The Electronic Properties of Semiconducting Copper–Chalcogenide Glasses

by

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This thesis has been written by myself as a record of my own work.
All other sources of information have been duly acknowledged.

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ABSTRACT

Several theoretical models have been developed to explain the nature of electronic transport in amorphous semiconductors. Experimental data can confirm the validity of these models with respect to specific materials.

In this work, the amorphous materials studied are alloys of copper with the chalcogenide glasses As$_2$Se$_3$ and As$_2$Se$_3$-As$_2$Te$_3$. These alloys contain copper in concentrations of between 5 and 7.89 atomic percent, as glasses with these compositions are known to have potentially useful ion-selective applications. A preliminary study was also made of alloys in the Cu-As-Se system with up to 27.5 atomic percent copper.

A general review is made of the band structure, conduction models and models of defect states in amorphous semiconductors. The structure and the electrical and optical properties of materials in the As-Se and As-Se-Te systems, including the effects of impurities, are also reviewed.

An account is given of the experimental techniques used in the preparation of the materials, the investigation of their structure and in the study of the dc and ac electrical properties, and optical absorption.

Measurements of dc and ac conductivity, thermoelectric power and optical absorption are interpreted to support a transport model of small polarons, although the model of Davis and Mott of transport
by variable range hopping in localised states at band edges and at the Fermi level is also considered.

Differential thermal analysis of the alloys shows that significant structural changes occur in the glasses with the introduction of copper. Evidence of tetrahedral coordination is observed, and in the Cu-As-Se system, the atomic arrangement resembles that of CuAsSe$_2$. 
1.1 THE AMORPHOUS STATE

A crystal is defined as a substance consisting of atoms in a pattern which repeats periodically in three dimensions. An amorphous solid is one which lacks this three-dimensional periodicity. The atoms in the amorphous solid lack the long range order of a crystalline solid, but there is short range order determined by the chemical bonding of the structure, although perhaps distorted from that present in a crystal.

The detailed theoretical understanding of crystalline materials followed the development of quantum mechanics, and was facilitated by the mathematical simplifications resulting from the periodicity. This in turn led to the development of solid-state semiconductor devices. The development of amorphous devices has progressed much more slowly because of the lack of theoretical understanding, due to the greater diversity and complexity of the properties of amorphous materials.

Amorphous solids, like crystalline solids, can be metals, insulators or semiconductors; they can be formed from each bonding type - covalent, ionic, metallic, Van der Waals and hydrogen. They
may be divided into three main categories.

(a) Transition-metal oxide glasses, in which a transition metal oxide is the major constituent.

(b) Materials with tetrahedral coordination like silicon and germanium which can only be obtained in amorphous thin film form by deposition from the vapour.

(c) Chalcogenide glasses, with which this thesis deals.

1.2 CHALCOGENIDE GLASSES

Glasses are a type of amorphous materials which are obtained by rapid cooling from the molten state, so that the material becomes rigid without crystallising. Hence the structure of the liquid is 'frozen in' to the solid.

Chalcogenide glasses are defined as those which contain a significant percentage of one or more of the chalcogen elements, sulphur, selenium and tellurium, so named because they are chemical analogies of oxygen in the periodic table. It is possible to form glasses by the combination of the chalcogen elements with one or more of a wide range of elements from groups III, IV and V of the periodic table. It has been established that such glasses have optical energy gaps from a few tenths of an eV to greater than 2eV, and electrical conductivities in the range $10^{-5}$ to $10^{-15} \Omega^{-1} \text{cm}^{-1}$, thus they can be classified as vitreous semiconductors.
1.3 APPLICATIONS OF CHALCOGENIDE GLASSES

There has been increasing interest in chalcogenide glasses, from both theoretical and experimental aspects, due to their potential practical uses. The wide range of optical and photoelectric properties of amorphous semiconductors has led to a number of important applications, as photoconductors, solar cells and switching devices. Electrophotography applications such as the 'Xerox' process and the 'Vidicon' television tubes make use of the photoconductive properties of amorphous materials such as Se, As$_2$Se$_3$ and Sb$_2$S$_3$.

In 1968, Ovshinsky (1) first reported the phenomenon of non-destructive fast electrical switching in thin-films of multi-component chalcogenide glasses. That is, for low applied electric fields, the current is ohmic and the resistivity high. When a certain critical voltage is reached, the resistance drops and the material is rapidly converted into a highly conductive state.

Subsequently, it has been shown that there are many forms of switching, which can occur in a wide variety of materials, and which may or may not remain in the on-state when the applied voltage is decreased.

Amorphous semiconductor devices have a number of advantages over similar devices made from crystalline semiconductors. Amorphous semiconductors are easier to manufacture - sophisticated crystal growing and doping techniques are not required, because amorphous semiconductors are not as sensitive to impurities.
Amorphous semiconductors are also more resistant to the effects of radiation.

More recently, it has been shown that "doped" chalcogenide glasses in an electrode configuration are capable of producing a response to particular ions. It is to such applications that this present work is directed.

1.4 IMPURITIES IN CHALCOGENIDE GLASSES

Kolomiets (2) was one of the first to show that the properties of chalcogenide glasses can be varied, according to the proportion of the component materials, and he extended his studies to the effect of impurities on the properties of these glasses. He showed that, in general, small deviations in composition (1 to 3 at%) did not cause any appreciable change in the properties of the chalcogenides. It has been observed that the bulk resistivities and hence the electrical properties of chalcogenide glasses are, in general, insensitive to impurities, which is in contrast to crystalline semiconductors where an impurity concentration of $10^{13} \text{cm}^{-3}$ or less can drastically affect the electrical and optical properties. Mott (3) suggested that this is because the nearest neighbour environment adjusts to satisfy the valence requirement of each impurity atom, that is, all electrons are taken up in bonding. Owen (4) stated that there are exceptions to that case and large conductivity increases are caused by the addition of
copper and silver to $a-$As$_2$S$_3$. However, Kolomiets further showed that deviations from the composition of between 10 and 30 atomic percent also result in significant changes in conductivity.

Since then, investigations have been made into the properties of chalcogenide alloys, with the intention of investigating how the impurity is incorporated into the glass structure, and how it affects the electrical properties of the glass. It has been suggested by Ovshinsky et al (5) that the introduction of impurities into chalcogenide glasses modifies the structure by introducing new bonding states, as well as altering the ones which are already there.

Liang (6) studied the structural effect of alloying copper with amorphous arsenic selenide, and he suggested that there is a progressive change in the structure of the glass due to the addition of copper. This is based on studies of the alloys of $a$-As$_2$Se$_3$ with up to 30 at% copper. He concluded that as the concentration of copper increases, the short-range order of the glass approaches that of crystalline CuAsSe$_2$. 

1.5 APPLICATIONS OF METAL–CHALCOGENIDE ALLOYS.

1.5.1 Photodoping

Photodoping of chalcogenide glasses is the photo-enhanced reaction of these glasses with metals. For example, when a layer of a metal, such as silver or copper, on a chalcogenide glass, such as arsenic sulphide, is exposed to light, the metal diffuses into the chalcogenide layer to a depth of up to 20 µm. Photodoping alters the structure of the chalcogenide and as a result changes to the electrical, optical and chemical properties take place. In particular, the undoped chalcogenide is soluble in alkali, whereas, when doped it is not. Hence, such a system may be used in photo-lithography and the optical definition is good enough to be used for submicron resolution in microfabrication technology.

1.5.2 Ion-Selective Properties

In 1974 Jasinski, Trachtenberg and Rice (7) showed that glassy alloys of copper and arsenic selenide, in the proportion of 0–30 at% of copper, are selective to $\text{Ca}^{2+}$ ions.

The ideas of Jasinski and Rice were developed in this Department by Drennan (8) and Wheatley (9). Drennan showed that copper-arsenic-sulphur alloys, although $\text{Cu}^{2+}$ selective, were unsuitable for long-term use as ion-selective electrode membranes,
due to the high resistivity of the material, and their liability to chemical attack.

Wheatley also investigated the ion-selective properties of copper-arsenic-selenium alloys and found that they were chemically more stable, but that their high resistivity led to instrumentation problems.

Kolomiets (2) and Segawa (10) showed that the conductivity of the glass $\text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3$ increases with the proportion of $\text{As}_2\text{Te}_3$. Wheatley substituted tellurium for 50% of the selenium in the copper-arsenic selenide alloy and this alloy proved to have similar copper selective properties, but a much lower resistivity and hence is a much better material for electrode applications.

1.6 CHOICE OF GLASS COMPOSITIONS

The work of Drennan and Wheatley outlined above was purely an investigation into the ion-selective properties of various metal-chalcogenide alloys. In this work a more detailed study of materials of the type used as ion-selective membrane materials was attempted to obtain a complete characterisation of their electronic properties and their conduction mechanisms.

Although the glasses of the As-Se-Te system have been fairly well investigated and documented, little is known about the properties of their alloys with copper or other metals.
More is known about the metallic alloys of arsenic selenide; in particular, Kolomiets et al (11) studied the effect of 0 to 2.4 atomic per cent of copper on the electronic properties of glassy arsenic selenide, and Liang (6) investigated the structure of alloys of copper with arsenic selenide.

For completeness, it was decided to investigate the properties of a range of materials in both the copper-arsenic-selenium and the copper-arsenic-selenium-tellurium systems. The glasses were of the compositions

\[ \text{Cu}_x [\text{As}_{0.4} (\text{Se}_{0.5} \text{Te}_{0.5})_{0.6}]_{100-x} \]

and

\[ \text{Cu}_y (\text{As}_{0.4} \text{Se}_{0.6})_{100-y} \]

where \( x \) and \( y \) are the atomic percentage of copper, with \( x \) in the range 5 to 7.89 and \( y \) in the range 5 to 27.5.
CHAPTER 2

THEORY OF AMORPHOUS SEMICONDUCTORS

2.1 BAND DIAGRAMS

The application of wave mechanics to electrons in solids has provided the basis for a 'band theory' which can be used to explain the electrical and optical properties of metals and semiconductors.

A crystalline solid consists of an array of atoms built up in three dimensions by the regular repetition over long distances of a fundamental unit, and the electrical potential characterising the crystalline structure is a periodic function in space, resulting from the mutual influence of all the atoms. Applying quantum mechanics, the Schrodinger wave equation can be solved for an electron moving in the varying potential. The allowed solutions give allowed bands of energies, and the energies for which there are no solutions are forbidden bands. Hence instead of the widely spaced energy levels of an atom, bands of closely spaced energy levels are available to an electron, separated from each other by forbidden gaps.

From Sze (12) we see that the distribution of electrons amongst the allowed energy states is given by \( n(E) \), where
\[ n(E) = f(E)N(E) \]  

(2.1)

\( N(E) \) is defined as the number of states in the energy range \( E \) to \( E+dE \), and \( f(E) \) is the probability that a quantum state with energy \( E \) is occupied by an electron. The function is the Fermi-Dirac probability function where

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

(2.2)

in which \( E_F \) is a constant for a particular material and is known as the Fermi level or Fermi energy. When \( E = E_F \), \( f(E) = 1/2 \). The one-dimensional and one-electron energy distribution of the density of states for a crystalline semiconductor is illustrated in fig 2.1(a). The valence and conduction bands have a definite structure with an abrupt transition at the band edges, giving a well defined forbidden energy gap. The Fermi level, which for an intrinsic semiconductor can be shown to be approximately \( (E_c+E_v)/2 \) is situated close to the centre of the forbidden gap. Within the bands, the states are extended, which means that the wave functions are continuous throughout the entire volume.

This band structure determines the electrical transport properties of the material.
Figure 2.1(a) Density of states for a crystalline semiconductor

Figure 2.1(b) Density of states for an ideal amorphous semiconductor.
2.2 THE EFFECTS OF DISORDER

It has been shown that certain liquids and amorphous solids can display the same range of electrical properties as a crystalline semiconductor, suggesting that the properties of solids are not determined simply by periodic structure.

In an amorphous solid, there is no long-range order, that is, over distances greater than a few tens of angstroms. However, it has been shown from x-ray diffraction (13) and extended x-ray absorption fine structure (EXAFS) (14) studies from which the radial distribution function (RDF) can be derived, that the nearest neighbour environment in many amorphous materials is very similar to that in equivalent crystalline materials. Short-range order is defined as the local atomic arrangement, over the first few coordination spheres, about a given reference atom. Materials which can be made into vitreous semiconductors, of which chalcogenide glasses are an example, generally contain elements of the groups III, IV, V and VI of the periodic table. Such elements possess highly directional interatomic binding forces, and consequently show strong local order in their glassy compounds.

In chalcogenide glasses, such as arsenic selenide, the chalcogen atoms possess a well-defined coordination number, and the structure consists of a network showing complete satisfaction of the two and three-fold bonding requirements of the selenium and arsenic atoms. The outer electronic configuration of a selenium atom is \((4s)^2\ (4p)^4\) and the two-fold coordination of selenium in arsenic
selenide means that there is a lone pair of electrons which take no part in bonding.

When chalcogenide glasses are prepared, defects such as vacancies, dangling bonds and non-bridging atoms occur. The effect of these defects are dealt with in section four of this chapter.

The concept of a density-of-states can also be applied to non-crystalline solids. The introduction of long-range disorder means that the band edges are no longer sharp, and that some states must exist beyond the crystalline band edges, and these are known as band tails. These tails contain localised states which are so called because they do not extend throughout the solid. Fig 2.1(b) shows a generalised density-of-states distribution for an amorphous solid.

2.3 BAND MODELS

Band models are used to interpret experimental electrical and optical data and several models have been proposed for the energy distribution of the density-of-states in amorphous semiconductors. They all agree on the concept of localised states in the band tails.
2.3.1 Cohen-Fritzsche-Ovshinsky (CFO) Model

Cohen et al (15) proposed the model shown in fig 2.2; as many amorphous semiconductors are observed to exhibit dc conductivities with a single thermal activation energy over a broad temperature range, they postulated that the non-crystalline structure would lead to tails of localised states, from the conduction and valence bands, but due to the extent of the disorder, the tails would overlap in the middle of the forbidden gap. This means that an electron in the valence band in some regions of the material may have a higher energy than an extra electron in a non-bonding state in other parts of the material. The Fermi level is pinned near the centre of the gap where the density-of-states is finite, but near its minimum value. The forbidden gap has filled (ie negatively charged) conduction band states below $E_F$ and empty (ie positively charged) valence band states above $E_F$.

This model also uses the idea of 'mobility edges', first introduced by Mott in 1966 (16), at energies $E_v$ and $E_c$. These are the energies at which the transition from extended to localised states occurs. At these mobility edges there is a sharp reduction in mobility of two to three orders of magnitude as the conduction process changes from low mobility band transport, with a finite mobility at $T=0$, to a thermally activated hopping between localised gap states, which disappears at $T=0$. These mobility edges define a mobility gap $E_c - E_v$ which contains only localised states.
Figure 2.2  Density of states proposed by Cohen et al (15)
The CFO model
Although this model was primarily proposed for the multicomponent chalcogenide alloys used for switching, it failed to account for the absence of an unpaired spin density and the sharp optical absorption edge in these materials. It is now almost certain that the extent of tailing in chalcogenides is much more limited than that proposed in this model.

2.3.2 Davis-Mott Model

Davis and Mott (17) proposed the model shown in fig 2.3, where, in contrast with the CFO model, the band tails are limited in extent, extending only a few tenths of an electron volt into the gap. In addition, they proposed a band of states near the centre of the gap, originating from defects in the network such as dangling bonds which may be split into separate donor-like and acceptor-like bands. (see fig 2.4)

Recent experimental evidence indicates that localised gap states exist, having been split off from the tail states. These states are associated with various defect centres.
Figure 2.3  Density of states proposed by Davis and Mott (17)

Figure 2.4  States in the gap according to the Davis-Mott model separated into Acceptor states $E_X$ and Donor states $E_Y$
2.3.3 Small Polaron Model

Emin et al (18) suggested that in an amorphous semiconductor, the charge carrier can be slowed down due to the disorder. This slowing down may lead to a localisation of a carrier and polarisation of the neighbouring lattice may take place if the carrier stays at one atomic site long enough. The resulting potential well traps the carrier and the unit created by the lattice deformation and the carrier is called a polaron.

In this state the carrier cannot move without changing the position of the neighbouring atoms. The polaron has a lower energy than the free electron, but a larger effective mass since any movement also involves its induced deformation. Transport of small polarons is possible by two mechanisms. At low temperatures band conduction takes place. At high temperatures the polaron can hop from one lattice position to an equivalent one which is created by a similar distortion of the lattice. This can be considered as phonon assisted tunnelling, as the necessary energy for the lattice deformation is provided by phonons.

The small polaron theory was developed for crystalline solids, but the absence of long-range order of non-crystalline materials was assumed to have no influence on the motion of polarons, due to their local nature. Emin argued that the probability of small polaron formation is increased when the material is disordered, and he showed that there is good agreement between experimental observations on some chalcogenide glasses and theoretical equations.
describing transport, developed for the motion of small polarons in a crystal.

2.4 CONDUCTION IN AMORPHOUS SEMICONDUCTORS

On the basis of the Davis-Mott model it is possible to distinguish four principal ways that charge may be transported in a vitreous semiconductor under the influence of an applied field. Their relative contribution to the total conductivity will vary according to temperature.

1. Extended State Conduction
Here conduction is due to the diffusive motion of carriers excited into the extended states just above $E_c$, or holes just below $E_v$. The mobility of carriers in the extended states is much higher than those in the localised states.

It can be shown (17) that for electrons

$$
\sigma = \sigma_0 \exp\left[-\frac{(E_c - E_F)}{kT}\right]
$$

(2.3)

where $\sigma_0$ is a constant known as the minimum metallic conductivity estimated theoretically by Mott to be $2 \times 10^4 \Omega^{-1} \cdot m^{-1}$.

2. Conduction in Band Tails
Where the wave functions are localised, conduction is due to carriers excited into localised states at the band edges, and then
transported by hopping through the localised states close to \( E_a \) or \( E_b \) (see fig 2.1); this tunnelling process involves the emission or absorption of a phonon. Hence, in order to raise the electron to the appropriate localised state at \( E \), a hopping energy \( W_1 \) is required in addition to the activation energy at \( E-E_F \):

\[
\sigma^- = \sigma_1^- \exp\left(-\frac{(E_a - E + W_1)}{kT}\right)
\]  

(2.4)

3. Conduction in Localised States near \( E_F \)

If the density-of-states at the Fermi level is finite, there will be a contribution to the conductivity from carriers with energies near \( E_F \), which can hop between localised states, by phonon assisted tunnelling.

\[
\sigma^- = \sigma_2^- \exp\left(-\frac{W_2}{kT}\right)
\]

(2.5)

where \( \sigma_2^- \ll \sigma_1^- \), and \( W_2 \) is the hopping energy

4. Variable range hopping

As the temperature is lowered, the number and energy of phonons available for absorption decreases, so that tunnelling is restricted to centres which are not nearest neighbours but which lie energetically closer and within the range \( kT \). This is so-called variable range hopping.
Here

\[ \sigma = \sigma_0 \exp\left(-\frac{3}{T^{1/4}}\right) \]  \hspace{1cm} (2.6)

The small polaron model predicts that the electrical conductivity will be thermally activated, that is

\[ \sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right) \]  \hspace{1cm} (2.7)

where \( E \) is the sum of the energy required to generate the carriers and an activation energy associated with the hopping of small polarons.

2.5 DEFECT STATES

The disorder occurring in amorphous semiconductors gives rise to localised states in the band tails, as described in section 2.2. Defects such as interstitial atoms and vacancies, impurity atoms of different valencies, compositional disorder in multi-component materials and variations in bond length and angles cause distortions of the perfect periodicity of the lattice. These distortions may be absorbed into the lattice by alterations in atomic bonding requirements, but they may give rise to regions of lower potential for a nearby electron or hole, resulting in a state displaced from the allowed band.
In section 2.3 it was suggested that there is little evidence for extensive band tails in amorphous semiconductors; however, in many materials, including chalcogenide glasses, the Fermi level seems to be pinned. A number of models of defect states have been devised to show that this apparent contradiction may be possible, if the states in the gap are caused by well-defined defects instead of the general disorder of the material.

Anderson (19) proposed that in amorphous semiconductors there is a strong tendency for electrons with anti-parallel spins to be paired in bonding configurations, the Coulomb repulsion between electrons at the same site being outweighed by a negative term in the energy due to electron-phonon interaction which leads to configuration changes in the local atomic structure. Street and Mott (20) applied Anderson's concepts specifically to point defects to obtain a model which explained a wider variety of phenomena, their considerations being based specifically on results of photoluminescence experiments. They suggested that a large density of dangling bonds in amorphous materials act as both acceptors and donors and that atomic motion sufficiently lowers the total energy to make the effective correlation energy negative, resulting in charged centres. These charged centres in turn give rise to states in the gap which can explain the opto-electronic properties of chalcogenide glasses.

To be more specific, the dangling bond is the point defect at which the normal coordination of the atom cannot be satisfied, because of constraints of local topography. In the absence of
ionicity, we would expect group VI (chalcogen) atoms to bond with twofold coordination and group VI atoms to bond with threefold coordination. However, depending on the strains imposed upon the material during glass formation, individual atoms may be forced into under-coordinated configurations, or other higher energy local environments. The dangling bond can contain zero, one or two electrons and are designated by $D^+$, $D^0$ and $D^-$ respectively. The negatively charged defect $D^-$ is a dangling bond associated with an under coordinated atom, in this case a chalcogen atom bonded to one other atom. When an electron is removed from the dangling bond, the neutral defect $D^0$, which has an orbital containing an unpaired electron, is formed. When a second electron is removed a $D^+$ is formed and the local environment around the $D^+$ may be highly distorted, as the lone pairs of nearby chalcogens tend to form coordinate bonds, which results in a threefold coordinated atom. Street and Mott assumed that local lattice distortion occurs when the electron occupancy of the dangling bond changes, and it is sufficiently strong for the reaction

$$2D^0 \rightarrow D^+ + D^- \quad (2.8)$$

to be exothermic. That is the total energy (electrons plus lattice) associated with a pair of charged defects (both without spin) is lower than that of two neutral defects (both with spin). The energy gain required to overcome the Coulomb repulsion between electrons at $D^-$ is provided by a distortion round $D^+$ owing to bonding with lone pair electrons on neighbouring atoms, hence the electron-phonon
interaction makes electron pairing energetically favourable at defects. This is what is meant by a negative effective correlation energy for the defect. Therefore all defect centres are either positively or negatively charged and $D^0$ occurs only by excitation.

In terms of energy levels, the addition of an electron from the valence band to $D^+$ costs an energy $E_1$. The addition of another electron to the resulting $D^0$ costs an energy $E_2$, but the negative correlation energy, designated $U_{\text{eff}}$, means that $E_2 < E_1$.

