CHAPTER 1

AN INTRODUCTION TO AMORPHOUS/GLASSY SEMICONDUCTORS AND SELECTION OF THE PROBLEM
CHAPTER - I

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1.1 AN INTRODUCTION TO AMORPHOUS/GLASSY SEMICONDUCTORS

All the glasses known before 1955 (silicate, phosphate and borate glasses) were insulators in the sense that electronic conduction was absent in these glasses. Though, some of these glasses may have appreciable conductivity particularly in impure state, even then they are not termed as semiconductors because conduction in them is ionic rather than electronic. Because of the absence of electronic conduction, these glasses could not be used in solid state devices unlike their crystalline counterparts where electronic conduction does exist. The theory of semiconductor was also based on the periodicity of atoms in solids. So, for a very long time, it was thought that non-crystalline solids could not be semiconductors. No experimental result was also available which showed the semiconducting behaviour of glassy substances. In 1955, however, B.T. Kolomiet's and his associates in USSR first used other sixth (B) group elements in the periodic Table, viz. S, Se, Te. Unlike the conventional oxide glasses, a special name 'chalcogenide glasses' was given to semiconducting glasses. There are two reasons for this division; one historic and one scientific [1]. Oxide materials particularly
those based on silica, are the oldest-known glass-forming system and it has become traditional to treat them separately from the more recently discovered chalcogenide materials. Although oxygen is also a group VI element, the physical behaviour of oxides is often rather different from that of chalcogenides, principally because the former have a much more significant ionic contribution to the chemical bonding than the latter, which are essentially completely covalent materials. For example, oxide glasses are generally insulators, with large values of the band-gap (~10 eV in the case of SiO₂), whereas for chalcogenides the gap is generally considerably smaller (1-3 eV), and hence these materials are semiconductors [2]. Later on, some other materials were also prepared in the glassy state which showed semiconducting properties [3].

A number of electronic applications of amorphous materials, almost all of them semiconductors, have been proposed or put into practice, especially after the discovery of doped n-type or p-type amorphous silicon. In many cases amorphous materials are used simply as passive elements in electronic devices made from conventional crystalline semiconductors. For example, a-SiO₂ or a-Si₃N₄ is used as the insulator layer in various thin film transistor configurations [4].

Amorphous semiconductors have also been found suitable for electrophotographic application. The material first used in xerography or document copying machines was a-Se in thin film form. More recently, a-Si:H films have also been used for this purpose.
Perhaps the most important application of the amorphous semiconductors, e.g., a-Si:H is in the direct conversion of sunlight to electrical power. The development of solar cells from amorphous semiconductors has been extremely active now a days.

Amorphous semiconductors, in particular, selenium and selenide alloys exhibit a unique property of reversible structural transformation which is useful in optical memory devices. Recent research and developments into optical disc memories have been carried out to achieve highly sensitive and stable memories.

1.2 BAND MODELS IN AMORPHOUS SEMICONDUCTORS

The carriers in amorphous system are strongly affected by the randomness of atomic arrangement due to the absence of long-range order. Mott [5] has argued that the spatial fluctuation in the potential, caused by the configurational disorder in amorphous materials may lead to the formation of localized states. A band gap may, however, exist in amorphous semiconductors due to short range order in them. Due to localized states, the valence and conduction bands do not have sharp cut-off but have a tail above and below the normal band. The extent of these tailing is expected to be enhanced in alloys which contain compositional disorder in addition to position disorder.
The conduction in localized states takes place by hopping process with the help of thermal energy. At absolute zero of temperature, no conduction is expected in localized states. The mobility of charge carriers therefore changes suddenly from a finite value to zero in the band tails.

Cohen, Fritzshe and Ovshinsky [6] first suggested that in the case of disordered covalent alloys, such as chalcogenide glasses, the valence and conduction band tails overlap each other close to the center of the forbidden gap. The mobility of the carriers has a finite value in high density states but it decreases abruptly in tail states (see Fig. 1.1). These boundaries are called mobility edges. The critical energies at mobility edges define a mobility gap.

Davis and Mott [7] proposed that there is a narrow band of compensated localized states which pin the Fermi level between the two tails (see Fig. 1.1). This model suggests that hopping conduction can take place in the localized states near the Fermi level.

Mott and his collaborators [8] further elaborated the model of gap states in the chalcogenide glasses. They considered the states near Fermi level due to defects which are discussed in detail in the next section.
Localized states

Mobility gap

(a) CFO Model

(b) Davis-Mott Model

(c) MDS Model

Electron energy (E)

Fig. 1.1
1.3 Defects in Amorphous Semiconductors

Defects can only be discussed sensibly in the context of some reference structure which is non-defective. In the case of crystalline materials, this requirement is readily satisfied, in terms of a perfect single crystal, but in the case of amorphous materials the situation is not as clear-cut; what is to be taken as the reference, non-defective, non-crystalline structure. In the case of covalently bonded systems, at stoichiometric compositions, the ideal reference structure may be taken to be a chemically - ordered continuous random network[9]. Thus, defects in such a structure can be wrong (homopolar) bonds and coordination defects, e.g. over-coordinated atoms or under-coordinated atoms (dangling bonds). However, in certain cases for amorphous materials it is difficult to decide whether or not a particular structural feature is a defect under the above definition. For instance, should the negatively charged non-bridging (NB) chalcogenide, denoted by the symbol \( \text{C}^-_1 \) (where \( \text{C} \) stands for chalcogen, and the superscript and subscript are the charge state and atomic coordination, respectively), resulting from the introduction into chalcogenide glasses of network-modifier cations and which compensate the positively charged cations [10], be regarded as defects.

