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Dynamics of the pseudogap transformation in semiconducting melts during metallization

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Abstract

Electrical conductivity $\sigma(T)$ and thermo-emf $\alpha(T)$ measurements, performed in a wide temperature range (from 700 to 1700 K) for binary $S_{0.35}Te_{0.65}$ and ternary $CuAsSe_2$ and $TlAsSe_2$ liquid alloys, suggest that a transition from semiconducting to metal conductivity occurs. The metallization temperature determined by thermo-emf measurements is lower than that determined by electrical conductivity. A temperature-dependent transformation of the pseudogap width is interpreted in the frame of a screening mechanism of the bound states by the free electron gas in the pseudogap region.

1. Introduction

Experimental investigations described in [1–6] strongly suggest that transition from semiconducting to metal conductivity occurred in liquid semiconductors at high temperatures. Based on electrical conductivity measurements, it was revealed essentially for all the semiconducting melts, that this transition to metal conductivity is accompanied by an increase in the pseudogap tailing velocity. At the same time, this phenomenon is not observed during the thermo-emf measurements. The observed narrowing dynamics of the pseudogap is manifested on the electrical conductivity dependencies as a jump increase in the activation energy. An interpretation of such peculiarity for Se–Te melts was based on the assumption of primary importance of the ambipolar mechanism of a charge transfer [7]. Nevertheless, it is the author's opinion that such a process requires a special thermo-emf behaviour [7]. According to Mott, holes in these liquid alloys form polarons of small radii, which behave similarly to Se_2^+ molecules and move like heavy ions [8]. In this case, an expression for the electrical conductivity must include an additional energy, W , connected to the polaron jumps, while an expression for the thermo-emf does not include such energy. As a result, different values of conductivity and thermo-emf activation energy, as well as the inflexion on the $\log \sigma = f(1000/T)$ curve occur. Another mechanism, proposed in [9], explained this behaviour of the Se–Te melt by both the change of the electron correlation and the ion contribution into

the conductivity. All these mechanisms are of a special case and could probably be adapted to individual systems.

In this paper we present a qualitative interpretation of the pseudogap behaviour in a wide temperature interval including a range of the semiconductor–metal transition. The analysis is based on experimental data of electrical conductivity and thermo-emf measurements.

2. Experimental details and results

Experimental results presented in this paper were obtained with a modified automated device, which measured jointly electrical conductivity and thermo-emf. The measurement procedure is based on a contact four-probe method and has been described completely in [10]. The experiments were performed under argon gas with pressures up to 50 MPa to minimize the change in chemical composition caused by volatilization of nonmetallic components. Original measuring cells, manufactured from 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. Graphite electrodes for the current (at the top and the bottom) and potential measurements were placed in the wall of the container along its vertical axis. The potential electrodes were provided with thermocouples. These thermocouples were used for temperature measurements and their single thermoelectrodes for $\sigma(T)$ and $\alpha(T)$ measurements. The melt temperature was determined by WRe-5/20 thermocouples in close contact with a liquid. Temperature gradients of about 3–4 K cm⁻¹ along the cell were maintained during $\alpha(T)$ measurements.

The cell construction permits us to carry out the electrical conductivity and thermo-emf measurements simultaneously in one run. The possibility of the determination of these parameters for different sections of the cell, which are formed by potential electrodes, is yet another advantage of the cell presented. Moreover, cell construction allows the elimination of analytically jamming and noise signals arising due to contact wires as well as systematic device deviation. A high-temperature heater with three independently controlled heating elements enables one to reach a temperature up to 1700 K. The components of samples employed were of 99.999% purity. The maximum errors of electrical conductivity and thermo-emf determination did not exceed 1.5 and 5%, correspondingly.

