CHAPTER - II

AMORPHOUS SEMICONDUCTOR

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Considerable work has been done on elementary semiconductors and large data is available; but in compression to crystalline materials very little literature is available for amorphous semiconductors. In order to understand amorphous semiconductors, band models of amorphous semiconductors are understood on the basis of band theory of crystalline solids.

2.1 BAND THEORY OF SOLIDS :

In sommerfeld model, it is considered that the electrons are free and the potential inside the solid is constant; but in solids the electrons are not ideally free and the potential in which they move is not constant but periodic in nature. The wave function of the electrons can be represented by the well known Bloch function :

i.e. $$\Psi_k (r) = u_k (r) \; e^{ikr} \qquad \ldots (2.1)$$

where $U_k(r)$ is known as modifying factor and it has the periodicity of lattice.

$$U_k (r + R_j) = U_k(r)$$

The lattice is described in terms of the lattice vector R_j such that,

$$R_j = j_1 a_1 + j_2 a_2 + j_3 a_3 \qquad \ldots (2.2)$$

where j_i are integers and a_i are the edges of the unit cells.

function is also periodic in nature.

$$\text{i.e.} \quad \Psi_k (x + R) = \Psi_k (x) \qquad \ldots (2.3)$$

The electron is moving in a potential which itself is periodic in nature (Figure 2.1).

$$\text{i.e.} \; V (x + R) = V (x)$$

The translational order is represented through the periodicity of the crystal. The periodic boundary conditions require the propogation vector,

$$k = \frac{2\pi n}{Na}$$

where N is number of atoms in the crystal and a is lattice constant, n is an integer. The motion of particles in such a periodic structure gives us an idea about the existence of forbidden zones, at the k values given by

$$k = \pm \frac{\pi}{a}, \quad \pm \frac{2\pi}{a}, \quad \pm \frac{3\pi}{a} \qquad \ldots (2.4)$$

The energy is represented as function of k shown in Figure (2.2).

The energy band in solids can be understood by different models existing in standard solid state books. The reduced zone, E-k diagram, the first Brillouin zone between $\pm \frac{\pi}{a}$ gives an idea about motion of particles in solids. In the forbidden zone, k values are complex and imaginary and the existence of particles in forbidden zone is not allowed for a perfect structure. In the allowed zone the electrons are occupied according to Pauli-exclusion principle i.e.

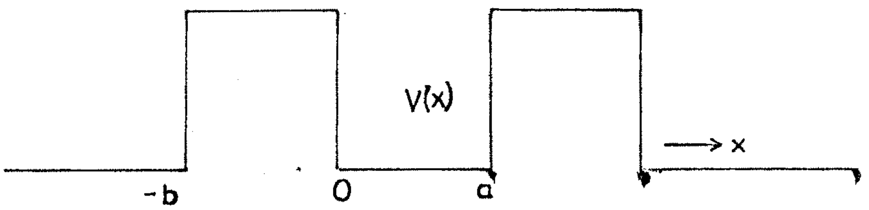


FIG. 2.1 Periodic nature of Potential

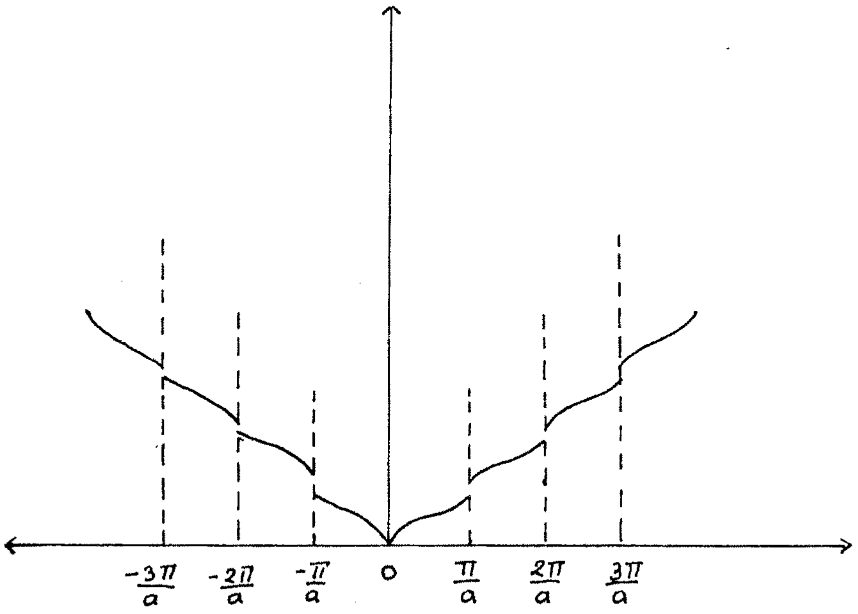


FIG. 2.2 'Modification of parabola rule" Brillowians zones.

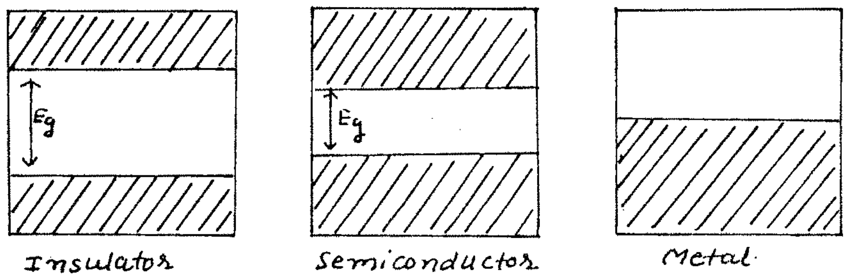


FIG. 2.3 Classification of solids.

two particles per state (with opposite spins). On the basis of this band approach, solids are divided into three groups, metals semiconductors and Insulators Figure (2.3).

2.2 SEMICONDUCTORS :

There are large number of materials which have resistivities lying between those of insulators (10^{14} to 10^{22} ohm cm) and conductors (10^{-6} ohm cm). Such material are known as semiconductors. Semiconductors have negative temperature coefficient of resistance i.e. conductivity of semiconductor increases rapidly with increase in temperature (Figure 2.4).

Semiconductor Germanium or Silicon, is having four valence electrons. When the two atoms of germanium are brought close to each other, the positive core of one atom interacts with one of the valence electrons of the other atom. Each core will attract the electrons of the other atom and the two electrons will be shared betweeen two atoms (Figure 2.5). Equilibrium state will reach when the attractive force is balanced by the repulsive force, betweeen two positive cores and a covalent bond is thus formed.

At ordinary temperature, because of thermal energy, crystal lattice is in continuous random motion. As a result an individual electron of a covalent bond acquires sufficient energy even at room temperature to break the bond and becomes free. These electrons move freely in crystal. When an electric field is applied, this random motion experiences a drift towards the positive electrode representing the flow of current.

When electron is escaped from covalent bond to become free then empty space left behind is called a hole. When a hole is created it moves in the crystal in a random way in the same manner as do free electrons. In the presence of an external electric field, a steady drift towards the negative electrode is superimposed upon the random motion of these holes and this represents a current flow which is transported by the absence of electrons.

2.3 BAND STRUCTURE OF SEMICONDUCTORS :

When two similar atoms are brought close together, there is an interaction of coupling betweeen the orbits of their electrons that causes splitting of each individual energy level into two slightly different levels. In solid, there are large number of atoms which are very close together, therefore, the energy levels are produced, after splitting due to interaction or coupling betweeen orbits of different electrons.

Figure (2.6) shows energy band diagram of diamond lattice as function of atomic spacing, when the atomic spacing is sufficiently large, interaction between atoms is negligible

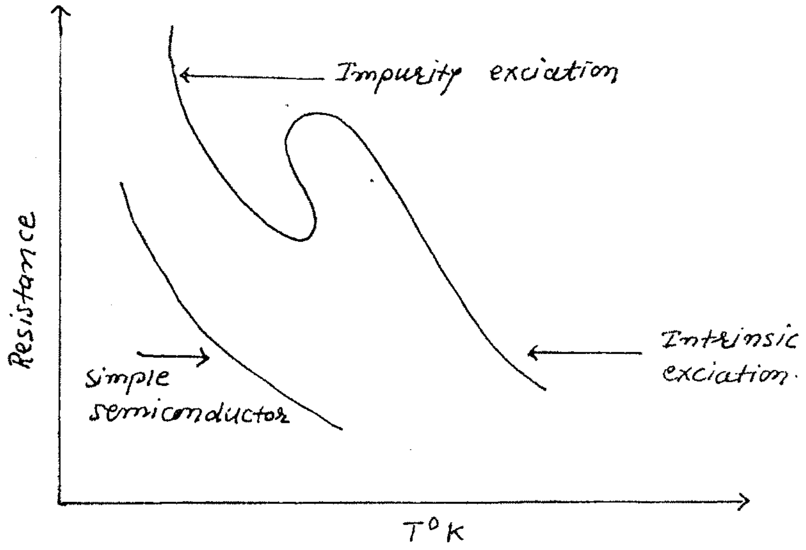


FIG-2.4 Resistance of semiconductor as function of temperature.

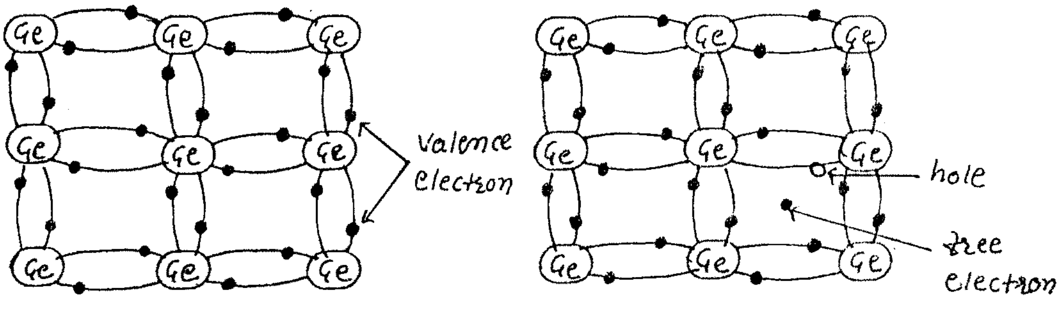


FIG-2.5 ⓐ covalent band in Ge ⓑ electron hole pair in Ge.

