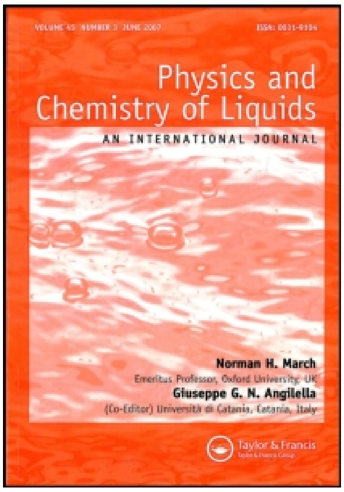

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THERMOELECTRIC POWER OF THE LIQUID (Pb-Sn)$_{1-x}$ Te$_x$ ALLOY

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The thermoelectric power of a $(Pb_{0.8}Sn_{0.2})_{1-x}Te_x$ liquid alloy has been measured as a function of composition and temperature. The well-known sigmoid shape for semiconductor to metal transition was observed. A mathematical expression for $\sigma(E)$ was found, based on the Enderby *et al.*, mobility edge model. We have compared the experimental data with our theoretical formula, by adjusting some physical parameters: Fermi energy, energy gap, α_C/α_V relation and the exponent ν. The fitting proved to be in good agreement with the physical assumptions.

KEY WORDS: Charge transport, liquid semiconductors.

INTRODUCTION

The interpretation of charge transport experimental results in liquid semiconductors is a complicated theoretical problem. It is generally admitted that the Seebeck coefficient is given by the following expression[1]

$$S(T) = -\frac{k}{e}\int_{-\infty}^{\infty} \frac{\sigma(E)}{\sigma}\frac{E-E_F}{kT}\frac{\partial f(E)}{\partial E}dE \tag{1}$$

where $f(E)$ is the Fermi-Dirac distribution function; σ the electrical conductivity, k the Boltzmann's constant and e the electron charge. Equation (1) is only applied to non-interacting carriers[2,3]. Hence, it is necessary to know the dependent energy function, in order to obtain exact results. In the case of an electronic conduction, it is proposed that[2]:

$$\sigma(E) = \alpha_C(E-E_C)^{\nu} \quad \text{for} \quad E \geqslant E_C \tag{2}$$

$$\sigma(E) = 0 \quad \text{for} \quad E \leqslant E_C$$

where E_C is the electron mobility edge. A similar expression is proposed for holes, being E_V replaced for the corresponding hole mobility edge. It has been argued that the value $\nu = 1$ is not valid when no interactions are present and the constant σ depends on the structural characteristics of the investigated system. Enderby and Barnes[2] have calculated the expression (1), assuming (2) for three different cases:

i) unipolar conduction; ii) $E_F = E_V = E_C = 0$; iii) $\Delta E \gg kT$.

The goal of this work is to use this theoretical approach, in order to achieve a better understanding of our experimental results.

EXPERIMENTAL

The Seebeck effect consists of the generation of an electromotive force in a non-uniformily heated material under zero current conditions. In an isotropic liquid sample the following equation is admitted[5,6]

$$\nabla U = -S \nabla T \tag{3}$$

where ∇U and $\nabla T$are the voltage and temperature gradients along the sample of the liquid respectively, and S is defined as its Seebeck coefficient. We have followed an experimental procedure which has been described by different authors[7,8,9]. The liquid sample filled a quartz container (80 mm long). At each end of the container there was a graphite electrode. A hole was drilled in both electrodes and a metallic junction (A–B) was placed within them, near the tip in contact with the liquid surface. The voltage drop between either the $A(U_A)$ or $B(U_A)$ leads, was measured by a potentiometric method. Hence, it holds the following expression:

$$S_{\text{liquid}} = S_A + \frac{U_A}{U_A - U_B}(S_B - S_A) \tag{4}$$

S_A and S_B being the corresponding absolute thermoelectric powers of each metal. In order to minimize the effect of non zero temperature gradients, the following measurement technique is employed: for each fixed mean temperature, the gradient is slightly changed and a relationship between U_A and $U_A - U_B$ is plotted. Due to the linear relation between both, it is easy to obtain the slope $U_A/(U_A - U_B)$[10]. This work was performed by using a three heating zone furnace and calibrated pairs of Chromel (or Ta)-Alumel (or Mo) wires. These were protected, against corrosion, by sealing the electrodes with a ceramic compound (sodium silicates, alumina and quartz mixtures). To prevent evaporation, all the experiments were carried out under Ar overpressure ($\sim$ 0.6 Mpa), after previous de-gassing under vacuums (up to 10^{-4} Pa.).

