CHAPTER 6

Electrons in a Crystal

In the preceding chapters we considered essentially only *one* electron, which was confined to the field of the atoms of a solid. This electron was in most cases an outer, i.e., a valence, electron. However, in a solid of one cubic centimeter at least 10^{22} valence electrons can be found. In this section we shall describe how these electrons are distributed among the available energy levels. It is impossible to calculate the exact place and the kinetic energy of each individual electron. We will see, however, that probability statements nevertheless give meaningful results.

6.1. Fermi Energy and Fermi Surface

The Fermi energy, E_F, is an important part of an electron band diagram. Many of the electronic properties of materials, such as optical, electrical, or magnetic properties, are related to the location of E_F within a band.

The Fermi energy is often defined as the "highest energy that the electrons assume at $T = 0$ K". This can be compared to a vessel, like a cup, (the electron band) into which a certain amount of water (electrons) is poured. The top surface of the water contained in this vessel can be compared to the Fermi energy. The more electrons are "poured" into the vessel, the higher the Fermi energy. The Fermi energies for aluminum and copper are shown in Figs. 5.21 and 5.22. Numerical values for the Fermi energies for some materials are given in Appendix 4. They range typically from 2 to 12 eV.

The above-stated definition, even though convenient, can occasionally be misleading, particularly when dealing with semiconductors. Therefore, a more accurate definition of the Fermi energy will be given in Section 6.2.

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We will see there that at the Fermi energy the Fermi function, F(E), equals $\frac{1}{2}$. An equation for the Fermi energy is given in (6.11).

In three-dimensional **k**-space the one-dimensional Fermi energy is replaced by a Fermi surface. The energy surface shown in Fig. 5.27 is the Fermi surface for copper.

6.2. Fermi Distribution Function

The distribution of the energies of a large number of particles and its change with temperature can be calculated by means of statistical considerations. The kinetic energy of an electron gas is governed by Fermi–Dirac statistics, which states that the probability that a certain energy level is occupied by electrons is given by the **Fermi function, F(*E*)**,

$$\mathrm{F}(E) = \frac{1}{\exp\left(\dfrac{E - E_{\mathrm{F}}}{k_{\mathrm{B}}T}\right) + 1}. \tag{6.1}$$

If an energy level E is completely occupied by electrons, the Fermi distribution function F(E) equals 1 (certainty); for an empty energy level one obtains $\mathrm{F}(E) = 0$. E_{F} is the Fermi energy which we introduced in Section 6.1, k_{B} is the Boltzmann constant, and T is the absolute temperature. In Fig. 6.1, the Fermi function is plotted versus the energy for $T \rightarrow 0$ by using (6.1). One sees from this figure that at $T = 0$ all levels that have an energy smaller than E_{F} are completely filled with electrons, whereas higher energy states are empty.

The Fermi distribution function for higher temperatures $(T \neq 0)$ is shown in Fig. 6.2. It is noticed there that F(E) varies around E_{F} in a gradual manner and not by a step as for $T = 0$. To characterize this behavior, one says that F(E) is "smeared out," i.e., it is extended to an energy interval $2\Delta E$. This

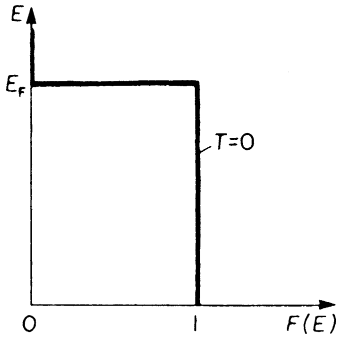

Figure 6.1. Fermi distribution function, F(E), versus energy, E, for $T = 0$. (For $E > E_F$ and $T \rightarrow 0$ (6.1) yields $F(E) \rightarrow 0$).

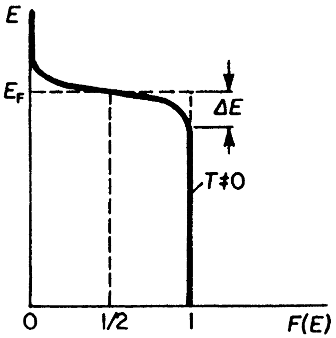

Figure 6.2. Fermi distribution function for $T \neq 0$.

decrease in F(E) with increasing energy is heavily exaggerated in Fig. 6.2. ΔE at room temperature is in reality only about 1% of E_F.