Coordination Defects (Positive U)

In covalently bonded materials with pronounced directional bonding and consequently a well defined local geometry, one type of point defect concerns the atomic coordination.
These can be of two type: involving under coordination or over coordination with respect to the normal coordination of the ideal structure. Under coordinated defects in covalent solids are simply dangling, broken or unsatisfied bonds. Over-coordinated defects, though less common, arise when an additional covalent bond is formed datively between a normally coordinated atom and another (utilizing non-bonding lone-pair electrons); the formation of such defects provides the mechanism for producing a negative effective correlation energy for dangling bonds in chalcogenide glasses. A similar type of over-coordinated site has been proposed in a Si-H, where hydrogen interacts interstitially with long (i.e. weak) Si-Si bonds [11].

The difference between coordination defects in amorphous and crystalline solids is that the isolated defects can occur in non-crystalline state but not in ordered structures.

A simple dangling bond normally contains one electron and is electrically neutral, however, it is amphoteric (being able to donate or accept an electron) and under certain circumstances the electronic occupancy can change, varying concomitantly the change of the centre. Isolated coordination defects in amorphous covalent materials are labelled in terms of the type of atom that is the site of the defect, together with its coordination number and charge state as subscript and superscript respectively. Thus, for tetrahedrally coordinated materials such as Si or Ge, the different charge states of
(under coordinated) dangling bonds are denoted by $T_3^0$, $T_3^+$ and $T_3^-$ (normally bonded atoms are denoted by $T_4^0$).

The energy levels for electron states associated with an isolated dangling bond may be discussed in terms of a simple molecular orbital picture. If we consider the case of a tetrahedral semiconducting material e.g., a-Si, having an atomic electronic configuration $S^2p^2$, the atomic levels hybridize to form four $S^3p^3$ molecular hybrids, each of which may admit a bonding or antibonding orbital; solid state interactions then broaden the molecular levels into bands separated by a band gap (Fig. 1.2). A dangling bond, or non-bonding orbital, containing a single electron will therefore, have an energy level lying at the zero energy for the $S^3p^3$ hybrids, viz near the middle of the gap (if atomic relaxations are neglected). Thus structural defects such as dangling bonds are expected to electron states deep into the gap; the precise position of the energy levels, however, will depend crucially on factors such as structural relaxation around the defect or the electronic character of the states at the top of the valence band and the bottom of the conduction band from which the eigenfunction of the defect state derives.

The density of states in the gap for an amorphous semiconductor containing dangling bonds has been depicted in Fig. 1.1c. The left mid-gap band in this figure corresponds to the neutral dangling bond containing a single electron(spin) and is 'donor-like' (i.e. neutral when occupied) and the right mid-band gap corresponds to a different charge state of the
Dangling bond

Fig. 1.2
same defect, namely when an extra electron is placed in it and is 'acceptor-like' (i.e. neutral when empty). Under normal circumstances, the net energy cost for this addition is positive, it costs an extra energy (the Hubbard or correlation energy):

$$U = \langle \frac{e^2}{4\pi \varepsilon \varepsilon_{r_{12}}} \rangle$$

where $r_{12}$ represents the appropriate separation for two electron at the same site and a configurational average has been taken in evaluating $U$.

Although the isolated dangling bond is a possible entity in a covalent random network structure, if dangling bonds occur at voids or other internal surfaces, they can reconstruct so as to lower the total energy, there by changing the electron occupancy and hence the charge state of the defects.

The essential features of the 'charged dangling bond' model may be understood by consideration of the mono-atomic system, amorphous Se, illustrated in Fig. [1.3]. The structure of amorphous Se, which is two fold coordinated is believed to consist mainly of chains (with perhaps a few rings). Any chain end will be the site of a dangling bond orbital, which in the simplest case will contain an unpaired electron and be electrically neutral relative to the bulk; this dangling bond defect can be written as $D^0$, in Mott's model [12] or equivalently $D_1^0$, referred to Kastner's model [13]. Mott et al. [12] postulated that, following Anderson [14], electrons residing
Fig. 1.3
at $D^0$ centres should experience a negative $U_{\text{eff}}$ and electron pairing should be energetically favourable as a result of atomic rearrangements. Electron-lattice coupling is strong in amorphous chalcogenide because of the low atomic coordination resulting in a high degree of network flexibility, but more importantly, there exist non-bonding, lone pair $\pi$ orbitals at the chalcogen atoms which may be utilized in forming additional bonds, and which are energetically accessible since they are high lying, forming the top of the valence bond [15]. The transfer of an electron from one $D^0$ ($C_1^0$) centre to another produces one site which has the original dangling bond orbital containing two spin paired electrons and which is consequently negatively charged ($D^-$ or $C_1^-$) and the other which has an empty orbital which is then free to form a dative bond with the long-pair of a fully connected neighbouring atom; the defect now becomes three fold coordinated and positive charged ($D^+$ or $C_3^+$), as shown in fig. 1.3. In the latter case, the site of the defect moves from the originally dangling bond to the atom providing lone-pair electrons for the dative bond which correspondingly becomes over-coordinated. The repulsive Hubbard energy $U$ involved in placing an extra electron on the same site to form a $D$ centre is postulated to be outweighed by the energy gained in forming the extra bond at the $D^+$ site, rendering the reaction

\[ 2D^0 \rightarrow D^+ + D^- \]
exothermic with an overall negative effective correlation energy (Fig. 1.4). This process can be illustrated in terms of a configurational coordinate diagram (Fig. 1.4). The appropriate configurational coordinate $q$ in this case may be taken to be the sum of the distances between two $D^0$ centres and their respective nearest neighbour, but non-directly bonded atoms $q_1 + q_2$. Transfer of an electron between $D^0$ centres without a change in configuration costs the Hubbard energy $U$, but the lowest energy state for the two resulting oppositely charged centres lies at a different configurational coordinate because of the atomic relaxation (bonding) that takes place at the $D^+$ centre; the energy for this equilibrium configuration is lower by $U_{\text{eff}}$ than that for the two $D^0$ centres.

