

CHAPTER

29

Band Theory of Solids

29.1 INTRODUCTION

X-ray diffraction studies show that a solid is an ordered structure. In the solid atoms occupy the lattice sites and the spacing between the atoms is of the same order as that of the linear dimensions of atoms. Therefore, atoms in a solid interact strongly and set up an internal electric field, which is *periodic* in nature. The periodic electric field affects the motion of free electrons. Electron is not an ordinary particle but possesses a wave character also. The application of quantum mechanics to the motion of electrons in solid shows that the allowed values of electron energy are distributed into bands, each band consisting of a sequence of closely spaced energy levels arranged in a manner akin to the steps of a ladder. In 1928 Felix Bloch developed **zone theory** for the electrons moving in a periodic field provided by a crystal lattice. This theory is popularly known as the **band theory of solids**. Knowledge of the formation of energy bands and the consequent restrictions imposed on electron motion in a solid are obtained from the band theory. Such considerations led to the invention of a gamut of solid state devices, which has revolutionized the field of electronics leading to miniaturization, micro-miniaturization and mass production of devices and systems.

29.2 THE BAND THEORY OF SOLIDS—A QUALITATIVE EXPLANATION

A solid may be imagined as formed by allowing initially free atoms to gradually approach one another. As long as the atoms are widely separated their interactions are negligible. Every atom has the *same* energy-level diagram. The energy-level diagram for the entire system of N atoms resembles the energy-level diagram for a single atom; now each state of the *system* can be occupied by N electrons instead of just one. As the atoms come together to create a close packed periodic structure, they interact strongly due to their proximity to each other. By **interaction** we mean that the positive nucleus of one atom attracts the electrons and repels the nucleus of the adjacent atom and vice versa. As a result, instead of one energy level the same for all N isolated atoms, there arise N closely spaced separate levels, which fall into groups. The energy levels are so closely spaced in the group that they form a virtual continuum, which is called an **energy band**. The formation of energy bands can be qualitatively understood using molecular orbital concept.

Let us consider an imaginary situation where N hydrogen atoms approach each other to form solid hydrogen. Each hydrogen atom is characterized by one electron residing at $1s$ energy level corresponding to an atomic orbital ψ . As long as the separation r of two atoms A and B is much larger than the size d of the atoms ($r \gg d$), the atoms do not interact and the atomic orbitals ψ_A and ψ_B are not affected (see Fig. 29.1 a). The two atoms have identical

energy levels marked E in Fig. 29.2. When the two atoms come into contact ($r = d$), the orbitals ψ_A and ψ_B overlap and form molecular orbitals, where each electron may be said to orbit around both nuclei. A linear combination of these two atomic orbitals yields two types molecular orbitals, namely

$$\psi_+ = C_1\psi_A + C_2\psi_B \quad \text{and} \quad \psi_- = C_3\psi_A - C_4\psi_B$$

where ψ_+ and ψ_- denote molecular orbitals and C_1, C_2, C_3 and C_4 are constants.

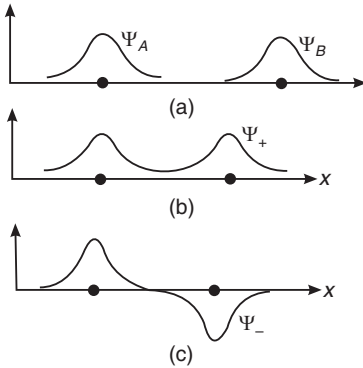


Fig. 29.1

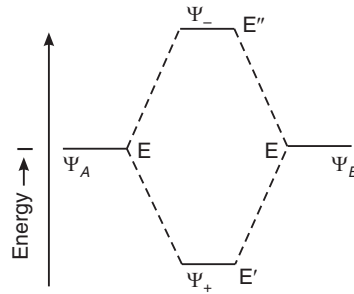


Fig. 29.2

The molecular orbital ψ_+ is called the **bonding orbital** and has a lower energy E' ($E' < E$). The molecular orbital ψ_- is called the **antibonding orbital** and has a higher energy E'' ($E'' > E$). Thus, the combination of two atomic orbitals results in two molecular orbitals, which extend over both the atoms. The first important consequence of the molecular orbital formation is that the individual valence electrons are not localized to their original atomic positions and they belong to both the atoms. The second important result is that one of the molecular orbitals (bonding orbital) is of lower energy than either of the individual atomic orbitals and the other molecular orbital (antibonding orbital) is of higher energy. It means that the original energy level E of each electron is split into two energy levels (see Fig. 29.2). *The transformation of a single energy level into two or more separate energy levels is known as energy level splitting.*

When two atoms come close, one energy level splits into two energy levels (Fig. 29.3 b). When three atoms approach each other closely, the original level splits into three levels; four atoms produce four levels and so on (Fig. 29.3 c). In general, N interacting atoms cause a particular energy level to split into N levels. The group of energy levels resulting from splitting is so closely spaced that it is called an *energy band* (see Fig. 29.3 d).

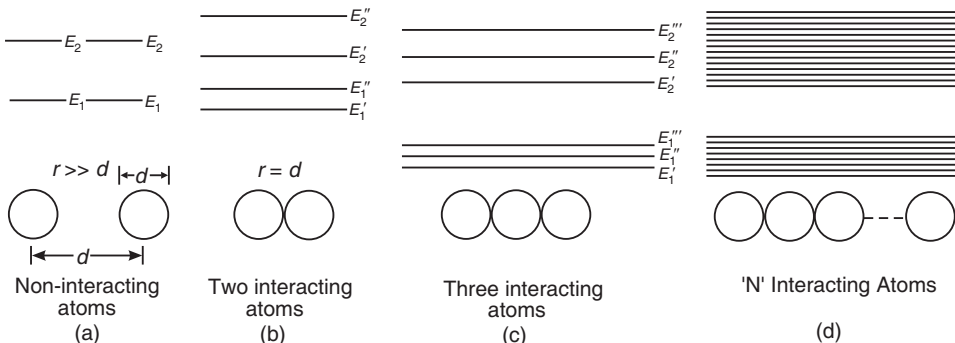


Fig. 29.3. Energy level splitting and band formation.

The individual valence electrons no longer belong to individual atoms; but they now belong to all nuclei in the solid.

29.3 THE BAND THEORY OF SOLIDS—QUANTUM MECHANICAL EXPLANATION

In order to find the allowed energies of electrons in solids, we have to apply Schrödinger wave equation for an electron in a crystal lattice. Fig. 29.4(a) shows the actual potential as seen by an electron in the crystal lattice in one dimension.

29.3.1 The Kronig-Penny Model

Kronig and Penny suggested a simplified model consisting of an infinite row of rectangular potential wells separated by barriers of width b . This one-dimensional representation of periodic lattice is known as *Kronig-Penny model* and is shown in Fig. 29.4 (b). Each well has a width b and a depth V_0 .

The period of the potential is $(a + b)$. In regions where $0 < x < a$, the potential energy is assumed to be zero and in regions such as $-b < x < 0$, it is V_0 . Through this model, Schrodinger equation can be solved explicitly in terms of elementary functions.

