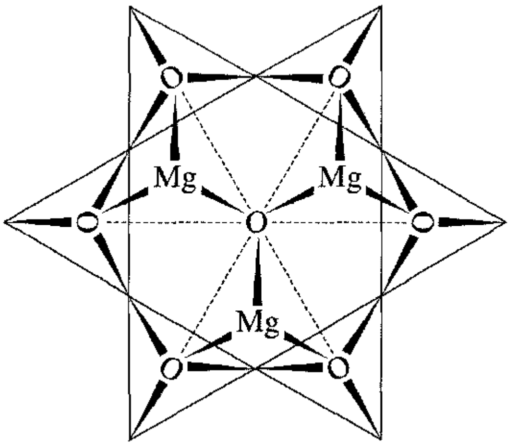

CHAPTER 7

The Crystalline Solid State

Solid-state chemistry uses the same principles for bonding as those for molecules. The differences from molecular bonding come from the magnitude of the "molecules" in the solid state. In many cases, a macroscopic crystal can reasonably be described as a single molecule, with molecular orbitals extending throughout. This description leads to significant differences in the molecular orbitals and behavior of solids compared with those of small molecules. There are two major classifications of solid materials: crystals and amorphous materials. Our attention in this chapter is on crystalline solids composed of atoms or ions.

We will first describe the common structures of crystals and then give the molecular orbital explanation of their bonding. Finally, we will describe some of the thermodynamic and electronic properties of these materials and their uses.

7-1 FORMULAS AND STRUCTURES

Crystalline solids have atoms, ions, or molecules packed in regular geometric arrays, with the structural unit called the **unit cell**. Some of the common crystal geometries are described in this section. In addition, we will consider the role of the relative sizes of the components in determining the structure. Use of a model kit, such as the one available from ICE,[1] makes the study of these structures much easier.

7-1-1 SIMPLE STRUCTURES

The crystal structures of metals are simple. Those of some minerals can be very complex, but usually have simpler structures that can be recognized within the more complex structure. The unit cell is a structural component that, when repeated in all

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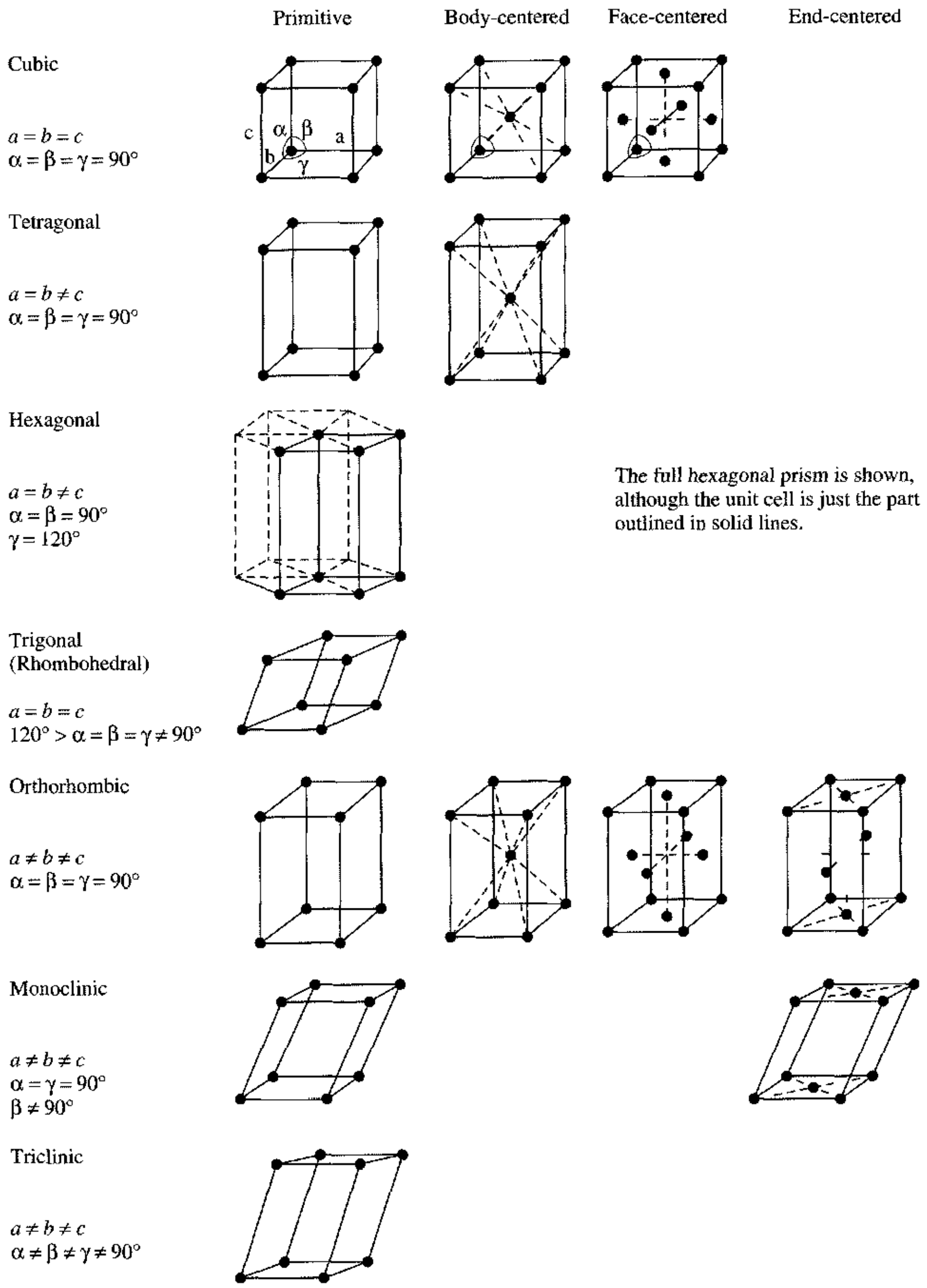
[1] Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave., Madison, WI 53706. Sources for other model kits are given in A. B. Ellis, M. J. Geselbracht, B. J. Johnson, G. C. Lisensky, and W. R. Robinson, *Teaching General Chemistry: A Materials Science Companion*, American Chemical Society, Washington, DC, 1993.

directions, results in a macroscopic crystal. Structures of the 14 possible crystal structures (Bravais lattices) are shown in Figure 7-1. Several different unit cells are possible for some structures; the one used may be chosen for convenience, depending on the particular application. The atoms on the corners, edges, or faces of the unit cell are shared with other unit cells. Those on the corners of rectangular unit cells are shared equally by eight unit cells and contribute $\frac{1}{8}$ to each ($\frac{1}{8}$ of the atom is counted as part of each cell). The total for a single unit cell is $8 \times \frac{1}{8} = 1$ atom for all of the corners. Those on the corners of nonrectangular unit cells also contribute one atom total to the unit cell; small fractions on one corner are matched by larger fractions on another. Atoms on edges of unit cells are shared by four unit cells (two in one layer, two in the adjacent layer) and contribute $\frac{1}{4}$ to each, and those on the faces of unit cells are shared between two unit



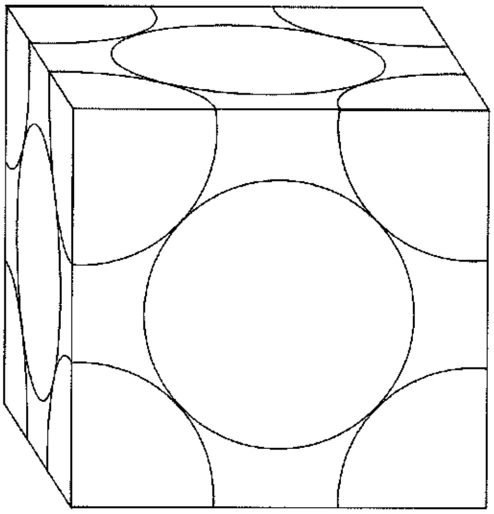
The full hexagonal prism is shown, although the unit cell is just the part outlined in solid lines.

FIGURE 7-1 The Seven Crystal Classes and Fourteen Bravais Lattices. The points shown are not necessarily individual atoms, but are included to show the necessary symmetry.

cells and contribute $\frac{1}{2}$ to each. As can be seen in Figure 7-1, unit cells need not have equal dimensions or angles. For example, triclinic crystals have three different angles and may have three different distances for the dimensions of the unit cell.

EXAMPLE

The diagram below shows a space-filling diagram of a face-centered cubic unit cell cut to show only the part of each atom that is inside the unit cell boundaries. The corner atoms are each shared among eight unit cells, so $\frac{1}{8}$ of the atom is in the unit cell shown. The face-centered atoms are shared between two unit cells, so $\frac{1}{2}$ of the atom is in the unit cell shown. The eight corners of the unit cell then total $8 \times \frac{1}{8} = 1$ atom, the six faces total $6 \times \frac{1}{2} = 3$ atoms, and there is a total of 4 atoms in the unit cell.



EXERCISE 7-1

Calculate the number of atoms in each unit cell of

a. A body-centered cubic structure.
b. A hexagonal structure.

The structures are shown in Figure 7-1.

The positions of atoms are frequently described in **lattice points**, expressed as fractions of the unit cell dimensions. For example, the body-centered cube has atoms at the origin $[x = 0, y = 0, z = 0, \text{ or } (0, 0, 0)]$ and at the center of the cube $\left[x = \frac{1}{2}, y = \frac{1}{2}, z = \frac{1}{2}, \text{ or } \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)\right]$. The other atoms can be generated by moving these two atoms in each direction in increments of one cell length.

Cubic

The most basic crystal structure is the simple cube, called the **primitive cubic** structure, with atoms at the eight corners. It can be described by specifying the length of one side, the angle 90°, and the single lattice point (0, 0, 0). Because each of the atoms is shared between eight cubes, four in one layer and four in the layer above or below, the total number of atoms in the unit cell is $8 \times \frac{1}{8} = 1$, the number of lattice points required. Each atom is surrounded by six others, for a **coordination number** (CN) of 6. This structure is not efficiently packed because the spheres occupy only 52.4% of the total volume. In the center of the cube is a vacant space that has eight nearest neighbors or a coordination number of 8. Calculation shows that a sphere with a radius $0.73r$ (where r is the radius of the corner spheres) would fit in the center of this cube if the corner spheres are in contact with each other.

Body-centered cubic

If another sphere is added in the center of the simple cubic structure, the result is called **body-centered cubic** (bcc). If the added sphere has the same radius as the others, the size of the unit cell expands so that the diagonal distance through the cube is $4r$, where r is the radius of the spheres. The corner atoms are no longer in contact with each other. The new unit cell is $2.31r$ on each side and contains two atoms because the body-centered atom is completely within the unit cell. This cell has two lattice points, at the origin $(0, 0, 0)$ and at the center of the cell $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$.

EXERCISE 7-2

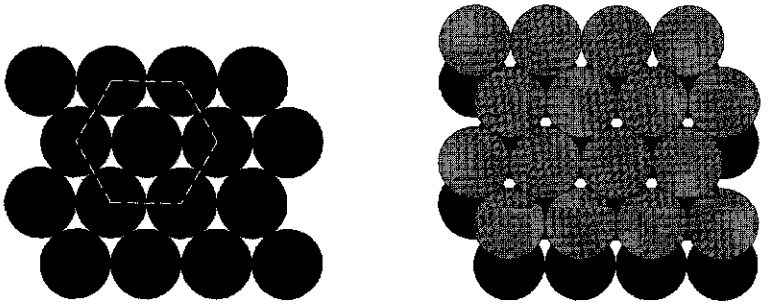
Show that the side of the unit cell for a body-centered cubic crystal is 2.31 times the radius of the atoms in the crystal.

Close-packed structures

When marbles or ball bearings are poured into a flat box, they tend to form a close-packed layer, in which each sphere is surrounded by six others in the same plane. This arrangement provides the most efficient packing possible for a single layer. When three or more close-packed layers are placed on top of each other systematically, two structures are possible: hexagonal close packing (hcp) and cubic close packing (ccp), also known as face-centered cubic (fcc). In both, the coordination number for each atom is 12, six in its own layer, three in the layer above, and three in the layer below. When the third layer is placed with all atoms directly above those of the first layer, the result is an ABA structure called **hexagonal close packing** (hcp). When the third layer is displaced so each atom is above a hole in the first layer, the resulting ABC structure is called **cubic close packing** (ccp) or **face-centered cubic** (fcc). These are shown in Figure 7-2. In both these structures, there are two tetrahedral holes per atom (coordination number 4, formed by three atoms in one layer and one in the layer above or below) and one octahedral hole per atom (three atoms in each layer, total coordination number of 6).

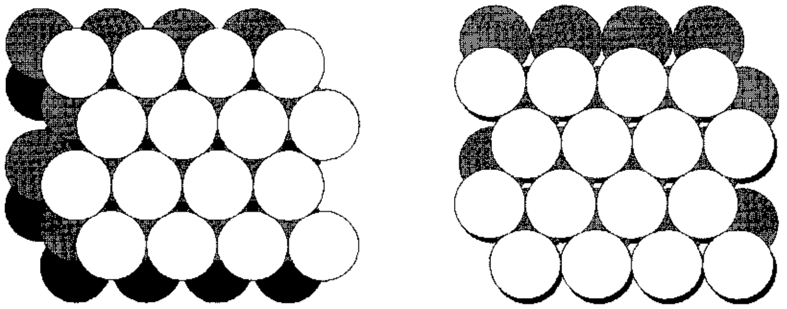
Hexagonal close packing is relatively easy to see, with hexagonal prisms sharing vertical faces in the larger crystal (Figure 7-3). The minimal unit cell is smaller than the hexagonal prism; taking any four atoms that all touch each other in one layer and extending lines up to the third layer will generate a unit cell with a parallelogram as the base. As shown in Figure 7-3, it contains half an atom in the first layer (four atoms averaging $\frac{1}{8}$ each), four similar atoms in the third layer, and one atom from the second layer whose center is within the unit cell, for a total of two atoms in the unit cell. The unit cell has dimensions of $2r$, $2r$, and $2.83r$ and an angle of 120° between the first two axes in the basal plane and 90° between each of these axes and the third, vertical axis. The atoms are at the lattice points $(0, 0, 0)$ and $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$.

