CHAPTER II

TRANSPORT PROPERTIES

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Electrical Properties of Amorphous Semiconductors :

In most semiconductors, the dc transport properties are very well understood. Electrical conductivity, and thermoelectrical power or (thermo power) measurements as function of temperature can be interpreted to yield the position of the Fermi-energy, the effective mass of the carriers, the band mobility, and the predominant carrier scattering mechanism. Small polaron formation and hopping transport can be identified if present. The most remarkable feature of the electrical conductivity data in amorphous chalcogenide alloys is the strong pinning of the Fermi-energy.

2.1 DC ELECTRICAL CONDUCTIVITY :

The essential features of the Davis-Mott model for band structure of amorphous semiconductors are the existance of narrow tails of localized states at the extremities of the valence and conduction bands. Fig.(2.1) and further more of a band of localized levels near the middle of the gap. This leads to three basically different channels for conduction.

2.1.1 EXTENDED STATE CONDUCTION :

Conduction due to carriers excited beyond the mobility edges in to non-localized or extended states.

The conductivity for any semiconductor can be expressed in the form

$$\sigma = -e\int g(E)\,\mu(E)\,KT\,\frac{\partial f(E)}{\partial E}\,dE \qquad ..(2.1)$$

where f(E) is the Fermi-Dirac distribution function.

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

using this relationship

$$\frac{\partial f(E)}{\partial E} = -\,f(E)\,[1-f(E)]/KT$$

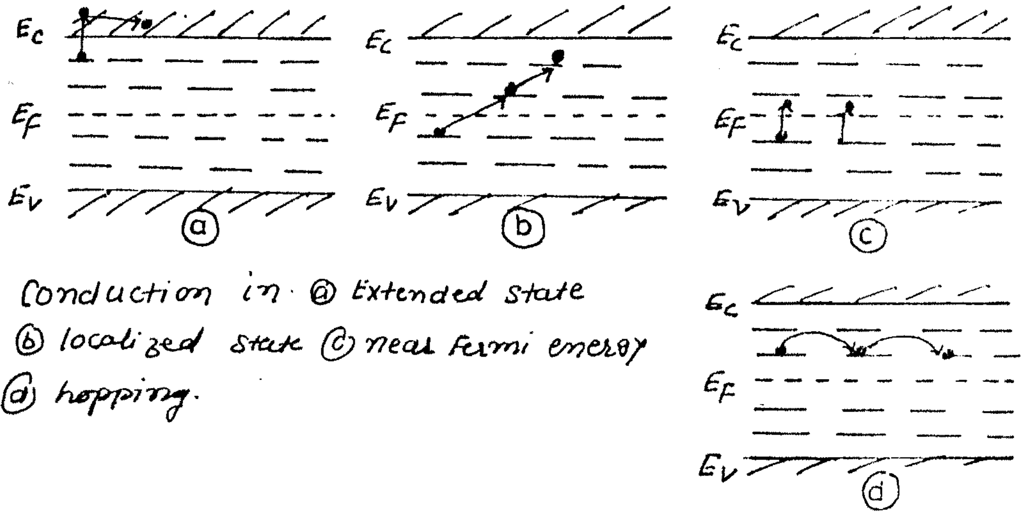
From this, σ can be written as

$$\sigma = e\int g(E)\,\mu(E)\,f(E)\,[1-f(E)]\,dE \qquad ..(2.2)$$

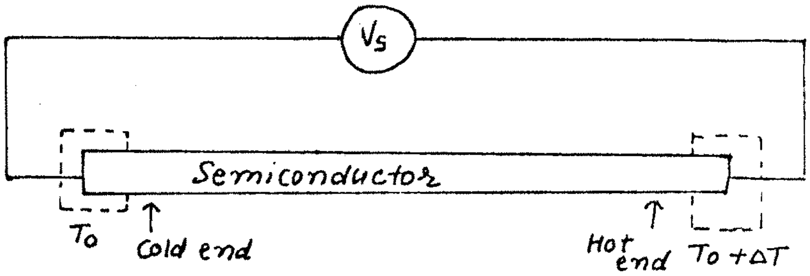
In the Davis-Mott[2.1] model, the Fermi-level E_F is situated near the middle of the gap and thus sufficiently far from conduction band i.e. the energy which separates the extended states from the localized states, so that Boltzmann statistics can be used to described the occupancy of states, Thus $f(E) = \exp.\,[-(E - E_F)/KT]$

According to Mott's view the mobility drops sharply at the critical energy E_C or E_V but at present it is not exactly known how the mobility depends on the energy in both conduction regimes.

