from: R. L. DeKock & H. B. Gray, "Chemical Structure and Bonding" (Benjamin Cummings, Menlo Park, 1980).

### *Electronic Bands in Metals*

The molecular-orbital theory provides an adequate model for metallic bonding. According to this model the entire block of metal is considered as a giant molecule. All of the atomic orbitals of a particular type in the crystal interact to form a set of delocalized orbitals that extend throughout the entire block. For a particular crystal, assume that the number of valence orbitals is of the order of $10^{23}$. To visualize the interaction of such a large number of valence orbitals, let us consider the hypothetical sequence of linear lithium molecules $Li_2$, $Li_3$, and $Li_4$, in which the important valence orbitals are 2*s* orbitals. Figure 7-25 shows the build-up of molecular orbitals for these three molecules. Notice that due to the delocalization of the molecular orbitals, none of the electrons is required to reside in antibonding orbitals. The spacing between the orbitals also becomes smaller. In the limit of $10^{23}$ equivalent atoms, the combination of atomic orbitals produces a band of closely spaced energy levels.

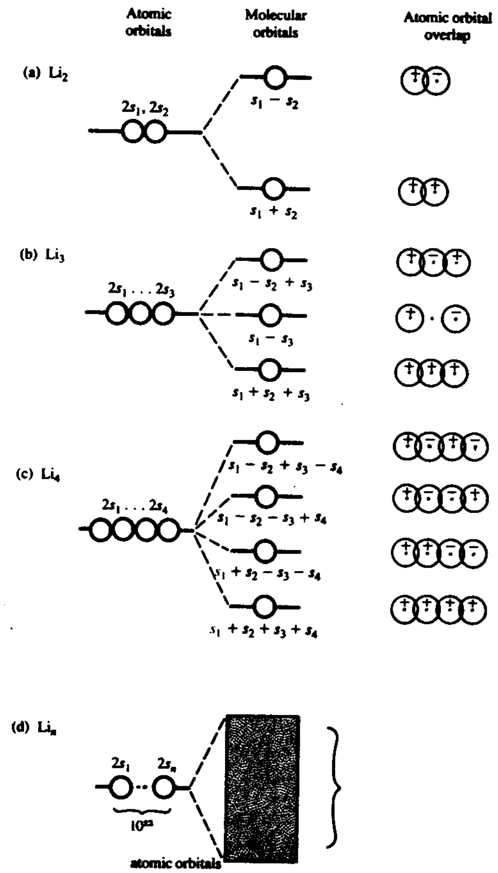

**Figure 7-25** Molecular-orbital development of the band theory of metals.

Figure 7-26 illustrates the three bands of energy levels formed by the 1*s*, 2*s*, and 2*p* orbitals of the simplest metal, lithium. The 1*s* molecular orbitals

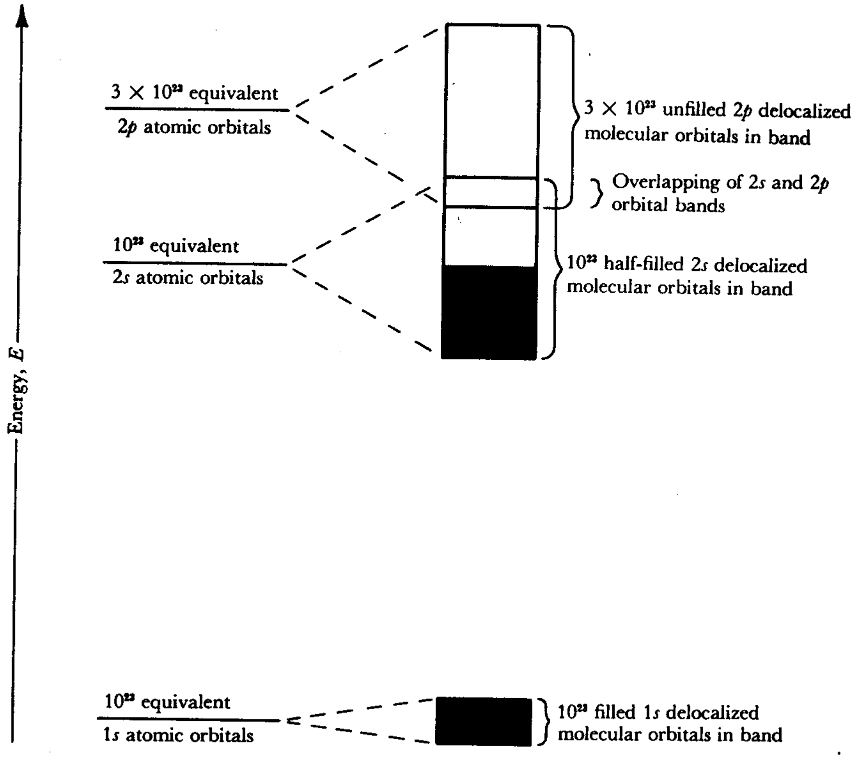

**Figure 7-26** Delocalized molecular-orbital bands in lithium. The original 2*s* and 2*p* atomic orbitals are so close in energy that the molecular-orbital bands overlap. Lithium has one electron in every 2*s* atomic orbital, hence only half as many electrons as can be accommodated in the 2*s* atomic orbitals or in the delocalized molecular-orbital band. There are unfilled energy states an infinitesimal distance above the highest-energy filled state, so an infinitesimal energy is required to excite an electron and send it moving through the metal. Thus lithium is a conductor.

are filled completely because the 1*s* atomic orbitals in isolated lithium atoms are filled. Thus the 1*s* electrons make no contribution to bonding. They are part of the positive ion cores and can be eliminated from the discussion. Atomic lithium has one valence electron in a 2*s* orbital. If there are $10^{23}$ atoms in a lithium crystal, the $10^{23}$ 2*s* orbitals interact to form a band of $10^{23}$ delocalized orbitals. As usual, each of these orbitals can accommodate two electrons, so the capacity of the band is $2 \times 10^{23}$ electrons. Lithium metal has enough electrons to fill only the lower half of the 2*s* band, as illustrated in Figure 7-26.

