

## WHAT'S AHEAD

- 12.1 ► Classification of Solids
- 12.2 ► Metallic Solids
- 12.3 ► Ionic Solids
- 12.4 ► Covalent Solids
- 12.5 ► Polymers
- 12.6 ► Nanomaterials

# 12

## SOLID S AND MODERN MATERIALS

### 12.1 | Classification of Solids



Modern devices like computers and cell phones are built from solids with very specific physical properties. For example, the integrated circuit that is at the heart of many electronic devices is built from semiconductors like silicon, metals like copper, and insulators like hafnium oxide.

Scientists and engineers turn almost exclusively to solids for materials used in many other technologies: *alloys* for magnets and airplane turbines, *semiconductors* for solar cells and light-emitting diodes, and *polymers* for packaging and biomedical applications. Chemists have contributed to the discovery and development of new materials either by inventing new substances or by developing the means to process natural materials to

form substances that have specific electrical, magnetic, optical, catalytic, or mechanical properties. In this chapter, we explore the structures and properties of solids. As we do so, we will examine some of the solid materials used in modern technology.

By the end of this section, you should be able to

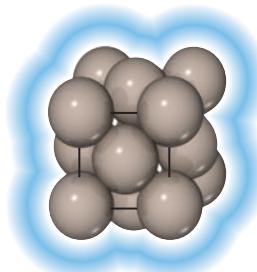
- Classify solids based on their bonding/intermolecular forces and understand how differences in bonding relate to physical properties.
- Describe the difference between crystalline and amorphous solids.
- Understand the terms used to describe a crystal lattice, recognize the five two-dimensional and the seven three-dimensional primitive lattices, and describe the locations of lattice points for body-centered and face-centered lattices.

Solids can be as hard as diamond or as soft as wax. Some readily conduct electricity, whereas others do not. The shapes of some solids can easily be manipulated, while others are brittle and resistant to any change in shape. The physical properties as well as the structures of solids are dictated by the types of bonds that hold the atoms in place. We can classify solids according to those bonds (**Figure 12.1**).

**Metallic solids** are held together by a delocalized “sea” of collectively shared valence electrons. This form of bonding allows metals to conduct electricity. It is also responsible for the fact that most metals are relatively strong without being brittle. **Ionic solids** are held together by the mutual electrostatic attraction between cations and anions. Differences between ionic and metallic bonding make the electrical and mechanical properties of ionic solids very different from those of metals: Ionic solids do not conduct electricity well and are brittle. **Covalent-network solids** are held together by an extended network of covalent bonds. This type of bonding can result in materials that are extremely hard, like diamond, and it is also responsible for the unique properties of semiconductors.

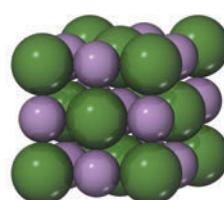
**Molecular solids** are held together by the intermolecular forces we studied in Chapter 11: dispersion forces, dipole–dipole interactions, and hydrogen bonds. Because these forces are relatively weak, molecular solids tend to be soft and have low melting points.

We will also consider two classes of solids that do not fall neatly into the preceding categories: polymers and nanomaterials. **Polymers** contain long chains of atoms (usually carbon), where the atoms within a given chain are connected by covalent bonds and adjacent chains are held to one another largely by weaker intermolecular forces. Polymers are normally stronger and have higher melting points than molecular solids, and they



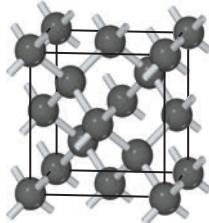
**Metallic solids**

Extended networks of atoms held together by metallic bonding (Cu, Fe)



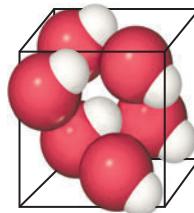
**Ionic solids**

Extended networks of ions held together by cation–anion interactions (NaCl, MgO)



**Covalent-network solids**

Extended networks of atoms held together by covalent bonds (C, Si)



**Molecular solids**

Discrete molecules held together by intermolecular forces (HBr, H<sub>2</sub>O)

▲ **Figure 12.1** Classification and examples of solids according to predominant bonding type.

Iron pyrite ( $\text{FeS}_2$ ), a crystalline solidObsidian (ca. 70%  $\text{SiO}_2$ ), an amorphous solid

**▲ Figure 12.2 Examples of crystalline and amorphous solids.** The atoms in crystalline solids repeat in an orderly, periodic fashion that leads to well-defined faces at the macroscopic level. This order is lacking in amorphous solids like obsidian (volcanic glass).

are more flexible than metallic, ionic, or covalent-network solids. **Nanomaterials** are solids in which the dimensions of individual crystals have been reduced to the order of 1–100 nm. As we will see, the properties of conventional materials change when their crystals become this small.

## Crystalline and Amorphous Solids

Solids contain large numbers of atoms. For example, a 1-carat diamond has a volume of  $57 \text{ mm}^3$  and contains  $1.0 \times 10^{22}$  carbon atoms. How can we hope to describe such a large collection of atoms? Fortunately, the structures of many solids have patterns that repeat over and over in three dimensions. We can visualize the solid as being formed by stacking a large number of small, identical structural units, much like a wall can be built by stacking identical bricks.

Solids in which atoms are arranged in an orderly repeating pattern are called **crystalline solids**. These solids usually have flat surfaces, or *faces*, that make definite angles with one another. The orderly arrangements of atoms that produce these faces also cause the solids to have highly regular shapes (Figure 12.2). Examples of crystalline solids include sodium chloride, quartz, and diamond.

**Amorphous solids** (from the Greek words for “without form”) lack the order found in crystalline solids. At the atomic level the structures of amorphous solids are similar to the structures of liquids, but the molecules, atoms, and/or ions lack the freedom of motion they have in liquids. Amorphous solids do not have the well-defined faces and shapes of a crystal. Familiar amorphous solids are rubber, glass, and obsidian (volcanic glass).

## Unit Cells and Crystal Lattices

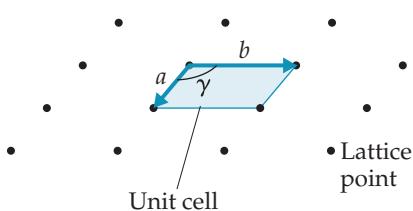
In a crystalline solid, there is a relatively small repeating unit, called a **unit cell**, that is made up of a unique arrangement of atoms and embodies the structure of the solid. The structure of the crystal can be built by stacking this unit over and over in all three dimensions. Thus, the structure of a crystalline solid is defined by (a) the size and shape of the unit cell and (b) the locations of atoms within the unit cell.

The geometrical pattern of points on which the unit cells are arranged is called a **crystal lattice**. The crystal lattice is, in effect, an abstract (that is, not real) scaffolding for the crystal structure. We can imagine forming the entire crystal structure by first building the scaffolding and then filling in each unit cell with the same atom or group of atoms.

Before describing the structures of solids, we need to understand the properties of crystal lattices. It is useful to begin with two-dimensional lattices because they are simpler to visualize than three-dimensional ones. Figure 12.3 shows a two-dimensional array of **lattice points**. Each lattice point has an identical environment. The positions of the lattice points are defined by the **lattice vectors**  $a$  and  $b$ . Beginning from any lattice point, it is possible to move to any other lattice point by adding together whole-number multiples of the two lattice vectors.\*

The parallelogram formed by the lattice vectors, the shaded region in Figure 12.3, defines the unit cell. In two dimensions the unit cells must *tile*, or fit together in space, in such a way that they completely cover the area of the lattice with no gaps. In three dimensions, the unit cells must stack together to fill all space.

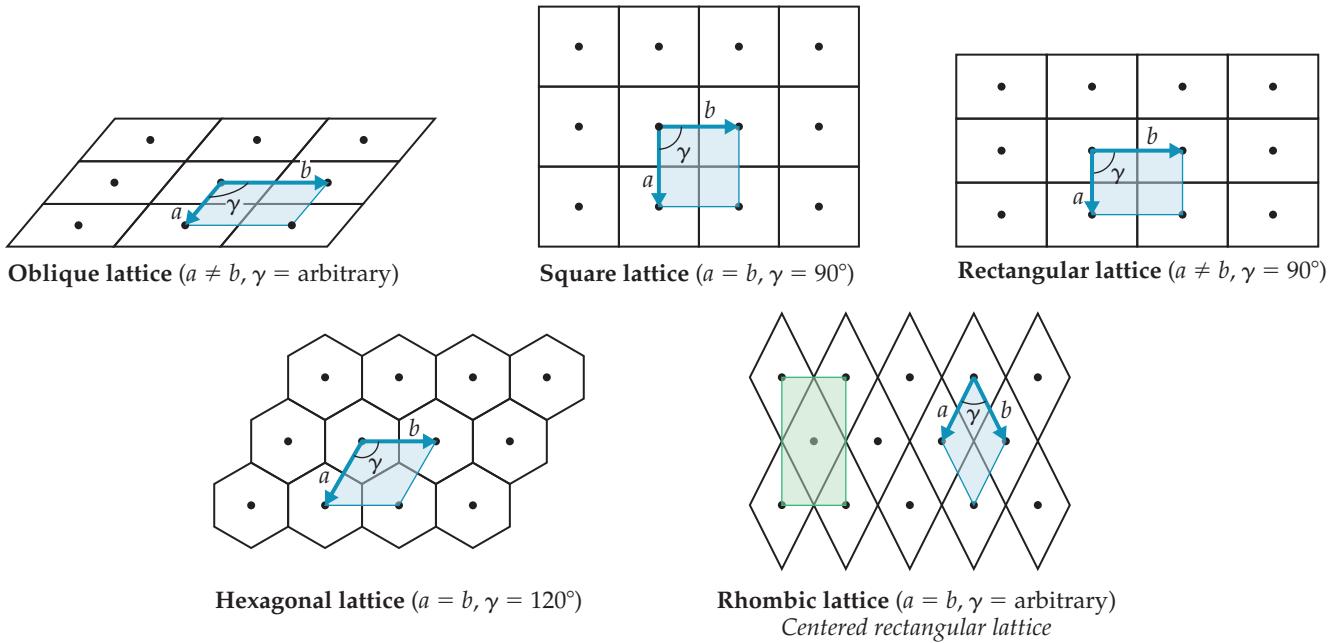
In a two-dimensional lattice, the unit cells can take only one of the five shapes shown in Figure 12.4. The most general type of lattice is the *oblique lattice*. In this lattice, the lattice vectors are of different lengths and the angle  $\gamma$  between them is of arbitrary size, which makes the unit cell an arbitrarily shaped parallelogram. The *square lattice*, *rectangular lattice*, *hexagonal lattice*,\*\* and *rhombic lattice* have a unique combination



**▲ Figure 12.3 A crystalline lattice in two dimensions.** An infinite array of lattice points is generated by adding together the lattice vectors  $a$  and  $b$ . The unit cell is a parallelogram defined by the lattice vectors.

\*A vector is a quantity involving both a direction and a magnitude. The magnitudes of the vectors in Figure 12.3 are indicated by their lengths, and their directions are indicated by the arrowheads.

\*\*You may wonder why the hexagonal unit cell is not shaped like a hexagon. Remember that the unit cell is by definition a parallelogram whose size and shape are defined by the lattice vectors  $a$  and  $b$ .



▲ **Figure 12.4** The five two-dimensional lattices. The primitive unit cell for each lattice is shaded in blue. For the rhombic lattice the centered rectangular unit cell is shaded in green. Unlike the primitive rhombic unit cell, the centered cell has two lattice points per unit cell.

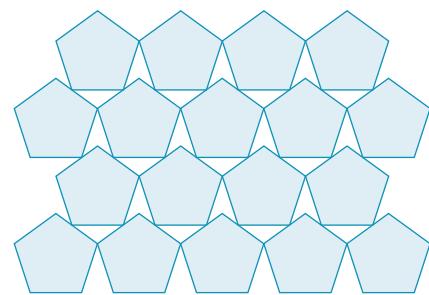
of  $\gamma$  angle and relationship between the lengths of lattice vectors  $a$  and  $b$  (shown in Figure 12.4). For a rhombic lattice an alternative unit cell can be drawn, a rectangle with lattice points on its corners *and* its center (shown in green in Figure 12.4). Because of this, the rhombic lattice is commonly referred to as a *centered rectangular lattice*. The lattices in Figure 12.4 represent five basic shapes: squares, rectangles, hexagons, rhombuses (diamonds), and arbitrary parallelograms. Other polygons, such as pentagons, cannot cover space without leaving gaps, as Figure 12.5 shows.

To understand real crystals, we must consider three dimensions. A three-dimensional lattice is defined by *three* lattice vectors  $a$ ,  $b$ , and  $c$  (Figure 12.6). These lattice vectors define a unit cell that is a parallelepiped (a six-sided figure whose faces are all parallelograms) and is described by the lengths  $a$ ,  $b$ ,  $c$  of the cell edges and the angles  $\alpha$ ,  $\beta$ ,  $\gamma$  between these edges. There are seven possible shapes for a three-dimensional unit cell, as shown in Figure 12.6.

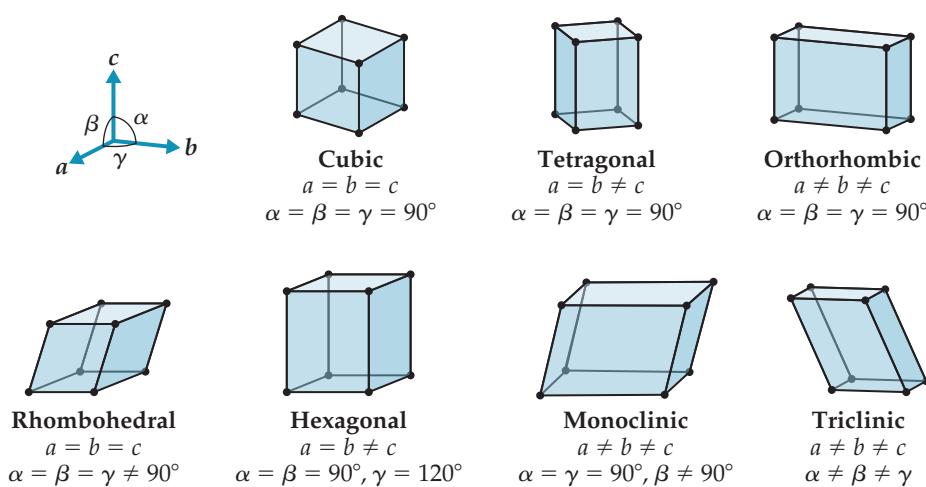
If we place a lattice point at each corner of a unit cell, we get a **primitive lattice**. All seven lattices in Figure 12.6 are primitive lattices. It is also possible to generate

### Go Figure

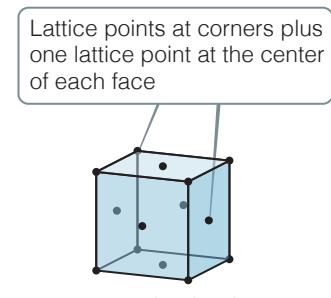
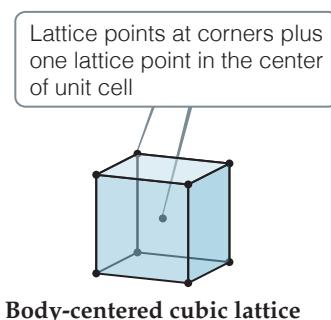
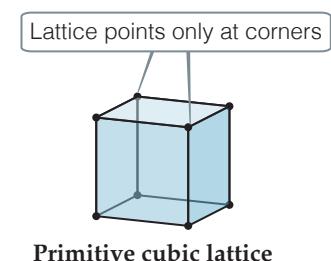
Why is there a centered rectangular lattice but not a centered square lattice?



▲ **Figure 12.5** Not all shapes tile space. Tiling means covering a surface entirely, which is impossible for some geometric shapes, as shown here for pentagons.



▲ **Figure 12.6** The seven three-dimensional primitive lattices.



▲ **Figure 12.7** The three types of cubic lattices.

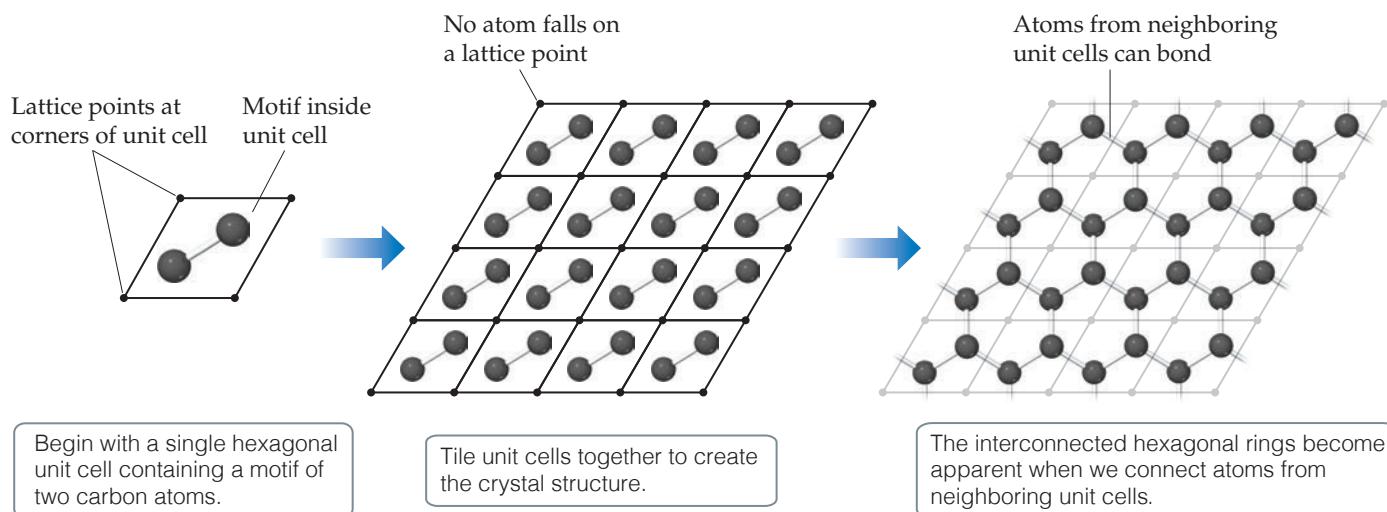
what are called *centered lattices* by placing additional lattice points in specific locations in the unit cell. This is illustrated for a cubic lattice in **Figure 12.7**. A **body-centered cubic lattice** has one lattice point at the center of the unit cell in addition to the lattice points at the eight corners. A **face-centered cubic lattice** has one lattice point at the center of each of the six faces of the unit cell in addition to the lattice points at the eight corners. Centered lattices exist for other types of unit cells as well. For the crystals discussed in this chapter we need consider only the lattices shown in Figures 12.6 and 12.7.

### Filling the Unit Cell

The lattice by itself does not define a crystal structure. To generate a crystal structure, we need to associate an atom or group of atoms with each lattice point. In the simplest case, the crystal structure consists of identical atoms, and each atom lies directly on a lattice point. When this happens, the crystal structure and the lattice points have identical patterns. Many metallic elements adopt such structures, as we will see in Section 12.2. Only for solids in which all the atoms are identical can this occur; in other words, *only elements* can form structures of this type. For compounds, even if we were to put an atom on every lattice point, the points would not be identical because the atoms are not all the same.

In most crystals, the atoms are not exactly coincident with the lattice points. Instead, a group of atoms, called a **motif**, is associated with each lattice point. The unit cell contains a specific motif of atoms, and the crystal structure is built up by repeating the unit cell over and over. This process is illustrated in **Figure 12.8** for a two-dimensional crystal based on a hexagonal unit cell and a two-carbon-atom motif. The resulting infinite two-dimensional honeycomb structure is a two-dimensional crystal called **graphene**, a material that has so many interesting properties that its modern discoverers won the Nobel Prize in Physics in 2010. Each carbon atom is covalently bonded to three neighboring carbon atoms in what amounts to an infinite sheet of interconnected hexagonal rings.

The crystal structure of graphene illustrates two important characteristics of crystals. First, we see that no atoms lie on the lattice points. While most of the structures we discuss in this chapter do have atoms on the lattice points, there are many examples, like graphene, where this is not the case. Thus, to build up a structure you must know the location and orientation of the atoms in the motif with respect to the lattice points. Second, we see that bonds can be formed between atoms in neighboring unit cells and the bonds between atoms need not be parallel to the lattice vectors.



▲ **Figure 12.8** Two-dimensional structure of graphene built up from a single unit cell.

## A CLOSER LOOK X-ray Diffraction

When light waves pass through a narrow slit, they are scattered in such a way that the wave seems to spread out. This physical phenomenon is called *diffraction*. When light passes through many evenly spaced narrow slits (a *diffraction grating*), the scattered waves interact to form a series of bright and dark bands, known as a diffraction pattern. The bright bands correspond to constructive overlapping of the light waves, and the dark bands correspond to destructive overlapping of the light waves. The most effective diffraction of light occurs when the wavelength of the light and the width of the slits are similar in magnitude.

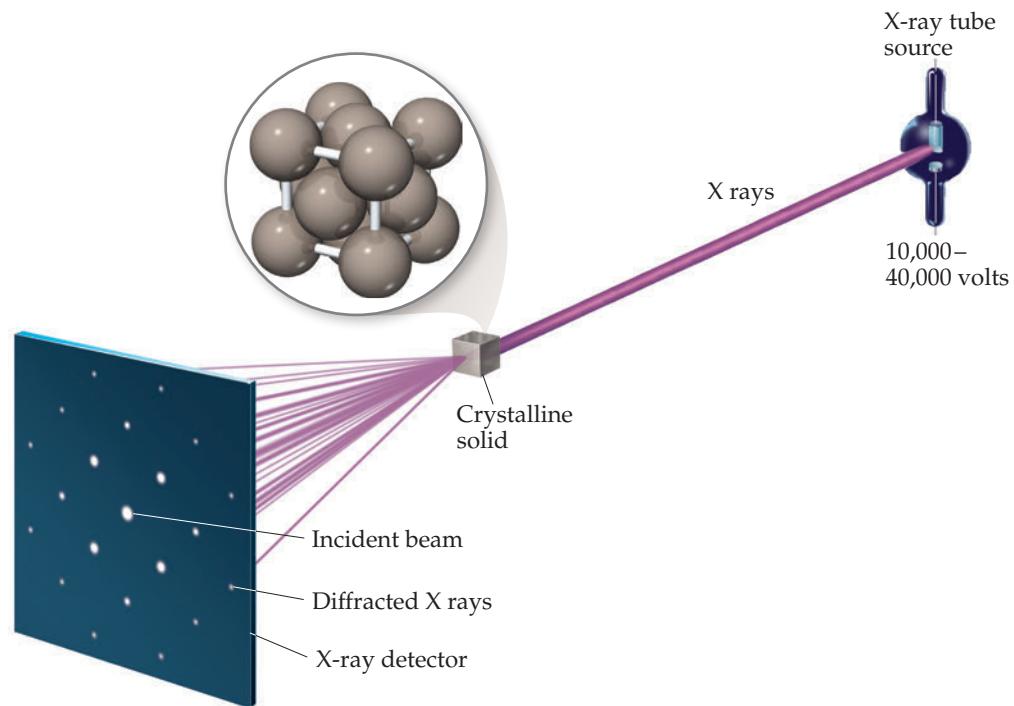
The spacing of the layers of atoms in solid crystals is usually about 0.2–2 nm. The wavelengths of X rays are also in this range. Thus, a crystal can serve as an effective diffraction grating for X rays. X-ray diffraction results from the scattering of X rays by a regular arrangement of atoms, molecules, or ions. Much of what we know about crystal structures has been obtained by looking at the diffraction patterns that result when X rays pass through a crystal, a technique known as *X-ray crystallography*. As shown in **Figure 12.9** a monochromatic beam of X rays is passed through a crystal. The diffraction pattern that results is recorded. For many years the diffracted X rays were detected by photographic film. Today, crystallographers use an

*array detector*, a device analogous to that used in digital cameras, to capture and measure the intensities of the diffracted rays.

The pattern of spots on the detector in Figure 12.9 depends on the particular arrangement of atoms in the crystal. The spacing and symmetry of the bright spots, where constructive interference occurs, provide information about the size and shape of the unit cell. The intensities of the spots provide information that can be used to determine the locations of the atoms within the unit cell. When combined, these two pieces of information give the atomic structure that defines the crystal.

X-ray crystallography is used extensively to determine the structures of molecules in crystals. The instruments used to measure X-ray diffraction, known as *X-ray diffractometers*, are now computer controlled, making the collection of diffraction data highly automated. The diffraction pattern of a crystal can be determined very accurately and quickly (sometimes in a matter of hours), even though thousands of diffraction spots are measured. Computer programs are then used to analyze the diffraction data and determine the arrangement and structure of the molecules in the crystal. X-ray diffraction is an important technique in industries ranging from steel and cement manufacture to pharmaceuticals.

**Related Exercises: 12.120–12.122**



▲ **Figure 12.9** Diffraction of X rays by a crystal. A monochromatic X-ray beam is passed through a crystal. The X rays are diffracted, and the resulting interference pattern is recorded. The crystal is rotated and another diffraction pattern recorded. Analysis of many diffraction patterns gives the positions of the atoms in the crystal.

## Self-Assessment Exercises

**12.1** How would you classify wax?

- (a) Metallic solid
- (b) Ionic solid
- (c) Molecular solid
- (d) Covalent-network solid

**12.2** Is soot an amorphous or crystalline form of carbon?

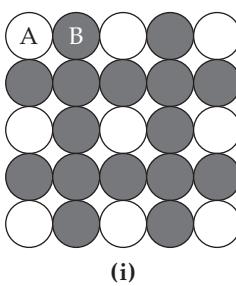
- (a) Amorphous
- (b) Crystalline

**12.3** How would you describe the lattice portrayed for the metallic solid in Figure 12.1?

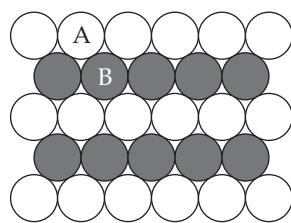
- (a) Body-centered cubic lattice
- (b) Face-centered cubic lattice

## Exercises

- 12.4** Silicon is the fundamental component of integrated circuits. Si has the same structure as diamond. (a) Is Si a molecular, metallic, ionic, or covalent-network solid? (b) Silicon readily reacts to form silicon dioxide,  $\text{SiO}_2$ , which is quite hard and is insoluble in water. Is  $\text{SiO}_2$  most likely a molecular, metallic, ionic, or covalent-network solid?
- 12.5** Which type (or types) of crystalline solid is characterized by each of the following? (a) High mobility of electrons throughout the solid; (b) softness, relatively low melting point; (c) high melting point and poor electrical conductivity; (d) network of covalent bonds.
- 12.6** You are given a white substance that melts at 1500 °C. The substance is brittle and soluble in water. Both the molten solid and the solution is a conductor of electricity. Which type of solid (molecular, metallic, covalent-network, or ionic) might this substance be?
- 12.7** Two patterns of packing two different circles of the same size are shown here. For each structure (a) draw the two-dimensional unit cell; (b) determine the angle between the lattice vectors,  $\gamma$ , and determine whether the lattice vectors are of the same length or of different lengths; (c) determine the type of two-dimensional lattice (from Figure 12.4).



(i)



(ii)

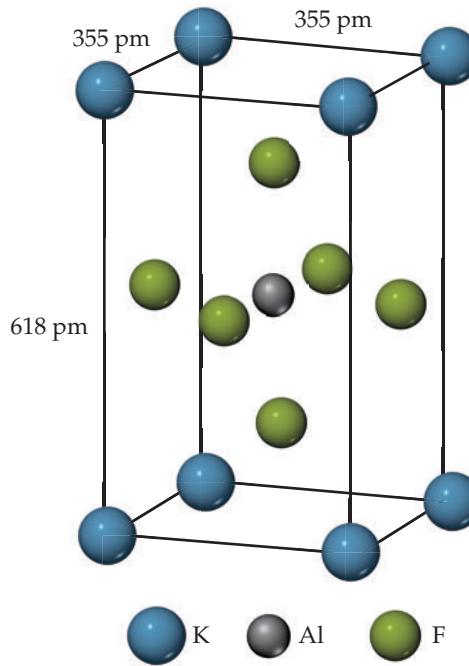
- 12.8** Imagine the primitive cubic lattice. Now imagine grabbing opposite corners and stretching it along the body diagonal while keeping the edge lengths equal. The three angles between the lattice vectors remain equal but are no longer 90°. What kind of primitive lattice have you made?



- 12.9** Besides the cubic unit cell, which other unit cell(s) has edge lengths that are all equal to each other? (a) Orthorhombic, (b) hexagonal, (c) rhombohedral, (d) triclinic, (e) both rhombohedral and triclinic.

- 12.10** What is the minimum number of atoms that could be contained in the unit cell of an element with a face-centered cubic lattice? (a) 1, (b) 2, (c) 3, (d) 4, (e) 5.

