inorganic nonmetallic solids that are prepared from powders usually mixed with water, formed into the desired shape and then heated. Ceramics are extensively used to make bricks, tiles, pottery, dishware, and insulating elements in electrical devices. They display a range of properties but are usually hard, strong, nonconductive, and brittle. The word “ceramics” originates from the Greek *keramikos*. Keramikos is an area of Athens that was the potters’ quarter of the city, and the Greeks were among the first accomplished potters. However, pottery itself predates recorded history. The oldest known example is the Venus of Dolni, a figurine that dates to 29,000–25,000 BCE. Ceramics can be categorized into three types: silicate, oxide, and nonoxide.

### Silicate Ceramics

Many ceramics are composed of aluminosilicates, a class of minerals in which some of the silicon atoms in the silicate structure are replaced by aluminum (see Section 24.3). The weathering of naturally occurring aluminosilicates produces **clays**, which are essentially powdered forms of the minerals mixed with water. When heated, reactions occur that transform the clay into the ceramic substance.

For example, the clay kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , undergoes irreversible chemical and structural changes when heated (or fired) above 1500 °C. These changes transform the clay into a white ceramic solid containing an extended network of Si-O and Al-O tetrahedra. Kaolinite is the most important component of porcelain, a ceramic substance that



▲ FIGURE 13.21  $\text{SiO}_4$

**Tetrahedron** In an  $\text{SiO}_4$  tetrahedron, silicon occupies the center of the tetrahedron, and one oxygen atom occupies each corner.



▲ FIGURE 13.22 Structure of

**Quartz** In the quartz structure, each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom is a bridge connecting the corners of two tetrahedrons.



▲ The Venus of Dolni, the oldest known ceramic object, dates to 29,000–25,000 BCE. It was discovered in 1925 in the Czech Republic.



▲ Ceramic electrical insulator



▲ Aluminum oxide crucible, a container in which substances can be subjected to high temperatures.



▲ The Roman Pantheon, still a popular tourist attraction, sits in the center of the ancient heart of Rome. It boasts a 2000-year-old 43.3 m diameter concrete dome.

originated in China during the Han dynasty about 2000 years ago. Chinese porcelain was superior to previous ceramics and became highly valued and prized for its beauty and durability, especially when formed into cups for drinking tea. The Chinese profitably exported their porcelain wares to the Middle East and the West and kept their recipe for making it a secret for hundreds of years. The term *china* today still refers to the fine plates, saucers, and cups made from porcelain and related ceramic materials. Silicate ceramics also find extensive use as insulators in electrical applications.

### Oxide Ceramics

Among the most common oxide ceramics are  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . These materials demonstrate the advantages and disadvantages of ceramic materials compared to metals.  $\text{Al}_2\text{O}_3$  melts at 2072 °C, compared to aluminum metal, which melts at 660 °C.  $\text{MgO}$  melts at an even higher temperature (2852 °C). Both are physically and chemically stable at high temperatures. The high melting point and chemical stability make  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  outstanding *refractory materials*—materials that can be used in high-temperature applications.

For example, aluminum oxide and magnesium oxide are used in industrial furnaces, high-speed cutting tools, crucibles, heating elements, and fire proofing. Engineers have long desired to take advantage of the high-temperature stability of ceramics to make ceramic engines. A ceramic engine can run at a higher temperature, which makes it more efficient and would require less cooling. However, certain less desirable characteristics of ceramics have made that pursuit difficult. Ceramic materials tend to be brittle and subject to thermal shock (they can crack upon fast changes in temperature). Metals can bend and stretch under stress, but ceramics break. Even though ceramics have found some limited use as components of engines, a completely ceramic mass-produced engine remains elusive.

### Nonoxide Ceramics

The nonoxide ceramics include substances such as  $\text{Si}_3\text{N}_4$ , BN, and SiC. Silicon nitride is a network covalent solid with a structure similar to silica; the silicon atoms sit in the center of nitrogen tetrahedra that are linked. Silicon nitride is used extensively in engine parts and nonmetallic ball bearings. Boron nitride is isoelectronic with  $\text{C}_2$  (BN and  $\text{C}_2$  have the same number of valence electrons) and forms structures similar to carbon. For example, BN can form layered sheets (similar to graphite), which are covalently bound within the sheets but with only dispersion forces between the sheets. As a result, this form of BN makes a good high-temperature lubricant. Another form of boron nitride has the diamond structure, which results in a hard, strong substance similar to diamond. This form of boron nitride is used as an abrasive and to make cutting tools. Boron nitride can even form nanotubes similar to those formed by carbon. Silicon carbide also has a diamond structure, but in silicon carbide, half of the carbon atoms are replaced by silicon atoms. It too finds applications as an abrasive, and it is also used as a refractory material and an additive to steel.

### Cement

Cement was first discovered by the Romans, who used lime, volcanic ash, and clay to make a pourable slurry that hardened into a rocklike substance. The Romans used cement to construct the 43.3-m-diameter dome of the Pantheon, a 2000-year-old edifice. This dome remains the largest unreinforced concrete dome in existence.

The majority of the cement used today is Portland cement. **Portland cement** is a powdered mixture consisting mostly of limestone ( $\text{CaCO}_3$ ) and silica ( $\text{SiO}_2$ ), with smaller amounts of alumina ( $\text{Al}_2\text{O}_3$ ), iron(III) oxide ( $\text{Fe}_2\text{O}_3$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The powdered mixture reacts with water in a number of complex reactions that produce a final rocklike substance. Unlike clays, which lose water upon setting, Portland cement reacts with water as it hardens. The hardening process involves the formation of Si-O-Si bridges that produce fibrous structures. These structures bond strongly to each other (and most other substances). The original Portland cement was patented in 1824 by an English bricklayer named Joseph Aspidin (1788–1855). The hardened cement resembles a prestigious building stone from the Isle of Portland in Southwest England and derives its name from this resemblance.

Portland cement is combined with sand and pebbles to make **concrete**, the most widely used building material in the world. Concrete dramatically revolutionized construction. Before concrete, buildings were made exclusively by arranging the materials piece by piece. With the development of concrete, buildings could literally be poured into place. Concrete is used extensively to make foundations, walls, buildings, bridges, aqueducts, roads, and dams. About half of all the structures humans construct are made of concrete.

## Glass

Silica melts when heated above 1500 °C. After melting, if cooled quickly, silica does not crystallize back into the quartz structure. Instead, the Si atoms and O atoms form a randomly ordered amorphous structure called a **glass**. Silicate glass is transparent, impervious to water, and an outstanding material for making windows and drinking vessels. The Egyptians and Greeks likely made glass objects; however, the Romans in the first century BCE were the first to extensively develop glass making. They discovered that adding sodium carbonate to silica dramatically lowers its melting point, allowing glass to form at much lower temperatures. In addition, they developed glassblowing, which involves melting glass and then using a tube to blow the glass into spherical shapes.

When  $\text{SiO}_2$  is made into a glass, the result is called **vitreous silica** or **fused silica**. This type of glass is hard, resists high temperatures, has a low thermal expansion, and is transparent to both visible light and ultraviolet light. Vitreous silica (because of the high temperatures required to produce it) is too expensive for most common applications. The most common modern glass is **soda-lime glass**, which is also referred to as *window glass*. Soda-lime glass is about 70%  $\text{SiO}_2$ ; the balance is mostly  $\text{Na}_2\text{O}$  and  $\text{CaO}$ . This type of glass is transparent to visible light (not ultraviolet) and has a high thermal expansion, but it is less expensive to make and form into desired shapes than vitreous silica.

One disadvantage of soda-lime glass is its tendency to crack under thermal shock. Adding boric oxide ( $\text{B}_2\text{O}_3$ ) to the glass mixture instead of  $\text{CaO}$  produces **borosilicate glass** (also known as **Pyrex®**), which expands less when heated. As a result, vessels made of Pyrex® can withstand heating and cooling cycles that would shatter soda-lime glass. The beakers, flasks, and other glassware found in most chemistry labs are made of borosilicate glass.

