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The electronic properties of liquid $\text{Ag}_{1-x}\text{Se}_x$

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Abstract. Measurements of the electrical conductivity σ , thermoelectric power S and magnetic susceptibility of liquid $\text{Ag}_{1-x}\text{Se}_x$ alloys have been measured as a function of composition and temperature. The unusual maximum in σ , along with the negative $d\sigma/dT$ observed around stoichiometry for Ag–S alloys is also observed in this system. The thermopower shows a p–n transition at $x = 0.36$ with a magnitude indicating that this is a liquid semiconductor with an essentially zero energy gap. It is demonstrated that the results cannot be explained using the Kubo–Greenwood expressions for σ and S if rigid band behaviour is assumed. The origins of this unusual behaviour are discussed in terms of an enhanced carrier mobility near the stoichiometric composition.

1. Introduction

Understanding the electronic properties of disordered electronic conductors remains a topic of intense theoretical interest despite many advances made during recent years. Of crucial importance is the effect of topological disorder in producing localized electron states and the consequences of this for the electronic transport properties. Most of the work has concentrated on the study of amorphous (quenched) solids, but due to the difficulties in producing uniform and homogeneous samples, there are often serious problems when interpreting experimental data. Liquid semiconductors by contrast are in true thermodynamic equilibrium and consequently their properties are not governed by preparation conditions (e.g. substrate temperatures, quenching rates etc). They can also in general be studied over a wide concentration range provided phase separation does not occur. In this paper we describe a material, liquid Ag–Se, which shows particularly unusual electronic properties, which cannot be explained in terms of the simple rigid band pictures used to date.

The electronic properties of a disordered conductor, within the independent particle approximation, can be described in terms of the Chester–Thellung–Kubo–Greenwood formulation based on the kinetic transport coefficients. The conductivity and thermopower are then given as

$$\sigma = - \int_0^\infty \sigma(E) \frac{\partial f(E)}{\partial E} dE \quad (1)$$

$$S = - \frac{k_B}{|e|} \int_0^\infty \frac{\sigma(E)}{\sigma} \frac{E - \mu}{k_B T} \frac{\partial f}{\partial E} dE \quad (2)$$

respectively, where $f(E)$ is the Fermi function

$$f(E) = \left[\exp\left(\frac{-(E - \mu)}{k_B T} + 1\right) \right]^{-1} \quad (3)$$

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and μ is the chemical potential. In these expressions the system dependent features are contained in the energy dependent conductivity $\sigma(E)$. These formulae omit the contribution from electron–electron and electron–phonon interactions, although it is possible to include effective approximations to them. It is the importance of these contributions that has been the subject of considerable theoretical debate. It should be realized that the majority of the expressions commonly used to interpret the behaviour of liquid and amorphous semiconductors and metals are in fact derived from these expressions in the degenerate (metallic) and non-degenerate ($\Delta E \gg kT$) limits using simple theories (such as the random phase approximation (RPA)) to describe the form of $\sigma(E)$. For example, the often quoted expressions for the conductivity σ , in the metallic and semiconducting limits are:

$$\sigma = A[N(E_F)]^2 \quad (4)$$

$$\sigma = \sigma_0 \exp \frac{-(E_c - \mu)}{k_B T} \quad (5)$$

respectively. However, care should be taken when using these expressions. For example, equation (5) is not universal and assumes a specific form for $\sigma(E)$ near the mobility edges.

Expressions for various models of $\sigma(E)$ in the degenerate and non-degenerate limits and in the intermediate regime have been fully discussed elsewhere (Enderby and Barnes 1990a, b). It was shown that by studying σ and S , the majority of liquid semiconductors close to stoichiometry can be well understood using simple models of $\sigma(E)$ and a rigid band type behaviour for the electronic density of states. However, both liquid Ag_2S and Ag_2Se are anomalous in the fact that they both show a negative $d\sigma/dT$ despite values of σ and S suggesting they are materials with a conductivity gap $\Delta E \simeq 0$. Recently, a detailed study of liquid $\text{Ag}_{1-x}\text{S}_x$ (Ohno *et al* 1990) revealed even more striking properties, notably a rise in σ as the stoichiometric composition Ag_2S is approached from both the silver and sulphur rich compositions. Due to phase separation problems, this material can only be studied for a narrow range of compositions near stoichiometry, and a p–n transition could not be observed. In this paper we present detailed results for liquid $\text{Ag}_{1-x}\text{Se}_x$ for which a broader composition range could be studied. Additionally, measurements of the magnetic susceptibility χ have also been carried out. With the results presented, we give a consideration of how the behaviour of χ can be interpreted within the framework of the independent particle model, particularly with reference to the limits of the rigid band picture.

2. Experimental details

The electrical conductivity and thermopower of liquid $\text{Ag}_{1-x}\text{Se}_x$ were measured simultaneously in a quartz cell using a four probe method described previously (Barnes 1986, Ohno *et al* 1990). Contact to the samples was made directly using small graphite electrodes inserted through a tapered hole in the quartz tube. These were secured in place using thin molybdenum bands to which molybdenum wires were attached. The temperature was measured using chromel–alumel thermocouples fastened immediately over each electrode using a nickel band. The cell was calibrated using high purity mercury at room temperature. To prevent evaporation of selenium from the sample, and bubbling, the apparatus was filled with argon gas which also prevented sample oxidation. Any bubbles that formed in the sample were removed by agitating it with a silica rod.

The thermopower measurements were made using a ΔT method. Accurate control of the electrode temperatures was obtained using a twin zone furnace with independent temperature control of the upper and lower cell thermocouples. The thermoelectric voltages were measured relative to molybdenum and chromel using a high accuracy (10 nV), high

impedance digital voltmeter. The absolute thermopower was determined using tabulated values of the thermopower of molybdenum given by Cusack and Kendall (1958).

The magnetic susceptibility was measured using the standard Faraday method with a torsion balance under feedback control. The field strength of the electromagnet was approximately 1 Tesla with a 50mm gap between the pole pieces. The constant value of $B dB/dx$ was $9.1 \pm 0.3 \text{ T}^2 \text{ m}^{-1}$. A standard sample of Mohr's salt ($\chi = 0.158 \text{ mol}^{-1}$) at room temperature was used to calibrate the apparatus. Samples of mass approximately 1.2g, sealed in an evacuated quartz capsule with an internal diameter of 5mm were used for the experiments.

