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The electrical and magnetic properties of molten AgCl–Ag₂S mixtures

S Ohno[†], A C Barnes[‡] and J E Enderby[‡]

[†] Niigata College of Pharmacy, Kamishin'eicho, Niigata, Japan

[‡] H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

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Abstract. The electrical conductivity σ , thermopower S and magnetic susceptibility χ of liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ have been measured as a function of c . It is found that σ decreases monotonically on addition of AgCl to Ag₂S and reaches a value typical of a molten salt when $c \sim 0.3$ at which point a semiconductor to molten salt transition takes place. The thermopower is negative for $c > 0.3$ at which composition it changes sign. The magnetic susceptibility measurements show a steady increase with c , consistent with the changes in the ionic diamagnetism and a significant Pauli contribution from the electrons for the Ag₂S rich compositions. The behaviour of the system is analysed and described in terms of a simple ionic band picture using a Kubo–Greenwood formalism in which the conductivity gap increases with increasing concentration of AgCl.

1. Introduction

The electrical conductivity of liquid AgCl–Ag₂S mixtures was first reported by Bell and Flengas (1964). However, there are some discrepancies in their measurement of the conductivity of the Ag₂S rich compositions which is probably due to problems associated with the high vapour pressure of sulphur in this system. Recently liquid Ag_{1-c}S_c alloys have been carefully studied (Ohno *et al* 1990). These results show that Ag₂S is a zero-gap liquid semiconductor with a highly unusual negative $d\sigma/dT$. From measurements of the thermopower it was deduced that the dominant transport mechanism is through electrons excited to the conduction band. In contrast liquid AgCl is a molten salt in which the dominant transport process is the motion of ions through the liquid. In this case the ionic transport is dominated by the Ag⁺ ions (AgCl is a good superionic conductor before it melts).

Liquid Ag₂S and AgCl are miscible in all proportions so that at some intermediate composition we expect to see evidence for a *metal–insulator* type transition taking place. In this paper we present results of detailed measurements of the electrical conductivity and thermopower of AgCl–Ag₂S mixtures in order to establish the point at which this transition takes place. In addition to these measurements, we have also carried out magnetic susceptibility measurements over the same range, in order to ascertain what is happening to the electronic density of states as this transition takes place. The data have been analysed using the Chester–Thellung–Kubo–Greenwood expressions for the electronic contribution in conjunction with the ionic diffusion picture for the molten salt.

2. Experimental procedures

The electrical conductivity and thermopower of liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ mixtures were measured simultaneously using a quartz cell (Ohno *et al* 1990). Electrodes of graphite were inserted into small tapered holes in the quartz cell and fastened by molybdenum bands. For the case of the AgCl rich compositions ($c \leq 0.4$) silver electrodes were used instead of graphite in order to avoid erroneous thermopower measurements due to the contact potentials between the liquid and the electrode. Molybdenum wires were attached to these in order to measure the conductivity and thermopower. The cell constant was determined by using liquid mercury at room temperature. The measurements were carried out in an argon atmosphere to prevent oxidation and vaporization of the sample. Any bubbles that formed in the sample during the course of the experiment were removed by agitating it with a silica rod. The temperature was measured using chromel–alumel (type K) thermocouples immediately above the electrodes.

The thermopower measurements were made using a ΔT method. A two-zone heater was used to maintain a given temperature difference across the sample. The voltage ΔE across the sample was measured using a digital voltmeter (Keithley 181) with a quoted precision of 10 nV. The measured value of $\Delta E/\Delta T$ gives the thermopower of the sample with respect to that of pure molybdenum. The value of the absolute thermopower was determined using the known thermopower of molybdenum quoted by Cusack and Kendall (1958).

Magnetic susceptibility measurements were made using the Faraday method. A field strength of approximately 10 kOe was used. A value of $H(dH/dx) = 9.1 \pm 0.3 \text{ kOe}^2 \text{ cm}^{-1}$ was produced using tapered pole pieces on the electromagnet. A standard sample of Mohr's salt ($\chi = 1.26 \times 10^{-2} \text{ emu mol}^{-1}$ at room temperature) was used to calibrate the balance. A master alloy of Ag_2S was produced using high-purity silver (99.999%) and sulphur (99.9%). Pure AgCl was purchased from Johnson Matthey plc. and Wako Pure Chemical Industries Ltd and used as received.