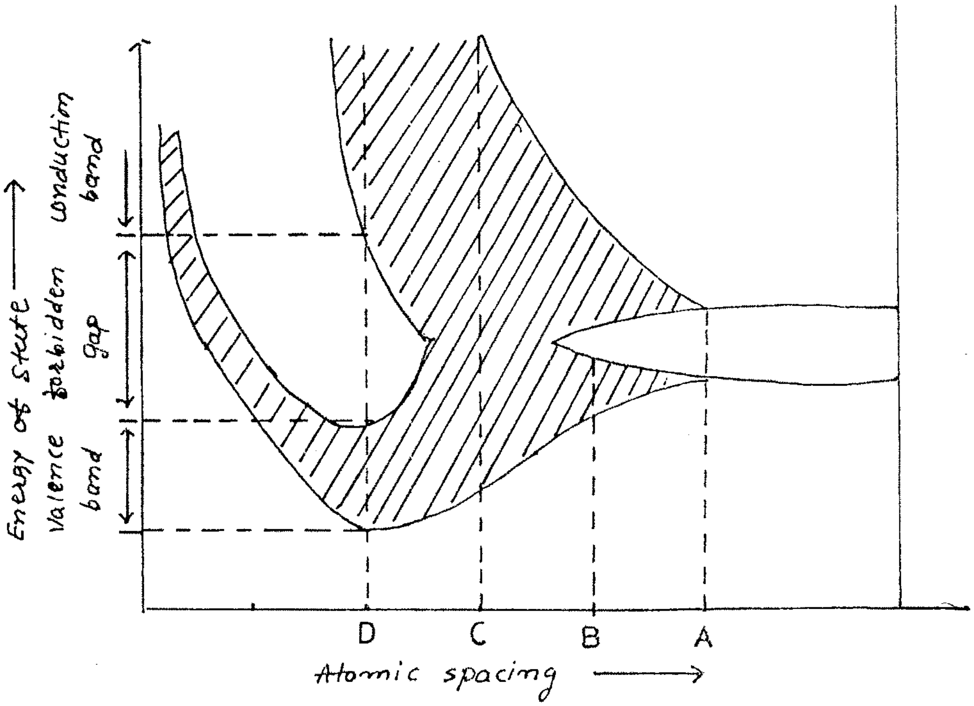


FIG-2.6 Energy band of lattice as function of atomic spacing.

and energy levels are those to be found in isolated atoms (position A). When atoms further come close to each other, their interaction increases and the two energy levels split into bands (position B). At position C, in figure the two bands overlap and when atomic spacing is further reduced (position D), the bands spread widely. The lower band is completely filled, is called valence band, where as the upper band is normally empty band, is called conduction band. The gap between these two bands is called forbidden zone, Eg. It is the minimum amount of energy that should be imparted to the electron in valence band to jump to conduction band.

2.4 TYPES OF SEMICONDUCTORS

2.4.1 INTRINSIC SEMICONDUCTOR :

When the conductivity in a crystalline semiconductor is due to breaking of covalent bonds, the substance is said to be an intrinsic semiconductor. The conductivity increases with increase in temperature. In case of germanium the forbidden energy gap is about 0.67 eV wide at 300 ^{o}K. At room temperature there is enough thermal energy to excite an appreciable number of electron-hole pairs. This process is called intrinsic excitation and the resultant conduction is called intrinsic conduction (Figure 2.7 a). The pure semiconductors are intrinsic semiconductors.

2.4.2 EXTRINSIC SEMICONDUCTOR :

Semiconductors in which impurities control the carrier density are called extrinsic semiconductors. The conductivity of crystalline materials could be changed by adding a very small amount of either a penta valent or tri-valent impurity. The process of adding impurity is known as doping. Semiconductors thus produced are called extrinsic semiconductors. Due to addition of impurity to any semi-conductor, one or more new energy level may appear in the band structure. The impurity may be termed as donor or acceptor depending upon the impurities contribute extra electrons or hole to the cause of conduction in the crystal. A crystal which has donors, is called as n type semiconductor (Figure 2.7b), because the charge carrier are negative and crystal with acceptor type impurity, is called p type semi-conductor, because the charge carrier are positive (Figure 2.7C).

2.5 FERMI LEVEL IN SEMICONDUCTOR :

In order to find out the total number of particles available in solid, one must know the density of states and the Fermi-Dirac distribution. The occupation number for electron is given by

$$f(E) = \frac{1}{\exp (E-E_F)/k_BT + 1} \qquad \ldots (2.5)$$

where E energy of electron = $\frac{\hbar^2 k^2}{2m^*}$

m* - effective mass of electron.

The density of state in conduction band is,

$$n_e = \int_0^{\infty} (\text{density of state}) \times (\text{occupation number}) dE$$

$$= \int_0^{\infty} N(E) \quad f(E) \; dE \qquad \ldots (2.6)$$

But

$$N(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} (E - E_g)^{1/2} \qquad \ldots (2.7)$$

Using equation (2.5) and (2.7) in equation (6) one can evaluate equation for Fermi energy,

$$E_F = \frac{E_g}{2} + \frac{3}{4} K_B T \ln \frac{m_h^*}{m_e^*} \qquad \ldots (2.8)$$

Equation (2.8) gives position of Fermi level in semiconductors. Fermi level is the energy of reference level at which the probability of filling is exactly half. The fermi level in semiconductor changes appreciably with change in impurity and concentration. The variation of fermi level with impurity concentration enables the operation of the various junction devices.

2.5.1. Intrinsic Semiconductor :

For intrinsic semiconductor , $m_h^* = m_e^*$. The concentration of electrons and holes is equal. Therefore from equation (8) we get,

$$E_F = \frac{E_g}{2} = \frac{E_c + E_v}{2} \quad \text{at } T = 0$$

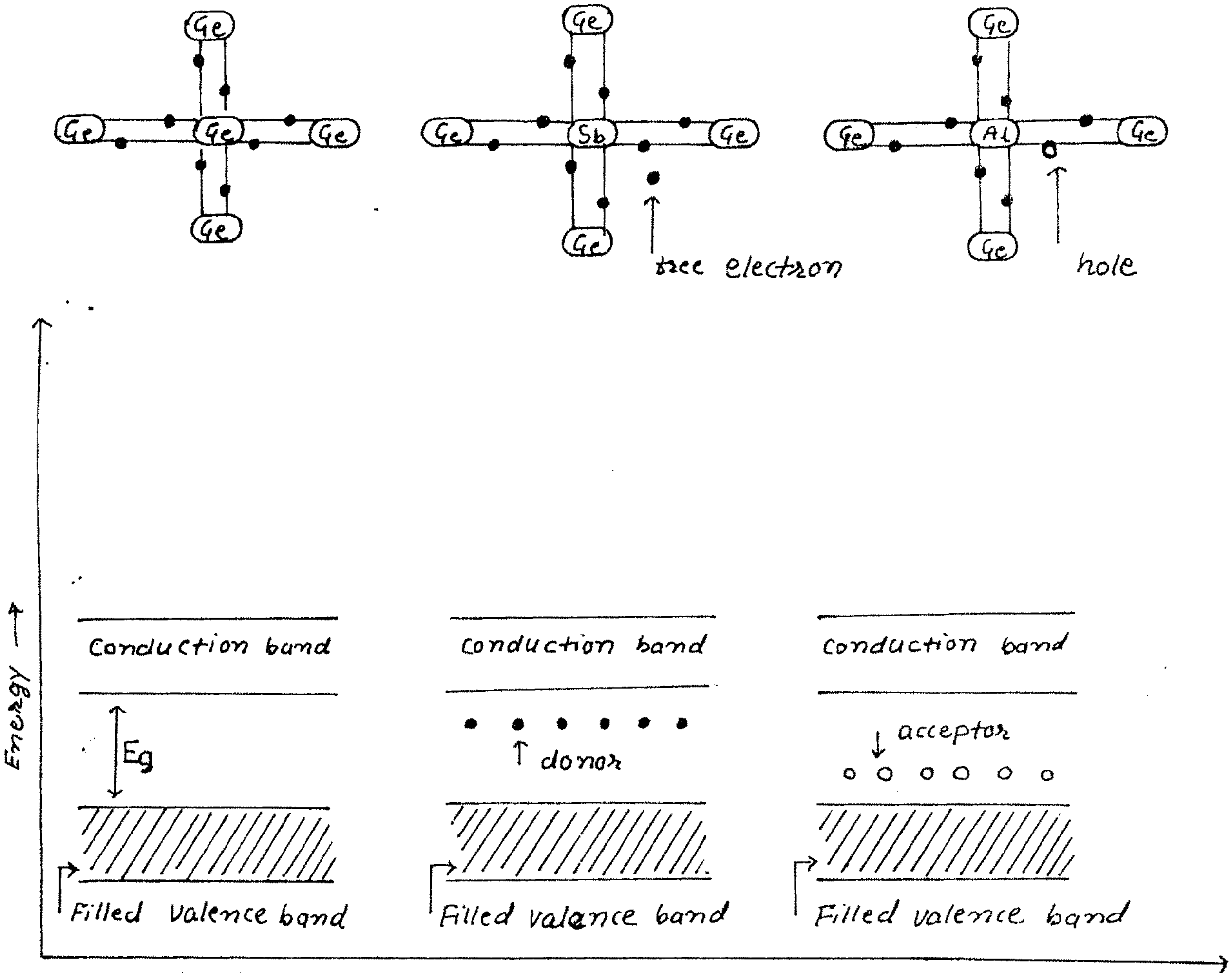
i.e. the fermi level lies exactly middle of the forbidden gap. In general m_h^* is slightly greater than m_e^*. The fermi level rises up as the temperature is increased; but for practical purpose, fermi level can be assumed to be constant for intrinsic semiconductor for a wide range of temperature (Figure 2.7 d).

2.5.2. n type semiconductor :

n type semiconductor consists of a conduction and below which there are donor levels of energy E_D. At absolute zero, the Fermi level lies midway between donor levels and bottom of the conduction band. As temperature increases the fermi level takes a very small initial rise upward after which it moves downward in the forbidden energy band. At high temperature, the Fermi level approaches the middle of the band gap which is the intrinsic position. As the crystal becomes more n type, the fermi level rises closer to the conduction band and may even go into conduction band, when doping becomes high as shown in Figure 2.8.

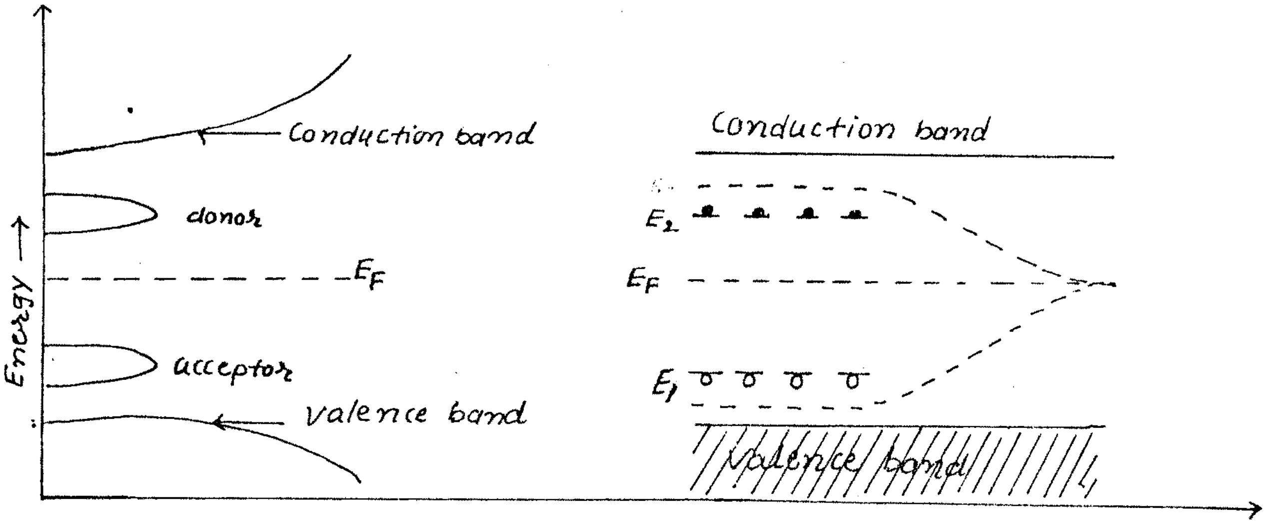
2.5.3. P type semiconductor :

At absolute Zero (T = 0), the Fermi level comes at $E_A/2$, midway between top of the valence band and acceptor level. As the temperature increases, the fermi level first



ⓐ Intrinsic semiconductor ⓑ n type semiconductor ⓒ p type semiconductor

FIG·2·7 Types of Semiconductors



FIG·2·7 ⓓ Position of Fermi level in intrinsic semiconductor lowers slightly and then it increases with increasing temperature. At high temperature the fermi level approaches to middle of the band gap which is intrinsic position. As crystal becomes more P type the fermi level comes closer to the valence band and may go even in the valence band when the doping level of acceptor impurities become very high (Figure 2.9).

