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THERMOELECTRIC POWER IN LIQUID COMPOSITIONS RICHER IN S THAN Tl_2S SEMICONDUCTOR COMPOUND

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A study was undertaken on the temperature and composition dependence of the thermoelectric power for five Tl-S liquid alloys in the composition range 45 up to 64.3at.%Tl in a temperature range including the pre-freezing region. An increase of the Seebeck coefficient with temperature and thallium content was found in the pre-feezing range for the alloys poor in thallium. This behavior was manifest both on the curves indicating the dependence of the Seebeck coefficent on the degree of overheating of the melt above the liquidus point as well as on the curves of equal overheating reflecting the composition dependence of the Seebeck cofficient. However at higher degrees of overheating the same alloys exhibited a semiconductor behavior consisting in a decrease of the thermoelectric power with temperature. In contrast to this, the thermoelectric power for the alloys richer in thallium has manifested a typical semiconductor behavior in the whole investigated temperature range starting with the liquidus point.

Keywords: thermoelectric power, liquid semiconductors, Tl-S alloys, pre-freezing range

1. Introduction

The thermoelectric effect is a physical phenomenon that finds nowadays a lot of applications either as new ways of energy conversion or as refrigerating devices. Indeed if operated in the Seebeck modality the thermoelectric effect works as an electricity generator by consuming the heat injected at the hot junction between two different materials. If operated in the Peltier modality the thermoelectric effect gives rise to a counter-entropic process since it works as a heat pump that produces refrigeration at the cold T_C point and heating at the hot T_H point as long as a continuous electric current passes in the circuit. Both phenomena are based on the flow of electrical charge carriers (electrons or holes) in the presence of a thermal gradient. Hence a thermoelectric couple works at its best if it consists in an *n*-type conducting element joined to a *p*-type element.

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Since a thermoelectric unicouple based on the Seebeck effect produces a thermoelectric power of only a few hundred of microvolt or less the unique application of this phenomenon consisted for a long time in using such a device for high temperature measurement. However nowadays higher thermoelectric power values are obtained by means of thermoelectric modules in which the couples are electrically connected in series and thermally in parallel. Even so the applications are not focussed on large scale energy generation but rather on niche domains that are crucial in modern high tech fields [1,2].

Space vehicles such as Apollo lunar missions, Viking Mars landers, outer-planet spacecrafts Voyager, Ulysses, Galileo, Cassini have their electronic devices powered for years by a reliable energy source based on the Seebeck effect, especially in the deep space where solar cells cannot work anymore [3]. Interesting enough while T_C is easy to be obtained in space, the hot temperature T_H is attained in the most ingenious, modern and reliable way by using the heat released from the radioactive decay of plutonium-238 radioactive isotope. Semiconductor Si-Ge alloys proved to be the choice material for such radioisotope thermoelectric generators.

Increased performance of microprocessors and further miniaturization in microelectronics and computer systems imply higher power input and higher on-chip power density. The refrigeration problems become stringent and external cooling by blast air has to be replaced by an internal cooling system incorporated in the integrated circuits [4]. Nano thin-film thermoelectric devices made of Bi_2Te_3 or based on Bi_2Te_3 - Sb_2Te_3 superlattice technology embedded as an internal cooling system in the package of the electronic integrated circuit seem to be a solution for the future [5].

A promising field of application consists in harvesting electricity from waste heat of automotive vehicles by means of thermoelectric devices [3]. Similar devices are already at work in Japan for plant-wide scale electricity harvesting from the decay heat of waste radioactive fuel in fast breeder plutonium-fueled nuclear reactors [6]. A Heusler type Fe_2VAl compound was used as a cheap thermoelectric material in this application.