Fig 2.5 is the energy level diagram for this system of defects, showing the gap states arising from the defects. In chalcogenides, lone pair orbitals form the upper part of the valence band; bonding states lie much deeper. Anti-bonding states form the conduction band. A $D^+$ state reacting with a lone pair of an adjacent atom forms a deep bonding state, but an electron introduced into this complex occupies the next highest level, the antibonding orbital. The latter state is a shallow donor level because of the charge on $D^+$. The two electrons on $D^-$ cannot form a covalent bond with a neighbouring atom, and instead form a lone pair at a level close to that of the lone pairs in a normally bonded configuration. However, a $D^-$ state is charged and can capture a hole from the valence band, so that it is similar to a shallow acceptor level. When a $D^0$ state is formed from $D^+$, electron-phonon interaction lowers the donor energy further by an amount $W^+$, so that it now has a depth $E_1^+ + W^+$. Hence the energy required to take one electron from $D^-$ and place it in the conduction band is $E_1^+ + W^+$. Hence the energy required to take one electron from $D^-$ and place it in the conduction band is $E_1^+ + W^+$. Hence the energy required to take one electron from $D^-$ and place it in the conduction band is $E_1^+ + W^+$.
Figure 2.5 Energy level diagram of the Street-Mott Model (20), showing the corresponding valence alternation states of Kastner et al (21)

Figure 2.6 Density of defect states for the Street-Mott Model
E⁻). The energy required to take a second electron from the same defect, which is now D⁰, is W⁺ + E⁺.

Fig 2.6 shows the equivalent density-of-states diagram; in the mobility gap there are two bands of states. For a negative U eff, the levels corresponding to double occupancy lie below those corresponding to single occupancy. As the electron occupancy is increased from zero, the electrons enter into the defect sites in pairs.

The Fermi level can now be determined; the energy required to take two electrons from the D⁻ state into the conduction band is:

\[
\begin{align*}
\text{for the first electron} & \quad \frac{1}{2} E_1 - (W^- + E^-) \\
\text{for the second electron} & \quad W^+ + E^+
\end{align*}
\]

giving a total energy of E₁ + E₂

hence the total for n electrons, per electron is:

\[
\frac{1}{2}[E_1+E_2]
\]

The Fermi level therefore is pinned halfway between the two levels of D⁰, if the concentration of D⁻ states is equal to that of D⁺ states.

As there are two electrons in D⁻, hopping conduction will only occur if two electrons hop simultaneously, which seems unlikely because of the strong interactions between them. This accounts for the absence of observed hopping conduction in chalcogenides. Esr signals also are absent in chalcogenides as D⁺ and states D⁻ have no unpaired spins.
The numbers of electrons in the outer shells of elements from the right hand side of the periodic table exceed their covalent coordination; therefore extra non-bonding electrons are available for bonding. Hence in materials in which such elements are present in large concentrations, the electrons of the free radicals form bonds.

Kastner et al (21) presented another description of these defects to describe the bonding configurations that give the gap states described above. They used simple chemical bond arguments to find the lowest energy bonding configurations for the atoms in the glass. In arsenic selenide, the arsenic is threefold coordinated, the selenium, twofold. They also showed that in lone-pair semiconductors the lowest energy neutral defect is a threefold coordinated chalcogen, represented by the notation $C^\circ_3$, where $C$ stands for the chalcogen, the subscript indicates the atomic coordination and the superscript the charge.

This model considers the neutral defect to have three equivalent covalent bonds, with one electron in the anti-bonding state. The energy required to create such a defect is low, because the number of covalent bonds is the same as for the normal bonding configuration.

An extra electron placed on a $C^+_3$ state is shared equally between the three bonds of the atom, which also leaves the number of bonds unchanged. This is in contrast to Street and Mott's model where it was suggested that the extra electron is located on one of
the three bonds.

The lowest energy defect is defined as the valence alternation pair (VAP), which comprises a single coordinated negatively charged atom, \( C_1^- \), and a positively charged threefold coordinated atom, \( C_3^+ \). The VAP is formed from a fully bonded network of atoms in the \( C_2^0 \) configuration shown by the equation:

\[
2C_2^0 \rightarrow C_3^+ + C_1^-(2.9)
\]

This is the equivalent of equation 2.10, and the energy levels of Fig 2.5 also apply; the corresponding valence alternation states are also shown.

Kastner et al also suggested that positively and negatively charged defect centres attract one another by Coulombic attraction. Two oppositely charged defect centres which are nearest neighbours are called intimate valence alternation pairs, or IVAPs. VAPs are also referred to as non-intimate VAPs, or NVAPs. Unlike a VAP, which is a pair of charged centres, an IVAP is regarded as a neutral centre.

The energy required to overcome the Coulomb repulsion of the extra electron on \( C_1^- \) comes not from a change in the number of bonds, but instead from the conversion of two pairs of bonding and anti-bonding electrons into lone-pairs. This is exothermic because anti-bonding states are raised in energy more than bonding states are lowered. Thus, the presence of the lone-pair electrons not only
explains the high density of defects, but also the origin of the large negative effective correlation energy. As the VAP is associated with the same number of bonds as the continuous random network, the energy required to form it may be quite low. As the creation of a VAP requires a relatively small energy, the density in a glass is assumed to be relatively large.

From this point of view, the negative correlation energy may be seen to be a result of the special chemistry of these materials, not as a result of disorder. It may be expected that similar structure and properties may occur in crystalline lone pair materials, albeit with more stringent spatial constraints.

Hence, both models show that the electronic properties of pure chalcogenide glasses are governed by charged defects.
CHAPTER 3

REVIEW OF ELECTRICAL AND OPTICAL PROPERTIES OF METAL-CHALCOGENIDE ALLOYS

3.1 PROPERTIES OF CHALCOGENIDE GLASSES IN THE As-Se AND As-Se-Te SYSTEMS

The study of the effect of impurities on the properties of glasses is a natural extension of the effect of the variation of their stoichiometry. Materials in the As-Se and the As-Se-Te systems have already been extensively studied, and both their structure and electrical properties are reasonably well known. This section summarises some of the properties of the chalcogenide glasses, $\text{As}_2\text{Se}_3$ and $\text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3$, which are the base glasses of the alloys investigated in this work.

Chalcogenide glasses, of which $\text{As}_2\text{Se}_3$ is a typical example, can be prepared in two different ways: by quenching from a melt or by thin film deposition by sputtering or evaporation. Fig 3.1 (22) shows the glass forming range of the As-Se-Te system. On the whole, these materials obey Mott’s BN bonding rule and large changes of conductivity with composition do not occur. However, they generally contain a large number of defects such as vacancies, dangling bonds and the D-centres (see section 2.5), and these defects give rise to well-defined energy levels in the mobility gap. It is expected that
Figure 3.1 Region of glass forming in the As-Se-Te system (22)
the density of defects would depend upon the method of preparation, for example, well-annealed melt-quenched glasses will probably have a lower density than evaporated thin films.

3.1.1 DC Conductivity

The dc conductivity of materials in the amorphous or disordered state, whether solid or liquid, rises rapidly with temperature.

The dc conductivity at low fields of most chalcogenides obeys the relation

\[ \sigma = C \exp(-\frac{E}{kT}) \]  

(3.1)

The separation between the Fermi level, \( E_F \), and the mobility edge will change with temperature, and assuming a linear temperature dependence,

\[ E_c - E_F = E(0) - \gamma T \]  

(3.2)

where \( E(0) \) is the value of \( E_c - E_F \) extrapolated to \( T=0 \).

Hence the experimental value of \( E_\sigma \) is \( E(0) \), assuming that the temperature coefficient, \( \gamma \), is a constant.

In an amorphous semiconductor the interpretation of the activation energy \( E_\sigma \) measured from conductivity, is not obvious. \( E_\sigma \) for chalcogenides is usually about half the value of the optical gap \( E_{opt} \) (see fig 2.1), so that they apparently show
'intrinsic' semiconductor behaviour, with extended state transport at room temperature.

Davis and Mott (17) noted that the values of the pre-exponential factor, \( C \) in equation 3.1, for various amorphous materials, and found their values to be in the range \( 10^2 - 10^4 \ \Omega^{-1} \text{cm}^{-1} \). They stated that values of \( C \) in the range \( 10^3 - 10^4 \ \Omega^{-1} \text{cm}^{-1} \) are often thought to indicate conduction at a mobility edge, and a small value of \( C \), as is found for \( \text{As}_2\text{S}_3 \), may indicate a wide range of localised states and conduction by hopping.

Seeger and Quinn (23) reported that for bulk \( \text{As}_2\text{Se}_3 \) a plot of the logarithm of the conductivity as a function of reciprocal temperature was linear over the temperature range investigated (273\(^\circ\)K to 430\(^\circ\)K). The room temperature parameters measured at low fields were:

- conductivity, \( \sigma \), \( 5 - 6 \times 10^{-13} \ \Omega^{-1} \text{cm}^{-1} \)
- \( E_\sigma \) typically 0.92eV
- pre-exponential factor, \( C \), \( 2 - 5 \times 10^3 \ \Omega^{-1} \text{cm}^{-1} \)

For \( \text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3 \) a value for \( E_\sigma \) of 0.29eV has been reported (34), and a room temperature conductivity (24) of \( 5 \times 10^{-8} \ \Omega^{-1} \text{cm}^{-1} \)

Kolomiets (2), also reported that conduction in \( \text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3 \) was purely electronic, as experimental investigation, using the Tubandt technique, had not revealed ionic conduction.
For \( \text{As}_2(\text{Se}_{1/3}\text{Te}_{2/3})_3 \), Arnoldussen et al (24) also reported a linear relationship between the logarithm of conductivity and reciprocal temperature, measured between 170°C and 335°C, with room temperature values of \( \sigma = 2.2 \times 10^3 \Omega^{-1} \text{cm}^{-1} \) and \( E_\sigma = 0.55 \text{eV} \). They also showed that these parameters were valid for both the bulk material and thin films.

Marshall and Owen (25) have shown that for \( \alpha\text{-As}_2\text{Te}_3 \) deviations in linearity occur at low temperatures. The variation of activation energy and conductivity with composition for materials in the As-Se-Te system (which includes \( \text{As}_2\text{Se}_3 \)) is reviewed in reference 23. Both quantities vary smoothly with the variation in stoichiometry, as does the optical gap, and the Fermi level seems to be pinned near mid-gap.

In \( \text{As}_2\text{Se}_3 \) the activation energy does not vary over an extended temperature range, which suggests that the conduction processes are not dominated by states near \( E_F \) as the temperature is decreased. Variable range hopping conduction, demonstrated by the conductivity varying with temperature according to the general relation:

\[
\sigma = A \exp(-B/T)^{1/4}
\]

is not observed. Mahadevan et al (26) reported \( T^{-1/4} \) behaviour for \( \text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3 \) up to room temperature, giving a density-of-states at the Fermi level of \( 1.14 \times 10^{16} \text{ eV}^{-1} \text{cm}^{-3} \).
3.1.2 AC Properties

With many amorphous semiconductors, including chalcogenide glasses, the ac conductivity has been observed, in a particular frequency range, to have a frequency dependence given approximately by the expression

$$\sigma(\omega) = A\omega^s$$

(3.4)

with $s<1$

This behaviour is generally taken to be evidence of hopping conduction.

Austin and Mott (27) interpreted these experimental observations in terms of a model in which conduction occurs through thermally assisted tunnelling between localised states near the Fermi level. They showed that the behaviour of the ac conductivity can be described by the relation

$$\sigma(\omega) = T[N(E_F)]^{1/2} \omega \ln^4 \left( \frac{V_{ph}}{\omega} \right)$$

(3.5)

The application of this equation to experimental observations of chalcogenide glasses produces a number of discrepancies. Values of the density-of-states at the Fermi level calculated from equation 3.5 are in the range $10^{18}$ to $10^{20}$ eV$^{-1}$ cm$^{-3}$, and are several orders of magnitude larger than values obtained from optical absorption or photo-induced ESR experiments. Also, equation 3.5
predicts that $\sigma(\omega)$ varies linearly with temperature, which implies that the gradient of the graph of $\sigma(\omega)$ plotted logarithmically as a function of inverse temperature should be $-T$. Although it has been shown experimentally that for chalcogenides (28) the slope of such a plot decreases with decreasing temperature, the slope is frequency dependent. Moreover, the frequency dependence derived from the factor $\ln^4(V_{ph}/\omega)$ in equation 3.4 predicts a maximum value of $s$ of 0.81, but values of up to 1 have been obtained experimentally. Thus it seems that this model is not appropriate for chalcogenide glasses.

An alternative approach was suggested by Elliot (29) based on the model for charged defect centres in chalcogenide glasses (20,21). He proposed that carrier motion occurs by means of hopping over the potential barrier between two defect centres rather than tunnelling through the barrier. Elliot considers the hopping process to occur when two electrons are ejected from a D$^-$ site and drop into a D$^+$ centre converting it into a D$^-$; the two centres thereby changing places. The model leads to the following expression for ac conductivity:

$$\sigma_{ac} = \pi^2/24[N(E_F)]^2 K [8e^2/kB] \omega^s/\tau o^{1-s}$$ (3.6)

where $B$ is the optical energy gap, $K$ is the dielectric constant, $N$ is the spatial density of defect sites and $\tau_o$ is a characteristic relaxation time. This expression gives no explicit temperature dependence, only an implicit dependence through $s$, which is $1-6kT/B$. 
Equation 3.6 predicts an ac conductivity whose frequency dependence is slightly sub-linear, and it gives a better agreement between theory and experiment. The temperature dependence obtained from this model is, to a first approximation,

\[ \ln \sigma_{ac} \propto T \]  \hspace{1cm} (3.7)

Fig 3.2(a) shows the temperature dependence of the conductivity of \( a-\text{As}_2\text{Se}_3 \) (28,30) measured at different frequencies. At high temperatures, \( \sigma_{\text{meas}} \) tends to the dc value, \( \sigma_{dc} \). Kitao (31) investigated the conductivity of \( \text{As}_2\text{Se}_3 \) in the temperature range 93\({}^\circ\)K to 227\({}^\circ\)K, at frequencies from 30Hz to 10.3 GHz. He found that at low temperatures \( \sigma_{\text{meas}} \) was nearly independent of temperature but strongly dependent on frequency. The frequency dependence of \( \sigma_{\text{meas}} \) was found to be linear up to 10\(^6\) Hz, quadratic between 10\(^6\)Hz and 10\(^8\)Hz and above 10\(^8\)Hz, independent of frequency. Similar temperature characteristics were obtained by Owen and Robertson (32) for \( \text{As}_2\text{S}_3 \) and an alloy of \( \text{As}_2\text{Se}_3 \) with 0.2 at\% Ag. Lakatos and Abkowitz (33) found that for \( \text{As}_2\text{Se}_3 \) \( s \) was between 0.9 and 1 in the frequency range 10\(^2\) to 10\(^7\) Hz, with no evidence of the \( \omega^2 \) dependence previously reported (31,32).

Lakatos and Abkowitz also reported that for \( \text{As}_2\text{Se}_3 \), Se and \( \text{As}_2\text{S}_3 \) the room temperature dc conductivity is at least a factor of 10 below the value of the low frequency ac conductivity. Andrievskii and Kashirin (34) found that the onset of the frequency dependent behaviour, as described by equation 3.4, is temperature
Figure 3.2 Temperature dependence of the conductivity of:

(a) amorphous As$_2$Se$_3$
(b) amorphous As$_2$Se$_3$ - As$_2$Te$_3$ (30)
dependent, and that it occurs at higher frequencies with increasing substitution of selenium by tellurium; $s$ for this system is in the range 0.7 to 0.9. At lower frequencies, they found that the conductivity was slightly greater than the dc conductivity, and showed an exponential temperature dependence. These results were interpreted in terms of conduction by hopping in localised states.

Fig 3.2(b) shows that the ac conductivity of $\text{As}_2\text{Se}_3$-$\text{As}_2\text{Te}_3$, (30) which has a lower resistivity, does not have a temperature dependent activation energy, and has a magnitude slightly greater than that of the dc conductivity over the same temperature range ($295^\circ \text{K}$ to $319^\circ \text{K}$). Ivkin et al (30) interpreted these results as evidence of extended state conduction. Segawa (22) investigated the ac conductivity of materials in the As-Se-Te system. He found that for $\text{As}_2\text{Se}_3$-$\text{As}_2\text{Te}_3$ the conductivity at low frequencies was about ten times that of the dc conductivity, and the onset of frequency dependent behaviour was at approximately $5\times10^6 \text{Hz}$.

Lakatos and Abkowitz (33) found that the dielectric constant, $\varepsilon'$, of $\text{As}_2\text{Se}_3$ at $10^2 \text{Hz}$ has a value of 11.2, which decreases to 10.5 when the frequency is increased to $10^7 \text{Hz}$, a dispersion of 15%.
3.1.3 Thermopower

Thermoelectric power measurements in chalcogenide glasses have shown a positive coefficient, $S$, indicating that hole conduction predominates; $S$ is inversely proportional to temperature and is shown by Mott and Davis (35) to be related to the band gap by the expression:

$$S = \frac{k}{e} \left( \frac{E_s}{kT} + A \right)$$  \hspace{1cm} (3.8)

where $E_s$ is a characteristic activation energy defined by $E_F - E_v$ (see fig 2.1) for conduction in extended states and $E_F - E_b$ for hopping in band-tail localised states. $A$ is a constant which depends on the scattering process, and is approximately unity for conduction in extended states, and $<<1$ for current carried in localised states.

If conduction is by holes alone, the thermal activation energy measured from thermopower, $E_s$, should be equal to $E_0$, unless the mobility of the holes is temperature dependent and can be approximated by

$$\mu(T) \propto \exp \left( \frac{-E_s}{kT} \right)$$  \hspace{1cm} (3.9)

over the temperature range of interest.
Uphoff and Healy (36) reported on the thermopower of glasses in the As-Se-Te system. For As$_2$Se$_3$ between 325°C and 380°C and for As$_2$Se$_3$-As$_2$Te$_3$ between 220°C and 375°C the Seebeck coefficient, $S$, is positive, (of the order of 1100μV/°K), and decreases linearly with increasing temperature. The thermal activation energies, calculated from graphs of resistivity versus reciprocal temperature are 0.60eV for As$_2$Se$_3$ and 0.54eV for As$_2$Se$_3$-As$_2$Te$_3$.

Kolomiets and Rospopova (37) reported a value of $E_s$ for As$_2$Se$_3$ of 0.97eV, which like the values of Seebeck coefficient, are higher than those of Uphoff and Healy. Seager and Quinn (22) reported a value for $E_s$ of 0.60 ± 0.07eV, which is substantially lower than the activation energy of 0.92eV, calculated from their dc conductivity measurements. Similarly, for As$_2$Te$_3$, a reported value of $E_s$ of 0.25 ± 0.02eV is lower than the $E_o$ of 0.42eV.

Arnoldussen et al (24) reported similar results for As$_2$(Se$_{1/3}$Te$_{2/3}$)$_3$, where a value of $E_s$ of 0.41eV was 0.15eV less than the activation energy measured from dc conductivity experiments. Measurements of thermopower suggest that materials in both systems are p-type, and the activation energy for conduction has been found to be greater than that for thermopower. The difference, $E_o - E_s$ of the order of 0.15eV. The difference between the two activation energies is interpreted by Seager and Quinn as additional evidence of conduction by small polaron hopping. Nagels et al (38) proposed a two-channel model of conduction in which they suggests that transport occurs simultaneously in extended
states and band-tail localised states. This model implies a gradual change in the slope of the semilogarithmic dc conductivity characteristics and a corresponding sudden rise in $S$ with increasing temperature.

3.1.4 Optical Absorption

In amorphous semiconductors the absorption of photons causes the excitation of electrons from filled states in the valence band to empty states in the conduction band. The absorption constant, $\alpha$, describes the decrease of light intensity with distance because of absorption; typically, this absorption edge has a shape as shown in fig 3.3. Its shape is usually different from that of crystalline materials, and the edge may shift towards higher or lower energies. It is often less steep, and in nearly all cases displays an exponential tail at low photon energies, below about $10^3 - 10^4 \text{ cm}^{-1}$, and saturates at high absorption coefficients.

In the high absorption region, where $\alpha > 10^4 \text{ cm}^{-1}$ indicated by the region $A$, the frequency dependence of the absorption coefficient is given by

$$\hbar\omega\alpha(\omega) = \text{const}(\hbar\omega - E_{\text{opt}})^r$$

(3.10)

where $r$ is a constant and $E_{\text{opt}}$ is the optical gap.

Both the cubic ($r=3$) and the quadratic ($r=2$) relationship have been observed in amorphous semiconductors. In most cases it appears that
Figure 3.3 The absorption edge of a typical amorphous semiconductor
the quadratic relation gives the best fit to optical absorption data.

The exponential part, B, or Urbach tail, extends over approximately four decades of absorption constant. Its origin is uncertain, but it is believed (39) that it may be due to internal electric fields produced by charged impurities.

Part C, the tail of the absorption edge, is generally attributed to inhomogeneities in the material, whose concentration, with careful preparation, can be minimised, and the tail reduced to values of the absorption coefficient of \( <<1 \).

For chalcogenide glasses, the absorption edge is usually not sharp. Part A of the absorption curve is usually associated with transitions from the localised valence band states into the delocalised conduction band states above \( E_c \). If imperfections are present in a material, energy levels are created in the gap, hence at energies less than the optical gap, it is possible to excite electrons to or from these imperfection levels, giving rise to optical absorption. This is why high imperfection densities have the effect of smoothing out the absorption edge.

Arnoldussen et al (24) investigated the optical absorption of bulk and thin film \( \text{As}_2(\text{Se}_{1/3}\text{Te}_{2/3})_3 \), and found no sharp absorption edge. They defined the optical gap at \( 0^\circ\text{K} \), \( (E_c-E_v) \), from equation 3.10, giving \( E_{\text{opt}} \), the value of \( E \) at zero absorption, as \( 1.24\text{eV} \) with \( r=2 \) and \( 1.15\text{eV} \) with \( r=3 \). This is greater than the mobility gap, which was defined by their dc
conductivity measurements.

Edmond (40) investigated the optical absorption of bulk and thin-film As$_2$Se$_3$, the former as both solid and liquid. He also investigated two materials in the As-Se-Te system. He found that the substitution of tellurium for selenium had the effect of shifting the absorption edge to lower energies. Edmond evaluated the optical gap as the energy corresponding to a value of $\alpha$ of 100 cm$^{-1}$, which for As$_2$Se$_3$ was 1.63 eV, 0.18 eV less than that of the mobility gap.

A sharper absorption edge has been observed by Stourac et al (41) for thin-films of As$_2$Te$_3$. At room temperature, the optical gap of 0.87 eV was close to the value of the mobility gap, 0.90 eV, which was interpreted as intrinsic conduction.

3.1.5 Transport Mechanisms

From time dependent transport studies, Pfister and Scher (42) deduced that holes in a-As$_2$Se$_3$ propagate by a hopping process through localised states, which is limited by various trapping events. This is trap controlled hopping, and Pfister and Scher suggested that D$^-$ levels close to the valence band may act as hole traps. Street (43) suggests that the defects can be considered as amphoteric centres, with D$^0$ being either a trapped hole or a trapped electron, as expressed by the reaction
Street states that unless the $D^0$ centre is particularly far from the nearest accessible valence band tail state, excitation of a hole will dominate because of the smaller activation energy. Consequently, electron transport is never observed, because, as soon as trapping at $D^+$ occurs, the above reaction ensures that $D^0$ centres excite holes to the valence band, and the propagation of electrons ceases.

3.2 THE EFFECT OF IMPURITIES

Kolomiets (11) showed that the conductivity of chalcogenide glasses generally increases with the increase of heavy components in the glass, for example, the introduction of tellurium increases the conductivity of glassy $\text{As}_2\text{Se}_3$. Following this work, it was believed that chalcogenide glasses could not easily be doped, as according to Mott's 8N rule (44) impurities in the glasses are coordinated in such a way that their bonding requirements are satisfied, and therefore they do not form donors or acceptors.

