TEMPERATURE DEPENDENCE OF THERMO-EMF OF Ag_2S

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ABSTRACT

The temperature dependences thermo-emf Ag_2S are explored in the range of temperatures 300-850 K. Concentration of charge carriers Ag_2S had values (10^{14}-10^{17}) cm^{-3} at 300K. For samples with $n=10^{14}$ cm^{-3} a thermo-emf incremented at diminution of concentration of charge carriers, attaining value 1,1-1,2 mV/K. With magnification of temperature the absolute value of thermo-emf decreases and at 448 K undergoes a sudden change because of polymorphic phase transformation α--β. Seeback coefficient changes continuously in polymorphic phase trans-formation temperature for samples with $n=10^{17}cm^{-3}$.

Keywords: the single crystals of Ag_2S, polycrystalline Ag_2S, electromotive, thermo-emf, Hall effect (R)

I. INTRODUCTION

The Seebeck constant, arising at temperature drop in one degree is one of the basic characteristic parameters of the semiconductor. The thermo-emf depends on such general parameters of the semiconductor, as a energetic zoned spectrum, a sign of conductance; concentration, effective mass and mechanism of a dispersion of current carriers.

II. EXPERIMENT DERIVING OF MATERIALS

Deriving of perfect Ag_2S monocrystals Ag_2S is a difficult problem. On this there are disagreements between the data both fundamental, and the characteristic parameters of polycrystal silver sulphide, obtained by different authors [1]. Ag_2S monocrystals obtained from gas-transport reaction [3] were acicular and mesh sizes. Ag_2S thin films had polycrystalline structure [4,5]. For the first time the large Ag_2S monocrystals have been obtained by us [1]. In this paper, monocrystals of silver sulphide were grown by an isothermical recrystalization method. For this purpose the temperature schedule, geometry of growth ampoules, requirements of the collective recrystallizing at a stage of a nucleation, annealing temperature and cooling rate have been selected. Homogeneity and monocrystallinity of Ag_2S were defined by a X-ray powder pattern and a Laue pattern.

III. INVESTIGATION OF TEMPERATURE DEPENDENCE OF THERMO-EMF Ag_2S

The electrical conductivity, Hall effect, thermo-emf in Ag_2S were explored in a wide temperature band(T_1-T_2) K. For a measuring of temperature dependence of a thermo-emf the sample from monocrystal of Ag_2S rectangular shape was positioned between two platinum plates. At blanket temperature T of a sample the difference of temperature between platinum plates was $\Delta T=T_2-T_1$. This temperature difference has matched with the electromotive force V_α. The thermo-emf at temperature $T_{ov}=(T_2-T_1)/2$ was defined by the formula $\alpha_{Tov}=V_\alpha/(T_2-T_1)$.The thermo-emf and Thomson coefficient of the semiconductor on an order of magnitude considerably exceed the relevant quantities for metals. On this the additive on the part of metal in a thermo-emf can be neglected. Routinely temperature difference ΔT was 5-15K. The temperature at butts of a sample was measured by the chromel-alumel thermocouple. For a measuring an electrical conductivity of samples were used 1 mm diameter molybdenic sondes. For diminution of transfer resistance of contact a sonde - sample, before measuring sondes were preformed by preheating of system up to 370 - 390 ^oC

IV. DISCUSSION OF RESULTS

Temperature dependences of thermo-emf of Ag_2S was investigated in the 300-850 K temperature range. Carrier concentration of investigated samples were varied in limits (10^{14}-10^{17}) sm^3 (T=300K). In extrinsic region (T=300K) the thermo-emf both monocrystal, and polycrystalline Ag_2S matters more than 0.8 mV/K. Thus the absolute value of $|\alpha|$ with diminution of concentration of charge carriers is incremented, attaining value 1,1-1,2 mV/K for samples with $n=10^{14}$ cm^{-3}. (fig. 1).

Temperature dependence of thermo-emf of Ag_2S is presented on fig. 2. Where as the course of dependence α (T) is typical for all investigated samples, we are restricted with that we give graphs α (T) only for two samples, where 1-is monocrystal with $n=2\cdot 10^{16}cm^{-3}$ and 2- is polycrystal with $n=1\cdot 10^{17}cm^{-3}$. With increasing of temperature the absolute value of $|\alpha|$ diminishes and at 448 K undergoes a sudden change because of polymer-

phic transformation. At temperature 300 K spring in dependence α (T) is significant for samples with smaller concentration of current carriers. For samples with $n=10^{17} cm^{-3}$ the thermo-emf in the the polymorphic transformation temperatures range varies so continuously, that it is difficult to define the temperature of $\alpha \to \beta$ polymorphic transformation. As can be seen from fig.2, thermo-emf, after polymorphic transformation, feebly varies of increasing of temperature that specifies as degeneracy of states. Behavior of temperature dependence of thermo-emf, electrical conductivity and Hall coefficient of Ag_2S at the temperatures, higher 450 K expels an opportunity of developing process of a self-admittance, because of noticeable participation of electron defects in transport process. In this case the small magnitude of the thermo-emf satisfactorily expresses by the equation not dependent on the mechanism of a carrier scattering.