**Leaded glass** (often called *crystal*, even though it is not a crystal) results when  $\text{PbO}$  is mixed with  $\text{SiO}_2$  and a couple of other minor components. This type of glass has a higher index of refraction (it bends light more than ordinary glass), which results in glassware with a more brilliant appearance than soda-lime glass. It also makes a ringing sound when tapped, which is a common test to distinguish lead crystal from ordinary glass. Recent concerns about the toxicity of lead in leaded glass have led to the development of lead-free alternatives (often called lead-free crystal) for stemware and drinking glasses, which have properties similar to those of leaded glass, but without the potentially negative health risks.

### 13.8

## Semiconductors and Band Theory

Recall that in Section 13.4 we discussed a model for bonding in metals called the *electron sea model*, which we first introduced and explained in Section 10.11. We now turn to a model for bonding in solids that is both more sophisticated and more broadly applicable—it applies to both metallic solids and covalent solids. The model is **band theory**, and it grows out of molecular orbital theory, first discussed in Section 11.8.

## Molecular Orbitals and Energy Bands

Recall that according to molecular orbital theory, the atomic orbitals of the atoms combine within a molecule to form molecular orbitals. These molecular orbitals are not localized on individual atoms but *delocalized over the entire molecule*. Similarly, in band theory, the atomic orbitals of the atoms within a solid crystal combine to form orbitals that are not localized on individual atoms, but delocalized over the entire *crystal*. In some sense, the crystal is like a very large molecule, and its valence electrons occupy the molecular orbitals formed from the atomic orbitals of each atom in the crystal.

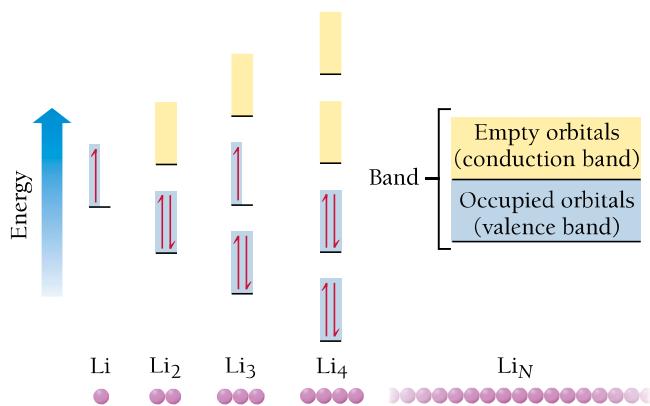


▲ Glassblowing involves blowing air into a hot piece of glass to form spherical shapes.



▲ Leaded glass has a higher index of refraction than ordinary glass, making it appear more brilliant.

The amount of lead that leaches into a drink from leaded glass over a short period of time is likely inconsequential. However, storing drinks in leaded glass for long periods of time can lead to elevated lead levels in the liquid.

**▲ FIGURE 13.23** Energy Levels of Molecular Orbitals in Lithium Molecules

**When many Li atoms are present, the energy levels of the molecular orbitals are so closely spaced that they fuse to form a band.** Half of the orbitals are bonding orbitals and contain valence electrons; the other half are antibonding orbitals and are empty.

Recall from Section 2.7 that a semiconductor is a substance of intermediate (and highly temperature-dependent) electrical conductivity.

**► FIGURE 13.24 Band Gap** In a conductor, there is no energy gap between the valence band and the conduction band. In semiconductors there is a small energy gap, and in insulators there is a large energy gap.

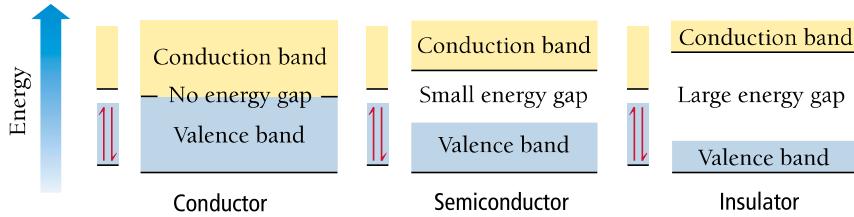
Consider a series of molecules constructed from individual lithium atoms. The energy levels of the atomic orbitals and resulting molecular orbitals for  $\text{Li}$ ,  $\text{Li}_2$ ,  $\text{Li}_3$ ,  $\text{Li}_4$ , and  $\text{Li}_N$  (where  $N$  is a large number on the order of  $10^{23}$ ) are shown in Figure 13.23. The lithium atom has a single electron in a single  $2s$  atomic orbital. The  $\text{Li}_2$  molecule contains two electrons and two molecular orbitals. The electrons occupy the lower-energy bonding orbital—the higher-energy, or antibonding, molecular orbital is empty. The  $\text{Li}_4$  molecule contains four electrons and four molecular orbitals. The electrons occupy the two bonding molecular orbitals—the two antibonding orbitals are completely empty.

The  $\text{Li}_N$  molecule contains  $N$  electrons and  $N$  molecular orbitals. However, because there are so many molecular orbitals,

the energy spacings between them are infinitesimally small; they are no longer discrete energy levels, but rather they form a **band** of energy levels. One half of the orbitals in the band ( $N/2$ ) are bonding molecular orbitals, and (at 0 K) these orbitals contain the  $N$  valence electrons; this band is called the **valence band**. The other  $N/2$  molecular orbitals are antibonding and (at 0 K) are completely empty; this band is called the **conduction band**. If the atoms composing a solid have  $p$  orbitals available, then the same process leads to another set of bands at higher energies.

In lithium metal, the highest occupied molecular orbital lies in the middle of a band of orbitals, and the energy difference between it and the next higher-energy orbital is infinitesimally small. Therefore, above 0 K, electrons can easily make the transition from the valence band to the conduction band. Because electrons in the conduction band are mobile, lithium, like all metals, is a good electrical conductor. Mobile electrons in the conduction band are also responsible for the thermal conductivity of metals. When a metal is heated, electrons are excited to higher-energy molecular orbitals. These electrons quickly transport the thermal energy throughout the crystal lattice.

In metals, the valence band and conduction band are energetically continuous—the energy difference between the top of the valence band and the bottom of the conduction band is infinitesimally small. In semiconductors and insulators, however, an energy gap, called the **band gap**, exists between the valence band and conduction band, as shown in Figure 13.24. Band gaps are usually specified in units of electron volts abbreviated as eV ( $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ ). In insulators, the band gap is large, and electrons are not promoted into the conduction band at ordinary temperatures, resulting in no electrical conductivity. In semiconductors, the band gap is smaller. As a result, the conductivity of semiconductors increases with increasing temperature because heat allows a greater number of electrons to be thermally promoted into the conduction band.



The group 4A elements exhibit a range of band gaps as shown in Table 13.2.

**TABLE 13.2** ■ Band Gap of Group 4A Elements

Group 4A Element	Atomic Radius (pm)	Band Gap	Classification
Carbon (diamond)	77	5.5 eV	Insulator
Silicon	118	1.11 eV	Semiconductor
Germanium	122	0.67 eV	Semiconductor
Tin	140	0.08 eV	Metal
Lead	180	none	Metal

Notice that the band gap decreases as you move down the column of elements. Why? We know from our discussion of periodic properties (see Section 9.6) that atomic radius increases as we move down a column in the periodic table. The increasing radius reduces the overlap between orbitals on neighboring atoms, which in turn reduces the energy difference between the antibonding orbitals (the conduction band) and the bonding orbitals (the valence band). This results in a decreasing band gap as you move down the column of elements.

## Doping: Controlling the Conductivity of Semiconductors

Doped semiconductors contain minute amounts of impurities that result in additional electrons in the conduction band or electron “holes” in the valence band. For example, silicon is a group 4A semiconductor. Its valence electrons just fill its valence band. The band gap in silicon is large enough that only a few electrons are promoted into the conduction band at room temperature; therefore, silicon is a poor electrical conductor. However, silicon can be doped with phosphorus, a group 5A element with five valence electrons, to increase its conductivity. The phosphorus atoms are incorporated into the silicon crystal structure, and each phosphorous atom brings with it one additional electron. Since the valence band is completely full, the additional electrons must go into the conduction band. These electrons are then mobile and can conduct electrical current. This type of semiconductor is an **n-type semiconductor** because the charge carriers are *negatively charged* electrons in the conduction band.

