

Carrier mobility in liquid semiconductors

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 A181

(<http://iopscience.iop.org/0953-8984/12/8A/321>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:27

Please note that [terms and conditions apply](#).

Carrier mobility in liquid semiconductors

J E Enderby and A C Barnes

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

Received 11 October 1999

Abstract. In high temperature liquid alloy semiconductors, the electronic conductivity (σ) is usually in the range $5\text{--}500\ \Omega^{-1}\ \text{cm}^{-1}$. Several workers have long argued that, since such values are lower than those predicted by the ‘Mooij’ limit or the Ioffe–Regel criterion ($k_{Fl} > 1$), the carriers in such systems are either localized or on the threshold of localization, i.e. they are characterized by a low mobility. There are no direct ways to measure the mobility of current carriers in high temperature liquids but we shall show that, with reasonable assumptions, reliable estimates of the mobility can be made by combining electron transport and magnetic susceptibility data. Our conclusions will challenge the idea that the apparent metal to non-metal transition observed in liquid alloy semiconductors is related to disorder induced localization.

Sir Nevill Mott, in his long and distinguished career, was responsible for bringing to the attention of the wide community of scientists the importance of the metal to non-metal (MNM) transition. The concept of localization induced either by disorder (the Anderson transition) or by suppression of charge fluctuations of the form $d^n + d^n \rightarrow d^{n+1} + d^{n-1}$ by correlation (the Mott transition) or by a combination of the two (the Mott–Anderson transition) has been central to the physics of the MNM transition for the last three decades. Nevertheless, scientists continue to be uneasy about the basis of the transition [1] and Mott himself, in his last letter to Professor Peter Edwards just before he died, expressed the view that the answer to the question ‘What is a metal?’ can be answered ‘only . . . at $T = 0$ K. Thus a metal conducts and a non-metal doesn’t’ (see preface to [1]). More recently, the very existence of the Mott-insulator phase has been questioned [2], but see, however, Anderson and Baskaran [3].

In spite of doubts and uncertainties about the nature of the transition, many hundreds of papers have been written about MNM transitions and, from an experimental viewpoint, have fallen into two principal categories: very low temperature measurements where extrapolation to 0 K is made or high temperature studies (say $T > 200$ K) where, for phase boundary reasons, extrapolation to low temperature is not an option. The first group of studies has, in the past, been largely driven by the wish to obtain the conductivity index and to understand its numerical value. The second group of experiments, which includes liquid semiconductors, liquid metals close to their critical points, metal–ammonia solutions, high temperature superconductors, bronzes, transition metal oxides etc, try to establish an effective minimum conductivity for delocalized current carriers in order, for example, to map out the concentration (or pressure or temperature) dependence of the MNM transition for a wide variety of systems. It is our belief that both approaches have their own difficulties [4, 5] and that from a strictly experimental standpoint, most of the accepted doctrine is at best unproven and much of it is probably wrong. In this paper, we will concentrate on the problems associated with liquid alloy systems in which, as the composition is varied, the conductivity dependence changes from that characteristic of a metal or semi-metal to that for a non-metal [6].

1. Conductivity scales

The so-called ‘Boltzmann conductivity’ σ_B is the conductivity derived from the Drude model of metals combined with the Boltzmann theory of transport. The usual expression for σ_B is

$$\sigma_B = S_F e^2 l / 12\pi^3 \hbar \quad (1)$$

where S_F is the surface area of the (spherical) Fermi surface and l is the mean free path. Equation (1) assumes that the electrons are completely degenerate. The lower limit of σ_B (the so-called minimum metallic conductivity, σ_M) is said to occur when l equals the interatomic spacing, a . For monovalent metals—again in the degenerate limit—and ignoring numerical corrections of order unity, we find [7]

$$\sigma_M \cong e^2 3\hbar a \quad (2)$$

which for $a = 3 \text{ \AA}$ yields a value of $2800 \Omega^{-1} \text{ cm}^{-1}$.

A third scale is the electron mobility, μ , defined by the relationship $\sigma = n|e|\mu$, where n is the electron density. Rewriting (2) we find that the minimum ‘metallic’ mobility μ_m , is given by

$$\mu_M \cong \frac{ea^2}{3\hbar} = 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \quad \text{for } a \sim 3 \text{ \AA}. \quad (3)$$

2. The inverse problem

Consider first the following problem confronted by an experimentalist. A hypothetical material of density 5.33 g cm^{-3} is found to have a conductivity of $2 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$. Can one deduce *from these data alone* that the current carriers are localized and that the mobility is much lower than the minimum value associated with ‘metallic’ behaviour? Some theoreticians seem to think that the answer is yes (see, for example, the discussions contained in [1]). In other words, the fact that $\sigma \ll \sigma_M$ is often taken as a direct proof that localization has occurred and that the independent particle/Boltzmann model is invalid [7]. Actually, the answer is *no* because the hypothetical material is in fact pure Ge which can be well understood in terms of the independent particle model and is characterized by high electron and hole mobilities ($\mu_e \sim 3800$, $\mu_h \sim 1800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Once the existence of a band gap is recognized and the appropriate statistics are used, of course, the ‘paradox’ disappears; the essential point is that *conductivity data alone* do not enable anything to be said about the onset of localization. Highly material specific information is required before any firm conclusions can be drawn about localization.

