Chapter 11 Density of States, Fermi Energy and Energy Bands

Contents

11.1 Current and Energy Transport

The electric field $\mathcal{E}$ is interfered with two processes which are the electric current density j and the temperature gradient ∇T. The coefficients come from the Ohm's law and the Seebeck effect. The field can be written as

$$\mathcal{E} = \frac{j}{\sigma} + \alpha \nabla T \tag{11.1}$$

where σ is the electrical conductivity and α is the Seebeck coefficient.

The heat flux (thermal current density) q is also interfered with both the electric field $\mathcal{E}$ and the temperature gradient ∇T. However, the coefficients are not readily attainable. Thomson in 1854 arrived at the relationship assuming that thermoelectric phenomena and thermal conduction are independent. Later, Onsager [1] supported that relationship by presenting the reciprocal principle which was experimentally verified. The heat flux can be written as

$$q = \alpha T j - k \nabla T \tag{11.2}$$

where k is the thermal conductivity consisting of the electronic and lattice (or phonon) contributions to the thermal conductivity as

$$k = k_e + k_l \tag{11.3}$$

In this chapter, only the electronic contribution to the total thermal conductivity is used.

$$q_e = \alpha T j - k_e \nabla T \tag{11.4}$$

We consider a one-dimensional analysis in this chapter because most thermoelectric devices reasonably holds one-dimension, so that tensor notations are avoided.

11.2 Electron Density of States

Dispersion Relation

From Equation (10.16) (combining the *Bohr mo*del and the *de Broglie wave*), we have

$$\lambda = \frac{h}{p} \tag{11.5}$$

This is known as the *de Broglie wavelength.* Using the definition of wavevector $k = 2\pi/\lambda$, we have

$$k = \frac{p}{\hbar} \tag{11.6}$$

Knowing the momentum $p = mv$, the possible energy states of a free electron is obtained

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{11.7}$$

which is called the *dispersion relation* (energy or frequency-wavevector relation).

Effective Mass

In reality, an electron in a crystal experiences complex forces from the ionized atoms. We imagine that the atoms in the linear chain form the electrical periodic potential. If the free electron mass m is replaced by the *effective mass m^**, we can treat the motion of electrons in the conduction band as free electrons. An exact defined value of the wavevector k, however, implies complete uncertainty about the electron's position in real space. Mathematically, localization can be described by expressing the state of the electron as a wave packet, in other words, a *group velocity*. The group velocity of electrons in Figure 11.1 is the slope of the dispersion relation.

$$v_g = \frac{\partial \omega}{\partial k} \tag{11.8}$$

Since the wavelength is twice the lattice constant a, the boundaries at the zone in k-space is $k = \pm \pi/a$. The frequency ω associated with a wavevector of energy E is

$$E = \omega\hbar \text{ and } k = \frac{p}{\hbar} \tag{11.9}$$

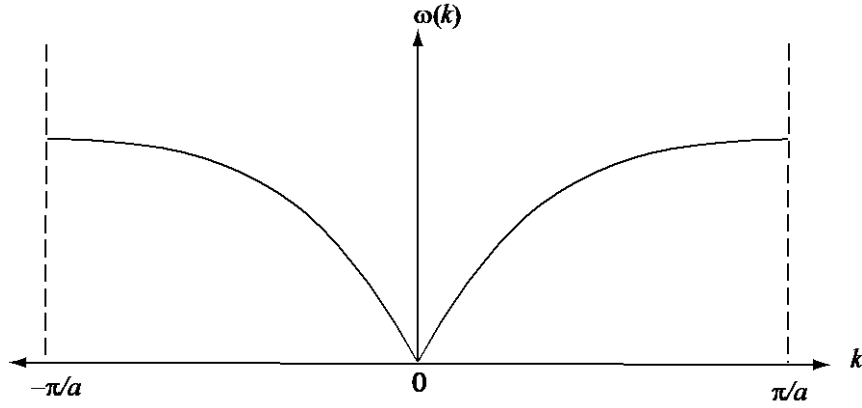where the two equations are known as the *Planck-Einstein relations*.

Figure 11.1 Dispersion relation of a group of electrons with a nearest neighbor interaction. Note that ω is linear for small k, and that $\partial\omega/\partial k$ vanishes at the boundaries of the *Brillouin zone* ($k = \pm \pi/a$)

$$v_g = \frac{1}{\hbar}\frac{\partial E}{\partial k} \qquad (11.10)$$

The derivative of Equation (11.10) with respect to time is

$$\frac{\partial v_g}{\partial t} = \frac{1}{\hbar}\frac{\partial^2 E}{\partial k \partial t} = \frac{1}{\hbar}\frac{\partial^2 E}{\partial k^2}\frac{\partial k}{\partial t} \qquad (11.11)$$

From Equation (11.9), we have $mv_g = \hbar k$ and $m\partial v_g/\partial t = \hbar \partial k/\partial t$. The force acting on the group of electrons is then

$$F = m\frac{\partial v_g}{\partial t} = \hbar \frac{\partial k}{\partial t} \qquad (11.12)$$

Combining Equations (11.11) and (11.12) yields

$$F = \frac{\hbar^2}{\partial^2 E/\partial k^2}\frac{\partial v_g}{\partial t} \qquad (11.13)$$

This indicates that there is an effective mass m^*, which will replace the electron mass m.

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2} \qquad (11.14)$$

The effective mass m^* is the second order of derivative of energy with respect to wavevector, which is representative of the local curvature of the *dispersion relation* in three dimensional space. The effective mass is a tensor and may be obtained experimentally or numerically.