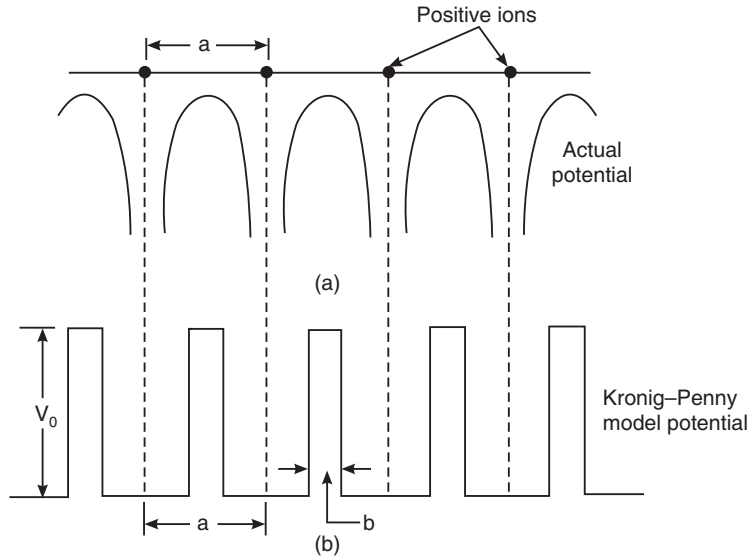


Fig. 29.4. Kronig-Penny Model

29.3.2 Bloch Theorem

The Schrodinger equation for the two regions can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} E\psi = 0 \quad \text{for } 0 < x < a \quad (29.1)$$

and
$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V_0)\psi = 0 \quad \text{for } -b < x < 0 \quad (29.2)$$

We rewrite the above equation as

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \quad \text{for } 0 < x < a \quad (29.3)$$

and
$$\frac{d^2\psi}{dx^2} + \beta^2 \psi = 0 \quad \text{for } -b < x < 0 \quad (29.4)$$

There is an important theorem known as the **Bloch theorem**. According to this theorem, the solution of the Schrodinger equation for a periodic potential would be of the form of a plane wave modulated with the periodicity of the lattice. It means that the solution can

be represented as the product of two functions: a free particle wave function and a periodic function $u(x)$ that has the same period as the lattice. Thus

$$\psi(x) = u(x)e^{ikx} \quad (29.5)$$

with

$$u(x) = u(x + a) \quad (29.6)$$

The wave functions of the above type are known as **Bloch functions** which change periodically with increasing x .

29.3.3 Energy Bands

We substitute the above wave functions into the Schrodinger equation and solve it in the usual way. When we apply the periodic boundary condition, we get the following expression.

$$\frac{maV_0b}{\hbar^2} \cdot \frac{\sin \alpha a}{a} + \cos \alpha a = \cos ka \quad (29.7)$$

where

$$\alpha = \frac{\sqrt{2mE}}{\hbar}$$

Equ. (29.7) provides the allowed solutions to the Schrodinger equation. As the relation involves trigonometric functions, only certain values of α are possible. The right hand side of equation (29.7)

is cosine function and can take values only between -1 and $+1$. Therefore, the left-hand side of the equation is restricted to vary between those two limits. Hence, only certain values of α are allowed. It means that energy E is restricted to lie within certain ranges.

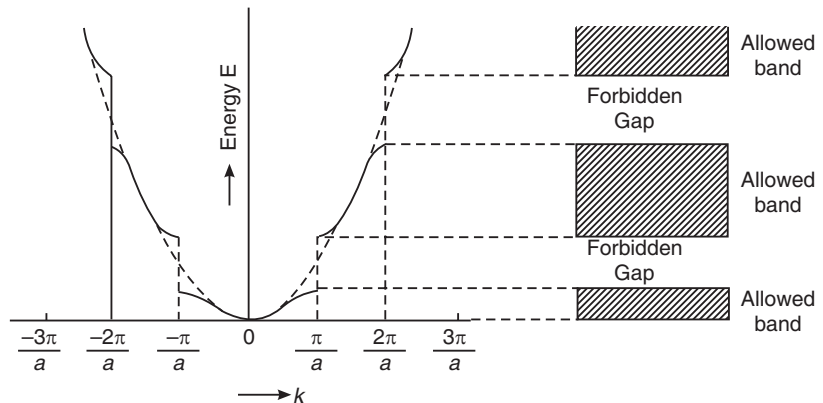


Fig. 29.5. Electron energy, E versus wave number, k plot for a solid

This concept is best understood by drawing the plot of energy E as a function of the wave number, k . The plot is shown in Fig. 29.5. The parabolic relation between E and k obtained in case of free electron is interrupted at certain values of k , as shown by the broken curve.

Fig. 29.5 shows discontinuities in E . The discontinuities occur at $ka = \pm n\pi$ i.e., at

$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots \quad (29.8)$$

The origin of the allowed energy bands and forbidden gaps is clear from Fig. 29.5.

29.4 ENERGY BAND STRUCTURE OF A SOLID

A crystal (i.e., solid) consists of an enormous number of atoms arranged in a regular periodic structure. The extent of energy level splitting in the solid depends on the nearness of atoms in it. Let us assume that N identical atoms form the crystal. The energy levels of the isolated atoms are shown in Fig. 29.6(c). All the N atoms have identical sets of energy levels. The electrons fill the energy levels in each atom independently. Fig. 29.6 (b) shows an atom sitting

at the origin of the coordinate system. Now let us imagine that other atoms approach this atom along the three axial directions and halt at the distance a_0 , which is the lattice constant of the crystal. As the atoms approach, a continuously increasing interaction occurs between the atoms. Each of the energy levels splits into many distinct levels and form energy bands, as shown in Fig. 29.6 (b). Fig. 29.6 (a) depicts the effect of slicing of Fig. 29.6 (b) at a_0 and it represents the *energy band structure* of the crystal. It is seen that corresponding to each allowed energy level of an isolated atom, there forms an allowed energy band; and that the allowed energy bands are separated by forbidden bands of energy.

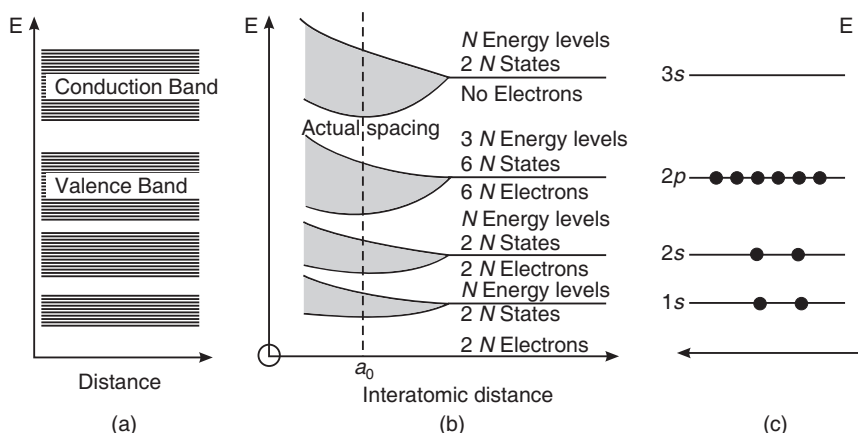


Fig. 29.6. Energy level splitting in a solid as a function of interatomic distance (a) Energy band structure of the solid corresponding to the actual spacing of atoms in the solid. (b) Energy level splitting as a function of distance. (c) Discrete energy levels in an isolated atom.