The electrical conductivity $\sigma(T)$ and thermo-emf $\alpha(T)$ data for the binary S_{0.35}Te_{0.65} liquid alloy are shown in figure 1 and for ternary CuAsSe₂ and TlAsSe₂ liquid alloys in figure 2, correspondingly. Inflexions on the curves observed for all the melts reflect an increase of the activation energy of conductivity. Nevertheless, such inflexions have not been found on the $\alpha(1000/T)$ curves for ternary CuAsSe₂ and TlAsSe₂ liquid alloys. Only for S_{0.35}Te_{0.65}, have similar inflexions been revealed. The constructed curves, $E(T)$, for the conductivity and thermo-emf activation energies, presented respectively in figure 3 (see also reference [11]), reflect not an increase in activation energy, but only an increase in the pseudogap tailing velocity.

It should be mentioned that similar peculiarities were also observed on the curves of energy dependence of the absorption coefficient in the course of the optical absorption edge measurements [2–4]. Like on the dependencies $\log \sigma = f(1000/T)$, an abrupt increase of activation energy took place.

Structural investigations performed for liquid S–Te [12, 13] and Tl–As–Se [14] alloys suggest that covalent bonds prevail. The coordination number of S–Te increases from 2.1 to 2.2. Such an insignificant increase leads to a rather trifling variation in the exchange interaction. This suggests that the ‘electron effects’ revealed by different studies do not reflect directly the structural changes, although the gradual structural variations undoubtedly affect the electron properties.

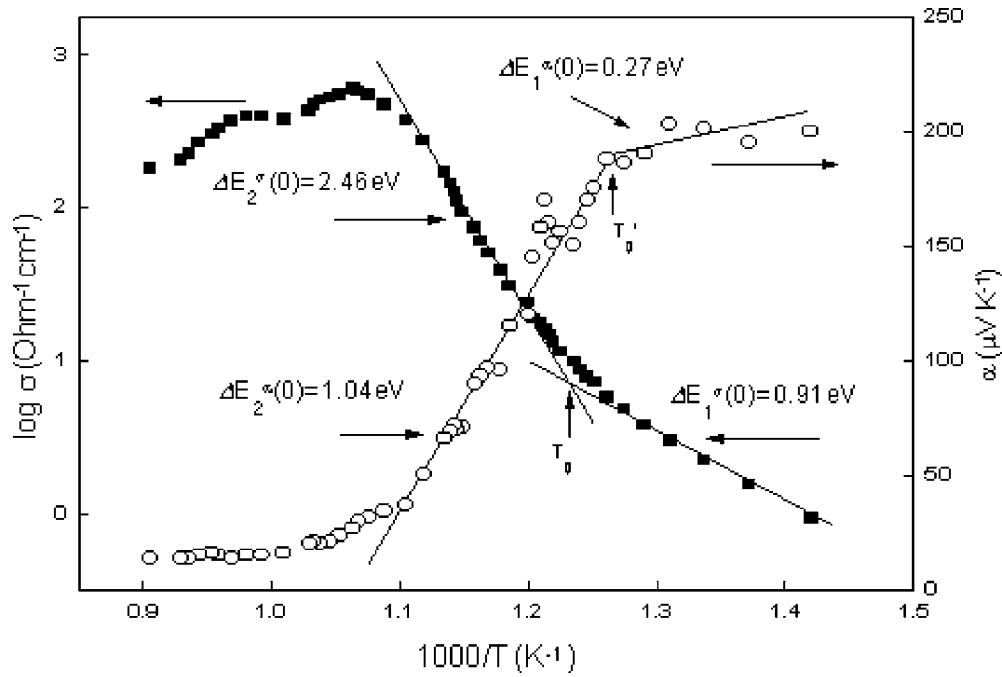


Figure 1. Electrical conductivity, $\log \sigma$, and thermo-emf, α , as a function of reciprocal temperature for the $S_{0.35}Te_{0.65}$ liquid alloy.

3. Discussion

An increase in the pseudogap tailing velocity at temperatures higher than some specific value T_0 suggests that none of the above-listed charge transfer mechanisms prevail in our melts. A many-electron mechanism of delocalization of extrinsic electron states by free electrons in 'metal-thin amorphous semiconductor-metal' systems has been described in reference [15]. Ideas based on this mechanism can also be applied to liquid semiconductors for the description of persistent or local electron states in the pseudogap region. It is suggested that delocalization of the electron states can be considered as the vanishing of pseudogap and a transition to metal conductivity.