Density of States

Thermoelectric materials typically exhibit the directional behavior. Therefore, in general we have

$$E = \frac{\hbar^2}{2}\left(\frac{k_x^2}{m_x} + \frac{k_y^2}{m_y} + \frac{k_z^2}{m_z}\right) \tag{11.15}$$

where m_x, m_y, and m_z are the principal effective masses in the x-, y-, z-directions and here k is the magnitude of the wavevector.

$$k^2 = k_x^2 + k_y^2 + k_z^2 \tag{11.16}$$

This represents the surface of a sphere with radius k in k-space. We introduce a new wavevectors k' and an effective mass m' as

$$E = \frac{\hbar^2 k'^2}{2m'} = \frac{\hbar^2}{2m'}\left(k_x'^2 + k_y'^2 + k_z'^2\right) \tag{11.17}$$

Equating Equations (11.15) and (11.17), we have a relationship between the original wavevector and the new wavevector as

$$k_x = \sqrt{\frac{m_x}{m'}}k_x', \ k_y = \sqrt{\frac{m_y}{m'}}k_y', \text{ and } k_z = \sqrt{\frac{m_z}{m'}}k_z' \tag{11.18}$$

In Figure 11.2, we have the volume of a thin shell of radius k and thickness dk.

$$dk = dk_x dk_y dk_z = \sqrt{\frac{m_x m_y m_z}{m'^3}}dk_x' dk_y' dk_z' = \sqrt{\frac{m_x m_y m_z}{m'^3}}4\pi k'^2 dk' \tag{11.19}$$

The volume of the smallest wavevector in a crystal of volume L^3 is $(2\pi/L)^3$ since L is the largest wavelength. The *number of states* between k and $k + dk$ in three-dimensional space is then obtained (see Figure 11.2)

$$N(k)dk = \frac{2 \cdot 4\pi k'^2}{\left(\frac{2\pi}{L}\right)^3} \sqrt{\frac{m_x m_y m_z}{m'^3}} dk' \tag{11.20}$$

where the factor of 2 accounts for the electron spin (Pauli Exclusion Principle). Now the density of states $g(k)$ is obtained by dividing the number of states N by the volume of the crystal L^3.

$$g(k)dk = \frac{k'^2}{\pi^2} \sqrt{\frac{m_x m_y m_z}{m'^3}} dk' \tag{11.21}$$
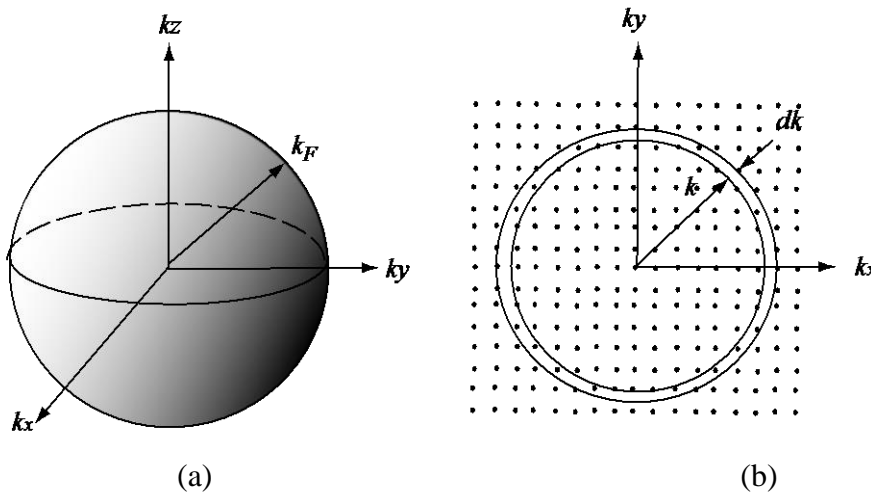

(a)   (b)

Figure 11.2 A constant energy surface in k-space: (a) three-dimensional view, (b) lattice points for a spherical band in two-dimensional view.

From Equation (11.17), we have

$$k' = \frac{\sqrt{2m'}}{\hbar} E^{\frac{1}{2}} \tag{11.22}$$

Differentiating this gives

$$\frac{dk'}{dE} = \frac{\sqrt{2m'}}{2\hbar} E^{-\frac{1}{2}} \tag{11.23}$$

Replacing this into Equation (11.21), m' is eliminated. The *density of states per valley* is finally obtained as

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m_d^*}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \qquad (11.24)$$

where

$$m_d^* = \left(m_x m_y m_z\right)^{\frac{1}{3}} \qquad (11.25)$$

which is called the *density-of-states effective mass*, and m_x, m_y, and m_z are the *principal effective masses* in the x-, y-, z-directions. Most actual band structures for semiconductors have ellipsoidal energy surfaces which require longitudinal and transverse effective masses in place of the three principal effective masses (Figure 11.3). Therefore, the density-of-states effective mass is expressed as

$$m_d^* = \left(m_l m_t^2\right)^{\frac{1}{3}} \qquad (11.26)$$

where m_l is the *longitudinal effective mass* and m_t is the *transverse effective mass*.
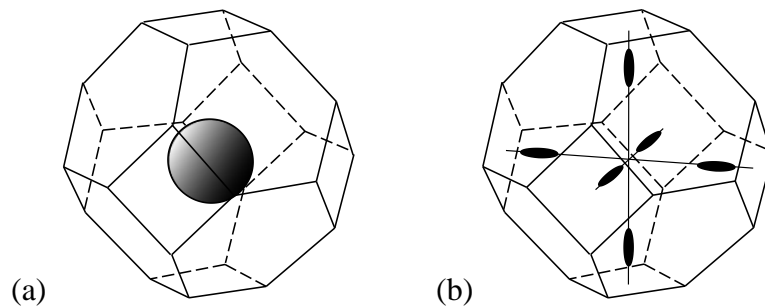

(a)   (b)

Figure 11.3 Constant electron energy surfaces in the *Brillouin zones* (space or *k*-space): (a) a *spherical band* such as GaAs; (b) an *ellipsoidal band* such as Si. Si has six identical conduction bands.

11.3 Fermi-Dirac Distribution

Although the classical free electron theory gave good results for electrical and thermal conductivities including *Ohm's law* in metals, it failed in certain other respects. These failure was eliminated by having the free electron obeys the *Fermi-Dirac distribution*.

The *ground state* is state of the *N* electron system at absolute zero. What happens as the temperature is increased? The solution is given by the *Fermi-Dirac distribution*. The kinetic energy of the electron increases as the temperature is increased: some energy levels are occupied

which were vacant at absolute zero, and some levels are vacant which were occupied at absolute zero (Figure 11.4). The *Fermi-Dirac distribution* f_o gives the *probability* that an orbital at energy E will be occupied by an ideal electron in *thermal equilibrium*.