The cube in cubic close packing is harder to see when each of the layers is close-packed. The unit cell cube rests on one corner, with four close-packed layers required to complete the cube. The first layer has only one sphere and the second has six in a triangle, as shown in Figure 7-4(a). The third layer has another six-membered triangle with the vertices rotated 60° from the one in the second layer, and the fourth layer again has one sphere. The cubic shape of the cell is easier to see if the faces are placed in the conventional horizontal and vertical directions, as in Figure 7-4(b).



A single close-packed layer, A, with the hexagonal packing outlined.

Two close-packed layers, A and B. Octahedral holes can be seen extending through both layers surrounded by three atoms in each layer. Tetrahedral holes are under each atom of the second layer and over each atom of the bottom layer. Each is made up of three atoms from one layer and one from the other.



Cubic close-packed layers, in an ABC pattern. Octahedral holes are offset, so no hole extends through all three layers.

Hexagonal close-packed layers. The third layer is exactly over the first layer in this ABA pattern. Octahedral holes are aligned exactly over each other, one set between the first two layers A and B, the other between the second and third layers, B and A.

● Layer 1 (A) ▨ Layer 2 (B) ○ Layer 3 (A or C)

FIGURE 7-2 Close-packed Structures.

The unit cell of the cubic close-packed structure is a face-centered cube, with spheres at the corners and in the middle of each of the six faces. The lattice points are at $(0, 0, 0)$, $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$, $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$, and $\left(0, \frac{1}{2}, \frac{1}{2}\right)$, for a total of four atoms in the unit cell, $\frac{1}{8} \times 8$ at the corners and $\frac{1}{2} \times 6$ in the faces. In both close-packed structures, the spheres occupy 74.1% of the total volume.

Ionic crystals can also be described in terms of the interstices, or holes, in the structures. Figure 7-5 shows the location of tetrahedral and octahedral holes in close-packed structures. Whenever an atom is placed in a new layer over a close-packed layer, it creates a tetrahedral hole surrounded by three atoms in the first layer and one in the second (CN = 4). When additional atoms are added to the second layer, they create tetrahedral holes surrounded by one atom in the one layer and three in the other. In addition, there are octahedral holes (CN = 6) surrounded by three atoms in each layer. Overall, close-packed structures have two tetrahedral holes and one octahedral hole per atom. These holes can be filled by smaller ions, the tetrahedral holes by ions with radius $0.225r$, where r is the radius of the larger ions, and the octahedral holes by ions with radius $0.414r$. In more complex crystals, even if the ions are not in contact with each other, the geometry is described in the same terminology. For example, NaCl has chloride ions in a cubic close-packed array, with sodium ions (also in a ccp array) in the

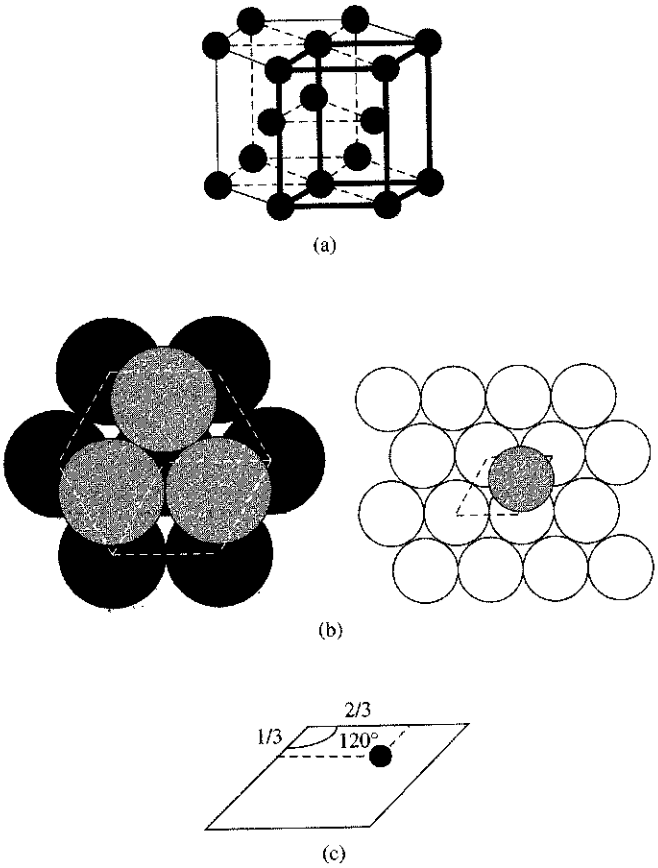


FIGURE 7-3 Hexagonal Close Packing. (a) The hexagonal prism with the unit cell outlined in bold. (b) Two layers of an hcp unit cell. The parallelogram is the base of the unit cell. The third layer is identical to the first. (c) Location of the atom in the second layer.

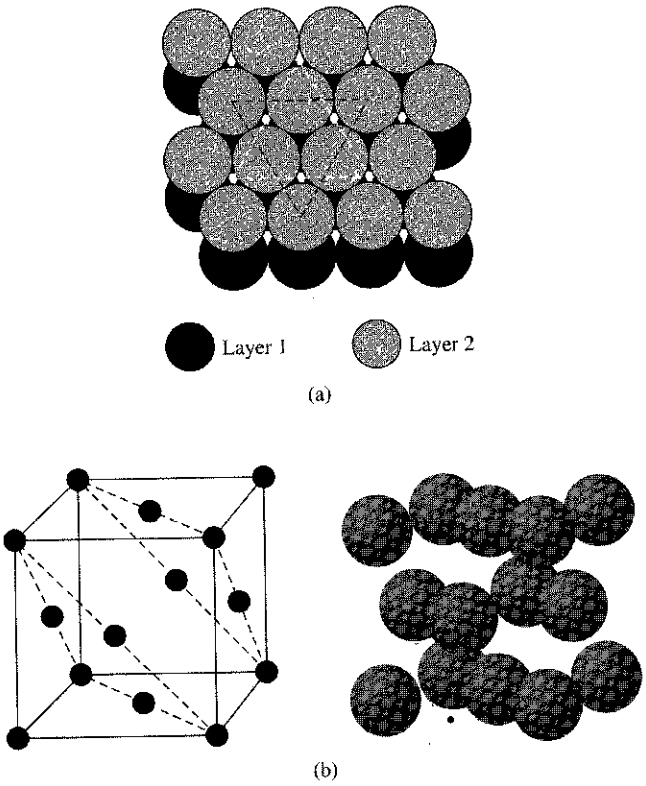


FIGURE 7-4 Cubic Close Packing. (a) Two layers of a ccp (or fcc) cell. The atom in the center of the triangle in the first layer and the six atoms connected by the triangle form half the unit cell. The other half, in the third and fourth layers, is identical, but with the direction of the triangle reversed. (b) Two views of the unit cell, with the close-packed layers marked in the first.

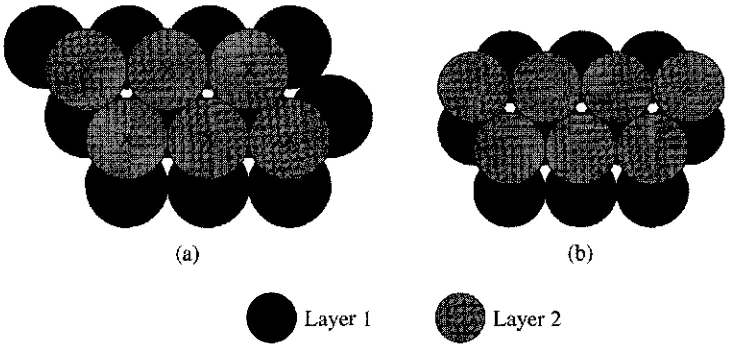


FIGURE 7-5 Tetrahedral and Octahedral Holes in Close-packed Layers. (a) Tetrahedral holes are under each x and at each point where an atom of the first layer appears in the triangle between three atoms in the second layer. (b) An octahedral hole is outlined, surrounded by three atoms in each layer.

octahedral holes. The sodium ions have a radius 0.695 times the radius of the chloride ion ($r_+ = 0.695r_-$), large enough to force the chloride ions apart, but not large enough to allow a coordination number larger than 6.

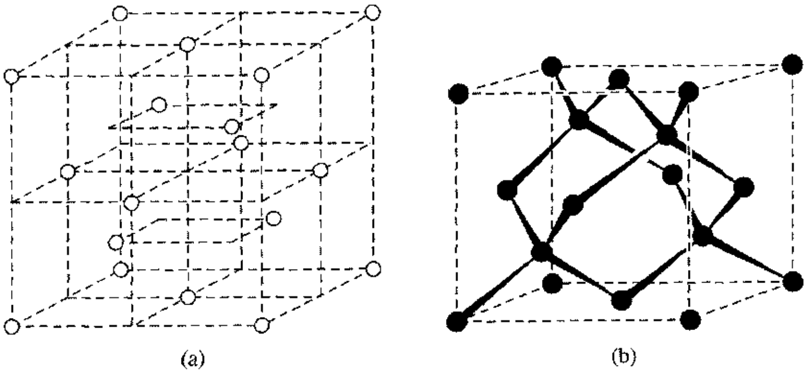
Metallic crystals

Except for the actinides, most metals crystallize in body-centered cubic, cubic close-packed, and hexagonal close-packed structures, with approximately equal numbers of each type. In addition, changing pressure or temperature will change many metallic crystals from one structure to another. This variability shows that we should not think of these metal atoms as hard spheres that pack together in crystals independent of electronic structure. Instead, the sizes and packing of atoms are somewhat variable. Atoms attract each other at moderate distances and repel each other when they are close enough that their electron clouds overlap too much. The balance between these forces, modified by the specific electronic configuration of the atoms, determines the net forces between them and the structure that is most stable. Simple geometric calculations cannot be relied on.

Properties of metals

The single property that best distinguishes metals from nonmetals is conductivity. Metals have high conductivity, or low resistance, to the passage of electricity and of heat; nonmetals have low conductivity or high resistance. One exception is diamond, which has low electrical conductivity and high heat conductivity. Conductivity is discussed further in Section 7-3 on the electronic structure of metals and semiconductors.

Aside from conductivity, metals have quite varied properties. Some are soft and easily deformed by pressure or impact, or malleable (Cu, fcc structure), whereas others are hard and brittle, more likely to break rather than bend (Zn, hcp). However, most can be shaped by hammering or bending. This is possible because the bonding is nondirectional; each atom is rather weakly bonded to all neighboring atoms, rather than to individual atoms, as is the case in discrete molecules. When force is applied, the atoms can slide over each other and realign into new structures with nearly the same overall energy. This effect is facilitated by **dislocations**, where the crystal is imperfect and atoms are out of place and occupy those positions because of the rigidity of the rest of the crystal. The effects of these discontinuities are increased by impurity atoms, especially those with a size different from that of the host. These atoms tend to accumulate at discontinuities in the crystal, making it even less uniform. These imperfections allow gradual slippage of layers, rather than requiring an entire layer to move at the same time. Some metals can be work-hardened by repeated deformation. When the metal is hammered, the defects tend to group together, eventually resisting deformation. Heating can restore flexibility by redistributing the dislocations and reducing the number of them. For different metals or alloys (mixtures of metals), heat treatment and slow or fast



(a) (b)

FIGURE 7-6 The Structure of Diamond. (a) Subdivision of the unit cell, with atoms in alternating smaller cubes. (b) The tetrahedral coordination of carbon is shown for the four interior atoms.

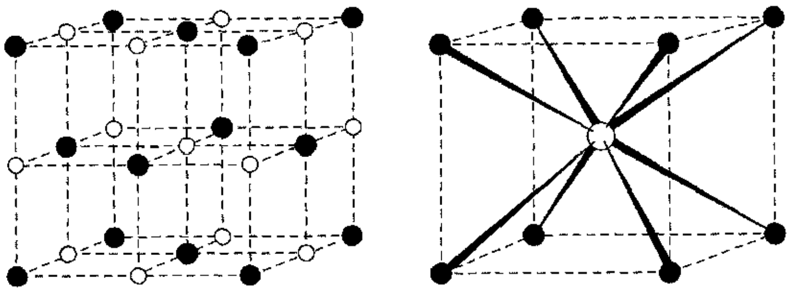
cooling can lead to much different results. Some metals can be tempered to be harder and hold a sharp edge better, others can be heat-treated to be more resilient, flexing without being permanently bent. Still others can be treated to have "shape memory." These alloys can be bent, but return to their initial shape on moderate heating.

Diamond

The final simple structure we will consider is that of diamond (Figure 7-6), which has the same overall geometry as zinc blende (described later), but with all atoms identical. If a face-centered cubic crystal is divided into eight smaller cubes by planes cutting through the middle in all three directions, and additional atoms are added in the centers of four of the smaller cubes, none of them adjacent, the diamond structure is the result. Each carbon atom is bonded tetrahedrally to four nearest neighbors, and the bonding between them is similar to ordinary carbon-carbon single bonds. The strength of the crystal comes from the covalent nature of the bonding and the fact that each carbon has its complete set of four bonds. Although there are cleavage planes in diamond, the structure has essentially the same strength in all directions. In addition to carbon, three other elements in the same group (silicon, germanium, and α-tin) have the same structure. Ice also has the same crystal symmetry (see Figure 3-21), with O—H—O bonds between all the oxygens. The ice structure is more open because of the greater distance between oxygen atoms.

