

A.C. Conduction in Amorphous Semiconductors

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Abstract | The recent developments in the theoretical and experimental study of frequency-dependent conductivity in amorphous semiconductors are reviewed, emphasising particularly on chalcogenide glasses. The striking similarity of a.c. conduction in quite different disordered solids is compared and discussed in terms of experimental results, modelling, and computer simulations. After giving an overview of experimental results, an existing macroscopic and a microscopic model are reviewed. More specifically, the factors such as random and non-random spatial distributions of electrically active centres responsible for the a.c. conductivity have been highlighted. Additionally, we have briefly discussed various aspects of a.c. loss behaviour on chalcogenide glasses such as effect of temperature, composition, doping, and other material properties. It is concluded that the a.c. conduction at intermediate to high temperatures is accounted for by the correlated barrier model, whereas at sufficiently low temperatures the behaviour is related to the atomic tunnelling.

1. Introduction

In recent years, exciting advances have been made in understanding the problem of how the disorder in amorphous semiconductors influences the band structure and hence the electrical and optical properties.¹⁻⁵ In crystalline solids one finds that the crystal structure plays a key to the various electronic conduction phenomena in both metals and semiconductors. But, of course, not all the solids are crystalline and not all the conductors are electronic. There are many disordered solids such as polymers and glass wherein the conduction of mobile charges includes electron, hole and *polaron* hopping is of considerable interest. Today, an interest in the dynamics in disordered materials is driven by multitude of novel applications these materials find in such devices as electronic and optical memories. So profound is the interest in devices based upon charge transport in both ordered and disordered materials that this expanding field

of research has come to be known as solid-state electronics.

In the context of electrical conduction phenomenon, a feature common to all amorphous semiconductors is a frequency-dependent conductivity that increases approximately linearly with frequency (see figure 1) at least in the frequency range below 10 MHz, i.e.,

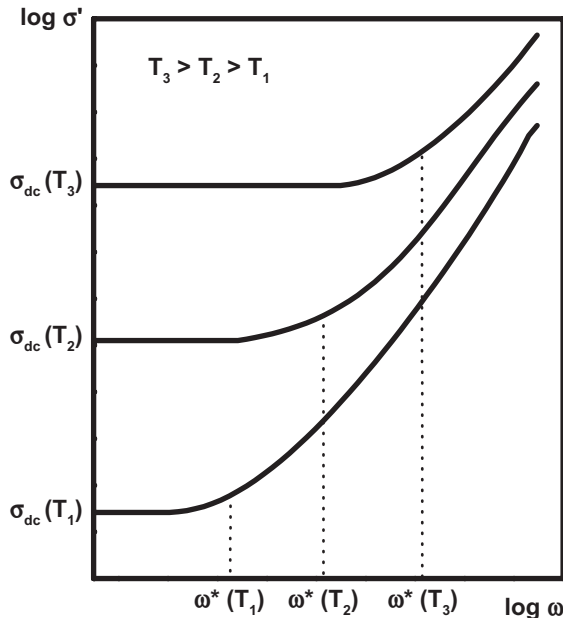
$$\sigma(\omega) = \sigma_0 + A\omega^s \quad (1)$$

where the pre factor A and the frequency exponent s are both weakly dependent on temperature and it is generally found that $s \leq 1$, tending to the limiting value of unity at low temperatures. The first term σ_0 is the low frequency (or d.c.) conductivity and found to be thermally activated with Arrhenius form. It has been observed that this type of behaviour in many other materials including polar polymers and ionic conductors. The only common feature of the numerous class

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Polaron: The quasiparticle formed by the electron and its self-induced distortion is called polaron

Figure 1: Schematic diagram showing the frequency dependence of real part of the conductivity at three different temperatures. When the temperature is lowered the d.c. conductivity decreases rapidly and correspondingly in the time scale the crossover frequency ω^* in the entire spectrum is displaced towards lower frequencies.



Mobility edge:

The mobility edge is the critical point at which a transition from localized to extended character of the eigenfunctions occurs in the random lattice

Variable range hopping:

It is a model describing low temperature electronic conductivity in a strongly disordered systems with localized states with characteristic temperature dependence of $T^{1/4}$

a.c. universality:

It is almost always possible to scale measurements of the frequency-dependent conductivity at different temperatures into one single "master" curve. Different solids have quite similar master curves and are the only common feature of the numerous different solids exhibiting this a.c. universality is their disorder

solids exhibiting this 'a.c. universality' is their disorder in either lattice or sublattice. This has been an open question ever since the full scope of a.c. universality was recognized in the 1970.⁶⁻⁹ The phenomenon has variously been ascribed to relaxation caused by the motion of electron, or atoms/ions, hopping or tunnelling between the equilibrium sites. The purpose of this article is therefore to review the available experimental evidence pertaining to a.c. conduction for a family of amorphous semiconductors, namely 'chalcogens' (elements from the Group VI) at the other, and 'chalcogenide' alloys of chalcogen with pnictogen (or tetrahedrally bonded semiconductors, such as Si or Ge) in between. The reasons for choosing to concentrate primarily upon this family of amorphous semiconductors are twofold: a unified picture of the behaviour of these solids emerges that is qualitatively different from that exhibited by other types of amorphous semiconductors such as amorphous silicon or germanium. Thus, the aim of this paper, then, is to complement and supplement with the existing reviews in this field.

An important two additional features make the study of the a.c. properties of chalcogenide glasses worthwhile: the first is that these materials appear to contain a certain type of structural defects,^{10,11} which controls many of the opto-electronic properties,

may also be responsible for the a.c. conduction. In addition they also contain a spectrum of low-energy states (two-level systems), which is responsible for the thermal and dielectric properties at low temperatures. The second feature characteristic of chalcogenide materials, and one that makes the interpretation of experimental data less ambiguous, is the fact that the d.c. conductivity of such materials is generally thermally activated, indicative of conduction by carriers in extended states beyond the *mobility edge*,¹² rather than exhibiting the temperature dependence, $\sigma \propto \exp(-T^{-1/4})$ indicative of *variable-range hopping* (tunnelling) of electrons between states at the Fermi level.¹³ This is of importance since, either in the case where a.c. and d.c. conduction arise from completely separate and different process, or where the same basic processes is responsible for both types of conductivity. Thus, in general, most of the chalcogenide glasses are expected to obey eqn. 1, since d.c. component (σ_{dc}) is due to band conduction and the a.c. component ($\sigma(\omega)$) is due to relaxation processes. If the same processes (e.g. hopping conduction) is responsible for both d.c. and a.c. conduction, σ_{dc} is simply the $\omega \rightarrow 0$ limit of $\sigma(\omega)$, and the validity of eqn. 1 is more doubtful, but is nevertheless still often used in the literature.¹⁴ However, since $\sigma(\omega)$ for amorphous semiconductors almost invariably increases monotonically with increasing frequency, and moreover is usually only weakly dependent on temperature. Therefore, the pure a.c. component of the conductivity will try to dominate at high frequencies and/or low temperatures because the temperature dependence of σ_{dc} is always much greater than that of σ_{ac} , and therefore the assumption of independent conduction mechanism within eqn. 1 becomes justified.

The layout of this review article is as follows: first we discuss in general the important terms of dielectric relaxation in solids and how a frequency-dependent conductivity can arise in amorphous materials, and follow this with a survey of the available theoretical models for a.c. conduction in amorphous semiconductors. The validity of these models will be discussed in the light of experimental data, allowing certain conclusions to be drawn as to those mechanisms of a.c. conduction in chalcogenide glasses.

