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# The electrical conductivity and thermopower of liquid $\text{Ag}_{1-x}\text{S}_x$ alloys near the stoichiometric composition $\text{Ag}_2\text{S}$

S Ohno†§, A C Barnes‡|| and J E Enderby†

† H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK

‡ Rutherford-Appleton Laboratory, Chilton, Oxon, OX11 0QX, UK

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**Abstract.** The electronic properties of liquid  $\text{Ag}_{1-x}\text{S}_x$  have been measured as a function of temperature and concentration near the stoichiometric composition  $\text{Ag}_2\text{S}$ . The unusual negative temperature dependence of the conductivity at stoichiometry found previously has been confirmed, and shown to extend over the composition range  $0.3250 \leq x \leq 0.3345$ . The concentration dependence of the conductivity shows a sharp peak at the stoichiometric composition reaching a value of  $250 \Omega^{-1}\text{cm}^{-1}$  at  $1000^\circ\text{C}$ ; such a feature has never been observed in a liquid semiconductor with a comparable conductivity. The thermopower of liquid  $\text{Ag}_{1-x}\text{S}_x$  is negative and shows a broad minimum centred around the composition  $x = 0.315$ .

## 1. Introduction

Liquid conductors have been classified into three types characterized by the value of their conductivity  $\sigma$  (Cutler 1977, Mott and Davies 1979, Enderby and Barnes 1990). Within this classification, electronic conductors with a deep minimum in the energy dependent conductivity  $\sigma(E)$  have  $\sigma$  values in the range  $500 \Omega^{-1}\text{cm}^{-1} \leq \sigma \leq 5000 \Omega^{-1}\text{cm}^{-1}$ . Most liquids with this conductivity range have a positive temperature dependence of  $\sigma$ . The conductivity of a liquid conductor can, in the independent particle model, be derived from

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

where  $f(E)$ , the Fermi function is given by

$$f(E) = \left[ \exp \left( \frac{E - E_F}{k_B T} \right) + 1 \right]^{-1} \quad (2)$$

with  $k_B$  the Boltzmann constant and  $E_F$  the Fermi energy. The positive temperature coefficient of the conductivity arises either because the Fermi energy lies close to a deep minimum (or pseudogap) in  $\sigma(E)$ , or from an increase in the density of states

§ On leave from Niigata College of Pharmacy, Kamishin'eicho, Niigata 950-21, Japan.

|| Present address: H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK.

(and consequently  $\sigma(E)$ ) at the Fermi energy with temperature, or a combination of both.

With the sole exceptions of  $\text{Ag}_2\text{S}$  and  $\text{Ag}_2\text{Se}$ , all liquid semiconductors studied so far with conductivities less than  $500 \Omega^{-1}\text{cm}^{-1}$  have  $d\sigma/dT > 0$ . Conductivities of this magnitude correspond to the point at which a pseudogap in  $\sigma(E)$  becomes sufficiently deep to give a real gap (i.e. an energy range where  $\sigma(E)$  becomes essentially zero) in the liquid (Enderby and Barnes 1990). The thermopower,  $S$ , is related to  $\sigma(E)$  in the independent particle model by

$$S = -\frac{k_{\text{B}}}{|e|} \int_0^{\infty} \frac{\sigma(E)}{\sigma} \frac{E - E_{\text{F}}}{k_{\text{B}}T} \frac{\partial f}{\partial E} dE \quad (3)$$

and plays an important role in the experimental determination of the conductivity gap and the slope of  $\sigma(E)$  at the conduction and valence band edges (Enderby and Barnes 1990).

The conductivity of liquid  $\text{Ag}_{1-x}\text{S}_x$  as a function of  $x$  was measured by Dancy and Derge (1963) who found a weak concentration dependence of  $\sigma$  around  $\text{Ag}_2\text{S}$  along with a *positive*  $d\sigma/dT$ . Ditman and Kulikova (1977) and Endo *et al* (1980) also measured the conductivity and thermopower of this system, observing a *negative*  $d\sigma/dT$  at stoichiometry and a negative thermopower. Glazov *et al* (1986) determined the Hall mobility in this system along with the conductivity and also found  $d\sigma/dT < 0$ . The aim of the experimental work described in this paper was first, to confirm the unusual behaviour of the liquid  $\text{Ag}_{1-x}\text{S}_x$  system reported by the authors above, especially at the stoichiometric composition  $\text{Ag}_2\text{S}$ , and second, to study in detail the composition dependence of  $\sigma$  and  $S$ . The measurements were carried out in a cell in which  $\sigma$  and  $S$  can be measured simultaneously and allowed estimates of the conductivity gap, its temperature dependence and the form of  $\sigma(E)$  to be made.

