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# The determination of the conductivity parameters for liquid semiconductors

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**Abstract.** A scheme to invert the conductivity and thermopower data to yield the fundamental parameters for liquid semiconductors is presented. As an illustrative example the method is applied to liquid thallium chalcogenides. Some comments on the thermoelectric figure of merit are included.

## 1. Introduction

The macroscopic conductivity  $\sigma$ , thermopower  $S$  and thermal conductivity  $\kappa_e$  for an electronic conductor are, in the absence of interactions, related to the energy-dependent conductivity  $\sigma(E)$  through the equations

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

$$S = \frac{k}{|e|} \int \frac{\sigma(E)}{\sigma} \frac{E - E_F}{kT} \frac{\partial f}{\partial E} dE \quad (2)$$

and

$$\kappa_e = \frac{1}{|e|^2 T} \left[ \frac{(\int (E - E_F) \sigma(E) (\partial f / \partial E) dE)^2}{\int \sigma(E) (\partial f / \partial E) dE} - \int (E - E_F)^2 \sigma(E) \frac{\partial f}{\partial E} dE \right] \quad (3)$$

where  $f$  is the Fermi function and  $k$  is the Boltzmann constant (Mott and Davis 1971, Ziman 1960). Evidence has been given elsewhere (Enderby and Barnes 1990) which suggests that for many liquid semiconductors  $\sigma(E)$  is proportional to  $E$ , the constant of proportionality being in the range  $1000-3000 \Omega^{-1} \text{ cm}^{-1} \text{ eV}^{-1}$ . In this model,  $\sigma(E)$  for a disordered *ambipolar* semiconductor will have the generic form shown in figure 1(a). The purpose of this paper is to propose a simple inversion scheme which allows  $\Delta E$  the conductivity gap,  $\alpha_v$  and  $r = \alpha_v / \alpha_c$ , the asymmetry factor, to be extracted from experimental data. Although the results here are embedded in a longer review article (Enderby and Barnes 1990), it was felt worthwhile to bring them together in the form of a paper.

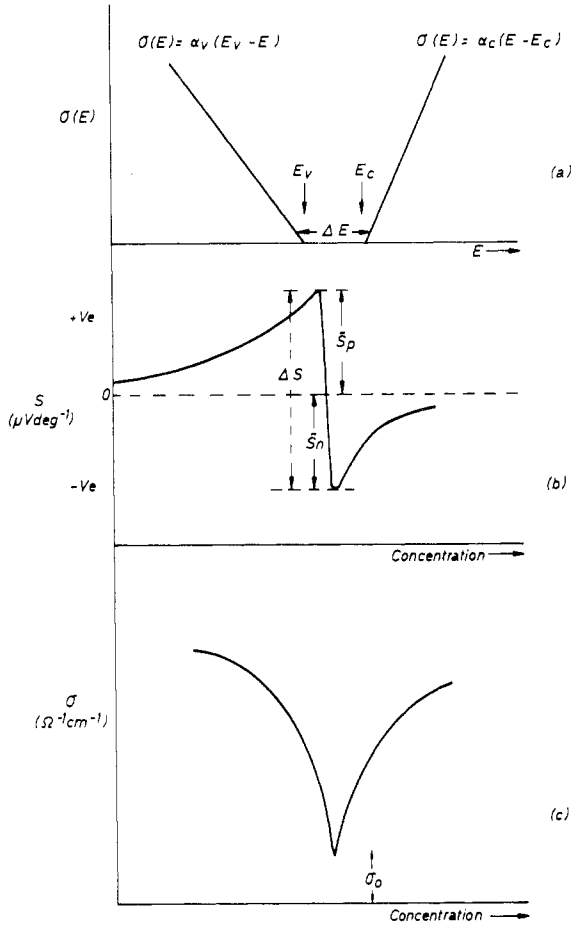


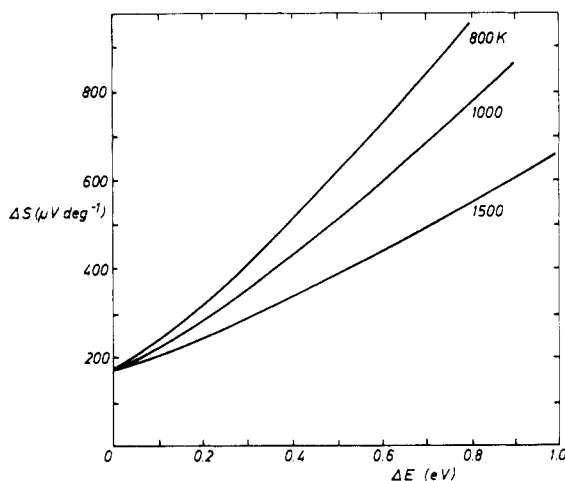
Figure 1. The conductivity and thermopower for the linear edge model as a function of  $E_F$ .

