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## The electrical properties of molten AgX–Ag<sub>2</sub>Se (X = Br, I) mixtures

S Ohno<sup>†</sup>, K Ishida<sup>†</sup>, M Togashi<sup>‡</sup>, A C Barnes<sup>§</sup> and J E Enderby<sup>§</sup>

<sup>†</sup> Niigata College of Pharmacy, Kamishin'eicho, Niigata 950-21, Japan

<sup>‡</sup> Niigata College of Technology, Kamishin'eicho, Niigata 950-21, Japan

<sup>§</sup> H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

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**Abstract.** The electrical conductivity,  $\sigma$ , and thermopower,  $S$ , of molten (AgX)<sub>1-c</sub>(Ag<sub>2</sub>Se)<sub>c</sub> mixtures (X = Br, I) have been measured as a function of temperature. The conductivity of the mixture is observed to decrease rapidly on the addition of AgX to Ag<sub>2</sub>Se and reaches a minimum on the AgX side. The thermopower on the Ag<sub>2</sub>Se side decreases gradually as the concentration of AgX increases until  $c = \sim 0.4$  at which point there is rapid change to large positive thermopowers. The value of  $S(+325 \mu\text{V K}^{-1}$  (AgBr),  $+420 \mu\text{V K}^{-1}$  (AgI)) on the AgX rich side decreases rapidly on addition of Ag<sub>2</sub>Se with the result that a minimum value of  $S(\sim -125 \mu\text{V K}^{-1})$  is observed at the composition  $c = \sim 0.4$  in both mixtures. A discussion of these results is presented in terms of the change from predominantly electronic transport in liquid Ag<sub>2</sub>Se to the predominantly ionic transport in AgX. The increasing importance of the contribution of the inhomogeneous thermopower to the total thermopower of the salt rich compositions is also discussed. The decrease in the electronic conductivity with composition for  $c \geq 0.6$  is analysed in terms of the Kubo–Greenwood equations.

### 1. Introduction

In recent years the electrical properties of liquid AgCl–Ag<sub>2</sub>Y (Y = S, Te) have been carefully studied and the results interpreted in terms of a simple theoretical model (Ohno *et al* 1996, 1999). In these systems the electrical conductivity is observed to decrease very rapidly on the addition of AgCl to Ag<sub>2</sub>Y. This rapid decrease in the conductivity corresponds to an increase in the conductivity gap  $\Delta E$  and/or a decrease in the slope  $\alpha_c$  and  $\alpha_v$  of the energy dependent conductivity  $\sigma(E)$  (Enderby and Barnes 1990) as the halide is added. The thermopower decreases on the addition of Ag<sub>2</sub>Y to molten AgCl and a p–n transition occurs close to the composition  $c = 0.3$  of Ag<sub>2</sub>Y where  $\sigma \sim 7 \Omega^{-1} \text{cm}^{-1}$ . The p–n transition in these mixtures appears to coincide broadly with the transition from predominantly electronic conduction to predominantly ionic conduction.

According to Enderby and Barnes (1990) liquid Ag<sub>2</sub>Se and liquid Ag<sub>2</sub>S are zero gap liquid semiconductors with a highly unusual negative temperature derivative of the conductivity  $d\sigma/dT$ . In contrast, liquid Ag<sub>2</sub>Te has a much smaller value of  $\sigma$  and more conventional positive  $d\sigma/dT$ . The region of low  $\sigma$  and negative  $d\sigma/dT$  exists for a narrow range of composition for the liquid Ag<sub>2</sub>Se and Ag<sub>2</sub>S systems ( $0.32 \leq c \leq 0.35$ ). On the addition of AgCl to both Ag<sub>2</sub>Se and Ag<sub>2</sub>S the negative value of  $d\sigma/dT$  is observed to remain until the concentration of AgCl reaches approximately 30% (Ohno *et al* 1998).

AgI and the silver chalcogenides (Ag<sub>2</sub>S, Ag<sub>2</sub>Se and Ag<sub>2</sub>Te) are solids that become superionic conductors at moderate temperatures (400–500 K). In all cases the high ionic

conductivity in the superionic phase is due to the diffusion of  $\text{Ag}^+$  ions through the crystal. It is believed that this high silver mobility extends into the liquid region and gives rise to some of the unusual properties noted above (Ohno *et al* 1994). In contrast  $\text{AgCl}$  and  $\text{AgBr}$  both have cubic crystal structures all the way to the melting temperature. Molten  $\text{AgCl}$  and  $\text{AgBr}$  have a value of  $\sigma$  ( $3\text{--}4 \Omega^{-1} \text{cm}^{-1}$ ) that is comparable to  $\text{AgI}$  in the superionic and liquid phase.

In this paper we report results concerning the electrical properties of the mixtures  $\text{AgBr}\text{--}\text{Ag}_2\text{Se}$  and  $\text{AgI}\text{--}\text{Ag}_2\text{Se}$ . We then attempt to understand the complex behaviour of these materials in terms of changes in the underlying conduction mechanism as the material changes from an electronic to an ionic conductor.

## 2. Experimental procedure

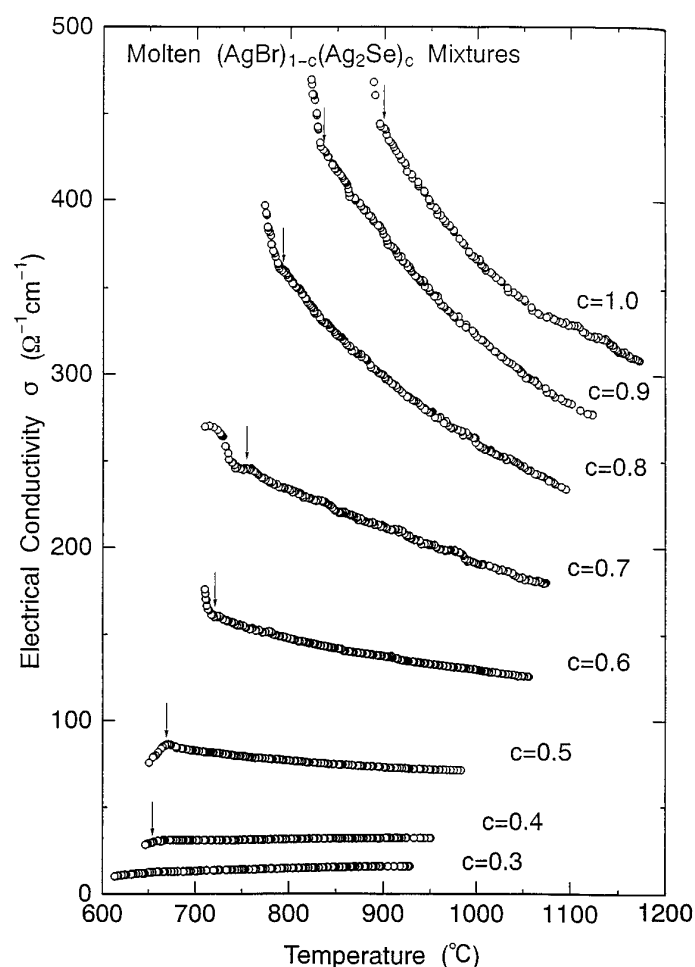
Conductivity and thermopower measurements on  $\text{Ag}_2\text{Se}$  rich mixtures of  $\text{Ag}_2\text{Se}\text{--}\text{AgBr}$  and  $\text{Ag}_2\text{Se}\text{--}\text{AgI}$  were made simultaneously using a quartz cell system as previously reported by Ohno *et al* (1996). Four graphite electrodes were inserted into small tapered holes in the quartz tube and electrical contact made by clamping molybdenum bands to them. External connections to the cell were made using molybdenum wires directly attached to these molybdenum bands. The cell constant was determined by reference to high purity mercury at room temperature. In order to prevent oxidation and evaporation of the sample all the measurements were carried out in an atmosphere of high purity argon. Any bubbles that formed during the measurements were removed by agitating the sample with a thin silica rod. The temperature of each electrode was measured using a type K (chromel–alumel) thermocouple attached to the molybdenum band immediately above the graphite electrode.

