Free Electrons in Crystals

10.1 INTRODUCTION

In the first five chapters while dealing with the structural aspect we ignored the effects arising due to electrons in the crystals. We assumed that the electrons surrounding the nucleus of an atom are tightly bound. This is valid for insulators, but not for semiconductors and metals. In order to understand the properties of semiconductors and particularly of metals, it is essential to take into account the behaviour of electrons in them. In this chapter, we shall concentrate mainly on the nature of existence and the role of electrons in deciding the properties of metals.

The outstanding properties of metals are their high electrical and thermal conductivities. Thus, soon after the discovery of electron, a number of investigators, particularly Drude and Lorentz attempted to explain these properties on the basis of free electron model. For the purpose, they made certain basic assumptions, which are as follows:

1. That a metal crystal consists of positive metal ions whose valence electrons are free to move between the ions as if they constitute an electron gas.
2. The crystal is then held together by electrostatic forces of attraction between the positively charged ions and the negatively charged electron gas.
3. The mutual repulsion between the electrons is ignored.
4. The potential field due to positive ions is completely uniform, so that electrons can move from place to place in the crystal without any change in their energy.
5. They collide occasionally with the atoms, and at any given temperature, their velocities could be determined according to Maxwell-Boltzmann distribution law.

The free electron model was successful in explaining the properties such as electrical and thermal conductivities, thermionic emission, thermoelectric and galvanomagnetic effects, etc. However, this model failed to explain the properties of solids which are determined by their internal structure. It was unable to explain even the observed facts that why some solids are conductors and some insulators.

The first success was achieved in 1927 when Pauli applied quantum statistics to explain the weak paramagnetism of alkali metals. The very next year Sommerfeld published a modified free electron theory by replacing classical statistics of Maxwell-Boltzmann by Fermi-Dirac statistics. The Sommerfeld free electron theory of metals could be better described as the statistical thermodynamical behaviour of a gas obeying Fermi-Dirac statistics.

10.2 ELECTRONS MOVING IN A ONE-DIMENSIONAL POTENTIAL WELL

Before we proceed further to discuss the modified free electron theory proposed by Sommerfeld and how it conforms with the quantum mechanical model of electrons, let us first determine the restrictions imposed by the laws of quantum mechanics on the energies of an electron inside a crystal. For the sake of mathematical simplicity, let us consider the case when an electron is limited to remain within a one-dimensional crystal of length a. Also, assume that the potential energy everywhere within this crystal is constant and equal to zero. However, at the two ends of the crystal the electron is prevented from leaving the crystal by a very high potential energy barrier ($V_0 \rightarrow \infty$) as shown in Fig. 10.1, i..e
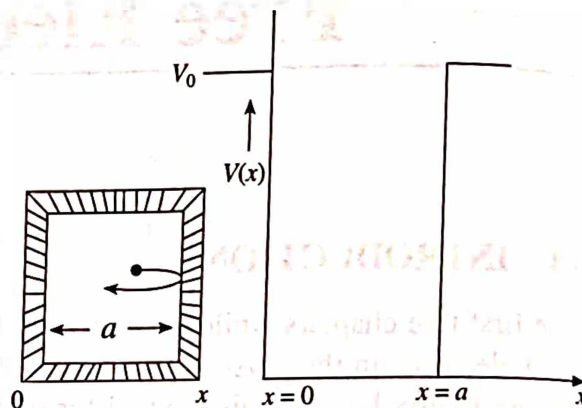
$$V(x) = \begin{cases} V_0 & \text{for } x \leq 0 \text{ and } x \geq a \\ 0 & \text{for } 0 < x < a \end{cases} \quad (1)$$

Fig. 10.1   A one dimensional potential box

Therefore, inside the crystal, the Schrodinger wave equation becomes

$$\frac{d^2 \psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi(x) = 0 \quad (2)$$

Any periodic function will satisfy this equation, and for the sake of simplicity let us suppose that the general solution of eq. 2 is of the type

$$\psi(x) = A \sin kx + B \cos kx \quad (3)$$

where A and B are arbitrary constants to be determined by applying boundary conditions. Since the electron is bound inside the crystal of length a, the electron wave function has to satisfy the following boundary conditions simultaneously, i.e.

(i) $\psi = 0$ at $x = 0$. This gives us $B = 0$ and hence $\psi = A \sin kx$.

(ii) $\psi = 0$ at $x = a$. This gives us $A \sin (ka) = 0$. Since A is not zero, therefore $\sin (ka) = 0$. Consequently,

$$k = \frac{n\pi}{a} \quad (4)$$

where $n = 1, 2, 3 \ldots$ represents the order of the state, $n = 0$ is not allowed because this will mean $k = 0$ and hence $\psi = 0$ everywhere in the box. Therefore, the solution to the Schrodinger wave eq. 2 in the region $0 < x < a$ becomes

$$\psi_n = A \sin \frac{n\pi x}{a} \quad (5)$$

For each value of "n" there is a corresponding quantum state ψ_n whose energy E_n can be obtained from eqs. 2 and 5 as

$$E_n = \frac{h^2 k^2}{8\pi^2 m} = \frac{h^2 n^2}{8 m a^2} \tag{6}$$

Equation 6 shows that:

(i) The bound electrons can have only discrete energy values corresponding to $n = 1, 2, 3,$ ... and not any arbitrary value of energy.

(ii) The lowest energy of the particle is obtained from this equation by putting $n = 1$. It is given by

$$E_1 = \frac{h^2}{8 m a^2}$$

$\Rightarrow \qquad\qquad E_n = n^2 E_1$

(iii) The spacing between the two consecutive levels increases as

$$(n + 1)^2 E_1 - n^2 E_1 = (2n + 1) E_1$$

Fig. 10.2 shows the energy level diagram for the particle. The value of the constant A could be determined by normalizing the wave function, according to which the total probability that the particle is somewhere in the box must be unity, i.e.
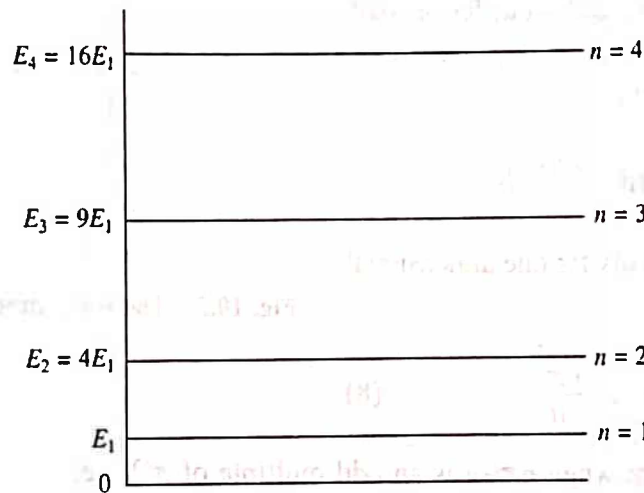
$E_4 = 16E_1$ ———————————————— $n = 4$

$E_3 = 9E_1$ ———————————————— $n = 3$

$E_2 = 4E_1$ ———————————————— $n = 2$

E_1 ———————————————— $n = 1$

0

Fig. 10.2 Schematic representation of energy levels

$$\int_0^a P(x)\,dx = \int_0^a |\psi_n|^2\,dx = 1$$

or

$$\int_0^a A^2 \sin^2 \frac{n\pi x}{a}\,dx = 1$$

or

$$A^2 \int_0^a \frac{1}{2}\left(1 - \cos \frac{2n\pi x}{a}\right) dx = 1$$

or
$$\frac{A^2}{2}\left[x - \frac{a}{2\pi n}\sin\frac{2n\pi x}{a}\right]_0^a = 1$$

Since the second term of the integrated expression becomes zero for both $x = 0$ and $x = a$, therefore this gives us

$$\frac{A^2 a}{2} = 1 \quad \text{or} \quad A = \left(\frac{2}{a}\right)^{1/2}$$

Thus the normalized wave function is

$$\psi_n = \left(\frac{2}{a}\right)^{1/2}\sin\frac{n\pi x}{a}$$

It can be shown that the wave function ψ_1 has two nodes at $x = 0$ and $x = a$, ψ_2 has three nodes at $x = 0$, $x = a/2$ and $x = a$ and ψ_3 has four nodes at $x = 0$, $x = a/3$, $x = 2a/3$ and $x = a$. Consequently, the wave function ψ_n will have $(n + 1)$ nodes. The wave function for the first three values of n are shown in Fig. 10.3.

To determine the probability distribution of particles within the potential well, let us start with the expression $P(x)\,dx = |\psi_n|^2\,dx$ over a small distance dx at x, i.e.

$$P(x)\,dx = \frac{2}{a}\sin^2\frac{n\pi x}{a}\,dx$$

Thus the probability density for one dimensional system is

Fig. 10.3   The wave function for $n = 1, 2,$ and 3

$$P(x) = \frac{2}{a}\sin^2\frac{n\pi x}{a} \qquad (8)$$

where $P(x)$ is maximum when $n\pi x/a$ is an odd multiple of $\pi/2$, i.e.

$$\frac{n\pi x}{a} = \frac{(2n - 1)\pi}{2}$$

or
$$\frac{n\pi x}{a} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$$

or
$$x = \frac{a}{2n}, \frac{3a}{2n}, \frac{5a}{2n}$$

Thus, the most probable positions corresponding to different quantum states of the particle can be obtained as
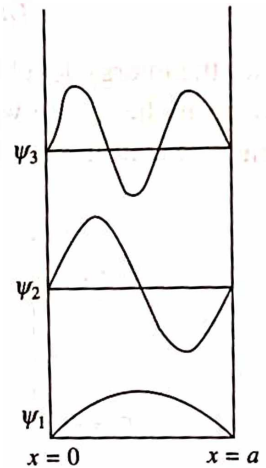
For $n = 1$, $\qquad\qquad\qquad x = \dfrac{a}{2}$

For $n = 2$,
$$x = \frac{a}{4}, \frac{3a}{4}$$

For $n = 3$,
$$x = \frac{a}{6}, \frac{3a}{6} = \frac{a}{2} \text{ and } \frac{5a}{6}$$

The probability density for the first three values of n are shown in Fig. 10.4. According to the classical mechanics, the probability for finding the particle within a small distance dx anywhere in the box is the same and is equal to dx/a. The probability density is simply $1/a$ throughout the box, which is contrary to the quantum mechanical result. Similarly, according to the classical prediction, there is a continuous range of possible energies. This is contrary to the quantum mechanical result, according to which the energy is quantized and so, it cannot vary continuously. Consequently, the quantum mechanical energy levels are discrete. However, if the particle becomes heavier and the length of the crystal is large (the electrons will be free within this length), the energy levels will be spaced very closely together and eventually may become continuous. For example, if $a = 1$ cm, then

Fig. 10.4 The probability density for $n = 1, 2$, and 3

$$E_n - E_{n\pm1} \sim 3.5 \times 10^{-19} \text{ eV}$$

The energy spectrum for such cases seems practically continuous. Thus the wave equation predicts that the bound particles (electrons) are associated with a discrete energy spectrum and free particles with a continuous spectrum.
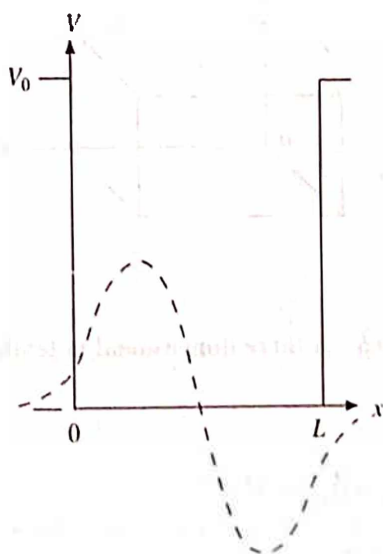

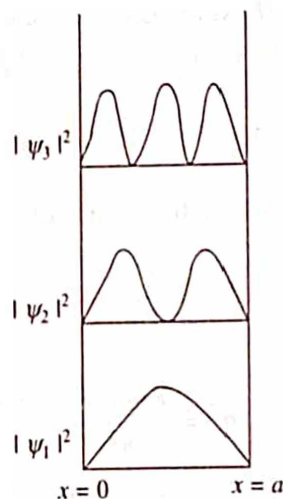Fig. 10.5 The wave function for $n = 2$ when the potential barrier is not infinite

In the interior of a real crystal the potential barriers for confining electrons are not infinitely high and are determined in a complex way by the surface energies of the crystal. If the potential barrier at the surface of a crystal is high but not infinite, the wave function for $n = 2$ will have the form as shown in Fig. 10.5. Note that the wave function is sinusoidal in the region $0 \le x \le a$ and exponential outside this region. It is expected that the extention of the wave function beyond the potential barrier is inversely proportional to the height of the barrier. Further, if the barrier is narrow, it is possible that the wave function can extend beyond it. In this case, there is a little but finite probability ($\sim |\psi|^2$) of finding the electrons on the other side of the barrier. The ability of electrons to penetrate

a potential barrier is called the "tunneling effect" and is a direct consequence of quantum mechanics to this problem.

