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The influence of the ionic component of the electrical conductivity on the semiconductor–metal transition in liquid Tl–Se alloys

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Abstract

Experimental investigations of electrical conductivity $\sigma(T)$ and thermo-e.m.f. $S(T)$ were performed for liquid Tl–Se alloys in the region of the stoichiometric compound Tl_2Se in a wide temperature range (from 600 K to 1700 K). It was shown that the existence of an ionic component in the electrical conductivity affects significantly the peculiarities of the metallization process of the liquid cells. A model explaining the unusual thermo-e.m.f. behavior, which forms a large deviation from the 'classical' dependence in a wide temperature range resulted from the effect of electron-hole compensation, has been proposed. The ionic contribution essentially changes the electrical conductivity resulting in a deformation of the exponential curve $\sigma(T)$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Liquid alloys; Semiconductors; Electrical transport; Thermoelectric; High pressure

1. Introduction

The existence of both, electron and hole mechanisms of the charge transfer, and their influence on the electron spectrum structure and hence on peculiarities of a metallization of semiconducting melt in the frame of the semiconductor–metal transition are poorly understood. Similar investigations especially in the metallization region are few in number [1–4]. Nakamura and Shimoji [5] measured the electrical conductivity and the thermo-e.m.f. of the Tl–Se and Tl–Te systems near the stoichiometric composition. They reported a deep minimum in the electrical conductivity at the stoichiometric composition and found that the thermo-e.m.f. rapidly changed a sign. This behavior is sometimes described as a change from p-type to n-type conduction according to whether the thermo-e.m.f. is positive or negative [4]. At this point, the liquid binary Tl–Se system suffering the p–n transition at the stoichiometric compound Tl_2Se seems to be convenient for such studies. Moreover, the fraction of the ionic conductivity in this system can not be neglected [2].

The purpose of this paper is to report a model explaining the unusual thermo-e.m.f. behavior. The analysis of both mechanisms of charge transfer is based on experimental results of electrical conductivity and thermo-e.m.f. measurements.

2. Experimental details

The samples used in this experiment were made from 99.999% Tl and 99.999% Se. The specimens were sealed in a vacuum in a quartz ampoule and reacted for about 20 h in a molten state and then quenched to room temperature. Before the experiment the sample was inserted by a special method into the measuring cell directly inside a high-pressure vessel [6]. The equipment design and the measurement procedure were also described in this paper.

Measurements were carried out under Ar gas atmosphere (up to 50 MPa) to reduce oxidation and vaporization of the liquid sample. The measurements have been carried out by a contact method in accordance with the four-point scheme. Measuring cells, manufactured of boron nitride ceramic in the form of two coaxial vertical cylindrical containers of different radii with an operating cavity height of 60 mm, were used for this purpose. The cell constant was determined by using Hg at room temperature. The cell construction permits to carry out the electrical conductivity

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and thermo-e.m.f. measurements simultaneously in one run. Six graphite electrodes, two for the current (at the top and the bottom) and four for potential measurements were placed in the wall of the container along its vertical axis. The potential electrodes were provided with thermocouples, which were used for temperature measurements and their single thermoelectrodes for electrical conductivity and thermo-e.m.f. measurements. In most runs the melt temperature was determined by WRe-5/20 thermocouples in close contact with the liquid, while for control measurements Pt/PtRh-10 thermocouples were employed. Temperature gradients of 2.5–3.33 K/cm along the cell were additionally controlled to within 0.1 K by a preliminary calibrated five-point differential thermocouple.

In order to prevent a development of convective flows a following stationary state equation has been taking into account [7]: $\beta\vec{\nabla}Tg + \beta'\vec{\nabla}cg = 0$, where β is a coefficient of the liquid's thermal expansion, β' is a concentration coefficient of expansion, g is a gravitational acceleration, $\vec{\nabla}T$ and $\vec{\nabla}c$ are temperature and concentration gradients, respectively. In order to suppress the convective flows, the horizontal components of the tensors $\vec{\nabla}T$ and $\vec{\nabla}c$ should be reduced to a minimum. The most simple and conventional solution to this problem is to construct a measuring cell as a vertical container with an inner diameter as small as possible. Based on the literature data on thermophysical properties of BN, we estimated the dimensions of the measuring cell as $l/r{\sim}25$. As it was shown in [6], the relationship l/r reached in our cell is about 32. Thus, we can state that no convection occurs. A high temperature heater with three independently controlled heating elements makes it possible to reach a temperature up to 1750 K. The experimental error in σ was less than ±2% and in S less than ±5%.

