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Liquid alloy semiconductors revisited

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In 1990 Enderby and Barnes reviewed the electrical properties of liquid alloys which show features associated with semiconducting behaviour. They proposed an empirical classification scheme based on the notion that some liquid semiconductors are characterized by a finite gap in $\sigma(E)$, the energy-dependent conductivity (narrow definition), whereas in others $\sigma(E)$ is continuous (broad definition). Interesting behaviour occurs for systems at the narrow/broad boundary and further analysis of these liquid alloys will form the subject matter of this paper. Particular attention will be focused on liquid silver chalcogenides as these offer a severe test of current theories.

Keywords: liquid alloys; liquid semiconductors; metal–non-metal transitions; silver chalcogenides

1. Introduction

Liquid alloys of the type $\mathrm{M}_a\mathrm{A}_m$, where M and A are metals or semimetals drawn from different parts of the periodic table with chemical valencies m and a, often form *liquid semiconductors*. Alloys of this type typically exhibit three signatures of semiconducting behaviour. First, they are characterized by electrical conductivities (σ) which are significantly lower than those typical of the metallic state. In most cases (but see below for two important exceptions) the temperature dependence of σ is positive. Secondly, the thermopower (S) changes sign from n-type to p-type as the alloy composition varies, at stoichiometry, from excess M to excess A. Thirdly, the microstructure of the alloy shows pronounced local order as evidenced both by structural and thermodynamic studies. An account of the properties of liquid alloy semiconductors has been given by Enderby & Barnes (1990) in an extensive review.

2. A phenomenological model

In their paper Enderby & Barnes (1990) introduced a phenomenological model to describe the behaviour of liquid alloy semiconductors close to stoichiometry. The formulation is based on the kinetic coefficients,

$$L_{11} = \int \sigma(E)\left[-\frac{\partial f}{\partial E}\right] \mathrm{d}E, \tag{2.1 a}$$

$$L_{12} = L_{21} = -\int \sigma(E)[E-\mu(T)]\left[-\frac{\partial f}{\partial E}\right] \mathrm{d}E, \tag{2.1 b}$$

where $f(E) = (1+\exp\{[E-\mu(T)]/k_{\mathrm{B}}T\}^{-1}$ is the Fermi function and $\sigma(E)$ includes all the system-dependent features. The conductivity and thermopower are related to L_{11} and L_{12} by

$$\sigma = L_{11}, \tag{2.2 a}$$

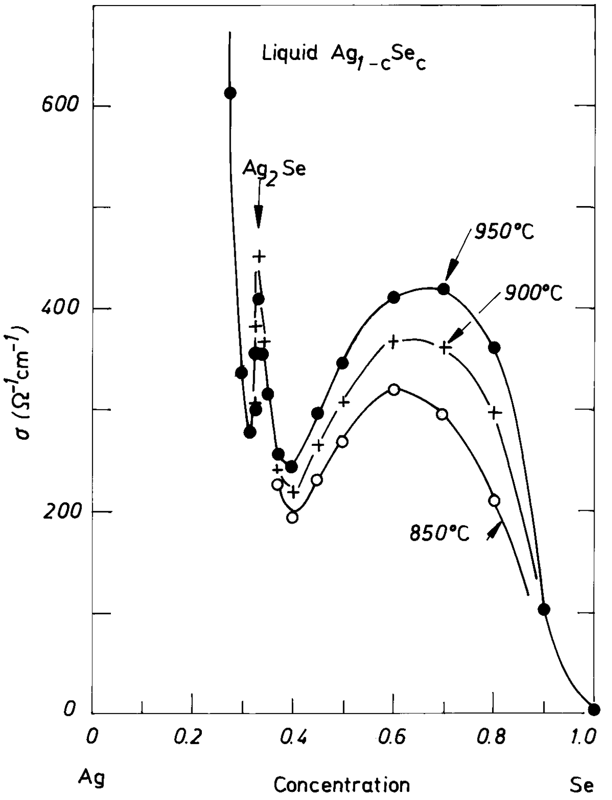

Figure 1. The electrical conductivity for l-$Ag_{1-c}Se_c$ (Ohno *et al.* 1996).

$$S = L_{12}/|e|TL_{11}. \tag{2.2 b}$$

However, in order to make use of equations (2.1) and (2.2), the form of $\sigma(E)$ has to be established. The recent application of Car–Parrrinello techniques by Gillan and co-workers has opened up the possibility of an *ab initio* theory. This work, though of considerable significance, is still in its infancy (Hollender & Gillan 1996).

