Thermoelectric power in two liquid Tl-S alloys (64.7 at.%Tl and 57.1 at.%Tl) in the low temperature range down to the liquidus point

S. ADAM, M. I. PETRESCU[*]
University Politehnica of Bucharest

Experimental determination of the thermoelectric power has been carried out in liquid Tl-S alloys containing various excess of sulfur compared to the stoichiometric composition of the semiconductor Tl_2S compound. In order to investigate the behavior of the liquid alloys in the pre-freezing range, experiments on the thermoelectric power have been performed in the low temperature range in the melt (maximum 110 K overheating, minimum 10 K overheating above the liquidus temperature). Spectral pure elements Tl and S have been used for preparing the alloys. An experimental device assuring that the thermocouples reflect accurately the temperature of the Mo electrodes and precise measurement of the thermoelectric power by a compensation method have been used. Two alloys containing 2% and 9.6% excess sulfur, respectively, have exhibited parallel curves showing a monotonous decrease of the Seebeck coefficient in the melt as the temperature increased above the liquidus point. A superposition of the two curves was obtained when the Seebeck coefficient was plotted against the degree of overheating of the melt. Theoretical calculation of the energy of activation has resulted in similar values, namely 0.8 eV at 2 at% excess sulfur and 0.65 eV at 9.6 at% excess sulfur, respectively.

1. Introduction

The chemical nature of liquid semiconductors is extremely important when studying the thermoelectric power of this class of materials. Among the elements, liquid Se and liquid Te are semiconductors, but well known solid semiconductors such as Ge and Si become metals on melting [1]. The same is true for the well known $A^{III} – B^V$ solid semiconductor compounds which become metallic when melted. The theoretical reasons for the shift to a metallic behavior upon melting undergone by the most important semiconductor material in electronic devices, namely Si, as well as its companion element Ge, is still a matter of interest [2]. Due to the wide range of stoichiometry that liquid semiconductors may have they are to be regarded rather as alloy systems, as for example Se-Te, Tl-Te, Tl-Se, Ag-Te, Mg-Bi, V-O a.s.o. The occurrence of a chalcogene element belonging to the VIB group (though not a universal rule) is very frequent in liquid semiconductors.

In our research we have focused attention on liquid semiconductor alloy systems in which the chalcogene element was sulfur instead of the more intensely studied tellurium or selenium. It is worth to mention that the interest in Te and Se alloys is still alive [3] but the number of researches in alloys in which Te or Se is replaced by S is poorer. In our research we have selected molten Tl-S alloys for investigating the thermoelectric power versus temperature and composition. The presence of Tl (a heavy metal, A=204.4 g/g.at.) is of outmost importance. Indeed on account of its large atomic mass the thermal vibrations frequency may decrease and therefore contribute to

obtaining high figures of merit by minimizing the phononic thermal conductivity κ_{ph} of the semiconductor chalcogenides. In a previous paper we [4] have presented a discussion of the various factors involved in the figure of merit of the materials used in modern thermoelectric devices as well as their recent applications. Previous researches carried out on liquid Tl-S alloys by other authors mainly focused on the stoichiometric Tl_2S compound or in alloys with a slight excess of Tl [5,6]. Instead we have focused attention on Tl-S alloys having a high content of sulfur, namely 2 up to ~22 at.% S in excess as compared to the stoichiometric composition Tl_2S (the latter being a well known semiconductor compound). Also in distinction from previous researches carried out in this alloy system at high degrees of overheating above the liquidus temperature [5,6], we have investigated the thermoelectric power in the low temperature range of the liquid state down to the liquidus point. In a previous paper [7] we have given more details on the reasons to undergo a research on the thermoelectric power of molten Tl-S alloys in the pre-freezing range.