7-1-2 STRUCTURES OF BINARY COMPOUNDS

Binary compounds (compounds consisting of two elements) may have very simple crystal structures and can be described in several different ways. Two simple structures are shown in Figure 7-7. As described in Section 7-1-1, there are two tetrahedral holes



Sodium chloride
○ Sodium (or chloride)
● Chloride (or sodium)
(a)

Cesium chloride
○ Cesium (or chloride)
● Chloride (or cesium)
(b)

FIGURE 7-7 Sodium Chloride and Cesium Chloride Unit Cells.

and one octahedral hole per atom in close-packed structures. If the larger ions (usually the anions) are in close-packed structures, ions of the opposite charge occupy these holes, depending primarily on two factors:

1. The relative sizes of the atoms or ions. The **radius ratio** (usually r_+/r_- but sometimes r_-/r_+, where r_+ is the radius of the cation and r_- is the radius of the anion) is generally used to measure this. Small cations will fit in the tetrahedral or octahedral holes of a close-packed anion lattice. Somewhat larger cations will fit in the octahedral holes, but not in tetrahedral holes, of the same lattice. Still larger cations force a change in structure. This will be explained more fully in Section 7-1-4.
2. The relative numbers of cations and anions. For example, a formula of M_2X will not allow a close-packed anion lattice and occupancy of all of the octahedral holes by the cations because there are too many cations. The structure must either have the cations in tetrahedral holes, have many vacancies in the anion lattice, or have an anion lattice that is not close-packed.

The structures described in this section are generic, but are named for the most common compound with the structure. Although some structures are also influenced by the electronic structure of the ions, particularly when there is a high degree of covalency, this effect will not be considered here.

Sodium chloride, NaCl

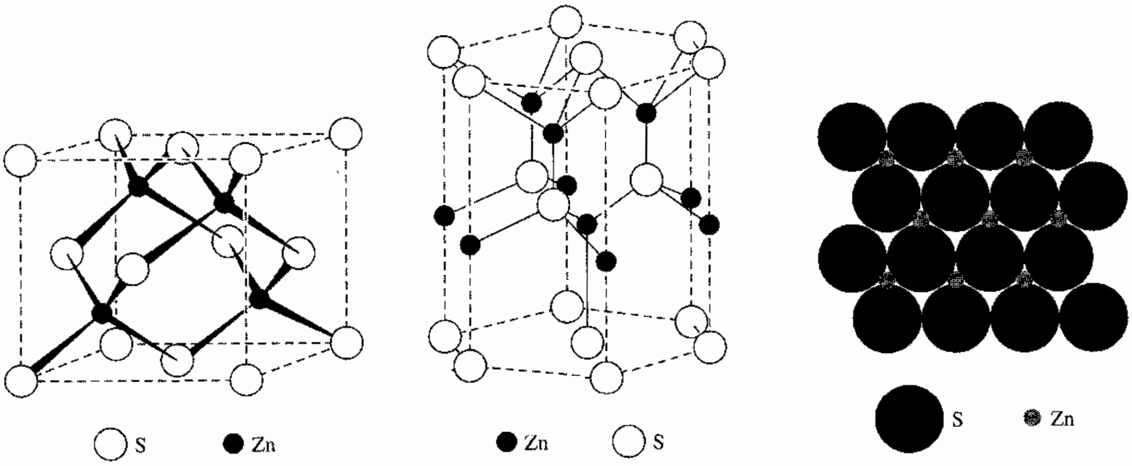
NaCl, Figure 7-7(a), is made up of face-centered cubes of sodium ions and face-centered cubes of chloride ions combined, but offset by half a unit cell length in one direction so that the sodium ions are centered in the edges of the chloride lattice (and vice versa). If all the ions were identical, the NaCl unit cell would be made up of eight simple cubic unit cells. Many alkali halides and other simple compounds share this same structure. For these crystals, the ions tend to have quite different sizes, usually with the anions larger than the cations. Each sodium ion is surrounded by six nearest-neighbor chloride ions, and each chloride ion is surrounded by six nearest-neighbor sodium ions.

Cesium chloride, CsCl

As mentioned previously, a sphere of radius $0.73r$ will fit exactly in the center of a cubic structure. Although the fit is not perfect, this is what happens in CsCl, Figure 7-7(b), where the chloride ions form simple cubes with cesium ions in the centers. In the same way, the cesium ions form simple cubes with chloride ions in the centers. The average chloride ion radius is 0.83 times as large as the cesium ion (167 pm and 202 pm, respectively), but the interionic distance in CsCl is 356 pm, about 3.5% smaller than the sum of the average ionic radii. Only CsCl, CsBr, CsI, TlCl, TlBr, TlI, and CsSH have this structure at ordinary temperatures and pressures, although some other alkali halides have this structure at high pressure and high temperature. The cesium salts can also be made to crystallize in the NaCl lattice on NaCl or KBr substrates, and CsCl converts to the NaCl lattice at about 469° C.

Zinc blende, ZnS

ZnS has two common crystalline forms, both with coordination number 4. Zinc blende, Figure 7-8(a), is the most common zinc ore and has essentially the same geometry as diamond, with alternating layers of Zn and S. It can also be described as having zinc



(a) Zinc blende (the same structure results if the Zn and S positions are reversed)

(b) Wurtzite

(c) One sulfide layer and one zinc layer of wurtzite. The third layer contains sulfide ions, directly above the zinc ions. The fourth layer is zinc ions, directly above the sulfides of the first layer.

FIGURE 7-8 ZnS Crystal Structures. (a) Zinc blende. (b, c) Wurtzite.

ions and sulfide ions, each in face-centered lattices, so that each ion is in a tetrahedral hole of the other lattice. The stoichiometry requires half of these tetrahedral holes to be occupied, with alternating occupied and vacant sites.

Wurtzite, ZnS

The wurtzite form of ZnS, Figure 7-8(b, c), is much rarer than zinc blende, and is formed at higher temperatures than zinc blende. It also has zinc and sulfide each in a tetrahedral hole of the other lattice, but each type of ion forms a hexagonal close-packed lattice. As in zinc blende, half of the tetrahedral holes in each lattice are occupied.

Fluorite, CaF_2

The fluorite structure, Figure 7-9, can be described as having the calcium ions in a cubic close-packed lattice, with eight fluoride ions surrounding each one and occupying all of the tetrahedral holes. An alternative description of the same structure, shown in

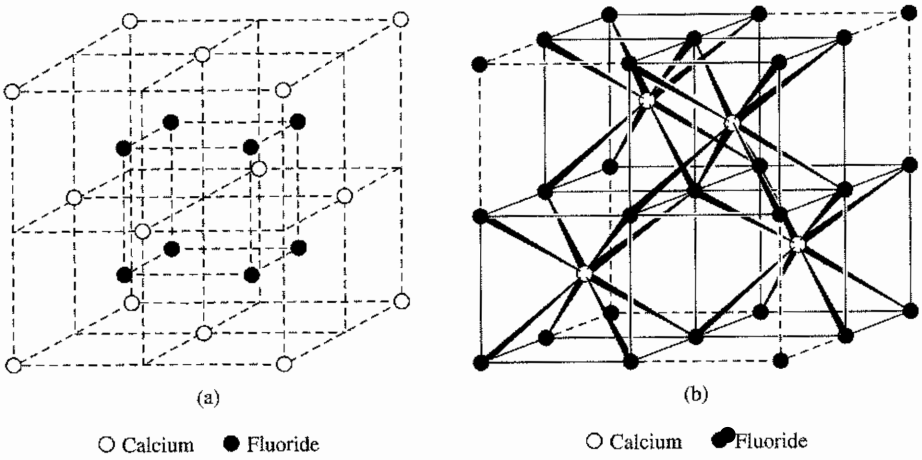


FIGURE 7-9 Fluorite and Antifluorite Crystal Structures. (a) Fluorite shown as Ca^{2+} in a cubic close-packed lattice, each surrounded by eight F^- in the tetrahedral holes. (b) Fluorite shown as F^- in a simple cubic array, with Ca^{2+} in alternate body centers. Solid lines enclose the cubes containing Ca^{2+} ions. If the positive and negative ion positions are reversed, as in Li_2O, the structure is known as antifluorite.

Figure 7-9(b), has the fluoride ions in a simple cubic array, with calcium ions in alternate body centers. The ionic radii are nearly perfect fits for this geometry. There is also an *antifluorite* structure in which the cation-anion stoichiometry is reversed. This structure is found in all the oxides and sulfides of Li, Na, K, and Rb, and in Li_2Te and Be_2C. In the antifluorite structure, every tetrahedral hole in the anion lattice is occupied by a cation, in contrast to the ZnS structures, in which half the tetrahedral holes of the sulfide ion lattice are occupied by zinc ions.

NiAs

The nickel arsenide structure (Figure 7-10) has arsenic atoms in identical close-packed layers stacked directly over each other, with nickel atoms in all the octahedral holes. The larger arsenic atoms are in the center of trigonal prisms of nickel atoms. Both types of atoms have coordination number 6, with layers of nickel atoms close enough that each nickel can also be considered as bonded to two others. An alternate description is that the nickel atoms occupy all the octahedral holes of a hexagonal close-packed arsenic lattice. This structure is also adopted by many MX compounds, where M is a transition metal and X is from Groups 14, 15, or 16 (Sn, As, Sb, Bi, S, Se, or Te). This structure is easily changed to allow for larger amounts of the nonmetal to be incorporated into nonstoichiometric materials.

Rutile, TiO_2

TiO_2 in the rutile structure (Figure 7-11) has distorted TiO_6 octahedra that form columns by sharing edges, resulting in coordination numbers of 6 and 3 for titanium and oxygen, respectively. Adjacent columns are connected by sharing corners of the octahedra. The oxide ions have three nearest-neighbor titanium ions in a planar configuration, one at a slightly greater distance than the other two. The unit cell has titanium ions at the corners and in the body center, two oxygens in opposite quadrants of the bottom face, two oxygens directly above the first two in the top face, and two oxygens in the plane with the body-centered titanium forming the final two positions of the oxide octahedron. The same geometry is found for MgF_2, ZnF_2, and some transition metal fluorides. Compounds that contain larger metal ions adopt the fluorite structure with coordination numbers of 8 and 4.

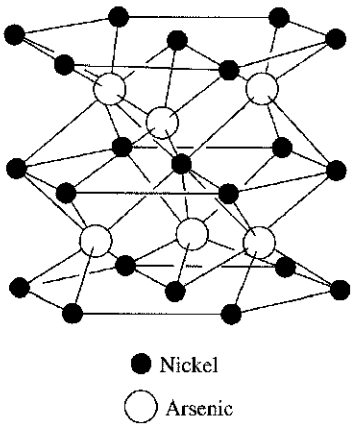


FIGURE 7-10 NiAs Crystal Structure.

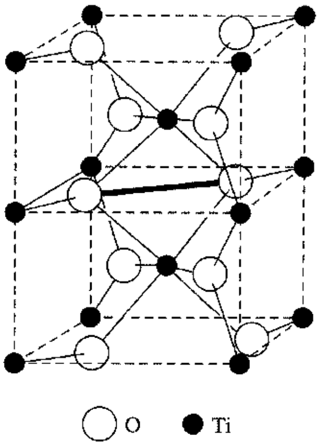


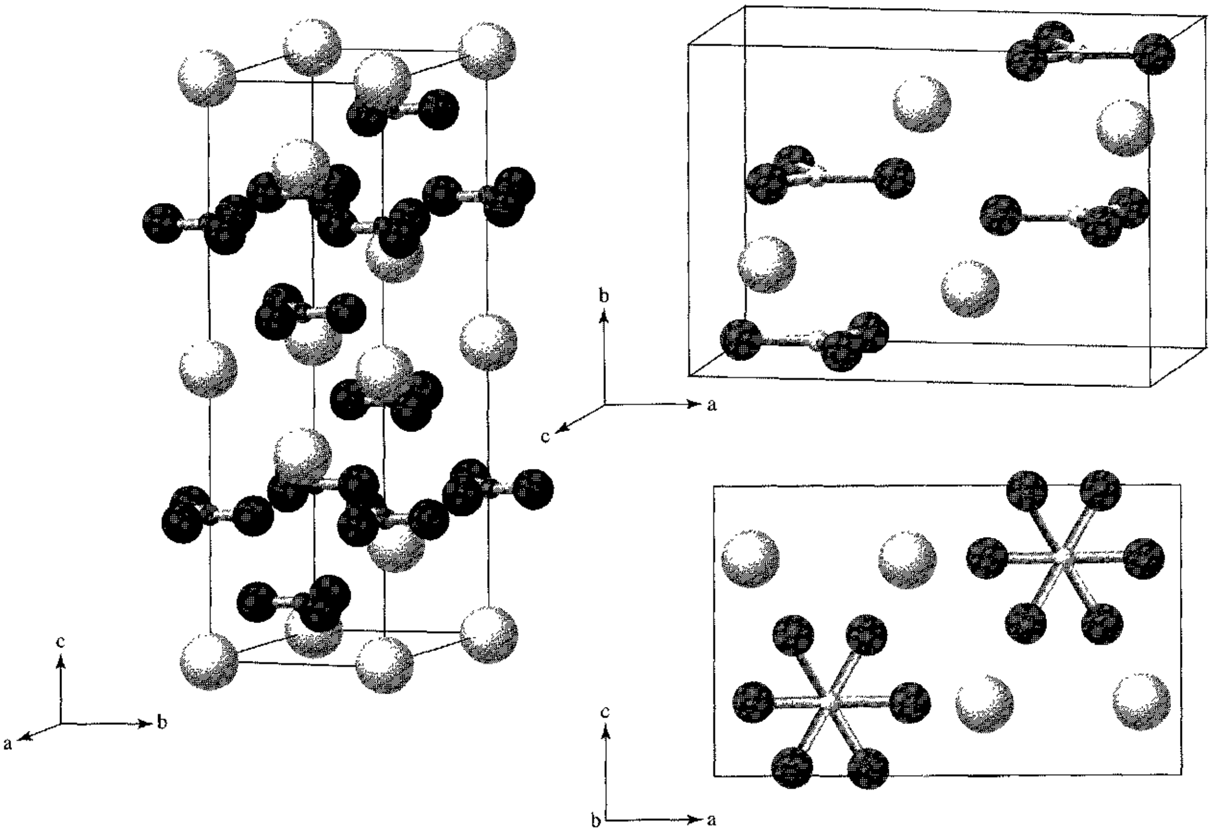
FIGURE 7-11 Rutile (TiO_2) Crystal Structure. The figure shows two unit cells of rutile. The heavy line across the middle shows the edge shared between two TiO_6 octahedra.