The thermopower measurements were made using the  $\Delta T$  method as outlined by Ohno *et al* (1998). For the halide rich samples the data was collected using silver electrodes in place of graphite in order to avoid erroneous thermopower measurements due to the contact potentials between the electrode and the liquid. Accurate control of the temperature difference between the two electrodes was obtained by using a two zone furnace. The voltage between the electrodes  $\Delta E_M$  was measured using a high impedance digital voltmeter with an accuracy of 10 nV. The value of  $\Delta E_M/\Delta T$  gives a measure of the thermopower of the sample with respect to that of molybdenum. The absolute thermopower was determined by subtracting the values of the thermopower of molybdenum as given by Cusack and Kendal (1958). A master alloy of  $\text{Ag}_2\text{Se}$  was prepared by mixing elemental Ag (99.999%) and Se (99.99%) of the appropriate mass in a sealed and evacuated silica tube that was heated in a furnace at a temperature in excess of 1400 K for 24 hours. Pure  $\text{AgBr}$  and  $\text{AgI}$  were purchased from Wako Pure Chemical Industries Ltd.

## 3. Experimental results

Figure 1 shows  $\sigma$  as a function of temperature for molten  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  for  $c \geq 0.3$ . The value of  $\sigma$  of liquid  $\text{Ag}_2\text{Se}$  is in good agreement with that obtained by Endo *et al* (1980). The value of  $(1/\sigma)(d\sigma/dT)$  for pure  $\text{Ag}_2\text{Se}$  was found to be  $-2.0 \times 10^{-3} \text{K}^{-1}$  immediately above the melting temperature.  $(1/\sigma)(d\sigma/dT)$  remained negative for all concentrations of  $c \geq 0.5$  and became positive for  $c \leq 0.4$ . The value of  $\sigma$  of molten  $\text{Ag}_3\text{SeBr}$  was found to be  $80 \Omega^{-1} \text{cm}^{-1}$  at the melting point.

Figure 2 shows  $\sigma$  as a function of temperature for molten  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  for  $c \geq 0.4$ . In this case  $(1/\sigma)(d\sigma/dT)$  becomes positive when  $c \leq 0.6$ . The value of  $\sigma$  of molten  $\text{Ag}_3\text{SeI}$  was found to be  $25 \Omega^{-1} \text{cm}^{-1}$  at the melting point. The values of  $\sigma$  for  $\text{AgBr}$  and  $\text{AgI}$  were found

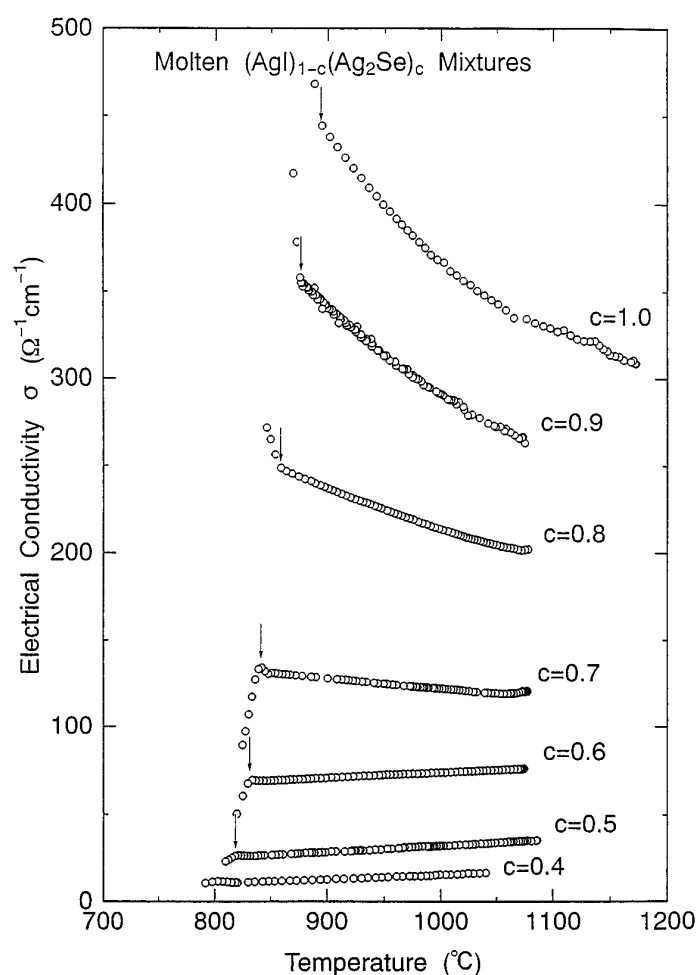


**Figure 1.** The electrical conductivity of liquid  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  as function of temperature for  $0.3 \leq c \leq 1.0$ . The arrows indicate the melting point of the mixture.

to be  $2.9 \Omega^{-1} \text{cm}^{-1}$  and  $2.4 \Omega^{-1} \text{cm}^{-1}$  at the melting point respectively—in good agreement with the results reported by Harrap and Heymann (1955) and Kvist and Josefson (1968).

Figure 3 shows the thermopower,  $S$ , as a function of temperature for  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  mixtures with  $c \leq 0.6$ . The convention for the measurement of  $S$  is that given according to Mott and Jones (1936) where the hotter molybdenum wire is connected to the positive terminal of the digital voltmeter. With this definition the thermopower of liquid AgBr was found to be  $+475 \mu\text{V K}^{-1}$  at the melting point. As  $c$  approaches 0.2 the thermopower of the mixtures shows a very strong temperature dependence such that it tends to decrease rapidly towards zero. Indeed, for  $c = 0.2$  the mixture has a thermopower of  $\sim +400 \mu\text{V K}^{-1}$  at the melting point ( $450^\circ\text{C}$ ) yet undergoes a p–n transition at  $\sim 800^\circ\text{C}$ . For  $0.3 \leq c \leq 0.6$   $S$  is typically  $\sim -100 \mu\text{V K}^{-1}$  at the melting point.

Figure 4 shows the thermopower of  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  for  $c \geq 0.7$ . In this case the data were collected using graphite electrodes. For all compositions in this range  $S$  was found to be negative with a gradual increase towards zero as the temperature increases.