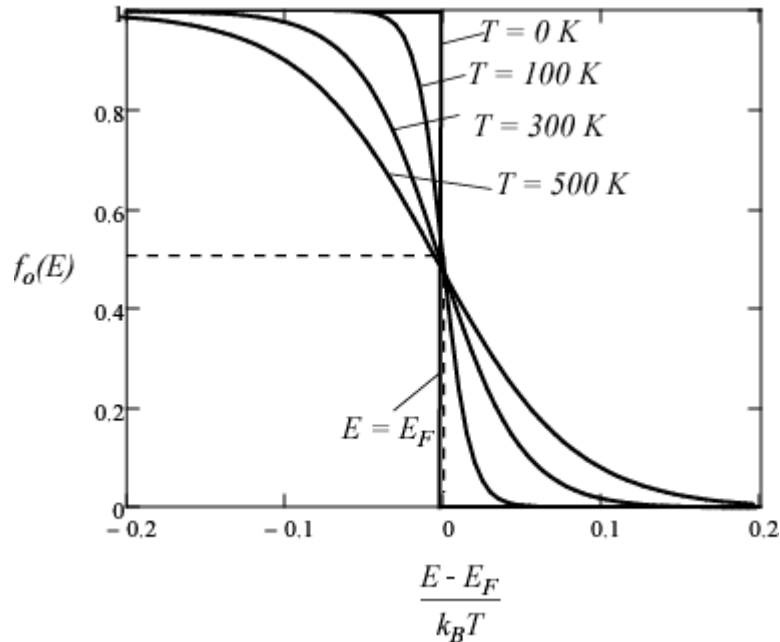$$f_o(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \qquad (11.27)$$

Figure 11.4 Fermi-Dirac distribution at the various temperatures.

11.4 Electron Concentration

The electron concentration n in thermal nonequilibrium is expressed as

$$n = \int_0^\infty g(E) f(E) dE \qquad (11.28)$$

where $f(E)$ is the temperature-dependent occupation *probability* in *thermal nonequilibrium*. It becomes the Fermi-Dirac distribution $f_o(E)$ in thermal equilibrium as shown in Equation (11.27), which becomes unity at absolute zero when E is less than E_F, and zero when E is greater than E_F (Figure 11.5). The electron concentration n in *thermal equilibrium* is

$$n = \int_0^\infty g(E) f_o(E) dE \tag{11.29}$$

Using Equations (11.24) and (11.27), the electron concentration n in thermal equilibrium is

$$n = \frac{1}{2\pi^2} \left(\frac{2m_d^*}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}}}{e^{(E-E_F)/k_B T} + 1} dE \tag{11.30}$$

11.5 Fermi Energy in Metals

The *Fermi-Dirac distribution* implies that at *absolute zero* (in the *ground state* of a system) the largest *Fermions* (electrons, holes, etc.) are filled up in the *density of states*, of which the energy is often called the *Fermi energy* (Figure 11.5), but here we specifically redefine it as the *Fermi energy at absolute zero*. So that the *Fermi energy* is temperature-dependent quantity. It is sometimes called the *Fermi level* or the *chemical potential*. In general, the *chemical potential* (temperature dependent) is not equal to the *Fermi energy at absolute zero*. The correction is very small at ordinary temperatures (under an order of 10^3 K) in ordinary metals.
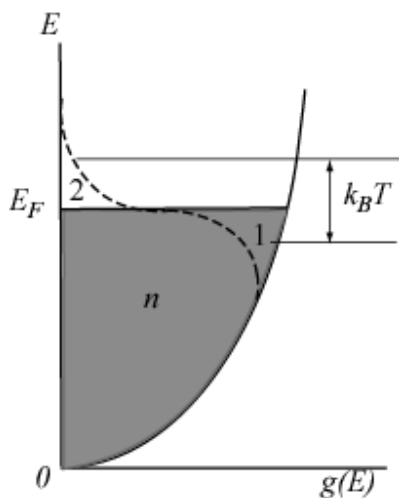

 Figure 11.5 Electron concentration n is given by the area under the density of states curve up to the Fermi energy E_F. The dashed curve represents the density of filled orbitals at a finite temperature. The electrons are thermally excited from region 1 to region 2.

The largest *number of states N* can be defined when a sphere of Fermi radius k_F is divided by the smallest volume $(2\pi/L)^3$ in k-space (see Figure 11.2 (a)).

$$N = \frac{2 \cdot \frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} \tag{11.31}$$

where the factor of 2 accounts for the *Pauli Exclusion Principle*. Since the crystal volume is defined as $V = L^3$, the *Fermi wavevector* is

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}} = \left(3\pi^2 n\right)^{\frac{1}{3}} \tag{11.32}$$

where N/V is the *electron density* (or *electron concentration*) n at the Fermi surface, which can be obtained from the lattice points, the lattice constant and the mass of the atom (n is usually a great number of about 10^{22} cm^{-3}). The Fermi wavevectors form the *Fermi surface*, which separates the occupied from the unoccupied levels. The *Fermi surface* is one of the fundamental constructions in the modern theory of metals; in general it is not spherical. The *Fermi en*ergy is

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{\frac{2}{3}} \tag{11.33}$$

or the electron concentration n is

$$n = \frac{2(2m)^{1/2}m}{3\pi^2\hbar^3} E_F^{\frac{3}{2}} \tag{11.34}$$

This can be also obtained by integrating Equation (11.30) from zero to E_F with $f_o \approx 1$ for $(E - E_F)/k_B T \ll 0$ in most metals. The *Fermi velocity* at the Fermi surface is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(3\pi^2 n\right)^{\frac{1}{3}} \tag{11.35}$$

For metals, the *Fermi velocity* is an order of 10^8 cm/s. This is a substantial velocity (about 1 percent of the speed of light). From the view point of classical statistical mechanisms, this is quite a surprising result, for we are describing the *ground state* ($T = 0$), and all particles in a classical gas have zero velocity at $T = 0$ (classical equipartition energy $1/2mv^2 = 3/2k_B T$). The *Fermi velocity* is only an approximation to the average electron velocity; this approximation works best in metals and in heavily doped semiconductors. The *electron mean free path* Λ can be approximated by

$$\Lambda \approx v_F \tau \tag{11.36}$$

where τ is the *relaxation time*. The *mean free path* is a measure of the average distance between successive scattering events. The *relaxation time* is the average time between successive collisions. The wavelength λ of electrons may be estimated by the *de Broglie* expression.

$$\lambda = \frac{h}{p} \approx \frac{2\pi\hbar}{mv_F} \tag{11.37}$$

EXAMPLE 11.1 Fermi Energy in Gold

A gold crystal has an *fcc* lattice with one gold atom per lattice point and a lattice constant of 4.08 Å. Every gold atom has one valence electron. Estimate the electron Fermi energy, Fermi velocity and electron wavelength in a gold crystal.