In the nondegenerate case and under the assumption of a constant density of states and constant mobility, the



FIG·2·1 Conduction in ⓐ Extended state ⓑ localized state ⓒ near Fermi energy ⓓ hopping.



FIG· 2·2

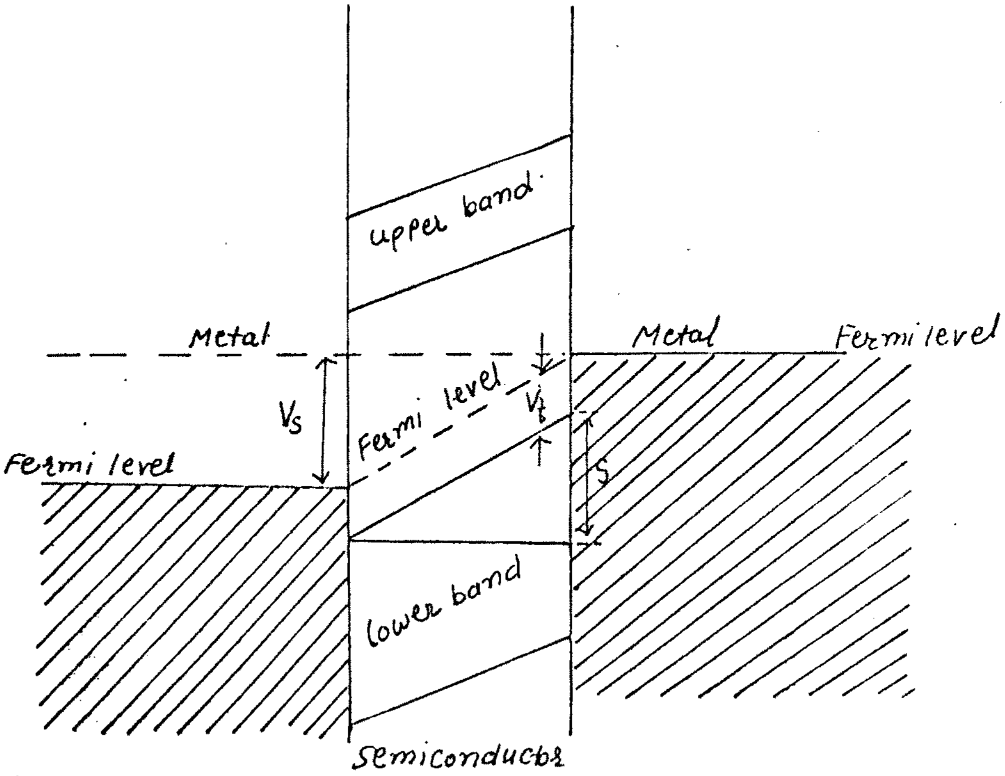


FIG 2·3

Variation of Fermi level in ptype material.

conductivity due to electrons excited beyond the mobility edge in to the extended states is given by

$$\sigma = e\, g(E_C)\, \mu_C KT \text{ exp. } [-(E_C - E_F)/KT] \qquad ..(2.3)$$

Where μ_C is the average mobility.

The number of electrons is given by

$$n = \int_{E_C}^{\infty} g(E_C) \text{ exp.}[-(E - E_F)/KT]\, dE$$

$$= g(E_C)\, KT \text{ exp.}[-(E_C - E_F)/KT] \qquad ..(2.4)$$

In order to get an idea of the order of magnitude of μ_C, we shall follow Mott's treatment. We define

$$\sigma\,(E_C) \equiv e\, g(E_C)\, \mu_C KT.$$

If $g(E_C) = \langle g(E_C) \rangle / 3$, where,

$\langle g(E_C) \rangle$ is the average density of states over the band, then

$$\sigma(E_C) = e \langle g(E_C) \rangle \mu_C KT/3$$

Mott[2.2] calculated the lowest value of the electrical conductivity before the start of an activated process, i.e. jsut at E_C.

This quantity he called the "minimum metallic conducitivity". He derived the expression

$$\sigma(\text{min}) = \frac{\text{Const } e^2}{\hbar a} \qquad ..(2.5)$$

Where the constant lies in the range between 0.026 and 0.1., σ_{min} is usually of the order 200-300 $\Omega^{-1}cm^{-1}$.