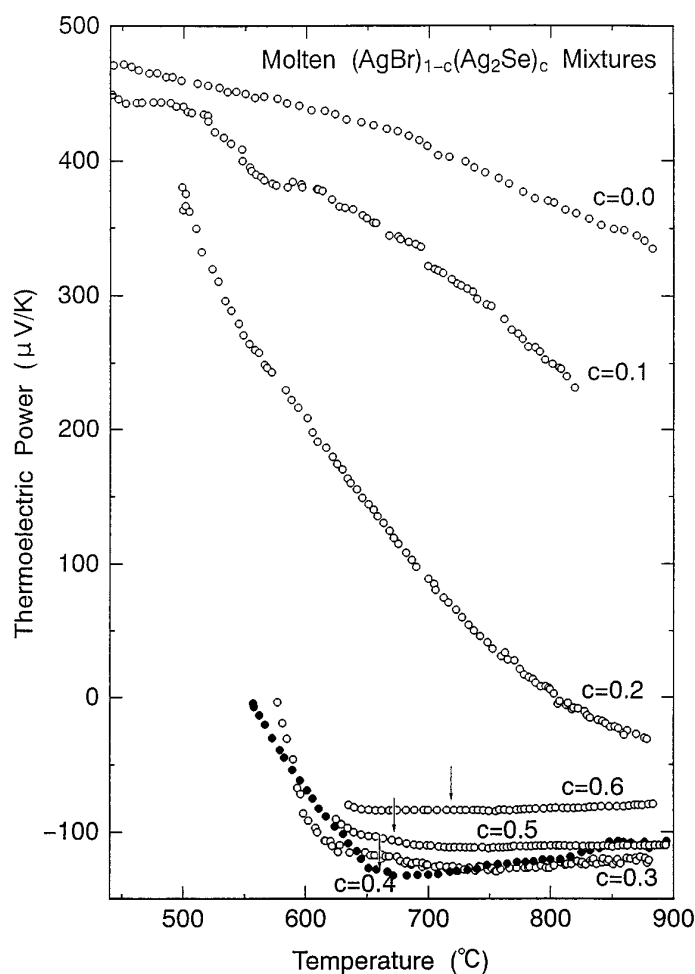


**Figure 2.** The electrical conductivity of liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  as function of temperature for  $0.4 \leq c \leq 1.0$ . The arrows indicate the melting point of the mixture.

Figure 5 shows the thermopower as a function of temperature for liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  mixtures for  $c \leq 0.6$ . The thermopower of pure liquid AgI just above the melting point was found to be  $+486 \mu\text{V K}^{-1}$  with a slight decrease with increasing temperature. For  $0.2 \leq c \leq 0.3$  the thermopower shows a rapid decrease in temperature similar to that observed in  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  mixtures. For  $0.4 \leq c \leq 0.6$  the thermopower is  $-100 \mu\text{V K}^{-1}$  just above the melting point.

Figure 6 shows the thermopower as a function of temperature for molten  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  mixtures with  $c \geq 0.7$ . In this case the data were collected using graphite electrodes. The behaviour of the thermopower in this region is very similar to the  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  mixtures.

Figure 7 shows the composition dependence of  $\sigma$  for the liquid  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$ ,  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  and  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$  (Ohno *et al* 1998) mixtures at  $900^\circ\text{C}$ . In all three cases  $\sigma$  decreases rapidly as the halide is added to  $\text{Ag}_2\text{Se}$ . The behaviours of AgCl and AgBr are very similar whereas AgI causes  $\sigma$  to decrease much more rapidly as a function of halide concentration. This is perhaps linked to the existence of the solid state ternary compound



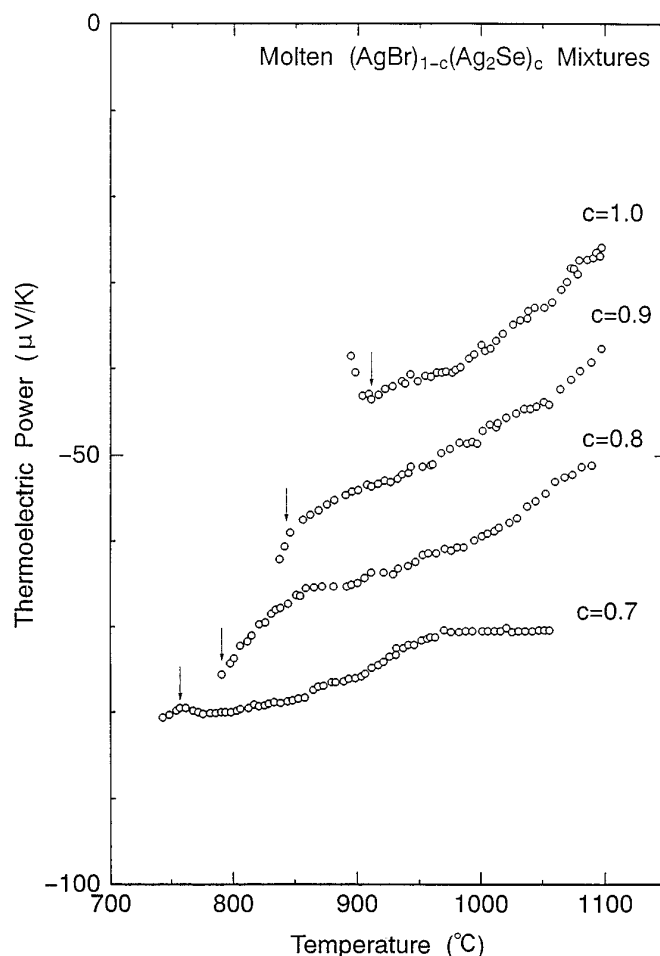
**Figure 3.** The thermopower of liquid  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  as function of temperature for  $0.0 \leq c \leq 0.6$ . The arrows indicate the melting point of the mixture.

$\text{Ag}_3\text{SeI}$  that has no analogue in the  $\text{AgCl}-\text{Ag}_2\text{Se}$  and  $\text{AgBr}-\text{Ag}_2\text{Se}$  mixtures (Blachnik and Kudermann 1973).

Figure 8 shows the composition dependence of  $S$  for liquid  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$ ,  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  and  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$  (Ohno *et al* 1998) mixtures at  $900^\circ\text{C}$ . In all cases  $S$  rapidly decreases from a large and positive thermopower ( $c = 0$ ) to reach a minimum negative value at  $c \sim 0.4, 0.3$  and  $0.5$  for  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$ ,  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  and  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  respectively. In all cases a p–n transition in  $S$  occurs at a composition that corresponds to a conductivity of between  $5.4$  and  $8.3 \Omega^{-1} \text{cm}^{-1}$ .

#### 4. Discussion

Pure liquid  $\text{Ag}_2\text{Se}$  has a conductivity of  $440 \Omega^{-1} \text{cm}^{-1}$  at a temperature of  $900^\circ\text{C}$ . By analysing the magnitude of the conductivity and the thermoelectric power Enderby and Barnes (1990) concluded that it was a liquid semiconductor with an energy gap of  $0 \text{ eV}$ . It also shows a

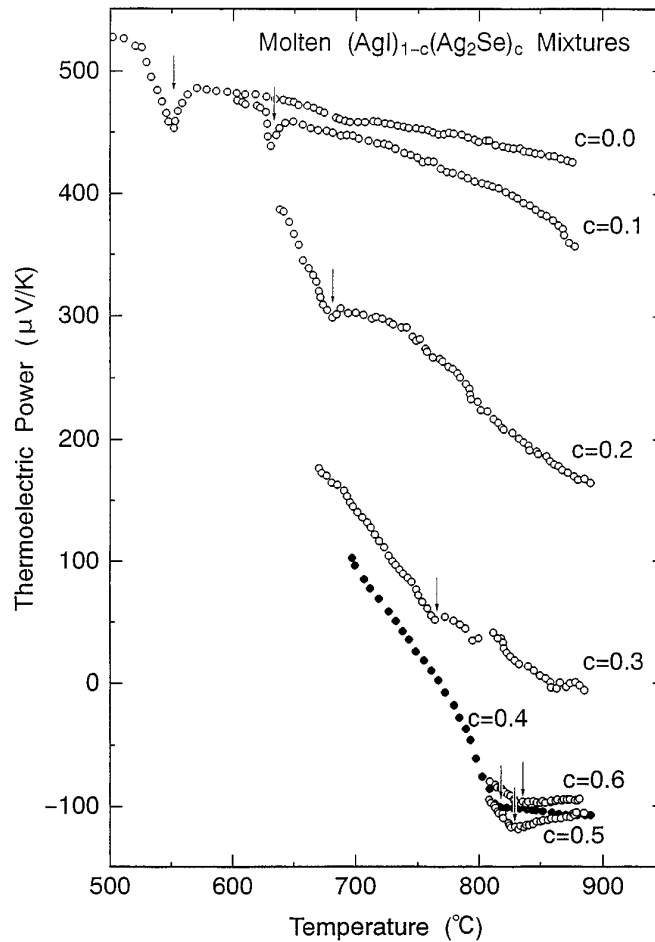


**Figure 4.** The thermopower of liquid  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  as function of temperature for  $0.7 \leq c \leq 1.0$ . The arrows indicate the melting point of the mixture.