Example: If a dust particle of one μgm requires 100 s to cross a distance of 1 mm which is the separation between two rigid walls of the potential, determine the quantum number described by this motion.

Solution: Given: Separation between the walls, $d = 1$ mm $= 10^{-3}$ m, the mass of the dust particle, $m = 1$ μgm $= 10^{-9}$ kg, $t = 100$ s, the quantum number, $n = ?$

Since in 100 s, the dust particle moves 10^{-3} m. So that in 1s, it will move 10^{-5} m. This is the velocity of the particle. The energy of the dust particle is then given by

$$E = \frac{1}{2} mv^2 = \frac{1}{2} \times 10^{-9} \times (10^{-5})^2 = 5 \times 10^{-20} \text{ J}$$

We also know that for a one-dimensional potential the energy eigen value is given by

$$E_n = \frac{h^2 n^2}{8 ma^2}$$

or

$$n^2 = \frac{8 ma^2 E}{h^2} = \frac{8 \times 10^{-9} \times (10^{-3})^2 \times 5 \times 10^{-20}}{(6.626 \times 10^{-34})^2} = 9.11 \times 10^{32}$$

or

$$n = 3 \times 10^{16}$$

10.3 THREE DIMENSIONAL POTENTIAL WELL

For simplicity, let us now consider a situation when the electrons are moving inside a three dimensional potential box of side "a" as shown in Fig. 10.6. Like one dimensional case, the potential energy inside the cube is taken as zero and very high (tending to infinity) outside it. Under this assumption, the Schrodinger wave equation becomes

$$\frac{d^2\psi(x,y,z)}{dx^2} + \frac{d^2\psi(x,y,z)}{dy^2} + \frac{d^2\psi(x,y,z)}{dz^2}$$

$$+ \frac{8\pi^2 m}{h^2} E\psi(x,y,z) = 0 \qquad (9)$$

Fig. 10.6 A three dimensional potential box

for which straightforward solution of the standing wave type may be assumed, i.e.

$$\psi(x, y, z) = A_x \sin(k_x x)\, A_y \sin(k_y y)\, A_z \sin(k_z z) \qquad (10)$$

where

$$k_x = \frac{n_x \pi}{a}, k_y = \frac{n_y \pi}{a}, k_z = \frac{n_z \pi}{a}.$$

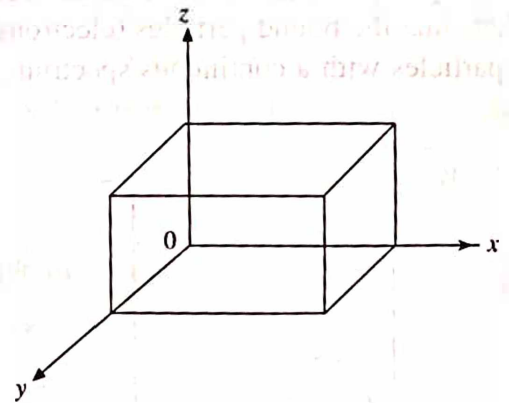Like one dimensional case, the value of the constants A_x, A_y and A_z can be determined by

applying the suitable boundary conditions, i.e. $\psi = 0$ at $x = 0$ and $x = a$, $y = 0$ and $y = a$ and $z = 0$ and $z = a$, we have

$$A_x = \left(\frac{2}{a}\right)^{1/2}, A_y = \left(\frac{2}{a}\right)^{1/2} \text{ and } A_z = \left(\frac{2}{a}\right)^{1/2}$$

Therefore, the normalized wave function for a cubical box becomes

$$\psi_n = \left(\frac{2}{a}\right)^{3/2} \sin\frac{n_x\pi x}{a}\cdot\sin\frac{n_y\pi y}{a}\cdot\sin\frac{n_z\pi z}{a} \tag{11}$$

The corresponding form of energy is given by

$$E_n = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{12}$$

or

$$E_n = \frac{h^2 n^2}{8ma^2}, \text{ where } n^2 = n_x^2 + n_y^2 + n_z^2 \tag{13}$$

Thus, in three-dimensions, we have three quantum numbers n_x, n_y and n_z which can take only positive integer values.

Example: Find the lowest energy of an electron confined to move in a three dimensional potential box of length 0.5 Å

Solution: Given: $a = 0.5\text{Å} = 0.5 \times 10^{-10}$ m, E (lowest) = ?
The possible energies of a particle in a cubical box of side a are given by

$$E_n = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

For lowest energy $n_x = n_y = n_z = 1$. Therefore

$$E_{111} = \frac{3h^2}{8ma^2} = \frac{3 \times (6.626 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.5 \times 10^{-10})^2}$$

$$= 7.24 \times 10^{-17} \text{ J} = \frac{7.24 \times 10^{-17}}{1.6 \times 10^{-19}} = 452 \text{ eV}$$

Example: Calculate the energy of an electron in the energy state immediately above the lowest energy level in a cubic box of side 1Å. Also find the temperature at which the average energy of the molecules of a perfect gas would be equal to the energy of the electron in the upper level.

Solution: Given: $a = 1$ Å $= 1 \times 10^{-10}$ m, E (next to the lowest) = ? T = ?

$$E \text{ (next to the lowest)} = 3/2 \ (k/T),$$

The lowest energy level is E_{111} and the next to the lowest level is E_{112}. Therefore,

$$E_{112} = \frac{6h^2}{8ma^2} = \frac{6 \times (6.26 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1.0 \times 10^{-10})^2}$$

$$= 3.62 \times 10^{-17} \text{ J} = \frac{3.62 \times 10^{-17}}{1.6 \times 10^{-19}} = 226 \text{ eV}$$

Further, according to the question

$$\frac{3}{2} kT = 226 \text{ eV} = 3.62 \times 10^{-17} \text{ J}$$

or

$$T = \frac{2 \times 3.62 \times 10^{-17}}{3 \times 1.38 \times 10^{-23}} = 1.75 \times 10^6 \text{ K}$$

10.4 QUANTUM STATE AND DEGENERACY

The most important consequence of the three quantum numbers appearing in eq. 12 is that several combinations can yield the same value of energy. Each combination of the quantum numbers is called a quantum state and several states having the same energy are said to be degenerate. To make this more clear, let us take an example and suppose that one of the quantum numbers is equal to 2 and the others as unity. This gives three possible combinations of quantum numbers which are as follows:

(i) $n_x = 1, n_y = 1, n_z = 2$
(ii) $n_x = 1, n_y = 2, n_z = 1$
(iii) $n_x = 2, n_y = 1, n_z = 1$

Substituting these values in eq. 11, the corresponding wave functions become

$$\psi_{112} = \left(\frac{2}{a}\right)^{3/2} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{2\pi z}{a}$$

$$\psi_{121} = \left(\frac{2}{a}\right)^{3/2} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi z}{a}$$

and

$$\psi_{211} = \left(\frac{2}{a}\right)^{3/2} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a}$$

From eq. 12, the corresponding energies are found to be

$$E_{112} = E_{121} = E_{211} = \frac{6h^2}{8ma^2} \tag{14}$$

In the above example, since three wave functions are associated with the same energy, the corresponding energy level is said to be three-fold degenerate. On the basis of this model, the level in which all the quantum numbers have the same value (e.g. $n_x = n_y = n_z = 1$ or 2, etc.) would be non-degenerate. Fig. 10.7 shows the energy level diagram for a particle in a three dimensional cubic box for the ground state and some excited states, together with the degree of degeneracy and quantum numbers.

It can be shown that the degeneracy breaks when a small modification is introduced to the system. For the purpose, let us consider the above discussed triply degenerate level which has
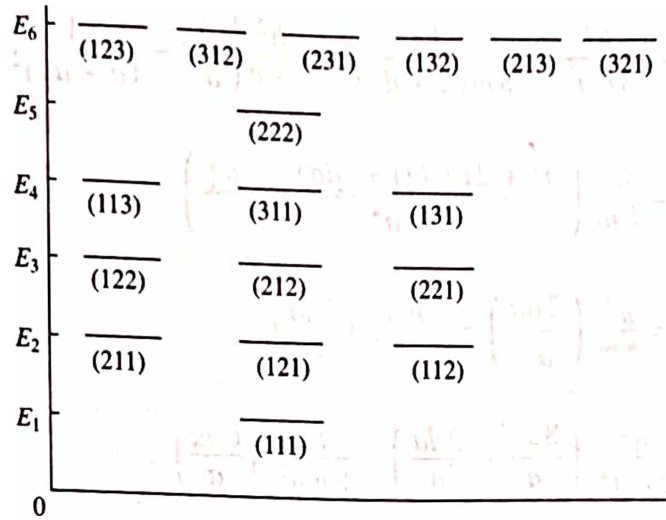
Fig. 10.7   Six lowest energy levels for an electron in a three dimensional potential box

three independent energy states with quantum numbers (2, 1, 1), (1, 2, 1) and (1, 1, 2). The energy associated with the x-direction of the state having quantum number (2, 1, 1) is given by

$$\frac{4h^2}{8ma^2}$$

On the other hand, the energy associated with the x-direction of each of the other two states is given by

$$\frac{h^2}{8ma^2}$$

Now, let the length of the cubical box be increased by a small amount da, along the x-axis while keeping the other dimensions unchanged. The corresponding change in the energy of the first state (2, 1, 1) is

$$\frac{4h^2}{8m(a+da)^2}$$

Hence, the decrease in the energy is, say

$$E_2 = \frac{4h^2}{8ma^2} - \frac{4h^2}{8m(a+da)^2} = \frac{4h^2}{8m}\left(\frac{1}{a^2} - \frac{1}{(a+da)^2}\right)$$

$$= \frac{4h^2}{8m}\left(\frac{a^2 + 2a(da) + (da)^2 - a^2}{a^4}\right)$$

$$= \frac{4h^2}{8m}\left(\frac{2\,da}{a^3}\right) = \frac{h^2}{8ma^2}\left(\frac{8da}{a}\right) \tag{15}$$

But for the remaining two states (1, 2, 1) and (1, 1, 2), the energy decrease is given by

$$E_1 = \frac{h^2}{8ma^2} - \frac{h^2}{8m(a+da)^2} = \frac{h^2}{8m}\left(\frac{1}{a^2} - \frac{1}{(a+da)^2}\right)$$

$$= \frac{h^2}{8m}\left(\frac{a^2 + 2a(da) + (da)^2 - a^2}{a^4}\right)$$

$$= \frac{h^2}{8m}\left(\frac{2\,da}{a^3}\right) = \frac{h^2}{8ma^2}\left(\frac{2da}{a}\right) \tag{16}$$