Taking constant = 0.026, one finds for the mobility

$$\mu_c = 0.078\ (e/\hbar a)\ /<g(E)>KT$$

In the nearly free electron model, g(E) is given by

$$g\ (E) = Km/2\Pi\hbar^2$$

on the other hand, the maximum energy Emax. of the band which also yields the width B of the band, is expressed by

$$Emax = \frac{\hbar^2\Pi^2}{2\ ma^2} \quad \text{and } K_{max} = \Pi/a$$

This yields $g(E) = \dfrac{1}{a^3\ B}$

Introducing this result in the expression for the μ_c: one gets.

$$\mu_c = 0.078\ \frac{ea^2B}{\hbar KT} \qquad ..(2.6)$$

Taking a = 2A°, B = 5 eV. One finds at room temperature that $\mu_c = 10\ cm^2\ V^{-1}\ S^{-1}$. This value corresponds to a mean free path comparable or less than interatomic distance.

Cohen (2.3) suggested that conduction in this case would be more properly described as a diffusion or Brownian-type motion. In this regime the mobility can be obtained with the help of Einstein equation,

$$\mu = eD/KT$$

The diffusion coefficient D may be written as $D = (1/6)\gamma a^2$

Where γ is the jump frequency and 'a' the interatomic separation. The mobility in the Brownian-Motion regime is then given by

$$\mu c = \frac{1}{6} \frac{ea^2}{KT} \gamma \qquad ..(2.7)$$

This expression yields the same temperature dependence as (2.6) derived by Mott. Since $\mu \propto 1/KT$, one expect that the expression for conductivity is of the form

$$\sigma = \sigma_0 \exp. [-(E_C-E_F) /KT] \qquad ..(2.8)$$

This equation is used for calculation of activation energy. Optical absorption of amorphous semiconductors has shown that band gap decreases with increasing temperature. The energy distance $(E_C - E_F)$ shows similar behaviour under the assumption of linear temperature dependence.

$$E_C - E_F = E(0) - \gamma T \qquad ..(2.9)$$

The expression for the conducitvity becomes

$$\sigma = \sigma o \exp.(\frac{\gamma}{k}) \exp.[-E(0)/KT] \qquad ..(2.10)$$

Here E(0) is energy disance at T = Ok.

We can write this formula in the form

$$\sigma = Co \exp. [-E(0)/KT] \qquad ..(2.11)$$

where

$$C_O = e\, g(E_C)\, KT\, \mu c \exp. (\gamma/k) \qquad ..(2.12)$$

As seen before μc is proportional to 1/T, So that the preexponential factor σ_o is temperature dependent. Mott(2.4) has made an estimate of the preexponential σ_o. In general σ_o may lie between 10 and 10^3 $\Omega^{-1}\text{cm}^{-1}$, in most amorphous semiconductors, An estimate of γ can be obtained from the temperature dependence of the optical gap. In chalcogenide glasses the temperature coefficient of optical gap generally lies between 4×10^{-4} and 8×10^{-4} eV deg^{-1}. As the Fermi-level is situated near the middle of the gap, values of γ is approximately half this magnitude are expected and hence values of exp.(γ/K) in the range 10 - 100 are most probable.

2.1.2 CONDUCTION IN BAND TAILS :

The conduction takes place due to the carriers excited in to the localized states at the band edges i.e. at E_A or E_B. Conduction can only occur by thermally activated hopping. Every time an electron moves from one localized state to another, it will exchange energy with a phonon. It may be expected that the mobility will have a thermally activated nature,

$$\mu_{hop} = \mu_o \exp.[- \frac{W(E)}{KT}] \qquad ..(2.13)$$

where $$\mu_o = (\frac{1}{6})\, \gamma_{ph}\, \frac{e^2 R^2}{KT} \qquad ..(2.14)$$

where γ_{ph} is the phonon frequency and R is the distance covered in one hop.