## 2. Experimental procedure and results

The electrical conductivity ( $\sigma$ ) and thermopower ( $S$ ), were measured simultaneously using a quartz cell and a four-point method. Contact to the sample was made through small graphite electrodes inserted through tapered holes in the quartz capillary. The electrodes were secured in place with thin molybdenum bands. The temperature of each electrode was determined from a chromel/alumel (type K) thermocouple fastened immediately over the electrode using another Mo band. The cell constant (used in determining the sample conductivity) was determined by using mercury at room temperature. Because of the relatively high S vapour pressures above the sample, the apparatus was filled with argon gas to prevent evaporation of S from the surface and to prevent oxidation of the sample. Any bubbles that formed in the liquid during the experimental run were removed by agitating the sample with a silica (S-rich samples) or a tungsten (Ag-rich samples) rod.

The thermopower measurements were made using a  $\Delta T$  method (Barnes 1986). A two-zone furnace was used to give accurate control of the electrode temperatures. The top and bottom thermocouples on the cell were used to regulate the furnace enabling a precisely determined temperature difference to be maintained across the sample. The thermoelectric voltages ( $\Delta V$ ) between two electrodes were measured using a Keithley 181 digital voltmeter with an accuracy of  $10^{-8}$  V. The thermoelectric voltages

obtained, which give the thermopower relative to the Mo contacts, were corrected to give the absolute thermopower using the tabulated values of the thermopower of Mo given by Cusack and Kendall (1958).

The master alloy of  $Ag_2S$  used for preparing the samples was purchased from Johnson Matthey plc as were the pure Ag (99.99%) and S (99.9%) used to change the composition. The concentration of each sample was determined by measuring the mass of the components before mixing. The accuracy in the value of  $x$  was limited by the loss of sulphur due to evaporation from the sample. Typically this amounted to 3–4 mg corresponding to a change in composition  $\delta x$  in the sample of 0.0005. A simplified phase diagram for this system is shown in figure 1 (Massalski 1986).

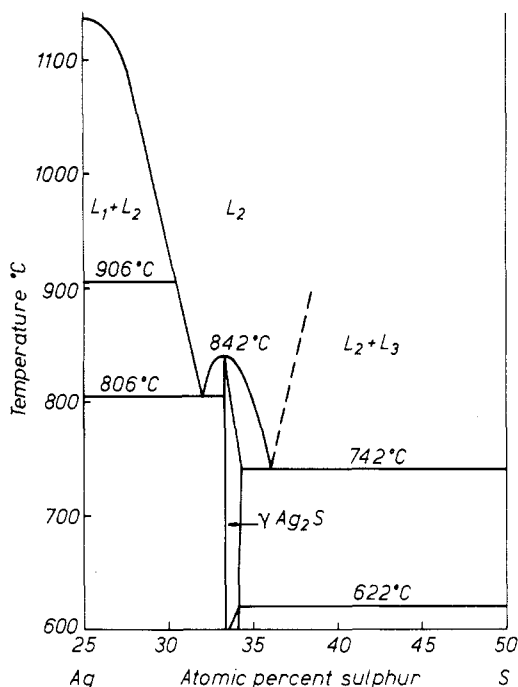


Figure 1. The binary phase diagram for  $Ag_{1-x}S_x$ .

The electrical conductivity as a function of temperature for liquid  $Ag_{1-x}S_x$  alloys with  $x \leq 0.315$  is shown in figure 2. The samples were heated to  $100^\circ\text{C}$  above the miscibility gap (shown in figure 1) and left at that temperature for 30 mins to ensure that the sample had completely mixed. The measurements were then made as the sample was cooled. The onset of phase separation was indicated by a marked change in the conductivity as shown by the arrows in figure 2. This proved to be a sensitive test for establishing that the liquid phase was properly mixed. All the alloys in this concentration range showed  $d\sigma/dT > 0$ .