Next, let us consider the temperature dependence of σ . Again it has often been argued that a positive $d\sigma/dT$ (i.e. opposite to that associated with metals) necessarily implies that the system is non-metallic or at any rate close to a transition. The so-called ‘Mooij’ limit (resistivity $\sim 150 \mu\Omega \text{ cm}$ corresponding to a conductivity of $6000 \Omega^{-1} \text{ cm}^{-1}$ which is of the same order as σ_M) is frequently invoked as a boundary between ‘normal’ and ‘anomalous’ behaviour [8]. Several counter-examples exist. Experimentally, liquid Zn ($\rho = 37 \mu\Omega \text{ cm}$) has a positive $d\sigma/dT$ at the melting point—a fact known since the 1930s and well explained by the weak scattering theory of Ziman [9]. On the other hand, the liquid alloy system Ag–S and Ag–Se [10] and liquid alloys in the composition range between Cu_2Te and CuTe and between Cu_2Se and CuSe [6] have resistivities substantially in excess of the Mooij limit but show a negative (i.e. metallic) $d\sigma/dT$. Yet another example is afforded by metallic $(\text{V}_{1-x}\text{Cr}_x)\text{O}_3$ where the magnitude of σ is a factor of 100 less than σ_M [11].

Theoretically, Enderby and Barnes [4] have show that $\sigma \sim T$ at the mobility edge in an Anderson-type system; Villagonzalo *et al* [4] in a further development have demonstrated that

above the mobility edge in the *metallic regime*, $\sigma \sim T^2$ at temperatures sufficiently low that the phonons can be neglected. Clearly as the temperature is increased, apparently anomalous temperature coefficients will be observed as the T^2 behaviour is attenuated by the $(1/T)$ term characteristic of phonons. All of this, note, refers to the delocalized region.

Finally, the phenomenon of ‘resistivity saturation’ has been closely related to the numerical value of σ_M [7]. In a recent paper Mills *et al* [12] revisited this effect and conclude that the essential physics is contained in the combined effect of electron–phonon interaction on the one hand, and static disorder on the other; as this is a balance of competing effects, the existence of saturation depends strongly on material specific details.

All of the above confirm our assertion that although one can, in principle, work upwards from a model to an observed conductivity, the converse is not true. There is no ‘universal’ value of σ or of $d\sigma/dT$ which, of itself, allows one to decide the localized versus non-localized question except, of course, at absolute zero.

Table 1. Derived properties of liquid semiconductors.

Liquid semiconductor	Temperature (K)	Minimum conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	ΔE (eV)	α ($\Omega^{-1} \text{ cm}^{-1} \text{ eV}^{-1}$)
Tl ₂ Te	800	110 ± 5	0.17 ± 0.01	2900 ± 100
	1000	320 ± 5	0.02 ± 0.01	2700 ± 100
Tl ₂ Se	800	15 ± 2	0.36 ± 0.01	1500 ± 100
	1000	52 ± 2	0.25 ± 0.01	1400 ± 100
Tl ₂ S	800	5 ± 1	0.50 ± 0.01	1000 ± 100
	950	13 ± 1	0.40 ± 0.01	900 ± 100
Cu ₂ Te	1400	540	0.09	4200 ± 200
Cu ₂ Se	1400	158	0.36	2800 ± 200
Cu ₂ S	1400	38	0.90	2400 ± 200
Ag ₂ Se	1200	400	0.00	4000 ± 200

3. A model for liquid semiconductors

In [6] Enderby and Barnes introduced a phenomenological model to describe the behaviour of liquid alloy semiconductors close to stoichiometry. The formulation is based on the kinetic coefficients,

$$L_{11} = \int \sigma(E) \left[-\frac{\partial f}{\partial E} \right] dE$$

$$L_{12} = L_{21} = - \int \sigma(E)[E - \mu(T)] \left[-\frac{\partial f}{\partial E} \right] dE$$

where $f(E) = (1 + \exp\{[E - \mu(T)]/k_B T\})^{-1}$ 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

$$\sigma = L_{11}$$

$$S = L_{12}/|e|TL_{11}.$$

A useful representation of $\sigma(E)$ is given by

$$\begin{aligned} \sigma(E) &= \alpha(E_v - E) & E \leq E_v \\ &= 0 & E_v \leq E \leq E_c \\ &= \alpha(E - E_c) & E \geq E_c \end{aligned}$$

where α is a constant. 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, ΔE is in the range 0–0.5 eV.