There are in fact two possible configurations for the neutral defect $D^0$ in chalcogenide glasses, one being under-coordinated ($C_1^0$) and the other over-coordinated ($C_3^0$). Kastner et al [13] proposed that the symmetric $C_3^0$ centre has the lowest total energy, whereas Mott et al.[12] believed that the actual configuration lie between the two, with one elongated bond.

The charged defects $C_3^+$ and $C_1^-$ have been called by Kastner a Valence–alteration pair (VAP), since the various under and over-coordinated sites can be considered as different charge states of the same defect. In compound chalcogenide glasses, $U_{\text{eff}}$ is expected to be negative, since the
Fig. 1.4
formation of a valence-alternation pair (VAP), \( C_3^+ \) and \( C_1^- \), from two normally bonded \( C_2^0 \) atoms via the reaction

\[
2 C_2^0 \rightarrow C_3^+ + C_1^-
\]

involves essentially just a bond flip, conserving the total number of bonds and therefore the VAP creation energy \( E_{\text{VAP}} \) might also be expected to be low [13]. Consequently, a relatively high density of coordination defects (charged in the case of compound materials) should be present in thermal equilibrium in chalcogenide melts, which will be frozen-in on quenching to form a glass, with a concentration depending on the temperature at which equilibrium was last established, namely the glass transition \( T_g \). Thus the concentration of randomly distributed VAP defect centres may be given by

\[
n_R \propto n_0 \exp (- E_{\text{VAP}} / 2k T_g)
\]

where \( n_0 \) is the total (chalcogen) atomic density. Since the VAP centres \( C_3^+ \) and \( C_1^- \) are equally and oppositely charged, there is a tendency for them to pair up in the melt under the action of their mutual coulomb interaction, thereby lowering the creation energy even further; the concentration \( n_I \) of such 'intimate-valence alternation pairs' - IVAPs [12] would therefore be higher than \( n_R \). It may be mentioned that VAPs pin the Fermi energy, IVAPs do not; the concentration of VAPs is expected to be far more sensitive than that of IVAPs to the addition of dopants that form charged centres. Luminescence could in principle arise from either VAPs or IVAPs.
1.4 ELECTRONIC TRANSPORT IN AMORPHOUS/GLASSY SEMI-CONDUCTORS AT LOW FIELD

Materials which can be transformed into the semi-conducting amorphous state generally contain elements of the groups III, IV, V and VI of the periodic table. These elements possess highly directional interatomic binding forces and, as a consequence, show rather strong local order in their glassy compounds. X-ray diffraction measurements have indeed revealed that the nearest-neighbor configuration in many amorphous materials is very similar to that of the crystalline state. Small deviations in the interatomic distance and in the bond angles lead, however, to a complete loss of translation order after a few coordination spheres. This immediately raised the important question concerning the applicability of special characteristics of the crystalline material, in particular its band structure model, to the amorphous state.

At present, there appears to be widespread agreement that, if the short-range order is the same in the amorphous state as in the crystalline one, some basic features of the electronic structure of crystal are preserved. This can be understood intuitively if one considers that the tight-binding approximation theory uses the atomic wave functions of the individual atoms perturbed only by the presence of the nearest neighbors. In order to account for the translational disordered, accompanied by a possible compositional disorder in multicomponent systems, modification have been proposed for the band structure of the amorphous solid. These are the
well-known Cohen-Fritzsche-Ovshinsky (CFO) [Fig. 1.1] and Davis-Mott [1.2] (Fig. 1.1), models. Introducing the basic idea of the presence of localized states at the band extremities, these models have been widely used to interpret experimental data in the field of electrical and optical properties. Nevertheless, in many respects the situation is far from clear at present, partly due to the absence of sophisticated theoretical work.

In contrast to the CFO and Davis-Mott ideas, a different approach to the understanding of the electrical properties of amorphous semiconductors has been put forward by Emin. He suggested that the charge carriers in some amorphous materials might be small polarons. It is generally accepted that hopping of small polarons is the mechanism responsible for electrical transport in oxide glasses, in which the major constituent is a transition-metal oxide. When the composition of the oxide deviates from stoichiometry, the transition-metal ion can occur in two valency states and conduction is due to hopping of charge carriers between aliovalent ions. A disagreement exists however, in the interpretation of the electrical data obtained on covalent amorphous semiconductors, such as a-Si, a-As, and the chalcogenide glasses. Here, it is not at all clear whether lattice deformation, induced by the incorporation of an extra charge at a given site, is strong enough to cause small-polaron formation.
DC Electrical Conductivity

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

(a) Extended state conduction

The conductivity for any semiconductor can be expressed in the form

\[ \sigma = -e \int N(E) \mu(E) \frac{\partial f(E)}{\partial E} \, dE \]  

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

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

Using the relationship

\[ \frac{\partial f(E)}{\partial E} = -f(E) \left(1 - f(E)\right)/kT \]

\( \sigma \) can be written as

\[ \sigma = e \int N(E) \mu(E) f(E) \left(1 - f(E)\right) \, dE \]  

In the Davis-Mott model, the Fermi level \( E_f \) is situated near the middle of the gap and thus sufficiently far from \( E_C \), the energy which separates the extended from the localized states, so the Boltzmann statistics can be used to describe the occupancy of state,
\[ f(E) = \exp\left[- \frac{(E - E_F)}{\kappa T}\right]. \]

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, under the assumption of a constant density of states and constant mobility, the conductivity due to electrons excited beyond the mobility edge into the extended states is given by

\[ \sigma = e N(E_C) \kappa T \mu_C \exp\left[- \frac{(E_C - E_F)}{\kappa T}\right] \quad (1.3) \]

where \( \mu_C \) is the average mobility. The number of electrons is given by

\[ n = \int_{E_C}^{\infty} N(E_C) \exp\left[- \frac{(E - E_F)}{\kappa T}\right] dE \]

\[ = N(E_C) \kappa T \exp\left[- \frac{(E_C - E_F)}{\kappa T}\right] \quad (1.4) \]

In order to get an idea of the order of magnitude of \( \mu_C \) we shall follow Mott's treatment. We define \( \sigma(E_C) = eN(E_C)\mu_C \kappa T \).