However, some additives can significantly affect the electronic properties of chalcogenide glasses. The electrical properties of Cu-$\text{As}_2\text{Se}_3$ were first reported in 1962 by Danilov and Myuller (45) who showed that a 5 at% addition of copper to $a$-$\text{As}_2\text{Se}_3$ increases the conductivity by approximately four orders of
magnitude. Danilov and El Mosli (46) investigated the temperature
dependence of the conductivity of a range of arsenic selenide
alloys, with up to 20 at% copper, and showed that the thermal and
optical gaps decreases with increasing copper content. Petursson
(47) confirmed that the addition of 1 at% or less of silver or
copper in the As-S or As-Se systems causes a considerable increase
in the conductivity and a reduction in the optical gap. Andreichin
(48) obtained similar results for copper impurities in arsenic
sulphide glasses.

Kolomiets et al (49) found that small additions of copper and
silver in As$_2$Se$_3$ up to 0.2 at% produces a decrease in
conductivity and an increase in activation energy. A further
increase in impurity concentration up to 2.4 at% results in an
increase in conductivity and a decrease in activation energy.
Kolomiets attributed the decrease in conductivity at very low
impurity levels to an increase in carrier scattering by the lattice
imperfections caused by the impurity. Also he suggested that the
subsequent increase in conductivity with increasing amounts of
copper are due to a transition to a more ordered structure.

Liang (6) sought a structural explanation for the reported
increase in conductivity and decrease in optical gap of
Cu-As$_2$Se$_3$ alloys with increasing copper concentration. He
showed that in these materials the nearest neighbour coordination
number and the glass transition temperature increases with copper
concentration.
Liang reported an optical gap for \( \text{a-As}_2\text{Se}_3 \) of approximately 1.5eV which decreases with increasing copper concentration to less than 1eV. Warnick and Benson (50) reported an optical gap for crystalline \( \text{CuAsSe}_2 \) also of less than 1eV; Liang suggested that a gap this magnitude is typical of a tetrahedral structure, and that the decrease in coordination with covalent bonding leads to a larger optical gap. The increase in \( T_g \) with copper concentration he attributed to the transition from the simple covalent structure of \( \text{As}_2\text{Se}_3 \) to the more complex three-dimensionally coordinated structure of \( \text{CuAsSe}_2 \) which will require more energy to devitrify.

Liang showed that the structure of glassy \( \text{CuAsSe}_2 \) was very similar to that of amorphous silicon and germanium, and that the increase in the average atomic coordination number from 2.4 in pure \( \text{As}_2\text{Se}_3 \) to nearly 4 in an alloy with 30 at% copper, is due to significant regions of the sample having an atomic arrangement and composition close to that of crystalline \( \text{CuAsSe}_2 \).

Pfister and Morgan (51) investigated the effect of very low concentrations of copper (<0.1 at%) on the electronic properties of \( \text{a-As}_2\text{Se}_3 \). The samples were prepared by co-evaporation at \( T_g \) of \( \text{a-As}_2\text{Se}_3 \) with copper, on to an aluminium substrate held at a temperature close to \( T_g \). The electrical properties which they studied were hole transit time and dc conductivity. For samples doped with between 0.015 and 0.3 at% copper, the activation energy varies from between 0.82 and 0.84eV, with an increase in conductivity of less than a factor of 10 over the same concentration range.
They found that doping a-As$_2$Se$_3$ with copper had similar effects on transport properties to doping it with nickel, manganese and iron.

Pfister and Morgan found that an increasing concentration of copper causes a large increase in hole transit time, with an associated increase in $\text{ec}_3$. They suggested that the copper generates traps at energies above the intrinsic trapping level located at 0.6eV above the hole transport states, as shown in fig 3.4.

They also interpreted their results as confirmation of the supposition that amorphous semiconductors cannot be doped when the dopant is added during the formation of the glass at $T_g$, that is, under conditions of thermal equilibrium. Very large conductivity increases and corresponding lowering of the activation energy have been observed by Ovshinsky (52) and Flasck et al (53) with metal additives in lone-pair semiconductors. These materials were prepared by co-deposition on to cold substrates. This method of preparation implies a different situation from that presented in this work, because the additives and the valence alternation centres are not permitted to equilibrate, and the concentration of the former exceeds that of the latter.

Kitao et al (54) investigated the effect of up to 4 at% copper on a-As$_2$Se$_3$. They found that the conductivity decreases with the addition of less than 0.5 at% copper and then increases with copper concentration. This is in agreement with the results of
Figure 3.4  Energy level diagram of As$_2$Se$_3$ doped with Mn, Fe, Ni or Cu (51)
Kolomiets et al (49). They also found that at a copper content of >1 at%, $E_{\text{opt}}$ decreases linearly with copper concentration. Kitao et al suggested that at copper concentrations of >1 at%, the decrease of the optical gap is caused by an 'alloying' effect, namely a compositional change in the material, due to the change in bond angles and/or bond lengths. In addition, they suggested that the Fermi level shifts downwards due to the creation of acceptor-like impurity states.

3.3 THEORETICAL MODELS

Many elements added to the melt of a chalcogenide material are incorporated in their lowest energy configuration, which means that they will remain relatively inactive electrically. However, there are some elements which will have a greater effect, including copper, the experimental effects of which have been described in section 3.2.

In chapter two the models which sought to identify the important intrinsic defects in chalcogenide glasses, were summarised. These models proposed that charge defects, derived from neutral bonding defects, intrinsic to the material and occurring in pairs, introduce a structure in the density of localised states, tailing from the band edges into the gap of the semiconductor. An assumption of these models is that impurities are not present, which implies that the defects occur in equal concentrations; however the
models have been extended in an attempt to predict the effect of additives.

Mott (55) analysed the effects of certain charged impurity centres on the conductivity of chalcogenide glasses. He suggested that the addition of certain elements to these glasses would alter the concentration of valence alternation centres by either destroying dangling bond centres of one sign, or forming charged centres which are compensated by D centres of the same sign as the impurity, which in the case of copper will be D⁺.

Mott showed how the conductivity of the glass would be expected to increase by exp(0.3/kT) when the density of the additives exceeds that of the intrinsic defects, that the activation energy would be reduced to 2/3 of the original value and that the Fermi energy would be unpinned. The results of Danilov and El Mosli (46) concide with this theory.

However, it is well established that whereas this is true for some additives, for others the conductivity is unaffected even by concentrations far in excess of that of the intrinsic defects.

To determine whether or not additives will alter the density of valence alternation centres, and thereby the transport properties, Kastner (56) extended his chemical bond arguments to the addition of metals to lone-pair glasses and analysed possible bonding configurations of charged and neutral bonding states.
Kastner pointed out that although foreign additives can alter the density of valence alternation centres, the effect is often smaller than might be expected. This is because many additives are incorporated into the semiconductor glass as a neutral species, which have their valence requirements satisfied, so it is only the unusual bonding configurations of the additives that are charged which affect the VAP density.

If the normal valence of a metal additive is \(n\), and the bonding of the metal in the glass is covalent, the lowest energy bonding configuration is one in which the metal has \(n\) normal bonds to twofold coordinated chalcogens and \(4-n\) coordinate or dative bonds to chalcogen atoms, which are threefold coordinated. Normally coordinated chalcogen atoms can lower their energy by moving closer to the metal atom and coordinate bonds are formed between the lone-pairs of the chalcogen and empty orbitals on the metal atom.

This complex is electrically neutral and is therefore electronically inactive; however, the entropy of mixing favours strongly its dissociation into ionised species. If the metal atom separates from the normally coordinated chalcogen, leaving the chalcogen negatively charged, an empty orbital is available for the formation of a fourth coordinate bond and the complex becomes a positive ion. This is a higher energy bonding configuration, and its formation can be described by the reaction

\[
A + C_2^O \rightarrow A^+ + C_1^-
\]  
(3.12)
indicating that the positively charged additive is compensated by a $C_1^-$ somewhere else in the material. It is only the charged additives which affect the density of the valence alternation defects, and through them, the conductivity. However, assuming that the additives are allowed to equilibrate at $T$, the dissociation is suppressed by the presence of the intrinsic charged defects in the glass. This strongly reduces the effectiveness of the foreign atoms for altering the conductivity. The generation of defects by the host material can be described by the reaction

$$2C_2^0 + 3C_3^+ + C_1^-$$  \hspace{1cm} (3.13)

Also charge neutrality requires that

$$xA_0 + [C_3^+] = [C_1^-]$$  \hspace{1cm} (3.14)

where $A_0$ is the total density of additives and $x$ is the fraction of additives that are ionised.

Applying the law of mass action to equations 3.12 and 3.13 and solving the three equations gives a maximum value of $x$ of

$$x_{\text{max}} = (1+K_i/K_d)^{-1}$$  \hspace{1cm} (3.15)

Where $K_d$ is the dissociation constant and $K_i$ is the equilibrium constant. This confirms that a large value of $K_i$, that is a high density of intrinsic defects, strongly represses the dissociation of
impurities, and hence reduces the effectiveness of the foreign additives for altering the conductivity. Fig 3.5 shows the concentration of ionised additives plotted as a function of the total additive concentration (56). As can be seen, the density of ionised additives increases with increasing concentration, but the rate of increase decreases rapidly with increasing concentration, even when the suppression of dissociation by intrinsic defects is negligible (ie $K_i/K_d \ll 1$).

Kastner states that the dissociation constant $K_d$ is inversely proportional to the dissociation energy, $E_d$, with an exponential dependence. Therefore, in general, additives with electronegativities near that of the host material are likely to have a large $E_d$ and be completely ineffective. Other additives, such as copper which has an electronegativity of 1.65 on the Pauling scale as compared with the value for selenium of 2.55, will have a greater effect.

Kastner and Fritszche (57) extended the KAF model (21) to predict the temperature dependence of the carrier concentrations and the conductivity as a function of the concentration of charged additives in chalcogenide semiconductors.

For the equilibrium situation, when additives are introduced into the melt, the positive additive centres of concentration $[A^+]$ remains fixed below $T_g$, as do the concentration of the defects. When equilibrium is permitted, the valence alternation defects not only retard the occurrence of charged additives, they increase in
Figure 3.5  Concentration of ionised additives, $\frac{xA_0}{K_d N_0}$ plotted as a function of additive concentration, $\frac{A_0}{K_d N_0}$. Also plotted is concentration of compensating valence alternating centres $\frac{c_1}{K_d N_0}$ (56)
number such that their concentration is always in excess of that of the charged additives.

Kastner and Fritsche related the quantities \([C_3^+], \[C_1^-]\), \(n\) and \(p\) (\(n\) and \(p\) are the electron and hole concentrations) by the laws of mass action, and in turn related them to \([A^+]\) by the condition for neutrality

\[
[C_3^+] + [A^+] + p = [C_1^-] + n \quad (3.16)
\]

Taking \(N_o\) as the defect density in the absence of dopants, they obtained the relation

\[
p^2(2N_o^2/[A^+]+p)^2=2[A^+]P_o^2 \quad (3.17)
\]

The solution derived by Mott (55), which leads to the reduction of the activation energy to \(2/3\) of its original value, can be obtained from equation 3.17 only when \(p \gg 2N_o^2/[A^+]\), that is at high temperatures. More commonly encountered is the case occurring at lower temperatures where \(p \ll 2N_o^2/[A^+]\), and equation 3.17 reduces to

\[
p = [A^+]P_o/N_o \quad (3.18)
\]

or, in the case of electrons

\[
n = [A^+]n_o/N_o \quad (3.19)
\]
The carrier concentration, \( p \), can be described by the relation

\[
p = N \exp\left(\frac{-E_p}{kT}\right)
\]  

(3.20)

where \( 2E_p = 2E_0 - E_1 - E_2 \), which is the energy needed to excite two holes to \( E_v \) by means of the reaction \( C_3^+ \rightarrow C_1^- + 2h \). This, therefore, is not expected to vary with the addition of \( [A^+] \).

Fritzsche's (58) suggested plot for \( \log p \) as a function of \( 1/T \) is shown in Fig 3.6 for both doped and undoped chalcogenide materials. The conductivity is expected to be related to the carrier concentration, and would display a kink at \( p = \frac{2N_0^2}{[A^+]} \). In addition they suggested that the conductivity prefactor would increase by \( [A^+] / N_o \), and that the presence of charged additives reduces the pinning effect of the valence alternation pairs.

Pfister and Morgan (51) investigated the effect of low concentrations (\(<1\) at\%) of a range of metallic impurities on the electronic properties of thin films of \( \alpha-\text{As}_2\text{Se}_3 \) in order to examine the predictions of charge defect models described above. Their results are described in the previous section. By doping the chalcogenide with electropositive or electronegative elements, Pfister and Morgan hoped to significantly alter the density of the \( C_1^- \) centres, which are the centres which affect the transport of holes in the materials. They suggested that copper was not suitable for probing the defect models because, although the impurity is
Figure 3.6 Hole concentration, $\log p$, as a function of $1/T$ of chalcogenide material (a) undoped and (b) containing a concentration $[O^-]$ of negatively charged doping centers (58)
positively charged, (in the form of Cu\(^+\)) it is not likely, at the
concentrations studied, to affect the C\(_1^-\) density, because
electrons released by the impurity atoms are taken up by the
neighbours bonding to the impurity.

They indicated a different doping mechanism for group IA metals
and thallium, which gave an increase in transit time proportional to
the impurity concentration, with a constant activation energy, which
is what could be expected from the model.

Fritszche and Kastner (59) predicted that at low concentrations
and/or higher temperatures, there is no change in the activation
energy, but there is a change in the conductivity prefactor C. They
suggested that observed increases in C and in conductivity, and a
decrease in activation energy may be due to changes in the VAP
ionisation energy E\(_1\) and E\(_2\), with alloying.
4.1 PREPARATION OF THE GLASSES

4.1.1 Formation of Glasses

Glasses can be made by many methods both in bulk and thin film form and several of these techniques have been reviewed by Owen (60). Since the composition of a glass is not limited by stoichiometry, the range of chalcogenide glass compositions is limited only by the ability to quench the melt rapidly enough to prevent crystallisation. For example, fig 4.1 (61) shows the large glass forming range of the Cu-As-Se system. Flasck et al (53) studied 'chemically modified' amorphous semiconductors prepared by RF sputtering of the chalcogen systems and the modifying metal on to substrates at low temperatures. The chemical modifiers are incorporated at a temperature sufficiently low that the material cannot reach a structural or configurational equilibrium. Ovshinsky found that attempts to incorporate nickel into a glass by quenching a melt of composition Ge$_{32}$Te$_{32}$Se$_{32}$As$_4$ resulted in partial crystallisation, even after rapid quenching. In contrast, Pfister and Morgan (51) deposited their films at or near the glass
Figure 4.1 Glass formation in the Cu-As-Se system
transition temperatures. In this work bulk glasses were mainly used in experiments, as their compositions could be more accurately determined than those of sputtered or evaporated films.

The formation of a glass by the cooling of a liquid requires conditions necessary for the prevention of crystallisation. As the temperature of the molten glass is lowered below the thermodynamic melting point, it passes a point where the rate of crystallisation is a maximum. If the temperature can be lowered through this maximum and the growth of crystals is avoided, then further cooling will make crystallisation less likely and the liquid will solidify into a glass. The rapidity of the required cooling is the determining factor in the prevention of crystallisation, and there is a wide range of quench rates for different materials to form glasses (60). For chalcogenide glasses, minimum cooling rates of a few degrees per second are sufficient. Multiple component chalcogenide glasses may suffer from inhomogeneity or phase separation, and the degree of inhomogeneity may depend on the preparation and heat treatment of the material.
4.1.2 Preparation of Bulk Glasses

The metal—chalcogenide alloys were prepared by the direct reaction of the pure elements, (99.9999% pure where possible). The component materials were prepared under dry nitrogen, and the appropriate weights were loaded into quartz tubes which were then sealed under vacuum. The tubes were heated at 850°C in a rocking furnace for 24 hours. To avoid the incorporation of bubbles in the material, the furnace was held steady for approximately 1 hour to allow any dissolved gases to escape. The tube was then cooled rapidly to ensure that the material formed was a glass.

During preliminary measurements of the electronic properties of these materials, it was noticed that the properties varied slightly from batch to batch of the glasses. In order to avoid such variations, careful precautions were taken to ensure that the cooling of the glasses was exactly the same in each case. The cooling pattern was as follows:

Cooling quickly from 850°C to $T_g$ by taking out of the furnace and placing in an oven at temperature $T_g$.
Holding at $T_g$ for 2 hours.
Reducing from $T_g$ to $T_g - 20°C$ in 1 hour cooling to ambient in the oven after it has been switched off.

This regime was planned to avoid phase separation by quenching as quickly as possible. Holding the material at $T_g$ allows mechanical relaxation to take place; this must be done at $T_g$ or lower to
avoid recrystallisation.

4.1.2.1 Preparation of Bulk Samples

For most experimental purposes thin slices of the bulk material are required; these were cut from the cooled ingot with a diamond saw. The slices were polished with carborundum powder so that their faces were flat and parallel. When broken, the materials exhibited conchoidal fractures typical of vitreous materials.

4.1.2.2 Preparation of Thin Samples

For measurements under high electric fields and thermopower studies, very thin sections of the glass are required. Suitable samples were prepared by pressing which is a method of producing bulk samples of known composition of approximately 200μm in thickness. A suitable small piece of bulk material was heated in a nitrogen atmosphere; when the glass became soft it was pressed into a film between two thin plates of mica. The best samples were obtained when the material is pressed at a temperature low enough for the glass to solidify after a few seconds of pressing, but high enough to permit the pressing to be done before the glass becomes too viscous. After pressing, the mica was peeled off; the samples were then polished with fine carborundum to remove any surface irregularities.
4.1.2.3 Preparation of Thin Films

The minimum thickness of samples obtained from splat cooling and/or hand polishing of bulk glasses was found to be in the region of 100μm. This proved to be too thick for optical absorption experiments as no transmission was detected through that thickness of material. Consequently, it was necessary to use films of chalcogenide glasses made by RF sputtering of the material on to glass substrates.

The films were produced using an RDM mkIII RF generator with an output of 1 kW at 13.56 MHz and an RDM mkIII impedance matching unit. The sputtering was carried out in an argon atmosphere at a pressure of 8x10⁻³ torr. The target was a 3.5in aluminium disc covered with powdered chalcogenide. It was found that sputtering at 50 watts for 1-2 hours gave reasonable films with properties similar to the bulk materials.

It is to be expected that the different elements in the melt will sputter at different rates but if the target glass is heated above its softening temperature, as was the case with a power of approximately 50 watts, these differences will be less.

Film thicknesses were measured using a Taylor Hobson Tallysurf 4.
4.2 ANALYSIS OF THE MATERIALS

4.2.1 Chemical Analysis

Chemical analyses were carried out by Miss Rona Belford on an Instrumentation Laboratory atomic absorption spectrophotometer, to confirm the chemical composition of both the bulk materials and the thin films. In atomic absorption spectroscopy a solution containing a metallic species is aspirated into an air-acetylene flame and an atomic vapour of the metal is formed. The metal atoms are irradiated with a light of their own characteristic resonant wavelength; the atoms will then absorb some of the radiation, the absorbance being proportional to the population density of the atoms in the flame. The spectrophotometer measures the reduction in light intensity compared with a blank solution. Calibration curves are obtained using solutions of known concentration of the elements to be determined, hence the contents of a known solution can be determined. Solutions of the chalcogenide alloys were obtained by dissolving the material in nitric acid.

The composition of the thin sputtered films were within 5% of the composition of the melts. As this technique is subject to experimental accuracy limits, samples of the target material before and after sputtering were also analysed, and were found also to be within 5% of the compositions expected.
4.2.2 Microprobe Studies

Normally, glasses cooled from a melt are microscopically homogeneous; however, in order to ascertain that this was the case, a sample from each melt was analysed using an electron microprobe. This is a technique whereby an electron beam is focused on a very small area of the sample surface and as a result of the electron bombardment the material emits x-rays. The characteristic x-ray spectrum is recorded and analysed to give qualitative information about the local atomic composition at the sample surface.

For these measurements a Microscan 5 electron probe microanalyser in the Department of Geology was used. A 1 μm 40kV electron beam was directed at the highly polished surface of a selection of the materials being studied. The instrument was adjusted to detect a specific spectral line, which is an indication of the presence and relative concentration of the corresponding element. The concentrations of each element were determined automatically by the instrument, by comparing the relative radiation intensities generated by the element in the specimen and a standard specimen (in this case either pure selenium, copper, tellurium or stoichiometric gallium arsenide were used). Corrections were also made for absorption and fluorescence of emitted x-rays and for background radiation. Table 4.1 shows the formulae of the materials determined from the microprobe measurements, and the nominal formulae of the melts.
<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Actual Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}<em>{25}(\text{As}</em>{0.4}\text{Se}<em>{0.6})</em>{75}$</td>
<td>$\text{Cu}<em>{24.75}(\text{As}</em>{0.42}\text{Se}<em>{0.58})</em>{75.25}$</td>
</tr>
<tr>
<td>$\text{Cu}<em>{5}(\text{As}</em>{0.4}\text{Se}<em>{0.6})</em>{95}$</td>
<td>$\text{Cu}<em>{4.88}(\text{As}</em>{0.45}\text{Se}<em>{0.55})</em>{95.2}$</td>
</tr>
<tr>
<td>$\text{Cu}<em>{27.5}(\text{As}</em>{0.4}\text{Se}<em>{0.6})</em>{62.5}$</td>
<td>$\text{Cu}<em>{27.26}(\text{As}</em>{0.40}\text{Se}<em>{0.60})</em>{72.74}$</td>
</tr>
<tr>
<td>$\text{Cu}<em>{5}(\text{As}</em>{0.4}\text{Se}<em>{0.5}\text{Te}</em>{0.5})_{95}$</td>
<td>$\text{Cu}<em>{4.93}(\text{As}</em>{0.40}\text{Se}<em>{0.5}\text{Te}</em>{0.5})_{94.01}$</td>
</tr>
<tr>
<td>$\text{Cu}<em>{7.89}(\text{As}</em>{0.4}\text{Se}<em>{0.5}\text{Te}</em>{0.5})_{92.11}$</td>
<td>$\text{Cu}<em>{7.19}(\text{As}</em>{0.4}\text{Se}<em>{0.49}\text{Te}</em>{0.49})_{92.81}$</td>
</tr>
</tbody>
</table>

**Table 4.1**

*Analysis by Electron Microprobe of some of the Chalcogenide Alloys*
Repeated measurements showed that there was no variation in composition in different parts of the melts, indicating complete homogeneity.

4.3 DIFFERENTIAL THERMAL ANALYSIS

4.3.1 Introduction

Differential thermal analysis (DTA) is a technique used to study the thermal behaviour of materials during heating or cooling at a controlled rate. A material which does not undergo any physical or chemical change through the temperature range of interest is selected as a reference material, and this material and the sample are placed close together in a temperature controlled environment. As the temperature is varied, changes occur in the sample; the temperature of the reference and the temperature difference between the sample and the reference material are plotted automatically as a function of time, the plot indicating where any changes in the sample have occurred. For example, when the sample converts from the amorphous to the crystalline state, the excess heat of the crystallisation of the sample means that its temperature increases relative to that of the reference, which is indicated by an exotherm, that is a positive peak in the trace. Similarly, an endotherm, which is a negative peak in the trace, indicates a
decrease in the sample temperature relative to the reference. Upon heating, a glass transition may be observed in the DTA trace for an amorphous material; it appears as a step, and $T_g$, the temperature of the onset of the glass transition, is at the intersection of the base line and the tangent to the maximum curve of the slope.

