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Investigation of the behavior of electrical resistance and thermal emf of polycrystals of europium monosulfide during temperature cycling in the range of 320−800 K

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The temperature dependences of the electrical resistance R and thermal S of polycrystals of europium monosulfide (EuS) in the range 320−800 K have been studied. It is shown that the processes of cyclic temperature action on polycrystalline EuS samples lead to the appearance of hysteresis on the dependences $\ln[R(10^3/T)]$, $S(T)$, as well as a subsequent change of the main free charge carriers in a narrow temperature range of 365−490 K. The analysis of the discovered patterns in the behavior of $\ln R$ and S suggests the presence of a significant influence on the indicated kinetic coefficients of the processes of exciton spectrum formation and destruction in temperature cycles.

Keywords: europium monosulfide, thermal EMF, electrical resistivity, excitons.

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1. Introduction

Europium monosulfide (EuS) is one of the members of the group of so-called „magnetoexcitonic semiconductors“ [1]. This compound has been attracting the attention of researchers for many years due to its unique physical properties, including magnetic phase transition, magneto-optical and magneto-electric effects, intermediate valence cation states, exciton states, etc. [1–4].

Recently, there has been renewed interest in the study of electron transfer processes in europium monosulfide in the temperature region corresponding to its paramagnetic state [5]. Such attention to EuS is attributable to the fact that it has been used to create SmS|EuS, PbS|EuS, InAs|EuS, SLG (single-layer graphene)|EuS, etc. heterostructures, which are promising materials for applications in spintronics, electronics devices, and exciton spectroscopy [6–9].

Based on the analysis of the available set of experimental data on the study of the physical properties of EuS in the temperature range of up to 1300 K, it is assumed that the subject compound is a semiconductor with an electronic type of conductivity [3,10]. Nevertheless, the results of studies of the temperature dependence of the thermo-emf of polycrystalline EuS obtained in Ref. [10] cast doubt on the validity of the above statement. Indeed, the character of the behavior of the temperature dependence of the thermal emfs $S(T)$ in the interval of 300−1300 K finds no explanation within the framework of the accepted zone model of EuS and is more consistent with the hole-type (p-type) conductivity. Hence, the claim of electrons as the main charge carriers in EuS over a wide temperature region needs further verification.

The analysis of optical and photoemission spectra of EuS in Refs. [2,3] allows concluding that exciton and impurity energy levels of different genesis are present in the forbidden zone of the above compound. However, neither the temperature range of existence of exciton states nor specific information on the structure of defects in the spectrum of impurity states, i. e. all that is necessary to understand the behavior of the temperature dependences of the kinetic coefficients of EuS, remain uncertain.

The behavior of the temperature dependences of the electrical resistivity (R) and thermo-emf (S) of EuS polycrystals in the temperature range of 320−800 K were studied in this paper for clarifying the electronic model of the EuS structure.

2. Experimental procedure

EuS polycrystals of nominally stoichiometric composition were prepared by method described in Ref. [4] followed by pressing of the synthesized powders and annealing at $T = 1600-1900\,^{\circ}\mathrm{C}$. Two samples were cut for the experiments and selected from different preformed blanks.

The test samples had the following parameters under normal conditions: lattice constant of NaCl type (space group $Fm\bar{3}m$) $a_{\mathrm{EuS}} = 5.96-5.97$ Å, coherent X-ray scattering region $L = 450-600$ Å, specific electrical resistance

$$\rho \approx (1.5-3) \cdot 10^5\ \Omega \cdot \mathrm{cm},$$

$$S \approx -(2.5-3.7)\ \mathrm{mV/K}.$$

The temperature dependences R and thermo-emf S of EuS polycrystals were studied in the temperature region

of 320–800 K using a setup described in Ref. [11]. The procedure for measuring the relationships $R(T)$ and $S(T)$ of test samples is described in Ref. [12].

