The electronic transport properties of liquid Ag–Te

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Abstract. We have systematically measured the conductivity and the thermopower of the Ag–Te system for concentrations in the neighbourhood of Ag_2Te. Our ability to stir the sample while taking measurements has allowed us to accurately study the immiscible region below 31 at.% Te and to measure the complete extent of the p–n transition in the thermopower as stoichiometry is crossed. Our results are compared to the recent experimental results of Ohno *et al* [1], and are found to be largely in excellent agreement for thermopower and conductivity; however, in our data approximately at stoichiometry, a previously unseen feature in the conductivity is observed, and a significant deviation from the thermopower data of Ohno *et al* is also seen. This conductivity feature is consistent with, but much smaller than, peaks that have been observed in the conductivities in liquid Ag_2Se and Ag_2S. We also include data for $d\sigma/dT$ and dS/dT that have not been previously available. Our results are discussed in terms of the Kubo–Greenwood equations, and are compared to the highly unusual systems Ag–Se and Ag–S.

1. Introduction

Silver chalcogenide systems have been the subject of intense scrutiny in recent years because of the observation in Ag_2Se [2] and Ag_2S [3] of an unexpected rise in the conductivity, σ, to a sharp peak at stoichiometry. At temperatures of about $1000\,^\circ C$, the peak has been observed to be about $100\ \Omega^{-1}\ cm^{-1}$ in height, approximately 6 at.% wide, and centred on stoichiometry. The peak in conductivity is accompanied in this narrow concentration range by a negative temperature coefficient; further from stoichiometry on either side, the temperature coefficient is positive. In the same range the thermopower, S, undergoes a p–n transition; for example, the thermopower of Ag_2Se changes from -60 to $+120\ \mu V\,^\circ C^{-1}$. Although a p–n transition is seen in a multitude of liquid semiconducting systems ($\sigma < 500\ \Omega^{-1}\ cm^{-1}$), the conductivity in these two unusual systems departs from the more regularly observed sharp minimum and positive temperature coefficient at stoichiometry. In this way, Ag–Se and Ag–S are unique among all liquid semiconductors. It is also interesting to consider whether these phenomena might be related to the fast-ion conducting character of Ag_2S and Ag_2Se in the high-temperature solid and in the liquid [4].

Perhaps just as curious as the feature in liquid Ag_2Se and Ag_2S is the apparent lack of such a phenomenon in the similar liquid alloy Ag_2Te. Early measurements of the conductivity of Ag–Te by Dancy [5], relying on convection alone to stir the sample, showed no evidence of the Ag–Se type conductivity behaviour, but rather displayed the

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more conventional sharp minimum at stoichiometry, associated with a positive temperature coefficient. The immiscible region below 31 at.% Te prevented the complete measurement of the conductivity and the p–n transition in the thermopower in previous experiments. Later results by Okada *et al* [6] were also measured only above 31 at.% Te, and the 31–40 at.% region was largely untouched.

Following these results, the apparent difference in behaviour between Ag_2Te and Ag_2Se was addressed at a structural level via neutron diffraction by Price *et al* [7], who found that in both liquid alloys the structure was very similar. Ag_2Se displayed a prepeak at $Q \sim 1.8$ Å^{-1}, which was found in a later analysis by *ab initio* simulations to be the result of Se–Se coordinations not unlike those seen in the fast-ion conducting solid. It was noted that the prepeak was absent in Ag_2Te, but this was expected to be a result of the similarity of scattering lengths of the two materials. Most importantly, there was no noticeable structural change as the concentration of selenium was varied in a narrow range about stoichiometry, suggesting that structure was not responsible for the anomalous peak in the conductivity.

Very recent results by Ohno *et al* [1] have sampled the neighbourhood of stoichiometry in more closely spaced concentration steps, and have again found no special features. No mention is made, however, of the stability of the liquid at temperatures below the miscible–immiscible boundary at Te concentrations between 9 and 31 at.%, although measurements appear to have been made at these temperatures. Such a boundary is seen in roughly the same concentration range in both Ag–S and Ag–Se, and the earlier studies have considered only data taken at higher temperatures, in the miscible region.