particularly unusual increase in its conductivity as a function of composition at stoichiometry—a property that is believed to be due to an increase in carrier mobility due to the increased local order at stoichiometry (Ohno *et al* 1994). The predominant current carrying mechanism is by electrons and holes although an ionic conductivity of  $5 \Omega^{-1} \text{cm}^{-1}$  has been reported by Endo *et al* (1980) using the residual potential method. In contrast the molten halides show purely ionic conduction in which the silver ions carry most of the current. In this work the conductivities of molten AgCl, AgBr and AgI were found to be 3.9, 2.9 and  $2.4 \Omega^{-1} \text{cm}^{-1}$  respectively at their melting points. Their ionic conductivities show a weak temperature dependence that is attributed to the very low activation energies needed for the silver ions to move through the liquid.

In order to discuss the electronic properties of these AgX–Ag<sub>2</sub>Se mixtures we will break down the discussion into three parts:

- (i) the region where electronic conduction is dominant (the Ag<sub>2</sub>Se rich region);
- (ii) the region where ionic conduction is dominant;



**Figure 5.** The thermopower of liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  as function of temperature for  $0.0 \leq c \leq 0.6$ . The arrows indicate the melting point of the mixture.

- (iii) the region where the transition from predominantly electronic to predominantly ionic conduction takes place.

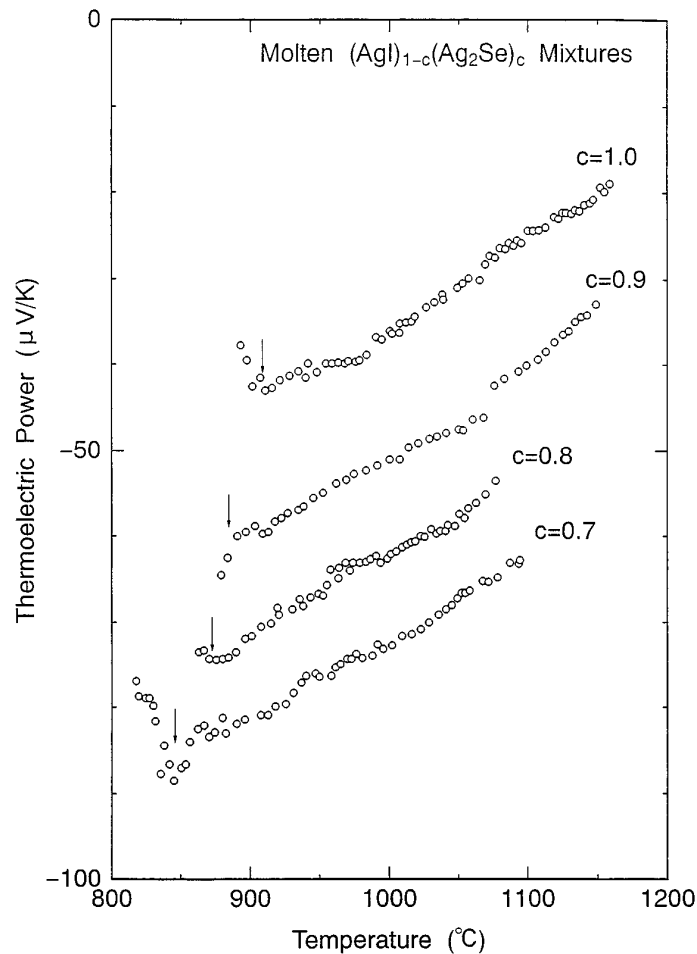
#### 4.1. Electronic conduction in the $\text{Ag}_2\text{Se}$ rich regime

On the addition of a silver halide to molten  $\text{Ag}_2\text{Se}$  the conductivity is immediately seen to decrease. In terms of the model for liquid semiconductors proposed by Enderby and Barnes (1990) this is due to one of three possibilities:

- (i) As the silver halide is added the conductivity gap  $\Delta E$  increases while  $\alpha_v$  and  $\alpha_c$  (that depend on density of electronic states  $N(E)$  at the band edges) remain constant.
- (ii) As the silver halide is added the values of  $\alpha_v$  and  $\alpha_c$  steadily decrease as  $N(E)$  near the band edges decreases.
- (iii) A combination of the two processes above.

In practice it is difficult to calculate precisely the effect of adding the salt to the semiconductor as the conductivity and thermopower are very sensitive to the value of the

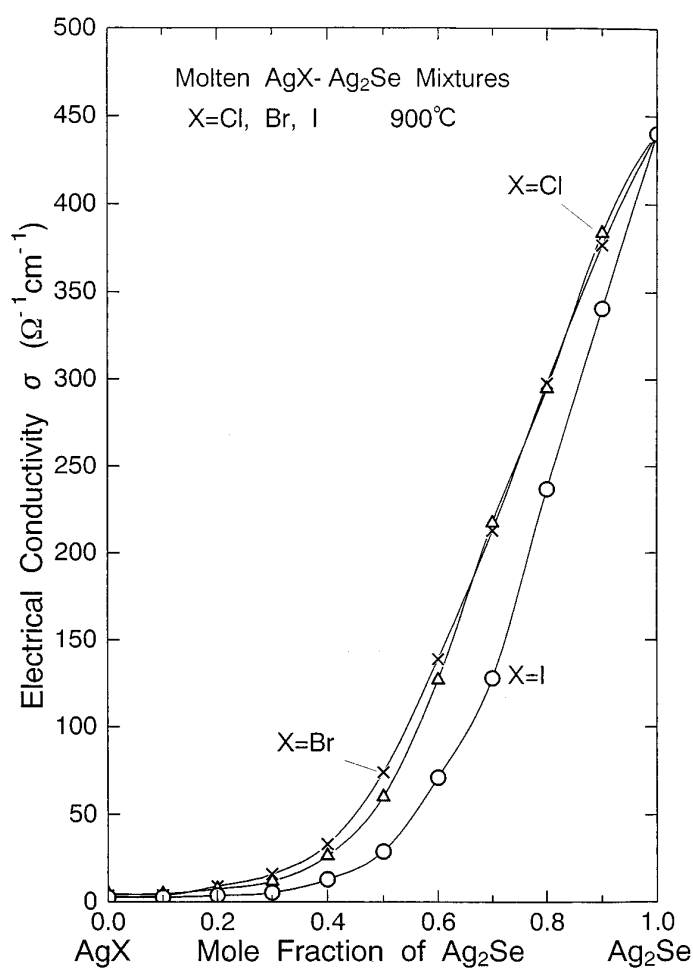




**Figure 6.** The thermopower of liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  as function of temperature for  $0.7 \leq c \leq 1.0$ . The arrows indicate the melting point of the mixture.

