Thermoelectric Power of the Liquid Sn—Te Alloy

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The Seebeck coefficient (S) of $Sn_{1-x}-Te_x$ liquid alloys was measured as a function of concentration and temperature. For $0 \leqq x < 0.45$ the behaviour is metallic; S values are small and negative, rising linearly with temperature. The predicted values of Ziman's theory when using the hard sphere approximation disagree with the experimental ones. The change in sign occurs for 0.45. For $x = 0.5$ (stoichiometric composition) the thermoelectric power decreases linearly with temperature. This fact is explained assuming a two-band model. For $x \geqq 0.6$ the liquid alloy becomes more semiconducting and presents a maximum in the isotherms of S for $x = 0.65$. For the excess tellurium concentration range we have calculated the difference $E_F - E_V$ and γ/k_B, assuming a $S(1/T)$ law. The experimental values are compared with those of Dancy and Glazov.

Introduction

The dependence of the electron properties of Sn-Te liquid alloys on temperature and concentration has been studied by several authors. It was observed that around the stoichiometric composition (0.5), the conductivity [1], the magnetic susceptibility [2], the enthalpy of mixing [3], and the fluidity [4] pass through a minimum. These data suggest the presence of associations in the melt. As for the thermoelectric power, there are Dancy's [1] and Glazov and coworkers [4] data. Dancy has measured S (the Seebeck coefficient) in the concentration range between 0.2 and 1.0 but presents only values for two or three temperatures at each concentration, so it is not easy to extract information about the variation of S with temperature. According to her curves, it is very difficult to know the concentration at which S changes sign, but at 900 °C it could be estimated to be at $x \cong 0.5$. On the other hand, Glazov et al. present only S values as a function of temperature for the compound $Sn_{0.5}$-$Te_{0.5}$. Their data are very different from those of Dancy. Therefore we have remeasured the thermoelectric power, both as a function of temperature and concentration. We were also interested in following the change of S through the melting point for each concentration.

Experimental Method

We have used the method described by Bradley [5]. A quartz container (80 mm long) was filled with the substance being investigated. At each end of the container a hole was made, through which a graphite electrode was passed. Pairs of alumel and molybdenum wires were connected to each of the graphite electrodes. With this device we protected both metals against corrosion. The voltage drop between either the Al(u_{Al}) leads or the Mo leads (u_{Mo}), was measured by a potentiometric method, while the "jump" at the melting point was registered using a digital microvoltmeter. Knowing the absolute thermoelectric power of the wires (S_{Mo} and S_{Al}), S_{Sn-Te} can be found by means of the relation

$$S_{Sn-Te} = S_{Mo} + \frac{u_{Mo}(S_{Al} - S_{Mo})}{(u_{Mo} - u_{Al})}.$$

We used the natural temperature difference in the furnace, which was always less than 12 °C. This small gradient makes thermodiffusion effects negligible. To prevent evaporation, all the experiments were performed under Ar overpressure ($\cong 3$ kg cm^{-2}) after previous de-gassing under vacuum. In order to check whether the composition was homogeneous, we measured S at a fixed temperature as a function of time (i. e. up to ten hours). Because the fluctuations in the Seebeck coefficient were less than the experimental error, it was concluded that the homogeneity of the samples did not change appreciably.

Experimental Results

We have measured the thermoelectric power of the liquid $Sn_{1-x}-Te_x$ for $x = 0.1$; 0.35; 0.45; 0.5 (compound composition), 0.65 and 0.85 (eutectic composition), in the temperature range $T_{melting} \leqq T \leqq 1400$ K. Basically, the behaviour of the alloy

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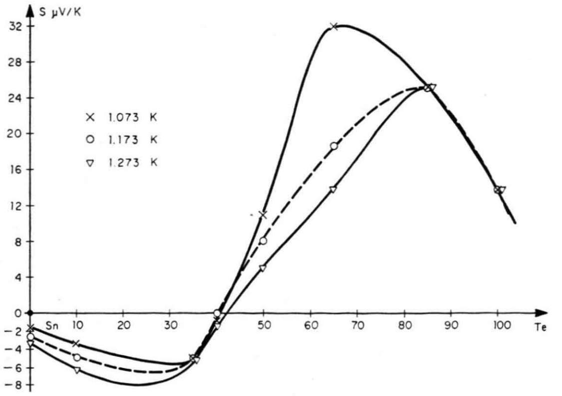

Fig. 1. Thermopower of liquid Sn-Te (x atomic fraction).