Solution:

We assume that the electron effective mass in gold is identical to that of free electrons. For an fcc lattice, there are four lattice points and thus four valence electrons. Consequently, the electron number density is

$$n = \frac{\text{Lattice points}}{(\text{Lattice constant})^3} = \frac{4}{(4.08 \times 10^{-8} cm)^3} = 5.89 \times 10^{22} cm^{-3}$$

From Equation (11.33), using $h = 6.6021 \times 10^{-34} Js$, $\hbar = h/2\pi$, $m_e = 9.10939 \times 10^{-31} kg$, and $1eV = 1.602 \times 10^{19} J$,

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{\frac{2}{3}} = 8.84 \times 10^{-19} J = 5.52 eV$$

The Fermi velocity is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} \left(3\pi^2 n\right)^{\frac{1}{3}} = 1.39 \times 10^6 m/s$$

The electron wavelength is estimated by

$$\lambda = \frac{h}{p} \approx \frac{2\pi\hbar}{mv_F} = 0.522\times10^{-9}\,m$$

Comments: We give the number of density in terms of cm^{-3} because such a unit is commonly used in semiconductors. Typical dopant levels for silicon-based semiconductor devices are $\sim10^{17} - 10^{19}$ cm^{-3}, which is much smaller than those in metals.

11.6 Fermi Energy in Semiconductors

In semiconductors, we usually have $(E - E_F)/k_BT \gg 1$, and then $\exp\big((E - E_F)/k_BT\big)$ becomes much greater than 1. Therefore, eliminating one we have

$$f_o(E) = \frac{1}{e^{(E-E_F)/k_BT}+1} = \exp\left(-\frac{E-E_F}{k_BT}\right) \tag{11.38}$$

The electron concentration n in equilibrium from Equation (11.30) is

$$n = \frac{1}{2\pi^2}\left(\frac{2m_d^*}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty E^{\frac{1}{2}}\exp\left(\frac{E_F - E}{k_BT}\right)dE \tag{11.39}$$

This can be solved using Gamma function. The electron concentration n in single band is reduced to (this is known as the *Boltzmann approximation*)

$$n = N_v 2\left(\frac{m_d^* k_B T}{2\pi\cdot\hbar^2}\right)^{\frac{3}{2}}\exp\left(\frac{E_F}{k_BT}\right) \tag{11.40}$$

where N_v is the degeneracy (number of bands or valleys having the same band edge energy and the same wavevector). For example, Si has the degeneracy of six valleys (see Figure 11.3). Solving for E_F, we have

$$E_F = k_B T \ln\left(\frac{n}{2N_v}\left(\frac{m_d^* k_B T}{2\pi\cdot\hbar^2}\right)^{-\frac{3}{2}}\right) \tag{11.41}$$

In typical semiconductors, the Fermi energy E_F may be below the conduction band edge E_C. The band gap E_g is the difference between E_C and E_V, which is usually much larger than k_BT as shown in Figure 11.6. The electron concentration n is the shaded area under the density of states curve

and the Fermi energy at room temperature. Note that the Fermi energy greatly affects the electron concentration n in the conduction band, which is much smaller than that of a metal (Figure 11.5).
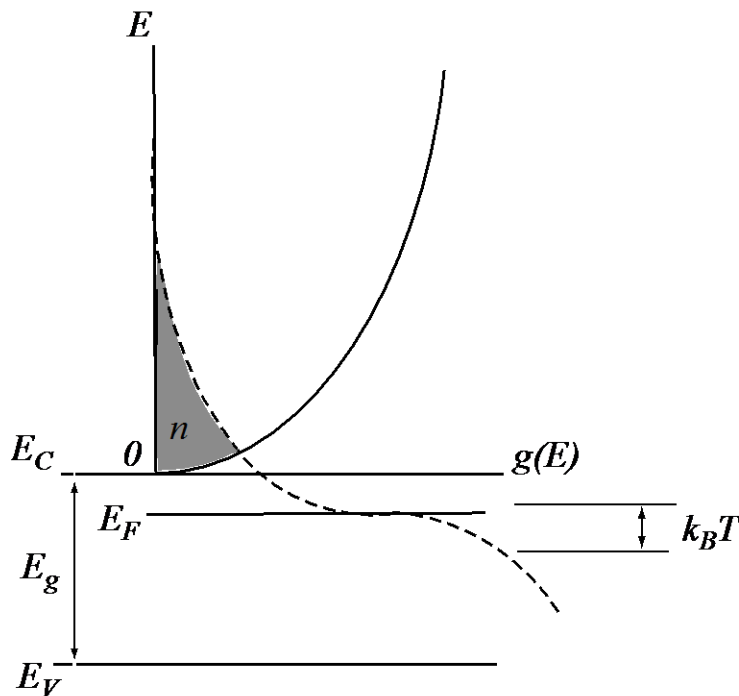

Figure 11.6 Electron concentration n in a semiconductor is given by the area under the density of states curve and the Fermi energy E_F at room temperature. The Fermi energy E_F is located under the minimum of conduction band. The dashed curve represents the density of filled orbitals at a finite temperature.

EXAMPLE 11.2 Fermi Energy in Doped Semiconductors

Silicon is widely used semiconductor material, and it is often doped with phosphorus to form an n-type semiconductor. Determine the Fermi energy of an n-type semiconductor doped with phosphorus with an electron concentration of 10^{17} cm^{-3} at 300 K, assuming that every phosphorus atom contributes one free electron to the conduction band and neglecting thermally excited electrons from the valence band. Si has six identical conduction bands with an effective mass equal to $0.33m$, where m is the free electron mass.

Solution:
Silicon has six identical conduction bands (Figure 11.3). When counting all six bands ($N_v = 6$), Equation (11.40) is written as

$$n = N_v 2 \left(\frac{m_d^* k_B T}{2\pi \cdot \hbar^2} \right)^{\frac{3}{2}} \exp\left(\frac{E_F}{k_B T} \right)$$

Taking $n = 10^{17}$ cm^{-3}, we can find the Fermi energy as

$$E_F = k_B T \ln\left(\frac{n}{2N_v} \left(\frac{m_d^* k_B T}{2\pi \cdot \hbar^2} \right)^{-\frac{3}{2}} \right)$$

$$= (1.38 \times 10^{-23})(300) \ln\left(\frac{10^{23}}{2(6)} \left(\frac{(0.33)(9.1 \times 10^{-31})(1.38 \times 10^{-23})(300)}{2\pi(6.626 \times 10^{-34}/2\pi)^2} \right)^{-3/2} \right) = -0.146 eV$$

Comments: The negative sign means that the Fermi energy is below the conduction band edge. The silicon bandgap at room temperature is 1.12 eV. Thus the Fermi energy is within the band gap. In fact, only in this case, the Boltzmann approximation we used in Equation (11.40) is applicable because the electron energy inside the conduction band, minus the Fermi energy, is much greater than $k_B T$ ($(E - E_F)/k_B T \gg 1$). If the Fermi energy is close to the band edge or falls inside the conduction band, which is the case when the semiconductors are heavily doped, we need to carry out numerical integration with the Fermi-Dirac distribution.