3. Experimental results

Figure 1 shows the electrical conductivity, σ , as a function of temperature for liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ mixtures with $c \geq 0.4$. The value of σ for liquid Ag_2S is in good agreement with that obtained by Ditman and Kulikova (1977). The conductivities of $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ with $c \geq 0.7$ decrease with increasing temperature in a similar way to that of pure Ag_2S . For mixtures with $c \leq 0.6$ the temperature coefficient of σ is positive. The values of σ for the AgCl rich mixtures are in good agreement with those reported by Bell and Flengas (1964).

Figure 2 shows the thermopower, S , as a function of temperature for liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ mixture with $c \geq 0.5$. Liquid Ag_2S has a negative value of S which gradually becomes more negative as AgCl is added and reaches its minimum at $c = 0.5$. Figure 3 shows S for the more AgCl rich compositions. The absolute value of the thermopower of liquid AgCl is in good agreement with that reported by Christy (1961). For all values of $c \lesssim 0.5$ S becomes more positive, crosses zero at $c \sim 0.3\text{--}0.4$ and becomes increasingly positive as the AgCl content increases.

Figure 4 shows the magnetic susceptibility χ as a function of temperature for liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$. Ag_2S has a large negative value of χ and a positive temperature coefficient $d\chi/dT$. The values of χ for liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ for $0.3 \leq c \leq 0.7$ decrease slightly at lower temperatures but then show a gradual increase with increasing

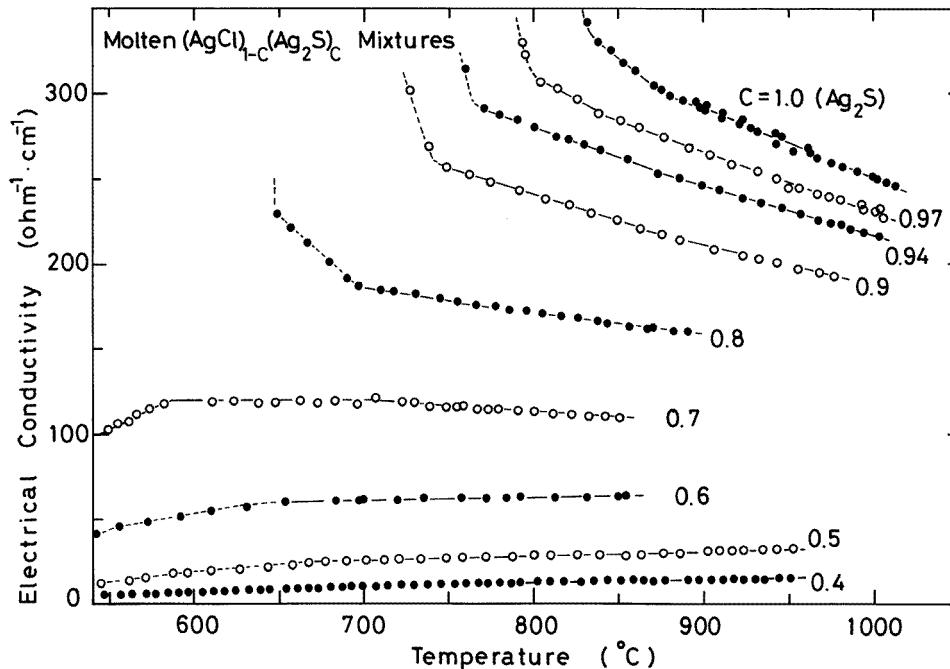


Figure 1. The electrical conductivity as a function of temperature of liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ for $c \geq 0.4$.

temperature. Molten AgCl on the other hand has a large negative value of χ and a small negative temperature dependence $d\chi/dT$.

As shown in figure 5 the value of σ decreases as AgCl is added to Ag₂S. The value of $(1/\sigma)d\sigma/dT$ is negative up until $c < 0.7$ and then becomes positive, reaching a maximum for $c = \sim 0.3$. For $c \leq 0.3$ $(1/\sigma)d\sigma/dT$ decreases but remains positive. The concentration dependence of S is shown in figure 6.

