1 Band Structure

1.1 Band Gaps from the Dispersion Relationship

The classification of a material as a metal, semiconductor, or insulator is generally stated in terms of the band structure of the material. Metals are materials in which there are no disallowed energies for the electrons near the Fermi level, i.e., there is no band gap. In contrast, for semiconductors and insulators, there exists a range of energies that an electron cannot take. For semiconductors, this range is relatively small, while for insulators it is larger. How, then, does this energy gap arise, and what consequences does it have for the behavior of the material?

First, consider an electron floating in vacuum. The energy of the electron is dependent only on its momentum p,

$$E(p) = \frac{p^2}{2m^\star} \rightarrow E(k) = \frac{\hbar^2 k^2}{2m^\star},$$

where $m^\star$ the effective mass of the electron. The relationship between electron energy and momentum is often stated using $p = \hbar k$, where k is the electron wavevector (inverse wavelength). The function $E(k)$ is called the *dispersion relationship*.

The effective mass of the electron is inversely proportional to the curvature of the dispersion relationship:

$$m^\star \propto \left(\frac{d^2E(k)}{d^2k}\right)^{-1}.$$

We can also use the dispersion relationship to understand the density of states $g(E)$ at $T = 0$ K, or the number of electron states within a given energy range $E + \Delta E$. In regions where the dispersion relationship is relatively flat, we have a larger number of electron states in an energy range $E + \Delta E$, and thus a higher density of states. In fact, the density of states is related to the inverse of the slope of $E(k)$:

$$g(E) = \frac{dN}{dE} = \left(\frac{dN}{dk}\right)\left(\frac{dk}{dE}\right) = \left(\frac{dN}{dk}\right)\left(\frac{dE}{dk}\right)^{-1}.$$

We can now think of our single electron existing not in vacuum, but in the periodic potential of a crystal. The effect of the potential is to modify the parabolic dispersion. At the periodic boundaries of the crystal, the electrons diffract and destructively interfere with one another. This destructive interference causes a gap to arise in the dispersion relationship, shown in Figure 1. The continuous segments of the dispersion are known as energy bands.

However, the gaps that arise at the periodic boundaries do not automatically make the material a semiconductor. For that, we need to introduce the *Fermi level* E_F. The Fermi level is the energy at which, at $T = 0$ K, all electron states below E_F are occupied and all electron states above E_F are unoccupied.

A material is a semiconductor or insulator if the Fermi level falls within an energy gap of the dispersion relationship. A metal has a Fermi level that falls in the middle of a band. These characteristics are represented in Figure 2.

1.2 Band Gaps from a Collection of Energy Levels

We can also think about band gaps from the perspective of energy levels. For this we will build a crystal atom-by-atom. First, consider an electron in a single atom. The electron can only occupy discrete energy levels. When we add another atom to begin building our crystal, the orbitals of our two atoms overlap.

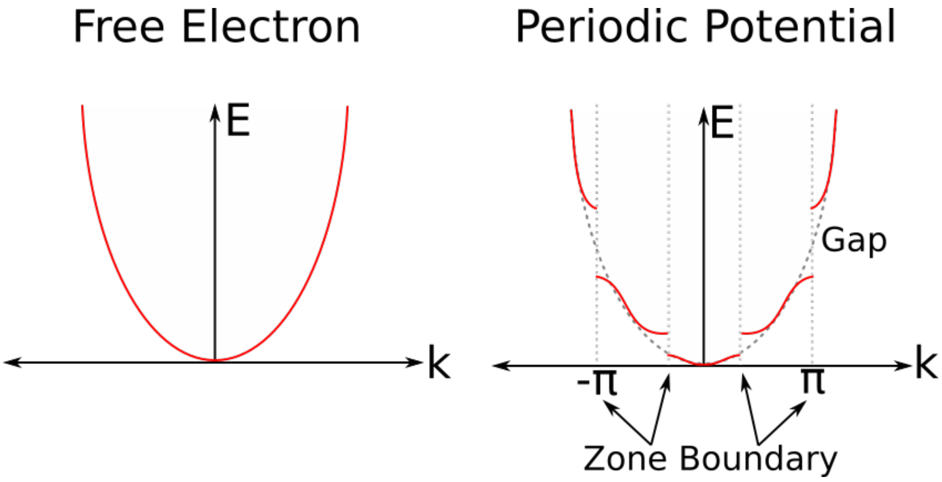

Figure 1: Dispersion relationship for a free electron and an electron in a periodic potential. In the case of the periodic potential, electron diffraction at the periodic boundaries results in destructive interference, yielding ranges of forbidden energies.