## 2. The conductivity gap $\Delta E$

As  $E_F$  moves from left to right across  $\Delta E$  the thermopower will peak at a maximum value  $\tilde{S}_p$ , go through zero, and then peak at a maximum negative value  $\tilde{S}_n$  (figure 1(b)). Numerical integration of equation (2) shows that  $\Delta S = \tilde{S}_p - \tilde{S}_n$  is independent of  $\alpha_v$  for a wide range of asymmetry factors ( $0.2 < r < 5$ ) and depends only on  $\Delta E$  and temperature. Thus provided the p-n transition occurs over a concentration range small enough so that  $\Delta E$  is unchanged, the observed value of  $\Delta S$  allows  $\Delta E$  to be determined directly (figure 2).

## 3. The asymmetry factor, $r$

Although  $\Delta S$  does not depend on  $r$  for  $0.2 < r < 5$ ,  $|\tilde{S}_p/\tilde{S}_n|$  does. The relationship between  $|\tilde{S}_p/\tilde{S}_n|$  and  $r$  is shown in figure 3.



**Figure 2.** The relationship between  $\Delta S$  and the conductivity gap  $\Delta E$  for three temperatures.

#### 4. The value of $\alpha_v$

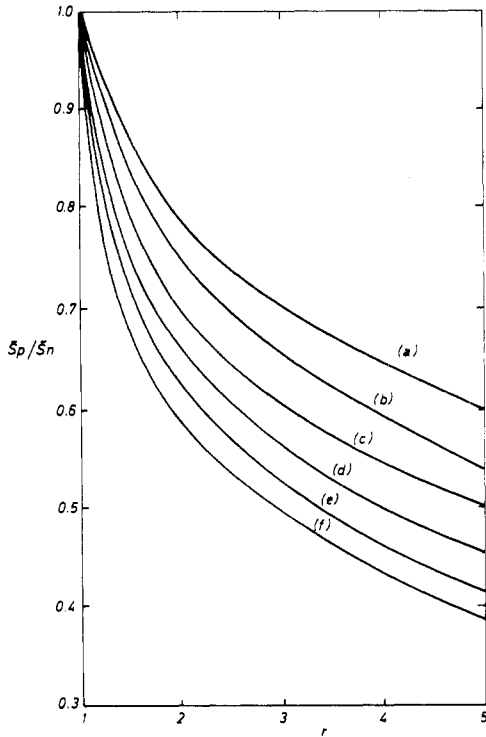
For many disordered semiconductors the energy-dependent conductivity is symmetric (i.e.  $r = 1$ ). In this case, the minimum value of the conductivity denoted by  $\sigma_0$  in figure 1(c) allows  $\alpha_v \simeq \alpha_c = \alpha$  to be determined. The relationship between  $\alpha$ ,  $\sigma_0$  and  $\Delta E$  is shown in figure 4.

#### 5. An illustrative example: liquid Tl-X (X = Te, Se, S)

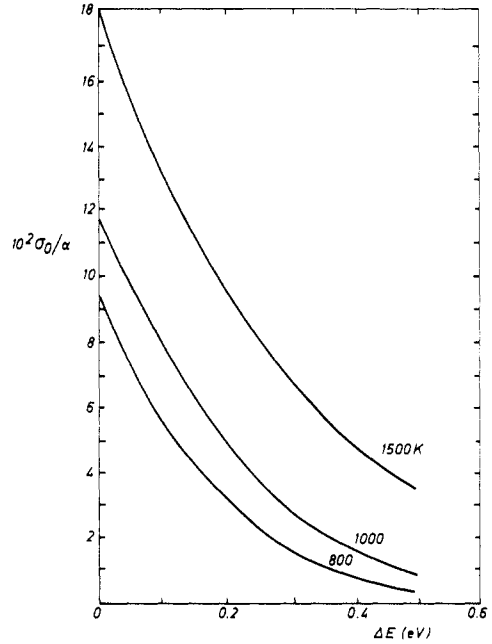
Conductivity and thermopower data are available for all three thallium chalcogenides, each of which is characterised by a minimum in the electrical conductivity at the stoichiometric composition  $Tl_2X$  and a p-n transition in  $S$ . As an example, the experimental data for liquid thallium selenide are shown in figure 5 and a summary of all the relevant data is given in table 1. It is clear that  $r \simeq 1$  for the three alloys so that  $\alpha_v \simeq \alpha_c = \alpha$ . The conductivity gaps and their temperature dependences obtained by the methods described above are shown in table 2. The magnitude of  $\Delta E$  and the temperatures at which  $\Delta E$  vanishes (the semiconductor-metal transition temperature) are well correlated with electronegativity differences. At present, the origin of the variation of  $\alpha$  with X is not clear, but it may be related to the broadening of the conductivity edge by effects specifically arising from the fluidity (as opposed to the disorder) characteristic of liquid systems (Mott private communication).