Silicon can also be doped with a group 3A element, such as gallium, which has only three valence electrons. When gallium is incorporated into the silicon crystal structure, gallium atoms trap some of the electrons in silicon’s valence band, resulting in electron “holes,” or empty molecular orbitals, in the valence band. The presence of holes also allows for the movement of electrical current because electrons in the valence band can move between holes. In this way, the holes move in the opposite direction as the electrons. This type of semiconductor is a **p-type semiconductor** because each hole acts as a *positive* charge.

At the heart of most modern electronic devices are silicon chips containing millions of **p-n junctions**, tiny spots that are p-type on one side and n-type on the other. These junctions can serve a number of functions, including acting as **diodes** (circuit elements that allow the flow of electrical current in only one direction) or *amplifiers* (elements that amplify a small electrical current into a larger one).

**SEMICONDUCTOR TYPE** Which element would you dope into germanium to create a p-type semiconductor?

- (a) indium      (b) tin      (c) arsenic

**13.6**

**Cc**

Conceptual Connection

**ANSWER NOW!**

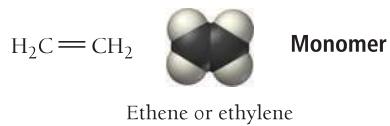


**13.9**

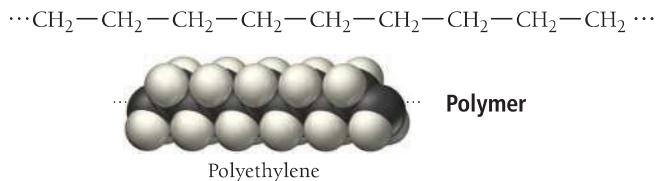
## Polymers and Plastics

**Polymers** are long, chainlike molecules composed of repeating units called **monomers**. In Chapter 23, we discuss natural polymers such as starches, proteins, and DNA, which play important roles in living organisms. In this section, we learn about synthetic polymers, which we encounter daily in plastic products such as PVC tubing, styrofoam coffee cups, nylon rope, and plexiglass windows. Polymeric materials are common in our everyday lives, found in everything from computers to toys to packaging materials. Most polymers are durable, partly because of the length of their molecules. In general, the longer a molecule, the greater the intermolecular forces between molecules and the higher the melting point and boiling point of the substance. Since breaking or tearing a polymeric material involves either overcoming the intermolecular forces between chains or actually breaking the covalent bonds between monomers, polymers tend to be durable materials.

One of the simplest synthetic polymers is polyethylene. The polyethylene monomer is ethene (also called ethylene):



Ethene monomers react with each other, breaking the double bond between carbons and bonding together to form a long polymer chain:

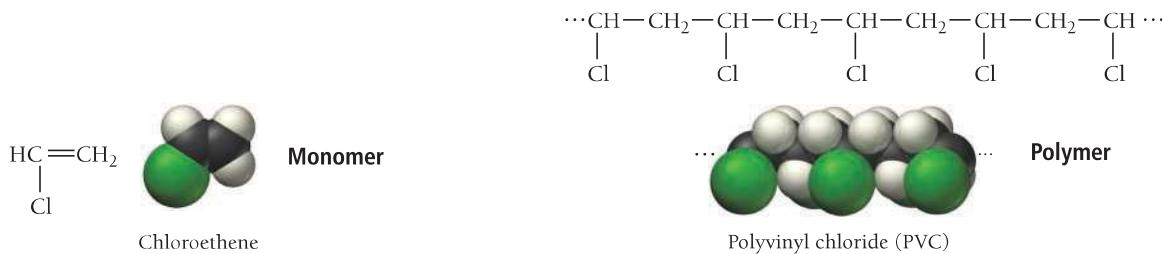


▲ **FIGURE 13.25** Polyethylene

Plastic milk bottles are made from polyethylene.

Polyethylene is an **addition polymer**, a polymer in which the monomers link together without the elimination of any atoms. Polyethylene is the plastic that is used for milk jugs, juice containers, and garbage bags. The properties of polyethylene depend on the exact structure of the ethylene chain and the resulting structure of the material. Although polymers are generally amorphous, they can have regions of crystallinity. For polyethylene, the degree of crystallinity depends in part on the degree of branching in the chain. High-density polyethylene (HDPE), for example, has little branching, so that the chains can align closer to one another, resulting in high crystallinity, high density, and good strength and heat resistance. Common plastic milk jugs are made of HDPE (Figure 13.25◀). Low-density polyethylene (LDPE), in contrast, has more highly branched chains. This branching prevents the chains from interacting as efficiently, resulting in lower crystallinity, density, and strength and heat resistance. Many common plastic bags are made of LDPE.

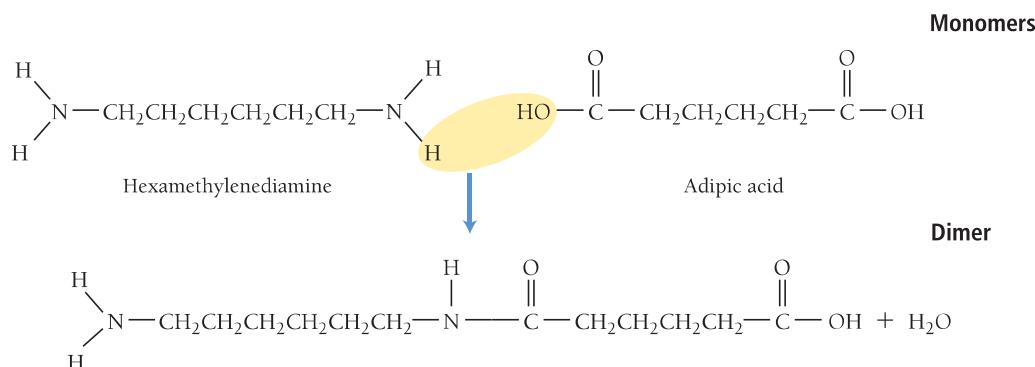
Substituted polyethylenes make up an entire class of polymers (Table 13.3). For example, polyvinyl chloride (PVC)—the plastic used to make certain kinds of pipes and plumbing fixtures—is composed of monomers in which a chlorine atom has been substituted for one of the hydrogen atoms in ethene (Figure 13.26▼). These monomers, which are shown here, react to form PVC:



► **FIGURE 13.26** Polyvinyl Chloride

Polyvinyl chloride is used for many plastic plumbing supplies, such as pipes and connectors.

Some polymers—called *copolymers*—consist of two different kinds of monomers. For example, the monomers that compose nylon 6,6 are hexamethylenediamine and adipic acid. These two monomers add together via a condensation reaction as follows:



**TABLE 13.3 ■ Polymers of Commercial Importance**

Polymer	Structure	Uses
<b>Addition Polymers</b>		
Polyethylene	$-(\text{CH}_2-\text{CH}_2)_n$	Films, packaging, bottles
Polypropylene	$\left[ \begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{CH}_3 \end{array} \right]_n$	Kitchenware, fibers, appliances
Polystyrene	$\left[ \begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Packaging, disposable food containers, insulation
Polyvinyl chloride	$\left[ \begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{Cl} \end{array} \right]_n$	Pipe fittings, clear film for meat packaging
<b>Condensation Polymers</b>		
Polyurethane	$\left[ \begin{array}{c} \text{C}(=\text{O})-\text{NH}-\text{R}-\text{NH}-\text{C}(=\text{O})-\text{O}-\text{R}'-\text{O} \\   \\   \end{array} \right]_n$ R, R' = $-\text{CH}_2-\text{CH}_2-$ (for example)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethylene terephthalate (a polyester)	$\left[ \begin{array}{c} \text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O} \\   \\   \end{array} \right]_n$	Tire cord, magnetic tape, apparel, soda bottles
Nylon 6,6	$\left[ \begin{array}{c} \text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O}) \\   \\   \end{array} \right]_n$	Home furnishings, apparel, carpet fibers, fish line, polymer blends

The product that forms between the reaction of two monomers is a **dimer**. The polymer (nylon 6,6) forms as the dimer continues to add more monomers. Polymers that eliminate an atom or a small group of atoms during polymerization are **condensation polymers**. Nylon 6,6 and other similar nylons are drawn into fibers and used to make consumer products such as panty hose, carpet fibers, and fishing line (see *Chemistry in Your Day: Kevlar*).