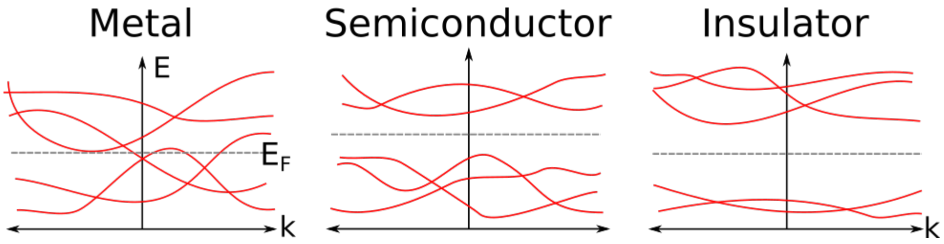

Figure 2: Schematic band structures for a metal, a semiconductor, and an insulator. In a metal, energy bands cross the Fermi level. In semiconductors and insulators, the Fermi level lies within an energy gap.

Because no two electrons can occupy the same energy state (the Pauli Exclusion Principle), the atomic orbitals split into molecular orbitals with different energies. Additional splitting occurs as we continue to add more atoms to the crystal, ultimately leading to several continuous ranges of allowed energies. This is represented schematically in Figure 3. However, even after adding all of our atoms to the crystal, there may be energy ranges that remain untouched. These energy ranges are thus inaccessible to electrons in the crystal, and if the Fermi energy lies in one of these gaps, the material will be a semiconductor.

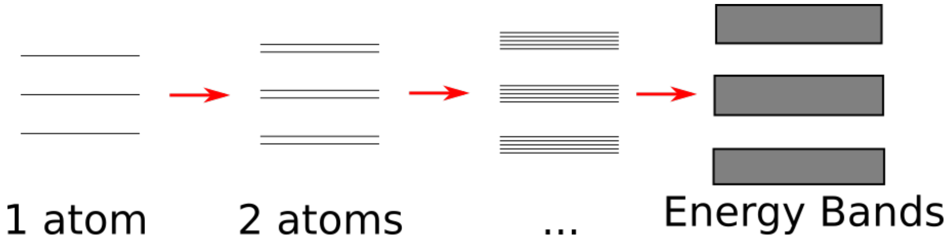

Figure 3: Schematic representation of orbital splitting giving rise to energy bands in bulk materials

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2 Intrinsic Semiconductors

Intrinsic semiconductors are semiconductors where thermal fluctuations can promote electrons in the valence band (the energy band just below the Fermi level) to the conduction band (the energy band just above the Fermi level). This promotion requires an energy equal to that of the energy gap E_g. This promotion can also occur if an electron adsorbs a photon with an energy greater than or equal to E_g.

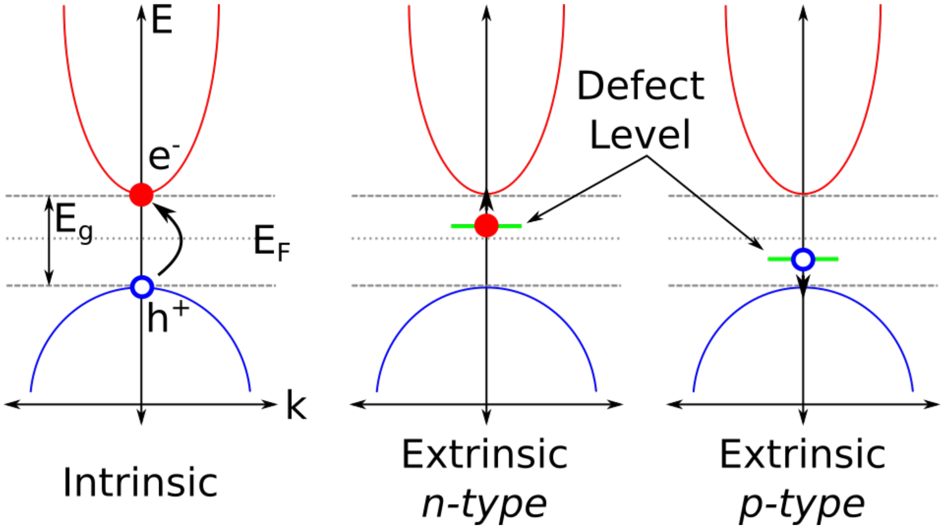

Figure 4: Schematic of electronic excitations in intrinsic and extrinsic semiconductors. In extrinsic semiconductors, dopants introduce defect levels within the band gap, from which electrons can jump directly into the conduction band. Additionally, an electron in the valence band can jump to the defect state and then to the conduction band.