For a typical phonon frequency $\gamma_{ph} = 10^{13}$ S^{-1} and W = KT, yields a mobility of the order $10^{-2}cm^2\ V^{-1}S^{-1}$ at room temperature. Comparison of this value with the one calculated for conduction in the extended states suggest, as postulated by Mott, that the mobility may drop by a factor of at least 100 at the energy which separates the localized and non-localized states. The conductivity, being an integral over all available energy states, will depend on the energy distribution of the density of localized states. If one assume that the density of states g(E) behaves as some power S of E,

$$g(E) = \frac{g(E\ )}{(\Delta E)^S}\ (E - E_A)^S \qquad ..(2.15)$$

with $\Delta E = E_C - E_A$, then the conductivity σ_{hop} due to electrons can be easily calculated, starting from (2.2).

$$\sigma_{hop} = \sigma_{ohop}\ (KT/\Delta E)^S\ C\ \exp.[-\frac{E_A - E_F + W}{KT}] \qquad ..(2.16)$$

where $\sigma_{ohop} = (\frac{1}{6})\ \gamma_{ph}\ e^2\ R^2\ g(E_C)$ ..(2.17)

and $$C = S! - (\frac{\Delta E}{KT})^S \exp.(-\frac{\Delta E}{KT})\ [1 + s(\frac{KT}{\Delta E}) + s(S+1)\ (\frac{KT}{\Delta E})^2 + ...]$$

For the specific case of s=1 (linear variation)

The conductivity is given by

$$\sigma_{hop} = \sigma_{ohop} \frac{KT}{\Delta E}\ c_1\ \exp.[-(E_A - E_F + W)/KT] \qquad ..(2.18)$$

with $c_1 = 1 - \exp.(\Delta E/KT)\ [1 + (\Delta E/KT)]$ ..(2.19)

2.1.3 CONDUCTION IN LOCALIZED STATES AT THE FERMI-ENERGY :

If the Fermi-energy lies in a band of localized states, as predicated by the Davis-Mott model, the carriers can move between the states via phonon assisted tunneling process. This is the transport analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures. An estimate for the temperature dependence of the hopping conductivity at E has been given by Mott(2.5) we shall follow his original derivation. Let us consider an electron that is scattered by phonons from one localized states to another. The jump probability between the states is denoted by three factors, which are the following :

1) The probability of finding a phonon with an exciatation energy equal to W, given by Boltzmann expression exp.(-w/kT).

2) An attempt frequency γph, which can not be greater than the maximum phonon frequency (in the range of 10^{12} - 10^{13} S^{-1})

3) The probability of electron transfer from one state to another.

This factor depends on the overlapping of the wave functions and should be given by exp.(-2αR). Here R is the jumping distance, which at high temperatures equals the interatomic spacing, and α is the quantity which is representative for the rate of fall-off the wave function at a site. If overlapping of the wave functions is important, the factor exp. $(-2\alpha R)$ becomes of the order of one.

The probability P that an electron jumps will then be expressed by.

$$P = \gamma_{ph.} \exp. (-2\alpha R - W/KT) \qquad ..(2.20)$$

By using Einstein relation for mobility.

$$\mu = \frac{eD}{KT}, \text{ with } D = \left(\frac{1}{6}\right) PR^2$$

so $$\sigma = (1/6)\, e^2R^2\, P\, g(E_F) \qquad ..(2.21)$$

where $g(E_F)$ is the density of the states at the Fermi-level. Using eq^h (2.20), the conductivity is represented by

$$\sigma = \left(\frac{1}{6}\right) e^2R^2\, \gamma_{ph}\, g(E_F) \exp. \left(-2\alpha R - \frac{W}{KT}\right) \qquad ..(2.22)$$

As the temperature is lowered, the number and energy of phonons decrease, and the more energetic phonon-assisted hops will progressively become less favourable. Carriers will tend to hop to large distances in order to find sites which lie energetically closer than the nearest neighbours. This mechanism is so called variable range hopping. The factor exp.$(-2\alpha R-W/KT)$ will not have its maximum value for the nearest neighbours. In order to find the most probable hopping distance, Mott used an optimization procedure. This is as follows, If g(w) is the density of states per unit volume per unit energy, then the number of states with energy difference W within a distance R from a perticular atom is given by

$$4\,\frac{\pi}{3}\,R^{3}\,g(w)\,W$$

The electron can leave its site only if the number of accessible sites is at least one. Taking this in to account one gets for the average energy spacing between states near Fermi level,

$$W = \frac{3}{4\pi R^{3}\,g(E_F)} \qquad ..(2.23)$$

and for the jump probability,

$$P = \gamma_{ph}\ \exp.[-2\alpha R-(\frac{4\pi}{3})\ g(E_F)R^{3}KT]^{-1} \qquad ..(2.24)$$