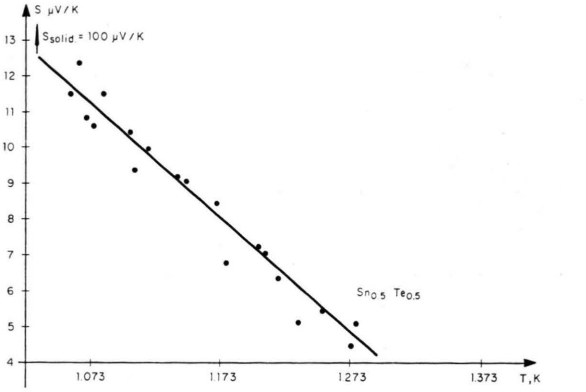

Fig. 3. Thermopower of liquid $Sn_{0.5}$-$Te_{0.5}$ (compound composition) as a function of temperature.

differs in three zones of concentration (Figure 1). For $0 \leqq x \leqq 0.4$ the liquid is metallic. The carriers are predominately electrons ($S<0$); S is small and increases with temperature (Figure 2). At $x = 0.45$, the transition from electron to hole transport takes place, and S changes from negative to positive. It is important to remark that this result is different from that of Dancy. For $x = 0.5$ (Fig. 3), the carriers are

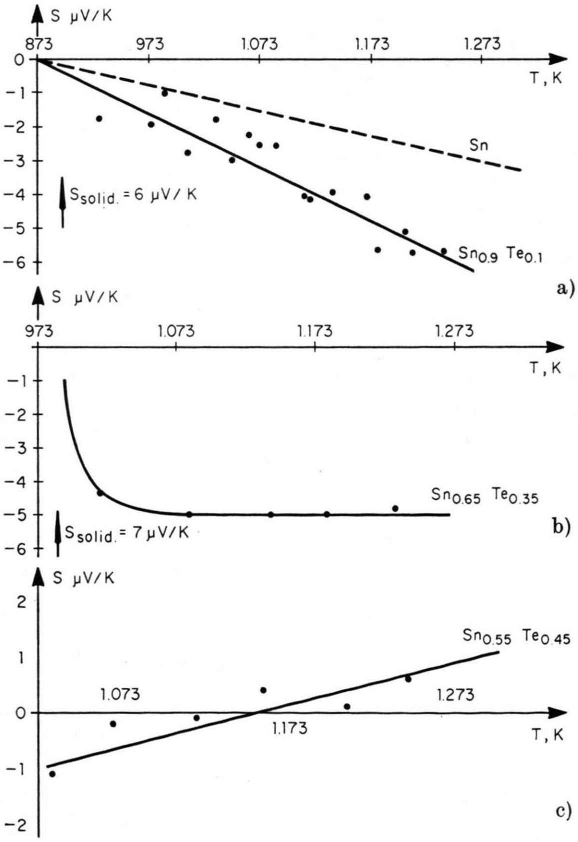

Fig. 2. a) Thermopower of liquid $Sn_{0.9}$-$Te_{0.1}$ as a function of temperature. b) Thermopower of liquid $Sn_{0.65}$-$Te_{0.35}$ as a function of temperature. c) Thermopower of liquid $Sn_{0.55}$-$Te_{0.45}$ as a function of temperature.

