TRANSPORT PHENOMENA IN THE SILVER SULFIDE SINGLE CRYSTAL

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ABSTRACT

The electrical conductivity (σ), Hall factor (R_H), thermo-e.m.f. (α) and spectral dependence of the absorption factor for silver sulfide single crystals received by the method of isotherical recrystallization from the solid phase have been investigated. The basic characteristic parameters have been determined: mobility, concentration of the charge carriers, the activation energy of donor levels, effective masses of the charge carriers, temperature factor of the width of the forbidden gap, degree of freedom for electrons, etc. The analysis of the temperature dependence of R_H and σ testify the presence of weak overlapping of the valence and conductivity bands in the β-phase.

Keywords: silver sulfide, single crystal, polycrystal, thermo-e.m.f., solid solution, recrystallization.

I. INTRODUCTION

Among semiconductor compounds of A_1^2B type being perspective materials for semiconductor electronics, silver sulfide also is interesting by an opportunity of use as an active material in massive and film arrangement in MSM and MDS-structures. The data available elsewhere [1, 2] on electrophysical and ohmic properties of silver sulfide relate to polycrystals and probably, therefore are inconsistent. We could not find out in the literature the data concerning to single crystals of Ag_2S, though still in [1] it was stated necessity of reception and study of Ag_2S single crystals. In the literature there were reports on reception of Ag_2S single crystals by the gas-transport reactions method [3]. Crystals were the needle form and the small sizes. Papers [4, 5] are devoted to study of thin films of Ag_2S.

II. METHOD OF RECEPTION OF MATERIALS

The present work is devoted to studying of the energy spectrum parameters of the silver sulfide single crystals which has been grown by the isotherial recrystallization method. To this choice selection of the temperature regime, geometry of growth ampoules, conditions of collective recrystallization at the nucleation stage, annealing temperatures and cooling rate have been preceded. Uniformity and single crystalline nature of the samples were confirmed by powder and electron-diffraction patterns. The electrical conductivity, Hall effect, thermo-e.m.f. in a wide temperature range and spectral dependence of the absorption coefficient have been investigated.

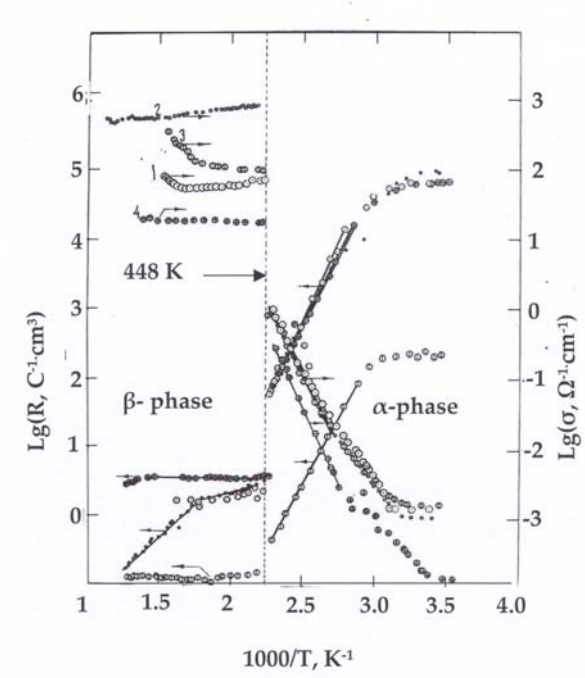

Fig. 1. Temperature dependence of the Hall factor R_H and electrical conductivity σ of the single crystalline (1-3) and polycrystalline samples of Ag_2S (4)

The choice of the temperature range (293÷770 K) has allowed us to calculate from electric and optical measurements characteristic parameters of the single crystalline silver sulfide for both low-temperature (α) and high-temperature (β) modifications. From [6] and other works it is known that silver sulfide of belongs to superionic conductors, therefore we have found expedient to carry out measurements of electrical conductivity and Hall effect on an alternating current that has enabled us to exclude influence of ionic conductivity.

Measurements of the temperature dependences of the Hall factor were carried out by the two-frequency method [7] in the argon atmosphere. Frequencies have been chosen: ω_H=87.5 Hz and ω_J=50 Hz. Intensity of the magnetic field was equal 1770 Oersted, the relative error was ~ 2-5 %. Accuracy of stabilization of the temperature was ~ 0.5 %. Advantages of the used method were: all collateral e.m.f. caused by the accompanying phenomena, asymmetry of the probes, pickups from the magnetic field are excluded; sensitivity of the given method many times over surpasses sensitivity of measurements on the direct current and a constant magnetic field. Samples for measurements of the Hall effect and electrical conductivity had a rectangular form; contacts - dot, clamping made of molybdenum. Uniformity of Ag_2S before the temperature measurements was checked on JXA-5A microanalyzer.