The presence of a partially filled band of delocalized orbitals accounts for bonding and electrical conduction in metals. Electrons in the lower filled orbital band move throughout the crystal in a random fashion in such a way that their motion results in no *net* separation of electrons and positive ions in the metal. For a metal to conduct an electric current, electrons must be excited to unfilled delocalized orbitals in such a way that their movement in one direction is not exactly canceled by electrons moving in the opposite direction. Such concerted electron movement occurs only when an electric potential difference is applied between two regions of a metal. Then electrons are excited to the unfilled delocalized molecular orbitals that are part of the same band (the 2*s* band for lithium) and just slightly higher in energy. Electrical conduction is restricted by the frequent collisions of electrons with positive ions, which have kinetic energy and thus vibrate randomly within their crystal sites. As temperature increases, vibration of the positive ions increases, and collisions with the conduction electrons are more frequent. Therefore electrical conduction in metals decreases as temperature increases.

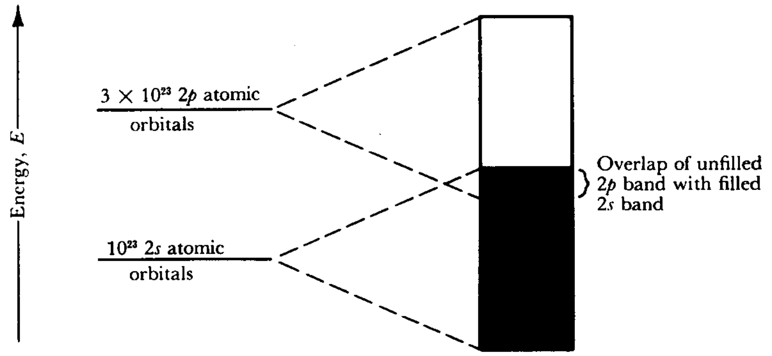

**Figure 7-27** Band-filling diagram for beryllium. A Be atom has enough electrons (two) to fill its 2*s* orbital, so Be metal has enough electrons to fill its 2*s* delocalized molecular orbital band. If the 2*s* and 2*p* bands did not overlap, Be would be an insulator, because an appreciable amount of energy would be required to make electrons flow in the solid. But with the band overlap shown here, an infinitesimal amount of energy excites the electrons to the 2*p* band orbitals, and electrons flow.

Beryllium is a more complicated example than lithium. An isolated beryllium atom has exactly enough electrons to fill its 2*s* orbital. Accordingly, beryllium metal has enough electrons to fill its 2*s* delocalized band. If the 2*p* band did not overlap the 2*s* (Figure 7-27), beryllium would not conduct well, because an energy equal to the gap between bands would be required before electrons could move through the solid. However, the two bands do overlap and beryllium has unoccupied delocalized orbitals that are an infinitesimal distance above the most energetic filled orbitals. Consequently beryllium is a metallic conductor.

## 7-5 Nonmetallic Network Solids

Nonmetallic network materials such as carbon or silicon are insulators; that is, they do not conduct electrical current. There is no simple way to apply the molecular-orbital model to a discussion of the bonding in nonmetallic network solids. Suffice it to say that in nonmetallic network solids it is usually possible to "count" electrons in the Lewis electron-dot sense and to show that the octet is achieved. That is, the atoms in nonmetallic network solids usually have at least as many valence electrons as the number of valence orbitals. Consequently, low coordination numbers are common and simple electron-pair bonds can be formed between each atom and its nearest neighbors. Due to the low coordination numbers, the potential energy is not constant throughout the crystal; rather, the energy is greatly lowered in the internuclear region, and the electrons are not free to move throughout the crystal as they are in metals.

In diamond, for example, each carbon atom has a coordination number of four. The hybrid-orbital model adequately describes the bonding by assigning to each carbon atom four localized tetrahedral $sp^3$ hybrid orbitals (Figure 7-28). The four valence electrons in each carbon atom are sufficient to fill these bonding orbitals. Thus all electrons in diamond are used for bonding, leaving none to move freely to conduct electricity.

The effect of coordination number on the electronic bands of a solid can be illustrated with respect to carbon. Calculations have shown that the electronic bands for carbon would be delocalized *if* carbon crystallized in a structure with a high coordination number such as is found for the metals (Figure 7-7). In that case the band structure would correspond to that shown in Figure 7-29(a), where one-half of the bands are occupied by electrons. (Carbon has four valence electrons and four valence orbitals, each of which can contain two electrons.) Consequently, carbon would be an electrical conductor. Experimentally it is found that carbon has a coordination number of four; this causes the extended bands shown in Figure 7-29(a) to split into