Thus, $\Delta E = E_2 - E_1 = \dfrac{h^2}{8ma^2}\left(\dfrac{8da}{a} - \dfrac{2da}{a}\right) = \dfrac{h^2}{8ma^2}\left(\dfrac{6da}{a}\right)$

This breakdown in the degeneracy is shown in Fig. 10.8. This aspect is relevant in explaining the fact such as the splitting of spectral lines in a magnetic or electric field. Under the action of the field, the degenerate level breaks up into separate levels.
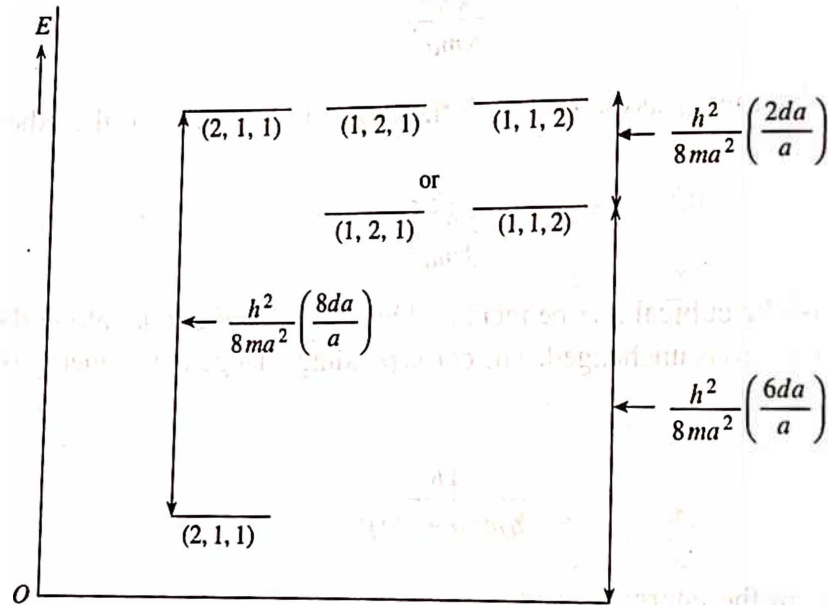

Fig. 10.8 The breakdown in degeneracy

Example: Determine the degree of degeneracy of the energy level $38h^2/8ma^2$ of a particle in a cubical box of side a.

Solution: Given: $(n_x^2 + n_y^2 + n_z^2) = 38$. By trial and error method, we can find that there exist two sets of values. They are:

$$n_x = 1, n_y = 1, n_z = 6$$

and

$$n_x = 2, n_y = 3, n_z = 5$$

Again, by simple manipulations, it is easy to determine the different members of the degenerate levels. They are:

116, 161, 611 three-fold degenerate

532, 325, 253, 352, 523, 235 six-fold degenerate

Thus, the given energy level is nine-fold degenerate.

10.5 THE DENSITY OF STATES

In ordre to determine the actual number of electrons in a given energy state, it is necessary to know the number of states in the system which have the energy under consideration multiplied by the probability distribution function. Therefore, if $g(E)dE$ is the number of available quantum states in the energy range E and $E + dE$ and $F(E)$ is the probability function of the electrons occupying a particular energy state E, then the actual number of electrons $N(E)dE$ present in the so called free state in the above energy range at any temperature is given by

$$N(E)dE = F(E)\ g(E)dE \tag{17}$$

Now, in order to calculate the density of states of electrons in the energy range E and $E + dE$, let us draw two spheres having radii n and $n + dn$ in the n-space as shown in Fig. 10.9. Any point (n_x, n_y, n_z) with integer values of coordinates represents an energy state. Thus, all the points on the surface of the sphere of radius n (where $n^2 = n_x^2 + n_y^2 + n_z^2$) will have the same energy. Since, n_x, n_y, n_z can have positive integral non-zero values; therefore the number of states of energy less than E will be given by the positive octant of the sphere, i.e.
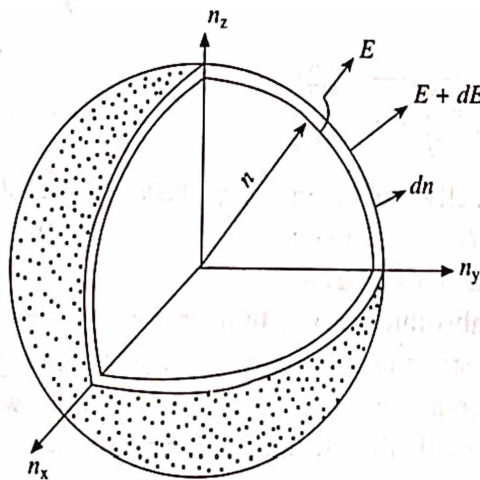

Fig. 10.9 Spheres representing density of states in n-space

$$g(E) = \frac{1}{8} \cdot \frac{4\pi n^3}{3} \tag{18}$$

Substituting the value of n from eq. 13, eq. 18 becomes

$$g(E) = \frac{1}{8} \cdot \frac{4\pi}{3} \left(\frac{8ma^2E}{h^2} \right)^{3/2} = \frac{4\pi V}{3h^3}(2m)^{3/2} E^{3/2} \tag{19}$$

where $V = a^3$. Now, differentiating both sides of the eq. 19 with respect to E, we obtain the density of states in the energy interval dE as

$$g(E)\, dE = \frac{2\pi V}{h^3}(2m)^{3/2} E^{1/2}\, dE$$

Since, the Pauli's exclusion principle allows two electrons in each state, so that the actual density of states in a volume V is given by

$$g(E)\, dE = \frac{4\pi V}{h^3}(2m)^{3/2} E^{1/2}\, dE \qquad (20)$$

Hence, the density of states per unit volume in an energy interval dE is given by

$$g'(E)\, dE = \frac{4\pi}{h^3}(2m)^{3/2} E^{1/2}\, dE \qquad (21)$$

The eq. 21 is diagramatically illustrated in Fig. 10.10. Now substituting the value of density of states and the probability distribution function (which is nothing but the Fermi-Dirac distribution function) in eq. 17, the density of states within the energy interval dE is given by

$$N(E)\, dE = F(E)\, g(E)\, dE$$

$$= \frac{4\pi V}{h^3}(2m)^{3/2} E^{1/2} \frac{dE}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} \qquad (22)$$
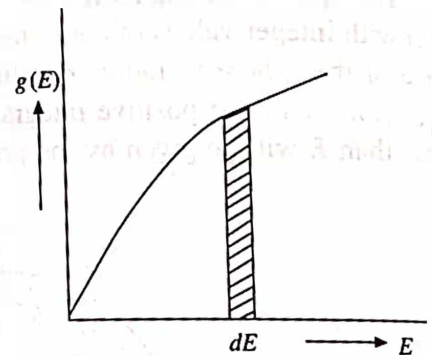

Fig. 10.10 Density of states as a function of electron energy

This distribution is diagramatically shown in Fig. 10.11. The calculation of $N(E)$ is illustrated in Fig. 10.12 which shows that the free electrons do not have zero energy at an absolute zero of temperature as one would have expected if the electrons were to obey classical statistics. Actually, the electron energy vary from zero to E_F and also the number of electrons increases with the increase of energy which becomes maximum at E_F. Since at absolute zero, $F(E) = 1$, therefore the total number of electrons is

$$\int N(E)\, dE = \frac{4\pi V}{h^3}(2m)^{3/2} \int_0^{E_F} E^{1/2}\, dE$$

or

$$N = \frac{2}{3} \times \frac{4\pi V}{h^3}(2m)^{3/2} E_F^{3/2} \qquad (23)$$

The number of electrons n per unit volume (called the density of electrons) is

$$n = \frac{N}{V} = \frac{8\pi}{3h^3}(2m)^{3/2} E_F^{3/2} \qquad (24)$$

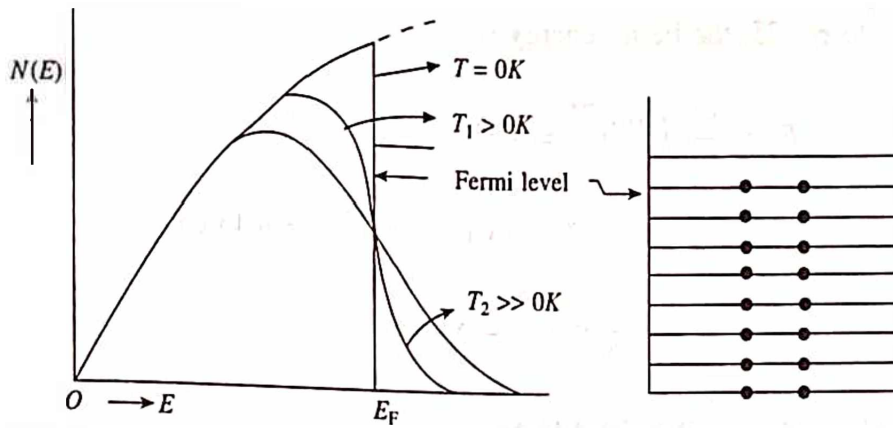Hence, the Fermi energy at absolute zero is given by

Fig. 10.11 Density of states as a function of electron energy at different temperature
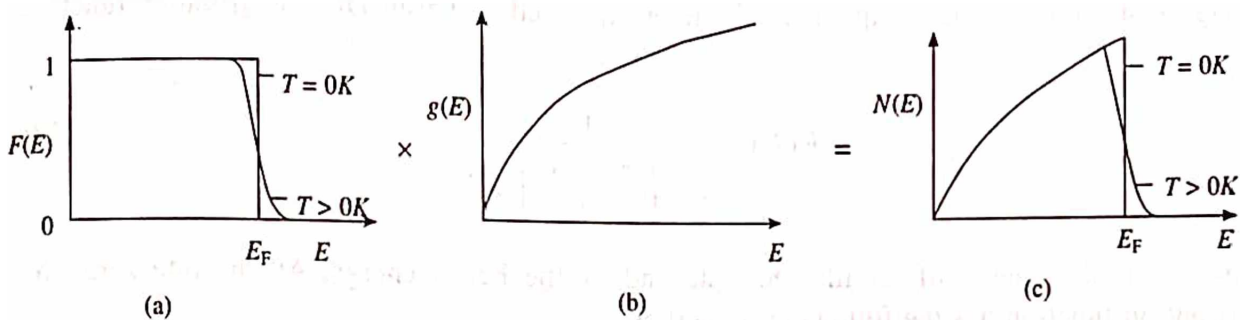

(a)   (b)   (c)

Fig. 10.12 The calculation of the density of occupied electron states $N(E)$ (a) Fermi-Dirac function, (b) Density of states, and (c) $N(E) = F(E) \times g(E)$

$$E_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} = 3.65 \times 10^{-19}\, n^{2/3}\ eV \tag{25}$$

Further, at absolute zero, the average energy of an electron is given by

$$\bar{E} = \frac{1}{N}\int_0^{E_F} E N(E)\,dE = \frac{4\pi V}{Nh^3}(2m)^{3/2}\int_0^{E_F} E^{3/2}\,dE = \frac{2}{5} \times \frac{4\pi V}{Nh^3}(2m)^{3/2} E_F^{5/2} \tag{26}$$

Substituting the value of N from eq. 23, we obtain

$$\bar{E} = \frac{3}{5} E_F \tag{27}$$

Example: The density of Zn is 7.13×10^3 kg/m³ and its atomic weight is 65.4. Calculate the Fermi energy in zinc. Also calculate the mean energy at 0K. The effective mass of the electron in zinc is $0.85\ m_e$.

