ЖУРНАЛ ФІЗИЧНИХ ДОСЛІДЖЕНЬ
т. 11, № 2 (2007) с. 190–194

JOURNAL OF PHYSICAL STUDIES
v. 11, No. 2 (2007) p. 190–194

METAL–NONMETAL TRANSITION IN SEMICONDUCTOR MELTS WITH 3d METAL ADMIXTURES

V. Sklyarchuk, Yu. Plevachuk, S. Mudry, I. Shtablavyi
Department for Metal Physics, Ivan Franko National University of Lviv
8 Kyryla i Mephodija St., Lviv, UA–79005, Ukraine
tel: +38 032 2394270, fax: +38 032 2970143,
e-mail: plevachuk@mail.lviv.ua

(Received January 29, 2007; received in final form May 7, 2007)

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 35 MPa). The structural changes were studied by means of the X-ray diffraction method. The structure factors are analyzed. The 3d metal admixtures increase the electrical conductivity, decrease the thermoelectric power and affect the temperature of the semiconductor–metal transition. The results are interpreted in the frame of the model describing a mechanism of the electron spectrum evolution in liquid semiconductors, which takes into account the charge resonance scattering on the virtual bound states, occurring due to the 3d admixture metal states in the semiconductor matrix.

Key words: semiconductor–metal transition, electrical conductivity, thermoelectric power, resonance scattering.

PACS number(s): 64.70.−p, 71.22.+i

I. INTRODUCTION

It was shown recently 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 the interpretation of this semiconductor–metal transition [5]. According to this theory, a pseudogap narrows linearly with the temperature increasing. When a pseudogap width reaches kT, the semiconductor-to-metal transition 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 complex $\sigma(T)$ and $S(T)$ experimental data obtained did not prove this expectation [4]. Contrary to theoretical predictions, parameters of an electron energy spectrum determined separately from $\sigma(T)$ and $S(T)$ measurements do not coincide. It was found that: 1) the metallization temperature $T^S_{\mathrm{s-m}} < T^\sigma_{\mathrm{s-m}}$; 2) the activation energy $E^\sigma(0)$ does not coincide with $E^S(0)$; 3) a condition $E^\sigma(0) > E^S(0)$ in the vicinity of the semiconductor–metal transition takes place; the points of inflexion on $\log\sigma = f(T^{-1})$ curves reflect the activation energy increasing from $E^\sigma(0)_1$ to $E^\sigma(0)_2$ at constant $E^S(0)$.

The first three points were explained in the frame of the model developed in [6, 7]. This model deals with the ideas of the percolation theory and suggests the existence of two percolation thresholds, high and low, in the three-dimensional space [7]. Two respective energy levels E^S_v and E^σ_v have been entered [6]. Similar to the mobility edge, E^σ_v, the concept of a formal “density of states edge”, E^S_v, in the energy spectrum of thermodynamically homogeneous semiconductors has been introduced. This edge is shifted towards the Fermi level, E_{F}, relative to E^σ_v. From this it follows that during the semiconductor–metal transition the “mobility pseudogap” determining an activation character of conductivity is always larger than the “density of states pseudogap”, which is responsible for the thermoelectric power.

At the same time, the model proposed was not able to explain the drastic activation energy $E^\sigma(0)$ increasing for some semiconductors. Another model for thermodynamically homogeneous semiconductors based on the delocalization mechanism of the electron bonded states was proposed recently [8]. The electron state delocalization was considered as the pseudogap vanishing leading in turn to metal conductivity. From the thermodynamic viewpoint a correction for the “enthalpy pseudogap” is introduced. On this basis it looks reasonable to enlarge the number of liquid semiconductors in order to study their metallization peculiarities. Thermodynamically homogeneous melts $Se_{0.5}Te_{0.5}$ doped by transition metals admixtures with localized d-states were chosen for this purpose. The common theoretical models for such systems are generally developed [9,10], and a procedure based on the virtual bonded states proposed in [11] can be used for describing the electrophysical properties of the d states in similar admixture states. Such a procedure has been developed also for describing magnetic properties of the admixture atoms, but it is also important for understanding the electron scattering processes in similar systems.