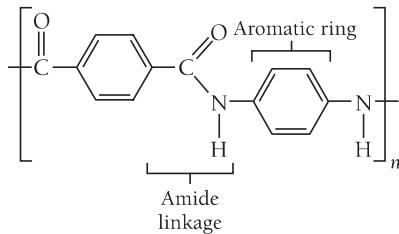


## CHEMISTRY IN YOUR DAY

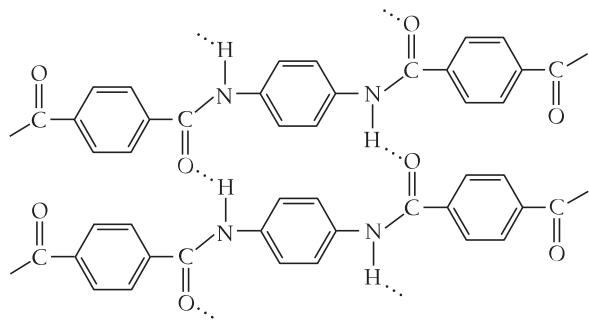
### Kevlar

In 1965, Stephanie Kwolek, working for DuPont to develop new polymer fibers, noticed an odd, cloudy product from a polymerization reaction. Some researchers might have rejected the product, but Kwolek insisted on examining its properties more carefully. The results were astonishing—when the polymer was spun into a fiber, it was stronger than any fiber known before. Kwolek had discovered Kevlar, a material that is pound for pound five times stronger than steel.

Kevlar is a condensation polymer featuring aromatic rings and amide linkages:



The polymeric chains within Kevlar crystallize in a parallel arrangement (like dry spaghetti noodles in a box), with strong cross-linking between neighboring chains resulting from hydrogen bonding. The hydrogen bonding occurs between the N—H groups on one chain and the C=O groups on neighboring chains:



This structure is responsible for Kevlar's high strength and its other properties, including fire resistance and chemical resistance (for example, resistance to acids).

Today, DuPont sells hundreds of millions of dollars worth of Kevlar every year. Kevlar is particularly well known for its use in bulletproof vests. This application of Kwolek's discovery has saved thousands of lives. In addition, Kevlar is used to make helmets, radial tires, brake pads, racing sails, suspension bridge cables, skis, and high-performance hiking and camping gear.



▲ Kevlar is used to make bulletproof vests.





# Self-Assessment Quiz

**Q1.** An X-ray beam of  $\lambda = 154$  pm is incident on the surface of an unknown metallic crystal. It produces a maximum diffraction at an angle of  $\theta = 29.1^\circ$ . Assuming  $n = 1$ , calculate the separation between layers of metal atoms in the crystal.

**MISSED THIS?** Read Section 13.2

- a) 316 pm
- b) 105 pm
- c) 154 pm
- d) 158 pm

**Q2.** How many atoms are in the body-centered cubic unit cell?

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3

- a) 1
- b) 2
- c) 4
- d) 5

**Q3.** What is the coordination number of an atom in a face-centered unit cell?

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3

- a) 4
- b) 6
- c) 8
- d) 12

**Q4.** What is the packing efficiency of the face-centered cubic unit cell?

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3

- a) 52%
- b) 68%
- c) 74%
- d) 88%

**Q5.** What is the edge length of a body-centered cubic unit cell made up of atoms that each has a radius of 168 pm?

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3, IWE 13.3

- a) 388 pm
- b) 336 pm
- c) 475 pm
- d) 84 pm

**Q6.** Rhodium crystallizes in a face-centered cubic unit cell. The radius of a rhodium atom is 135 pm. Determine the density of rhodium in g/cm<sup>3</sup>.

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3, IWE 13.4

- a) 3.07 g/cm<sup>3</sup>
- b) 12.3 g/cm<sup>3</sup>
- c) 278 g/cm<sup>3</sup>
- d) 0.337 g/cm<sup>3</sup>

**Q7.** Which type of solid is dry ice (solid carbon dioxide)?

**MISSED THIS?** Read Section 13.4

- a) ionic
- b) molecular
- c) atomic
- d) none of the above

**Q8.** Which solid has the highest melting point?

**MISSED THIS?** Read Section 13.4

- a) CS<sub>2</sub>(s)
- b) CaF<sub>2</sub>(s)
- c) C<sub>8</sub>H<sub>18</sub>(s)
- d) Ar(s)

**Q9.** Which material is a common oxide ceramic?

**MISSED THIS?** Read Section 13.7

- a) N<sub>2</sub>O
- b) Al<sub>2</sub>O<sub>3</sub>
- c) Fe<sub>2</sub>O<sub>3</sub>
- d) CuO

**Q10.** What is the main component of glass?

**MISSED THIS?** Read Section 13.7

- a) Al<sub>2</sub>O<sub>3</sub>
- b) SiO<sub>2</sub>
- c) CaF<sub>2</sub>
- d) SiC

**Q11.** Which substance has the greatest band gap?

**MISSED THIS?** Read Section 13.8

- a) silicon
- b) germanium
- c) lead
- d) gold

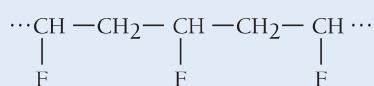
**Q12.** Which element produces a p-type semiconductor when doped into silicon?

**MISSED THIS?** Read Section 13.8

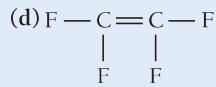
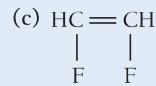
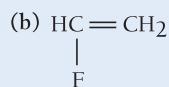
- a) Ge
- b) As
- c) Ga
- d) Sb

**Q13.** Which monomer produces the addition polymer shown here?

**MISSED THIS?** Read Section 13.9



(a) H<sub>2</sub>C=CH<sub>2</sub>



# CHAPTER 13 IN REVIEW

## TERMS

### Section 13.1

graphene (541)

### Section 13.2

X-ray diffraction (542)

X-ray crystallography (544)

### Section 13.3

crystalline lattice (545)

unit cell (545)

simple cubic (546)

coordination number (547)

packing efficiency (547)

body-centered cubic (547)

face-centered cubic (549)

hexagonal closest packing (551)

cubic closest packing (552)

### Section 13.4

molecular solids (553)

polymorphs (554)

ionic solids (555)

atomic solids (555)

nonbonding atomic  
solids (555)

metallic atomic solids (555)

network covalent atomic  
solids (556)

### Section 13.6

graphite (558)

diamond (558)

fullerenes (560)

nanotubes (560)

silicates (561)

quartz (561)

silica (561)

### Section 13.7

ceramics (561)

clay (561)

Portland cement (562)

concrete (563)

glass (563)

vitreous silica (fused silica)  
(563)

soda-lime glass (563)

borosilicate glass (Pyrex®)  
(563)

leaded glass (563)

### Section 13.8

band theory (563)

valence band (564)

conduction band (564)

band gap (564)

n-type semiconductor (565)

p-type semiconductor (565)

p-n junctions (565)

diodes (565)

### Section 13.9

polymer (565)

monomer (565)

addition polymer (566)

dimer (568)

condensation polymer (568)

## CONCEPTS

### Crystalline Structures (13.2–13.4)

- X-ray crystallography uses the diffraction pattern of X-rays to determine the crystal structure of solids.
- The crystal lattice is represented by a unit cell, a structure that reproduces the entire lattice when repeated in all three dimensions.
- Three basic cubic unit cells are the simple cubic, the body-centered cubic, and the face-centered cubic.
- Some crystal lattices can also be depicted as closest-packed structures, including the hexagonal closest-packing structure (not cubic) and the cubic closest-packing structure (which has a face-centered cubic unit cell).
- The basic types of crystal solids are molecular, ionic, and atomic solids. We divide atomic solids into three different types: nonbonded, metallic, and network covalent.

### Ionic Solids (13.5)

- Unit cells in the structures of ionic solids are charge neutral. The unit cells must also accommodate the difference in size between the anion and cation.
- Common unit cells for ionic compounds include the sodium chloride unit cell, the zinc blende unit cell, and the calcium fluoride unit cell.