Figure 3 shows the electrical conductivity as a function of temperature for alloys with  $0.325 \leq x \leq 0.333$ , a sign change in  $d\sigma/dT$  occurring at  $x = 0.325$ . The value of  $(1/\sigma)(d\sigma/dT)$  for liquid  $Ag_2S$  is  $-13.7 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$  at  $900^\circ\text{C}$  and rapidly approaches zero with decreasing concentration of S. The values of  $\sigma$  and  $d\sigma/dT$  obtained are in good agreement with those obtained by Ditman and Kulikova (1977) and in moderate agreement with those due to Glazov *et al* (1986). In particular, the present work

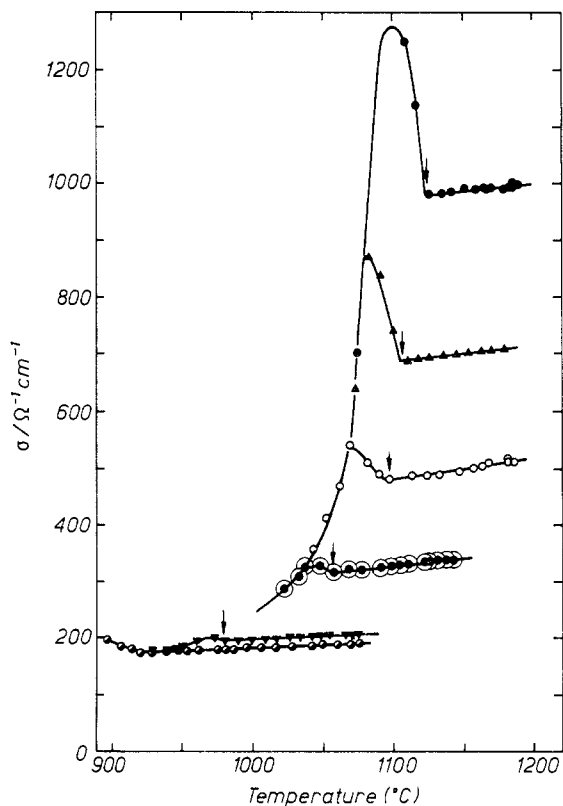


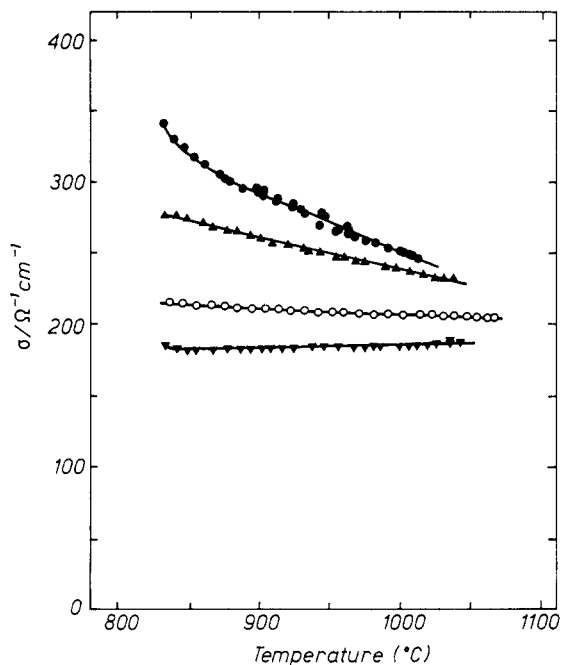
Figure 2. The conductivity,  $\sigma$ , of liquid  $\text{Ag}_{1-x}\text{S}_x$  for  $x \leq 0.315$ . ( $x$ ;  $\bullet = 0.25$ ,  $\blacktriangle = 0.27$ ,  $\circ = 0.285$ ,  $\odot = 0.295$ ,  $\blacktriangledown = 0.305$ ,  $\bullet = 0.315$ .)

confirms the *negative* temperature dependence of  $\sigma$ . Figure 4 shows  $\sigma$  as a function of temperature for  $0.333 \leq x \leq 0.3345$ . Again  $d\sigma/dT$  is less than zero for all compositions. Unfortunately, the maximum amount of S that could be added was limited due to the fact that, at one atmosphere, liquid  $\text{Ag}_2\text{S}$  can contain only a very small excess of S before phase separation and decomposition occurs (figure 1).