Figure 6 shows how the thermopower of liquid Ag₂S decreases gradually as AgCl is added. At $c = 0.5$ it reaches a minimum and then starts to become increasingly positive.

The value of χ changes smoothly with the addition of AgCl as shown in figure 7. This suggests that there is no ternary compound in this system, which would manifest itself as dip in χ as a function of composition. Figure 7 also shows $d\chi/dT$ at 850 °C. This is positive for all compositions above $c = 0.3$ but decreases as AgCl is added. The experimental value of χ for liquid AgCl is in good agreement with the value predicted from the core diamagnetism of Ag⁺ and Cl⁻ ($\chi_d = -65.0 \times 10^{-6}$ emu mol⁻¹; Angus 1932). The value of χ_d for (Ag⁺)₂S²⁻ is -116.9×10^{-6} emu mol⁻¹ which is much lower than the experimental value of χ (-89×10^{-6} emu mol⁻¹) indicating that there is a significant contribution to the susceptibility from the conduction electrons (Pauli susceptibility) in Ag₂S.

4. Discussion

An attempt to understand the electronic transport properties of liquid AgCl–Ag₂S is complicated as there are two processes that can contribute to the conductivity, namely the transport of electrons and the transport of ions in the liquid. The absence of any

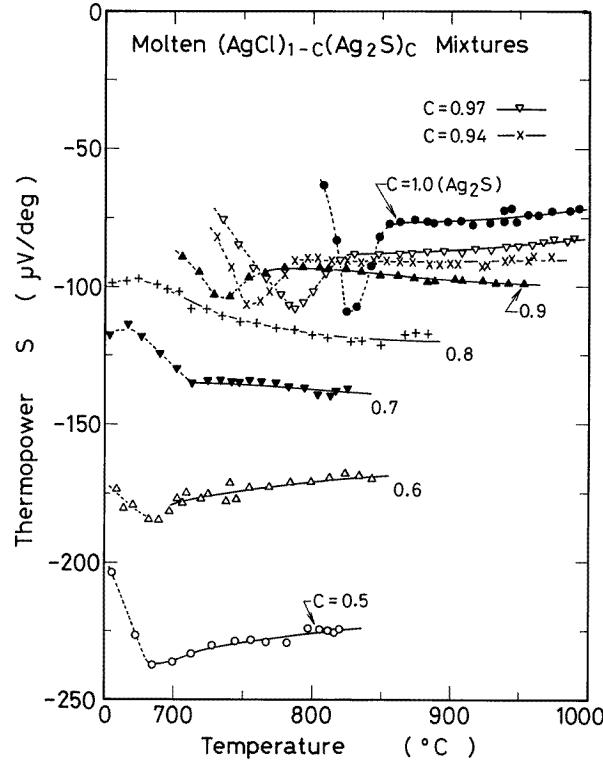


Figure 2. The thermopower as a function of temperature of liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ for $c \geq 0.5$.

Pauli paramagnetism in liquid AgCl is in agreement with the assertion that it is a molten salt whose conductivity is dominated by diffusive ionic motion. In contrast, for Ag_2S the significant difference between the susceptibility observed and that predicted from the atomic diamagnetism is in agreement with the conclusion that Ag_2S is a liquid semiconductor for which the dominant conduction mechanism is electronic in origin. The positive $d\chi/dT$ observed for $c > 0.3$ is consistent with the narrow definition of a liquid semiconductor (Enderby and Barnes 1990) in which the chemical potential lies within a deep pseudogap in the material. It also suggests that the transition between the two regimes occurs at approximately $c = 0.3$.

We will attempt to interpret the behaviour of liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ using a model that includes conduction from both electrons and ions. The electrical current densities in the liquid can be written as (Haga 1960)

$$j = j_e + j_i = \sigma_e(E + (Q_e/eT)\nabla T) + \sigma_i(E - (Q_i/eT)\nabla T) \quad (1)$$

where σ_e and σ_i are the conductivities due the electrons and the Ag^+ ions respectively. It is assumed that the conduction due to the S^{2-} ions can be neglected. Q_e/eT and Q_i/eT are the corresponding thermopowers. From this expression an attempt can be made to understand the properties of quasi-ionic liquid semiconductors as the transition from electronic to ionic conduction takes place.