The degree of splitting of energy levels depends on their depth in the atom. The electrons in outer shells screen the core electrons belonging to inner shells. Consequently, the energy levels of inner shell electrons are split to a lesser degree. They form narrow core bands. They are always completely filled and do not participate in electrical conduction. In contrast the energy levels of valence electrons are split more and form wider bands.

In general, N interacting atoms cause an energy level to split into $(2l + 1)N$ levels. Thus, s -level ($l = 0$) splits into N levels whereas the p -level, consisting of three sublevels p_x , p_y , and p_z , splits into $3N$ levels. Thus, in a solid each level of an individual atom splits into $(2l + 1)N$ number of levels where N is the number of atoms in the system. Consequently, the maximum electron capacity of an s -band is $2N$ electrons whereas the capacity of a p -band is $6N$ electrons.

While occupying an energy band, electrons start from the lowest energy level in the band and fill the levels one after the other in the ascending order of energy. When $2N$ electrons occupy the N levels available in the band, the band is said to be **completely filled**. In case of non-availability of $2N$ electrons, the energy band gets **partially filled**. When there are no electrons to occupy the levels, the energy band remains **vacant**.

The width of an allowed or forbidden energy band is generally of the order of a few electron-volts. As N is very large, the energy separation between successive energy levels in an allowed band is very small and is of the order of 10^{-27} eV. At room temperature, the kinetic energy of the electrons of the order of kT (≈ 0.026 eV) which is very large compared to the energy level separation in an allowed band. Consequently, electrons can easily move into higher vacant levels within the allowed energy band either due to thermal energy or due to a small externally applied electric field. On the other hand, electrons cannot jump across a

forbidden band under normal thermal energy possessed by them or due to an applied electric field. High temperatures are required to cause inter-band electron transitions.

29.5 ELECTRICAL CONDUCTION FROM THE VIEW POINT OF BAND THEORY

In a solid, the allowed values of electron energy are distributed into bands (Fig. 29.6), each band consisting of a sequence of closely spaced discrete energy levels arranged in a manner akin to the rungs of a ladder. The electrons are distributed in the energy levels according to the Pauli exclusion principle. The motion of an electron corresponds to its transition from a lower energy level to an upper vacant energy level. This implies that the following two conditions are to be fulfilled for electrical conduction to take place in a solid:

- (i) There should be free electrons available in the solid.
- (ii) Vacant energy levels should be available immediately above the levels occupied by free electrons.

If a band has vacant energy levels but is devoid of electrons, there would be no carriers to move through the vacant levels when energy is supplied to the solid from a source such as a battery. Hence current does not flow through the solid.

On the other hand, if all the energy levels within a band were completely occupied by electrons, there would be no energy level to which an electron can jump. Therefore, even though the energy is supplied to the solid from a source such as a battery, the electrons cannot acquire energy and electrical conduction cannot occur in the solid.

If an energy band is partially filled, then the electrons will have vacant upper energy levels into which they can jump. On acquiring energy from the electric field applied across the solid, the electrons move into successive upper energy levels and cause electrical conduction. Thus, *partially filled energy band is required for electrical conduction in a solid.*

29.6 ENERGY BAND DIAGRAM

An energy band diagram is a graphic representation of the energy levels associated with top energy band and the next lower energy band in a solid. The energy band diagram shows two bands with a gap in-between (see Fig. 29.7). The upper band is called the **conduction band** and the lower energy band is called the **valence band**. These two bands are separated by a *forbidden gap*. This energy gap is more popularly called **band gap** and is denoted by the symbol E_g . The conduction band corresponds to the energy values of *free electrons* that have broken their valence bonds, and hence have become free to move in the crystal. The bottom of the conduction band represents the smallest energy that the electron must possess to become free.

Only the free electrons can move in the crystal under the influence of the externally applied electric field. Hence, these electrons are called **conduction electrons** and the energies of such electrons constitute the **conduction band**. The band showing the energy values of **valence electrons** that are engaged in covalent bonding is called the **valence band**.

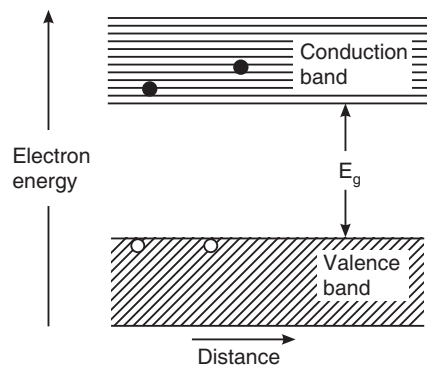


Fig. 29.7. Energy band diagram

29.7 CLASSIFICATION OF SOLIDS

The concept of energy bands helps us in understanding the division of solids into three groups. The nature of the energy bands determines whether the solid is an electrical conductor

or insulator. According to the band theory, the electrical conductivity a solid is characterized by the energy gap E_g separating the outermost energy bands namely, the valence band and the conduction band. The ability of electrical conduction is decided by the order of magnitude of the energy gap E_g .

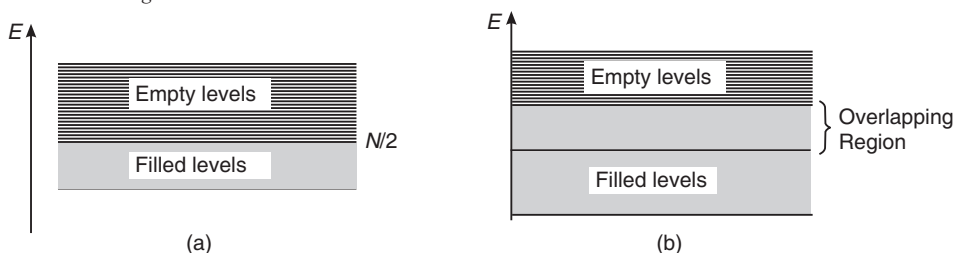


Fig. 29.8. Energy band formation in a conductor (a) Half filled conduction band. (b) Empty upper band overlaps on a totally filled lower band.

In some solids, an upper vacant band overlaps the valence band or the valence band itself is half-filled, as shown in Fig. 29.8. It means that electrons in the valence band have easy access to levels in the upper vacant band. For this reason, very large numbers of electrons are available for conduction, even at extremely low temperatures. When electric field is impressed across the solid, electrons readily jump into upper unoccupied energy levels of the vacant band and current flows in a large measure in the solid. Therefore, these solids exhibit good electrical conductivity and are called **conductors**.

In some solids the band gap is narrow and of the order of 2 eV or less, as shown in Fig. 29.9. Acquisition of small amounts of energy from the vibrations of atom can raise electrons from the valence band to the conduction band. The conduction band is then partially filled. If a potential is applied across the material, it causes the electrons in the conduction band to move to upper levels. As a result, current flows in a modest measure in the solid. Such solids are called **semiconductors**.