2. Fundamental Concepts

In the presence of an externally applied electric field a material's response is often characterized in two generic ways within the literature. A conductive response is associated with a current comprised of mobile charge carriers which in the case of electronic conductors are electrons, and in the case of an

ionic conductor are ions. If a material's response is limited to the local displacement of bound charges, often characterized by a change in a local dipole moment, then the response is commonly termed dielectric.¹⁵ In the present investigation, since the interest lies in understanding the response of charged species to the presence of an applied electric field, the response will simply be referred to as the conductivity to avoid trying to continuously define the length scale over which displacements of a given response mechanism occur. The response of a given material often changes drastically depending on the measurement environment, thus making conductivity spectroscopy particularly well suited to the task of exploring the dynamic behaviour of materials. By the application of an harmonically varying electric field to a dielectric sample produces a time-dependent polarization $P(t)$. In the frequency domain, the spectral dependence of the polarization is related to the electric field variation¹⁵ by

$$P(\omega) = \epsilon_0 \chi(\omega) E(\omega) \quad (2)$$

where ϵ_0 is the permittivity of free space, and the dielectric *susceptibility* $\chi(\omega)$ is, in general, a complex quantity i.e.,

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (3)$$

the imaginary part $\chi''(\omega)$ is termed the 'dielectric loss' (and the resulting current due to this is in phase with the driving field). The dielectric loss in disordered solids usually exhibits a peak, much like that characterizing dielectric relaxation in dipolar liquids. The components of the dielectric susceptibility are related to those of the complex relative *permittivity*

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (4)$$

$$\epsilon'(\omega) = 1 + \chi'(\omega) \quad (4a)$$

$$\epsilon''(\omega) = \chi''(\omega) \quad (4b)$$

Furthermore, the frequency-dependent relative dielectric constant $\epsilon^*(\omega)$ can be expressed in terms of conductivity. By

$$\begin{aligned} \sigma^*(\omega) &= \sigma'(\omega) + i\sigma''(\omega) \\ &= i\omega\epsilon_0\epsilon^*(\omega) \\ &= i\omega\epsilon_0[\epsilon'(\omega) - i\epsilon''(\omega)] \end{aligned} \quad (5)$$

The real part of $\sigma^*(\omega)$ is usually denoted by $\sigma'(\omega)$ and is given by

$$\sigma'(\omega) = \epsilon_0\omega\epsilon''(\omega) \quad (6)$$

to which should be added any d.c. conductivity component, and, equivalently, the imaginary part of the a.c. conductivity is given by

$$\sigma''(\omega) = \epsilon_0\omega\epsilon'(\omega) \quad (7)$$

Clearly, $\sigma''(\omega) \neq 0$ reflects a phase difference between field and free charge carrier. Below phonon frequencies, whenever the conductivity is frequency dependent the charge carrier displacement always lags behind the electric field.

The "loss tangent" is defined by

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (8)$$

And although it is a useful quantity since it is independent of sample geometry. However, it is of only limited to general utility since its behaviour with frequency and temperature does not in general reflect those of ϵ_1 and ϵ_2 independently.

In order to calculate the a.c. conductivity, we first consider the Debye¹⁶ model for the dielectric response to an alternating electric field of either an isolated charge that can occupy one of two localized sites or equivalently an inertialess dipole that can assume one of only two spatial configurations.¹⁵ The Debye response is defined by the relaxation of the polarization obeying a first-order rate equation characterized by a single, fixed time constant τ , namely

$$\frac{dP(t)}{dt} = -\frac{P}{\tau} \quad (9)$$

which has the solution

$$P(t) = P_0 \exp\left(-\frac{t}{\tau}\right) \quad (10)$$

The dielectric susceptibility is obtained from the Laplace transform of the polarization decay function $-\frac{dP(t)}{dt}$, given by the Debye response:

$$\begin{aligned} \chi(\omega) &= \frac{\chi(0)}{1 + i\omega\tau} \\ &= \chi(0) \left[\frac{1 - i\omega\tau}{(1 + \omega^2\tau^2)} \right] \end{aligned} \quad (11)$$

The dielectric loss $\chi''(\omega)$ is thus predicted to exhibit a peak, since the function $\frac{\omega\tau}{(1 + \omega^2\tau^2)}$ has a peak at $\omega\tau = 1$, if the relaxation time τ has a fixed value. However, in disordered systems, and amorphous

Loss tangent: It is a parameter of a dielectric material that quantifies its inherent dissipation of electric energy in the material

Susceptibility: Susceptibility of dielectric material is a measure of how easily it polarizes in response to an external electric field

Permittivity: Permittivity, also called electric permittivity, is a constant of proportionality that exists between electric displacement and electric field intensity

materials in particular, it is more reasonable to assume that a broad distribution of relaxation times, $n(\tau)$ should exist if relaxation occurs by processes involving either with respect to distances or activation energies intimately related to the disordered structure of the material. Thus a peak exhibited by a given solid is not necessarily Debye like, it can be exhibited by the dielectric loss. The distribution of relaxation time indicates that each individual microscopic process giving rise to a relaxation time τ is independent of all others. Therefore, the overall conductivity is given by a summation over all contributions each acting in parallel. For a continuous spectrum of $n(\tau)$, the real part of the a.c. conductivity can be written as

$$\sigma'(\omega) = \int_0^{\infty} \alpha n(\tau) \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} d\tau \quad (12)$$

where α is the *polarizability* of a pair of sites, for the moment assumed to be independent of τ . The linear frequency dependence that is observed in chalcogenides and other amorphous semiconductors can be obtained from eqn. 12 for $n(\tau) \propto \frac{1}{\tau}$, where

$$\sigma'(\omega) \propto \int \frac{\omega}{1 + \omega^2 \tau^2} d(\omega\tau) \propto \omega \quad (13)$$

The form of $n(\tau)$ required implies that the relaxation time τ itself must be an exponential function of a random variable ξ , i.e.,

$$\tau = \tau_0 \exp(\xi) \quad (14)$$

where τ_0 is a characteristic *relaxation time*, and where ξ has a flat distribution, $n(\xi) = \text{constant}$. In practice, n and α may each be function of ξ , giving rise to a slightly sub linear frequency dependence. Remarkably, two microscopic relaxation mechanisms that can give rise to the functional form for τ given in eqn. 14 are:

- (i) classical hopping of a carrier over the potential barrier separating two energetically favourable sites, i.e., in a double-well potential, in which

$$\xi = \frac{W}{kT} \quad (14a)$$

- (ii) phonon-assisted quantum-mechanical tunnelling through the barrier separating two equilibrium positions, in which the case

$$\xi = 2\alpha R \quad (14b)$$

where W is the barrier height and R is the equilibrium distance between the two states. It can be assumed that the wave function of a carrier localized at a given site is proportional to $\exp(-\alpha R)$. Both cases (i) and (ii), and variants, will be considered in interpreting the experimental data for amorphous chalcogenide materials. However, it should be stressed here in the light of the discussion above that information on the physical mechanism responsible for the a.c. loss resides primarily in the departure from unity to the exponent of the frequency dependence of the real part of the a.c. conductivity and in the temperature dependence of $\sigma(\omega)$.