Because energy conversion is aimed at both in Seebeck and in Peltier based devices the main point is the efficiency of this conversion. The maximum efficiency η expected in a thermoelectric device for converting heat into electricity may be calculated according to Joffe [7] as follows:

$$\eta=\{[(T_H-T_C)/T_H]\}\{[(1+ZT)^{1/2}-1]/\{[(1+ZT)^{1/2}]+(T_C/T_H]]\} \qquad (1)$$

If the thermoelectric device is used for refrigeration the efficiency is expressed as:

$$\eta=\{[T_H/(T_H-T_C)]\}.\{[(1+ZT)^{1/2}-T_H/T_C]/\{[(1+ZT)^{1/2}]+1]]\} \qquad (2)$$

In both equations the term $[(T_H-T_C)/T_H]$ is the Carnot efficiency that depends only on the difference between the temperature of the hot point T_H and the temperature of the cold point T_C and it represents the upper limit for a device based on the Seebeck or Peltier effect. The remaining terms contain a characteristic of the thermoelectric material used, namely the adimensional figure of merit **ZT**, where **T** is the average temperature and **Z** is the thermoelectric figure of merit that may be expressed as follows:

$$Z = S^2 \sigma/\kappa \tag{3}$$

According to eqs. (1) and (2) increasing the figure of merit Z results in a better efficiency η. At its turn Z depends on a proper balance between several characteristics of the thermoelectric material, i.e its Seebeck coefficient S (or its thermoelectric power), its electrical conductivity σ and its thermal conductivity κ. The last value is the sum of the electronic conductivity κ_{el} and the phononic conductivity κ_{ph}. The analysis of the simultaneous action of these material characterisctics shows that the best materials for building a thermoelectric device are the semiconductors with narrow forbidden band and high-mobility carriers. Metals make not good thermoelectric materials since κ is high and S is low (1-10μV/K, much less than 87μV/K which is the theoretical thermopower for a classical electron gas) and the thermopower decreases with decreasing temperature [1].

For decades (between 1940s and early 1990) no better materials were discovered that would exceed a value for the figure of merit ZT higher than 1 (the semiconductor compounds Bi_2Te_3, PbTe, $CsBi_4Te_6$, $Si_{1-x}Ge_x$). Recent researches have found thermoelectric compounds that exhibit values ZT>1 ($AgPb_mSbTe_{2+m}$, Zn_4Sb_3 $Yb_{0.19}Co_4Sb_{12}$, $CeFe_{4-x}Co_xSb_{12}$) [8,9], for some of them ZT attaining values as high as 3.6 [10]. Such discoveries have reinvigorated the interest in thermoelectric technologies. However calculations show [3] that even for a figure of merit ZT~3 the efficiency cannot exceed half of the Carnot efficiency.

Creating a data base for the physical properties involved in the figure of merit implied in the thermoelectric energy conversion requires many experimental efforts and it is just such a contribution that was aimed at in this paper. Extending the area of research to liquid semiconductors as done in this paper greatly increases the opportunities to obtain better figures of merit. Extending the temperature range in the pre-freezing region of the melt undertaken in this research may bring additional information.

2. Experimental methods and materials

The thermoelectric power (quantitatively characterized at each temperature by the Seebeck coefficient S expressed in $\mu V/^oC$) was measured by using an apparatus based on the principle of small temperature gradients. Purified argon was used as a protective atmosphere in the measuring cell of the apparatus as well as in the sealed vials in which the alloys were prepared. The elements for preparing the alloys (Tl and S) were of spectral purity delivered by Johnson-Mathew Comp.

The liquid alloy contained in a U shaped quartz cell (set in vertical position) was heated in a resistance electric furnace. A small temperature difference between the liquid in the two columns was created by slightly overheating the liquid in one column by means of an additional heating coil. This small temperature gradient ΔT gives rise to a small thermoelectric power ΔE measured between two molybdenum electrodes immersed in each liquid alloy column. Each Mo electrode consisted in a Mo sheath and a Mo wire welded to the inner bottom of the Mo sheath. The thermoelectric power between the Mo wires was measured by means of a high precision galvanometer. Each Mo sheath also contained an insulated Ni-NiCr thermocouple for measuring the temperature in each liquid alloy column. A high precision was assured when measuring the thermoelectric power between the Mo electrodes as well as between the thermocouple wires by applying the compensation method. The melting points of several pure metals were used to experimentally calibrate the thermocouples. The following correlation was obtained between the thermoelectric power U_{Tc} in μV recorded by the thermocouple and T in °C:

$$U_{Tc} = -0.237243 + 2.730684 \cdot 10^{-2} T + 3.02324 \cdot 10^{-6} T^2 \qquad (4)$$