### Network Covalent Atomic Solids (13.6)

- Network covalent solids are composed of extended arrays of atoms held together by covalent bonds.
- Well known network covalent solids include diamond, graphite, graphene, and silica.

### Ceramics, Cement, and Glass (13.7)

- Ceramics are inorganic nonmetallic solids that are prepared from powders typically mixed with water, formed into the desired

shape, and then heated. Ceramics are usually hard, strong, nonconductive, and brittle.

- Cement is a powdered mixture consisting mostly of limestone ( $\text{CaCO}_3$ ) and silica ( $\text{SiO}_2$ ), with smaller amounts of other substances. When cement is mixed with water, it reacts to form a hard, stone-like substance.
- Glass is primarily amorphous  $\text{SiO}_2$  or silica. Silicate glass is transparent, impervious to water, and an outstanding material for making windows and drinking vessels.

### Semiconductors and Band Theory (13.8)

- Band theory is a model for bonding in solids in which the atomic orbitals of the atoms are combined and delocalized over the entire crystal solid. In band theory, solids form energy bands that are occupied by electrons.
- In metals, the valence band (composed of bonding molecular orbitals) is continuous with the conduction band (composed of antibonding molecular orbitals).
- Semiconductors have a small energy gap—called the band gap—between the valence band and the conduction band.
- Semiconductors can be doped with small amounts of impurities to modify their conductivity.

### Polymers and Plastics (13.9)

- Polymers are long, chainlike molecules that consist of repeating units called monomers. They can be natural or synthetic.
- Polyethylene is an addition polymer, a polymer formed without the elimination of any atoms.
- Condensation polymers, such as nylon, are formed by the elimination of small groups of atoms.

## EQUATIONS AND RELATIONSHIPS

Bragg's Law: Relationship between Light Wavelength ( $\lambda$ ), Angle of Reflection ( $\theta$ ), and Distance ( $d$ ) between the Atomic Layers (13.2)  $n\lambda = 2d \sin \theta$  ( $n = \text{integer}$ )

## LEARNING OUTCOMES

Chapter Objectives	Assessment
Perform X-ray diffraction calculations using Bragg's law (13.2)	Example 13.1 For Practice 13.1 Exercises 27–28
Analyze crystalline solids in terms of unit cell type, coordination number, and packing efficiency (13.3)	Example 13.2 For Practice 13.2 Exercises 29–32
Relate unit cell volume, edge length, and atomic radius (13.3)	Example 13.3 For Practice 13.3 Exercises 33–34
Solve problems involving the density of crystalline solids (13.3)	Example 13.4 For Practice 13.4 Exercises 35–38
Classify crystalline solids by type (molecular, ionic, or atomic) (13.4)	Example 13.5 For Practice 13.5 Exercises 39–40
Predict relative melting points of crystalline solids (13.4)	Exercises 41–44
Analyze atomic solids in terms of structure and properties (13.6)	Exercises 45–52
Describe the properties of silicates and silicate-based materials (13.7)	Exercises 53–58
Analyze semiconductors in terms of band theory and type (n or p) (13.8)	Exercises 59–68
Analyze polymers and plastics in terms of structure and properties (13.9)	Exercises 69–76

## EXERCISES

**Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

## REVIEW QUESTIONS

- What is graphene? Why is graphene unique?
- Explain the basic principles involved in X-ray crystallography. Include Bragg's law in your explanation.
- What is a crystalline lattice? How is the lattice represented with the unit cell?
- Make a drawing of each unit cell: simple cubic, body-centered cubic, and face-centered cubic.
- For each of the cubic cells in the previous problem, give the coordination number, edge length in terms of  $r$ , and number of atoms per unit cell.
- What is the difference between hexagonal closest packing and cubic closest packing? What are the unit cells for each of these structures?
- What are the three basic types of solids and the composite units of each? What types of forces hold each type of solid together?
- What are the three categories of atomic solids?
- What kinds of forces hold each of the three basic categories of atomic solids together?
- What is a polymorph?
- In an ionic compound, how are the relative sizes of the cation and anion related to the coordination number of the crystal structure?
- Show how the cesium chloride, sodium chloride, and zinc blende unit cells each contain a cation-to-anion ratio of 1:1.
- Show how the fluorite structure accommodates a cation-to-anion ratio of 1:2.
- Name and describe the different allotropes of carbon.
- What are silicates? What is quartz?
- What is the definition of a *ceramic*? What are the three categories of ceramics?
- List the major and minor components of Portland cement. What is the difference between the hardening process of Portland cement and the hardening process of clays?
- How is concrete made from Portland cement? What advantage does concrete have for building compared to the construction methods that predated the development of concrete?
- Describe what happens on the molecular level when silica is heated and then cooled to make glass.
- Describe the difference between vitreous silica and soda-lime glass. What are some advantages and disadvantages of each of these types of glass?
- In band theory of bonding for solids, what is a *band*? What is the difference between the *valence band* and the *conduction band*?
- In band theory of bonding for solids, what is a band gap? How does the band gap differ in metals, semiconductors, and insulators?
- Explain how doping can increase the conductivity of a semiconductor. What is the difference between an n-type semiconductor and a p-type semiconductor?
- What is the trend in the size of the band gap as you move down the column of the group 4A elements?
- What is a polymer? What is the difference between a polymer and a copolymer?
- How do an addition polymer and a condensation polymer differ from each other?

## PROBLEMS BY TOPIC

### Types of Solids and Their Structures

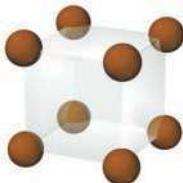
- 27.** An X-ray beam with  $\lambda = 154$  pm incident on the surface of a crystal produced a maximum reflection at an angle of  $\theta = 28.3^\circ$ . Assuming  $n = 1$ , calculate the separation between layers of atoms in the crystal.

**MISSED THIS?** Read Section 13.2

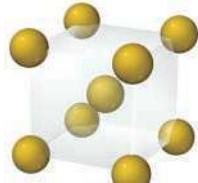
- 28.** An X-ray beam of unknown wavelength is diffracted from a NaCl surface. If the interplanar distance in the crystal is 286 pm, and the angle of maximum reflection is found to be  $7.23^\circ$ , what is the wavelength of the X-ray beam? (Assume  $n = 1$ .)

- 29.** Determine the number of atoms per unit cell for each metal.

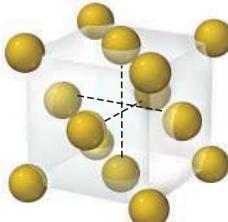
**MISSED THIS?** Read Section 13.3; Watch KCV 13.3



(a) Polonium

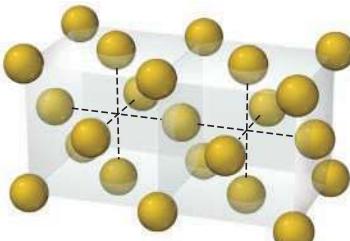


(b) Tungsten

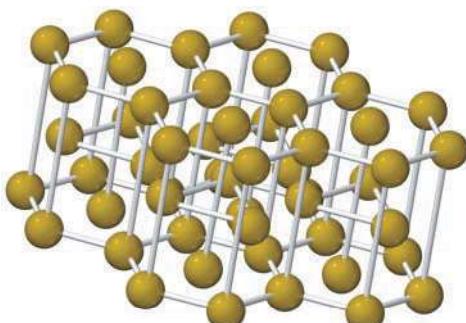


(c) Nickel

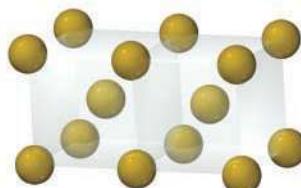
- 30.** Determine the coordination number for each structure.



(a) Gold



(b) Ruthenium



(c) Chromium

- 31.** Calculate the packing efficiency of the body-centered cubic unit cell. Show your work.

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3

- 32.** Calculate the packing efficiency of the face-centered cubic unit cell. Show your work.

- 33.** Platinum crystallizes with the face-centered cubic unit cell. The radius of a platinum atom is 139 pm. Calculate the edge length of the unit cell and the density of platinum in g/cm<sup>3</sup>.