3. A.C. Conduction in Disordered Solids: Facts

Most commonly, the solids are classified into metals and non-metals. A metallic solid has large weakly temperature-dependent d.c. conductivity, a non-metallic solids has a much smaller d.c. conductivity which, however, increases strongly with increasing temperature.¹⁷ Only for disordered non-metallic solids the origin of a.c. conduction is different from the d.c. observed far below the phonon frequencies. As mentioned earlier, these solids have quite similar a.c. conductivity behaviour, '*universality*'. Among the non-metallic solids, there is sub-class of solids exhibits the universal a.c. properties includes ion conducting crystal and glasses, polycrystalline and amorphous semiconductors, semiconductors, mixed (ion/electron) conducting polymers, transition metal oxides and organic/inorganic composites.¹⁸⁻²⁸

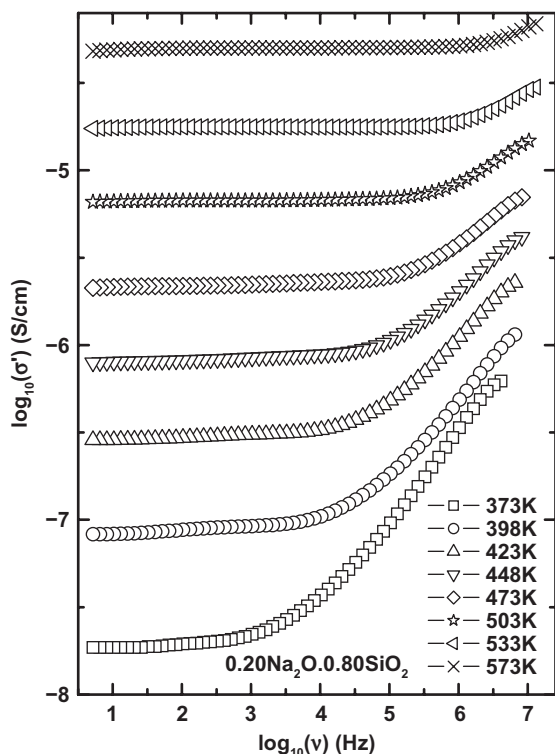
Figure 2 shows the frequency dependent conductivity data for four different disordered solids including ion, electron and polaron conducting solids at different temperatures. Clearly, the observed a.c. conductivities are quite similar in all the solids. While ion conduction is a classical barrier crossing processes, an electron conduction in amorphous materials usually proceeds via quantum mechanical tunnelling between the localized states. Now the question arises that why do these conduction mechanisms have in common in disordered solids? One reason is the ubiquities disorder in the material which causes energy barrier between the sites to vary randomly or the variations in inter site separations. As a result, a very broad distribution of jump rates/tunnelling rates/local mobilities.

Different strategies were made in the past to characterize the quite similar a.c. responses observed for different types of solids in the frequency regimes not exceeding 10 MHz. The simplest description is power-law frequency

Polarizability: It is defined as the ratio of the induced dipole moment of an atom to the electric field that produces this dipole moment

Relaxation time: In dielectrics, the time required for an exponential variable (polarization) to decrease to 1/e of its initial value

Figure 2a: Experimental frequency-dependent conductivity spectra of 0.2Na₂O.0.8SiO₂ glass at various temperatures.



Time-temperature superposition principle: The validity of the TTSP suggests that the basic microscopic mechanisms of the dynamic processes do not depend on temperature, although the time window of these processes exhibits generally strong temperature dependence

dependence as proposed by Jonscher.⁸ However, the power-law description is slightly inaccurate, because the exponent must generally increase somewhat with frequency in order to fit with experimental data. A more general approach is to consider the scaling formalism associated with *time-temperature superposition* (TTS) principle. The scaling ansatz reads as:

$$\frac{\sigma(\omega, T)}{\sigma_o(T)} = F\left(\frac{\omega}{\omega_o(T)}\right) \quad (15)$$

defining $u = \frac{\omega}{\omega_o(T)}$, where F(u) is the scaling function which is independent of temperature and ω_o is the angular frequency making onset of a.c. conduction and has been defined in a variety of ways over time. Any solid that obeys TTS is, equivalently, referred to as obeying scaling law. Barton, Nakijama and Namikawa long ago proposed independently^{7,29,30} and verified that for many ion and electron conducting disordered solids the scaling parameter ω_o as

$$\omega_o = \frac{\sigma_{dc}}{p\epsilon_o\Delta\epsilon} \quad (16)$$

where p is a constant of order of unity and $\Delta\epsilon$ is the dielectric relaxation strength, i.e., the difference between the static and high-frequency dielectric constants. Eqn. 16 is also known as the BNN relation.

A.c. universality was first discovered for ion conducting oxide glasses. Taylor has been shown that the dielectric loss for different ion conducting glasses fell on a single plot against scaled frequency.³¹⁻³³ Additionally, he found from the same analysis that the activation energy of the d.c. conductivity was the same as that of the onset frequency of a.c. conduction. Subsequently, Israd modified Taylor's scaling parameter by plotting dielectric loss against the log of frequency and d.c. resistivity, equivalent to the following representation:

$$\frac{\sigma(\omega)}{\sigma_o} = F\left(\frac{\omega}{\sigma_o T}\right) \quad (17)$$

Since then the above equation, which we shall refer to as "Taylor-Isard scaling",³⁴ has been used by several authors. For instance, Taylor-Isard scaling was used by Scher and Lax for the continuous time random-walk approximation,³⁵ by Balkan et al., for amorphous semiconductors,³⁶ and by Summerfield for hopping models solved in a certain approximation in tetrahedrally bonded amorphous semiconductors.³⁷ For ion conducting

Figure 2b:

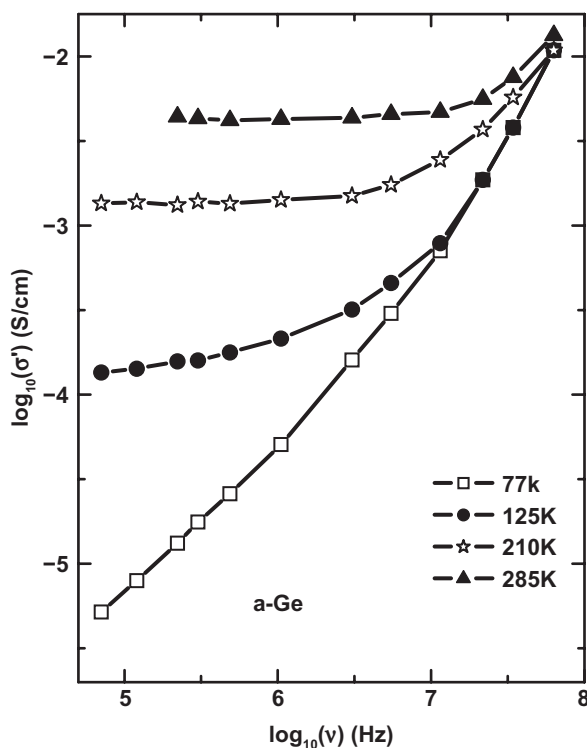


Figure 2c:

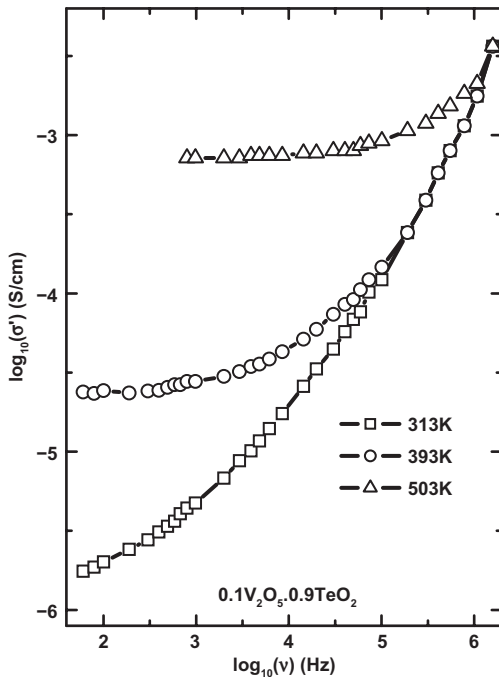
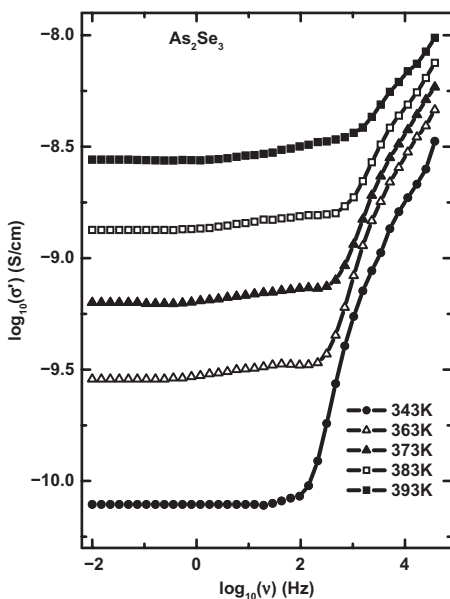