At each proposed temperature T the thermoelectric power ΔE between the two Mo electrodes was measured at several (at least 4) small temperature gradients ΔT (5°C, 10°C, 15°C, 20°C, or nearly so). According to the definition of the Seebeck coefficient (eq.5) the graph ΔE versus ΔT should be a straight line whose slope is just the Seebeck coefficient S expressed in μV/ °C:

$$\Delta E / \Delta T = S \qquad (5)$$

A correction was applied because the experimentally obtained Seebeck coefficient S_{ab} was actually a relative quantity since two materials were involved when the thermoelectric power was measured, namely the liquid alloy (material *a*) and solid Mo (material *b*). The values for the Seebeck coefficient S_b of solid Mo were available from the literature [11,12]. By using the values reported by Cusack and Kendall [11] which extended far below 700°C we have obtained the absolute Seebeck coefficient S_a of the investigated liquid alloy from eq.(6):

$$S_{ab} = S_a - S_b \qquad (6)$$

Concerning the compositions proposed for study they belong to a system comprising thallium (a heavy metal which contributes to a higher figure of merit by the bias of a minimized phononic thermal conductivity) and a chalcogenide element (namely sulfur) different from the more extensively investigated Se and Te as components in molten thermoelectric materials. The presence of sulfur enlarges the opportunities to obtain semiconductors with various values for the forbidden energy gap. In the Tl-S system Tl_2S is a recognized semiconductor compound whose thermoelectric power has been thoroughly investigated in liquid state [13,14]. Outside this composition the possibilities to investigate the thermoelectric power in liquid state are limited in the Tl- rich region especially in the pre-freezing range on account of an immiscibility phenomenon (decomposition in two immiscible liquids L_3+L_4) that sets in at compositions higher than ~70at.% Tl. However in the sulfur rich region the possibilities to investigate the thermoelectric power in liquid state in a wide composition range do exist because the immiscibility region L_1+L_2 is far away from the composition of the semiconductor compound Tl_2S**.** Actually the immiscibility phenomenon sets in at compositions lower than ~26.5at.% Tl. Taking these facts into account five Tl-S compositions in the S-rich side, have been selected in our research on the thermoelectric power in liquid state, namely composition I (64.7at.%Tl+35.3at.%S), composition II (57.1at.%Tl+42.9at.%S), composition III (54at.%Tl+46at.%S), composition IV (50at.%Tl+50at.%S), composition V (45at.%Tl+55at.%S).

3. Results

The experimental data for all compositions are plotted in Fig.1 in a series of diagrams, each comprising a set of straight lines, each line referring to a given temperature at which the thermoelectric power was measured. The points on each straight line represent the thermoelectric power measured at a specific value for the imposed temperature gradient.

According to ec.(5) the slope of the straight line $\Delta E/\Delta U$ is just the Seebeck coefficient measured at the proposed temperature. This procedure is very accurate as compared to simply measuring a unique thermoelectric power at a single temperature gradient as used in other researches. A value $r^2 > 0.999$ was obtained in each instance when correlating the experimental points by the best fit straight line. The values of the investigated temperatures indicated in frame on each diagram are expressed in ^{o}C.