When an electron of charge $-q$ is promoted to the conduction band, it leaves behind an empty space in the valence band (Figure 4). This empty space is referred to as a *hole*, which has charge $+q$. This separation of charges allows current flow in the semiconductor. Note, however, that the material as a whole remains electrically neutral. In an pure, intrinsic semiconductor, the density of holes and electrons are equal.

At finite temperature, the Fermi-Dirac distribution,

$$f(E) = \frac{1}{1 + e^{(E-\mu)/(k_B T)}}$$

gives the average occupation n of an energy level with energy E. Here, μ is the chemical potential, the energy at which $f(E) = 1/2$. At $T = 0$ K, $\mu = E_F$ (but this is not necessarily true at higher temperatures). The general shape of $f(E)$ at different temperature is given in Figure 5.

Thus, at higher temperature, more electrons are likely to occupy the conduction band (with an equal number of holes occupying the valence band), leading to an increase in the carrier concentration.

3 Extrinsic Semiconductors

Unlike intrinsic semiconductors, where charge separation and current flow occurs as a result of electron promotion directly from the valence band to the conduction band, extrinsic semiconductors rely on the introduction of electronic defect states within the band gap.

These defect states are produced by introducing a physical defect into the crystal lattice. In most extrinsic semiconductors, this is achieved through substitution of one atom in the crystal lattice for another.

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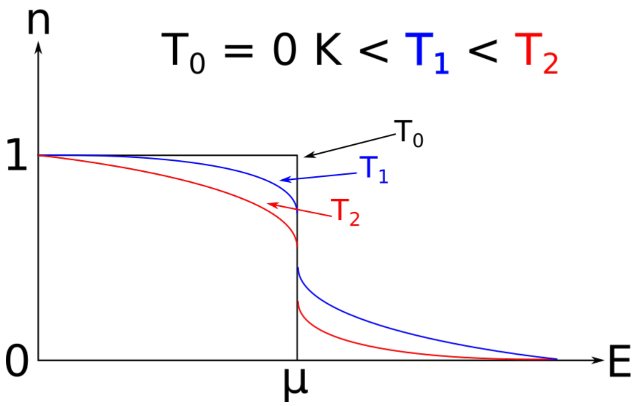

Figure 5: General shape of the Fermi function at different temperatures. At absolute zero, the distribution is a step function. As the temperature increases, the distribution acquires a sigmoidal shape.

The substituted atoms are called *dopants*, and the behavior of the extrinsic semiconductor depends on the chemistry of the dopant.

For example, consider replacing a few Si atoms in bulk silicon with P atoms. Phosphorus has one more electron than silicon, and this extra electron is allowed to roam about the material as it is not involved in bonding. In terms of energy, this extra electron sits at the energy level of the defect state in the band structure created by introducing the P atom. This energy is closer to the conduction band, making it easier for thermal fluctuations (or photon absorption) to promote the electron to the conduction band.

Similarly, we can dope silicon with an atom with fewer electrons, like boron. This situation is similar, except we have a roaming hole instead of a roaming electron. This hole sits in a defect state near the valence band, making it easier for the hole to jump into the valence band and serve as a charge carrier.

Doping with an element with more electrons is known as *n-type* doping; doping with an element with fewer electrons is known as *p-type* doping. Schematic band structures of *n-* and *p-type* extrinsic semiconductors are given in Figure 4.

It is important to note that in extrinsic semiconductors, the densities of electrons and holes acting as charge carriers are not equal. In *n-type* semiconductors, the electron density is larger than that of holes. The opposite is true for *p-type* semiconductors. However, in both cases charge neutrality is still preserved, as we have merely replaced one neutral atom in the crystal lattice with another.

Reference

Charles Kittel (2004), *Introduction to Solid State Physics*, 8th Ed. Wiley.

The End.