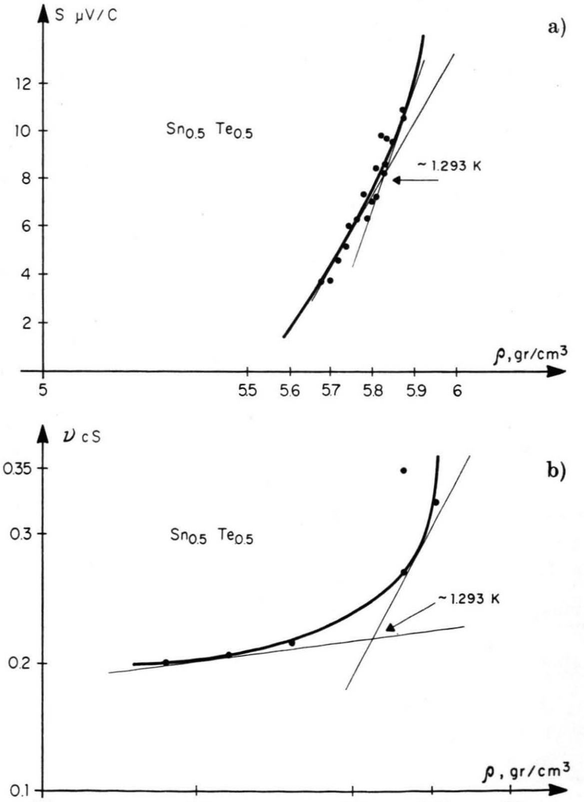

Fig. 4. a) Thermopower of liquid $Sn_{0.5}$-$Te_{0.5}$ as a function of density. b) Viscosity of liquid $Sn_{0.5}$-$Te_{0.5}$ as a function of density.

predominately holes and S decreases with temperature. At this concentration Glazov's results ($41\,\mu V/K \leqq S \leqq 8.5\,\mu V/K$ for a temperature interval of $1074\,K \leqq T \leqq 1233\,K$) are very different from ours. It is difficult to make any numerical comparison with Dancy's results (see Introduction), nevertheless her values are much lower than Glazov's. The change at the melting point is more pronounced for $x = 0.35$

$$\left|\frac{\Delta S}{S_{\text{solid}}}\right| = \left|\frac{S_{\text{liquid}} - S_{\text{solid}}}{S_{\text{solid}}}\right| = 1.6\,.$$

For $x \gg 0.6$ (Fig. 4), the liquid presents features of a semiconductor. The values of S are higher (i. e. $S = 65\,\mu V/K$ at $T = 1049\,K$ for $x = 0.65$), they decrease with temperature and also tend to saturate, this last effect being remarkable at the eutectic composition.

Discussion

Recently, Robertson [6, 7] has carried out a general qualitative analysis of electronic transport properties of non-crystalline semiconductor alloys, either liquid or amorphous. He relates these properties with the type of bonding which he classfies: metal simple (i. e. liquid $Cu_x - Sn_{1-x}$), random semiconductor (i. e. liquid $Se_x - Te_{1-x}$), ordered compensated semiconductor (i. e. amorphous $Ge_x - Te_{1-x}$), ionic semiconductor (i. e. liquid $Mg_x - Bi_{1-x}$) and substitutional semiconductor (i. e. amorphous $Ga_x - As_{1-x}$). In the ionic case each atom is surrounded, as much as possible, by ions of the other element. In this case, the co-ordination number depends on the composition, whereas in simple covalent systems the co-ordination number remains constant He indicates a difference between ionic, covalent and metallic sites: an ionic site is one which introduces extra states in the density of states of the host lattice only above (cation) or below (anion) the gap. A covalent or metallic site adds states in both bands; for the covalent site the number of states added is twice its co-ordination number, but it is less for the metallic site. Besides Robertson's groups there are a great number of binary alloys in structural stability plots where the two co-ordinates respectively represent the degree of ionicity or covalency of each alloy. Accordingly, his analysis suggests that liquid $Sn_{1-x} - Te_x$ is an ionic ordered semiconductor at the stoichiometric composition but that slightly away from $x = 0.5$ each excess component enters as an interstitial one: atoms of the kind in excess are bounded to those of the other class. Assuming that at the compound composition liquid Sn – Te is in the Sn^{2+}- Te^{2-} form, any Sn atom in excess produces an n-type liquid semiconductor:

$$Sn + Te^{2-} \rightarrow Sn^{2+} + Te \uparrow + 4\,e\,.$$

On the other hand, a Te atom gives rise to a p-type liquid semiconductor:

$$Te + Sn^{2+} \rightarrow Te^{2-} + Sn \uparrow + 4\,h\,.$$

It must be noted that Robertson's work suggests that his doping mechanism is always produced just around the stoichiometry.

In the concentration range $0 \leqq x \leqq 0.45$, we have seen above that the alloy is metallic, since the thermoelectric power is small and the conductivity is high. Now, if we apply the electron gas formula [8]

$$\sigma = e^2\, n^2\, \lambda_s / \pi\, (3\,\pi^2)^{1/2}\,,$$

where λ_S is the scattering length, then $\lambda_S \gg \lambda_D$ (de Broglie's wavelength) and $k_f\, L \gg 1$ can be deduced. In this case, in principle, Ziman's theory, which relates S with the structure factors and interatomic potentials, can be applied. Unfortunately, there are no experimental data for $S_{ij}(Q)$ for this liquid alloy.

The rigid sphere approximation of the Ziman formula, where the partial interference function is deduced from the Percus-Yevick approximation [9], predicts a positive value, which is obviously wrong. We suppose that the failure is due to the presence of associations in the melt [10]. It is interesting to point out that the Nordheim-Gorter rule also fails. We suppose, as a first approximation, that the liquid is a mixture of free Sn and Te atoms, and Te atoms which are surrounded by Sn atoms as Robertson has proposed. Accordingly, in this model the majority of free electrons is brought by Sn atoms. When the concentration of Te rises, the number of Sn atoms which participate in Sn-Te bonds also rises. For this reason the number of free electrons decreases, since the conductivity falls and the thermoelectric power rises. At a certain concentration ($x \cong 0.45$) the numbers of electrons and holes are nearly equal and the thermoelectric power tends to vanish. At the compound composition S is small and decreases with the temperature, the transport process being dominated by holes. Although the Hall constant is negative [11], Friedman's theory [12] gives an account of the discrepancy between the signs of S and R_{H}. We suppose that the Seebeck e.m.f. is due to electrons in the conduction band and holes in the valence band. Faber [13] has used his two band hypothesis to explain the liquid Pb-Te alloy behaviour by supposing that $\sigma_{\mathrm{e}} \cong \sigma_{\mathrm{h}}$. Also we consider that, at this composition, the liquid alloy is an intrinsic semiconductor and the Fermi energy, E_{F}, is in the middle of the pseudogap. We can apply the relation [13]

$$S = \frac{\sigma_{\mathrm{h}} S_{\mathrm{h}} + \sigma_{\mathrm{e}} S_{\mathrm{e}}}{\sigma_{\mathrm{h}} + \sigma_{\mathrm{e}}} \simeq \frac{k_{\mathrm{B}}}{e^2} \left[1 - \frac{\gamma}{k_{\mathrm{B}}}\right] \frac{\Delta E}{2T},$$

where $\Delta E = E_{\mathrm{F}} - E_{\mathrm{V}} = E_{\mathrm{C}} - E_{\mathrm{F}}$; E_{C} and E_{V} are the energies which divide the extended states zone from the localized states region. In our case ΔE is very small because $\Delta E \cong 0.08\ \mathrm{eV} \cong k_{\mathrm{B}} T$, so we conclude that this liquid alloy is a semimetal [14], So, a transition metal → semimetal → semiconductor takes place while the Te concentration increases. The value $\gamma / k_{\mathrm{B}} = 1.326$ does not agree with Mott's estimation $(2 \leqq \gamma / k_{\mathrm{B}} \leqq 3)$. It is interesting to compare the value of ΔE obtained from conductivity data with those calculated from our thermoelectric measurements. If both values would be the same the relation