The value of the Fermi energy needs a reference point. Equation (11.39) indicates that the reference is the conduction band edge at zero energy, which is shown in Figure 11.6.

11.7 Energy Bands

The free electron model of metals gives us good insight into the electrical conductivity and electrodynamics of metals. But the model fails to help us with other questions, for example the relation of conduction electrons in the metal to the valence electrons of free atoms and many transport properties. Every solid contains electrons. The important question for electrical conductivity is how electrons respond to an applied electric field. We shall see that electrons in crystals are arranged in *energy bands* separated by regions in energy for which no wavelike electron orbits exist. Such forbidden regions are called *energy gaps* or *band gaps* (E_G) which are shown in Figure 11.7, wherein the differences between a metal, a semiconductor and an insulator are summarized schematically.

The crystal behaves as an insulator if the allowed energy bands are all either filled or empty, for then no electrons can move in an electric field. The crystal behaves as a metal if one or more bands are partly filled. The crystal is a semiconductor or semimetal if one or two bands are slightly filled or slightly empty.

To understand the difference between insulators and conductors, we must extend the free electron model to take account of the periodic lattice of the solid. The possibility of a band gap is the most important new property that emerges.
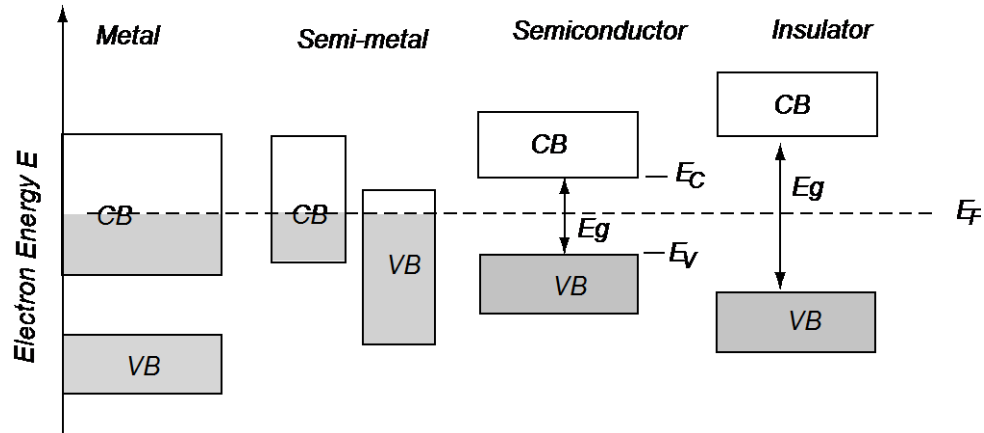

Figure 11.7 Energy level diagrams for a metal, a semiconductor, and an insulator. Metals have a partly occupied band (shaded). For semiconductors and insulators, the Fermi level lies between the occupied valence band and the unoccupied conduction band.

11.7.1   Multiple Bands

There may be two separate bands: a conduction band for electrons and a valence band for holes as shown in Figure 11.8 (a). In many semiconductors such as Si and PbTe, there may be also multiple bands that have the same energy levels, whereby it is called degeneracy. The heavy and light holes are degenerate and the split-off hole in the valence band is slightly off the valence band edge (maximum).
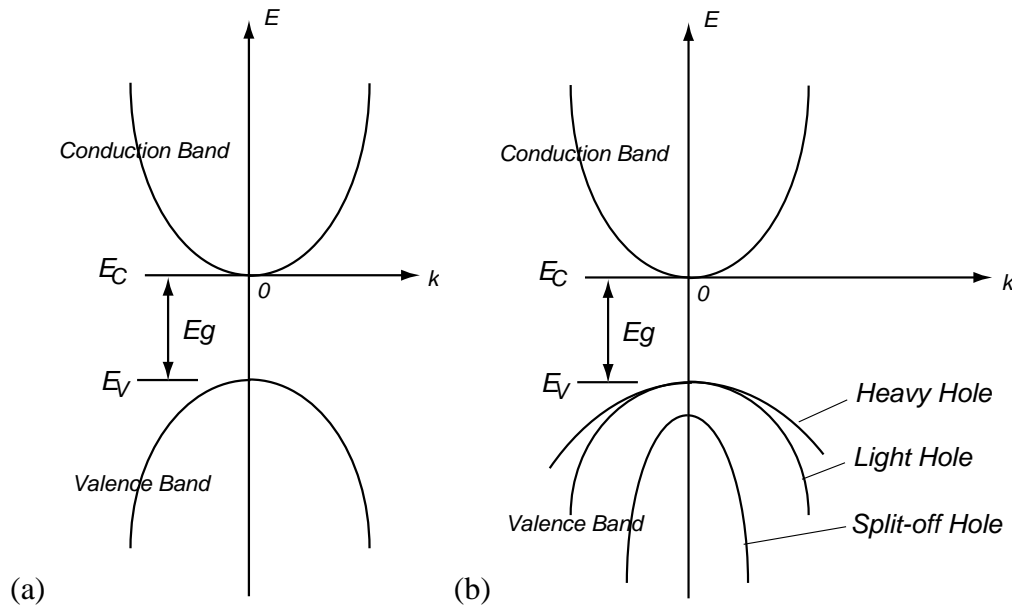
Figure 11.8 Band structures of a semiconductor including the conduction band and the valence bands. (a) A model of a conduction band and a valence band, and (b) a model of multiple bands.

11.7.2   Direct and Indirect Semiconductors

The type of band gap in semiconductors is important for the selection of material for many electronic devices including thermoelectric devices, solar cells and lasers. There are two types of band gaps in semiconductors, which are *direct* and *indirect band gap*. The energy E of a particle is always associated with a wavevector k (or momentum), which implies that, for any transition between bands, both energy and momentum must be conserved. When an electron absorbs enough energy to exceed the energy gap Eg, the electron can jump from the valence band into the conduction band. The source of the energy could be photons, phonons, or electric field.