An empirical approach developed by Enderby & Barnes relies on the unique electronic structure of Mn_xTe_{1-x} and yields a representation of $\sigma(E)$ given by

$$\begin{aligned}\sigma(E) &= \alpha(E_v - E), && E \leqslant E_v,\\ &= 0, && E_v \leqslant E \leqslant E_c,\\ &= \alpha(E - E_c), && E \geqslant E_c,\end{aligned}$$

where α is a constant of the order of 1000–3000 Ω^{-1} cm^{-1} eV^{-1}. The characteristic energies E_v and E_c are defined as 'conductivity edges' and $\Delta E = E_c - E_v$ as the 'conductivity gap'. For most liquid semiconductors when defined in the narrow sense (Enderby & Barnes 1990), ΔE is in the range of 0–0.5 eV.

This simple model enables a range of experimental measurements to be put on a systematic footing; moreover, an inversion procedure involving data for σ and S allows ΔE to be established. As an example consider the three thallium chalcogenides Tl_cX_{1-c} (X = Te, Se, S) each of which is characterized by a minimum in the electrical conductivity at the stoichiometric composition Tl_2X and a p–n transition in S. Conductivity data, the derived conductivity gaps and their temperature depen-

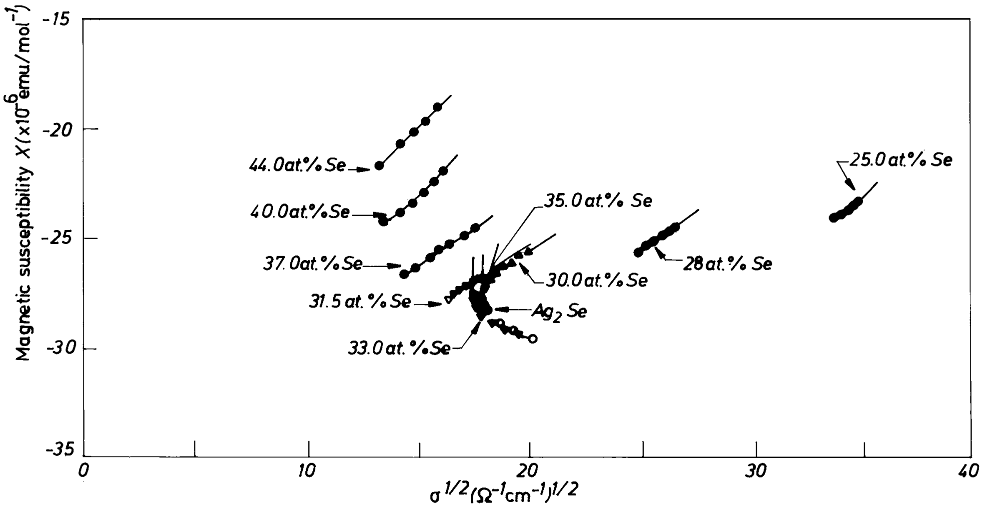

Figure 2. (Conductivity)$^{1/2}$ versus magnetic susceptibility for l-$Ag_{1-c}Se_c$ (Ohno *et al.* 1994).