3. Results and discussion

The data of temperature dependence of electrical conductivity and thermo-e.m.f. for all the investigated alloys are presented in Figs. 1 and 2 and summarized in Table 1. The exponential temperature dependence of the electrical conductivity of the Tl_2Se alloy with an activation energy $E^{\sigma}(0)=0.49$ eV is typical for intrinsic semiconductors. At the same time the thermo-e.m.f. decreases reaching nearly metallic values [3]. For the alloy $Tl_{0.68}Se_{0.32}$ with a higher thallium content than in the stoichiometric compound Tl_2Se a jump-like increase of the activation energy from $E^{\sigma}{}_1(0)=0.45$ eV to $E^{\sigma}{}_2(0)=0.56$ eV occurs (see Fig. 1). For both of these compositions the conductivity changes its slope and tends to saturate at a level of about 630 $Ohm^{-1}cm^{-1}$ for $Tl_{0.68}Se_{0.32}$ and 550 $Ohm^{-1}cm^{-1}$ for Tl_2Se. This can be considered as the beginning of a metallization process of the alloys based on electrical conductivity [3].

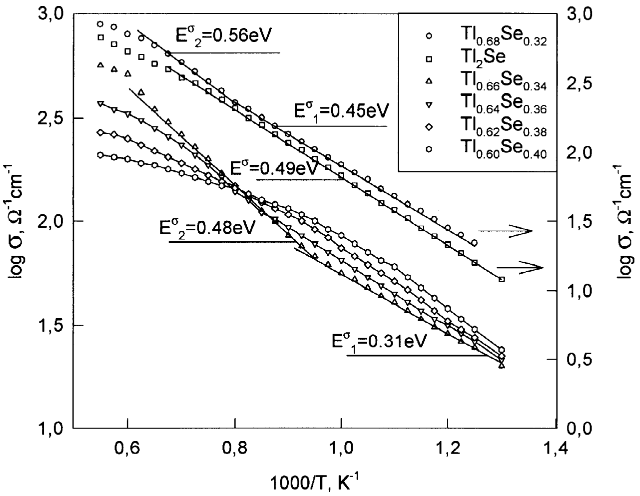

Fig. 1. Electrical conductivity as a function of reciprocal temperature for liquid Tl–Se alloys.

An increase of the electrical conductivity with temperature for $Tl_{0.66}Se_{0.34}$, accompanied by a drastic increase of the activation energy from $E^{\sigma}{}_1(0)=0.31$ eV to $E^{\sigma}{}_2(0)=0.48$ eV and further trend to saturation are also in agreement with the metallization concept [3]. An increase of the selenium content reduces the temperature whereby the electrical conductivity begins to deviate from linearity and lowers the corresponding absolute values of σ. It should be pointed out that for the $Tl_{0.64}Se_{0.36}$, $Tl_{0.62}Se_{0.38}$, and $Tl_{0.60}Se_{0.40}$ liquid alloys a tendency of the $\Delta\sigma/\Delta T$ decreasing is well-defined. For the $Tl_{0.66}Se_{0.34}$ composition a trend toward saturation is most pronounced beginning from 1600 K at a level of about 490 $Ohm^{-1}cm^{-1}$. In all instances the thermo-e.m.f. decreases sharply with a sign

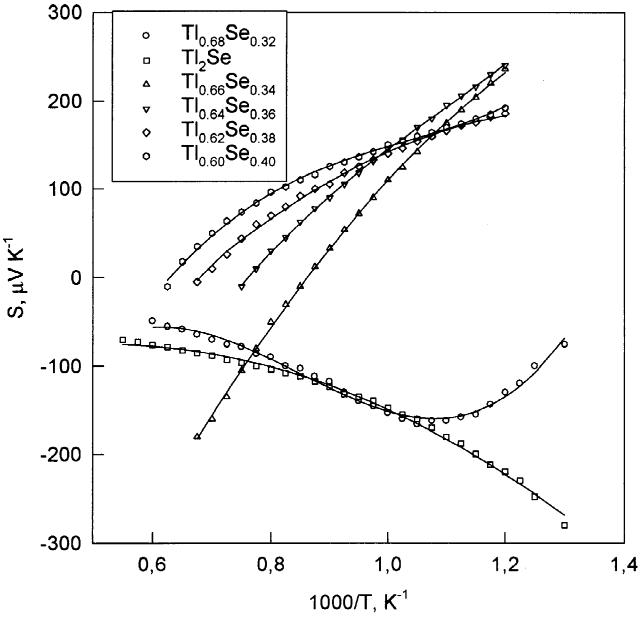

Fig. 2. Thermo-e.m.f. as a function of reciprocal temperature for liquid Tl–Se alloys.