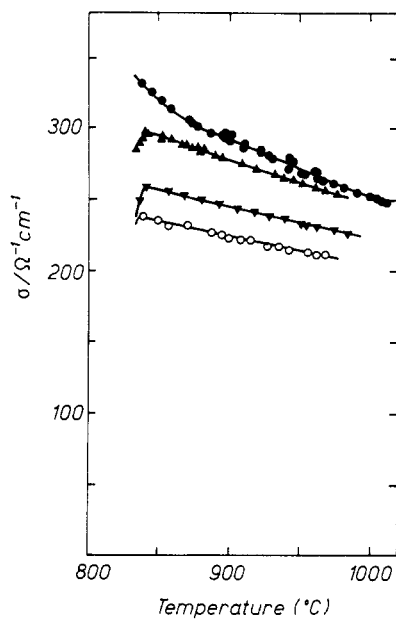
The thermopower  $S$ , as a function of  $x$  for alloys with  $0.25 \leq x \leq 0.3345$ , is shown in figures 5 and 6. At compositions close to the stoichiometric composition,  $S$  has a weak dependence on temperature with  $|dS/dT| < 0$ . The absolute value of  $S$  for liquid  $\text{Ag}_2\text{S}$  is in good agreement with the value obtained by Ditman and Kulikova (1977) at the same composition.

### 3. Discussion

The conductivity of liquid  $\text{Ag}_{1-x}\text{S}_x$  alloys decreases smoothly with increasing concentration of S, levelling off in the range between  $x = 0.305$  and  $x = 0.325$ , and then shows an increase to give a sharp peak at the stoichiometric composition  $\text{Ag}_2\text{S}$  as shown in figure 7. The width of this peak is about 1.0 at. % in concentration. We are unaware of any other liquid with this magnitude of conductivity which shows similar behaviour. The more usual observation is to find a deep minimum in the conductivity



**Figure 3.** The conductivity,  $\sigma$ , of liquid  $\text{Ag}_{1-x}\text{S}_x$  for  $0.325 \leq x \leq 0.333$ . ( $x$ ;  $\bullet$  = 0.333,  $\blacktriangle$  = 0.331,  $\circ$  = 0.328,  $\blacktriangledown$  = 0.325.)



**Figure 4.** The conductivity,  $\sigma$ , of liquid  $\text{Ag}_{1-x}\text{S}_x$  for  $0.333 \leq x \leq 0.3345$ . ( $x$ ;  $\bullet$  = 0.333,  $\blacktriangle$  = 0.3336,  $\blacktriangledown$  = 0.3343,  $\circ$  = 0.3345.)

at the stoichiometric composition as observed, for example, in liquid  $\text{Ag}_{1-x}\text{Te}_x$  alloys (Okada *et al* 1983).

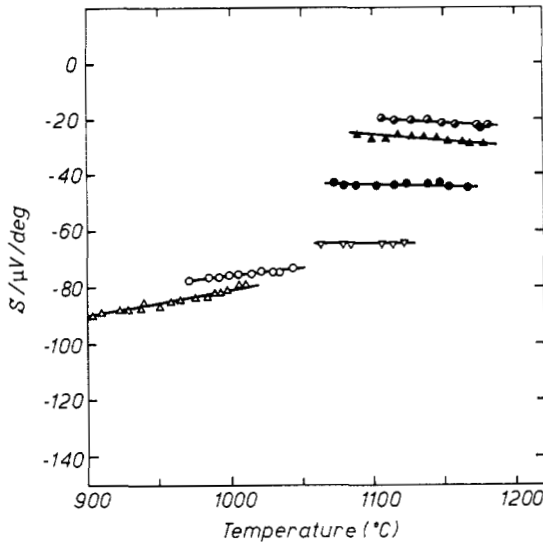


Figure 5. The thermopower,  $S$ , of liquid  $\text{Ag}_{1-x}\text{S}_x$  for  $0.25 \leq x \leq 0.315$ . ( $x$ ;  $\bullet$  = 0.25,  $\blacktriangle$  = 0.27,  $\bullet$  = 0.285,  $\nabla$  = 0.295,  $\circ$  = 0.305,  $\Delta$  = 0.315.)