2.6 AMROPHOUS SEMICONDUCTORS :

As stated earlier in crystalline solids, the atoms are stacked in a regular manner, forming a three dimensional pattern. When the periodicity of pattern extends through certain piece of material, one speaks of single crystal. In polycrystalline material the periodicity of structure is interrupted at grain boundaries. When the size of a grain becomes to size of pattern unit, then one speaks of amorphous substance.

Amorphous semicohductors are non-crystalline materials. They lack long range periodic ordering of their constituent atoms. Amorphous semiconductors do not consist of closed packed atoms but they contain covalently bounded atoms arranged in an open network. The Bloch function in existing form does not hold in amorphous materials. The disorder in amorphous semiconductor is as follows :

(1) Topological disorder - This is due to (a) Atoms are not

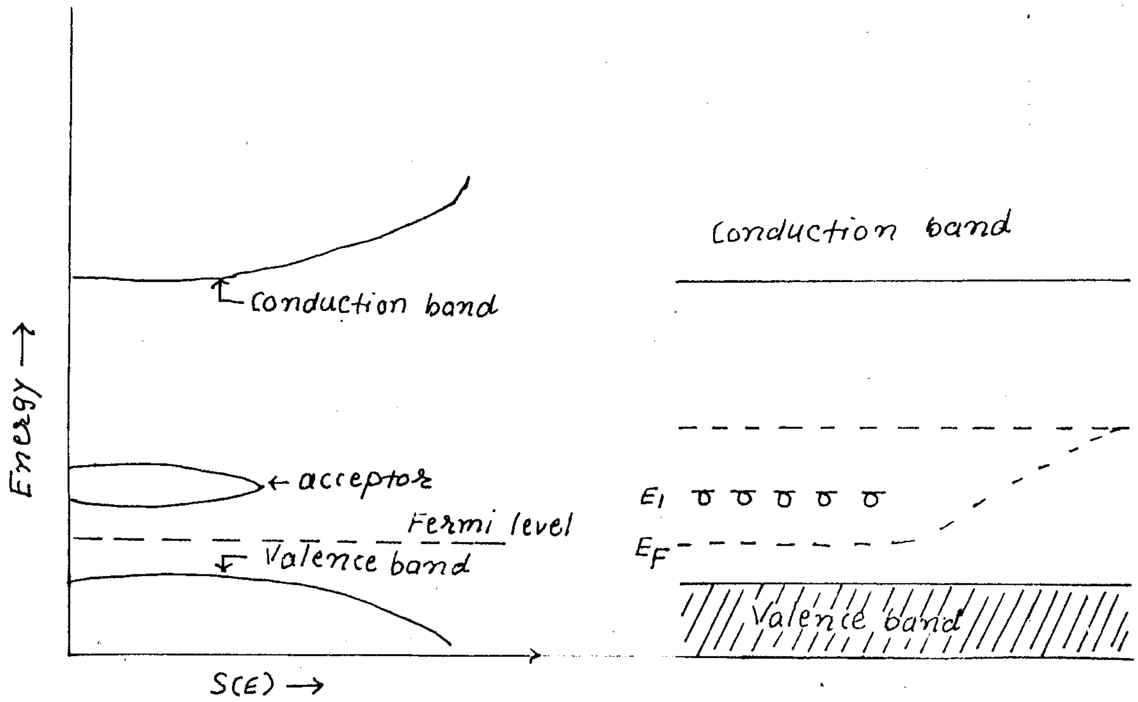


FIG. 2.8 Position of Fermi level in p type semiconductor

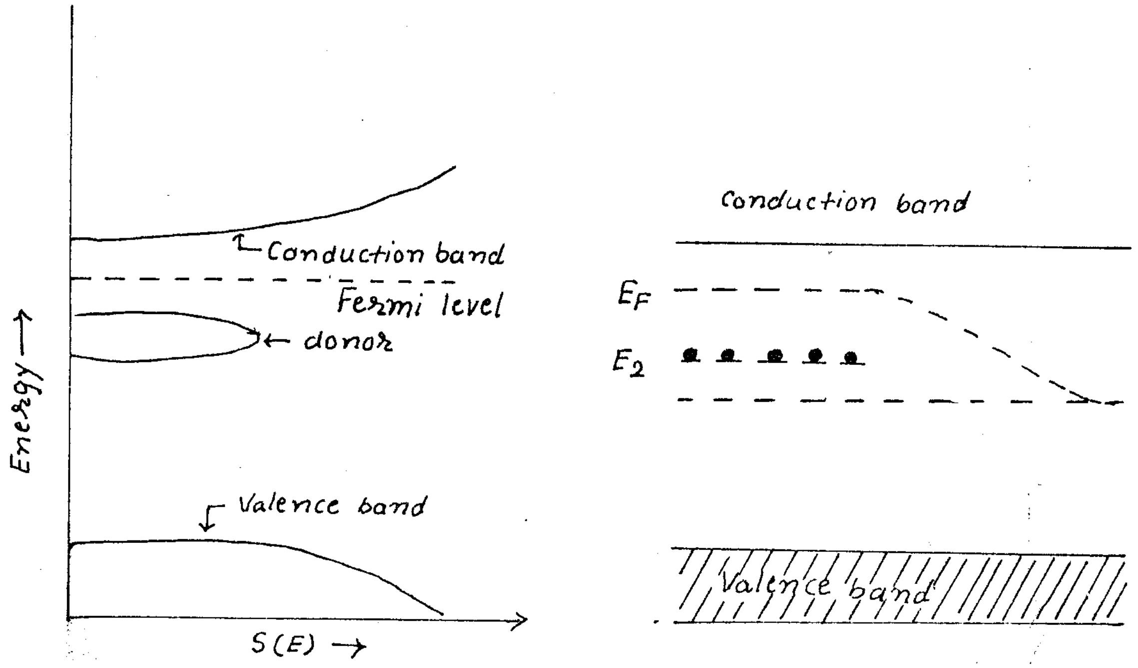


FIG. 2.9 Position of Fermi level in n type semiconductor

occupying regular sites (b). They are crowded at one place forming clusters (c) Planes are missing from the structure. It is heavily perturbed system and because of perturbation the potential fluctuations give rise to localized states.

(2) Translational disorder : The long range order is absent but short range order is responsible for observable properties. The potential in amorphous material is periodic for few atoms i.e. periodicity of potential is limited. The Bloch function in the existing form does not hold in amorphous material.

(3) Compositional disorder : The composition of elements in amorphous material may not be in the same ratio and it will give rise to localized states in forbidden zone. This may be considered on same line, when crystalline semiconductors are doped by different impurities.

The amorphous semiconductors include two classes - (1) Chalcogenide glasses (2) Oxide glasses. The chalcogenide glasses are materials like Se, As, Ge, Te, etc. They are semiconductors with forbidden gap that range from 1.5 to 2.5 eV. They are very good glass formers with transition temperature (T_g) in the range of $300^{o}K$ to $600^{o}K$, where as oxide glasses are made of oxides of group III, IV and V elements.

Scientific investigation of amorphous semiconductor was originated in the work of A.F. Ioffe and A.R.Regal[2.5].

Ioffe discussed the principle features of electronic structure of amorphous semiconductors. The band gap depends upon short range order than long range order. Anderson[2.6, 2.7] in 1958 showed that sufficient disorder could localize all states in an energy gap. In 1961, Mott and Towse[2.8] discussed one dimensional state.

In order to throw light on the nature of type of short range order, a radial distribution analysis of electron diffraction is important. The observed radial distribution function for an amorphous GeTe film is taken as an example. Figure (2.10) shows the radial distribution function of amorphous GeTe film. Not only the magnitude of order can be obtained from such a graph but also the bond length can be obtained since the location of peaks or maxima in radial distribution curves gives the sequence of characteristics bond length of specimen. The area under the peaks gives an average value of the number of atoms at radial distance r from some origin atom in the specimen. The width of peaks indicates some spread in the interatomic distance and the decreasing amplitude of the oscillations with r shows the lack of long range order.

Further discussion of the structure of amorphous semiconductors is obtained by X-ray diffraction studies. Structural models of amorphous solids can be constructed to give the best fit to the experimental radial distribution curves, together with any other conditions required by the nature of the bonds surrounding each atom. Structural changes in an amorphous solid, as a function of temperature, can be obtained from Differential thermal analysis.

A lot of interest has now diverted to the study of amorphous solids and is thus the subject of number of theoretical and experimental investigations. The main purpose of these investigations, is to -

(a) ascertain whether the amorphous structure is homogeneously random or microscopic crystalline in nature.

(b) compare structural characteristics (short range order and bonding nature) of amorphous and crystalline phases of the same materials.

(c) understand how the energy band diagram, the character of energy state and transition probability between states and transport processes are changed going from crystalline to the amorphous phase of the same material.

The answer to such questions are expected to be revealed by the study of structural, optical and electrical properties of suitably chosen semiconductors which exist in both the crystalline and amorphous states.

2.7 LOCALIZED STATES :

The concept of density of state is applicable equally to both crystalline and non-crystalline materials. The density of state is denoted by $N(E)$ and is defined so that $N(E)dE$ is the number of states in unit volume for an electron in the system with given spin direction and with energy E and $E + dE$. The number of electrons in the energy range dE for each spin direction is,

$$N\ (E)\ f(E)\ dE$$

where $f(E)$ the Fermi distribution function

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1} \qquad \ldots (2.9)$$

The Fermi energy E_F is function of temperature when the scattering of electron is weak, in which electrons are described by wave functions, each having a fairly well defined wave number k. The mean free path L is large and the uncertainty Δk in k is given by relation,

$$L\Delta k \sim 1, \text{ such that } \frac{\Delta k}{k} \sim\ll 1$$

In this case energy E of each electron is a parabolic function of k, so that

$$E = \frac{\hbar^2\ k^2}{2m} \qquad \ldots (2.10)$$

The density of states for the electrons is given for each spin direction by the free-electron formula,

$$N(E) = \frac{4\pi k^2}{8\pi^3}\left(\frac{dE}{dk}\right)$$

$$= \frac{km}{2\pi^2 h^2} \qquad \ldots (2.11)$$

The other possibility is that the interaction is strong so that $\frac{\Delta k}{k}$ 1. The mean free path is short ($kL \sim 1$) the states are localized as shown in figure (2.11).

The density of state N(E) that is continuous function of E remains a valid concept; but if $\frac{\Delta k}{k} \sim 1$ large deviations from the free electron form is possible. Some of these are shown in figure (2.11). We shall see that Figure (2.11(b),(c), (d)) all imply $\frac{\Delta k}{k} \sim 1$ (or localization) in the regions where the deviation of N(E) from the free electron value is large.