For all the measurements, a master alloy of Ag_2Se was prepared from pure (99.99%) Ag and Se. The composition of each sample was determined by accurately measuring the mass of each component before mixing.

3. Experimental results

The electrical conductivity and thermopower of liquid $Ag_{1-x}Se_x$ were measured at fifteen different compositions ($0 \leq x \leq 0.44$). A simplified phase diagram of this system derived from the values of σ is shown in figure 1. In all cases the sample was heated to approximately 150 °C above the liquidus and agitated by a quartz rod to ensure complete mixing. The point of phase separation was observed as an abrupt change in σ .

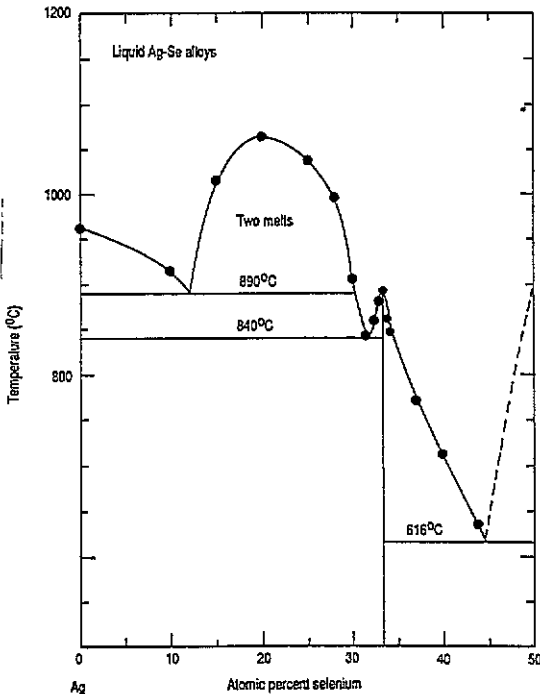


Figure 1. The phase diagram of Ag-Se derived from the conductivity data.

Figures 2, 3 and 4 show σ as a function of T and x . For $x \leq 0.315$, the behaviour appears to be typical of many liquid alloys with a negative $d\sigma/dT$ in the metallic regime which becomes progressively more positive as σ decreases. In the regime $0.315 \leq x \leq 0.35$ highly unusual behaviour becomes apparent, notably σ increases as the stoichiometric composition is approached from either side. The temperature coefficient $1/\sigma(d\sigma/dT)$

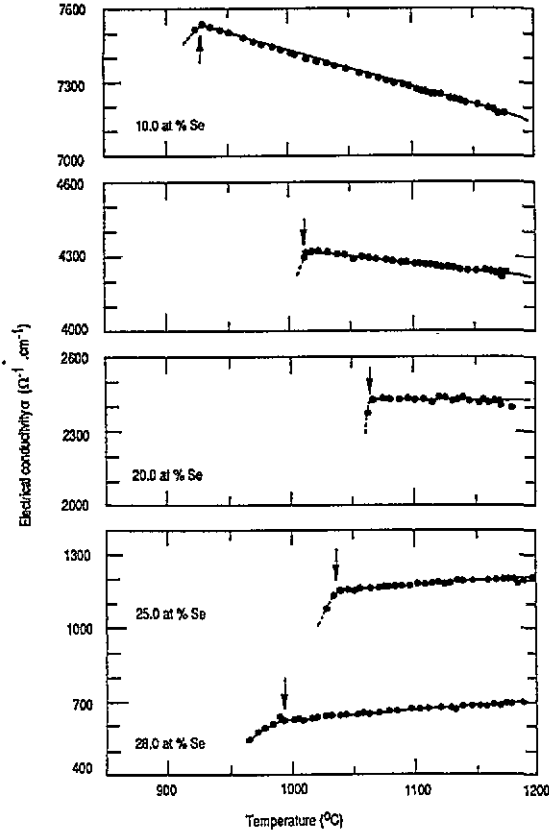


Figure 2. The conductivity of liquid $\text{Ag}_{1-x}\text{Se}_x$ for $x \leq 0.28$.

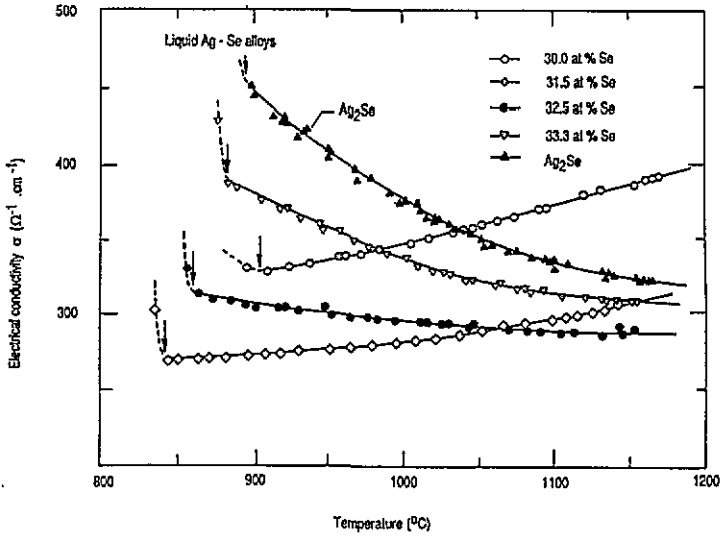


Figure 3. The conductivity of liquid $\text{Ag}_{1-x}\text{Se}_x$ for $0.3 \leq x \leq 0.333$.

becomes large and negative and reaches its minimum value at precisely $x = 1/3$. For $0.35 \leq x \leq 0.45$, $1/\sigma(d\sigma/dT)$ again becomes positive, and is more typical of that