Figure 2d: Experimental frequency-dependent conductivity spectra of typical ion (a), an electron (b) and polaron (c, d) conducting disordered solids. Each figure shows a log-log plot of the real part of the conductivity as a function of frequency at various temperatures. At low temperatures the conductivity is constant; at high frequencies it follows an approximate power law with an exponent less than one. The data shown for the following systems: (a) $0.2\text{Na}_2\text{O}\cdot 0.8\text{SiO}_2$ glass; (b) a-Ge (Mott and Davis 1979); (c) $0.1\text{V}_2\text{O}_5\cdot 0.9\text{TeO}_2$ (Sankarappa et al., J. Mol. Str., 889, (2008) 308); (d) As_2Se_3 glass.



glasses Taylor-Isard scaling approach was used recently by various authors. In summary, we now list the most important characteristic features of a.c. conductivity spectra of the vast majority of disordered solids.

- i. The real part of the a.c. conductivity increases with frequency, the imaginary part is non-negative.
- ii. At high frequencies $\sigma'(\omega)$ follows an apparent power law, i.e., $\sigma'(\omega) \propto \omega^s$. The deviations from this power law corresponds to s increasing weakly with frequency and as temperatures decreases, i.e. $s \rightarrow 1$ for $T \rightarrow 0$. At low frequencies, the conductivity is independent of frequency and is attributed to the d.c. conductivity.
- iii. The real part of a.c. conductivity $\sigma'(\omega)$ is generally only weakly dependent on temperature as compared to d.c. conductivity. In the case of low energy gap materials the temperature dependence of $\sigma'(\omega)$ is stronger at intermediate temperatures than at low temperatures.
- iv. The a.c. conductivity obeys time-temperature superposition principle, i.e. the shape of $\sigma'(\omega)$ in a double logarithmic plot is temperature independent and is roughly the same for all disordered solids (universality).
- v. When the cross-over frequency ω_0 satisfies the BNN relation then the activation energy for ω_0 and σ_{dc} would be identical.

4. Macroscopic Models for A.C. Conduction

In essence, three quantities are required in order to calculate the a.c. conductivity. As can be seen from eqn. 12, these are the polarizability α , the distribution function $n(\tau)$ for relaxation times, and the relaxation time expressed in terms of a relaxation variable ξ . The form of this latter quantity, $\tau(\xi)$, depends on the particular type of microscopic process under consideration.

4.1. Polarizability Factor within the Pair Approximation

An evaluation of the polarizability factor within the pair approximation was suggested by Pollak and Geballe³⁸ in analysing the a.c. conductivity data of impurity conduction in crystalline silicon. For two sites, separated in space by R and in energy by Δ , the polarizability can be calculated by using the rate equations for the charge transfer between the two sites, i.e.

$$F_1 = \omega_{21}f_2 - \omega_{12}f_1 = -F_2 \quad (18)$$

where f_1 and $f_2 (= 1 - f_1)$ are the occupation probabilities for states 1 and 2, and ω_{ij} are the transition rates. The application of an electric field E to the system perturbs the levels, causing a change in the occupation numbers from their equilibrium values, which, if the field is small ($eER \ll kT$), means that the response can be linearized to

$$\alpha = \frac{e^2 R^2}{12kT} \frac{1}{\cosh^2\left(\frac{\Delta}{2kT}\right)} \left(\frac{1}{1 + i\omega\tau} \right) \quad (19)$$

where an average over an angle (between R and E) has been performed. It is interesting to note that the Debye form for the frequency dependence has been obtained; this is a direct result of the particular form of rate equation embodied in eqn. 18, whose solution is exponential time dependent as given in eqn. 10. The effective relaxation time τ that appears in eqn. 19 is given by

$$\tau = \frac{1}{2} \tau_o \left[\cosh\left(\frac{\Delta}{2kT}\right) \right]^{-1} \quad (20)$$

if the transition rate is written as¹⁴

$$\omega_{ij} = \frac{1}{\tau_o} \exp\left(\frac{\Delta_{ij} + \Delta_{ji}}{2kT}\right) \quad (21)$$

Above equation is valid for the multiphonon frequencies, i.e. when the energies involved in the transition are larger than the Debye energy. In the following, we shall be concerned almost exclusively with multiphonon processes giving rise to dielectric loss. Based on above considerations, we now turn to a discussion of the various basic types of models that have been proposed for the a.c. conduction in amorphous semiconductors before considering in more detail the a.c. conductivity of chalcogenide glassy semiconductors.

4.2. Relaxation Due to the Quantum-Mechanical Tunnelling

4.2.1. Electronic tunnelling

The tunnelling of charge carriers was observed first by Pollak and Geballe³⁸ in connection with the effect of impurity on the conductivity of doped crystalline silicon, and subsequently extended to the other amorphous semiconductors by Austin and Mott.³⁹ If the electronic relaxation is regarded as the origin of the dielectric loss observed in amorphous semiconductors then quantum-mechanical tunnelling (QMT) is perhaps an obvious phenomenon to consider, because the d.c. conductivity (solids such as a-Ge and a-Si) below room temperature exhibits an $\exp(-T^{-1/4})$

dependence believed to results from the phonon assisted tunnelling between defect states.¹² Thus, at sufficiently low temperatures the frequency dependent conductivity has been ascribed to the QMT of the charge carriers. The relaxation time is given in this case by a combination of eqn. 14 & 14b i.e. $\tau \propto \exp(2\alpha R)$ or equivalently substituting $\tau_o = 2\tau_{ot} \exp(2\alpha R)$ in eqn. 20 giving

$$\tau = \frac{\tau_{ot} \exp(2\alpha R)}{\cosh\left(\frac{\Delta}{2kT}\right)} \quad (22)$$

It is generally assumed that the sites between which electron transfer occurs are randomly distributed in space i.e.

$$P(R)dR = 4\pi NR^2 dR \quad (23)$$

Based on the above considerations, an expression for the real part of the a.c. conductivity can then be obtained rather straight forwardly and simply using the above relations correlating the polarizability, relaxation time and spatial distribution of random sites. Based on the above considerations,

$$\sigma(\omega) = \frac{\pi N^2 e^2 \omega}{6\alpha kT} \int_{\tau_{min}}^{\tau_{max}} R^4 \frac{d(\omega\tau)}{1 + \omega^2 \tau^2} \quad (24)$$

It is important to note that the factor R^4 arises from two contributions: a factor R^2 from the polarizability and a factor of R^2 from the spatial distribution of centres. The lower limit of the integral in eqn. 24 represents the $\tau_{min} = \tau_o$ (often taken to be of the order of an inverse of phonon frequency), which for the purposes of evaluation of the integral can be approximated by $\tau_{min} \approx 0$. The upper limit τ_{max} corresponds to the maximum tunnelling distance, which according to eqn. 22 can in principle increase without limit, and hence it can be approximated as $\tau_{max} \approx \infty$. The integral in eqn. 24 can be evaluated in an approximate manner by noting that the function $\frac{\omega\tau}{1 + \omega^2 \tau^2}$ is sharply peaked in τ space, and extremely sharply peaked in R space, and therefore it effectively acts as a δ -function. The factor R^4 can therefore be removed from the integral part, having been given the value of R_ω at which $\frac{\omega\tau}{1 + \omega^2 \tau^2}$ is a maximum i.e. at $\omega\tau = 1$.