Fig 4.2 shows a typical heating thermogram for a chalcogenide glass, for example $\text{a-As}_2\text{Se}_3$. It has three points of interest: the onset of the glass transition at $T_g$, the recrystallisation/devitrification exotherm with a maximum at $T_c$ and a melting endotherm with a minimum at $T_m$.

The glass transition and recrystallisation are kinetic processes and will depend on the heating rate, that is, their values should be lower for slow heating rates than for fast heating rates. $T_m$ has little or no dependence on the heating rate. $T_g$ and $T_c$ are also affected by particle size; small particle size, and hence greater surface area provides more surface nucleation sites for crystallisation and gives a lower value of $T_c$. $T_g$ will probably be affected only slightly due to the different thermal transfer properties of powder and lump materials, bulk material having a slightly larger value of $T_g$. 
Figure 4.2 Typical heating thermogram for a chalcogenide glass
4.3.2 Experimental Method

An evaluation of the thermal properties of the copper–chalcogenide alloys was made using a Stanton Redcroft 673-4 Differential Thermal Analyser, connected to a Servoscribe 2s chart recorder.

Immediately before the DTA measurements were made, a sample of each bulk glass was crushed to a coarse powder in an agate mortar, in air. The reference material was Alumina, Al$_2$O$_3$, according to the manufacturer's recommendation. Equal weights of both materials were placed in small platinum-rhodium crucibles which were placed in a ceramic stem inside a furnace. A 3mm dent in the base of the crucibles allowed the junctions of platinum/platinum-rhodium thermocouples to measure the temperature of the centre of the material within the crucibles. The furnace was then heated at a constant rate.

After the heating programme was completed, the sample was rapidly cooled in air in order to retain the high temperature disordered state, and the heating programme was repeated. This was done once only, as it was suspected that the resulting oxidation of the sample could lead to inaccurate results.
4.3.3 Results

The thermograms resulting from the differential thermal analysis experiments are shown in fig 4.3. Also shown is the trace obtained for a sample of a-As$_2$Se$_3$ made by quenching a melt of the elements in cold water. At a heating rate of 5deg/min the points of interest for the Cu-As-Se-Te and Cu-As-Se systems are well defined. It can be seen in some of the traces that there are two values of $T_m$ and $T_c$ indicating a two-phase structure in the glasses, although this is not apparent from the microprobe measurements. Table 4.2 gives the temperatures of the points of interest on the traces. The values in table 4.2 were the average of at least two determinations and were obtained with a reproducibility of better than $\pm 2^\circ$C. (Accuracy of the temperature readings was $\pm 1^\circ$C.)

For a-As$_2$Se$_3$, $T_g$ is 169$^\circ$K at a heating rate of 5deg/min. This is a similar result to that of Barakati (62) and Seager and Quinn (23). Liang's (6) results, obtained at the higher heating rate of 20deg/min, show $T_g$ as being much higher, confirming that $T_g$ is dependent on the heating rate, and $T_c$ and $T_m$ are not shown at all.
Figure 4.3  DTA traces measured at a heating rate of 5 deg./min.
<table>
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<tr>
<th>MATERIAL</th>
<th>rate</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;</th>
<th>T&lt;sub&gt;c1&lt;/sub&gt;</th>
<th>T&lt;sub&gt;c2&lt;/sub&gt;</th>
<th>T&lt;sub&gt;m1&lt;/sub&gt;</th>
<th>T&lt;sub&gt;m2&lt;/sub&gt;</th>
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<td>As&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5°C/min</td>
<td>172</td>
<td>344</td>
<td>374</td>
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<tr>
<td>Cu&lt;sub&gt;5&lt;/sub&gt;(As&lt;sub&gt;0.4&lt;/sub&gt;Se&lt;sub&gt;0.6&lt;/sub&gt;)&lt;sub&gt;95&lt;/sub&gt;</td>
<td>5°C/min</td>
<td>159</td>
<td>277</td>
<td>303</td>
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<td>397</td>
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<tr>
<td>Cu&lt;sub&gt;6.25&lt;/sub&gt;(As&lt;sub&gt;0.4&lt;/sub&gt;Se&lt;sub&gt;0.6&lt;/sub&gt;)&lt;sub&gt;93.75&lt;/sub&gt;</td>
<td>5°C/min</td>
<td>160</td>
<td>296</td>
<td>323</td>
<td>367</td>
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<tr>
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<td>5°C/min</td>
<td>165</td>
<td>266</td>
<td>344</td>
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<tr>
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<td>5°C/min</td>
<td>136</td>
<td>264</td>
<td>295</td>
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<td></td>
</tr>
</tbody>
</table>

**TABLE 4.2**

Results of Differential Thermal Analysis Experiments
5.1 INTRODUCTION

This work is not primarily concerned with the structure of copper-chalcogenide alloys but as a major previous investigation of the effects of metallic alloying on $\alpha$-$\text{As}_2\text{Se}_3$ was made from the structural point of view, (6), some experiments were carried out in order to further define the structure of metal-chalcogenide alloys, and to augment the information obtained by studying the electrical and optical properties.

Amorphous $\text{As}_2\text{Se}_3$ is thought to have a two-dimensional layer structure (63); the layers being composed of $\text{AsSe}_{3/2}$ linked rings of sheet-like structures bonded together in parallel layers by van der Waals forces. The short range order in these glasses is similar to that in the corresponding crystalline forms. Seregin and Vasilev (63) found that the structure of $\alpha$-$\text{As}_2\text{Te}_3$ is similar to that $\alpha$-$\text{As}_2\text{Se}_3$, which is unlike the crystalline structure of $\text{As}_2\text{Te}_3$.

X-ray studies carried out by Vaipolin and Porai-Koshits (64) have shown that in the $\alpha$-$\text{As}_2(\text{Se},\text{Te})$ system the $\alpha$-$\text{As}_2\text{Se}_3$ structure is preserved, and that Te substitutionally replaces Se in
the structure. The $\text{As}_2(\text{Se},\text{Te})_3$ glasses consist of corrugated layers in which As atoms occasionally act to hold adjacent layers together, and in which the Se and Te atoms are randomly dispersed relative to each other, but in which each chalcogen is bonded to two As atoms and each As is bonded to three chalcogens.

Liang's (6) radial distribution function (rdf) studies of glassy $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})^{100-x}$ alloys indicate that the average coordination number increases linearly from 2.40 at $x=0$ to 3.83 at $x=30$. He considered two possible atomic arrangements; in one the As and Se retain the three and two fold coordinations of $\text{As}_2\text{Se}_3$, while the copper is coordinated by eight to ten atoms; this is known as the random covalent model. Alternatively, the Cu and a large portion of the Se atoms are four-fold coordinated in a tetrahedral complex. The latter is the model which Liang's experimental evidence supports.

Liang also used x-ray diffraction techniques to identify the devitrified materials obtained during DTA experiments. He found that the major phase had a diffraction pattern similar to sphalerite and his literature search revealed two crystalline compounds with a structure close to sphalerite, namely, $\text{CuAsSe}_2$ and $\text{Cu}_3\text{AsSe}_4$. Further x-ray diffraction measurements on these materials showed that the structure of the devitrified alloys resembled that of $\text{CuAsSe}_2$ more closely. Fig 5.1 (65) shows the structure of chalcopyrite, which is crystalline $\text{CuFeS}_2$, where each Cu and Fe atom is tetrahedrally coordinated by four S atoms, and each S atom is tetrahedrally coordinated by two Cu and two Fe atoms.
Figure 5.1 Clinographic projection of the unit cell of the tetragonal structure of chalcopyrite $\text{CuFeS}_2$ (66)
Crystalline CuAsSe$_2$ has a similar structure.

Using extended x-ray absorption fine structure (EXAFS), Hunter et al (66) found that the coordination number of copper in alloys of composition $Cu_x(\text{As}_{0.4}\text{Se}_{0.6})_{100-x}$ was in the range 3.5 to 4. The nearest neighbour contribution indicated that the coordination of Cu in these materials is closer to that of crystalline CuAsSe$_2$ than that of crystalline Cu$_3$AsSe$_4$. These results conclusively exclude the validity of the random covalent model for these materials.

5.2 SCANNING ELECTRON MICROSCOPY

A scanning electron microscope was used to obtain topographical images of the fractured surface of the materials, at a high magnification. If a material is truly amorphous, there should be no evidence of form or structure in the image obtained. The images of most of the materials were completely featureless. However for the Cu-As-Se materials with low percentages of copper a very faint structure could be discerned at high magnifications (x2000 approximately). This suggests that this material may have a crystalline component. This will be discussed later.
5.3 X-RAY DIFFRACTION

X-ray diffraction experiments were carried out, using a Debye-Scherrer powder diffraction camera, in the Physics Department. Many materials in the Cu-As-Se and Cu-As-Se-Te system were investigated and were proved to be amorphous, except for the Cu-As-Se materials with low percentages of copper, which were partially crystalline. The crystalline phase was shown to be CuAsSe$_2$ (67). This corresponds to the results obtained with the scanning electron microscope. Materials in the Cu-As-Se system which were quenched in air more rapidly than described in chapter four, were proved to be truly amorphous.

5.4 DIFFERENTIAL THERMAL ANALYSIS

The technique of differential thermal analysis was described in detail in chapter four; the results are shown in section 4.3.3. It should be noted that the thermograms of fig 4.3 for the Cu-As-Se system show crystallisation and melting of two phases. This is the case for both the amorphous and the partially crystalline materials. Analysis of the thermograms indicate that the two phases are As$_2$Se$_3$, which has a melting point of 375°C and CuAsSe$_2$, which has a melting point of 415°C. Cu$_3$AsSe$_4$ is reported to have a melting point of 460°C (63), but a melting endotherm at this temperature was not observed. Liang (6) also detected two phases in the Cu-As-Se system, but only in the materials containing
more than 25 at% copper. Remembering that the electron microprobe
did not detect any compositional variations, there can be no phase
separation in the materials, however, it is possible that the
materials have a structure resembling a mixture of As$_2$Se$_3$ and
CuAsSe$_2$.

The thermograms for the Cu-As-Se-Te system exhibit only single
crystallisation and melting points.

5.5 ELECTRON SPIN RESONANCE

Paramagnetic materials possess a permanent atomic or magnetic
moment; only unpaired electrons contribute to the magnetic moment
of the atom as a whole, and in the absence of a magnetic field the
net magnetisation is zero.

Electron spin resonance (ESR) is a technique used for the
detection and investigation of unpaired spins. By applying an
alternating magnetic field to a paramagnetic material to which has
already been applied a perpendicular unvarying magnetic field,
transitions of unpaired electrons between states of energy $E_1$ and
$E_2$ are stimulated by radiation of the appropriate frequency (in
the microwave region), according to the relationships:

\[
E = E_2 - E_1 = \hbar = gBH
\]

where \( B \) = Bohr magneton, \( H \) = magnetic field strength and \( g \) is a constant of proportionality.

The density of unpaired spins may be obtained from measurements of \( g \).

In chalcogenide glasses such as \( \text{As}_2\text{Se}_3 \), the number of unpaired spins is very small. By contrast, in tetrahedrally coordinated semiconductors, where unpaired broken bonds are quite stable, strong spin resonance signals can be detected.

Pfister and Morgan (51) observed no ESR in thin-films of \( \text{As}_2\text{Se}_3 \) doped with copper in concentrations of less than 0.1 at% deposited on substrates heated to the glass transition temperature of \( \text{As}_2\text{Se}_3 \). They interpreted their results as evidence that the preferred ionic state of the copper is \( \text{Cu}^+ \). However, they observed that samples prepared by evaporation on to substrates held at room temperature exhibit paramagnetism resulting from \( \text{Cu}^{2+} \) and on annealing, the \( \text{Cu}^{2+} \) signal decreased substantially.

In this department preliminary ESR experiments (67) have indicated that materials in the Cu-As-Se system give ESR signals, but as yet no quantitative information has been obtained.
5.6 CONCLUSIONS

From the above investigations it can be concluded that in the materials in the Cu-As-Se system there is some tetrahedral coordination, where the atomic arrangement resembles that of CuAsSe$_2$, which is known to be tetrahedrally coordinated. It should also be noted that materials the Cu-As-Se system require to be quenched more rapidly than is described in section 4.1 in order to obtain a truly amorphous material. However, these materials which were quenched in air had mechanical properties which led to difficulties in the preparation of uniform samples for electrical measurements and for use in electrodes.

Little could be concluded about the structure of the materials in the Cu-As-Se-Te system. However, as it is known that the structure of As$_2$(Se$_{0.5}$Te$_{0.5}$)$_2$ resembles that of As$_2$Se$_3$ with tellurium atoms substituted for selenium atoms, it is reasonable to assume that the materials in the Cu-As-Se-Te system will also have a tetrahedral structure.
6.1 DC CONDUCTIVITY

In chapter two, the transport mechanisms of amorphous semiconductors in various temperature regions were discussed. From this, it can be seen that conductivity and other electrical measurements are required over as wide a temperature range as possible in order to study the electronic structure of the materials. The resistivities of the copper-chalcogenide alloys were low enough to permit measurement of conductivity over an appreciable temperature range. The dc conductivity of the bulk glasses was measured using polished slices of the material, approximately 1mm thick. The conductivity was measured from about 120\(^{\circ}\)K to approximately 30\(^{\circ}\)K below the glass transition temperature, to avoid any irregularities in results due to the softening of the glass; the glass transition temperatures having previously been determined by DTA measurements.
6.1.1 Experimental method

DC conductivity measurements on the bulk glasses were carried out using the circuit shown in fig. 6.1. Temperature control was achieved with an Oxford Instruments CF 100 continuous flow cryostat. This instrument used a controlled continuous flow of coolant to a vacuum insulated, radiation-shielded sample block. In this case the coolant is liquid nitrogen, so the temperature of the sample block could be controlled to within 0.1°K from 77°K upwards, by balancing the flow of coolant against heat leaks into the cryostat. The temperature was controlled by an Oxford Instruments Harwell temperature controller, which used an iron-gold thermocouple at 77°K as the reference junction. The controller compared the set voltage corresponding to the required temperature, with the thermocouple emf, and the derived error signal was used to control the heater power to obtain a balance.

Contacts of gold, copper or aluminium were evaporated on each face of the slices of the bulk glasses; to ensure good thermal contact to the sample block and good electrical contact with the connecting wires, a coating of colloidal graphite was put on the contacts. The samples were then clamped to the sample block. This arrangement gave good electrical connection down to temperatures of approximately 120°K. A voltage, supplied by a Coutant voltage source with a voltage divider, was applied across the sample, and the current measured using a Cary 410 vibrating-reed electrometer. The apparatus used is shown in fig 6.2; with this apparatus it was possible to measure conductances down to 1x10^-15 siemens.
Figure 6.1 Circuit used for measurement of DC conductivity
6.2 AC CONDUCTIVITY

6.2.1 Instrumentation

A common way of measuring the ac impedance or dielectric constant of a material is with a bridge. However, the limitation of this method is the length of time required to carry out a series of measurements.

More sophisticated experimental arrangements were used in the present work with a Solarton 1174 Frequency Response Analyser for frequencies between 0.1mHz and 1MHz, and a Hewlett Packard 4191A RF Impedance Analyser for frequencies in the range 1MHz to 1000MHz.

The Frequency Response Analyser (FRA) is an instrument which provides a means of measuring the frequency response of a system to a sinusoidal input signal. It consists of a programmable generator which produces an accurate stimulating sinusoidal signal, and an analyser which resolves the response to the stimulus, in terms of gain and phase shifts.

The generator provides an output signal of known amplitude and frequency of the form \( A \sin(\omega t) \), where \( \omega t \) can be in the range \( 10^{-4} \) Hz to \( 10^6 \) Hz and \( A \) can be in the range \( 10^{-3} \) V to 10V.

The output signal is in the form \( R \sin(\omega t + \theta) \), and the instrument displays the amplitude, \( R \), and phase angle, \( \theta \) of the test sample, relative to the original signal. Alternatively, it will give the
output in the form \( a + jb \), giving separately the real and imaginary parts. The instrument measures two voltages, \( X \) and \( Y \), its output is the ratio \( Y/X \). The FRA frequency sweep facility enables measurements to be made automatically over any part of the specified frequency range. This instrument is included in the experimental arrangement shown in fig 6.2.

The RF Impedance Analyser is an instrument which can be programmed to measure impedance parameters automatically over its frequency range, over a measurement range of \( 1\text{m}\Omega \) to \( 100\text{K}\Omega \).

The 4191A measures the reflection and/or transmission coefficient parameters of the sample to obtain the desired impedance characteristics. The instrument applies a measurement frequency test signal to the sample, which is terminated at the test port, and detects the vector voltage ratio of the reflected wave to the incident wave from/to the sample to measure the reflection coefficient. From the reflection coefficient the impedance value of the sample can be derived. Measured data is corrected according to stored calibration data, and the corrected data is converted into the selected parameters and displayed. Calibration is achieved by measuring error data for 51 calibration frequencies, and is stored in a non-destructive memory. The instrument carries out error corrections for frequencies other than the calibration frequencies by automatic interpolation.
Figure 6.2 Apparatus used for AC and DC conductivity measurements

1 Frequency response analyser (FRA)
2 FRA Plotter interface
3 Temperature controller
4 Millivoltmeter for temperature measurement
5 Pump unit for liquid nitrogen
6 Electrometer
7 DC supply
8 Evacuated sample chamber
A frequency synthesiser generates the test signal which remains phase locked to an internal quartz reference oscillator. The frequency of the test signal can be varied in 100Hz steps from 1MHz to 1000MHz. The impedance analyser is shown in fig 6.3.

6.2.2 Experimental Method

The FRA was used in the configuration shown in fig 6.4. The voltage measured across the sample is X and Y is the voltage measured across both the sample and a fixed resistor. Here the fixed resistors are of the type Vishay-Welwyn 4802, correct to within ±0.05% of their stated value, and with a negligible capacitive or inductive impedance over the frequency range of interest. On this instrument the outputs are not floating, hence it is not possible to make \( \frac{Y}{X} \) the ratio of the known to the unknown impedances. Therefore the results cannot be displayed directly on the XY plotter attached to the FRA. Here the calculations were worked out on a PDP11 computer, and the graphs plotted on a Hewlett Packard 7220S graph plotter. The instrument was checked using standard components.

In order to investigate the AC conductivity as a function of temperature, the samples were mounted directly on to the stage of the cryostat sample holder. This enabled accurate control of the sample temperature. To minimise stray capacitances, the coaxial leads between the parts of the apparatus were made as short as
Figure 6.3 The Hewlett Packard 4191A RF impedance analyser
Figure 6.4 Frequency response analyser configuration

Figure 6.5 Coaxial sample holder for the RF impedance analyser
possible. In order to maximise the sample capacitance, pressed samples less than 300\,\mu m in thickness were used. As sample capacitances were still only in the order of 20\,pF, large errors were still introduced by the stray capacitances in the leads and sample holder. These were evaluated by measuring the complex impedance of the circuit, including the evacuated sample holder, but without a sample in place. This measured impedance did not vary with temperature, and was used to correct the values measured with the sample in place, and which varied with temperature. Measurements were carried out in the frequency range 0.1\,mHz to 1000\,kHz and in the temperature range 220\,^\circ\,K to \( T < 300\,^\circ\,K \); the instrument was not sensitive enough to measure impedances at low temperatures.

On the impedance analyser the desired test parameters were programmed through the front panel controls, and the sample was mounted in a coaxial test fixture, as shown in fig 6.5. The impedance values calculated by the instrument were also processed on the PDP11 and associated graph plotter.
6.3 CAPACITANCE-VOLTAGE CHARACTERISTICS

6.3.1 Experimental Method

The Hewlett Packard 419A Impedance Analyser was used, and is described in section 6.2. This instrument can apply a bias voltage of up to +40 volts to the sample, which was again mounted in the coaxial sample holder. Because the sample has a relatively high resistivity, the applied voltage is less than that indicated on the instrument, and was measured directly on a Gould digital voltmeter, as shown in fig 6.3.

6.4 THERMOPOWER

6.4.1 Experimental Method

The 'coldfinger' apparatus shown in fig 6.6 was used for thermopower measurements. Temperature control of the sample was achieved by the use of a sample holder, shown in fig 6.7, which had two independent heating units. Each unit comprised two 300Ω, 6 watt vitreous wire-wound resistors mounted in parallel in an aluminium pier. The aluminium piers were bolted to, but partially thermally insulated from, a copper flange, which was connected by means of a hollow vacuum-jacketed copper rod to a liquid nitrogen
Figure 6.6 Apparatus used for thermopower measurements
reservoir. Each heater was manually controlled using two Farnell E30/1 power supplies to balance the heater input powers against the heat loss to the liquid nitrogen reservoir. Adjustment of the power to the heaters established a temperature gradient between the two units.

The samples were thin (about 300μm) irregularly shaped pieces of pressed glass. The sample was mounted on an insulating substrate of mica, which was mounted between the aluminium piers. Contacts of conducting silver paint were used to keep the sample clear of the mica, and to connect leads for the measurement of the emf.

The whole assembly, which is shown in fig 6.7 was placed in a brass box which was evacuated with a rotary pump. The thermocouple leads passed unbroken through vacuum feedthroughs. The temperatures at either end of the samples were measured by two copper-constantan thermocouples.

The thermocouple leads were connected through a switch, to enable the outputs of the thermocouple to be measured using the same digital multimeter (Keithley 160). The emf across the sample was measured with a Cary 410 vibrating reed electrometer.

With this apparatus it was possible to measure the thermopower over a temperature range of 200°K to 310°K. The temperature difference was kept small – always <20°C and usually <6°C – in order to avoid errors. The measured emfs were correct to within 20μV and the measured temperatures correct to within 0.4°K.
thermocouple for absolute temperature measurements

aluminium piers

mica sheet mounted on aluminium piers

heaters mounted within aluminium piers

thermocouples for differential temperature measurement

gold contacts

sample

Figure 6.7 Sample holder used for thermopower measurements
6.4.2 Zero Offset Voltage

When the temperature gradient across the sample is reduced to zero, there should be no thermovoltage; with this apparatus this was not the case. When the temperature gradient was zero, a small voltage, the zero offset voltage, could be measured. In order to find the true value of the thermopower several measurements of thermovoltage were made at the same mean temperature $T$, but with different temperature gradients across the sample. Fig 6.8 shows typical characteristics of the variation of $V$ with $\Delta T$ of a sample, with the value of $T$ being held constant. The graphs are straight lines, showing that $S = V/\Delta T$ is a constant for a particular value of $T$, and has a value equal to the slope of the line. Linear regression methods were used to calculate the shape of the straight line of best fit for the data points. The offset voltage may be due to the distance of the thermocouple from the actual sample, which could result in a discrepancy between the actual and measured values of $T$. 
Figure 6.8   Thermovoltage of Cu$_{625}$[As$_{0.4}$Se$_{0.5}$Te$_{0.6}$]$_{93.75}$ as a function of $\Delta T$ at fixed mean $T$
6.5 OPTICAL ABSORPTION

6.5.1 Experimental Method

For optical measurements a Zeiss Spectrophotometer, which comprises a lamp unit, a monochromator, a sample holder and a detector unit with an indicator meter, was used. The light source is a 30watt 6V tungsten filament lamp. Small pieces of the glass were held by a spring loaded sample holder across a hole; the holder also has a reference hole. Thus either the sample or the reference hole can be placed in the light beam. The detector unit has a photomultiplier tube for wavelengths of less than 0.67μm and a PbS photocell for wavelengths in the range 0.67μm to 2.5μm, and an amplifier unit which gives an output meter reading between 0 and 100.