2. Experimental

An apparatus (Fig.1) based on the principle of small temperature gradients was built for measuring the thermoelectric power (quantitatively characterized by the Seebeck coefficient in $\mu V/^oC$) in molten Tl-S alloys.
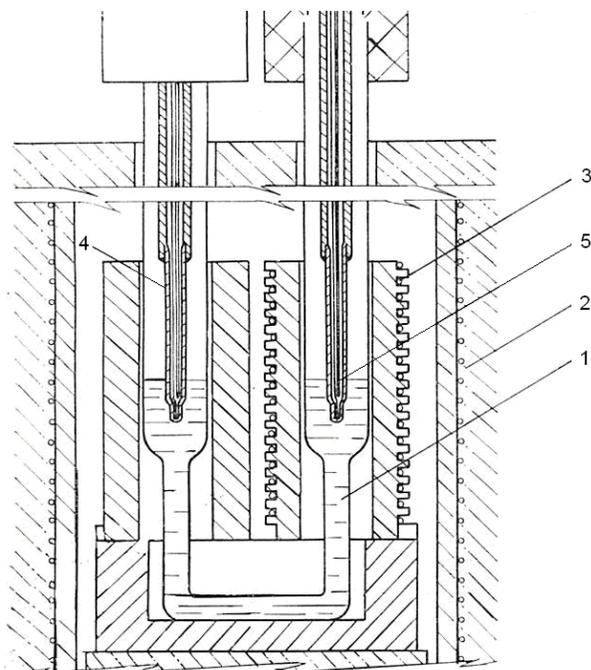
Fig.1 Schematic depiction of the apparatus devised for the experimental measurement of the Seebeck coefficient in liquid Tl-S alloys

The main part of the apparatus was a U shaped quartz cell containing the liquid alloy in its two connected vertical columns (1). The cell was heated at the desired temperature by means of a resistance electric furnace (2). In order to create a slight temperature difference between the liquid in the two columns one column was slightly overheated by means of an additional heating coil (3). This slight temperature difference gives rise to a small thermoelectric power measured between two Mo electrodes. Each Mo electrode consisted in a Mo sheath (4) immersed ten mm deep in the liquid alloy and a Mo wire welded to the inner bottom of the Mo sheath. Each Mo sheath also contained a Ni-NiCr thermocouple (5) for measuring the temperature in each liquid alloy column. Each thermocouple (having its wires electrically insulated) was introduced down to the bottom of the Mo sheath in order to make sure that the temperature of the thermocouple was the same as the temperature of the lower end of the Mo sheath.

In order to maintain the slight temperature gradient between the two vertical liquid columns the horizontal connection branch of the U-shaped quartz cell was far thinner than the vertical branches. As a rule four temperature gradients (5°C, 10°C, 15°C, 20°C, or nearly so) were used at each temperature at which the Seebeck coefficient was measured. The temperature in each liquid alloy column was so adjusted that the proposed temperature was located midway between the lower temperature in one column and the higher temperature in the second column. To perform a measurement, time was allowed for the temperature gradient to reach a steady-

state value. The atmosphere used in the cell was pure argon.

A high precision was ensured when measuring the thermoelectric power generated both between the two Mo electrodes as well as for the thermocouples by applying the compensation method. A galvanometer of high sensitivity was used for capturing the exact moment of compensation. The sign of the measured thermoelectric power was asigned according to the convention that it is negative when the cold end is negative.

At each applied temperature gradient ΔT (in ^{o}C) a thermoelectric power ΔE (in μV) was measured between the Mo electrodes. For small temperature gradients one may expect a linear dependence of the thermoelectric power ΔE versus the temperature gradient ΔT and this was attested to be so in our experiments (Fig.3 and 4). The constant in this linear dependence is just the Seebeck coefficient S that characterizes the thermoelectric power of the investigated material at a given temperature:

$$\Delta E/ \Delta T = S \quad (\mu V/\,^o C) \tag{1}$$

It is worth to remark that what one actually measures is a relative Seebeck coefficient S_{ab} because two materials are involved when the thermoelectric power is measured, namely the liquid alloy (material a) and the solid molybdenum electrode (material b). The relative Seebeck coefficient S_{ab} is the difference between the absolute Seebeck coefficient S_a of the liquid alloy and the absolute Seebeck coefficient S_b of the solid molybdenum electrode:

$$S_{ab} = S_a - S_b \tag{2}$$

The values for the Seebeck coefficient of solid Mo were available from the literature [8,9]. However it is worth to mention that Howe and Enderby [8] have studied the temperature dependence of the Seebeck coefficient of solid Mo at temperatures higher than 700°C, while the determinations of Cusack and Kendall [9] were extended far below 700°C. This is why we have used the data of Cusack and Kendall to derive the absolute Seebeck coefficient of liquid Tl-S alloys from our experimental determinations which have been performed at low temperatures down to the liquidus point.