7-1-3 MORE COMPLEX COMPOUNDS

It is possible to form many compounds by substitution of one ion for another in part of the locations in a lattice. If the charges and ionic sizes are the same, there may be a wide range of possibilities. If the charges or sizes differ, the structure must change, sometimes balancing charge by leaving vacancies and frequently adjusting the lattice to accommodate larger or smaller ions. When the anions are complex and nonspherical, the crystal structure must accommodate the shape by distortions, and large cations may require increased coordination numbers. A large number of salts ($LiNO_3$, $NaNO_3$, $MgCO_3$, $CaCO_3$, $FeCO_3$, $InBO_3$, YBO_3) adopt the calcite structure, Figure 7-12(a), named for a hexagonal form of calcium carbonate, in which the metal has six nearest-neighbor oxygens. A smaller number (KNO_3, $SrCO_3$, $LaBO_3$), with larger cations, adopt the aragonite structure, Figure 7-12(b), an orthorhombic form of $CaCO_3$, which has 9-coordinate metal ions.

7-1-4 RADIUS RATIO

Coordination numbers in different crystals depend on the sizes and shapes of the ions or atoms, their electronic structures, and, in some cases, the temperature and pressure under which they were formed. A simple, but at best approximate, approach to predicting coordination numbers uses the radius ratio, r_+/r_-. Simple calculation from tables of



(a) (b)

FIGURE 7-12 Structures of Calcium Carbonate, $CaCO_3$. (a) Calcite. (b) Two views of aragonite.

ionic radii or of the size of the holes in a specific structure allows prediction of possible structures, treating the ions as if they were hard spheres.

For hard spheres, the ideal size for a smaller cation in an octahedral hole of an anion lattice is a radius of $0.414r_-$. Similar calculations for other geometries result in the radius ratios (r_+/r_-) shown in Table 7-1.

TABLE 7-1
Radius Ratios and Coordination Numbers

Radius Ratio Limiting Values	*Coordination Number*	*Geometry*	*Ionic Compounds*
	4	Tetrahedral	ZnS
0.414			
	4	Square planar	None
	6	Octahedral	NaCl, TiO_2 (rutile)
0.732			
	8	Cubic	CsCl, CaF_2 (fluorite)
1.00			
	12	Cubooctahedron	No ionic examples, but many metals are 12-coordinate

EXAMPLE

NaCl Using the radius of the Na^+ cation (Appendix B-1) for either CN = 4 or CN = 6, $r_+/r_- = 113/167 = 0.677$ or $116/167 = 0.695$, both of which predict CN = 6. The Na^+ cation fits easily into the octahedral holes of the Cl^- lattice, which is ccp.

ZnS The zinc ion radius varies more with coordination number. The radius ratios are $r_+/r_- = 74/170 = 0.435$ for the CN = 4 and $r_+/r_- = 88/170 = 0.518$ for the CN = 6 radius. Both predict CN = 6, but the smaller one is close to the tetrahedral limit of 0.414. Experimentally, the Zn^{2+} cation fits into the tetrahedral holes of the S^{2-} lattice, which is either ccp (zinc blende) or hcp (wurtzite).

EXERCISE 7-3

Fluorite (CaF_2) has fluoride ions in a simple cubic array and calcium ions in alternate body centers, with $r_+/r_- = 0.97$. What are the coordination numbers of the two ions predicted by the radius ratio? What are the coordination numbers observed? Predict the coordination number of Ca^{2+} in $CaCl_2$ and $CaBr_2$.

The predictions of the example and exercise match reasonably well with the facts for these two compounds, even though ZnS is largely covalent rather than ionic. However, all radius ratio predictions should be used with caution because ions are not hard spheres and there are many cases in which the radius ratio predictions are not correct. One study[2] reported that the actual structure matches the predicted structure in about two-thirds of cases, with a higher fraction correct at CN = 8 and a lower fraction correct at CN = 4.

There are also compounds in which the cations are larger than the anions; in these cases, the appropriate radius ratio is r_-/r_+, which determines the CN of the anions in the holes of a cation lattice. Cesium fluoride is an example, with $r_-/r_+ = 119/181 = 0.657$, which places it in the six-coordinate range, consistent with the NaCl structure observed for this compound.

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[2] L. C. Nathan, *J. Chem. Educ.*, **1985**, *62*, 215.

When the ions are nearly equal in size, a cubic arrangement of anions with the cation in the body center results, as in cesium chloride with CN = 8. Although a close-packed structure (ignoring the difference between cations and anions) would seem to give larger attractive forces, the CsCl structure separates ions of the same charge, reducing the repulsive forces between them.

Compounds whose stoichiometry is not 1:1 (such as CaF_2 and Na_2S) may either have different coordination numbers for the cations and anions or structures in which only a fraction of the possible sites are occupied. Details of such structures are available in Wells[3] and other references.

7-2 THERMODYNAMICS OF IONIC CRYSTAL FORMATION

Formation of ionic compounds from the elements appears to be one of the simpler overall reactions, but can also be written as a series of steps adding up to the overall reaction. The Born-Haber cycle is the process of considering the series of component reactions that can be imagined as the individual steps in compound formation. For the example of lithium fluoride, the first five reactions added together result in the sixth overall reaction.

$Li(s) \longrightarrow Li(g)$	$\Delta H_{sub} = 161$ kJ/mol	Sublimation	(1)
$\frac{1}{2}F_2(g) \longrightarrow F(g)$	$\Delta H_{dis} = 79$ kJ/mol	Dissociation	(2)
$Li(g) \longrightarrow Li^+(g) + e^-$	$\Delta H_{ion} = 531$ kJ/mol	Ionization energy	(3)
$F(g) + e^- \longrightarrow F^-(g)$	$\Delta H_{ion} = -328$ kJ/mol	−Electron affinity	(4)
$Li^+(g) + F^-(g) \longrightarrow LiF(s)$	$\Delta H_{xtal} = -1239$ kJ/mol	Lattice enthalpy	(5)
$Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$	$\Delta H_{form} = -796$ kJ/mol	Formation	(6)

Historically, such calculations were used to determine electron affinities when the enthalpies for all the other reactions could either be measured or calculated. Calculated lattice enthalpies were combined with experimental values for the other reactions and for the overall reaction of $Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$. Now that it is easier to measure electron affinities, the complete cycle can be used to determine more accurate lattice enthalpies. Although this is a very simple calculation, it can be very powerful in calculating thermodynamic properties for reactions that are difficult to measure directly.

7-2-1 LATTICE ENERGY AND MADELUNG CONSTANT

At first glance, calculation of the lattice energy of a crystal may seem simple: just take every pair of ions and calculate the sum of the electrostatic energy between each pair, using the equation below.

$$\Delta U = \frac{Z_i Z_j}{r_0}\left(\frac{e^2}{4\pi\varepsilon_0}\right)$$

where Z_i, Z_j = ionic charges in electron units

r_0 = distance between ion centers

e = electronic charge = 1.602×10^{-19} C

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[3] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1988.

$$4\pi\varepsilon_0 = \text{permittivity of a vacuum} = 1.11 \times 10^{-10}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1}$$

$$\frac{e^2}{4\pi\varepsilon_0} = 2.307 \times 10^{-28}\ \text{J m}$$

Summing the nearest-neighbor interactions is insufficient, because significant energy is involved in longer range interactions between the ions. For a crystal as simple as NaCl, the closest neighbors to a sodium ion are six chloride ions at half the unit cell distance, but the set of next-nearest neighbors is a set of 12 sodium ions at 0.707 times the unit cell distance, and the numbers rise rapidly from there. The sum of all these geometric factors carried out until the interactions become infinitesimal is called the **Madelung constant**. It is used in the similar equation for the molar energy

$$\Delta U = \frac{NMZ_+Z_-}{r_0}\left(\frac{e^2}{4\pi\varepsilon_0}\right)$$

where N is Avogadro's number and M is the Madelung constant. Repulsion between close neighbors is a more complex function, frequently involving an inverse sixth- to twelfth-power dependence on the distance. The Born-Mayer equation, a simple and usually satisfactory equation, corrects for this using only the distance and a constant, ρ:

$$\Delta U = \frac{NMZ_+Z_-}{r_0}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(1 - \frac{\rho}{r_0}\right)$$

For simple compounds, $\rho = 30$ pm works well when r_0 is also in pm. Lattice enthalpies are twice as large when charges of 2 and 1 are present, and four times as large when both ions are doubly charged. Madelung constants for some crystal structures are given in Table 7-2.

TABLE 7-2
Madelung Constants

Crystal Structure	*Madelung Constant, M*
NaCl	1.74756
CsCl	1.76267
ZnS (zinc blende)	1.63805
ZnS (wurtzite)	1.64132
CaF_2	2.51939
TiO_2 (rutile)	2.3850
Al_2O_3 (corundum)	4.040

SOURCE: D. Quane, *J. Chem. Educ.*, **1970**, *47*, 396, has described this definition and several others, which include all or part of the charge (Z) in the constant. Caution is needed when using this constant because of the different possible definitions.

The lattice enthalpy is $\Delta H_{xtal} = \Delta U + \Delta(PV) = \Delta U + \Delta nRT$, where Δn is the change in number of gas phase particles on formation of the crystal (e.g., -2 for AB compounds, -3 for AB_2 compounds). The value of ΔnRT is small (-4.95 kJ/mol for AB, -7.43 kJ/mol for AB_2); for approximate calculations, $\Delta H_{xtal} \approx \Delta U$.

EXERCISE 7-4

Calculate the lattice energy for NaCl, using the ionic radii from Appendix B-1.

7-2-2 SOLUBILITY, ION SIZE (LARGE-LARGE AND SMALL-SMALL), AND HSAB

Thermodynamic calculations can also be used to show the effects of solvation and solubility. For the overall reaction $AgCl(s) + H_2O \longrightarrow Ag^+(aq) + Cl^-(aq)$, the following reactions can be used:

$AgCl(s) \longrightarrow Ag^+(g) + Cl^-(g)$	$\Delta H = 917\ kJ/mol$	−Lattice enthalpy
$Ag^+(g) + H_2O \longrightarrow Ag^+(aq)$	$\Delta H = -475\ kJ/mol$	Solvation
$Cl^-(g) + H_2O \longrightarrow Cl^-(aq)$	$\Delta H = -369\ kJ/mol$	Solvation
$AgCl(s) + H_2O \longrightarrow Ag^+(aq) + Cl^-(aq)$	$\Delta H = 73\ kJ/mol$	Dissolution

If any three of the four reactions can be measured or calculated, the fourth can be found by completing the cycle. It has been possible to estimate the solvation effects of many ions by comparing similar measurements on a number of different compounds. Naturally, the entropy of solvation also needs to be included as part of the thermodynamics of solubility.

Many factors are involved in the thermodynamics of solubility, including ionic size and charge, the hardness or softness of the ions (HSAB), the crystal structure of the solid, and the electronic structure of each of the ions. Small ions have strong electrostatic attraction for each other, and for water molecules, whereas large ions have weaker attraction for each other and for water molecules but can accommodate more water molecules around each ion. These factors work together to make compounds formed of two large ions or of two small ions less soluble than compounds containing one large ion and one small ion, particularly when they have the same charge magnitude. In the examples given by Basolo,[4] LiF, with two small ions, and CsI, with two large ions, are less soluble than LiI and CsF, with one large and one small ion. For the small ions, the larger lattice energy overcomes the larger hydration enthalpies, and for the large ions, the smaller hydration enthalpies allow the lattice energy to dominate. The significance of entropy can be seen by the fact that a saturated CsI solution is about 15 times as concentrated as a LiF solution (molarity) in spite of the less favorable enthalpy change.

Cation	*Hydration Enthalpy (kJ/mol)*	*Anion*	*Hydration Enthalpy (kJ/mol)*	*Lattice Energy (kJ/mol)*	*Net Enthalpy of Solution (kJ/mol)*
Li^+	−519	F^-	−506	−1025	0
Li^+	−519	I^-	−293	−745	−67
Cs^+	−276	F^-	−506	−724	−58
Cs^+	−276	I^-	−293	−590	+21

In this same set of four compounds, the reaction $LiI(s) + CsF(s) \longrightarrow CsI(s) + LiF(s)$ is exothermic ($\Delta H = -146\ kJ/mol$) because of the large lattice enthalpy of LiF. This is contrary to the simple electronegativity argument that the most electropositive and the most electronegative elements form the most stable compounds. However, these same compounds fit the hard-soft arguments, with LiF, the hard-hard combination, and CsI, the soft-soft combination, the least soluble salts (Section 6-3). Sometimes these factors are also modified by particular interactions because of the electronic structures of the ions.

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[4] F. Basolo, *Coord. Chem. Rev.*, **1968**, *3*, 213.

7-3 MOLECULAR ORBITALS AND BAND STRUCTURE

When molecular orbitals are formed from two atoms, each type of atomic orbital gives rise to two molecular orbitals. When n atoms are used, the same approach results in n molecular orbitals. In the case of solids, n is very large (similar to Avogadro's number). If the atoms were all in a one-dimensional row, the lowest energy orbital would have no nodes and the highest would have $n - 1$ nodes; in a three-dimensional solid, the nodal structure is more complex but still just an extension of this linear model. Because the number of atoms is large, the number of orbitals and energy levels with closely spaced energies is also large. The result is a **band** of orbitals of similar energy, rather than the discrete energy levels of small molecules.[5] These bands then contain the electrons from the atoms. The highest energy band containing electrons is called the **valence band**; the next higher empty band is called the **conduction band**. In elements with filled valence bands and a large energy difference between the highest valence band and the lowest conduction band, this **band gap** prevents motion of the electrons, and the material is an **insulator**, with the electrons restricted in their motion. In those with partly filled orbitals, the valence band-conduction band distinction is blurred and very little energy is required to move some electrons to higher energy levels within the band. As a result, they are then free to move throughout the crystal, as are the **holes** (electron vacancies) left behind in the occupied portion of the band. These materials are **conductors** of electricity because the electrons and holes are both free to move. They are also usually good conductors of heat because the electrons are free to move within the crystal and transmit energy. As required by the usual rules about electrons occupying the lowest energy levels, the holes tend to be in the upper levels within a band. The band structure of insulators and conductors is shown in Figure 7-13.

