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Investigation of the behavior of electrical resistance and thermal EMF of polycrystals of ytterbium monosulfide during temperature cycling in the range of 320−790 K

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The temperature dependences of the electrical resistance R and thermal EMF S of polycrystals of ytterbium monosulfide (YbS) in the range 320−790 K have been studied. It was found that cyclic temperature exposure to YbS samples leads to the appearance of hysteresis on the dependences $\ln[R(10^3/T]$ and $S(T)$. The analysis of the discovered patterns in the behavior of R and S allowed us to suggest a significant influence of the processes of occurrence and destruction of the exciton spectrum during temperature changes on the transport properties of charge carriers in YbS.

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

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1. Introduction

Monochalcogenides of rare earth metals with the charge state of cations 2+ ($RE^{2+}X$, where RE — Sm, Yb, X — O, S, Se, Te) under normal conditions These conditions form the „group of magnetoexitonic semiconductors" [1,2]. The principle quantum number in the ground state is RE^{2+} $J = 0$, but the energy of its transfer to the state with $J = 1$ is low according to experimental data and theoretical calculations [3–6]. Heating of $RE^{2+}X$ samples resulted in the activation of $4f^n$-electrons in the $5d_{t_{2g}}(6s)$-conduction band in electronic systems of such materials and transitions of such electrons into bound (exciton) states $4f^{n-1}5d^{ex}$ with $J = 1$, which have a significant impact on their physical properties. For instance, an exciton mechanism of phase transformation of the first kind under pressure in SmS [7] is theoretically substantiated in Ref. [6], while the behavior of the baric dependence of the electrical resistance of SmTe in the field of semiconductor conductivity is explained in Ref. [8] by a change of the concentration of the exciton states under the action of uniform compression that play the role of traps for electrons activated from $4f^6$-levels. The observed anomalies in the behavior of temperature dependences of electrical resistance (R) and thermal EMF (S) of SmS and SmSe single crystals in the region 500−800 K as a result of cyclic temperature treatment of samples in the range 320−800 K were consistently interpreted in Refs. [9,10] by assuming the processes of exciton pair formation and decay in the studied materials.

This paper presents the results of experimental studies of the behavior of R and S polycrystals of ytterbium monosulfide (YbS) in case of temperature cycling in the region of 320−790 K. Based on the analysis of the data obtained, it is suggested that exciton states are generated and subsequently destroyed in ytterbium monosulfide in a certain temperature range, similar to what occurs in SmS and SmSe [9,10], as well as the influence of these processes on the parameters of electrical transfer in YbS polycrystals.

2. Experimental methodology

YbS polycrystals of nominally stoichiometric composition were prepared according to the method [11]. Three samples were selected for the study, which were cut from various pre-synthesized blanks.

The constants of the crystal FCC lattice (spatial group $Fm\bar{3}m$) and the coherent X-ray scattering region (CSR) L of the YbS samples, according to the X-ray phase analysis, had the following values under normal conditions: sample 1 — $a_{\text{YbS}} = 5.686$ Å; $L_{(200)} \approx 860$ Å (which corresponds to a large-block polycrystal), sample № 2 — $a_{\text{YbS}} = 5.695$ Å; $L_{(200)} \approx 255$ Å, sample № 3 — $a_{\text{YbS}} = 5.699$ Å; $L_{(200)} \approx 650$ Å. The values of the lattice constant a_{YbS} obtained in this work at $T = 300$ K and atmospheric pressure $P = 0.1$ MPa are slightly higher than values: $a_{\text{YbS}} = 5.677$ Å and $a_{\text{YbS}} = 5.69$ Å, listed for reference in Ref. [12]. The electrical resistivity ρ and thermal EMF S of the tested samples under normal conditions are as follows: sample № 1 — $\rho \approx 1.35\,\Omega \cdot$ cm and $S \approx +270\,\mu$V/K; sample № 2 — $\rho \approx 1.04\,\Omega \cdot$ cm and $S \approx +500\,\mu$V/K and sample № 3 — $\rho = 8.57\,\Omega \cdot$ cm and $S \approx +560\,\mu$V/K.

The temperature dependences R and S of polycrystals in the above-mentioned temperature range were studied using the facility described in Ref. [13]. The details of the procedure for measuring the dependencies $R(T)$ and $S(T)$ of the test samples are given in Ref. [10].