The most probable distance is found by minimizing the exponent of the above expression as a function of R,

$$R = [\ \frac{9}{8\pi\ \alpha g(E_F)\ KT}\ ]^{1/4} \qquad ..(2.25)$$

This gives the jump frequency of the form

$$P = \gamma_{ph}\ \exp.\ (-\ \frac{A}{T^{1/4}}\ ) \qquad ..(2.26)$$

where $A = 2.1\ [\ \frac{\alpha^{3}}{K\ g(E_F)}\ ]^{1/4}$ ..(2.27)

Mott's treatment of variable range hopping leads to a temperature dependence for the conductivity of the form

$$\sigma = (1/6)\ e^2R^2\ \gamma_{ph}\ g(E_F)\ \exp.\ (-A/T^{1/4}) \qquad ..(2.28)$$

or

$$\sigma = \sigma_0(T)\ \exp.(-A/T^{1/4}) \qquad ..(2.29)$$

In the recent literature many experimental studies, especially on the tetrahedral bonded materials, dealt with variable range hopping. In many cases, unreasonable high values were calculated for $g(E_F)$ or $N(E_F)$, very often by use of the pre exponential factor $\sigma_0(T)$. Although the $T^{-1/4}$ dependence of $\ln \sigma$ is widely observed, these findings seem to indicate that the above expression do not describe in an exact quantitative way the conductivity. A review article on hopping conductivity in disordered solids has recently been published by overhof (2.6).

2.2 THERMO ELECTRIC EFFECT IN SEMICONDUCTOR.

Fundamental information about the mechanism of conduction in solids can be obtained from studies of the thermoelectric effect. In 1821 Thomas Seeback found that if a metal is connected at its two ends with a second metal, and if one of the junctions is heated, a voltage is developed across the open ends of the second metal.

The schematic circuit for the measurement of thermoelectric voltages for a semiconductor is given in fig(2.2).If the metal contacts are applied to the two ends of a semiconductor rod and it one junction is maintained at a higher temperature than the other, a potential difference will be developed between the two electrodes. This thermoelectric or seeback voltage is produced partly because of the majority carriers in semiconductor defused from hot to cold junction per second, thus giving a potential difference between the two ends. This voltage builds up a value such that the return current just balances the diffusion current, when a steady voltage is reached.

In the experimental arrangement of Fig.(2.2). If the charge carriers in semiconductcrs are predominantly electrons, the cold junction becomes negatively charged, if the carriers are positive holes, the cold junction becomes positively charged. The magnitude of the voltage Vs is proportional to the difference in temperature between the hot and cold junction.

From the sign of the thermoelectric voltages, it is thus possible to deduce whether a specimen exhibits n-type or p-type conductivity further from the magnitude of the thermoelectric voltage one can determine the concentration of charge carries in the specimen.

Semiconductors exhibit thermoelectric behavior in circuits with metals, the magnitude of the thermoelectric quantities exhibited by semiconductors are often much larger than those exhibited by metals. The thermoelectric properties of semiconductors can be used to know the position of Fermi level with respect to band edges.

A typical thermoelectric circuit containing a semiconductor in the form of long thin rod, with metal contacts at its two ends is shown in Fig.(2.2). One end of the rod is kept at a reference temperature To, while the other end is placed at To + T. Let us suppose that, a linear temperature gradient exists along the rod, which is p-type. Under these conditions, the Fermi-level in the metal and semiconductor and the edges of the semiconductor band assume the position shown in the lower part of the Fig.(2.3). The semiconductor band edges, become tilted as indicated. While the Fermi-level also become tilted, with a somewhat diferent slope. The Fermi level in the semiconductor is continuous with the Fermi levels in the metals at two contacts. The Fermi level in metal wires leading away from the contacts do not change with temperature as compared to the magnitude of change in Fermi level in semiconductor, hence the Fermi level in metal wires are shown horizontal in Fig.(2.3). The seebeck voltage of the circuit is essentially given by the difference in the Fermi level from one end of the semiconductor rod to the other end. In the case of uniform p-type semiconductor taken as an example, the right end of the rod becomes negative with respect to left hand side.

If the temperature difference is small the effects depicted in Fig.(2.3) will be linear with temperature and hence linear with horizontal distance across the diagram. The quotient between V(s) and ΔT is called the thermoelectric power. Its physical dimensions are volt per degree, it is distignated by a symbol S. If both the hot and cold junctions are raised or lowered in temperature keeping T same. It will be found that S varies with mean temperature. The variation of S with temperature can just be well observed by keeping the cold junction at temperature T and plotting the thermoelectric voltage V(S) against the variable temperature $T_o + \Delta T$ of the hot junction. The slope of this plot at temperature T gives the value of S at that temperature.