3. Measurement results

Figures 1 and 2 show, respectively, the dependences of the logarithm of the electrical resistivity $\ln[R(10^3/T)]$ on the inverse temperature (with weighted multiplier 10^3) and thermo-emf S of two EuS polycrystals in the temperature region of 320–800 K for „heating–cooling“ cycles (thermocycles). The experimental data obtained in the temperature range of 320–400 K required their computer processing to identify the useful signal against the background of noise

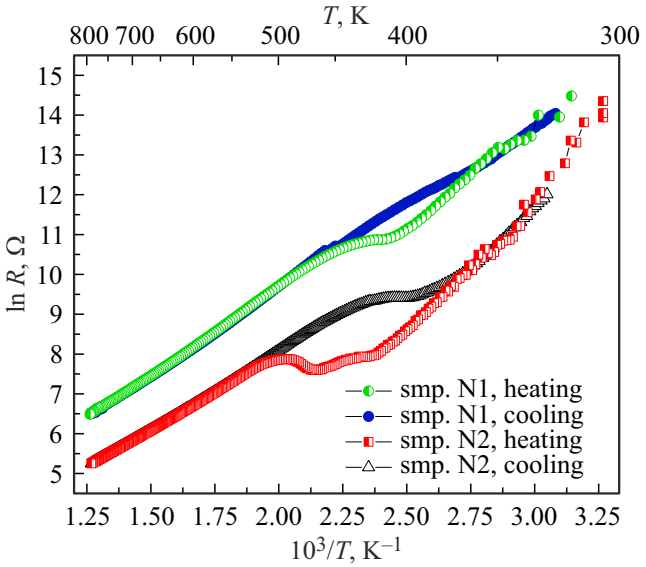

Figure 1. Temperature dependences $\ln R(10^3/T)$ of samples № 1 and № 2 of EuS polycrystals.

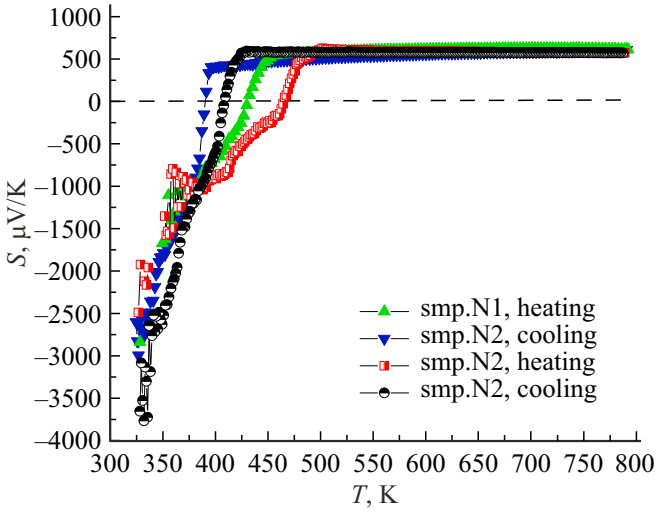

Figure 2. Temperature dependences $S(T)$ of samples № 1 and № 2 of EuS polycrystals.

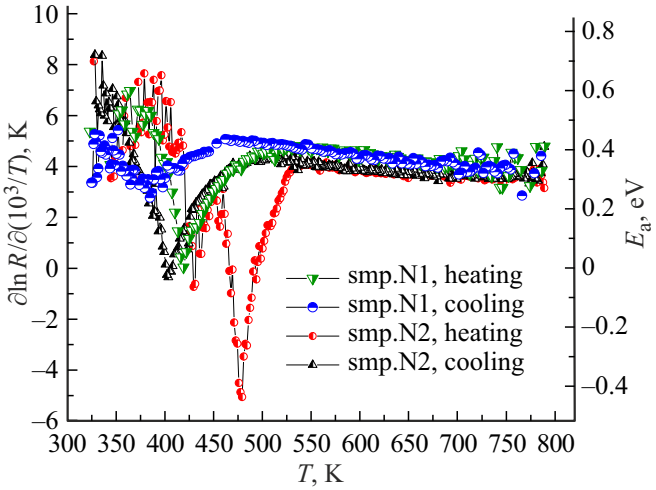

Figure 3. Temperature dependences of the local activation energy E_a of samples № 1 and № 2 of EuS polycrystals.

recorded by the recording equipment for further calculation of R ($\ln R$) and S in EuS samples.