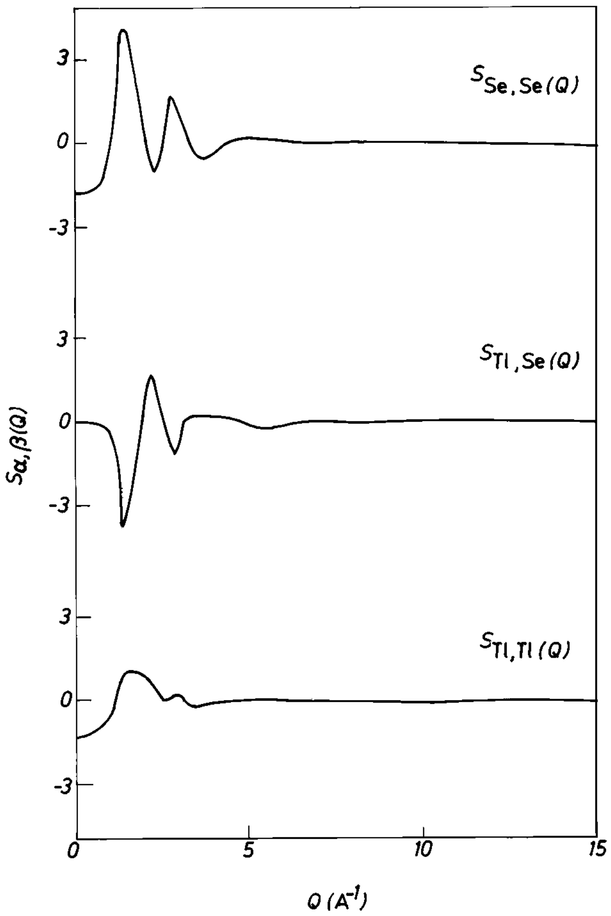

Figure 3. The partial structure factors for l-Tl_2Se obtained by neutron diffraction.

Table 1. *Derived properties of liquid semiconductors*

liquid semiconductor	temperature (K)	minimum conductivity (Ω^{-1} cm^{-1})	ΔE (eV)	$\Delta E = \Delta E_0 - \beta T$	temperature for a zero gap (K)
Tl_2Te	800	110 ± 5	0.17 ± 0.01	$0.77–7.5 \times 10^{-4} T$	1030
	1000	320 ± 5	0.02 ± 0.01		
Tl_2Se	800	15 ± 2	0.36 ± 0.01	$0.80–5.5 \times 10^{-4} T$	1450
	1000	52 ± 2	0.25 ± 0.01		
Tl_2S	800	5 ± 1	0.50 ± 0.01	$1.03–6.6 \times 10^{-4} T$	1565
	950	13 ± 1	0.40 ± 0.01		

dences are shown in table 1. The magnitude of ΔE and the temperatures at which ΔE vanishes are well correlated with electronegativity differences and are consistent with the trend to higher ionicities as X = Te → Se → S.

3. Beyond the phenomenological model

We first note that the energy-dependent conductivity can be expressed in terms of a density of states factor $g(E)$ and a mobility $\mu(E)$. There are therefore three possibilities for the existence of ranges of energy for which $\sigma(E)$ is zero. These are

(i) $\mu(E) = 0$ for $E_v \leqslant E \leqslant E_c$, otherwise finite: $g(E)$ finite;

(ii) $g(E) = \mu(E) = 0$ for $E_v \leqslant E \leqslant E_c$, otherwise finite;

(iii) $g(E) = 0$ for $E_v \leqslant E \leqslant E_c$, otherwise finite: $\mu(E)$ finite.

The *Anderson model*, which corresponds to (i), allows for vanishing mobility at finite values of $g(E)$ and leads to the so-called mobility edge. The *random phase approximation* corresponds to (ii) and has been advocated by Mott (see Cutler 1977), who based his ideas on the experimental observation that there exists a linear relationship between $\sigma^{1/2}$ and the magnetic susceptibility for Tl_cTl_{1-c} (Cutler 1997).