3. Measurement results

Figure 1 shows the dependences of the logarithm of electrical resistance of a YbS polycrystal on the reverse temperature with a weighting factor of 10^3 for the „heating-cooling" cycle in the temperature range of 320–790 K. Features in the form of bends in the temperature range near 720 K in case of heating and 690 K in case of cooling on the graphs of functions $\ln[R(10^3/T)]$ YbS are revealed by the analysis of experimental data. The following fact is also noteworthy: a slight decrease of the value $\ln R$ of the sample is observed at the beginning of the cooling process (near the temperature peak). The graph of the dependence $\ln[R(10^3/T)]$ exhibits an increase in full accordance with the semiconductor nature of electrical conductivity in YbS as the temperature decreases further.

Additional information about the effect of temperature on the transport properties of charge carriers in the sample № 1 YbS can be obtained by analyzing the temperature dependence of the derivative $\partial \ln[R(10^3/T)]/\partial(1/T)$ (see Figure 2). The temperature dependence of the local activation energy $E_a(T)$ of YbS polycrystal was calculated over the entire temperature range of the experiment based on the results of differentiation, using the ratio $E_a = \partial(\ln R)/\partial(1/T) \cdot k_B$, where k_B is the Boltzmann constant. $E_a \approx 0.23$ eV at $T = 320$ K, which is slightly less than the value given in Ref. [12]. It should be noted that the value of E_a is a characteristic of charge carriers of p-type, since the thermal EMF of the test sample is $S > 0$. The dependence $E_a(T)$ weakly changes at the initial temperature range of 320–625 K, and its significant increase up to $E_a \approx 0.77$ eV at the maximum temperature is observed only in the high-temperature range of 625–790 K.

The transition from the heating mode of the YbS crystal to its cooling leads to a change of the behavior of the dependence $E_a(T)$ at high temperatures: a sharp drop of the value of E_a is observed with a transition to the region of negative values. Further cooling leads to a rapid increase of E_a, followed by a change of its sign and reaching a maximum at $T \approx 720$ K. The dependences $E_a(T)$ are almost identical in the range of $320\,\text{K} \le T \le 700$ K in case of heating and cooling of the sample.

The analysis of the temperature dependence $S(T)$ of YbS sample № 1, shown in Figure 3, allows drawing additional conclusions about the features of charge carrier transport in this compound. The thermal EMF of the tested sample increases and reaches a maximum of $S \approx +425\,\mu$V/K at ≈ 625 K as its temperature increases. Further, the value of S begins to drop as the temperature increases and its value is $\approx +290\,\mu$V/K at $T = 786$ K.

The behavior of thermal EMF of YbS in the high-temperature region in the cooling mode demonstrates the following features: *a*) decrease of S to $+281\,\mu$V/K when the sample is cooled by 18 K; *b*) increase of $S(T)$ with a further decrease of temperature to the intersection at $T \approx 675$ K with its temperature dependence in the heating mode and the formation of a hysteresis loop on the curve $S(T)$.

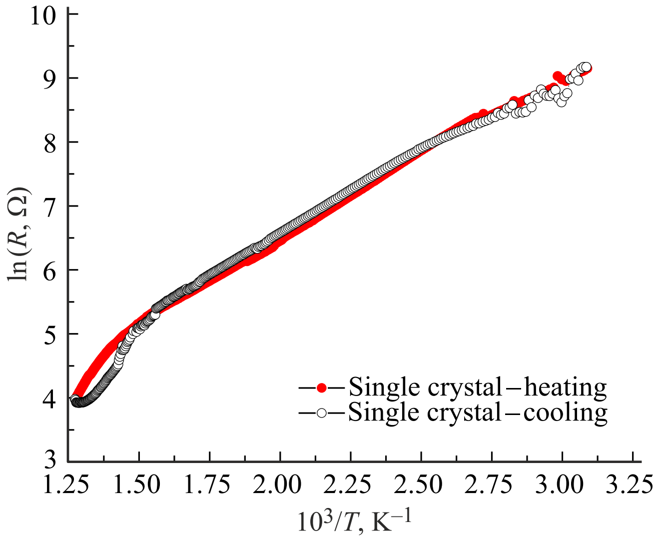

Figure 1. Temperature dependence $\ln R$ of the sample № 1 of YbS polycrystal.