In the absence of a temperature gradient ($\nabla T = 0$) equation (1) can be written as

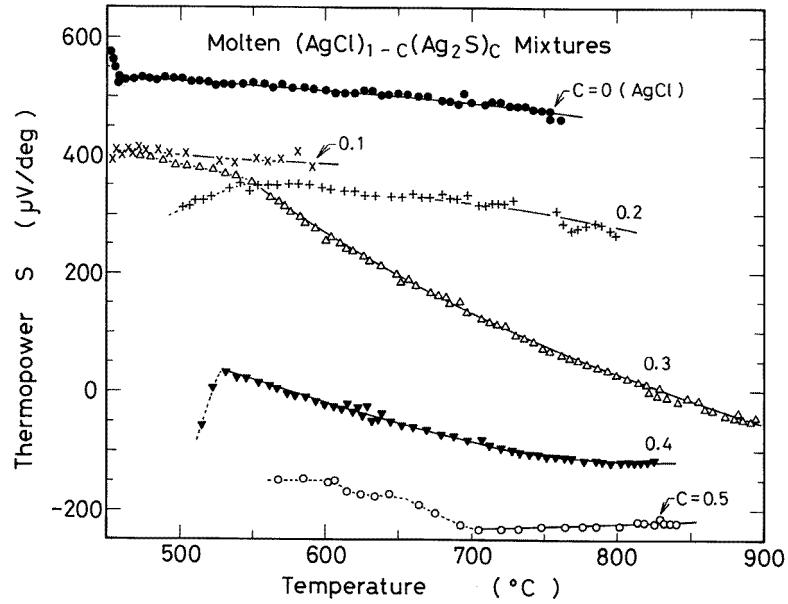


Figure 3. The thermopower as a function of temperature for liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ with $c \leq 0.5$.

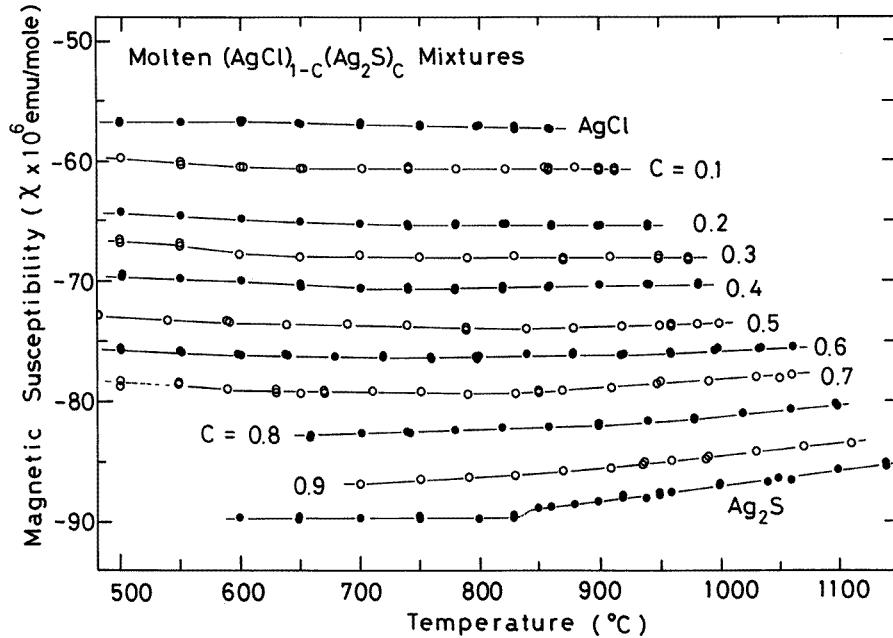


Figure 4. The magnetic susceptibility as function of temperature for $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$.