It is assumed that an increase in the concentration of free electrons leads to the shift and vanishing of local levels and the energy width of a pseudogap can be described as

$$E(T) = E(T_0) - \frac{n}{n^*}kT \quad (1)$$

where E is the activation energy of local states, n is the concentration of free electrons, n^* is a specific concentration of carriers wherein E lowers by kT owing to screening of persistent electron states by free carriers. For $E(T)$ calculation, an equation allowing the determination of the free carriers concentration, n , is needed. According to reference [15], the n value can be obtained from the thermodynamic analysis of states where the system is stable. A system-free energy, F , is expressed as

$$F = U - TS \quad (2)$$

where U is the internal energy, S is the entropy.

Assuming that n represents the carriers transferred from the valence band with the density of states N_v into the conduction band with the density of states N_c , and the energy expenditure

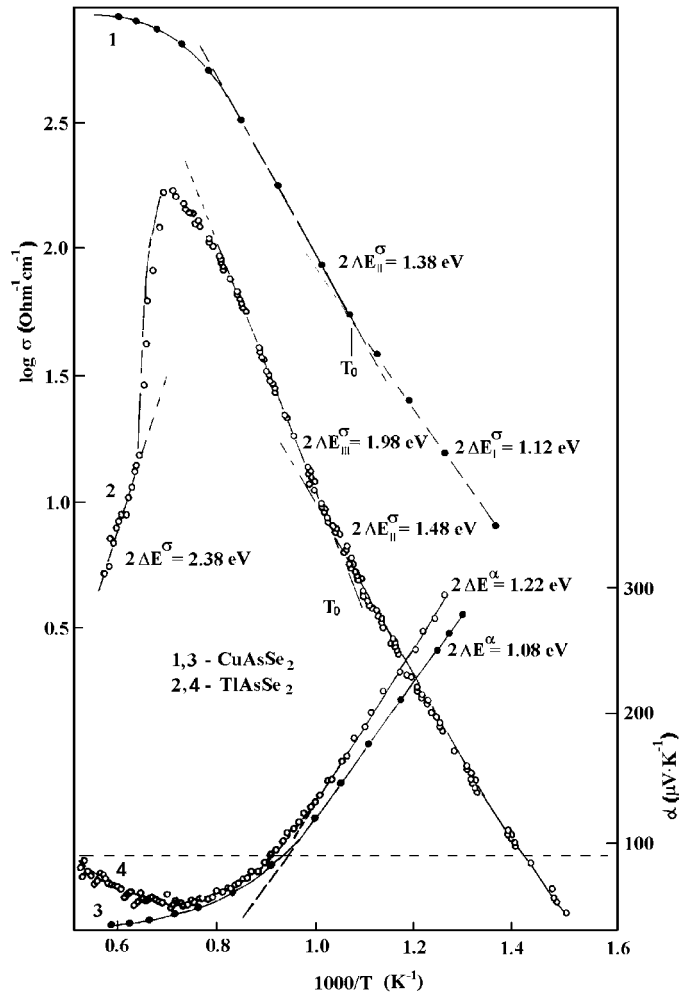


Figure 2. Electrical conductivity, $\log \sigma$, and thermo-emf, α , as a function of reciprocal temperature for the CuAsSe_2 and TIAsSe_2 liquid alloys.

for the transfer of each carrier is equal to the energy width of the pseudogap $E(T)$, the internal energy can be written as [15]

$$U = nE(T) = nE(T_0) - \frac{n^2}{n^*}kT. \tag{3}$$

The entropy involves entropies of both the valence and conductive bands

$$S = k(\ln W_1 + \ln W_2) \tag{4}$$

where W_1 is the number of all possible free carrier positions among the common quantity of states in the conductive band, N_c , and can be expressed as

$$W_1 = \frac{N_c!}{n!(N_c - n)!}. \tag{5}$$

W_2 is the number of all possible hole positions in the valence band, N_v , expressed as