Additionally, the experimental thermopower data taken at concentrations and temperatures within the immiscible portion of the phase diagram suggest by the asymmetry of the p–n transition that the slopes of the valence and conduction bands are highly asymmetric, following the formalism of Enderby *et al* [8]. But rigid band modelling, comparing experimental data to those generated by numerical integration of the Kubo–Greenwood equations, is incapable of reproducing even the general features of the conductivity and the thermopower. We have therefore studied Ag–Te once more in the neighbourhood of stoichiometry, proceeding in even finer concentration steps, and examining only the well stirred liquid.

2. Experimental details

The experimental apparatus used to study liquid Ag–Te has been described in detail elsewhere [9]. The only modification is the addition of graphite plugs, used to seal the contact holes in the alumina containment tubes; these more securely contain the liquid and allow electrical contact to be made with the sample. The alloy showed no evidence of attack on the Al_2O_3, and the solidified sample separated easily from the post-experiment tube. The tubes were open at the top to allow stirring, and all of the samples were agitated repeatedly during the experiments. Even in Te rich samples, the cool upper inside of the sample tube was free from condensed Te after the experiments, leading us to believe our concentrations were largely unaffected by evaporation. Conductivity was measured with the four-probe DC technique, and thermopower was measured with a chromel counterelectrode, with $S(T)$ for chromel from [10]. Our calibration for chromel is in excellent agreement with that of Cook and Laubitz [11], and we estimate the uncertainty in the absolute thermopower of chromel to be ± 0.2 μV $^{\circ}$C^{-1}. The sample concentration was not varied continuously during the experiment to avoid any possibility of progressive contamination; the majority of the samples were independently prepared in different alumina tubes from pure Ag and Te, making most data points completely independent of all others.
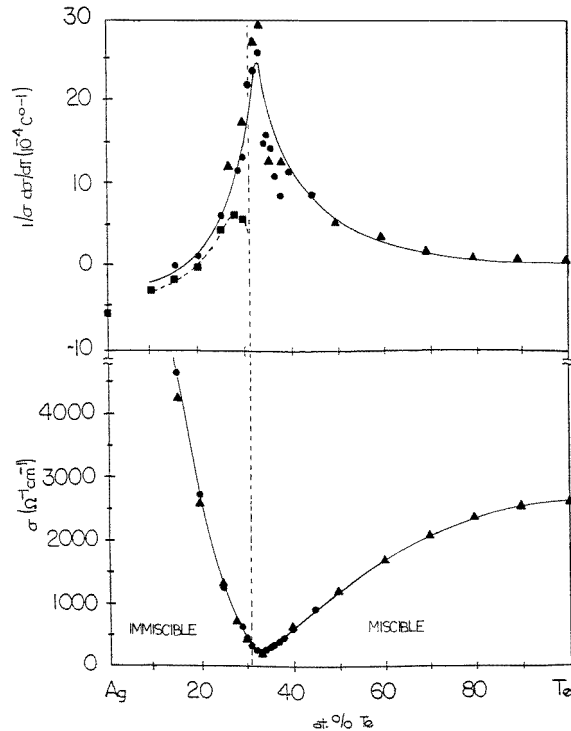
Figure 1. Measurements of σ and $1/\sigma \, d\sigma/dT$ for liquid Ag–Te. $\bullet$, current results as a function of Te concentration on the isotherm $T = 960\,°\mathrm{C}$; $\blacktriangle$, results of Ohno *et al* [1] for Ag–Te, $T = 1000\,°\mathrm{C}$; $\blacksquare$, results for Ohno *et al* [2] for Ag–Se. The upper concentration boundary of the immiscible region, 31 at%. Te, is denoted by a dashed vertical line; the other boundary is at 9 at.% Te. The uncertainty in σ is smaller than the extent of the points.