(Enderby and Barnes 1990, Haga 1960)

$$\sigma = \sigma_e + \sigma_i = - \int \sigma(E) \left(\frac{\partial f}{\partial E} \right) dE + \frac{n_i e^2 D_i}{kT} \quad (2)$$

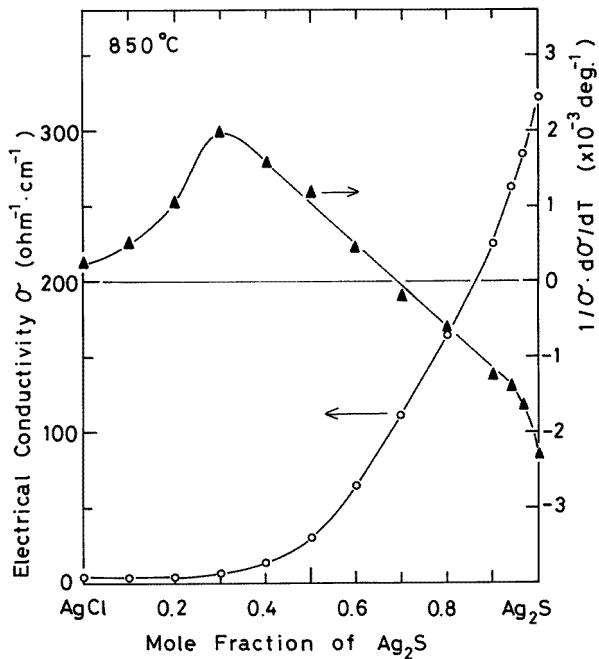


Figure 5. σ and $(1/\sigma)d\sigma/dT$ as functions of composition for $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$.

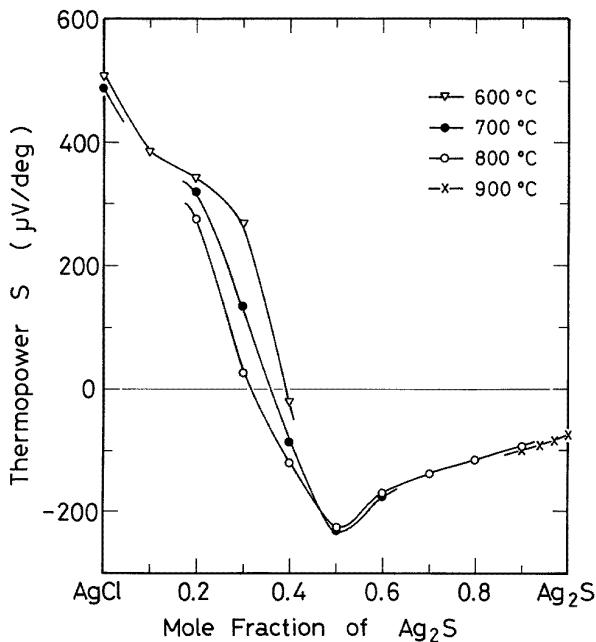


Figure 6. The thermopower S as a function of composition for $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$.

where $\sigma(E)$ is the energy dependent conductivity which determines the electronic processes and D_i and n_i are the diffusion coefficient and density of the ions respectively. Equation (2)

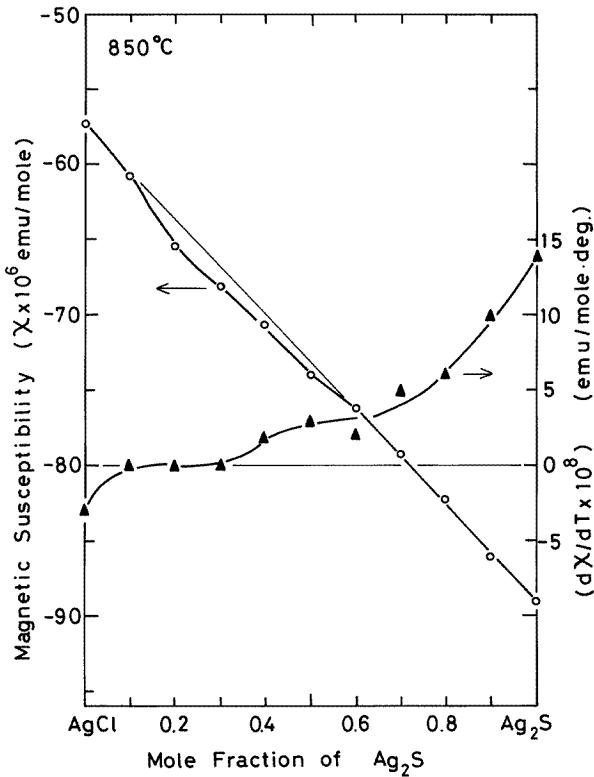


Figure 7. χ and $d\chi/dT$ as functions of composition for $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$.

