

12.8: Semiconductors and Band Theory

Recall from [Section 12.4](#) the simple model for bonding in metals called the electron sea model. We now turn to a model for bonding in solids that is both more sophisticated and more broadly applicable—it applies to both metallic solids and covalent solids. The model is **band theory**, and it grows out of molecular orbital theory, first discussed in [Section 6.4](#).

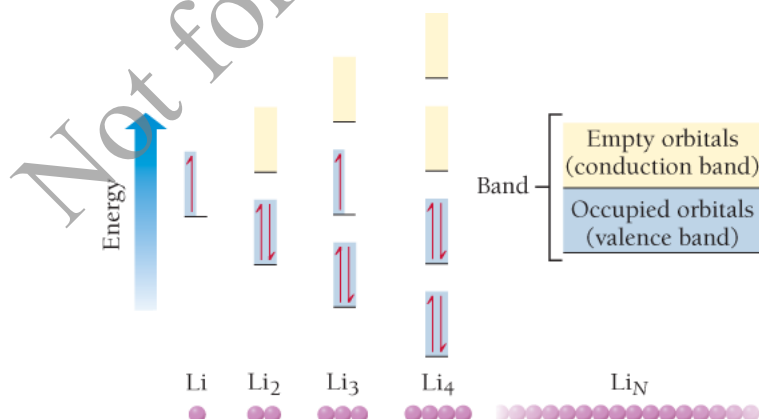
Molecular Orbitals and Energy Bands

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

Consider a series of molecules constructed from individual lithium atoms. The energy levels of the atomic orbitals and resulting molecular orbitals for Li, Li₂, Li₃, Li₄, and Li_N (where *N* is a large number on the order of 10²³) are shown in [Figure 12.21](#). The lithium atom has a single electron in a single 2s atomic orbital. The Li₂ molecule contains two electrons and two molecular orbitals. The electrons occupy the lower-energy bonding orbital—the higher-energy, or antibonding, molecular orbital is empty. The Li₄ molecule contains four electrons and four molecular orbitals. The electrons occupy the two bonding molecular orbitals—the two antibonding orbitals are completely empty.

Figure 12.21 Energy Levels of Molecular Orbitals in Lithium Molecules

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



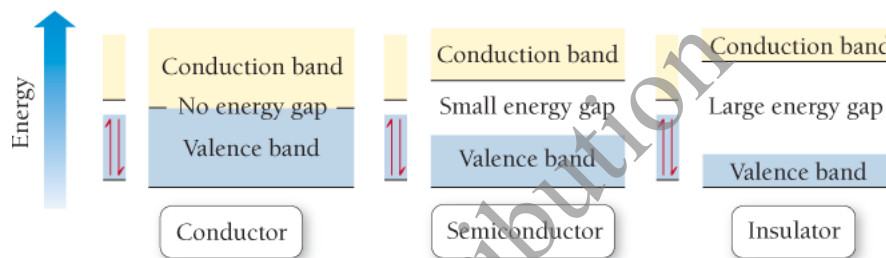
The Li_N molecule contains *N* electrons and *N* molecular orbitals. However, because there are so many molecular orbitals, the energy spacings between them are infinitesimally small; they are no longer discrete energy levels, but rather they form a *band* of energy levels. One-half of the orbitals in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

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

In metals, the valence band and conduction band are energetically continuous—the energy difference between the top of the valence band and the bottom of the conduction band is infinitesimally small. In semiconductors and insulators, however, an energy gap, called the **band gap**, exists between the valence band and conduction band as shown in [Figure 12.22](#). Band gaps are usually specified in units of electron volts or eV ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$). In insulators, the band gap is large, and electrons are not promoted into the conduction band at ordinary temperatures, resulting in no electrical conductivity. In semiconductors, the band gap is smaller. As a result, the conductivity of semiconductors increases with increasing temperature because heat allows a greater number of electrons to be thermally promoted into the conduction band.

Figure 12.22 Band Gap

In a conductor there is no energy gap between the valence band and the conduction band. In semiconductors there is a small energy gap, and in insulators there is a large energy gap.



The group 4A elements exhibit a range of band gaps, as shown in [Table 12.1](#).

Table 12.1 Band Gap of Group 4A Elements

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

Notice that the band gap decreases as we move down the column of elements. Why? We know from our discussion of periodic properties (see [Section 3.6](#)) that atomic radius increases as we move down a column in the periodic table. The increasing radius reduces the overlap between orbitals on neighboring atoms, which in turn reduces the energy difference between the antibonding orbitals (the conduction band) and the bonding orbitals (the valence band).

Doping: Controlling the Conductivity of Semiconductors

Doped semiconductors contain minute amounts of impurities that result in either additional electrons in the

conduction band or electron “holes” in the valence band. For example, silicon is a group 4A semiconductor. Its valence electrons just fill its valence band. The band gap in silicon is large enough that only a few electrons are promoted into the conduction band at room temperature; therefore, silicon is a poor electrical conductor. However, silicon can be doped with phosphorus, a group 5A element with five valence electrons, to increase its conductivity. The phosphorus atoms are incorporated into the silicon crystal structure, and each phosphorus atom brings with it one additional electron. Since the valence band is completely full, the additional electrons must go into the conduction band.

These additional electrons are then mobile and can conduct electrical current. This type of semiconductor is called an **n-type semiconductor** because the charge carriers are *negatively* charged electrons in the conduction band.

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

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

Conceptual Connection 12.5 Semiconductor Type

Interactive

Not for Distribution

Not for Distribution