When mean free path is short, the elementary methods of quantum mechanics are used to deduce $\sigma(w)$, the conductivity at frequency w. At T = 0 and for states filled up to a fermi energy E, we denote the result of $\sigma_E (w)$. This is related to the absorption coefficient α by the equation,

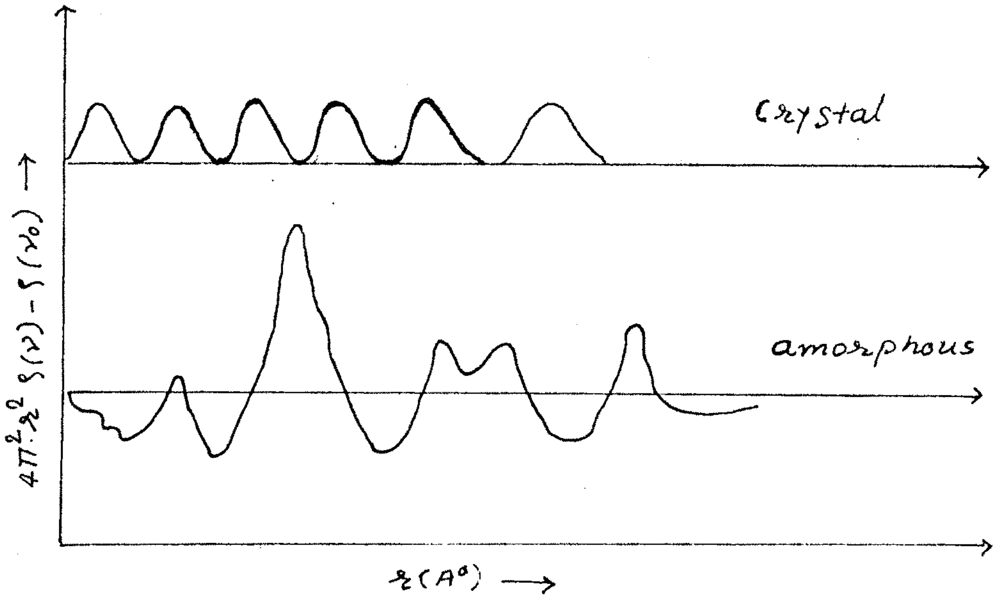
$$\alpha = \frac{4\pi\, \sigma_E (w)}{n_0} \qquad \ldots (2.12)$$

where n_0 is the real part of the refractive index.

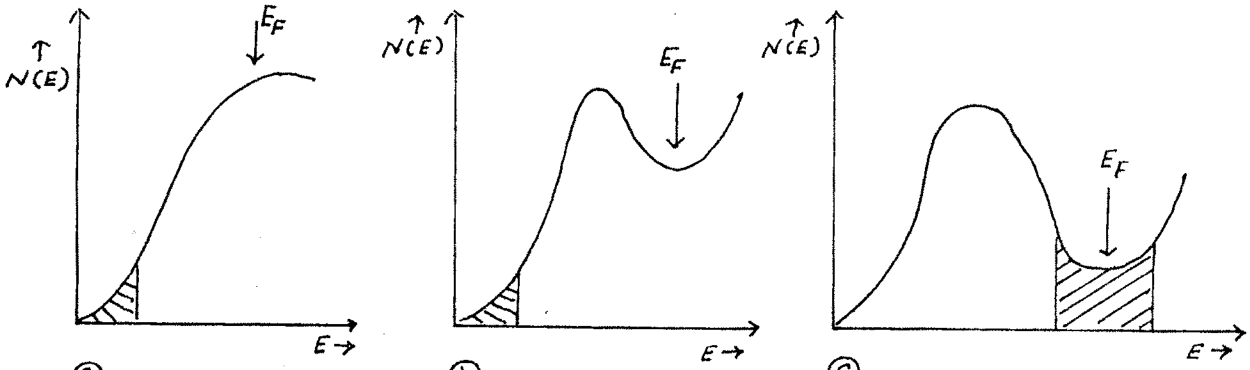
For the d.c. conductivity at zero temperature for a system with states filled upto an energy E, we get

$$\sigma_E (0) = \lim_{w \to 0} \sigma_E (w) \qquad \ldots (2.13)$$

This is called as the Kubo-Green formula[2.9].



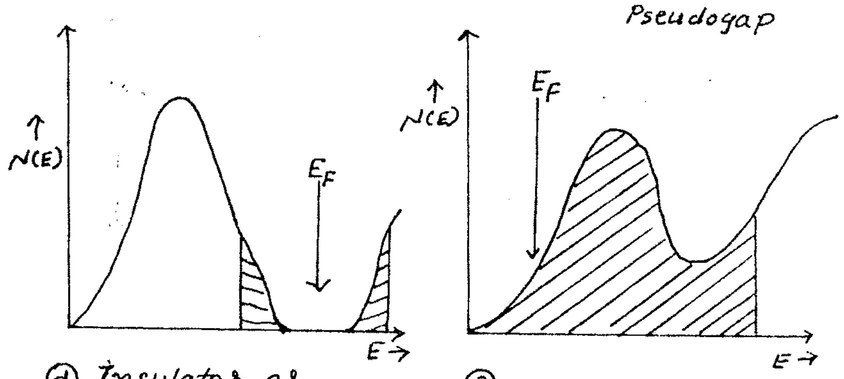
FIG·2·10 Typical radial distribution curve for Ge-Te



ⓐ Amorphous metal

ⓑ Semi metal

ⓒ Semi metal with deep Pseudogap



ⓓ Insulator or intrinsic Semiconductor

ⓔ Impurity band in heavy compensated n type semiconductor

FIG·2·11 Density of state in non crystalline material. E_F is Fermi energy at absolute zero temperature.

At low temperature, we may consider two cases (1) situations in which the conductivity is determined by the properties of electrons with energies near E_F. In this case, the range of energies may exist in which N(E) is finite but states are localized and mobility of electrons with such an energy is zero, at T = 0. The vanishing of σ_E (0) can surve as definition of localization for electrons with energy E.

(2) Situations where the mobility of electrons with energies near E_F is zero or small for non-localized state $\sigma_E(0)$ can then be interpreted as eN(E) kTμ. where μ is mobility of carriers with energy E. If the states are localized, mobility vanishes at T = 0. At finite temperature mobility is due to interaction with phonons and smaller than for non-localized state (extended). For any model of non-crystalline system, the states with energy E are localized if,

$$\langle \sigma_E (0) \rangle = 0 \qquad \ldots (2.14)$$

But for assembly of N atoms, a range of electrons energies may exist such that the number of configuration for which σ does not vanish tends to zero as $N \rightarrow \infty$. In other words σ tends to zero. Thus our defihition of localization is that, for a Fermi gas of non-interacting electrons with Fermi energy E,

$$\lim_{N \rightarrow \infty} \langle \sigma_E (0) \rangle = 0 \qquad \ldots (2.15)$$

2.8 ANDERSONS LOCALIZATION :

Our problem is to consider what happends to band of energies when the potential energy function is non-periodic. A non-periodic potential can be formed in two ways.

(1) By the displacement of each centre by a random amount, as for instance by lattice vibrations or by destroying the long range order.

(2) By addition of random potential energy $\frac{1}{2}U$ to each well in such a way that energy level W_o for electrons in the well is changed to $W_o + \frac{1}{2} U$

We write,

$$\langle U^2 \rangle = U_0^2 \qquad \text{... (2.16)}$$

where W_o - energy level for an electron in single well U_o - measures of disorder.

The resulting potential is shown in Figure (2.12b). This is called Anderson potential[2.6, 2.7]. If U_o is small and using golden rule,

$$\frac{1}{L} = \frac{2\pi}{\hbar} \left(\frac{1}{2} U_o \right)^2 \frac{a^3 N(E)}{u} \qquad \text{... (2.17)}$$

where u - velocity of electron, a^3 - atomic volume L - mean free path.

Using equation (2.11) for N(E) we may write,

$$\frac{1}{L} = 4\pi \left(\frac{m}{2\pi\hbar^2} \right)^2 a^3 \left(\frac{1}{2} U_o \right)^2 \qquad \text{... (2.18)}$$

m - mass of electron OR

$$\frac{a}{L} = \frac{(U_o/T)^2}{16\pi} \qquad \ldots (2.19)$$

where I is related to J by equation

$$J = 2\ ZT$$

J = band width, I - overlap integral

Z = coordination number.

In middle of band ka $\sim$ 1, a is minimum free path under this condition the wave function ψ will vary in random way from well to well (Figure 2.13a). The equation (2.19) suggest that the wave function is vary randomely, when U_o/I reaches the value 7.

Consider a pair of wells at distance R from each other with energies shifted from the mean amounts U_a, U_b. The two wave functions for a pair of electrons in these states are,

$$\psi_1 = A\phi_a + B\phi_b$$

$$\psi_2 = B\phi_a - A\phi_b$$

where ϕ_a - overlap between atomic wave functions of well a
ϕ_b - ,, ,, ,, ,, ,, ,, b

We consider following limiting cases

(1) If $|U_a - U_b| \ll I$, then $A \sim B$ and $E_1 - E_2 \simeq 2I$

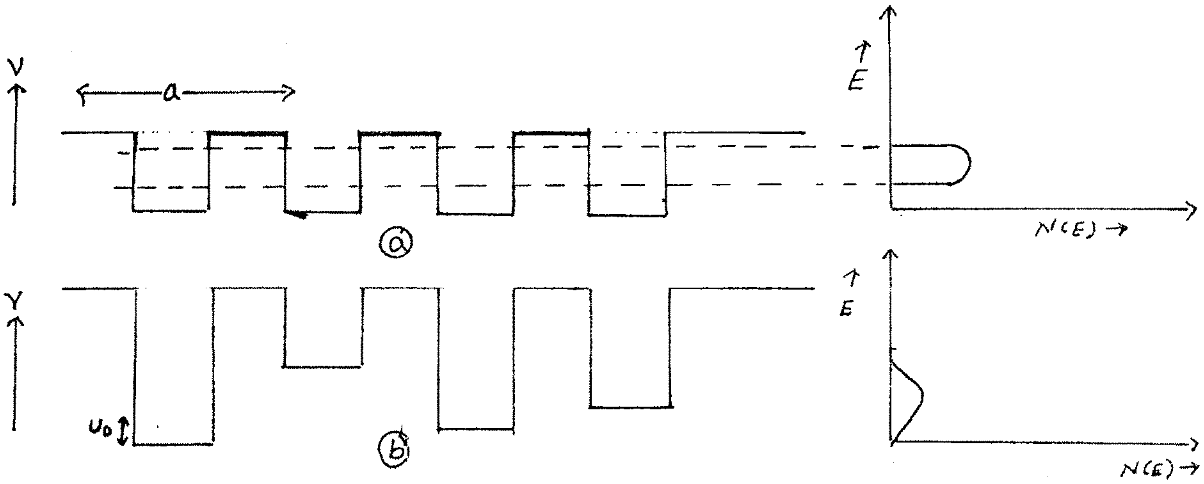
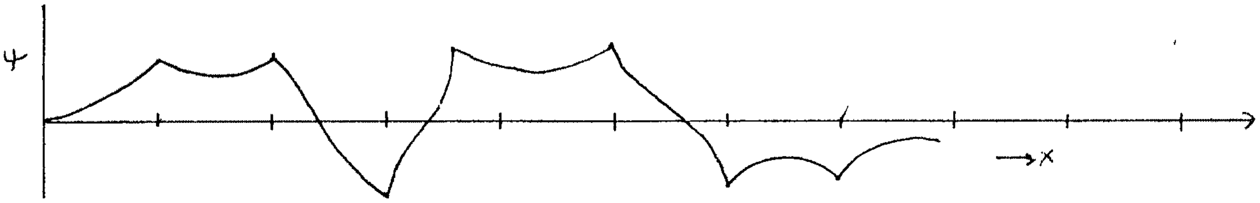
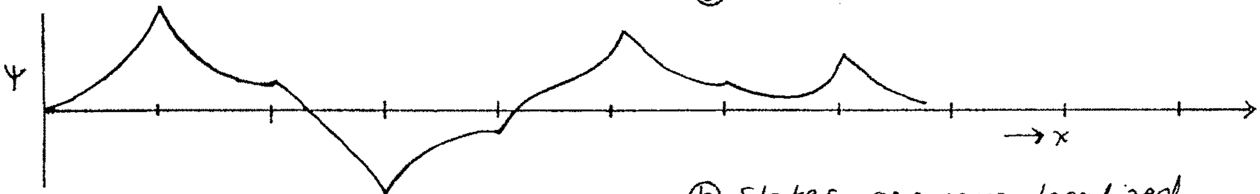