II. EXPERIMENTAL DETAILS

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. The chamber of the X-ray diffractometer was filled with pure helium (above 0.1 MPa) in order to avoid the sample oxidation and vaporization during the experiment. Cu–K_α 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 a different angular step, which was equal to 0.05° within the region of the principal peak and 0.5° at the remaining values of wave vectors. The measuring of scattered intensity was done with accuracy higher than 2%. In order to obtain the more accurate scattered intensities, 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. The sample was placed in a rounded cup of 20 mm diameter. Intensity curves were corrected on polarization, absorption and incoherent scattering [12]. After this procedure they were normalized to electron units by the Krogh–Moe method [13]. The obtained intensity curves were used to calculate the SF and then the pair correlation function PCF.

The measurements of the electrical conductivity and thermoelectric power have been carried out by a contact method in accordance with the 4-point scheme as described elsewhere [14]. The samples were contained in the measuring cells manufactured of BN ceramics in the form of vertical cylinders with an operating cavity height of 60 mm. Six graphite electrodes, two for the current and four for the potential measurements, were inserted into the wall of the container along its vertical axis. The potential electrodes were provided with WRe–5/20 thermocouples. This permitted simultaneous determination of the temperature as well as measurement of the electrical conductivity and thermoelectric power in one run. Moreover, the cell construction allowed eliminating analytically jamming and noise signals arising due to contact wires as well as a systematic device deviation. Temperature gradients of 15–20 K along the cell were additionally controlled to within 0.1 K by preliminary calibrated five-point differential thermocouple. The experiments were performed under Ar gas pressures of up to 30 MPa. The sample compositions were accurate within 0.02 wt.%. The resultant error of the electrical conductivity is about 2% and 5% of the thermoelectric power.

III. RESULTS

The 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 Fig. 1, where the structure factors for $Se_{0.5}Te_{0.5}$ and $Se_{0.5}Te_{0.5} + 2\,\text{at.\%Ti}$ are compared, significant changes in the short range order structure occur. Particularly, a pre-peak is significantly lower. The principal 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 the Ti-admixture revealed similar peculiarities.

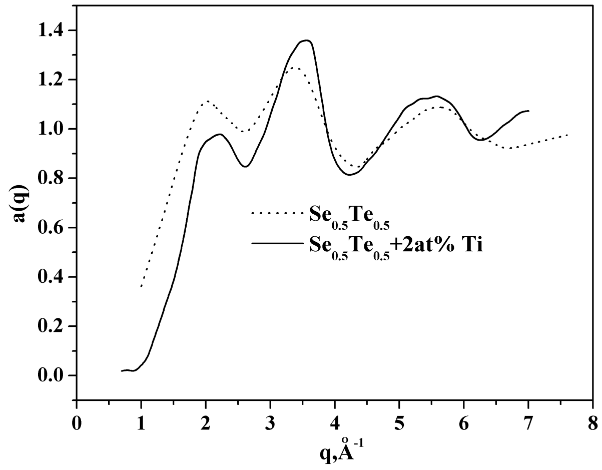

Fig. 1. Structure factors of liquid $Se_{0.5}Te_{0.5}$ and with Ti admixture.

More significant structural changes are observed upon V-atoms addition (Fig. 2). Pre-peak in a structure factor reduces its height and becomes more symmetric. The main maximum significantly decreases its width and looks sharper. Consequently, as a result of the V-atoms addition to the $Se_{0.5}Te_{0.5}$ molten alloy the correlation radius increases, indicating an increase of the topological ordering degree.