RESULTS

We have measured the thermoelectric power of the liquid $(\mathrm{Pb}_{0.8}\,\mathrm{Sn}_{0.2})_{1-x}\mathrm{Te}_x$ alloy for $x = 0, 0.2, 0.3, 0.6, 0.65, 0.7, 0.8, 0.9$ and 1, up to 1250 °K. The alloy thermoelectric behaviour differs in three concentration zones. For $0 \leqslant x \leqslant 0.3$ the system is a liquid metal, because S is negative, small and it increases with temperature[11,12] (Fig. 1-a). Between $x = 0.3$ and $x = 0.6$ a metal to semiconductor transition takes place, and S changes from negative values to positive ones. For $0.6 \leqslant x \leqslant 1$ the liquid alloy may be characterized as a liquid semiconductor. S assumes positives values, higher than metallic (in magnitude), and it decreases with temperature (Fig. 1-b).

DISCUSSION

The S results obtained are consistent with those found by other authors: at x close to zero ($\mathrm{Pb}_{0.8}\,\mathrm{Sn}_{0.2}$[13]) and x near one (pure Te[14,15]). The S behavior for semiconductor zone does not belong to the situation described by Enderby and Barnes[1] for

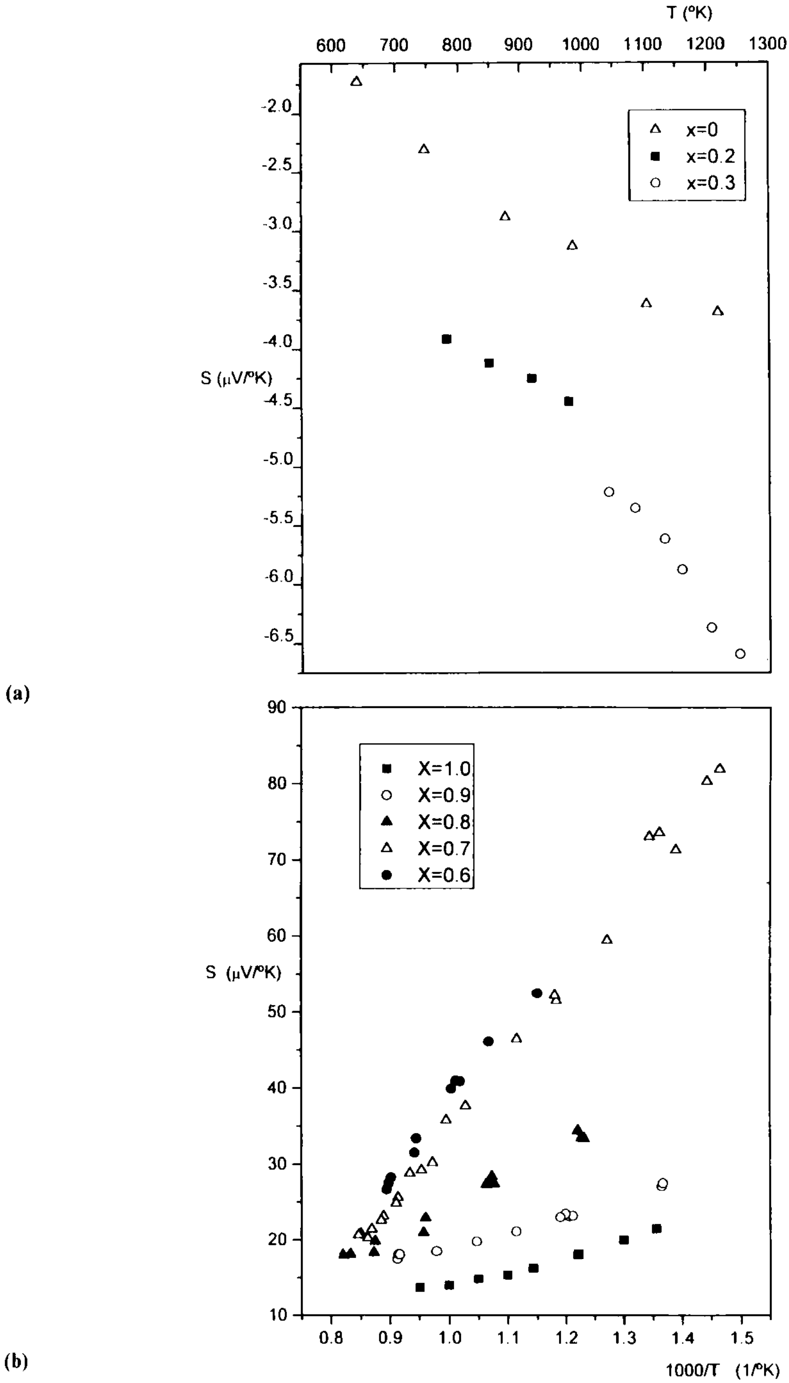

Figure 1 (a) Seebeck coefficient as a function of temperature and concentration in metallic region. (b) Seebeck coefficient as a function of temperature and concentration in semiconductor region.

high S values and for n to p semiconductor transition. Cases where neither Maxwell-Boltzmann nor metallic regime are valid have been described by Cutler[22] a few years ago ("intermediate regime").