The measurements of the optical transmission and reflection were carried out on two-beam spectrometer IKS-14 and UR-20. The absorption factors depending on the radiation energy have been determined from the reflection and transmission spectra by using the technique described elsewhere [8].

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Temperature dependences of the electrical conductivity and Hall factor for several samples of Ag_2S with various concentration of the charge carriers are presented in Fig. 1. Prominent feature of the temperature dependence of the electrical conductivity is the semiconductor course in the of temperature range 235÷446 K. At 443 K σ and R_H undergo discontinuous change; this is a temperature of the polymorphic transition between α (low-temperature) and β (high-temperature) modifications. β-Ag_2S exists in the temperature range 448÷860 K. To study of the transport phenomena of high-temperature phases (670 ÷ 1478 K) of polycrystalline silver sulfide devoted works [9, 10], and it was established that β-$Ag_2S \rightarrow$ γ-Ag2S transition (BCC structure $\rightarrow$ FCC structure) occurs at 860 K without appreciable changes in the electric properties.

The Hall factor R_H remains negative in all range of the temperatures for all investigated Ag_2S samples. A course of the dependence of the Hall factor on room temperature up to 448 K is semiconducting one (R_H falls in 2 - 3 order of magnitude with increasing of the temperature). Sharp reduction of R_H in the phase transition point specifies increase in the free charge carriers concentration. In β-phase R_H remains constant in the temperature range 448 ÷ 580 K.

If for all investigated samples dependence R_H *(T)* in the temperature range from room temperature up to temperature of the phase transition practically has semiconducting character, then at transition to β- phase degeneration and metallic conductivity is observed. In the relation β-phases of silver sulfide Junod interpreted his data starting from the concept of metallic character of the conductivity. He supported this point of view by the discussion on the population degree of Jones bands and summarized that metallic character of the conductivity in β-Ag2S is caused by its crystal structure and does not depend on details of structure, an impurity, etc.[1].

In Fig. 2 temperature dependence of the Hall factor is presented from which the activation energy of the charge carriers in silver sulfide (α-Ag_2S) single crystal appeared equal to (1.45 ± 0.05) eV that is larger than value known from the literature, i.e. ~1.3 eV [1] relating to polycrystalline silver sulfide; the activation energy of polycrystalline silver sulfide determined by us (curve 4, Fig. 2) is ~ 1.32 eV that insignificantly differs from known from the literature. The analysis of the temperature dependence of R_H *(T)* shows that the character of dependence is identical for all investigated samples and for the majority of samples in the temperature range 448÷625 K a relationship $lgRT^{3/2}$ = const is satisfied.

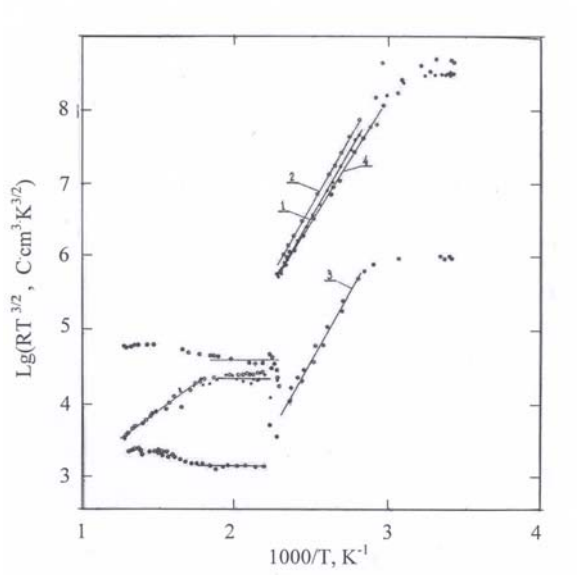

Fig. 2. Temperature dependence of the Hall factor for single crystalline (1-3) and polycrystalline samples of Ag_2S (4)

Such dependence can be received only in the case if weak overlapping of the valence and conductivity bands takes place, i.e. the semi-metallic structure is realized. Further dependence of the Hall factor on temperature has an activation character and the activation energy equals to 0.62 eV.

The mobility of electrons μ_n, and holes μ_p and their ratio were determined by a technique described elsewhere [11].

The mobility of the holes were determined by extrapolation of rectilinear intrinsic section in $lgR \sim 1/T$ and $lg\ \sigma \sim 1/T$ dependences to crossing with a perpendicular restored from an abscissa axis in point T = 293 K. The mobility of the holes were calculated by formula

$$\mu_p = R_n\,(T)\,\sigma_n\,(T) - R_i\,(T)\,\sigma_i\,(T) \qquad (1)$$

where R_i and σ_i are the Hall factor and electrical conductivity, respectively, at temperature T, caused by intrinsic charge carriers.