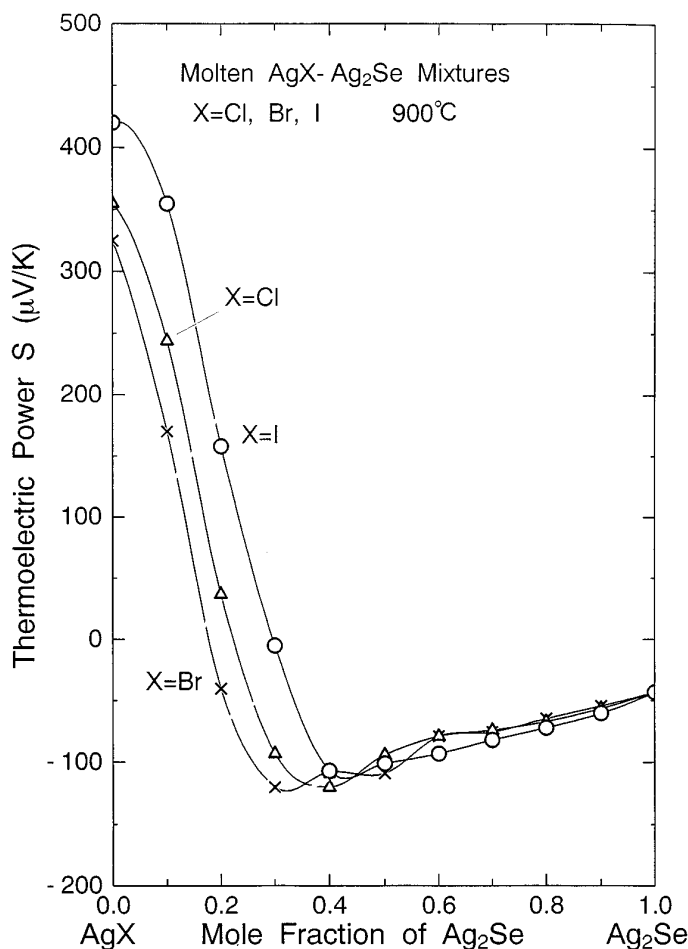
chemical potential  $\mu$  of the system (Barnes 1993) and to the relationship between  $N(E)$  and the energy dependent conductivity  $\sigma(E)$ . The value of the chemical potential is itself sensitive to the precise form of the density of states  $N(E)$  near the band edges. The form of  $N(E)$  is strongly dependent on the nature of the bonding and interactions in the material and is theoretically difficult to calculate precisely. However, by using a simple rigid band ionic model of the density of states it is possible to calculate the *trends* in  $\sigma$  and  $S$  as the halide is added. We carried this out using a similar method to that used in by Barnes (1993) to calculate the composition dependence of  $\sigma$  and  $S$  for liquid  $\text{Tl}_2\text{Se}$ .  $\sigma$  and  $S$  are calculated by determining the value of the chemical potential in the model and using the random phase approximation to determine  $\sigma(E)$  and hence  $\sigma$  and  $S$  via the Kubo–Greenwood relations.

Figure 9 shows a calculation of the composition dependence of  $\sigma$  and  $S$  using two different assumptions. The initial density of states of  $\text{Ag}_2\text{Se}$  has been determined to match closely the values of  $\sigma$  and  $S$  for pure  $\text{Ag}_2\text{Se}$  in a similar way as for  $\text{Tl}_2\text{Se}$  as described by Barnes (1993) and is shown schematically in figure 10(a).



**Figure 7.** The composition dependence of the conductivity of liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  (circles),  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  (crosses) and  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$  (triangles) at  $900^\circ\text{C}$ .

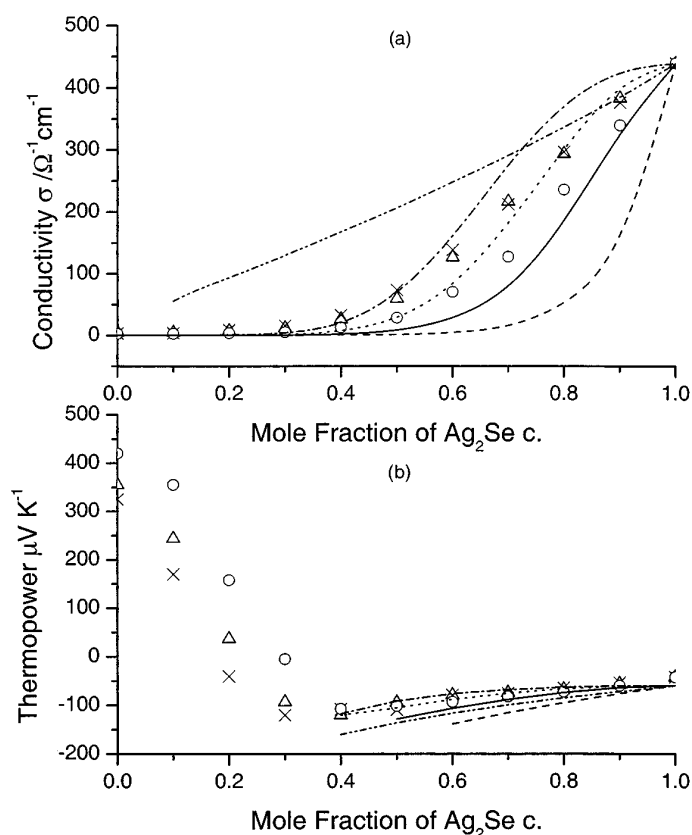
- Case 1.** The shape of the density of states  $N(E)$ , and hence the values of  $\alpha_v$  and  $\alpha_c$  (calculated using the random phase approximation) have been kept constant but the energy gap  $\Delta E$  has been increased according to the relation  $\Delta E = 2.5c^n$  eV. This corresponds to a change of  $\Delta E$  from 0 eV for pure  $\text{Ag}_2\text{Se}$  to 2.5 eV typical of a molten silver halide (cf the band gaps for the solid halides, 3.0, 2.5 and 2.4 eV for  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  respectively (Victoria 1997)). Figure 9 shows the comparison of this model for  $n = 1.0, 1.5, 2.0$  and  $2.5$  with the data for the mixtures. The trends in the data are reasonably well reproduced for values of  $n$  between 1.5 and 2.0.
- Case 2.** The density of states  $N(E)$  is modelled as a simple linear combination of the model density of states of  $\text{Ag}_2\text{Se}$  as in case 1, and a model density of states of the silver halide that has a gap of 2.5 eV. In this case the values of  $\alpha_c$  and  $\alpha_v$  have been calculated using the random phase approximation as outlined by Barnes (1993) and will decrease in size as the concentration of the halide increases. In this case the energy gap  $\Delta E$  remains at 0 eV and  $\alpha_v$  and  $\alpha_c$  are calculated from  $N(E)$  using the random phase approximation. A



**Figure 8.** The composition dependence of the thermopower of liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  (circles),  $(\text{AgBr})_{1-c}(\text{Ag}_2\text{Se})_c$  (crosses) and  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$  (triangles) at 900 °C.

schematic diagram of this model density of states and its change with halide concentration is shown in figure 10(b). In this model the conduction band, that we consider as arising from the Ag 5s states, is assumed to have the same width and position for both  $\text{Ag}_2\text{Se}$  and  $\text{AgX}$ . In this case  $\alpha_c$  remains essentially constant but there is a steady decrease in  $\alpha_v$  as the salt is added. The conductivity and thermopower of the mixture using this model are also shown in figure 9. In contrast to case 1,  $\sigma$  decreases more slowly than experimentally observed and still remains large at the point where the experimental  $\sigma$  is clearly dominated by the ionic contribution. As in case 1, the magnitude of the thermopower shows a steady but small increase on the addition of the halide.