Silver and tellurium sample materials were supplied by Aesar–Johnson Matthey Co. and were of 99.99% and 99.999+% purity, respectively. The samples were prepared in air, but all measurements were made in a system that was baked under vacuum, and maintained during the experiment under 1 atmosphere of argon.

3. Results

Our results for the conductivity of Ag–Te as a function of Te content are shown in figure 1, and are seen to be in good general agreement with the results of Ohno *et al* [1]. Our points result from the evaluation at 960 °C of a linear fit to all of the data at each concentration. We also provide our data for the temperature coefficient of the conductivity, which also agree well with the limited data of Ohno *et al* [1], and appear to be rather asymmetric. Also shown on this graph are the boundaries of the immiscible region, according to Massalski [12]; the immiscible region extends from 31 at.% Te to 9 at.% Te, with a very sharply concentration dependent temperature boundary.

Figure 2 shows a curve fit to our data outside the immediate neighbourhood of stoichiometry. This curve falls below our data close to stoichiometry, and would suggest that our conductivity data do form a peak approximately at stoichiometry, extending from
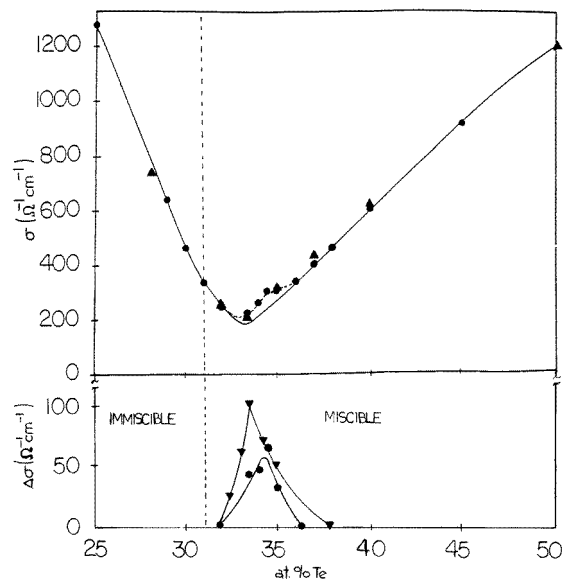
Figure 2. The conductivity of Ag–Te for a narrow range of Te concentrations, shown with a line drawn as a guide to the eye. Symbols are the same as for figure 1, and the immiscible boundary is again marked by a dashed line. The lower portion of the graph is the difference between the curve extrapolated from the experimental data at higher Te concentrations and our data near stoichiometry. ●, present data; ▲, data for Ag–Te from Ohno *et al* [1]; ▼, similar difference curve for Ag$_2$Se, from Ohno *et al* [2].

roughly 32 at.% to 36 at.% Te, with a maximum height of about 65 Ω^{-1} cm^{-1}. Also included on this graph is the difference between this curve and our experimental data; for comparison, similar difference data at 1000 °C for the peak in the Ag–Se system have been plotted as well (data from Ohno *et al* [2]). The peak in the conductivity of Ag–Te begins at roughly 32 at.% Te, and extends to roughly 36 at.% Te. It is quite similar to the peak in Ag–Se, which begins at roughly 31 at.% chalcogenide, and extends to 37 at.%, and which shows a significant broadening toward higher Se content as temperature is increased.