The monochromator is used for separating a small wavelength band from the continuous spectrum of the light source. The width of this band depends on the width of the entrance and exit slits which are always the same and are controlled automatically by a servo mechanism. When the reference hole is in the beam of light, the automatic slit unit changes the slit width until the indicator gives a transmittance of 100%. Thus when the sample is placed in the light beam, the transmission can be read in % directly from the scale.
The transmission was measured in suitable steps of wavelengths over the instrument range of 360 - 2500\textmu m; at longer wavelengths interference fringes appeared.

For a thin film on a non-absorbing substrate, taking account of multiple reflections from all three interfaces, but neglecting interference, one obtains the following expression for the optical absorption constant (69):

\[ T = \frac{(1-R_1)(1-R_2)(1-R_3)e^{-\alpha d}}{1-R_2^2R_3^2[1-(R_1R_2+R_1R_3(1-R_2)^2)e^{-2\alpha d}]} \] (6.1)

where \( T \) is the ratio of the intensities of the transmitted and reflected light and \( R_1, R_2 \) and \( R_3 \) are the reflectances at the air-film, film-substrate and the substrate-air interfaces respectively. The reflectances can be calculated from the expression:

\[ R = \frac{(n_a - n_b)^2}{(n_a + n_b)^2} \] (6.2)

where \( n_a \) and \( n_b \) are the refractive indices. The refractive index of materials conforms to a semi-classical theory in which the macroscopic properties of a material can be related to microscopic properties which take some account of the atomic nature of matter and the resonant frequencies of the atoms.
The refractive index of a material, \( n \), is complex, and may be defined by \( n - jk \), where \( k \) is the extinction coefficient or absorption index which describes the absorption of light by the material according to the relation

\[
k = \frac{\alpha \lambda}{4\pi}
\]

(6.2a)

The reflectivity at normal incidence on a flat absorbing surface can also be expressed in terms of \( n \) and \( k \) as (88)

\[
R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}
\]

(6.2b)

The refractive index and its frequency dependence can be related to the response, to an oscillating electric field, of the atomic oscillators of the material, represented by the polarisation, or dipole moment per unit volume of the material. The behaviour of the atomic oscillator corresponds closely to that of a classical resonator, which shows resonant characteristics at particular frequencies of the varying field.

According to the model of absorption or dispersion on the atomic scale (88), the behaviour of absorption and refractive index in the region of a resonance is as shown in fig 6.9. This characteristic is typical for the behaviour of the optical constants for any of the electronic, atomic or molecular resonances with appropriate resonant frequencies. In a solid, the atomic oscillators are tightly coupled and their resonances are widened into a broader
Figure 6.9  The variation of absorption ($K$) and refractive index ($n$) in the region of a resonance.
band. Hence, at a region of absorption, a decrease in the magnitude of refractive index is expected.

In the calculation of the absorption coefficient, $\alpha$, the contribution to the reflectivity of the extinction coefficient is assumed to be negligible, and values of $R$ are calculated using equation 6.2.

The thickness of the films were measured directly using a Taylor Hobson Talysurf 4. On this instrument the step between a film and the substrate deflects the stylus on a mechanical arm, and the instrument displays the magnitude of the step.
Equation 6.1 can be rewritten in the form

\[ T = \frac{A/y}{1-B/y^2} \]  \hspace{1cm} (6.3)

where \( y = \exp(\alpha d) \)

Solving equation 6.3 for \( y \) and taking natural logarithms gives:

\[ \alpha d = \ln\left[\frac{A}{2T} + \frac{(A/2T^2+B)}{1-B/y^2}\right] \]  \hspace{1cm} (6.4)

A PDP11 was used to calculate the quantity \( \alpha d \) and to plot the graphs of \( \alpha \) vs T and \( h\nu \) vs \( (\alpha h\nu)^{1/2} \).

6.5.2 Refractive Index Measurements

For air, the refractive index is 1; 1.5 was used as the refractive index of the glass substrate. The refractive index of the film \( \alpha d \) be calculated from the interference fringes in the transmission measurements:

\[ 2nd = m\lambda_1 \]  \hspace{1cm} (6.5)

(for maximum transmission)
\[ 2nd = (m+1/2) \lambda_2 \]  \hspace{1cm} (6.6)

(for minimum transmission)

where \( d \) is the film thickness, \( m \) is an integer and \( \lambda \) is the wavelength in free space of the incident light.

Refractive indices were obtained directly using an Applied Materials Ellipsometer II. This instrument enables the determination of the refractive index of thin isotropic films deposited on silicon, utilising the properties of polarised light.

The ellipsometer has a laser which emits monochromatic light at a wavelength of 6328Å; the components of the polariser produce elliptically polarised light at a fixed angle of 70° with respect to the normal of a sample on the instrument stage. An analyser mounted at the same angle examines the reflected light beam using a polarising prism.

The rotation of the polariser and the analyser causes variable intensities of light to be reflected off the wafer and to be sensed by the detector. A null meter indicates a minimum of light transmission and at this point the degree readings of the polariser and analyser are used to calculate two numbers which, with the aid of a computer program, are used to calculate the refractive index.
7.1 DC CONDUCTIVITY

The variation of the dc conductivity with temperature was investigated for materials in the Cu$_x$(As$_{0.4}$Se$_{0.5}$Te$_{0.5}$)$_{100-x}$ systems, with $x$ taking the values 5, 6.25 and 7.89 and in the Cu$_y$(As$_{0.4}$Se$_{0.6}$)$_{100-y}$ system, with $y$ taking the values 5, 6.25, 7.89, 20, 25 and 27.5. The experimental details are described in chapter six. Figs 7.1 and 7.2 show the temperature dependence of the dc conductivity in the Cu-As-Se and Cu-As-Se-Te systems respectively.

Conductivity at high temperatures can be expressed by the general equation

$$\sigma = C \exp\left[-\frac{E_o}{kT}\right]$$

(7.1)

where $E_o$ is an activation energy, and hence the activation energy, $E_o$, and the pre-exponential constant $C$ can be calculated. As the temperature decreases, the slopes of the curves in figs 7.1 and 7.2 decrease, to varying extents, according to the material composition,
Figure 7.1 Variation of DC conductivity with reciprocal temperature for Cu\(_x\) (As\(_{0.4}\) Se\(_{0.6}\) \(_{100-x}\)

1. \(x = 5\)   2. \(x = 6.25\)   3. \(x = 7.89\)
4. \(x = 20\)   5. \(x = 25\)   6. \(x = 27.5\)
Figure 7.2  Variation of DC conductivity with reciprocal temperature for

\[ \text{Cu}_x \left[ \text{As}_{0.4} \left( \text{Se}_{0.5} \text{Te}_{0.5} \right)_{0.6} \right]_{1.0-x} \]

1 \( x = 5 \), 2 \( x = 6.25 \), 3 \( x = 7.89 \)
but without any distinctive breakpoint. Hence the values of $E_0$ and $C$ also decrease with temperature. Table 7.1 summarises the electrical parameters obtained by the application of equation 7.1.

All the results were obtained from bulk samples with evaporated gold contacts. Measurements were also made with copper and aluminium contacts, but no significant variation in conductivity was observed.

Figs 7.3 and 7.4 show the variation of room temperature activation energy and room temperature conductivity for the CuAs-S$_2$ system as a function of the percentage of copper in the composition. In Fig 7.3, the data for low percentages of copper, ie $< 2.4$ at%, are from the work of Kolomiets et al (49), who have extrapolated measurements between $330^\circ K$ and $453^\circ K$ to room temperature. It can be seen that as the percentage of copper increases, the activation energy decreases, but this decrease is progressively less with increasing amounts of copper.

Fig 7.5 shows some of the same conductivity data plotted as a function of $T^{-1/4}$. The straight lines obtained at low temperatures suggests that the formula for hopping conduction at low temperatures (44) may be applied, ie
Figure 7.3 Variation of activation energy with copper concentration for the Cu - As - Se system
Figure 7.4 Variation of DC conductivity with copper concentration in the Cu-As-Se system

1. at 300°K  
2. at 161°K
Figure 7.5 Variation of DC conductivity with $T^{-1/4}$
\[ \sigma = A \exp\left[-B/T\right]^{1/4} \]  
(7.2)

where \[ B = \left[ \frac{16\alpha^3}{kN(E_F)} \right]^4 \]  
(7.3)

From equation 7.3 the density-of-states at the Fermi level, \( N(E_F) \), can be calculated. Following Fritzsche (70), the coefficient of exponential decay of the localised wavefunction, \( \alpha \), is assumed to be 0.125Å\(^{-1}\). Table 7.2 shows the values of \( N(E_F) \) obtained in this manner, and the maximum temperatures at which equation 7.2 appears to be valid, that is where the plotted curves deviate from a straight line.

7.2 OPTICAL ABSORPTION

The refractive indices and optical absorption coefficients of the materials were determined from measurements of the optical transmission and reflection at room temperature, using the experimental method described in chapter six. These were carried out on thin films of the materials \( \text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{100-x} \) and \( \text{Cu}_x[\text{As}_{0.4}(\text{Se}_{0.5}\text{Te}_{0.5})_{0.6}]_{100-x} \), with \( x \) taking the values 5, 6.25 and 7.89.
<table>
<thead>
<tr>
<th>Material</th>
<th>$N(E_F)$ ($\text{cm}^{-3}\text{eV}^{-1}$)</th>
<th>$T_{\text{max}}$ ($^\circ\text{K}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>5$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{95}$</td>
<td>1.56x10$^{18}$</td>
<td>260</td>
</tr>
<tr>
<td>Cu$<em>{6.25}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{93.75}$</td>
<td>2.33x10$^{18}$</td>
<td>230</td>
</tr>
<tr>
<td>Cu$<em>{7.89}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{92.11}$</td>
<td>2.96x10$^{18}$</td>
<td>220</td>
</tr>
<tr>
<td>Cu$<em>{20}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{80}$</td>
<td>2.37x10$^{20}$</td>
<td>130</td>
</tr>
<tr>
<td>Cu$<em>{25}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{75}$</td>
<td>3.86x10$^{23}$</td>
<td>140</td>
</tr>
<tr>
<td>Cu$<em>{27}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{73}$</td>
<td>5.58x10$^{23}$</td>
<td>150</td>
</tr>
<tr>
<td>Cu$<em>5$[As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$<em>{0.6}$]$</em>{95}$</td>
<td>1.10x10$^{18}$</td>
<td>170</td>
</tr>
<tr>
<td>Cu$<em>{6.25}$[As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$<em>{0.6}$]$</em>{93.75}$</td>
<td>5.28x10$^{18}$</td>
<td>140</td>
</tr>
<tr>
<td>Cu$<em>{7.89}$[As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$<em>{0.6}$]$</em>{92.11}$</td>
<td>1.40x10$^{19}$</td>
<td>140</td>
</tr>
</tbody>
</table>

**TABLE 7.2**

*Values of the Density-of-States at the Fermi Level*
Fig 7.6 shows typical optical transmission data for two films of composition Cu$_{7.89}$(As$_{0.4}$Se$_{0.6}$)$_{92.11}$ and fig 7.7 shows the optical absorption characteristics obtained for some of the materials investigated. Values of $\alpha$ calculated from equation 5.4 were applied to equation 3.10; the best straight line was obtained when $r=2$, which indicates that for these materials the equation

$$h\nu = \text{const} (h\nu - E_{\text{opt}})^2$$

is valid.

Fig 7.8 shows $(\alpha h\nu)^{1/2}$ plotted as a function of $h\nu$ for $\alpha > 10^4$. The extrapolation of the linear portion of these graphs intersect the x axis at the energy, $E_{\text{opt}}$, the optical gap. The refractive indices used to calculate the absorption coefficient, were measured at a wavelength of 6328Å on the ellipsometer, as described in chapter six. Table 7.3 shows the values of refractive index and $E_{\text{opt}}$ obtained for each material studied. Fig 7.9 shows the variation of $E_{\text{opt}}$ with the concentration of copper in the Cu-As-Se alloys.

As the refractive index for a-As$_2$Se$_3$ is 2.79 at a wavelength of 5 μm (87) and for materials in the a-As$_2$Se$_3$-As$_2$Te$_3$ system, the indices are between 3.5 and 4.5 (2), the values presented in table 7.3 seem low.
The value of the refractive index of a material decreases with increasing wavelength, but not uniformly. Well away from resonance, as defined in chapter six, the refractive index decreases steadily with frequency and absorption is small. As the light frequency approaches the resonant frequency, absorption increases and the dispersion in refractive index changes sign, as shown in figure 6.9. Glassy As$_2$Se$_3$ and its alloys with tellurium have been shown (40) to be highly absorbing at the wavelength at which the ellipsometric measurements were made (0.6328µm). The effect of alloying a heavy element such as copper with these glasses will be to increase the effect and range of the dispersion caused by absorption, and further decrease the refractive indices at the wavelength of measurement.

Values of $n$ of approximately 2.4, calculated from dielectric measurements at frequencies of $10^7$ Hz from the relation

$$\varepsilon = n^2$$

confirm that higher values of $n$ could reasonably be expected at optical frequencies. The unexpectedly low values of refractive index may be due to dispersion, which is the outcome of the absorption of light at the ellipsometer frequency. However, anomalous values of refractive index are likely to be the result of uncertainty in the interpretation of the ellipsometer measurements. The results obtained were not within the ellipsometer nomograph, and the computer program used to obtain values for refractive indices used assumptions which may only be valid in relation to silicon
technology, not for the materials studied in this work. The accurate evaluation of the refractive indices of chalcogenide alloys would require a detailed investigation into the theory of ellipsometry in relation to the instrument used here.

The observed discrepancies (\(\pm 0.2 \mu m\)) between the thicknesses measured by mechanical and ellipsometric means would also be accounted for by the preceding considerations. Sample uneveness and the accuracy of thickness measurements of submicron samples in the Tallysurf may also affect the refractive index calculations to within \(\pm 0.1\). However, it must be pointed out that variations in refractive indices do not significantly affect the values of \(\alpha\) obtained from equation 5.4, and hence the values of \(E_{\text{opt}}\) used in this work.
Figure 7.6 Optical transmission characteristics for thin films of Cu$_{7.89}$ (As$_{0.4}$ Se$_{0.6}$)$_{92.11}$

Film thicknesses are

1. 0.185 μm
2. 1.035 μm
Figure 7.7 Optical absorption of:

1. Cu$_{7.89}$ (As$_{0.4}$ Se$_{0.6}$)$_{92.11}$
2. Cu$_{5}$ (As$_{0.4}$ Se$_{0.6}$)$_{95}$
3. Cu$_{7.89}$ [As$_{0.4}$ (Se$_{0.5}$ Te$_{0.5}$)$_{0.6}$]$_{92.11}$
4. Cu$_{5}$ [As$_{0.4}$ (Se$_{0.5}$ Te$_{0.5}$)$_{0.6}$]$_{95}$
Figure 7.8 The variation of $(\alpha \hbar \nu)^2$ with $\hbar \nu$ for 
$\text{Cu}_x \left[ \text{As}_{0.4} (\text{Se}_{0.5} \text{Te}_{0.5})_{0.6} \right]_{100-x}$

1. $x = 5$  
2. $x = 6.25$  
3. $x = 7.89$

and for $\text{Cu}_y (\text{As}_{0.4} \text{Se}_{0.6})_{100-y}$

4. $y = 5$  
5. $y = 6.25$  
6. $y = 7.89$
Figure 7.9  Variation of $E_{\text{opt}}$ with copper concentration in the Cu-As-Se system
<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Index</th>
<th>$E_{\text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}<em>5(\text{As}</em>{0.4}\text{Se}<em>{0.6})</em>{95}$</td>
<td>1.96</td>
<td>1.62</td>
</tr>
<tr>
<td>$\text{Cu}<em>{6.25}(\text{As}</em>{0.4}\text{Se}<em>{0.6})</em>{93.75}$</td>
<td>1.93</td>
<td>1.55</td>
</tr>
<tr>
<td>$\text{Cu}<em>{7.89}(\text{As}</em>{0.4}\text{Se}<em>{0.6})</em>{92.11}$</td>
<td>1.89</td>
<td>1.52</td>
</tr>
<tr>
<td>$\text{Cu}<em>5[\text{As}</em>{0.4}(\text{Se}<em>{0.5}\text{Te}</em>{0.5})<em>{0.6}]</em>{95}$</td>
<td>1.92</td>
<td>1.28</td>
</tr>
<tr>
<td>$\text{Cu}<em>{6.25}[\text{As}</em>{0.4}(\text{Se}<em>{0.5}\text{Te}</em>{0.5})<em>{0.6}]</em>{93.75}$</td>
<td>1.43</td>
<td>1.26</td>
</tr>
<tr>
<td>$\text{Cu}<em>{7.89}[\text{As}</em>{0.4}(\text{Se}<em>{0.5}\text{Te}</em>{0.5})<em>{0.6}]</em>{92.11}$</td>
<td>1.10</td>
<td>1.25</td>
</tr>
</tbody>
</table>

**TABLE 7.3**

**Optical Properties**
7.3 THERMOPOWER

Using the apparatus described in chapter six, measurements of thermopower were made for the materials Cu\(_x\)(As\(_{0.4}\)Se\(_{0.6}\))\(_{100-x}\) and Cu\(_x\)(As\(_{0.4}\)Se\(_{0.5}\)Te\(_{0.5}\))\(_{0.6}\)\(_{100-x}\) with \(x = 5, 6.25\) and 7.89. Fig 7.10 shows the measured thermopower as a function of reciprocal temperature for the six different compositions. As was stated in chapter three, the temperature dependence of thermopower for p-type material can be expressed as

\[
S = \frac{k}{e}[E_s/kT + A]
\] (7.5)

where \(A\) is a constant. Using equation 7.5, the thermopower activation energy, \(E_s\), was calculated from the slope of the thermopower versus reciprocal temperature characteristics. The slopes were determined using linear regression methods. Values of \(E_s\) for all the materials investigated are shown in table 7.4.

The values of thermopower, for the materials reviewed in section 3.3, are always positive, indicating hole conduction.
Figure 7.10  Variation of thermopower with reciprocal temperature for Cu$_x$[As$_{0.4}$Se$_{0.6}$Te$_{0.5}$]$_{100-x}$

1. $x = 5$
2. $x = 6.25$
3. $x = 7.89$

and for Cu$_y$(As$_{0.4}$Se$_{0.6}$)$_{100-y}$

4. $y = 5$
5. $y = 6.25$
6. $y = 7.89$
### TABLE 7.4

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_\sigma$ (eV)</th>
<th>$E_s$ (eV)</th>
<th>$E_{opt}$ (eV)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>5$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{95}$</td>
<td>0.58</td>
<td>0.42</td>
<td>1.62</td>
<td>0.16</td>
</tr>
<tr>
<td>Cu$<em>{6.25}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{93.75}$</td>
<td>0.52</td>
<td>0.37</td>
<td>1.55</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu$<em>{7.89}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{92.11}$</td>
<td>0.51</td>
<td>0.37</td>
<td>1.52</td>
<td>0.14</td>
</tr>
<tr>
<td>Cu$<em>5$[As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$_{0.6}$]$^{95}$</td>
<td>0.52</td>
<td>0.39</td>
<td>1.28</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu$<em>{6.25}$[As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$_{0.6}$]$^{93.75}$</td>
<td>0.47</td>
<td>0.36</td>
<td>1.26</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu$<em>{7.89}$[As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$_{0.6}$]$^{92.11}$</td>
<td>0.45</td>
<td>0.32</td>
<td>1.25</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**Comparison of Room Temperature Activation Energies**
7.4 DISCUSSION

7.4.1 DC Electrical Properties

A preliminary study of the graphical results indicates that the dc properties of the alloys investigated differ markedly from those of their base glasses, but variations in composition do not introduce significant changes in properties, until very high percentages (>25%) of copper are incorporated, and then only at low temperatures.

However, the complete absence of any time dependent effect in the dc conductivity measurements, over periods of up to 24 hours indicate that, as in the base glasses, conduction is purely electronic in nature.

Detailed investigation of the temperature dependence of the dc conductivity together with that of the thermopower should give further information about the nature of the transport mechanisms in the materials being studied.

The exponential variation of the dc conductivity of the form described in equation 7.1, has been reported for many chalcogenide glasses, over a wide range of temperatures. The behaviour of the base glasses for the materials investigated here is reported in chapter three.
The results show that, in contrast with the base glasses, the dc conductivity, measured over a wide temperature range cannot be represented by a single exponential. The best fit to the data reported in section 7.1, and plotted as shown in figs 7.1 and 7.2, is given by smooth curves with no distinctive breakpoint, showing that the activation energy decreases continuously with decreasing temperature. Therefore the general equation describing transport in these materials becomes:

$$\sigma(T) = \sigma_0(T)\exp[-E(T)B]$$  \hspace{1cm} (7.9)

where $B = \frac{1}{kT}$ and $\sigma_0(T)$ and $E(T)$ cannot be uniquely determined from the log conductivity versus reciprocal temperature characteristics.

Conductivity characteristics with slight but continuous curvature have been reported for other chalcogenide glasses, for example As$_2$Te$_3$ (25), where this change in slope is attributed to a transition, with decreasing temperature, from conduction in extended states below $E_v$ to hopping conduction in localised states between $E_v$ and $E_b$, as shown in the density-of-states diagram in fig 7.11. This continuous curvature may also be accounted for by variable range hopping, conduction by small polarons, or conduction in parallel paths.

Possible conduction mechanisms are discussed more fully later, however, in the high temperature range, the conductivity data for the materials under investigation is superficially consistent with trap limited conduction, in this case hole conduction by holes in
Figure 7.11  Density-of-states of a typical amorphous semiconductor
extended states.

Information about the conduction processes in glasses which are quasi-intrinsic semiconductors, may be derived from the pre-exponential coefficient, which is the quantity $C$ as defined in equation 7.1. The constant $C$ corresponds to the quantity $\sigma_0 \exp(\beta/k)$ where $\sigma_0$ is defined in equation 3.1 and is temperature independent or weakly temperature dependent. Extrapolated from the upper temperature limit of the experimental measurements, the values of $C$ are shown in table 7.1 and are between $15 \Omega^{-1} \text{cm}^{-1}$ and $2.13 \times 10^2 \Omega^{-1} \text{cm}^{-1}$, which are lower than Davis and Mott's (17) theoretical estimates for conduction in the extended states close to the mobility edges, which give values for $C$ between $10^3 \Omega^{-1} \text{cm}^{-1}$ and $10^4 \Omega^{-1} \text{cm}^{-1}$. At lower temperatures, the values of the pre-exponential, referred to as $\sigma_1$ in equation 2.4, are much smaller, which suggests, according to Davis and Mott, conduction by hopping in the localised states. However, the value of the pre-exponential factor is not considered to be valid, by itself, as a test for conduction at a mobility edge.

From figs 7.5 and 7.6 it can be seen that at low temperatures the conductivity shows a $T^{-1/4}$ dependence, as described in equation 7.3, which, according to Mott (44), indicates variable range hopping between states near the Fermi level. This expression should be valid for low temperatures only, but table 7.2 shows that in the Cu-As-Se system, this is not the case, and the range of $T^{-1/4}$ behaviour extends almost to room temperature. The $T^{-1/4}$ behaviour has also been observed up to higher temperatures for
materials in the As-Se-Te system by Mahadevan et al (26), and for materials with very high copper concentrations in the Cu-As-Se system by Mooney (71).