Now, the Kubo-Greenwood formula[1,3,4] for electrical conductivity is known

$$\sigma = -\int_{-\infty}^{\infty} \sigma(E)\frac{\partial f(E)}{\partial E}\,dE \tag{5}$$

If the energy origin is taken in the middle of the energy gap, $\nabla E = E_C - E_V$ and replacing the electron, $f_N(E)$, and hole $f_P(E)$ distributions

$$f_N(E) = 1/(e^{\beta(E-E_F)} + 1) = 1 + f_P(E) \tag{6}$$

with $\beta = 1/kT$ and Fermi's Energy, E_F it can be obtained by (2), (5) and (6)

$$\sigma = \int_{-\infty}^{E_V} \alpha_V(E_V - E)^{\nu}\frac{\partial f_P(E)}{\partial E}\,dE - \int_{E_C}^{\infty} \alpha_C(E - E_C)^{\nu}\frac{\partial f_N(E)}{\partial E}\,dE \tag{7}$$

where σ_P and σ_N denote the contribution of valence and conductions band, respectively (both positive due to $\partial f_P(E)/\partial E \geqslant 0$ and $\partial f_N(E)/\partial E \leqslant 0$).
The integration of σ_P leads to

$$\sigma_P = \frac{\alpha_v \nu}{\beta^{\nu}} F_{\nu-1}(\eta_v) \tag{8}$$

where $F_{\nu-1}(\eta_v)$ is Fermi's integral[16] of the form

$$I_{\nu-1}(\eta) = \frac{1}{\Gamma(\nu)}\int_0^{\infty} \frac{\varepsilon^{\nu-1}}{e^{\beta(\varepsilon-\eta)}+1}\,d\varepsilon = \frac{1}{\Gamma(\nu)}F_{\nu-1}(\eta) \tag{9}$$

and

$$\eta_v = \beta(Ev - E_F) = -\beta(\Delta E/2 + E_F) \tag{10}$$

(where $\Gamma(\nu)$ is the gamma function).
For σ_N one has

$$\sigma_N = \frac{\alpha_C \nu}{\beta^{\nu}} F_{\nu-1}(\eta_C) \tag{11}$$

with $\eta_C = \beta(E_F - E_C) = \beta(E_F - \Delta E/2)$

Thus, the ambipolar conductivity is from (8) and (11) in (7):

$$\sigma = (kT)^{\nu}\alpha_v \nu\,[F_{\nu-1}(\eta_v) + rF_{\nu-1}(\eta_C)] \tag{12}$$

the ratio being $r = \alpha_C/\alpha_P$.

The calculus of ambipolar thermoelectric power is resolved from (1) as follows

$$S = \frac{k\beta}{e\sigma}\left[-\int_{-\infty}^{E_V} \sigma_P(E)(E - E_F)\frac{\partial f_P(E)}{\partial E}\,dE + \int_{E_C}^{\infty} \sigma_N(E)(E - E_F)\frac{\partial f_N(E)}{\partial E}\,dE\right] = S_P + S_N \tag{13}$$

It must be pointed out that the results are consistent with $S_P \geqslant 0$ and $S_N \leqslant 0$.

The evaluation of S_P implies the calculus of

$$S_P = \frac{k\beta}{e\sigma}\left[\int_{-\infty}^{E_V} \sigma_P(E) E \frac{\partial f_P(E)}{\partial E} dE - E_F \int_{-\infty}^{E_V} \sigma_P(E) \frac{\partial f_P(E)}{\partial E} dE\right] \tag{14}$$

Performing some variable changes and using (8) in (14)

$$S_P = \frac{k\beta}{e\sigma}\left[-\int_{-\infty}^{E_V}\left(E\frac{d\sigma_P(E)}{dE} + \sigma_P(E)\right) f_p(E) dE + E_F\sigma_P\right]. \tag{15}$$