Figure 3 shows a graph of the conductivity at 30 at.% Te, which we have included to demonstrate the apparent lack of any mixing difficulties within the immiscible region. Our graph includes data for two different 30 at.% samples, both of which were measured during repeated stirring at temperatures above and below the boundary of the immiscible region. The Ag–Te phase diagram indicates the boundary is at roughly 1075 °C for this concentration, indicated with an arrow in the figure; the conductivity varies smoothly through this temperature. At no temperature in any of the Te alloys in this region is there a dramatic change of the slope or the magnitude of the conductivity which would indicate the presence of a mixed–unmixed boundary. In particular, the temperature coefficient is quite small and positive over all temperatures surveyed, in contrast to the very large positive slopes displayed by the unmixed Ag–Se and Ag–S alloys, which change to small positive slopes when the miscibility boundary is crossed. Furthermore, at various temperatures within the immiscible region, the sample was stirred, measured, and allowed to settle for several hours, at which time more measurements were taken. There was no time dependence of the electronic properties, which makes us believe that these components separate far more slowly in the immiscible region than in the other silver chalcogenide alloys.
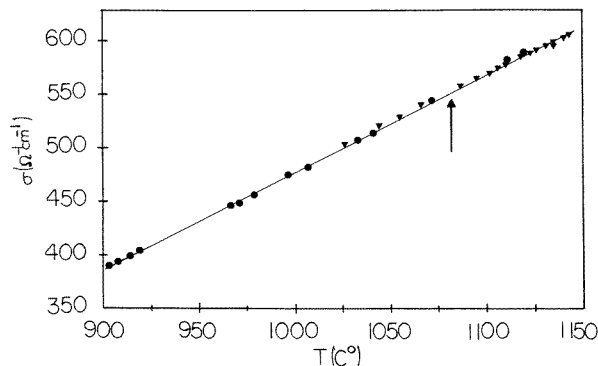
Figure 3. The conductivity for 30 at.% Te as a function of temperature. All of the data are current data, but different symbols denote separate experiments. Only a fraction of the data is shown of graphical clarity. The arrow denotes the temperature of the immiscible–miscible boundary of the liquid.

Our thermopower data (figure 4) we are generally in good agreement with Ohno *et al* [1]. Our study includes thermopower measurements in the immiscible region, and has verified that the thermopower extends at its lowest point to only -13 μV $^{\circ}$C^{-1}. The dramatic dip in the thermopower seen in Ag–Se or Ag–S between 29% and 32% chalcogenide is absent in our Ag–Te data. Interestingly, the concentration dependence of our thermopower data through stoichiometry is very close to that in Ag$_2$Se, about 20 μV $^{\circ}$C at.%$^{-1}$. (Measurements on Ag–S were not completed in this region because of miscibility problems.) The zero of the thermopower is at the same concentration as in the data of Ohno *et al* [1], 31.5 at.% Te, and less than the 36 at.% zero seen in Ag$_2$Se; it is not surprising that this is at a lower chalcogen concentration than in Ag–Se, as the deeply negative thermopower is not seen in our data. Additionally, our data recognize a small positive temperature coefficient of the thermopower at stoichiometry, in contradiction to the earlier study of Endo *et al* [4]. A positive temperature coefficient is also seen in Ag$_2$Se and Ag$_2$S.

It is interesting to note that while the data of Ohno *et al* [1] lie consistently 3–4 μV $^{\circ}$C^{-1} below ours outside the neighbourhood of stoichiometry, perhaps due to their different counterelectrode material, in the area from $\sim$34 at.% Te to 40 at.% Te their thermopower is above ours by as much as 25 μV $^{\circ}$C^{-1}. The difference between these measurements is well beyond the error quoted for their measurements ($\sim$10 μV $^{\circ}$C^{-1}), and far greater than our estimated errors, about 3–5 μV $^{\circ}$C^{-1}. These concentrations are crucial to the definition of the curvature on the conductivity graph as stoichiometry is approached from the tellurium rich side, and ultimately to the identification of the peak in σ at stoichiometry.