Each Tl-S alloy was prepared by introducing spectral pure elements (thallium and sulfur) in a quartz vial filled with pure argon which was flame sealed. The vial was introduced in horizontal position in an electrical furnace and rotated during melting for obtaining a perfectly homogenized alloy. After solidification the vial was broken and the alloy introduced in one of the vertical columns of the quartz cell of the apparatus (Fig.1).

According to this description one may see that the measurement of the Seebeck coefficient in the liquid alloy in our method was time consuming. Nevertheless it has the advantage to give results based on direct, independent and precise measurements of temperature and thermoelectric power performed in thermal equilibrium conditions. Especially the method complies with the requirement that the thermocouples reflect accurately the temperature of the

electrodes. As specified in [10] the most certain way to assure that the temperature of the thermocouple is the same as that of the Mo electrode is the one we have applied, namely to keep each electrode together with the thermocouple in the same separate compartment which is at a uniform temperature measured by the thermocouple. Less intricate design of the measuring cell frequently applied may failure in this respect and as appreciated by Cutler [10] this is probable responsible for a good deal of error on thermoelectric power in liquid alloys published in the literature. Even more the high purity of the chemical elements from which we have prepared the alloys makes the results on the Seebeck coefficients really representative for the binary alloys without interference of trace foreign elements that may significantly alter the thermoelectric power [3, 11].

3. Results

Two liquid Tl-S alloys richer in sulfur than the stoichiometric Tl_2S compound have been identified in this paper to exhibit a uniform increase of the thermoelectric power when the temperature was lowered down to the liquidus point and they will be discussed here. The remaining S rich Tl-S alloys with a different behavior of the thermoelectric power in liquid state will be presented in a next to come paper intended to be published in the same journal.

The two alloys discussed here are the following:

Alloy I: 64.7 at.%Tl + 35.3 at.%S (2 at.% excess S as compared to Tl_2S). As seen in the phase equilibrium diagram in Fig.2 in solid state this alloy consists of a mixture of Tl_2S and Tl_4S_3 crystals.

Alloy II: 57.1 at.%Tl + 42.9 at.%S, (9.6 at.% excess S as compared to Tl_2S). As seen in the phase equilibrium diagram in Fig.2 in solid state this alloy consists of a single phase namely the stoichiometric Tl_4S_3 compound.

The location of these two alloys in the phase equilibrium diagram of the binary Tl-S system is indicated in Fig.2, together with the temperatures at which the Seebeck coefficient has been measured for each alloy. It is worth to mention that the phase equilibrium diagram in Fig.2 is the latest form for the Tl-S system as published in 1992 by Massalski [12] which differs considerably from the previous form presented in 1958 by Hansen [13].
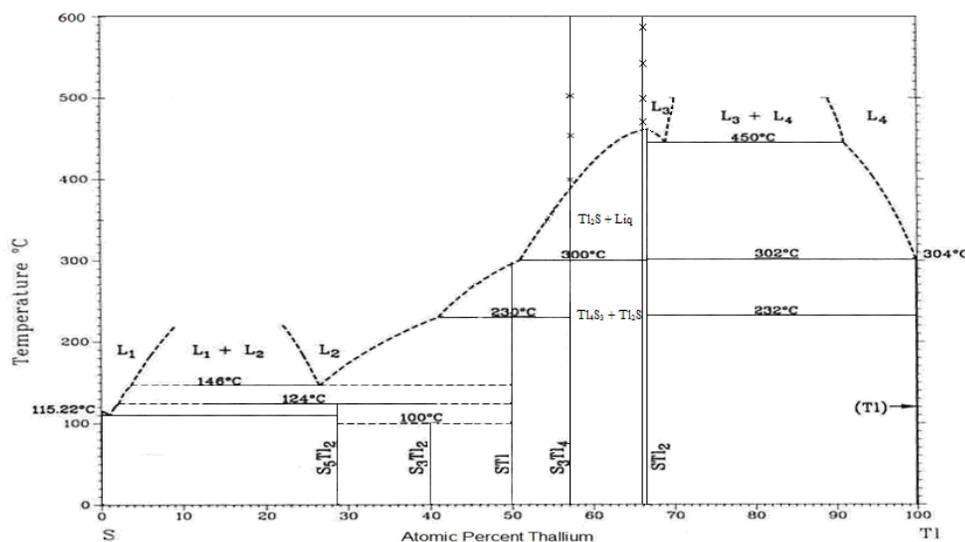

