Semiconductor-Metal Transition in Semiconductor Melts with 3d Metal Admixtures

V Sklyarchuk, Yu Plevachuk, S Mudry, I Shtablavyi, B Sokolovskii

Ivan Franko National University, Department of Metal Physics
Lviv, Ukraine, sklyarchuk@ukr.net

Abstract. Electrical conductivity and thermoelectric power measurements were performed for liquid semiconductor alloys Se$_{0.5}$Te$_{0.5}$ doped with 3d metals in a wide temperature range (up to 1600 K) under ambient pressures of argon gas (up to 30 MPa). Structure changes were studied by means of X-ray diffraction method. The 3d metal admixtures affect electrophysical properties and a temperature of the semiconductor-metal transition (SMT).

Introduction

It was shown that transition to metal conductivity in liquid semiconductors in a high temperature region above a melting point occurs [1-4]. The Mott concept on the energy electron spectrum in the thermodynamic homogeneous semiconductors was used for interpretation of this SMT [5]. According to this theory, a pseudogap in density of states narrows linearly with temperature increasing. When a pseudogap width reaches ~kT, the SMT takes place. Moreover, the onset of this transition determined both from the electrical conductivity, \( \sigma(T) \), and thermoelectric power, \( S(T) \), measurements should be observed at the same temperatures. Nevertheless, the obtained experimental data on \( \sigma(T) \) and \( S(T) \) did not prove this expectation [4]. It was found that: 1) the metallization temperature determined from \( S(T) \) \( T_{s-m} \) was almost lower then \( T_{s-m} \) determined from \( \sigma(T) \) data; 2) the activation energy \( E_s(0) \) do not coincide with \( E_s(0) \); 3) a condition \( E_s(0) > E_s(0) \) in the vicinity of the SMT takes place, and a drastic activation energy increasing from \( E_s(0) \) to \( E_s(0) \) at constant \( E_s(0) \) is observed at certain temperatures. The first three points were explained in the frames of the model developed in [6,7]. This model deals with ideas of the percolation theory and suggests an existence of two percolation thresholds, high and low, in the three-dimensional space [7]. Two respective energy levels \( E_s^\nu \) and \( E_s^\sigma \), have been entered [6]. Similar to the mobility edge, \( E_s^\sigma \), the concept of a formal "density of states edge", \( E_s^\nu \), in the energy spectrum of thermodynamically homogeneous semiconductors has been introduced. This edge is shifted towards the Fermi level, \( E_F \), in relation to \( E_s^\nu \). From this it follows that during the SMT the "mobility pseudogap" determining an activation character of conductivity is always larger than the "density of states pseudogap", which is responsible for the \( S(T) \) power.

At the same time, the model proposed was not able to explain the drastic increasing of activation energy \( E_s(0) \) for some semiconductors. Another model for thermodynamically homogeneous semiconductors based on the delocalization mechanism of the electron bonded states has been proposed [8]. The electron state delocalization was considered as the pseudogap vanishing, leading in turn to the metal conductivity. From the thermodynamic viewpoint a correction for the "enthalpy pseudogap" is introduced. On this basis it looks reasonable to enlarge a number of liquid semiconductors in order to study their metallization peculiarities. Thermodynamically homogeneous melts Se$_{0.5}$Te$_{0.5}$ doped by transition metals (TM) admixtures with localized d-states were chosen for this purpose.
2. Experimental details

The diffraction studies were carried out using a high-temperature diffractometer with a special attachment that allows to investigate the solid and liquid samples at different temperatures up to 1800 K. Cu-Kα radiation monochromatized by means of LiF single crystal as a monochromator and Breg-Brentano focusing geometry were used. The scattered intensities as a function of the scattering angle were recorded within the range $1\text{Å}^{-1} < k < 7\text{Å}^{-1}$, with different angular step, which was equal to 0.05° within the region of principal peak and 0.5° at rest values of wave vectors. The measuring of scattered intensity was done with accuracy, better then 2%, the scan time was equal to 100 s. The diffracted intensity was recorded using a NaI(Tl) scintillator detector in conjunction with an amplification system. Intensity curves were corrected on polarization, absorption and incoherent scattering [9]. After this procedure they were normalized to electron units by Krogh-Moe method [10]. The intensity curves were used to calculate the SF and than the pair correlation function PCF.

The $\sigma(T)$ and $S(T)$ were measured by a contact method in accordance with the 4-point scheme [11]. A measuring cell was manufactured of BN ceramic, and its construction allows eliminating analytically jamming and noise signals. The experiments were performed under Ar gas pressures up to 30 MPa. The sample compositions were accurate within 0.02 wt. %. The resultant error of the $\sigma(T)$ was $\sim 2 \%$ and that of the $S(T)$ was $\sim 5 \%$.