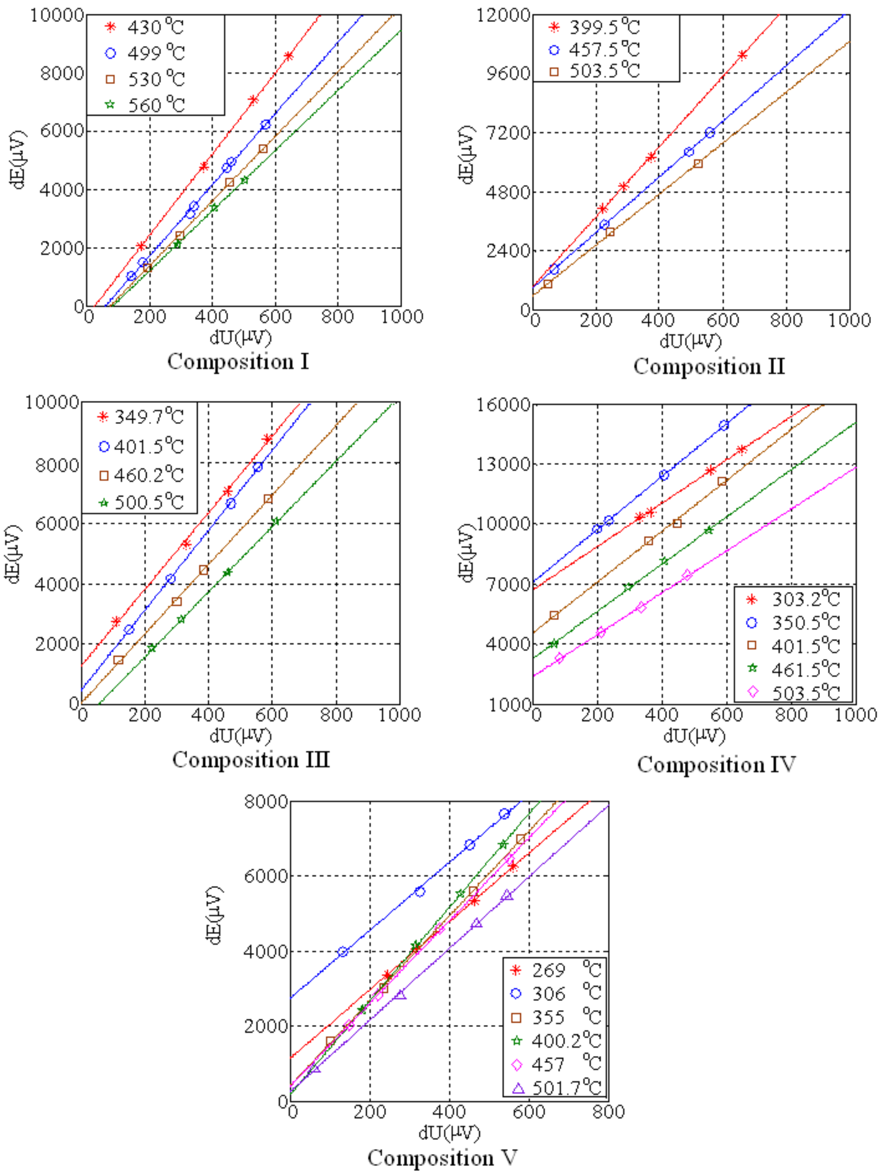

Fig.1 Experimental data on the thermoelectric power for the investigated compositions

For a better accuracy the temperature gradient on the abscissa of each diagram in Fig.1 was expressed in μV as directly recorded by the thermocouples. Further on, the Seebeck coefficient obtained from all points on the straight line was subject to a single transformation in order to be expressed in μV/^{o}C, namely multiplication of the slope by a parameter ε derived from ec (4). The absolute values S_a of the Seebeck coefficient were calculated from the experimental relative values S_{ab} by applying the correction for the Seebeck coefficient S_b of solid molybdenum according to ec.(6).

Table 1 presents the results on the thermoelectric power for all compositions. For putting in evidence how far apart from the liquidus point the melt was when the thermoelectric power was measured, for each temperature is indicated the corresponding value for the overheating of the melt ΔT (=$T-T_{liq}$) where T is the temperature of the melt and T_{liq} is the liquidus temperature (end of melting).