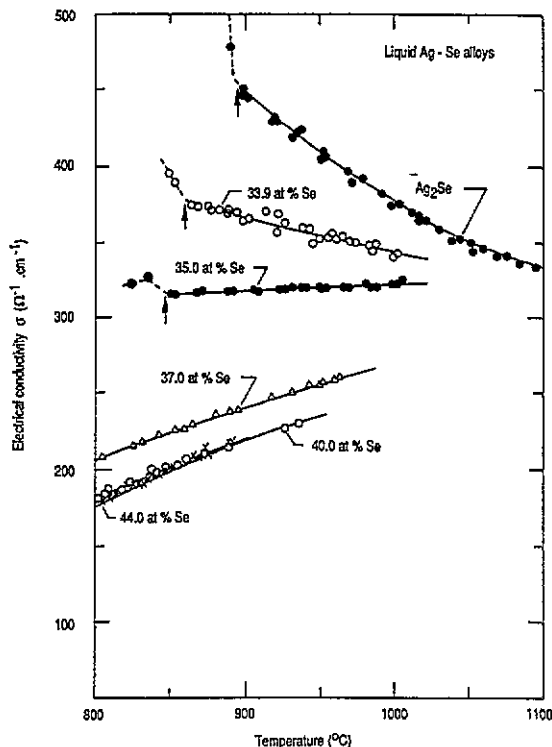


Figure 4. The conductivity of liquid $\text{Ag}_{1-x}\text{Se}_x$ for $0.333 \leq x \leq 0.44$.

observed in other liquids of comparable conductivity. The composition dependence of σ and $(1/\sigma)(d\sigma/dT)$ are shown in figures 5 and 6.

The results for the thermopower S as a function of temperature are shown in figures 7 and 8. For the concentration range $0 \leq x \leq 0.2$ the thermopower is small ($< 25 \mu\text{V K}^{-1}$) and negative with essentially no temperature dependence. This is consistent with the position of the chemical potential lying within the conduction band, and the observed conductivities. For the range $0.2 \leq x \leq 0.3$, the behaviour is more unusual as it shows a significant temperature dependence for approximately 150°C above the liquidus and then levels out to more metallic like magnitudes with $dS/dT \approx 0$. For $0.3 \leq x \leq 0.35$, S remains negative with a strong temperature dependence such that $d|S|/dT$ is negative. A p-n transition is observed to take place between $0.35 \leq x \leq 0.37$ at which point S becomes positive. For $0.4 \leq x \leq 0.44$, S is positive with $d|S|/dT$ strongly negative. S as a function of composition is shown in figure 9. It should be noted that the results for the composition Ag_2Se obtained here are in close agreement with those obtained by Endo *et al* (1980), and Glazov *et al* (1986).

Figure 10 shows the molar magnetic susceptibility (χ) as a function of temperature for liquid $\text{Ag}_{1-x}\text{Se}_x$ in the range $0 \leq x \leq 0.333$. There is generally a small increase in χ as T increases. A minimum of $\chi = -375.0 \times 10^{-6} \text{ mol}^{-1}$ occurs at the stoichiometric composition along with a relatively large temperature dependence. χ as a function of T for $0.333 \leq x \leq 0.444$ is shown in figure 11, again showing a small increase with temperature. A plot of χ versus x is shown in figure 12. There is a very small apparent shift in the minimum of χ to 0.336 at higher temperatures.

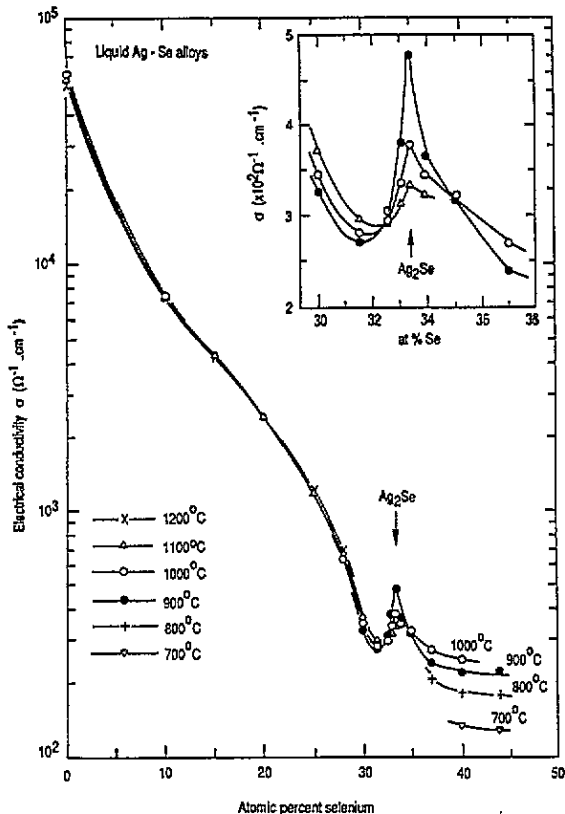


Figure 5. The conductivity of liquid $\text{Ag}_{1-x}\text{Se}_x$ as a function of composition and temperature.

4. Discussion

The results presented for liquid $\text{Ag}_{1-x}\text{Se}_x$ and those obtained previously for $\text{Ag}_{1-x}\text{S}_x$ are unique among liquid semiconductors. Typically for a compound forming system (for example Tl-Te, Cu-As, K-Pb etc) the general behaviour is that σ remains metallic over the majority of the composition range but decreases rapidly to a deep minimum at the stoichiometric composition. Similarly, the total magnetic susceptibility, which includes the Pauli susceptibility term also shows a minimum reflecting the minimum in the electron density of states at the position of the chemical potential at stoichiometry. The thermopower shows a characteristic rise in magnitude as stoichiometry is approached with a sudden p-n transition as the stoichiometric composition is crossed. For the typical systems referred to above the underlying structure at stoichiometry is considered to be similar to that of a molten salt except that the energy gap is now of the order $k_B T$ so that excitation of electrons from one band to the other can take place. For example, the physical and electronic structure of liquid Tl_2Te can be understood assuming it consists of essentially Tl^+ and Te^{2-} ions. The valence and conduction bands then originate from the Te p and Tl s states respectively. The conductivity gap is then determined by the separation of these bands and the degree of electron localization taking place. It might be expected that Ag-S and Ag-Se would show similar behaviour to Tl-Te, as the monovalent Tl^+ and Ag^+ ions often show chemical similarity. Indeed, liquid Ag-Te (Dancy 1965) does show very similar properties to Tl-Te.