A review of the experimental data reveals singularities in the graphs of the functions $\ln[R(10^3/T)]$ of europium monosulfide in the form of bends and hysteresis loops in the temperature region of 365–520 K (see Figure 1). Dependencies $S(T)$ for EuS shown in Figure 2 exhibit the same specific features as $\ln[R(10^3/T)]$. It is noteworthy that the functions $S(T)$ change sign in thermocycles in the region of 370–490 K, which indicates a consistent change of the main free charge carriers (in the absence of their degeneracy) in the studied samples: the transition from electrons to holes and vice versa.

The study of the behavior of the dependences of the derivatives $\partial \ln[R(10^3/T)]/\partial(1/T)$ of EuS samples on temperature allows obtaining additional information about the influence of the latter on the transport properties of charge carriers in the studied material. Based on the results of differentiation of the functions $\ln[R(10^3/T)]$, using the relation $E_a \approx \partial(\ln R)/\partial(1/T)k_B$, where k_B is the Boltzmann constant, the temperature dependences of the local activation energy $E_a(T)$ of EuS polycrystals in the whole temperature range of the experiment were calculated (see Figure 3). A characteristic feature of the behavior of $E_a(T)$ is the presence, firstly, of sharp minima at points corresponding to the temperatures of vanishing of $S(T)$, and, secondly, the presence of hysteresis in the temperature cycles.

4. Discussion of results

Before proceeding to analyze the results obtained in these studies, it should be noted that the latter were performed in the temperature range corresponding to the impurity conductivity region of EuS [4,10].

The electrotransport mechanism in EuS polycrystals similar to those used in this paper has been previously studied

in Ref. [5] in the temperature range of 150−400 K. The electrical parameters of several polycrystalline EuS samples were studied in the paper, and a significant variation in the values of their resistivity ρ, concentration of conduction electrons n, and their mobility μ under normal conditions was found. The variation of the kinetic coefficients ρ and μ was explained in Ref. [5] by the presence of a combined (including hopping and zone) charge transport mechanism in EuS polycrystals. A similar situation occurs in the EuS samples studied in this paper in the temperature region up of to 390 K. This is indicated by the rapid growth of $E_a(T)$ when they are heated in the interval of 320−390 K (see Figure 3). A necessary condition for the realization of hopping conduction is the presence of vacancies in the system of donor states. Such can be ensured as partial compensation of donors by third-party impurities present in the material, acting as acceptors, and structural defects that form vacancies in the crystal lattice [4]. The latter circumstance was first pointed out in Ref. [13].

The functions $\ln R$ of the tested samples are non-linearly decreasing dependences on $1/T$ (with weighted multiplier 10^3) in the temperature region of 320−390 K, consisting of a number of fragments (see Figure 1) and their local activation energies $E_a(T)$ increase and reach maximum values: ~ 0.52 eV in sample № 1 and ~ 0.65 eV in sample № 2 (see Figure 3). Further increase in temperature leads to a sharp decrease in activation energy. When the temperature of 412 K is exceeded for sample № 1 and 420 K for sample № 2, a typical semiconductor behavior pattern of the dependence $\ln[R(1/T)]$ is observed in the impurity depletion region [14], culminating in the transition of the electrical conductivity of the samples to the hole conduction region. The latter is confirmed by the reversion to zero and even by the transition to the region of negative values of the local activation energy $E_a(T)$ at the indicated temperatures (see Figure 3), as well as by the subsequent change of sign of $S(T)$ of the samples in the interval of 430−465 K (see Figure 2).