Table 1

Experimental values of the absolute Seebeck coefficient S_a in the Tl-S liquid compositions

Composition, at.%	T, (°C) of the measurement	T_{liq} ,(°C) of the alloy	ΔT, (°C) (overheating of the melt)	S_a μV/°C
64.7%Tl+35.3%S (composition I)	470	460	10	436.46
	499		39	387.57
	530		70	355.75
	560		100	333.98
57.1%Tl+42.9%S (composition II)	399.5	390	9.5	437.42
	457.5		67.5	354.87
	503.5		113.5	329.73
54%Tl+46%S (composition III)	349.7	340	9.7	389.29
	401.5		61.5	410.54
	460.2		120.2	363.16
	500.5		160.5	345.04
50%Tl+50%S (composition IV)	303.2	295	8.2	328.5
	350.5		55.5	402.37
	401.5		106.5	392.13
	461.5		166.5	370.69
	503.5		208.5	332.85
45%Tl+55%S (composition V)	269	265	4	276.42
	306		41	277.35
	355		90	347.55
	400.2		135.2	386.24
	457		192	347.65
	500.75		235.75	305.92

4. Discussion

In Fig.2 the temperature dependence of the absolute Seebeck coefficient is represented taking as an independent variable not the temperature itself but the overheating of the melt above the liquidus point, namely $\Delta T=T-T_{liq}$.

In our opinion this less usual representation in which temperature is replaced by the overheating of the melt has many advantages. The overheating clearly shows how far apart from the liquidus point the melt was when the thermoelectric power was measured. Indeed Fig.2 shows that for all compositions the first measured point was close to the melting point in spite of the fact that in Table 1 the temperature itself of this point is very different. So a comparison of the thermoelectric power at various compositions in physically comparable states becomes possible.

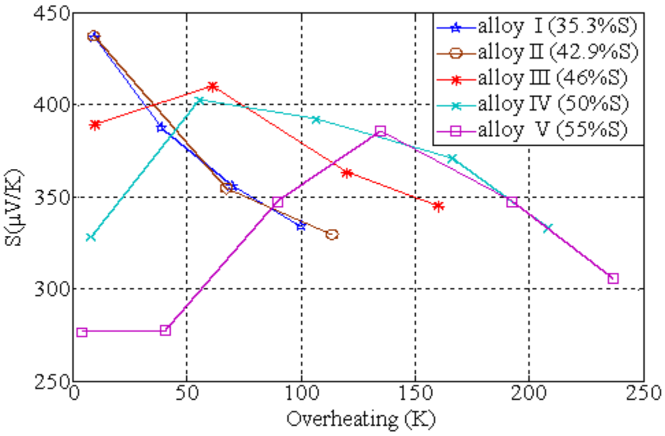

Fig.2 Temperature dependence of the Seebeck coefficient for the investigated liquid compositions

A closer examination of Fig.2 shows that the liquid compositions richer in thallium (I and II) exhibit a decrease of the thermoelectric power as the temperature increases. This behavior is specific for a one band semiconductor and it is valid starting with the melting point. We think interesting to emphasize that according to the Tl-S phase equilibrium diagram [15] for both composition belonging to this group the last crystals persisting up to the liquidus point consist in the semiconductor compound Tl_2S.

For the remaining compositions poorer in thallium and richer in sulphur (III, IV and V) such a behavior is manifest only at high temperatures starting with an overheating that was specific for each composition, namely $\Delta T=61.5K$ for composition III (46at.%S), $\Delta T=55K$ for composition IV (50at.%S), $\Delta T=135K$ for composition V (55at.%S). In the overheating range lower than the above mentioned values, compositions III, IV and V exhibit a different behaviour, namely an increase of the thermoelectric power as the temperature increases. We think interesting to remark that in compositions manifesting a dual behavior the last crystals persisting up to the liquidus point consist no more in the semiconductor compound Tl_2S, but in a different compound Tl_4S_3. To be more specific composition III is on the border-line, exhibiting in Fig.2 a less pronounced dual behaviour and belonging rather to the first group (the last crystals persisting up to the liquidus point consisting in the semiconductor compound Tl_2S).

Our finding on a special behaviour in compositions rich in sulfur is confirmed by an older research [16] in which such a behaviour was noticed for an even higher sulfur content of the Tl-S melt, namely 65 at.%S. For this composition Belascenko [16] has noticed an increase of the thermoelectric power with temperature for an overheating range of more than 100 ºC. We remark that for the composition investigated in [16] the last crystals persisting up to the liquidus point consist no more in the semiconductor compound Tl_2S but in the TlS compound.