The unusual properties of Ag-S and Ag-Se cannot be explained using this generalized

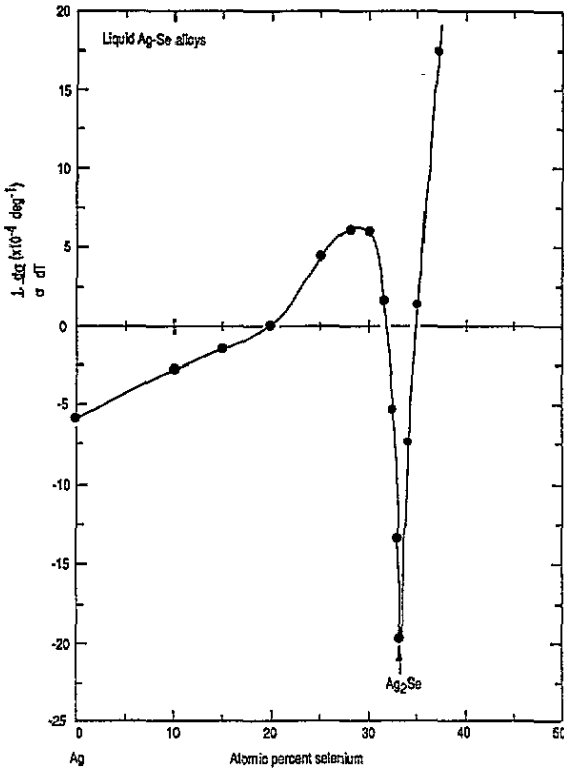


Figure 6. $1/\sigma(d\sigma/dT)$ for $Ag_{1-x}Se_x$ as a function of composition.

ionic picture, and they therefore raise interesting questions concerning the theoretical description of electronic processes in liquid systems.

The transport properties of poor liquid metals and semiconductors are usually interpreted in terms of Chester–Thellung–Kubo–Greenwood kinetic coefficients (equations (1) and (2)) or approximations to them in the appropriate limits (equations (4) and (5)). In these relations the important parameter is the energy dependent conductivity $\sigma(E)$, which in principle can be calculated theoretically for specific systems, or parametrized to some simple generic form (Enderby and Barnes 1990). For the metallic region, and using the simple approach based on the RPA (which is still a commonly used approximation when interpreting experimental data), $\sigma(E)$ is given by:

$$\sigma(E) = A[N(E)]^2 \tag{6}$$

where $N(E)$ is the density of states at energy E , and A is a constant given by

$$A = \frac{1}{6} \frac{\pi e^2 a^5 \Gamma^5}{\hbar z} \tag{7}$$

where Γ is the bandwidth, a the nearest neighbour separation and z the coordination number of the atoms in the system (Cutler (1977), Hindley (1970)). In practice, when considering liquid semiconductors near stoichiometry, the rigid band model (where $N(E)$ is assumed to remain unchanged for small variations in composition), is used to discuss their behaviour. As stoichiometry is approached μ moves towards the minimum (or zero) in $N(E)$ and the effects of strong disorder on the electron system become more important. The relationship between $\sigma(E)$ as $N(E)$ approaches zero is still the subject of considerable theoretical debate.

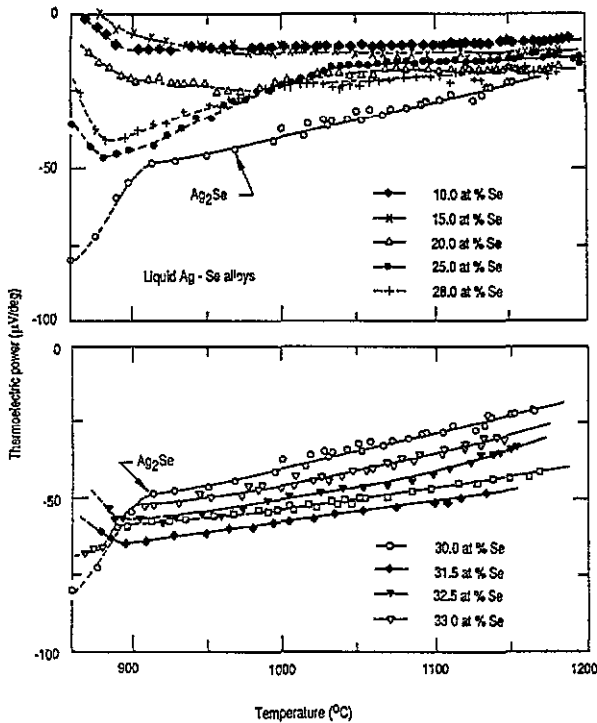


Figure 7. The thermopower of liquid $\text{Ag}_{1-x}\text{Se}_x$ for $x \leq 0.33$.

In the presence of sufficient disorder (Anderson (1958), Mott and Davis (1979)), some of the electron states may become localized and essentially non-conducting so that $\sigma(E) \simeq 0$ and a conductivity gap forms. The energies at which the electron states change from the localized to the delocalized state are the valence (E_v) and conduction band (E_c) mobility edges so that $\Delta E = E_c - E_v$. Enderby and Barnes (1990) showed how ΔE could be determined from the magnitude of the p-n transition in the thermopower when passing through stoichiometry and gave the condition $\Delta E \geq 0$ as the narrow definition of a liquid semiconductor. Following this procedure, the thermopower results show that Ag_2Se is a semiconductor with $\Delta E \simeq 0$.

However, if rigid band behaviour around stoichiometry is assumed, then in order to reproduce the observed peak in σ at stoichiometry a similar peak in $\sigma(E)$ with a width much greater than $k_B T$ is required. This leads to a 'double S' type structure in the thermopower (Enderby and Barnes (1990)). This is not observed in the experimental data. It is also difficult to envisage, using any simple bonding scheme for Ag and Se, why $\sigma(E)$ would have this form and why the observed conductivity peaks precisely at stoichiometry. Consequently we conclude that the experimental data cannot be explained using a rigid band model for $\sigma(E)$.

Moving away from the rigid band picture of $\sigma(E)$, there are several other possible explanations for the behaviour of Ag-S and Ag-Se.