In *direct band gap semiconductors*, such as GaAs, the maximum and minimum of energy versus momentum relationship occur at the same value of the wavevector (Figure 11.9 (a)). In *indirect band gap semiconductors* like Si and Ge, the maximum and minimum of the energy versus momentum relationship occurs at different wavevectors, which is pictured in Figure 11.9 (b). In this case, the electron cannot directly jump into the conduction band, but once the electron at the valence band edge E_V absorbs energy (photon, phonon, or electric field) and reaches the energy level of the conduction band edge E_C across the energy band E_g, it can indirectly jump into the conduction band with the aid of phonon energy because phonon usually exists anyway.
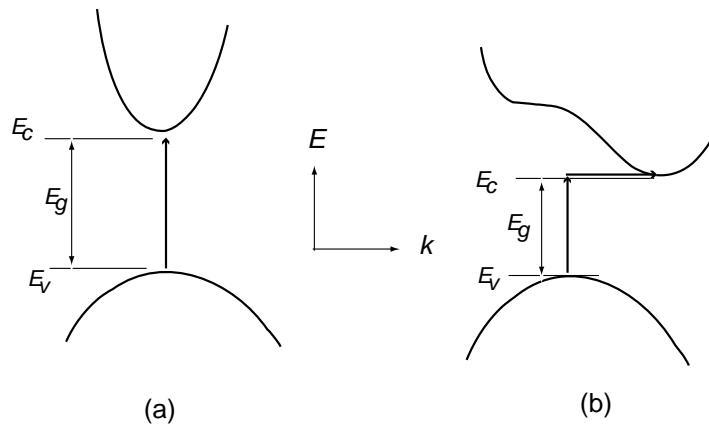
Figure 11.9 Energy versus wavevector diagrams in (a) direct bandgap and (b) indirect bandgap semiconductors.

Direct and indirect gap semiconductors have major differences in their optical properties. Direct band gap semiconductors are more efficient photon emitters, semiconductor lasers are made of direct gap semiconductors such as GaAs, whereas most electronic devices including thermoelectric devices are built on indirect semiconductors.

11.7.3   Periodic Potential (Kronig-Penney Model)

So far we have dealt with a free electron. In fact the electron in a crystal experiences a periodic potential which is along a line of the ionized atoms. Assuming one-dimensional lattice with the lattice constant a as shown in Figure 11.10 (a), resembling the individual atomic potentials as the atom is approached closely and flattening off in the region between atoms. We approximate this by a square periodic potential in Figure 11.10 (b) as introduced by Kronig and Penney.
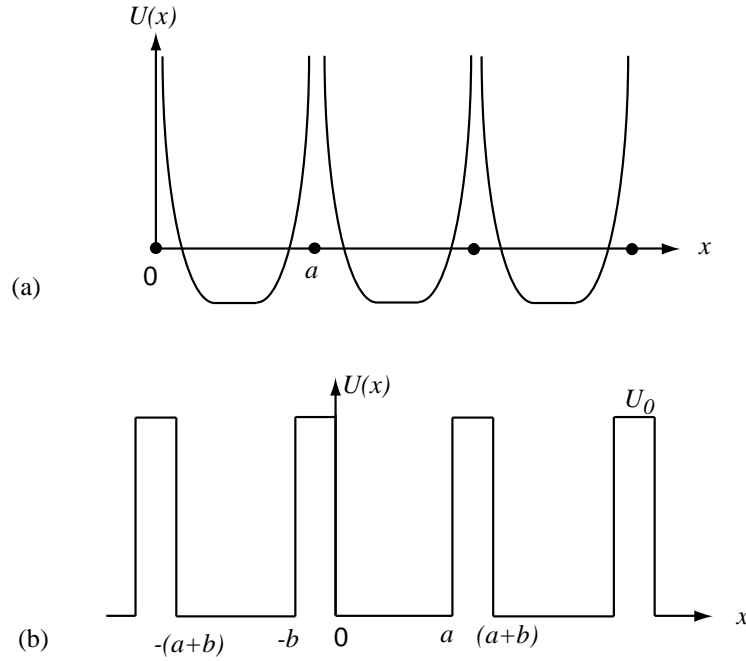
Figure 11.10 One-dimensional periodic potential energy model. (a) Sketch of potential model, and (b) *Kronig-Penney model*.

The Schrodinger equation for the wavefunction is then

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+\left(U(x)-E\right)\Psi=0 \tag{11.42}$$

The potential distribution is given by

$$U(x)=\begin{cases}0 \text{ for } 0<x\leq a \\ U_0 \text{ for } -b\leq x\leq 0\end{cases} \tag{11.43}$$

Subject to the following periodicity requirement

$$U(x+a+b)=U(x) \tag{11.44}$$

The general solution for Equation (11.42) are

$$\Psi=Ae^{iKx}+Be^{-iKx} \quad \left(0<x\leq a\right) \tag{11.45}$$

$$\Psi=Ce^{Qx}+De^{-Qx} \quad \left(-b<x\leq 0\right) \tag{11.46}$$

where

$$E = \frac{\hbar^2 K^2}{2m} \quad \text{and} \quad U_0 - E = \frac{\hbar^2 Q^2}{2m} \tag{11.47}$$

And K and Q are to be determined, from which the eigen energy E of the electron inside such a periodic potential is to be extracted.

Four boundary conditions are needed to determine the unknown coefficient A, B, C, and D. We can use the continuity of the wavefunction and its derivative at $x = 0$, which gives

$$A + B = C + D \tag{11.48}$$

$$iK(A - B) = Q(C - D) \tag{11.49}$$

Two more boundary conditions are necessary to determine the four unknown coefficients. Due to the periodicity in the potential, the wavefunction at any two points separated by a lattice vector is related through the *Bloch theorem* in the x-direction,

$$\Psi(x + a + b) = \Psi(x) e^{ik(a+b)} \tag{11.50}$$

We should distinguish the wavevector k from the propagation vector of the solution K in Equation (11.45). The latter contains the energy of the electrons that we want to find. We want to find a relation between k and E, which is equivalent to a relation between k and K. The continuity requirements for the wavefunction and its derivative at $x = a$ are then

$$Ae^{iKa} + Be^{-iKa} = \left(Ce^{-Qb} + De^{Qb}\right)e^{ik(a+b)} \tag{11.51}$$

$$iK\left(Ae^{iKa} - Be^{-iKa}\right) = Q\left(Ce^{-Qb} - De^{Qb}\right)e^{ik(a+b)} \tag{11.52}$$

Four equations with four unknowns have a solution only if the determinant of the coefficients vanishes, yielding

$$\frac{Q^2 - K^2}{2KQ} \sinh(Qb)\sin(Ka) + \cosh(Qb)\cos(Ka) = \cos(k(a+b)) \tag{11.53}$$