Fig.2 Location in the Tl-S phase equilibrium diagram of the compositions and temperatures at which the thermoelectric power in liquid state has been investigated

In Fig 3 we give the experimental results we have obtained for alloy I (64.7 at.%Tl + 35.3 at.%S; 2at.% excess sulfur as compared to Tl_2S) at four proposed temperatures, going down as close as possible to the liquidus point (T_{liq}=460°C). As seen in Fig.3, at each

temperature a linear dependence has been obtained for the thermoelectric power ΔE measured at several temperature gradients. The best fit straight line equation is given in each figure. It is worth to mention that the correlation coefficient in each instance was R^2>0.999.
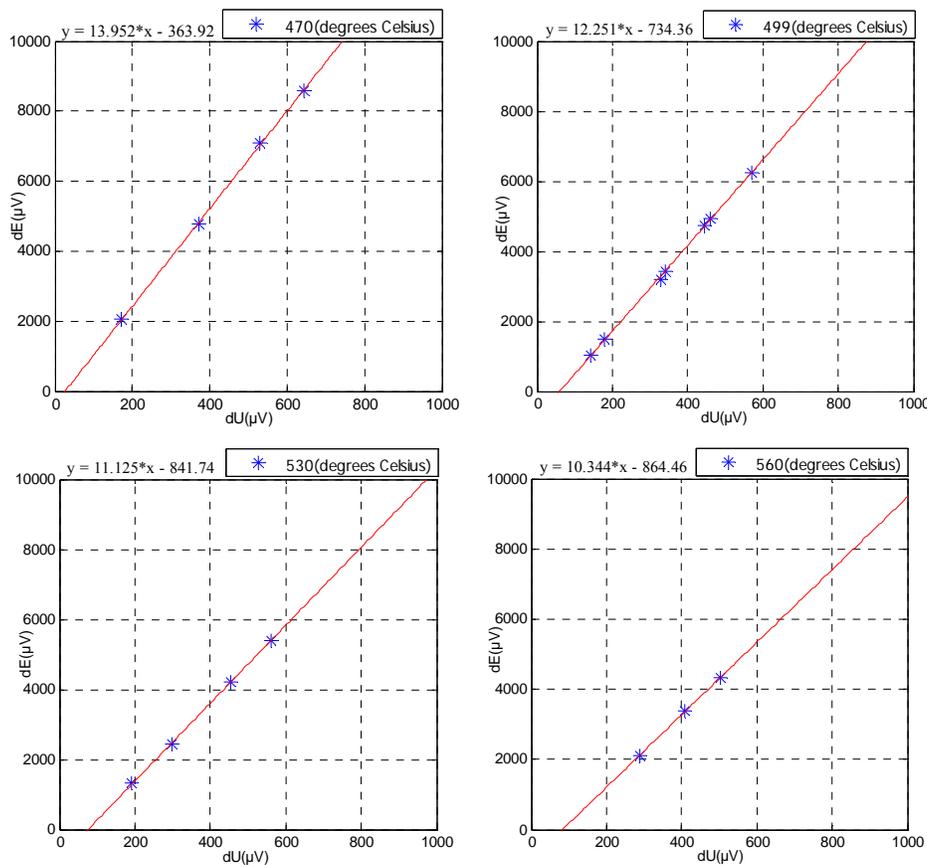
Fig.3 Linear dependence of the thermoelectric power ΔE versus the temperature gradient ΔU for the molten alloy I (2 at. % excess sulfur) obtained experimentally at various temperatures: 470°C; 499°C; 530°C; 560°C

A closer examination of the graphs in Fig.3 shows that for each point the thermoelectric power ΔE measured between the two Mo electrodes is expressed in μV. Concerning the temperature gradient between the two columns of liquid alloy in which the two thermocouples were plunged it was indicated in each graph in Fig.3 directly by ΔU representing the difference in μV between the thermoelectric power recorded by the two thermocouples. In so doing we have aimed at improving the accuracy of the results by avoiding a manifold transformation from μV to °C.