The result of these model calculations suggests the most important effect of adding the salt is to increase the size of the energy gap  $\Delta E$  in the liquid. At low halide concentration the increase in  $\Delta E$  is relatively slow and then accelerates as the concentration is increased. Surprisingly,  $\text{AgBr}$  and  $\text{AgCl}$  reduce the conductivity of  $\text{Ag}_2\text{Se}$  less slowly than  $\text{AgI}$  despite their having larger band gaps. A model in which the effect of the halide is to reduce  $N(E)$  (and hence  $\alpha_v$  and  $\alpha_c$ ) at the band edges while  $\Delta E$  remains near zero does not produce a



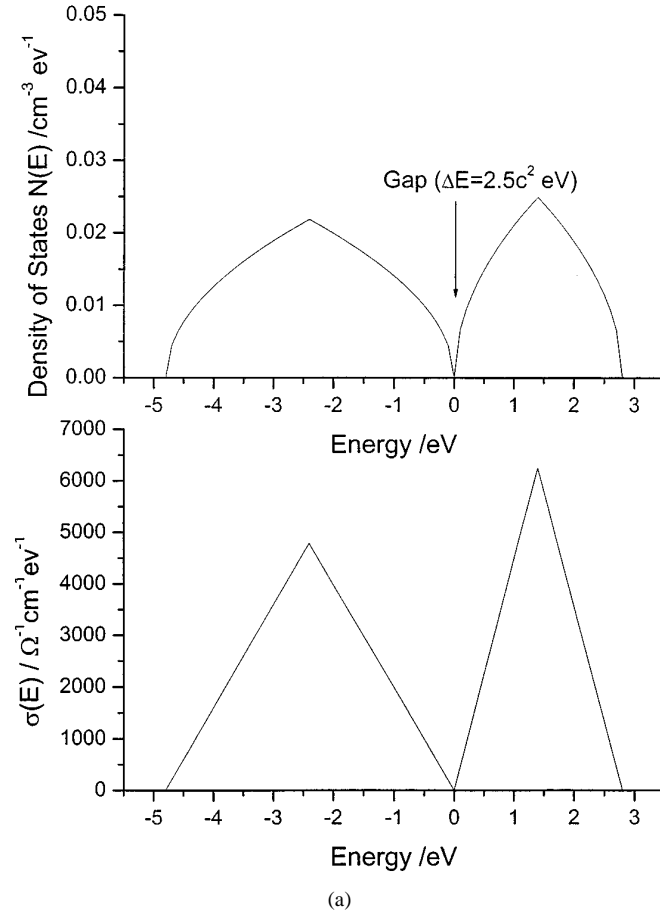
**Figure 9.** A comparison of the composition dependence of (a) the conductivity and (b) the thermopower of liquid (AgI)<sub>1-c</sub>(Ag<sub>2</sub>Se)<sub>c</sub> (circles), (AgBr)<sub>1-c</sub>(Ag<sub>2</sub>Se)<sub>c</sub> (crosses) and (AgCl)<sub>1-c</sub>(Ag<sub>2</sub>Se)<sub>c</sub> (triangles) at 900 °C and model calculations based on a conductivity gap that increases according to  $\Delta E = 2.5c^n$  for  $n = 1.0$  (dashed line),  $n = 1.5$  (solid line),  $n = 2.0$  (dotted line) and  $n = 2.5$  (dot-dashed line). The two dot-dashed line corresponds to the case when  $\Delta E$  remains at 0.0 eV but  $N(E)$  is reduced at the band edges as AgCl is added.

sufficiently rapid decrease in  $\sigma$ , in comparison with the experimental data with increasing halide concentration.

#### 4.2. Ionic conduction in the halide rich regime.

For the pure halide the conduction process is due to the diffusion of ions through the liquid. In all cases the conduction due to the Ag<sup>+</sup> ions is much higher than that of the halide ions. In this case the ionic conductivity  $\sigma_i$  can be described in terms of the Nernst–Einstein equation (Hansen and Macdonald 1986). In contrast the thermopower of a molten salt is more difficult to treat theoretically and more difficult to measure experimentally because of the problems of avoiding false readings due to unwanted electrode potentials and polarization effects. The experimental thermopower measurements on the halide rich samples were all made using silver electrodes in order to minimize these experimental difficulties. The electrical conductivity, neglecting the effects of cross-correlations between ions (March and Tosi 1984), can be written as

$$\sigma = \frac{n^+ e^2 D^+}{kT} + \frac{n^- e^2 D^-}{kT} = \sigma_+ + \sigma_- \quad (1)$$



**Figure 10.** Schematics of the model density of states  $N(E)$  and energy dependent conductivity  $\sigma(E)$  used to calculate the curves shown in figure 9. (a) and (b) correspond to case 1 ( $\Delta E$  steadily increasing) and case 2 ( $N(E)$  at the band edges reduces as  $\Delta E$  stays constant) as described in section 4.1.

where  $n^+$  and  $n^-$  are the number densities of the positive and negative ions respectively, and  $D^+$  and  $D^-$  are their associated diffusion constants. This relation typically gives molten salt conductivities in the range 1–10  $\Omega^{-1} \text{ cm}^{-1}$ . In this regime the temperature dependence of the ionic conductivity is directly related to the temperature dependence of the diffusion coefficients  $D^+$  and  $D^-$ .

The thermopower of a molten salt is more difficult to treat theoretically. For a sample that is subject to a temperature gradient we can write the current densities for the positive and negative ions as

$$j_+ = eD^+ \left( \frac{n^+ eE}{kT} - \frac{\partial n^+}{\partial x} - \frac{n^+ Q^+}{kT^2} \frac{\partial T}{\partial x} \right) \quad (2)$$

$$j_- = eD^- \left( \frac{n^- eE}{kT} + \frac{\partial n^-}{\partial x} + \frac{n^- Q^-}{kT^2} \frac{\partial T}{\partial x} \right) \quad (3)$$

where  $E$  is the electric field, and  $Q^+$  and  $Q^-$  are the heats of transport of the ions. If two neighbouring points in the system (I and II) are at temperatures of  $T$  and  $T + dT$ , and the ion

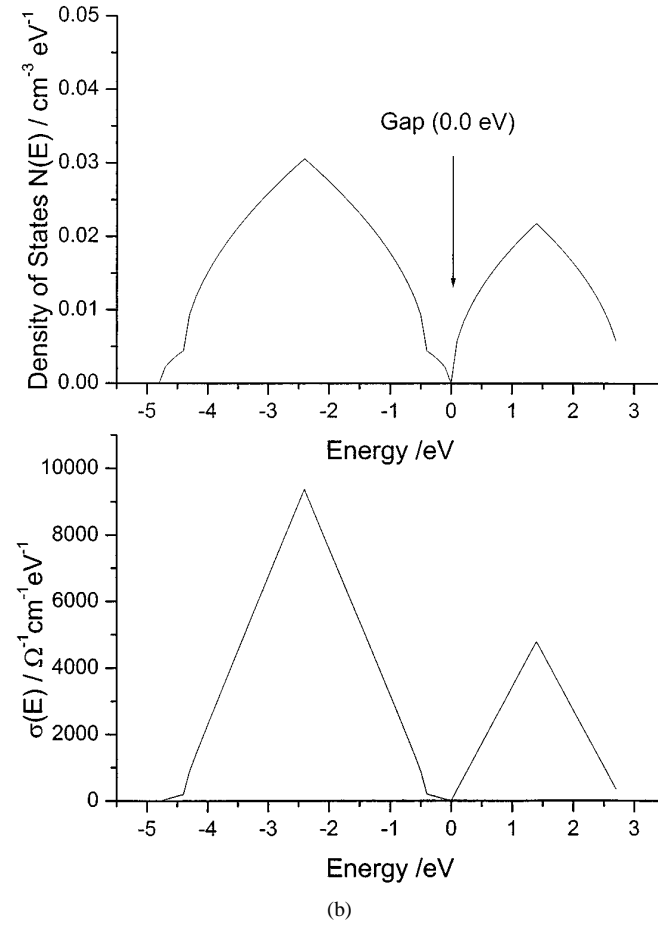


Figure 10. (Continued)