Solution: Given: $\rho = 7.13 \times 10^3$ kg/m³, $M = 65.4$, $m_{eff} = 0.85\ m_e$, $E_F = ?$ $\bar{E}_0 = ?$

Since zinc is a divalent metal, the number of electrons per unit volume will be

$$n = \frac{2\rho N}{M} = \frac{2 \times 7.13 \times 10^3 \times 6.023 \times 10^{26}}{65.4} = 13.13 \times 10^{28}$$

Now, according to eq. 25, the Fermi energy is

$$E_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} = 3.65 \times 10^{-19} n^{2/3} eV$$

$$= 3.65 \times 10^{-19} \times (13.13 \times 10^{28})^{2/3} = 9.43 \text{ eV}$$

and

$$\bar{E}_0 = \frac{3}{5} E_F = \frac{3}{5} \times 9.43 = 5.66 \text{ eV}$$

10.6 FERMI-DIRAC STATISTICS

Since, the electrons are Fermions and also obey the Pauli's exclusion principle, therefore, their energy distribution at any temperature T can be expressed by Fermi-Dirac distribution function as

$$F(E) = \frac{1}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} \tag{28}$$

where E is the energy of an allowed state and E_F the Fermi energy. At absolute zero, the distibution function has the following properties:

$$F(E) = 1 \text{ for all values of } E < E_F$$

$$F(E) = 0 \text{ for all values of } E > E_F$$

That is the levels below E_F are completely filled, and all those above E_F are completely empty. Hence, E_F is the maximum energy of the filled state. However, for any temperatue greater than zero, $F(E) = 1/2$ at $E = E_F$. Therefore, the Fermi level in a metal is that energy level for which the probability of occupation is half. Further, at very high temperatures, as T tends to infnity, $kT \gg E_F$. The electrons lose their quantum mechanical character and Fermi-Dirac distribution function reduces to classical Boltzmann distribution, $\exp(-E/kT)$. Fig. 10.13 gives a plot of the Fermi function versus allowed energy E at different temperatures.

Example: At what temperature we can expect a 10% probability that electrons in silver have an energy which is 1% above, the Fermi energy? The Fermi energy of silver is 5.5 eV.
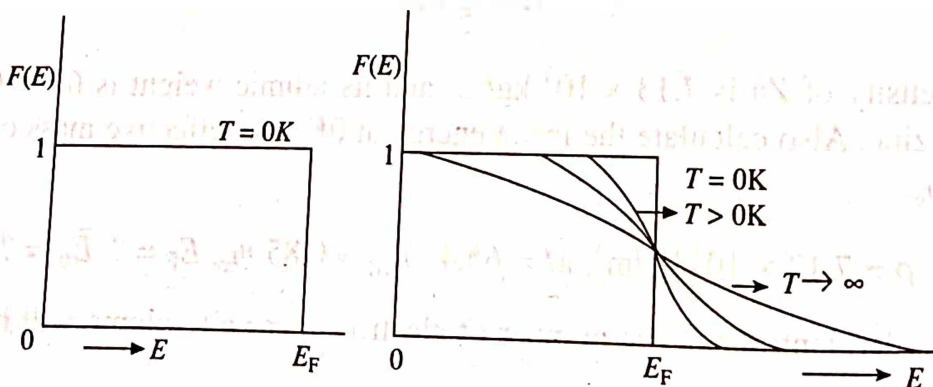

Fig. 10.13 The Fermi distribution function at different temperatures

Solution: Given: $F(E) = 10\%$, $E = E_F + 1\%$ of E_F, $E_F = 5.5$ eV, $T = ?$ Here,

$$E = 5.5 + \frac{5.5}{100} = 5.5 + 0.055 = 5.555 \quad \text{or} \quad E - E_F = 0.055$$

Now, substituting the value of $E - E_F$ in eq. 28, we have

$$0.1 = \frac{1}{\exp\left(\dfrac{0.055 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times T}\right) + 1} = \frac{1}{\exp\left(\dfrac{637.7}{T}\right) + 1}$$

or $\quad \exp\left(\dfrac{637.7}{T}\right) = 9 \quad$ or $\quad \dfrac{637.7}{T} = \ln 9 \quad$ or $\quad T = \dfrac{637.7}{\ln 9} = 290\,\text{K}$

10.7 EFFECT OF TEMPERATURE ON FERMI DISTRIBUTION FUNCTION

As we increase the temperature, the electrons lying just below the Fermi level gain energy and get excited. They occupy the energy level which were vacant at absolute zero. The number of free electrons lying in the energy interval dE at any temperature greater than absolute zero is given by

$$N = \int_0^\infty N(E)\,dE = \int_0^\infty g(E)\,dE \cdot F(E) = \int_0^\infty \frac{g(E)\,dE}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1}$$

$$= \frac{4\pi V}{h^3}(2m)^{2/3} \int_0^\infty \frac{E^{1/2}\,dE}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} \tag{29}$$

Now, let us evaluate the integral in eq. 29 using the method of integration by parts, i.e. using the formula

$$\int u\,dv = uv - \int v\,du$$

we have

$$I = \int_0^\infty \frac{E^{1/2}\,dE}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1}$$

$$= \left| \frac{2E^{3/2}}{3} \times \frac{dE}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} \right|_0^\infty + \frac{2}{3} \int_0^\infty \frac{E^{3/2}\exp\left(\dfrac{E - E_F}{kT}\right)dE}{\left[\exp\left(\dfrac{E - E_F}{kT}\right) + 1\right]^2 \cdot kT} \tag{30}$$

The first term on the right side of eq. 30 is zero for both the limits, because the probability of finding an electron for both (zero energy and infinite energy) is zero. The second term can be evaluated by making use of the Taylor's series, according to which any function $g(E)$ in the neighbourhood of $E = E_F$ can be expanded in powers of $(E - E_F)$ as

$$g(E) = g(E_F) + (E - E_F) g'(E_F) + \frac{(E - E_F)^2}{2!} g''(E_F) + \ldots \tag{31}$$

This will give us

$$E^{3/2} = E_F^{3/2} + (E - E_F) \frac{3}{2} E_F^{1/2} + \frac{(E - E_F)^2}{2} \frac{3}{4} E_F^{-1/2} + \ldots \tag{32}$$

Substituting eq. 32 into 30, the integral I becomes

$$\frac{2}{3kT} \int_0^\infty \frac{\exp\left(\dfrac{E - E_F}{kT}\right)}{\left[\exp\left(\dfrac{E - E_F}{kT}\right) + 1\right]^2} \left[E_F^{3/2} + \frac{3}{2}(E - E_F) E_F^{1/2} + \frac{3}{8}(E - E_F)^2 E_F^{-1/2} + \ldots \right] dE \tag{33}$$

In order to simplify the above integral, let us put

$$\frac{E - E_F}{kT} = x, \text{ so that } dE = kT \, dx$$

Further, taking into account the fact that at low temperatures such as $kT \ll E_F$, the derivative $F'(E)$ is large only at energies near $E = E_F$ as shown in Fig. 10.14.
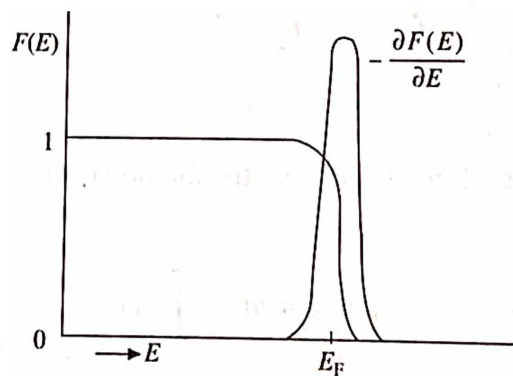

Fig. 10.14   The Fermi distribution function and its derivative at $E = E_F$

where

$$F(E) = \frac{1}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} = \left[\exp\left(\frac{E - E_F}{kT}\right) + 1\right]^{-1}$$

and

$$F'(E) = \frac{dF(E)}{dE} = - \frac{\left[\exp\left(\dfrac{E - E_F}{kT}\right) + 1\right]^{-2}}{kT} \cdot \exp\left(\frac{E - E_F}{kT}\right)$$

$$= -\left(\frac{1}{kT}\right)\frac{\exp\left(\dfrac{E-E_F}{kT}\right)}{\left[\exp\left(\dfrac{E-E_F}{kT}\right)+1\right]^2}$$

For other values of E (particularly for negative values of E), $F'(E)$ is negligible. Therefore, the lower limit in the integral may be taken as $-\infty$ instead of $(-E_F/kT)$. The above integral becomes

$$I = \frac{2}{3kT}\int_{-\infty}^{\infty}\frac{e^x}{(e^x+1)^2}\left[E_F^{3/2} + \frac{3}{2}kTxE_F^{1/2} + \frac{3}{8}(kT)^2 x^2 E_F^{-1/2} + \ldots\right]kT\,dx$$

$$= \frac{2}{3}\left[E_F^{3/2}\int_{-\infty}^{\infty}\frac{e^x\,dx}{(e^x+1)^2} + \frac{3}{2}kTE_F^{1/2}\int_{-\infty}^{\infty}\frac{xe^x\,dx}{(e^x+1)^2} + \frac{3}{8}(kT)^2 E_F^{-1/2}\int_{-\infty}^{\infty}\frac{x^2 e^x\,dx}{(e^x+1)^2} + \ldots\right] \quad (34)$$

Now, making use of the standard integrals such as

$$\int_{-\infty}^{\infty}\frac{e^x\,dx}{(e^x+1)^2} = 1, \int_{-\infty}^{\infty}\frac{xe^x\,dx}{(e^x+1)^2} = 0 \text{ and } \int_{-\infty}^{\infty}\frac{x^2 e^x\,dx}{(e^x+1)^2} = \frac{\pi^2}{3}$$

eq. 34 becomes

$$I = \frac{2}{3}\left[E_F^{3/2} 2 \cdot \frac{1}{2} + 0 + \frac{3}{8}(kT)^2 2 \cdot \frac{\pi^2}{6}E_F^{-1/2} + \ldots\right] = \frac{2}{3}E_F^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{kT}{E_F}\right)^2 + \ldots\right] \quad (35)$$

Taking into account only upto the second term and substituting the value of this integral (eq. 35) into eq. 29, we obtain

$$N = \frac{4\pi V}{h^3}(2m)^{3/2} \times \frac{2}{3}E_F^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{kT}{E_F}\right)^2\right] \quad (36)$$

At absolute zero, $E_F = E_{F_0}$. Therefore, eq. 36 reduces to

$$N = \frac{4\pi V}{h^3}(2m)^{3/2} \times \frac{2}{3}E_{F_0}^{3/2} \quad (37)$$

This is same as eq. 23, except subscript 0 in eq. 37. Now, substituting eq. 37 into 36, we obtain

$$E_{F_0}^{3/2} = E_F^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{kT}{E_F}\right)^2\right] \quad \text{or} \quad E_F = E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2\right] \quad (38)$$

Equation 38 indicates that the Fermi energy is not constant but decreases slightly as the temperature is increased. However, the value of the factor $(kT/E_{F_0})^2$ is very small at room temperature and the Fermi energy is considered to be a constant. Hence, subscript 0 is dropped from eq. 37.

10.8 THE ELECTRONIC SPECIFIC HEAT

According to Drude and Lorentz, the conduction electrons are treated as free particles as if they are electron gas molecules which obey the classical laws of mechanics and statistical mechanics (sec. 10.1). Further, from classical statistical mechanics (the kinetic theory of gases), the average energy of a free electron is $(3/2)kT$. Thus if a metal contains N free electrons per mole then the average energy of the electrons per mole should be

$$\langle \overline{E} \rangle = \frac{3}{2} NkT = \frac{3}{2} RT \tag{39}$$

where N is the Avogadro's number and $R = Nk$. Therefore, the electronic specific heat is given by

$$C_e = \frac{\partial(\overline{E})}{\partial T} = \frac{3}{2} R \cong 3 \, \text{cal/mol.} \, ^\circ\text{K} \tag{40}$$

However, the experimental measurements show that the electronic specific heat is smaller than the classical value (eq. 40) by a factor of about 10^{-2}. This discrepancy was removed by the introduction of quantum statistics developed by $E.$ Fermi and P.A.M. Dirac and is known as Fermi-Dirac statistics (eq. 28).