The Seebeck coefficient S (in μV/ °C) defined as ΔE/ΔT was obtained at each temperature as the slope of the straight line in Fig.3, calculated by derivation against ΔT of the equation type y=ax + b (where y= ΔE and x= ΔU). If the slope of the straight line is multiplied by a constant ε that helps to transform the thermoelectric power

of the thermocouples in °C, one obtains the relative Seebeck coefficient S_{ab} of the liquid alloy in μV/ °C. This constant ε was calculated at the temperature of each measurement by using the equation specific for the thermocouple we have used, namely:

$$U_{Tc}(T)= -0.237243 +2.730684 \cdot 10^{-2}T+3.02324 \cdot 10^{-6}T^2 \quad (3)$$

where U_{Tc} (T) is the thermoelectric power in μV recorded by the thermocouple at the temperature T in °C. We have obtained the coefficients in eq.(3) by experimental calibration of the thermocouple we have used by the method of the melting points of five pure metals.

Table 1 summarises the steps and final results for the Seebech coefficients we have calculated from the experimental data in Fig.3.

*Table 1. Calculation of the absolute Seebeck coefficient of the liquid alloy I (64.7 at.%Tl+35.3 at.%S
(2 at.% excess S) at various temperatures*

T (^{O}C)	ΔT (^{O}C)	ΔU (μV)	ΔE (μV)	y=ax+b	ε	S_{ab} (μV/^{O}C)	S_b (μV/^{O}C)	S_a (μV/^{O}C)
470	10	172.7 373 530 643	2067 4782 7081 8594	a= 13.95 b= -363.92	30.148	420.64	15.82	436.46
499	39	178 445 570 142 329 460 340	1478 4745 6240 1020 3186 4950 3426	a = 12,25 b = -734.36	30.234	371.48	16.09	387.57
530	70	297 562 454 192	2427 5407 4228 1314	a = 11,12 b = -841. 4	30.511	339.43	16.32	355.75
560	100	503 407 290	4320 3380 2120	a = 10,34 b = -864.46	30.693	317.50	16.48	333.98

The meaning of the values in the columns of Table 1 is as follows: T= temperature at which the Seebeck coefficient was measured; ΔT=T-T$_{liq}$ (overheating of the melt above alloy's liquidus temperature T$_{liq}$=460°C); ΔU= difference between the thermoelectric power recorded by the two thermocouples at each thermal gradient; ΔE= thermoelectric power recorded between the two Mo electrodes at each proposed thermal gradient; equation of the straight line in Fig.3; ε = factor for transforming the slope of the straight line in Fig.3 in

μV/^{o}C; S$_{ab}$= relative Seebeck coefficient of the liquid alloy at temperature T; S$_b$= absolute Seebeck coefficient of solid molybdenum at temperature T; S$_a$= absolute Seebeck coefficient of the liquid alloy at temperature T.

For alloy II (57.1 at.%Tl+42.9 at.%S; stoichiometry Tl$_4$S$_3$ in solid state; 9.6 at.% excess S as compared toTl$_2$S) the thermoelectric power in liquid state was investigated at three temperatures going down as close as possible to the liquidus point (T$_{liq}$=390°C). The results are given in Fig.4 and Table 2 (built with the same columns as Table 1).
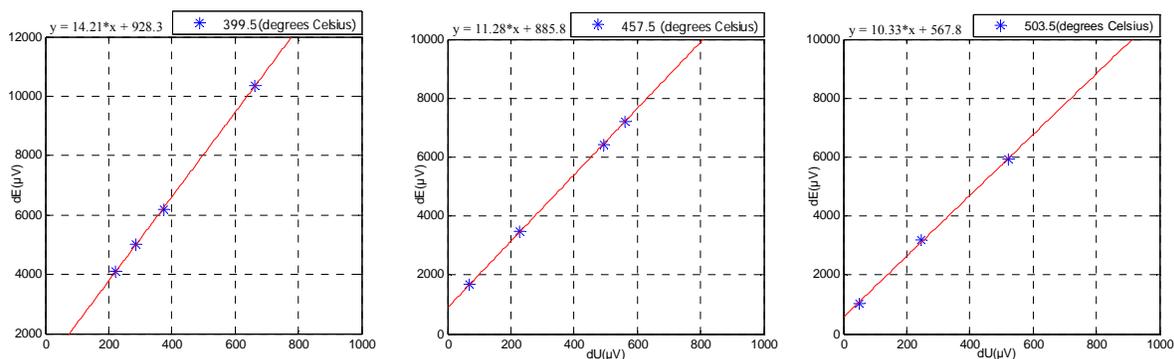