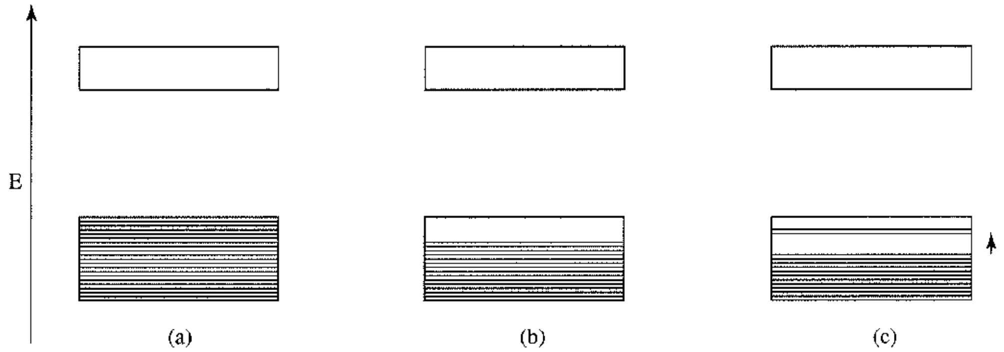

FIGURE 7-13 Band Structure of Insulators and Conductors. (a) Insulator. (b) Metal with no voltage applied. (c) Metal with electrons excited by applied voltage.

The concentration of energy levels within bands is described as the **density of states**, $N(E)$, actually determined for a small increment of energy dE. Figure 7-14 shows three examples, two with distinctly separate bands and one with overlapping bands. The shaded portions of the bands are occupied, and the unshaded portions are empty. The figure shows an insulator with a filled valence band, and a metal, in which the valence band is partly filled. When an electric potential is applied, some of the electrons can move to slightly higher energies, leaving vacancies or holes in the lower part of the band. The electrons at the top of the filled portion can then move in one direction and the holes in the other, conducting electricity. In fact, the holes appear to move because an electron moving to fill one hole creates another in its former location.

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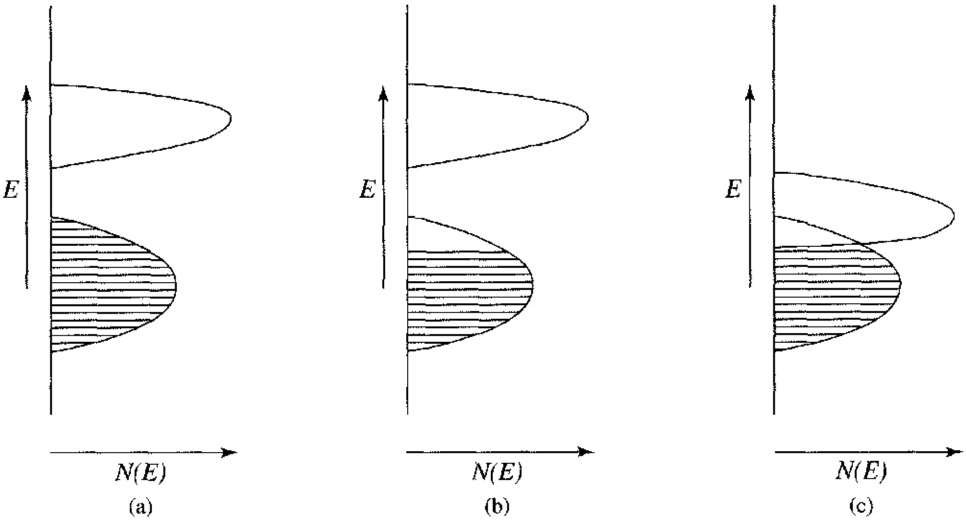
[5] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH Publishers, New York, 1988, pp. 1–7.



(a) (b) (c)

FIGURE 7-14 Energy Bands and Density of States. (a) An insulator, with a filled valence band. (b) A metal, with a partly filled valence band and a separate empty band. (c) A metal with overlapping bands caused by similar energies of the initial atomic orbitals.

EXERCISE 7-5

Hoffmann uses a linear chain of hydrogen atoms as a starting model for his explanation of band theory. Using a chain of eight hydrogen atoms, sketch the phase relationships (positive and negative signs) of all the molecular orbitals that can be formed. These orbitals, bonding at the bottom and antibonding at the top, form a band.

The conductance of metals decreases with increasing temperature, because the increasing vibrational motion of the atoms interferes with the motion of the electrons and increases the resistance to electron flow. High conductance (low resistance) in general, and decreasing conductance with increasing temperature, are characteristics of metals. Some elements have bands that are either completely filled or completely empty, but differ from insulators by having the bands very close in energy (near 2 eV or less). Silicon and germanium are examples. Their diamond structure crystals have bonds that are more nearly like ordinary covalent bonds, with four bonds to each atom. At very low temperatures, they are insulators, but the conduction band is very near the valence band in energy. At higher temperatures, when a potential is placed across the crystal, a few electrons can jump into the higher (vacant) conduction band, as in Figure 7-15(a). These electrons are then free to move through the crystal. The vacancies, or holes, left in the lower energy band can also appear to move as electrons move into them. In this way, a small amount of current can flow. When the temperature is raised, more electrons are excited into the upper band, more holes are created in the lower band, and conductance *increases* (resistance decreases). This is the distinguishing characteristic of **semiconductors**. They have much higher conductivity than insulators and have much lower conductivity than conductors.

It is possible to change the properties of semiconductors within very close limits. As a result, the flow of electrons can be controlled by applying the proper voltages to some of these modified semiconductors. The entire field of solid-state electronics (transistors and integrated circuits) depends on these phenomena. Silicon and germanium are **intrinsic semiconductors**, meaning that the pure materials have semiconductive properties. Both molecular and nonmolecular compounds can also be semiconductors. A short list of some of the nonmolecular compounds and their band gaps is given in Table 7-3. Other elements that are not semiconductors in the pure state can be modified by adding a small amount of another element with energy levels close to those of the host to make **doped semiconductors**. Doping can be thought of as replacing a few atoms of the origi-

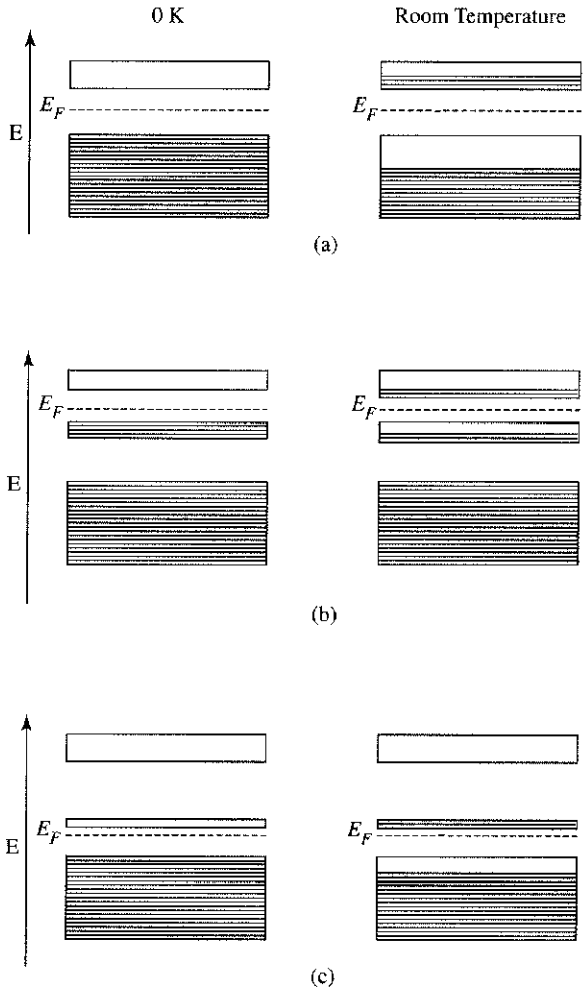


FIGURE 7-15 Semiconductor Bands at 0 K and at Room temperature. (a) Intrinsic semiconductor. (b) *n*-type semiconductor. (c) *p*-type semiconductor.

TABLE 7-3
Semiconductors

Material	*Band Gap (eV)*
Elemental	
Si	1.11
Ge	2.2
Group 13–15 Compounds	
GaP	2.25
GaAs	1.42
InSb	0.17
Group 12–16 Compounds	
CdS	2.40
ZnTe	2.26

nal element with atoms having either more or fewer electrons. If the added material has more electrons in the valence shell than the host material, the result is an ***n*-type semiconductor** (*n* for negative, adding electrons), shown in Figure 7-15(b). Phosphorus is an example in a silicon host, with five valence electrons compared with four in silicon. These electrons have energies just slightly lower in energy than the conduction band of silicon. With addition of a small amount of energy, electrons from this added energy level can jump up into the empty band of the host material, resulting in higher conductance.

If the added material has fewer valence electrons than the host, it adds positive holes and the result is a ***p*-type semiconductor**, shown in Figure 7-15(c). Aluminum is a *p*-type dopant in a silicon host, with three electrons instead of four in a band very close in energy to that of the silicon valence band. Addition of a small amount of energy boosts electrons from the host valence band into this new level and generates more holes in the valence band of the host, thus increasing the conductance. With careful doping, the conductance can be carefully tailored to the need. Layers of intrinsic, *n*-type, and *p*-type semiconductors together with insulating materials are used to create the integrated circuits that are so essential to the electronics industry. Controlling the voltage applied to the junctions between the different layers controls conductance through the device.

The number of electrons that are able to make the jump between the valence and the conduction band depends on the temperature and on the energy gap between the two bands. In an intrinsic semiconductor, the **Fermi level** (E_F, Figure 7-15), the energy at which an electron is equally likely to be in each of the two levels, is near the middle of

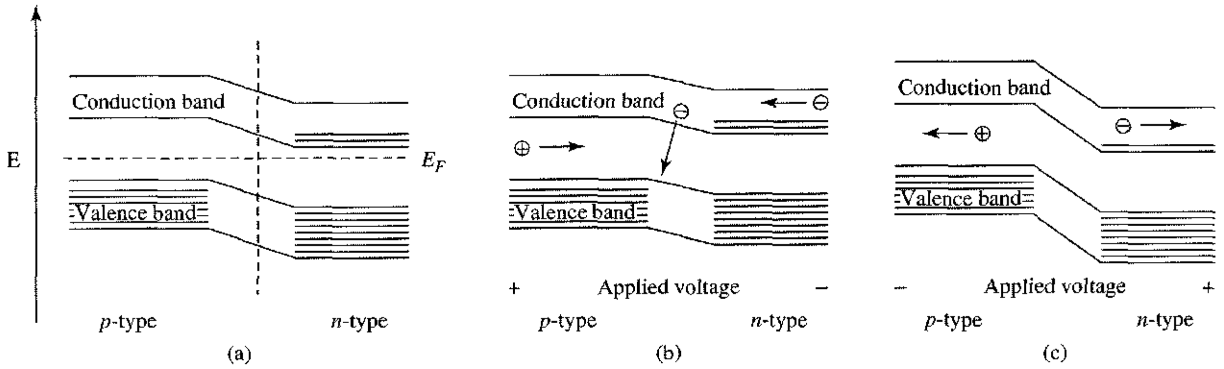


FIGURE 7-16 Band-energy Diagram of a *p-n* Junction. (a) At equilibrium, the two Fermi levels are at the same energy, changing from the pure *n*- or *p*-type Fermi levels because a few electrons can move across the boundary (vertical dashed line). (b) With forward bias, current flows readily. (c) With reverse bias, very little current flows.

the band gap. Addition of an *n*-type dopant raises the Fermi level to an energy near the middle of the band gap between the new band and the conduction band of the host. Addition of a *p*-type dopant lowers the Fermi level to a point near the middle of the band gap between the new conduction band and the valence band of the host.

7-3-1 DIODES, THE PHOTOVOLTAIC EFFECT, AND LIGHT-EMITTING DIODES

Putting layers of *p*-type and *n*-type semiconductors together creates a *p-n junction*. A few of the electrons in the conduction band of the *n*-type material can migrate to the valence band of the *p*-type material, leaving the *n* type positively charged and the *p* type negatively charged. An equilibrium is quickly established because the electrostatic forces are too large to allow much charge to accumulate. The separation of charges then prevents transfer of any more electrons. At this point, the Fermi levels are at the same energy, as shown in Figure 7-16. The band gap remains the same in both layers, with the energy levels of the *n*-type layer lowered by the buildup of positive charge. If a negative potential is applied to the *n*-type and a positive potential to the *p*-type side of the junction, it is called a forward bias. The excess electrons raise the level of the *n*-type conduction band and then have enough energy to move into the *p*-type side. Holes move toward the junction from the left and electrons move toward the junction from the right, canceling each other at the junction, and current can flow readily. If the potential is reversed (reverse bias), the energy of the *n*-type levels is lowered compared with the *p*-type, the holes and electrons both move away from the junction, and very little current flows. This is the description of a **diode**, which allows current to flow readily in one direction, but has a high resistance to current flow in the opposite direction, as in Figure 7-17.

A junction of this sort can be used as a light-sensitive switch. With a reverse bias applied (extra electrons supplied to the *p* side), no current would flow, as described for diodes. However, if the difference in energy between the valence band and the conduction band of a semiconductor is small enough, light of visible wavelengths is energetic

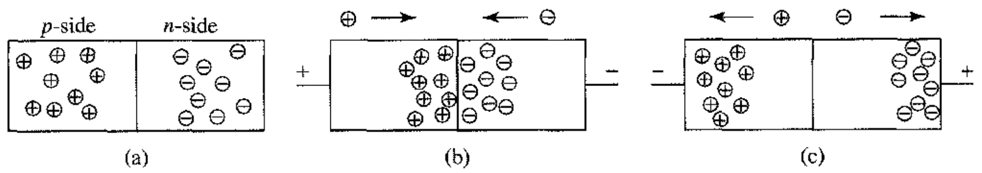


FIGURE 7-17 Diode Behavior. (a) With no applied voltage, no current flows, and few charges are neutralized near the junction by transfer of electrons. (b) Forward bias: current flows readily, with holes and electrons combining at the junction. (c) Reverse bias: very little current can flow because the holes and electrons move away from each other.