It is rather tedious to obtain this equation. The result is simplified if we represent the potential by the periodic delta function obtained when we pass to the limit $b = 0$ and $U_0 = \infty$ in such a way that $Q^2 ba/2 = P$, a finite quantity. In this limit $Q \gg K$ and $Qb \ll 1$. Then, Equation (11.53) reduces to

$$\frac{P}{Ka}sin(Ka) + cos(Ka) = cos(ka) \qquad (11.54)$$

The range of K for which this equation has solutions are plotted in Figure 11.11, for the case $P = 3\pi/2$. We can convert the solution for K into energy, and redraw the graph as a function of ka as shown in Figure 11.12. The figure shows that, for each wavevector k, there are multiple values for the electron energy E.
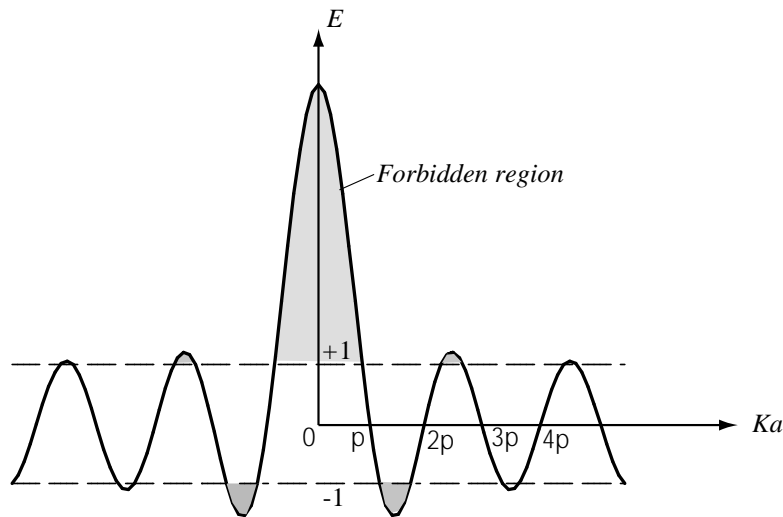

Figure 11.11 Left-hand side of Equation (11.54) as function of Ka. Because the right-hand side is always less than or equal to one, there are regions (the shaded area) where no solution for Ka exists, and thus no electrons exist with energy corresponding to the values of K in these regions.

The electron energy forms quasi-continuous bands (because k itself is quasi-continuous) separated from each other by a minimum gap that occurs at $ka = s\pi$ ($s = 0, \pm1, \pm2, \ldots$), or $k = s\pi/a$, at which the right-hand side of Equation (11.54) is ±1. Figure 11.12 (b) implies that there are multiple values of k for each E. However, the *Bloch theorem* says that wavefunctions corresponding to the wavevectors k separated by $m(2\pi/a)$ (since $b = 0$) are identical, they are the same quantum state and should be counted only once. Thus, rather than plotting the energy eigenvalues for all the wavevectors, we can plot them in one period, as shown in Figure 11.13. This way of representation is called the reduced-zone representation. The relationship between the energy and the wavevector is the *dispersion relation*.
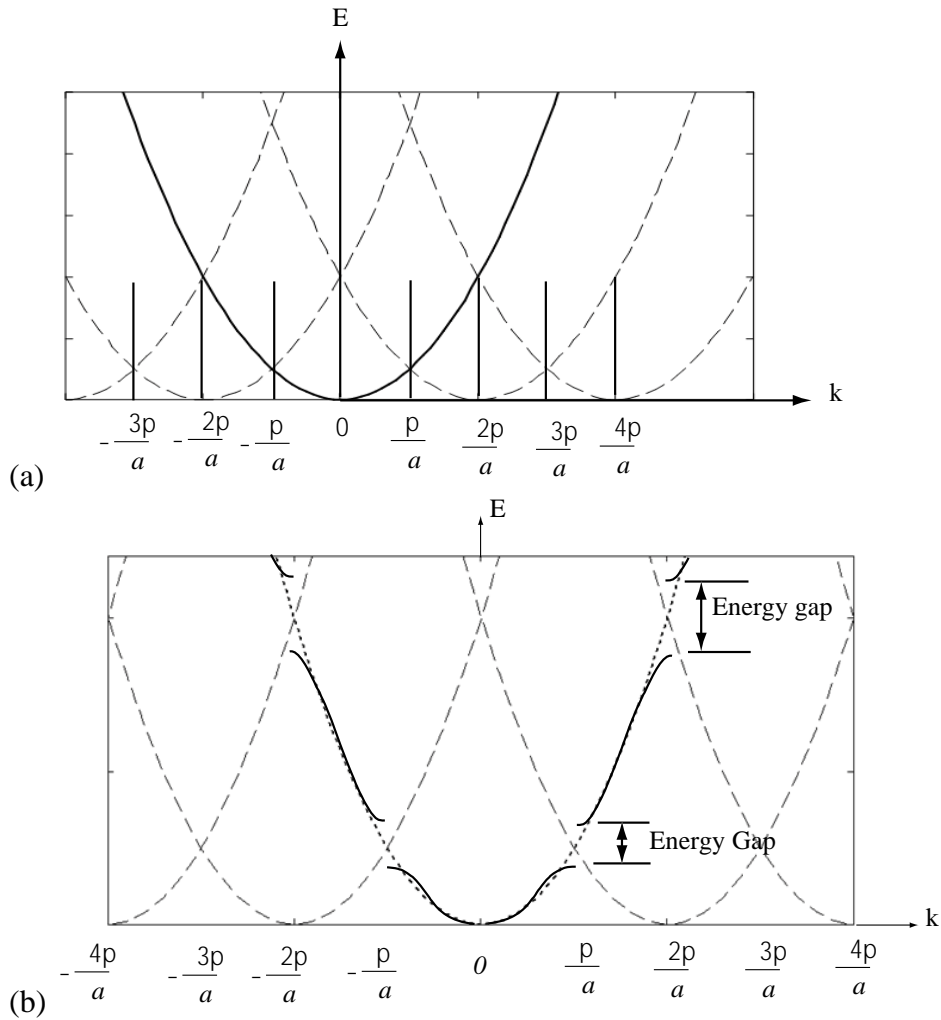
(a)

(b)

Figure 11.12 (a) Parabolic energy curves of a free electron in one dimension, periodically continued in reciprocal space. The periodicity in real space is *a,* and (b) extended zone: splitting of the energy parabola at the boundaries of the first Brillouin zone. The energy gaps are forbidden regions. The solid lines from Kronig-Penney model.