Fig.4 Linear dependence of the thermoelectric power ΔE versus the temperature gradient ΔU for molten alloy II (9.6 at.% excess sulfur) obtained experimentally at various temperatures: 399.5^{o}C; 457.5^{o}C; 503.5 ^{o}C

Table 2. Calculation of the absolute Seebeck coefficient of the liquid alloy II (57.1 at.%Tl + 42.9 at.%S (9.6 at.% excess S) at various temperatures

T (°C)	ΔT (°C)	ΔU (μV)	ΔE (μV)	ΔE =aΔU +b	E	S_{ab} (μV/°C)	S_b (μV/°C)	S_a (μV/°C)
399.5	9.5	222 287 374 662	4105 5017 6200 10352	a= 14.2141 b= 928.30	29.7224	422.48	14.94	437.42
457.5	67.5	70 228 493 560	1670 3468 6433 7210	a = 11.2788 b = 885.84	30.0731	339.19	15.68	354.87
503.5	113.5	50 245 522	1040 3175 5930	a = 10.3323 b = 567.84	30.3512	313.60	16.13	329.73

4. Discussion

In order to make clear the type of temperature dependence in liquid state of the thermoelectric power for the investigated alloys we have plotted in Fig.5 our experimental data on the temperature variation of the absolute Seebeck coefficient for both molten alloys. It appears obvious that the two curves point to the same type of variation, namely an increase of the thermoelectric power as the temperature decreases and this was true down to the liquidus temperature of each alloy (liquidus temperature indicated by a bar for each alloy).
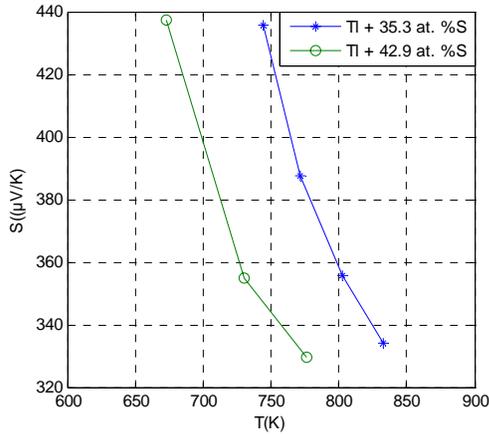

*Fig.5 Temperature dependence of the Seebeck coefficient for the investigated alloys: * = alloy I (Tl+35.3 at.%S) $T_{liq.}$ =460° C; ∘= alloy II (Tl+42.9 at.%S) $T_{liq.}$ =490° C*

An interestig finding put in evidence in Fig.5 consists in the fact that the two curves for the Seebeck coefficient in the liquid alloys are seemingly parallel. This similitude is confirmed by the energy of activation for the process calculated as follows:

We take as a basis the expression that correlates the Seebeck coefficient S with the electrical conductivity σ:

$$S = \frac{k}{e}\int_0^\infty \frac{\sigma(E)}{\sigma}\frac{(E-E_f)}{kT}\left(\frac{\partial f}{\partial E}\right)dE \qquad (4)$$

which may be written:

$$S = \frac{k}{e}\int_0^\infty \frac{BE^n}{\sigma}\frac{(E-E_f)}{kT}\left(\frac{\partial f}{\partial E}\right)dE \qquad (5)$$

if one admits to express the electrical conductivity σ as:

$$\sigma(E) = BE^n \qquad (6)$$

where B is a constant

By integrating eq. (5), one obtains:

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

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

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

and

$$\xi = \frac{E-E_f}{kT} \qquad (9)$$

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

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

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

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

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

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

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

In the graphical representation in Fig.6 we have plotted on the ordinate the left member in eq.(10) and on the abscisa the reciprocal absolute temperature. It is to note the excelent agreement between the theoretical curves and the experimental points. As a result we have succeded to obtain the activation energy E_1 for each alloy, which according to eq.(8) represents the slope of the straight line.