3. Results

An influence of Ti and V admixtures on the structure of liquid Se$_{0.5}$Te$_{0.5}$ has been studied. The alloy exhibits a random atomic distribution with a similar to liquid tellurium topology. As seen from Figure 1, where the structure factors for Se$_{0.5}$Te$_{0.5}$ and Se$_{0.5}$Te$_{0.5}$+ 2 at. % Ti are compared, significant changes in the short range order structure occur. Particularly, a prepeak is significantly lower. A principle maximum increases, and slightly shifts to the large $q$ values. It is suggested that the Ti-admixture promotes changes in the Se$_{0.5}$Te$_{0.5}$ atomic topology and a transformation from the covalent to metallic chemical bonds as well as an increase of the structural units size. Note that other Se-Te compositions with Ti-admixture revealed similar peculiarities. More significant structure changes are observed upon V-atoms addition (Figure 2). Prepeak in a structure factor reduces its height and becomes more symmetric. The main maximum significantly decreases its width and looks more sharp. Consequently, in result of V-atoms addition to Se$_{0.5}$Te$_{0.5}$ molten alloy the correlation radius increases, indicating an increase of the topological ordering degree.

![Figure 1. Structure factors of liquid Se$_{0.5}$Te$_{0.5}$ and with Ti admixture](image1.png)

![Figure 2. Structure factors of liquid Se$_{0.5}$Te$_{0.5}$ and with V admixture](image2.png)

Typical $\sigma(T)$ and $S(T)$ dependencies are presented in Figures 3,4 for Se$_{0.5}$Te$_{0.5}$ doped with cobalt and in Figures 5,6 for Se$_{0.5}$Te$_{0.5}$ doped with samarium.
Similar dependencies were revealed for the liquid Se$_{0.5}$Te$_{0.5}$ alloys with Ti and V admixtures. The common peculiarities for all the alloys take place. The exponential $\sigma(T)$ dependence is typical for the intrinsic conductivity of semiconductors. A saturation of the electrical conductivity exponential curve $\sigma(T)$ is observed with heating. Admixtures of the transition metals increase the absolute conductivity values but do not change the trend of the curve. As shown for pure Se-Te alloys [1,2], upon reaching the temperature, peculiar for each alloy, an inflexion on the log $\sigma = f(1000/T)$ curves reflecting an increase of the activation energy from $E_s^0 (1)$ to $E_s^0 (2)$ at constant $E_s^0$, occurs.

Table 1. Density of states at the Fermi level, eV$^{-1}$m$^{-3}$

| Alloy          | N(E$_f$), 10$^{-34}$ | $T_{s-m}^\sigma$, K | $T_{s-m}^S$, K |
|----------------|----------------------|---------------------|----------------|
| Se$_{0.5}$Te$_{0.5}$         | 0.64                 | 1037                | 893            |
| Se$_{0.5}$Te$_{0.5}$ + Ti     | 0.7                  | 952                 | 873            |
| Se$_{0.5}$Te$_{0.5}$ + Co     | 0.98                 | 1020                | 892            |
| Se$_{0.5}$Te$_{0.5}$ + V      | 0.65                 | 961                 | 887            |
| Se$_{0.5}$Te$_{0.5}$ + Sm     | 0.79                 | 1000                | 890            |

Some deviation from linearity of the log $\sigma = f(1000/T)$ dependence towards decreasing (SMT) was observed for Se$_{0.5}$Te$_{0.5}$ at $T_{s-m}^\sigma=1037$ K, at 952 K for Se$_{0.5}$Te$_{0.5}$ + Ti, 1020 K for Se$_{0.5}$Te$_{0.5}$ + Co, 961 K for Se$_{0.5}$Te$_{0.5}$ + V, and 1000 K for Se$_{0.5}$Te$_{0.5}$ + Sm (see Table 1). Further $\sigma(T)$ increasing up to the saturation above the mentioned temperatures is caused by a temperature dependent increasing of the density states at the Fermi level. The later has been calculated from the Mott equation [5]:

![Figure 3. Electrical conductivity vs. reciprocal temperature for liquid Se$_{0.5}$Te$_{0.5}$ and with Co](image)

![Figure 4. Thermoelectric power vs. reciprocal temperature for liquid Se$_{0.5}$Te$_{0.5}$ and with Co](image)

![Figure 5. Electrical conductivity vs. reciprocal temperature for liquid Se$_{0.5}$Te$_{0.5}$ and with V](image)

![Figure 6. Thermoelectric power vs. reciprocal temperature for liquid Se$_{0.5}$Te$_{0.5}$ and with V](image)
\[ \sigma_0 = \frac{2\pi e^2 \hbar^3}{m^2} N(E_f) \] 

The values of the density of states at 1100 K are listed in Table 1. Based on [3] the temperatures of the SMT \( T_{S-m} \) were also evaluated from the S(T) data (Table 1).