However, plots of $\ln \sigma$ for the same data, versus $T^{-1/3}$ and other fractional functions of $T$ are also linear, and in general, it seems that $\ln \sigma$ versus $T^{-1/n}$ plots are insensitive to the values of $n$. Therefore it is difficult to decide the nature of charge transport on the basis of this linearisation alone.

The room temperature values of activation energy and conductivity as a function of atomic percent copper in $As_2Se_3$ are shown in figs 7.3 and 7.4. Also included in these figure are the data of Kolomiets (49) and Seager and Quinn (23). In fig 7.4, the variation of the dc conductivity with increasing Cu concentration is shown also for lower temperatures ($167^0\text{K}$), where it can be seen that the conductivity rises smoothly with increasing copper concentration and no discontinuities are observed at atomic percents greater than 20, despite the change in the behaviour of the dc conductivity of the high copper alloys at low temperatures, which can be seen in Fig 7.1. The dc conductivity of the high copper alloys will be discussed separately.

Meurier et al (72) showed that experimental results obtained at low temperatures, where the log conductivity versus reciprocal temperature characteristics are not linear, can be used in conjunction with equations obtained from previously derived electronic transport models to determine the best transport model for a particular
Meurier et al used two models which are plausible for low temperature conductivity; variable range hopping and conduction by small polarons. Assuming a general function for the density of states of

\[ N(E) = N_0 (E - E_F)^p \]  \hspace{1cm} (7.7)

Hamilton (73) showed that for variable range hopping, the dc conductivity is related to the density-of-states in the region of the Fermi energy by:

\[ \sigma(T) = \sigma(0) \exp \left( -BT \frac{(p+1)}{(p+4)} \right) \]  \hspace{1cm} (7.8)

Where \( B \) is a constant. If \( W'(T)k^{-1} \) is the slope of the log conductivity versus \( 1/T \) plot,

\[ W'(T) = -\frac{d\ln \sigma}{dT} = Bk \left[ \frac{p+1}{p+4} \right] T^{(3/p+4)} \]  \hspace{1cm} (7.9)

where \( \beta = 1/kT \)

The constants \( p \) and \( B \) can be found from the slope and intercept of a plot of \( \log W' \) as a function of \( \log T \).

- Mott's \( T^{-1/4} \) law, mentioned previously, corresponds to the case of \( p=0 \), but for the variable range hopping model to be valid, \( p \) may take any value between 0 and \( \infty \), so long as \( W' \) satisfies the relation:
\[ W'(T) < 2^{(p/p+4)}kT \]  

(7.10)

Examination of the results presented in section 7.1 for the Cu-As-Se-Te system and the Cu-As-Se system where Cu is present in concentrations of <25 at%, show negative values for \( p \) and hence the relationship in equation 7.10 does not hold, which indicates that variable range hopping is not the transport model appropriate for low temperature conduction of the materials investigated.

For the model of conduction by small polarons, Schnackenberg (74), deduced the following relation:

\[
W(T) = W_h \left[ \tanh(\theta_d/4T) \right] + W_d/2 \tag{7.11}
\]

where \( W(T) \) is the non-adiabatic hopping energy of small polarons at temperatures above \((\theta_d/4)\), where \( W_d \) and \( W_h \) are the disorder energy and high temperature small polaron hopping energy respectively, and \( \theta_d \) is the Debye temperature of the solid.

From the expression for conductivity (equation 7.8) the following can be derived:

\[
W'(T) = W_h \text{sech}^2(\theta_d/4T) + W_d/2 \tag{7.12}
\]

assuming that \( \sigma(t) \) is independent of temperature.
The values of the constants $\Theta_d$ and $W_h$ can be obtained from the slope of a $W'$ versus $T^{-2}$ plot for temperatures above $\Theta_d/4$, assuming $W_d$ is zero. A further plot of $W'$ versus $\text{sech}^2 \Theta_d/4$ yields better values of $W_h$ and $W_d$ from the slope and intercept. Table 7.5 shows the values of these constants derived in this manner for the materials investigated. The accuracy of these values are influenced by the accuracy to which the slopes of the characteristics in figs 7.1 and 7.2 can be measured. This gives an uncertainty in the resultant values of $W_h$ of $\pm 0.03 \text{eV}$. Values of $W_d$ are very small - close to zero. Values of Debye temperature are expected to decrease as the mass of the atomic constituents in a glass increases. In these results this trend is observed between the Cu-As-Se and Cu-As-Se-Te systems, but not consistently within the systems. Schnaus et al (76) report values of Debye temperature for $\text{As}_2\text{Se}_3$ and $\text{As}_2\text{Se}_{1.5}\text{Te}_{1.5}$ of $350^\circ \text{K}$ and $300^\circ \text{K}$ respectively, and in comparison, the values obtained here seem rather high. Fig 7.12 shows typical $\text{sech}^2 \Theta_d/4$ versus $W'$ characteristics indicating a linear relationship. The values of $W$ obtained from equation 7.11 are also shown in table 7.5. For the Cu-As-Se-Te system these are close to the measured room temperature values of $E_o$; in the Cu-As-Se system, the values of $W$ are slightly larger than $E_o$. The correlation between $E_o$ and $W$ indicate that it is plausible to consider the motion of small polarons as the transport mechanism in the copper-chalcogenide alloys.
Figure 7.12 Variation of $SECH^2 \theta_4$ with $\omega/k$ for $\theta_4/k = 4$

$\text{Cu}_{6.25}(\text{As}_{0.4}\text{Se}_{0.6})_{93.75}$

$\text{Cu}_{7.89}(\text{As}_{0.4}\text{Se}_{0.6})_{92.11}$
### TABLE 7.5

Values of Conductivity Constants and Debye Temperature derived from Equations 7.8, 7.9 and 7.11
The concept of small polarons was introduced in chapter two. Emin et al (18) suggested that in disordered chalcogenide systems both electrons and holes interact with their atomic environment with sufficient strength to form small polarons, and that as the holes interact less strongly, their mobility will be higher and they will dominate the observed electrical conduction processes of the material. At low temperatures, polaron transport is by band conduction. At higher temperatures, polarons move by phonon assisted hopping between equivalent sites. Thus, polaron hopping is dependent on what are called 'coincident events', which are dependent on the occurrence of occasional structural fluctuations, causing adjacent occupied and unoccupied sites to have momentarily coincident deformations. Two cases are generally distinguished:

1. The adiabatic regime in which the carrier jumps between the two equivalent sites during the period they have the same energy.

2. The non-adiabatic regime in which the carrier cannot follow the lattice vibrations, and the time required for a carrier to hop is large compared with the duration of a coincident event.

The transport properties which Emin et al associated with the motion of small polarons will be further discussed in relation to the chalcogenide alloys investigated in this work.
Emin (76) also introduced the concept of a dominant constituent in a disordered material; this is a conductive structural unit or chemical bonding configuration associated with the small polaron, and the easiest conductive path for the movement of the small polarons self-trapped in these structural units in the glass is between similar structural units. The existence of a dominant constituent does not mean that detectable phase separation will occur, as the scale of the structural unit associated with phase separation is larger (>20Å) than that necessary for a dominant constituent. The microprobe, used in the present work as described in chapter five, will only detect areas of phase separation greater than 3μm. Emin suggested that if the mobility and conductivity of this constituent are sufficiently high compared with other constituents, then the measured transport properties of the material would be closely related to the properties of the dominant constituent. Hence glasses with different compositions but with the same dominant constituent will have similar electrical properties, due to the similarities in their microscopic structure.

Seager, Emin and Quinn (23) suggested that the As-Te structural unit in As-Te-I and As-Te-Ge glasses is an example of a dominant constituent and that charge transport occurred by means of hole-like polarons, associated with the As-Te bonds, hopping between similar structural units.

Emin et al (18) deduced that for small polaron motion the dc conductivity is thermally activated and can be expressed by the relation:
\[
\sigma = \sigma_0 \exp\left[-\frac{E}{kT}\right] \tag{7.13}
\]

where the activation energy \( E \) is the sum of the energy, \( E_0 \), required to generate the carriers and the activation energy, \( W_H \), associated with the intrinsic hopping of small polarons. For glasses with the same dominant constituent, \( W_H \) is not expected to vary significantly, however, \( E_0 \) may vary considerably between glasses. Emin et al (18) stated that \( \sigma_0 \) can be expressed by the relation

\[
\sigma_0 = \frac{N e^2 a^2 \nu P}{kT} \tag{7.14}
\]

where \( N \) is the number of equivalent carrier sites (in the dominant material) approximately \( 10^{22} \, \text{cm}^{-3} \), \( P \) is a factor which in the non-adiabatic theory of small polaron motion is \( <1 \), \( a \) is the lattice constant and \( \nu^{-1} \) is a vibrational period of the time characterising the establishment of new atomic equilibrium positions. The parameter \( \sigma_0 \), obtained by extrapolation of measurements made at approximately \( 300^\circ \text{K} \), should be, according to the small polaron hopping model, within an order of magnitude of \( 10^2 - 10^3 \Omega^{-1} \text{cm}^{-1} \) and should vary by less than an order of magnitude among glasses with the same dominant constituent. The results shown in table 7.1 give as good agreement with this theory as that of Davis and Mott (17) mentioned earlier.
According to Emin (76), the continuous curvature of the log conductivity versus reciprocal temperature characteristics is due to a fundamental feature of small polaron motion, whereby the mobility of the small polarons is thermally activated at and above the Debye temperature and non-activated below a fraction (typically one third) of the Debye temperature.

The values of thermopower for the materials investigated are positive, as are the values for the base glasses reviewed in section 3.3. The sign of the thermopower is believed to give a reliable indication of whether the conduction is dominated by holes or electrons; the positive sign is taken to indicate that holes are the most numerous carriers. Mott (55) suggested that hole conduction predominates because the range of localised states in the conduction band is wider than that of the valence band.

The temperature dependence of the thermopower can be used to ascertain the energy difference between the Fermi energy and the energy level where charge transport occurs. In a simple one-band model where conduction is assumed to be through only one energy level or channel, and the Fermi energy is pinned near the centre of the gap, the thermopower, $S$, is thermally activated with an activation energy $E_s$. The results in section 7.3 show that the thermopower data, plotted with respect to reciprocal temperature, gives a slightly curved characteristic, with continuously varying values of $E_s$. 
By comparison, it can be seen that the dc conductivity has a stronger temperature dependence than the thermopower, and that the difference in the activation energies calculated from the thermopower data and those measured from dc conductivity experiments can be expressed by

\[ \Delta E = E_0 - E_s \] (7.15)

The room temperature values of \( \Delta E \) are between 0.11 and 0.16eV, and are shown in table 7.4. Seager and Quinn (23) obtained values of \( \Delta E \) of 0.17eV and 0.31eV for a-As\(_2\)Se\(_3\) and a-As\(_2\)Te\(_3\) respectively. The curved nature of the thermopower characteristics makes it difficult to evaluate \( A \), but extrapolation of the characteristics indicates that \( A \) is probably very small.

This difference in activation energies, like the variation in \( E_0 \) with temperature, may be accounted for by the small polaron hopping model, or by one of two further explanations: by one carrier conduction in the localised states, involving an activation energy for hopping, or by a two parallel path conduction process.

According to Mott and Davis (35), thermopower measurements can be used to determine whether conduction is by hopping at \( E_a \) (see fig 7.11). If current is carried by holes at an energy level \( E \) from the Fermi level,

\[ E_0 = E + W \] (7.16)
where $W$ is a hopping energy. $E$ is the thermopower activation energy, $E_s$. The difference between the conductivity and thermopower activation energies is attributed to a thermally activated mobility with an activation energy

$$E_\mu = E_\sigma - E_s \tag{7.17}$$

where $E_\mu$ is the same as $\Delta E$ in equation 7.15. If conduction takes place in extended states, $\Delta E$ will be zero.

Emin et al (18) suggested that it is unlikely that so large a value for hopping energy is due only to disorder, and that the hopping is due to small polaron formation. In the small polaron hopping model, $\Delta E$ is interpreted as the polaron hopping energy, $W_H$. The thermopower can be expressed by the formula of the usual form shown in equation 7.5, where $E_s$ is the energy required to generate carriers. If there is no transfer of vibrational energy associated with the small polaron hop, the kinetic term $A$, which is a constant dependent on the carrier scattering mechanism, could be very small. The difference between $E_\sigma$ and $E_s$ is the polaron hopping energy $W_H$, which is a characteristic of the dominant constituent and which should not vary between glasses with the same dominant constituent. Any variation of $E_s$ is related to the difference in the energy level that is associated with the states other than that of the dominant constituent. These levels are characteristic of defects, compositional disorder and structural fluctuation in the remaining material, that is the non-dominant constituent.
The results reported above for dc conductivity and thermopower can be seen to resemble those obtained by Nagels et al (38) for glasses in the As-Te-Si system. Nagels et al attributed the curvature in the dc conductivity and thermopower characteristics to a gradual transition from conduction by holes in the valence band to conduction by hopping in the localised states between $E_v$ and $E_b$. To explain these results, Nagels et al proposed that parallel conduction occurs via holes in the extended states just below $E_v$ and holes hopping in localised states just above $E_v$. The total thermopower for parallel conduction mechanisms is the sum of the individual thermopowers weighted according to the contribution each mechanism makes to the conductivity. This implies that the curved thermopower characteristics indicate a parallel conduction mechanism, but that the actual slope of the characteristics has little meaning. Nagels et al showed that the contribution to the conduction due to hopping between localised states was non-negligible even at temperatures of up to 400°K.

The small polaron model also predicts an n-type Hall effect (Emin et al, (18)) due to the local geometry of the material. It also predicts that the Hall mobility is low and is activated with an energy one third of that found for the conductivity mobility.

Support for the validity of the small polaron model in amorphous $\text{As}_2\text{Te}_3$ and its alloys is given by its agreement with the experimental observation of Seager et al (77). However, in the present work, the Hall mobility of the materials has not been measured.
The measurements of Pfister and Morgan (51) of hole transit time in \( \text{As}_2\text{Se}_3 \) doped with up to 0.1 at% copper were reported in chapter three. They suggested that the copper generates traps at energies extending from the intrinsic trapping level at 0.6eV above the hole transport states, to the middle of the band gap, as was shown in fig 3.4.

Pfister and Morgan’s spin resonance measurements indicate that a substantial fraction of the copper is incorporated into the glass as positively charged impurities; but at the doping level concerned, the \( C_1^- \) density will not be affected because the electrons released by the impurity atoms will all be taken up in bonding, with the result that impurities introduce additional localised valence states, rather than increase the number of free charge carriers. Hence Pfister and Morgan admit that copper is not a suitable dopant to use to verify the predictions of the defect models.

Pfister and Morgan’s measurements were carried out on materials with very small copper concentrations and so cannot be directly compared with the alloys investigated in this work, because the dopant concentration was too small to observe any change in dc conductivity. In their materials, no fourfold coordination was observed, a structure which is central to the arguments in this work.
Taylor and Ngai (78) have interpreted the results of Pfister and Scher (42) and Pfister and Morgan's (51) transient hole transport measurements without assuming the presence of defects or traps. They observed that in pure As$_2$Se$_3$ the microscopic activation energy of the thermally activated transport processes is equal to the small polaron hopping energy measured from thermopower and dc conductivity measurements.

However, Taylor and Ngai do not believe that impurities in As$_2$Se$_3$ form defects; instead, they suggest that the impurities are incorporated into the glass network in such a way as to satisfy their normal bonding requirements. Hence, impurities do not act as traps for electrons or holes. Consequently, they suggest that the conduction processes in both pure and doped As$_2$Se$_3$ involve small polarons.

In this work, the only evidence of states near the Fermi level is the apparent agreement between the low temperature dc conductivity measurements and Mott's $T^{-1/4}$ rule.

7.4.2 Optical Absorption

The values of the optical gap, $E_{\text{opt}}$, reported in section 7.2 are greater than twice the room temperature values of $E_\infty$ reported in section 7.1. $E_{\text{opt}}$ is the energy which is associated with the excitation of an electron from the extended states of the valence to the extended states of the conduction band. According to the energy band theory, the magnitude of the optical gap is defined as the
mobility gap, $E_c - E_v$ (see fig 7.11), whereas, $E_\sigma$ represents the energy difference between $E_F$ and $E_b$.

Kitao et al (54) observed that for alloys of $\text{As}_2\text{Se}_3$ with copper, the variation of $E_\sigma$ with copper concentration is much greater than that of $E_{\text{opt}}$, although the difference decreases as copper concentration increases. Kitao et al define this as an impurity effect caused by either a shift of the Fermi level towards the valence band, or a displacement of the mobility edge of the valence band to higher energies. In this work, as shown in fig 7.9, when the copper concentration increases, the variation of $E_\sigma$ and $E_{\text{opt}}$ with copper concentration appears similar, which suggests that only a decrease in the band gap occurs. Kitao et al define this as an alloying effect due to a compositional change in the material itself, and that the larger rate of decrease of $E_\sigma$ compared with $E_{\text{opt}}$ with increasing copper concentration is due to the transition from the impurity effect to the alloying effect.

In the small polaron model (18), the atoms remain in their rigid lattice positions during the process of excitation by incident radiation. Subsequently, the atoms may adjust to the presence of the carriers, allowing the formation of small polarons. In the energy level structure associated with small polarons, the activation energy, $E_p$, is less than half of the magnitude of the optical gap because it is related to the energy difference between the electron and hole small polaron levels. This is shown in fig 7.13 where it can be seen that the optical gap is not simply related to the carrier generation energy. This coincides with the
Figure 7.13  Energy level scheme associated with small polaron formation
observations from the measurements carried out in this work.

7.4.3 Structure

It is clear from the results that, in both systems of copper-chalcogenide alloys investigated, the differences between the thermopower and conductivity activation energies, and the values of C are not significantly affected by composition. It seems likely that this can be related to similarities in the microscopic structure of the glasses. These similarities could be due to the occurrence of certain common chemical bonding configurations, which exist with the smallest amount of copper present in the alloys, and which are more conducting than the rest of the material.

In chapter three, it was shown how the lowest energy defect in a chalcogenide glass was the valence alternation pair, \( \text{C}_3^+ + \text{C}_1^- \), and that these defects determined the properties of chalcogenides such as \( \text{As}_2\text{Se}_3 \) and \( \text{As}_2(\text{Se}_{0.5}\text{Te}_{0.5})_3 \). According to the reaction

\[
\text{C}_3^+ + 2e \rightarrow \text{C}_1^-
\]  

(7.18)

\( \text{C}_3^+ \) can be converted to \( \text{C}_1^- \) centres and vice versa. With the introduction of two electrons from a modifying material such as copper, and spontaneous bond breaking, \( \text{C}_1^- \) centres will be formed from \( \text{C}_3^+ \).
Pnictides, such as arsenic, can also undergo valence alternation. The lowest energy defect is considered to be $P_4^0$, analogous to the $C_3^0$ defect of a chalcogen atom. This defect is formed from hybridisation of the $s$ and $p$ orbitals containing five valence electrons, two of which remain in a non-bonding pair. In this case, the equivalent of the $D^+$ and $D^-$ defects are the VAP $P_4^+ + P_2^-$. This structure is only slightly energetically less favourable than the threefold coordinated structure occurring in $As_2Se_3$. When both selenium and arsenic are combined in a glass, all the defects $C_3^+$, $C_1^-$, $P_4^+$ and $P_2^-$ will be present in different concentrations. When copper is introduced into this glass, it will combine with the positive defects into a tetrahedral formation, leaving an excess of $C_1^-$ and $P_2^-$ states; Kastner and Fritszchle (57) believe that the $C_1^-$ is the dominant negative defect.

Hence it seems reasonable to suggest that the introduction of a copper modifier to $As_2Se_3$ and $As_2(Se_{0.5}Te_{0.5})_3$ results in regions with a tetrahedral structure, the extent of the tetrahedral formation being proportional to the concentration of modifier. In the Cu-As-Se system, the arsenic, copper and selenium atoms will all be tetrahedrally coordinated, the selenium if its lone-pair electrons are used in dative bonding, and the copper atoms forming three bonds with surrounding selenium atoms. This is the structure of CuAsSe$_2$, which has the same structure as chalcopyrite shown in fig 5.1, and was the tetrahedral component suggested as a result of the structural studies reported in chapter five.
7.4.4 High Copper Alloys in the Cu-As-Se System

As reported in section 7.4.3, it seems likely that in the Cu-As-Se system there are structural units with a tetrahedral structure similar to that of crystalline CuAsSe$_2$. As copper is alloyed to amorphous As$_2$Se$_3$, the Se lone pairs are used in bonding and the coordination number of the Se increases. Hence, for the materials in the system Cu$_x$[As$_{0.4}$Se$_{0.6}$]$_{100-x}$ the copper is incorporated in a tetrahedral formation for values of $x$ up to 23, where $x$ is the concentration of copper in atomic per cent, because 23 is the maximum value of $x$ for which 

$$\text{Cu}_x\text{As}_{0.4(100-x)}\text{Se}_{0.6(100-x)}$$

is equivalent to $x$(CuAsSe$_2$).

This is assuming that all the copper impurity is ionised. For values of $x$ greater than 23, there are no further lone pairs available, therefore, at higher values of $x$, up to the glass formation limit (when $x$=36), the microscopic structure of the materials may vary if configurations with a selenium to copper ratio of less than two to one are formed. Hence the electrical properties of such high copper alloys may also vary.

Although the primary purpose of this work was to investigate alloys with lower percentages of copper, glasses in the Cu-As-Se system were prepared with $x$ = 20, 25 and 27.5, in order to observe trends in thermal behaviour and dc conductivity in the composition region where the structure is likely to vary. The variation of the logarithm of dc conductivity of these materials with temperature, shown in fig 7.1, shows that the decrease in slope is observed with decreasing temperature, and that there is a significant but gradual
change in the low temperature conductivity characteristics between 20 and 25 at% copper.

As the concentration of copper increases, the low temperature dc conductivity increases significantly, and the slope of the low temperature part of the characteristic decreases, until at the two highest levels of copper concentration where measurements were made, there appear to be two separate characteristics with very different activation energies. Hence it seems that at these levels of copper concentration there is a transition from quasi-intrinsic to extrinsic conduction as the temperature is lowered.

Ovshinsky (5) has reported similar dc conductivity characteristics, obtained from the chemical modification of a number of amorphous intrinsic semiconductors. This behaviour he attributes to extrinsic conduction, although this conclusion is not generally recognised. Extrinsic conduction is not usually associated with chalcogenide glasses, because it is believed that the Fermi level is pinned by the valence alternation pairs present in the materials, as shown in fig 7.14. Crystalline tetrahedral semiconductors substitutionally doped with trivalent impurities show extrinsic conduction due to the movement of the Fermi level as a result of the shallow donor levels. A typical density-of-states diagram is shown in fig 7.15.

In section 7.4.3 it was reported that the copper modifier was most likely to be in a tetrahedral configuration with the formation of three dative bonds to surrounding chalcogen atoms. According to
Figure 7.14 Density-of-states diagram showing the pinning of the Fermi level by valence alternation states.

Figure 7.15 Density-of-states diagram for an extrinsic semiconductor.
equation 7.17, The electrons produced by the ionisation of copper convert some of the $C_3^+$ centres to $C_1^-$. The Fermi level will remain pinned until there is a sufficient concentration of copper to saturate the $C_3^+$ centres, and allow the Fermi level to move. Any further copper added may not be incorporated into the tetrahedral structure, and additional ionised impurities will form donor states, hence n-type conduction will result. The donor states shown in fig 7.15 will in this case be $Cu^+$ states.