$$\sigma = \sigma_0 \exp(e\, S / k_{\mathrm{B}} + A)$$

would be valid, but this is not true in this case as $\Delta E_{\sigma} \gg \Delta E_{\mathrm{S}}$. In the case of an amorphous semiconductor Mott and Davies [14] have explained this difference by electronic conduction being an activated process, while ΔE_{S} is due to a mean potential along the electronic path. It is not clear whether the same explanation could be applied to liquid semiconductors. On the other hand, when the temperature rises, the interatomic distance and the difference $E_{\mathrm{C}} - E_{\mathrm{V}}$ become greater and therefore the thermoelectric power must decrease. So, we have plotted S as a function of the density (Figure 4 a). The curve shows an inflection near 930 °C, which is coincident with self diffusion [15] and viscosity [4] measurements (Figure 4 b).

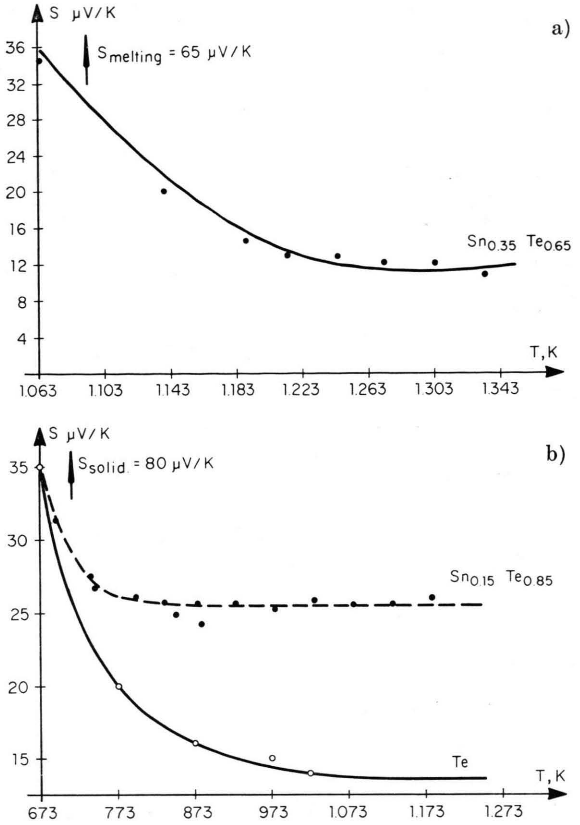

Fig. 5. a) Thermopower of liquid $Sn_{0.35}$-$Te_{0.65}$ as a function of temperature. b) Thermopower of liquid $Sn_{0.15}$-$Te_{0.85}$ as a function of temperature.

$Sn_{0.35} - Te_{0.065}$ – For this alloy the following formula can be applied:

$$S_{\mathrm{h}} = \frac{k_{\mathrm{B}}}{e} \left[\frac{E_{\mathrm{F}} - E_{\mathrm{V}}}{k_{\mathrm{B}} T} - \frac{\gamma}{k_{\mathrm{B}}} + 1\right].$$

In this case $E_{\mathrm{F}} - E_{\mathrm{V}} = 0.16\ \mathrm{eV}$. Because E_{F} can lie on the lower energy side of the minimum in the density of states, we can estimte that $E_{\mathrm{V}} - E_{\mathrm{C}} = 0.32\ \mathrm{eV}$ at least. On the other hand, $\gamma / k_{\mathrm{B}} = 1$. There are no accurate data for the conductivity at this composition, so we cannot establish a comparison between ΔE_{S} and ΔE_{σ}.

$Sn_{0.15} - Te_{0.85}$ (eutectic) – Due to the fact that the curve $S = f(T)$ saturates very quickly, it is not possible to apply the formula we have used above. It must be remarked that pure tellurium also tends to saturate [16] but less strictly than this alloy.

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