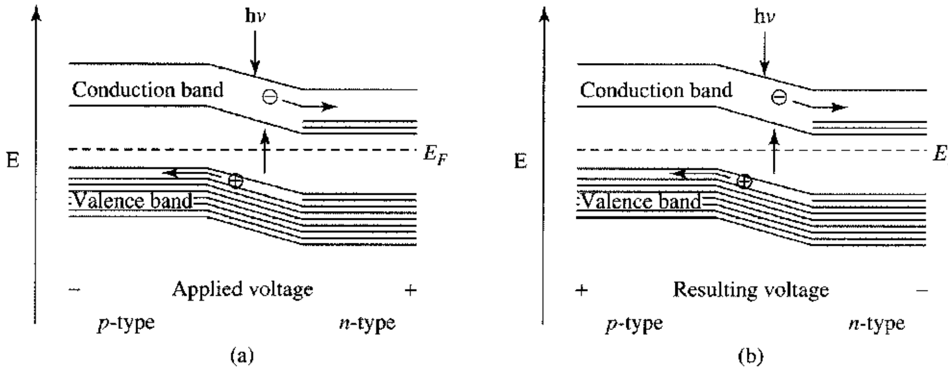


FIGURE 7-18 The Photovoltaic Effect. (a) As a light-activated switch. (b) Generating electricity. Light promotes electrons into the conduction band in the junction.

enough to lift electrons from the valence band into the conduction band, as shown in Figure 7-18. Light falling on the junction increases the number of electrons in the conduction band and the number of holes in the valence band, allowing current to flow in spite of the reverse bias. Such a junction then acts as a photoelectric switch, passing current when light strikes it.

If no external voltage is applied and if the gap has the appropriate energy, light falling on the junction can increase the transfer of electrons from the *p*-type material into the conduction band of the *n*-type material. If external connections are made to the two layers, current can flow through this external circuit. **Photovoltaic cells** of this sort are commonly used in calculators or in remote locations, and are increasingly being used to generate electricity for home and commercial use.

A forward-biased junction can reverse this process and emit light as a **light-emitting diode (LED)**. The current is carried by holes on the *p*-type side and by electrons on the *n*-type side. When electrons move from the *n*-type layer to the *p*-type layer, they recombine with the holes. If the resulting energy change is of the right magnitude, it can be released as visible light (luminescence) and an LED results. In practice, GaP_xAs_{1-x} with $x = 1.00$ to 0.40 can be used for LEDs that emit red light (band gap of 1.88 eV) to green light (2.23 eV). The energy of the light emitted can be changed by adjusting the composition of the material. GaAs has a band gap of about 1.4 eV; GaP has a band gap of about 2.25 eV. The band gap increases steadily as the fraction of phosphorus is increased, with an abrupt change in slope at $x = 0.45$, where there is a change from a direct band gap to an indirect band gap.[6] In arsenic-rich materials, the electrons drop directly across the energy gap into holes in the lower level (a direct band gap) and the light is emitted with high efficiency. In phosphorus-rich materials, this process must be accompanied by a change in vibrational energy of the crystal (an indirect band gap). This indirect process is less efficient and requires addition of a dopant to give efficient emission by relaxing these rules. These materials also have more complex emission or absorption spectra because of the addition of the dopant, in contrast to the arsenic-rich materials, which have spectra with one simple band. The efficiency of emission is also improved for both types at lower temperatures, at which the intensity of vibrations is reduced. Similar behavior is observed in $Al_xGa_{1-x}As$ LEDs; emission bands (from 840 nm for $x = 0.05$ to 625 nm for $x = 0.35$) shift to shorter wavelengths and much greater intensity on cooling to the temperature of liquid nitrogen (77 K).

Adding a third layer with a larger band gap and making the device exactly the right dimensions changes the behavior of an LED into a solid-state laser. Gallium arsenide doped to provide an *n*-type layer, a *p*-type layer, and then a larger band gap in a *p*-type layer with Al added to the GaAs is a commonly used combination. The general

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[6] A. G. Thompson, M. Cardona, K. L. Shaklee, and J. C. Wooley, *Phys. Rev.*, **1966**, *146*, 601; H. Mathieu, P. Merle, and E. L. Ameziane, *Phys. Rev.*, **1977**, *B15*, 2048; M. E. Staumanis, J. P. Krumme, and M. Rubenstein, *J. Electrochem. Soc.*, **1977**, *146*, 640.

behavior is the same as in the LED, with a forward bias on the junction creating luminescence. The larger band gap added to the p-type layer prevents the electrons from moving out of the middle p-type layer. If the length of the device is exactly a half-integral number of wavelengths of the light emitted, photons released by recombination of electrons and holes are reflected by the edges and stimulate release of more photons in phase with the first ones. The net result is a large increase in the number of photons and a specific direction for their release in a laser beam. The commonly seen red laser light used for pointers and in supermarket scanners uses this phenomenon.

7-4 SUPERCONDUCTIVITY

The conductivity of some metals changes abruptly near liquid helium temperatures (frequently below 10 K), as in Figure 7-19, and they become **superconductors**, an effect discovered by Kammerling Onnes in 1911[7] while studying mercury at liquid helium temperature. In this state, the metals offer no resistance to the flow of electrons, and currents started in a loop will continue to flow indefinitely (several decades at least) without significant change. For chemists, one of the most common uses of this effect is in superconducting magnets used in nuclear magnetic resonance instruments, in which they allow generation of much larger magnetic fields than can be obtained with ordinary electromagnets.

7-4-1 LOW-TEMPERATURE SUPERCONDUCTING ALLOYS

Some of the most common superconducting materials are alloys of niobium, particularly Nb-Ti alloys, which can be formed into wire and handled with relative ease. These Type I superconductors have the additional property of expelling all magnetic flux when cooled below the critical temperature, T_c. This is called the Meissner effect. It prevails until the magnetic field reaches a critical value, H_c, at which point the applied field destroys the superconductivity. As in the temperature dependence, the change between superconducting and normal conduction is abrupt rather than gradual. The highest T_c found for niobium alloys is 23.3 K for Nb_3Ge.[8]

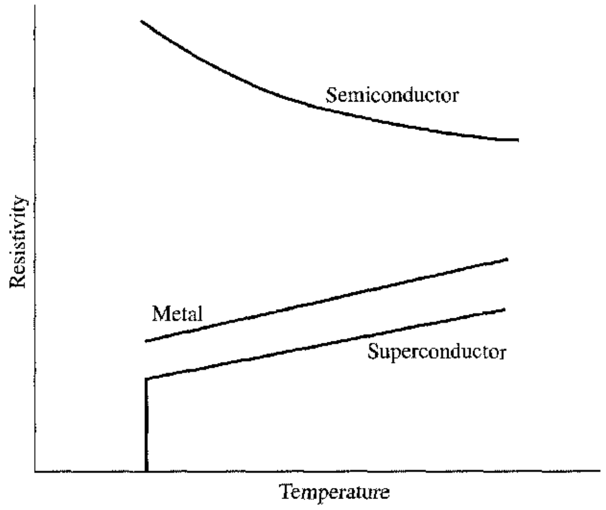

FIGURE 7-19 Temperature Dependence of Resistivity in Semiconductors, Metals, and Superconductors.

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[7] H. Kammerlingh Onnes, *Akad. Van Wetenschappen (Amsterdam)*, **1911**, *14*, 113, and *Leiden Comm.*, **1911**, *122b*, 124c.

[8] C. P. Poole, Jr., H. A. Farach, and R. J. Creswick, *Superconductivity*, Academic Press, San Diego, 1995, p. 22.

Type II superconductors have a more complicated field dependence. Below a given critical temperature, they exclude the magnetic field completely. Between this first critical temperature and a second critical temperature, they allow partial penetration by the field, and above this second critical temperature they lose their superconductivity and display normal conductance behavior. In the intermediate temperature region, these materials seem to have a mixture of superconducting and normal regions.

The Meissner effect is being explored for practical use in many areas, including magnetic levitation of trains, although other electromagnetic effects are presently being used for this. A common demonstration is to cool a small piece of superconducting material below its critical temperature and then place a small magnet above it. The magnet is suspended above the superconductor because the superconductor repels the magnetic flux of the magnet. As long as the superconductor remains below its critical temperature, it expels the magnetic flux from its interior and holds the magnet at a distance.

The levitation demonstration works only with Type II superconductors because the magnetic field lines that do enter the superconductor resist sideways motion and allow the balance of magnetic repulsion and gravitation to "float" the magnet above the superconductor. With Type I superconductors, the magnetic field lines cannot enter the superconductor at all and, because there is no resistance to sideways motion, the magnet will not remain stationary over the superconductor.

The materials used in the coils of superconducting magnets are frequently Nb-Ti-Cu or Nb_3Sn-Cu mixtures, providing a balance between ductility for easier formation into wire and T_c, which is about 10 K for these materials.

Superconducting magnets allow very high currents to flow with no change indefinitely as long as the magnet is kept cold enough. In practice, an outer Dewar flask containing liquid nitrogen (boiling point 77.3 K) reduces boil-off of liquid helium (boiling point 4.23 K) from the inner Dewar flask surrounding the magnet coils. A power supply is attached to the magnet, electrical current is supplied to bring it to the proper field, and the power supply is then removed and current flows continuously, maintaining the magnetic field.

A major goal of superconductor research is a material that is superconducting at higher temperatures, to remove the need for liquid helium and liquid nitrogen for cooling.

7-4-2 THE THEORY OF SUPERCONDUCTIVITY (COOPER PAIRS)

In the late 1950s, more than 40 years after its discovery, Bardeen, Cooper, and Schrieffer[9] (BCS) provided a theory to explain superconductivity. Their BCS theory postulated that electrons travel through the material in pairs in spite of their mutual electrostatic repulsion, as long as the two have opposite spins. The formation of these Cooper pairs is assisted by small vibrations of the atoms in the lattice; as one electron moves past, the nearest positively charged atoms are drawn very slightly toward it. This increases the positive charge density, which attracts the second electron. This effect then continues through the crystal, in a manner somewhat analogous to a sports crowd doing the wave. The attraction between the two electrons is small, and they change partners frequently, but the overall effect is that the lattice helps them on their way rather than interfering, as is the case with metallic conductivity. If the temperature rises above T_c, the thermal motion of the atoms is sufficient to overcome the slight attraction between the electrons and the superconductivity ceases.

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[9] J. Bardeen, L. Cooper, and J. R. Schrieffer, *Phys. Rev.*, **1957**, *108*, 1175; J. R. Schrieffer, *Theory of Superconductivity*, W. A. Benjamin, New York, 1964; A. Simon, *Angew. Chem., Int. Ed.*, **1997**, *36*, 1788.

7-4-3 HIGH-TEMPERATURE SUPERCONDUCTORS ($YBa_2Cu_3O_7$ AND RELATED COMPOUNDS)

In 1986, Bednorz and Müller discovered that the ceramic oxide La_2CuO_4 was superconducting above 30 K when doped with Ba, Sr, or Ca to form compounds such as $(La_{2-x}Sr_x)CuO_4$.[10] This opened many more possibilities for the use of superconductivity. Then, in 1987, $YBa_2Cu_3O_7$ was discovered to have an even higher T_c, 93 K.[11] This material, called 1-2-3 for the stoichiometry of the metals in it, is a Type II superconductor, which expels magnetic flux at low fields, but allows some magnetic field lines to enter at higher fields and consequently ceases to be superconducting at high fields. A number of other similar compounds have since been prepared and found to be superconducting at these or even higher temperatures. These high-temperature superconductors are of great practical interest, because they would allow cooling with liquid nitrogen rather than liquid helium, a much more expensive coolant. However, the ceramic nature of these materials makes them more difficult to work with than metals. They are brittle and cannot be drawn into wire, making fabrication a problem. Researchers are working to overcome these problems by modifying the formulas or by depositing the materials on a flexible substrate. The present record is a critical temperature of 164 K for $HgBa_2Ca_2Cu_3O_{8-\delta}$ under pressure.[12]

The structures of all the high-temperature superconductors are related, most with copper oxide planes and chains, as shown in Figure 7-20. In $YBa_2Cu_3O_7$, these are

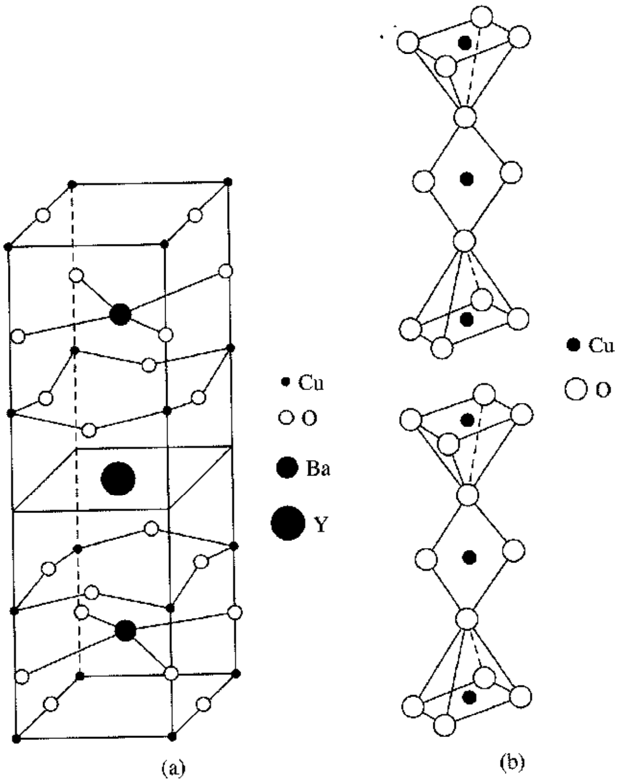

FIGURE 7-20 Two Views of Orthorhombic $YBa_2Cu_3O_7$. (a) The unit cell. The Y atom in the middle is in a reflection plane. (Adapted from C. P. Poole, Jr., H. A. Farach, and R. J. Creswick, *Superconductivity*, Academic Press, San Diego, 1995, p. 181, with permission.) (b) Stacking of copper oxide units. (Adapted from C. P. Poole, Jr., T. Datta, and H. A. Farach, *Copper Oxide Superconductors*, John Wiley & Sons, New York, 1988, p. 100. © John Wiley & Sons, used by permission.)