Some solids (Fig. 29.10) have band gaps that are very wide ($E_g > 3$ eV). It would require the acquisition of very large amounts of energy to cause an electron to jump from the valence band to the conduction band. Very few electrons can get this large amount of energy to jump from valence band to conduction band at ambient temperature. Hence, there are very few electrons in the conduction band. When a voltage is applied across

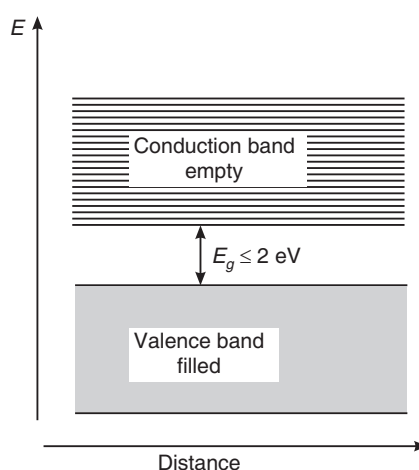


Fig. 29.9. Energy band structure of a semiconductor

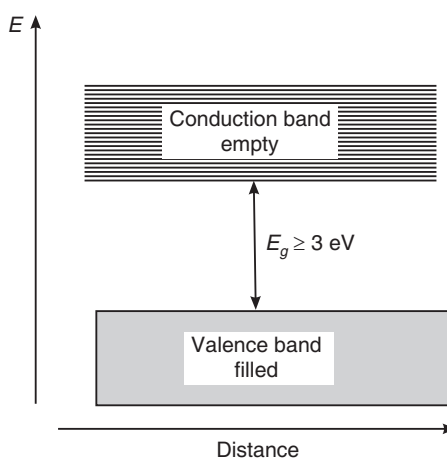


Fig. 29.10. Energy band structure of an insulator

the solid, negligible current flows and the solid exhibits very low electrical conductivity. These solids are called **insulators**.

29.8 ENERGY BAND DIAGRAMS FOR SOME TYPICAL SOLIDS

29.8.1 Lithium

Let us consider the element lithium belonging to Group I in the periodic table. The electron configuration of lithium atom is $1s^2 2s^1$. The $1s$ shell is closed and there is only one electron at the $2s$ level. In solid lithium, $1s$ and $2s$ bands form corresponding to the $1s$ and $2s$ levels, as illustrated in Fig. 29.11.

Both $1s$ and $2s$ bands have N levels each. The $1s$ band is completely filled as $2N$ electrons occupy N energy levels whereas the $2s$ band is half-filled because the N available electrons fill $N/2$ lower levels in the band leaving the upper $N/2$ levels vacant. In general, the solids of Group-I elements form such half-filled energy bands at the top and therefore belong to the group of conductors.

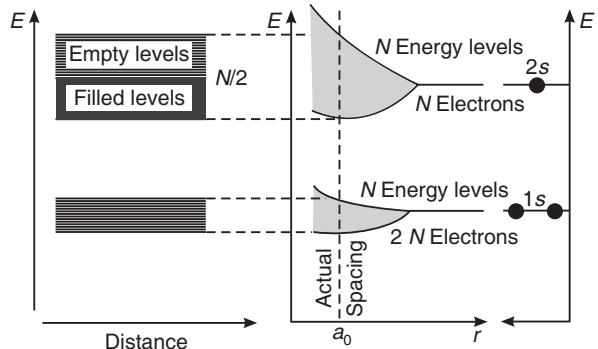


Fig. 29.11. Energy level splitting and energy band configuration in lithium solid showing half-filled $2s$ band.

29.8.2 Beryllium

Let us next consider the case of alkaline earth elements of Group-II. The first element in this group is beryllium. Its electron configuration is $1s^2 2s^2$. From the electron configuration, it is expected that beryllium solid would be an insulator. However, it is known to be a conductor. The reason is that the upper vacant $2p$ band overlaps the lower completely filled $2s$ band leading to the formation of a partially filled hybrid band, as shown in Fig. 29.12.

In general, solids of Group-II elements exhibit such partially filled bands, and therefore belong to the conductors group.

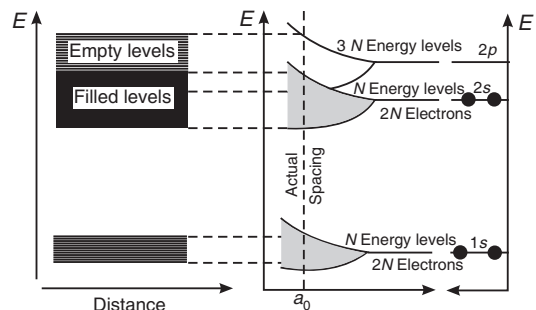


Fig. 29.12. Energy level splitting and energy band configuration in beryllium solid showing overlapping of completely filled $2s$ band and vacant $2p$ band.

29.8.3 Energy Band Diagrams for Silicon and Diamond

Silicon belongs to Group IV elements in the periodic table. The electron configuration of silicon atom is $1s^2 2s^2 2p^6 3s^2 3p^2$. It is seen that the inner K and L shells are closed and the corresponding bands would be completely filled. In the outer subshells $3s$ and $3p$, $3s$ -subshell is closed. The $3p$ sub-shell is partially filled. Hence it is expected to behave as a good conductor. But because of formation of a hybrid band, which later branches out, the Si solid behaves as a semiconductor.

In the crystal formation process, when the atoms are very far apart, as at position 'd' in Fig. 29.13, the electrostatic interaction among them is negligible. Consequently, the electronic

energy levels of the crystal will be the same as those of isolated atoms. As the separation between atoms decreases, the $3s$ and $3p$ levels split and two bands are formed, as shown at position 'c' in Fig. 29.13. The band corresponding to $3s$ level has N energy levels and the band corresponding to $3p$ level has $3N$ levels. $2N$ electrons occupy N levels in $3s$ -band and $2N$ electrons occupy N levels in $3p$ -band. It may now be noted that there is an energy gap between the two bands. The energy gap is seen to decrease with the decrease in atomic spacing. At

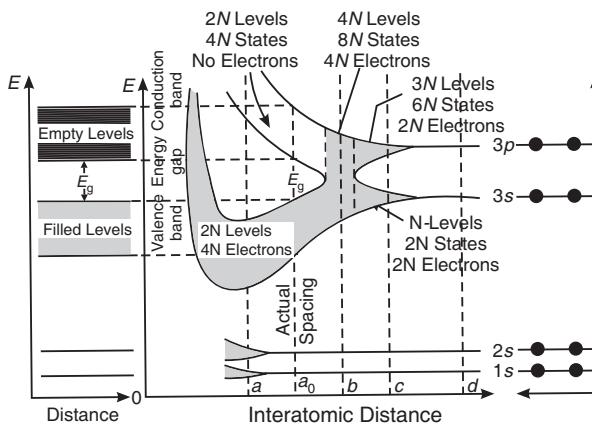


Fig. 29.13. Energy level splitting and band formation in crystals of Group IV A elements

position 'b' in Fig. 29.13 the two bands merge and form a composite band. The $3N$ upper levels merge with N lower levels, giving rise to a total of $4N$ levels. These levels have to be occupied by the $4N$ electrons available in total, and so the lowermost $2N$ levels are filled. When the atomic distance in our imaginary crystal is further reduced, the interaction among the atoms becomes very strong. Beyond the lattice spacing 'b' in Fig. 29.13, we find that the composite band branches out and once again two bands are formed, separated by a forbidden gap, E_g . The significant point is that the $4N$ energy levels are equally divided between the two branches. There is an equal distribution of levels, $2N$ in each, in the two bands. The $4N$ electrons available in total at $3s$ and $3p$ levels, now occupy the lower energy band and leave the upper band vacant. The lower band constitutes the valence band and the upper band the conduction band. This is the situation at the actual spacing ' a_0 ' in the silicon crystal. At position a_0 the two bands are not widely separated from each other. The value of E_g at 0 K is 1.12 eV. At normal temperatures, a significant number of electrons will be thermally excited from valence band to conduction band. The electrons excited to conduction band respond to the external voltage and produce a modest flow of current. Thus, Si behaves as a semiconductor.