As the temperature increases, the electrons whose energy is close to the Fermi energy (E_F), gain thermal energy of the order of kT, and go to the higher energy state above the Fermi level. That is the electrons having the energies between E_F and $(E_F - kT)$ alone are likely to be raised above E_F and the electrons below $(E_F - kT)$ remain unaffected. An electron at the Fermi level may increase its energy from E_F to $(E_F + kT)$ at the most, so that a fraction kT/E_F of the electrons is affected. Therefore, the number of electron excited per mole is approximately given by NkT/E_F. And since on an average each electron absorbs an energy of the order of $3kT/2$, it follows that the thermal energy per mole is approximately given by

$$\overline{E} = \frac{NkT}{E_F} \times \frac{3kT}{2} = \frac{3Nk^2}{2E_F} \cdot T^2 \tag{41}$$

and hence the specific heat

$$C_e = \frac{\partial \overline{E}}{\partial T} = 3Nk\left(\frac{kT}{E_F}\right) = 3R\left(\frac{kT}{E_F}\right) \tag{42}$$

The approximate value of the electronic specific heat (eq. 42) obtained after the introduction of quantum statistics is in agreement with the experimental value. For a better agreement between the theoretically estimated value and the experimental result, it is necessary to know the average energy possessed by a free electron at any temperature T greater than absolute zero. It is given by

$$\overline{E} = \frac{1}{N} \int_0^\infty EN(E) \, dE = \frac{4\pi V}{Nh^3} (2m)^{3/2} \int_0^\infty \frac{E^{3/2} \, dE}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} \tag{43}$$

From a calculation similar to the above, the average energy of an electron at any temperature T is obtained as

$$\overline{E}_T = \overline{E}_0\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2\right] \tag{44}$$

Equation 44 indicates that the average energy is not constant and increases slightly as the temperature is increased. Now, the electronic specific heat at constant volume per electron can be obtained as

$$C_e = \frac{\partial(\overline{E}_T)}{\partial T} \cong \frac{5\pi^2 k^2 T}{6 E_{F_0}^2}(\overline{E}_0) \tag{45}$$

Making use of the eq. 27 after putting the subscript 0 for absolute zero, eq. 45 becomes

$$C_e = \frac{\pi^2 k^2 T}{2 E_{F_0}} \tag{46}$$

If we define the Fermi temperature by $T_F = E_F/k$, then eq. 46 becomes

$$C_e = \frac{\pi^2}{2} \times \frac{kT}{T_F} \tag{47}$$

This result is in fair agreement with the experimental values. It is interesting to note that the electronic specific heat varies linearly with the temperature whereas the lattice specific heat varies as cube of the absolute temperature at low temperatures (eq. 36 of chapter 9) and so that the total specific heat of a metal at low temperature may be written as

$$C_v = C_e + C_l$$

or
$$C_v = AT + BT^3 \tag{48}$$

Fig. 10.15a shows the variation of the two specific heats with temperature, indicating that the electronic contribution dominates in the helium region and only after certain temperature the lattice contribution becomes predominant. On the other hand, a plot between C_v/T versus T^2 shows a straight line having the intercept A and the slope B (Fig. 10.15b).

Example: Estimate the electronic contribution of specific heat kmol of copper at 4 K and 300 K. The Fermi energy of copper is 7.05 eV and is assumed to be temperature independent.
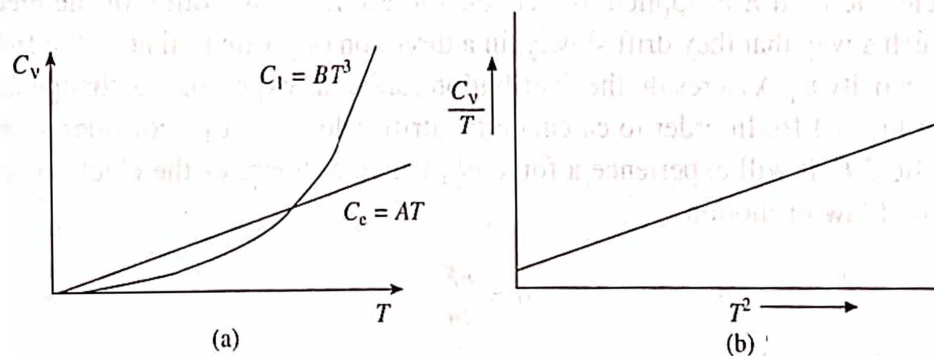

Fig. 10.15 (a) The variation of two specific heats of metal at low temperatures, (b) A plot between C_v/T versus T^2

Solution: Given: $E_F = 7.05$ eV $= 7.05 \times 1.6 \times 10^{-19}$ J, $T_1 = 4$ K, $T_2 = 300$ K, $C_e = ?$

Making use of eq. 46, and substituting various values, we obtain at 4 K,

$$C_e = \frac{\pi^2 k^2 T}{2 E_{F_0}} \times N = \frac{\pi^2 \times (1.38 \times 10^{-23})^2 \times 4 \times 6.023 \times 10^{26}}{2 \times 7.05 \times 1.6 \times 10^{-19}}$$

$$= 2.00 \text{ J kmol}^{-1} \text{ K}^{-1}$$

At 300 K,

$$C_e = 150 \text{ J kmol}^{-1} \text{ K}^{-1}$$

10.9   THE ELECTRICAL CONDUCTIVITY OF METALS

Electron Drift in an Electrical Field

According to the free electron theory, electrons move freely in a conductor. In the absence of an electric field, the electron gas is in an equilibrium state described by equilibrium distribution functions, viz, the Fermi-Dirac distribution function for a degenerate electron gas and the Maxwell-Boltzmann distribution function for non-degenerate electron gas (Fig. 10.16). Because of the fact that in a conductor the number of electrons moving in opposite directions is always the same, their average velocity in any direction is zero and consequently the distribution functions are symmetric about the axis of ordinates. This explains the fact that in the absence of an external electric field there is no electric current in a conductor, no matter how many free electrons it contains.
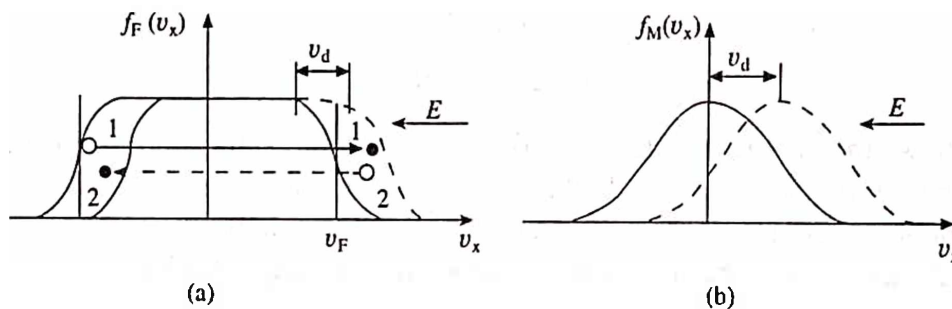

Fig. 10.16 (a)   Fermi-Dirac and (b) Boltzmann distribution function

When an electric field E is applied to a conductor, the random motion of the electrons gets modified in such a way that they drift slowly, in a direction opposite to that of the field, with an average drift velocity v_d. As a result, the distribution functions experience a change as shown by dotted lines in Fig. 10.16. In order to calculate the drift velocity, let us consider a free electron in an electric field E. It will experience a force eE, which accelerates the electron according to Newton's second law of motion

$$a = \frac{eE}{m} \tag{49}$$

where e is the electronic charge and m is the electronic mass, respectively. Prima facie, it appears that the electrons should be accelerated indefinitely and their velocity should grow continuously

as a result of the electric field. However, this is not correct. In fact, during their motion the electrons collide with the phonons, impurities and lattice imperfections. As a result, they regularly lose their kinetic energy and hence the velocity they gained in the field. In other words, the electrons have to surmount a reaction force F_r during their motion through the lattice. The reaction force is proportional to the drift velocity v_d and is directed against it.

$$F_r = -\frac{1}{\tau} m v_d \tag{50}$$

where τ is called the relaxation time. Taking into account the eqs. 49 and 50, the equation of directional motion of the electron in the lattice may be written as

$$m \frac{dv_d(t)}{dt} = eE - \frac{m v_d}{\tau} \tag{51}$$

Equation 51 tells us that the velocity of the directional motion of the electrons will rise and they will be accelerated until the two forces on the right hand side become equal when the resultant force acting on the electron, and accordingly the acceleration will become zero. Consequently,

$$v_d = \frac{eE\tau}{m} \tag{52}$$

Since an electron has a negative charge, it drifts in a direction opposite to that of the field.

In a chemically pure and structurally perfect crystal where the resistance force approaches zero, even a small field is enough to accelerate the electron indefinitely so that its velocity grows continuously which could become infinitely high. Actually, in a perfect lattice, electron wave propagates in an optically transparent medium.

10.10 RELAXATION TIME AND MEAN FREE PATH

Let us suppose that as soon as the velocity of the directional motion of the electrons attains a constant value v_d, the field is turned off. This velocity starts diminishing as a result of collisions of the electrons with the phonons, impurities and lattice imperfections, and the electron gas ultimately return to an equilibrium state. Such a process leading to the establishment of equilibrium in a system is termed as relaxation process. Thus for $E = 0$, the eq. 51 becomes

$$\frac{dv_d(t)}{dt} = -\frac{v_d(t)}{\tau}$$

so that

$$v_d(t) = v_d \exp\left[-\frac{t}{\tau}\right] \tag{53}$$

where $v_d(t)$ is the velocity of the directional motion of the electrons and t is the time after the field is turned off. In eq. 53, τ characterizes the rate at which the equilibrium state of a system is reached; smaller is the t sooner the system reaches to equilibrium state. For $t = \tau$, the velocity of the directional motion decreases by $1/e$ of its initial value. For pure metals, $\tau \simeq 10^{-14}$ s.

The motion of an electron in a crystal may be conveniently described in terms of mean free path. By analogy with the kinetic theory of gases one may presume that an electron in a crystal

moves along a straight line until it collides with the lattice imperfection and gets scattered. The average distance λ that the electron travels between two successive collisions is taken as the mean free path of the electron. At room temperature, since the velocity imparted to the electrons by an applied electric field is much smaller thermal velocity, the time τ taken by the electrons is travelling the distance λ will thus be decided not by the drift velocity due to the field but by the average velocity v, due to random thermal motion. Therefore,

$$\tau = n\frac{\lambda}{v} \tag{54}$$

where n is the number of collisions that are required to nullify the directional velocity completely.

10.11   ELECTRICAL CONDUCTIVITY AND OHM'S LAW

Ohm's law is the most established experimental law relating to the conduction in metals and can be used to test the validity of the theory of electrical conductivity.