The characteristic tunnelling distance R_ω at a given frequency ω is thus given by

$$R_\omega = \frac{1}{2\alpha} \ln\left(\frac{1}{\omega\tau_o}\right) \quad (25)$$

where $\omega\tau = 1$ has been substituted into eqn. 24. Hence, the final expression for the real part

of the a.c. conductivity for the QMT can be written as

$$\sigma'(\omega) = \frac{Ce^2kT}{\alpha} N^2(E_F)\omega R_\omega^4 \quad (26)$$

where $N(E_F)$ is the density of states at the Fermi level and $N = kTN(E_F)$ is the number of states actually contributing to the a.c. loss. The constant C is equal to $\frac{1}{24}\pi^2$ in the simple treatment case; a more rigorous analysis yields a slightly different value of $\frac{1}{24}\pi^4$, but the functional form for $\sigma(\omega)$ remains the same.

4.2.2. Small Polaron Tunnelling

A small polaron may be formed in a covalent solid if the addition of a charge carrier to a site causes such a large degree of local lattice distortion that the total energy (electronic + distortion) of the system is thereby lowered by an amount W_p , the polaron energy. The small polarons are generally assumed to be so localized that their distortion clouds do not overlap. A small polaron behaves as a free particle with enhanced mass (m_p) at low temperatures but moves by thermally activated hopping at high temperatures (i.e. $kT > \frac{1}{2}\hbar\omega$, where ω is the phonon frequency). Therefore, the activation energy for polaron transfer, $W_H \approx \frac{1}{2}W_p$ and is not dependent on the intersite separation. The relaxation time for small-polaron tunnelling at high temperatures can be written as⁴⁰

$$\tau = \tau_o \exp\left(\frac{W_H}{kT}\right) \exp(2\alpha R) \quad (27)$$

whereas at sufficiently low temperatures, below the Debye temperatures, the transition rate, and hence the relaxation time, are independent of temperatures, i.e.

$$\tau = \tau_o \exp\left(\frac{W_H}{\frac{1}{4}\hbar\omega_o}\right) \exp(2\alpha R) \quad (28)$$

where ω_o is the vibrational frequency describing the lattice distortion. The frequency dependent conductivity at the high temperature limit expected for the tunnelling of the carriers trapped at the structural defects (which are randomly distributed in space) and which form small polarons can be evaluated in exactly the same way as in the earlier section by using eqn. 27, i.e. the characteristic relaxation time is now temperature dependent, $\tau' = \tau_o \exp(\frac{W_H}{kT})$. The tunnelling distance at a frequency ω now written as

$$R_\omega = \frac{1}{2\alpha} \left[\ln\left(\frac{1}{\omega\tau_o}\right) - \frac{W_H}{kT} \right] \quad (29)$$

and the a.c. conductivity is given in eqn. 26, but with the above expression for R_ω used instead of eqn. 25. It is interesting to note that the tunnelling distance decreases more rapidly with increasing frequency than in case of QMT (eqn. 25). Indeed, R_ω and hence $\sigma(\omega)$ are predicted to go to zero at sufficiently high frequency with the frequency is equal to

$$\omega_c = \frac{1}{\tau_o} \exp\left(-\frac{W_H}{kT}\right) \quad (30)$$

The validity of above equation (30) becomes pathological, since for frequencies greater than ω_c a negative value for R_ω is predicted. The frequency dependence of s for this model is negative, i.e. there is a maxima in the frequency dependence of $\sigma'(\omega)$ prior to $R_\omega \rightarrow 0$. In practice, of course, the tunnelling distance cannot become equal to zero; the minimum value of R_ω is equal to the interatomic spacing. At higher frequencies (or lower temperature) than given by the critical condition eqn. 30, the contribution to the overall a.c. conductivity due to the small-polaron tunnelling mechanism would tends to zero.

4.3. Relaxation Due to Hopping Process

We treat the term 'hopping' for those transfer processes that involve thermal activation over the barrier separating two different well defined sites, rather than quantum mechanical tunnelling through the barrier. Thus such processes are inherently relatively high temperature phenomena. In such cases, the relaxation time is given in more commonly as $\tau \propto \exp(\frac{W}{kT})$, and no explicit dependence on the intersite separation is generally included. Here, we shall see this basic model can be modified to include an implicit dependence on separation.

4.3.1. Atomic Hopping

Pollak and Pike had developed first hopping model to the dielectric relaxation in amorphous semiconductors⁴¹ and subsequently extended by Leclac'h,⁴² who assumed that the atoms or ions hopped over the barrier of height W separating two sites, having an energy difference, Δ . This model had its origin that the low-temperature thermal anomalies mentioned in the earlier section, but because of the thermal-activation nature of the charge transfer its applicability is at higher temperatures. The relaxation variable in this case is obviously W , which in the simplest case is independent of the intersite separation R . Furthermore, the dipole moment p and the change in p involved in an atomic transition are

not known a priori, and so p may be set equal to a constant value of p_0 and independent of W and R . The relaxation time can be written as $\tau = \tau_0 \exp(\frac{W}{kT})$ if $W \gg kT$ and $\Delta \gg kT$.^{14,41} Assuming that the distribution $p(W)$ of barrier heights is uniform in the range $0 \leq W \leq W_0$, and also that Δ is randomly distributed between 0 and Δ_0 . Based on the above considerations, the real part of the a.c. conductivity for this model can be evaluated as⁴¹

$$\sigma'(\omega) = \pi p_0^2 \frac{NkT}{6W_0\Delta_0} \omega \tanh\left(\frac{\Delta_0}{2kT}\right) \quad (31)$$

The above eqn. 31 clearly predicts a strictly linear dependence on both frequency and temperature. The linear frequency dependence arises because there is no dependence of the hopping distance R_ω on frequency ω .

4.3.1. Correlated Barrier Hopping Model

The correlated barrier-hopping (CBH) model was originally proposed by Pike⁴³ in order to calculate the frequency dependent conductivity in scandium oxide films, and then extended by Elliott,⁴⁴ in the study of chalcogenide glasses. It should be emphasized that the CBH model is based on several assumptions. The assumption made in the simple hopping model described above is that the relaxation variable W is independent of the distance between the two sites R , and hence the hopping is independent of frequency. This restriction was lifted by CBH model, where the electron transfer by thermal activation over the barrier between two sites, each having a coulombic potential well associated with it. For neighbouring sites at a distance R , the coulomb wells overlaps and resulting in a lowering of the effective barrier from W_M (at an infinite separation) to a value

W , as shown in figure 3. Now, for single electron transition is given by

$$W = W_M - \frac{e^2}{\pi\epsilon\epsilon_0 R} \quad (32)$$

The a.c. conductivity expressed for the case of single-electron transfer by the CBH model can be evaluated in exactly the same manner as employed previously using the expression for the polarizability given by eqn. 19 and the relaxation time corresponding as follows:

$$\tau = \frac{\tau_0 \exp(\frac{W}{kT})}{\cosh(\frac{\Delta}{2kT})} \quad (33)$$

In the narrow band limit ($\Delta_0 \ll kT$), and assuming that the a.c. conductivity is given approximately as

$$\sigma'(\omega) = \frac{1}{24} \pi^3 N^2 \epsilon\epsilon_0 \omega R_\omega^6 \quad (34)$$

where the hopping distance at a frequency ω is given by

$$R_\omega = \frac{e^2}{\pi\epsilon\epsilon_0 [W_M - kT \ln(\frac{1}{\omega\tau_0})]} \quad (35)$$