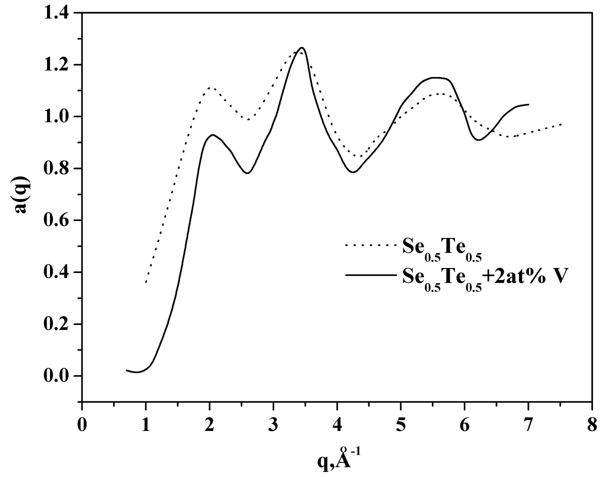

Fig. 2. Structure factors of liquid $Se_{0.5}Te_{0.5}$ and that with V admixture.

Typical temperature dependencies of electrical conductivity and thermoelectric power are presented in Fig. 3, 4 for $Se_{0.5}Te_{0.5}$ doped with titanium and in Fig. 5, 6 for $Se_{0.5}Te_{0.5}$ doped with vanadium. Similar dependencies were revealed for the liquid $Se_{0.5}Te_{0.5}$ alloys with cobalt and samarium admixtures. Same common peculiarities for all the alloys are aparently valid. The exponential temperature dependence of electrical conductivity is typical of the intrinsic conductivity of semiconductors. A saturation of the electrical conductivity exponential curve $\log\sigma(T)$ 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 SeTe 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 $E^{\sigma}(0)_1$ to $E^{\sigma}(0)_2$ at constant $E^{S}(0)$ occurs.

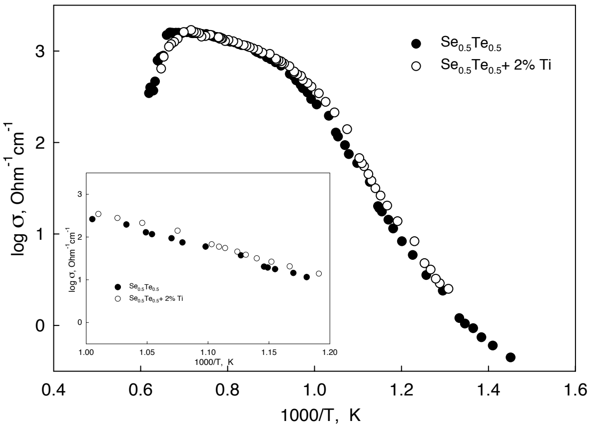

Fig. 3. Electrical conductivity as a function of reciprocal temperature for liquid $Se_{0.5}Te_{0.5}$ and with Ti admixture.

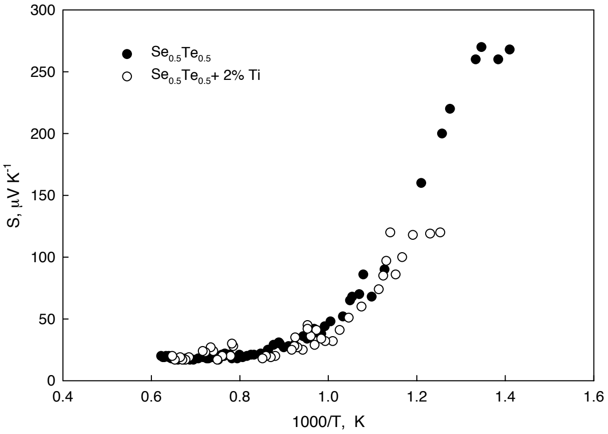

Fig. 4. Thermoelectric power as a function of reciprocal temperature for liquid $Se_{0.5}Te_{0.5}$ and with Ti admixture.

Some deviation from a linearity of the $\log\sigma = f(1000/T)$ dependence towards decreasing (semiconductor–metal transition) has been observed for $Se_{0.5}Te_{0.5}$ at $T^{\sigma}_{\mathrm{s-m}} = 1037$ 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 obviously caused by a temperature dependent increasing of the density of states at the Fermi level. The later has been calculated from the Mott equation [5]:

$$\sigma_0 = \frac{2\pi e^2\hbar^3}{m^2}L\{N(E_f)\}^2 \tag{1}$$

The values of the density of states at 1100 K are listed in Table 1.