After simple algebraic calculations in (15)

$$S_P = \frac{k\beta}{e\sigma}\left[\sigma_P\left(\frac{\Delta E}{2} + E_F\right) + \frac{\alpha_v(v+1)}{\beta^{v+1}} F_v(\eta_v)\right] \tag{16}$$

S_N is found in an analogous way

$$S_N = \frac{k\beta}{e\sigma}\left[\sigma_N\left(E_F - \frac{\Delta E}{2}\right) - \alpha_C \frac{(v+1)}{\beta^{v+1}} F_v(\eta_C)\right] \tag{17}$$

Adding the Eqs. (16) and (17):

$$S = S_P + S_N = \frac{k\beta}{e\sigma}\left[\frac{(v+1)}{\beta^{v+1}}[\alpha_v F_v(\eta_v) - \alpha_C F_v(\eta_C)] + \frac{\Delta E}{2}(\sigma_P - \sigma_N) + E_F(\sigma_P + \sigma_N)\right] \tag{18}$$

and ordering the different terms one obtains

$$S = \frac{k}{e}\left[\frac{1}{[F_{v-1}(\eta_v) + rF_{v-1}(\eta_C)]}\left[\left(\frac{v+1}{v}\right)[F_v(\eta_v) - rF_v(\eta_C)]\right.\right.$$
$$\left.\left. + \left(\frac{\Delta E}{2kT}\right)[F_{v-1}(\eta_v) - rF_{v-1}(\eta_C)]\right] + \frac{E_F}{kT}\right] \tag{19}$$

To compare experimental data, represented by $S(T) = A/T + B$ (displayed in Tab. 1) by using Eq. (19) it is necessary to adjust $\Delta E, E_F, v$ and r for the whole temperature range. We have used a fitting procedure based on a modified Simplex Method[17].

For physical reasons we choose the fitting parameters to obey the conditions:

$$-\frac{\Delta E}{2} \leqslant E_F \leqslant 0$$

$$1 \leqslant v \leqslant 2.5$$

$$0.4 \leqslant r \leqslant 1.2$$

Numerical results are shown in Table 2.

Table 1 Constants A and B for $(Pb_{0.8}Sn_{0.2})_{1-x}Te_x$ alloy; with $S = A/T + B$ law in $0.6 \leqslant X \leqslant 1$ range, and $S = AT + B$ law in $0 \leqslant X \leqslant 0.3$ range.

X	$A(\mu V)$	$B(\mu V/{}^\circ K)$
1.0	$(18.8 \pm 0.6)\ 10^3$	-5 ± 0.5
0.9	$(20.7 \pm 0.2)\ 10^3$	-1.4 ± 0.5
0.8	$(41.4 \pm 0.4)\ 10^3$	-17 ± 1
0.7	$(101.4 \pm 0.7)\ 10^3$	-67 ± 4
0.6	$(106 \pm 0.8)\ 10^3$	-68 ± 5
0.3	$-(7.1 \pm 0.6)\ 10^{-3}$	2.3 ± 0.7
0.2	$-(2.7 \pm 0.2)\ 10^{-3}$	1.1 ± 0.6
0.0	$-(3.5 \pm 0.2)\ 10^{-3}$	0.3 ± 0.3

Table 2 Theoretical fitting parameters for different Tellurium compositions.

X	$\Delta E(eV)$	$E_F(eV)$	ν	r
0.9	0.25 ± 0.01	-0.12 ± 0.005	1.33 ± 0.03	0.65 ± 0.03
0.8	0.25 ± 0.01	-0.11 ± 0.005	1.37 ± 0.03	0.78 ± 0.03
0.7	0.31 ± 0.01	-0.10 ± 0.005	1.32 ± 0.03	1.10 ± 0.03
0.6	0.31 ± 0.01	-0.10 ± 0.005	1.31 ± 0.03	1.10 ± 0.03

CONCLUSIONS

As far as we know, there are neither analytical expressions nor computational results for the ambipolar case. Enderby and Barnes have applied to Kubo-Greenwood formula for the symmetric p–n transitions, and high S values. It must be pointed out, that our expression (19) is coincident with their limit approximations for the situation described above. On the other hand, it is possible to obtain an adequate fitting of the mobility edge structure parameters. The results obtained are physically reasonable becasue:

- The energy gap is small.
- E_F is near E_v.
- r reflects a nearly similar structure between valence and conduction bands.
- The exponent ν is clearly larger than unity, which is indicative of rapid growth of $\sigma(E)$ conductivity.

Our mathematical analysis is limited to the semiconductor regime, because to obtain a functional relationship $\sigma(E)$ in the metallic case has proved difficult to date.

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