The tilting of the energy bands and Fermi level in the semiconductor sustaining a temperature gradient can be explained as follows. Because of the temperature gradient, there will be a diffusion of positive holes down the temperature gradient from right to left. The cooler end of the specimen, therefore becomes positively charged and a steady state potential difference in question is given by the vertical distance d on the diagram.

Even if there were no concentration gradient of majority carriers, there would still be a small potential difference generated between the two ends of the specimen. This difference would result from the fact that those holes crossing an imaginary cross section of the specimen by random thermal motion would be going slightly faster in the right to left direction than in left to right because they come from a warmer region of the specimen and hence have higher thermal kinetic energies. For semiconductor in the impurity dominated and intrinsic temperature range, however this effect is small compared with the effect of diffusion and may be neglected in approximate theory.

2.3 SEEBECK EFFECT AND THERMOELECTRIC POWER :

The Fermi-level in p-type semiconductor rises with temperature towards the middle of the forbidden gap. Hence the total rise of the Fermi-level in Fig.(2.3) from cold end of the specimen to the warm end is given by the sum of rise in the upper edge of the valence band and the additional increase due to the rise of the Fermi level above the valence band edge. In other words,

$$V_S = d + \frac{d\,V_F}{dT} \quad \Delta T \qquad ..(2.31)$$

Where Vs is voltage which would be indicated by a high resistance voltmeter in the metallic part of the circuti.

The calculation of the thermoelectric quantity Vs) in terms of basic physical quantitis is straight forward for simple cases of semiconductors in which only one type of conducting particles need be considered. In the p-type specimen indicated in Fig.(2.3) the right to left current density due to diffusion is

$$I_{RL} = D_p \, q \, \frac{dp}{dx}$$

Where D_p is diffusion constant, dp/dx is rate of change of holes with distance and q is charge on the hole.

The left to right return current due to electric field set up by this process is.

$$I_{RL} = p \, \mu_p \, q \, E_x$$

Where E_x is electric field, p-number of holes and μp is hole mobility.

In steady state, these two currents are equal giving

$$D_p \, q \, \frac{dp}{dx} = p \, \mu_p \, q \, E_x \qquad ..(2.32)$$

using Einstein relationship, we may write $D_p = KT \, \mu p/q$ and assuming the electric field to be uniform (as it will be for a small temperature difference and uniform gradient) we may set d/L for E_x where L is the length of the specimen, with these substitutions, and rearranging above equation we get.

$$\frac{dp}{dx} = \frac{pq}{KT} \, \frac{d}{L} \qquad ..(2.33)$$

However $$\frac{dp}{dx} = \frac{dp}{dT} \, \frac{dT}{dx} = \frac{dp}{dT} \, \frac{\Delta T}{L}$$

Therefore above equation becomes

$$\frac{dp}{dT} = \frac{pq}{KT} \quad \frac{d}{\Delta T} \qquad ..(2.34)$$

From the Fermi statistics,

$$p = 2UT^{3/2} \qquad e^{-qV_F/KT}$$

where $u = 2.42 \times 10^{15}\ \text{cm}^{-3}\ \text{AB}\ S^{-3/2}$

Differentiating with respect to T, and putting the result in above equation and simplifying

we get,

$$d = \left(- \frac{d\,V_F}{dT} + \frac{V_F}{T} + \frac{3K}{2q}\right) \Delta T \qquad ..(2.35)$$

combining equation (34 & 35)

$$V_S = \left(\frac{V_F}{T} + \frac{3K}{2q} \right) \Delta T \qquad ..(2.36)$$

Since $S = V_S/\Delta T$, we have

$$S = \frac{V_F}{T} + \frac{3K}{2q} \qquad ..(2.37)$$

These last two equations for seebeck voltage and thermoelectric power are only approximate. Their derivation neglected the effect described earlier in which a small contribution to S comes from the difference in mean thermal kinetic energy of particles diffusing randomly in two directions in the specimen. The correction to take account of this effect yields for V_s and S.

$$V_S = \left(\frac{V_F}{T} + \frac{2K}{T}\right) \Delta T$$

and

$$S = \frac{V_F}{T} + \frac{2K}{q}$$

Therefore $S = \frac{k}{q} \left(2 + \frac{E_F}{KT} \right)$ ..(2.38)