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[10] J. G. Bednorz and K. A. Müller, *Z. Phys. B*, **1986**, *64*, 189.

[11] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.*, **1987**, *58*, 908.

[12] L. Gao, Y. Y. Xue, F. Chen, Q. Ziong, R. L. Meng, D. Ramirez, C. W. Chu, J. H. Eggert, and H. K. Mao, *Phys. Rev. B*, **1994**, *50*, 4260.

stacked with square-pyramidal, square-planar, and inverted square-pyramidal units. The copper atoms in the top and bottom layers of Figure 7-20(a) are those in the square-planar units of Figure 7-20(b); two units are shown. In a related tetragonal structure, the oxygen atoms of the top and bottom planes in 7-20(a) are randomly dispersed in the four equivalent edges of the plane; the resulting material is not superconducting. Oxygen-deficient structures are also possible and are superconducting until about $\delta = 0.65$; materials closer to the formula $YBa_2Cu_3O_6$ are not superconducting.

The understanding of superconductivity in the high-temperature superconductors is incomplete, but at this point an extension of the BCS theory seems to fit much of the known data. The mechanism of electron pairing and the details of the behavior of the electron pairs are less clear. Other theories have been proposed, but none has gained general acceptance yet.

7-5

BONDING IN IONIC CRYSTALS

The simplest picture of bonding in ionic crystals is of hard-sphere ions held together by purely electrostatic forces. This picture is far too simple, even for compounds such as NaCl that are expected to be strongly ionic in character. It is the deviation from this simple model that makes questions about ion sizes so difficult. For example, the Pauling radius of Li^+ is 60 pm. The crystal radius given by Shannon (Appendix B-1) for a six-coordinate structure is 90 pm, a value that is much closer to the position of minimum electron density between ions determined by X-ray crystallography. The four-coordinate Li^+ has a radius of 73 pm, and estimates by Goldschmidt and Ladd are between 73 and 90 pm.[13] The sharing of electrons or the transfer of charge back from the anion to the cation varies from a few percent in NaCl to as much as 0.33 electron per atom in LiI. Each set of radii is self-consistent, but mixing some radii from one set with some from another does not work.

Some of the structures shown earlier in this chapter (e.g., ZnS, in Figure 7-8, and NiAs, in Figure 7-10) are given as if the components were simple ions, when we know that the bonding is strongly covalent. In any of these structures, this ambiguity must be kept in mind. The band structures described previously are much more complete in their descriptions of the bonding. Hoffmann[14] has described the bands in VS, an example of the NiAs structure. The crystal has layers that could be described as ABACA in the hexagonal unit cell, with the identical A layers made up of a hexagonal array of V atoms, and the B and C layers made up of S atoms in the alternate trigonal prisms formed by the metal (Figure 7-21). In this structure, both atoms are six-coordinate, with V atoms octahedrally coordinated to S atoms and S atoms in a trigonal prism of V atoms. The very complex band structure derived from this structure has been analyzed by Hoffmann in terms of smaller components of the crystal.

Hoffmann has also shown that the contributions to the density of states of specific orbitals can be calculated.[15] In rutile (TiO_2), a clear separation of the d orbital contribution into t_{2g} and e_g parts can be seen, as predicted by ligand field theory (Chapter 10).

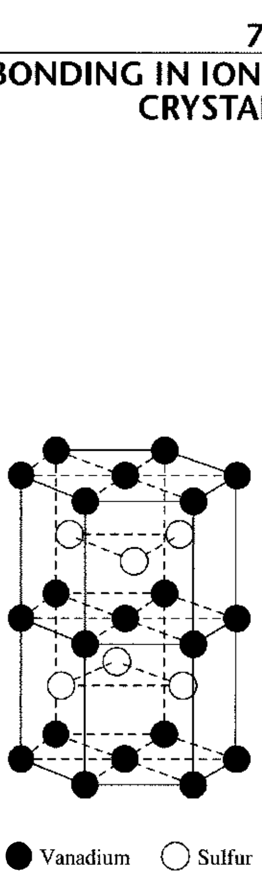

FIGURE 7-21 Structure of VS.

7-6

IMPERFECTIONS IN SOLIDS

In practice, all crystals have imperfections. If a substance crystallizes rapidly, it is likely to have many more imperfections, because crystal growth starts at many sites almost simultaneously. Each small crystallite grows until it runs into its neighbors; the boundaries between these small crystallites are called grain boundaries, which can be

[13] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997, p. 81.

[14] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH Publishers, New York, 1988, pp. 102–107.

[15] R. Hoffmann, *Solids and Surfaces*, p. 34.

seen on microscopic examination of a polished surface. Slow crystal growth reduces the number of grain boundaries because crystal growth starts from a smaller number of sites. However, even if a crystal appears to be perfect, it will have imperfections on an atomic level caused by impurities in the material or by dislocations within the lattice.

Vacancies and self-interstitials

Vacancies are missing atoms and are the simplest defects. Because higher temperatures increase vibrational motion and expand a crystal, more vacancies are formed at higher temperatures. However, even near the melting point, the number of vacancies is small relative to the total number of atoms, about 1 in 10,000. The effect of a vacancy on the rest of the lattice is small, because it is a localized defect and the rest of the lattice remains unaffected. Self-interstitials are atoms displaced from their normal location and appear in one of the interstices in the lattice. Here, the distortion spreads at least a few layers in the crystal because the atoms are much larger than the available space. In most cases, the number of these defects is much smaller than the number of vacancies.

Substitutions

Substitution of one atom for another is a common phenomenon. These mixtures are also called solid solutions. For example, nickel and copper atoms have similar sizes and electronegativities and the same fcc crystal structures. Mixtures of the two are stable in any proportion, with random arrangement of the atoms in the alloys. Other combinations that can work well have a very small atom in a lattice of larger atoms. In this case, the small atom occupies one of the interstices in the larger lattice, with small effects on the rest of the lattice but potentially large effects on behavior of the mixture. If the impurity atoms are larger than the holes, lattice strains result and a new solid phase may be formed.

Dislocations

Edge dislocations result when atoms in one layer do not match up precisely with those of the next. As a result, the distances between the dislocated atoms and atoms in adjacent rows are larger than usual and the angles between atoms are distorted for a number of rows on either side of the dislocation. A screw dislocation is one that has part of one layer shifted a fraction of a cell dimension. This kind of dislocation frequently causes a rapidly growing site during crystal growth and forms a helical path, which leads to the name. Because they provide sites that allow atoms from the solution or melt to fit into a corner where attractions from three directions can hold them in place, screw dislocations are frequently growth sites for crystals.

In general, dislocations are undesirable in crystals. Mechanically, they can lead to weakness that can cause fracture. Electrically, they interfere with conduction of electrons and reduce reliability, reproducibility, and efficiency in semiconductor devices. For example, one of the challenges of photocell manufacture is to raise the efficiency of cells made of polycrystalline silicon to levels that are reached by single crystals.

7-7 SILICATES

Oxygen, silicon, and aluminum are the most abundant elements in the surface of the earth (more than 80% of the atoms in the solid crust are oxygen or silicon, mostly in the form of silicates). The number of compounds and minerals that contain these elements is very large, and their importance in industrial uses matches their number. We can give only a very brief description of some of these compounds and will focus on a few of the silicates.

Silica, SiO_2, has three crystalline forms, quartz at temperatures below 870° C, tridymite from 870° to 1470° C, and cristobalite from 1470° to 1710° C, at which temperature it melts. The high viscosity of molten silica makes crystallization slow; instead of crystallizing, it frequently forms a glass which softens near 1500° C. Conversion from one crystalline form to another is difficult and slow even at high temperatures because it requires breaking Si — O bonds. All forms contain SiO_4 tetrahedra sharing oxygen atoms, with Si — O — Si angles of 143.6°.

Quartz is the most common form of silica and contains helical chains of SiO_4 tetrahedra, which are chiral, with clockwise or counterclockwise twists. Each full turn of the helix contains three Si atoms and three O atoms, and six of these helices combine to form the overall hexagonal shape (Figure 7-22).[16]

The four-coordination of silicon is also present in the silicates, forming chains, double chains, rings, sheets, and three-dimensional arrays. Al^{3+} can substitute for Si^{4+}, requiring addition of another cation to maintain charge balance. Aluminum, magnesium,

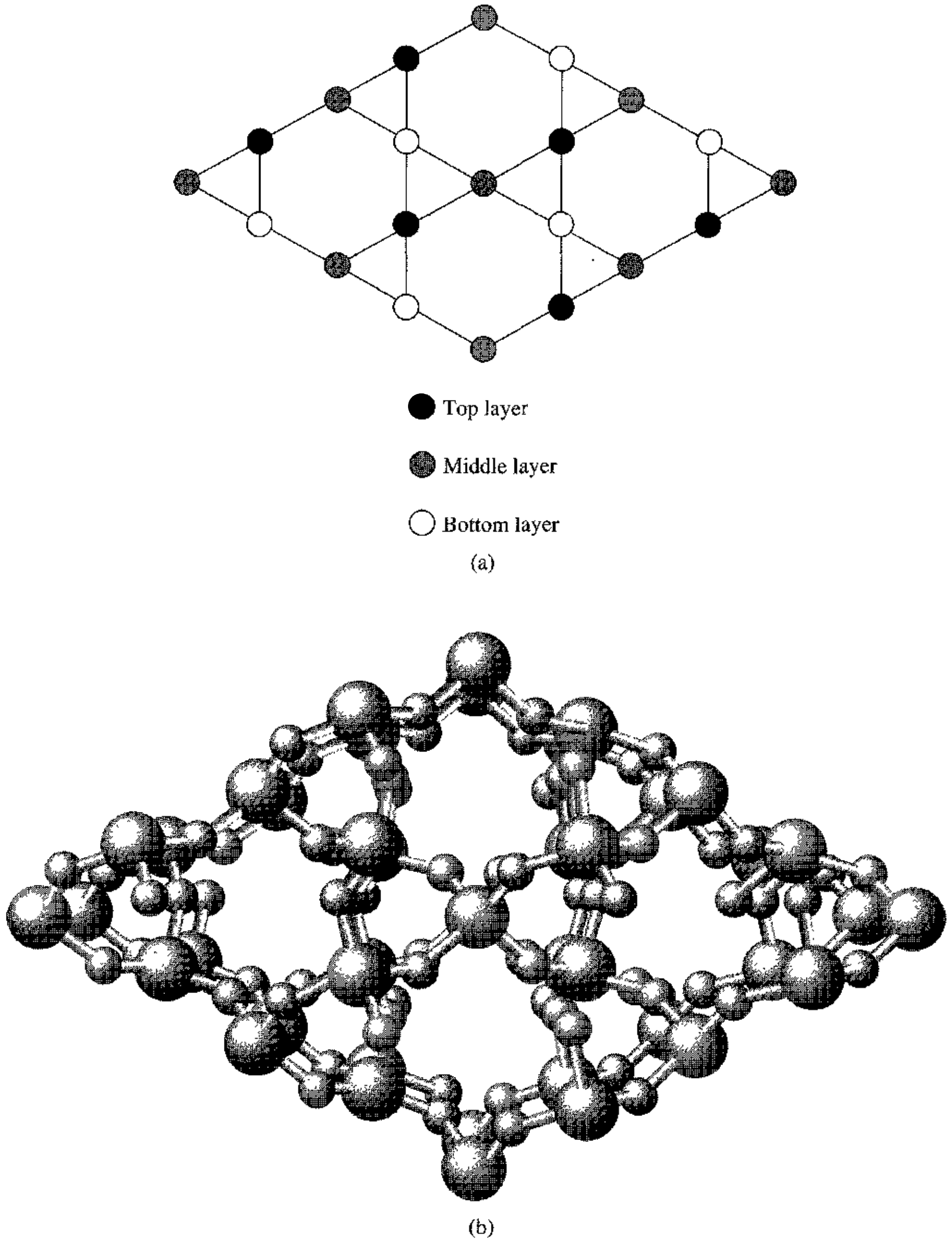

FIGURE 7-22 Crystal Structure of β-Quartz. (a) Overall structure, showing silicon atoms only. (b) Three-dimensional representation with both silicon (larger) and oxygen atoms. There are six triangular units surrounding and forming each hexagonal unit. Each triangular unit is helical, with a counterclockwise twist, three silicon atoms and three oxygen atoms per turn. α-Quartz has a similar, but less regular, structure.

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[16] This figure was prepared with the assistance of Robert M. Hanson's Origami program and the Chime plug-in (MDL) to Netscape.