assumes that the electrons are non-interacting (or can be approximated to the non-interacting case) and that the ionic conduction is described by the Nernst–Einstein equation (Hansen and Macdonald 1986). That is, there is no coupling between the diffusion of the Ag^+ and S^{2-} ions. The ionic conductivity due to the Ag^+ ions in AgCl rich mixtures (where σ_e is negligible) has been determined from the temperature dependence of σ by Bell and Flengas (1964). The ionic conductivity of Ag_2S was measured using the residual current technique by Endo *et al* (1980). From these results the ionic conductivity was found to be $\sim 5 \Omega^{-1} \text{ cm}^{-1}$ at 800°C for AgCl rich mixtures and $\sim 5 \Omega^{-1} \text{ cm}^{-1}$ for Ag_2S at the melting point.

In the absence of an applied electric field the thermopower can be written as

$$S = E/\nabla T = (\sigma_i/\sigma)Q_i/eT - (\sigma_e/\sigma)Q_e/eT \quad (3)$$

where Q_e is obtained from the Kubo–Greenwood expression as (Enderby and Barnes 1990)

$$Q_e \int \frac{\sigma(E)}{\sigma} (E - E_F) \left(\frac{\partial F}{\partial E} \right) dE \quad (4)$$

where E_F is the Fermi energy. A theoretical expression for Q_i has been derived by Howard and Liddiard (1957) and Haga (1960).

Equations (1) and (2) agree with the observation that the conductivity decreases smoothly as AgCl is added to Ag_2S until the limiting ionic conductivity of AgCl is reached. From the σ – x data, the point where the change from predominantly electronic to predominantly ionic conduction occurs is difficult to determine, but would appear to take place in the range

$0.2 < x < 0.4$ in agreement with the susceptibility data. The thermopower data also show a rapid change of sign in this region in agreement with the change from the negative charge carriers (electrons) in the Ag_2S rich region to the positive charge carriers (Ag^+ ions) in pure AgCl .

In practice, it is extremely difficult to calculate the precise effect of adding salt to a liquid semiconductor. As shown by Barnes (1993) the conductivity and thermopower of a liquid semiconductor are very sensitive to the position of the chemical potential μ , which in turn is strongly dependent on the precise shape of the density of states $N(E)$.

Despite these difficulties it is useful to carry out an analysis based on some simple assumptions that contain the essential physics. In terms of the model outlined by Enderby and Barnes (1990) and Barnes (1993) the addition of AgCl to Ag_2S could have three possible effects:

- (i) as AgCl is added the conductivity gap ΔE increases while α_c and α_v (the slope in $\sigma(E)$ at the conduction and valence band mobility edges respectively) remain constant;
- (ii) as AgCl is added α_c and α_v for the Ag_2S bands steadily decrease and reach zero for pure AgCl ;
- (iii) a combination of the first two effects occurs.

Figure 8 shows the results from an analytical calculation of σ and S using the Boltzmann approximation for a material with ΔE increasing from 0.2 to 1 eV with α_c and α_v fixed at 2400 and $930 \Omega^{-1} \text{cm}^{-1} \text{eV}^{-1}$ respectively (Ohno *et al* 1990). The ionic conductivity and thermopower are taken as $5 \Omega^{-1} \text{cm}^{-1}$ and $450 \mu\text{V K}^{-1}$ respectively. The chemical potential (μ) has been fixed at mid-gap. This approximation, although inapplicable for liquid Ag_2S (which has $\Delta E \sim 0$), should be reasonable for liquid $(\text{AgCl})_{1-c}(\text{Ag}_2\text{S})_c$ for $c \lesssim 0.6$. The results of the calculation are similar to the experimental results. The conductivity steadily decreases as ΔE increases, and levels off at a value corresponding to purely ionic conduction. This occurs somewhere in the region $0.6 < \Delta E < 0.8$. The thermopower starts negative (this is ensured when $\alpha_c > \alpha_v$), becomes increasingly positive as ΔE increases, and crosses zero for $\Delta E \sim 0.38$ eV. At this point the conductivity has reached a value of approximately $10 \Omega^{-1} \text{cm}^{-1}$, which corresponds to the point where the electronic contribution to the conductivity has become equal to the ionic contribution. As ΔE increases further, S increases until it reaches the value for the purely ionic conduction. This again occurs at $0.6 < \Delta E < 0.8$.