Diamond

It is evident from Fig. 29.13 that the energy gap between the two branches goes on increasing with decreasing atomic distance. At the interatomic distance corresponding to line at 'a' in Fig. 29.13, the distance between the two bands becomes considerably large. In case of diamond the two bands are separated by 5.47 eV. Even at high temperatures, the thermal energy would be insufficient to excite enough number of electrons to the conduction band. Because of the non-availability of electrons in the conduction band electrical conduction cannot take place in the material and hence diamond behaves as insulator.

29.9 ENERGY BAND STRUCTURE OF A CONDUCTOR

Conductors are characterized by a single energy band, namely conduction band which contains more energy levels than free electrons. At the temperature 0K, electrons occupy the lower energy levels in the conduction band up to a certain energy level called the Fermi level E_F .

29.9.1 Fermi-Dirac Distribution Function

We are next interested in knowing how electrons are distributed among the various energy levels in the conduction band at a given temperature. We cannot apply Maxwell-Boltzmann distribution to electrons because (i) they obey exclusion principle and (ii) they are indistinguishable particles. The statistical distribution function applicable to quantum particles is the Fermi-Dirac distribution function.

The probability that an electron occupies an energy level E at thermal equilibrium is given by

$$f(E) = \frac{1}{1 + \exp[(E - E_F) / kT]}$$

where E_F is known as **Fermi level**. In general E_F may or may not correspond to an energy level but it provides a reference with which other energies can be compared. The function $f(E)$ is known as **Fermi factor**.

The above equation is known as *Fermi-Dirac equation* or *Fermi-Dirac distribution function*. Note that the probability of the electron to occupy the energy level E increases with temperature. We first discuss about the distribution function and the related topics with reference to conductors. We shall find later that these concepts are equally applicable to other cases.

Example 29.1. Evaluate the Fermi function for energy kT above the Fermi energy.

Solution. The Fermi function is given by $f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}$

Gvn : $E = E_F + kT$

Therefore, If $(E - E_F) = kT$, then $f(E) = \frac{1}{1 + e^{(E - E_F)/kT}} = \frac{1}{1 + e^1} = \frac{1}{1 + 2.78} = \frac{1}{3.78} = 0.269$.

Example 29.2. In a solid, consider the energy level lying 0.01 eV below Fermi level. What is the probability of this level not being occupied by an electron?

Gvn : $E = E_F - 0.01$ **Solution.** $(E_F - E) = [E_F - (E_F - 0.01)] = 0.01$ eV and $kT = 0.026$ eV at $T = 300$ K

The probability of an energy level E not being occupied by an electron is given by $[1 - f(E)]$.

$$\begin{aligned} [1 - f(E)] &= 1 - \frac{1}{1 + e^{(E - E_F)/kT}} = \frac{1}{1 + e^{(E_F - E)/kT}} = \frac{1}{1 + e^{0.01\text{eV}/0.026\text{eV}}} = \frac{1}{1 + e^{0.385}} \\ &= \frac{1}{1 + 1.47} = 0.405 \end{aligned}$$

29.9.2 Fermi Level

The occupancy of the energy levels by electrons in conductors is described by the Fermi-Dirac distribution function.

$$f(E) = \frac{1}{1 + \exp[(E - E_F) / kT]} \quad (29.9)$$

We distinguish two situations - one at absolute zero and the other at higher temperatures.

Case 1: $T = 0$ K

Fig. 29.14 (a) depicts the conduction band of a conductor at 0K. At absolute zero, electrons occupy energy levels in pairs starting from the bottom of the band up to an upper level designated as E_F , leaving the upper levels vacant. **Fermi level** can be, therefore, defined as the uppermost filled energy level in a conductor at 0K. Correspondingly, **Fermi energy**

is defined as **maximum energy that a free electron can have in a conductor at 0K**. To use an analogy, the electron distribution in the conduction band can be likened to water at rest in a container. The Fermi level corresponds to the top surface of water. The **Fermi function at 0K** is shown in Fig. 29.14 (b).

Let us now apply equ. (29.9) to the solid taking the value of T as 0 K .

(i) For energy levels E lying below E_F , $E < E_F$, $(E - E_F)$ is a negative quantity.

$$\therefore f(E) = \frac{1}{1 + e^{-(E-E_F)/0}} = \frac{1}{1 + e^{-\infty}} = \frac{1}{1 + 0} = 1$$

$f(E) = 1$ indicates that all the energy levels lying below the level E_F are occupied.

(ii) For energy levels located above E_F , $E > E_F$, $(E - E_F)$ is a positive quantity.

$$\therefore f(E) = \frac{1}{1 + e^{(E-E_F)/0}} = \frac{1}{1 + e^{\infty}} = \frac{1}{1 + \infty} = \frac{1}{\infty} = 0$$

The result $f(E) = 0$ implies that all the levels above E_F are vacant at $T = 0\text{ K}$.

(iii) For $E = E_F$, the quantity $(E - E_F) = 0$.

$$\therefore f(E) = \frac{1}{1 + e^{0/0}} = \text{indeterminate}$$

The above result implies that the occupancy of Fermi level at 0 K ranges from zero to one.

Case 2: $T > 0\text{ K}$

On heating the conductor, electrons are excited to higher energy levels. In general, $E_F \gg kT$. Therefore, for most of the electrons lying

deep in the conduction band, the thermal energy is not sufficient to cause a transition to an upper unoccupied level. **At normal temperatures, only those electrons occupying the energy levels near the Fermi level can be thermally excited.** These levels make up a narrow band of width kT directly adjacent to the Fermi level. Therefore, upon heating the solid, electrons having energy a little below E_F , jump into levels with energy somewhat above E_F and a new energy distribution of electrons is obtained.