jumps from region I to region II, then the heat of transport  $Q$  of the ion is defined as the heat absorbed in region I from that produced in region II in such a way as to preserve the initial temperatures (Lidiard 1957). For the thermoelectric power no net currents are flowing through the material so that  $j_+ + j_- = 0$  and we obtain

$$E = \frac{\sigma_+}{\sigma} \left( \frac{kT}{en^+} \frac{\partial n^+}{\partial x} + \frac{Q^+}{eT} \frac{\partial T}{\partial x} \right) - \frac{\sigma_-}{\sigma} \left( \frac{kT}{en^-} \frac{\partial n^-}{\partial x} + \frac{Q^-}{eT} \frac{\partial T}{\partial x} \right). \quad (4)$$

The thermopower then becomes

$$\begin{aligned} S &= \frac{\partial V}{\partial T} = \frac{E}{(\partial T / \partial x)} = \frac{\sigma_+}{\sigma} \left( \frac{kT}{en^+} \frac{\partial n^+}{\partial T} + \frac{Q^+}{eT} \right) - \frac{\sigma_-}{\sigma} \left( \frac{kT}{en^-} \frac{\partial n^-}{\partial T} + \frac{Q^-}{eT} \right) \\ &= \frac{\sigma_+ S_+ + \sigma_- S_-}{\sigma} \end{aligned} \quad (5)$$

where  $S_+$  and  $S_-$  are the contributions to the thermopower from the positive and negative ions, respectively. At this point we clarify the definition of the thermopower of a material. When measuring the thermopower of a liquid metal or semiconductor the potential difference between two points on the sample at different temperatures is measured and the thermopower

of the sample is usually calculated according to the relation (Tauc 1974, p 388)

$$S = \frac{\Delta V}{\Delta T} - S_M \quad (6)$$

where  $S_M$  is the absolute thermopower of the metal electrodes connected to the sample.  $S_M$  is the sole correction made for the connecting electrodes. However, in the case of a molten salt the situation is more complicated due to the existence of electrochemical voltages between the electrode wires and the sample. Therefore in order to determine the thermopower of a molten salt we need to use the relation

$$S = \frac{\Delta V}{\Delta T} - S_M + \frac{1}{e} \frac{\Delta \zeta}{\Delta T} \quad (7)$$

where  $(1/e)\Delta\zeta/\Delta T$  corresponds to the difference in the electrochemical potential at the electrodes at the two temperatures (Haga 1958, 1960, Howard and Lidiard 1957). This third term on the right is often denoted the *inhomogeneous* thermopower in the discussion of the thermopower of ionic crystals (Lidiard 1957). It depends on the material of the electrodes used and is not an intrinsic property of the sample itself. The expression for the thermopower of a liquid metal/semiconductor,  $S$ , given in equation (5) does not include the effects of the electrode potentials and is generally known as the homogeneous thermopower. In the literature the thermopower of ionic materials is normally given as the sum of the homogeneous and inhomogeneous thermopower. We have adopted this definition of the thermopower here. The values of the inhomogeneous thermopower of AgI, AgBr and AgCl have been reported as 188, 140 and 210  $\mu\text{V K}^{-1}$  respectively as measured by Reinhold and Blachny (1933) and Janes (1967). In the case of the silver halides and chalcogenides it is known that the  $\text{Ag}^+$  ions are much more mobile than the anions, in which case the homogeneous thermopower is dominated by the transport of  $\text{Ag}^+$  so that equation 5 can be reduced to

$$S = \frac{\sigma_+}{\sigma} \left( \frac{k T}{e n^+} \frac{\partial n^+}{\partial T} + \frac{Q^+}{eT} \right). \quad (8)$$

From equation (1) and assuming  $\sigma_+ \gg \sigma_-$  we can write the first term in equation (8) as

$$\frac{k T}{e n^+} \frac{\partial n^+}{\partial T} = \frac{k}{e} \left( \frac{T}{\sigma_+} \frac{\partial \sigma_+}{\partial T} + 1 - \frac{E_v}{kT} \right) \quad (9)$$

where we have assumed that the diffusion of the ions follows Arrhenius behaviour of the form  $D_+ = D_0 \exp(-E_v/kT)$ . In the case of AgI and substituting the values of  $\sigma_+$ ,  $(\partial\sigma_+/\partial T)$  and  $E_v (= 0.095 \text{ eV})$  given by Kvist and Tärneberg (1970) equation (9) gives a value of 67  $\mu\text{V K}^{-1}$  at 1173 K. As  $E_v$  is small and  $\sigma_+$  has a weak temperature dependence we have assumed that this term has a weak temperature dependence so that we can estimate  $Q^+$  for the pure silver halides by plotting  $S$  against  $1/T$  and calculating  $Q^+$  from the gradient. With this method we have obtained  $Q^+ = 0.1 \text{ eV}$ , 0.14 eV and 0.2 eV for AgCl, AgBr and AgI respectively. Using this expression for the thermopower, the slow decrease in  $S$  with  $T$  for the molten halides is attributed to the  $1/T$  dependence associated with the heat of transport term  $Q^+/eT$ .

#### 4.3. The transition from predominantly electronic to predominantly ionic conductivity

In the experimental data there is a clear indication that the change from predominantly ionic conduction to predominantly electronic conduction takes place in the range  $0.3 \leq c \leq 0.5$ . This is observed as a rapid change of the sign of the thermopower and the observation that the conductivity has approached a value roughly double that of the pure molten salt. In order to understand this transition we need to combine the theoretical frameworks given in section 4.1

and 4.2 into a unified scheme that covers the entire composition range. For the case of the conductivity the total conductivity is given simply by

$$\sigma_{TOTAL} = \sigma_{ionic} + \sigma_{electronic}. \quad (10)$$

For the homogeneous thermopower we can extend the arguments for the pure molten salt to include the effects of the second anion and the electrons and holes in the system to give

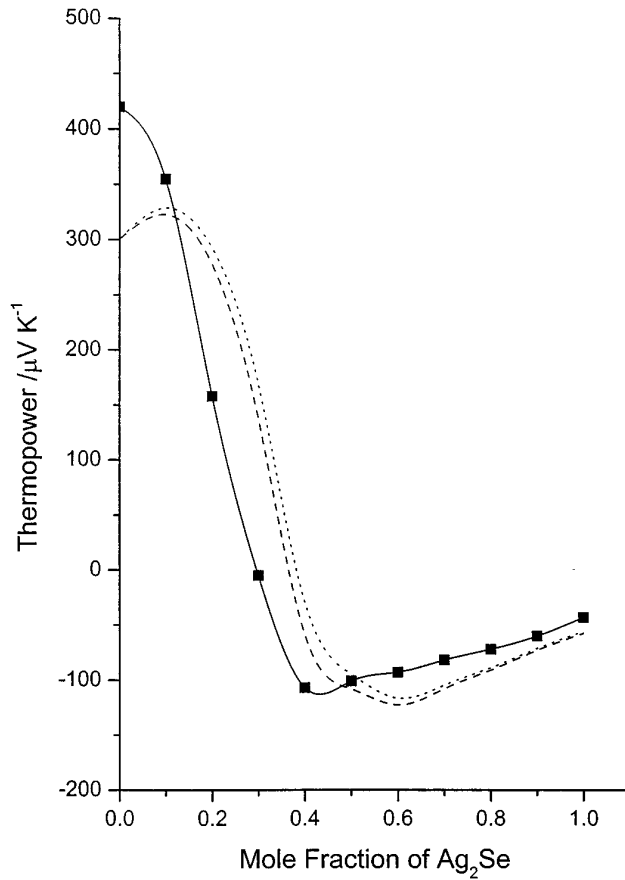
$$S_{TOTAL} = \frac{\sigma_+ S_+ + \sigma_- S_- + \sigma'_- S'_- + \sigma_{elect} S_{elect} + \sigma_{hole} S_{hole}}{\sigma_{TOTAL}} \quad (11)$$