- 12.11** The unit cell of a compound containing potassium, aluminum, and fluorine is shown here. (a) What type of lattice does this crystal possess (all three lattice vectors are mutually perpendicular)? (b) What is the empirical formula?



K

Al

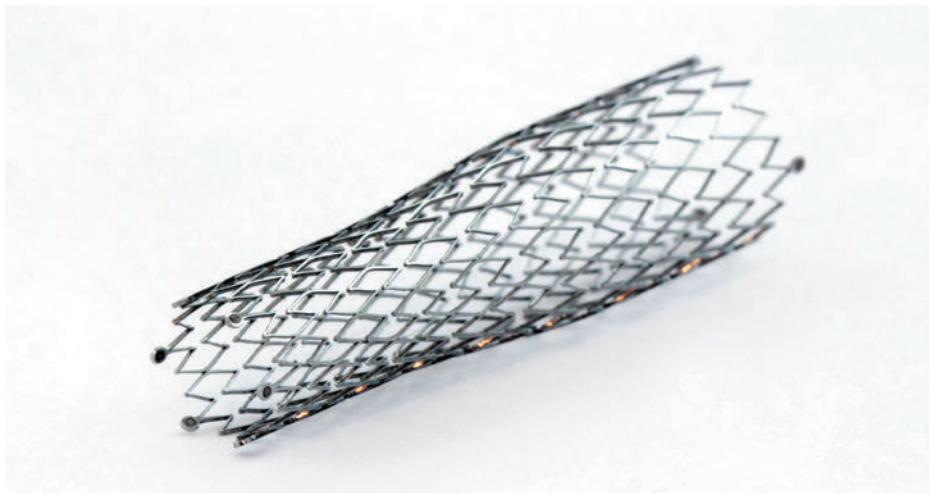
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12.1 (c) 12.2 (a) 12.3 (b)

Answers to Self-Assessment Exercises



## 12.2 | Metallic Solids



Nitinol is a 1:1 nickel–titanium alloy that has ‘shape memory’. This remarkable property was discovered by accident when the alloy was presented to a management meeting of the US Naval Ordnance Laboratory (from where it derived its name: Ni-Ti-N-O-L) in 1961. The folded wire was passed around the room and one of the participants used a cigarette lighter to heat the sample. To the astonishment of those present, the wire uncoiled and took on its original shape. The wire has two crystal structures that are easily interconverted but that are stable at different temperatures. Heating the wire while holding the desired shape fixes the shape and crystal structure. On cooling, the wire may be deformed into another shape and transform to a more complicated crystal structure. Subsequent warming reforms the original crystal lattice and shape.

There are several applications of nitinol in dentistry and medicine. For example, stents used to treat heart conditions can be ‘set’ in their open, functioning shape before cooling and compacting for easy insertion into a blocked coronary artery. At body temperature, the nitinol reforms its open shape, allowing blood to flow more freely.

By the end of this section, you should be able to

- Describe the lattice structure of metals and alloys
- Relate the physical properties of metals to the bonding present

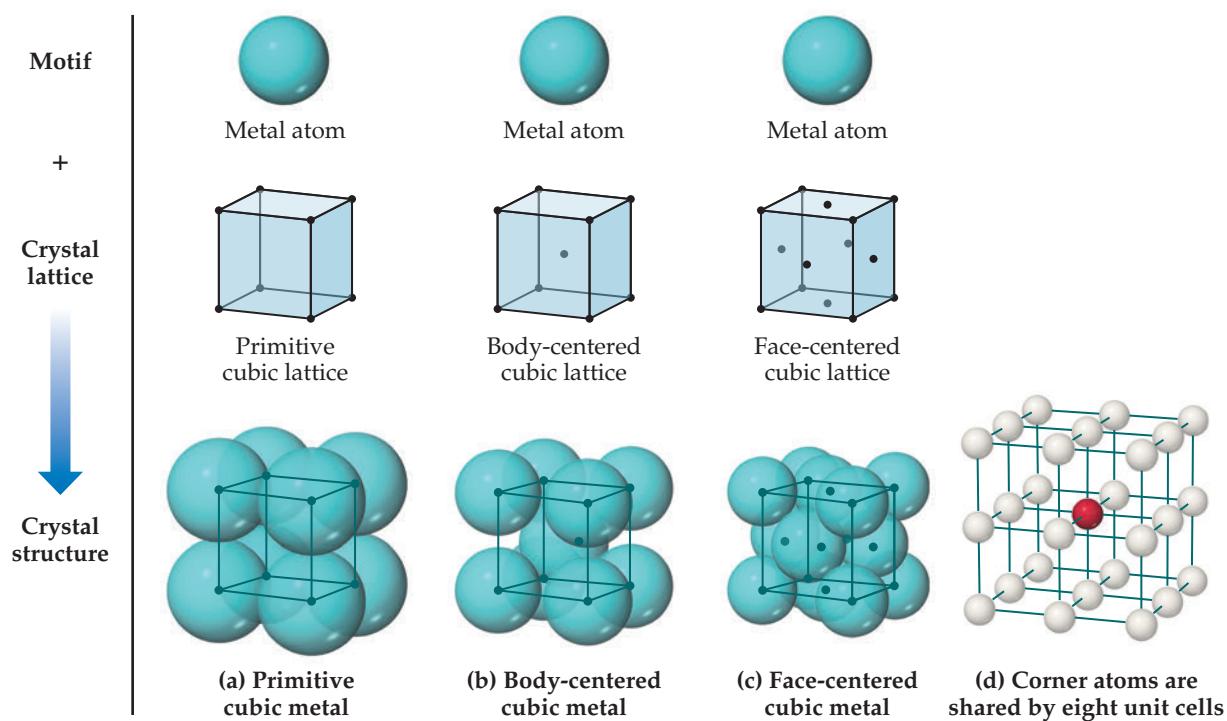
**Metallic solids**, also simply called *metals*, consist entirely of metal atoms. The bonding in metals is too strong to be due to dispersion forces, and yet there are not enough valence electrons to form covalent bonds between atoms. The bonding, called *metallic bonding*, happens because the valence electrons are *delocalized* throughout the entire solid. That is, the valence electrons are not associated with specific atoms or bonds but are spread throughout the solid. In fact, we can visualize a metal as an array of positive ions immersed in a “sea” of delocalized valence electrons.

The chemical bonding in metals is reflected in their properties. You have probably held a length of copper wire or an iron bolt. Perhaps you have even seen the surface of a freshly cut piece of sodium metal. These substances, though distinct from one another, share certain similarities that enable us to classify them as metallic. A clean metal surface has a characteristic luster. Metals have a cold feeling when you touch them, related to their high thermal conductivity (ability to conduct heat). Metals also have high electrical conductivity, which means that electrically charged particles flow easily through them. The thermal conductivity of a metal usually parallels its electrical conductivity. Silver and copper, for example, which possess the highest electrical conductivities among the elements, also possess the highest thermal conductivities.

Most metals are *malleable*, which means that they can be hammered into thin sheets, and *ductile*, which means that they can be drawn into wires (Figure 12.10). These properties indicate that the atoms are capable of slipping past one another. Ionic and covalent-network solids do not exhibit such behavior; they are typically brittle.



▲ **Figure 12.10** Malleability and ductility. Gold leaf demonstrates the characteristic malleability of metals, and copper wire demonstrates their ductility.



**▲ Figure 12.11** The structures of (a) primitive cubic, (b) body-centered cubic, and (c) face-centered cubic metals. Each structure can be generated by the combination of a single-atom motif and the appropriate lattice. (d) Corner atoms (one shown in red) are shared among eight neighboring cubic unit cells.

### The Structures of Metallic Solids

The crystal structures of many metals are simple and can be generated by placing a single atom on each lattice point. The structures corresponding to the three cubic lattices are shown in Figure 12.11. Metals with a primitive cubic structure are rare, one of the few examples being the radioactive element polonium. Body-centered cubic metals include iron, chromium, sodium, and tungsten. Examples of face-centered cubic metals include aluminum, lead, copper, silver, and gold.

Notice in the bottom row of Figure 12.11 that the atoms on the corners and faces of a unit cell do not lie wholly within the unit cell. These corner and face atoms are shared by neighboring unit cells. An atom that sits at the corner of a unit cell is shared among eight unit cells, and only  $1/8$  of the atom is in one particular unit cell. Because a cube has eight corners, each primitive cubic unit cell contains  $(1/8) \times 8 = 1$  atom, as shown in Figure 12.12(a). Similarly, each body-centered cubic unit cell [Figure 12.12(b)] contains two atoms,  $(1/8) \times 8 = 1$  from the corners and 1 at the center of the unit cell. Atoms that lie on the face of a unit cell, as they do in a face-centered cubic metal, are shared by two unit cells so that only one-half of the atom belongs to each unit cell. Therefore, a face-centered cubic unit cell [Figure 12.12(c)] contains four atoms,  $(1/8) \times 8 = 1$  atom from the corners and  $(1/2) \times 6 = 3$  atoms from the faces.

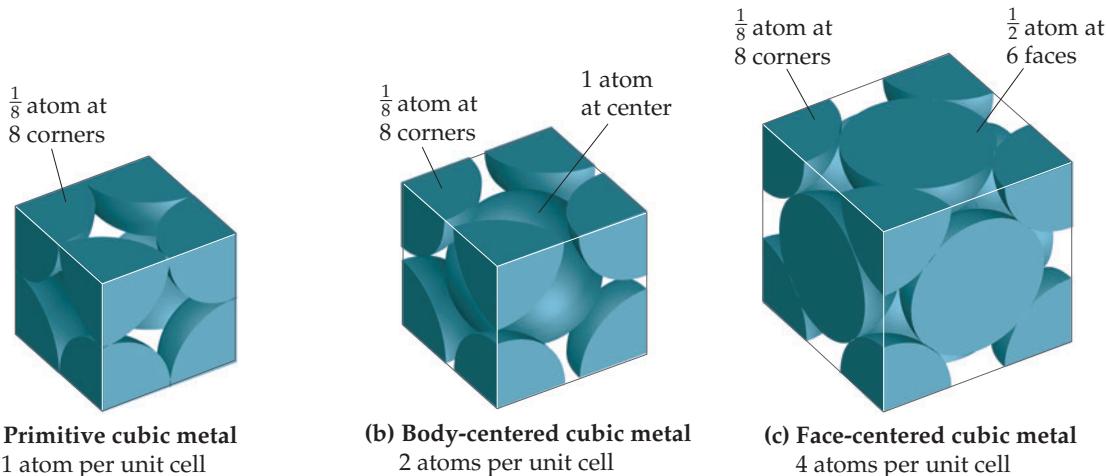
Table 12.1 summarizes how the fractional part of each atom that resides within a unit cell depends on the atom's location within the cell.

### Close Packing

The shortage of valence electrons and the fact that they are collectively shared make it favorable for the atoms in a metal to pack together closely. Because we can consider the shape of an atom to be a sphere, we can understand the structures of metals by considering how spheres pack. The most efficient way to pack one layer of equal-sized spheres is to surround each sphere by six neighbors, as shown at the top of Figure 12.13. To form a three-dimensional structure, we need to stack additional layers on top of this base layer. To maximize packing efficiency, the second layer of spheres must sit in the depressions

 Go Figure

Which one of these unit cells would you expect to represent the densest packing of spheres?



▲ Figure 12.12 A space-filling view of unit cells for metals with a cubic structure. Only the portion of each atom that falls within the unit cell is shown.

**TABLE 12.1 Fraction of Any Atom as a Function of Location within the Unit Cell\***

Atom Location	Number of Unit Cells Sharing Atom	Fraction of Atom within Unit Cell
Corner	8	1/8 or 12.5%
Edge	4	1/4 or 25%
Face	2	1/2 or 50%
Anywhere else	1	1 or 100%

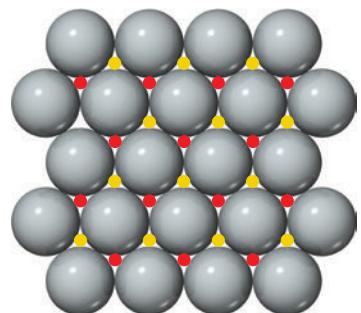
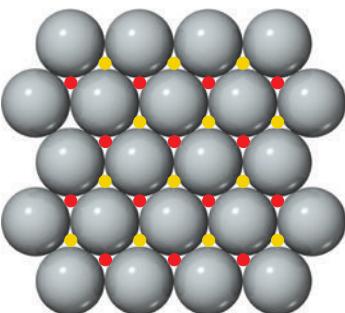
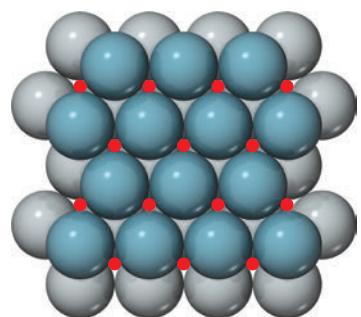
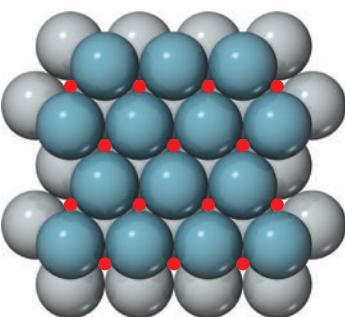
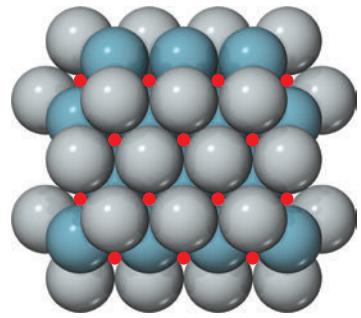
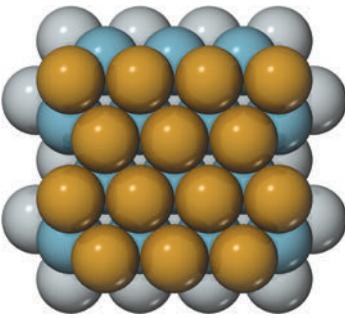
\*It is only the position of the center of the atom that matters. Atoms that reside near the boundary of the unit cell but not on a corner, edge, or face are counted as residing 100% within the unit cell.

formed by the spheres in the first layer. We can either put the next layer of atoms into the depressions marked by the yellow dot or the depressions marked by the red dot (realizing that the spheres are too large to simultaneously fill both sets of depressions). For the sake of discussion we arbitrarily put the second layer in the yellow depressions.

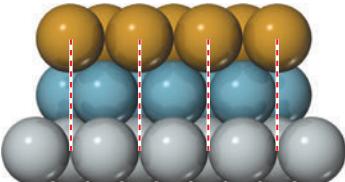
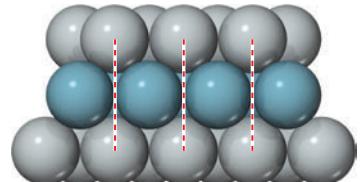
For the third layer, we have two choices for where to place the spheres. One possibility is to put the third layer in the depressions that lie directly over the spheres in the first layer. This is done on the left-hand side of Figure 12.13, as shown by the dashed red lines in the side view. Continuing with this pattern, the fourth layer would lie directly over the spheres in the second layer, leading to the ABAB stacking pattern seen on the left, which is called **hexagonal close packing** (hcp). Alternatively, the third-layer spheres could lie directly over the depressions that were marked with red dots in the first layer. In this arrangement, the spheres in the third layer do not sit directly above the spheres in either of the first two layers, as shown by the dashed red lines on the lower right-hand side of Figure 12.13. If this sequence is repeated in subsequent layers, we derive an ABCABC stacking pattern shown on the right known as **cubic close packing** (ccp). In both hexagonal close packing and cubic close packing, each sphere has 12 equidistant nearest neighbors: six neighbors in the same layer, three from the layer above, and three from the layer below. We say that each sphere has a **coordination number** of 12. The coordination number is the number of atoms immediately surrounding a given atom in a crystal structure.

**Go Figure**

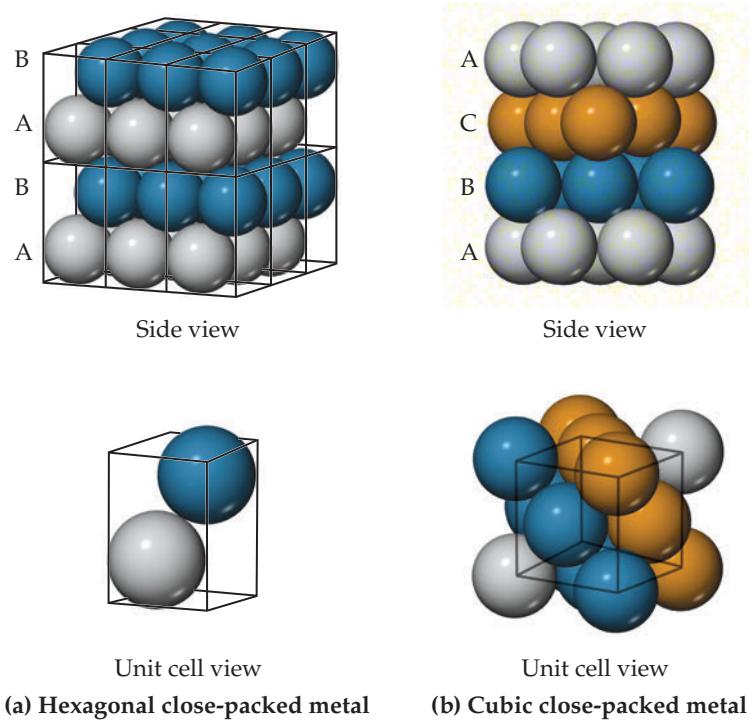
What type of two-dimensional lattice describes the structure of a single layer of close-packed atoms?

**Hexagonal close packing (hcp)****Cubic close packing (ccp)**First layer  
top viewSecond layer  
top viewSpheres sit in depressions  
marked with yellow dots.Spheres sit in depressions  
marked with yellow dots.Third layer  
top viewSpheres sit in depressions  
that lie directly over spheres of  
first layer, ABAB stacking.Spheres sit in depressions  
marked with red dots; centers of  
third-layer spheres offset from centers  
of spheres in first two layers,  
ABCABC stacking.

Side view

A  
B  
AC  
B  
A

**▲ Figure 12.13 Close packing of equal-sized spheres.** Hexagonal (left) close packing and cubic (right) close packing are equally efficient ways of packing spheres. The red and yellow dots indicate the positions of depressions between atoms.



◀ Figure 12.14 The unit cells for (a) a hexagonal close-packed metal and (b) a cubic close-packed metal. The solid lines indicate the unit cell boundaries. Colors are used to distinguish one layer of atoms from another.

The extended structure of a hexagonal close-packed metal is shown in Figure 12.14(a). There are two atoms in the primitive hexagonal unit cell, one from each layer. Neither atom sits directly on the lattice points, which are located at the corners of the unit cell. The presence of two atoms in the unit cell is consistent with the two-layer ABAB stacking sequence associated with hcp packing.

Although it is not immediately obvious, the structure that results from cubic close packing possesses a unit cell that is identical to the face-centered cubic unit cell we encountered earlier [Figure 12.11(c)]. The relationship between the ABC layer stacking and the face-centered cubic unit cell is shown in Figure 12.14(b). In this figure, we see that the layers stack perpendicular to the body diagonal of the cubic unit cell.

### Sample Exercise 12.1

#### Calculating Packing Efficiency

It is not possible to pack spheres together without leaving some void spaces between the spheres. *Packing efficiency* is the fraction of space in a crystal that is actually occupied by atoms. Determine the packing efficiency of a face-centered cubic metal.

#### SOLUTION

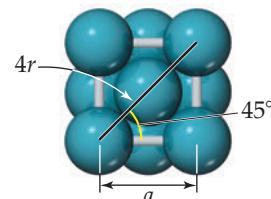
**Analyze** We must determine the volume taken up by the atoms that reside in the unit cell and divide this number by the volume of the unit cell.

**Plan** We can calculate the volume taken up by atoms by multiplying the number of atoms per unit cell by the volume of a sphere,  $4\pi r^3/3$ . To determine the volume of the unit cell, we must first identify the direction along which the atoms touch each other. We can then use geometry to express the length of the cubic unit cell edge,  $a$ , in terms of the radius of the atoms. Once we know the edge length, the cell volume is simply  $a^3$ .

**Solve** As shown in Figure 12.12, a face-centered cubic metal has four atoms per unit cell. Therefore, the volume occupied by the atoms is

$$\text{Occupied volume} = 4 \times \left( \frac{4\pi r^3}{3} \right) = \frac{16\pi r^3}{3}$$

For a face-centered cubic metal, the atoms touch along the diagonal of a face of the unit cell:



Therefore, a diagonal across a face of the unit cell is equal to four times the atomic radius,  $r$ . Using simple trigonometry, and the identity  $\cos(45^\circ) = \sqrt{2}/2$ , we can show that

$$a = 4r \cos(45^\circ) = 4r(\sqrt{2}/2) = (2\sqrt{2})r$$

Finally, we calculate the packing efficiency by dividing the volume occupied by atoms by the volume of the cubic unit cell,  $a^3$ :

$$\begin{aligned} \text{Packing efficiency} &= \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{\left(\frac{16}{3}\pi r^3\right)}{(2\sqrt{2})^3 r^3} \\ &= 0.74 \text{ or } 74\% \end{aligned}$$

*Continued*

### ► Practice Exercise

Consider the two-dimensional square lattice of Figure 12.4. The “packing efficiency” for a two-dimensional structure would be the area of the atoms divided by the area of the

unit cell, times 100%. What is the packing efficiency for a square lattice for atoms of radius  $a/2$  that are centered at the lattice points?

- (a) 3.14% (b) 15.7% (c) 31.8% (d) 74.0% (e) 78.5%

## Alloys

An **alloy** is a material that contains more than one element and has the characteristic properties of a metal. The alloying of metals is of great importance because it is one of the primary ways of modifying the properties of pure metallic elements. Nearly all the common uses of iron, for example, involve alloy compositions (for example, stainless steel). Bronze is formed by alloying copper and tin, while brass is an alloy of copper and zinc. Pure gold is too soft to be used in jewelry, but alloys of gold are much harder (see “Chemistry Put to Work: Alloys of Gold”). Other common alloys are described in [Table 12.2](#).

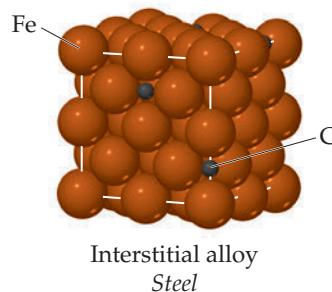
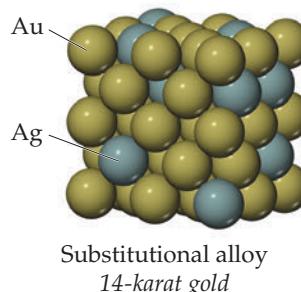
Alloys can be divided into four categories: substitutional alloys, interstitial alloys, heterogeneous alloys, and intermetallic compounds. Substitutional and interstitial alloys are both homogeneous mixtures in which components are dispersed randomly and uniformly ([Figure 12.15](#)). Solids that form homogeneous mixtures are called solid solutions. When atoms of the solute in a solid solution occupy positions normally occupied by a solvent atom, we have a **substitutional alloy**. When the solute atoms occupy interstitial positions in the “holes” between solvent atoms, we have an **Interstitial alloy** ([Figure 12.15](#)).

**TABLE 12.2 Some Common Alloys**

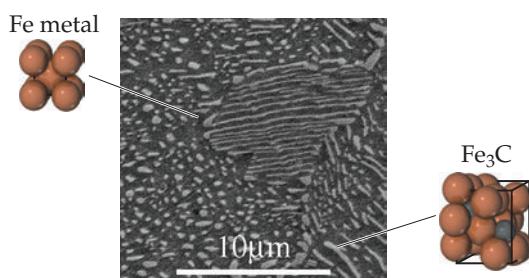
Name	Primary Element	Typical Composition (by Mass)	Properties	Uses
Wood's metal	Bismuth	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70 °C)	Fuse plugs, automatic sprinklers
Yellow brass	Copper	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for early civilizations
Stainless steel	Iron	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Cookware, surgical instruments
Plumber's solder	Lead	67% Pb, 33% Sn	Low melting point (275 °C)	Soldering joints
Sterling silver	Silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Dental amalgam	Silver	70% Ag, 18% Sn, 10% Cu, 2% Hg	Easily worked	Dental fillings
Pewter	Tin	92% Sn, 6% Sb, 2% Cu	Low melting point (230 °C)	Dishes, jewelry

### Go Figure

What determines which species in a solid solution is the solute and which is the solvent?



▲ **Figure 12.15** The distribution of solute and solvent atoms in a substitutional alloy and an interstitial alloy. Both types of alloys are solid solutions and, therefore, homogeneous mixtures.



◀ **Figure 12.16** Microscopic view of the structure of the heterogeneous alloy pearlite. The dark regions are body-centered cubic iron metal, and the lighter regions are cementite,  $\text{Fe}_3\text{C}$ .

Substitutional alloys are formed when the two metallic components have similar atomic radii and chemical-bonding characteristics. For example, silver and gold form such an alloy over the entire range of possible compositions. When two metals differ in radii by more than about 15%, solubility is generally more limited.

For an interstitial alloy to form, the solute atoms must have a much smaller bonding atomic radius than the solvent atoms. Typically, the interstitial element is a non-metal that makes covalent bonds to the neighboring metal atoms. The presence of the extra bonds provided by the interstitial component causes the metal lattice to become harder, stronger, and less ductile. For example, steel, which is much harder and stronger than pure iron, is an alloy of iron that contains up to 3% carbon. Other elements may be added to form *alloy steels*. Vanadium and chromium may be added to impart strength, for instance, and to increase resistance to fatigue and corrosion.

One of the most important iron alloys is stainless steel, which contains about 0.4% carbon, 18% chromium, and 1% nickel. The ratio of elements present in the steel may vary over a wide range, imparting a variety of specific physical and chemical properties to the materials.

In a **heterogeneous alloy**, the components are not dispersed uniformly. For example, the heterogeneous alloy pearlite contains two phases (Figure 12.16). One phase is essentially pure body-centered cubic iron, and the other is the compound  $\text{Fe}_3\text{C}$ , known as cementite. In general, the properties of heterogeneous alloys depend on both the composition and the manner in which the solid is formed from the molten mixture. The properties of a heterogeneous alloy formed by rapid cooling of a molten mixture, for example, are distinctly different from the properties of an alloy formed by slow cooling of the same mixture.

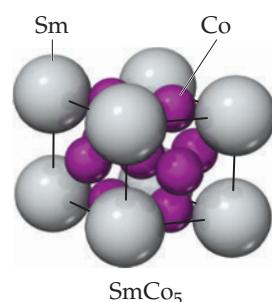
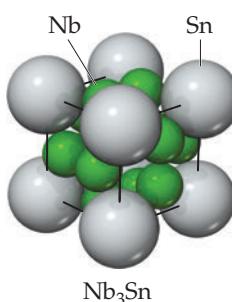
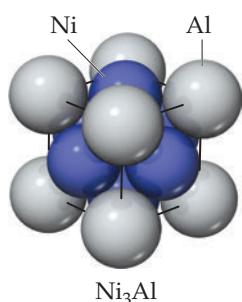
**Intermetallic compounds** are compounds rather than mixtures. Because they are compounds, they have definite properties and their composition cannot be varied. Furthermore, the different types of atoms in an intermetallic compound are ordered rather than randomly distributed. The ordering of atoms in an intermetallic compound generally leads to better structural stability and higher melting points than what is observed in the constituent metals. These features can be attractive for high-temperature applications. On the negative side, intermetallic compounds are often more brittle than substitutional alloys.

Intermetallic compounds play many important roles in modern society. The intermetallic compound  $\text{Ni}_3\text{Al}$  is a major component of jet aircraft engines because of



### Go Figure

In the unit cell drawing on the right, why do we see eight Sm atoms and nine Co atoms if the empirical formula is  $\text{SmCo}_5$ ?



▲ **Figure 12.17** Three examples of intermetallic compounds.

its strength at high temperature and its low density. Razor blades are often coated with Cr<sub>3</sub>Pt, which adds hardness, allowing the blade to stay sharp longer. Both compounds have the structure shown on the left-hand side of Figure 12.17. The compound Nb<sub>3</sub>Sn, also shown in Figure 12.17, is a superconductor, a substance that, when cooled below a critical temperature, conducts electricity with no resistance. In the case of Nb<sub>3</sub>Sn superconductivity is observed only when the temperature falls below 18 K. Superconductors are used in the magnets in MRI scanners widely employed for medical imaging. The need to keep the magnets cooled to such a low temperature is part of the reason why MRI devices are expensive to operate. The hexagonal intermetallic compound SmCo<sub>5</sub>, shown on the right-hand side of Figure 12.17, is used to make the permanent magnets found in lightweight headsets and high-fidelity speakers. A related compound with the same structure, LaNi<sub>5</sub>, is used as the anode in nickel-metal hydride batteries.