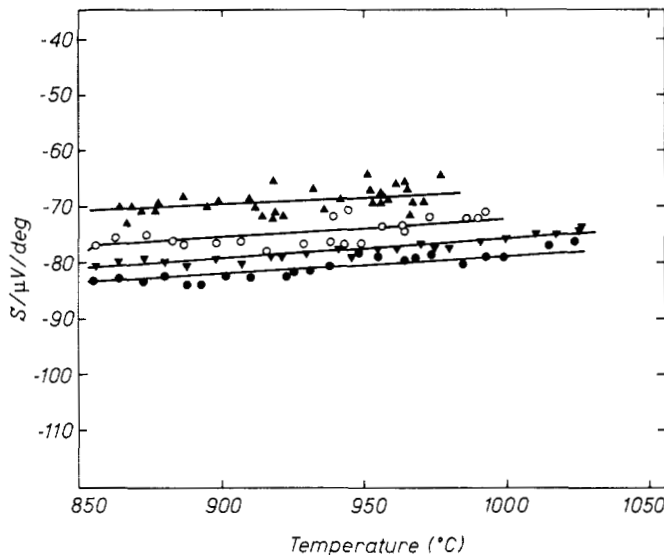
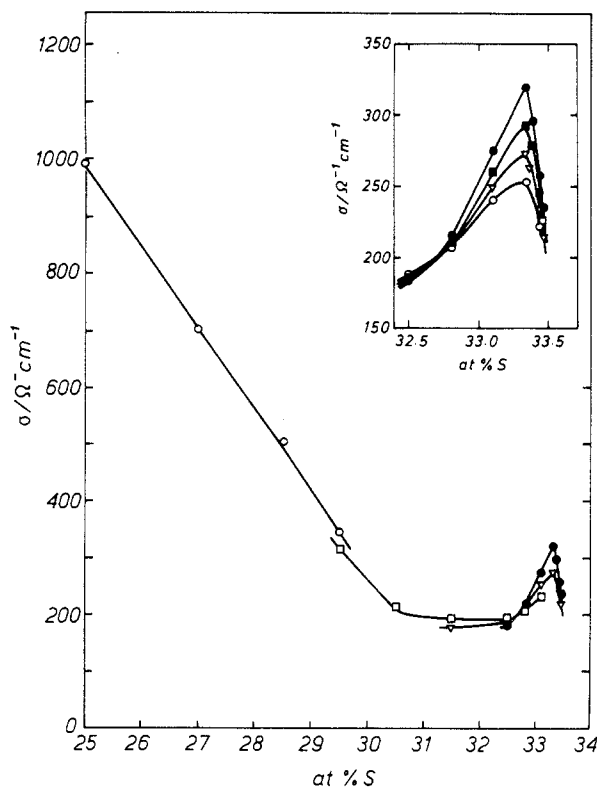


Figure 6. The thermopower,  $S$ , of liquid  $\text{Ag}_{1-x}\text{S}_x$  for  $0.325 \leq x \leq 0.3345$ . ( $x$ ;  $\blacktriangle$  = 0.3345,  $\circ$  = 0.333,  $\nabla$  = 0.331,  $\bullet$  = 0.325.)

To make progress in analyzing these data, the generic form for  $\sigma(E)$  suggested by Enderby and Barnes (1990) has been used. It is impossible (because of phase separation in the liquid) to add sufficient S to  $\text{Ag}_2\text{S}$  for this alloy to undergo a p-n transition in the thermopower, which Enderby and Barnes (1990) have shown to be a reliable method for the determination of  $\Delta E$ . The conductivity gap can, however, be estimated by assuming that  $\Delta S = 2\tilde{S}_n$  where  $\tilde{S}_n$  is the maximum value of  $|S_n|$  close to stoichiometry. For  $\text{Ag}_2\text{S}$ ,  $|\tilde{S}_n| \simeq 90 \mu\text{V K}^{-1}$  at  $1000^\circ\text{C}$  (figure 8), corresponding to a value of  $\Delta E \simeq 0.0 \text{ eV}$ . If  $\Delta E$  is indeed  $0.0 \text{ eV}$  then according to Enderby and