Guided both by behaviour in the solid state and the fact that they exhibited an unusual temperature-dependent conductivity (negative), $d\sigma/dT$, Ohno *et al.* (1994, 1996) have made a systematic study of the systems l-Ag_cX_{1-c} (see, as an example, figure 1). These are small gap materials and as such, may show directly the influence of finite carrier mobilities. The breakdown of the linear relationship between the magnetic susceptibility versus $\sigma^{1/2}$ close to stoichiometry for l-$Ag_{1-x}Se_x$ (figure 2) shows clearly that $\mu(E)$ is finite and actually *increases* as $g(E)$ *decreases*. This observation effectively rules out the first two possibilities. Similar results have recently been found for a variety of small gap systems including Ag–S and In–Se.

We therefore conclude, by elimination, that model (iii) contains the essential physics and that the zero or very small conductivity in the range $E_v \leqslant E \leqslant E_c$ is a consequence of a deep minimum or gap in the denisty of states. This gap arises from charge transfer from electropositive elements like Ag or Tl to the electronegative chalcogenide and is therefore 'chemical' in origin. The mobility, as in conventional semiconductors, remains finite at E_v or E_c.

In structural terms, the existence of charge transfer is evident in the studies of partial structure factors carried out by Barnes and his colleagues (Barnes & Guo 1994). Thus the data shown in figure 2 together with the structural data in figure 3 strongly suggest that the localization of charge induced by chemical bonding is central to our understanding of the metal–non-metal transition in liquid alloys of the type considered here.

We note finally that the effect of temperature produces two competing mechanism so far as $d\sigma/dT$ is concerned. On the one hand equation (2.1 *a*) indicates that L_{11} will increase with temperature as the Fermi function broadens in width. This effect will dominate in wide gap semiconductors and leads to the usual observation that the conductivity has a positive temperature coefficient. On the other hand, the structural order which characterizes systems described in this paper will be reduced at elevated temperatures and on rather general grounds will tend to lower carrier mobilities. This effect is likely but not necessarily to become dominant in the small gap case and is the key finding so far as the silver chalcogenides are concerned. The increase in σ very close stoichiometry discovered by Ohno and co-workers (1996) reflects the fact that the effective mobility of the current carriers is high.

I am very grateful for many helpful discussions with Adrian Barnes and the EPSRC for their continued support.

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Discussion

C. N. R. RAO (*Indian Institute of Science, Bangalore, India*). Ag_2S and Ag_2Se undergo β–α transition in the solid state with a marked jump in conductivity. The Ag^+ ions move randomly in the high temperature form. Does the ionic conductivity not contribute to Professor Enderby's measurements?

Would an ionicity scale (such as the Philip's scale) not be better than the electronegativity difference to understand the molten chalcogenides?

J. E. ENDERBY. As Professor Rao says, the high temperature form of Ag_2S and Ag_2Se is a superionic conductor. The ionic conductivity is about $2\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and does not change significantly on melting and is therefore about 1–2% of the total.

Ionicity scales are certainly useful but they often fail in detail. For example, LiAu is metallic as is NiTe, whereas CsAu is a wide gap semiconductor as is MgTe. Nevertheless, there is a correlation between 'ionicity' and liquid semiconductor behaviour and this is outlined in Enderby & Barnes (1990).

R. MCGREEVY (*Studsvik Neutron Research Laboratory, Sweden*). Professor Enderby's structural measurements on molten Ag_2Se compare well with the absolute simulations by Kirchhoff *et al.* (1996). However, while the structural measurements have been interpreted as indicating the importance of two-fold coordinated Se, i.e. Se chains, the simulations indicate that Se–Se bonds are 'surprisingly shortlived', of the order of 1 ps. Can he comment on this apparent contradiction in interpretation, particularly in relation to the electronic conductivity of this stoichiometric composition?

J. E. Enderby. It is necessary to distinguish between l-Ag_2Se and l-Ga_2Te_3. For l-Ag_2Se, experiment, simulation and *ab initio* work agree that a predominately ionic model is appropriate. There is little evidence of Se–Se pairs. On the other hand, for l-Ga_2Te_3 or Se_2Se_3 there are predicted chain-like conformations and these appear to be consistent with diffraction data, albeit at the total level. It is correct that the Se–Se chains appear to be shortlived but, on the timescale relevant to electron transport, are probably sufficiently well defined to account for the observed conductivity effects. But I agree that this is an area where further study is needed.