## CHEMISTRY PUT TO WORK

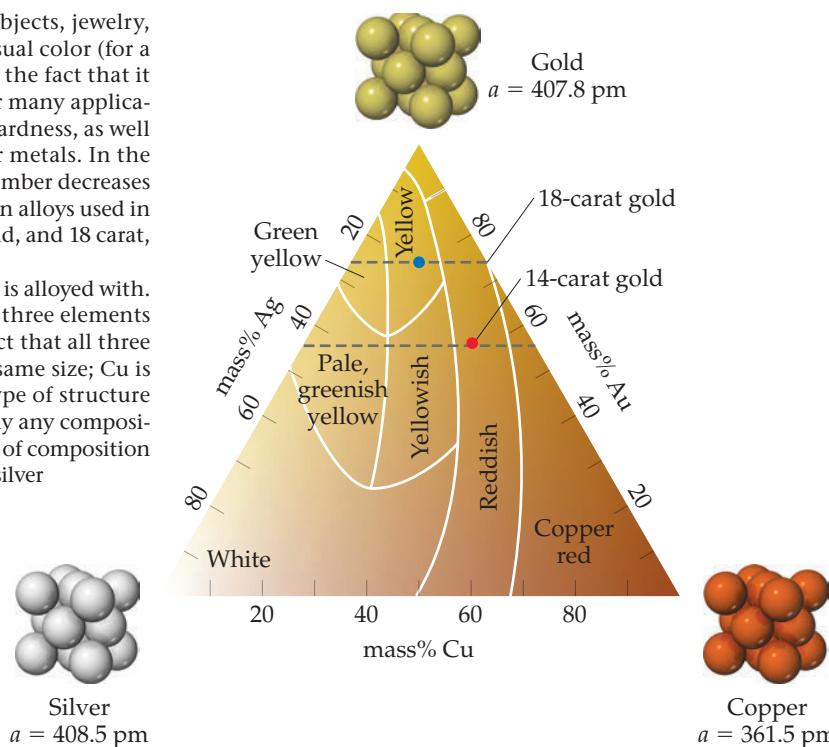
### Alloys of Gold

Gold has long been a metal of choice for decorative objects, jewelry, and coins. The popularity of gold is driven by its unusual color (for a metal), its resistance to many chemical reactions, and the fact that it can easily be worked. However, pure gold is too soft for many applications, including jewelry. To increase its strength and hardness, as well as to modify its color, gold is often alloyed with other metals. In the jewelry trade pure gold is termed 24 carat. The carat number decreases as the mass percent of gold decreases. The most common alloys used in jewelry are 14 carat, which is  $(14/24) \times 100 = 58\%$  gold, and 18 carat, which is  $(18/24) \times 100 = 75\%$  gold.

The color of gold varies depending on the metals it is alloyed with. Gold is typically alloyed with silver and/or copper. All three elements crystallize with a face-centered cubic structure. The fact that all three elements have similar radii (Au and Ag are nearly the same size; Cu is roughly 11% smaller) and crystallize with the same type of structure make it possible to form substitutional alloys with nearly any composition. The variations in color of these alloys as a function of composition are shown in Figure 12.18. Gold alloyed with equal parts silver and copper (blue dot) takes on the golden yellow color we associate with 18-carat gold jewelry. Red (14-carat) or rose gold is a copper-rich alloy (red dot). Silver-rich alloys take on a greenish hue, eventually giving way to silvery-white colors as silver becomes the majority constituent.

**Related Exercises:** 12.17, 12.78, 12.124

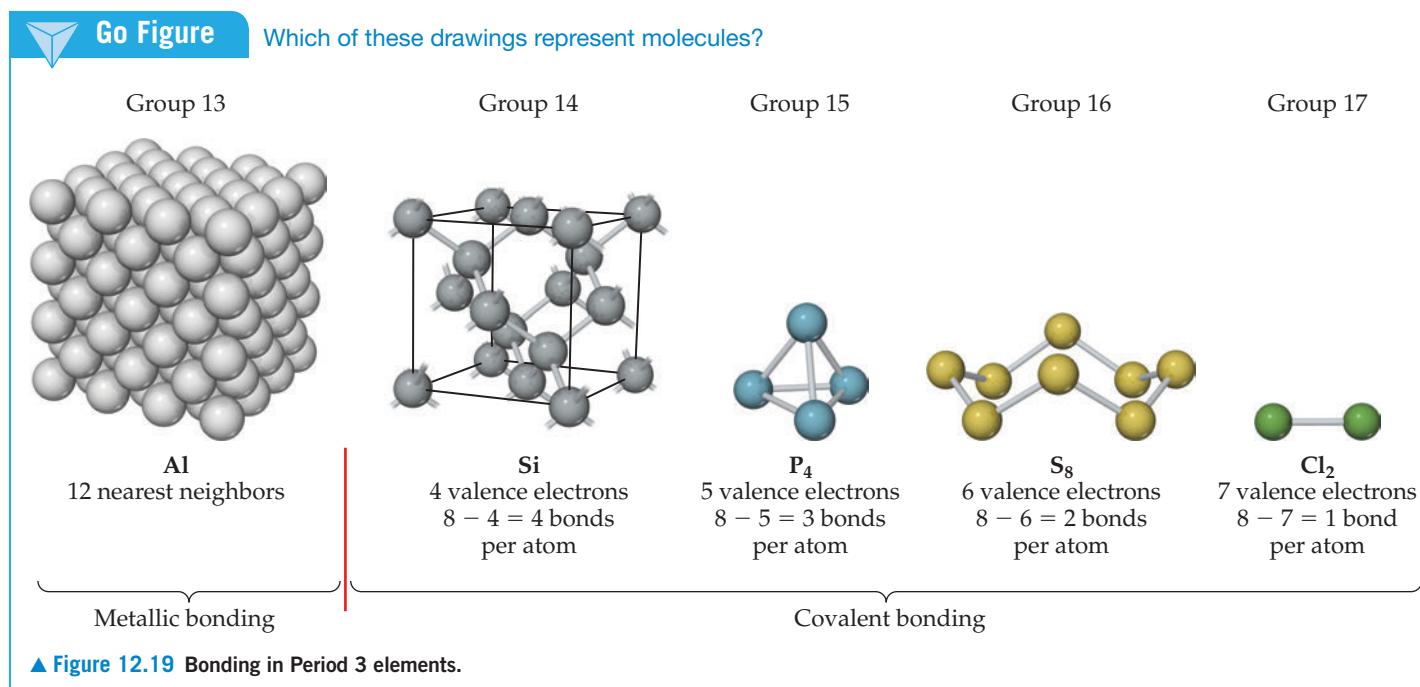
► **Figure 12.18** Colors of Au–Ag–Cu alloys as a function of composition.



## Metallic Bonding

Consider the elements of the third period of the periodic table (Na–Ar). Argon with eight valence electrons has a complete octet; as a result it does not form any bonds. Chlorine, sulfur, and phosphorus form molecules (Cl<sub>2</sub>, S<sub>8</sub>, and P<sub>4</sub>) in which the atoms make one, two, and three bonds, respectively (Figure 12.19). Silicon forms an extended network solid in which each atom is bonded to four equidistant neighbors. Each of these elements forms  $8 - N$  bonds, where  $N$  is the number of valence electrons. This behavior can easily be understood through the application of the octet rule.

If the  $8 - N$  trend continued as we move left across the periodic table, we would expect aluminum (three valence electrons) to form five bonds. Like many other metals, however, aluminum adopts a close-packed structure with 12 nearest neighbors. Magnesium and sodium also adopt metallic structures. What is responsible for this abrupt change in the preferred bonding mechanism? The answer, as noted earlier, is that metals do not have enough valence-shell electrons to satisfy their bonding requirements by forming localized electron-pair bonds. In response to this deficiency, the valence electrons are collectively shared. A structure in which the atoms are close-packed facilitates this delocalized sharing of electrons.



### Electron-Sea Model

A simple model that accounts for some of the most important characteristics of metals is the **electron-sea model**, which pictures the metal as an array of metal cations in a “sea” of valence electrons (Figure 12.20). The electrons are confined to the metal by electrostatic attractions to the cations, and they are uniformly distributed throughout the structure. The electrons are mobile, however, and no individual electron is confined to any particular metal ion. When a voltage is applied to a metal wire, the electrons, being negatively charged, flow through the metal toward the positively charged end of the wire.

The high thermal conductivity of metals is also accounted for by the presence of mobile electrons. The movement of electrons in response to temperature gradients permits ready transfer of kinetic energy throughout the solid.

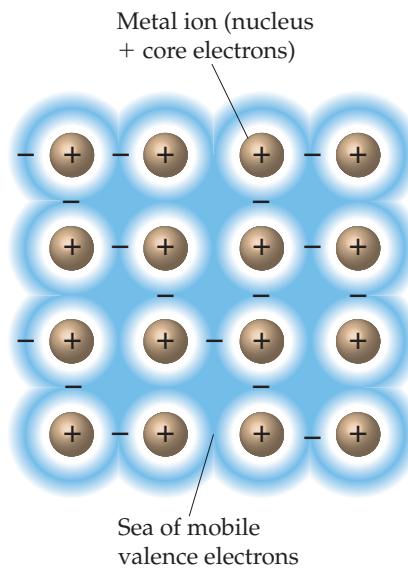
The ability of metals to deform (their malleability and ductility) can be explained by the fact that metal atoms form bonds to many neighbors. Changes in the positions of the atoms brought about in reshaping the metal are partly accommodated by a redistribution of electrons.

### Molecular Orbital Model

Although the electron-sea model works surprisingly well given its simplicity, it does not adequately explain many properties of metals. According to the model, for example, the strength of bonding between metal atoms should steadily increase as the number of valence electrons increases, resulting in a corresponding increase in the melting points. However, elements near the middle of the transition metal series, rather than those at the end, have the highest melting points in their respective periods (Figure 12.21). This trend implies that the strength of metallic bonding first increases with increasing number of electrons and then decreases. Similar trends are seen in other physical properties of the metals, such as the boiling point, heat of fusion, and hardness.

To obtain a more accurate picture of the bonding in metals, we must turn to molecular orbital theory. In Sections 9.7 and 9.8, we learned how molecular orbitals are created from the overlap of atomic orbitals. Let's briefly review some of the rules of molecular orbital theory:

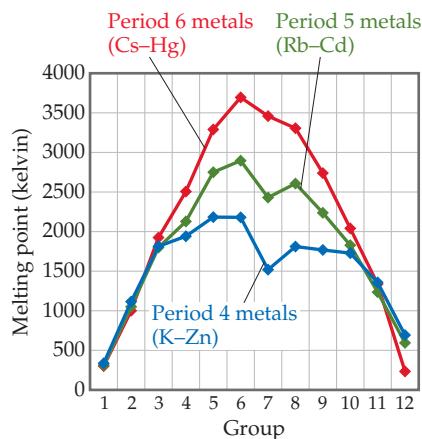
1. Atomic orbitals combine to make molecular orbitals that can extend over the entire molecule.
2. A molecular orbital can contain zero, one, or two electrons.



▲ Figure 12.20 Electron-sea model of metallic bonding. The valence electrons delocalize to form a sea of mobile electrons that surrounds and binds together an extended array of metal ions.

### Go Figure

Which element in each period has the highest melting point? In each case, is the element you named at the beginning, middle, or end of its period?



▲ Figure 12.21 The melting points of metals from Periods 4, 5, and 6.

- The number of molecular orbitals in a molecule equals the number of atomic orbitals that combine to form molecular orbitals.
- Adding electrons to a bonding molecular orbital strengthens bonding, while adding electrons to antibonding molecular orbitals weakens bonding.

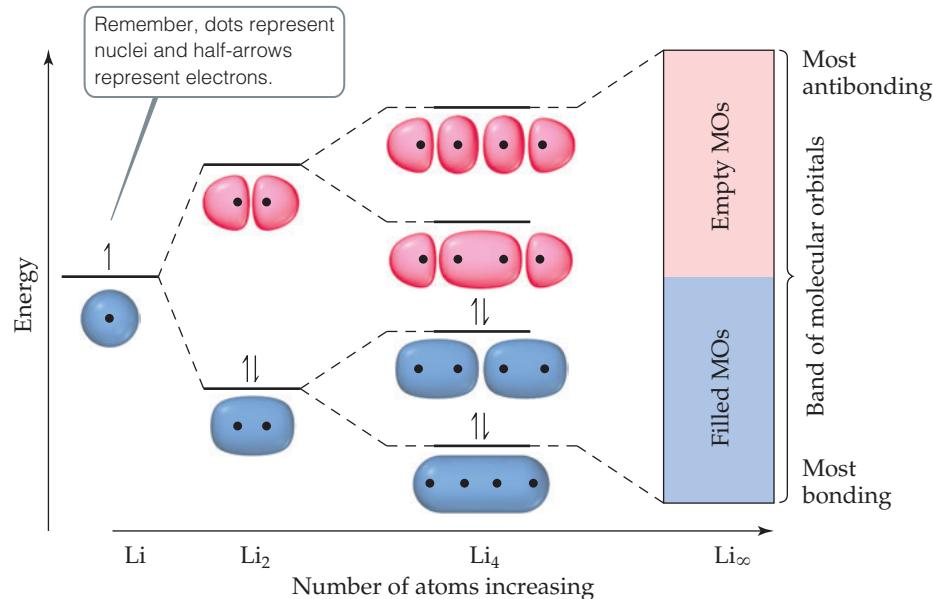
The electronic structures of crystalline solids and small molecules have similarities as well as differences. To illustrate, consider how the molecular orbital diagram for a chain of lithium atoms changes as we increase the length of the chain (Figure 12.22). Each lithium atom contains a half-filled 2s orbital in its valence shell. The molecular-orbital diagram for  $\text{Li}_2$  is analogous to that of an  $\text{H}_2$  molecule: one filled bonding molecular orbital and one empty antibonding molecular orbital with a nodal plane between the atoms. For  $\text{Li}_4$ , there are four molecular orbitals, ranging from the lowest-energy orbital, where the orbital interactions are completely bonding (zero nodal planes), to the highest-energy orbital, where all interactions are antibonding (three nodal planes).

As the length of the chain increases, the number of molecular orbitals increases. Regardless of chain length, the lowest-energy orbitals are always the most bonding and the highest-energy orbitals always the most antibonding. Furthermore, because each lithium atom has only one valence shell atomic orbital, the number of molecular orbitals is equal to the number of lithium atoms in the chain. Because each lithium atom has one valence electron, half of the molecular orbitals are fully occupied and the other half are empty, regardless of chain length.\*

**Electronic Band Structure** If the chain becomes very long, there are so many molecular orbitals that the energy separation between them becomes vanishingly small. As the chain length goes to infinity, the allowed energy states become a continuous **band**. For a crystal large enough to see with the eye (or even an optical microscope), the number of atoms is extremely large. Consequently, the electronic structure of the crystal is like that of the infinite chain, consisting of bands, as shown on the right-hand side of Figure 12.22.

### Go Figure

How does the energy spacing between molecular orbitals change as the number of atoms in the chain increases?

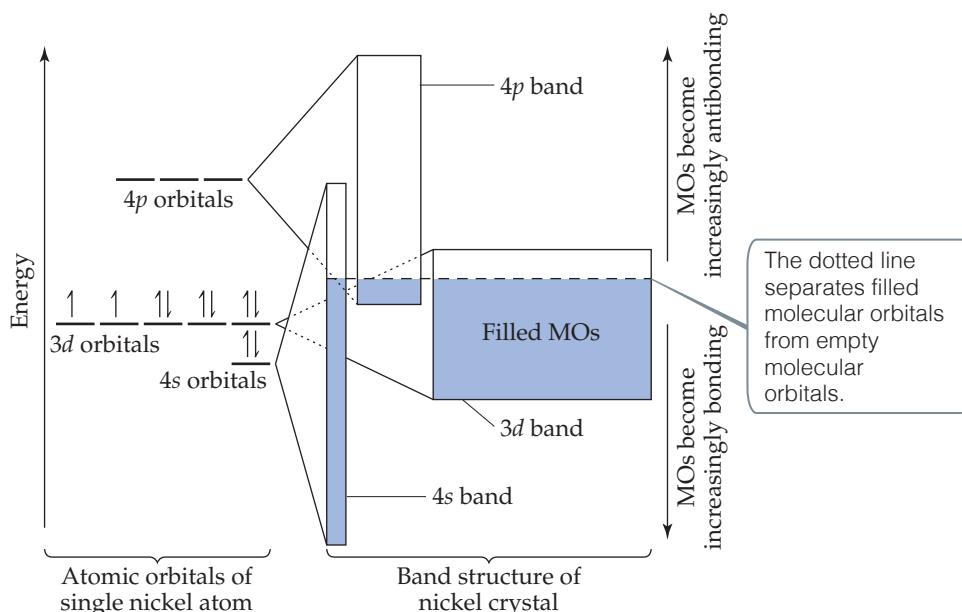


▲ Figure 12.22 Discrete energy levels in individual molecules become continuous energy bands in a solid. Occupied orbitals are shaded blue, and empty orbitals pink.

\*This is strictly true only for chains with an even number of atoms.


**Go Figure**

If the metal were potassium rather than nickel, which bands—4s, 4p, and/or 3d—would be partially occupied?



▲ Figure 12.23 The electronic band structure of nickel.

The electronic structures of most metals are more complicated than those shown in Figure 12.22 because we have to consider more than one type of atomic orbital on each atom. Because each type of orbital can give rise to its own band, the electronic structure of a solid usually consists of a series of bands. The electronic structure of a bulk solid is referred to as a **band structure**.

The band structure of a typical metal is shown schematically in Figure 12.23. The electron filling depicted corresponds to nickel metal, but the basic features of other metals are similar. The electron configuration of a nickel atom is  $[Ar]4s^23d^8$ , as shown on the left side of the figure. The energy bands that form from each of these orbitals are shown on the right side. The 4s, 4p, and 3d orbitals are treated independently, each giving rise to a band of molecular orbitals. In practice, these overlapping bands are not completely independent of each other, but for our purposes this simplification is reasonable.

The 4s, 4p, and 3d bands differ from one another in the energy range they span (represented by the heights of the rectangles on the right side of Figure 12.23) and in the number of electrons they can hold (represented by the area of the rectangles). The 4s, 4p, and 3d bands can hold 2, 6, and 10 electrons per atom, respectively, corresponding to two per orbital, as dictated by the Pauli exclusion principle. The energy range spanned by the 3d band is smaller than the range spanned by the 4s and 4p bands because the 3d orbitals are smaller and, therefore, overlap with orbitals on neighboring atoms less effectively.

Many properties of metals can be understood from Figure 12.23. We can think of the energy band as a partially filled container for electrons. The incomplete filling of the energy band gives rise to characteristic metallic properties. The electrons in orbitals near the top of the occupied levels require very little energy input to be “promoted” to higher-energy orbitals that are unoccupied. Under the influence of any source of excitation, such as an applied electrical potential or an input of thermal energy, electrons move into previously vacant levels and are thus freed to move through the lattice, giving rise to electrical and thermal conductivity.

Without the overlap of energy bands, the periodic properties of metals could not be explained. In the absence of the d- and p-bands, we would expect the s-band to be half-filled for the alkali metals (Group 1) and completely filled for the alkaline-earth metals (Group 2). If that were true, metals like magnesium, calcium, and strontium would

not be good electrical and thermal conductors, in disagreement with experimental observations.

While the conductivity of metals can be qualitatively understood using either the electron-sea model or the molecular orbital model, many physical properties of transition metals, such as the melting points plotted in Figure 12.21, can be explained only with the latter model. The molecular orbital model predicts that bonding first becomes stronger as the number of valence electrons increases and the bonding orbitals are increasingly populated. Upon moving past the middle elements of the transition metal series, the bonds grow weaker as electrons populate antibonding orbitals. Strong bonds between atoms lead to metals with higher melting and boiling points, higher heats of fusion, higher hardness, and so forth.

## Self-Assessment Exercises

**12.12** Sterling silver is 92.5% silver and 7.5% copper. Both pure metals crystallize with a face-centered cubic structure. What sort of alloy is sterling silver?

- (a) Substitution alloy
- (b) Interstitial alloy
- (c) Heterogeneous alloy
- (d) Intermetallic compound

**12.13** Which element, Pt or Re, has the greater number of electrons in antibonding orbitals? Which one would you expect to have the higher melting point?

- (a) Pt has the greater number of electrons in antibonding orbitals and the lower melting point
- (b) Pt has the greater number of electrons in antibonding orbitals and the higher melting point
- (c) Re has the greater number of electrons in antibonding orbitals and the lower melting point
- (d) Re has the greater number of electrons in antibonding orbitals and the higher melting point

## Exercises

**12.14** The densities of the elements Cr, Mn, Fe, and Cu are 7.15, 7.30, 7.87, and 8.96 g/cm<sup>3</sup>, respectively. One of these elements crystallizes in a face-centered cubic structure; the other three crystallize in a body-centered cubic structure. Which one crystallizes in the face-centered cubic structure? Justify your answer.

**12.15** Barium crystallizes in a body-centered cubic structure. (a) How many Ba atoms are contained in each unit cell? (b) How many nearest neighbors does each Ba atom possess? (c) Estimate the length of the unit cell edge, *a*, from the atomic radius of barium (0.215 nm). (d) Estimate the density of Ba metal at this temperature.

**12.16** Determine if each statement is true or false: (a) Substitutional alloys are solid solutions, but interstitial alloys are heterogeneous alloys. (b) Substitutional alloys have “solute” atoms that replace “solvent” atoms in a lattice, but interstitial alloys have “solute” atoms that are in between the “solvent” atoms in a lattice. (c) The atomic radii of the atoms in a substitutional alloy are similar to each other, but in an interstitial alloy, the interstitial atoms are a lot smaller than the host lattice atoms.

**12.17** For each of the following alloy compositions, indicate whether you would expect it to be a substitutional alloy, an interstitial alloy, or an intermetallic compound:

- (a) Cu<sub>0.66</sub>Zn<sub>0.34</sub>, (b) Ag<sub>3</sub>Sn, (c) Ti<sub>0.99</sub>O<sub>0.01</sub>.

**12.18** Indicate whether each statement is true or false:

- (a) Intermetallic compounds have a fixed composition.
- (b) Copper is the majority component in both brass and bronze.
- (c) In stainless steel, the chromium atoms occupy interstitial positions.

**12.19** Imagine that you have a metal bar sitting half in the sun and half in the dark. On a sunny day, the part of the metal that has been sitting in the sun feels hot. If you touch the part of the metal bar that has been sitting in the dark, will it feel hot or cold? Justify your answer in terms of thermal conductivity.

**12.20** The molecular-orbital diagrams for two- and four-atom linear chains of lithium atoms are shown in Figure 12.22. Construct a molecular-orbital diagram for a chain containing six lithium atoms and use it to answer the following questions: (a) How many molecular orbitals are there in the diagram? (b) How many nodes are in the lowest-energy molecular orbital? (c) How many nodes are in the highest-energy molecular orbital? (d) How many nodes are in the highest-energy occupied molecular orbital (HOMO)? (e) How many nodes are in the lowest-energy unoccupied molecular orbital (LUMO)? (f) How does the HOMO-LUMO energy gap for this case compare to that of the four-atom case?

**12.21** Which would you expect to be the more ductile element, (a) Ag or Cr, (b) Zn or Ge? In each case, explain your reasoning.

12.12 (a)    12.13 (a)



## 12.3 | Ionic Solids



A piezoelectric crystal responds to applied pressure by generating a voltage difference across two crystal faces. The effect works in both directions as an applied voltage can cause a deformation of the crystal structure by up to 0.1%. There are many applications that utilize the piezoelectric effect including gas ignition lighters, sonar, balances for weighing, ultrasound nozzles, ink-jet printers, amplification ‘pick-ups’ for musical instruments, clock generators to synchronize computer circuit boards and probes for scanning microscopes. While there is a wide range of types of material that show a piezoelectric effect, Rochelle salt (potassium sodium tartrate) was used in the early days for gramophone pick-ups as well as microphones and earpieces where the crystal could have an output of as much as 2 V. Unfortunately, the salt absorbs water easily and deteriorated quickly in humid climates.

In this section, we examine the crystal structures of ionic solids, and, by the end of the section, you should be able to

- Relate the structure of an ionic solid to its empirical formula

**Ionic solids** are held together by the electrostatic attraction between cations and anions: ionic bonds. The high melting and boiling points of ionic compounds are a testament to the strength of the ionic bonds. The strength of an ionic bond depends on the charges and sizes of the ions. As discussed in Chapters 8 and 11, the attractions between cations and anions increase as the charges of the ions increase. Thus NaCl, where the ions have charges of 1+ and 1–, melts at 801 °C, whereas MgO, where the ions have charges of 2+ and 2–, melts at 2852 °C. The interactions between cations and anions also increase as the ions get smaller, as we see from the melting points of the alkali metal halides in [Table 12.3](#). These trends mirror the trends in lattice enthalpy discussed in Section 8.2.

Although ionic and metallic solids both have high melting and boiling points, the differences between ionic and metallic bonding are responsible for important differences in their properties. Because the valence electrons in ionic compounds are confined to the anions, rather than being delocalized, ionic compounds are typically electrical insulators. They tend to be brittle, a property explained by repulsive interactions between ions of like charge. When stress is applied to an ionic solid, as in [Figure 12.24](#), the planes of

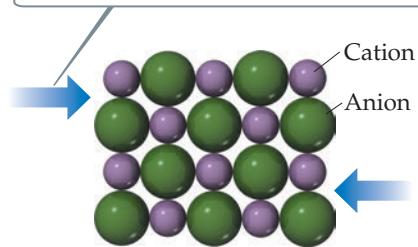
**TABLE 12.3 Properties of the Alkali Metal Halides**

Compound	Cation–Anion Distance (pm)	Lattice Enthalpy (kJ/mol)	Melting Point (°C)
LiF	201	1030	845
NaCl	283	788	801
KBr	330	671	734
RbI	367	632	674

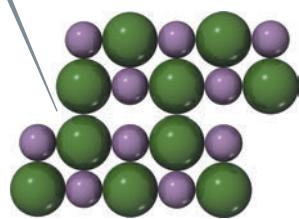
## Go Figure

Why don't metals cleave in the way depicted here for ionic substances?

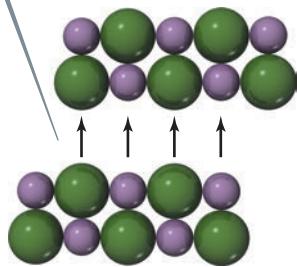
- 1 A shear stress is applied to an ionic crystal.



- 2 Planes of atoms slide in response to stress.



- 3 Repulsive interactions between ions of like charge lead to separation of the layers.



(a)



(b)

▲ **Figure 12.24** Brittleness and faceting in ionic crystals.

(a) When a shear stress (blue arrows) is applied to an ionic solid, the crystal separates along a plane of atoms as shown. (b) This property of ionic crystals is used to facet gemstones, such as rubies.

atoms, which before the stress were arranged with cations next to anions, shift so that the alignment becomes cation–cation, anion–anion. The resulting repulsive interaction causes the planes to split away from each other, a property that lends itself to the carving of certain gemstones (such as ruby, composed principally of  $\text{Al}_2\text{O}_3$ ).

## Structures of Ionic Solids

Like metallic solids, ionic solids tend to adopt structures with symmetric, close-packed arrangements of atoms. However, important differences arise because we now have to pack together spheres that have different radii and opposite charges. Because cations are often considerably smaller than anions, the coordination numbers in ionic compounds are smaller than those in close-packed metals. Even if the anions and cations were the same size, the close-packed arrangements seen in metals cannot be replicated without letting ions of like charge come in contact with each other. The repulsions between ions of the same type make such arrangements unfavorable. The most favorable structures are those where the cation–anion distances are as close as those permitted by ionic radii, but the anion–anion and cation–cation distances are maximized.

Three common ionic structure types are shown in **Figure 12.25**. The cesium chloride ( $\text{CsCl}$ ) structure is based on a primitive cubic lattice. Anions sit on the lattice points at the corners of the unit cell, and a cation sits at the center of each cell. (Remember, there is no lattice point inside a primitive unit cell.) With this arrangement, both cations and anions are surrounded by a cube of eight ions of the opposite type.