Knowing the drift velocity of the electrons, it is easy to calculate the current density and hence the conductivity of a metal. For the purpose, let us consider a cylindrical conductor of length v_d and area of cross-section of unity as shown in Fig. 10.17. Suppose it contains N electrons per unit volume. Imagine any section of the conductor and count the number of charges passing through this section per second. Obviously, it will be equal to all the electrons inside this cylinder of volume $1. v_d$. Therefore, a current flowing through the conductor with a density
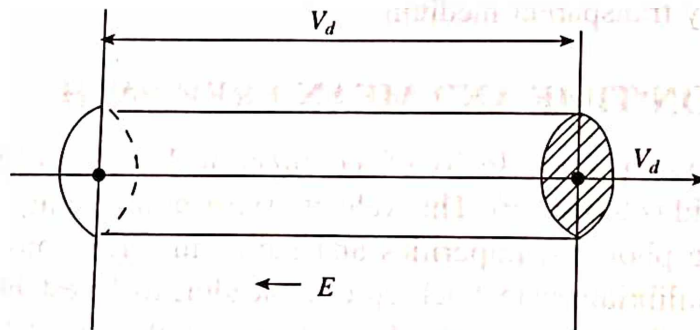
Fig. 10.17   Calculation of current density

$$I = N (1.v_d) e = Ne\left(\frac{eE\tau}{m}\right) \quad \text{(from eq. 52)}$$

$$= \left(\frac{Ne^2\tau}{m}\right)E \tag{55}$$

This is at once recognizable as Ohm's law ($I = \sigma E$) where the conductivity σ is given by

$$\sigma = \left(\frac{Ne^2\tau}{m}\right) = Ne\mu \tag{56}$$

where $\mu = e\tau/m$ is called the carrier mobility and is defined as the average drift velocity per unit electric field, i.e.

$$\mu = \frac{v_d}{E} = \frac{e\tau}{m}$$

and the resistivity ρ is given by

$$\rho = \frac{m}{Ne^2\tau} \qquad (57)$$

Equation 56 can be easily understood as follows: we expect the charge transported in the medium to be proportional to the charge density ($n = Ne$), the factor (e/m) enters because the acceleration in a given electric field is proportional to e and inversely proportional to m (eq. 49) and the time τ describes the time during which the field acts on the carrier. This equation is of fundamental importance. The electrical conductivity σ depends on two factors, the number n of carriers per unit volume and their mobility μ. The dependence of these quantities particularly on temperature provides the basic understanding of the electrical properties of materials. For example, in metals, n is constant and μ varies relatively slowly with temperature. In semiconductors, the exponential dependence of n is of primary importance while in some insulators, it is the exponential dependence of μ on temperature that is significant while n is constant. An understanding of the relative contributions of n and μ to σ enables us to explain the whole spectrum of values of σ.

Example: Sodium metal with a bcc structure has two atoms per unit cell. The radius of the sodium atom is 1.85 Å. Calculate its electrical resistivity at 0°C if the classical value of the mean free time at this temperature is 3×10^{-14} s.

Solution: Given: $\tau = 3 \times 10^{-14}$ s, Na has bcc structure with $n = 2$, $R_{Na} = 1.85$ Å $= 1.85 \times 10^{-10}$ m, $\rho = ?$
For a bcc structure, we know that

$$\sqrt{3}a = 4R,$$

or $$a = \frac{4}{\sqrt{3}}R = \frac{4}{\sqrt{3}} \times 1.85 \times 10^{-10} = 4.27 \times 10^{-10} \text{ m}$$

Further, the number of electrons per unit volume in sodium atom is given by

$$n' = \frac{\rho N}{M} = \frac{n}{a^3} = \frac{2}{(4.27 \times 10^{-10})^3} = 2.57 \times 10^{28}/\text{m}^3$$

Making use of eq. 57 and substituting different values, we can obtain

$$\rho = \frac{m}{n'e^2\tau}$$

$$= \frac{9.1 \times 10^{-31}}{2.57 \times 10^{28} \times (1.6 \times 10^{-19})^2 \times 3.1 \times 10^{-14}} = 4.46 \times 10^{-8} \ \Omega\text{m}$$

Example: A uniform copper wire whose diameter is 0.16 cm carries a steady current of 10 amp. Its density and atomic weight are respectively, 8920 kg/m³ and 63.5. Calculate the current density and the drift velocity of the electrons in copper.

Solution: Given: Density, $\rho = 8920$ kg/m³, At. wt. = 63.5, $I = 10$ A, Diameter, $d = 0.16$ cm = 16 $\times 10^{-4}$ m, and hence $r = 8 \times 10^{-4}$ m, $J = ?$ $v_d = ?$ The number of electrons per unit volume in copper is given by

$$n = \frac{\rho N}{M} = \frac{8920 \times 6.023 \times 10^{26}}{63.5} = 8.46 \times 10^{28} / m^3$$

Now, the current density

$$J = \frac{I}{a} = \frac{10}{\pi r^2} = \frac{10}{\pi (8 \times 10^{-4})^2} = \frac{10^9}{64 \pi} = 4.97 \times 10^6 \ A/m^2$$

The drift velocity can be obtained by using the relation

$$v_d = \frac{J}{ne} = \frac{4.97 \times 10^6}{8.46 \times 10^{28} \times 1.6 \times 10^{-19}} = 3.67 \times 10^{-4} \ m/s$$

Example: A uniform silver wire has a resistivity of 1.54×10^{-8} Ωm at room temperature. For an electric field along the wire of 1 Volt/cm, compute the average drift velocity of the electrons, assuming that there are 5.8×10^{28} conduction electrons/m³. Also calculate the mobility and the relaxation time of the electron.

Solution: Given: $\rho = 1.54 \times 10^{-8}$ Ωm, $E = 1$ V/cm = 100 V/m, $n = 5.8 \times 10^{28}/m^3$, $v_d = ?$

From eq. 56, the mobility is found to be

$$\mu = \frac{\sigma}{ne} = \frac{1}{\rho n e} = \frac{1}{1.54 \times 10^{-8} \times 5.8 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$$= 6.99 \times 10^{-3} \ m^2/Vs$$

Further, the drift velocity is given by

$$v_d = \mu E = 100 \times 6.99 \times 10^{-3} = 0.69 \ m/s$$

Also, the relaxation time τ is given by

$$\tau = \frac{\mu m}{e} = \frac{6.99 \times 10^{-3} \times 9.1 \times 10^{-31}}{1.6 \times 10^{-19}} = 3.97 \times 10^{-14} s$$

10.12 WIEDEMANN-FRANZ-LORENTZ LAW

From earlier discussions, we have come to know that the electrons are not only the agencies of electrical conduction in an electric field but also responsible for the transport of the thermal energy in a solid. For this reason, it would be natural to expect a relationship between the two conductivities, i.e.

$$\frac{K_e}{\sigma} = \left(\frac{\pi^2 N k^2 T \tau}{3m} \right) \cdot \left(\frac{m}{Ne^2 \tau} \right) = \left(\frac{\pi^2 k^2}{3e^2} \right) T \tag{58}$$

This relationship was first experimentally established by G. Wiedemann and P. Franz and then

theoretically explained by L. Lorentz for metals. Wiedemann and Franz observed that the ratio K_c/σ remains constant for all metals at a fixed temperature. However, this was modified by Lorentz, who observed that it is $K_c/\sigma(T)$ which remains constant. Accordingly, eq. 58 reduces to

$$\frac{K_c}{\sigma(T)} = \frac{\pi^2}{3}\left(\frac{k^2}{e^2}\right) = L \tag{59}$$

where $L = \frac{\pi^2}{3}\left(\frac{k^2}{e^2}\right) = 2.45 \times 10^{-8}$ Watt ohm deg^{-2}, and is known as Lorentz number. Table 10.1 shows the experimental values of L for some metals at 0°C and 100°C, respectively. They are found to agree with the theoretical value (eq. 59). At low temperatures ($T \ll \theta_D$), Lorentz number tends to decrease because the collision time involved in the two conductivities is not identical.

Table 10.1   Experimental Lorentz numbers for some metals

Metals	Lorentz numbers ($L \times 10^{-8}$ Watt-ohm/deg^2)	
	0°C	100°C
Aq	2.31	2.37
Au	2.35	2.40
Cd	2.42	2.43
Cu	2.23	2.33
Ir	2.49	2.49
Mo	2.61	2.79
Pb	2.47	2.56
Pt	2.51	2.60
Sn	2.52	2.49
W	3.04	3.20
Zn	2.31	2.33

Example: A uniform copper wire of length 0.5 m and dimeter 0.3 mm has a resistance of 0.12 Ω at 293 K. If the thermal conductivity of the specimen at the same temperature is 390 Wm^{-1} K^{-1}, calculate the Lorentz number. Compare this value with the theoretical value.

Solution: Given: $1 = 0.5$ m, $d = 0.3$ mm $= 0.3 \times 10^{-3}$ m, so that $r = 0.15 \times 10^{-3}$ m, $R = 0.12$ W, the Lorentz number = ?

We know that the resistance of a wire in terms of its length and its radius is given by

$$R = \rho\,\frac{1}{\pi r^2} = \frac{1}{\sigma \pi r^2}$$

or
$$\sigma = \frac{1}{R\pi r^2} = \frac{0.5}{0.12 \times \pi\,(0.15 \times 10^{-3})^2} = 5.89 \times 10^7 \ \Omega^{-1} m^{-1}$$

Hence, using eq. 59, we can obtain the Lorentz number as

$$L = \frac{K_c}{\sigma(T)} = \frac{390}{5.89 \times 10^7 \times 293} = 2.26 \times 10^{-8} \ \text{W}\Omega\text{K}^{-2}$$

On the other hand, the theoretical value of the Lorentz number can be obtained by using the expression

$$L = \frac{\pi^2}{3}\left(\frac{k^2}{e^2}\right) = \frac{\pi^2}{3}\left(\frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}}\right)^2 = 2.84 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$$

Comparing the above two values of Lorentz numbers, we observe that the theoretical value is about 1.26 times higher than the experimental one.

10.13 THE ELECTRICAL RESISTIVITY OF METALS

At room temperature (~300 K) the electrical resistivity of most metals is dominated by the collisions of conduction electrons with the phonons of the lattice (arising due to any perturbation in the normal positions of the atoms). On the other hand, at liquid helium temperature (or around absolute zero) it is due to the collisions of electrons with the impurity atoms or other imperfections (such as vacancies, dislocations, grain boundaries, etc.) that are present in a real crystal (Fig. 10.18). Thus in general, the resistivity of a metal containing imperfections is given by

$$\rho = \rho_l + \rho_i \tag{60}$$

where ρ_l is the resistivity caused by the thermal vibrations of the lattice, ρ_i (also called the residual resistivity) is the resistivity caused by the scattering of electrons by impurity atoms. For small impurity content, ρ_l is often independent of the number of defects N_i, and ρ_i is proportional to the N_i but independent of temperature. Equation 60 is known as Matthiessen's rule. This becomes less accurate at high temperatures or at high impurity content.
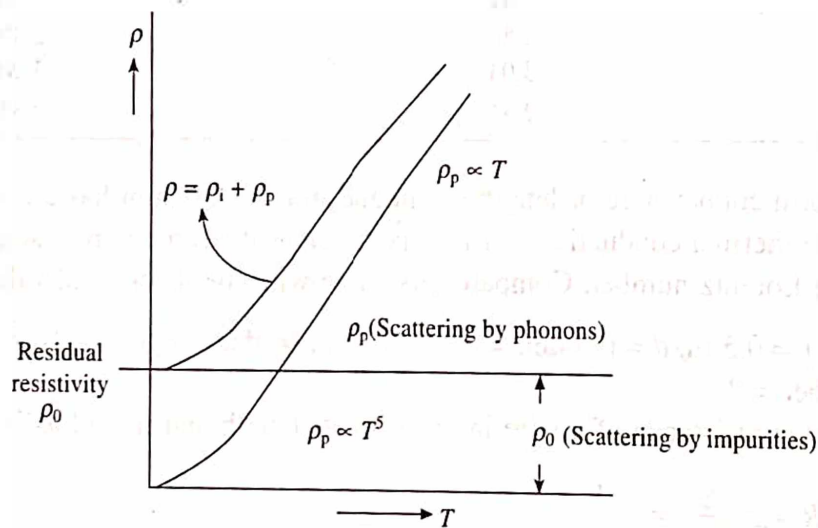

Fig. 10.18 The electrical resistivity in a real crystal

At very low temperatures, the scattering by phonon is negligible because of negligibly small amplitude of vibration. Therefore, as T approaches zero, τ_l tends to infinity so that ρ_l approaches zero and hence $\rho = \rho_i$ from eq. 60. This is in agreement with the experimental results. Measurements on sodium show that $\rho_i(0)$ may vary from specimen to specimen, whereas $\rho_l(T) = \rho - \rho_i(0)$ is independent of the specimen. As the temperature increases, the scattering by phonons becomes

more effective and $\rho_i(T)$ increases linearly with temperature. This again, is in agreement with the experimental results.