It should be noted in passing that the behaviour of CBH model might also be regarded pathological as a function of frequency in the same sense as for the small-polaron QMT model. In the other extreme limit, namely the broad-band case ($\Delta_0 \gg kT$) and for single-electron hopping motion, Long has calculated the a.c. conductivity as follows:

$$\sigma'(\omega) = \frac{1}{12} \pi^3 g_0^2 (kT)^2 \omega R_\omega^6 \quad (36)$$

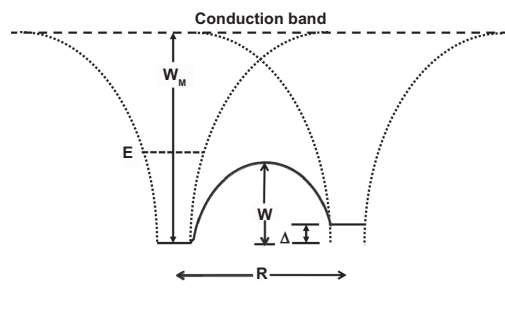
where a constant density of states $g_0 = \frac{N}{\Delta_0}$ has been assumed. The frequency dependence in the CBH model (for both limits) is embodied in the ωR_ω^6 factor, and can be expressed in terms of the frequency exponent s as

$$s = 1 - \frac{6kT}{[W_M - kT \ln(\frac{1}{\omega\tau_0})]} \quad (37)$$

It is interesting to note that s is predicted to be both frequency and temperature dependent. It should be noted that, at least for small values of $\frac{W_M}{kT}$, s increases with increasing the frequency and for large values of $\frac{W_M}{kT}$, the exponent s is nearer unity.

Finally it should be mentioned that the d.c. conductivity can also be predicted by the CBH model. In this case the 'extended-pair

Figure 3: Schematic illustration of the lowering of the barrier height for two closely spaced charged centres on the CBH model.



approximation' has been used, where carrier motion is not just confined to pairs of states, but the contributions of other sites to the d.c. current are taken into account in an average way and a percolation condition is imposed. In this way, the d.c. conductivity for *bipolaron* transport within the CBH model is given by

$$\sigma_{dc} = \sigma_o \exp\left(\frac{-W(R_p)}{kT}\right) \quad (38)$$

where the pre-exponential factor given by

$$\sigma_o = \frac{g_o N^2}{15} [R_p^5 - R_{min}^5] \exp\left(\frac{W_M}{kT}\right) \quad (39)$$

where N is the defect concentration and the conductance term g_o is given by⁴⁵

$$g_o = \frac{e^2}{4kT\tau_o \exp\left(\frac{W_M}{kT}\right)} \quad (40)$$

where the symbols have their usual meaning. R_p is the critical percolation radius which in three dimensions is given by

$$R_p = \left(\frac{8}{4\pi N}\right)^{\frac{1}{3}} \quad (41)$$

and R_{min} is a lower limit of the hopping distance R_o , given by

$$R_{min} = \left(\frac{2e^2}{\pi\epsilon\epsilon_o W_M}\right) \quad (42)$$

which is necessary to preclude any unphysical values of the hopping energy W_o . Therefore, the activation energy for the d.c. conductivity in this model namely $W(R_p)$ is simply the barrier between the two sites separated by the critical percolation radius R_p .

$$W(R_p) = W_M - \frac{2e^2}{\pi\epsilon\epsilon_o R_p} \quad (43)$$

Based on the above considerations and with the defect density $N \approx 10^{16} \text{ cm}^{-3}$ in the case of a-As₂Se₃, the predicted d.c. conductivity is $\sigma_{dc} = 10^{-13} \text{ S/cm}$,⁴⁵ which is comparable but still less than the measured d.c. conductivity. Thus, for most cases, it is expected that the a.c. and d.c. conductivities in chalcogenide materials are not due to the same mechanism, and so a separation of the total measured conductivity into separate a.c. and d.c. components, as in eqn. 1, is in general a valid procedure.

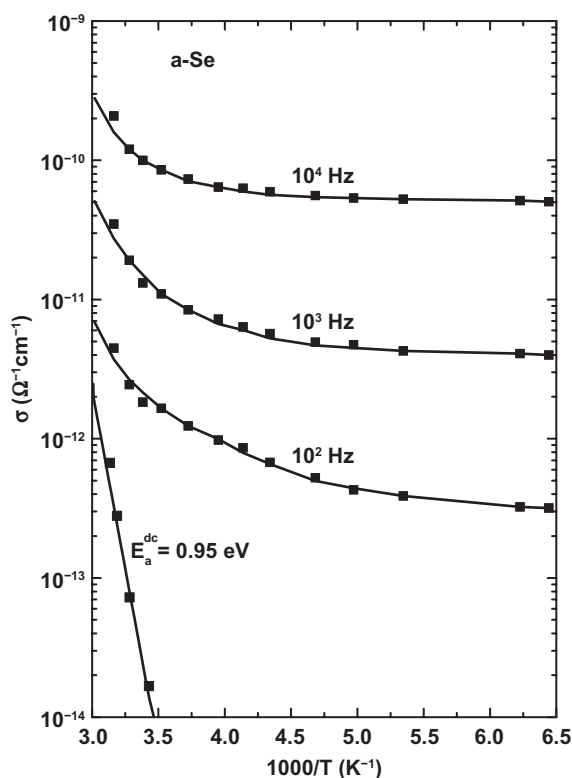
5. Experimental Results on Chalcogenide Glasses

An experimental a.c. conductivity measurement has been reported for a wide variety of amorphous chalcogenides including simple selenium, binary and ternary semiconductors. Although there would appear to be an excess of a.c. data for these materials, in fact many of the reports are rather restricted in scope, describing a.c. measurements taken over a limited range of frequencies and temperatures. We note in passing here that in order to make detailed comparison with existing theories, and hence ultimately to decide between models on the basis of experimental evidence for the a.c. loss data (both conductance and capacitance) should be measured over as wide a range of frequencies and temperatures as possible, ideally for a range of compositions of the material as well. Nevertheless, we show in figures 4 and 5 representative experimental data typical of chalcogenide materials available in the literature measured over range of temperatures and frequencies. In figure 4 we show the temperature dependence of conductivity of a-Se at different frequencies.⁴⁶ The temperature dependence of these data is shown more explicitly by plotting against the inverse of temperature. It can be seen from these figures that the a.c. conductivity has only weak temperature dependence, which is considerably less than that exhibited by the d.c. conductivity. The frequency exponent of the conductivity s shows the strong dependence on temperature, where at low temperatures the exponent found to be unity and at high temperatures the value decreases to 0.85. Similar results were obtained on other Se based alloys such as As₂S₃ and As₂Se₃, however, the exponent found to vary ± 0.05 among the different samples at a given temperature.⁴⁷ In figure 5, we show the temperature dependent conductivity of ternary chalcogenide glass system measured at different frequencies, where all the results show the similar features relating to the a.c. conductivity. It is worthwhile to mention that there are discrepancies in the magnitude of the a.c. conductivity between the bulk and vapour-deposited thin-film of the same material at a given temperature.