If \( N(E_C) \approx \frac{<N(E)>}{3} \), where \( <N(E)> \) is average density of states over the band, then

\[ \sigma(E_C) = e <N(E)> \mu_C \kappa T/3 \]

Mott calculated the lowest value of the electrical conductivity before the start of an activated process, i.e. just at \( E_C \). This quantity he called the 'minimum metallic conductivity.'
He derived the expression

$$\sigma_{\text{min}} = \text{const.} \frac{e^2}{h_\text{a}}$$  \quad (1.5)$$

where the constant lies in the range between 0.026 and 0.1; \( \sigma_{\text{min}} \) is usually of the order 200 - 300 \( \text{cm}^{-1} \). Taking const. = 0.026, one finds for the mobility

$$\mu_C = 0.078 \left( \frac{e}{h_\text{a}} \right) \langle N(E) \rangle \exp(\frac{E}{kT})$$

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

$$N(E) = \frac{K_m}{2\pi^2 h^2}$$

On the other hand, the maximum energy \( E_{\text{max}} \) of the band, which also yields the width \( B \) of the band, is expressed by

$$E_{\text{max}} = \frac{\hbar^2 \pi^2}{2ma^2} \quad \text{and} \quad K_{\text{max}} = \frac{\pi}{a}$$

This yields \( N(E) = \frac{1}{a^2} B \).

Introducing this result in the expression for \( \mu_C \) one gets

$$\mu_C = 0.078 e a^2 B/hkT$$  \quad (1.6)$$

Taking \( a = 2 \text{ Å} \), \( B = 5 \text{ eV} \) one finds at room temperature that \( \mu_C \approx 10 \text{ cm}^2\sqrt{\text{V}^{-1}s^{-1}} \). This value corresponds to a mean free path comparable or less than the interatomic distance. Cohen[1.7] suggested that conduction in this case would be more properly described as a diffusive or Brownian-type motion. In this regime the mobility can be obtained with the help of Einstein's relation,

$$\mu = \frac{eD}{kT}$$
The diffusion coefficient $D$ may be written as

$$D = \left(\frac{1}{6}\right) \nu a^2$$

where $\nu$ is the jump frequency and 'a' the interatomic separation. The mobility in the Brownian-motion regime is then given by

$$\mu_C = \frac{1}{6} \left(\frac{e^2}{\kappa T}\right) \nu$$  \hspace{1cm} (1.7)

This expression yields the same temperature dependence as (1.6) derived by Mott. Since $\mu_C \propto \frac{1}{kT}$, one expects that the expression for the conductivity is of the form

$$\sigma = \sigma_0 \exp\left[- \frac{(E_C - E_F)}{kT}\right]$$ \hspace{1cm} (1.8)

(b) **Conduction in Band Tails**

If the wave function are localized, so that $\sigma(E) = 0$, 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.

$$\mu_{\text{hop}} = \mu_0 \exp\left[- \frac{W(E)}{kT}\right]$$ \hspace{1cm} (1.9)

The pre-exponential $\mu_0$ has the form

$$\mu_0 = \left(\frac{1}{6}\right) \gamma_{\text{ph}} \frac{eR^2}{\kappa T}$$ \hspace{1cm} (1.10)

where $\gamma_{\text{ph}}$ is the phonon frequency and $R$ is the distance covered in one hop.

For a typical phonon frequency $\gamma_{\text{ph}} = 10^{13} \text{ s}^{-1}$ and
\( W \approx kT \) \((1.9)\) yields a mobility of the order \(10^{-2} \text{ cm}^2\text{v}^{-1}\text{s}^{-1}\) at room temperature. Comparison of this value with the one calculated for conduction in the extended states suggests, 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 assumes that the density of states \(N(E)\) behaves as some power \(S\) of \(E\),

\[
N(E) = \frac{N(E_C)}{(\Delta E)^S} (E - E_A)^S
\]

with \(E = E_C - E_A\), then the conductivity \(\sigma_{\text{hop}}\) due to electrons can be easily calculated starting from \((1.2)\)

\[
\sigma_{\text{hop}} = \sigma_0 \text{ hop} \left(\frac{kT}{\Delta E}\right)^S C \exp\left[-(E_A - E_F + W)/kT\right] \quad (1.12)
\]

where

\[
\sigma_0 \text{ hop} = (\frac{1}{2}) \gamma_{\text{ph}} e^2 R^2 N(E_C) \quad (1.13)
\]

and

\[
C = S! - (\frac{\Delta E}{kT})^S \exp\left(-\frac{\Delta E}{kT}\right) \left[1 + S(\frac{kT}{\Delta E}) + S(S-1)(\frac{kT}{\Delta E})^2 + \cdots\right] \quad (1.14)
\]

For the specific case of \(S = 1\) (linear variation), the conductivity is given by

\[
\sigma_{\text{hop}} = \sigma_0 \text{ hop} \frac{kT}{\Delta E} C_1 \exp\left[-(E_A - E_F + W)/kT\right] \quad (1.15)
\]
where

\[
C_1 = 1 - \exp\left(-\frac{\delta}{kT}\right) \left[1 + \left(\frac{\delta}{kT}\right)\right]
\]  
(1.16)

(c) **Conduction in Localized states at Fermi energy**

If the Fermi energy lies in a band of localized states, as predicted by the Davis-Mott model, the carriers can move between the states via a 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 \(E_F\) has been given by Mott. We shall follow here his original derivation.

Let us consider an electron that is scattered by phonons from one localized state to another. The energy difference between the states is denoted by \(W\). The probability \(p\) that an electron will jump from one state to another is determined by three factors, which are the following.

(I) The probability of finding a phonon with an excitation energy to \(W\), given by a Boltzmann expression \(\exp\left(-\frac{W}{kT}\right)\).