Thus, as a result of thermal excitation, the probability of finding electrons in the levels immediately below E_F will decrease. On the same hand, the probability of finding electrons in

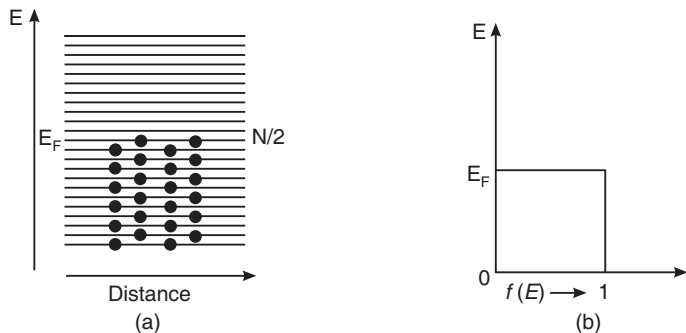


Fig. 29.14

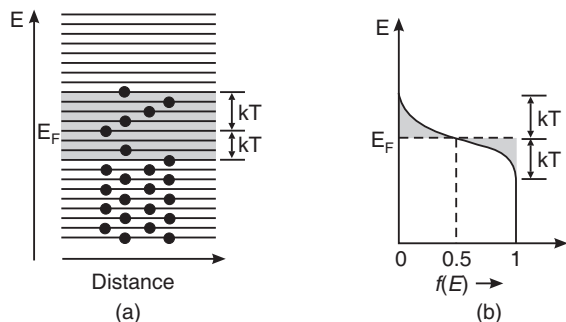


Fig. 29.15

the levels immediately above E_F increases. This fact is reflected in the graph (Fig. 29.15 b) as a blurring of the step plot.

At $T > 0\text{K}$, if we consider an electron at Fermi level, then $E = E_F$.

$$\therefore f(E) = \frac{1}{1 + e^{0/kT}} = \frac{1}{1+1} = \frac{1}{2}$$

This implies that the probability of occupancy of Fermi level at any temperature above 0K is 0.5 or 50% . Now we can define Fermi level as the energy level, which has a probability of occupancy of 0.5 . An operational definition of Fermi energy can be given now. **Fermi energy is the average energy possessed by electrons participating in conduction in metals at temperatures above 0K .**

29.9.3 Effect of Temperature on Fermi Function

The Fermi-Dirac distribution curves for different temperatures are shown in Fig. 29.16. At $T = 0\text{K}$, there is an abrupt jump in the value of $f(E)$ from 1 to zero at E_F . At $T > 0\text{K}$ the change is gradual. The higher the temperature, more gradual is the change.

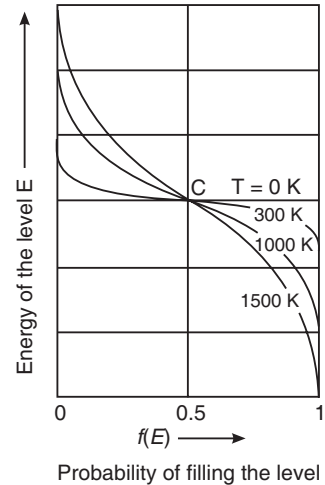


Fig. 29.16

It is seen from the curves for different temperatures in Fig.

29.16 that they all pass through a **crossover point C**, at which the probability of occupancy is 0.5 . This is due to the fact that $f(E)$ has a value of 0.5 for any temperature greater than 0K .

We may deduce from the curves that **Fermi energy E_F is the average energy possessed by electrons that participate in conduction process in a conductor at temperatures above absolute zero.**

Example 29.3. The Fermi level for potassium is 2.1 eV . Calculate the velocity of the electrons at the Fermi level.

Solution: $E_F = \frac{1}{2} m v_F^2$

$$\therefore v_F^2 = \frac{2E_F}{m} = \frac{2 \times 2.1 \times 1.602 \times 10^{-19} \text{ C} \cdot \text{V}}{9.10 \times 10^{-31} \text{ kg}} = 0.74 \times 10^{12} \text{ m}^2/\text{s}^2$$

$$v_F = 8.6 \times 10^5 \text{ m/s.}$$

Example 29.4. The Fermi level of silver is 5.5 eV . Calculate the fraction of free electrons at room temperature located up to a width of kT on either side of the Fermi level.

Solution. The number of electrons that occupy levels above E_F at a temperature T is proportional to kT . Therefore, the fraction of electrons that occupies levels higher than E_F is given by

$$\frac{kT}{E_F} = \frac{0.026 \text{ eV}}{5.5 \text{ eV}} = 0.0047$$

Similarly, the fraction of electrons that are deprived of partners $\cong 0.0047$

$$\therefore \text{The fraction of free electrons that is located up to a width } kT \text{ on either side of } E_F \\ = 2 \times 0.0047 = 0.0094 \approx \mathbf{0.01}$$

Example 29.5. 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 .

Solution. Given that the electron energy is $E = E_F + 1\%E_F$.

$$\therefore E - E_F = 1\%E_F = \frac{5.5 \text{ eV}}{100} = 0.055 \text{ eV}$$

Also
$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

Putting $\frac{E - E_F}{kT} = x$,
$$f(E) = \frac{1}{1 + e^x}$$

As $f(E) = 10\% = 0.1$, we get $\frac{1}{1 + e^x} = 0.1$ or $x = 2.197$

$$\therefore \frac{E - E_F}{kT} = 2.197$$

or
$$T = \frac{E - E_F}{2.197 \times k} = \frac{0.055 \text{ eV}}{2.197 \times 8.61 \times 10^{-5} \text{ eV/K}} = \mathbf{290 \text{ K.}}$$

Example 29.6. Find the temperature at which there is 1% probability that a state with energy 2 eV is occupied. Given that Fermi energy is 1.5 eV.

Solution. The probability of an energy state E being occupied by an electron is given by

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

$$E - E_F = 2 \text{ eV} - 1.5 \text{ eV} = 0.5 \text{ eV} \quad \text{and} \quad f(E) = 1\%$$

$$\therefore \frac{1}{100} = \frac{1}{1 + e^{0.5/kT}} \quad \text{or} \quad e^{0.5/kT} = \frac{0.99}{0.01} = 99$$

Taking logarithm on both the sides, we get

$$\frac{0.5 \text{ eV}}{kT} = 2.303 \log 99$$

or
$$\frac{0.5 \text{ eV}}{kT} = T = \frac{0.5 \text{ eV}}{2.303 \log 99 \times 8.61 \times 10^{-5} \text{ eV/K}} = 1262 \text{ K.}$$

Example 29.7. Show that the probability of finding an electron of energy ΔE above the Fermi level is same as probability of not finding an electron at energy ΔE below the Fermi level.

OR

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

Solution. Let us consider an energy level E_2 that is above the Fermi level by an amount of energy ΔE . The probability that the energy level E_2 is occupied is given by

$$\begin{aligned} f(E_2) &= f(E_F + \Delta E) = \frac{1}{1 + \exp[(E_2 - E_F) / kT]} \\ &= \frac{1}{1 + \exp[(E_F + \Delta E - E_F) / kT]} \end{aligned}$$

$$\therefore f(E_2) = \frac{1}{1 + \exp(\Delta E / kT)} \quad (1)$$

Next, let us consider the energy level E_1 that is below the Fermi level by energy ΔE . $[1 - f(E_1)]$ gives the probability that the level E_1 is not occupied.

$$\begin{aligned}
 [1 - f(E_1)] &= [1 - f(E_F - \Delta E)] \\
 &= 1 - \frac{1}{1 + \exp[(E_F - \Delta E - E_F) / kT]} \\
 &= 1 - \frac{1}{1 + \exp[(-\Delta E) / kT]} \\
 &= \frac{\exp[(-\Delta E) / kT]}{1 + \exp[(-\Delta E) / kT]}
 \end{aligned}$$

$$\text{or} \quad [1 - f(E_1)] = \frac{1}{1 + \exp[(\Delta E) / kT]} \quad (2)$$

The R.H.S of equation (1) and (2) are the same.

$$\therefore f(E_2) = [1 - f(E_1)]$$

It means that the probability of an energy level $[E_F + \Delta E]$ (ΔE above the Fermi level) being occupied is the same as the probability of an energy level $[E_F - \Delta E]$ (ΔE below E_F), being vacant.