Based on [3] the temperatures of the semiconductor–metal transition $T^{S}_{\mathrm{s-m}}$ were also evaluated from the $S(T)$ data (Table 1).

Alloy	$N(E_f)$, 10^{-28}	$T^{\sigma}_{\mathrm{s-m}}$, K	$T^{S}_{\mathrm{s-m}}$, 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

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

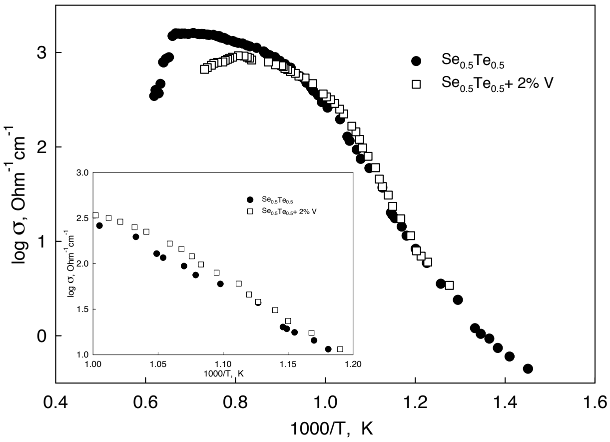

Fig. 5. Electrical conductivity as a function of reciprocal temperature for liquid $Se_{0.5}Te_{0.5}$ and with V admixture.

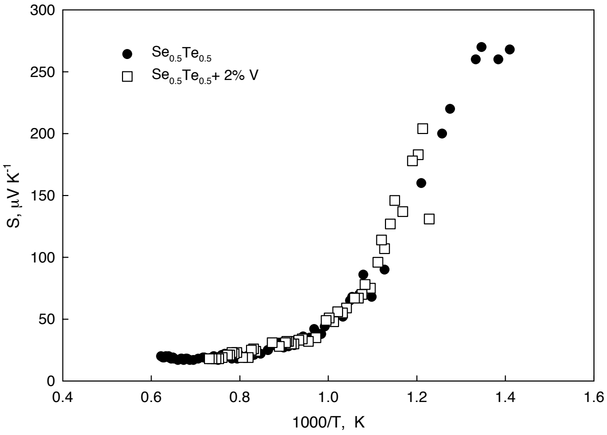

Fig. 6. Thermoelectric power as a function of reciprocal temperature for liquid $Se_{0.5}Te_{0.5}$ and with V admixture.

IV. DISCUSSION

The peculiarities of the semiconductor–metal transition studied were discussed in detail elsewhere [3]. A drastic increase of the conduction activation energy or, in other words, an increase of the pseudogap tailing has been also discussed [8]. In our case, however, the energy spectrum of the $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ matrix solvent is perturbed by Ti, V, Co or Sm admixtures with localized $3d$ states.

The temperature dependence of electrical conductivity, $\sigma(T)$, and thermopower, $S(T)$, are described by well-known equations [5]:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_c - E_v}{2kT}\right) \tag{2}$$

$$S(T) = -\frac{k}{e}\left(\frac{E_c - E_v}{2kT} + A\right) \tag{3}$$

where σ_0 is a minimum metallic conductivity, E_c and E_v are energies at the mobility edges of conduction and valence bands correspondingly, and the scattering parameter A equals 1.

The calculations according to equations (1) and (2) revealed a drastic increase of the conduction activation energy until the temperature peculiar for each alloy has been reached: from 0.87 to 1.43 eV for $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$, from 1.03 to 1.75 eV for $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ + Ti, and from 0.86 to 1.9 eV $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ + Co. The activation energies determined from $S(T)$ are constant and their values are 0.7 eV, 0.78 eV and 1 eV correspondingly. 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, γ, can be determined according to the procedure proposed in [3]. The following increasing of γ has been observed: from 1.12×10^{-3} to 1.38×10^{-3} eV/K for $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$, from $1.26v10^{-3}$ to 1.84×10^{-3} eV/K for $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ + Ti, and from 1.10×10^{-3} to 1.87×10^{-3} $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ + Co. The temperature coefficient of the pseudogap tailing determined from the S data has lower values and equals to 0.78×10^{-3}, 0.89×10^{-3} and 1.12×10^{-3} eV/K, respectively. It could be stated therefore that the process of the semiconductor–metal transition generally corresponds to the concept proposed in [15] taking into account the many electron mechanism of the electron states delocalization. The 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 semiconductor–metal transition temperature. A number of the electrons at the d shell (2 for Ti or 7 for Co) is also important, but it requires more detailed studies.