(II) An attempt frequency \(\gamma_{ph}'\) which cannot be greater than the maximum phonon frequency in the range \((10^{12} - 10^{13} \text{ s}^{-1})\).

(III) 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 \(\exp(-2\alpha R)\).

Here \(R\) is the jumping distance, which at high temperatures equals the interatomic spacing, and \(\alpha\) is a
quantity which is representative for the rate of fall-off of the wave function at a site. If overlapping of the wave functions is important, the factor \( \exp(-2aR) \) becomes of the order of one.

The probability \( P \) that an electron jumps will then be expressed by

\[
P = \gamma_{\text{ph}} \exp(-2aR - \frac{W}{kT})
\]

By making use of Einstein's relation

\[
\mu = \frac{eD}{kT}
\]

with \( D = \frac{1}{6} p R^2 \), the conductivity can be written as

\[
\sigma = \left( \frac{1}{6} \right) e^2 p R^2 N(E_F)
\]

Here \( N(E_F) \) is the density of states at the Fermi level and \( N(E_F) kT \) is the number of electrons that contribute to the conductivity.

\[
\sigma = \left( \frac{1}{6} \right) e^2 R^2 \gamma_{\text{ph}} N(E_F) \exp(-2aR) \exp\left( -\frac{W}{kT} \right)
\]

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

\[
\frac{4\pi}{3} R^3 N(W) W
\]

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

\[
W = \frac{3}{4\pi R^3 N(E_F)}
\]

and for the jump probability,

\[
P = \gamma_{ph} \exp \left\{ -2\alpha R - \left[ (\frac{4\pi}{3}) N(E_F) R^3 kT \right]^{-1} \right\}
\]

The most probable jump distance is found by minimizing the exponent of the above expression as a function of \( R \):

\[
R = \left[ \frac{9}{8\pi\alpha N(E_F) kT} \right]^{1/4}
\]

This gives a jump frequency of the form

\[
P = \gamma_{ph} \exp\left( -\frac{A}{T^{1/4}} \right)
\]

where

\[
A = 21[\alpha^3/K N(E_F)]^{1/4}
\]
Mott's treatment of variable range hopping leads to a temperature dependence for the conductivity of the form

\[ \sigma = \left( \frac{1}{6} \right) e^{2\gamma_{ph} R^2} N(E_F) \exp\left(-\frac{A}{T^{1/4}}\right) \quad (1.24) \]

or

\[ \sigma = \sigma_0(T) \exp\left(-\frac{A}{T^{1/4}}\right) \quad (1.25) \]

There have been several more derivations of the conductivity formula for variable range hopping. In general the \( T^{-1/4} \) relationship remains unchanged, but slightly different values were found for the numerical factor in \( A \). In Mott's derivation the pre-factor \( \sigma_0(T) \) is given by

\[ \sigma_0(T) = \frac{e^{2\gamma_{ph} R^2} N(E_F)}{6} \left[ \frac{9}{8\pi \alpha N(E_F) kT} \right]^{1/2} \]

\[ \sigma_0(T) = \frac{e^{2\gamma_{ph} R^2}}{2(8\pi)^{1/2}} \gamma_{ph} \left[ \frac{N(E_F)}{\alpha kT} \right]^{1/2} \quad (1.26) \]

In principle, the two parameters \( \alpha \) and \( N(E_F) \) can be evaluated from the slope of a plot of \( \ln[\sigma(T) T^{1/2}] \) vs \( T^{-1/4} \) and from the intercept at \( T^{-1/4} = 0 \), if one makes a reasonable assumption for \( \gamma_{ph} \). Alternatively, one can get an idea of the most probable hopping distance \( R \) at a given temperature by inserting values for \( \alpha \) and \( N(E_F) \) in (1.21).

In the recent literature many experimental studies, especially on the tetrahedral bonded materials, dealt with variable range hopping. In many case, unreasonably high values were calculated for \( N(E_F) \), very after by use of the pre-exponential factor \( \sigma_0(T) \). Although the \( T^{-1/4} \) dependence of \( \ln \sigma \)
in wide observed these finding seem to indicate that the above expressions do not describe in an exact quantitative way the conductivity. It must be mentioned here that Mott's derivations are based on certain assumptions of which the most important are: energy independence of the density of states at $E_F$, neglection of correlation effects in the tunneling process, omission of multi-phonon processes, and neglection of the electron phonon interaction. Several authors have investigated the effect of departure from a constant density of states and have clearly demonstrated that the energy distribution of density of states is of major importance in the theory of variable range hopping [16].

1.5 **HIGH FIELD CONDUCTION IN AMORPHOUS SEMICONDUCTORS**

The study of the electrical conductivity of any medium gives us an insight into the transport mechanisms for the prevailing carrier species, be they electrons, holes, Polarons or ions. The starting point for experimental work and for theoretical analysis is usually the low-field condition, defined by the requirements that the applied field should not significantly disturb the thermal equilibrium of the system. In this situation one may treat transport as a small perturbation of the equilibrium system [17] usually through Boltzmann's equation, with the distribution of electrons in energy remaining to first order unchanged in comparison with the equilibrium situation. When dealing with a free-carrier system, such as a semiconductor or a metal, one derives an expression for the mobility
µ of the carriers, in terms of their effective mass m*, change q and mean collision time τd : μ = q τp/m*. The density of free carriers is assumed to be the equilibrium density n0, so that the resulting low field conductivity is given by

$$\sigma_0 = q \mu n_0$$  \hspace{1cm} (1.27)

The application of a high field to a free carrier system may influence both the mobility and the number of available carriers. The mobility may be influenced by the change in the effective distribution of carriers in energy, which could be described in terms of a rise of carrier temperature Tc above the lattice temperature T0. This may be seen most readily by considering that an electric field E acting on a carrier system moving with an average velocity \( V_d = \mu E \) will give rise to a power input \( q \mu E^2 \). Under steady state conditions this power input has to be dissipated to the lattice through collisions which take the energy away from the carriers.