4. Discussion

The peculiarities of the SMT behavior were discussed in details elsewhere [3]. A drastic increase of the conduction activation energy or, in other words, an increase of the pseudogap tailing has been discussed also [8]. In our case however, the energy spectrum of the \( \text{Se}_{0.5}\text{Te}_{0.5} \) matrix solvent is perturbed by Ti, V, Co, and Sm admixtures with localized 3d states. \( \sigma(T) \) and \( S(T) \) are described by [5]:

\[ \sigma(T) = \sigma_0 \exp \left( -\frac{E_c - E_v}{2k_B T} \right) \] 

\[ S(T) = -\frac{k_B}{e} \left( \frac{E_c - E_v}{2k_B T} + A \right) \]

where \( \sigma_0 \) is a minimum metallic conductivity, \( E_c \) and \( E_v \) are the energies at the mobility edges of conduction and valence bands correspondingly, and a scattering parameter \( A \) is equal to 1. The calculations according to equations (1) and (2) revealed a drastic increase of the conduction activation energy upon reaching the temperature peculiar for each alloy: from 0.87 to 1.43 eV for \( \text{Se}_{0.5}\text{Te}_{0.5} \), from 1.03 to 1.75 eV for \( \text{Se}_{0.5}\text{Te}_{0.5} + \text{Ti} \), and from 0.86 to 1.9 eV \( \text{Se}_{0.5}\text{Te}_{0.5} + \text{Co} \). The activation energies determined from S(T) are constant and their values are 0.7 eV, 0.78 eV and 1 eV respectively. Doping by admixtures leads to an increase both of the conduction and thermopower activation energies.

Taking into account the Mott theory about a linear decrease of the pseudogap with heating according to \( E(T) = E(0) - \gamma T \) [5], the temperature coefficient of the pseudogap tailing, \( \gamma \), can be determined according to the procedure proposed in [3]. The following increasing of \( \gamma \) has been observed: from \( 1.12\times10^{-3} \) to \( 1.38\times10^{-3} \) eV/K for \( \text{Se}_{0.5}\text{Te}_{0.5} \), from \( 1.26\times10^{-3} \) to \( 1.84\times10^{-3} \) eV/K for \( \text{Se}_{0.5}\text{Te}_{0.5} + \text{Ti} \), and from \( 1.10\times10^{-3} \) to \( 1.87\times10^{-3} \) eV/K for \( \text{Se}_{0.5}\text{Te}_{0.5} + \text{Co} \). The temperature coefficient of the pseudogap tailing determined from the S data has lower values and equal to \( 0.78\times10^{-3} \), \( 0.89\times10^{-3} \) and \( 1.12\times10^{-3} \) eV/K respectively. It could be stated therefore that a process of the SMT generally corresponds to the concept proposed in [12], taking into account the manyelectron mechanism of the electron states delocalization. Doping of the 3d admixture leads to an increase of density of states at the Fermi level and acceleration of the delocalization process. The later leads in turn to the shift of the SMT temperature. A number of electrons in d shell (2 for Ti and 7 for Co) is also important, but requires more detailed studies.

References

[1] Cutler M 1977 Liquid Semiconductors (New York: Academic Press)
[2] Perron Y C 1967 Adv. Phys. 16(64) 657
[3] Sklyarshchuk V, Plevachuk Yu 2000 J. Alloys Comp. 312/1-2 25
[4] Sklyarshchuk V, Plevachuk Yu 2002 High Temperatures - High Pressures 34 29
[5] Mott F, Davis E 1979 Electron processes in non-crystalline materials (Oxford: Clarendon Press)
[6] Sokolovskii B 1982 Ph. D. Thesis, (Lviv: Ivan Franko University)
[7] Shklovskii B I, Efros A L 1975 Uspekhi Fizicheskikh Nauk 117(3) 401
[8] Sklyarshchuk V, Plevachuk Yu 2001 J. Phys.: Condens. Matter 13(41) 9179
[9] Cromer D T, Waber T J 1965 Acta Cryst. 18(5) 104
[10] Krogh-Moe J, 1956 Acta Cryst. 9 951
[11] Plevachuk Yu, Sklyarshchuk V 2001 Meas. Sci. Technol. 12(1) 23
[12] Sandomirskii V, Sukhanov A and Zhdan A 1970 J. Exper. Theor. Phys. 58 (5) 1683