#### 6. The 'edge' value of the transport coefficients

Consider a system for which  $\Delta E \gg kT$  so that at the point where  $E_F$  crosses the conductivity edges  $E_v$  and  $E_c$ , ambipolar effects can be neglected. What is the value of  $S$ , for example, at a conductivity edge? It is frequently, but incorrectly, stated, following



**Figure 3.** The relationship between  $\tilde{S}_p/\tilde{S}_n$  and the asymmetry factor  $r$  at 1500 K for six values of the conductivity gap  $\Delta E =$ : 0.5 (a), 0.4 (b), 0.3 (c), 0.2 (d), 0.1 (e) and 0 eV (f).



**Figure 4.** The relationship between  $100\sigma_0/\alpha$  and  $\Delta E$  for three temperatures.

Mott and Davis (1971), that the ‘edge’ value of  $S$  is  $k/e = \pm 86 \mu\text{V K}^{-1}$ . The error arises from the incorrect extrapolation of the non-degenerate forms of equation (2):

$$S = \frac{k}{|e|} \left[ \frac{E_F - E_v}{kT} + 1 \right] \quad (\text{holes}) \quad (4)$$

$$S = -\frac{k}{|e|} \left[ \frac{E_c - E_F}{kT} + 1 \right] \quad (\text{electrons}) \quad (5)$$

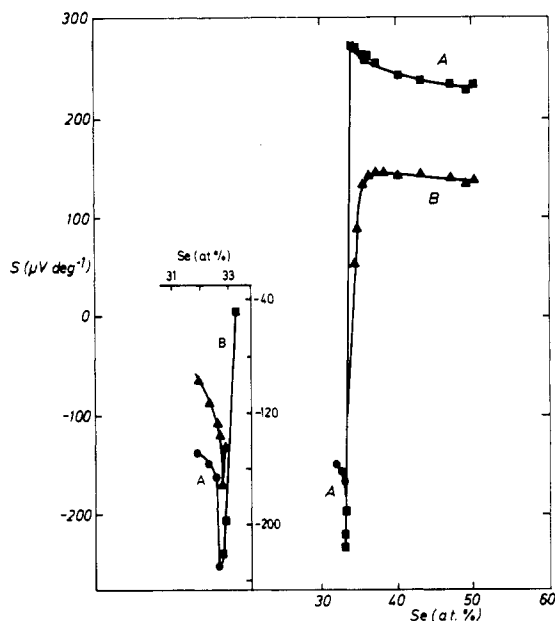
to the limit  $E_F = E_v$  or  $E_F = E_c$ . In fact, for  $\sigma = \alpha E^\nu$ , the edge value of  $S$  is universal and depends only on the conductivity exponent  $\nu$  and is independent of temperature. Equation (2) can be integrated exactly for  $E_F = E_v$  or  $E_F = E_c$  with the result

$$S = \pm \left( \frac{k}{|e|} \right) \left( \frac{\nu + 1}{\nu} \right) \frac{I_{\nu+1}}{I_\nu} \quad (6)$$

where

$$I_\nu = [1 - 2^{1-\nu}] \Gamma(\nu) \zeta(\nu) \quad (7)$$

and  $\Gamma(x)$ ,  $\zeta(x)$  are the usual gamma and Riemann functions. The thermopower for various values of  $\nu$  are given in table 3. It is clear that the often quoted value of



**Figure 5.** The change in thermopower with composition for  $\text{Tl}_2\text{Se}$  close to stoichiometry (Regel 1970). A, 750 K and B, 1000 K.

**Table 1.**  $\alpha$  values for liquid thallium chalcogenides.

Liquid semiconductor	Temperature (K)	$\sigma_0$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	$\alpha$ ( $\Omega^{-1} \text{ cm}^{-1} \text{ eV}^{-1}$ )
$\text{Tl}_2\text{Te}$	800	$110 \pm 5$	$2900 \pm 100$
	1000	$320 \pm 5$	$2700 \pm 100$
$\text{Tl}_2\text{Se}$	800	$15 \pm 2$	$1500 \pm 200$
	1000	$52 \pm 2$	$1400 \pm 100$
$\text{Tl}_2\text{S}$	800	$5 \pm 1$	$1000 \pm 200$
	950	$13 \pm 1$	$900 \pm 100$