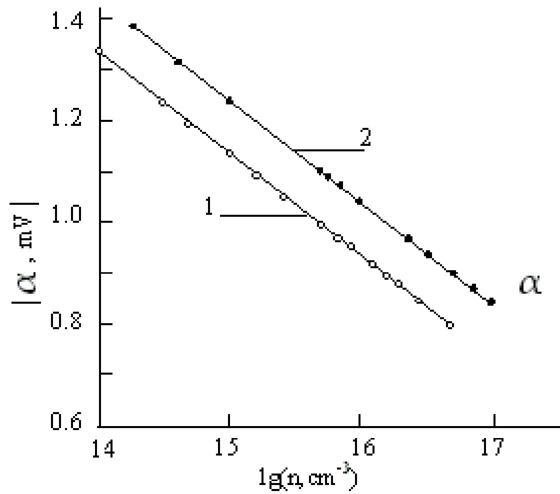

Fig. 1. Dependence of Seeback coefficient Ag_2S from concentration of current carriers. 1-monocrystal, 2-polycrystal

In case of square-law dependence of energy of carriers on a quasimomentum $E = \hbar^2 k^2 /(2m_n)$ and a power characteristic of a relaxation time on energy [6]:

$$\tau(E) = \tau_{02}(T)(\frac{E}{k_0 T})^{r-\frac{1}{2}} \quad (1)$$

The formula for a thermo-emf in the semiconductor with any degeneracy of electronic gas in a standard band is expressed as follows [6]:

$$\alpha = -\frac{k_0}{q}(\frac{F_{r+2}}{F_{r+1}} - \eta^*) \quad (2)$$

Interval of change r in the formula (1) and (2), according to the theory of a dispersion, depending on the mechanism of a dispersion, are the following.

r=0; 1; 2 (3) ,

which are defined from temperature dependences of Hall mobility $R\sigma \sim f(T)$, and at a dispersion on acoustic vibrations of a lattice r=0 and $R\sigma \sim AT^{-\frac{3}{2}}$; at a dispersion on optical vibrations of ions of a lattice r=1 and $R\sigma \sim AT^{-\frac{1}{2}}$; at a dispersion on ions of an impurity r=2 and $R\sigma \sim AT^{\frac{3}{2}}$.

The given chemical potential of investigated Ag_2S, in the room temperature range had the negative value. In this range of temperatures we used formula of Pisarenko [6]:

$$\alpha = -\frac{k_0}{q}(r+2-\eta^*) = -86{,}25\cdot(2-\eta^*)\mu V\cdot K^{-1} \quad (4)$$

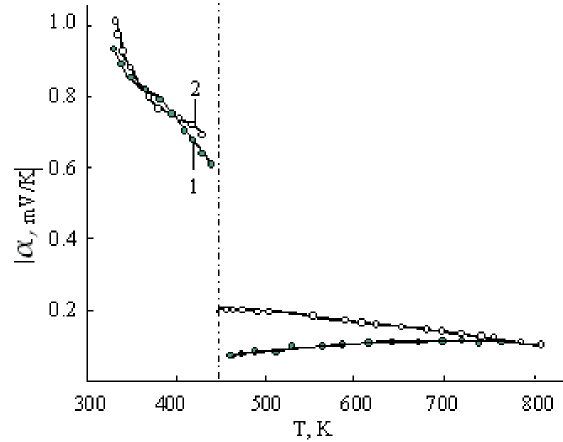

Fig. 2. Temperature dependences of thermo-emf of Ag_2S. 1-monocrystal, 2-polycrystal.

The method of definition of effective mass of current carriers is set up on measuring of temperature dependence of a thermo-emf, an electrical conductivity and a Hall effect on same sample Ag_2S.

Effective mass of current carriers in Ag_2S was defined by a measuring of temperature dependence of the thermo-emf, the electrical conductivity and Hall effect on the same sample. By collateral measuring of the electrical conductivity and Hall effect we defined parameter r, which describes mechanism of dispersion and from the formula (4) we defined the reduced chemical potential $\eta^* = -11.91$. By substitution of this parameter in the formula for concentration of current carriers in the C-band [7]:

$$n = \frac{2N_c}{\sqrt{\pi}} f_{\frac{1}{2}}(\eta^*) \quad (5),\ \text{where}$$

$$N_c = (\frac{2\pi m_n^* k_0 T}{h^2})^{\frac{3}{2}} = 4.82\cdot 10^{15}(\frac{m_n^*}{m_0})^{\frac{3}{2}} T^{\frac{3}{2}} \quad (6)$$

We determine effective mass of electrons by the following formula:

$$\frac{m_n^*}{m_0} = \frac{1}{T}[\frac{n\sqrt{\pi}}{5.44\cdot 10^{15}\cdot f_{\frac{1}{2}}(\eta^*)}]^{\frac{3}{2}} \quad (7)$$

The integral of Fermi - Dirac for nondegenerate semiconductors is the following expression:

$$f_{\frac{1}{2}} = \frac{\sqrt{\pi}}{2} e^{\eta^*} \quad (\text{при } -\infty < \eta^* < -1) \quad (8)$$

Tables of these values are given in the work [6].