Similar calculations were carried out for the second model. The results give the same broad conclusion: the thermopower crosses zero when the ionic and electronic conductivities become equal.

The experimental results in the region $c > 0.6$ are more difficult to interpret. The results above imply that the thermopower becomes increasingly positive as the salt is added. The data, however show that S decreases at first (becomes more negative) and then starts to rise. In this regime the energy gap ΔE is still small and the Maxwell–Boltzmann approximation cannot be used. In this case it is not possible to predict the behaviour of the thermopower with composition using a simple analytical model. Previous calculations for liquid semiconductors in which the position of the chemical potential is calculated from a model density of states (Barnes 1993, Ohno *et al* 1994) have shown that this kind of behaviour can still be understood using a quasi-ionic model. However, in order to understand fully the system in this regime it is necessary to model the density of states as a function of c .

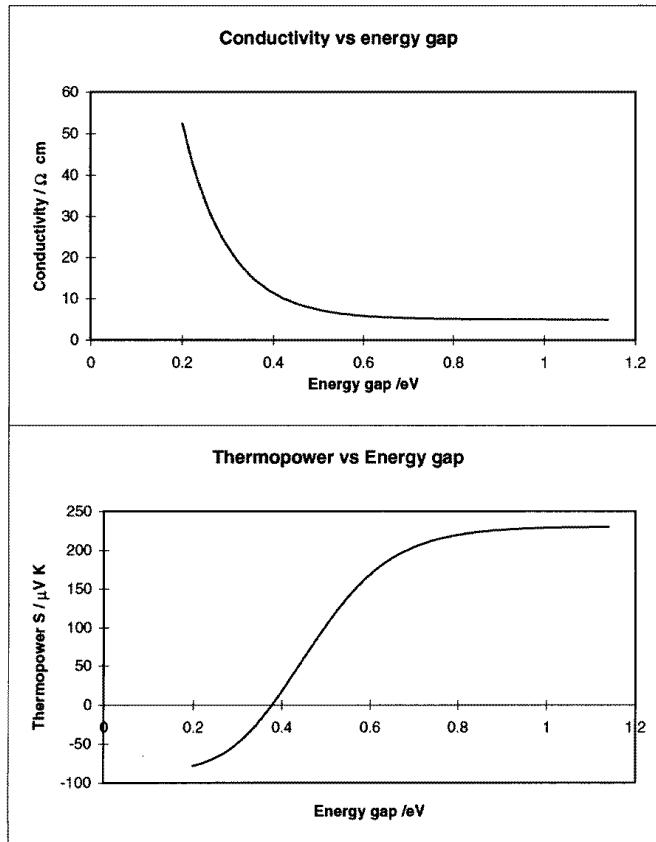


Figure 8. Calculations of the conductivity and thermopower in the Maxwell–Boltzmann limit for $0.2 < \Delta E < 1.0$ eV. The parameters used in the calculation are given in the text.

5. Conclusions

Experiments have been carried out to measure the electrical conductivity, thermopower and magnetic susceptibility of liquid $\text{AgCl}_{1-c}\text{Ag}_2\text{S}_c$ liquid alloys. The results show a steady decrease in the conductivity on the addition of AgCl to Ag₂S as the salt is added. Similarly the thermopower shows a change in sign from negative in pure Ag₂S to large and positive in pure AgCl. This is consistent with the change from predominantly electronic carriers in Ag₂S to the purely ionic carriers in AgCl. This transition is found to occur at $c \sim 0.3$. Simple calculations based on the Chester–Thellung–Kubo–Greenwood expressions in the Maxwell–Boltzmann approximation show that the behaviour of this mixture is fully consistent with a picture in which the conductivity gap ΔE increases steadily as AgCl is added.

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