Such a dual behavior for the sulfur rich liquid Tl-S alloys has not been remarked by previous researchers who have investigated the thermoelectric power in liquid alloys belonging to the Tl-S system. These researches have been performed years ago [17-19] at temperatures far above the liquidus point.

In our opinion another peculiarity of the curves in Fig.2 may be put in connection with the last crystals persisting up to the liquidus point. Indeed in the semiconductor behavior range the curves „Seebeck coefficient versus overheating of the melt" are almost superposed for the pair of compositions I and II on one hand and for the the pair of compositions IV and V on the other hand. This similitude within each group of compositions is confirmed by the energy of activation for the process calculated from the values of the Seebeck coefficient expressed as follows:

$$S = -\left(\frac{k}{e}\right)\left[\frac{(n+1)F_n(\xi)}{nF_{n-1}(\xi)} - \xi\right] \tag{7}$$

where $F_n(\xi)$ is the Fermi integral order n that may be expressed as:

$$F_n(\xi) = \int_0^\infty \frac{x^{n-1}}{e^{x-\xi}+1}dx \tag{8}$$

and

$$\xi = \frac{E - E_f}{kT} \tag{9}$$

where E_f is the Fermi energy, and $E=xkT$, respectively.

From the above mentioned equations one finally obtains in the framework of the Fermi-Dirac statistics the following dependence:

$$\ln\left(h_r\left(\tfrac{S_e}{k}\right)\right) - \frac{3}{2}\ln(T) = c_2 + \frac{E_1}{kT} \tag{10}$$

where h_r is a funcion that expresses the dependence of $\dfrac{N_v}{p}$ on S, namely:

$$\frac{p}{N_v} = \left(\frac{2}{\sqrt{\pi}}\right)e^{\left(r+\frac{5}{2}\right)-S\frac{e}{k}}\Gamma\left(\frac{3}{2}\right) \tag{11}$$

where $\Gamma(n)$ is the well known gamma function.

By taking $r=-0.5$ (in fact value r plays a negligible role) the left member of eq. (10) becomes a quantity known from the experimental data for each composition, whereas the right member contains the activation energy E_1.

The values of the activation energy calculated as outlined above (with an accuracy reflected in a coefficient r^2 >0.97) are as follows for each group:
$E_1=0.8eV$ for composition I (35.3at.%S) and $E_1=0.65\ eV$ for composition II (42.9 at.%S);
$E_1=0.3\ eV$ for composition IV (50 at.%S) and $E_1=0.5\ eV$ for composition V (55 at.%S).

The composition dependence of the transport properties in liquid alloys is usually represented on isotherms. In our opinion in this instance too it would be more meaningful to represent the composition dependence of the thermoelectric power on curves of equal overheating instead of isotherms. As seen in Table 1 the end of melting temperature (T_{liq}) of the investigated alloys is strongly dependent on composition (T_{liq}=460°C for alloy I, T_{liq}=390°C for alloy II, T_{liq}=340°C for alloy III, T_{liq}=295°C for alloy IV, T_{liq}=265°C for alloy V). As a consequence an isotherm at 470°C for instance would mean an extremely small value for the overheating of the melt above the liquidus temperature namely 10°C for alloy I, but an extremely large value namely 205°C for alloy V.

In Fig.3 we have represented the composition dependence of the thermoelectric power for all investigated alloys at four values (equally spaced) for the overheating of the melt, namely $\Delta T=T-T_{liq}$=10°C, 40°C, 70°C, and 100°C, respectively. Because the experimental determinations have not been carried out exactly at these values for the overheating, we have obtained the necessary values for the thermoelectric power at the proposed overheating by interpolation on the temperature dependence curves (expressed in terms of overheating) for each composition (Fig.2).