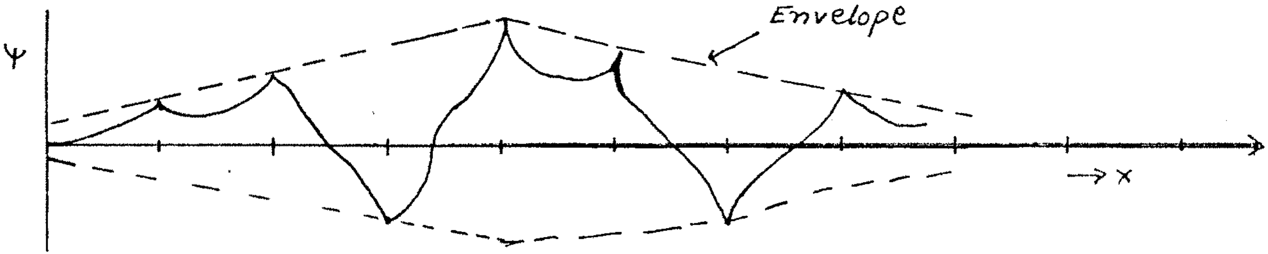
FIG. 2.12 ⓐ Potential wells for crystalline lattice
ⓑ potential wells for Anderson lattice.



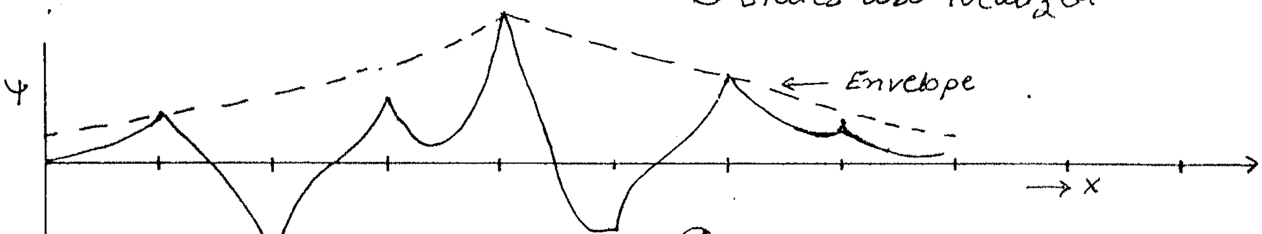
ⓐ L ~ a



ⓑ States are non localized



ⓒ States are localized



ⓓ strong localization

FIG. 2.13 Wave function in Anderson model

It can not be less than 2I.

(2) If $U_a - U_b \gg I$ the $\frac{A}{B} \simeq \frac{U_a - U_b}{2I}$ ... (2.20)

The wave functions for the two cases and also plot of $E_1 - E_2$ as function of $|U_a - U_b|$ are shown in Figure (2.14).

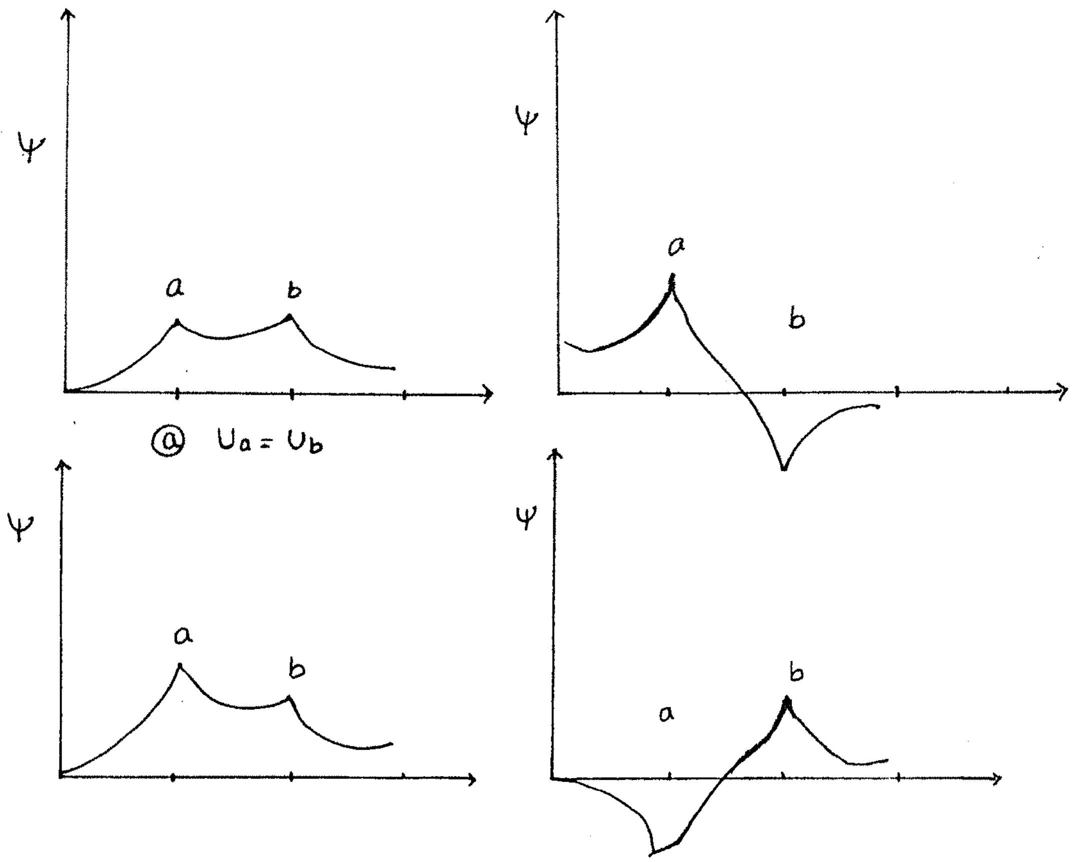
If we consider infinite array of wells, there will be random fluctuations of amplitude of wave function ψ in going from well to well. If U_o/J increases, these fluctuations get larger (Figure 2.13b). However if U_o/J is very large, the wave function of each well would be little perturbed by all other wells and so would fall exponentially with distance. This is shown in Figure (2.13 (c) (d)).

Anderson find that there is no diffusion if U_o/J is greater than a constant that depends upon coordination number z = 6. This means that $U_o/J > 5$. All the wave functions for an electron in system are shown in Figure (2.13(c)) decaying exponentially with distance r from some well n. The initial state of the wave function is of the form,

$$\sum a_m \Psi_m$$

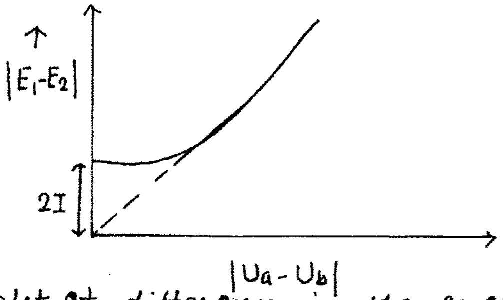
The coefficient a_m will fall exponentially with distance between wells m and n.

The critical value of U_o/J depends upon coordination number Z. The Andersons plot of $U_o/2I$ is shown in figure (2.15). U_o/J has the value ~ 5 for Z = 6.



ⓐ $U_a = U_b$

ⓑ $U_a < U_b$ and $U_b - U_a >> 2I$



ⓒ plot of difference in the energies of the two states.

FIG-2.14 wave function of even parity for pair of wells.

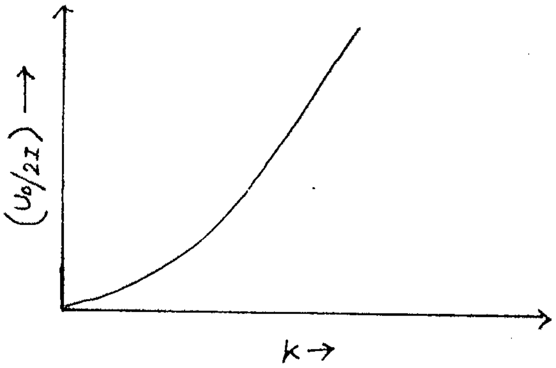


FIG. 2.15 Critical value of $U_0/2I$ taken for Anderson

Some more recent work of Anderson localization has concentrated on the quantity $\sigma(0)$. If there is no diffusion, the conductivity σ must vanish for all energies in the band i.e. $\langle u^2 \rangle = U_o^2$
when U is small , o does not vanish.
For finite number of wells, $\langle \sigma \rangle$ tends to zero exponentially for large N. This problem was investigated by Mott$^{2.10}$.
This method is used to evaluate the conductivity at frequency w , $\sigma(w)$ and to show that for all configurations except a proportion that gives a vanishing contribution as $\sigma \to \infty$, $\langle \sigma (w) \rangle$ behave like w^2 for small w $\langle \sigma(0) \rangle$ therefore vanishes.

2.8.1 Situations in which state are localized in one range of energies and not localized in another : In this case a critical energy E_c must separate the two regions, as follows

$$\langle \sigma_E \ (0) \rangle = 0 \quad E < E_c \qquad \ldots (2.21)$$

$$\neq 0 \quad E > E_c$$

This is shown for density of state resulting from the Anderson potential in Figure (2.16).

Mott (1970)$^{2.10}$ has suggested that for values of E, slightly less than E_c, the wave function is as shown in Figure (2.13c), for such a wave function each localized orbital will overlap many others. If the states are localized, an electron can move only by hopping from one state to another exchanging energy with a phonon in the process. If the overlap of orbitals is small, so the hopping probability should be small. On the other hand, the electron can tunnel i.e. AS E -- E_c from below the activation energy W, hopping tends to zero (Figure 2.17 b).

For E greater than E_c, the wave function should be as shown in figure (2.13(b), we call such a wave function extended, the value of $\langle \sigma (0) \rangle$ is finite. There will be therefore discontinuity in $\langle \sigma_E (0) \rangle$ at $E = E_c$ as shown in figure 2.17 (a). There will be no discontinuities in $\sigma (w)$ at finite value of T.