At high energies ($E \gg E_F$) the upper end of the Fermi distribution function can be approximated by the classical (Boltzmann) distribution function. This is best seen from (6.1) in which for large energies the exponential factor becomes significantly larger than 1. Then, F(E) is approximately

$$\mathrm{F}(E) \approx \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right]. \tag{6.1a}$$

Equation (6.1a) is known to be the Boltzmann factor, which gives, in classical thermodynamics, the probability that a given energy state is occupied. The F(E) curve for high energies is thus referred to as the "**Boltzmann tail**" of the Fermi distribution function.

Of particular interest is the value of the Fermi function F(E) at $E = E_F$ and $T \neq 0$. As can be seen from (6.1) and Fig. 6.2, F(E) is in this particular case $\frac{1}{2}$. This serves as a definition for the Fermi energy, as outlined in Section 6.1.

6.3. Density of States

We are now interested in the question of how energy levels are distributed over a band. We restrict our discussion for the moment to the lower part of the valence band (the 3s-band in aluminum, for example) because there the electrons can be considered to be essentially free due to their weak binding force to the nucleus. We assume that the free electrons (or the "electron gas") are confined in a square potential well (box) from which they cannot escape. The dimensions of this potential well are thought to be identical to the dimensions of the crystal under consideration. Then our problem is similar to the case of *one* electron in a potential well of size a, which we treated in Section 4.2. By using the appropriate boundary conditions, the solution of the Schrödinger equation yields an equation that has the same form as (4.18) or (4.26),

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right), \tag{6.2}$$

where n_x, n_y, and n_z are the principal quantum numbers and a is now the *length*, etc., of the crystal. Now we pick an arbitrary set of quantum numbers n_x, n_y, n_z. To each such set we can find a specific energy level E_n, frequently called "**energy state**". An energy state can therefore be represented by a point in quantum number space (Fig. 6.3). In this space, n is the radius from the origin of the coordinate system to a point (n_x, n_y, n_z) where

$$n^2 = n_x^2 + n_y^2 + n_z^2. \tag{6.3}$$

Equal values of the energy E_n lie on the surface of a sphere with radius n. All points within the sphere therefore represent quantum states with energies smaller than E_n. The number of quantum states, η, with an energy equal to or smaller than E_n is proportional to the volume of the sphere. Since the quantum numbers are positive integers, the n-values can only be defined in the positive octant of the n-space. One-eighth of the volume of the sphere with radius n therefore gives the number of energy states, η, the energy of which is equal to or smaller than E_n. Thus, with (6.2) and (6.3), we obtain

$$\eta = \frac{1}{8}\cdot\frac{4}{3}\pi n^3 = \frac{\pi}{6}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2} E^{3/2}. \tag{6.4}$$

Differentiation of η with respect to the energy E provides the **number of energy states per unit energy** in the energy interval dE, i.e., the density of the energy states, briefly called **density of states**, $Z(E)$:

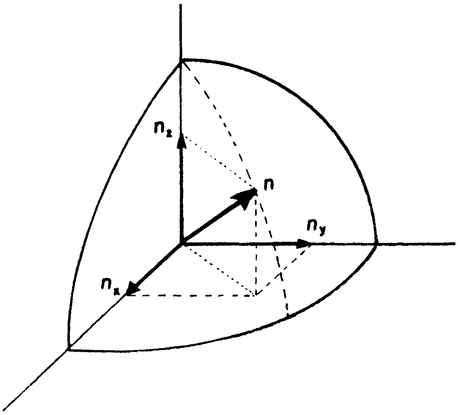

Figure 6.3. Representation of an energy state in quantum number space.

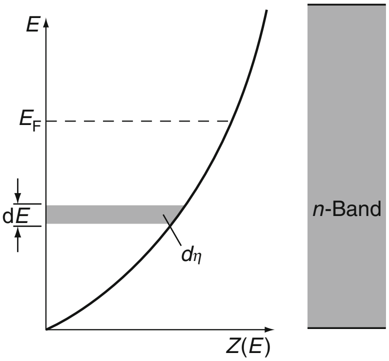

Figure 6.4. Density of states $Z(E)$ within a band. The electrons in this band are considered to be free. Note, that the density of states, as shown in this figure, is only parabolic for the three-dimensional case (solids). Z(E) looks different for the two-dimensional case (quantum well), one-dimensional case (quantum wire), or zero-dimensional case (quantum dot). See for example Fig. 8.33(c). However, since we are discussing here only solids, the representation as shown above is correct and sufficient.

$$\frac{d\eta}{dE} = Z(E) = \frac{\pi}{4}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2} E^{1/2} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \tag{6.5}$$

(a^3 is the volume, V, that the electrons can occupy).