We shall focus in the following sections in more detail on a.c. conductivity spectra and their temperature dependences in different chalcogenide glasses and compare with the different theoretical model predictions. More specifically, we divide the temperature range into three different regimes such as (i) low temperatures (below 100 K), (ii) intermediate temperature (100 K–300 K) and (iii) high temperatures (above 300 K). Certain features of the experimental observations relating to

Bipolaron: Those for which the special extent of the polaron is large as compared with the interatomic spacing and the distortion clouds overlap with each other

Figure 4: The real part of the a.c. conductivity for a-Se is plotted against the inverse of the temperature for three different frequencies (Lakatos and Abkowitz 1971). The temperature dependence of the d.c. conductivity is also shown in the figure.



the a.c. conduction in chalcogenide materials serve to rule out immediately several of the theoretical models described earlier. In particular, the behaviour of the frequency exponent s with both temperature and frequency is an important factor.

5.1. Low Temperatures

The behaviour of the a.c. conductivity of chalcogenide glasses at low temperature regime, i.e. below 100 K has been attributed to the QMT phenomenon. The conductivity spectra appear to become temperature-independent and the frequency dependence becomes linear at the lower temperatures with an exponent value of nearly unity. Obviously, at very low temperatures the transition mechanism must tend towards the quantum limit of atomic tunnelling model (Sec. 4.2.1). The parameters that appear in the conductivity expression for this model, namely two level system (TLS) asymmetry-energy bandwidth Δ_0 , the width λ_0 of the distribution of tunnelling parameters and the dipole moment p_0 are not

known explicitly, and so estimates for the density of atomic sites responsible cannot be obtained. The only way to isolate this parameter is to study a given material in detail, varying the density of active sites in a systematic way if possible, perhaps by doping or irradiation.

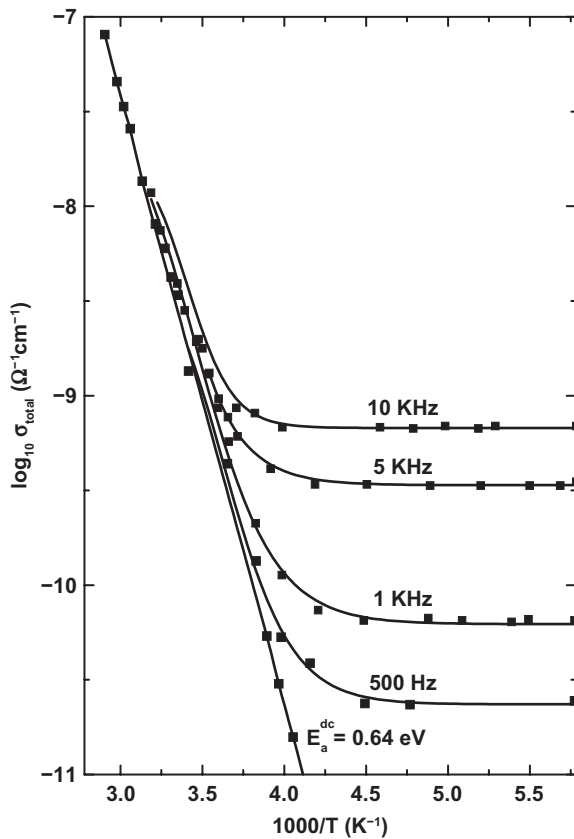
The involvement of atomic motion in low-temperature a.c. loss has been unequivocally determined in simple system like amorphous SiO_2 containing an appreciable amount of OH impurity.^{47,48} In this case, the terminal OH groups can rotate about the Si-O bond between a number n of positions corresponding to various potential minima. In the case of chalcogenide glasses, Philips has examined the low temperatures results obtained on glassy As_2S_3 via a.c. conductivity, specific-heat and photo-echo measurements and concluded that in this material there exists a subset of polar states, which are responsible for the temperature variation of the dielectric constant and sound velocity.⁴⁹ It is interesting to note that the density of polar states deduced in this way ($\sim 1.6 \times 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$) is almost identical with the value obtained from a.c. conductivity data at high temperatures, assuming that bipolaron motion via the CBH mechanism is responsible. A possible candidate for the atomic tunnelling centre is therefore the D^- centre, which is sufficiently polar by virtue of the charge density localized on the defect. Additionally, it has been shown by the photo-echo measurements that the induced dipole moment which gives an intersite separation of $\approx 10 \text{ \AA}$,⁵⁰ which is consistent with the hopping distance, deduced from the a.c. conductivity measurements assuming CBH bipolaron transport. Therefore, the low temperature a.c. conductivity measurements show that a close link between tunnelling states and the charged defect states (D^+ and D^- centres).

5.2. Intermediate Temperature Regime

In the intermediate temperature regime, the observation that the frequency exponent s is temperature-dependent and it indicates the signature of the fact that the hopping distance at a particular frequency becomes a function of temperature or in other words that the effective dipole moment is temperature-dependent. In this context, there are two models which take into account for the experimental observation: they are the CBH model and the overlapping large polaron model.

The CBH model was first proposed by Pike in 1972 to account for the a.c. conduction in amorphous scandium oxide films⁴³ and later it has been extended to chalcogenide glasses by Elliott.⁴⁴ In chalcogenide glasses, the intrinsic charged

Figure 5: The temperature dependence of the total measured conductivity $\sigma(\omega)$ and d.c. conductivity of $\text{Pb}_{20}\text{Ge}_{19}\text{Se}_{61}$ glass sample at various frequencies. The temperature dependence of the d.c. conductivity is also shown in the figure.



defect states that give rise to the Coulombic potentials, and which, when they overlap, lead to a lowering of the activation-energy barrier to hopping. It is assumed that for most of the materials in the intermediate temperatures only charged defect states are present, i.e. the effective Hubbard correlation energy U_{eff} is sufficiently large ($U_{\text{eff}} > kT$) indicating that all neutral D^0 centres are converted to D^+ and D^- centres. In this case the only possible form of electron transfer between defects that preserves the identity of the defects if a.c. field is applied. However, it should be mentioned that in certain materials there is evidence for the presence of D^0 centres at room temperature, and that in these cases single-polaron transport would be predominant.

5.3. High Temperature Regime

In this section we shall discuss the a.c. behaviour of chalcogenide glasses at temperatures higher than 300 K. Above this temperature range the

measured conductivity approaches the d.c. limit and here the temperature dependence of σ_{dc} is usually much greater than the frequency dependence part. However, we are not interested in this rather trivial instance of strongly temperature-dependent behaviour, since we are assuming that, at least for the case of chalcogenide glasses, a.c. and d.c. conductivities are due to *different* mechanisms. The temperature dependent behaviour under consideration can be seen in the experimental data reported in the literature by various authors and in different chalcogenide systems. Based on these results at longer time scale, the motion of charge carriers has been characterized by the long-range diffusive behaviour, i.e. random motion. On the other hand, in a short time scale the charge carriers are characterized by the subdiffusive behaviour, i.e. the charge carriers perform the correlated forward backward hopping motions. The temperature dependence of $\sigma'(\omega)$ predicted by CBH model does in fact increase with increasing temperature, but it is insufficient to account for the increase observed experimentally. The a.c. conductivity resulting from the CBH motion of single electron has been discussed earlier and in the narrow-band limit ($kT > \Delta_0$), valid at high temperatures.