4. Discussion

For the majority of liquid semiconductors, an analysis according to the method of Enderby *et al* [8] can yield a good qualitative agreement with experimental data. This method involves the numerical integration of the Kubo–Greenwood equations
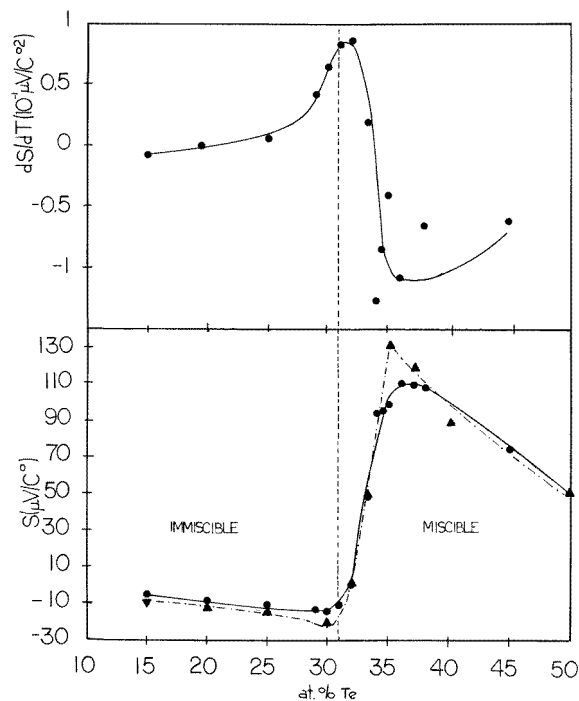
$$\sigma = -\int_0^\infty \sigma(E)\frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E$$

Figure 4. The thermopower, S, and temperature coefficient of the thermopower, dS/dT, for liquid Ag–Te. Again, ●, current results at $T = 960\,°C$; ▲, results of Ohno *et al* [1] for Ag–Te, $T = 950\,°C$. Estimated uncertainties in S are 3–5 $\mu V\,°C^{-1}$. Again, the boundary of the immiscible region is marked by a vertical dashed line.

$$S = -\frac{k_B}{|e|} \int_0^\infty \frac{\sigma(E)}{\sigma} \frac{E - E_f}{k_B T} \frac{\delta f}{\delta E}\, dE$$

where f is the Fermi function, k_B is Boltzmann's constant, and E_f is the Fermi energy. $\sigma(E)$ is the energy dependent conductivity, and the valence and conduction band contributions may be expressed generally as

$$\sigma_c(E) = a_c(E - E_c) \qquad (E \geqslant E_c)$$
$$\sigma_v(E) = a_v(E_v - E) \qquad (E \leqslant E_v)$$

where E_c and E_v are the energies that denote the edges of the bands. The variables a_c and a_v may be calculated using the band width, the atomic separation, and the total number of electron states per unit volume in the band.

Our new data would suggest that the behaviour of AgTe around stoichiometry is rather more complex than a simple $\sigma(E)$ could explain. A consideration of the overall shape of $\sigma(c)$ for Ag–Te, neglecting the feature near stoichiometry, and of the behaviour of $S(c)$ on the Te rich side of stoichiometry would suggest that $\sigma(E)$ falls rather steeply to a gap or pseudogap within a few atomic per cent of stoichiometry. Using the random phase approximation and a model $\sigma(E)$ according to Barnes [13], with bandwidths from a calculation of the density of states for liquid Ag$_2$Te by Koslowski [14], we have calculated $a_c \sim 1300\ \Omega^{-1}\ cm^{-1}\ eV^{-1}$, in reasonable agreement with the choice of Ohno *et al* of $2000\ \Omega^{-1}\ cm^{-1}\ eV^{-1}$ [1]. A choice of $a_c = 2a_v$ for Ag–Te, similar to that chosen for Ag–Te [1], does indeed reproduce the asymmetry and magnitude of $\sigma(c)$ about stoichiometry, and

the thermopower rises to a maximum of roughly 100 μV$\,^\circ$C^{-1}. However, no choice of a_c, a_v, or band gap ΔE could reproduce the shallow $S(c)$ and steep $\sigma(c)$ in this concentration range simultaneously. A small feature can indeed be reproduced in the conductivity and the thermopower on the tellurium rich side of stoichiometry with a more detailed $\sigma(E)$ similar to that suggested by Enderby *et al* [8] for Cu$_2$Te, but only with the same inability to reproduce even the general shape of both $\sigma(c)$ and $S(c)$. We conclude that a rigid band model is not appropriate for liquid Ag–Te.