**Table 2.** The conductivity gap for liquid thallium chalcogenides.

Liquid semiconductor	Temperature (K)	$\Delta S$ ( $\mu\text{V K}^{-1}$ )	$\Delta E$ (eV)	$\Delta E = \Delta E_0 - \beta T$	Temperature for a zero gap (K)
$\text{Tl}_2\text{Te}$	800	$300 \pm 10$	$0.17 \pm 0.01$	$0.77 - 7.5 \times 10^{-4} T$	1030
	1000	$190 \pm 10$	$0.02 \pm 0.01$		
$\text{Tl}_2\text{Se}$	800	$470 \pm 10$	$0.36 \pm 0.01$	$0.80 - 5.5 \times 10^{-4} T$	1450
	1000	$320 \pm 10$	$0.25 \pm 0.01$		
$\text{Tl}_2\text{S}$	800	$620 \pm 10$	$0.50 \pm 0.01$	$1.03 - 6.6 \times 10^{-4} T$	1565
	950	$440 \pm 10$	$0.40 \pm 0.01$		

$\pm 86 \mu\text{V K}^{-1}$  at the edge value for  $S$  is seriously in error. It is also worth noting that  $S(\text{edge})$  is independent of  $T$  and that the values as shown in table 3 apply as  $T \rightarrow 0$ . At very low temperatures,  $\Delta E$  is necessarily  $\gg kT$  so that ambipolar effects

can be neglected. Thus provided equation (2) remains valid at low temperatures, a measurement of the thermopower of any disordered semiconductor will yield directly the value of the critical exponent  $\nu$ .

**Table 3.** The thermoelectric power when  $E_F$  coincides with a conductivity edge (single band).

Conductivity exponent $\nu$	Thermopower ( $\mu\text{V K}^{-1}$ ) <sup>†</sup>
1.0	$\pm 205$
1.5	$\pm 241$
2.0	$\pm 282$

<sup>†</sup> Positive if  $E_F = E_v$ , negative if  $E_F = E_c$ .

It is also possible to write down explicit expressions for the edge value of  $\sigma$  and  $\kappa_e$ . Thus for  $\sigma = \alpha E^\nu$

$$\sigma = \alpha \nu (kT)^\nu I_\nu \quad (8)$$

$$\kappa_e = \frac{\alpha (kT)^{\nu+2}}{|e|^2 T} \left[ (2 + \nu) I_{\nu+2} - \frac{(\nu + 1)^2}{\nu} \frac{I_{\nu+1}^2}{I_\nu} \right]. \quad (9)$$

If we take the special case of  $\nu = 1$ , we find that

$$S = 205 \mu\text{V K}^{-1} \quad (10)$$

and is independent of  $\alpha$

$$\sigma = \alpha kT \ln 2 \quad (11)$$

and

$$\kappa_e = 1.47 \frac{\alpha (kT)^3}{|e|^2 T} \quad (12)$$

## 7. The figure of merit for thermoelectric generation

The device efficiency for a thermoelectric generator depends on the figure of merit,  $\gamma$ . This is defined as

$$\gamma = \frac{S^2 \sigma T}{\kappa} \quad (13)$$

where  $\kappa$  is the total thermal conductivity (i.e. electronic and atomic).  $\gamma$  should be of the order unity for effective thermoelectric generation. As  $E_F$  crosses the conductivity edge, the electronic contribution to  $\gamma$  (denoted  $\gamma_e$ ) can be evaluated from equations (6)–(12) and turns out to be independent of  $\alpha$  and  $T$ . For the special case of  $\nu = 1$ ,  $\gamma_e = 2.66$ , a very high value, suggesting that liquid semiconductors offer device possibilities. However, the atomic part of  $\kappa$  degrades the electronic contribution to  $\gamma$  and if the atomic component of  $\kappa$  is taken as  $4 \times 10^{-3} \text{ W K}^{-1}$  (Cutler 1977), the actual figure of merit evaluated at the conductivity edge is, for  $\alpha = 1000 \Omega^{-1} \text{ cm}^{-1} \text{ eV}^{-1}$ , 0.67 at 1000 K. At 1500 K,  $\gamma$  approaches unity and increases further if  $\alpha$  exceeds  $1000 \Omega^{-1} \text{ cm}^{-1} \text{ eV}^{-1}$ .

The simple model proposed here satisfactorily explains the values of  $\gamma$  reported by the Russian school and discussed in some detail by Cutler (1977). In particular it suggests that highly effective thermoelectric generators might be based on unipolar liquid semiconductors with  $E_F$  tuned to the conductivity edge.

## **Acknowledgments**

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