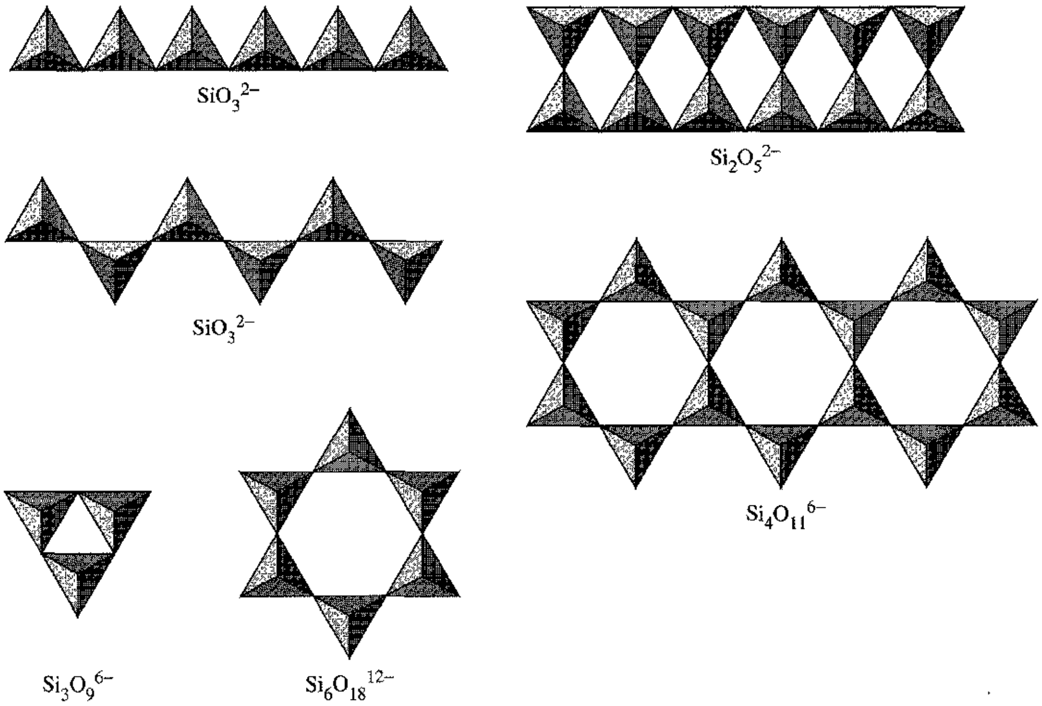

FIGURE 7-23 Common Silicate Structures. Reproduced with permission from N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Elmsford, N. Y., 1984, pp. 403, 405, © 1984; and from A. F. Wells, Structural Inorganic Chemistry, 5th ed., Oxford University Press, New York, 1984, pp. 1006, 1024.

iron, and titanium are common cations that occupy octahedral holes in the aluminosilicate structure, although any metal cation can be present. Some of the simpler examples of silicate structures are shown in Figure 7-23. These subunits pack together to form octahedral holes to accommodate the cations required to balance the charge. As mentioned previously, aluminum can substitute for silicon. A series of minerals is known with similar structures but different ratios of silicon to aluminum.

EXAMPLE

Relate the formulas of SiO_3^{2-} and $Si_2O_5^{2-}$ to the number of corners shared in the structures shown in Figure 7-23.

Consider the first tetrahedron in the chains of SiO_3^{2-} to have four oxygen atoms, or SiO_4. Extending the chain by adding SiO_3 units with the fourth position sharing an oxygen atom of the previous tetrahedron results in an infinite chain with the formula SiO_3. The charge can be calculated based on Si^{4+} and O^{2-}.

$Si_2O_5^{2-}$ can be described similarly. Beginning with one Si_2O_7 unit can start the chain. Adding Si_2O_5 units (two tetrahedra sharing one corner and each with a vacant corner for sharing with the previous unit) can continue the chain indefinitely. Again, the charge can be calculated from the formula.

EXERCISE 7-6

Describe the structure of $Si_3O_9^{6-}$ in a similar fashion.

One common family has units of two layers of silicates in the $Si_4O_{11}^{6-}$ geometry bound together by Mg^{2+} or Al^{3+} (or other metal ions) and hydroxide ions to form $Mg_3(OH)_4Si_2O_5$ or $Al_4(OH)_8Si_4O_{10}$ (kaolinite). Kaolinite is a china-clay mineral that forms very small hexagonal plates. If three magnesium ions substitute for two alu-

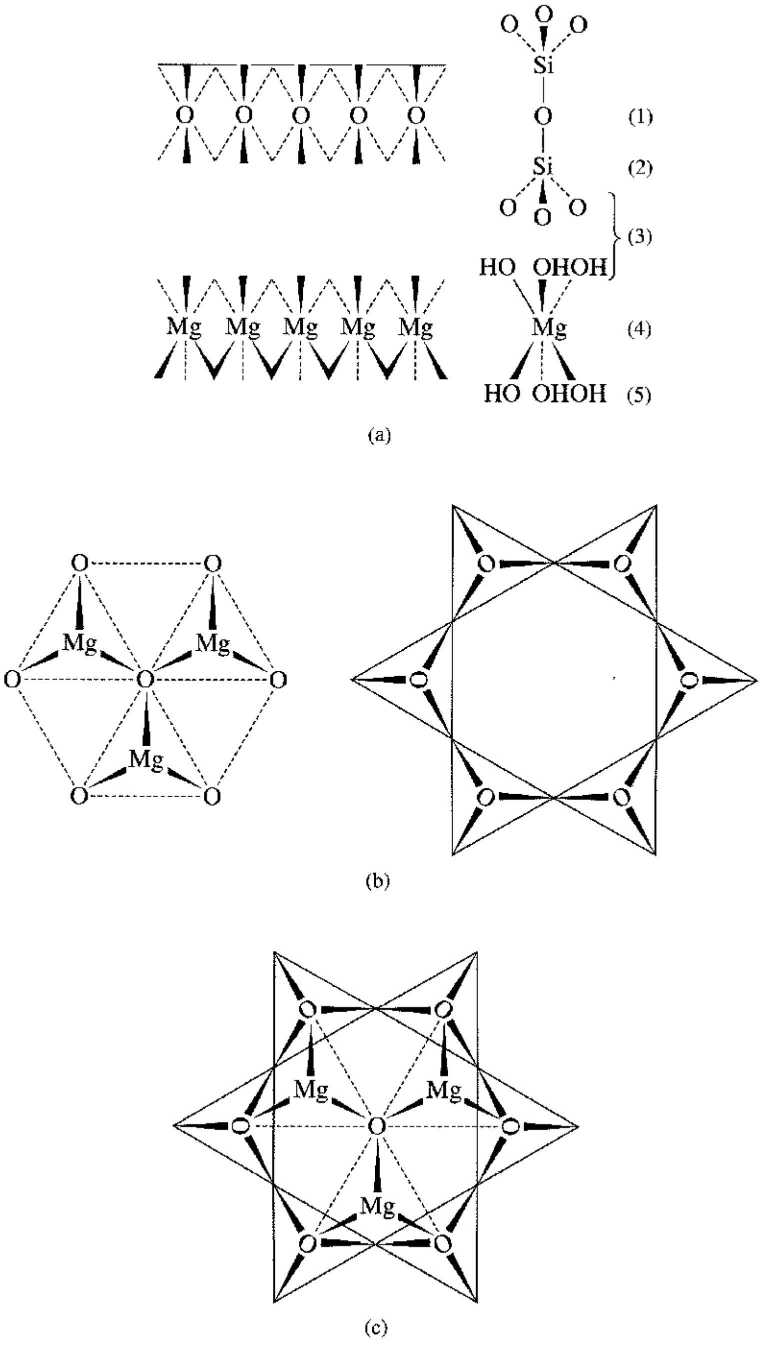

FIGURE 7-24 Layer Structure of $Mg(OH)_2$-Si_2O_5 Minerals. (a) Side view of the separate layers. (b) Separate views of the layers. (c) The two layers superimposed, showing the sharing of O and OH between them.

minum ions (for charge balance), the result is talc, $Mg_3(OH)_2Si_4O_{10}$. In either case, the oxygen atoms of the silicate units that are not shared between silicon atoms are in a hexagonal array that fits with the positions of hydroxide ions around the cation. The result is hydroxide ion bridging between Al or Mg and Si, as shown in Figure 7-24(a). The layers in talc are (1) all oxygen (the three shared by silicate tetrahedra); (2) all silicon; (3) oxygen and hydroxide in a 2:1 ratio (shared by silicon and magnesium); (4) magnesium; and (5) hydroxide (shared between magnesium ions). If another silicate layer (made up of individual layers 3, 2, and 1) is on top of these layers, as in kaolinite, the mineral is called pyrophyllite. In both pyrophyllite and talc, the outer surfaces of these layered structures are the oxygen atoms of silicate tetrahedra, resulting in weak attractive forces and very soft materials. Soapstone and the talc used in cosmetics, paints, and ceramics are commercial products with these structures.

Hydrated montmorillonite has water between the silicate-aluminate-silicate layers. The micas (e.g., muscovite) have potassium ions in comparable positions and also have aluminum substituting for silicon in about 25% of the silicate sites. Changes in the proportions of aluminum and silicon in either of these allow the introduction of other cations and the formation of a large number of minerals. The layered structures of some micas is very obvious, allowing them to be cleaved into sheets used for high-temperature applications in which a transparent window is needed. They also have valuable insulating properties and are used in electrical devices. If the *octahedral* Al^{3+} is partially replaced by Mg^{2+}, additional cations with charges of 1+ or 2+ are also added to the structures, and montmorillonites are the result. These clays have ion exchange properties, swell on the absorption of water, and have **thixotropic** properties. They are gels when undisturbed but become liquid when stirred, making them useful as oil field "muds" and in paints. Their formulas are variable, with $Na_{0.33}[(Mg_{0.33}Al_{1.67}(OH)_2(Si_4O_{10})] \cdot n\ H_2O$ as an example. The cations can include Mg, Al, and Fe in the framework and H, Na, K, Mg, or Ca in the exchangeable positions.

The term asbestos is usually applied to a fibrous group of minerals, including the amphiboles, such as tremolite, $Ca_2(OH)_2Mg_5(Si_4O_{11})_2$, with double-chain structures, and chrysotile, $Mg_3(OH)_4Si_2O_5$. In chrysotile, the dimensions of the silicate and magnesium layers are different, resulting in a curling that forms the characteristic cylindrical fibers.

The final group we will consider are the zeolites, mixed aluminosilicates containing $(Si, Al)_nO_{2n}$ frameworks with cations added to maintain charge balance. These minerals contain cavities that are large enough for other molecules to enter. In fact, it is now possible to make synthetic zeolites with cavities tailored for specific purposes. The holes that provide entrances to the cavities can have from 4 to 12 silicon atoms around them. A common feature of many of these is a cubo-octahedral cavity formed from 24 silicate tetrahedra, each sharing oxygens on three corners. These units can then be linked by sharing of the external oxygen atoms to form cubic or tetrahedral units with still larger cavities. These minerals exhibit ion exchange properties, in which alkali and alkaline earth metal cations can exchange, depending on concentration. They were used as water softeners to remove excess Ca^{2+} and Mg^{2+} until the development of polystyrene ion exchange resins. They can also be used to absorb water, oil, and other molecules and are known in the laboratory as molecular sieves; a larger commercial market is as cat litter and oil absorbent. They are also used in the petroleum industry as catalysts and as supports for other surface catalysts. A large number of zeolites have been described and illustrated in the *Atlas of Zeolite Structure Types*.[17] The references by Wells and Greenwood and Earnshaw, cited previously in this book, also provide more information about these essential materials.

Figure 7-25 shows an example of the type of structure possible in the zeolites. Others have larger or smaller pores and larger or smaller entries into the pores (from 4 to 12 Si—O units are possible).

The extreme range of sizes for the pores (260 to 1120 pm) makes it possible to control entry to and escape from the pores based on the size and branching geometry of the added material. In addition, the surfaces of the pores can be prepared with reactive metal atoms, providing opportunities for surface-catalyzed reactions. Although much of the design of these catalytic zeolites is of the "try it and see what happens" style, patterns are emerging from the extensive base of data and planned synthesis of catalysts is possible in some cases.

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[17] W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, 2nd ed., Structure Commission of the International Zeolite Commission, Butterworths, London, 1988.

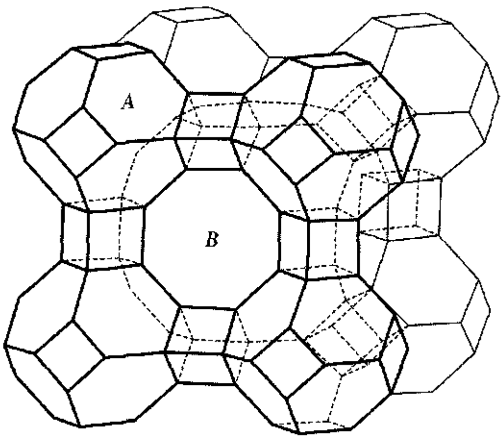

FIGURE 7-25 An Example of an Aluminosilicate Structure. Illustrated is the space-filling arrangement of truncated octahedra, cubes, and truncated cuboctahedra. (Reproduced with permission from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1975, p. 1039.)

GENERAL REFERENCES

Good introductions to most of the topics in this chapter (and many others) are in A. B. Ellis, et. al., *Teaching General Chemistry: A Materials Science Companion*, American Chemical Society, Washington, DC, 1993; P. A. Cox, *Electronic Structure and Chemistry of Solids*, Oxford University Press, Oxford, 1987; and L. Smart and E. Moore, *Solid State Chemistry*, Chapman & Hall, London, 1992. Cox presents more of the theory and Smart and Moore present more description of structures and their properties. Superconductivity is described by C. P. Poole, Jr., H. A. Farach, and R. J. Creswick, *Superconductivity*, Academic Press, San Diego, 1995; and G. Burns, *High-Temperature Superconductivity*, Academic Press, San Diego, 1992. A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, 1984, and N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997, describe the structures of a very large number of solids and discuss the bonding in them. A very good web site on superconductors is www.superconductors.org.

PROBLEMS

7-1 What experimental evidence is there for the model of alkali halides as consisting of positive and negative ions?

7-2 LiBr has a density of 3.464 g/cm^3 and the NaCl crystal structure. Calculate the interionic distance and compare your answer with the value from the sum of the ionic radii found in Appendix B-1.

7-3 Compare the CsCl and CaF_2 lattices, particularly their coordination numbers.

7-4 Using the diagrams of unit cells shown below, count the number of atoms at each type of position (corner, edge, face, internal) and each atom's fraction in the unit cell to determine the formulas (M_mX_n) of the compounds represented. Open circles represent cations and closed circles represent anions.