(i) For this, and possibly many other liquids, the kinetic coefficients for the transport behaviour are inadequate and more general theories including the effects of interactions are needed. It is beyond the scope of this paper to discuss the necessity of using a more sophisticated framework for discussing this, and other liquid semiconductors, although it is still hard to envisage, using any reasonable model, how such a peak in σ against x could

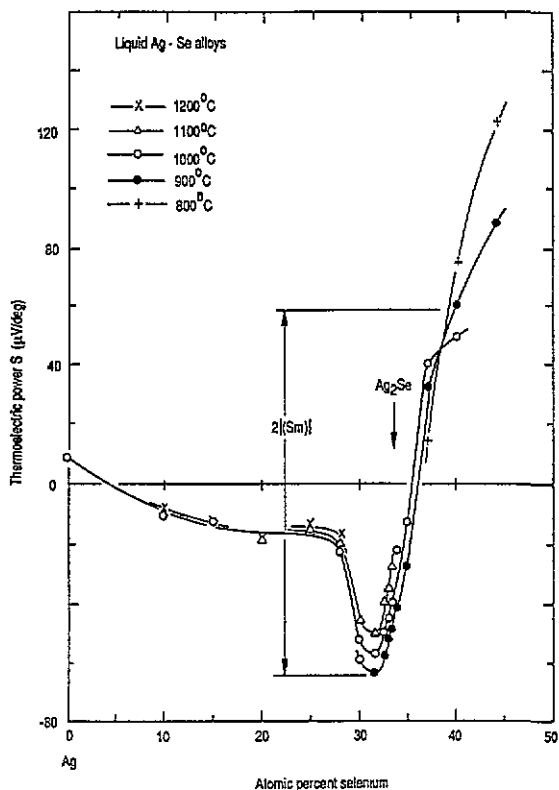


Figure 8. The thermopower of liquid $\text{Ag}_{1-x}\text{Se}_x$ for $0.333 \leq x \leq 0.44$.

be predicted.

(ii) Rigid band behaviour of $\sigma(E)$ does not occur because the underlying physical structure, and consequently the electronic structure are changing rapidly as a function of concentration near stoichiometry. This hypothesis is more difficult to reject as there is very limited experimental data relating to direct measurements of the electronic and physical structure. For liquids at these temperatures the principle solid state spectroscopic techniques for measuring the density of states such as XPS, BIS and UPS cannot be readily applied. However, neutron data at the total structure factor level have been obtained for $\text{Ag}_{1-x}\text{Se}_x$ for $x = 0.3033, 0.3333$ and 0.3633 (Saboungi *et al* (1992)). Although these are only total structure factor measurements, no major changes in the structure could be observed over this concentration range (the first peak in $S(Q)$ remains constant at $Q = 2.5 \text{ \AA}^{-1}$ and a shoulder at $Q = 1.8 \text{ \AA}^{-1}$ remains present in all samples). Also the results show broad agreement with the molecular dynamics simulations of Rino *et al* (1988) which are based on essentially ionic potentials, leading us to believe that a quasi-ionic origin of the density of states for $\text{Ag}_{1-x}\text{Se}_x$ is reasonable.

(iii) Rigid band behaviour occurs in terms of $N(E)$, but the conductivity gap Δ reduces as stoichiometry is approached due to a decrease in the degree of localization in the system at stoichiometry. Although this seems plausible at first sight, detailed consideration of the changes in S corresponding to the decrease in ΔE show that this is entirely inconsistent with the observed thermopower data. That is, as ΔE decreases and σ increases, a corresponding decrease in $|S|$ is predicted to occur.

(iv) The density of states can be approximated by rigid band behaviour but the

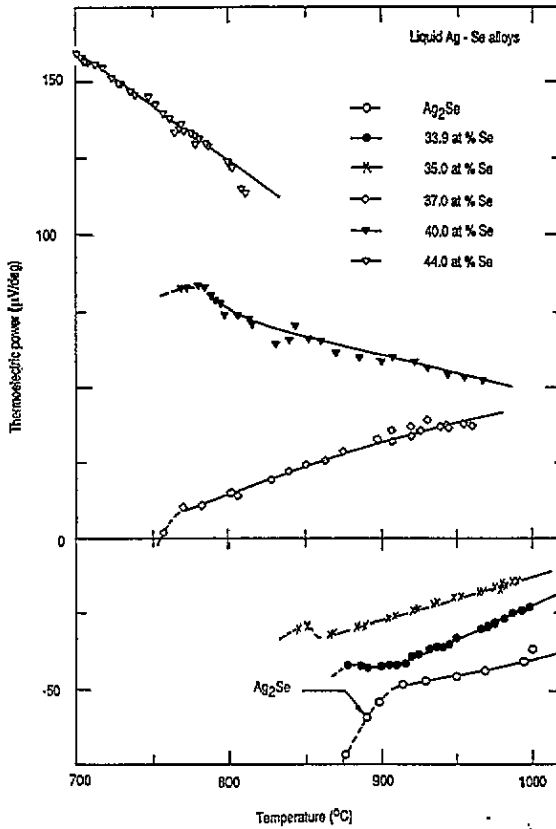


Figure 9. The thermopower of liquid $\text{Ag}_{1-x}\text{Se}_x$ as a function of composition.

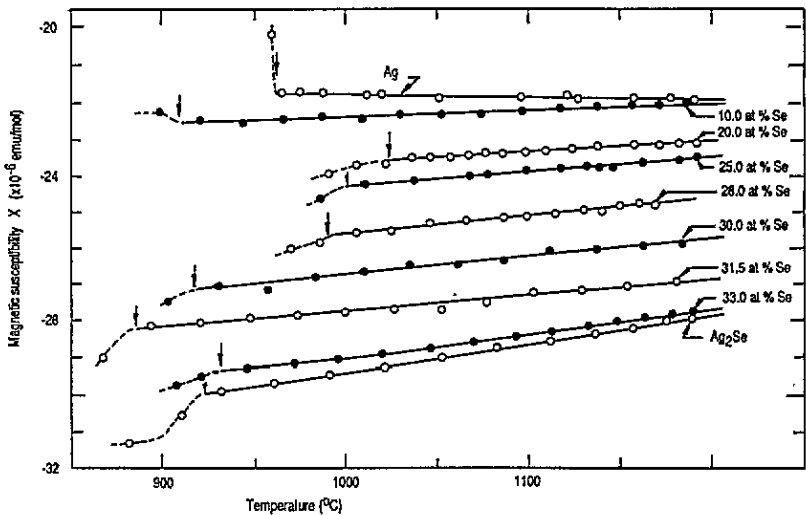


Figure 10. The molar magnetic susceptibility of $\text{Ag}_{1-x}\text{Se}_x$ for $0 \leq x \leq 0.333$.

carrier mobility (reflected in the slope of $\sigma(E)$ near the mobility edge) increases as the stoichiometric composition is reached.