Let us consider separately the behavior of the dependence $\ln R(10^3/T)$ of sample № 2. It is almost independent of temperature in the interval of 420−435 K, but it exhibits a semiconducting decreasing course up to $T \approx 470$ K in case of the further heating. The genesis of this behavior is most likely activation-donor, because the above function begins to increase again already in the interval from 470 to 490 K, apparently, as a result of the change of the main current carriers of n-type — conduction electrons to current carriers of p-type — holes, possessing a greater effective mass, and a natural drop in mobility with increasing temperature.

When the samples are heated above 490 K, their functions $\ln R(10^3/T)$ decrease almost linearly up to the upper limit of the temperature range of measurements. The plot of dependence $E_a(T)$ in the stabilization region of p-type of conductivity in EuS ($T \geq 490$ K) also decreases with the increase of the temperature up to 800 K with an average rate of $\sim 3.1 \cdot 10^{-4}$ eV/K.

The temperature dependences $S(T)$ of EuS exhibit unusual behavior when the samples are heated: rapid growth with reaching saturation with S, approximately equal to $-900\,\mu$V/K (averaging over two samples) in the narrow temperature range of 355−380 K, and further increasing with a transition to the region of positive values. Further increase in temperature leads to a smooth increase of S from $\sim 555\,\mu$V/K at $T = 460$ K to $\sim 626\,\mu$V/K at $T = 700$ K, followed by a slight decrease to $\sim 610\,\mu$V/K at $T = 795$ K.

The stabilization of EuS thermo-emf in the region of 355−380 K is apparently attributable to the beginning of the process of mass activation of electrons to the levels of third-party acceptors and vacancies from the valence band with the formation of holes in the latter. A further increase of the hole concentration with increasing temperature naturally leads to a change of the sign of the EuS thermal emf. The behavior of $S(T)$ in the high-temperature region can be explained using the example of a model of a non-degenerate semiconductor having two types of free current carriers with opposite signs (electrons and holes) and standard with a quadratic zone dispersion law: conduction and valence. Then the formula for the thermal emf corresponding to this case has the following form [11]

$$S = -\frac{k_B}{e^-}\left\{\frac{\left[2+\ln\frac{N_c}{n}\right]n\mu_n - \left[2+\ln\frac{N_p}{p}\right]p\mu_p}{n\mu_n + p\mu_p}\right\}, \qquad (1)$$

where e^- is the electron charge; n, μ_n, N_c is the conduction electron concentration, their mobility and effective density of states (DOS) in the conduction band, respectively; p, μ_p, N_p is the hole concentration, their mobility and DOS in the valence band. If the first summand in the numerator of the fraction of formula (1) under normal conditions prevails over the second summand, but weakly increases with increasing temperature (due to the low concentration of small donors), and the second summand rapidly increases (due to the increasing concentration of holes), then S changes sign.

The conduction band in the high-temperature region is filled with electrons activated from different energy depths of the donor levels, including $4f$-levels. At the same time, the process of transition of electrons both to the remaining unfilled acceptor levels and, apparently, to the donor $4f$-states, which have become free, from the valence zone, with an increase in the concentration of holes in the latter, compensating the electronic component of the thermo-emf, is increasing. A very weak temperature dependence of the EuS thermo-emf is observed at $T \geq 500$ K. Since the mobility of conduction electrons exceeds that of holes in the valence band, the dependence $S(T)$ slightly decreases with increasing temperature.

Let us now try to understand the reasons for the hysteresis of functions $\ln[R(10^3/T)]$ and $S(T)$ in the thermal cycles of EuS samples. We would like to note the following circumstance: at the end of the temperature effects on the EuS samples, the indicated kinetic coefficients retain the

initial values of their magnitudes within the permissible errors. This fact suggests that cyclic heating of samples up to 800 K does not lead to noticeable violations of the spectrum of energy states in the band gap of EuS. Taking into account the existing experimental data on the study of optical and photoemission spectra of EuS crystals, it is possible to conclude that the hysteresis loops present in the dependences $\ln[R(10^3/T)]$ and $S(T)$ of thermocycles of the samples are attributable to the processes of nucleation and disintegration of exciton states $3p4s^{\mathrm{ex}}$, $4f^6 5d^{\mathrm{ex}}_{t_{2g}}$ [2,15]. It is reasonable to assume that the disintegration of exciton states begins in EuS samples, when a certain temperature threshold is reached as a result of heating, culminating at higher temperatures in the transition of electrons to the conduction band and the formation of holes in the valence band. Accordingly, the recovery of the exciton spectrum is possible only when the temperature decreases below the boundary of the onset of its destruction. The question of the low-temperature boundary of exciton existence in EuS is still open due to the lack of data on the structure of the energy spectrum of impurity and intrinsic defect states.