where  $\sigma_-$  and  $\sigma'_-$  correspond to the conductivity due to the Cl<sup>-</sup> and Se<sup>2-</sup> ions. For the case where the thermopower on the semiconductor side is dominated by the electrons (as in the case of Ag<sub>2</sub>Se) and on the molten salt side is dominated by the cations (as in the case of AgCl) this expression for the thermopower can be written as

$$S_{TOTAL} \approx \frac{\sigma_+ S_+ + \sigma_{elect} S_{elect}}{\sigma_{TOTAL}}. \quad (12)$$

However these expressions (Lidiard 1957) do not include the effect of the electrode potentials (inhomogeneous thermopower) that we have seen is an important contribution to the measured voltage in the case of a molten salt. In the case of liquid semiconductors and metals this is generally assumed to be negligible as the electronic conductivity is assumed to internally short the potential due to the electrodes. However, when the electronic and ionic conductivities are comparable, the electrode potentials will continue to make an important contribution to the measured voltage. In the case of the Ag/AgX–Ag<sub>2</sub>Se electrode system in this experiment the important electrochemical reaction at the electrodes is  $\text{Ag} \leftrightarrow \text{Ag}^+ + \text{e}^-$ . In a completed circuit this would lead to the removal of silver from one electrode, the transport of silver ions through the salt and the deposition of silver on the opposite electrode. The electrode potential originates physically from the voltage that is induced at the electrodes as Ag<sup>+</sup> ions migrate to or from the electrodes to reach chemical equilibrium with the liquid. In the absence of charged species this is equivalent to the normal thermodynamic requirement that the chemical potentials in the two phases (electrode and liquid) are equal at equilibrium. In the case of charged species the diffusion of Ag<sup>+</sup> in or out of the liquid leads initially to a space charge developing at the interface between the two phases. It is this space charge that gives rise to the electrode potential, that is, the extra work needed to move an Ag<sup>+</sup> ion against the potential difference induced at the electrode. To recover the thermodynamic description of the two phases the requirement is that the electrochemical potential should be constant across the interface at equilibrium. The electrochemical potential incorporates the potential drop at the electrode. The effects of screening reduce the work needed to move an Ag<sup>+</sup> ion to and from the electrode under equilibrium conditions such that the magnitude of the electrode potential is reduced. In aqueous electrolytes the screening comes from the movement of the ions in the solution and is normally discussed in terms of Debye–Hückel theory (or extensions to it, Atkins 1982). In the case of Debye–Hückel theory the screening length remains quite long (of the order of a nanometre for the most concentrated solutions). However, free electrons (those contributing to the electronic conductivity) will be much more effective at screening and we expect the screening length to become significantly smaller as the concentration of free electrons increases (a typical metal has a screening length of less than 0.1 nm). In this case a more appropriate description of the screening would be in terms of Thomas–Fermi or Lindhard theory. Hence we expect to see a rapid reduction in the contribution to the total thermopower from the electrode potentials as the electronic conductivity of the sample increases. Accurate first principles calculations of the electrode potentials in electrolyte solutions are still not feasible and the addition of free electrons to the problem makes the task even more intractable.





**Figure 11.** The composition dependence of the thermopower of liquid  $(\text{AgI})_{1-c}(\text{Ag}_2\text{Se})_c$  in comparison to the results of the simple model described in section 4.3. The dotted line assumes that  $\sigma_{\text{ionic}}$  is constant over the composition range; the dashed line is the case where  $\sigma_{\text{ionic}}$  increases from 2.4 to  $5 \Omega^{-1} \text{ cm}^{-1}$  as  $c$  changes from 0.0 to 1.0.

We will therefore not attempt to calculate theoretically the change in electrode potential as a function of  $\text{Ag}_2\text{Se}$  concentration. However, making a crude assumption that the screening depends directly on the concentration and mobility of the electrons in the sample, in other words it is proportional to  $\sigma_{\text{elect}}$ , we write the difference in the electrode potentials as a function of concentration as

$$\frac{1}{e} \frac{\Delta \zeta}{\Delta T}(c) = \frac{1}{e} \frac{\Delta \zeta}{\Delta T}(c=0) \frac{\sigma_{\text{ionic}}}{\sigma_{\text{TOTAL}}}. \quad (13)$$

With this expression, and in the case of pure liquid  $\text{Ag}_2\text{Se}$ , we estimate the contribution to the electrode potential is approximately 1% of that of the pure halides (i.e. a few  $\mu\text{V K}^{-1}$ ). Using this simple expression we have calculated the *trends* in the expected behaviour as the transition in conduction mechanism takes place.

Figure 11 shows the experimental results for the thermopower of liquid  $\text{Ag}_2\text{Se}-\text{AgI}$  as a function of composition along with the combined calculations using the two models for the electronic conduction outlined in section 4.1. Two models of the ionic conduction have been used:

- (i) a model in which the ionic conductivity is assumed to be constant and equal to the ionic conductivity of pure AgI ( $2.4 \Omega^{-1} \text{ cm}^{-1}$ );
- (ii) a model in which the ionic conduction,  $\sigma_{\text{ionic}}$ , is assumed to change smoothly and slowly between  $2.4$  and  $5 \Omega^{-1} \text{ cm}^{-1}$  (Endo *et al* 1980) with composition dependence as outlined by Ohno *et al* (1999). The value of  $Q_i$  was taken to be that for pure molten AgI (0.2 eV) and was assumed to be constant on the addition of Ag<sub>2</sub>Se.

It can be seen that the broad trends in the experimental results are reproduced in the calculations. Similar results are found in the case of Ag<sub>2</sub>Se–AgBr and Ag<sub>2</sub>Se–AgCl suggesting that this represents a reasonable phenomenological picture of the transition between ionic and electronic conduction in these mixtures.

## 5. Conclusions

We have presented results for the concentration dependence of the electrical conductivity and thermoelectric power of AgX–Ag<sub>2</sub>Se (X=Cl,Br or I) mixtures. The results suggest that the primary mechanism for the reduction of the electrical conductivity is a progressive opening of the conductivity gap  $\Delta E$  as the halide is added to Ag<sub>2</sub>Se rather than a progressive reduction in the density of states  $N(E)$  at the band edges. The thermopower measured at the Ag<sub>2</sub>Se rich compositions is consistent with these conclusions but a large deviation from the predicted behaviour arises when the electronic conductivity and ionic conductivities reach comparable magnitudes. In this region of composition we have demonstrated that the effect of the electrode potentials (inhomogeneous thermopower) makes an important contribution to the measured thermoelectric voltages. The reduction in the size of the electrode potentials as Ag<sub>2</sub>Se is added to the pure salt is attributed to the high degree of screening of the bare ion potentials afforded by the mobile free electrons added to the system.

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