A similar derivation holds for n-type semiconductor leading to equations similar to the two above, expect that the signs of V_s and S will be negative and that $(V_g - V_F)$ will appear instead of V_F. Equation (2.38) gives us an independent method for determining V_F in a p-type semiconductor sample and hence for obtaining by calculation a value for the hole concentration P. Therefore we have,

$$P = 2U T^{3/2} e^{-q Q/K+2} \quad ..(2.39)$$

In case of an n-type semiconductor above formula becomes

$$S = \frac{-K}{q} \left(2 + \frac{E - E_F}{KT} \right) \quad ..(2.40)$$

2.4 THERMO-ELECTRIC POWER :

Important information about the transport mechanism in amorphous semiconductors has been obtained from thermo power data. In this section we shall derive the formulas for the thermopower associated with the three possible processes of conduction.

Fritzsche (2.7) has given a general expression for the tnermopower S

$$S = -\frac{k}{q} \frac{\int \mu(E)\, g(E)\, [(E - E_F)/KT]\, f(1-f)\, dE}{\int \mu(E)\, g(E)\, f(1-f)\, dE} \quad ..(2.41)$$

where f is the Fermi-Dirac distribution function. For nondegenerate semiconductor classical Boltzmann statistics are appropriate. In this case the factor f(1-f) in (41) reduces to a Boltzmann factor $f = \exp.[-(E - E_F)/KT]$.

2.4.1 CONDUCTION IN EXTENDED STATES :

Under the assumption of a constant density of states and an energy independent mobility the thermopower can be readily found by integrating equation (41). This yields an expression for the familiar form for band conduction of electrons

$$S = -\frac{k}{q}\left(\frac{E_c - E_F}{KT} + A\right) \qquad ..(2.42)$$

with $A = 1$

In crystalline semiconductors it is well known that the kinetic term A depends on the scattering mechanism. Hindley (2.8) has found a similar expression for using the random phase model. If both the electrons and holes contribute to the conductivity, then the thermoelectric power is the algebraic sum of individual contributions S_e and S_h. Thus we have

$$S = \frac{S_e\sigma_e + S_h\,\sigma_h}{\sigma_e + \sigma_h} \qquad ..(2.43)$$

where S_e = Thermoelectric power of electron.

S_h = Thermoelectric power of hole.

σ_e = Conducitivity of electrons.

σ_h = Conductivity of holes.

2.4.2 MOTION OF CARRIER IN LOCALIZED STATE NEAR THE MOBILITY EDGE :

The thermoelectric power by carrier in the localized states of a band tails will be given by

$$S = -\frac{k}{q} \frac{\int [(E-E_F)/KT] \exp.[-(E-E_F)/KT]\, g(E)^{dE}}{n} \quad ..(2.44)$$

If density of localized state behave like some power 'S' of the energy E,

$$g(E) \text{ or } N(E) = \frac{g(E_c)}{(E_c - E_A)^3} (E - E_A)^s,$$

then we have

$$S = -\frac{k}{q} \left(\frac{E_A - E_F}{KT} + \frac{c^*}{c} \right)$$

where C is defined as before, in dc conductivity,

$$C^* = \int^{\Delta E/KT} e^{-x} x^{s+1} dx$$

Here $\Delta E = E_c - E_A$ is the width of the tail and $x = (E - E_A)/KT$.

If the carriers move by hopping in the localized states, the conductivity varies nearly exponentially with temperature, and the measured activation energy is the sum of the activation energies for carrier creation and for hopping. The activation for hopping does not appear in the expression for S and, therefore, one expects a difference in slope between the conductivity and thermopower curve.

2.4.3. MOTION OF CARRIERS IN LOCALIZED STATES AT THE FERMI-ENERGY :

At low temperature, charge transport can arise from electron tunneling between states at E_F. Cutler and Mott(2.9) Suggested that the thermoelectric power in this regime should be identical to equation used for metalic conduction.

$$S = \frac{\Pi^2 K^2 T}{3 e} \left[\frac{d \ \ln\sigma(E)}{dE} \right]_{E_F} \qquad ..(2.45)$$

Since the Fermi level lies in a region where the density of states is finite. The thermoelectric power is small. Its sign may be negative or positive depending on whether the major contribution to the current will lie below or above the Fermi energy. Several authors (2.10-2.13) have calculated the thermoelectric power in the variable range hopping regime.