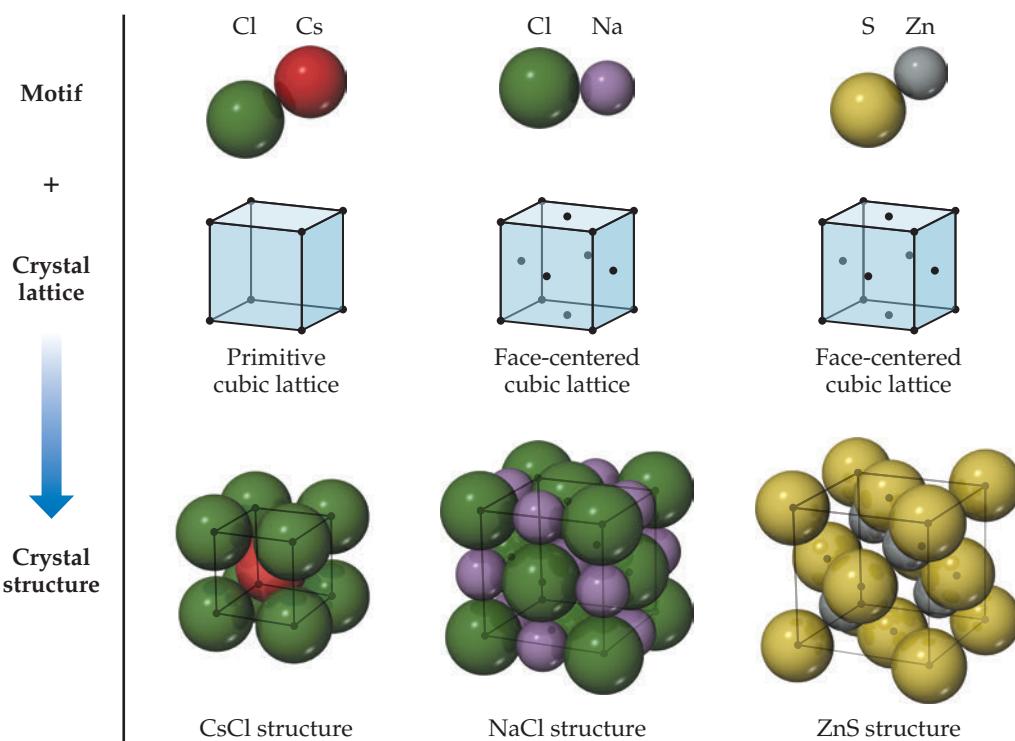
The sodium chloride ( $\text{NaCl}$ ; also called the rock salt structure) and zinc blende ( $\text{ZnS}$ ) structures are based on a face-centered cubic lattice. In both structures the anions sit on the lattice points that lie on the corners and faces of the unit cell, but the two-atom motif is slightly different for the two structures. In  $\text{NaCl}$  the  $\text{Na}^+$  ions are displaced from the  $\text{Cl}^-$  ions along the edge of the unit cell, whereas in  $\text{ZnS}$  the  $\text{Zn}^{2+}$  ions are displaced from the  $\text{S}^{2-}$  ions along the body diagonal of the unit cell. This difference leads to different coordination numbers. In sodium chloride, each cation and each anion are surrounded by six ions of the opposite type, leading to an octahedral coordination environment. In zinc blende, each cation and each anion are surrounded by four ions of the opposite type, leading to a tetrahedral coordination geometry. The cation coordination environments can be seen in **Figure 12.26**.

For a given ionic compound, we might ask which type of structure is most favorable. A number of factors come into play, but two of the most important are the relative sizes of the ions and the stoichiometry. Consider first ion size. Notice in **Figure 12.26** that the coordination number changes from 8 to 6 to 4 on moving from  $\text{CsCl}$  to  $\text{NaCl}$  to  $\text{ZnS}$ . This trend is driven in part by the fact that for these three compounds the ionic radius of the cation gets smaller while the ionic radius of the anion changes very little. When the cation and anion are similar in size, a large coordination number is favored and the  $\text{CsCl}$  structure is often realized. As the relative size of the cation gets smaller, eventually it is no longer possible to maintain the cation–anion contacts and simultaneously keep the anions from touching each other. When this occurs, the coordination number drops from 8 to 6, and the sodium chloride structure becomes more favorable. As the cation size decreases further, eventually the coordination number must be reduced again, this time from 6 to 4, and the zinc blende structure becomes favored. Remember that, in ionic crystals, ions of opposite charge touch each other but ions of the same charge should not touch.

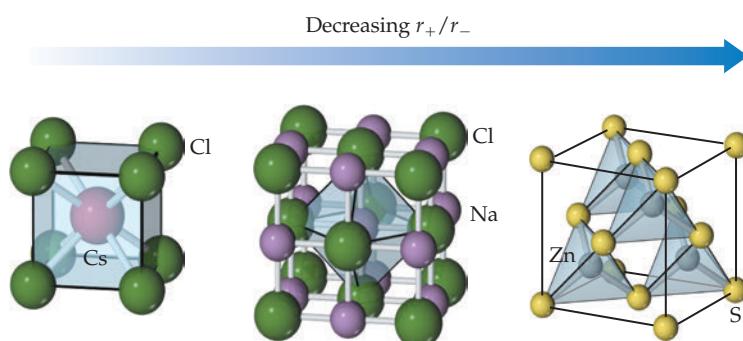
The relative number of cations and anions also helps determine the most stable structure type. All the structures in **Figure 12.26** have equal numbers of cations and anions. These structure types (cesium chloride, sodium chloride, zinc blende) can be realized only for ionic compounds in which the number of cations and anions is equal. When this is not the case, other crystal structures must result.

 Go Figure

Do the anions touch each other in any of these three structures? If not, which ions do touch each other?



▲ Figure 12.25 The structures of CsCl, NaCl, and ZnS. Each structure type can be generated by the combination of a two-atom motif and the appropriate lattice.



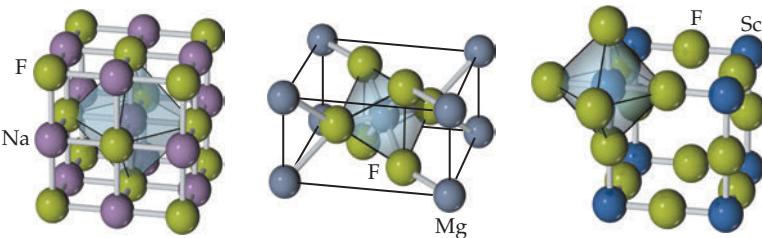
	CsCl	NaCl	ZnS
Cation radius, $r_+$ (pm)	181	116	88
Anion radius, $r_-$ (pm)	167	167	170
$r_+/r_-$	1.08	0.69	0.52
Cation coordination number	8	6	4
Anion coordination number	8	6	4

▲ Figure 12.26 Coordination environments in CsCl, NaCl, and ZnS. The sizes of the ions have been reduced to show the coordination environments clearly.

**Go Figure**

How many cations are there per unit cell for each of these structures?  
How many anions per unit cell?

Increasing anion-to-cation ratio



	NaF	MgF <sub>2</sub>	ScF <sub>3</sub>
Cation coordination number	6	6	6
Cation coordination geometry	Octahedral	Octahedral	Octahedral
Anion coordination number	6	3	2
Anion coordination geometry	Octahedral	Trigonal planar	Linear

▲ **Figure 12.27 Coordination numbers depend on stoichiometry.** The sizes of the ions have been reduced to show the coordination environments clearly.

As an example, consider NaF, MgF<sub>2</sub>, and ScF<sub>3</sub> (Figure 12.27). Sodium fluoride has the sodium chloride structure with a coordination number of 6 for both cation and anion, as you might expect since NaF and NaCl are quite similar. Magnesium fluoride, however, has two anions for every cation, resulting in a tetragonal crystal structure called the *rutile structure*. The cation coordination number is still 6, but the fluoride coordination number is now only 3. In the scandium fluoride structure, there are three anions for every cation; the cation coordination number is still 6, but the fluoride coordination number has dropped to 2. As the cation/anion ratio goes down, there are fewer cations to surround each anion, and so the anion coordination number must decrease. The empirical formula of an ionic compound can be described quantitatively by the relationship

$$\frac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \frac{\text{anion coordination number}}{\text{cation coordination number}} \quad [12.1]$$

**Sample Exercise 12.2****Calculating the Density of an Ionic Solid**

Rubidium iodide crystallizes with the same structure as sodium chloride. (a) How many iodide ions are there per unit cell? (b) How many rubidium ions are there per unit cell? (c) Use the ionic radii and molar masses of Rb<sup>+</sup> (166 pm, 85.47 g/mol) and I<sup>-</sup> (206 pm, 126.90 g/mol) to estimate the density of rubidium iodide in g/cm<sup>3</sup>.

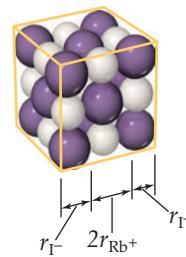
## SOLUTION

### Analyze and Plan

- (a) We need to count the number of anions in the unit cell of the sodium chloride structure, remembering that ions on the corners, edges, and faces of the unit cell are only partially inside the unit cell.
- (b) We can apply the same approach to determine the number of cations in the unit cell. We can double-check our answer by writing the empirical formula to make sure the charges of the cations and anions are balanced.
- (c) Because density is an intensive property, the density of the unit cell is the same as the density of a bulk crystal. To calculate the density we must divide the mass of the atoms per unit cell by the volume of the unit cell. To determine the volume of the unit cell, we need to estimate the length of the unit cell edge by first identifying the direction along which the ions touch and then using ionic radii to estimate the length. Once we have the length of the unit cell edge, we can cube it to determine its volume.

### Solve

- (a) The crystal structure of rubidium iodide looks just like NaCl with Rb<sup>+</sup> ions replacing Na<sup>+</sup> and I<sup>-</sup> ions replacing Cl<sup>-</sup>. From the views of the NaCl structure in Figures 12.25 and 12.26, we see that there is an anion at each corner of the unit cell and at the center of each face. From Table 12.1 we see that the ions sitting on the corners are equally shared by eight unit cells ( $\frac{1}{8}$  ion per unit cell), while those ions sitting on the faces are equally shared by two unit cells ( $\frac{1}{2}$  ion per unit cell). A cube has eight corners and six faces, so the total number of I<sup>-</sup> ions is  $8(\frac{1}{8}) + 6(\frac{1}{2}) = 4$  per unit cell.
- (b) Using the same approach for the rubidium cations, we see that there is a rubidium ion on each edge and one at the center of the unit cell. Using Table 12.1 again, we see that the ions sitting on the edges are equally shared by four unit cells (1/4 ion per unit cell), whereas the cation at the center of the unit cell is not shared. A cube has 12 edges, so the total number of rubidium ions is  $12(\frac{1}{4}) + 1 = 4$ . This answer makes sense because the number of Rb<sup>+</sup> ions must be the same as the number of I<sup>-</sup> ions to maintain charge balance.
- (c) In ionic compounds, cations and anions touch each other. In RbI the cations and anions touch along the edge of the unit cell as shown in the following figure.



The length of the unit cell edge is equal to  $r(I^-) + 2r(Rb^+) + r(I^-) = 2r(I^-) + 2r(Rb^+)$ . Plugging in the ionic radii we get  $2(206 \text{ pm}) + 2(166 \text{ pm}) = 744 \text{ pm}$ . The volume of a cubic unit cell is just the edge length cubed. Converting from pm to cm and cubing we get

$$\text{Volume} = (7.44 \times 10^{-8} \text{ cm})^3 = 4.12 \times 10^{-22} \text{ cm}^3$$

From parts (a) and (b) we know that there are four rubidium and four iodide ions per unit cell. Using this result and the molar masses, we can calculate the mass per unit cell

$$\text{Mass} = \frac{4(85.47 \text{ g/mol}) + 4(126.90 \text{ g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.411 \times 10^{-21} \text{ g}$$

The density is the mass per unit cell divided by the volume of a unit cell

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{1.411 \times 10^{-21} \text{ g}}{4.12 \times 10^{-22} \text{ cm}^3} = 3.43 \text{ g/cm}^3$$

**Check** The densities of most solids fall between the density of lithium (0.5 g/cm<sup>3</sup>) and that of iridium (22.6 g/cm<sup>3</sup>), so this value is reasonable.

### ► Practice Exercise

Estimate the length of the cubic unit cell edge and the density of CsCl (Figure 12.25) from the ionic radii of cesium, 181 pm, and chloride, 167 pm. (Hint: Ions in CsCl touch along the body diagonal, a vector running from one corner of a cube through the body center to the opposite corner. Using trigonometry it can be shown that the body diagonal of a cube is  $\sqrt{3}$  times longer than the edge.)

## Self-Assessment Exercise

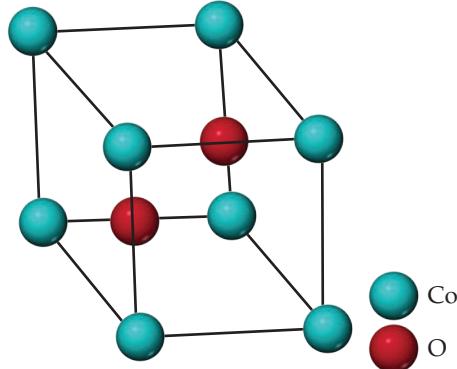
- 12.22 In the crystal of titanium dioxide, the oxide ions are coordinated by three titanium ions. What is the coordination number of titanium?

- (a) 1  
(b) 2

- (c) 3  
(d) 6

## Exercises

- 12.23** The unit cell of a compound containing Co and O has a unit cell as illustrated here. The Co atoms are on the corners, and the O atoms are completely within the unit cell. What is the empirical formula of this compound? What is the oxidation state of the metal?

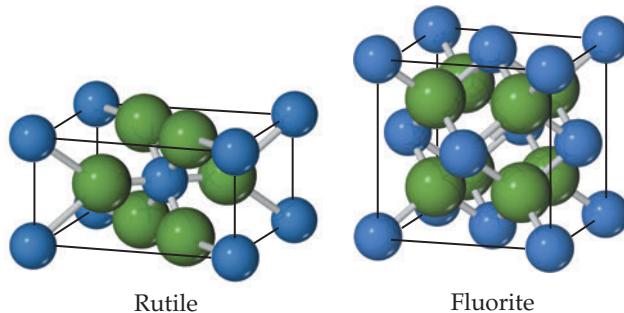


- 12.24** Silver chloride ( $\text{AgCl}$ ) adopts the rock salt structure. The density of  $\text{AgCl}$  at  $25^\circ\text{C}$  is  $5.56 \text{ g/cm}^3$ . Calculate the length of an edge of the  $\text{AgCl}$  unit cell.

- 12.25** At room temperature and pressure  $\text{RbCl}$  crystallizes with the  $\text{NaCl}$ -type structure. **(a)** Use ionic radii to predict the length of the cubic unit cell edge. **(b)** Use this value to estimate the density. **(c)** At high temperature and pressure, the structure transforms to one with a  $\text{CsCl}$ -type structure. Use ionic radii to predict the length of the cubic unit cell edge for the

high-pressure form of  $\text{RbCl}$ . **(d)** Use this value to estimate the density. How does this density compare with the density you calculated in part (b)?

- 12.26** The rutile and fluorite structures, shown here (anions are colored green), are two of the most common structure types of ionic compounds where the cation to anion ratio is 1:2. **(a)** For  $\text{CaF}_2$  and  $\text{ZnF}_2$  use ionic radii,  $\text{Ca}^{2+}$  ( $r = 114 \text{ pm}$ ),  $\text{Zn}^{2+}$  ( $r = 88 \text{ pm}$ ), and  $\text{F}^-$  ( $r = 119 \text{ pm}$ ), to predict which compound is more likely to crystallize with the fluorite structure and which with the rutile structure. **(b)** What are the coordination numbers of the cations and anions in each of these structures?



- 12.27** The coordination number for the  $\text{Al}^{3+}$  ion is typically between four and six. Use the anion coordination number to determine the  $\text{Al}^{3+}$  coordination number in the following compounds: **(a)**  $\text{AlF}_3$  where the fluoride ions are two coordinate, **(b)**  $\text{Al}_2\text{O}_3$  where the oxygen ions are six coordinate, **(c)**  $\text{AlN}$  where the nitride ions are four coordinate.

12.22 (d)

Answers to Self-Assessment Exercise



## 12.4 | Covalent Solids



Diamond was long considered the hardest known substance, but that does not appear to be the case anymore. If you were to investigate very hard substances, you might start by looking at ones that have a similar structure to that of diamond. We have seen that the structure depends on bonding and size. Boron nitride (BN) is a material that is both isostructural and isoelectronic with diamond. Calculations suggest it can withstand about 18% more stress than diamond, but it occurs rarely in nature, so this has yet to be verified on a natural sample. It can be manufactured in the lab and the strength of BN, coupled with a resistance to oxidation at high temperatures, makes it an ideal candidate for cutting and grinding tools and other high-temperature applications.

There are two classes of covalent solid with very different properties. By the end of this section, you should be able to

- Interpret melting point and boiling point data in terms of crystal structure
- Predict how n-type and p-type doping can be used to control the conductivity of semiconductors

## Molecular Solids

**Molecular solids** consist of atoms or neutral molecules held together by dipole–dipole forces, dispersion forces, and/or hydrogen bonds. Because these intermolecular forces are weak, molecular solids are soft and have relatively low melting points (usually below 200 °C). Most substances that are gases or liquids at room temperature form molecular solids at low temperature. Examples include Ar, H<sub>2</sub>O, and CO<sub>2</sub>.

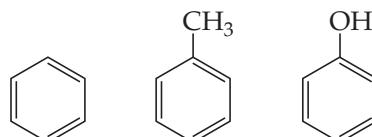
The properties of molecular solids depend in large part on the strengths of the forces between molecules. Consider, for example, the properties of sucrose (table sugar, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>). Each sucrose molecule has eight —OH groups, which allow for the formation of multiple hydrogen bonds. Consequently, sucrose exists as a crystalline solid at room temperature, and its melting point, 184 °C, is relatively high for a molecular solid.

Molecular shape is also important because it dictates how efficiently molecules pack together in three dimensions. Benzene (C<sub>6</sub>H<sub>6</sub>), for example, is a highly symmetrical planar molecule. It has a higher melting point than toluene, a compound in which one of the hydrogen atoms of benzene has been replaced by a CH<sub>3</sub> group (**Figure 12.28**). The lower symmetry of toluene molecules prevents them from packing in a crystal as efficiently as benzene molecules. As a result, the intermolecular forces that depend on close contact are not as effective and the melting point is lower. In contrast, the boiling point of toluene is *higher* than that of benzene, indicating that the intermolecular attractive forces are larger in liquid toluene than in liquid benzene. The melting and boiling points of phenol, another substituted benzene shown in Figure 12.28, are higher than those of benzene because the OH group of phenol can form hydrogen bonds.



### Go Figure

In which substance, benzene or toluene, are the intermolecular forces stronger? In which substance do the molecules pack more efficiently?



Benzene

Toluene

Phenol

Melting point (°C)

Boiling point (°C)

5

—95

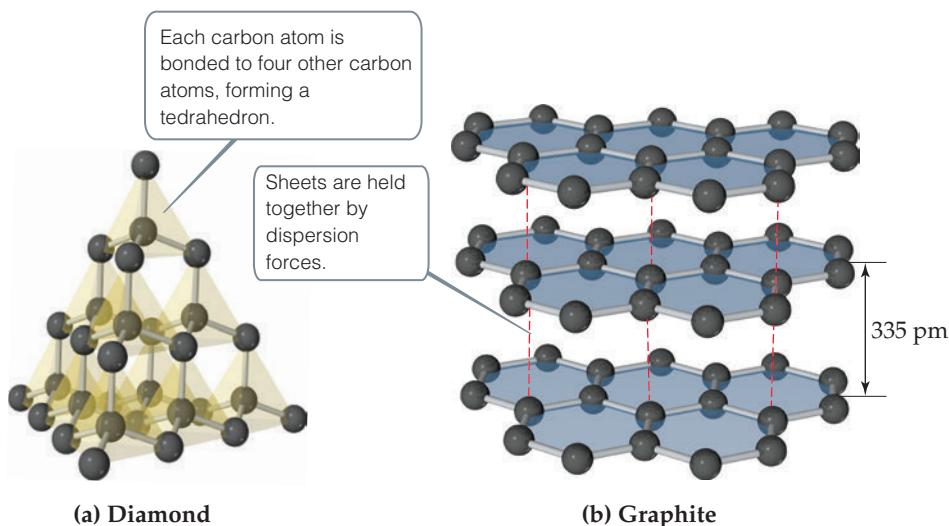
43

111

182

▲ **Figure 12.28** Melting and boiling points for benzene, toluene, and phenol.

► **Figure 12.29** The structures of (a) diamond and (b) graphite.



### Covalent-Network Solids

**Covalent-network solids** consist of atoms held together in large networks by covalent bonds. Because covalent bonds are much stronger than intermolecular forces, these solids are much harder and have higher melting points than molecular solids. Diamond and graphite, two allotropes of carbon, are two of the most familiar covalent-network solids. Other examples are silicon, germanium, quartz ( $\text{SiO}_2$ ), silicon carbide (SiC), and boron nitride (BN). In all cases, the bonding between atoms is either completely covalent or more covalent than ionic.

In diamond, each carbon atom is bonded tetrahedrally to four other carbon atoms (Figure 12.29). The structure of diamond can be derived from the zinc blende structure (Figure 12.26) if carbon atoms replace both the zinc and sulfide ions. The carbon atoms are  $sp^3$  hybridized and held together by strong carbon–carbon single covalent bonds. The strength and directionality of these bonds make diamond one of the hardest known material. For this reason, industrial-grade diamonds are employed in saw blades used for the most demanding cutting jobs. The stiff, interconnected bond network also explains why diamond is one of the best-known thermal conductors, yet is not electrically conductive. Diamond has a high melting point, 3550 °C.

In graphite, [Figure 12.29(b)], the carbon atoms form covalently bonded layers that are held together by intermolecular forces. The layers in graphite are the same as those in the graphene sheet shown in Figure 12.8. Graphite has a hexagonal unit cell containing two layers offset so that the carbon atoms in a given layer sit over the middle of the hexagons of the layer below. Each carbon is covalently bonded to three other carbons in the same layer to form interconnected hexagonal rings. The distance between adjacent carbon atoms in the plane, 142 pm, is very close to the C–C distance in benzene, 140 pm. In fact, the bonding resembles that of benzene, with delocalized  $\pi$  bonds extending over the layers. Electrons move freely through the delocalized orbitals, making graphite a good electrical conductor along the layers. (In fact, graphite is used as a conducting electrode in batteries.) These  $sp^2$  hybridized sheets of carbon atoms are separated by 335 pm from one another, and the sheets are held together only by dispersion forces. Thus, the layers readily slide past one another when rubbed, giving graphite a greasy feel. This tendency is enhanced when impurity atoms are trapped between the layers, as is typically the case in commercial forms of the material.

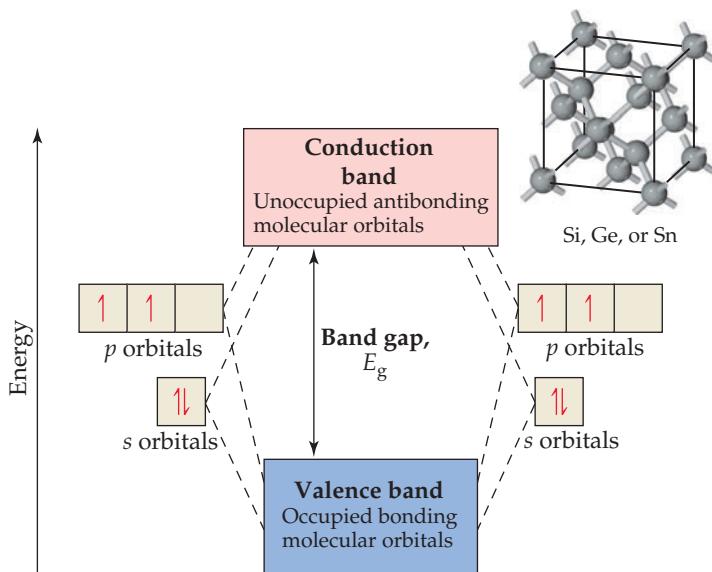
Graphite is used as a lubricant and as the “lead” in pencils. The enormous differences in physical properties of graphite and diamond—both of which are pure carbon—arise from differences in their three-dimensional structure and bonding.

### Semiconductors

Metals conduct electricity extremely well. Many solids, however, conduct electricity somewhat, but nowhere near as well as metals, which is why such materials are called **semiconductors**. Two examples of semiconductors are silicon and germanium, which

 Go Figure

If you draw a second diagram next to this one to represent an insulator, what aspect of the second diagram would be different?



▲ Figure 12.30 The electronic band structure of semiconductors that have the diamond crystal structure.

lie immediately below carbon in the periodic table. Like carbon, each of these elements has four valence electrons, just the right number to satisfy the octet rule by forming single covalent bonds with four neighbors. Hence, silicon and germanium, as well as the gray form of tin, crystallize with the same infinite network of covalent bonds as diamond.

When atomic *s* and *p* orbitals overlap, they form bonding molecular orbitals and antibonding molecular orbitals. Each pair of *s* orbitals overlaps to give one bonding and one antibonding molecular orbital, whereas the *p* orbitals overlap to give three bonding and three antibonding molecular orbitals. The extended network of bonds leads to the formation of the same type of bands we saw for metals in Section 12.2. However, unlike metals, in semiconductors an energy gap develops between the filled and empty states, much like the energy gap between bonding and antibonding orbitals. The band that forms from bonding molecular orbitals is called the **valence band**, and the band that forms the antibonding orbitals is called the **conduction band** (Figure 12.30). In a semiconductor, the valence band is filled with electrons and the conduction band is empty. These two bands are separated by the energy **band gap**  $E_g$ . In the semiconductor community, energies are given in electron volts (eV);  $1\text{ eV} = 1.602 \times 10^{-19}\text{ J}$ . Band gaps greater than  $\sim 3.5\text{ eV}$  are so large that the material is not a semiconductor; it is an **insulator** and does not conduct electricity.

Semiconductors can be divided into two classes: elemental semiconductors, which contain only one type of atom, and compound semiconductors, which contain two or more elements. The elemental semiconductors all come from Group 14. As we move down the periodic table, bond distances increase, which decreases orbital overlap. This decrease in overlap reduces the energy difference between the top of the valence band and the bottom of the conduction band. As a result, the band gap decreases on going from diamond ( $5.5\text{ eV}$ , an insulator) to silicon ( $1.11\text{ eV}$ ) to germanium ( $0.67\text{ eV}$ ) to gray tin ( $0.08\text{ eV}$ ). In the heaviest Group 14 element, lead, the band gap collapses altogether. As a result, lead has the structure and properties of a metal.

Compound semiconductors maintain the same *average* valence electron count as elemental semiconductors—four per atom. For example, in gallium arsenide, GaAs, each Ga atom contributes three electrons and each As atom contributes five, which averages out to four per atom—the same number as in silicon or germanium. Hence, GaAs is a semiconductor. Other examples are InP, where indium contributes three valence electrons

**TABLE 12.4 Band Gaps of Select Elemental and Compound Semiconductors**

Material	Structure Type	$E_g$ eV <sup>†</sup>						
Si	Diamond	1.11			13 Al	14 Si	15 P	
AlP	Zinc blende	2.43			30 Zn	31 Ga	32 Ge	33 As
Ge	Diamond	0.67						34 Se
GaAs	Zinc blende	1.43						
ZnSe	Zinc blende	2.58			48 Cd	49 In	50 Sn	51 Sb
Sn <sup>‡</sup>	Diamond	0.08						52 Te
InSb	Zinc blende	0.18						
CdTe	Zinc blende	1.50						

<sup>†</sup> Band gap energies are room temperature values, 1 eV =  $1.602 \times 10^{-19}$  J.

<sup>‡</sup> These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.

and phosphorus contributes five, and CdTe, where cadmium provides two valence electrons and tellurium contributes six. In both cases, the average is again four valence electrons per atom. GaAs, InP, and CdTe all crystallize with a zinc blende structure.

The band gap of a compound semiconductor tends to increase as the difference in group numbers increases. For example,  $E_g = 0.67$  eV in Ge, but  $E_g = 1.43$  eV in GaAs. If we increase the difference in group number to four, as in ZnSe (Groups 12 and 16), the band gap increases to 2.70 eV. This progression is a result of the transition from pure covalent bonding in elemental semiconductors to polar covalent bonding in compound semiconductors. As the difference in electronegativity of the elements increases, the bonding becomes more polar and the band gap increases.

Electrical engineers manipulate both the orbital overlap and the bond polarity to control the band gaps of compound semiconductors for use in a wide range of electrical and optical devices. The band gaps of several elemental and compound semiconductors are given in **Table 12.4**.

### Sample Exercise 12.3

#### Qualitative Comparison of Semiconductor Band Gaps

Will GaP have a larger or smaller band gap than ZnS? Will it have a larger or smaller band gap than GaN?

#### SOLUTION

**Analyze** The size of the band gap depends on the vertical and horizontal positions of the elements in the periodic table. The band gap will increase when either of the following conditions is met: (1) The elements are located higher up in the periodic table, where enhanced orbital overlap leads to a larger splitting between bonding and antibonding orbital energies, or (2) the horizontal separation between the elements increases, which leads to an increase in the electronegativity difference and bond polarity.