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3, IWE 13.3, 13.4

- 34.** Molybdenum crystallizes with the body-centered unit cell. The radius of a molybdenum atom is 136 pm. Calculate the edge length of the unit cell and the density of molybdenum.

- 35.** Rhodium has a density of 12.41 g/cm<sup>3</sup> and crystallizes with the face-centered cubic unit cell. Calculate the radius of a rhodium atom. **MISSED THIS?** Read Section 13.3; Watch KCV 13.3, IWE 13.3, 13.4

- 36.** Barium has a density of 3.59 g/cm<sup>3</sup> and crystallizes with the body-centered cubic unit cell. Calculate the radius of a barium atom.

- 37.** Polonium crystallizes with a simple cubic structure. It has a density of 9.3 g/cm<sup>3</sup>, a radius of 167 pm, and a molar mass of 209 g/mol. Use these data to calculate Avogadro's number (the number of atoms in one mole).

**MISSED THIS?** Read Section 13.3; Watch KCV 13.3, IWE 13.4

- 38.** Palladium crystallizes with a face-centered cubic structure. It has a density of 12.0 g/cm<sup>3</sup>, a radius of 138 pm, and a molar mass of 106.42 g/mol. Use these data to calculate Avogadro's number.

- 39.** Identify each solid as molecular, ionic, or atomic.

**MISSED THIS?** Read Section 13.4

- |                        |                        |
|------------------------|------------------------|
| a. Ar(s)               | b. H <sub>2</sub> O(s) |
| c. K <sub>2</sub> O(s) | d. Fe(s)               |

- 40.** Identify each solid as molecular, ionic, or atomic.

- |                          |                        |
|--------------------------|------------------------|
| a. CaCl <sub>2</sub> (s) | b. CO <sub>2</sub> (s) |
| c. Ni(s)                 | d. I <sub>2</sub> (s)  |

- 41.** Which solid has the highest melting point? Why?

Ar(s), CCl<sub>4</sub>(s), LiCl(s), CH<sub>3</sub>OH(s)

**MISSED THIS?** Read Section 13.4

- 42.** Which solid has the highest melting point? Why?

C(s), diamond, Kr(s), NaCl(s), H<sub>2</sub>O(s)

- 43.** Which solid in each pair has the higher melting point and why?

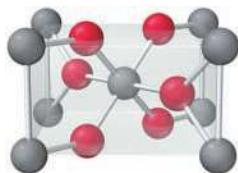
**MISSED THIS?** Read Section 13.4

- |                                    |  |
|------------------------------------|--|
| a. TiO <sub>2</sub> (s) or HOOH(s) | b. CCl <sub>4</sub> (s) or SiCl <sub>4</sub> (s) |
| c. Kr(s) or Xe(s)                  | d. NaCl(s) or CaO(s)                             |

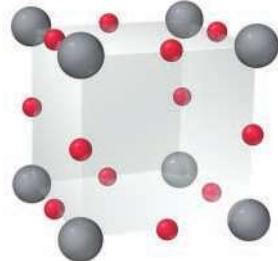
- 44.** Which solid in each pair has the higher melting point and why?

- |                                  |   |
|----------------------------------|---|
| a. Fe(s) or CCl <sub>4</sub> (s) | b. KCl(s) or HCl(s)                           |
| c. Ti(s) or Ne(s)                | d. H <sub>2</sub> O(s) or H <sub>2</sub> S(s) |

45. An oxide of titanium crystallizes with the unit cell shown here (titanium = gray; oxygen = red). What is the formula of the oxide? **MISSED THIS? Read Section 13.5; Watch KCV 13.5**

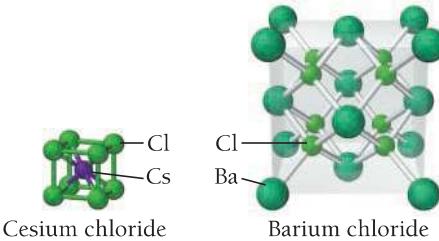


46. An oxide of rhenium crystallizes with the unit cell shown here (rhenium = gray; oxygen = red). What is the formula of the oxide?

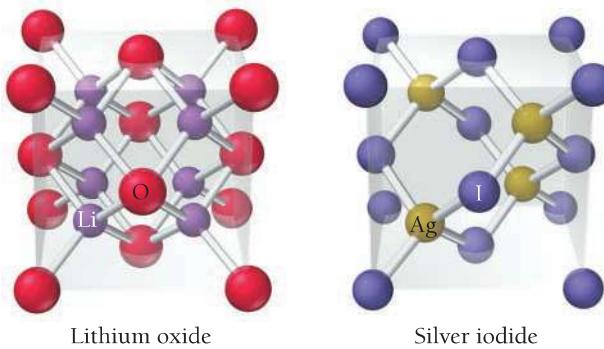


47. The unit cells for cesium chloride and barium chloride are shown here. Show that the ratio of cations to anions in each unit cell corresponds to the ratio of cations to anions in the formula of each compound.

**MISSED THIS? Read Section 13.5; Watch KCV 13.3**



48. The unit cells for lithium oxide and silver iodide are shown here. Show that the ratio of cations to anions in each unit cell corresponds to the ratio of cations to anions in the formula of each compound.



49. Identify the structure of each of the two unit cells shown in Problem 47 as the rock salt structure, zinc blende structure, fluorite structure, antifluorite structure, or none of these.

**MISSED THIS? Read Section 13.5**

50. Identify the structure of each of the two unit cells shown in Problem 48 as the rock salt structure, zinc blende structure, fluorite structure, antifluorite structure, or none of these.

51. Consider the rock salt structure in Figure 13.15. What type of structure would result if all the anions were somehow removed, leaving only cations?

**MISSED THIS? Read Section 13.5; Watch KCV 13.3**

52. Consider the zinc blende structure in Figure 13.16. What type of structure would result if the remaining tetrahedral sites in the unit cell were also filled with cations?

### Ceramics, Cement, and Glass

53. Classify each of the following as a component of a silicate ceramic, an oxide ceramic, or a nonoxide ceramic.

**MISSED THIS? Read Section 13.7**

- B<sub>4</sub>C
- Mg<sub>2</sub>SiO<sub>4</sub>
- MoSi<sub>2</sub>

54. Classify each of the following as a component of a silicate ceramic, an oxide ceramic, or a nonoxide ceramic.

- TiB<sub>2</sub>
- ZrO<sub>2</sub>
- NaAlSi<sub>3</sub>O<sub>8</sub>

55. What are the name and formula of the compound commonly used in the manufacture of glass to reduce its tendency to crack or shatter under thermal shock?

**MISSED THIS? Read Section 13.7**

56. What are the name and formula of the compound commonly used in the manufacture of glass to increase the index of refraction?

57. One of the key components in the manufacture of Portland cement is Ca<sub>3</sub>SiO<sub>5</sub>, a compound that is obtained by firing the reactants in a kiln at 1400–1500 °C. Assign an oxidation state to each element in this compound.

**MISSED THIS? Read Section 5.9, 13.7; Watch KCV 5.13**

58. Replacement of aluminum ions in kaolinite with magnesium ions yields a compound with the formula Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. Assign an oxidation state to each element in this compound.

### Semiconductors and Band Theory

59. Which solid would you expect to have little or no band gap?

**MISSED THIS? Read Section 13.8**

- Zn(s)
- Si(s)
- As(s)

60. Which solid would you expect to have the largest band gap?

- As(s)
- Sb(s)
- Bi(s)

61. How many molecular orbitals are present in the conduction band of a lithium crystal with a mass of 11.2 g?

**MISSED THIS? Read Section 13.8**

62. How many molecular orbitals are present in the valence band of a sodium crystal with a mass of 5.45 g?

63. A substance has a band gap of 6.9 eV at 273 K. Is this substance best classified as an insulator, a semiconductor, or a metal?

**MISSED THIS? Read Section 13.8**

64. A substance has a band gap of 0.85 eV at 273 K. Is this substance best classified as an insulator, a semiconductor, or a metal?