An energy relaxation time \( \tau_\varepsilon \) may be defined by the relation

$$q \mu E^2 = \frac{\kappa (T_c - T_0)}{\tau_\varepsilon}$$  \hspace{1cm} (1.28)

equating the power output from the field to the power loss to the lattice. Since the conditions for energy relaxation are quite different from those for momentum randomisation \( \tau_\varepsilon \) is not necessarily equal to \( \tau_p \). The time \( \tau_\varepsilon \) being usually much longer [18,19]. Depending upon the prevailing scattering
mechanism, the mobility may either increase or decrease with increasing electric field due to this carrier heating effect. It appears, however, that at fields in excess of some $10^3 - 10^4$ V/cm, the proportionality between drift velocity and field is largely lost and $V_d$ increases much more slowly, saturating in most instances at values of the order of $10^7$ cm/s [20].

At much higher electric fields, of the order of $10^6$ V/cm, the heating of the carrier population by the electric field becomes sufficiently effective to impart to a finite number of carriers energies comparable with the width of the forbidden gap, thus leading a rapid multiplication of carrier numbers by the avalanche process [21]. This causes a corresponding rise of current with field.

In the case of free-carrier systems high field effects are most readily observable in materials with a small number of equilibrium carriers since heating effects are kept to reasonable proportions. Highly conducting solids do not readily lend themselves to this type of study. For the same reason, the study of high field effects is particularly favoured in low-conductivity solid, many of which are such because of their low mobility. It is here that the amorphous semiconductors come into consideration, since the mobility of localized carriers in them is very low. Some of these materials may have so low an equilibrium conductivity that they may be classified as insulators and the only observable transport occurs under high field conditions. In this work present, will be concerned
with the theory and experimental results relating to high field conduction in a wide range of low mobility solids, most of which are amorphous or heavily disordered.

Classification of High Field Phenomena

In the context of low mobility solids it is possible to distinguish four broad classes of phenomena which could arise in the presence of high electric fields to the system.

(i) Contact-induced effects, e.g. injection of non-equilibrium carriers, space charge limited flow, blocking effects, tunnelling through the barriers etc.

(ii) purely thermal effect arising from Joule heating of the sample.

(iii) Bulk effects due to the enhancement of the conduction by the high electric field, without resulting thermal effects and structural changes breakdown, switching etc.

The problem of contacts will be discussed very briefly in the following section, but the remainder of the first category of effects will not be dealt with here since they form a vast subject in their own right for which there is ample literature [22-26]. The second category of purely thermal effects will not be considered either, except for mentioning the obvious precautions which have to be taken avoid overheating of samples.

The last category of catastrophic effects, whether they are reversible or irreversible, forms the subject of two well-developed directions of study dielectric breakdown effects[27]
and switching phenomena in amorphous semiconductors which have been dealt within the context of the summer school [28]. Accordingly, we do not propose to discuss them at present. This only leaves the third category of bulk effects due to high electric fields. It is inevitable that in most cases the experiments have to be performed on relatively thin films of the material under study, to avoid excessive dissipation of heat and to keep the required potential difference across the sample down to manageable values. The resulting 'sandwich' geometry, metal-semiconductor-metal, makes it impracticable to apply separate potential probes to eliminate any contact effects and considerable caution is necessary in this interpretation of experimental results on that account [29].

Contacts to low mobility solids

An electrical contact represents an interface between two different materials, one of which is our case in non-metallic and the other metallic. In general, a potential difference exists between the two materials even in the absence of an external bias. This may be due to a difference between the contact potentials of the two materials, or to the formation of surface charge on the semiconductor due to the peculiar charge conditions of the electronic surface states [27]. In either case, the resulting potential difference is screened within a distance related to the "screening length" \( \lambda \) in the semiconductor, which depends on the number of ionizable
centres in the vicinity of the interface. This number is in turn dependent on the density of available electronic states in the forbidden gap of the material in question, especially in the range of energy close to the Fermi-level. If the density of ionizable centres is high, in excess of $10^{19} \text{ cm}^{-3}$ say, a barrier of 1 eV height would have a width of 100 Å, the resulting energy barrier being as shown in fig. 1.5(a). In this situation it is very likely that the dominant process of carrier injection into the semiconductor is by direct tunnelling near the Fermi-level into the localized levels in the forbidden gap of the material. In this situation the observed behaviour would not depend strongly on contact phenomena. If the semiconductor has very few localized levels in the forbidden gap, then the screening length is very large and may exceed the total thickness of a relatively thin sample (Fig. 1.5(b)). The potential of the bulk material is now determined entirely by the contact potential difference and the transport properties depend on the motion in the conduction or valence bands of carriers injected over the contact barrier. The presence of contact barriers leads to two kinds of effects - asymmetry with respect to the polarity of the applied bias and the failure of the voltage-current. Characteristics to scale according to the thickness of the sample, since barrier phenomena depend on voltage while bulk effects depend on field. A test for symmetry, for correct thickness dependence and for independence of the type of metal electrode used should
eliminate any doubts as to the significance of contact effects in any particular experiment.

**Bulk High field effects**

We begin our discussion of bulk high field effects with a brief review of the types of localized levels which are likely to be found in the forbidden gap of a disordered solid. It is possible to distinguish two basic types, according to the state of charge of the centre which is assumed to be capable of existing in two states, one of which contains one electron more than the other. The electron-rich state will be referred to as 'occupied' or 'full' and the other as 'unoccupied' or empty. A centre is called a donor if it is neutral when full and positively charged when empty; it is called a trap if it neutral when empty and negatively charged when full. The basic difference for our present purpose consists in the nature of the forces binding the electron to the centre - in a donor the force is Coulombic and therefore of relatively long range, in a trap it is non-coulombic and much shorter range.