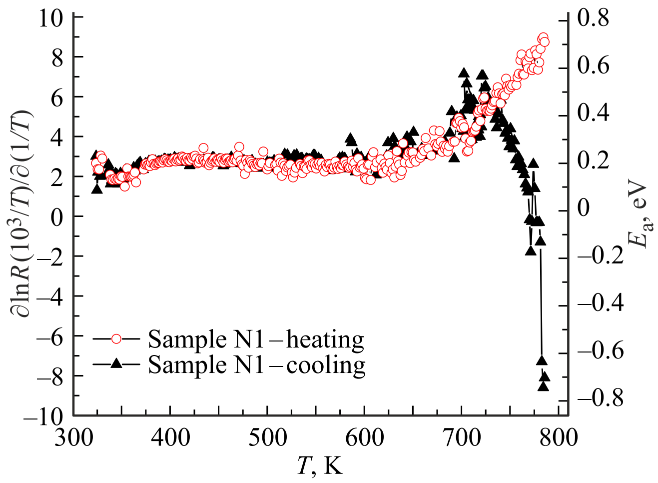

Figure 2. Temperature dependence of the derivative $\partial(\ln R)/\partial(1/T)$ of the sample № 1 of YbS polycrystal.

Studies of the behavior of dependencies $\ln[R(10^3/T)]$, $\partial \ln[R(10^3/T)]/\partial(1/T)$ and $S(T)$ in thermal cycles based on experimental data on the study of temperature dependencies R and S of YbS samples № 2 and № 3 show the same features that were observed in the sample № 1. It necessary to note the instability of electrical and thermoelectric parameters inherent in each test sample at a certain temperature range of 525–700 K, as well as differences in the sizes of hysteresis loops based on the dependences $\ln R(10^3/T)$ and $S(T)$ (see Figures 4–6).

4. Discussion of the results

The analysis of the experimental research results was conducted on the basis of the scheme of the structure of the YbS band spectrum, given in Ref. [4] and shown in Figure 7. Unlike the original in Ref. [4], the energy transitions E_1 and E_2 (see Figure) are considered to be related to excitonic excitations $4f^{13}5d^{ex}_{t_{2g}}$ and $4f^{13}5d^{ex}_{e_g}$. Transitions of $4f$-electrons into the conduction band ($4f^{14} \to 4f^{13}6s$, $4f^{14} \to 4f^{13}5d_{t_{2g}}$, $4f^{14} \to 4f^{13}5d_{e_g}$) are not shown in Figure 7.

The dark conductivity of stoichiometric YbS (as well as other ytterbium monochalcogenides) under normal conditions of p-type according to Ref. [3]. Possible reasons for the occurrence of hole conduction: firstly, deviations of the composition of the compound towards an excess

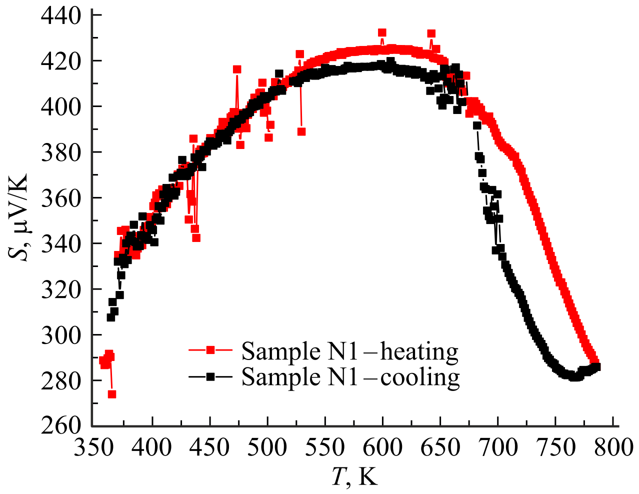

Figure 3. Temperature dependence of thermal EMF S of sample № 1 of YbS polycrystal.

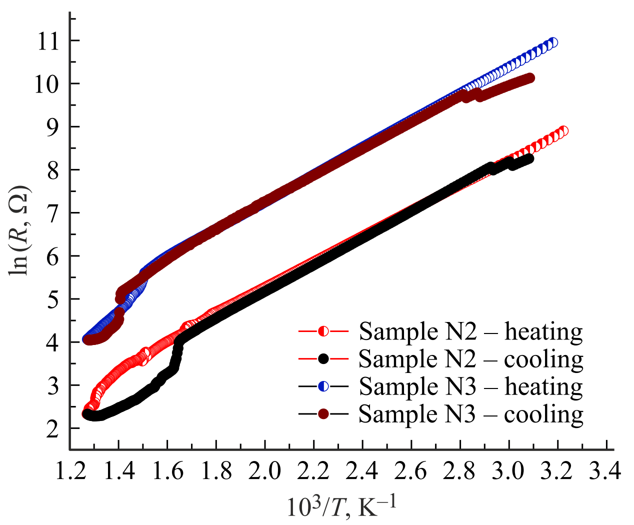

Figure 4. Temperature dependences $\ln R(10^3/T)$ of samples № 2 and № 3 of YbS polycrystal.