65. Indicate if each solid forms an n-type or a p-type semiconductor.

**MISSED THIS?** Read Section 13.8

- germanium doped with gallium
- silicon doped with arsenic

66. Indicate if each solid forms an n-type or a p-type semiconductor.

- silicon doped with gallium
- germanium doped with antimony

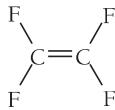
67. Does a photon of red light with a frequency of  $4.29 \times 10^{14}$  Hz have sufficient energy to promote an electron from the valence band to the conduction band in a sample of silicon (the band gap in silicon is 1.11 eV)? **MISSED THIS?** Read Section 13.8

68. Which wavelength of light (in nm) is emitted if an electron moves from the conduction band to the valence band in a sample of diamond (diamond has a band gap of 5.5 eV)?

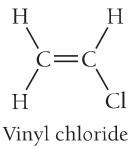
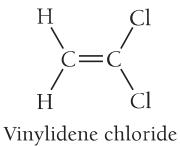
## Polymers

69. Teflon is an addition polymer formed from the monomer shown here. Draw the structure of the polymer.

**MISSED THIS?** Read Section 13.9



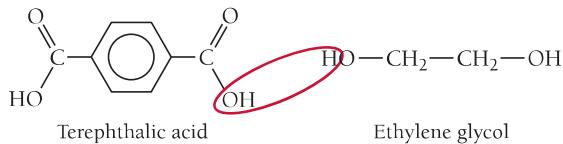
70. Saran, the polymer used to make Saran Wrap, is an addition polymer formed from two monomers—vinylidene chloride and vinyl chloride. Draw the structure of the polymer. (*Hint:* The monomers alternate.)



Vinylidene chloride

Vinyl chloride

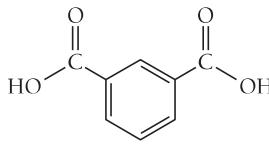
71. One kind of polyester is a condensation copolymer formed from terephthalic acid and ethylene glycol. Draw the structure of the dimer. [*Hint:* Water (circled) is eliminated when the bond between the monomers forms.] **MISSED THIS?** Read Section 13.9



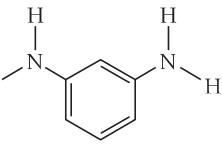
Terephthalic acid

Ethylene glycol

72. Nomex, a condensation copolymer used by firefighters because of its flame-resistant properties, forms from isophthalic acid and *m*-aminoaniline. Draw the structure of the dimer. (*Hint:* Water is eliminated when the bond between the monomers forms.)



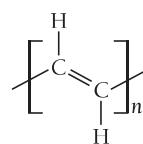
Isophthalic acid



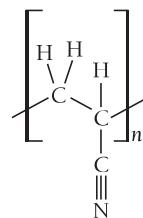
*m*-Aminoaniline

73. Polyacetylene is an addition polymer with the structure shown here. Draw the structure of the monomer.

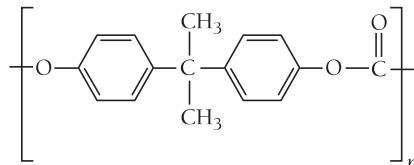
**MISSED THIS?** Read Section 13.9



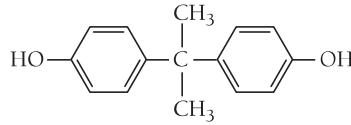
74. Polyacrylonitrile (PAN) is an addition polymer with the structure shown here. Draw the structure of the monomer.



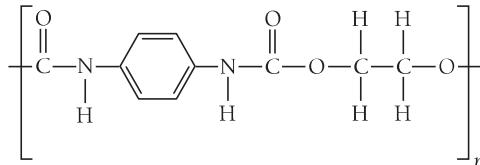
75. The polycarbonate Lexan is a condensation polymer and has the structure shown here: **MISSED THIS?** Read Section 13.9



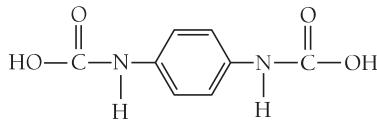
Assuming this polymer was formed from the monomer shown here plus another monomer, provide a possible structure for the other monomer that would be required to form Lexan.



76. Consider the condensation polymer with the structure shown here:

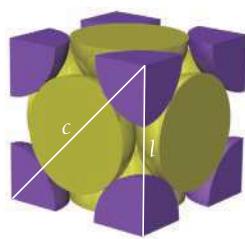


Assuming this polymer was formed from the monomer shown here plus another monomer, provide the structure of the other monomer that would be required to form this polymer.

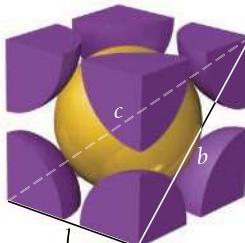


## CUMULATIVE PROBLEMS

- 77.** Silver iodide crystallizes in the zinc blende structure. The separation between nearest-neighbor cations and anions is approximately 325 pm, and the melting point is 558 °C. Cesium chloride, by contrast, crystallizes in the structure shown in Figure 13.14. Even though the separation between nearest-neighbor cations and anions is greater (348 pm), the melting point of cesium chloride is higher (645 °C). Explain.
- 78.** Copper iodide crystallizes in the zinc blende structure. The separation between nearest-neighbor cations and anions is approximately 311 pm, and the melting point is 606 °C. Potassium chloride, by contrast, crystallizes in the rock salt structure. Even though the separation between nearest-neighbor cations and anions is greater (319 pm), the melting point of potassium chloride is higher (776 °C). Explain.
- 79.** Consider the face-centered cubic structure shown here:



- a. What is the length of the line (labeled  $c$ ) that runs diagonally across one of the faces of the cube in terms of  $r$  (the atomic radius)?
- b. Use the answer to part a and the Pythagorean theorem to derive the expression for the edge length ( $l$ ) in terms of  $r$ .
- 80.** Consider the body-centered cubic structure shown here:



- a. What is the length of the line (labeled  $c$ ) that runs from one corner of the cube diagonally through the center of the cube to the other corner in terms of  $r$  (the atomic radius)?
- b. Use the Pythagorean theorem to derive an expression for the length of the line (labeled  $b$ ) that runs diagonally across one of the faces of the cube in terms of the edge length ( $l$ ).
- c. Use the answer to parts a and b along with the Pythagorean theorem to derive the expression for the edge length ( $l$ ) in terms of  $r$ .

- 81.** The volume of a unit cell of diamond is  $0.0454 \text{ nm}^3$ , and the density of diamond is  $3.52 \text{ g/cm}^3$ . Find the number of carbon atoms in a unit cell of diamond.
- 82.** The density of an unknown metal is  $12.3 \text{ g/cm}^3$ , and its atomic radius is  $0.134 \text{ nm}$ . It has a face-centered cubic lattice. Find the atomic mass of this metal.
- 83.** An unknown metal is found to have a density of  $7.8748 \text{ g/cm}^3$  and to crystallize in a body-centered cubic lattice. The edge of the unit cell is  $0.28664 \text{ nm}$ . Calculate the atomic mass of the metal.
- 84.** When spheres of radius  $r$  are packed in a body-centered cubic arrangement, they occupy 68.0% of the available volume. Use the fraction of occupied volume to calculate the value of  $a$ , the length of the edge of the cube, in terms of  $r$ .
- 85.** Potassium chloride crystallizes in the rock salt structure. Estimate the density of potassium chloride using the ionic radii provided in Chapter 9.
- 86.** Calculate the fraction of empty space in cubic closest packing to five significant figures.
- 87.** A tetrahedral site in a closest-packed lattice is formed by four spheres at the corners of a regular tetrahedron. This is equivalent to placing the spheres at alternate corners of a cube. In such a closest-packed arrangement the spheres are in contact, and if the spheres have a radius  $r$ , the diagonal of the face of the cube is  $2r$ . The tetrahedral hole is inside the middle of the cube. Find the length of the body diagonal of this cube and then find the radius of the tetrahedral hole.
- 88.** X-ray diffractometers often use metals that have had their core electrons excited as a source of X-rays. Consider the  $2p \rightarrow 1s$  transition for copper, which is called the  $K\alpha$  transition. Calculate the wavelength of X-rays (in Å) given off by the  $K\alpha$  transition if the energy given off by a mole of copper atoms is  $7.77 \times 10^5 \text{ kJ}$ . ( $1 \text{ \AA} = 10^{-10} \text{ m}$ )
- 89.** Why is it necessary to use the  $K\alpha$  transition ( $2p \rightarrow 1s$ ) in copper (see Problem 88) to generate X-rays? Why not use, for example, the  $4s \rightarrow 3p$  transition?
- 90.** In certain cases where X-ray diffraction is unsuitable for determining the structure of a crystal, *neutron diffraction* can be used. Instead of X-rays, a beam of neutrons is used to analyze the sample. Calculate the velocity of a beam of neutrons with a wavelength of  $2.00 \text{ \AA}$ .