This simple model enabled a range of experimental measurements to be put on a systematic footing; moreover, an inversion procedure involving data for σ and S allows ΔE and α to be established. The results for a variety of systems are shown in table 1.

Table 2. Effective value of α for conventional semiconductors.

Semiconductor	ΔE (eV)	σ ($\Omega^{-1} \text{ cm}^{-1}$) (at 300 K)	α ($\Omega^{-1} \text{ cm}^{-1} \text{ eV}^{-1}$)	Electron mobility (μ) ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	α/μ (numerical value)
Ge	0.67	0.021	2.7×10^5	3900	69
InSb	0.17	174	2.6×10^6	8×10^4	33
Te	0.35	2.5 (av)	5.5×10^4	1170	47
Sn (grey)	0.075	0.5×10^4	1.4×10^5	2500	56
				Average	50 ± 10

Table 3. Estimated mobilities for a selection of liquid semiconductors.

Liquid semiconductors	Temperature (K)	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
Tl ₂ Te	800	58
	1000	54
Tl ₂ Se	800	30
	1000	28
Tl ₂ S	800	20
	950	18
Cu ₂ Te	1400	84
Cu ₂ Se	1400	56
Cu ₂ S	1400	48
Ag ₂ Se		56

Table 4. Hall mobilities.

	σ ($\Omega^{-1} \text{ cm}^{-1}$)	R ($\text{cm}^3 \text{ V}^{-1}$)	$ R\sigma $ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
Pb	10 500	-4.4×10^{-5}	0.46
Bi	7750	-4.0×10^{-5}	0.31
CdSb	5000	-8×10^{-5}	0.40
ZnSb	5300	-5×10^{-5}	0.26
Tl ₂ Te	140	-3×10^{-3}	0.42
In ₂ Te ₃	100	-1×10^{-3}	0.10
As ₂ Te ₃	40	-5×10^{-2}	0.20

4. The density of states factor

We have argued above the low values of σ shown in table 1 do not, by themselves, enable any conclusions to be drawn about the localization of electrons. Other experimental data are required, particularly those relating to the density of states. Recognizing this, Mott [7] introduced the (density of states)² or g^2 factor into (2); he regarded the experimental evidence

derived from plotting the Pauli paramagnetic susceptibility against the square root of the conductivity as strong support for the view that new physics arises once σ is less than σ_M . Data on Tl_xTe_{1-x} were consistent with Mott's approach but subsequent work by Ohno and co-workers [10] on a range of silver based chalcogenides provided a series of counter-examples. There is *no* correlation between the susceptibility and the electrical conductivity. Indeed, close to the stoichiometric compositions As_2S and Ag_2Se , the conductivity *increases* as the susceptibility *decreases*—exactly opposite to the behaviour expected if the g^2 factor were significant.

5. Are current carriers in liquid semiconductors mobile?

The constant α in table 1 is closely connected with the value of the mobility. It is therefore instructive to compare values of α derived from the inversion scheme given in [6] for liquid alloys with those for crystalline semiconductors. This is, of course, an approximation because there is no guarantee that $\sigma(E) \propto E^s$ with $s = 1$ will necessarily apply to solid semiconductors but the errors involved are probably not significant. The results for materials with energy gaps comparable with those found in liquid semiconductors are shown in table 2.

The fact that for a wide variety of semiconductors α/μ is a constant to within a factor of 2 suggests that we can estimate the carrier mobility of liquid semiconductors with the results shown in table 3.

Even allowing for a factor of three error in the numerical value of α/μ , it is clear that the current carrier mobilities in a representative selection of liquid semiconductors are greatly in excess of the minimum 'metallic' mobility given in equation (3). Although the temperature range for thallium based chalcogenides is small, there is evidence that the mobility decreases with temperature, reflecting the reduction in short range order.

6. The Hall mobility (μ_H)

There is no complete theory of the Hall coefficient in liquid semiconductors; setting $\mu_H = R\sigma$ is incorrect once the fully degenerate limit ceases to be satisfied (see especially Ghibaudo in [13]). There are also severe experimental difficulties in making Hall measurements so $R\sigma$ values need to be interpreted with care. In spite of these problems it is interesting to consider *trends* in the data and, in particular, to compare $R\sigma$ values for liquid semiconductors with the higher valence liquid metals (table 4).