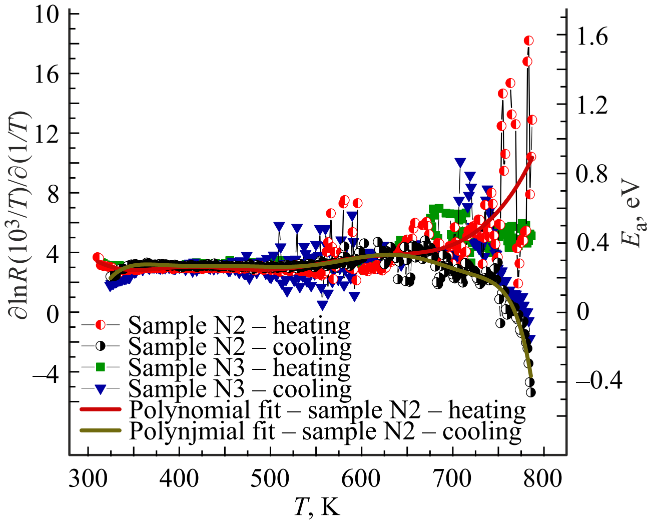

Figure 5. Temperature dependences $\partial \ln R/\partial(1/T)$ of samples № 2 and № 3 of YbS polycrystals and polynomial approximations of temperature dependence $\partial \ln R/\partial(1/T)$ for sample № 2.

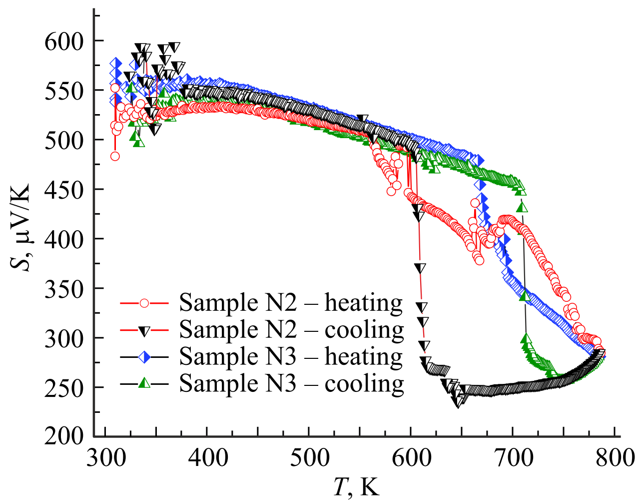

Figure 6. Temperature dependences of thermal EMF S of samples № 2 and № 3 of YbS polycrystal.

of chalcogen atoms during synthesis, and secondly, the occurrence of vacancies in the cationic sublattice as a result of the location of a certain number of cations outside the regular crystal structure in the interstices and at the boundaries of defects of the latter. According to Ref. [12] „the occurrence of a cationic vacancy is accompanied by the transition of two neighboring ions Yb^{2+} (4/14) to the trivalent state Yb^{3+} ($4f^{13}$) and the formation of acceptor levels, which capture electrons from the valence band, create a conductivity of p-type“. It is only necessary to add that these energy levels are located close to the ceiling of the valence band, below the $4f^{14}$ levels.

The electrical resistance of YbS samples decreases in the temperature range of ≤ 625 K during heating due to an increase of the concentration of holes in the valence

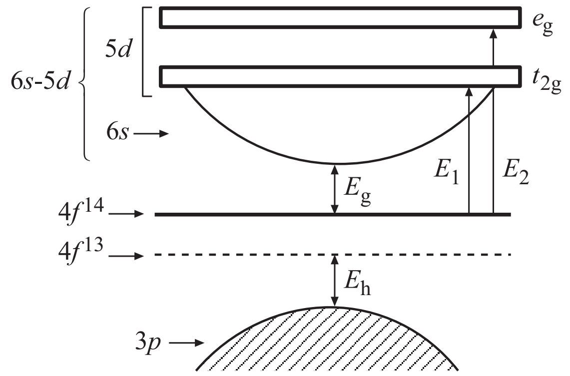

Figure 7. YbS semiconductor phase band diagram: E_g is the energy gap between $4f$-levels and the bottom of the conduction band; E_h is the energy gap between the ceiling of the valence band and the hole states; E_1 and E_2 are minimum energy gaps between $4f$-levels and exciton states in t_{2g}- and e_g-subbands of $5d$-conduction band.