2.5 CONDUCTION BY SMALL-POLARON MOTION :

The formation of small polaron in non-crystalline materials has been discussed by Emin(2.14). He argued that the probability of small polaron formation in disorder state is largely increased as compared to the crystalline state. It may be remembered in Davis and Mott model that existence of mobility edges at the energies which saparates the localized tail states from the extended states. The existance of such tail states does not appear in a small polaron band.

If the charge carrier remains in the vicinity of a perticular atomic site over a time interval long enough for displacement of the surrounding atoms to take place, a potential well may be created which can lead to trapping of the carrier. The unit built up by the trapped carrier and its induced lattic deformation is called a polaron. The polaron has a lower energy than the free electron but has a larger effective mass, since it must carry its induced deformation with it as it moves through the lattice. The decrease in energy of a small polaron relative to that of the electron in the undistorted lattice is called the small-polaron binding energy.

In paper on 'small polaron motion' Holstein (2.15) introduced the fundamental concept called coincident event which characterizes the hopping mechanism. In 'adiabatie' regime, the electron goes backwards and forwards several times during the period that the two potential wells have equal depth. The carrier will possess a high probability to hope to the adjacent site. In 'nonadiabatic' regime the electron can not follow the lattice vibrations and the time required for an electron to hop is large compared to the duration of a coincident event. In this case carrier will have many coincident events before it hops, its probability for transfer being much smaller than in the adiabatic case.

The dc conductivity for small polarons, being proportional to the probability for hopping, is given by

$$\sigma = \left(\frac{ne^2 a^2}{KT} \right) P \qquad ..(2.46)$$

The jump probability P, can be written as a product of two terms: the probability P_1 for the occurance of a coincidence event and the probability P_2 of charge transfer during this event. The probability for a configuration with equal potential can be expressed by

$$P_1 = \frac{\omega_o}{2\Pi} \exp. \left(\frac{-W}{KT} \right) \qquad ..(2.47)$$

where $\omega_o/2\Pi$ is an average phonon frequency and w is the minimum energy necessary to obtain two equivalent sites.

The total probability P becomes

$$P = \frac{\omega_o}{2\Pi} \exp.(-W/KT)\, P_2 \qquad ..(2.48)$$

In the adiabatic regime, where the carrier can follow the motion of the lattice, the probability for jumping during coincidence is high, and one can put $P_2 = 1$. In the non adiabatic regime where the carrier is slow, one expects $P_2 \ll 1$ Holstein (2.17) derived the following expression for P_2:

$$P_2 = \frac{2\Pi}{\hbar\,\omega_o} \left(\frac{\Pi}{wKT} \right)^{1/2} J^2 \qquad ..(2.49)$$

The electronic transfer in integral J is a measure of the overlapping of the wave functions.

The transport property, thermoelectric power S, received special attention in the experimental studies on small polarons. For small polaron hopping, S was found to be expressed by a formula of the classical form

$$S = - \frac{K}{e} \left(\frac{E}{KT} + A \right) \qquad ..(2.50)$$

Where E is the energy associated with the thermal generation of the carriers.

2.6 SWITCHING IN NON CRYSTALLINE SEMICONDUCTORS :

Amorphous chalcogenide alloys were among the first and certainly have been the most investigated materials which exhibit the phenomenon of "threshold switching" discussed by ovshinsky in his landmark paper (2.18). When electric field in excess of about 10^5 V/CM. are applied to this materials, a metastable state of high conductance appears, in which of the order of 10^{19} cm^{-3} free electrons move with mobilities of approximately 10 $cm^2/V\text{-}S$ (2.18). When the current is reduced below a critical value, the material returns to its original low conductance state.

The detailed experimental observations of switching in chalcogenide can be explained by VAP Model (   ) Near equillibrium, the charged centres, e.g. C_3^+ and P_2^+, act as efficient traps for field-generated as well as photogenerated carriers, and the trapping time is considerably shorter than the transit time. However, beyond the critical value of the applied field, sufficiently free-carrier generation takes place so that the charged traps are all occupied and thus netural. Since the concentration of the positively and negatively charged centres were originally equal, the material remains neutral after charged trap saturation. Only neutral traps remain, so that the trapping time increases. Sharply if it becomes large compared to the transit time, the current rises dramatically, initiating the switching. Note that it is essential that a sufficiently high carrier to netural defect interconversion exist to retard this possibility over the time necessary for the switching transition, since such interconversion would tend to pin the quasi-fermi energies. When the current is reduced below the values necessary to sustain sufficiently carrier concentrations to keep the charged traps filled, the material quickly transforms to the nonconducting state.

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