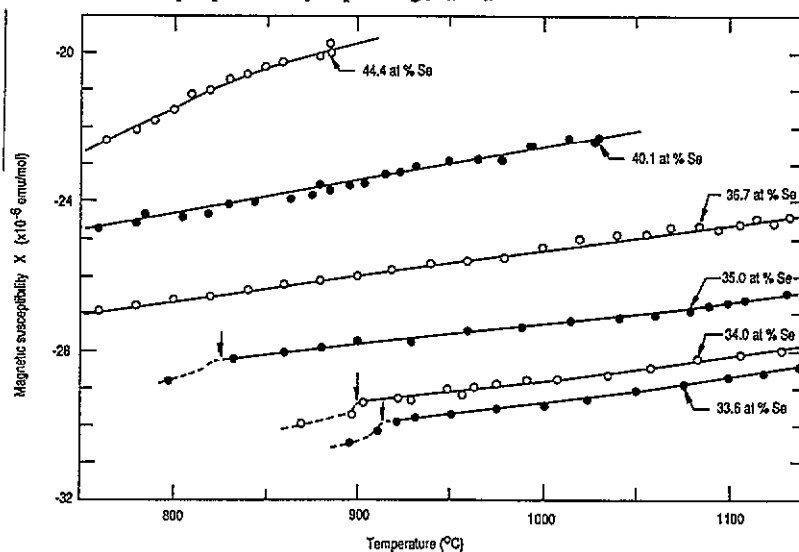


Figure 11. The molar magnetic susceptibility of $Ag_{1-x}Se_x$ for $0.333 \leq x \leq 0.44$.

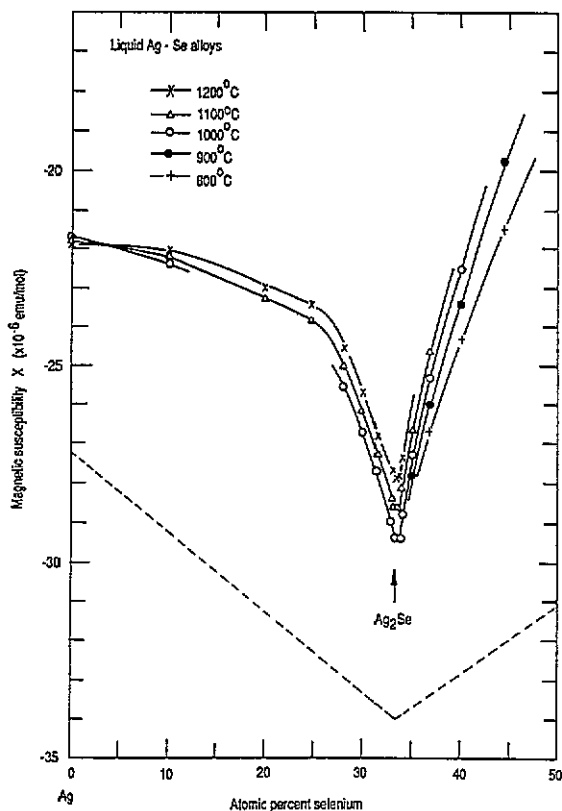


Figure 12. The molar magnetic susceptibility of $Ag_{1-x}Se_x$ as a function of composition.

It is this fourth possibility that will be considered in the rest of this paper. It should be noted that $\sigma(E)$ does not map directly to the density of states in the system, and could in fact change quite significantly with changes in the underlying disorder (which may not significantly change the density of states). As a consequence of the changes in disorder,

E_c and E_v could move positions within the band, thus changing ΔE , or a change in the slope of $\sigma(E)$ near the mobility edges could occur due to changes in the carrier mobilities. In order to probe more carefully the effects of localization and the interrelation between $N(E)$ and $\sigma(E)$, a more direct measure of $N(E)$ in this system is needed. The magnetic susceptibility of a material after subtraction of the atomic diamagnetism and paramagnetism, is such a measure.

The total susceptibility of the sample (in the absence of paramagnetism) is a combination of the Pauli susceptibility from the conduction electrons and the atomic diamagnetism of the ion cores such that

$$\chi_{\text{total}} = \chi_{\text{Pauli}} + \chi_{\text{diam}}. \quad (8)$$

For liquids, χ_{diam} will depend on the atomic concentration of each component and their chemical environment. There is no unambiguous way of experimentally separating the atomic diamagnetism from the Pauli term, so this technique only gives qualitative measurements of $N(E)$. For quasi-ionic liquid semiconductors, it is often assumed that the diamagnetic contribution to the susceptibility can be written as the average susceptibility of the ion cores in the material, with the excess 'free' electrons contributing to the Pauli term. Therefore we can write

$$\chi_{\text{diam}} = (1 - x)\chi_{\text{diam}}(\text{Ag}^+) + x\chi_{\text{diam}}(\text{Se}^{2-}). \quad (9)$$