The density of states plotted versus the energy gives, according to (6.5), a parabola. Figure 6.4 shows that at the lower end of the band considerably fewer energy levels (per unit energy) are available than at higher energies. One can compare the density of states concept with a high-rise apartment building in which the number of apartments per unit height (e.g., 8 ft) is counted. To stay within this analogy, only a very few apartments are thought to be available on the ground level. However, with increasing height of the building, the number of apartments per unit height becomes larger.

The area within the curve in Fig. 6.4 is, by definition, the number of states that have an energy equal to or smaller than E_n. Therefore, one obtains, for an area element $d\eta$,

$$d\eta = Z(E) \cdot dE, \tag{6.6}$$

as can be seen from (6.5) and Fig. 6.4.

6.4. Complete Density of States Function Within a Band

We have seen in Section 6.3 that for the free electron case the density of states has a parabolic E versus $Z(E)$ relationship. In actual crystals, however,

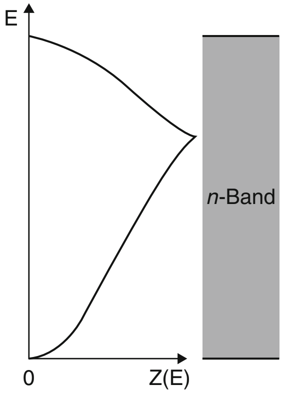

Figure 6.5. Schematic representation of the complete density of states function within a band.

the density of states is modified by the energy conditions within the first Brillouin zone. Let us consider, for example, the curves of equal energy depicted in Fig. 5.26. For low energies, the equal energy curves are circles. Thus, the electrons behave free-electron like for these low energies. The density of states curve is then, as before, a parabola. For larger energies, however, fewer energy states are available, as is seen in Fig. 5.26. Thus, $Z(E)$ decreases with increasing E, until eventually the corners of the Brillouin zones are filled. At this point $Z(E)$ has dropped to zero. The largest number of energy states is thus found near the center of a band, as shown schematically in Fig. 6.5.

6.5. Population Density

The number of electrons per unit energy, $N(E)$, within an energy interval dE can be calculated by multiplying the number of possible energy levels, $Z(E)$, by the probability for the occupation of these energy levels. We have to note, however, that because of the **Pauli principle**, each energy state can be occupied by one electron of positive spin and one of negative spin,[16] i.e., each energy state can be occupied by two electrons. Therefore,

$$N(E) = 2 \cdot Z(E) \cdot F(E) \tag{6.7}$$

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[16] See Appendix 3.

or, with (6.1) and (6.5),

$$N(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}. \tag{6.8}$$

$N(E)$ is called the (electron) **population density**. We see immediately that for $T \to 0$ and $E < E_F$, the function $N(E)$ equals $2 \cdot Z(E)$ because $F(E)$ is unity in this case. For $T \neq 0$ and $E \simeq E_F$, the Fermi distribution function (6.1) causes a smearing out of $N(E)$ (Fig. 6.6).

The area within the curve in Fig. 6.6 represents the number of electrons, N^*, that have an energy equal to or smaller than the energy E_n. For an energy interval between E and $E + dE$, one obtains

$$dN^* = N(E)dE. \tag{6.9}$$

We are now in a position to calculate the Fermi energy by making use of (6.8) and (6.9). We consider the simple case $T \to 0$ and $E < E_F$, which yields $F(E) = 1$. Integration from the lower end of the band to the Fermi energy, E_F, provides

$$N^* = \int_0^{E_F} N(E)dE = \int_0^{E_F} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\, dE = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}. \tag{6.10}$$

Rearranging (6.10) yields

$$E_F = \left(3\pi^2 \frac{N^*}{V}\right)^{2/3} \frac{\hbar^2}{2m}. \tag{6.11}$$

We define $N' = N^*/V$ as the **number of electrons per unit volume**. Then we obtain