The study of the high copper alloys was recently extended by Mooney (71) who carried out a detailed investigation of the variation of dc conductivity with temperature of materials in the system $Cu_x(As_{0.4}Se_{0.6})^{100-x}$ with $20 \leq x \leq 25$. Mooney's results, which are presented in Appendix II, indicate that the general trend in low temperature conductivity is interrupted by anomalous behaviour of materials containing $21 - 22$ at% copper. The conductivity characteristics of these anomalous compositions resemble that with $x = 25$ and 27.5 in fig 7.1. Mooney attributes this anomalous behaviour to the presence of regions in the material with a structure similar to crystalline $Cu_3AsSe_4$; he identified this composition from DTA results. However, as reported in chapter five, in this work the DTA results did not show any sign of $Cu_3AsSe_4$, possibly due to the different cooling methods used in the material preparation. Consequently, no anomalous dc conductivity results were observed for high copper Cu-As-Se alloys.
8.1 AC CONDUCTIVITY

The variation of conductivity with the frequency of an applied electric field was investigated, according to the methods described in chapter six, for the materials $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{100-x}$ and $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.5}\text{Te}_{0.5})_{100-x}$, with $x$ taking the values 5, 6.25 and 7.89.

Figs 8.1 and 8.2 show the relationship between conductivity and frequency at room temperature for the materials in the Cu-As-Se and Cu-As-Se-Te systems. The conductivity, $\sigma(\omega)$, is the real component of the complex conductivity, and is the measured conductivity resulting from the application of a varying electric field. The conductivity $\sigma(\omega)$ can be resolved into frequency independent and frequency dependent components

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac}$$  \hspace{1cm} (8.1)

where $\sigma_{ac}$ is frequency dependent and $\sigma_{dc}$ is the dc conductivity.
Figure 8.1 Variation of conductivity with frequency for \( Cu_x(As_{0.4}Se_{0.6})_{100-x} \)

- ① \( X = 5 \)
- ② \( X = 6.25 \)
- ③ \( X = 7.89 \)
Figure 8.2 Variation of conductivity with frequency for \( \text{Cu}_x[\text{As}_{0.4}(\text{Se}_{0.5}\text{Te}_{0.5})]_{100-x} \):

1. \( x = 5 \)
2. \( x = 6.25 \)
3. \( x = 7.89 \)
At low frequencies, the conductivity is constant, but as the frequency increases above $10^4$ Hz for the Cu-As-Se system and $10^6$ Hz for the Cu-As-Se-Te system, the conductivity increases. This is similar to the behaviour of the base glasses described in chapter three, where the onset of frequency dependence was seen to shift towards greater frequencies as selenium is substituted by tellurium, because of the increase in the dc conductivity. At higher frequencies the conductivity increases according to the expression

$$\sigma(\omega) = A\omega^s$$  \hspace{1cm} (8.2)

The room temperature values of $s$, obtained from equation 8.2 are shown in table 8.1.

The characteristics of the materials in the Cu-As-Se system shown in fig 8.1, level out towards the upper frequency limit of measurement, $10^9$ Hz, indicating that this is a saturation region where there is no frequency dependence. A quadratic dependence as reported for As$_2$Se$_3$ (31,32) was not observed.

The variation of the conductivity of the materials as a function of temperature and frequency was investigated in the frequency range $10^{-4}$ Hz to $10^9$ Hz and from approximately 240$^\circ$K to 350$^\circ$K. Figs 8.3 and 8.4 show the measured conductivity, $\sigma(\omega)$, plotted logarithmically as a function of inverse temperature, at various frequencies, for a representative material from each system. At low temperatures $\sigma(\omega)$ has a weak temperature dependence, which becomes stronger as the temperature increases. At low temperatures, a
Figure 8.3 Variation of AC conductivity with temperature for Cu$_5$(As$_{0.4}$Se$_{0.6}$)$_{95}$
Figure 8.4 Variation of AC conductivity with temperature for Cu$_5$[As$_{0.4}$Se$_{0.5}$Te$_{0.5}$)$_{0.6}$]$_{95}$
<table>
<thead>
<tr>
<th>Material</th>
<th>s</th>
<th>$W_{m1}$</th>
<th>$W_{m2}$</th>
<th>$E_{opt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>5$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{95}$</td>
<td>0.99</td>
<td>*</td>
<td>*</td>
<td>1.62</td>
</tr>
<tr>
<td>Cu$<em>{6.25}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{93.75}$</td>
<td>0.91</td>
<td>1.67</td>
<td>0.55</td>
<td>1.55</td>
</tr>
<tr>
<td>Cu$<em>{7.89}$(As$</em>{0.4}$Se$<em>{0.6}$)$</em>{92.11}$</td>
<td>0.99</td>
<td>*</td>
<td>*</td>
<td>1.52</td>
</tr>
<tr>
<td>Cu$<em>5$(As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$<em>{0.6}$)$</em>{95}$</td>
<td>0.77</td>
<td>0.65</td>
<td>0.22</td>
<td>1.28</td>
</tr>
<tr>
<td>Cu$<em>{6.25}$(As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$<em>{0.6}$)$</em>{93.75}$</td>
<td>0.89</td>
<td>1.36</td>
<td>0.45</td>
<td>1.26</td>
</tr>
<tr>
<td>Cu$<em>{7.89}$(As$</em>{0.4}$(Se$<em>{0.5}$Te$</em>{0.5}$)$<em>{0.6}$)$</em>{92.11}$</td>
<td>0.88</td>
<td>1.25</td>
<td>0.42</td>
<td>1.25</td>
</tr>
</tbody>
</table>

TABLE 8.1

AC Parameters

* Not possible to obtain accurate values as $s$ is very close to unity.
frequency dependence of the slope of the curves is observed, which decreases slightly with increasing frequency. At high temperatures, \( \sigma(\omega) \) tends to \( \sigma_{dc} \). Similar characteristics were obtained by Rockstad (79) from measurements of the ac conductivity of thin films of \( \text{As}_2\text{Se}_3 \).

At room temperature the dc conductivity of the materials in the Cu-As-Se system, is less than the ac conductivity, whereas, in the Cu-As-Se-Te system, the dc and ac conductivities are virtually the same. This corresponds to the results obtained by Ivkin et al (30) for the base glasses, \( \text{As}_2\text{Se}_3 \) and \( \text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3 \).

Extensive temperature dependence measurements could not be carried out because of instrumentation shortcomings. The temperature controlled cryostat and the connecting leads to the Frequency Response Analyser (FRA) had an appreciable impedance, compared to that of the sample under investigation, and it was not possible, owing to the nature of the materials, to further increase the impedance of the samples by altering their dimensions. The FRA gives values of \( a+jb \), as described in chapter six, to four significant figures; at temperatures of more than a few tens of degrees below room temperature, the FRA could not detect the difference between 'sample' and 'no sample'. At higher temperatures where measurement was possible, the variation in conductivity occurred at frequencies above the range of the FRA. Hence measurements of the temperature dependence of the exponent, \( s \), were not possible. In addition, accurate measurements of conductivity variation with temperature were
not possible with the high frequency impedance analyser.

As reported in chapter three, Austin and Mott (27) derived an expression for conductivity, \( \sigma(\omega) \), assuming that conduction is dominated by states near \( E_F \). Applying this expression,

\[
\sigma(\omega) = T[N(E_F)]^2 \omega \ln^4(\nu_{ph}/\omega)
\]

(8.3)

values for the density-of-states at the Fermi level were calculated. These were unreasonably large, in the range \( 10^{24} - 10^{25} \) eV\(^{-1}\) cm\(^{-3}\), when the atomic densities of the materials are only in the order of \( 10^{22} \) cm\(^{-3}\).

An alternative model proposed by Elliot (29) for ac conduction in chalcogenide glasses is also summarised in chapter three. The values for the density-of-states at the Fermi level were calculated using Elliot's expression for \( \sigma_{ac} \) which to a first order approximation is:

\[
\sigma_{ac} = (\pi^2/24)[N(E_F)]^2 \kappa [8\pi^2/k_B] \omega^s / \tau_0^{1-s}
\]

(8.4)

where \( \kappa \) is the optical energy gap, \( \kappa \) is the dielectric constant and \( \tau_0 \) is the effective relaxation time, which is expected to have a value of the order of an inverse phonon frequency of about \( 10^{-13} \) s. The values of \( N(E_F) \) obtained in this way were within an order of magnitude of those obtained from \( \log \sigma \) versus \( T^{-1/4} \) characteristics in section 7.1.
8.2 DIELECTRIC PROPERTIES

It is sometimes more appropriate to analyse $\sigma_{ac}$, as defined in the preceding section, in terms of the relative permittivity, defined (80) as

$$e = e' + je''$$  \hspace{1cm} (8.5)

from which an expression for conductivity can be derived

$$\sigma_{ac} = we''e_0 + jwe'e_0$$  \hspace{1cm} (8.6)

where $e'$ is the dielectric constant, $e''$ the dielectric loss and $e_0$ is a constant, the permittivity of free space.

Fig 8.5 shows examples of the room temperature frequency dependence of $e'$ and $e''$, for frequencies at which the ac conductivity varies from the dc conductivity, for some of the materials investigated.

8.3 CAPACITANCE-VOLTAGE CHARACTERISTICS

Fig 8.6 shows the variation of capacitance with applied voltage for a representative material from each system. The results for these materials are typical for their systems, and as can be seen the capacitance does not vary over a wide range of bias voltage.
Figure 8.5  Frequency variation of $\varepsilon'$ and $\varepsilon''$
for (1) Cu$_{6.25}$[As$_{0.4}$Se$_{0.5}$Te$_{0.6}$] 93.75
and (2) Cu$_{6.25}$ (As$_{0.4}$ Se$_{0.6}$) 93.75
Figure 8.6 Variation of capacitance with bias voltage for:

1. $\text{Cu}_6\text{As}_0.4\text{(Se}_{0.5}\text{Te}_{0.5})_3$ at $1\text{ MHz}$

2. $\text{Cu}_7\text{As}_{0.4}\text{Se}_{0.6}$ at $5\text{ MHz}$
The variation of capacitance with applied voltage shows no change within the range of voltage bias applied. The maximum field applied to the samples was approximately $2 \times 10^3$ volts/cm, which is sufficiently high to demonstrate any electrode effects. The measurements were carried out on samples with electrodes in a sandwich configuration; if depletion regions exist in the glass adjacent to the electrodes, the dimensions of these regions, and hence the measured capacitances, will vary with applied bias. As this does not occur, it can be assumed that the electrodes are non-blocking, and that the measured ac properties described in the preceding sections are related to the bulk materials.

8.4 DISCUSSION

Information on the nature of the conduction mechanism in an amorphous material may be obtained from investigations of the ac conductivity. According to the Davis-Mott model, the three mechanisms of charge transport, summarised in chapter two, can all contribute to ac conductivity.

When conduction occurs by carriers excited across the mobility edges to extended states near $E_c$ or $E_v$, Mott and Davis (35) state that for frequencies up to approximately $10^7$ Hz, no frequency dependence of the conductivity associated with carriers in extended states is expected.
When carrier transport is by carriers excited into localized states near the edges of the valence or conduction band, Mott and Davis suggest that the conductivity dependence on frequency varies as $\omega^s$, where $s \leq 1$. The temperature dependence of this component of the ac conductivity should be the same as that of the carriers at the band edges, that is for the conduction band the ac conductivity should vary as $\exp[-(E_a-E_F)/kT]$. They state further that conductivity due to hopping of carriers at energies near the Fermi level should have a similar frequency dependence, but no exponential temperature dependence. Hence, the two hopping processes may be distinguished by observing their temperature dependence.

The increase in ac conductivity with increasing frequency may be interpreted as an indication of hopping conduction between localized states at the Fermi level, or in band tails, or by Maxwell-Wagner dispersion, which is caused by interfacial polarisation, set up from the inhomogeneity of the materials. The dielectric constants (fig 8.5) show little variation with frequency, until the frequencies associated with the saturation of the ac conductivity, which suggests that there is no significant dielectric relaxation in this frequency range, and hence no interfacial polarisation.

As reported in chapter three, few results have been reported for chalcogenide glasses where the values of $N(E_F)$ obtained from Austin and Mott's expression for ac conductivity (equation 8.3) have been in agreement with those obtained from other measurements. This is also the case in this work, as shown in section 8.1. These observations
imply that a frequency dependent conductivity of the form $\omega^s$ may not necessarily be due to hopping conduction of carriers of the form associated with dc conduction.

For chalcogenide glasses, the accepted models for the gap states, summarised in chapter three, suggest that electrons are trapped in pairs at defect sites, designated $D^-$ or $C_1^-$, and that tunnelling of these electrons to $D^+$ or $C_3^+$ sites is a possible mechanism for ac conduction.

Elliot (29), proposed that the two electrons in a $D^-$ site transfer to a $D^+$ site by hopping over, rather that tunnelling through the potential barrier separating the sites. This model predicts that the density-of-states responsible for ac conductivity lie in a energy range lower than that predicted by other models. Elliot (81) suggested that the barrier height, $W_m$, is approximately equal to the band gap, (that is the optical band gap, $E_{opt}$) and, for non-intimate valence alternation pairs can be related to $s$ by the expression:

$$1-s = 6kT/W_m$$  \hspace{1cm} (8.7)

For intimate valence alternation pairs this becomes

$$1-s = 2kT/W_m$$  \hspace{1cm} (8.8)

giving a larger value for the frequency exponent, $s$, and a smaller
temperature dependence than for NVAPs. Table 8.1 shows the values obtained for the barrier height, \( W_{m1} \) from equation 8.7 and \( W_{m2} \) from equation 8.8. The values for \( s \) were derived from the graphs in figs 8.1 and 8.2. However, as \( s \) approaches unity, the accuracy of \( s \) significantly affects the accuracy of \( W_{m1} \) and \( W_{m2} \), hence the results obtained for \( s = 0.99 \) have little meaning.

For the materials in the Cu-As-Se-Te system, there is reasonable agreement between the experimentally obtained values of \( E_{opt} \) and \( W_{m1} \). For the materials in the Cu-As-Se system, the higher values of \( s \) give a better agreement between \( E_{opt} \) and \( W_{m2} \). Some discrepancies in these values may be accounted for in the uncertainty of the evaluation in \( s \) because of slight non-linearity in some of the characteristics.

The characteristics shown in figs 8.3 and 8.4 showing the temperature dependence of \( \sigma(\omega) \), measured at different frequencies, have two distinct regions. At low frequencies and at high temperatures, the ac conductivity does not show \( \omega^s \) behaviour; under these conditions the ac conductivity of the mechanism just described is smaller than the dc conductivity. If at low frequencies and high temperatures dc conduction occurs via holes excited into the extended states of the valence band, the conductivity will have no frequency dependence.

Rockstad (79) suggested that at any frequency the ac conductivity may be represented by a sum of two components, and that the study of temperature dependence of conductivity may be used to
detect different hopping processes. The two components of $\sigma_{ac}$ can be described as, $\sigma_1(\omega)$ which is due to hopping transport in states at the Fermi level, and $\sigma_2(\omega)$ which is due to hopping transport at localised states near the band edges. Rockstad observed that at lower temperatures, where $\sigma_{ac}$ is $\sigma_1$, $\sigma_{ac}$ is proportional to temperature. As the temperature increases, $\sigma_{ac}$ increases much more rapidly than the temperature. Hence $\sigma_2$ is thermally activated with an activation energy less than that calculated from dc conductivity measurements.

If the dc conductivity is due to the hopping of carriers in the localised states close to the band edge, a frequency dependence of the conductivity should be observed.

In figs 8.3 and 8.4 the high temperature regions are frequency independent and their slopes correspond to the activation energy of the dc conductivity measured at the same temperatures.

In the low temperature regions, the conductivity decreases with decreasing temperature and slightly with decreasing frequency, which is not in accordance with Austin and Mott's model for tunnelling in states at the Fermi level, which predicts that the slope of the characteristics would be $-T$, with no frequency dependence.

If conduction at low temperatures is by means of carrier hopping between defect centres, according to Elliot's model, equation 8.4 applies, and the ac conductivity is dependent on temperature only through the exponent $s$. It can also be seen that the slope of the
log conductivity versus reciprocal temperature characteristics, \([\text{d} \ln \sigma_{\text{ac}} / \text{d}(1/T)]\), will have a frequency dependence; as the frequency increases, the slope decreases, and \(\ln \sigma_{\text{ac}}\) to a first approximation will be proportional to temperature. The model also implies that \(s\) is a decreasing function of temperature, and Elliot (82) suggests that this behaviour is due to hopping between NVAP centres. Elliot also observed that the ac conductivity of some chalcogenides shows \(\omega^s\) behaviour but with \(s\) independent of temperature. He attributes this behaviour to hopping between IVAPs.

In this work the temperature dependence of \(s\) has not been measured, so it is not possible to confirm the predictions derived from equations 8.7 and 8.8 whether NVAPs or IVAPs are responsible for the behaviour of the materials in the Cu-As-Se-Te and Cu-As-Se systems respectively.

Elliot (82) applied his model to Rockstad's results and showed that there was agreement at low temperatures. However, at higher temperatures, it was apparent that the experimental values were higher than the predicted characteristic, which suggested that a different conduction mechanism occurs. At higher temperatures, Elliot showed that \(\ln \sigma_{\text{ac}}\), that is \(\ln \sigma_{\text{2}}\), plotted as a function of \(1/T\), yields a straight line. The slope of the line was found to be 0.03 eV less than the activation energy for dc conductivity, he attributed this difference to carriers tunnelling at 0.03 eV from the mobility edge. He suggested that this behaviour dominated the conduction at temperatures greater than 200°K, and that his model accounted for the component, \(\sigma_1\), which dominated the conduction.
below $200^\circ K$. Hence, it should be possible to distinguish between conduction by quantum mechanical tunnelling between localised states at the band edges, and conduction due to two electrons hopping between defect sites, as the two processes will have different activation energies.

Values of $\sigma_1$ may be derived from equation 8.4, but without a quantitative knowledge of the temperature dependence of $E_{\text{opt}}$ and $s_0$, which have not been obtained during this work, it is not possible to predict the temperature dependence of $\sigma_2$ and hence the ac conductivity according to Elliot's model. However, the characteristics in figs 8.3 and 8.4 are similar to those drawn by Rockstad, therefore, it seems reasonable to assume that the same theoretical deductions may apply, and that the ac conductivity may be shown to have two contributions:

$$\sigma_{\text{ac}} = \sigma_1 + \sigma_2 \quad (8.9)$$

where $\sigma_1$ is the contribution at low temperatures due to the correlated barrier hopping of carriers, as defined by Elliot. The activation energies of $\sigma_1$ vary with frequency, but are very small, in the order of 0.03eV, indicating that the defect states are close to the Fermi level. Following Rockstad and Elliot, it is possible that $\sigma_2$ is caused by carriers undergoing quantum mechanical tunnelling in the localised states at the band edges, and that this behaviour is dominant at temperatures above approximately $250^\circ K$. 

At temperatures above approximately 350\textdegree K for materials in the Cu-As-Se system, and 300\textdegree K for materials in the Cu-As-Se-Te system, the ac and dc conductivities coincide, suggesting that conduction in extended states predominates. The increase in low temperature ac conductivity with the addition of copper to the base glasses, may be accounted for by a consequent increase in $C^+_3$ centres, due to the mechanism discussed in chapter seven, and resulting in the increased probability of electrons hopping in pairs from $C^-_1$ centres. In figs 8.1 and 8.2 it can be seen that the ac conductivities of the materials within each system are much closer in value than their dc conductivities. This suggests that the mechanism which is responsible for the ac conductivity, is similar in all the materials, and is not dependent purely on composition.

Hill and Jonscher (82) considered the effect of the response of the lattice in which the proposed hopping charges are moving, and they suggest that the closeness of the ac conductivity values indicate that the carriers have a negligible effect on the ac behaviour of the materials. They also suggest that values of $s$ close to unity are virtually independent of temperature, hence are associated with a lattice response, and not that of carriers. Without knowing the temperature dependence of $s$, the validity of Hill and Jonscher's theory cannot be ascertained.

In addition, Hill and Jonscher suggest that smaller values of $s$ are due to dipoles associated with defects or impurities, the presence of such dipoles are indicated by a slowly varying
conductivity at low frequencies corresponding to a strong dispersion of both the dielectric loss and dielectric constant. The low frequency instrumentation used in this work was not sensitive enough to show any slight deviation from the dc conductivity at low frequencies.

Saturation of the ac characteristics occurs at high frequencies for materials in the Cu-As-Se system. Segawa (22) observed similar saturation of the ac conductivity of $\text{As}_2\text{Se}_3$-$\text{As}_2\text{Te}_3$ at frequencies above $10^9$ Hz. Therefore, it is possible that at microwave frequencies, the materials in the Cu-As-Se-Te system may show the same high frequency saturation of ac conductivity as observed for materials in the Cu-As-Se system.

Segawa attributes this behaviour to hopping within a short-range ordered cluster; hopping between clusters occurs at lower frequencies, and gives rise to an ac conductivity with a linear frequency dependence. However, Segawa's theory shows that hopping within the cluster at lower frequencies gives rise to an $\omega^2$ relationship, which was not observed here.

Kitao (31) observed high frequency saturation of ac conductivity in $\text{As}_2\text{Se}_3$ at frequencies above $10^8$ Hz. Kitao showed that this behaviour may be explained using a simple pair model of a carrier hopping back and forward between two localised states near the Fermi level. However, as this model could not account for the sub-linear relationship at low frequencies, Kitao suggested that the material is inhomogeneous and consists of layers of different conductivities,
which dominate the behaviour at different frequencies and that it is
the hopping conduction as outlined above in the highest conducting
layer, which accounts for the behaviour of the conductivity at the
highest frequencies of measurement. Therefore the ac conductivity of
As$_2$Se$_3$ would be strongly influenced by inhomogeneity of the
material, and hence would be affected by the method of sample
preparation.

In this work, all the materials were prepared in the same way,
so it was not possible to observe any effect on ac conductivity of
variations in sample preparation techniques.

The measured ac conductivity $\sigma_{ac}(\omega)$ is directly related to the
loss component of the complex permittivity, as described in equation
8.5, by the expression

$$\sigma_{ac}(\omega) = e''(\omega)$$

(8.10)

Therefore from equation 8.2

$$e'' = A\omega^{s-1}$$

(8.11)

Thus, if $s < 1$, $e''$ should decrease with increasing frequency throughout
the range in which equation 8.2 applies.

Fig 8.5 shows the expected reduction of $e''$ with increasing
frequency, although, the change is small, as the values of $s-1$ are
small. In the saturation region, where conductivity is independent
of frequency, \( s=0 \), hence, as can be seen, \( e'' \) decreases more sharply with frequency. \( e' \) reduces by approximately 10% for materials in the Cu-As-Se-Te system, and by approximately 8% for materials in the Cu-As-Se system for frequencies up to the onset of saturation, that is greater than \( 10^8 \) Hz.

The results, presented in terms of dielectric loss and dielectric constant, as shown in figures 8.5 and 8.6, suggest that, in dielectric terms, the response up to the onset of saturation is from the high frequency side of a loss peak, the low frequency response being below the level of experimental detection. At higher frequencies, the dispersion of the dielectric constant may show the beginning of a further relaxation or absorption mechanism. This data may be extrapolated, to show resonance absorption in the infra-red region.