Band 5

Band 4

Band 3

Band 2

Band 1

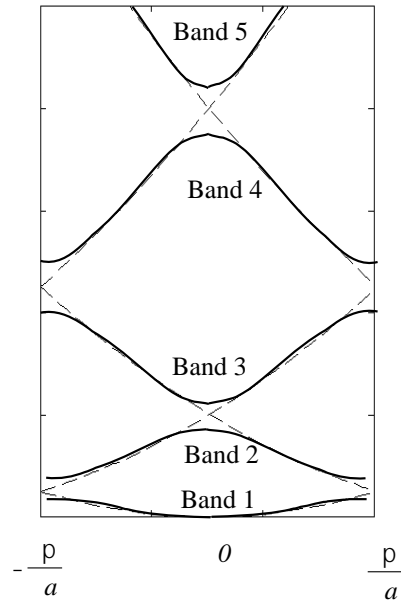$-\dfrac{p}{a}$ 0 $\dfrac{p}{a}$

Figure 11.13 The solid lines show the energy bands in the reduced zone. The free electron dispersion relations are shown as dashed lines.

The *ab initio* calculated electronic band structure using the density functional theory (DFT) depicted in Figure 11.14 shows the *indirect energy gap* and the *threefold degeneracy* of the valence band at the Fermi energy. It is seen that the approximate sum of the energy bands for a specific energy level in Figure 11.14 (a) corresponds to the density of states for the energy level in Figure 11.14 (b). From this approach, we can estimate the effective mass using Equation (11.14) that is the second derivative of energy with respect to wavevector. Also we obtain the band gap from the figure.
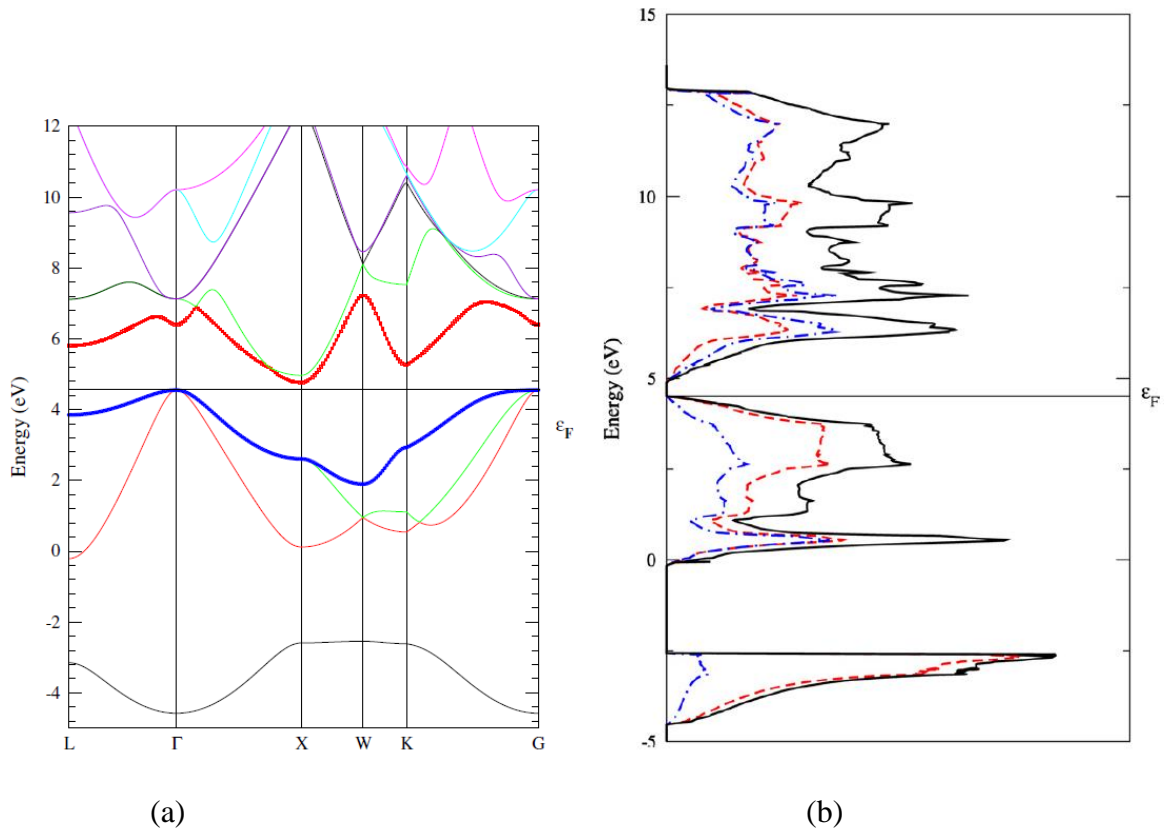
(a)   (b)

Figure 11.14 (a) Electronic band structure of Mg$_2$Si calculated with the density functional theory (DFT), and (b) total electron density of states (DOS) projected on magnesium and silicon atoms, the solid line for total DOS, the dashed line for silicon contribution, and the dot-dashed line for magnesium contribution. Boulet at al. (2011)

Problems

11.1 A copper crystal has an *fcc* lattice with one *Cu* atom per lattice point and a lattice constant of 3.61 Å. Every copper atom has one valence electron. Estimate the electron Fermi energy, Fermi velocity and electron wavelength in a copper crystal.

11.2 Derive Equation (11.33) by using Equation (11.30).

11.3 Germanium *Ge* is widely used semiconductor material, and it is often doped with *As* to form an n-type semiconductor. Determine the Fermi energy of an n-type semiconductor doped with *As* with an electron concentration of 10^{19} cm^{-3} at 300 K. Assume that every *As* atom contributes one free electron to the conduction band and neglect thermally excited electrons from the valence band. *Ge* has 4 identical conduction bands with an effective mass equal to 0.55*m*, where *m* is the free electron mass.

11.4 PbTe is widely used semiconductor material, and it is often doped with *Na* to form an n-type semiconductor. Determine the Fermi energy of an n-type semiconductor doped with Na with an electron concentration of 10^{18} cm^{-3} at 300 K, assuming that every *Na* atom contributes one free electron to the conduction band and neglecting thermally excited electrons from the valence band. *PbTe* has 4 identical conduction bands with an effective mass equal to 0.22*m*, where *m* is the free electron mass.

11.5 Describe the important concept of the band structures.

11.6 Describe briefly the important concept and results of the Kronig-Penney model.

References

1. Onsager, L., *Reciprocal Relations in Irreversible Processes. I.* Physical Review, 1931. **37**(4): p. 405-426.