Example 29.8. Show that the occupancy probabilities of two states whose energies are equally spaced above and below the Fermi energy add up to one.

Solution. Let us consider two energy levels E_2 and E_1 , which are equally spaced above and below the Fermi energy E_F .

$$\text{Let} \quad \begin{aligned} E_2 &= E_F + \Delta E & \text{and} \\ E_1 &= E_F - \Delta E \end{aligned}$$

The probability of occupancy of the level E_2 is given by

$$\begin{aligned}
 F(E_2) &= F(E_F + \Delta E) = \frac{1}{1 + \exp[(E_2 - E_F) / kT]} \\
 &= \frac{1}{1 + \exp[(E_F + \Delta E - E_F) / kT]}
 \end{aligned}$$

$$\therefore F(E_2) = \frac{1}{1 + \exp(\Delta E / kT)}$$

The probability of occupancy of the level E_1 is given by

$$f(E_1) = f(E_F - \Delta E) = \frac{1}{1 + \exp[(E_F - \Delta E - E_F) / kT]}$$

$$\text{or} \quad f(E_1) = \frac{1}{1 + \exp[-\Delta E / kT]}$$

$$\begin{aligned}
 \therefore f(E_1) + f(E_2) &= \frac{1}{1 + \exp(\Delta E / kT)} + \frac{1}{1 + \exp(-\Delta E / kT)} \\
 &= \frac{1}{1 + \exp(\Delta E / kT)} + \frac{\exp(\Delta E / kT)}{1 + \exp(\Delta E / kT)} \\
 &= \frac{1 + \exp(\Delta E / kT)}{1 + \exp(\Delta E / kT)}
 \end{aligned}$$

$$\therefore f(E_1) + f(E_2) = 1$$

Thus, the occupancy probabilities of two states whose energies are equally spaced above and below the Fermi energy add up to one.

29.10 ENERGY BAND STRUCTURE OF AN INSULATOR

Insulators are characterized by two energy bands – conduction band and valence band, separated by a large energy gap. At 0K all valence electrons are engaged in covalent bonds, the valence band is full. The absence of mobile charge carriers keeps the conduction band vacant. The situation is same even at higher temperatures (300K), as the valence band and conduction bands are separated by a large gap (> 3 eV) and it is not possible to excite electrons from valence band to conduction band by thermal energy ($kT \cong 0.026$ eV). Consequently, insulators do not allow flow of current even at temperatures higher than room temperature.

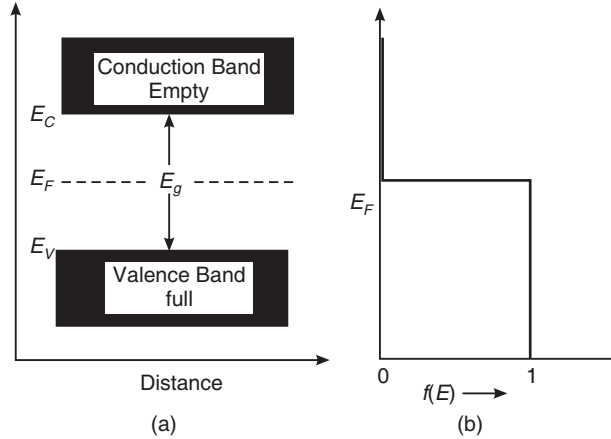


Fig. 29.17

The concept of Fermi level can be extended to insulators also. As the energy levels in valence band are filled, $f(E)$ is equal to unity throughout the valence band. As there are no electrons in the conduction band, $f(E)$ is equal to zero throughout the conduction band. Since the Fermi function is symmetrical about E_F , the Fermi level may be expected to be situated in the middle of the energy gap. Even though there are no energy levels and no electrons in the band gap, the meaning of Fermi level remains the same. It is a *reference energy position*. The energy band diagram for an insulator is shown in Fig. 29.17 along with probability function.

29.11 ENERGY BAND STRUCTURE OF A SEMICONDUCTOR

A semiconductor is characterized by two energy bands – conduction band and valence band separated by a smaller energy gap. At normal temperatures, a significant number of electrons are thermally excited from valence band to conduction band. An equal number of vacancies are produced in the valence band. These vacancies are treated as particles having a mass equal to that of electron and carry positive charge. They are called **holes**.

The Fermi-Dirac distribution function is applicable to a semiconductor. Fig. 29.18 depicts the probability function plotted alongside the band diagram for a semiconductor. Because the probability of electron occupancy of the conduction

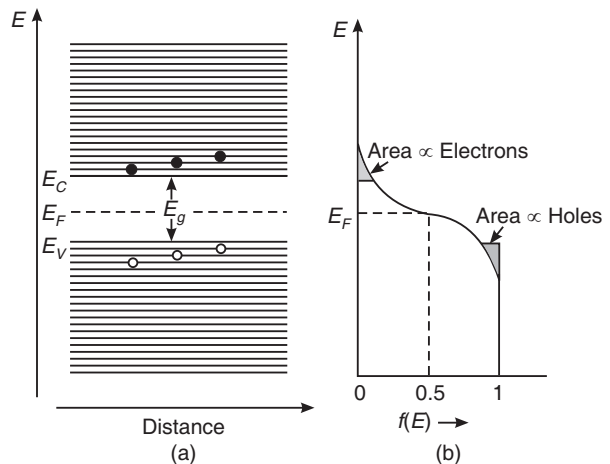


Fig. 29.18

band increases at temperatures greater than 0K, the probability function is blurred and tapers off towards higher energy in the conduction band. Similarly, the probability of hole occupancy of the valence band increases, and the probability curve is blurred near the top edge of the valence band. The extent of blurring of probability curve in both the bands is equal indicating that the concentration of electrons in the conduction band and that of holes in the valence band are equal. Secondly, the probability function $f(E)$ rapidly approaches zero value with increasing E . It suggests that the electrons in the conduction band are clustered very close to the bottom edge of the band. In a similar way, the holes are grouped very close to the top edge of the valence band. Therefore, it may be approximated that electrons are located right at the bottom edge of the conduction band whereas the holes are at the top edge of the valence band.

The Fermi level represents the average energy of charge carriers participating in conduction. Both electrons and holes participate in conduction in semiconductor and they lie in two different bands separated by a forbidden gap. Therefore, it is expected that the Fermi level lies in the middle of the forbidden gap. If the Fermi level is located elsewhere, it would mean that the number of electrons in the conduction band would be different from the number of holes in the valence band. It, in turn, would imply that the material does not exhibit overall neutrality which is not at all true.