Table 1
The electrical conductivity and thermo-e.m.f. data of liquid Tl–Se alloys

T, K	$Tl_{0.60}Se_{0.40}$	$Tl_{0.62}Se_{0.38}$	$Tl_{0.64}Se_{0.36}$	$Tl_{0.66}Se_{0.34}$	Tl_2Se	$Tl_{0.68}Se_{0.32}$
σ, Ohm^{-1} cm^{-1}						
770	24	22	21	20	12	18
830	38	33	31	29	22	28
900	60	50	45	42	38	47
1000	85	74	65	56	67	81
1100	118	107	100	89	120	141
1250	151	151	154	154	204	229
1430	179	200	225	257	347	446
S, μV K^{-1}						
770	220	280	270	280	−250	−70
830	198	230	230	240	−200	−120
900	185	180	185	190	−150	−140
1000	150	130	145	120	−145	−145
1100	130	115	100	50	−120	−120
1250	100	90	50	−50	−100	−105

inversion. Figs. 3 and 4 show the concentration variation of electrical conductivity, $\sigma(x)$, and thermo-e.m.f., $S(x)$, for the liquid Tl–Se alloys at certain temperatures. As is seen, the minimum in the $\sigma(x)$-curves shifts towards the alloys with higher concentration of selenium with increasing temperature. At a first glance, an increase of the electrical conductivity in a high temperature region appears unexpected (see Fig. 1). It can be explained either by an increase of the charge carriers amount or by additional contribution of other mechanisms of the charge transfer to the conductivity. A joint analysis of the electrical conductivity and thermo-e.m.f. data provides strong evidence that electron-hole compensation occurs in similar melts [4,8]. Moreover, a relationship between the partial contributions depends on temperature and concentration.

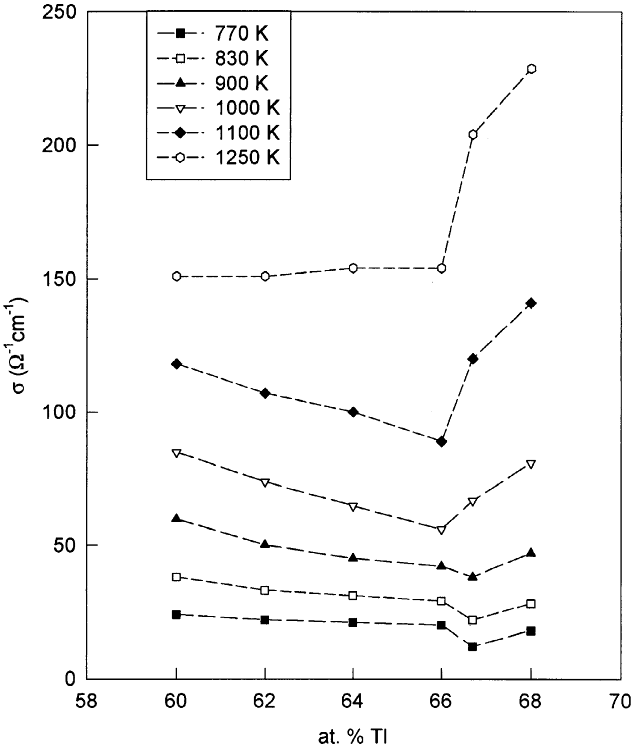

Fig. 3. Concentration variation of electrical conductivity for liquid Tl–Se alloys at different temperatures. Lines are drawn as guides to the eye.

A well-known model for the alloys with a strong composition dependence of transition coefficients like Tl–Te, Tl–Se, Tl–S etc. rests on the hypotheses for cluster formation. The later leads to the pseudogap formation in the density of states [9]. The energy bands of these clusters form the conducting and valence bands divided by an area of low-density states corresponding to the band gap. An electron in the metallic area with energy higher than the energies of the clusters conducting and valence bands can penetrate into the inner cluster area, while the later acts like a scatterer.

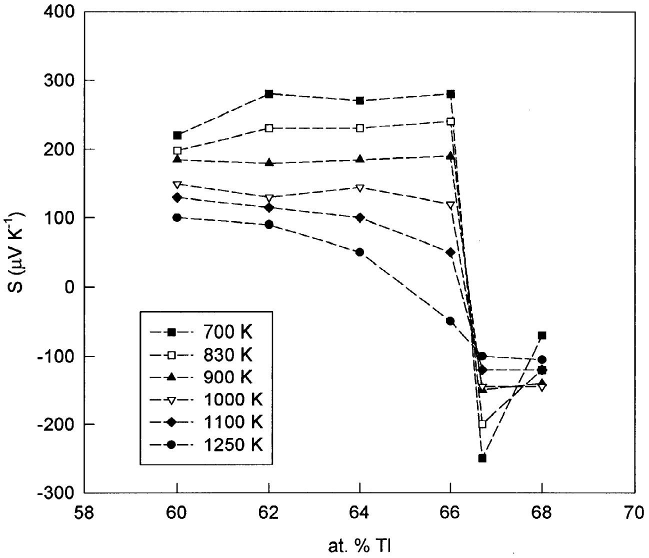

Fig. 4. Concentration variation of thermo-e.m.f. for liquid Tl–Se alloys at different temperatures. Lines are drawn as guides to the eye.