V. CONCLUSION

Admixtures of the $3d$ metals to the liquid $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ alloys change the shape of the principle maximum of the structure factor. The pseudogap at the Fermi level remains and the conductivity and thermoelectric power changes due to the increase of the common density of states at the Fermi level if the $sp-d$ mixes. A shift of the semiconductor–metal transition temperature, the changes of the activation energy and of the pseudogap tailing velocity are explained by the changes of the density of states at the Fermi level.

[1] M. Cutler, *Liquid Semiconductors* (Academic Press, New York, 1977).

[2] Y. C. Perron, Adv. Phys. **16(64)**, 657 (1967).

[3] V. Sklyarchuk, Yu. Plevachuk, J. Alloys Comp. **312(1)**, 25 (2000).

[4] V. Sklyarchuk, Yu. Plevachuk, High Temp. – High Pressure **34**, 29 (2002).

[5] N. Mott, E. Davis, *Electron processes in non-crystalline materials* (Clarendon Press, Oxford, 1979).

[6] B. Sokolovskii, Ph.D. Thesis, Ivan Franko University, Lviv (1982).

[7] B. I. Shklovskii, A. L. Efros, Usp. Fiz. Nauk **117**, 401 (1975).

[8] V. Sklyarchuk, Yu. Plevachuk, J. Phys.: Cond. Matt. **13**, 9179 (2001).

[9] I. Vakarchuk, Yu. Rudavsky, G. Ponedilok, *A Microscopic Theory of the Liquid state of a Magnetic Atom System* (Institute of theoretical Physics AN UkrSSR, December 1980).

[10] I. Vakarchuk, Yu. Rudavsky, G. Ponedilok, *Free Energy of Amorphic Ferromagnet with the Heisenberg Exchange Interaction* (Institute of theoretical Physics AN UkSSR, May 1981).

[11] J. Friedel, Nuovo Cimento, Suppl. **7**, 287 (1958).

[12] D. T. Cromer, J. T. Waber, Acta Crystallogr. **18(5)**, 104 (1965).

[13] J. Krogh-Moe, Acta Crystallogr. **9**, 951 (1956).

[14] Yu. Plevachuk, V. Sklyarchuk, Meas. Sci. Technol. **12**, 23 (2001).

[15] V. Sandomirskii, A. Sukhanov, A. Zhdan, J. Exper. Theor. Phys. **58**, 1683 (1970).

ПЕРЕХІД МЕТАЛ–НЕМЕТАЛ У НАПІВПРОВІДНИКОВИХ РОЗПЛАВАХ ІЗ ДОМІШКАМИ 3*d* МЕТАЛІВ

В. Склярчук, Ю. Плевачук, С. Мудрий, І. Штаблавий
Львівський національний університет імені Івана Франка,
кафедра фізики металів,
вул. Кирила і Мефодія, 8, Львів, 79005, Україна

У широкому температурному інтервалі (до 1600 К) в умовах високого тиску аргону (до 35 МПа) виміряно електропровідність та термо-е.р.с. напівпровідникових розплавів $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ з домішками 3*d* металів. Методом дифракції рентґенівських променів проведено структурні дослідження і проаналізовано структурні чинники. Домішки 3*d* металів підвищують електропровідність, знижують термо-е.р.с. і впливають на температуру переходу метал–неметал. Результати інтерпретовано в межах моделі, що описує механізм еволюції електронного спектра в рідких напівпровідниках, із урахуванням резонансного розсіяння заряду на віртуальних станах унаслідок появи домішкових станів 3*d* металів у напівпровідниковій матриці.