**Plan** We must look at the periodic table and compare the relative positions of the elements in each case.

**Solve** Gallium is in the fourth period and Group 13. Phosphorus is in the third period and Group 15. Zinc and sulfur are in the same periods as gallium and phosphorus, respectively. However, zinc, in Group 12, is one element to the left of gallium; sulfur in Group 16

is one element to the right of phosphorus. Thus, we would expect the electronegativity difference to be larger for ZnS, which should result in ZnS having a larger band gap than GaP.

For both GaP and GaN the more electropositive element is gallium. So we need only compare the positions of the more electronegative elements, P and N. Nitrogen is located above phosphorus in Group 15. Therefore, based on increased orbital overlap, we would expect GaN to have a larger band gap than GaP.

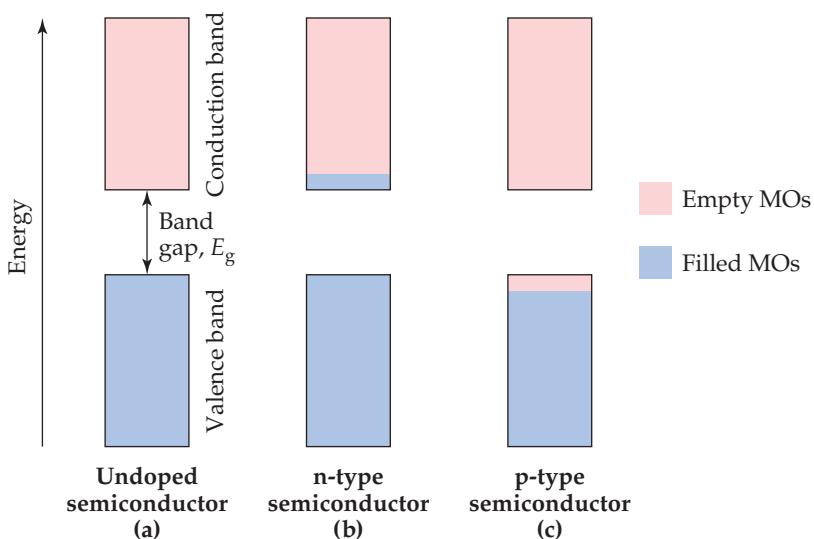
**Check** External references show that the band gap of GaP is 2.26 eV, ZnS is 3.6 eV, and GaN is 3.4 eV.

#### ► Practice Exercise

Will ZnSe have a larger or smaller band gap than ZnS?

 Go Figure

Predict what would happen in panel (b) if you doubled the amount of doping shown in the n-type semiconductor.



▲ Figure 12.31 The addition of small amounts of impurities (doping) to a semiconductor changes the electronic properties of the material.

## Semiconductor Doping

The electrical conductivity of a semiconductor is influenced by the presence of small numbers of impurity atoms. The process of adding controlled amounts of impurity atoms to a material is known as **doping**. Consider what happens when a few phosphorus atoms (known as dopants) replace silicon atoms in a silicon crystal. In pure Si, all of the valence-band molecular orbitals are filled and all of the conduction-band molecular orbitals are empty, as Figure 12.31(a) shows. Because phosphorus has five valence electrons but silicon has only four, the “extra” electrons that come with the dopant phosphorus atoms are forced to occupy the conduction band [Figure 12.31(b)]. The doped material is called an *n-type* semiconductor, *n* signifying that the number of negatively charged electrons in the conduction band has increased. These extra electrons can move very easily in the conduction band. Thus, just a few parts per million (ppm) of phosphorus in silicon can increase silicon’s intrinsic conductivity by a factor of a million!

The dramatic change in conductivity in response to the addition of a trace amount of a dopant means that extreme care must be taken to control the impurities in semiconductors. The semiconductor industry uses “nine-nines” silicon to make integrated circuits; what this means is that Si must be 99.99999999% pure (nine nines after the decimal place) to be technologically useful! Doping provides an opportunity for controlling the electrical conductivity through precise control of the type and concentration of dopants.

It is also possible to dope semiconductors with atoms that have fewer valence electrons than the host material. Consider what happens when a few aluminum atoms replace silicon atoms in a silicon crystal. Aluminum has only three valence electrons compared to silicon’s four. Thus, there are electron vacancies, known as **holes**, in the valence band when silicon is doped with aluminum [Figure 12.31(c)]. Since the negatively charged electron is not there, the hole can be thought of as having a positive charge. Any adjacent electron that jumps into the hole leaves behind a new hole. Thus, the positive hole moves about in the lattice like a particle.\* A material like this is called a *p-type* semiconductor, *p* signifying that the number of positive holes in the material has increased.

\*This movement is analogous to watching people changing seats in a classroom; you can watch the people (electrons) move about the seats (atoms), or you can watch the empty seats (holes) “move.”

As with n-type conductivity, p-type dopant levels of only parts per million can lead to a millionfold increase in conductivity—but in this case, the holes in the valence band are doing the conduction [Figure 12.31(c)].

The junction of an n-type semiconductor with a p-type semiconductor forms the basis for diodes, transistors, solar cells, and other devices.

### Sample Exercise 12.4

#### Identifying Types of Semiconductors



Which of the following elements, if doped into silicon, would yield an n-type semiconductor: Ga, As, or C?

#### SOLUTION

**Analyze** An n-type semiconductor means that the dopant atoms must have more valence electrons than the host material. Silicon is the host material in this case.

**Plan** We must look at the periodic table and determine the number of valence electrons associated with Si, Ga, As, and C. The elements with more valence electrons than silicon are the ones that will produce an n-type material upon doping.

**Solve** Si is in column 14, and so has four valence electrons. Ga is in column 13, and so has three valence electrons. As is in column 15, and so has five valence electrons; C is in column 14, and so has

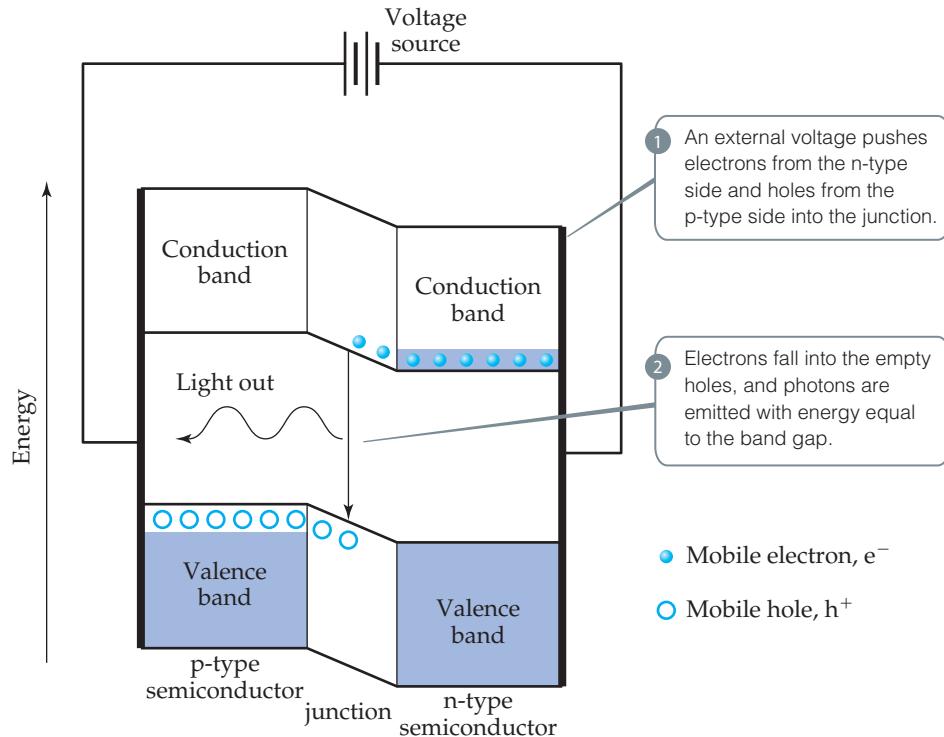
four valence electrons. Therefore, As, if doped into silicon, would yield an n-type semiconductor.

#### ► Practice Exercise

Compound semiconductors can be doped to make n-type and p-type materials, but the scientist has to make sure that the proper atoms are substituted. For example, if Ge were doped into GaAs, Ge could substitute for Ga, making an n-type semiconductor; but if Ge substituted for As, the material would be p-type. Suggest a way to dope CdSe to create a p-type material.

### CHEMISTRY PUT TO WORK Solid-State Lighting

Artificial lighting is so widespread we take it for granted. Major savings in energy would be realized if incandescent lights could be replaced by light-emitting diodes (LEDs). Because LEDs are made from semiconductors, this is an appropriate place to take a closer look at the operation of an LED.



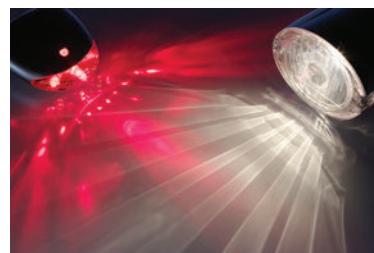
The heart of an LED is a p-n diode, which is formed by bringing an n-type semiconductor into contact with a p-type semiconductor. In the junction where they meet, there are very few electrons or holes to carry the charge across the interface between them, and the conductivity decreases. When an appropriate voltage is applied, electrons are driven from the conduction band of the n-doped side into the junction, where they meet holes that have been driven from the valence band of the p-doped side. The electrons fall into the empty holes, and their energy is converted into light whose photons have energy equal to the band gap (Figure 12.32). In this way electrical energy is converted into optical energy.

Because the wavelength of light that is emitted depends on the band gap of the semiconductor, the color of light produced by the LED can be controlled by appropriate choice of semiconductor. Most red LEDs are made of a mixture of GaP and GaAs. The band gap of GaP is 2.26 eV ( $3.62 \times 10^{-19}$  J), which corresponds to a green photon with a wavelength of 549 nm, while GaAs has a band gap of 1.43 eV ( $2.29 \times 10^{-19}$  J), which corresponds to an infrared photon with a wavelength of 867 nm. By forming solid solutions of these two compounds, with stoichiometries of  $\text{GaP}_{1-x}\text{As}_x$ , the band gap can be adjusted to any intermediate value. Thus,  $\text{GaP}_{1-x}\text{As}_x$  is the solid solution of choice for red, orange, and yellow LEDs. Green LEDs are made from mixtures of GaP and AlP ( $E_g = 2.43$  eV,  $\lambda = 510$  nm).

▲ **Figure 12.32 Light-emitting diodes.** The heart of a light-emitting diode is a p-n junction in which an applied voltage drives electrons and holes together, where they combine and give off light.

Red LEDs have been in the market for decades, but to make white light, an efficient blue LED was needed. The first prototype bright blue LED was demonstrated in a Japanese laboratory in 1993. In 2010, less than 20 years later, over \$10 billion worth of blue LEDs were sold worldwide. The blue LEDs are based on combinations of GaN ( $E_g = 3.4$  eV,  $\lambda = 365$  nm) and InN ( $E_g = 2.4$  eV,  $\lambda = 517$  nm). Many colors of LEDs are now available and are used in everything from barcode scanners to traffic lights (Figure 12.33). Because the light emission results from semiconductor structures that can be made extremely small and because they emit little heat, LEDs are replacing standard incandescent and fluorescence light bulbs in many applications.

**Related Exercises:** 12.29, 12.33, 12.94, 12.95



▲ Figure 12.33 LEDs are all around us.

## Self-Assessment Exercises

**12.28** Sulfur has a melting point of 115 °C. How would you classify the solid?

- (a) Molecular solid
- (b) Covalent-network solid

**12.29** If you want to dope GaAs to make a p-type semiconductor with an element to replace As, which element(s) would you pick?

- (a) Si
- (b) P
- (c) Se

## Exercises

**12.30** Classify each of the following statements as true or false:

- (a) For molecular solids, the melting point generally increases as the strengths of the covalent bonds increase.
- (b) For molecular solids, the melting point generally increases as the strengths of the intermolecular forces increase.

**12.31** Which of the following properties are typical characteristics of a covalent-network solid, a metallic solid, or both: (a) ductility, (b) hardness, (c) high melting point?

**12.32** For each of the following pairs of semiconductors, which one will have the larger band gap: (a) InP or InAs, (b) Ge or AlP, (c) AgI or CdTe?

**12.33** Cadmium telluride is an important material for solar cells.

- (a) What is the band gap of CdTe? (b) What wavelength of light would a photon of this energy correspond to? (c) Draw a vertical line at this wavelength in the figure shown in Exercise 12.95, (towards the end of this chapter) which shows the light output of the sun as a function of wavelength. (d) With respect to silicon, does CdTe absorb a larger or smaller portion of the solar spectrum?

**12.34** The first LEDs were made from GaAs, which has a band gap of 1.43 eV. What wavelength of light would be emitted from an LED made from GaAs? What region of the electromagnetic spectrum does this light correspond to: ultraviolet, visible, or infrared?

12.28 (a)      12.29 (a)

Answers to Self-Assessment Exercises

## 12.5 | Polymers



Silicone is a polymer composed of an alternating chain of Si and O atoms with two carbon groups (typically CH<sub>3</sub>- groups) attached to each Si atom. The polymer is resistant to water and inert under normal circumstances making it useful as a sealant and in medicine. For example, breast implants, used for reconstructive or cosmetic surgery can be made of silicone.

By the end of this section, you should be able to

- Define the terms relating to polymers.
- Explain how the interactions between polymer chains impact the physical properties of polymers.

In nature we find many substances of very high molecular weight, running up to millions of u, that make up much of the structure of living organisms and tissues. Some examples are starch and cellulose, which abound in plants, as well as proteins, which are found in both plants and animals. In 1827, Jöns Jakob Berzelius coined the word **polymer** (from the Greek *polys*, “many,” and *meros*, “parts”) to denote molecular substances of high molecular weight formed by the *polymerization* (joining together) of **monomers**, molecules with low molecular weight.

Historically, natural polymers, such as wool, leather, silk, and natural rubber, were processed into usable materials. During the past 70 years or so, chemists have learned to form synthetic polymers by polymerizing monomers through controlled chemical reactions. A great many of these synthetic polymers have a backbone of carbon–carbon bonds because carbon atoms have an exceptional ability to form strong stable bonds with one another.

**Plastics** are polymeric solids that can be formed into various shapes, usually by the application of heat and pressure. There are several types of plastics.

**Thermoplastics** can be reshaped. For example, plastic milk containers are made from the thermoplastic polymer *polyethylene* (polyethylene). These containers can be melted down and the polymer recycled for some other use. If you look at the bottom of a plastic container, you are likely to see a recycle symbol containing a number, as shown in [Figure 12.34](#). The number and the letter abbreviation below it indicate the kind of polymer from which the container is made, as summarized in [Table 12.5](#). These symbols make it possible to sort containers by composition. In general, the lower the number, the greater the ease with which the material can be recycled.

Unlike a thermoplastic, a **thermosetting plastic** (also called a *thermoset*) is shaped through irreversible chemical processes and, therefore, cannot be reshaped readily. Vulcanized rubber and polyurethanes found in commercial products including insulating foams and mattresses are familiar examples of thermosetting plastics.

Another type of plastic is the **elastomer**, which is a material that exhibits rubbery or elastic behavior. When subjected to stretching or bending, an elastomer regains its original shape upon removal of the distorting force, if it has not been distorted beyond some elastic limit. Rubber is the most familiar example of an elastomer.

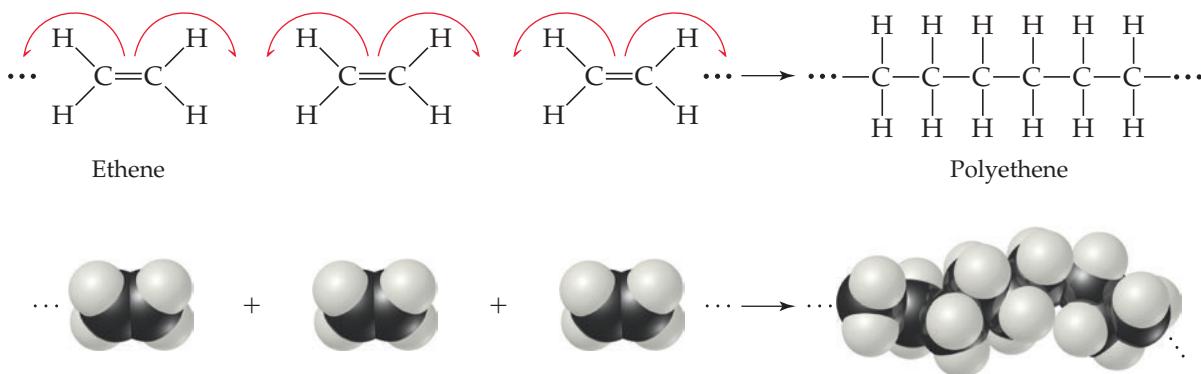
Some polymers, such as nylon and polyesters, both of which are thermosetting plastics, can be formed into fibers that, like hair, are very long relative to their



▲ **Figure 12.34** Recycling symbols. Most plastic containers manufactured today carry a recycling symbol indicating the type of polymer used to make the container and the polymer's suitability for recycling.

**TABLE 12.5 Categories Used for Recycling Polymeric Materials in the United States**

Number	Abbreviation	Polymer
1	PET or PETE	Polyethene terephthalate
2	HDPE	High-density polyethene
3	PVC	Polyvinyl chloride
4	LDPE	Low-density polyethene
5	PP	Polypropene
6	PS	Polystyrene
7	None	Other



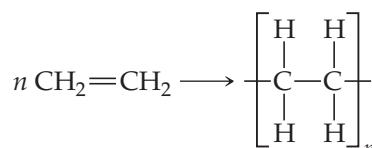
▲ Figure 12.35 The polymerization of ethene monomers to make the polymer polyethene.

cross-sectional area. These fibers can be woven into fabrics and cords and fashioned into clothing, tire cord, and other useful objects.

### Making Polymers

A good example of a polymerization reaction is the formation of polyethene from ethene molecules (Figure 12.35). In this reaction, the double bond in each ethene molecule “opens up,” and two of the electrons originally in this bond are used to form new C—C single bonds with two other ethene molecules. This type of polymerization, in which monomers are coupled through their multiple bonds, is called **addition polymerization**.

We can write the equation for the polymerization reaction as follows:



Here  $n$  represents the large number—ranging from hundreds to many thousands—of monomer molecules (ethene in this case) that react to form one polymer molecule. Within the polymer, a repeat unit (the unit shown in brackets in the previous equation) appears over and over along the entire chain. The ends of the chain are capped by carbon–hydrogen bonds or by some other bond, so that the end carbons have four bonds.

Polyethene is an important material; its annual production exceeds 190 billion pounds each year. Although its composition is simple, the polymer is not easy to make. The right manufacturing conditions were identified only after many years of research. Today many forms of polyethene, varying widely in physical properties, are known.

Polymers of other chemical compositions provide still greater variety in physical and chemical properties. Table 12.6 lists several other common polymers obtained by addition polymerization.

A second general reaction used to synthesize commercially important polymers is **condensation polymerization**. In a condensation reaction two molecules are joined to form a larger molecule by elimination of a small molecule, such as H<sub>2</sub>O. For example, an amine (a compound containing —NH<sub>2</sub>) reacts with a carboxylic acid (a compound containing —COOH) to form a bond between N and C plus an H<sub>2</sub>O molecule (Figure 12.36).

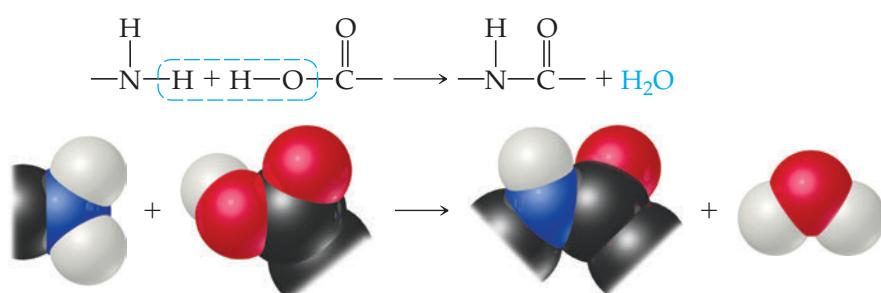
Polymers formed from two different monomers are called **copolymers**. In the formation of many nylons, a *diamine*, a compound with the —NH<sub>2</sub> group at each end, is reacted with a *diacid*, a compound with the —COOH group at each end. For example, the copolymer nylon 6,6 is formed when a diamine that has six carbon atoms and an amino group on each end is reacted with adipic acid, which also has six carbon atoms (Figure 12.37). A condensation reaction occurs on each end of the diamine and the acid. Water is released, and N—C bonds are formed between molecules.

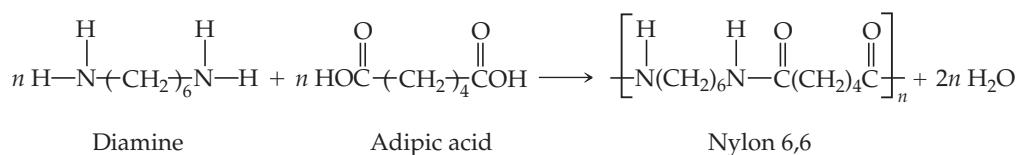
**TABLE 12.6 Polymers of Commercial Importance**

Polymer	Structure	Uses
<b>Addition Polymers</b>		
Polyethene	$\text{--}(\text{CH}_2\text{--CH}_2)_n\text{--}$	Films, packaging, bottles
Polypropene	$\left[\text{CH}_2\text{--}\overset{\text{CH}}{\underset{\text{CH}_3}{\text{CH}}}\right]_n$	Kitchenware, fibers, appliances
Polystyrene	$\left[\text{CH}_2\text{--}\overset{\text{CH}}{\underset{\text{C}_6\text{H}_5}{\text{CH}}}\right]_n$	Packaging, disposable food containers, insulation
Polyvinyl chloride (PVC)	$\left[\text{CH}_2\text{--}\overset{\text{CH}}{\underset{\text{Cl}}{\text{CH}}}\right]_n$	Pipe fittings, plumbing
<b>Condensation Polymers</b>		
Polyurethane	$\left[\text{NH--R--NH--C=O--O--R'--O--C=O}\right]_n$ R, R' = $-\text{CH}_2\text{--CH}_2-$ (for example)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethene terephthalate (a polyester)	$\left[\text{O--CH}_2\text{--CH}_2\text{--O--C=O--}\text{C}_6\text{H}_4\text{--C=O}\right]_n$	Tire cord, magnetic tape, apparel, soft-drink bottles
Nylon 6,6	$\left[\text{NH--(CH}_2\text{)}_6\text{--NH--C=O--(CH}_2\text{)}_4\text{--C=O}\right]_n$	Home furnishings, apparel, carpet, fishing line, toothbrush bristles
Polycarbonate	$\left[\text{O--}\text{C}_6\text{H}_4\text{--C(CH}_3\text{)}_2\text{--C}_6\text{H}_4\text{--O--C=O}\right]_n$	Shatterproof eyeglass lenses, CDs, DVDs, bulletproof windows, greenhouses

Table 12.6 lists nylon 6,6 and some other common polymers obtained by condensation polymerization. Notice that these polymers have backbones containing N or O atoms as well as C atoms.

► **Figure 12.36** A condensation polymerization.





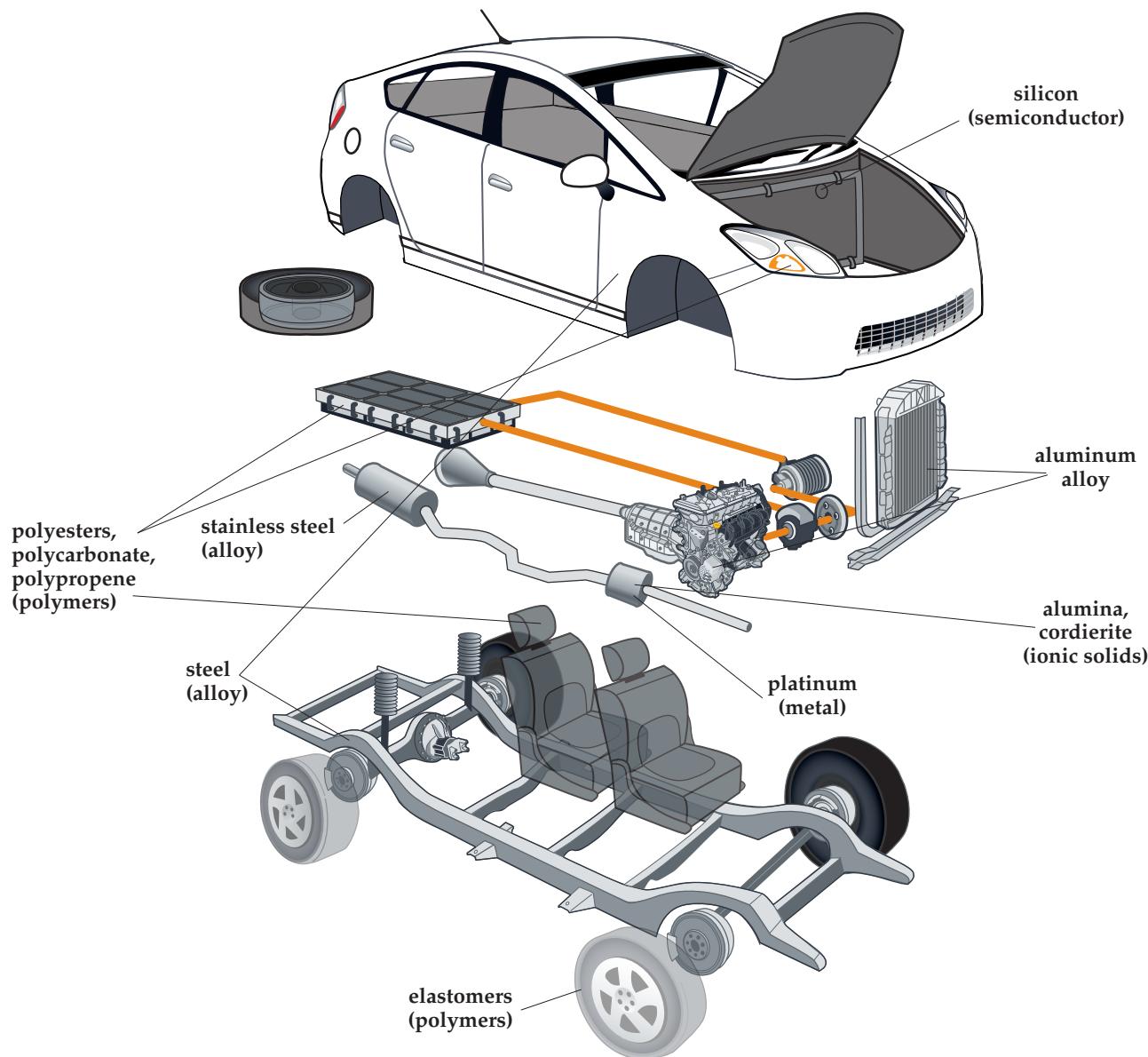
▲ Figure 12.37 The formation of the copolymer nylon 6,6.

## CHEMISTRY PUT TO WORK Modern Materials in the Automobile

There are over a billion motor vehicles in the world. Improvement in the fundamental understanding of the structure and properties of materials has enabled the development of motor vehicles that are safer, more powerful, more comfortable, and more fuel efficient. Let's take a look at some of these modern materials (**Figure 12.38**).

Metals and metal alloys are incorporated into many parts of an automobile. For example, aluminum is the primary component of the radiator, intake manifold, and engine block. Steel is typically the material used for the frame and body. Stainless steel is utilized in mufflers, exhaust silencers, and catalytic converters. The inside

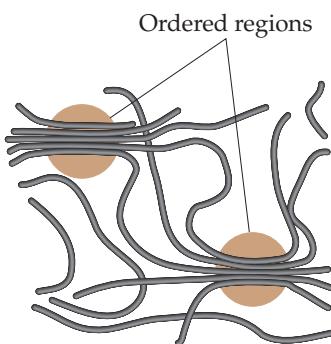
of the catalytic converter contains small particles of platinum group metals that are deposited onto a honeycomb-shaped structural ceramic. The ceramic is composed of the ionic solids alumina ( $\text{Al}_2\text{O}_3$ ) coated onto cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ). Semiconducting oxides are used for the oxygen sensor to monitor the air/fuel ratio in the exhaust gases, which is controlled by the engine control computer that is based on silicon, a covalent network solid. Polymers are found in a motor vehicle too, with polyesters in seat covers and carpets, polycarbonate optical reflectors, and polypropene in bumpers and car batteries.



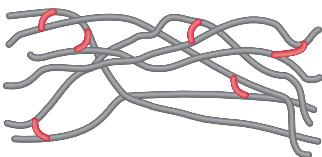
▲ Figure 12.38 Selected modern material components of an automobile.