A simple method to estimate the overall impurity and perfection of a metal (conductor) is to measure the ratio of the resistivities at room temperature and at helium temperature, i.e.

$$\frac{\rho(300 \text{ K})}{\rho(4.2 \text{ K})}$$

Since, at 4.2 K, $\rho = \rho_i$, the resistivity ratio is approximately given by

$$\frac{\rho_1(300 \text{ K}) + \rho_i}{\rho_i}$$

For chemically pure and structurally perfect metals, the resistivity ratio may be as high as 10^6. On the other hand, for commercial purity materials, this ratio is of the order of 10^2, while for some alloys, it is as low as 1.

Matthiessen's rule is not always valid. Calculation of resistivity due to lattice vibration ρ_1, have been quite successful in some metals. Empirically, one finds that ρ_1 is rather well represented by a universal function,

$$\rho_1 \propto \left(\frac{T}{M\theta_R^2}\right) \cdot f\left(\frac{T}{\theta_R}\right) \tag{61}$$

where the function f goes to unity at high temperatures. However, at low temperatures, $f \propto (T/\theta_R)^4$. The resistive characteristic temperature θ_R is close to the Debye temperature for metals.

Example: Calculate the percentage increase in the resistivity of nichrome when it is heated from 300 K to 1000 K. The temperature coefficient of resistance of nichrome is 0.0001.

Solution: Given: $T_1 = 300$ K, $T_2 = 1000$ K, $\alpha = 0.0001$, $(\rho_{1000} - \rho_{300}) = ?$ According to Matthiessen's rule, we know that the resistivity of a metal containing impurity can be written as

$$\rho = \rho_i + \rho_1(T) = \rho_i + \alpha T$$

Therefore, $\qquad \rho_{300} = \rho_i + \alpha T_1$ and $\rho_{1000} = \rho_i + \alpha T_2$

or $\qquad \rho_{1000} - \rho_{300} = \alpha(T_2 - T_1) = 700\alpha = 700 \times 0.0001 = 0.07$

Therefore the percentage increase in the resistivity is

$$0.07 \times 100 = 7\%$$

10.14 THERMIONIC EMISSION

When a metal is heated, electrons are emitted from its surface, a phenomenon called thermionic emission. In sections 10.2 and 10.3, we considered that the height of the potential barrier is infinitely large. However, this is not actually the case in real crystals. At absolute zero:

(i) the height of the potential energy barrier can be taken equal to $E_F + e\phi$ as shown in Fig. 10.19, where E_F is the Fermi energy and $e\phi$ is the work function.

(ii) all the levels upto the Fermi level are filled, and all the levels above the Fermi level are empty.

(iii) no electrons can escape from the metals.

The work function $e\phi$ is the minimum energy required to remove an electron from the Fermi surface to the vacuum outside the metal, where ϕ is expressed in volts and $e\phi$ in electron volts (eV). The voltage ϕ is required to overcome the attraction due to positive ions at the surface of the metal. Fig. 10.20 shows an ideal potential (periodic in nature) encountered by electrons along a row of atoms near the surface and the potential energy barrier at the surface of the metal. In our day to day life, we do not observe any electron emission from metal surface even at room temperature. However, as the temperature is increased further, the electrons lying near the Fermi level get exited and begin to fill the levels above E_F. Thus, when a metal is heated, (i.e. when an energy greater than $E_F + e\phi$ is supplied), electrons are observed to be emitted from its surface. This phenomenon is known as thermionic emission.
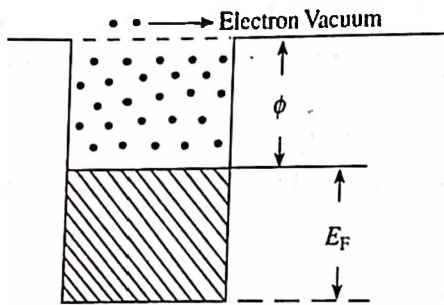

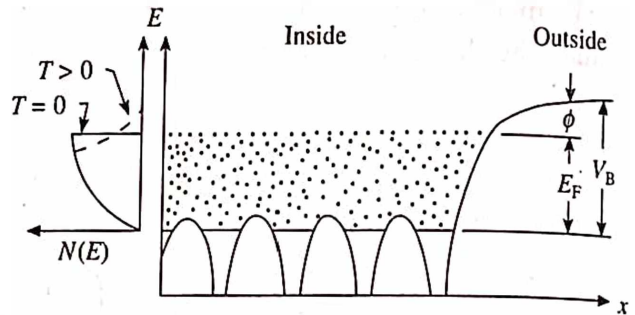Fig. 10.19   Thermionic emission

Fig. 10.20   Idealized potential energy of an electron along a row of atoms near the surface, and the potential energy barrier at the surface of the metal. The shaded area represents electron energy as given by the Fermi distribution shown on the left

In order to evaluate the current density for the emitted electrons, let us consider a metal surface held normal to the x-direction. Then, for an electron to escape from the metal surface, we must have

$$\frac{1}{2} mv_x^2 \geq (E_F + e\phi) \tag{62}$$

where v_y and v_z can have any values including $+\infty$ and $-\infty$.

Now, let us write the density of occupied states (eq. 19) per unit volume in terms of velocity of electrons by substituting $E = 1/2(mv^2)$, so that $dE = mvdv$. The modified equation becomes

$$N(v)dv = F(v)g(v)dv = \frac{8\pi m^3}{h^3} \cdot \frac{v^2 dv}{\exp\left(\dfrac{E - E_F}{kT}\right) + 1} \tag{63}$$

Then the current density J_x will be eV_x times the density of occupied states per unit volume. To simplify the problem, let us integrate the resulting equation over all electron velocities using cartesian coordinate system instead of spherical coordinate system. Thus replacing the quantity $\int 4\pi v^2 dv$ by $\int dv_x dv_y dv_z$, the current density J_x can be written as

$$J_x = \frac{2em^3}{h^3} \int\limits_{v_x = \sqrt{\frac{2(E_F + e\phi)}{m}}}^{\infty} \int\limits_{V_y = -\infty}^{\infty} \int\limits_{V_z = -\infty}^{\infty} \frac{v_x \, dv_x \, dv_y \, dv_z}{\exp\left(\frac{E - E_F}{kT}\right) + 1} \tag{64}$$

In general, $(E - F_F) \gg kT$, therefore the exponential term in the above equation is also very very large than unity. Thus neglecting the digit 1 which is appearing in the denominator, the eq. 64 reduces to

$$J_x = \frac{2em^3}{h^3} \int\limits_{v_x = \sqrt{\frac{2(E_F + e\phi)}{m}}}^{\infty} \int\limits_{V_y = -\infty}^{\infty} \int\limits_{V_z = -\infty}^{\infty} \exp\left[-\frac{1}{kT}\left(\frac{mv_x^2}{2} + \frac{mv_y^2}{2} + \frac{mv_z^2}{2} - E_F\right)\right] \tag{65}$$

Now, making use of the standard form of the integral, i.e.

$$\int\limits_{-\infty}^{\infty} \exp(-\alpha x^2) = \left(\frac{\pi}{\alpha}\right)^{1/2}$$

the above integrals separately can be given by

$$\int\limits_{-\infty}^{\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z = \int\limits_{-\infty}^{\infty} \exp\left(-\frac{mv_y^2}{2kT}\right) dv_y = \left(\frac{2\pi kT}{m}\right)^{1/2} \tag{66}$$

and

$$\int\limits_{v_x = \sqrt{\frac{2(E_F + e\phi)}{m}}}^{\infty} v_x \cdot \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x = \frac{kT}{m} \cdot \exp\left(-\frac{E + e\phi}{kT}\right) \tag{67}$$

Hence, the current density is given by

$$J_x = \frac{4\pi emk^2}{h^3} T^2 \cdot \exp\left(-\frac{e\phi}{kT}\right) = AT^2 \cdot \exp\left(-\frac{e\phi}{kT}\right) \tag{68}$$

where $A = (4\pi em\, k^2/h^3) = 1.20 \times 10^6 \text{ Am}^{-2}\text{K}^{-2}$. Equation 68 is commonly known as Richardson-Dushman equation. This is in agreement with the experimental results. The eq. 68 can further be written as

$$\frac{J_x}{T^2} = A \exp\left(-\frac{e\phi}{kT}\right)$$

or

$$\ln\frac{J_x}{T^2} = \ln A - \left(\frac{e\phi}{k}\right)\frac{1}{T} \tag{69}$$

If we plot a curve between $\ln (J_x/T^2)$ versus $1/T$, we obtain a straight line which has a slope of $(e\phi/k)$ and the intercept equal to $\ln A$ as shown in Fig. 10.21.

Example: The work function of tungsten is 4.5 eV. Calculate the thermionic emission of a filament 0.05 m long and 10^{-4} m diameter at 2400 K.

Solution: Given: ϕ = 4.5 eV, $2r = D = 10^{-4}$ m, l = 0.05m, T = 2400K, A = 1.20 × 10^6 Am^{-2} K^{-2}, I = ?

The surface area of the filament, $a = 2\pi r l = \pi \times 10^{-4} \times 0.05 = 5\pi \times 10^{-6}$ m^2. Now, making use of the eq. 68 and substituting different values, the value of the current can be obtained as

Fig. 10.21 A plot between 1/T and log J/T^2

$$I = a \times J = a \times AT^2 \cdot \exp\left(-\frac{e\phi}{kT}\right)$$

$$= 5\pi \times 10^{-6} \times 1.20 \times 10^6 \,(2400)^2 \times \exp\left(-\frac{4.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 2400}\right)$$

$$= 5\pi \times 10^{-6} \times 1.20 \times 10^6 \,(2400)^2 \times \exp\,(-21.739)$$

$$= 5\pi \times 10^{-6} \times 1.20 \times 10^6 \,(2400)^2 \times 3.62 \times 10^{-10} = 393 \times 10^{-4} \text{ amp}$$

10.15 THE HALL EFFECT

Let us consider a rectangular metal slab carrying a current density J_x in the positive x-direction and placed in a uniform magnetic field of induction B acting perpendicular to both the conductor and the current as shown in Fig. 10.22. Under such an experimental arrangement, in 1879 G. Hall found that a voltage (called the Hall voltage) is developed at right angles to both the current and the magnetic field.

In the absence of the magnetic field, the conduction electrons drift with a velocity v_x in the negative x-direction. However, when the field is applied, a force (called the Lorentz force) causes the electron path to deflect towards the front face of the rectangular block. As a result, an excess of electrons accumulate on the front face of the slab. Simultaneously, equal number of positive charge appears (due to the deficiency

Fig. 10.22 The Hall effect

of electrons) on the opposite face of the slab. The appearance of the opposite charges on the opposite faces creates an electric field (called the Hall field) directed towards the positive y-axis.