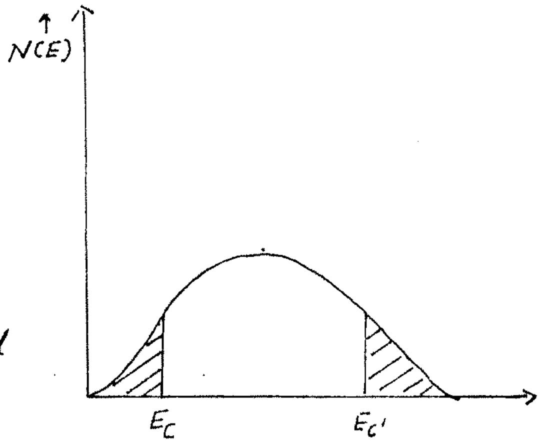
2.9 DENSITY OF STATES :

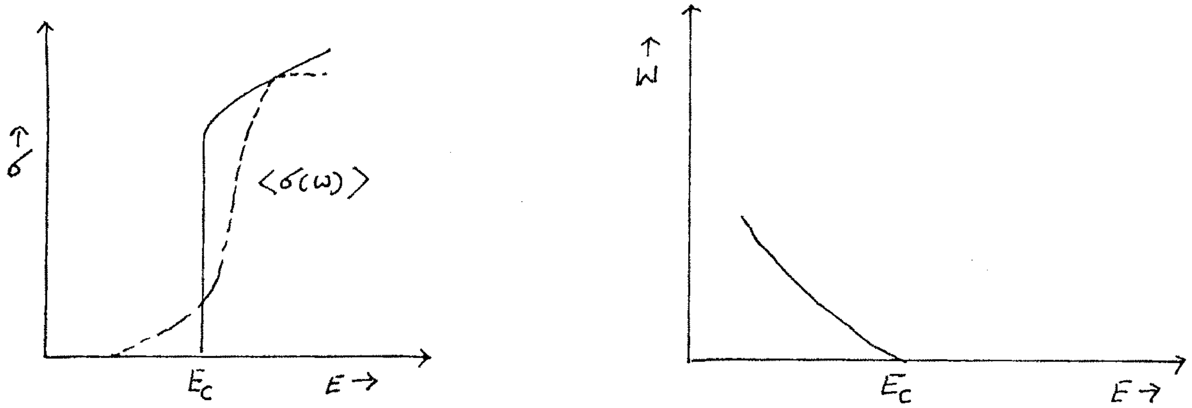
In the Bloch theory of crystalline solids the allowed energies for an electron are divided into bands. In insulators and semiconductors, valence and conduction bands do not overlap. There is a band of forbidden gap in which density of states is zero and Fermi level lies between this gap. For semi-metal there is small overlap and density of state can be low at the fermi energy as shown in Figure (2.18).

The density of state in non-crystalline material is determined by the actual potential of the atom and its nearest neighbour. When the tails of conduction and valence band overlap, the density of state show a minimum which we call a pseudogap as shown in Figure (2.19). For an amorphous material gap must appear, if there is no dangling bonds.

FIG·2·16

Density of state in the Anderson model when states are non localized in centre of band. localized states are shown shaded. E_c & E_c' represent the ranges of energy where states are localized and non localized.





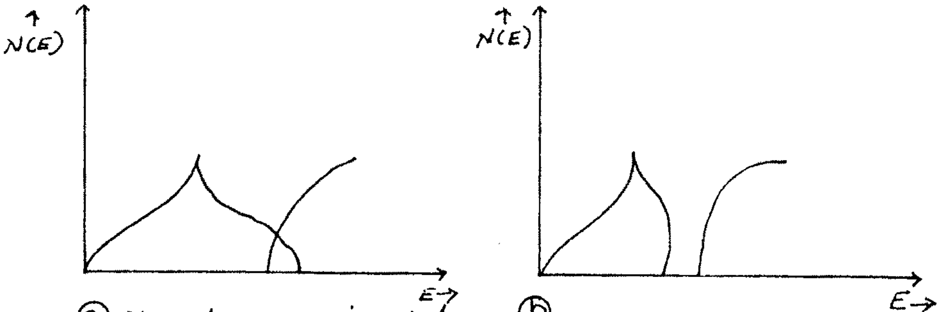
FIG· 2·17

ⓐ The conductivity $\langle \sigma_E(0)\rangle$ as function of E when $T=0$ in Anderson model.

ⓑ The hopping activation energy 'w' as function of E. dotted lines show $\langle\sigma(\omega)\rangle$ for small (ω) OR $\langle\sigma(0)\rangle$ for Small T

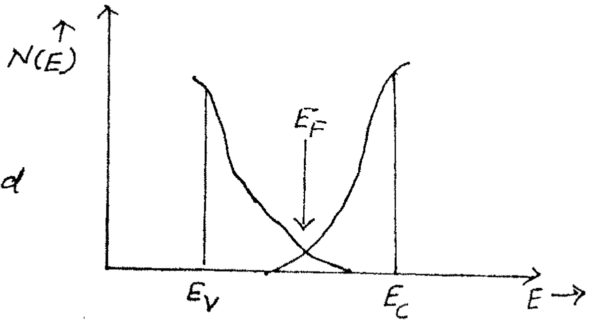
FIG·2·18

Density of State in divalent crystalline material



ⓐ Metal or semimetal with overlapping bands

ⓑ Semiconductor



FIG·2·19

Density of state in valence and conduction band of an amorphous non metal with overlapping tails

If pseudogap is deep enough, the states are localized. So the material is non-conducting at T = 0,
If N (E_F) is not zero, we define factor g by,

$$g = \frac{N(E_F)}{N(E_F)_{free}} \qquad \ldots (2.22)$$

then for localization g is order of 0.3. We thus have three possibilities if E_F lies in pseudogap.

(a) $g > 0.3$, the behaviour is metallic, σ tends to finite value as $T \rightarrow 0$

(b) $g < 0.3$, but not too small conduction at low temperature is then by thermally activated hopping but at higher temperature carriers will be excited to non-localized states.

(c) g is small or zero, the tunneling factor between localized states will make thermally activated hopping. The current is carried by electrons excited into conduction band.

2.10 MOBILITY SHOULDER :

We now consider the case when $\langle \sigma_E \rangle$ is negligible at $E = E_F$ and current is carried by electrons excited into conduction band. Let us consider the contribution made by carriers with extended wave functions. The contribution to the conductivity is given by equation

$$\sigma = - \int \langle \sigma_E (0) \rangle \frac{\partial f}{\partial E} \, dE \qquad \ldots (2.23)$$

Since for a semiconductor,

$f = e^{-(E-E_F)/kT}$, this gives,

$$\sigma = \sigma_o \exp\left[-(E_c - E_F)/kT\right] \qquad \ldots (2.24)$$

where $\sigma_o = \langle \sigma(0) \rangle_{E} = E_c$

σ_o is order of 350 Ω^{-1} cm^{-1} for Z = 6. The mobility can be deduced only if $N(E_c)$ is known. Since the number of electrons with energies above E_c is,

$$N(E_c)KT \exp\left[-(E_c - E_F)/kT\right]$$

The mobility μ_{ext} at E_c is,

$$\langle \sigma (0) \rangle /eN(E)\ kT_{\,E=E_c} \qquad \ldots (2.25)$$

If band width $B = \frac{h^2}{mR^2}$ and $N(E_c) = \frac{0.2}{R^3B}$

then we find $\mu_{ext} = \frac{0.3eh}{mKT} \sim 12\ cm^2\ V^{-1}\ S^{-1}$ ... (2.26)

at room temperature. This formula enables us to write the mobility in the form of diffusive motion.

$$\mu_{ext} = \frac{1}{6}\, e\ \nu_{el}\ \frac{R^2}{kT} \qquad \ldots (2.27)$$

where ν_{el} - electronic frequency, R - jump distance

$$\nu_{el} \quad \frac{e\hbar^2}{mR^3} \sim 3 \times 10^{15}\ 5^{-1}$$

For $E \lesssim E_c$ conduction will be by hopping and given by equation

$$\mu_{hop} = \frac{1}{6} \nu_{ph} \left(\frac{eR^2}{kT} \right) \exp \left(- \frac{W}{kT} \right) \qquad \ldots (2.28)$$

where ν_{ph} is the phonon frequency.

Near E_c we may assume $W \ll kT$. Thus drop in the mobility by a factor $\sim 10^3$ is expected as the energy E goes through the value E_c. This drop in the mobility has been called the mobility shoulder and was first described by Cohen[2.11]. It must also be assumed that the carriers are excited to mobility shoulder of Figure (2.20).

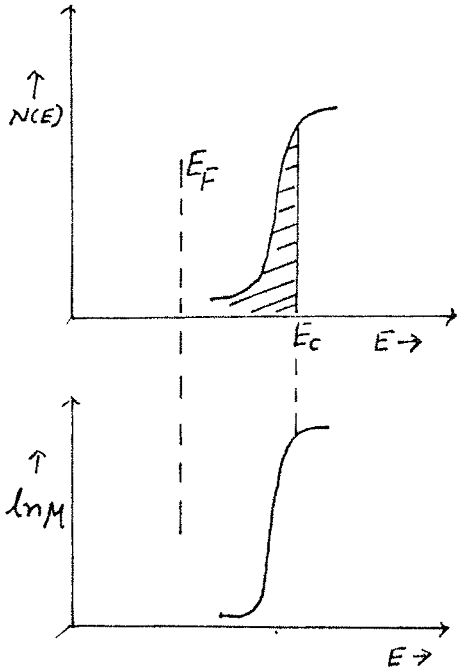
2.11 DEFECT MODEL :

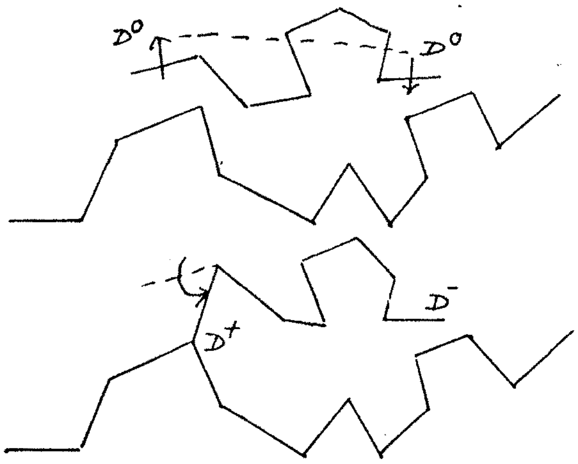
The model will be illustrated with reference to selenium consider two dangling bands at the end of selenium chain as shown in Figure 2.21 (a). When they contain single electron the defects are neutral and will be designated D^o. Transfer of an electron from one chain to other will lead to the creation of two charged defects D^+ and D^-.It is proposed that the reaction $2D^o \rightarrow D^+ + D^-$ is exothermic. ... (2.29)

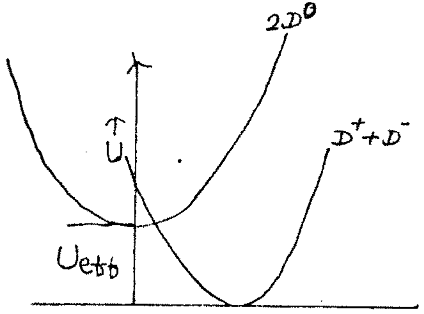
From Figure (2.21 (b)) the positive correlation energy U associated with the two electrons at D^- in the absence of configurational changes become negative (U_{eff}) after lattice relaxation. The chemical reason for the exothermic nature of the reaction is that, at D^+ an extra bond with neighbouring

FIG·2·20

Mobility Shoulder showing the rapid drop of mobility as E drops below E_c







FIG·2·21

ⓐ The transfer of the electron from one chain end to another creating two charged defects D^- and D^+.