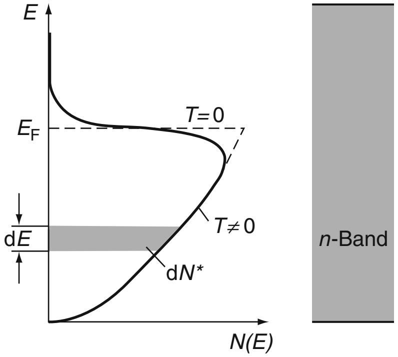

Figure 6.6. Population density $N(E)$ within a band for free electrons. dN^* is the number of electrons in the energy interval dE.

$$E_F = \left(3\pi^2 N'\right)^{2/3} \frac{\hbar^2}{2m}. \tag{6.11a}$$

It should be noted that N^* was calculated for simplicity for $T \to 0$ and $E < E_F$. This does not limit the applicability of (6.11), however, since the number of electrons does not change when the temperature is increased. In other words, integrating from zero to infinity and using $T \neq 0$ would yield essentially the same result as above.

6.6. Consequences of the Band Model

We mentioned in Section 6.4 that, because of the **Pauli principle**, each s-band of a crystal, consisting of N atoms, has space for $2N$ electrons, i.e., for two electrons per atom. If the highest filled s-band of a crystal is occupied by two electrons per atom, i.e., if the band is completely filled, we would expect that the electrons cannot drift through the crystal when an external electric field is applied (as it is similarly impossible to move a car in a completely occupied parking lot). An electron has to absorb energy in order to move. Keep in mind that for a completely occupied band higher energy states are not allowed. (We exclude the possibility of electron jumps into higher bands.) Solids in which the highest filled band is completely occupied by electrons are, therefore, **insulators** (Fig. 6.7(a)).

In solids with one valence electron per atom (e.g., **alkali metals**) the valence band is essentially half-filled. An electron drift upon application of an external field is possible; the crystal shows metallic behavior (Fig. 6.7(b)).

Bivalent metals should be insulators according to this consideration, which is not the case. The reason for this lies in the fact that the upper

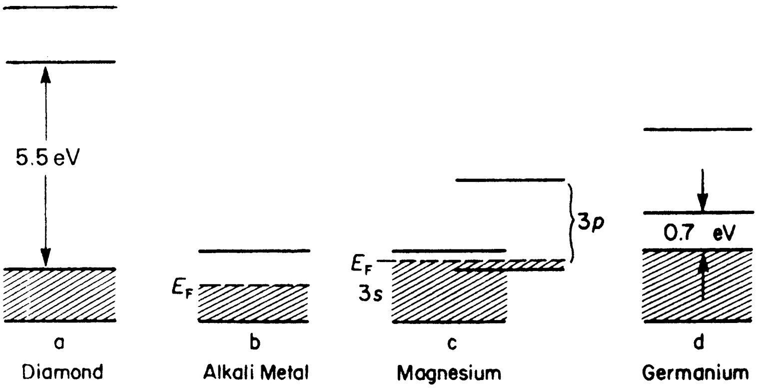

Figure 6.7. Simplified representation for energy bands for (a) insulators, (b) alkali metals, (c) bivalent metals, and (d) intrinsic semiconductors.

bands partially overlap, which occurs due to the weak binding forces of the valence electrons on their atomic nuclei (see Fig. 5.9). If such an overlapping of bands occurs, the valence electrons flow in the lower portion of the next higher band, because the electrons tend to assume the lowest potential energy (Fig. 6.7(c)). As a result, bivalent solids may also possess partially filled bands. Thus, they are also conductors.

We shall see in Chapter 8 that the valence as well as the conduction bands of **semiconductors** can accommodate $4N$ electrons. Because germanium and silicon possess four valence electrons, the valence band is completely filled with electrons. Intrinsic semiconductors have a relatively narrow forbidden energy zone (Fig. 6.7(d)). A sufficiently large energy can, therefore, excite electrons from the completely filled valence band into the empty conduction band and thus provide some electron conduction.

This preliminary and very qualitative discussion on electronic conduction will be expanded substantially and the understanding will be deepened in Part II of this book.

6.7. Effective Mass

We implied in the previous sections that the mass of an electron in a solid is the same as the mass of a free electron. Experimentally determined physical properties of solids, such as optical, thermal, or electrical properties, indicate, however, that for some solids the mass is larger while for others it is slightly smaller than the free electron mass. This experimentally determined electron mass is usually called the effective mass, m^*. The deviation of m^* from the free electron mass[17] m_0 can be easily appreciated by stating the ratio m^*/m_0, which has values slightly above or below 1 (see Appendix 4). The cause for the deviation of the effective mass from the free electron mass is usually attributed to interactions between the drifting electrons and the atoms in a crystal. For example, an electron which is accelerated in an electric field might be slowed down slightly because of "collisions" with some atoms. The ratio m^*/m_0 is then larger than 1. On the other hand, the electron wave in another crystal might have just the right phase in order that the response to an external electric field is enhanced. In this case, m^*/m_0 is smaller than 1.