**▲ Figure 12.39** A segment of a polyethylene chain. This segment consists of 28 carbon atoms. In commercial polyethylenes, the chain lengths range from about  $10^3$  to  $10^5 \text{ CH}_2$  units.



**▲ Figure 12.40** Interactions between polymer chains. In the circled regions, the forces that operate between adjacent segments of the chains lead to ordering analogous to the ordering in crystals, though less regular.



**▲ Figure 12.41** Cross-linking of polymer chains. The cross-linking groups (red) constrain the relative motions of the polymer chains, making the material harder and less flexible than when the cross-links are not present.

## Structure and Physical Properties of Polymers

The simple structural formulas given for polyethylene and other polymers are deceptive. Because four bonds surround each carbon atom in polyethylene, the atoms are arranged in a tetrahedral fashion, so that the chain is not straight as we have depicted it. Furthermore, the atoms are relatively free to rotate around the C—C single bonds. Rather than being straight and rigid, therefore, the chains are flexible, folding readily (Figure 12.39). The flexibility in the molecular chains causes any material made of this polymer to be very flexible.

Both synthetic and natural polymers commonly consist of a collection of *macromolecules* (large molecules) of different molecular weights. Depending on the conditions of formation, the molecular weights may be distributed over a wide range or may be closely clustered around an average value. In part because of this distribution in molecular weights, polymers are largely amorphous (noncrystalline) materials. Rather than exhibiting a well-defined crystalline phase with a sharp melting point, polymers soften over a range of temperatures. They may, however, possess short-range order in some regions of the solid, with chains lined up in regular arrays as shown in Figure 12.40. The extent of such ordering is indicated by the degree of **crystallinity** of the polymer. Mechanical stretching or pulling to align the chains as the molten polymer is drawn through small holes can frequently enhance the crystallinity of a polymer. Intermolecular forces between the polymer chains hold the chains together in the ordered crystalline regions, making the polymer denser, harder, less soluble, and more resistant to heat. Table 12.7 shows how the properties of polyethylene change as the degree of crystallinity increases.

The degree of crystallinity in polyethylene strongly depends on the average molecular weight. Polymerization results in a mixture of macromolecules with varying values of  $n$  (numbers of monomer molecules) and, hence, varying molecular weights. Low-density polyethylene (LDPE), used in forming films and sheets, has an average molecular weight in the range of  $10^4$  u, has a density of less than  $0.94 \text{ g/cm}^3$ , and has substantial chain branching. That is, there are side chains off the main chain of the polymer. These side chains inhibit the formation of crystalline regions, reducing the density of the material. High-density polyethylene (HDPE), used to form bottles, drums, and pipes, has an average molecular weight in the range of  $10^6$  u and has a density of  $0.94 \text{ g/cm}^3$  or higher. This form has fewer side chains and thus a higher degree of crystallinity.

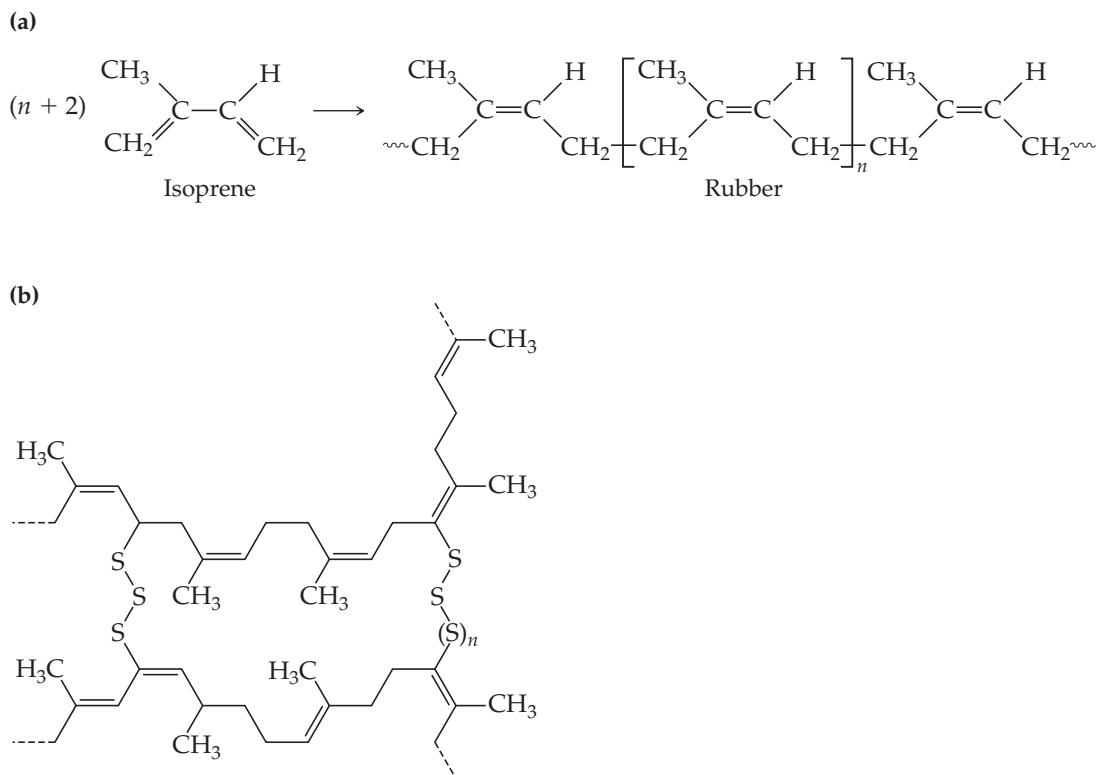
Polymers can be made stiffer by introducing chemical bonds between chains. Forming bonds between chains is called **cross-linking** (Figure 12.41). The greater the number of cross-links, the more rigid the polymer. Whereas thermoplastic materials consist of independent polymer chains, thermosetting plastics become cross-linked when heated; the cross-links allow them to hold their shapes.

An important example of cross-linking is the **vulcanization** of natural rubber, a process discovered by Charles Goodyear in 1839. Natural rubber is formed from a liquid resin derived from the inner bark of the *Hevea brasiliensis* tree. Chemically, it is a polymer of isoprene,  $\text{C}_5\text{H}_8$  (Figure 12.42). Because rotation about the carbon–carbon double bond does not readily occur, the orientation of the groups bound to the carbons is rigid.

**TABLE 12.7 Properties of Polyethylene as a Function of Crystallinity**

Properties	Crystallinity				
	55%	62%	70%	77%	85%
Melting point (°C)	109	116	125	130	133
Density (g/cm <sup>3</sup> )	0.92	0.93	0.94	0.95	0.96
Stiffness*	170	325	520	820	1140
Yield stress*	11.72	17.24	22.75	28.96	35.16

\*These test results show that the mechanical strength of the polymer increases with increased crystallinity. The physical units for the stiffness test are pascals; those for the yield stress test are megapascals. Discussion of the exact meaning and significance of these tests is beyond the scope of this text.

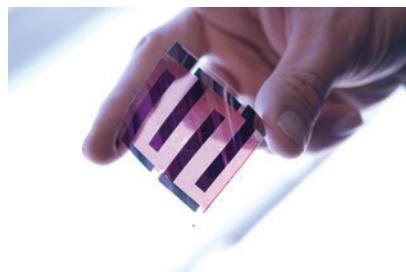


**▲ Figure 12.42 Vulcanization of natural rubber.** (a) Formation of polymeric natural rubber from the monomer isoprene. (b) Adding sulfur to rubber creates carbon–sulfur bonds and sulfur–sulfur links between chains.

In natural rubber, the chain extensions are on the same side of the double bond, as shown in Figure 12.42(a).

Natural rubber is not a useful polymer because it is too soft and too chemically reactive. Goodyear accidentally discovered that adding sulfur and then heating the mixture make the rubber harder and reduce its susceptibility to oxidation and other chemical degradation reactions. The sulfur changes rubber into a thermosetting polymer by cross-linking the polymer chains through reactions at some of the double bonds, as shown schematically in Figure 12.42(b). Cross-linking of about 5% of the double bonds creates a flexible, resilient rubber. When the rubber is stretched, the cross-links help prevent the chains from slipping, so that the rubber retains its elasticity. Because heating was an important step in his process, Goodyear named it after Vulcan, the Roman god of fire.

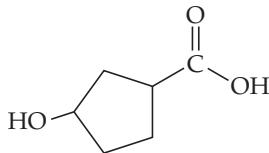
Most polymers contain  $sp^3$ -hybridized carbon atoms lacking delocalized  $\pi$  electrons, so they are usually electrical insulators and are colorless (which implies a large band gap). However, if the backbone of the polymer has resonance, the electrons can become delocalized over long distances, which can lead to semiconducting behavior in the polymer. Such “plastic electronics” are of great current interest for lightweight and flexible organic solar cells, organic transistors, organic light-emitting diodes, and other devices that are based on carbon rather than inorganic semiconductors like silicon (Figure 12.43).



**▲ Figure 12.43 Plastic electronics.** Flexible organic solar cells are made from conducting polymers.

## Self-Assessment Exercises

**12.35** Is this molecule a better starting material for an addition polymer or a condensation polymer?



**(a)** Addition polymer

**(b)** Condensation polymer

**12.36** Bakelite is a thermosetting polymer used as an insulator in early electrical appliances. The rigid structure is due to:

**(a)** The high molecular weight of the polymer

**(b)** Formation from a rigid monomer molecule

**(c)** Extensive cross-linking between polymer chains

## Exercises

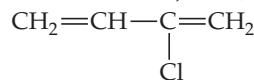
**12.37** The molecular formula of *n*-decane is  $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ . Decane is not considered a polymer, whereas polyethene is. What is the distinction?

**12.38** Indicate whether the following statement is true or false: For an addition polymerization, there are no by-products of the reaction (assuming 100% yield).

**12.39** Write a balanced chemical equation for the formation of a polymer via a condensation reaction from the monomers 1,4-phenylenediamine ( $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$ ) and terephthalic acid ( $\text{HOOC}_6\text{H}_4\text{COOH}$ ).

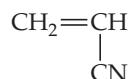
**12.40** Write the chemical equation that represents the formation of

- (a) polychloroprene from chloroprene (polychloroprene is used in highway-pavement seals, expansion joints, conveyor belts, and wire and cable jackets)



Chloroprene

(b) polyacrylonitrile from acrylonitrile (polyacrylonitrile is used in home furnishings, craft yarns, clothing, and many other items).



Acrylonitrile

**12.41** What molecular structural features cause high-density polyethylene to be denser than low-density polyethylene?

**12.42** Indicate whether each statement is true or false:

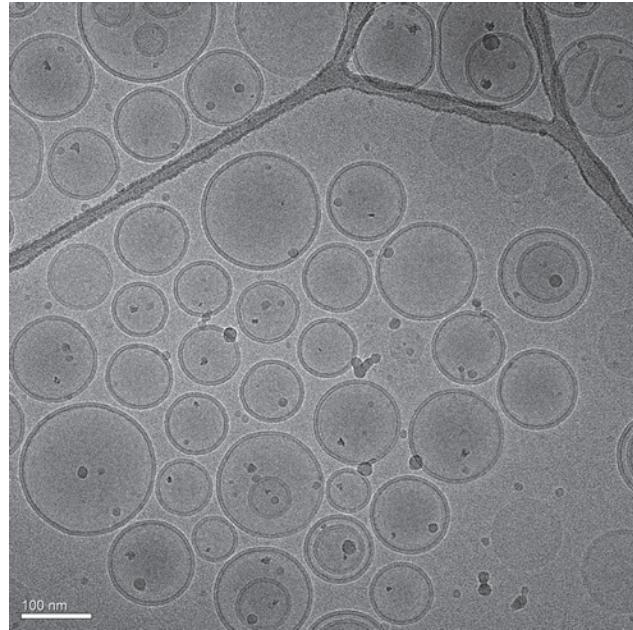
- (a) Elastomers are rubbery solids.
- (b) Thermosets cannot be reshaped.
- (c) Thermoplastic polymers can be recycled.

12.35 (b)    12.36 (c)

Answers to Self-Assessment Exercises



## 12.6 | Nanomaterials



The prefix *nano* means  $10^{-9}$ . When people speak of “nanotechnology,” they usually mean making devices that are on the 1–100 nm scale. It turns out that the properties of semiconductors and metals change in this size range. **Nanomaterials**—materials that have dimensions on the 1–100 nm scale—are under intense investigation in research laboratories around the world, and chemistry plays a central role in this investigation. Nanoparticles are between 10 and 1000 times larger than an atom.

By the end of this section, you should be able to

- Recognize that very small particles may have different properties to a bulk material.

## Semiconductors on the Nanoscale

Figure 12.22 shows that, in small molecules, electrons occupy discrete molecular orbitals, whereas in macroscale solids the electrons occupy delocalized bands. At what point does a molecule get so large that it starts behaving as though it has delocalized bands rather than localized molecular orbitals? For semiconductors, both theory and experiment tell us that the answer is roughly at 1 to 10 nm (about 10–100 atoms across). The exact number depends on the specific semiconductor material. The equations of quantum mechanics that were used for electrons in atoms can be applied to electrons (and holes) in semiconductors to estimate the size where materials undergo a crossover from molecular orbitals to bands. Because these effects become important at 1 to 10 nm, semiconductor particles with diameters in this size range are called *quantum dots*.

One of the most spectacular effects of reducing the size of a semiconductor crystal is that the band gap changes substantially with size in the 1–10 nm range. As the particle gets smaller, the band gap gets larger, an effect observable by the naked eye. On the macro level, the semiconductor cadmium phosphide looks black because its band gap is small ( $E_g = 0.5$  eV), and it absorbs all wavelengths of visible light. As the crystals are made smaller, the material progressively changes color until it looks white! It looks white because now no visible light is absorbed. The band gap is so large that only high-energy ultraviolet light can excite electrons into the conduction band ( $E_g > 3.0$  eV).

Making quantum dots is most easily accomplished using chemical reactions in solution. For example, to make CdS, you can mix  $\text{Cd}(\text{NO}_3)_2$  and  $\text{Na}_2\text{S}$  in water. If you do not do anything else, you will precipitate large crystals of CdS. However, if you first add a negatively charged polymer to the water (such as polyphosphate,  $-(\text{OPO}_2^-)_n-$ ), the  $\text{Cd}^{2+}$  associates with the polymer, like tiny “meatballs” in the polymer “spaghetti.” When sulfide is added, CdS particles grow, but the polymer keeps them from forming large crystals. A great deal of fine-tuning of reaction conditions is necessary to produce nanocrystals that are of uniform size and shape.

As we learned in Section 12.7, some semiconductor devices can emit light when a voltage is applied. Another way to make semiconductors emit light is to illuminate them with light whose photons have energies larger than the energy of the band gap of the semiconductor, a process called *photoluminescence*. A valence-band electron absorbs a photon and is promoted to the conduction band. If the excited electron then falls back down into the hole it left in the valence band, it emits a photon having energy equal to the band gap energy. In the case of quantum dots, the band gap is tunable with the crystal size, and thus all the colors of the rainbow can be obtained from just one material, as shown for CdSe in Figure 12.44.

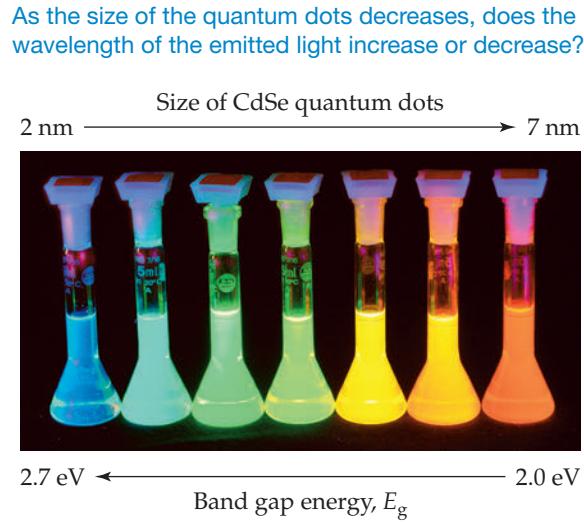
Quantum dots are being explored for applications ranging from electronics to lasers to medical imaging because they are very bright, very stable, and small enough to be taken up by living cells even after being coated with a biocompatible surface layer.

Semiconductors do not have to be shrunk to the nanoscale in all three dimensions to show new properties. They can be laid down in relatively large two-dimensional areas on a substrate but be only a few nanometers thick to make *quantum wells*. *Quantum wires*, in which the semiconductor wire diameter is only a few nanometers but its length is very long, have also been made by various chemical routes. In both quantum wells and quantum wires, measurements along the nanoscale dimension(s) show quantum behavior, but in the long dimension, the properties seem to be just like those of the bulk material.

## Metals on the Nanoscale

Metals also have unusual properties on the 1–100 nm length scale. Fundamentally, this is because the mean free path of an electron in a metal at room temperature is typically about 1–100 nm. So when the particle size of a metal is 100 nm or less, one might expect unusual effects because the “sea of electrons” encounters a “shore” (the surface of the particle).

### Go Figure



▲ **Figure 12.44** Photoluminescence depends on particle size at the nanoscale. When illuminated with ultraviolet light, these solutions, each containing nanoparticles of the semiconductor CdSe, emit light that corresponds to their respective band gap energies. The wavelength of the light emitted depends on the size of the CdSe nanoparticles.

## CHEMISTRY PUT TO WORK Microporous and Mesoporous Materials

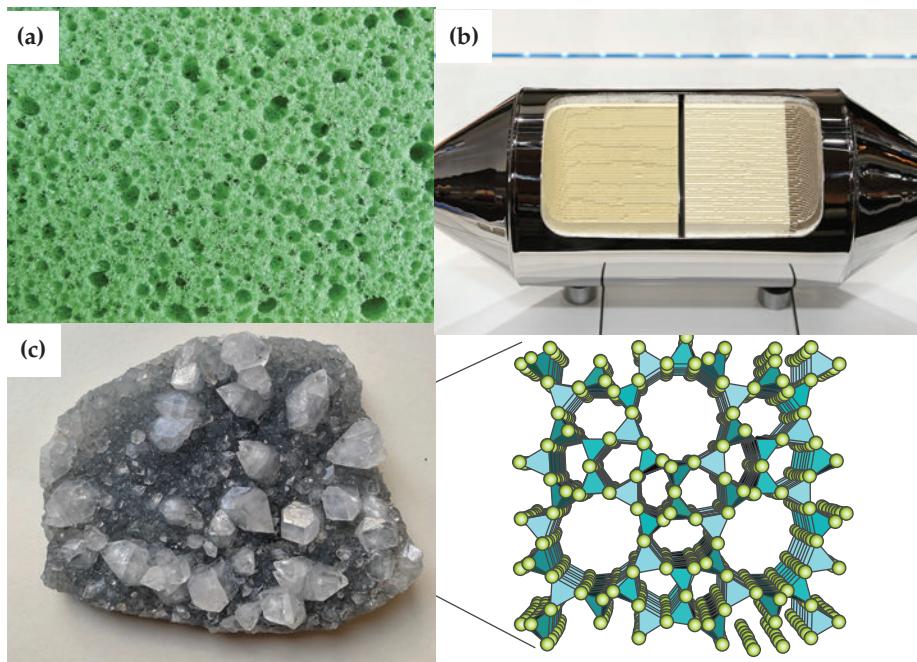
**Macroporous** materials have pores that are visible to the naked eye. Examples include the everyday synthetic sponge [Figure 12.45(a)] and the honeycomb-like cordierite core of an automobile catalytic converter [Figure 12.45(b)], with pore sizes in the mm size range and the tens of  $\mu\text{m}$  size range, respectively. **Microporous** and **mesoporous** materials have much smaller pores that are not visible to the naked eye. **Microporous** solids have pores up to 2 nm in size, whereas **mesoporous** solids have pore sizes in the range 2 to 50 nm.

Microporous and mesoporous materials have a large surface area relative to their volume because of their numerous pores and cavities. **Nanomaterials**, on the other hand, have a large surface area relative to their volume because of their small particle size. The size-dependent properties of these materials has led researchers to investigate their fundamental science and application.

**Zeolites**, which occur naturally and can also be synthesized, are a class of aluminosilicates that have been known since 1756. There are several hundred types of microporous and mesoporous zeolites. These substances adopt a variety of structures with polyhedral cavities connected by tunnels that often resemble a honeycomb [Figure 12.45(c)]. The interior surfaces attract ions and molecules that weakly interact with the rigid framework of aluminum, silicon,

and oxygen atoms. Various pore and cavity sizes can be prepared by varying the chemical composition and synthesis method.

Zeolites may be synthesized with weakly interacting ions occupying the cavities. Upon exposure to ions that interact more strongly with the interior surfaces, there is a preferential exchange of weakly interacting ions for more strongly interacting ions. This effectively creates what we might think of as an ionic sponge. An example that illustrates this behavior is the use of a sodium zeolite to remove radioactive cesium ( $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ ) from contaminated areas around the Fukushima Daiichi nuclear power plants in Japan, which were damaged by an earthquake and tsunami in 2011. The cesium ions are attracted into the cavities of the zeolite where an ion exchange occurs ( $\text{Cs}^+$  for  $\text{Na}^+$ ). Another example is treatment of water from wells that contain relatively high concentrations of calcium, magnesium, and iron ions—so-called hard water. Heated hard water can cause problems by forming deposits inside of pipes, reducing flow over time. Hard water can be “softened” by passing it through zeolites containing sodium ions that are replaced or exchanged for calcium ions in the hard water. Periodic flushing of the zeolite with an aqueous solution containing a high concentration of sodium ions removes the calcium ions and renews the zeolite for further use.



▲ **Figure 12.45** Porous materials. Sponges (a) and the core of an automobile catalytic converter (b) are macroporous. Zeolite ZSM-5 (c) is a microporous material with pore sizes near 0.5 nm.

Although it was not fully understood, people have known for hundreds of years that metals are different when they are very finely divided. Dating back to the Middle Ages, the makers of stained-glass windows knew that gold dispersed in molten glass made the glass a beautiful deep red (Figure 12.46). Much later, in 1857, Michael Faraday reported that dispersions of small gold particles could be made stable and were deeply colored—some of the original colloidal solutions that he made are still in the Royal Institution of Great Britain’s Faraday Museum in London (Figure 12.47).

Other physical and chemical properties of metallic nanoparticles are also different from the properties of the bulk materials. Gold particles less than 20 nm in diameter



▲ **Figure 12.46** Stained glass window from the Chartres Cathedral in France. Gold nanoparticles are responsible for the red color in this window, which dates back to the twelfth century.

melt at a far lower temperature than bulk gold, for instance, and when the particles are between 2 and 3 nm in diameter, gold is no longer a “noble,” unreactive metal; in this size range it becomes chemically reactive.

At nanoscale dimensions, silver has properties analogous to those of gold in its beautiful colors, although it is more reactive than gold. Currently, research laboratories around the world are showing great interest in taking advantage of the unusual optical properties of metal nanoparticles for applications in biomedical imaging and chemical detection.

## Carbon on the Nanoscale

We have seen that elemental carbon is quite versatile. In its bulk  $sp^3$  hybridized solid-state form, it is diamond; in its bulk  $sp^2$  hybridized solid-state form, it is graphite. Over the past three decades, scientists have discovered that  $sp^2$  hybridized carbon can also form discrete molecules, one-dimensional nanoscale tubes, and two-dimensional nanoscale sheets. Each of these forms of carbon shows very interesting properties.

Until the mid-1980s, pure solid carbon was thought to exist in only two forms: the covalent-network solids diamond and graphite. In 1985, however, a group of researchers led by Richard Smalley and Robert Curl of Rice University and Harry Kroto of the University of Sussex, England, vaporized a sample of graphite with an intense pulse of laser light and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer. The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of 60 carbon atoms,  $C_{60}$ .

Because  $C_{60}$  clusters were so preferentially formed, the group proposed a radically different form of carbon, namely, nearly spherical  $C_{60}$  molecules. They proposed that the carbon atoms of  $C_{60}$  form a “ball” with 32 faces, 12 of them pentagons and 20 hexagons (Figure 12.48), exactly like a soccer ball. The shape of this molecule is reminiscent of the geodesic dome invented by the U.S. engineer and philosopher R. Buckminster Fuller, so  $C_{60}$  was whimsically named “buckminsterfullerene,” or “buckyball” for short. Since the discovery of  $C_{60}$ , other related molecules made of pure carbon have been discovered. These molecules are now known as fullerenes.

Appreciable amounts of buckyball can be prepared by electrically evaporating graphite in an atmosphere of helium gas. About 14% of the resulting soot consists of  $C_{60}$  and a related molecule,  $C_{70}$ , which has a more elongated structure. The carbon-rich gases from which  $C_{60}$  and  $C_{70}$  condense also contain other fullerenes, mostly containing more carbon atoms, such as  $C_{76}$  and  $C_{84}$ . The smallest possible fullerene,  $C_{20}$ , was first detected in 2000. This small, ball-shaped molecule is much more reactive than the larger fullerenes. Because fullerenes are molecules, they dissolve in various organic solvents, whereas diamond and graphite do not. This solubility permits fullerenes to be separated from the other components of soot and even from one another. It also allows the study of their reactions in solution.

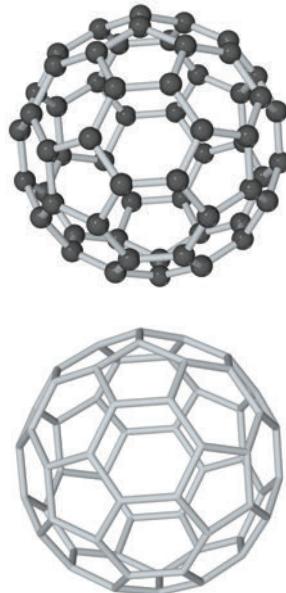
Soon after the discovery of  $C_{60}$ , chemists discovered carbon nanotubes (Figure 12.49). You can think of these as sheets of graphite rolled up and capped at one or both ends by half of a  $C_{60}$  molecule. Carbon nanotubes are made in a manner similar to that used to



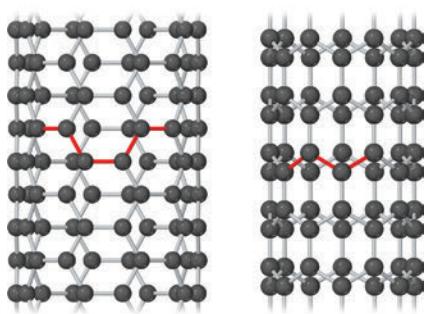
▲ **Figure 12.47** The solution of colloidal gold nanoparticles made by Michael Faraday in the 1850s. This is on display in the Royal Institution, London.

### Go Figure

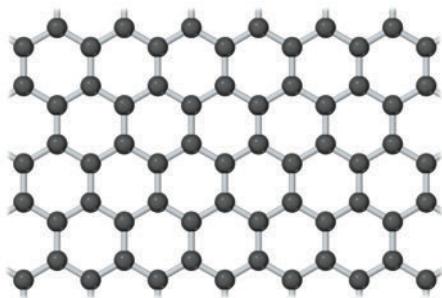
How many bonds does each carbon atom in  $C_{60}$  make? Based on this observation, would you expect the bonding in  $C_{60}$  to be more like that in diamond or that in graphite?



▲ **Figure 12.48** Buckminsterfullerene,  $C_{60}$ . The molecule has a highly symmetric structure in which the 60 carbon atoms sit at the vertices of a truncated icosahedron. The bottom view shows only the bonds between carbon atoms.



**▲ Figure 12.49** Atomic models of carbon nanotubes. Left: “Armchair” nanotube, which shows metallic behavior. Right: “Zigzag” nanotube, which can be either semiconducting or metallic, depending on tube diameter.



**▲ Figure 12.50** A portion of a two-dimensional graphene sheet.

make C<sub>60</sub>. They can be made in either *multiwall* or *single-walled* forms. Multiwall carbon nanotubes consist of tubes within tubes, nested together, whereas single-walled carbon nanotubes consist of single tubes. Single-walled carbon nanotubes can be 1000 nm long or even longer but are only about 1 nm in diameter. Depending on the diameter of the graphite sheet and how it is rolled up, carbon nanotubes can behave as either semiconductors or metals.

The fact that carbon nanotubes can be made either semiconducting or metallic without any doping is unique among solid-state materials, and laboratories worldwide are making and testing carbon-based electronic devices. Carbon nanotubes are also being explored for their mechanical properties. The carbon–carbon bonded framework of the nanotubes means that the imperfections that might appear in a metal nanowire of similar dimensions are nearly absent. Experiments on individual carbon nanotubes suggest that they are stronger than steel, if steel were the dimensions of a carbon nanotube. Carbon nanotubes have been spun into fibers with polymers, adding great strength and toughness to the composite material.