D. E. Logan (*Physical and Theoretical Chemistry Laboratory, University of Oxford, UK*). If I have understood it correctly, much of Professor Enderby's analysis assumes, at least implicitly, non-interacting (or at best weakly interacting) electrons. I would have thought that in many of the complex liquid alloy semiconductors he considers, electron attractions in one guise or another would play an important role. Does he have evidence to suggest that the majority of systems he considers are only weakly interacting?

He also mentioned that there does not appear to be evidence for the importance of disorder-induced Anderson localizations in any of the systems considered. I feel one needs to be cautious here, since I think it unlikely (a) that any *single* mechanism underlies a metal–insulator transition in these complex materials, or (b) that the electrons are in essence non-interacting, and he appears to have assumed both in reaching the above conclusions. It would be surprising if, in these beautifully rich systems, there was not simultaneous occurrence of (and a subtle interplay between) disorder, interactions and other effects. And I do not see how, from current experimental information, it is possible to disentangle such factors; or, specifically, to conclude that localization is irrelevant.

J. E. Enderby. I agree that there is probably no single unifying mechanism which can account for all the observations on liquid alloys. In that sense, the detailed chemistry of each system needs to be considered and this was the main point of my paper. Enderby & Barnes used the simplest possible (non-trivial) model and found that the experimental data could be rationalized in terms of an energy-dependent conductivity of the form $\sigma(E) = \alpha E$, where α is a constant of order $1000\ \Omega^{-1}\ \mathrm{cm}^{-1}\ \mathrm{eV}^{-1}$. This value of α is remarkably high and implies that localization effects are probably absent; indeed the work on l-Ag_cX_{1-c} (X = S, Se, Te) strongly suggests that the carrier mobility is much higher than had been previously thought.

R. L. Johnston (*Department of Chemistry, University of Birmingham, UK*). In stoichiometric systems is it not possible (especially at elevated temperatures) that there are regions, perhaps metallic, of non-stoichiometry? Would this mean that the problem is essentially one of percolation?

J. E. Enderby. There is no evidence for inhomogeneous regions of scale required for percolation. For example, there is no small angle scattering in Tl_2Se as the work of Barnes & Guo (1994) makes clear. Several years ago, Hawker *et al.* (1974) showed that an inhomogeneous model for Cu_2Te–CuTe was not appropriate either.

D. M. Edwards (*Department of Mathematics, Imperial College, London, UK*). Is there evidence for gaps from optical experiments?

J. E. Enderby. The group at Marburg has shown that optical gaps do exist in low conductivity systems such as liquid Au–Cs. For many of the systems with intermediate conductivity, the high temperatures involved together with free carrier absorption masks optical gaps, however.

P. P. Edwards (*School of Chemistry, University of Birmingham, UK*). Professor Enderby mentioned the case of Cs^+Au^-, caesium auride, in which Au contains the 'Hg' $6s^2$ closed shell electronic structure. What is known of the status of Au in chalcogenides and related compounds and melts?

Regarding Ag_2S, is there any change in conductivity (both electronic and ionic) as the crystal melts?

I do agree with his comments in relation to the 'potency' of incipient chemical compound formation, cf. incipient electron localization via other means. I suppose it's a case of, *if the physics doesn't get you, the chemistry will!*

J. E. Enderby. Little is known about AuX (X = S, Se, Te) except that $AuTe_2$ is metallic.

The ionic conductivity in both liquid and solid Ag_2S is about $2\,\Omega^{-1}\,\text{cm}^{-1}$ and is therefore about 2% of the total. The electronic conductivity changes by about 10% at the melting transition.

I agree. Chemical bonding (which of course ultimately can be derived from physical principles) is at the heart of the structural and related properties of liquid semiconductors.

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