We shall now attempt to find an expression for the effective mass. For this, we shall compare the acceleration of an electron in an electric field calculated by classical as well as by quantum mechanical means. At first, we write an expression for the velocity of an electron in an energy band.

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[17] We shall use the symbol m_0 only when we need to distinguish the free electron (rest) mass from the effective mass.

We introduced in Chapter 2 the group velocity, i.e., the velocity with which a wave packet moves. Let ω be the angular frequency and $|\mathbf{k}| = 2\pi/\lambda$ the wave number of the electron wave. Then, the group velocity is, according to (2.10),

$$v_g = \frac{d\omega}{dk} = \frac{d(2\pi\nu)}{dk} = \frac{d(2\pi E/h)}{dk} = \frac{1}{\hbar}\frac{dE}{dk}. \tag{6.12}$$

From this we calculate the acceleration

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}. \tag{6.13}$$

The relation between the energy E and the wave number $|\mathbf{k}|$ is known from the preceding sections. We now want to determine the factor dk/dt. Forming the first derivative of (4.7) $(p = \hbar k)$ with respect to time yields

$$\frac{dp}{dt} = \hbar\frac{dk}{dt}. \tag{6.14}$$

Combining (6.14) with (6.13) yields

$$a = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\frac{dp}{dt} = \frac{1}{\hbar^2}\cdot\frac{d^2E}{dk^2}\cdot\frac{d(mv)}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F, \tag{6.15}$$

where F is the force on the electron. The classical acceleration can be calculated from Newton's law (1.1)

$$a = \frac{F}{m}. \tag{6.16}$$

Comparing (6.15) with (6.16) yields the effective mass

$$m^* = \hbar^2\left(\frac{d^2E}{dk^2}\right)^{-1}. \tag{6.17}$$

We see from (6.17) that the effective mass is inversely proportional to the curvature of an electron band. Specifically, if the curvature of $E = f(k)$ at a given point in **k**-space is large, then the effective mass is small (and vice versa). When inspecting band structures (Fig. 5.4 or Figs. 5.21–5.24) we notice some regions of high curvature. These regions might be found, particularly, near the center or near the boundary of a Brillouin zone. At these places, the effective mass is substantially reduced and may be as low as 1% of the free electron mass m_0. At points in **k**-space for which more than one electron band is found (Γ-point in Fig. 5.23, for example) more than one effective mass needs to be defined.

We shall demonstrate the **k**-dependence of the effective mass for a simple case and defer discussions about actual cases to Section 8.4. In Fig. 6.8(a) an

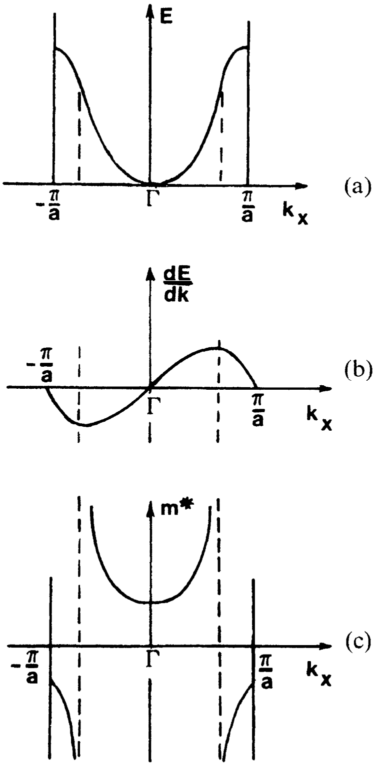

Figure 6.8. (a) Simple band structure, as shown in Fig. 5.4. (b) First derivative and (c) inverse function of the second derivative of the curve shown in (a).

ideal electron band within the first Brillouin zone is depicted. From this curve, both the first derivative and the reciprocal function of the second derivative, i.e., m^*, have been calculated. These functions are shown in Fig. 6.8(b) and (c). We notice in Fig. 6.8(c) that the effective mass of the electrons is small and positive near the center of the Brillouin zone and eventually increases for larger values of k_x. We likewise observe in Fig. 6.8(c) that electrons in the upper part of the given band have a negative effective mass. A negative mass means that the "particle" under consideration travels in the opposite direction to an applied electric force (and opposite to an electron.) An electron with a negative effective mass is called a "defect electron" or an "**electron hole**". (It is, however, common to ascribe to the hole a *positive effective mass and a positive charge* instead of a negative mass and a negative charge.) Electron holes play an important role in crystals whose valence bands are almost filled, e.g., in semiconductors. Solids which possess different properties in various directions (anisotropy) have a different m^* in each direction. The effective mass is a tensor in this case. An electron/hole pair is called an "**exciton**".