$$W_2 = \frac{N_v!}{n!(N_v - n)!}. \tag{6}$$

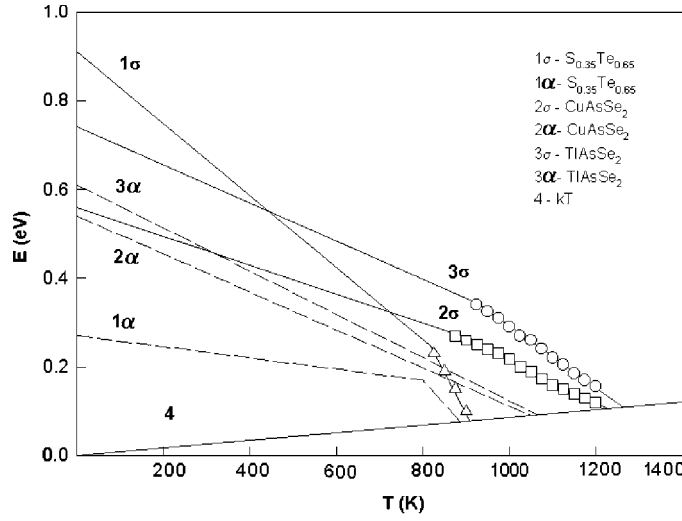


Figure 3. Second derivative of free energy, F , as a function of a free electrons concentration, n .

For high n , N_c , N_v , $N_c - n$, and $N_v - n$ values, the Stirling equation $\ln N! = N \ln N - N$ can be employed. Assuming $n \ll N_c$, we obtain

$$F = nE(T_0) - \frac{n^2}{2n^*}kT + nkT \ln \frac{n^2}{(N_v - n)N_c} - N_vkT \ln \frac{N_v}{N_v - n} \quad (7)$$

$$\frac{\partial F}{\partial n} = E(T_0) - \frac{n}{n^*}kT + kT \ln \frac{n^2}{(N_v - n)N_c}. \quad (8)$$

Analysis of an equation similar to equation (8), performed in reference [15] gave three roots corresponding to the extreme values of function F . In the vicinity of the first extreme point a semiconducting melt exhibits only semiconducting properties, i.e.

$$n = n_i. \quad (9)$$

The vicinity of the second extreme point includes a region of the semiconductor–metal transition, that is

$$n = 2n^* \ln \left(\frac{n^*}{n_i} \right). \quad (10)$$

Finally, at the third extreme point the system has only metallic properties:

$$n = N_v. \quad (11)$$

Stability of all these states is determined by a sign of a second derivative:

$$\frac{\partial^2 F}{\partial n^2} = \frac{kT}{n^*} \frac{n^2 - n(N_v + n^*) + 2N_v n^*}{n(N_v - n)}. \quad (12)$$

Equation (12) has two roots. Stability of semiconducting or metallic states is determined by a sign of a function of the free energy increasing (see figure 4). It is clearly seen that the states where $n = n_i$, $n = N_v$ corresponds to the F minimum, and $n = n_s$ corresponds to the F maximum. In this case region I corresponds only to the semiconducting states. Region II represents the stable semiconducting and metastable metallic states; region III represents the metastable semiconducting and stable metallic states; and region IV represents the stable

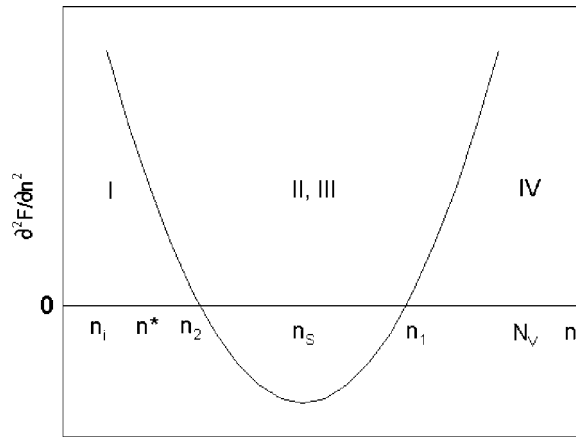


Figure 4. Temperature dependence of pseudogaps width for $S_{0.35}Te_{0.65}$, $CuAsSe_2$, and $TlAsSe_2$ liquid semiconductors.

metallic state. So, a transition region, II–III, from the stable semiconducting to the stable metallic state exists.