ⓑ The same reaction on a configurational coordinate diagram. The positive correlation energy U is associated with two electrons at one site is turned in to an effective negative correlation energy U_{eff} becuase of the configurational changes.

chain can be formed by utilizing the normally non-bonding lone-pair electrons. The coordination of Se atoms at D^+ is therefore three, in contrast to that at D^- where it is one and at a normally bonded Se atom where it is two. Mott, Davis and Street[2.12] proposed that the lattice distortion at D^- is negligible, at D^+ it is considerable, at D^o it is intermediate. In a chemical band description of these defects given by Kastner et al.[2.13,2.14], the charged states of the defect are designated C_1^- and C_3^+, 'C' standing for chalcogenide and the subscript indicating the atomic coordination. The neutral centre is labelled by C_3^o.

The structure and energies of several simple bonding configurations for chalcogen is shown in Figure (2.22). The normal bonding configuration is C_2^o , the straight lines represent bonds (σ states) and dots the lone pair (LP). In this configuration the antibonding (σ^*) states are empty and energy relative to the lone pair is $-2E_b$ as shown. Antibonding states are pushed up from lone pair energy more than bonding states are pushed down. Thus the next configuration C_3^o - a neutral three-fold coordinated atom with extra electron placed in the bonding orbital has higher energy than C_2^o by amount Δ. The C_3^+ with energy of $-3E_b$ is defect having the lowest energy. The energy of C_3^- is $- E_b + 2\Delta + U_{\sigma^*}$ the positive correlation energy term U_{σ^*} arising because two electrons are in indistinguishable from the two lone pair electrons at the site and so energy of this defect is $-E_b$, finally a negative charged dangling bond C_1^- has four valence electrons in the lone pair state, its energy is $- E_b + UL_p$, the second ferm arising from the correlation energy in this level. The reaction corresponding to 2.29 in Kastner's notation is,

$$2C_3^o \rightarrow C_3^+ + C_1^- \qquad \ldots (2.30)$$

which can be seen to be exothermic if,

$$-4E_b + 2\Delta > - 3E_b - E_b + U_{LP}$$

i.e. if $2\Delta - U_{LP} > U$

The charged defect C_3^+ and C_1^- in equation (2.30) have been called valence alternation pair (VAP). Their creation starting from a fully bonded network in which all atoms are in the C_3^o configuration can be described by,

$$2C_2^o \rightarrow C_3^+ + C_1^- \qquad \ldots (2.31)$$

which costs an energy

$$-3E_b - E_b + U_{LP} + 4E_b = U_{LP} \qquad \ldots (2.32)$$

The concentrations of VAPS present in a sample prepared by cooling a melt assuming equilibrium at the glass transition temperature T_g is then,

$$N = \exp (- U_{LP} / 2KT_g)$$

where N is concentration of lattice sites. For T 500 K, the fraction of lattice sites that could be VAPS is 10^{-6} if U_{LP} 1.1 ev.

Another way of looking at the negative energy which makes reaction 2.30 exothermic is as follows. Let the addition of an electron from, say the valence band to D^+ cost an energy E_1 and the addition of electron resulting D^o and energy E_2, then we write

$$D^+ + e\ (+E_1) \rightarrow D^o \qquad \ldots (2.33)$$

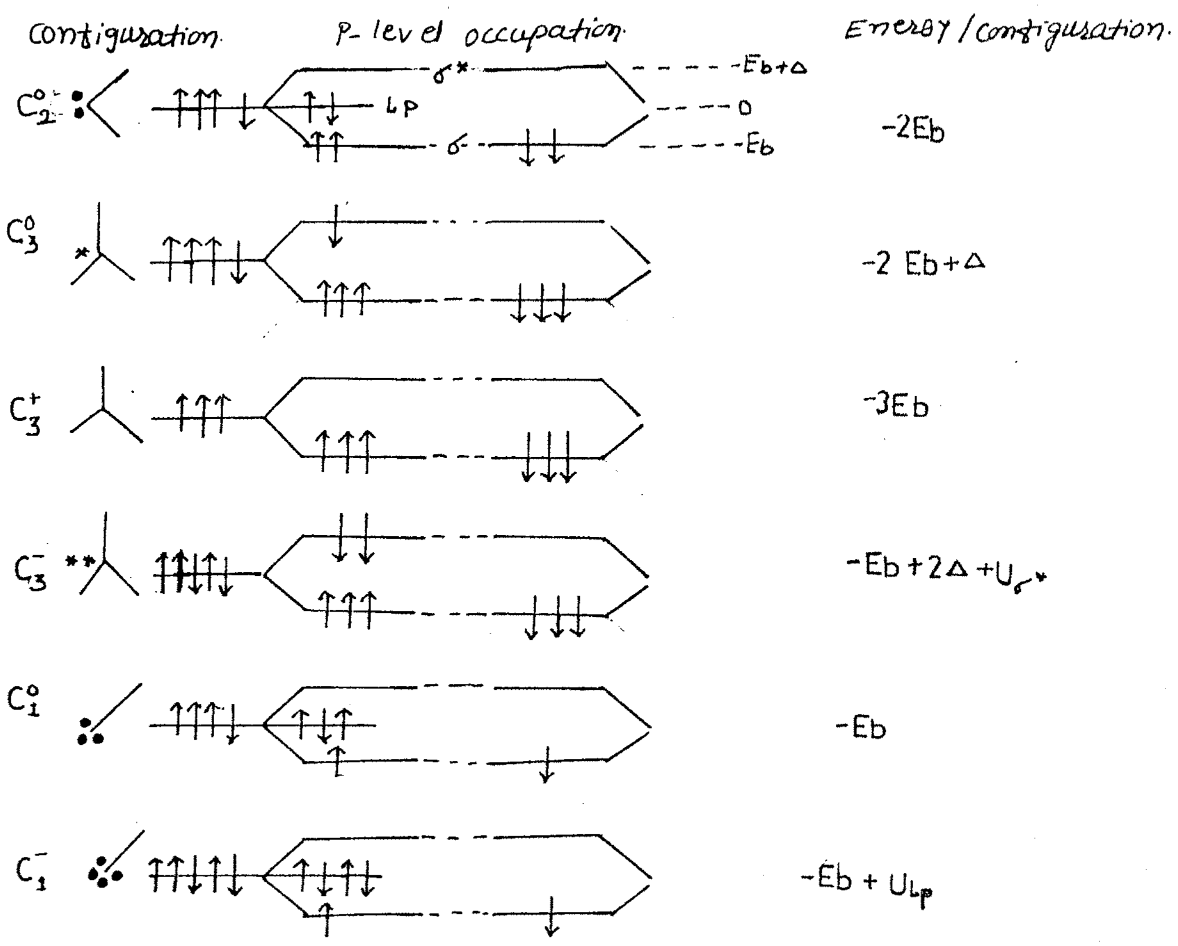
$$D^o + e\ (+E_2) \rightarrow D^-$$

$$\text{Thus} \quad 2D^o \rightarrow D^+ + D^- + (E_1 - E_2) \qquad \ldots (2.34)$$

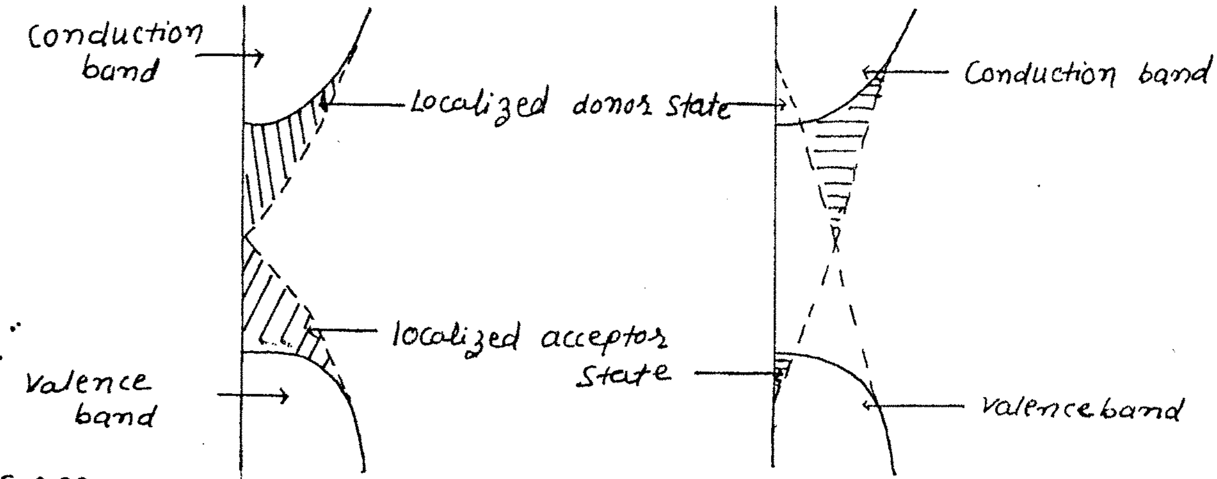
If the addition of second electron to D^+ costs less energy than the first (i.e. $E_2 < E_1$) then $E_1 - E_2$ is positive and the total reaction is exothermic.

2.12 ENERGY BAND DIAGRAM FOR AMORPHOUS SEMICONDUCTOR :

Having seen the model for perfect and imperfect crystals, we now proceed to establish the models for the amorphous semiconductors. We have already remarked that short range order exists in amorphous material. This short range order is due to the random distribution of extremely small crystallites within the sample. But as we already pointed out that the imperfection gives rise to localized states in mobility gap, since the order of imperfection is because of translational topological and compositional disorder.



FIG·2·22 Structure and energy of various defect configurations in a two fold coordinated material. Arrows represent the spin of electron



FIG·2·23 Energy band diagram of amorphous Ge-Te

ⓐ Intrinsic semiconductor like Ge ⓑ same as crystalline Ge-Te

solid dashed curves corresponds to crystalline lattice and dotted curve to those of disordered lattice.

One and three dimensional disordered lattice concludes that as long as short range order is maintained the essential feature of the crystalline band structure are retained with following significant modifications. Due to fluctuations of the neighbouring atoms, the periodic potential shows fluctuations of two types.

(a) The maxima and minima of the periodic potential shift in a random fashion and there by produce tailing of the band edges.

(b) The heights of the maxima and minima fluctuates randomely. As a result, allowed states which extend through the lattice become localized in the disorder lattice.

Localization means that the wave function has the probability amplitude decreasing exponentially with distance from the centre of localization. Average conductivity is zero at $T = 0$. It is not possible to calculate the degree of tailing of band edges without a detailed knowledge of the fluctuation potential. It is clear, however, that the larger the fluctuation, larger the tailing. Thus the effective gap becomes narrower in disorder lattice. Tailing may extend deep in overlapping of the conduction and valence bands.

Mott[2.15] discussed the behaviour of the carrier mobility in localized and non-localized states. He has shown that the mobility due to conduction by hopping in the completely localized states (phonon assisted conduction) is considerably smaller than that in non-localized states. Further he concluded that at low temperature (when conduction in localized state is by tunneling alone) the mobility of conduction is 10 times smaller than that of hopping electrons.

Gubanov[2.16] has suggested a procedure for extending the crystal theories to disordered structure. He assumes that the difference between the short range order arrangements in an amorphous body and in corresponding crystal is small. The necessarily large difference over long distance may be taken care of by transformation of co-ordinates. In place of usual cartesian, Co-ordinates, Gubanov introduced certain curvilinear co-ordinates and showed that the ground state wave functions are linear combinations of wave functions which are Bloch functions in these curvillinear co-ordinates. Their usefulness is limited, but they make it possible to calculate roughly the electron energy states. Gubanov has shown that they form bands not too different from those of the corresponding crystal. It is worth while to remark here that, the results obtained by Gubanov's method are in good agreement with those obtained by Mott and others, based upon band theory.