It should be noted here for clarification that an electron hole is not identical with a **positron**. The latter is a subatomic particle like the electron, however with a positive charge. Positrons are emitted in the β-decay or are found in cosmic radiation. When positrons and electrons react with each other they are both annihilated under emission of energy.

6.8. Conclusion

The first part of this book is intended to provide the reader with the necessary tools for a better understanding of the electronic properties of materials. We started our discussion by solving the Schrödinger equation for the free electron case, the bound electron case, and for electrons in a crystal. We learned that the distinct energy levels which are characteristic for isolated atoms widen into energy bands when the atoms are moved closer together and eventually form a solid. We also learned that the electron bands have "fine structure," i.e., they consist of individual "branches" in an energy versus momentum (actually **k**) diagram. We further learned that some of these energy bands are filled by electrons, and that the degree of this filling depends upon whether we consider a metal, a semiconductor, or an insulator. Finally, the degree to which electron energy levels are available within a band was found to be nonuniform. We discovered that the density of states is largest near the center of an electron band. All these relatively unfamiliar concepts will become more transparent to the reader when we apply them in the chapters to come.

Problems

1. What velocity has an electron near the Fermi surface of silver? ($E_F = 5.5$ eV).
2. Are there more electrons on the bottom or in the middle of the valence band of a metal? Explain.
3. At what temperature can we expect a 10% probability that electrons in silver have an energy which is 1% above the Fermi energy? ($E_F = 5.5$ eV).
4. Calculate the Fermi energy for silver assuming 6.1×10^{22} free electrons per cubic centimeter. (Assume the effective mass equals the free electron mass.)
5. Calculate the density of states of 1 m^3 of copper at the Fermi level ($m^* = m_0$, $E_F =$ 7 eV). *Note*: Take 1 eV as energy interval. (Why?)
6. The density of states at the Fermi level (7 eV) was calculated for 1 cm^3 of a certain metal to be about 10^{21} energy states per electron volt. Someone is asked to calculate the number of electrons for this metal using the Fermi energy as the maximum kinetic energy which the electrons have. He argues that because of the Pauli principle, each

energy state is occupied by two electrons. Consequently, there are 2×10^{21} electrons in that band.

(a) What is wrong with that argument?
(b) Why is the answer, after all, not too far from the correct numerical value?

7. Assuming the electrons to be free, calculate the total number of states below $E = 5$ eV in a volume of 10^{-5} m^3.

8. (a) Calculate the number of free electrons per cubic centimeter in copper, assuming that the maximum energy of these electrons equals the Fermi energy ($m^* = m_0$).
   (b) How does this result compare with that determined directly from the density and the atomic mass of copper? Hint: Consider equation (7.5)
   (c) How can we correct for the discrepancy?
   (d) Does using the effective mass decrease the discrepancy?

9. What fraction of the 3*s*-electrons of sodium is found within an energy k_BT below the Fermi level? (Take room temperature, i.e., $T = 300$ K.)

10. Calculate the Fermi distribution function for a metal at the Fermi level for $T \neq 0$.

11. Explain why, in a simple model, a bivalent material could be considered to be an insulator. Also explain why this simple argument is not true.

12. We stated in the text that the Fermi distribution function can be approximated by classical Boltzmann statistics if the exponential factor in the Fermi distribution function is significantly larger than one.
   (a) Calculate $E - E_F = nk_BT$ for various values of n and state at which value for n,

$$\exp\left(\frac{E - E_F}{k_BT}\right)$$

   can be considered to be "significantly larger" than 1 (assume $T = 300$ K). (*Hint*: Calculate the error in $F(E)$ for neglecting "1" in the denominator.)
   (b) For what *energy* can we use Boltzmann statistics? (Assume $E_F = 5$ eV and $E - E_F = 4k_BT$.)

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