The temperature dependence of the Hall mobility for a sample No.2 α-Ag_2S and β-Ag_2S are presented in Fig. 3. In the intrinsic conductivity region of α-Ag_2S the Hall mobility versus the temperature obeys the law $R_i\sigma_i \sim T^{\nu}$, where ν = - 3/2, that indicates the presence of thermal scattering of electrons on acoustic phonons of the lattice in the specified temperature range. In the temperature range 450÷630 K the Hall mobility of the charge carriers in α-Ag_2S decreases under the power law $\sigma R \sim T^{\nu}$, where ν <-2.2. Ditman in [10] observed the dependence $\sigma R \sim T^{-3.6}$ in the high-temperature phase (β-Ag_2S) and connected it with the presence of strong dependence of effective mass on temperature $(m^* \text{-} T^{2.6})$ that can be caused by increase in number of vacancies in connection with the sulfur's volatilization. In the given case small duration of measurements of σ (T) and R_H (T), and results of the X-ray microanalysis allow us to assume that during experiment structure of Ag_2S samples were not broken. Starting from this observable power dependence $\sigma R \sim T^{\nu}$, where ν <-2.2 can be attri-buted to multiphonon processes.

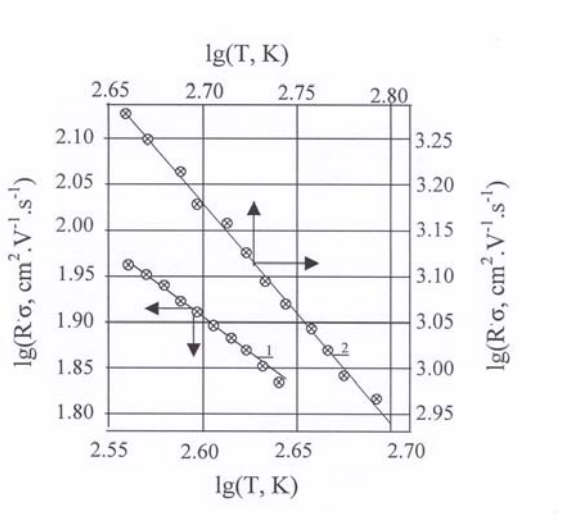

Fig. 3. Temperature dependence of the Hall mobility for Ag_2S single crystal : 1 - α- phase; 2 – β- phase

At increase in temperature kinks are observed in $lg\,(R\,\sigma) \sim (lgT)$ dependence.

On Fig. 4 dependence of the concentration of free charge carriers for single crystalline (1) and poly-crystalline (2) silver sulfide on temperature are presented.

The concentration of the intrinsic charge carriers were calculated by formula:

$$n_i = -\frac{3\pi}{8}\frac{1}{qR_i}\frac{\mu-1}{\mu+1} \qquad (2)$$

with the assumption of the constant mobility ratio in all interval of temperatures.

The activation energy of the charge carriers determined from dependences $lgRT^{3/2} \sim f\,(10^3/T)$, $lgn_iT^{3/2} \sim f\,(10^3/T)$ (Fig. 5) appeared equal to 1.45 eV for single crystalline and 1.32 eV for a polycrystalline α-Ag_2S. The activation energy of the donor levels determined from the temperature dependence of the Hall factor equals to 0.327 eV. The concentration of the donor centers was determined under the following formula and at T = 293 K made 10^{14} cm^{-3}:

$$\Delta E = kT\left[\frac{k\pi^{3a}h^2N_g}{2m_n^*k_0T^{40}}\right] \qquad (3)$$

Degree of freedom for electrons was determined by formula:

$$f_n = \frac{m_n}{m_n^*} = \mu^{1/5}(4{,}82\cdot10^{15}T^{3/2})\frac{1}{n_i}e^{-E_g/2kT} \qquad (4)$$

$$f_p = \frac{m_0}{m_p^*} = \mu^{-1/5}(4{,}82\cdot10^{15}T^{3/2})\frac{1}{n_i}e^{-E_g/2kT} \qquad (5)$$

where - E_g = 0.93 eV; $n_i = 1{,}2\cdot10^{12}$ cm^{-3}; f_n = 0.5.