A neutron diffraction study by Price *et al* [7] indicates a prepeak exists in liquid Ag$_2$Se at $Q \sim 1.8$ Å^{-1}, which has been determined experimentally by partial structure factor analysis to be most substantially composed of a contribution from the comparatively immobile Se ions. There is no apparent change in structure as concentration of Se is scanned through stoichiometry, making it unlikely that a structural change is the source of the unusual conductivity peak. Price *et al* also note the strong similarity of liquid Ag$_2$Se structure to liquid Ag$_2$Te; an absence of the prepeak in Ag$_2$Te is attributed to the similarity in scattering lengths of Ag and Te. It should be noted that all three silver chalcogenides have been shown to be fast-ion conductors.

It is therefore interesting that a recent neutron diffraction study of liquid Mg$_3$Bi$_2$ by Guo *et al* [15] indicates an ordering in the liquid similar to the fast-ion conducting solid phase of the same material. Furthermore, the structure shows broad similarity to that of Ag$_2$Se, including the presence of a prepeak at low wavenumber. Reverse Monte Carlo analysis suggests that the Bi–Bi distances generate the prepeak in Mg$_3$Bi$_2$, and that a shallow first minimum in the Mg–Mg real space distribution indicates that Mg ions are indeed quite mobile. Additionally, transport studies of Mg–Bi have shown that the inadequacy of a rigid $\sigma(E)$ is not limited to the silver chalcogenides. Guo *et al* find that fast-ion conducting liquid Mg$_3$Bi$_2$ is also difficult to explain using the Kubo–Greenwood formalism with any simple model $\sigma(E)$, because the conductivity drops to a sharp minimum while $|S| < 10$ μV$\,^\circ$C^{-1} around stoichiometry. By changing the concentration by only 1.5 at.% on either side of stoichiometry, the conductivity rises to values expected of a material with a shallow pseudogap.

In the absence of a structural explanation for the conductivity anomaly in Ag–Se, Ohno *et al* [3] suggested that the density of states in Ag$_2$Se may be modelled by rigid band behaviour, but that a sudden change in d$\sigma(E)/$dE may be responsible for the unusual peak in the conductivity which spans the concentration range 31–37 at.% Se. The change in $\sigma(E)$ is believed to occur as a result of changes in mobility; magnetic susceptibility measurements indicated $N(E)$ was at a minimum at stoichiometry. The susceptibility measurements are in agreement with the conclusions of Koslowski [14], who calculated the density of states for all three silver chalcogenides using a simple tight-binding method, and found that with sufficient introduction of chemical bonds, the Fermi energy was indeed located in a pseudogap located between the silver s and tellurium p bands. Guo also postulated a change in $N(E)$ *and* the mobility to explain the small d$S/$dc through stoichiometry and shallow d$\theta/$dc away from stoichiometry in Mg$_3$Bi$_2$, and further pointed to the work of Fortner *et al* [16] which suggests a possible link between mobile ions and enhanced mobility. Our new data, and the similarity in structure and transport to other similar alloys, suggest that a similar dramatic change in mobility or density of states occurs in Ag$_2$Te around stoichiometry.

At least four liquid fast-ion conductors have now been identified as being inadequately explained by the Kubo–Greenwood equations. Our study has revealed the presence of a peak in the conductivity near stoichiometry similar to that seen in the other silver chalcogenides, though smaller in magnitude. Ag–Te has also been studied at temperatures above and below

the immiscible boundary, and found at temperatures inside this region to be a surprisingly stable liquid.

Acknowledgment

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