A disordered solid may contain a wide distribution of both donors and traps in energy and in space and fig. 1.6 shows a schematic representation of such a distribution, donors being represented by squares, traps by circles and shading denoting full centres. All transitions giving rise to transport must be between full and empty centres and the most energetically favourable are those involving the smallest
charge of energy. In low field transport there is no significant difference between donors and traps and all transitions marked in fig. 1.6 contribute to the flow of current. At high fields, however, an important distinction arises between traps and donors and we shall distinguish the following cases:

(i) donor - donor hopping
(ii) trap - trap hopping
(iii) donor - trap hopping [30].

(i) **Donor - donor hopping**

At low electric fields this mechanism is responsible for conduction in compensated crystalline silicon and germanium in the impurity conduction range, at very low temperature [31,32]. The presence of high electric field $E$ will affect the potential barrier of a coulombic centre situated at the point $r = 0$ in the following manner:

$$\phi(r) = -\frac{e^2}{4\pi\varepsilon_0 k'r} - e E r$$

(1.29)

as shown in fig. 1.7. The maximum of the potential barrier in the direction of the electric field occurs at point $x_m = \frac{e}{2E^{1/2}}$ and the lowering with respect to the zero level in the absence of field is

$$\phi_m = -e \beta E^{1/2} \quad \text{where} \quad \beta = \left(\frac{e}{\pi k'}\right)^{1/2}$$

(1.30)

If the ground state of the donor is at $\phi_i$ in the absence of the field, the probability of emission from this ground state due to thermal excitation is
P \propto \exp\left(-\frac{\varphi_{1}}{kT}\right) \exp\left(\frac{e\varepsilon E}{kT}\right) \quad (1.31)

The electric current arising from the transport of the emitted carriers in the conduction band will depend not only on $P$ but also on the distance $l$ moved by the carriers before recapture, we may postulate that $l = \text{const}$, if the distance travelled is independent of the field or $l \propto E^a$ where 'a' is an exponent of the order of 1 or 2. The current will therefore be of the form:

$$I = A(T) E^a \exp\left(\frac{e\varepsilon E}{kT}\right) \quad (1.32)$$

where $A(T)$ is a function of temperature incorporating, among other factors the first exponential term in equation (1.31).

Since the dominant field dependence in equation (1.32) is through the exponential term, the $E^a$ factor giving a relatively weak contribution, it is possible to write equation (1.32) in the following form

$$\log I = \text{const} + \frac{e\varepsilon}{kT} E^{1/2} \quad (1.33)$$

This shows that a graph of $\log I$ versus $E^{1/2}$ ought to give a straight line with a slope $\frac{e\varepsilon}{kT}$ which should be easily checked experimentally, with the value of $\beta$ taken from equation (1.30). This mechanism is known as Poole-Frenkel conduction and has been observed in a range of amorphous materials. Such as SiO [34], Ge [35], C [36], to name only a few.

A different situation arise if the Coulombic centres are situated so close together that their fields overlap. In this case the lowering of the barrier is given by $e\varepsilon S$, where
2S is the distance between centres. One would therefore expect this model to be characterized by a current-field dependence of the type:

\[ \log I = \text{const} + \frac{eS}{kT} E \]  

(1.34)

and this is known as the Poole effect. Again, this type of behaviour has been found in a number of materials [37,38].

The simple theory discussed so far provided for emission over the lowest point of the barrier, directly in line with the electric field. A more realistic assumption is that the emission attempts are distributed isotropically in all directions and that they succeed according to the barrier lowering in any particular direction. This treatment has been applied [33-39], and has been further extended by Hill [37] to include emission 'upstream', i.e. against the field. The final result is that the exponential term in equation (1.32) is replaced by function

\[ f(\alpha) = \alpha \cosh \alpha - \sinh \alpha \]  

(1.35)

where \( \alpha = \frac{e\phi E^{1/2}}{kT} \) for the Poole-Frenkel mechanism and \( \alpha = \frac{eSE}{kT} \) for Poole mechanism. Hill expresses the current in a reduced form

\[ J = I \Gamma^{-b} \exp\left(\frac{e\phi_1}{kT}\right) \]  

(1.36)

where \( \Gamma^{-b} \) term corresponds to \( \frac{1}{A(T)} \) in equation (1.32), \( \phi_1 \) is the donor activation energy in the absence of field. With
these notations it is possible to write a general equation

\[ J = f(\alpha) \]  

(1.37)

which contains both field and temperature dependence implicitly through the variable \( \alpha \).

Trap - trap hopping

By contrast with the relatively well-developed understanding of the Poole-Frenkel and Poole mechanisms in donor-dominated hopping at high electric fields, the behaviour of hopping between traps is much less well understood. The high field has a much smaller direct effect on the strongly localized barrier of a trapping centre than on the comparatively much more extended coulombic potential of a donor. The most pronounced effect that one would expect in this case is that the distribution of carriers in energy among the traps will be affected if the energy gained per hop is appreciably larger than the thermal energy:

\[ e E_{ij} > kT \]  

(1.38)

Fig.(1.8) shows an assumed distribution of trapping levels in energy in the presence of a high electric field with three types of transitions indicated by arrows. On average, the carriers are unlikely to lose as much energy to the lattice as they gain from the field and this leads to an increase of their 'effective temperature' in the traps. This situation is analogous to hot electrons in a free band which are described
Fig. 1.8
levels. It was suggested [40] that the further apart in energy the localized level are, the longer the relaxation time, since it is more difficult to dissipate this energy to the lattice. As the density of levels in energy increases towards the band edges, so the energy relaxation time decreases towards the free band value which may be $10^{-14}$ - $10^{-13}$ sec.

This heating of the carrier population in localized levels by a high electric field would bring about an increase of mobility with field, since the more energetic electrons are moving in regions of higher mobility. In those cases where a field-dependence of mobility has been postulated in amorphous materials it is very likely that the mechanism responsible is of this type.