Once again, there is no evidence that the carrier mobilities in liquid semiconductors are significantly less than those characteristic of higher valence liquid metals which have been shown to be well described by the weak scattering theory of Ziman.

It is also worth pointing out that the one example [14] where $|R\sigma|$ can be derived as a function of composition (figure 1) shows that the Hall mobility actually increases as stoichiometry is approached. This is consistent with the view that enhanced short range order increases the carrier mobility as predicted by weak scattering theory.

7. Conclusion

Contrary to much that has been written in the past, we do not consider that carrier localization plays any significant role in the observed reduction in the conductivity of liquid alloy semiconductors as stoichiometry is approached. The carrier mobility remains well above the minimum value postulated for the application of Boltzmann transport theory. The driver for

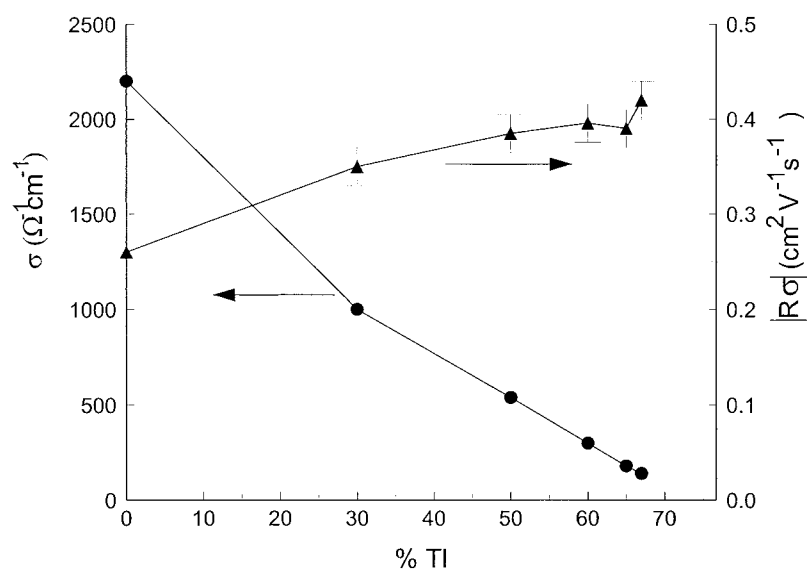


Figure 1. The conductivity and Hall mobility for liquid $\text{Tl}_x\text{Te}_{1-x}$ at 800 K.

the reduction in conductivity is the development of a deep gap in the density of states brought about by chemical bonding. At stoichiometry, liquid semiconductors are characterized by substantial short range order as the neutron diffraction experiments have established [15]. This is completely consistent with the approach developed in this paper.

Acknowledgments

We wish to thank our colleagues at Bristol (Professor Evans) and Argonne (Drs Saboungi and Price) for their many helpful discussions about the problem posed by liquid semiconductors. The views expressed here are, however, our own and are not necessarily endorsed by them. We also are grateful to the Engineering and Physical Sciences Research Council for their generous support.

References

- [1] Edwards P P, Johnston R L, Rao C N R and Tunstall D P (eds) 1998 *Phil. Trans. R. Soc. A* **356** 1
- [2] Laughlin R E 1998 *Adv. Phys.* **47** 943
- [3] Anderson P W and Baskaran G *Preprint Cond-Mat/9711197*
- [4] Enderby J E and Barnes A C 1994 *Phys. Rev. B* **49** 5062
Villagonzalo C, Römer R A and Schröder M 1999 *Euro. Phys. J.* submitted
- [5] von Lohneysen H 1998 *Phil. Trans. R. Soc. A* **356** 139 and references therein
- [6] Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85
- [7] Mott N F 1990 *Metal Insulator Transitions* (London: Taylor and Francis)
- [8] Mooij J J 1973 *Phys. Status Solidi* **179** 521
- [9] Ziman J M 1961 *Phil. Mag.* **6** 1013
- [10] Ohno S, Okada T, Barnes A C and Enderby J E 1996 *J. Noncryst. Solids* **205–207** 98
- [11] Honig J M 1985 *The Metallic and Non Metallic States of Matter* ed P P Edwards and C N R Rao (London: Taylor and Francis) p 261
- [12] Mills A J, Hu J and Das Sarma S 1999 *Phys. Rev. Lett.* **82** 2354
- [13] Ghibaudo G 1987 *J. Phys. C: Solid State Phys.* **20** L769

- [14] Enderby J E and Simmons C J 1969 *Phil. Mag.* **20** 125
Enderby J E 1974 *Amorphous and Liquid Semiconductors* ed J Tauc (New York: Plenum) p 361
- [15] Barnes A C, Lague S B, Salmon P S and Fischer H E 1997 *J. Phys.: Condens. Matter* **9** 6159