Lewis (84) considers the dielectric response of donor and acceptor states in amorphous materials, which when ionised produce dipoles. Dipole re-orientation in an applied field can come about in several ways; by the transfer of an electron from a donor to an ionised donor (dipole \( D^+, D \)), or from an ionised acceptor to an acceptor (dipole \( A^-, A \)), ionisation occurring by the transfer of an electron from a donor to an adjacent acceptor (dipole \( D^+, A^- \), which is the same as a VAT, \( C_3^+, C_1^- \)). Lewis shows that the \( A^- A \) and \( D^+ D \) dipoles give rise to dielectric relaxation and \( D^+ A^- \) dipoles, resonance absorption.
The conventional dielectric approach suggests that the loss arises from Debye-type relaxation processes having a broad distribution of relaxation times. At the frequencies considered here, dielectric loss is usually due to ionic and molecular movements, therefore, it seems likely that these types of movements will be responsible for the relaxation phenomena. A number of models for ac and dc conduction in chalcogenide glasses have been considered which postulate several possible molecular and ionic configurations which may be responsible for electronic conduction, but which may also be dipolar in a dielectric sense.
9.1 INTRODUCTION

The main purpose of this work was to study some of the physical, electronic and optical properties of the alloys of copper with amorphous $\text{As}_2\text{Se}_3$ and $\text{As}_2(\text{Se}_{0.5}\text{Te}_{0.5})_3$ which have been shown to have ion-selective properties. These materials investigated contained 5, 6.25 and 7.89 at% copper. Some dc conductivity measurements were also carried out on materials in the Cu-As-Se system with concentrations of copper between 20 and 27.5 atomic percent. In this work the properties of the alloys were studied using recognised techniques. The experimental investigation into the structure of the materials, as described in chapter five, with the exception of differential thermal analysis, was carried out on specialised apparatus, mainly located in other departments of the University, and with the assistance of the appropriate staff. Differential thermal analysis, and measurements of dc conductivity and optical absorption were carried out using previously tested apparatus, regarded as standard in these laboratories.
The sample holder used in the thermopower experiments was developed specifically for this work, as the existing apparatus proved unsuitable for the type of samples available. The nature and the positioning of the thermocouples facilitated measurement of absolute and differential temperature, which was necessary for the accurate evaluation of thermopower when a zero offset voltage is anticipated.

The measurement of the ac properties of the materials was attempted using several techniques. Initially, a Lynch bridge was assembled, but subsequently a method was sought to reduce the time and instrumentation required for measurements over a large frequency range. A preliminary investigation was made into time domain spectroscopy techniques; apparatus was set up and results obtained, although no measurements were made. The results of ac conductivity experiments presented in this work were obtained using techniques developed for the Solartron Frequency Response Analyser and a Hewlett Packard Impedance Analyser, which were acquired during the course of this work. The former, being an instrument not specifically designed for the measurement of impedances, required a significant effort in setting up and in interpreting the results.

From a comparison of the results presented in chapters seven and eight, and the properties of chalcogenide glasses described in chapter three, it can be seen that the alloying of copper with chalcogenide glasses in the As-Se and As-Se-Te systems introduces significant changes in the properties of the glasses. Gradual changes in these properties result from variations in the concentration of copper in the alloys.
9.2 STRUCTURAL PROPERTIES

The results of differential thermal analysis experiments, reported in chapter five, indicate the existence in the Cu-As-Se system of two different types of structure. Therefore, it seems likely that there is significant structural alteration to As$_2$Se$_3$, with the addition of copper. This confirms Liang's (6) observations on materials with high copper concentrations; the higher resolution obtained using lower heating rates showed that the formation of two types of structure extends to materials with small concentrations of copper.

From Kastner's model (56), summarised in chapter three, impurities are associated with chalcogen atoms only through their lone pair electrons. Chalcogen atoms which are normally twofold coordinated in As$_2$Se$_3$ or As$_2$(Se$_{0.5}$Te$_{0.5}$)$_3$ lower the energy of their lone pair electrons by moving closer to the copper atom. Thus, chalcogen atoms which are normally twofold coordinated will become threefold coordinated by forming dative bonds with the copper atom, hence each atom will be surrounded by three threefold coordinated and one twofold coordinated selenium atoms. Kastner suggests that dissociation is favoured; that is the copper atom will separate from the normally coordinated selenium atom, leaving the selenium atom negatively charged, ($\text{Se}^-$), and a positively charged copper complex. Intrinsic charged defects in the glass will tend to repress dissociation, and an equilibrium situation will result. Therefore, according to Kastner's model, the addition of
certain elements to a glass can alter the density of valence alternation centres.

From the melting points observed in the DTA experiments, the two components in the Cu-As-Se system are As₂Se₃ and CuAsSe₂, the latter having a tetrahedral structure similar to chalcopyrite, shown in fig 5.1, where, unlike in Kastner's model, both the copper and arsenic are fourfold coordinated. Although the melting point in the DTA traces for materials in the Cu-As-Se-Te system were not of recogniseable components, it seems reasonable to assume that similar structural alterations will take place, with the addition of copper to As₂(Se₀.₅Te₀.₅)₃, and that the copper atoms will be incorporated in a tetrahedral formation.

In this situation, dissociation is not anticipated, which is confirmed by the gradual change in the dc conductivity with concentration of added copper, until the concentration where approximately all the selenium lone pairs have been used in bonding. Here significant changes are seen in the low temperature dc conductivity, as reported in chapter seven, due to copper now being incorporated into the glass as Cu⁺ ions.

The results of previous researchers indicate that at low impurity levels, (less than approximately 1 at%), the structure of the glass is sufficiently flexible to accommodate the bonding requirements of the impurity. However, in alloys with higher copper concentrations, such as studied in this work, it has been shown that the copper forms a tetrahedral structure, which in the Cu-As-Se...
system is similar to that of CuAsSe$_2$.

9.3 ELECTRICAL AND OPTICAL PROPERTIES

For an intrinsic semiconductor, the activation energy is generally assumed to represent half an energy gap, here designated $E_{\text{opt}}$, the optical gap, which is interpreted as being the energy difference between the mobility edges. Values obtained for $E_{\text{opt}}$ are shown in table 7.3. For each material investigated, a comparison of the measured optical energy gap and the measured room temperature dc conductivity activation energy, shown in table 7.1, indicates that the Fermi level appears to be close to the centre of the gap, a distance $E_\text{F}$ from the valence band edge. This is close to the behaviour of many other chalcogenide glasses, described as quasi-intrinsic, where the Fermi level is apparently fixed near the centre of the gap, irrespective of doping levels.

From an investigation of the dc conductivity, it appears that the values of the pre-exponential constant, $C$, derived from the dc conductivity measurements, are, in some cases, close to $10^3 \Omega^{-1}$ cm$^{-1}$ which are consistent with Davis and Mott's (17) theoretical estimates for conduction in extended states at the mobility edge. For some of the materials, the values of $C$ are smaller, between $10^{-1}$ and $10^{-3} \Omega^{-1}$ cm$^{-1}$, and according to the same model, may be taken to indicate room temperature conduction by hopping in localised states at the band edges.
In the materials studied, the simple activated behaviour does not persist to temperatures much below room temperatures. The reducing curvature of the $\ln \sigma$ versus $1/T$ plots and the linear relationship between the logarithm of conductivity and $T^{-1/4}$ indicates the possibility of a high density-of-states at or near the Fermi level, with transport occurring by hopping between these states.

The measured thermopower is always positive, therefore, the high temperature transport involves holes at or close to the mobility edge. The thermopower has a smaller temperature dependence than the dc conductivity, with $(E_F - E_s) = 0.14 \pm 0.02$eV. The difference between the measured thermopower and dc conductivity activation energies may be accounted for by the activation energy of the hole mobility. Therefore, according to the Davis-Mott model, these materials may, in general, be represented by a density-of-states as shown in fig 9.1 for Cu$_{7.89}$As$_{0.4}$Se$_{0.6}$Cu$_{92.11}$. This diagram shows the states responsible for the three processes leading to conduction, and which predominate in different temperature regions. The main transport mechanism involves holes either moving in extended states or hopping in localised states, both near to the mobility edge. This is consistent with the continuous curvature of the dc conductivity characteristics which suggests that there is no distinct change between conduction in extended states and localised states.
Figure 9.1 Proposed density-of-states diagram for Cu$_{76}$As$_{0.4}$Se$_{0.6}$

$N(E_f) = 2.96 \times 10^{18}$

$E_f - E_f = 1.52 \text{ eV}$

$E_f - 0.51 \text{ eV}$

CONDUCTION BAND

VALENCE BAND
At low temperatures, conduction occurs via thermally assisted tunnelling between states at the Fermi level. Values for the density-of-states at the Fermi level, $N(E_F)$, have been determined according to Mott's $T^{-1/4}$ rule, and are shown in table 7.2. The dc conductivity activation energies are slightly less than half the values of the optical gap determined by optical absorption. This may be taken to indicate that the Fermi level lies slightly closer to the valence band.

The curvature in the thermopower characteristic may also indicate a two path conduction process, with parallel conduction occurring in extended and localised states on either side of the mobility edge.

However some aspects of the transport behaviour do not appear to be consistent with the Davis-Mott model. On the other hand, some of the transport coefficients calculated from the experimental results are consistent with Emin's small polaron model (76). Further evidence for the small polaron hopping model is the substantial value for $E_p$ and the values of $C$ which are compatible with small polaron hopping transport, and are slightly low for the Davis-Mott model. Fig 9.2 shows a possible energy level scheme for small polaron transport. $E_s$, obtained from thermopower measurements, is the carrier generation energy, which varies from the conductivity activation energy, $E_a$, by the small polaron hopping energy, $W_H$. The Fermi level generally lies halfway between the electron and hole small polaron bands. $W_H$ in the Cu-As-Se system is $0.15 \pm 0.01$ eV and in the Cu-As-Se-Te system is
Figure 9.2  Energy level scheme for small polaron transport in Cu$_{7.89}$ (As$_{0.4}$ Se$_{0.6}$) 92-11
0.12 ± 0.01 eV. A constant value for $W_H$ within a material system suggests a common dominant constituent. $E_s$ is less than half the optical gap, because $E_{opt}$ is associated with electronic transitions in which the material is not able to adjust to the presence of the carriers, and form small polarons.

An investigation of the room temperature ac conductivity of these materials showed that at low frequencies the ac conductivity is independent of frequency, implying conduction in the extended states - similar to dc conduction at the same temperature. At higher frequencies, above approximately $10^6$ Hz, the conductivity is frequency dependent, being proportional to $w^s$, where $s$ is a constant <1. The experimental evidence suggests that at higher frequencies conduction is by a carrier hopping mechanism.

At low temperatures, the conductivity decreases with decreasing temperature and slightly with increasing frequency. This suggests that Austin and Mott's model (27) of hopping conduction, which predicts no frequency dependence, is not appropriate for the chalcogenide materials investigated here. At temperatures below approximately 250K, the ac conductivity data supports Elliot's (29) correlated barrier hopping model, where it is suggested that conduction occurs by two electrons simultaneously hopping over a barrier between charged defect centres. Elliot's predictions for the barrier height suggest that the ac response is due to hopping of pairs of electrons between non-intimate or intimate pairs of defects in the Cu-As-Se-Te and Cu-As-Se systems respectively. At higher temperatures, it is possible that conduction via quantum mechanical
tunnelling between localised states at the band edge predominates. However, this cannot be definitely ascertained without a knowledge of the temperature dependence of $s$.

The dielectric response of the materials suggests that one or more dipolar mechanism is responsible for the frequency response. Several models suggest possible molecular and ionic configurations which may be responsible for electronic conduction and which are also dipolar. Electrons (27) or pairs of electrons (29) hopping between states behave like dipoles; VAPs and IVAPs by their nature are dipolar, as are small polarons, which suggest that the material lattice may also have a dielectric response (83). However, the experimental evidence from the present work does not indicate conclusively that any one model is applicable to these materials.

Defect states in chalcogenide glasses are due to lattice deformations; according to the KAF model, the defect states $C_1^{-}$ occur when electrons are trapped in pairs at defect sites, the coulomb repulsive energy between the electrons being outweighed by an energy gain associated with lattice distortion. Such a doubly occupied defect site is sometimes referred to as a bipolaron. The $C_1^{-}$ defect centres occur in conjunction with $C_3^{+}$ defect centres, according to equation 2.9. The traps which control the hole mobility in amorphous chalcogenides (42) are thought to be these negatively charged $C_1^{-}$ centres.
If the copper atoms are incorporated into the glass structure by the utilisation of the lone-pair electrons of the chalcogen atoms in dative bonding, the density of the defects will not change. Hence the variation in conductivity and activation energy with the addition of copper is not due to a variation in hole mobility, but the result of the formation of CuAsSe$_2$ type complexes, which have smaller activation energies.

Emin’s small polaron theory (76) includes the concept of a dominant constituent, which was defined in chapter two. There is strong evidence obtained from the structural studies reported in chapter five, that each glass in the same system has the same dominant constituent, and that this is a tetrahedral component based on the copper atoms. The gradual change in the electrical and optical properties of the glasses are due to the gradual increase in the amount of the dominant constituent.

For alloys in the Cu-As-Se system with copper concentrations of greater than 20 at%, the high temperature dc conductivity follows the trend of the alloys with lower copper concentrations, but significant changes were observed in the low temperature conductivity. At low temperatures the plots of dc conductivity versus reciprocal temperature showed an uncharacteristic flattening out, which is similar to that associated with extrinsic conduction. This occurs at approximately the composition where all the available lone-pairs are used up in bonding. Any additional copper will be incorporated into the material as donor atoms, which give rise to the apparently extrinsic behaviour.
The results, presented in this work, of investigations into the electrical and other properties of the chalcogenide alloys have been interpreted in terms of several conduction mechanisms summarised above. Although definitive proof was not obtained, the experimental results in this work strongly support the small polaron theory of conduction, as indicated in the following discussion.

The values of the pre-exponential constant, $C$, at room temperature are slightly low to be associated with extended state conduction, but are consistent with the values predicted by the small polaron model. In addition, the values of $C$ are too high to be attributed to the hopping of carriers in the localised bandtail states, which is the explanation favoured by the Davis-Mott model for the discrepancies between the values of $E_0$ and $E_s$. In addition, it is unlikely that such a large discrepancy is due only to disorder.

Nagels et al's (38) theory of parallel conduction, described in chapter seven, was developed to account for observed curvatures in the dc conductivity and thermopower characteristics, as well as the differences in activation energies obtained from the two experiments. The fitting of this theory to the experimental results in this work requires that the contributions to the conductivity from extended state motion and bandtail hopping are approximately equal, and hence in all cases the measurements of thermopower require to have been made in the transition temperature range between the temperature above which transport in extended states predominates and the temperature below which hopping transport in
localised states predominates. It seems implausibly fortuitous that this should have occurred in all six of the materials for which thermopower measurements were carried out.

A more satisfactory explanation is that conduction is by small polarons and that the difference $E_\sigma - E_s$ is the polaron hopping energy, $W_H$, the magnitude of $W_H$ indicating that the hopping processes are multiphonon transitions.

At temperatures below room temperature, the dc conductivity shows $T^{-1/4}$ behaviour, which is consistent with variable range hopping between states at the Fermi level, according to the Davis-Mott model. However, the $T^{-1/4}$ relationship cannot be taken as definite proof of the existence of such states, and the negative values of $\rho$ obtained from equation 7.8 confirm that this model is not applicable to the results obtained in this work. On the other hand, the low temperature conductivity data is shown, in chapter seven, to fit Schnackenberg's (74) equations for conduction by small polarons.

In summary, the experimental data obtained from structural and steady state transport studies indicate that conduction in these copper-chalcogenide alloys is due to hole-like small polarons hopping through a dominant constituent, which is a copper-based tetrahedral component.
9.4 FURTHER WORK

Some aspects of the properties of the materials investigated have not been fully defined by the results of the experiments carried out in this work.

Further evidence for the small polaron model might be provided by Hall effect measurements, as the small polaron theory predicts that the Hall mobility will be thermally activated with an activation energy one third of that derived from the dc conductivity. The theory also predicts the sign anomaly which has been observed in some chalcogenides, where the Hall coefficient has an opposite sign to that of the thermopower.
APPENDIX 1

ION-SELECTIVE PROPERTIES OF COPPER-CHALCOGENIDE ALLOYS

1. INTRODUCTION

Ion-selective electrodes function in the configuration shown in fig 1. The potential measured between the electrode and the reference electrode varies with ion concentration according to Nernst's equation:

\[ E = E^0 + \frac{RT}{2F} \ln[A^{2+}] \]  

for a divalent cation \( A^{2+} \) where \( E^0 \) is a constant, \( F \) the Faraday constant and \( R \) the gas constant.

A solid state ion-selective electrode is one in which the internal filling solution is replaced by a metal contact, giving advantages of robustness and possible reduction in size. It has been postulated that electronic conduction in the membrane material would enable stable metal contacts to be formed with reversible electrode behaviour. Insight into the conduction mechanisms of suitable membrane materials would enable the development of solid-state sensors to be less empirical.
Figure 1 Conventional ion-selective electrode configuration
As was mentioned in chapter one, this study of the conduction mechanisms of copper-chalcogenide alloys followed from the observations that these materials were suitable for use as membranes in microelectronic copper-selective electrodes.

In this department, a program of research into the electrochemical behaviour of ion-selective electrodes based on the results of Jasinski et al (7) with Cu-As-S membranes has been ongoing since 1976. Drennan (8) showed that the materials used by Jasinski et al were unsuitable for long term use due to their susceptibility to chemical attack and the resulting disintegration of the membrane surface.

Jasinski et al asserted that the presence of a crystalline compound within the sulphide glass was essential for ion-selective activity, however, it seemed possible that this structure aggravated the problem of chemical attack.

Wheatley (9) studied the response of materials in the Cu-As$_2$Se$_3$-As$_2$Te system, in which relatively large amounts of copper (up to 30 at%) can be incorporated whilst still retaining an entirely glassy structure. The results obtained refuted the claims of Jasinski et al, that the presence of a crystalline compound was a pre-requisite for ion-selectivity. The advantage of using alloys which incorporate some tellurium is that the resistivity is lower and hence instrumentation is easier.
Wheatley also obtained preliminary results with membranes of \( \text{Pb}_{20}\text{Cu}_5(\text{As}_2\text{Se}_3)_{75} \) in lead-sensitive solid-state electrodes, although again the high resistivity of the materials introduced problems.

2. MEASUREMENTS OF ION-SELECTIVITY

Prior to the investigation of the properties of the copper-chalcogenide alloys, experiments were carried out to confirm the ion-selectivity of the materials.

2.1 Manufacture of Electrodes

The electrode membranes were made from 1mm slices of the cooled ingot, prepared according to the method described in chapter four, which had been polished on both sides to a roughness of 1µm, and ultrasonically cleaned in trichloroethylene. A gold contact was evaporated on one side of the membrane, and a contact lead attached using Acheson colloidal silver dag. The disc was then mounted with ICI Silicoset silicone rubber adhesive, at the end of a perspex tube of length 12cm approximately, as shown in fig 2.
Figure 2  Solid-state copper-selective electrode as used in the present work
2.2 Electrochemical measurements

The potentiometric response of the electrodes was tested in solutions of Cu(II) of varying concentrations. These test solutions were made by repeated tenfold dilutions of 10 M Cu(II) with a base electrolyte of 0.1M KNO₃ down to a minimum of 10⁻⁵ M. The reference electrode used was a Radiometer saturated calomel electrode or a Simac double junction electrode (for use in lead solutions). The potential between the reference and ion-selective electrodes was measured by a Keithley 610C electrometer; a connection to a Vitatron chart recorder enabled the stability of the response to be observed over a period of several hours. In order to shield the cell from external electrical interference it was housed in an aluminium box.

2.3 Results

Fig 3 shows the electrochemical response of an electrode with a membrane of Cu₆·₂₅[As₀·₄(Se₀·₅Te₀·₅)₀·₆]₉₃·₇₅. These results show that for Cu(II) concentrations down to approximately 10⁻⁵ M the electrode response is linear and with a slope of approximately 30mV/decade of concentration, which corresponds to equation 1. Hence the electrode response is nearly Nernstian; it is also but not completely reproducible.
Figure 3  Response of electrode with membrane
of Cu$_{5.25}$[As$_{0.4}$Se$_{0.5}$Te$_{0.5}$]$^{33.75}$
These preliminary measurements confirm the previous work of Wheatley and justified further investigations into the properties of the membrane material.

3. CURRENT ELECTROCHEMICAL STUDIES

The detailed studies of the properties of copper-chalcogenide alloys have been concurrent with investigations into their electrochemical behaviour. Kennedy (69) has been studying the effects of several variables in the copper-selective electrode system based on the copper-chalcogenide alloys. He found that variations in the percentage of copper in the alloy, and in the metal used as the back contact did not affect the electrode response. He has also made a detailed study of the effect on the electrode response of pH and cations in the form of nitrates, in the unknown solution. It was found that interference did not occur, except in the case of Ag⁺, Hg⁺ and Fe³⁺. Illumination also affects the response in electrodes with Cu-As-Se membranes; the electrode becomes more positive with increasing intensity of light.

Analyses of these results and of the results of Kennedy's experiments with dc sweep and cyclic voltammetry and chronopotentiometry will be presented at a later date. The electrode response of pH and cations in the form of nitrates, in the unknown solution. It was found that interference did not occur, except in the case of Ag⁺, Hg⁺ and Fe³⁺. Illumination also
affects the response in electrodes with Cu-As-Se membranes; the electrode becomes more positive with increasing intensity of light.
VARIATION OF CONDUCTIVITY OF MATERIALS IN THE Cu-As-Se SYSTEM WITH TEMPERATURE AND COMPOSITION

A detailed investigation of the variation with temperature of dc conductivity of materials in the \( \text{Cu}_x (\text{As}_{0.4} \text{Se}_{0.6})_{100-x} \) system with high concentrations of copper has recently been carried out by Mooney (71). The variation of the logarithm of conductivity with reciprocal temperature is shown in figs 1 and 2 for \( 20>x>25 \).

These results show the same continuous curvature also evident in the results presented in chapter seven. The results for materials with \( x \) between 21 and 22 show an anomaly in the trend, as shown in Fig 2. The plots for these materials indicate two distinct regions, similar to those presented in chapter seven for the material with 25 and 27.5 at% copper. This anomalous behaviour at low temperatures is further evident in fig 3 where the logarithm of conductivity is plotted as a function of at% copper in \( \text{As}_2 \text{Se}_3 \), at various temperatures.

For most compositions, the plot of the logarithm of conductivity versus \( T^{-1/4} \) is a straight line, as shown in fig 4, which indicates that the data fits the variable range hopping equation predicted by Mott (44). The dc conductivity of the
Figure 1 Log $\sigma$ versus $\frac{1000}{T}$
Figure 2: Log $\sigma$ vs $\frac{1000}{T}$ for $x = 21$ and $x = 22$
Figure 3  Variation of conductivity with copper content in As$_2$Se$_3$ at constant temperatures
Figure 4  Log $\sigma$ versus $\frac{10}{T^{1/4}}$
materials which have anomalous behaviour is not linear with respect to $T^{-1/4}$ as can be seen in Fig 5.
Figure 5  
Log $\sigma$ vs $T^{-\frac{1}{4}}$ for $x = 21$ and $x = 22$.
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