## CHALLENGE PROBLEMS

- 91.** The structure of the addition polymer polypropylene is shown in Table 13.3.
- Draw the structure of the monomer.
  - Show how an alternate version of the polypropylene polymer (with a different arrangement) could be formed from the monomer you found in part a.
- 92.** Perovskite is a compound with a cubic unit cell and has a strontium atom at the center of the cell, titanium atoms at the corners of the unit cell, and oxygen atoms at the centers of each face of the unit cell.
- What is the formula of perovskite?
  - What is the coordination number of strontium in the perovskite structure?
  - If the edge length of the unit cell is  $3.905\text{ \AA}$ , calculate the density of perovskite in  $\text{g/cm}^3$ .
- 93.** A compound with the formula  $\text{Rb}_3\text{C}_{60}$  has been shown to demonstrate superconductivity below 30.0 K. Given that the  $\text{C}_{60}$  molecules have a face-centered cubic arrangement, which of the tetrahedral and octahedral sites are occupied by Rb atoms?
- 94.** Despite Dalton's laws, it is now known that many ionic compounds do not always contain atoms in small integer ratios. For example, a sample of iron(II) oxide may, in fact, contain a significant amount of  $\text{Fe}^{3+}$  in addition to  $\text{Fe}^{2+}$ . This is an example of a *nonstoichiometric* compound. A sample of iron(II) oxide is found to be 75.65% iron by mass. Determine the percentage of  $\text{Fe}^{3+}$  ions in the sample.

## CONCEPTUAL PROBLEMS

- 95.** During the glass manufacturing process, the liquid must be cooled relatively quickly to form the glass. Why?
- 96.** Why are X-rays used for crystallography? Why not use some other, more accessible type of electromagnetic radiation such as ultraviolet light?
- 97.** Compare the crystal structure of diamond (C) and zinc blende ( $\text{ZnS}$ ). What are the key similarities and differences between the two structures?
- 98.** In X-ray crystallography, a small amount of oil is often used to mount the crystal sample on a glass fiber. Explain why neither

the oil nor the glass fiber interferes with the diffraction pattern of the crystal.

- 99.** Which is not likely to lead to an increase in electrical conductivity?
- Increasing the temperature of a semiconductor
  - Choosing a semiconductor with a smaller band gap
  - Doping the semiconductor
  - All of the above would likely lead to an increase in electrical conductivity.

## QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 100.** Have each group member select one of the cubic crystalline lattices. Learn everything you can about your lattice and present it to the group.
- 101.** Using group members to play the role of atoms or molecules, demonstrate the main structural features of the following categories of crystalline solids: molecular solid, ionic solid, nonbonded solid, metallic solid, network covalent solid. Clearly identify what you represent and how you are representing various interactions between particles (e.g., covalent bond, ionic bond).
- 102.** Make a list of questions you would need to ask in order to classify a solid into one of the categories of crystalline solids (molecular solid, ionic solid, nonbonded solid, metallic solid, and network covalent solid). Determine a good order to ask them. (You may

### Active Classroom Learning

need a branching decision tree.) Once you have agreed on a good set of questions, have each group member choose a substance from the chapter and then have the other group members ask the questions in turn until the correct classification is reached. You may agree to edit your questions if you discover ways to improve them when you are using your decision tree.

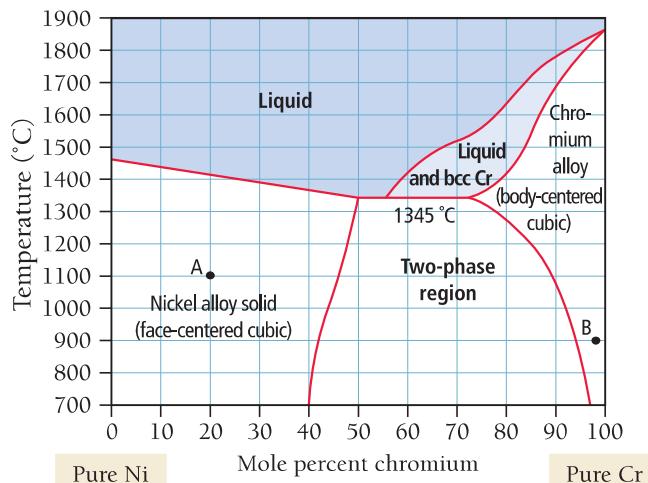
- 103.** Have each group member select and study a material from the section on ceramics, cement, and glass. Take turns describing your material to the group, and see if they can identify the type of material based on your description (without consulting the text).
- 104.** Describe how a common object or toy (e.g., a train, building blocks, or beads on a string) could represent the structure of a polymer. Describe how the following terms would be represented using your model: monomer, dimer, addition polymer, condensation polymer, branching.



## DATA INTERPRETATION AND ANALYSIS

### Alloy Composition and Phase

**105.** An *alloy* is a metallic mixture composed of two or more elements. As is the case in all mixtures, the relative amounts of the elements in an alloy can vary. In some cases, the components of an alloy can have different crystal structures. For example, a nickel-chromium alloy consists of nickel, which has face-centered cubic structure, and chromium, which has a body-centered cubic structure. Which structure does the alloy adopt? It depends on the relative compositions. The phase diagrams for alloys such as these reveal the structure as a function of the alloy composition and temperature. For example, the nickel and chromium phase diagram from 700 °C to 1900 °C is shown here:



▲ Cr-Ni Phase Diagram

Notice that the diagram has two different solid phases: face-centered cubic and body-centered cubic. From pure nickel (0 mol % chromium) to about 40–50 mol % chromium, the structure is face-centered cubic. In this structure, Cr atoms substitute for Ni atoms in the face-centered cubic structure of nickel. However, when an amount of chromium beyond a certain percentage (which depends on temperature) is added, that structure is no longer stable. At the other end of the diagram, from pure chromium to about 75% chromium (depending on temperature), the structure is body-centered cubic, with nickel substituting into the body-centered cubic structure of the chromium. The region in between the two phases is called the *two-phase region*. At these compositions, the two phases (nickel-rich face-centered cubic and chromium-rich body-centered cubic) exist together (the solution is not homogeneous in this region). Use the phase diagram to answer the following questions.

- What is the relative composition of the mixture at point A? At what temperature does a solid mixture having this composition melt?
- Is it possible to have a homogeneous solid mixture that is 50% Ni and 50% Cr? If so, what crystalline structure would it have?
- What is the relative composition at point B? What is the crystalline structure at point B?
- At what temperature does the solid present at point B begin to melt?



## ANSWERS TO CONCEPTUAL CONNECTIONS

### Edge Length and Atomic Radius

**13.1 (c)** 255 pm The relationship between the edge length and the radius for the body-centered cubic unit cell is  $l = 4r\sqrt{3}$ . Therefore,  $r = l/\sqrt{3}/4$ .

### Cubic Structures

**13.2 (c)** The face-centered cubic structure has four atoms per unit cell.

### Crystalline Solid Types and Melting Points

**13.3 (a)** MgO, an ionic compound, has the highest melting point because the solid is held together by ionic bonds. I<sub>2</sub> is a molecular compound with only dispersion forces, and Kr is a nonbonding atomic solid with only dispersion forces. As a result, these two substances have much lower melting points.

### Ionic Crystalline Solid Unit Cells

**13.4 (c)** The zinc blende structure occurs in ionic compounds with a one-to-one cation-to-anion ratio in which the cation is much smaller than the anion.

### Phase Changes and Pressure

**13.5 (a)** An increase in pressure favors the denser phase, in this case diamond.

### Semiconductor Type

**13.6 (a)** Since indium has three valence electrons and germanium has four, the presence of indium would introduce holes into the valence band, resulting in a p-type semiconductor.