The Lorentz force F_L acting on an electron which is moving from right to left with a velocity v is

$$F_L = -\,ev_x \times B_z = -\,ev_x B_z \text{ (since } v_x \text{ is } \perp B) \tag{70}$$
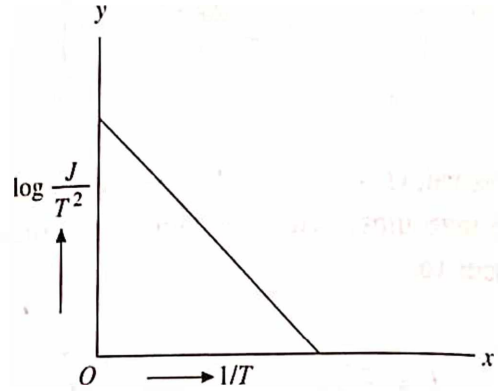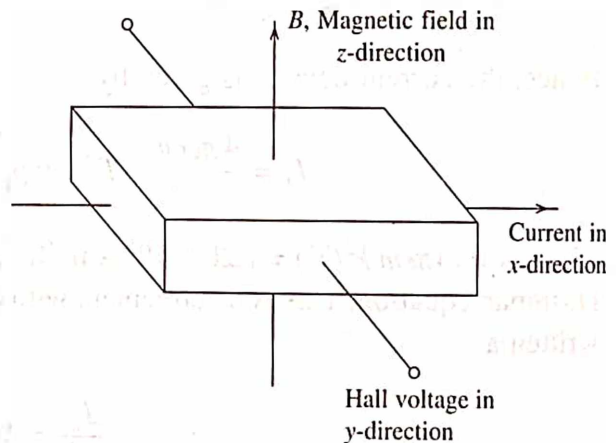
Further, the accumulated charges on the oppositive faces produce a force (called Hall force) opposite to the Lorentz force. Hence, the accumulation process continues until the Hall force completely cancels the Lorentz force. In equilibrium, $F_H = F_L$, i.e.

$$eE_H = -ev_x B_z \quad \text{or} \quad E_H = -v_x B_z \tag{71}$$

Further, the current density, J_x is given by the equation

$$J_x = nev_x \quad \text{or} \quad E_H = -\left(\frac{1}{ne}\right)B_z J_x \tag{72}$$

This shows that the Hall field is proportional to both the magnetic field and the current density. The constant of proportionality in eq. 72 is known as Hall constant and is defined by

$$R_H = -\frac{1}{ne} \tag{73}$$

which is inversely proportional to the density of charge carrier, n. The sign of the Hall constant indicates the nature of the charge carrier that predominate in the conduction process. If R_H is negative, the predominant charge is electron and vice versa. The measurement of Hall voltage helps us to know the following:

1. The sign of the predominant charge carrier.
2. The charge density.
3. The mobility of the charge carriers.

Example: Calculate the Hall coefficient of sodium based on free electron model. Sodium has bcc structure and the side of the cube is 4.28Å.

Solution: Given: $a = 4.28$ Å $= 4.28 \times 10^{-10}$ m, crystal has a bcc structure indicating it contains 2 atoms per unit cell, Hall coefficients = ?
The number of electrons per unit volume for the sodium crystal is given by

$$n = \frac{2}{a^3} = \frac{2}{(4.28)^3 \times 10^{-30}} = 2.55 \times 10^{28}/m^3$$

Now, making use of eq. 73, the Hall coefficient can be obtained as

$$R_H = -\frac{1}{ne} = -\frac{1}{2.55 \times 10^{28} \times 1.6 \times 10^{-19}} = -2.45 \times 10^{-10} \text{ m}^3\text{C}^{-1}$$

10.16 SUMMARY

1. The free electron model successfully explains some of the properties of solids, such as electrical and thermal conductivities, thermionic emission, etc. However, it fails to explain many other important properties such as behaviour of solids as conductors, semiconductors or insulators, etc.

2. Free electrons are associated with a continuous energy spectrum and bound electrons with a discrete energy spectrum. The energy corresponding to the electrons moving in box of side a is given by

$$E_n = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

where n_x, n_y and n_z are quantum numbers and can take only positive integer values.

3. Each combination of these quantum numbers is called a quantum state while several states having the same energy are said to be degenerate.

4. At absolute zero, the density of electrons (the number of electrons per unit volume) below the Fermi level is given by

$$n = \frac{8\pi}{3h^3}(2m)^{3/2} E_F^{3/2}$$

5. As the temperature is increased (particularly above room temperature) the Fermi energy is found to decrease according to the relation.

$$E_F = E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2\right]$$

6. At low temperatures, the electronic specific heat of solids is found to be predominant and varies linearly with T. The electronic specific heat per mole is given by

$$C_e = \frac{\pi^2}{2} \times \frac{kT}{T_F}$$

7. The electrical conductivity of conduction electrons, treated as free particles with a collision time τ is given by

$$\sigma = \frac{Ne^2\tau}{m}$$

8. Wiedemann-Franz-Lorentz law connects the thermal and electrical conductivities according to the relation

$$\frac{K_e}{\sigma} = \frac{\pi^2}{3}\left(\frac{k^2}{e^2}\right)$$

9. Taking into account the lattice vibrations and static impurities, the electrical resistivity of a solid is governed by Matthiessen's rule

$$\rho = \rho_l + \rho_i$$

10. When a metal is heated, some electrons which are lying just below the Fermi level acquire sufficient energy and escape from the surface of the metal. The thermionic current density is given by

$$J_x = AT^2 \cdot \exp\left(-\frac{e\phi}{kT}\right)$$

where A is constant and ϕ is the work function of the metal.

11. Hall effect helps us to determine the following:

(i) The sign of the current carrying charges.

(ii) The charge density.

(iii) The mobility of the charge carriers

10.17 DEFINITIONS

Current Density: The electric current per unit area, amperes per square meter.

Electrical conductivity: The proportionality constant in Ohm's law as stated below.

Electric Current: The time rate of passage of charge through a conductor. In SI units, coulomb per second, called amperes.

Electrical Resistivity: The inverse of the electrical conductivity, so that the Ohm's law is also $E = \rho J$.

Electronic Specific Heat: The contribution to the total specific heat due to transitions of electrons to states of higher energy.

Fermi Level: In a partially filled energy band at 0K, the Fermi level is the energy of the highest filled state. At higher temperatures, one half of the states at the Fermi level are full.

Manthiessen's Rule: The total resistivity of a conductor is the sum of lattice contribution as a result of lattice vibrations and the impurity contribution as a result of presence of imperfections.

Residual Resistivity: The temperature independent part of the resistivity of a conductor. This is due to imperfections.

Resistivity Ratio: Usually, it is defined as $\rho(300K)/\rho(4.2K)$, although the lower temperature may vary. In order to estimate the value of residual resistivity $\{\rho_i(300K) + \rho_i\}/\rho_i$ is approximately taken as $\rho_i(300K)/\rho_i$.

REVIEW QUESTIONS AND PROBLEMS

1. A particle moving in a one dimensional potential, is given by

$$V(x) = 0 \quad \text{for} \quad x < 0$$

$$\text{and } V(x) = V_0 \quad \text{for} \quad x \geq 0$$

Write down the Schrodinger wave equation for the particle and solve it.

2. What is an infinite potential well? Obtain Schrodinger's time independent wave equation. Solve it for a particle in a cubical box of side "a" and hence obtain expressions for the allowed wave functions and discrete energy values of the particle.

3. Obtain the eigen values and normalized wave functions for a particle in a one dimensional infinite potential box of side "a".

4. A particle of mass m is confined in a field free region between impenetrable walls at $x = 0$ and $x = a$. Show that the stationary energy levels of the particle is given by

$$E_n = \frac{h^2 n^2}{8 m a^2}$$

Discuss the physical significance of the wave function ψ.

5. Define Fermi energy. Write down the expression for Fermi-Dirac distribution function. Derive an expression for Fermi energy of a system of free electrons.

6. Based the Fermi-Dirac statistics, state the nature of the Fermi distribution function. How does it vary with temperature?

7. What are the density of states in metals? Derive an expression for the density of energy states and hence obtain the Fermi energy of a metal.

8. What is meant by the Fermi level in metals? How does it vary with temperature in metals?

9. Show that the wavelength associated with an electron having an energy equal to the Fermi energy is given by

$$2\left(\frac{\pi}{3n}\right)^{1/2}$$

Calculate the molar specific heat of metals on the basis of Fermi-Dirac statistics and compare it with the classical predicted value.

10. The Fermi energy expression at room temperature is given by

$$E_F = E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2\right]$$

where E_{F_0} is the Fermi energy at 0K.

Using the above equation, obtain the expression for the mean energy of the electron at room temperature. Also obtain the expression for the molar specific heat of metals on the basis of this distribution.

11. What do you understand by "degenerate" and "non degenerate" states? Taking the example of a particle in a cubical box of side "a", obtain first few states and present them graphically.

12. Derive an expression for the electrical conductivity of a free electron gas using the collision time concept. Does this result explain the experimental value of resistivity of a normal metal like sodium.

13. On the basis of free electron theory derive an expression for the electrical and thermal conductivity of metal and hence establish Wiedemann-Franz-Lorentz law.

14. What are the main sources of electrical resistance in metals? Discuss the effect of impurity, temperature and alloying on the electrical conductivity of metals.

15. Explain the variation of electrical conductivity with temperature both at low and high temperature regions. Hence explain Matthiessen's rule.

16. Discuss electron-scattering mechanisms in metals and show that the mean free path is inversely proportional to absolute temperature for $T \gg \theta_D$.

17. Obtain the expression of Lorentz number on the basis of quantum theory. Compare it with the one predicted on the basis of classical theory.

18. Discuss the Hall effect. Explain how the measurement of Hall coefficient helps one to determine the mobility of electrons in metals.

19. Show that the Hall coefficient is independent of the applied magnetic field and is inversely proportional to the current density and electronic charge. Mention the important applications of Hall effect.

20. Discuss the phenomenon of thermionic emission in metals. Obtain Richardson Dushman equation for the emission of current density.

21. The thermal conductivity of aluminium at 20°C is 210 $Wm^{-1}K^{-1}$. Calculate the electrical resistivity of aluminium at this temperature. The Lorentz number for aluminium is 2.02×10^{-8} $W\Omega K^{-2}$.

Ans. 2.82×10^{-8} Ωm

22. A copper wire of cross sectional area 5×10^{-2} sq. cm. carries a steady current of 50 ampere. Assume one electron per atom, calculate the density of free electrons, the average drift velocity and the relaxation time. Given: the resistivity of copper = 1.7×10^{-8} Ωm.

Ans. $8.46 \times 10^{28}/m^3$, 7.4×10^{-4} m/s and 2.46×10^{-14} s.

23. (a) Find the lowest energy of an electron confined in a box of side 1 Å.

(b) Find the temperature at which the average energy of the molecule of a perfect gas would be equal to the lowest energy of the electron.

Ans. 112.9 eV, 8.72×10^5 K.

24. The electrons in a cubical box of a metal are subject to the influence of a magnetic field such that the length increases by da while the width and thickness remain the same. Show that the energy difference between the states (311) and (131) is $(h^2/8ma^2)$ $(16da/a)$ in the new position.

25. Evaluate the temperature at which there is 1% probability that a state with an energy 0.5 eV above the Fermi energy will be occupied by an electron.

Ans. 1264 K.

26. Calculate the number of states lying in an energy interval of 0.02 eV above the Fermi energy of sodium crystal of unit volume. For sodium, $E_F = 3.22$ eV. *Ans.* 2.47×10^{26}

27. Use the Fermi distribution function to obtain the value of $F(E)$ for $E - E_F = 0.01$ eV at 200 K.

Ans. 0.36

28. Show that the probability that a state ΔE above the Fermi level E_F is filled equals the probability that a state ΔE below is empty.

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

Ans. 5.1×10^{23}.

30. The Fermi energy of silver is 5.5 eV. Calculate the fraction of free electrons at room temperature located upto a width of kT on either side of E_F.

Ans. 0.01.

31. Calculate the heat capacity of electron gas at room temperature in copper assuming one free electron per atom. Compare this with the lattice specific heat value of 2.4×10^4 J kmol^{-1} K^{-1}. The Fermi energy of copper is 7 eV.

Ans. 1.52×10^2 J kmol^{-1} K^{-1}, 0.633%.

32. An alloy of a metal is found to have a resistivity of 10^{-6} Ωm at 0°C. When it is heated to a temperature of 700°C, the resistivity increases by 8%. Using Matthiessen's rule, find the resistivity of the alloy.

Ans. 0.969×10^{-6} Ωm.

33. The electrical and thermal conductivities of silver at 20°C are 6.22×10^7 Ω^{-1} m^{-1} and 423 Wm^{-1}K^{-1}, respectively. Calculate the Lorentz number on the basis of quantum free election theory.

Ans. 2.32×10^{-8} WΩK^{-2}.