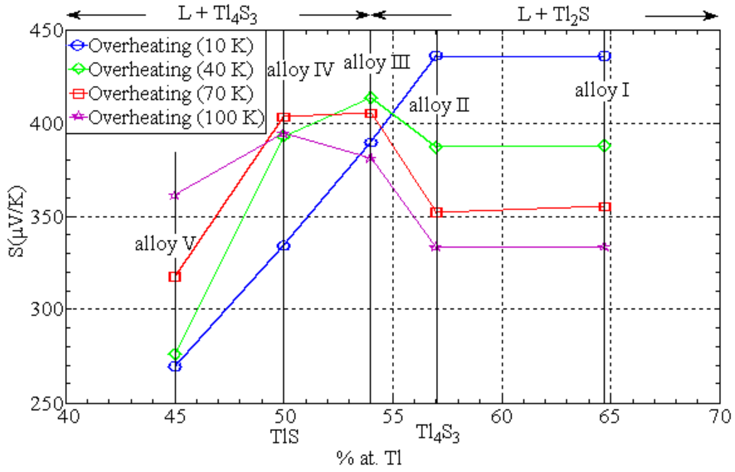

Fig.3 Curves of equal overheating for the Seebeck coefficient at various degrees of overheating of the melt

A close examination of the curves of equal overheating in Fig.3 shows that the composition dependence of the thermoelectric power is different for compositions I and II on one hand and compositions III, IV and V on the other hand. For compositions I and II richer in thallium the thermoelectric power keeps constant for both alloys and it gradually decreases as the overheating of the melt increases from 10°C to 100°C.

On the contrary in the composition range poorer in thallium and richer in sulfur (compositions III, IV and V) the thermoelectric power strongly depends on composition in a way that is specific for each degree of overheating. This specificity may be an indication that heating induces some structural transformations in the melts.

We think that a clue to the kind of transformation occurring in the structure of the melt may be looked for in some old papers of Belascenko et al [20,21]. Indeed these authors have found that when the melt 65at.%S+35 at.%Tl was heated between 300°C and 460°C the efective electric charge of thallium increases from 0.186 up to 0.93 fraction of the electric charge of an electron. This experimental finding was interpreted in [16] as indicating an increase from ~ 20 up to ~ 90% of the amount of electrically charged thallium ions (Tl^+ and even Tl^{3+} above 400°C) at the expense of the amount of Tl^o (meaning neutral thallium atoms bonded in molecular complexes).

This fact agrees with Roth's model [22] for the electronic structure of alloy systems comprising an M_aA_m semiconductor compound (where M is a metal and A is a chalcogenide element,-S, Se,Te-) that states that increasing the ionicity of the interatomic bond modifies the energy band structure and consequently the electron transport properties (including the thermoelectric power).

5. Conclusions

The investigation of the thermoelectric power in liquid Tl-S compositions poorer in thallium than the semiconductor Tl_2S compound have indicated new phenomena in the temperature and composition dependence of the Seebeck coefficient in the pre-freezing range of the melts.

The measurements carried out starting with temperatures as close as possible to the melting point (overheating of the order of 10°C or less) have indicated a temperature dependence of the thermoelectric power specific for a one band semiconductor (decrease of the Seebeck coefficient as the temperature raises) only in the group of liquid compositions in which the last crystals to melt consisted in the semiconductor compound Tl_2S. On the contrary in the liquid alloys poorer in thallium in which the last crystals to melt consisted in a different compound namely Tl_4S_3 the thermoelectric power has manifested a dual behavior. At high temperatures the behavior was similar to the one manifested in the first group (decrease of the Seebeck coefficient as the temperature raises). However at low temperatures starting with the melting point an increase of the thermoelectric power when the temperature raised was manifest.

The same disjunction between the two groups of alloys was manifest on the curves of equal overheating versus composition. In the first group of alloys in which the last crystals to melt consisted in the semiconductor compound Tl_2S the thermoelectric power was seemingly composition independent. In the second group of alloys in which the last crystals to melt consisted in the Tl_4S_3 compound the thermoelectric power was strongly composition dependent, this dependence increasing as the overheating of the melt became lower. The calculated values for the energy of activation support this different behaviour.

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