Ultimately, we conclude that the amorphous materials can be looked upon as having one conduction band and valence band with many localized levels in between. The levels lying near the conduction band can trap the electrons very easily and behave as electron traps. In the same sense the levels near the valence band behave as the hole traps. The fermi level is supposed to lie between the conduction and valence bands. To account for the neutrality, it is assumed that, the hole traps and the electron traps are equal in number so that they counter balance each other.

The above argument is supported by experimental evidence. The photoconductivity and re-combination experiments have been interpreted as giving the evidence for presence of localized states, while activation energy, which is comparatively small confirms the tailing of conduction and valence bands (Figure 2.23).

BAND MODELS FOR AMORPHOUS SEMICONDUCTOR :

1) COHEN-FRITZSCHE-OVSHINSKEY MODEL :

Cohen, Fritzsche and Ovashinskey (CFO)$^{2.11}$ constructed a simple basic band model of disorder semiconductors. In the CFO model the mobility edges, the energies at which states change their character from localized to extended state play an important role. In 1969, Cohen showed that the conductivity σE_c vanishes at the mobility edge.

Cohen showed that, an electron in localized state is effectively trapped by the polarised or disorted lattice and it can move from one localized state to another by hopping or tunneling. This hopping process of conduction produces an energy gap in disordered lattice in which the mobility is negligible. This energy gap has also been described by CFO as, mobility gap in contrast with the conventional crystalline semiconductor band gap in which the density of states is zero. The edges of mobility gap are sharp but sharpness remains unresolved.

Figure (2.24) shows that tail states extend across the gap in the structureless distribution. The decrease of localized state destroy sharpness of conduction and valence band edges. The author said that in chalcogenide alloys disorder is high the tails of conduction and valence bands overlap leading density of state in the middle of gap. This band overlapping is due to the fact that there are states in the valence band, ordinarily filled, that have higher energies than states in the conduction band that are ordinarily unfilled. A redistribution of electrons takes place forming filled state in conduction band tail which are negatively charged and empty state in valence band, which are positively charged. This model therefore pins the fermi level close to the middle of the gap. The major objection against CFO model was high transparency of amorphous chalcogenide below well defined absorption edge.

2) DAVIS-MOTT MODEL :

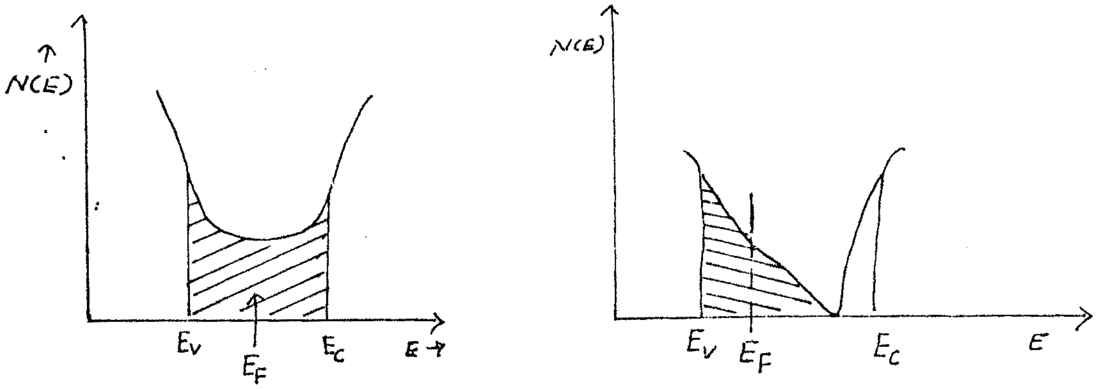
Mott[2.17] has discussed the behaviour of carrier mobility to be expected in localized and non-localized states. He has shown the mobility due to conduction by hopping in the completely localized state is smaller than in non-localized state. Further he concludes that at low temperature the mobility of conduction is 10 times smaller than that of hopping electrons.

According to Davis and Mott, the tails of localized state should be narrow and extend few tenths of electron volt into forbidden gap . (Figure 2.25a) E_c and E_v represent energies which separate the ranges where states are localized and extended. The centre band split into donor and acceptor bands which also pins the fermi level as shown in Figure (2.24b). Mott suggested that transition from extended to localized state, mobility drops by several order of magnitude producing mobility edge. The concept of localization state says that mobility is zero at $T = 0^{\circ}K$. The interval between E_c and E_v is called mobility gap.

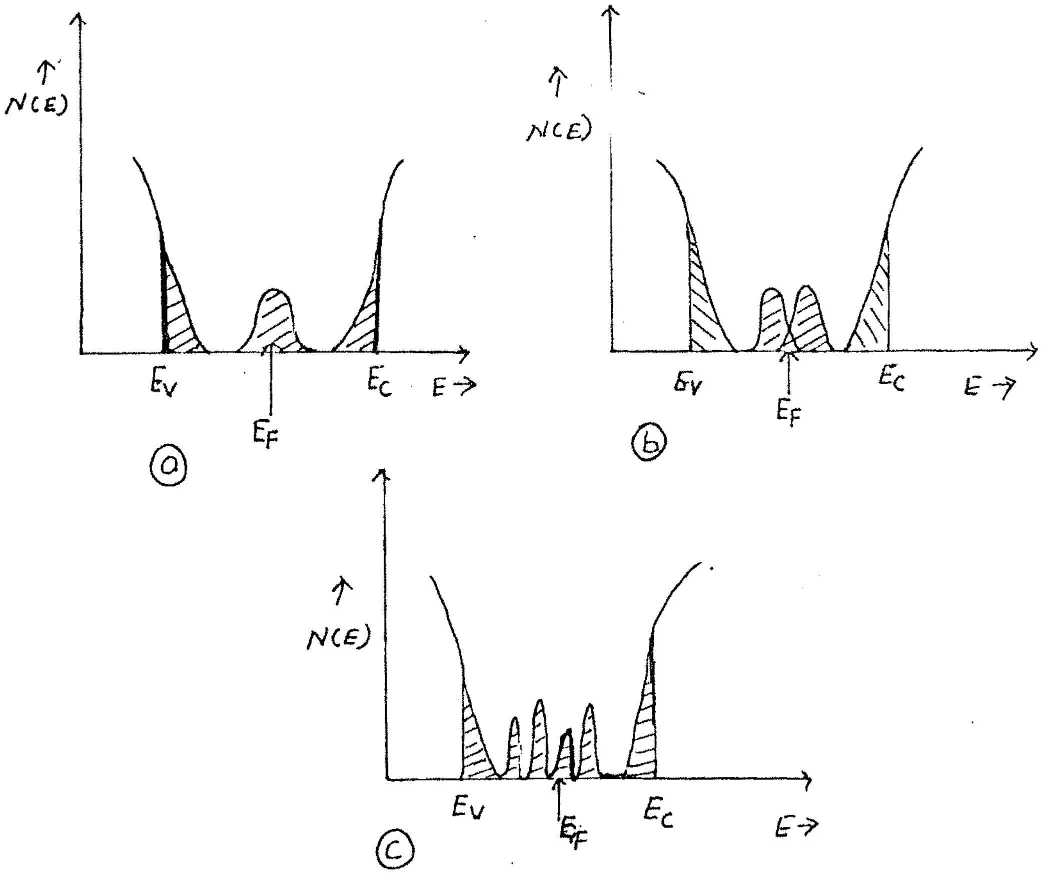
Cohen[2.18] suggested for dependence of mobility that there should not be an abrupt but rather continuous drop of mobility occurring in the extended state just inside mobility edge. In this intermediate range the mean free path of carriers becomes of the order of the interatomic spacing so that ordinary transport theory based on Boltzmann equation cannot be used. Cohen described the transport as Brownian motion in which the carriers are under the influence of the continuous scattering.

3) SMALL-POLARON MODEL :

The role of lattice distortion in the presence of an extra charge carrier in an amorphous solid has been discussed by E_{min}[2.19] He suggested that the charge carriers in some amorphous semiconductors may enter a self-trapped state as a result of polarization of the surrounding atomic lattice. In support of this hypothesis E_{min} argued that the presence of disorder in non-crystalline solid tends to slow down carrier. This slowing down may lead to a localization of the carrier and, if the carrier stays at an atomic site, sufficiently long enough for atomic rearrangements to take place, it may induce displacements of the atoms in its immediate vicinity, causing small polaron formation since the small polaron is local in nature, the absence of long range order in non-crystalline solids may be expected to have no significant influence on its motion.



FIG·2·24 Energy band diagram for CFO model



FIG· 2·25

ⓐ Davis Mott model showing a band of compensated levels near the middle of the gap

ⓑ modified Davis- Mott model

ⓒ A "real" glass with defect states·

REFERENCES

2.1 Kittle, Charles, Introduction to Solid State Physics 4th Ed. Willey Eastern (1971).

2.2 Blackemore, J.S., Solid State Physics 2nd Ed. (1974).

2.3 Smith, R.A., Semiconductors 2nd Edition Cambridge University Press (1978).

2.4 Levy, Robert A., Principles of Solid State Physics Academic Press Inc. (1968).

2.5 Ioffe, A.F., and Regal, A.R., Prog. semiconductor 4 (1960) 237.

2.6 Anderson, P.W., Phy. Rev. 109 (1958) 1492.

2.7 Anderson, P.W., Comments Solid State Phys. 2(1970) 193.

2.8 Mott and Towse Advs. Phys. Vol. 10 (1961) 107.

2.9 Kubo, R., Phy. Rev. 86 (1952) 929.

2.10 Mott, N.F., Rew. mod. phys. 40 (1970) 677.

2.11 Cohen, Fri~~t~~zsche and Ovshinsky, Phy. Rev. lett. 22 (1969). 1065.

2.12 Mott, N.F., Davis, E.A., Street, R.A., Philos. Mag. 32 (1975) 961.

2.13 Kastner, M., Adler, D, Frizsche, H., Phys. Rev. Lett. 37 (1976) 1504.

2.14 Kastner, M. Fritzsche, H., Philos. Mag. 37 (1978) 199.

2.15 Mott, N.F., Adv. Phys. 13 (1964) 325.

2.16 Gubanov, A.I., Quantum electron theory of amorphous conductors.Consultants Bureau New York (1965).

2.17 Davis, E.A., Mott, N.F., Philos. Mag. 22 (1970) 903.

2.18 Cohen, M.H., J. non-crystal solids 4, (1970) 391.

2.19 E_{min}, "Aspects of the theory of small polarons in disordered materials" on electronic and structural properties of Amrophous semiconductors Ed. by Lecomber, Mort J., Academic Press London, New York (1973) p. 261.

2.20 Mott, N.F., J. non-crystal solids. (1969 a).

2.21 Mott, N.F., Adv. Phy. 16 (1967) 49.

2.22 Brodsky, M.H., Amrophous semiconductor springer-verlag Berlin Heidelberg New York Vol. 36 (1979) 1-21, 27-30, 53.

2.23 Mott, N.F., Davis, E.A., Electronic process in non-crystalline materials, Clarendon Press, Oxford (1971) 6-22, 29-34, 43.

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