**Figure 7.** The conductivity,  $\sigma$ , of liquid  $Ag_{1-x}S_x$  as a function of composition. ( $T$ ;  $\bullet$  = 850 °C,  $\nabla$  = 950 °C,  $\square$  = 1050 °C,  $\circ$  = 1150 °C. For inset,  $T$ ;  $\bullet$  = 850 °C,  $\square$  = 900 °C,  $\nabla$  = 950 °C,  $\circ$  = 1000 °C.)

Barnes (1990)

$$S = \left( \frac{1-r}{1+r} \right) 205 \mu\text{V K}^{-1} \quad (4)$$

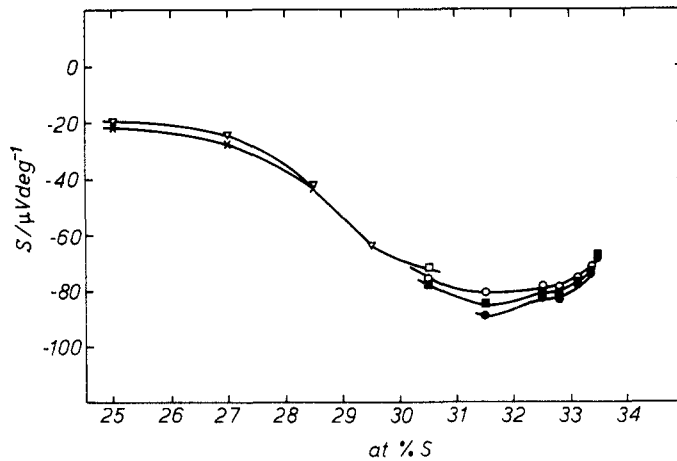
and

$$\sigma = \alpha_v (1+r) k_B T \ln 2 \quad (5)$$

which yields a value of  $r = 2.6$  and  $\alpha_v \simeq 930 \Omega^{-1}\text{cm}^{-1} \text{eV}^{-1}$ . The value of  $\alpha_v$  can be compared with that for  $Tl_2S$  ( $900 \Omega^{-1}\text{cm}^{-1} \text{eV}^{-1}$ ) and is typical for a wide range of liquid semiconductors (Enderby and Barnes 1990). However, the behaviour of  $Ag_{1-x}S_x$  around  $x = 0.333$ , cannot be explained in terms of a rigid band model. The fact that there is a peak in the concentration dependence of  $\sigma$  and that the conductivity and thermopower have unusual temperature dependences at this composition suggests that interesting changes in the chemical bonding are occurring with  $x$  and  $T$  (see, for example, Endo *et al* 1980) and that these are influencing the electrical properties.

Two systems of particular interest for comparison with Ag-S are Ag-Te and Ag-Se. Ag-Te has been well studied by Dancy and Derge (1963) and Okada *et al* (1983). This alloy is characterized by a positive  $d\sigma/dT$  and a minimum in  $\sigma$  at stoichiometry, the usual type of behaviour associated with liquid semiconductors. A detailed study





**Figure 8.** The thermopower of liquid  $\text{Ag}_{1-x}\text{S}_x$  as a function of composition. ( $T$ ;  $\times = 1150^\circ\text{C}$ ,  $\nabla = 1100^\circ\text{C}$ ,  $\square = 1050^\circ\text{C}$ ,  $\circ = 1000^\circ\text{C}$ ,  $\blacksquare = 950^\circ\text{C}$ ,  $\bullet = 900^\circ\text{C}$ .)

of liquid Ag–Se is in progress by one of us (SO). Preliminary data indicate that  $\text{Ag}_2\text{Se}$  closely resembles Ag–S, and in particular also shows a maximum in  $\sigma$  near stoichiometry as well as a negative  $d\sigma/dT$ . To develop a deeper understanding of these liquids requires a knowledge of the short-range order and experiments using the method of isotopic substitution and neutron diffraction are in progress.

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