Let $n_i = B_1 \exp(-E(T_0)/2kT_0)$, and we formally assume that $n^* = B_2 \exp(-E(T)/2kT)$, where $E(T) = E(T_0) - kT$. So, we obtain:

$$\frac{n}{n^*} = 2 \ln \left(\frac{B_2}{B_1} \right) + \frac{E(T_0)}{kT_0} \left(1 - \frac{T_0}{T} \right) + 1. \quad (13)$$

Taking into account that $B_1 \approx B_2$ and substituting (13) into (1) we get

$$E(T) = E(T_0) - \frac{E(T_0)}{kT} \left(1 - \frac{T_0}{T} \right) kT - kT. \quad (14)$$

It should be noted that $E(T)$ has been obtained from the condition of a free energy extremum in the transition region and represents, in fact, a gap, calculated from the expression for free energy. Actually, comparing equation (14) with high-temperature experimental data, a gap, calculated from the enthalpy expression should be considered. As the latter differs from the ‘free energy gap’ by kT [11, 15], we finally obtain

$$E(T) = E(T_0) - \frac{E(T_0)}{kT} \left(1 - \frac{T_0}{T} \right) kT = E(T_0) \left(2 - \frac{T}{T_0} \right). \quad (15)$$

The $E(T)$ dependence computed from formula (15) is in good agreement with experimental values (see figure 3). However, only the $\sigma(T)$ data can satisfactorily explain the behaviour of the melt, although similar inflexions were noticed earlier during the edge absorption investigations [3]. The experimental $\alpha = f(1000/T)$ curves are deprived of such inflexions. Only for $S_{0.35}Te_{0.65}$, the observed inflexion on the $\alpha = f(1000/T)$ curve has been observed and, like in reference [16], lies at a much lower temperature than that on the $\log \sigma(1000/T)$ curves. Returning to equations (2) and (8), we recall from the thermodynamics of irreversible processes [17] that an enthalpy in the transition region can be presented as ‘a transfer entropy’ [18]: $S = 1/T((\langle \tau_m E \rangle / \tau_m) - E_F)$ where E is the energy of the carrier, E_F is the Fermi energy, τ_m is the impulse relaxation time. Taking into account the connection between the transfer entropy, S , and a differential thermo-emf, α , [19, 20] we obtain: $S = \alpha n$. Thus, equation (2) can be rewritten as

$$F = U + n\alpha T \quad (16)$$

so that

$$\frac{\partial F}{\partial n} = E(T_0) - \frac{n}{n^*}kT + \alpha_0 T. \quad (17)$$

Comparing (8) and (17), we obtain

$$\alpha = k \ln \frac{n^2}{(N_v - n)N_c}. \quad (18)$$

For high n , N_v , and N_c values, we have a constant α contribution into equation (18), weakly dependent on temperature. In the energy sense, it will be a constant correction for the ‘enthalpy gap’. It means that the energy gap computed from the thermo-emf will be lower than that computed from the electrical conductivity. A specific temperature of inflexion on the $\alpha = f(1000/T)$ dependence is practically missing in the liquid state or is much more lower than on the $\log \sigma = f(1000/T)$ curves.

4. Conclusion

The dynamics of the pseudogap transformation on the semiconductor–metal transition in the high temperature region can be analysed using experimental results of electrical conductivity and thermo-emf measurements. Considering the electron spectrum characteristics of semi-conducting melts, namely, an existence of the localized states region in the energy spectrum, it is suggested that the bound states screening effect in the pseudogap region by the free carriers is the basis for the semiconductor–metal transition. As a consequence of this screening, delocalization of these bound states and pseudogap tailing occur. The metallization temperature determined by the thermo-emf measurements is lower than that determined by electrical conductivity.

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