5. Conclusion

The results of experimental studies of the temperature dependences $\ln R[(10^3/T)]$ and thermo-emf S of two polycrystalline EuS samples cut from blanks of different batches of synthesized material in the temperature range of 320−800 K are presented. It is shown that the sign of the main free charge carriers sequentially changes in the studied samples in the processes of temperature cycling: the transition from electronic conductivity to hole conductivity in case of heating and vice versa, from hole conductivity to electronic conductivity in case of cooling.

It was also found in the course of studies that hysteresis loops are formed on their dependences $\ln[R(10^3/T)]$ and $S(T)$ f as a result of cyclic temperature effects on samples of europium monosulfide, the appearance of which can be consistently explained by the processes of formation and destruction of the system of exciton states in EuS.

Finally, we would like to note that the experimental facts obtained by studying the transport properties of charge carriers in EuS in thermocycles in the high-temperature region are established for the first time.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] E.L. Nagaev. Fizika magnitnykh poluprovodnikov. Nauka, M. (1979). p. 431. (in Russian).
[2] S. Methfessel, D. Mattis. Magnetic Semiconductors. Handb. f. Physik. Springer Verlag, Berlin (1968).
[3] P. Wachter. Handbook Phys. Chem. Rare Earth **2**, 507 (1979).
[4] A.V. Golubkov, E.V. Goncharova, V.P. Zhuze, G.M. Loginov, V.M. Sergeeva, I.A. Smirnov. Fizicheskie svoistva khal'kogenidov redkozemel'nykh elementov. Nauka, L. (1973). p. 304. (in Russian).
[5] M.M. Kazanin, V.V. Kaminskii, M.V. Romanova, N.N. Stepanov, A.V. Golubkov, N.V. Sharenkova. Phys. Solid State **58**, *11*, 2282 (2016).
[6] V.V. Kaminsky, N.N. Stepanov, S.M. Soloviev. FTVD **25**, *3–4*, 74 (2015). (in Russian).
[7] Yu.F. Golovnev, L.V. Nikolskaya. Izv. TulGU, ser. Fizika *5*, 104 (2005). (in Russian).
[8] N.V. Blümel, A. Goschew, Y.A. Shokr, P. Fumagalli. AIP Advances **9**, *3*, 035016 (2019).
[9] S.Yu. Davydov. FTT **67**, *2*, 372 (2025). (in Russian).
[10] G.G. Gadzhiev, G.N. Dronova, B.N. Magdiyev. TVT **24**, *4*, 812 (1986). (in Russian).
[11] A.T. Burkov, A.I. Fedotov, A.A. Kas'yanov, R.I. Panteleev, T. Nakama. Nauch.-tekh. vestn. informacionnyh tekhnologij, mekhaniki i optiki **15**, *2*, 173 (2015).
[12] N.N. Stepanov, G.A. Kamenskaya, S.V. Novikov. FTT **66**, *1*, 22 (2024). (in Russian).
[13] N.V. Sharenkova, V.V. Kaminskiĭ, M.V. Romanova, L.N. Vasil'ev, G.A. Kamenskaya. Phys. Solid State **50**, *7*, 1207 (2008).
[14] K.V. Shalimova. Fizika poluprovodnikov. Energoatomizdat, M. (1985). P. 392, il. (in Russian).
[15] A.B. Lakovtsev. Sovremennye problemy fundamental'nyh i prikladnyh nauk: Trudy 50-j nauchnoj konferencii MFTI, ch. 5, 118 (2007). (in Russian).

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