It should be noted that this model considers two types of localized states. The first one contains the states responsible for cluster stabilization, while the second one consists of some states in the metallic area, which could become localized when the forbidden volume will exceed the critical value. In real alloys the Fermi level lies within the gap. As the concentration of 'metal' electrons as well as the Fermi level change with the alloy concentration, the gap shifts. Location of the Fermi level relating to the gap depends strongly on concentration, especially when the latter crosses a stoichiometric relationship ($x=2/3$) corresponding to the compound Tl_2Se. Since the Fermi level falls in the pseudogap, the states close to the Fermi level make no contribution to the conductivity, and a sharp electrical conductivity decreasing is expected.

It should be noted that changes of conductivity with concentration for alloys with a higher selenium content than in the Tl_2Se are not so drastic as those for the alloys with an excess of thallium. Our data, however, show that these changes are smaller than those reported in [9], where changes of resistivity reached orders of magnitude. Such discrepancy can be explained by the existence of a region with a miscibility gap close to Tl_2Se, extending towards higher thallium content in the phase diagram. A phase separation affects considerably the conductivity values [10], which in turn are very sensible to concentration, especially for the Tl_2Se+Tl liquid alloys.

The thermo-e.m.f. value near the stoichiometric composition is rather high and changes its sign when crossing it. The $\sigma(T)$ and $S(T)$ behavior are in good qualitative agreement with experimental results. Nevertheless, it is highly complicated to explain the heating dependent sign changes in the alloys with an excess of Se. Some efforts to explain this phenomenon have been based on magnetic susceptibility measurements in [11], where an unusual behavior of the density of states has been revealed. According to [1,2,12], the ionic and electronic components of conductivity are available in all the liquid Tl–Se alloys, but their relative contribution can change. The gradual increase of the ionic component in the Tl–Se system [2] allows to consider these liquid alloys as electron-ion liquids [12,13]. This statement has been confirmed by several structural studies [14–16].

It follows from these investigations that the main interaction occurs between the Tl–Se and Tl–Tl layers. The X-ray scattering data in a liquid state point to the fact that the short-range structure of the melt remains stable with temperature variation. The structural investigations in the liquid state indicate that the short-range structure and a type of the interatomic bonds in Tl_2Se change very little in the course of melting. As a result, two mechanisms of the charge transfer are possible in similar melts, namely, the electron tunneling between charged centers (the clusters can also manifest themselves as the charge centers) and the ion drift. In the thermodynamic theory for irreversible processes a phenomenological expression for thermo-e.m.f. is given as [17]:

$$S=\sum t_i(Q_i-\mu_i)/q_iT \quad (1)$$

where t_i is a fraction of current transferred by a single particle, μ_i is a chemical potential, $Q_i$is a heat transfer, q_i is a particle charge. It is clear that $\mu_i=E_f$ and $q_i=-e$ for both mechanisms of the charge transfer.

Eq. (1) includes the ionic, S_I, and electronic, S_E, contributions of the charge transfer. A final expression for the thermo-e.m.f. is as follows:

$$S=t_ES_E+t_I S_I \quad (2)$$

Assuming a change of t_I with temperature, peculiarities of the thermo-e.m.f. behavior can be satisfactory explained. Considering the ionic and electronic contributions to the charge transfer as independent ones, the common electrical conductivity σ is the sum of the ionic $\sigma_I$and electronic σ_E components. These ionic and electronic terms were separated in [2,15]. The increase of the activation energy on the log $\sigma=f(1000/T)$ dependencies has been interpreted by an increase of the σ_E/σ_I ratio, based probably on a many component screening mechanism.

4. Conclusion

The analysis of the temperature dependence of the electrical conductivity and the thermo-e.m.f. for liquid Tl–Se alloys proves that at low temperatures (<1000 K) their behavior can be explained by both electron and hole conduction. The aim of the present work was to show that at higher temperatures (>1000 K) the ion component has a significant impact on the charge transfer processes in the Tl–Se liquid alloys and can not be neglected.

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