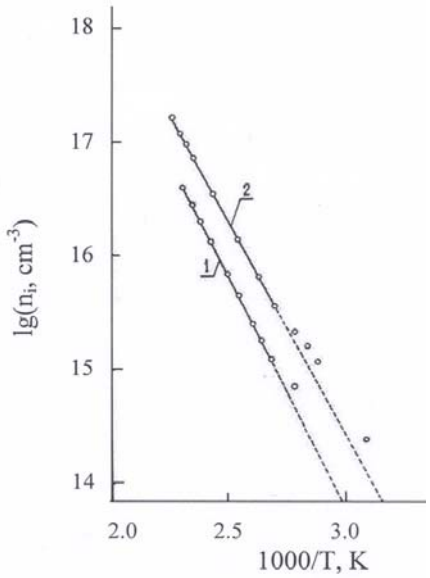

Fig. 4. The dependence of the intrinsic concentration of the charge carriers lg (n_i, cm^3) on temperature for single crystalline (1) and polycrystalline Ag_2S (2)

The used technique has allowed us to determine average values of effective masses m_n^* and m_p^* and the ratio of electron and hole mobilities at room temperature:

$$m_o / m_n^* = 0{,}5; \quad m_0 / m_p^* = 0{,}32;$$

$$\mu = \frac{\mu_n}{\mu_p} = 2{,}82 \qquad \text{(sample No. 2)}$$

The dielectric constant calculated by formula

$$\frac{m_0}{m_n^*} = \frac{13{,}5}{\varepsilon^2\Delta E_D} \qquad (5)$$

(where ΔE_D is the activation energy of donor levels, ε is dielectric constant) has made $\varepsilon = 8.8$ that also is in accordance with the literary data.

In Fig. 6 the temperature dependence of the thermo-e.m.f. is presented. In the region of the existence of the low-temperature phases thermo-e.m.f. monotonously falls with the rise of the temperature and at the phase transition temperature jump takes place.

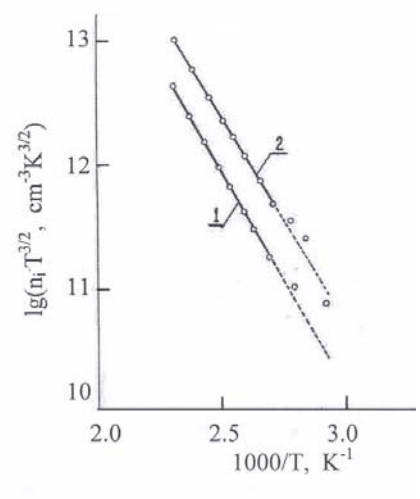

Fig. 5. Dependence of $n_iT^{3/2}$ on temperature for single crystalline (1) and polycrystalline (2) Ag_2S

As it is seen from Fig. 6, thermo-e.m.f. at 500 K and above weakly depends on temperature that apparently denotes degeneration. Calculations of the reduced chemical potential (η = 4.32) also specifies degeneration of the high-temperature phase Ag_2S; the chemical potential at 500 K equals to ξ = 0.186 eV, that is above a bottom of the conductivity band.

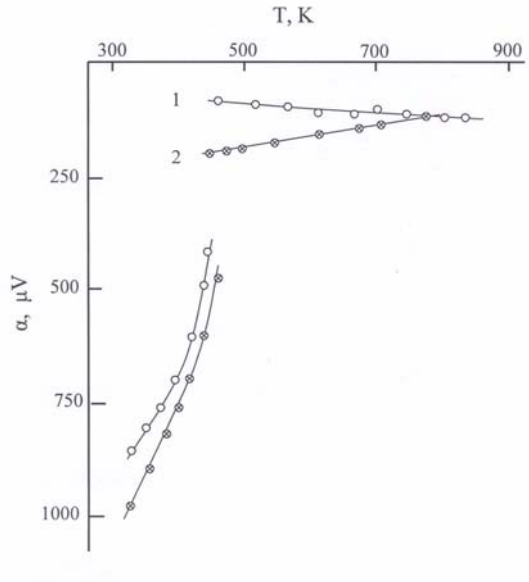

Fig. 6. The temperature dependence of the thermo-e.m.f. for Ag_2S single crystal

From the dependence $\alpha = f\ (10^3/T)$ ratio of mobilities have been calculated by a technique described elsewhere [11] and values obtained coincide with above-stated ones.

The absorption factor has been calculated from the curves of spectral dependence of the transmission and reflection. The width of the forbidden gap for α-Ag_2S single crystal at room temperature makes 0.93 eV. Abrupt growth of the absorption factor enables us to assume that silver sulfide is the direct band gap semiconductor.

At the assumption of linear change with temperature of width of the forbidden gap, temperature factor of width of the forbidden gap was determined: $a = 1.44 \cdot 10^{-3}$ eV/K.

IV. CONCLUSION

Summarizing above-stated data it is possible to say that the silver sulfide single crystal in α-phase is the semiconductor with the band gap 0.93 eV and in β-phase weak overlapping of the valence and conductivity bands takes place - the structure of semi-metal is realized.

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