29.12 EFFECTIVE MASS

We generally assume that the mass of an electron in a solid is the same as the mass of a free electron. However, experimentally measured values indicate that in some solids the electron mass is larger while for others it is slightly smaller than the free electron mass. The experimentally determined electron mass is called the **effective mass m^*** . The cause

for the deviation of the effective mass from the free electron mass is due to the interactions between the drifting electrons and the atoms in a solid. It has been found that the effective mass is inversely proportional to the curvature of an allowed energy band. It means that the effective mass depends on the location of an electron in the allowed energy band (Fig. 29.19). Considering the electron as a wave packet having a group velocity, v_g , an expression for the effective mass is derived as

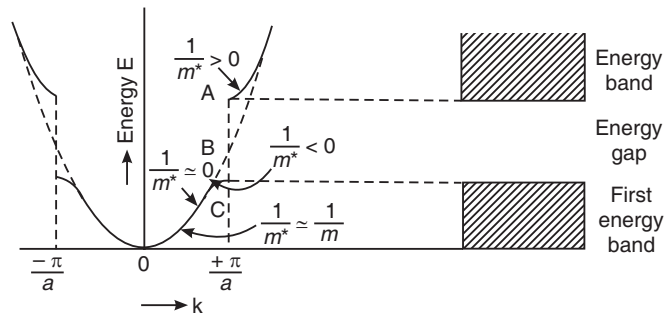


Fig. 29.19. The effective mass of electron in a solid depends on electron's location in the band.

- (i) Near the bottom of the band, the form of the $E - k$ curve does not differ much from the curve for free electron. Therefore, in these regions $m^* \approx m$.
- (ii) At the point of inflection B, the derivative $d^2E/dk^2 = 0$. Therefore, in these regions $m^* \approx \infty$. It means that an external field cannot exert any action on the motion of the electron in the region.

$$m^* = \frac{\hbar^2}{d^2E/dk^2} \quad (29.10)$$

- (iii) Near the top of the allowed band, C the derivative $d^2E/dk^2 < 0$. Therefore, the effective mass m^* of the electrons occupying levels near the top of the band is negative.

The concept of effective mass provides a satisfactory description of the charge carriers in crystals. In crystals such as alkali metals, which have partially filled energy band, the conduction takes place mainly through electrons. However, in crystals for which the energy band is nearly full, the negative charge and negative mass vacancies may be considered as positive charge and positive mass particles called *holes*. It explains the origin of positive Hall coefficient in certain metals such as zinc.

QUESTIONS

1. Define energy level and energy band. Explain with proper diagrams, how on the basis of band theory, solids are classified as conductors, insulators and semiconductors.
(C.S.V.T.U., 2005, 2007, 2009)
2. Describe the formation of energy bands in a crystalline solid.
Define valence band, conduction band and forbidden gap in the energy band structure.
Hence classify solids into conductors, semiconductors and insulators. (Bombay Univ.)
3. Explain formation of energy bands in solids on the basis of band theory of solids.
(R.T.M.N.U., 2007)
4. Explain the 'Kronig-Penny' model of solids and show that it leads to energy band structure of solids.
(RGPV, 2010)
5. (a) Discuss with suitable mathematical expressions, the motion of an electron in a periodic potential.
(b) Explain how the above theory leads to the concept of band structure of solids.
(c) What is effective mass of electron ? (JNTU, 2010)
6. Explain quantitatively band theory of solids. Explain energy band diagram and distinguish metal, semiconductor and insulator on the basis of above theory.
(RGPV, 2008)
7. Explain how solids are classified on the basis of energy band gap. (Calicut Univ., 2005)
8. Describe in short the formation of energy bands in solids and hence explain how it helps to classify the materials into conductors, semiconductors and insulators (with an example in each).
(C.S.V.T.U., 2008)
9. Explain how the materials are classified into conductors, semiconductors and insulators with the help of energy band diagrams. (G.T.U., 2009)
10. Explain the formation of energy bands in solids and briefly explain how solids are classified on the basis of energy band gap. (Calicut Univ., 2006)
11. According to band theory, a completely filled or empty band is not associated with electrical conduction. Only partially filled band is responsible for electrical conduction. Explain, why?
(R.T.M.N.U., 2007)
12. How does the band theory differ from the free electron model in explaining the properties of metals?
13. Explain energy band diagram of silicon showing a graph of variation of potential energy with distance. Explain semi-conducting nature of silicon. With similar band structure why is diamond insulator?
14. Draw a graph showing variation of electron energy in germanium crystals as a function of interatomic distance and explain why it shows semiconducting behaviour?

15. Draw a graph showing variation of electron energy levels of germanium as a function of its interatomic distance. Explain from it why germanium is an insulator at 0°K and semiconductor at 7°K. **(R.T.M.N.U., 2007)**
16. What is Fermi level and Fermi energy?
17. Explain Fermi energy function. How does it vary with temperature? **(RGPV, 2008)**
18. Write and explain Fermi function. Explain with the help of a diagram how it varies with change of temperature.
19. Write down the Fermi-Dirac equation for the probability of occupation of an energy level E by an electron. Show that the probability of its occupancy by an electron is zero if $E > E_F$ and unity if $E < E_F$ at temperature 0K.
20. Define Fermi distribution function. Show that at all temperatures ($T > 0K$) probability of occupancy of Fermi level is 50%.
21. What is Fermi function? Draw a graph showing its variation with energy at different temperatures and discuss it.
22. Write down Fermi distribution function $f(E)$. Show graphically and analytically that $f(E)$ as function of E always passes through a point $\left(E_F, \frac{1}{2}\right)$ at different temperatures.
23. Why is that only the electrons near the Fermi level contribute to electrical conductivity?
24. Explain the concept of hole. **(R.T.M.N.U., 2006)**
25. What is meant by effective mass of electron?
26. Explain the concept of negative mass on the basis of band theory.
27. Write down an expression for the probability of occupancy of a particular energy state of an electron in an intrinsic semiconductor. Represent it graphically at 0° K and at room temperature.
28. Explain in brief the concept of Fermi level. Show diagrammatically the Fermi level in metals, intrinsic semiconductors and insulators at 0° K and at higher temperature. **(R.T.M.N.U., 2006)**
29. How are the band structures of insulators and semiconductors similar? How are they different? **(R.T.M.N.U., 2006)**

PROBLEMS

1. In a solid, consider the energy level lying 0.01 eV above Fermi level. What is the probability of this level being *occupied* by an electron at 200 K? **[Ans: 0.359]**
2. In a solid, consider the energy level lying 0.01 eV below Fermi level. What is the probability of this level being occupied by an electron at 300 K? **[Ans: 0.595]**
3. In a solid, consider the energy level lying 0.01 eV above Fermi level. What is the probability of this level being *occupied* by an electron at 300 K? **[Ans: 0.405]**
4. In a solid, consider the energy level lying 0.01 eV above Fermi level. What is the probability of this level being *not occupied* by an electron at 300 K? **[Ans: 0.595]**