The two-dimensional form of carbon, graphene, is the most recent low-dimensional form of carbon to be experimentally isolated and studied. Although its properties had been the subject of theoretical predictions for over 60 years, it was not until 2004 that researchers at the University of Manchester in England isolated and identified individual sheets of carbon atoms with the honeycomb structure shown in **Figure 12.50**. Amazingly, the technique they used to isolate single-layer graphene was to successively peel away thin layers of graphite using adhesive tape. Individual layers of graphene were then transferred to a silicon wafer having a precisely defined overcoat of SiO<sub>2</sub>. When a single layer of graphene is left on the wafer, an interference-like contrast pattern results that can be seen with an optical microscope. If not for this simple yet effective way to scan for individual graphene crystals, they would probably still remain undiscovered. Subsequently, it has been shown that graphene can be deposited on clean surfaces of other types of crystals. The scientists who led the effort at the University of Manchester, Andre Geim and Konstantin Novoselov, were awarded the 2010 Nobel Prize in Physics for their work.

The properties of graphene are remarkable. It is very strong and has a record thermal conductivity, topping carbon nanotubes in both categories. Graphene is a semimetal, which means its electronic structure is like that of a semiconductor in which the energy gap is exactly zero. The combination of graphene’s two-dimensional character and the fact that it is a semimetal allows the electrons to travel very long distances, up to 0.3 μm, without scattering from another electron, atom, or impurity. Graphene can sustain electrical current densities six orders of magnitude higher than those sustainable in copper. Even though it is only one atom thick, graphene can absorb 2.3% of sunlight that strikes it. Scientists are currently exploring ways to incorporate graphene in various technologies, including electronics, sensors, batteries, and solar cells.

## Sample Integrative Exercise

### Putting Concepts Together

Polymers that can conduct electricity are called *conducting polymers*. Some polymers can be made semiconducting; others can be nearly metallic. Polyacetylene is an example of a polymer that is a semiconductor. It can also be doped to increase its conductivity.

Polyacetylene is made from acetylene in a reaction that looks simple but is actually tricky to do:



- (a) What is the hybridization of the carbon atoms, and the geometry around those atoms, in acetylene and in polyacetylene?
- (b) Write a balanced equation to make polyacetylene from acetylene.
- (c) Acetylene is a gas at room temperature and pressure (298 K, 101.3 kPa). How many grams of polyacetylene can you make from a 5.00-L vessel of acetylene gas at room temperature and room pressure? Assume that acetylene behaves ideally and that the polymerization reaction occurs with 100% yield.
- (d) Using the average bond enthalpies in Table 8.4, predict whether the formation of polyacetylene from acetylene is endothermic or exothermic.
- (e) A sample of polyacetylene absorbs light from 300 nm down to 650 nm. What is its band gap, in electron volts?

## SOLUTION

**Analyze** For part (a), we need to recall what we have learned about  $sp$ ,  $sp^2$ , and  $sp^3$  hybridization and geometry. For part (b), we need to write a balanced equation. For part (c), we need to use the ideal-gas equation. For part (d), we need to recall the definitions of endothermic and exothermic and how bond enthalpies can be used to predict overall reaction enthalpies. For part (e), we need to relate the absorption of light to the differences in energy levels between filled and empty states in a material.

**Plan** For part (a), we should draw out the chemical structures of the reactant and product. For part (b), we need to make sure the

### Solve

- (a) Carbon usually forms four bonds. Thus, each C atom must have a single bond to H and a triple bond to the other C atom in acetylene. As a result, each C atom has two electron domains and must be  $sp$  hybridized. This  $sp$  hybridization also means that the H—C—C angles in acetylene are  $180^\circ$  and the molecule is linear. We can write out the partial structure of polyacetylene as follows: Each carbon is identical but now has three bonding electron domains that surround it. Therefore, the hybridization of each carbon atom is  $sp^2$ , and each carbon has local trigonal planar geometry with  $120^\circ$  angles.

(b) We can write:

Note that all atoms originally present in acetylene end up in the polyacetylene product.

(c) We can use the ideal-gas equation as follows:

Acetylene has a molar mass of 26.0 g/mol; therefore, the mass of 0.204 mol is:

Note that from the answer to part (b), all the atoms in acetylene go into polyacetylene. Due to conservation of mass, then, the mass of polyacetylene produced must also be 5.32 g, if we assume 100% yield.

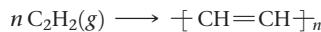
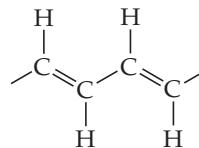
- (d) Let's consider the case for  $n = 1$ . We note that the reactant side of the equation in part (b) has one  $C \equiv C$  triple bond and two C—H single bonds. The product side of the equation in part (b) has one  $C=C$  double bond, one C—C single bond (to link to the adjacent monomer), and two C—H single bonds. Therefore, we are breaking one  $C \equiv C$  triple bond and are forming one  $C=C$  double bond and one C—C single bond. Accordingly, the enthalpy change for polyacetylene formation is:

Because  $\Delta H$  is a negative number, the reaction releases heat and is exothermic.

- (e) The sample of polyacetylene absorbs many wavelengths of light, but the one we care about is the longest one, which corresponds to the lowest energy.

We recognize that this energy corresponds to the energy difference between the bottom of the conduction band and the top of the valence band, and so is equivalent to the band gap  $E_g$ . Now we have to convert the number to electron volts. Since  $1.602 \times 10^{-19} \text{ J} = 1 \text{ eV}$ , we find that:

equation is properly balanced. For part (c), we need to convert from liters of gas to moles of gas, using the ideal-gas equation ( $PV = nRT$ ); then we need to convert from moles of acetylene gas to moles of polyacetylene using the answer from part (b); finally, we can convert to grams of polyacetylene. For part (d), we need to recall that  $\Delta H_{rxn} = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed})$ . For part (e), we need to realize that the lowest energy absorbed by a material will tell us its band gap  $E_g$  (for a semiconductor or insulator) and combine  $E = h\nu$  and  $c = \lambda\nu$  together ( $E = hc/\lambda$ ) to solve for  $E_g$ .



$$\begin{aligned} PV &= nRT \\ (101.3 \text{ kPa})(5.00 \times 10^{-3} \text{ m}^3) &= n(8.314 \text{ m}^3\text{-Pa/K-mol})(298 \text{ K}) \\ n &= 0.204 \text{ mol} \end{aligned}$$

$$(0.204 \text{ mol})(26.0 \text{ g/mol}) = 5.32 \text{ g acetylene}$$

$$\begin{aligned} \Delta H_{rxn} &= (\text{C}\equiv\text{C enthalpy}) - (\text{C}=\text{C enthalpy}) - (\text{C---C enthalpy}) \\ &= (839 \text{ kJ/mol}) - (614 \text{ kJ/mol}) - (348 \text{ kJ/mol}) \\ &= -123 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} E &= hc/\lambda \\ &= (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1})/(650 \times 10^{-9} \text{ m}) \\ &= 3.06 \times 10^{-19} \text{ J} \end{aligned}$$

$$E_g = 1.91 \text{ eV}$$

## Self-Assessment Exercise

- 12.43** Large crystals of ZnS can show photoluminescence, emitting ultraviolet photons with energies equal to the band gap energy and a wavelength of 340 nm. Is it possible to shift the luminescence so that the emitted photons are in the visible region of

the spectrum by making appropriately sized nanocrystals?

- (a) Yes  
(b) No

## Exercises

**12.44** GaP has a band gap of 2.26 eV. If GaP is illuminated with ultraviolet light, it emits light equal to the band gap energy. (a) What color is the emitted light? (b) Would appropriately sized GaP quantum dots be able to emit blue light? (c) What about red light?

**12.45** Indicate whether this statement is true or false:

If you want a semiconductor that emits blue light, you could either use a material that has a band gap corresponding to the energy of a blue photon or you could use a material that has a smaller band gap but make an appropriately sized nanoparticle of the same material.

**12.46** Gold adopts a face-centered cubic structure with a unit cell edge of 408 pm (Figure 12.11). How many gold atoms are

there in a sphere that is 20 nm in diameter? Recall that the volume of a sphere is  $\frac{4}{3}\pi r^3$ .

**12.47** What evidence supports the notion that buckyballs are actual molecules and not extended materials?

- (a) Buckyballs are made of carbon.
- (b) Buckyballs have a well-defined atomic structure and molecular weight.
- (c) Buckyballs have a well-defined melting point.
- (d) Buckyballs are semiconductors.
- (e) More than one of the previous choices.

12.43 (b)

Answers to Self-Assessment Exercise



## Chapter Summary and Key Terms

**CLASSIFICATION OF SOLIDS (SECTION 12.1)** The structures and properties of solids can be classified according to the forces that hold the atoms together. **Metallic solids** are held together by a delocalized sea of collectively shared valence electrons. **Ionic solids** are held together by the mutual attraction between cations and anions. **Covalent-network solids** are held together by an extended network of covalent bonds. **Molecular solids** are held together by weak intermolecular forces. **Polymers** contain very long chains of atoms held together by covalent bonds. These chains are usually held to one another by weaker intermolecular forces. **Nanomaterials** are solids where the dimensions of individual crystals are on the order of 1–100 nm.

In **crystalline solids**, particles are arranged in a regularly repeating pattern. In **amorphous solids**, however, particles show no long-range order. In a crystalline solid the smallest repeating unit is called a **unit cell**. All unit cells in a crystal contain an identical arrangement of atoms. The geometrical pattern of points on which the unit cells are arranged is called a **crystal lattice**. To generate a crystal structure a **motif**, which is an atom or group of atoms, is associated with each and every **lattice point**.

In two dimensions, the unit cell is a parallelogram whose size and shape are defined by two **lattice vectors** ( $a$  and  $b$ ). There are five **primitive lattices**, lattices in which the lattice points are located only at the corners of the unit cell: square, hexagonal, rectangular, rhombic, and oblique. In three dimensions the unit cell is a parallelepiped whose size and shape are defined by three lattice vectors ( $a$ ,  $b$ , and  $c$ ), and there are seven primitive lattices: cubic, tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic, and triclinic. Placing an additional lattice point at the center of a cubic unit cell leads to a **body-centered cubic lattice**, while placing an additional point at the center of each face of the unit cell leads to a **face-centered cubic lattice**.

**METALLIC SOLIDS (SECTION 12.2)** **Metallic solids** are typically good conductors of electricity and heat, *malleable*, which means that they can be hammered into thin sheets, and *ductile*, which means that they can be drawn into wires. Metals tend to form structures where the atoms are closely packed. Two related forms of close packing, **cubic close packing** and **hexagonal close packing**, are possible. In both, each atom has a **coordination number** of 12.

**Alloys** are materials that possess characteristic metallic properties and are composed of more than one element. The elements in an alloy can be distributed either homogeneously or heterogeneously. Alloys which contain homogeneous mixtures of elements can either be substitutional or interstitial alloys. In a **substitutional alloy** the

atoms of the minority element(s) occupy positions normally occupied by atoms of the majority element. In an **interstitial alloy** atoms of the minority element(s), often smaller nonmetallic atoms, occupy interstitial positions that lie in the “holes” between atoms of the majority element. In a **heterogeneous alloy** the elements are not distributed uniformly; instead, two or more distinct phases with characteristic compositions are present. **Intermetallic compounds** are alloys that have a fixed composition and definite properties.

The properties of metals can be accounted for in a qualitative way by the **electron-sea model**, in which the electrons are visualized as being free to move throughout the metal. In the molecular orbital model the valence atomic orbitals of the metal atoms interact to form energy **bands** that are incompletely filled by valence electrons. Consequently, the electronic structure of a bulk solid is referred to as a **band structure**. The orbitals that constitute the energy band are delocalized over the atoms of the metal, and their energies are closely spaced. In a metal the valence shell  $s$ ,  $p$ , and  $d$  orbitals form bands, and these bands overlap, resulting in one or more partially filled bands. Because the energy differences between orbitals *within a band* are extremely small, promoting electrons to higher-energy orbitals requires very little energy. This gives rise to high electrical and thermal conductivity, as well as other characteristic metallic properties.

**IONIC SOLIDS (SECTION 12.3)** **Ionic solids** consist of cations and anions held together by electrostatic attractions. Because these interactions are quite strong, ionic compounds tend to have high melting points. The attractions become stronger as the charges of the ions increase and/or the sizes of the ions decrease. The presence of both attractive (cation–anion) and repulsive (cation–cation and anion–anion) interactions helps to explain why ionic compounds are brittle. Like metals, the structures of ionic compounds tend to be symmetric, but to minimize direct contact between ions of like charge, the coordination numbers (typically 4 to 8) are necessarily smaller than those seen in close-packed metals. The exact structure depends on the relative sizes of the ions and the cation-to-anion ratio in the empirical formula.

**COVALENT SOLIDS (SECTION 12.4)** **Molecular solids** consist of atoms or molecules held together by intermolecular forces. Because these forces are relatively weak, molecular solids tend to be soft and possess low melting points. The melting point depends on the strength of the intermolecular forces, as well as the efficiency with which the molecules can pack together.

**Covalent-network solids** consist of atoms held together in large networks by covalent bonds. These solids are much harder and have higher melting points than molecular solids. Important examples include diamond, where the carbons are tetrahedrally coordinated to each other, and graphite, where the  $sp^2$ -hybridized carbon atoms form hexagonal layers. **Semiconductors** are solids that do conduct electricity, but to a far lesser extent than metals. **Insulators** do not conduct electricity at all.

Elemental semiconductors, like Si and Ge, as well as compound semiconductors, like GaAs, InP, and CdTe, are important examples of covalent-network solids. In a semiconductor the filled bonding molecular orbitals make up the **valence band**, while the empty antibonding molecular orbitals make up the **conduction band**. The valence and conduction bands are separated by an energy that is referred to as the **band gap**,  $E_g$ . The size of the band gap increases as the bond length decreases and as the difference in electronegativity between the two elements increases.

**Doping** semiconductors changes their ability to conduct electricity by orders of magnitude. An n-type semiconductor is one that is doped so that there are excess electrons in the conduction band; a p-type semiconductor is one that is doped so that there are missing electrons, which are called **holes**, in the valence band.

**POLYMERS (SECTION 12.5)** **Polymers** are molecules of high molecular weight formed by joining large numbers of small molecules called **monomers**. **Plastics** are materials that can be formed into various shapes, usually by the application of heat and pressure. **Thermoplastic** polymers can be reshaped, typically through heating, in contrast to **thermosetting plastics**, which are formed into objects through an irreversible chemical process and cannot readily be reshaped. An **elastomer** is a material that exhibits elastic behavior; that is, it returns to its original shape following stretching or bending.

In an **addition polymerization** reaction, the molecules form new linkages by opening existing  $\pi$  bonds. Polyethene forms, for

example, when the carbon–carbon double bonds of ethene open up. In a **condensation polymerization** reaction, the monomers are joined by eliminating a small molecule between them. The various kinds of nylon are formed, for example, by removing a water molecule between an amine and a carboxylic acid. A polymer formed from two different monomers is called a **copolymer**.

Polymers are largely amorphous, but some materials possess a degree of **crystallinity**. For a given chemical composition, the crystallinity depends on the molecular weight and the degree of branching along the main polymer chain. Polymer properties are also strongly affected by **cross-linking**, in which short chains of atoms connect the long polymer chains. Rubber is cross-linked by short chains of sulfur atoms in a process called **vulcanization**.

**NANOMATERIALS (SECTION 12.6)** When one or more dimensions of a material become sufficiently small, generally smaller than 100 nm, the properties of the material change. Materials with dimensions on this length scale are called **nanomaterials**. Quantum dots are semiconductor particles with diameters of 1–10 nm. In this size range the material's band gap energy becomes size-dependent. Metal nanoparticles have different chemical and physical properties in the 1–100-nm size range. Nanoparticles of gold, for example, are more reactive than bulk gold and no longer have a golden color. Nanoscience has produced a number of previously unknown forms of  $sp^2$ -hybridized carbon. Fullerenes, like C<sub>60</sub>, are large molecules containing only carbon atoms. Carbon nanotubes are sheets of graphite rolled up. They can behave as either semiconductors or metals depending on how the sheet was rolled. Graphene, which is an isolated layer from graphite, is a two-dimensional form of carbon. These nanomaterials are being developed now for many applications in electronics, batteries, solar cells, and medicine.

## Learning Outcomes After studying this chapter, you should be able to:

- Classify solids based on their bonding/intermolecular forces and understand how differences in bonding relate to physical properties. (Section 12.1) *Related Exercises: 12.4, 12.5, 12.58, 12.59, 12.60*
- Describe the difference between crystalline and amorphous solids. (Section 12.1) *Related Exercises: 12.62, 12.63*
- Define and describe the relationships between unit cells, crystal lattice, lattice vectors, and lattice points. (Section 12.1)  
*Related Exercises: 12.7, 12.64*
- Explain why there are a limited number of lattices. Recognize the five two-dimensional and the seven three-dimensional primitive lattices. Describe the locations of lattice points for body-centered and face-centered lattices. (Section 12.1)  
*Related Exercises: 12.7, 12.9, 12.10, 12.64, 12.66, 12.67*
- State the characteristics and properties of metals. (Section 12.2)  
*Related Exercises: 12.14, 12.50, 12.69, 12.70*
- Calculate the empirical formula and density of ionic and metallic solids from a picture of the unit cell. Estimate the length of a cubic unit cell from the radii of the atoms/ions present. (Sections 12.2 and 12.3) *Related Exercises: 2.15, 12.71–12.73, 12.75, 12.76*
- Explain how homogeneous and heterogeneous alloys differ. Describe the differences between substitutional alloys, interstitial alloys, and intermetallic compounds. (Section 12.2)  
*Related Exercises: 12.16–12.18, 12.77–12.79*
- Explain the electron-sea model of metallic bonding. (Section 12.2)  
*Related Exercise: 12.82*
- Use the molecular orbital model of metallic bonding to generate the electronic band structures of metals and qualitatively predict the trends in melting point, boiling point, and hardness of metals. (Section 12.2) *Related Exercises: 12.20, 12.84, 12.85*
- Predict the structures of ionic solids from their ionic radii and empirical formula. (Section 12.3) *Related Exercises: 12.26, 12.89*
- Predict the empirical formula from the structure of an ionic solid. (Section 12.3) *Related Exercises: 12.23, 12.86*
- Interpret melting point and boiling point data of molecular solids in terms of intermolecular forces and crystalline packing. (Section 12.4) *Related Exercise: 12.26*
- Identify the valence band, conduction band, and band gap, for semiconductors and insulators. (Section 12.4)  
*Related Exercise: 12.55*
- Account for the relative band gap energies of semiconductors in terms of periodic trends. Calculate the wavelength of a photon emitted from an LED given its band gap. (Section 12.4) *Related Exercises: 12.32–12.34, 12.93, 12.95–12.98*
- Predict how n-type and p-type doping can be used to control the conductivity of semiconductors. (Section 12.4)  
*Related Exercises: 12.29, 12.94*
- Define the terms monomer, plastic, thermoplastic, thermosetting plastic, elastomer, copolymers, and cross-linking. (Section 12.5)  
*Related Exercise: 12.99*
- Describe how polymers are formed from monomers and recognize the features of a molecule that allow it to react to form a polymer. Explain the differences between addition polymerization and condensation polymerization. (Section 12.5)  
*Related Exercises: 12.39, 12.101*
- Explain how the interactions between polymer chains impact the physical properties of polymers. (Section 12.5)  
*Related Exercises: 12.41, 12.42, 12.104, 12.105*

- Describe how the properties of bulk semiconductors and metals change as the size of the crystals decreases to the nanometer-length scale. (Section 12.6) *Related Exercises: 12.44, 12.107, 12.108*

- Describe the structures and unique properties of fullerenes, carbon nanotubes, and graphene. (Section 12.6) *Related Exercises: 12.47, 12.109*

## Key Equations

$$\frac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \frac{\text{anion coordination number}}{\text{cation coordination number}}$$

[12.1]

Relationship between cation and anion coordination numbers and the empirical formula of an ionic compound

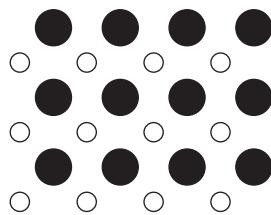
## Exercises

### Visualizing Concepts

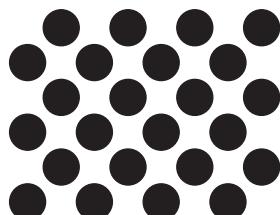
- 12.48** Two solids are shown here. One is a semiconductor and one is an insulator. Which one is which? Explain your reasoning. [Sections 12.1, 12.4]



- 12.49** For each of the two-dimensional structures shown here **(a)** draw the unit cell, **(b)** determine the type of two-dimensional lattice (from Figure 12.4), and **(c)** determine how many of each type of circle (white or black) there are per unit cell. [Section 12.1]

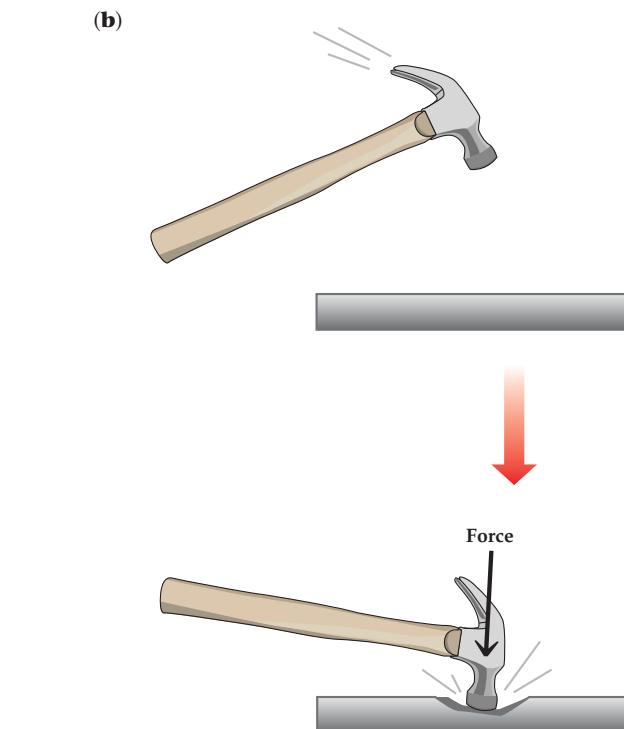
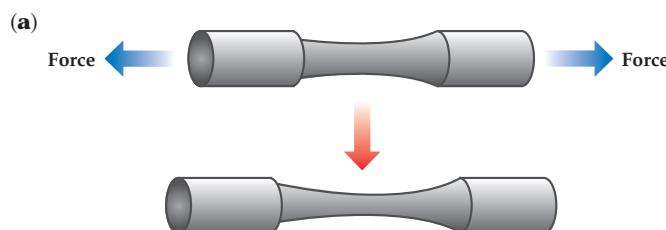


(i)

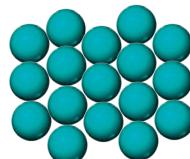


(ii)

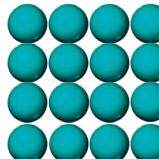
- 12.50** Shown here are sketches of two processes. Which of the processes refers to the ductility of metals and which refers to malleability of metals? [Section 12.2]



- 12.51** Which arrangement of atoms in a lattice represents close-packing? (Section 12.2)



(i)

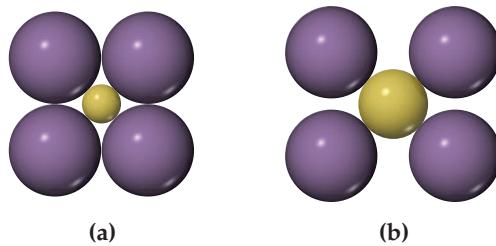


(ii)

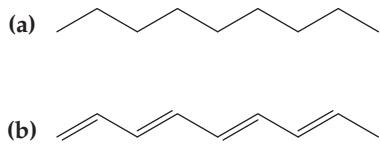
- 12.52** **(a)** What kind of packing arrangement is seen in the following photo? **(b)** What is the coordination number of each cannonball in the interior of the stack? **(c)** What are the coordination numbers for the numbered cannonballs on the visible side of the stack? [Section 12.2]



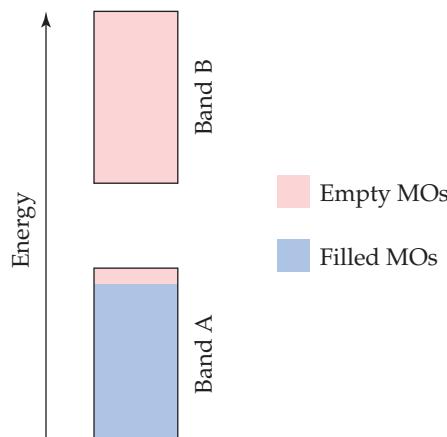
- 12.53** Which arrangement of cations (yellow) and anions (blue) in a lattice is the more stable? Explain your reasoning. [Section 12.3]



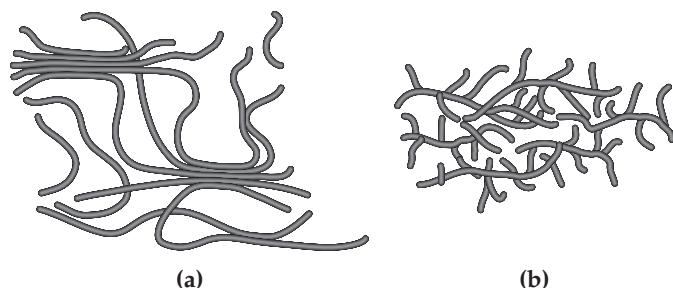
- 12.54** Which of these molecular fragments would you expect to be more likely to give rise to electrical conductivity? Explain your reasoning. [Sections 12.4, 12.5]



- 12.55** The electronic structure of a doped semiconductor is shown here. (a) Which band, A or B, is the valence band? (b) Which band is the conduction band? (c) Which region of the diagram represents the band gap? (d) Which band consists of bonding molecular orbitals? (e) Is this an example of an n-type or p-type semiconductor? (f) If the semiconductor is germanium, which of the following elements could be the dopant: Ga, Si, or P? [Section 12.4]



- 12.56** Shown here are cartoons of two different polymers. Which of these polymers would you expect to be more crystalline? Which one would have the higher melting point? [Section 12.5]



### Classification of Solids (Section 12.1)

- 12.57** Covalent bonding occurs in both molecular and covalent-network solids. Which of the following statements best explains why these two kinds of solids differ so greatly in their hardness and melting points?

- (a) The molecules in molecular solids have stronger covalent bonding than covalent-network solids do.
- (b) The molecules in molecular solids are held together by weak intermolecular interactions.
- (c) The atoms in covalent-network solids are more polarizable than those in molecular solids.
- (d) Molecular solids are denser than covalent-network solids.

- 12.58** What kinds of attractive forces exist between particles (atoms, molecules, or ions) in (a) molecular crystals, (b) covalent-network crystals, (c) ionic crystals, (d) and metallic crystals?

- 12.59** Indicate the type of solid (molecular, metallic, ionic, or covalent-network) for each compound: (a) B, (b) Li, (c) LiCl, (d) diethylether ( $C_4H_{10}O$ ), (e) chloroform ( $CHCl_3$ ), (f)  $Li_2O$ .

- 12.60** Indicate the type of solid (molecular, metallic, ionic, or covalent-network) for each compound: (a) SiC, (b) Ni, (c)  $CaCl_2$ , (d) camphor ( $C_{10}H_{16}O$ ), (e)  $SiO_2$ .

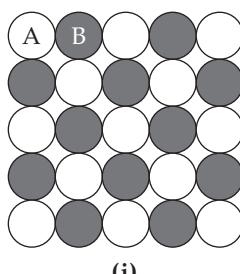
- 12.61** You are given a gray substance that melts at  $700^\circ C$ ; the solid is a conductor of electricity and is insoluble in water. Which type of solid (molecular, metallic, covalent-network, or ionic) might this substance be?

- 12.62** (a) Draw a picture that represents a crystalline solid at the atomic level. (b) Now draw a picture that represents an amorphous solid at the atomic level.

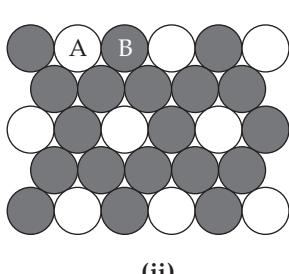
- 12.63** Amorphous silica,  $SiO_2$ , has a density of about  $2.2\text{ g/cm}^3$ , whereas the density of crystalline quartz, another form of  $SiO_2$ , is  $2.65\text{ g/cm}^3$ . Which of the following statements is the best explanation for the difference in density?

- (a) Amorphous silica is a network-covalent solid, but quartz is metallic.
- (b) Amorphous silica crystallizes in a primitive cubic lattice.
- (c) Quartz is harder than amorphous silica.
- (d) Quartz must have a larger unit cell than amorphous silica.
- (e) The atoms in amorphous silica do not pack as efficiently in three dimensions as compared to the atoms in quartz.