This term is shown along with susceptibility data for $\text{Ag}_{1-x}\text{Se}_x$ in figure 12. The values of χ_{diam} for Ag^+ and Se^{2-} are those given by Mendolsohn and Biggs (1970) and Angus (1932) respectively. Theoretically the Pauli susceptibility can be expressed (again in the absence of significant electron-electron interactions) as (Faber (1972), Ashcroft and Mermin (1976))

$$\chi \propto \int (N_+(E) - N_-(E))f(E) dE \quad (10)$$

where $N_+(E)$ and $N_-(E)$ are the density of states for spin up and spin down levels respectively and are given by

$$N_+(E) = N(E - \mu_B B) \quad (11)$$

and

$$N_-(E) = N(E + \mu_B B) \quad (12)$$

where $N(E)$ is the zero field density of states. Alternatively this may be written as

$$\chi \propto \int (f_+(E) - f_-(E))N(E) dE \quad (13)$$

where

$$f_{\pm}(E) = \frac{1}{\exp((E \pm \mu_B B - \mu)/k_B T) + 1}. \quad (14)$$

In the degenerate (metallic) regime these expressions reduce to the well known expression

$$\chi = \alpha \mu_B^2 N(\mu) \quad (15)$$

where α is a constant of order 1, which is introduced to approximate electron-electron effects. It also shows that χ should be essentially independent of temperature for liquid metals. Assuming the absence of electron localization and combining this with equation (4) the relationship between χ and σ is

$$\chi = \frac{a\mu_B^2\sigma^{1/2}}{\sqrt{A}} \quad (16)$$

Plotting χ against $\sqrt{\sigma}$ for many poor liquid metals and semiconductors has shown good agreement with this expression and this is often quoted as evidence in support of the RPA theory when discussing their behaviour, at least to the first approximation. A plot of this for $Ag_{1-x}Se_x$ is shown in figure 13. Again no particularly unusual deviation from the usual behaviour is observed, except for compositions close to stoichiometry corresponding to the anomaly in σ . Equation (15) is valid provided μ , the chemical potential, is greater than $\approx 2k_B T$ away from the band edge. As μ moves towards the band edge (as stoichiometry is approached) and into the gap in $N(E)$ then equation (13) must be numerically integrated to obtain χ . However it will show a steady decrease as μ moves towards the edge.

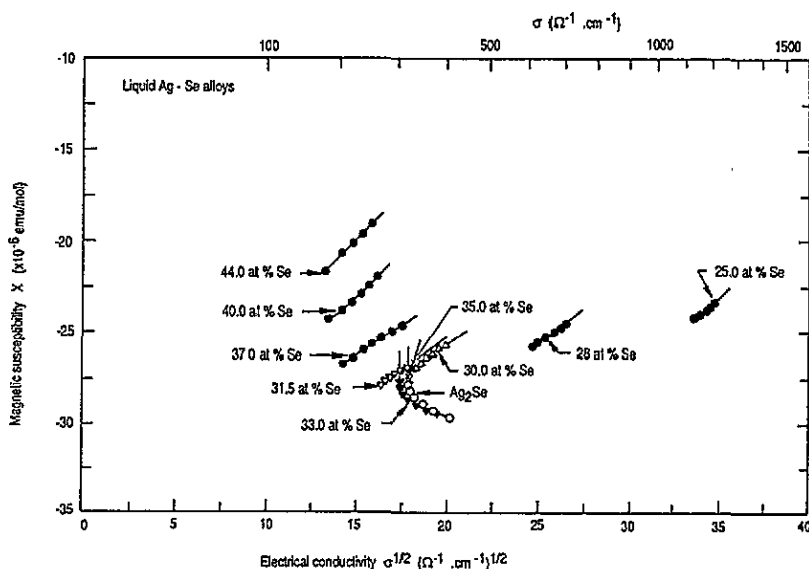


Figure 13. The graph of $\sqrt{\sigma}$ against χ for $Ag_{1-x}Se_x$.

In the non-degenerate (Boltzmann) limit, and assuming $\mu_B B \ll k_B T \ll \mu$, then for $N(E)$ with parabolic band edges given by

$$N(E) = a(E - E_c)^{1/2} \tag{17}$$

the relationship between χ and σ for unipolar conduction becomes

$$\chi = a\mu_B^2 \sigma \sqrt{\frac{\pi}{k_B T}} \tag{18}$$

This expression shows that χ is now essentially proportional to σ but also has a weak $1/\sqrt{T}$ temperature dependence.

At the stoichiometric composition Ag_2Se , and given that $\Delta E \approx 0$, the conduction will be bipolar with a contribution from both electrons and holes. It is not possible to give analytical results for the relationship between χ and σ in this region and so a full numerical integration of equations (1) and (13) must be carried out. In principle this requires a full knowledge of $N(E)$ as a function of composition and the relationship between $N(E)$ and $\sigma(E)$. At the current time this is not theoretically tractable. However the *general* behaviour

of σ , S and χ can be investigated using the simple model density of states and $\sigma(E)$ for a charge transfer liquid semiconductor given by Barnes (1993). This is based on a simple two band picture of complete charge transfer, with the valence band formed from the anion states and the conduction band by the cation states. The shape of $N(E)$ near the band edges is fixed as parabolic (as in equation (17)) with $\sigma(E)$ given by equation (6). Thus $\sigma(E)$ will have the generic form discussed extensively by Enderby and Barnes (1990). The only other parameters included are the widths of the valence and conduction bands which effectively determine the constant a in (17), and A . Using this model, μ , σ , S and χ have been calculated as a function of composition and temperature from the density of states and equations (1) and (2). The parameters and the method used are similar to those used by Barnes (1993) for modelling the properties of liquid Tl_2Te . Figure 14 shows the calculated curves of χ against $\sqrt{\sigma}$ for $\Delta E = 0$ at various compositions near stoichiometry using this model. Although the parameters chosen are rather arbitrary, the features observed are typical of the kind of behaviour expected for a system showing rigid band behaviour. It should be noted that the susceptibility shown here is only the Pauli contribution. In the metallic regime ($x < 0.32$, $x > 0.35$) the relationship between χ and $\sqrt{\sigma}$ is broadly linear over the temperature range considered (300–1500 K) but does not pass through the origin as predicted by equation (16). The reason is that although equation (16) is essentially correct, it does not account for the variation of μ with temperature. A better approximation (in which the temperature dependence of μ is included by approximating it through the Sommerfeld expansion) gives

$$\chi = \mu_b^2 a \sqrt{\frac{\sigma}{A}} \left(1 - \frac{1}{24} \left(\frac{\pi k_B T A}{\sigma} \right)^2 \right) \quad (19)$$

where the term in brackets is the correction to equation (16). This term can amount to a few percent for typical values of A at temperatures typical of liquid metals.