The values obtained are as follows, being close one to another for the two liquid alloys:

$E_1=0.8\ eV \pm 0.001$ for alloy I (64.7 at.%Tl + 35.3 at.%S)
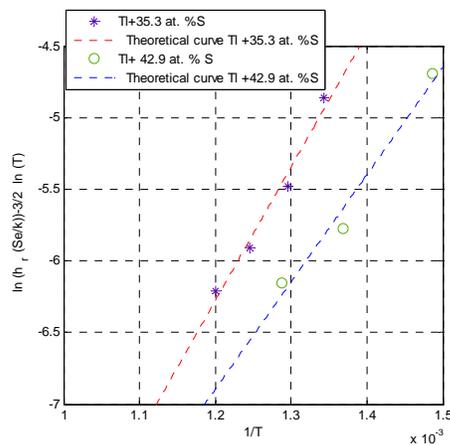$E_1=0.65\ eV \pm 0.001$ for alloy II (57.1 at.%Tl + 42.9 at.%S), respectively.

Fig.6 Theoretical dependence of the Seebeck coefficient on temperature used to determine the activation energy R^2 coef for (*) is 0.9816 and for (○) is 0.974.

Another interpretation that may bring support to this agreement may come from correlating the composition of the alloys with the phase equilibrium diagram of the Tl-S system.

Acording to the phase equilibrium diagram in Fig. 2 the two alloys have a different phase constitution at room temperature, namely alloy II consists entirely of Tl_4S_3 crystals whereas alloy I comprises 0.2 Tl_4S_3 crystals plus ~0.8 Tl_2S crystals (by molar fractions).

However when heated for melting a phase transformation occurs in both alloys and this makes them to adopt the same type of phase constitution. This is so because the compound Tl_4S_3 (which exists in both alloys but in different amount) is unstable when heated and at a temperature equal to 300^oC decomposes by a peritectic reaction as follows:

$$Tl_4S_3 \rightarrow Tl_2S + liquid\ _{(59at.\%S)}$$
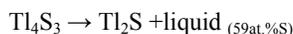
One may conclude that above 300^oC both alloys consist in a mixture of $liquid_{59(at.S)}$ and Tl_2S crystals. There is however a difference between the two alloys concerning the amount of Tl_2S crystals existing along with the liquid.

By performing the necessary calculations on the phase equilibrium based on the Gibbs rule, it is easy to establish that above 300^oC alloy II contains a fraction of 0.395 Tl_2S crystals whereas alloy I contains a larger fraction namely 0.874 Tl_2S crystals.

Theoretical thermodinamical calculations involving the pseudo-binary entropy of mixing in liquid state carried out for the Tl-Te system [14] have concluded that molecular Tl_2Te clusters may persist in the melt together with a Te-rich or a Tl-rich liquid, depending on the element in excess. If this is also true for the akin Tl-S system in which the chalcogene element is sulfur instead of tellurium, the same type of clusters namely Tl_2S are to be expected to exist in different proportions in the melt of the two S-rich alloys we have investigated. This may be an explanation for the parallelism of the curves in Fig.5 as well as for the similar values of the activation energy.

An interesting feature of the behavior of the investigated alloys appears in Fig.7 in which we have plotted the Seebeck coefficients for the two alloys in a way that is different from the usual one. Instead of using the temperature T as the independent variable as usual, we have taken as the independent variable the value $\Delta T=T-T_{liq}$ representing the overheating of the melt above the alloy's liquidus temperature (as indicated in Tables 1 and 2). In so doing we have reasoned that from a physical point of view what really matters in the behavior of the melt is not its temperature but how far apart this temperature is from the liquidus point (end of melting). Surprisingly in this new type of plotting the two curves appear superposed, the experimental values of the Seebeck coefficient measured at the same overheating in the two alloys appearing as common points on the two curves.
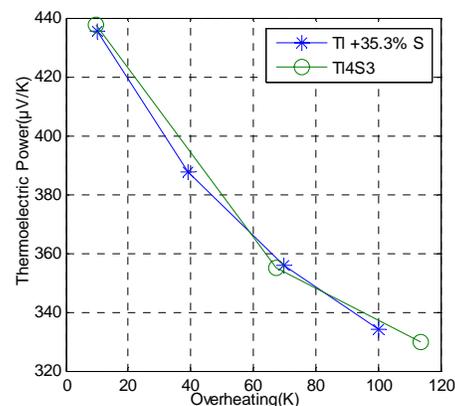

Fig. 7. Temperature dependence of the Seebeck coefficient expressed as a function of the overheating of the melt above the liquidus temperature of each alloy ($\Delta T=T-T_{liq}$) * = alloy I (Tl+35.3 at.%S), $T_{liq.} = 460^o C$; ○= alloy II (Tl+42.9 at.%S), $T_{liq.} =390^o C$

This finding suggests that using the overheating instead of temperature as a parameter may better reflect what happens in the melt upon heating. As discussed above in connection with the phase equilibrium diagram, at the end of melting (liquidus temperature) the two

investigated alloys inherit from the solid the same type of preferential atomic association, namely Tl_2S clusters and a sulfur rich liquid. When the melt is heated the effect of increased thermal vibration on the atomic associations in the melt may be better reflected when one considers the same degree of overheating.