- 12.64** Two patterns of packing for two different circles of the same size are shown here. For each structure (a) draw the two-dimensional unit cell; (b) determine the angle between the lattice vectors,  $\gamma$ , and determine whether the lattice vectors are of the same length or of different lengths; and (c) determine the type of two-dimensional lattice (from Figure 12.4).

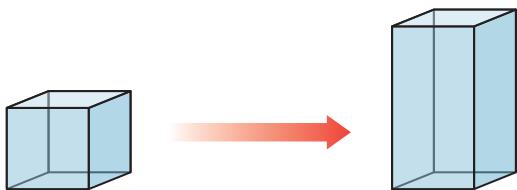


(i)



(ii)

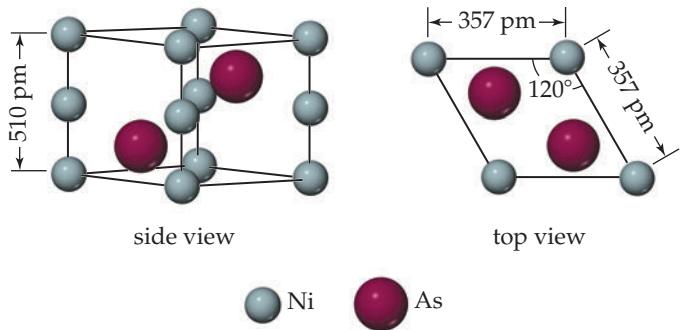
- 12.65** Imagine the primitive cubic lattice. Now imagine grabbing the top of it and stretching it straight up. All angles remain  $90^\circ$ . What kind of primitive lattice have you made?



- 12.66** Which of the three-dimensional primitive lattices has a unit cell where none of the internal angles is  $90^\circ$ ?  
**(a)** Orthorhombic, **(b)** hexagonal, **(c)** rhombohedral, **(d)** triclinic, **(e)** both rhombohedral and triclinic.

- 12.67** What is the minimum number of atoms that could be contained in the unit cell of an element with a body-centered cubic lattice? **(a)** 1, **(b)** 2, **(c)** 3, **(d)** 4, **(e)** 5.

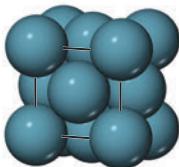
- 12.68** The unit cell of nickel arsenide is shown here. **(a)** What type of lattice does this crystal possess? **(b)** What is the empirical formula?



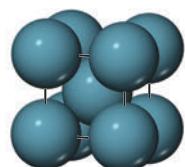
## Metallic Solids (Section 12.2)

- 12.69** For each of these solids, state whether you would expect it to possess metallic properties: **(a)**  $\text{TiCl}_4$ , **(b)** NiCo alloy, **(c)** W, **(d)** Ge, **(e)**  $\text{ScN}$ .

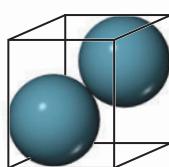
- 12.70** Consider the unit cells shown here for three different structures that are commonly observed for metallic elements. **(a)** Which structure(s) corresponds to the densest packing of atoms? **(b)** Which structure(s) corresponds to the least dense packing of atoms?



Structure type A



Structure type B



Structure type C

- 12.71** Potassium metal (atomic weight 39.10 g/mol) adopts a body-centered cubic structure with a density of  $0.856 \text{ g/cm}^3$ . **(a)** Use this information and Avogadro's number ( $6.022 \times 10^{23}$ ) to estimate the atomic radius of potassium. **(b)** If potassium didn't react so vigorously, it could float on water. Use the answer from part (a) to estimate the density of K if its structure were that of a cubic close-packed metal. Would it still float on water?

- 12.72** Rhodium crystallizes in a face-centered cubic unit cell that has an edge length of  $0.381 \text{ nm}$ . **(a)** Calculate the atomic radius of a rhodium atom. **(b)** Calculate the density of rhodium metal.

- 12.73** Calcium crystallizes in a face-centered cubic unit cell at room temperature that has an edge length of  $558.8 \text{ pm}$ . **(a)** Calculate the atomic radius of a calcium atom. **(b)** Calculate the density of Ca metal at this temperature.

- 12.74** Calculate the volume in  $\text{\AA}^3$  of each of the following types of cubic unit cells if it is composed of atoms with an atomic radius of  $182 \text{ pm}$ . **(a)** primitive **(b)** face-centered cubic. Note  $1 \text{\AA} = 1 \times 10^{-10} \text{ m}$

- 12.75** Aluminum metal crystallizes in a face-centered cubic unit cell. **(a)** How many aluminum atoms are in a unit cell? **(b)** What is the coordination number of each aluminum atom? **(c)** Estimate the length of the unit cell edge,  $a$ , from the atomic radius of aluminum (143 pm). **(d)** Calculate the density of aluminum metal.

- 12.76** An element crystallizes in a face-centered cubic lattice. The edge of the unit cell is  $0.408 \text{ nm}$ , and the density of the crystal is  $10.49 \text{ g/cm}^3$ . Calculate the atomic weight of the element and identify the element.

- 12.77** Which of these statements about alloys and intermetallic compounds is false? **(a)** Bronze is an example of an alloy. **(b)** "Alloy" is just another word for "a chemical compound of fixed composition that is made of two or more metals." **(c)** Intermetallics are compounds of two or more metals that have a definite composition and are not considered alloys. **(d)** If you mix two metals together and, at the atomic level, they separate into two or more different compositional phases, you have created a heterogeneous alloy. **(e)** Alloys can be formed even if the atoms that comprise them are rather different in size.

- 12.78** For each of the following alloy compositions, indicate whether you would expect it to be a substitutional alloy, an interstitial alloy, or an intermetallic compound:

- (a)**  $\text{Fe}_{0.97}\text{Si}_{0.03}$ , **(b)**  $\text{Fe}_{0.60}\text{Ni}_{0.40}$ , **(c)**  $\text{SmCo}_5$

- 12.79** Indicate whether each statement is true or false:

- (a)** Substitutional alloys tend to be more ductile than interstitial alloys.  
**(b)** Interstitial alloys tend to form between elements with similar ionic radii.  
**(c)** Nonmetallic elements are never found in alloys.

- 12.80** Which element or elements are alloyed with gold to make the following types of "colored gold" used in the jewelry industry? For each type, also indicate what type of alloy is formed: **(a)** white gold, **(b)** rose gold, **(c)** green gold.

- 12.81** An increase in temperature causes most metals to undergo *thermal expansion*, which means the volume of the metal increases upon heating. How does thermal expansion affect the unit cell length? What is the effect of an increase in temperature on the density of a metal?

- 12.82** State whether each sentence is true or false:

- (a)** Metals have high electrical conductivities because the electrons in the metal are delocalized.  
**(b)** Metals have high electrical conductivities because they are denser than other solids.

- (c) Metals have large thermal conductivities because they expand when heated.
- (d) Metals have small thermal conductivities because the delocalized electrons cannot easily transfer the kinetic energy imparted to the metal from heat.

**12.83** Which of the following statements does not follow from the fact that the alkali metals have relatively weak metal–metal bonding?

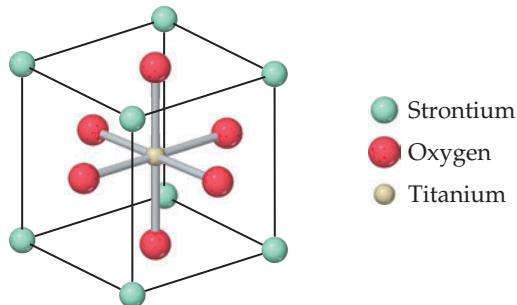
- (a) The alkali metals are less dense than other metals.
- (b) The alkali metals are soft enough to be cut with a knife.
- (c) The alkali metals are more reactive than other metals.
- (d) The alkali metals have higher melting points than other metals.
- (e) The alkali metals have low ionization energies.

**12.84** Arrange the following metals in increasing order of expected melting point: La, W, Ta, Hf. Explain this trend in melting points.

**12.85** For each of the following groups, which metal would you expect to have the highest melting point: (a) gold, rhenium, or cesium; (b) rubidium, molybdenum, or indium; (c) ruthenium, strontium, or cadmium?

### Ionic Solids (Sections 12.3)

**12.86** Tausonite, a mineral composed of Sr, O, and Ti, has the cubic unit cell shown in the drawing. (a) What is the empirical formula of this mineral? (b) How many oxygens are coordinated to titanium? (c) To see the full coordination environment of the other ions, we have to consider neighboring unit cells. How many oxygens are coordinated to strontium?



**12.87** Galena, also called lead glance, is a mineral composed of lead(II) sulfide (PbS). The mineral adopts the rock salt structure. The length of an edge of the PbS unit cell is 0.593 nm at 25 °C. Determine the density of PbS in g/cm<sup>3</sup>.

**12.88** Boron phosphide (BP) adopts the zinc blende structure. The length of the unit cell edge is 0.457 nm. (a) Calculate the density of BP in this form. (b) Boron arsenide (BAs) also forms a solid phase with the zinc blende structure. The length of the unit cell edge in this compound is 0.478 nm. What accounts for the larger unit cell length? (c) Which of the two substances has the higher density? How do you account for the difference in densities?

**12.89** CuI, CsI, and NaI each adopt a different type of structure. The three different structures are those shown in Figure 12.26. (a) Use ionic radii, Cs<sup>+</sup> ( $r = 181$  pm), Na<sup>+</sup> ( $r = 116$  pm), Cu<sup>+</sup> ( $r = 74$  pm), and, I<sup>-</sup> ( $r = 206$  pm), to predict which compound will crystallize with which structure. (b) What is the coordination number of iodide in each of these structures?

**12.90** The coordination number for Mg<sup>2+</sup> ion is usually six. Assuming this assumption holds, determine the anion coordination number in the following compounds: (a) MgS, (b) MgF<sub>2</sub>, (c) MgO.

### Covalent Solids (Section 12.4)

**12.91** Classify each of the following statements as true or false:

- (a) Although both molecular solids and covalent-network solids have covalent bonds, the melting points of molecular solids are much lower because their covalent bonds are much weaker.
- (b) Other factors being equal, highly symmetric molecules tend to form solids with higher melting points than asymmetrically shaped molecules.

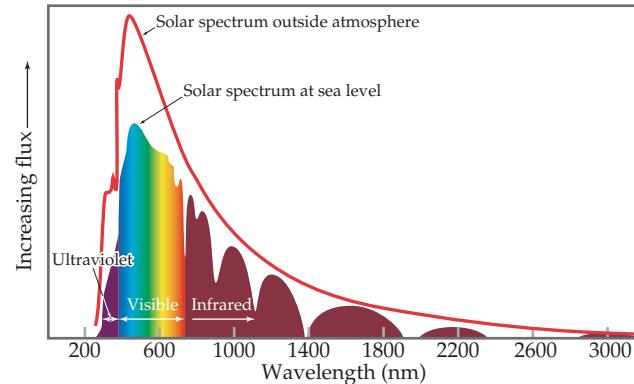
**12.92** Both covalent-network solids and ionic solids can have melting points well in excess of room temperature, and both can be poor conductors of electricity in their pure form. However, in other ways their properties are quite different.

- (a) Which type of solid is more likely to dissolve in water?
- (b) Which type of solid can become a considerably better conductor of electricity via chemical substitution?

**12.93** For each of the following pairs of semiconductors, which one will have the larger band gap: (a) CdS or CdTe, (b) GaN or InP, (c) GaAs or InAs?

**12.94** If you want to dope GaAs to make an n-type semiconductor with an element to replace Ga, which element(s) would you pick?

**12.95** Silicon has a band gap of 1.1 eV at room temperature. (a) What wavelength of light would a photon of this energy correspond to? (b) Draw a vertical line at this wavelength in the figure shown, which shows the light output of the Sun as a function of wavelength. Does silicon absorb all, none, or a portion of the visible light that comes from the Sun? (c) You can estimate the portion of the overall solar spectrum that silicon absorbs by considering the area under the curve. If you call the area under the entire curve “100%,” what approximate percentage of the area under the curve is absorbed by silicon?



**12.96** The semiconductor gallium nitride (GaN) has a band gap of 3.4 eV. What wavelength of light would be emitted from an LED made from GaN? What region of the electromagnetic spectrum is this?

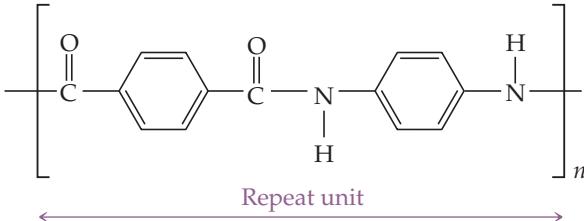
**12.97** GaAs and GaP make solid solutions that have the same crystal structure as the parent materials, with As and P randomly distributed throughout the crystal.  $\text{Ga}_x\text{As}_{1-x}$  exists for any value of  $x$ . If we assume that the band gap varies linearly with composition between  $x = 0$  and  $x = 1$ , estimate the band gap for  $\text{GaP}_{0.8}\text{As}_{0.2}$ . (GaAs and GaP band gaps are 1.43 eV and 2.26 eV, respectively.) What wavelength of light does this correspond to?

**12.98** Orange light-emitting diodes are made from GaAs and GaP solid solutions,  $\text{GaP}_x\text{As}_{1-x}$  (see Exercise 12.97). The original orange LEDs emitted light with a wavelength of 590 nm. If

we assume that the band gap varies linearly with composition between  $x = 0$  and  $x = 1$ , estimate the composition (the value of  $x$ ) that is used in these LEDs.

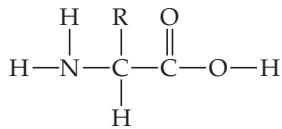
### Polymers (Section 12.5)

- 12.99** (a) What is a monomer? (b) Which of these molecules can be used as a monomer: ethanol, ethene, methane?
- 12.100** State whether each of these numbers is a reasonable value for a polymer's molecular weight: 100 u, 10,000 u, 100,000 u, 1,000,000 u?
- 12.101** An addition polymerization forms the polymer originally used as Saran™ wrap. It has the following structure  $\text{+CCl}_2-\text{CH}_2\text{+}_n$ . Draw the structure of the monomer.
- 12.102** The polymer Kevlar, a condensation polymer, is used as reinforcement in car tires, strings of archery bows, and as a component of bulletproof vests.



Draw the structures of the two monomers that yield Kevlar.

- 12.103** Proteins are naturally occurring polymers formed by condensation reactions of amino acids, which have the general structure



In this structure, —R represents —H, —CH<sub>3</sub>, or another group of atoms; there are 20 different natural amino acids, and each has one of 20 different R groups. (a) Draw the general structure of a protein formed by condensation polymerization of the generic amino acid shown here. (b) When only a few amino acids react to make a chain, the product is called a "peptide" rather than a protein; only when there are 50 amino acids or more in the chain would the molecule be called a protein. For three amino acids (distinguished by having three different R groups, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>), draw the peptide that results from their condensation reactions. (c) The order

in which the R groups exist in a peptide or protein has a huge influence on its biological activity. To distinguish different peptides and proteins, chemists call the first amino acid the one at the "N terminus" and the last one the one at the "C terminus." From your drawing in part (b) you should be able to figure out what "N terminus" and "C terminus" mean. How many different peptides can be made from your three different amino acids?

- 12.104** (a) What molecular features make a polymer flexible? (b) If you cross-link a polymer, is it more flexible or less flexible than it was before?
- 12.105** If you want to make a polymer for plastic wrap, should you strive to make a polymer that has a high or low degree of crystallinity?

### Nanomaterials (Section 12.6)

- 12.106** Explain why "bands" may not be the most accurate description of bonding in a solid when the solid has nanoscale dimensions.
- 12.107** Indicate whether each statement is true or false:
- (a) The band gap of a semiconductor decreases as the particle size decreases in the 1–10-nm range.
  - (b) The light that is emitted from a semiconductor, upon external stimulation, becomes longer in wavelength as the particle size of the semiconductor decreases.
- 12.108** An ideal quantum dot for use in TVs does not contain any cadmium due to concerns about disposal. One potential material for this purpose is InP, which adopts the zinc blende (ZnS) structure (face-centered cubic). The unit cell edge length is 586.9 pm. (a) If the quantum dot is shaped like a cube, how many of each type of atom are there in a cubic crystal with an edge length of 3.00 nm? 5.00 nm? (b) If one of the nanoparticles in part (a) emits blue light and the other emits orange light, which color is emitted by the crystal with the 3.00-nm edge length? With the 5.00-nm edge length?
- 12.109** Which statement correctly describes a difference between graphene and graphite?
- (a) Graphene is a molecule but graphite is not. (b) Graphene is a single sheet of carbon atoms and graphite contains many, and larger, sheets of carbon atoms. (c) Graphene is an insulator but graphite is a metal. (d) Graphite is pure carbon but graphene is not. (e) The carbons are  $sp^2$  hybridized in graphene but  $sp^3$  hybridized in graphite.

## Additional Exercises

- 12.110** Selected chlorides have the following melting points: NaCl (801 °C), MgCl<sub>2</sub> (714 °C), PCl<sub>3</sub> (−94 °C), SCl<sub>2</sub> (−121 °C) (a) For each compound, indicate what type its solid form is (molecular, metallic, ionic, or covalent-network). (b) Predict which of the following compounds has a higher melting point: CaCl<sub>2</sub> or SiCl<sub>4</sub>.
- 12.111** A face-centered tetragonal lattice is not one of the 14 three-dimensional lattices. Show that a face-centered tetragonal unit cell can be redefined as a body-centered tetragonal lattice with a smaller unit cell.
- 12.112** Imagine the primitive cubic lattice. Now imagine pushing on top of it, straight down. Next, stretch another face by pulling it to the right. All angles remain 90°. What kind of primitive lattice have you made?



- 12.113** Pure iron crystallizes in a body-centered cubic structure, but small amounts of impurities can stabilize a face-centered cubic structure. Which form of iron has a higher density?
- 12.114** Introduction of carbon into a metallic lattice generally results in a harder, less ductile substance with lower electrical and thermal conductivities. Explain why this might be so.
- 12.115** Ni<sub>3</sub>Al is used in the turbines of aircraft engines because of its strength and low density. Nickel metal has a cubic

close-packed structure with a face-centered cubic unit cell, while  $\text{Ni}_3\text{Al}$  has the ordered cubic structure shown in Figure 12.17. The length of the cubic unit cell edge is 353 pm for nickel and 356 pm for  $\text{Ni}_3\text{Al}$ . Use these data to calculate and compare the densities of these two materials.

- 12.116** For each of the intermetallic compounds shown in Figure 12.17 determine the number of each type of atom in the unit cell. Do your answers correspond to the ratios expected from the empirical formulas:  $\text{Ni}_3\text{Al}$ ,  $\text{Nb}_3\text{Sn}$ , and  $\text{SmCo}_5$ ?

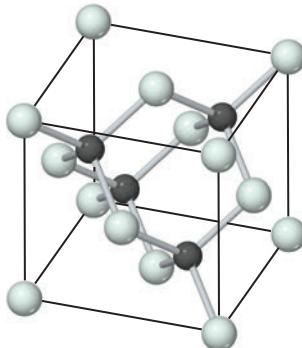
- 12.117** What type of lattice—primitive cubic, body-centered cubic, or face-centered cubic—does each of the following structure types possess: (a)  $\text{NaF}$ , (b)  $\text{Ag}$ , (c)  $\text{Fe}$ , (d)  $\text{CsCl}$ , (e)  $\text{ScF}_3$ ?

- 12.118** Greenockite ( $\text{CdS}$ ) was utilized as a pigment known as vermillion. It has a band gap of 2.6 eV near room temperature for the bulk solid. What wavelength of light (in nm) would a photon of this energy correspond to?

- 12.119** The electrical conductivity of aluminum is approximately  $10^9$  times greater than that of its neighbor in the periodic table, silicon. Aluminum has a face-centered cubic structure, and silicon has the diamond structure. A classmate of yours tells you that density is the reason aluminum is a metal but silicon is not; therefore, if you were to put silicon under high pressure, it too would act like a metal. Discuss this idea with your classmates, looking up data about Al and Si as needed.

- 12.120** Silicon carbide,  $\text{SiC}$ , has the three-dimensional structure shown in the figure.

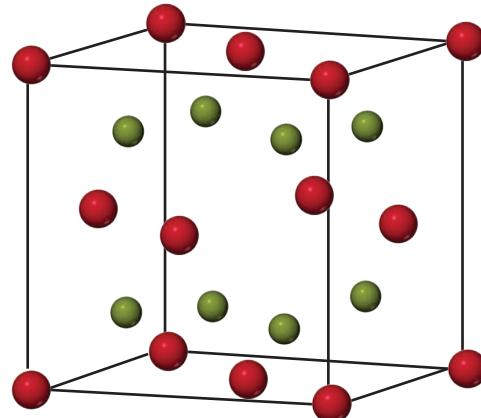
(a) Name another compound that has the same structure. (b) Would you expect the bonding in  $\text{SiC}$  to be predominantly ionic, metallic, or covalent? (c) How do the bonding and structure of  $\text{SiC}$  lead to its high thermal stability (to 2700 °C) and exceptional hardness?



- 12.121** Energy bands are considered continuous due to the large number of closely spaced energy levels. The range of energy levels in a crystal of copper is approximately  $1 \times 10^{-19} \text{ J}$ . Assuming equal spacing between levels, the spacing between energy levels may be approximated by dividing the range of energies by the number of atoms in the crystal. (a) How many copper atoms are in a piece of copper metal in the shape of a cube with edge length 0.5 mm? The density of copper is  $8.96 \text{ g/cm}^3$ . (b) Determine the average spacing in J between energy levels in the copper metal in part (a). (c) Is this spacing larger, substantially smaller, or about the same as the  $1 \times 10^{-18} \text{ J}$  separation between energy levels in a hydrogen atom?

- 12.122** Unlike metals, semiconductors increase their conductivity as you heat them (up to a point). Suggest an explanation.

- 12.123** Sodium oxide ( $\text{Na}_2\text{O}$ ) adopts a cubic structure with Na atoms represented by green spheres and O atoms by red spheres.



- (a) How many atoms of each type are there in the unit cell?  
 (b) Determine the coordination number and describe the shape of the coordination environment for the sodium ion.  
 (c) The unit cell edge length is 555 pm. Determine the density of  $\text{Na}_2\text{O}$ .

- 12.124** Teflon is a polymer formed by the polymerization of  $\text{F}_2\text{C}=\text{CF}_2$ . (a) Draw the structure of a section of this polymer. (b) What type of polymerization reaction is required to form Teflon?

- 12.125** Hydrogen bonding between polyamide chains plays an important role in determining the properties of a nylon such as nylon 6,6 (Table 12.6). Draw the structural formulas for two adjacent chains of nylon 6,6 and show where hydrogen-bonding interactions could occur between them.

- 12.126** Explain why X rays can be used to measure atomic distances in crystals but visible light cannot be used for this purpose.

- 12.127** In their study of X-ray diffraction, William and Lawrence Bragg determined that the relationship among the wavelength of the radiation ( $\lambda$ ), the angle at which the radiation is diffracted ( $\theta$ ), and the distance between planes of atoms in the crystal that cause the diffraction ( $d$ ) is given by  $n\lambda = 2d \sin \theta$ . X rays from a copper X-ray tube that have a wavelength of 154 pm are diffracted at an angle of 14.22 degrees by crystalline silicon. Using the Bragg equation, calculate the distance between the planes of atoms responsible for diffraction in this crystal, assuming  $n = 1$  (first-order diffraction).

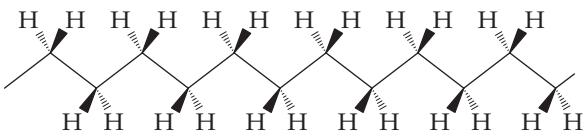
- 12.128** Germanium has the same structure as silicon, but the unit cell size is different because Ge and Si atoms are not the same size. If you were to repeat the experiment described in the previous problem but replace the Si crystal with a Ge crystal, would you expect the X rays to be diffracted at a larger or smaller angle  $\theta$ ?

- 12.129** (a) The density of diamond is  $3.5 \text{ g/cm}^3$ , and that of graphite is  $2.3 \text{ g/cm}^3$ . Based on the structure of buckminsterfullerene, what would you expect its density to be relative to these other forms of carbon? (b) X-ray diffraction studies of buckminsterfullerene show that it has a face-centered cubic lattice of  $\text{C}_{60}$  molecules. The length of an edge of the unit cell is 142 pm. Calculate the density of buckminsterfullerene.

- 12.130** When you shine light of band gap energy or higher on a semiconductor and promote electrons from the valence band to the conduction band, do you expect the conductivity of the semiconductor to (a) remain unchanged, (b) increase, or (c) decrease?

## Integrative Exercises

- 12.131** The carat scale used to describe gold alloys is based on mass percentages. (a) If an alloy is formed that is 75 mol% silver and 25 mol% gold, what is the carat number of the alloy? Use Figure 12.18 to estimate the color of this alloy. (b) If an alloy is formed that is 75 mol% copper and 25 mol% gold, what is the carat number of the alloy? What is the color of this alloy?
- 12.132** Spinel is a mineral that contains 37.9% Al, 17.1% Mg, and 45.0% O, by mass, and has a density of  $3.57\text{ g/cm}^3$ . The unit cell is cubic with an edge length of 809 pm. How many atoms of each type are in the unit cell?
- 12.133** (a) What are the C—C—C bond angles in diamond? (b) What are they in graphite (in one sheet)? (c) What atomic orbitals are involved in the stacking of graphite sheets with each other?
- 12.134** Employing the bond enthalpy values listed in Table 8.4, estimate the molar enthalpy change occurring upon (a) polymerization of ethene, (b) formation of nylon 6,6, (c) formation of polyethene terephthalate (PET).
- 12.135** Although polyethene can twist and turn in random ways, the most stable form is a linear one with the carbon backbone oriented as shown in the following figure:



The carbon atoms of the backbone are not shown for clarity. The solid wedges in the figure indicate bonds from carbon that come out of the plane of the page; the dashed wedges indicate bonds that lie behind the plane of the page.

- (a) What is the hybridization of orbitals at each carbon atom? What angles do you expect between the bonds?
- (b) Now imagine that the polymer is polypropene rather than polyethene. Draw structures for polypropene in which (i) the  $\text{CH}_3$  groups all lie on the same side of the plane of the paper (this form is called isotactic polypropene), (ii) the  $\text{CH}_3$  groups lie on alternating sides of the plane (syndiotactic polypropene), or (iii) the  $\text{CH}_3$  groups are randomly distributed on

either side (atactic polypropene). Which of these forms would you expect to have the highest crystallinity and melting point, and which the lowest? Explain in terms of intermolecular interactions and molecular shapes.

- (c) Polypropene fibers have been employed in athletic wear. The product is said to be superior to cotton or polyester clothing in wicking moisture away from the body through the fabric to the outside. Explain the difference between polypropene and polyester or cotton (which has many  $-\text{OH}$  groups along the molecular chain) in terms of intermolecular interactions with water.

- 12.136** (a) In polyvinyl chloride shown in Table 12.6, which bonds have the lowest average bond enthalpy? (b) When subjected to high pressure and heated, polyvinyl chloride converts to diamond. During this transformation which bonds are most likely to break first? (c) Employing the values of average bond enthalpy in Table 8.3, estimate the overall enthalpy change for converting PVC to diamond.

- 12.137** Silicon has the diamond structure with a unit cell edge length of 543 pm and eight atoms per unit cell. (a) How many silicon atoms are there in  $1\text{ cm}^3$  of material? (b) Suppose you dope that  $1\text{ cm}^3$  sample of silicon with 1 ppm of phosphorus that will increase the conductivity by a factor of a million. How many milligrams of phosphorus are required?

- 12.138** One method to synthesize ionic solids is by the heating of two reactants at high temperatures. Consider the reaction of  $\text{MgO}$  with  $\text{TiO}_2$  to form  $\text{MgTiO}_3$ . Determine the amount of each of the two reactants to prepare 3.250 g  $\text{MgTiO}_3$ , assuming the reaction goes to completion.

- (a) Write a balanced chemical reaction.  
 (b) Calculate the formula weight of  $\text{MgTiO}_3$ .  
 (c) Determine the moles of  $\text{MgTiO}_3$ .  
 (d) Determine moles and mass (g) of  $\text{MgO}$  required.  
 (e) Determine moles and mass (g) of  $\text{TiO}_2$  required.

- 12.139** Look up the diameter of a silicon atom, in pm. The latest semiconductor chips have fabricated lines as small as 14 nm. How many silicon atoms does this correspond to?

## Design an Experiment

Polymers were commercially made by the DuPont Company starting in the late 1920s. At that time, some chemists still could not believe that polymers were molecules; they thought covalent bonding would not "last" for millions of atoms, and that polymers were

really clumps of molecules held together by weak intermolecular forces. Design an experiment to demonstrate that polymers really are large molecules and not little clumps of small molecules that are held together by weak intermolecular forces.