band. Electrons activated in the conduction band from $4f$-levels of cations located both in the interstices and other defective regions of the polycrystal and in the nodes of the regular crystal lattice begin to take an active part in electrical transfer at higher temperatures. This statement is supported by a rapid decrease of the value of S YbS in the high-temperature region.

It is possible to specify the temperature on the dependencies $\ln R(1/T)$ in the half-cycles of heating for each of the studied YbS samples exceeding which accelerates the decrease of electrical resistance of the YbS samples. This is 720 K for sample № 1, this is 690 K for sample № 2 and 660 K for sample № 3. The behavior of $R(T)$ of samples at temperatures exceeding those indicated cannot be explained solely by the connection of the $5d$-conduction band of YbS to charge transport processes, since it is not possible to explain hysteresis phenomena on dependencies $\ln R(10^3/T)$ based on such electrotransport model (see Figures 1, 4). It is reasonable to assume that the exciton generation process begins at a certain temperature in the studied material during the heating process. A characteristic feature of this is the noticeable fluctuations of the electrical voltage measured during the study of $R(T)$ and $S(T)$ on YbS polycrystals (cf. with [9,10]). Such areas of instability are quite easy to identify visually on the charts $E_a(T)$ (see Figures 2 and 5). An increase of the temperature of YbS samples above $T \approx 784$ K leads to a sharp drop of the value of $\ln R(10^3/T)$, which is undoubtedly attributable to the destruction of the exciton spectrum, which takes on a landslide character. The upper limit of the temperature measurements in this study was $T \approx 786$ K. Unfortunately, the capabilities of the facility [13] did not allow further expanding the range of the study into the field of higher temperatures. Nevertheless, it clearly follows from the analysis of the obtained data that uncontrolled processes of a sharp increase of the concentration of conduction electrons take place in YbS crystals at extremely high experimental temperatures. Indeed, the concentration of charge carriers in YbS continues to increase in a certain temperature range characteristic of each test sample even after the end of the half-cycle of heating and the transition of the facility to the cooling mode. An uncontrolled increase of the concentration of conduction electrons at the boundary of changes in the temperature regime of thermal treatment of the studied samples determines a decrease of electrical resistance R, respectively, and $\ln R$, $S(T)$ in these samples, as well as a change of the sign of $E_a = \partial(\ln R)/\partial(1/T) \cdot k_B$ at the point the maximum heating temperature (the latter is clearly a consequence of the so-called „hardware effect“ and, therefore, has no physical meaning). The process of decrease of R (and $\ln R$), $S(T)$ continues over a fairly wide temperature range, after which the transition to the semiconductor type of charge carrier transport takes place. It is not difficult to notice that both the values of the temperature range of abnormal behavior of R ($\ln R$) and S and the hysteresis phenomena on these dependences are determined by the structural features of the studied polycrystal: the largest temperature range of positive values $\partial R/\partial T$, $\partial S/\partial T$ inside the hysteresis loop and the region of the latter itself correspond to the smallest value of $L_{(200)} \approx 255$,Å.

5. Conclusion

This paper presents the results of experimental studies of the temperature dependences of electrical resistance R and thermal EMF S of three polycrystalline YbS samples cut from blanks of various batches of synthesized material in the temperature range from 320 to ≈ 790 K. The experimental studies found a significant effect of temperature cycling of samples on the parameters of charge carrier transport. A qualitative model of the temperature-induced evolution of the spectrum of exciton states in YbS is proposed for explaining the observed effects: 1) the occurrence of excitons at the stage of sample heating at $T \geq 525$ K, 2) the beginning of collective dissipation of exciton states upon reaching a critical temperature of ≈ 784 K in the material, 3) restoration of the exciton spectrum in case of sufficient sample cooling (up to 680−700 K depending on № of sample) and 4) low-temperature dissipation of the exciton spectrum at $T < 525$ K.

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Conflict of interest

The authors declare that they have no conflict of interest.

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