5. Conclusions

The experimental measurement of the thermoelectric power versus temperature in molten Tl-S alloys with a large excess of sulfur (2 up to ~22 at.% excess S if compared to the semiconductor stoichiometric Tl_2S compound) have indicated that in the composition range (2 up to 9.6 at.% excess S) the molten alloys manifest a behavior specific for a one band semiconductor substance, namely decrease of the Seebeck coefficient as the temperature increases. Such a behavior was shown to be valid down to the lowest temperature accessible to thermoelectric power measurement in the melt, meaning a temperature very close to the liquidus point (~ 10^oC overheating of the melt above the liquidus temperature).

For the two investigated alloys that fall in this category (alloy I= 64.7 at.%Tl + 35.3 at.%S; 2 at.% excess S as compared toTl_2S and alloy II= 57.1 at.%Tl+42.9 at.%S; 9.6 at.% excess S as compared toTl_2S) the experimental curves showing the Seebeck coefficient dependence versus temperature were seemingly parallel. Even more if the dependence of the Seebeck coefficient was presented in a less usual way, namely versus the degree of overheating of the melt, the two curves appear superposed. The reason for this similitude in behavior may be ascribed to the structure of the liquid resulting when melting the two alloys. This structure is the same for both of them consisting in a sulfur rich atomic liquid and Tl_2S clusters resulting from the persistence in the liquid phase of reminiscences of the structure of Tl_2S crystals.

A theoretical calculation of the activation energy of thermoelectric transport process has resulted in similar values namely *E_1=0.8 eV ± 0.001* for alloy I (64.7 at.%Tl + 35.3 at.%S) and *E_1=0.65 eV ± 0.001* for alloy II (64.7 at.%Tl + 35.3 at.%S), respectively. This difference may be due to the different amount of Tl_2S crystals existing in the two alloys above the peritectic reaction responsible for the disappearance of the unstable compound Tl_4S_3 that exists at room temperature in different amounts in the two alloys.

References

[1] H. S. Schneiders, J. B.van Zytveld, J.Phys.Condens.Mat. **8,** 10875 (1996).
[2] A. M. Vora, Commun.Theor.Phys. (Beijing-China) **51**(3), 550 (2009).
[3] V. Sklyarchuk, Yu.Plevachuk, S.Mudry, I.Shtablavyi, Journal of Physical Studies **11**(2), 190 (2007).
[4] A. M. Adam, S. Adam, M. I. Petrescu, Metalurgia International, Special Issue **1**, 77 (2013).
[5] Kazandzhan, A. A.Tsurikov, Akad. Nauk SSSR **48**,746 (1974).
[6] Y. Nakamura, K. Matsumura, M.Shimoji, J. Chem.Soc. Faraday Trans. **70,** 273 (1974).
[7] S. Adam, A. M. Adam, M.I.Petrescu, Metalurgia International, Special Issue 1, 73 (2013).
[8] R. A. Howe, J. E. Enderby, Phil.Mag. **16**, 467 (1967).
[9] N. Kusack, P.Kendall, Proc. Phys. Soc. **72,** 898 (1958).
[10] M. Cutler, Liquid semicoductors, Academic Press, New York (1977).
[11] B. Wölfing,**"***Tl$_9$BiTe$_6$: A new thermoelectric material with record performancies",* Ph.D.Thesis,Universität Konstanz, Switzerland 2000.
[12] T. B. Massalski, H. Okamoto, P. R. Subramanian, L. Kacprzak (editors), Binary alloys phase diagrams, 2nd edition, ASM Publications, USA, 1992.
[13] M. Hansen, K. Anderco, Constitution of the binary alloys, Mc.Graw-Hill Book Comp., New York (1958).
[14] Y. Nakamura M. Shimoji, Trans.Faraday Soc. **67**, 1270 (1971).

*Corresponding author: ipetrescu@yahoo.com