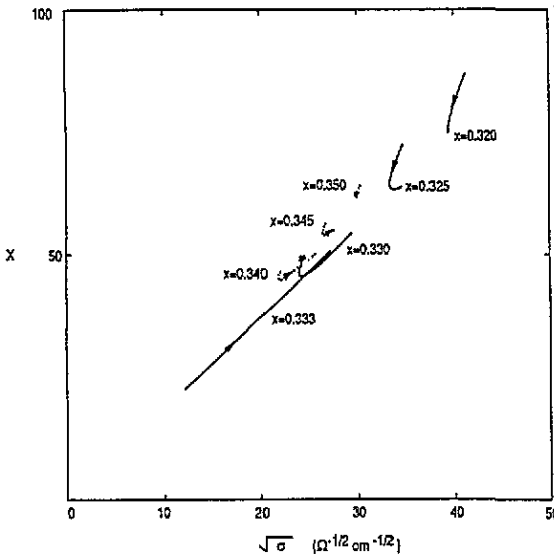


Figure 14. The behaviour of $\sqrt{\sigma}$ against χ for a typical 2:1 liquid semiconductor $A_{1-x}B_x$ with $\Delta(E) \simeq 0$. The solid line is for $0.320 \leq x \leq 0.333$ and the broken line $0.333 \leq x \leq 0.350$. The arrows indicate the direction of increasing temperature.

Approaching the semiconducting limit the behaviour predicted is unusual and shows a characteristic bending of the curves as the temperature changes. This has not been noted before and few studies of χ have been carried out on liquid semiconductors in this regime to test the prediction. The shape depends on the precise relationship between $N(E)$ and

$\sigma(E)$, but arises from the pronounced temperature dependence of μ when it is close to, or in, the energy gap (precisely the situation we expect for Ag_2Se near stoichiometry). The turn in the graph is a characteristic of the change from semiconducting behaviour at low T ($\Delta E \gg k_B T$) to metallic behaviour at high T ($\Delta E \ll k_B T$). For a large gap semiconductor (i.e. with $\Delta E \gg k_B T$ and μ mid-gap), χ exhibits a behaviour more characteristic of equation (18). Note however, that in reality this only occurs at the precise stoichiometric composition—minor deviations from it quickly push μ towards the band edges.

Although the curves in figure 14 broadly resemble the experimental data, the temperature dependence is incorrect. At the point where the conductivity begins to rise again, χ continues to decrease but very quickly starts to increase again along with σ . Experimentally it is found that as the temperature increases and σ decreases (for $0.3 \leq x \leq 0.333$), χ continues to increase. This effect cannot be reproduced for any model density of states using a rigid band picture. It is possible, within this model, to include the effects of electron localization by defining the mobility edges at some finite value of $N(E)$ (rather than $N(E) = 0$). However this does not change the conclusions for $\Delta E \simeq 0$ above. It therefore appears that the increase in σ with decreasing χ (corresponding to a decrease in $N(E)$) can only be explained by a rapidly increasing carrier mobility.

Glazov *et al* (1986) conducted a series of measurements of the conductivity and Hall effect of liquid Ag_2S , Ag_2Se and Ag_2Te , in both the solid and liquid phase. They derived the Hall mobility of the carriers from the measured σ and R_H for each system. The results obtained were $\mu_H = 1.5, 3.5$ and $0.21 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, if the conventional relationships between σ , R and μ_H are assumed. The fact that Ag_2Te has a carrier mobility an order of magnitude lower than Ag_2S and Ag_2Se is in agreement with the conclusion above, i.e. the carrier mobility is unusually high. Furthermore, from the experimental data it can be inferred that the corresponding mobilities at $T = 1400 \text{ K}$ for the three systems are approximately 0.2, 0.4 and $0.2 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. Thus at temperatures greater than a few hundred degrees above the liquidus the mobility has dropped by an order of magnitude in Ag_2S and Ag_2Se whereas for Ag_2Te it has remained essentially the constant. In their study of Ag_2Se Endo *et al* (1980) found that at approximately 1500 K the temperature coefficient for the conductivity becomes positive. Extrapolation of our data to these temperatures indicates that the peak in σ against x will disappear at about this temperature. It therefore appears that these materials become, in some sense 'conventional' for temperatures in excess of 1500 K.

In summary, an explanation for the behaviour of this system which is consistent with the observed conductivity and susceptibility data is that there is a considerably enhanced carrier mobility around the stoichiometric composition in Ag_2Se and Ag_2S . The reasons for its absence in Ag_2Te and its structural origin are unclear (see also Price *et al* 1993).

It would be interesting to carry out similar, careful studies of the relationship between σ and χ for a wider range of liquid semiconductors (those with $\Delta E > 0$) to observe if they show agreement with the predictions of the numerical calculations, or whether large variations in carrier mobilities are common in these materials near stoichiometric compositions.

5. Conclusions

Experimental measurements of the conductivity, thermopower and magnetic susceptibility of liquid $\text{Ag}_{1-x}\text{Se}_x$ have been carried out as a function of temperature and composition. The results not only confirm the previously observed negative temperature coefficient of the conductivity for the stoichiometric composition Ag_2Se but also show that this corresponds

to a local maximum in the conductivity versus composition graph (the only other case to our knowledge being $\text{Ag}_{1-x}\text{S}_x$). Attempts have been made to explain this property using a model density of states and $\sigma(E)$ for the system. It is shown that these data cannot be understood using standard transport theory using a rigid band picture for $\sigma(E)$. We have demonstrated by consideration of the conductivity and magnetic susceptibility data, that the observed properties are consistent with an enhanced carrier mobility around the stoichiometric composition, in agreement with the conductivity and Hall effect measurements by Glazov *et al* (1986) on the stoichiometric alloys. Similar measurements should now be carried out to confirm the rapid reduction in mobility away from stoichiometric compositions. At higher temperatures (above 1500 K) we conclude that Ag–Se shows properties more typical of other liquid semiconductors. At present, we do not have an explanation for the origin of this enhanced carrier mobility at stoichiometry—behaviour which is atypical of the majority of liquid semiconductors so far studied.

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