6. Correlation of the A.C. Conductivity to Material Properties

In this section, we shall discuss the relationship of the a.c. conductivity to other material parameters of a given material, in particular the band gap and defect concentrations, in the context of the CBH model. The parameter W_M appearing in eqn. 32 is the maximum energy required to remove, in the case of bipolaron transport, two electrons from a D^- centre, i.e. when infinitely separated from a D^+ centre. An estimate for the value of W_M can be obtained from a consideration of the properties of centres suffering a negative U_{eff} . The activation energy required to take two electrons out of a D^- centre and to place them in the conduction band is given by

$$W_M = B - W_1 + W_2 \quad (44)$$

where B is the optical energy gap, W_1 is the energy required to take an electron from the valence band and place it on a D^0 centre thereby turning it into D^- , and W_2 is the total energy necessary to take an electron from a D^0 centre and place it in the conduction band. W_M can also be understood as being simply twice the energy difference between the Fermi level and the conduction

band. Amorphous chalcogenide glasses are in general p-type, exhibiting simply activated d.c. conductivity of activation energy ΔE . Thus W_M can be written equivalently as

$$W_M = 2(B - \Delta E) \quad (45)$$

which has the advantage that W_M can be estimated using commonly measured experimental parameters. Since the Fermi level of these materials often lies near the mid-gap (so $\Delta E \approx \frac{1}{2}B$), a consequence of the fact that $W_1 \approx W_2$, which further leads us both eqn. 44 and eqn. 45 indicate that to a first approximation we may take $W_M \approx B$. From the above results, it is clear that W_M is associated with the band gap of a material exhibiting a negative U_{eff} is that the a.c. and d.c. conductivities should therefore be correlated if the loss mechanism is CBH involving D^- and D^+ centres. Such correlation of experimental data for chalcogenide glasses has previously been noted by Davis and Mott⁵¹ but without any reasons for the observed correlations. If the a.c. and d.c. conductivities arise from different mechanisms (as mentioned earlier), it is not obvious at first sight why there should be any correlation whatsoever between a.c. and d.c. behaviour. The possible resolution of this paradox is that there are defect states exists in the gap, which effectively control the d.c. conductivity by governing the position of E_F within the gap, and which also act as relaxation centres giving rise to dielectric loss. Thus, the energy gap B is an important parameter in determining the magnitude of the both a.c. and d.c. conductivities of chalcogenide materials and consequently the charge transport are predominantly governed by bipolaran mechanism. In addition to the band gap dependence of $\sigma'(\omega)$, there is a concomitant dependence of the frequency exponent s of the a.c. conductivity with the energy gap predicted by the CBH model. It has been observed that the exponent s is predicted to increase with increasing W_M and consequently with B in the As_xSe_{1-x} glasses.⁵² It can be seen that the behaviour of s with arsenic content qualitatively follows that of ΔE .

7. Doping Effects

It is well known that amorphous chalcogenides are normally insensitive to electrical doping by the addition of impurities, because of the pinning of the Fermi level at midgap by the *valence-alternation pairs* (VAP).⁵³ However, it has been realized by Mott that charged additives could change the ratio of valence-alternation pairs to such an extent that the Fermi energy could become unpinned.⁵⁴ Metallic additives such as Bi and Pb in chalcogenide glasses

enter the network as charged species, altering the concentration of VAP.^{55,56} When the concentration of charged additives exceeds that of intrinsic VAP, the chalcogenide glasses can exhibit carrier-type reversal, i.e. p-n transition has been observed in different alloyed chalcogenide glasses, with the addition of Bi and Pb.⁵⁷⁻⁶¹ In order to understand the change in the conduction mechanism in these materials by using the conductivity spectroscopy technique few attempts have been made in the literature. The addition of Pb impurities is found to change the conduction mechanism and it appears to occur by two processes, namely single-polaron hopping between randomly distributed defect sites and bipolaron hopping between non-randomly distributed defect sites. At lower temperatures the calculations based on CBH model for bipolaron-hopping contribution agrees quite well with the experimental data points. The single-polaron-hopping process becomes the predominant contributor to $\sigma'(\omega)$ at higher temperatures.⁶²⁻⁶⁴ More specifically, the Pb or Bi metal doping brings out a relative diminishing in D^+ defects as compared D^- ones. As the doping concentration increases, the bipolaron hopping contribution decreases due to the decrease in the density of D^+ defect states. But single polaron hopping contribution increases because of the shift of the Fermi level towards the conduction band as discussed earlier. Due to the shift of E_F towards conduction band, W_2 will decrease and it seems that single polaron hopping starts to dominate over bipolaron hopping as the concentration of metal dopant increases.

Additionally, the incorporation of transition (e.g. Mn) and certain other metals such as (Ag, Cu and Tl) has been observed to cause pronounced changes in the electrical and optical properties⁶⁵⁻⁶⁷ of chalcogenide glasses. The changes are most pronounced when the materials are '*chemically modified*', i.e. when the impurity is introduced into the amorphous solid under the conditions of thermal non-equilibrium. The increase in the total d.c. conductivity can be attributed to one of the three possible causes: (i) impurity induced movement of the Fermi level, (ii) hopping conduction in impurity-related gap states and (iii) partial contribution of ionic conduction from the incorporated metallic species. In order to differentiate between the various contributions more clearly, additional experiments need to be performed, for example thermopower or transport—number measurements. If the CBH mechanism involving charged structural defects is assumed to be operative for the undoped chalcogenide glasses, several consequences may result from doping with impurities. Kitao and

Valence-alternation pairs: In chalcogenide glasses, contain positively and negatively charged defect states known as valence-alternation pairs

co-workers have found that Ag-doped glassy As_2Se_3 exhibits an ω^s frequency dependence over the entire frequency range measured, but that the value of the frequency exponent found to decrease with the addition of Ag.⁶⁵ More interestingly, it was found that the frequency exponent s is much more strongly temperature-dependent when the glass is doped with metallic impurities than when it is undoped. The necessity of assuming single-polaron motion for the doped glasses implies that either D^+ , D^0 or D^- , D^0 centres are involved, but it is then difficult to understand why these centres are paired in accordance with a Coulombic interaction. A more likely situation is for an Ag^+ ion, acting as an ionized donor,⁶⁵ to trap an electron from a neighbouring D^- centre, thereby forming a D^0 centre; single-electron hopping between a D^+ and the D^0 can take place. Similar arguments involving single-polaron transport have been used by Takano et al. to explain the data on Cu doped glassy As_2Se_3 , except that in addition a contribution due to bipolaron CBH was found to be necessary in order to fit the data at lower temperatures.⁶⁶

8. Conclusions

The motivation of this review has been to survey the various theories for a.c. conduction in amorphous semiconductors, emphasising towards the recent developments that have taken place. The experimental a.c. loss behaviour of chalcogenide glasses have been reviewed in more detail. Based on the available experimental results, at least for temperatures above 100 K, it appears that the a.c. conductivity of chalcogenide glasses can be described by the ‘correlated-barrier-hopping’ (CBH) model in a more appropriate manner. At very low temperatures, the CBH is no longer valid, since it considers the charge transport by classical hopping rather than quantum mechanical tunnelling. In order to understand the a.c. loss behaviour on an atomic scale level, two advances need to be made. One of the major stumbling blocks is the relative paucity of high-quality experimental data taken in a systematic fashion in a series of compositions for a given material. More specifically, the experiments to be carried out over wide range frequency and temperatures, particularly at low temperatures, where there is very little data extant. Additionally, the validity of any theory requires a comparison between the real and imaginary part the dielectric functions, and such comparisons are very limited at present. The other area in which the further development needed and equally important is our present understanding of the theory. An advanced theory should be developed in a self-

consistent fashion the changeover from classical hopping to quantum-mechanical tunnelling in a single theory, i.e. it should be able to consider the transition from high-temperature behaviour to low-temperature behaviour of the a.c. conductivity of *all* amorphous semiconductors, not just chalcogenide glasses. The other aspect in which further theoretical development is required concerns the coupling between lattice distortion and electronic states at defect sites. The small-polaron theory of Emin has addressed this to a certain extent, but for the case of essentially normally bonded sites, rather than for intrinsic defect sites, which we believe are responsible for the a.c. conductivity behaviour of most amorphous materials. With such improvements, we confidently expect the a.c. loss technique to yield important information about the nature and distribution of defects in amorphous semiconductors in the years to come.

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