(iii) **Donor - trap hopping**

This mechanism has been introduced to explain some experimental observations of high field photo-conduction in SiO [41], although its relevance to dark conduction is fairly clear. It applies in situations where there exist a large density of trapping levels distributed in energy together with some donor levels which effectively supply carriers to these traps.

Figure 1.9 shows a donor surrounded by trapping levels in the presence of high field. The electron does not have to be excited to the 'band edge' for emission to take place. It is sufficient that it should acquire enough energy
Average energy in equilibrium of lattice temperature $T_0$

Average energy required for escape

Fig. 1.9
to move into the upper range of localized traps in which the mobility is relatively high. It then moves by the trap-hopping process described above and may move even closer to the 'band edge', without necessarily ever reaching it, because of the rapidly decreasing energy relaxation time. In the final process of recapture in an empty donor site, the thermalization of the carrier has to be taken into account [40], and it has been postulated that the carrier may be re-emitted before reaching the donor ground state. This would account for the effective temperature in the Poole-Frenkel mechanism which may be responsible for the abnormally low values of the slope of the log I versus $E^{1/2}$ graphs mentioned earlier. A different but related approach to the interpretation of high field photoconductivity in amorphous Se and Te postulates a field-dependent quantum efficiency [42,43]. Most of the known examples of Poole-Frenkel or Poole mechanism of high field conduction occur in amorphous semiconductors and it is interesting to consider the reasons for the absence of this effect in crystalline materials. Simple consideration of energy balance in the presence of high field shows [44], that the field-lowering mechanism for carrier emission is in competition with the carrier heating mechanism which leads to the avalanche ionization process either from impurity levels or across the energy gap. It is easily shown that in high mobility semi-conductors and for low ionization energies the avalanche process has a
much higher probability than the field-lowering mechanism. Only in very low mobility solids is the probability of avalanche ionization significantly lower than the Poole-Frenkel mechanism. Experiments on layered crystalline structures show that in the direction normal to the layers, i.e., in the direction of low mobility, there appears to be good evidence of the latter mechanisms [45,46].

1.6. SELECTION OF THE PROBLEM

Chalcogenide glasses belong to a special category of amorphous semi-conductors which have recently been found suitable for various solid state devices. Amorphous materials, in general, have many advantages over their crystalline counterpart due to their easy preparation techniques. As thermodynamic equilibrium is not required for these materials, multi-component alloys with varying compositions can be prepared and hence the properties can be changed according to one's will. These materials are, therefore, called tailor made materials.

In spite of the technical advantages of amorphous semi-conductors over their crystalline counterpart, the progress in the devices made from these materials has been rather slow as the basic physics of these materials is not understood to a level which is required to improve the quality of the devices. Scientists and engineers have taken keen interest in
the study of these materials during the last 25 years. However, the field is found to be highly intriguing. More and more experimental data is required to arrive at a conclusion.

Among chalcogenide glasses, Se-Te glassy alloys have recently gained much importance because of their superiority over amorphous Se. Alloying of Se with Te reduces the electronic band gap of Se and thus results in a photoreceptor having more desirable spectral response for Xerographic purposes. Apart from this, these alloys have higher photosensitivity, greater hardness, higher crystallization temperature and smaller aging effects as compared to Se glass and hence can be used in various other devices.

The addition of third element to the binary Se-Te alloys have been useful to obtain stable glassy systems having higher glass transition and crystallization temperature. The present author has chosen two binary glasses in Se-Te system, i.e. Se_{70}Te_{30} and Se_{80}Te_{20}. In Se_{70}Te_{30}, Cd is added to get ternary Se_{70}Te_{30-x}Cd_{x} system where x is varied from 0 to 8.

In Se_{80}Te_{20} binary system, Sb and Ge is added to obtain ternary Se_{80-x}Te_{20}Sb_{x} and Se_{80-x}Te_{20}Ge_{x} systems where x is varied from 0 to 15. One more ternary glassy system, Ge_{22}Se_{78-x}Bi_{x}, has been chosen for the present study. This system has been an important one as p-n transition takes place at a particular composition. A study of the electrical conductivity of any medium gives us an insight into the transport mechanisms for the prevailing carrier species. The mobility and free carrier concentration is assumed to be constant with field in this situation.
The application of a high field to a free carrier system may influence both the mobility and the number of carriers available.

In the case of free-carrier systems, high field effects are most readily observed in materials with a small number of equilibrium carriers since heating effects are kept to reasonably small. For this reason, the study of high field effects is particularly favoured in low conductivity solids.

High field effects have been studied in amorphous semiconductors [47-71] and the results have been interpreted in terms of the space charge limited conduction or in terms of high field conduction due to Poole-Frenkel effect.

This shows that the electrical conduction at high fields is still not fully understood in chalcogenide glasses. The present work is an attempt to provide some important conclusions in this direction.

Chapter 2 describes the results of d.c. conductivity measurements, at low fields, as a function of temperature, composition dependence of d.c. conductivity and the activation energy is also discussed. The author has established a relation between pre-exponential factor and the activation energy which is known as Meyer-Neldel rule which has been observed in many other kinds of solids also. The details of preparation of glassy samples and their thin films, have also been mentioned in this chapter. Characterization of the samples by X-ray
diffraction and DSC technique has also been done and the results reported in the same chapter.

Chapter 3 of the thesis deals with the high field conduction studies in the same glasses in which low field conduction measurements have been reported in chapter 2. Results of high field conduction have been analysed in terms of existing mechanisms reported for high field conduction and it is found that the conduction in these glasses is Poole-Frenkel type.

Chapter 4 of the thesis deals with the high field conduction studies in Ge-Se-Bi glassy system. The results indicate that, unlike Se-Te based glasses reported in chapter 3, Ge-Se-Bi glasses show the presence of space charge limited conduction. This may be because of lower density of defects in this system as discussed later in this chapter.