Calculation of effective mass of electrons in samples of Ag_2S with various concentration of current carriers between $n=10^{15}sm^{-3}$ and $n=10^{17}sm^{-3}$ up has shown, that the effective mass in the given interval of concentrations (at 300 K) does not depend from concentration. Hence the effective state density N_c is a stationary value and is equal $7.8 \cdot 10^{19}$ cm^{-3}. Knowing this parameter of Ag_2S from the formula (5) represents an opportunity to specify the dependence of Fermi level from carrier density :

$$E_F = kT\ln(\frac{N_c}{n}) \qquad (9)$$

It is possible to specify temperature dependence of the effective mass by the expression (7) . Substituting values N_c, n at various temperatures in the formula (9) represents an opportunity to specify the temperature dependence of the Fermi level in Ag_2S.

Concentration dependence of the relaxation time of electrons was defined by the expression

$$\mu_n = \frac{\tau \cdot q}{2m_n^*} \quad (10),$$

where $\mu_n = \sigma_n/(qn)$ is the electron mobility and m_n^* - effective mass of electron.

As the electron effective mass with concentration does not vary, variation of electron mobility is bound with the change of time of the relaxation. A relaxation time of conduction electrons have an order of magnitude $\tau \sim 10^{-14}$ s that has a good conformity with the data of work [9].

The activation energy of donor levels, defined of temperature dependence of Hall coefficient has made 0.327 eV. Concentration of donor centers was defined under the formula:

$$\Delta E = kT[\frac{4\pi^{\frac{3}{2}}h^2 N_D}{(2m_n^* k_0 T)^{\frac{3}{2}}} \qquad (11)$$

and for sample under №2 at 293 K was equal $10^{14}cm^{-3}$. Concentration of intrinsic carrier concentration at temperature 300 K, defined an extrapolation of the graph $\lg n_i \sim (10^3/T)$ was $n_i = 7\cdot 10^{12}$ cm^{-3} (fig. 27) . Dielectric constant of monocrystal Ag_2S was calculated under the formula

$$\frac{m_0}{m_n^*} = \frac{13.5}{\varepsilon^2 \Delta E_D} = 0.47 \qquad (12)$$

where ΔE_D - the activation energy of donor levels, ε - a dielectric constant, was equal 8.8 and had a good conformity with literary values of ε.

If its are known values of m_0/m_n^* and ε from the other measuring , it is possible to define an activation energy of donor levels under the formula (12). As is known the dielectric constant of the semiconductor equal to a quadrate of its reflection coefficient

$$\varepsilon = (n_r - ik)^2 = n_r - k^2 \qquad (13)$$

is defined by concentration of n , of effective mass of current carriers, of charge q and of circular frequency of an incident wave [8]. In the range of the basic absorption band, where k is few, sufficiently to have only values of index of refraction n_r. When is only known value of forbidden gap (and optical constants are not defined), for evaluation of E_g it is possible to use Moss rule of thumb [8]:

$$E_g \cdot n_r^4 = 173 \qquad (14)$$

As have shown calculations, relations (14) is precisely enough applicable for monocrystal Ag_2S. Since temperature dependence $n_r(T)$ is bound with change of forbidden gap, it is possible to define n_r at a wide range of temperatures $n_r(300K) = 3.68$.

The analysis of temperature dependence of Hall effect showed, that in a temperature band 448-625 K for the majority samples the relation $\lg RT^{3/2} = const$ is fulfilled. Such dependence at presence of the negative course of an electrical conductivity with temperature can be obtained in case if feeble band overlap is takes place i.e. if the structure of semimetal with the negative forbidden band is implemented .

$$E_C - E_V = -\Delta E \qquad (15)$$

As is known, at $kT << |\Delta E|$ a semimetal can be degenerate simultaneously both on electrons, and on electron defects. For such a case, concentrations of electrons and electron defects express accordingly [7]:

$$n = \frac{8\pi}{3}(\frac{2m_n^*}{h^2})^{3/2}(F - E_C)^{3/2} \qquad (16), \text{ and}$$

$$p = \frac{8\pi}{3}(\frac{2m_p^*}{h^2})^{3/2}(E_V - F)^{3/2} \qquad (17)$$

where $F - E_C = E_n$ и $E_V - F = E_p$ (18)

and $E_n + E_p = E_V - E_C = \Delta$ (19)

Using (16), (17), (18) and (19) we can define the band overlap Δ:

$$\Delta = E_n + E_p = \frac{(3\pi^2)^{2/3}\hbar^2}{2m_n^*}\cdot n^{2/3} + \frac{(3\pi^2)^{2/3}\hbar^2}{2m_p^*}\cdot p^{2/3} \qquad (20)$$

For intrinsic concentration of current carriers in a semimetal in the range of degeneration of electronic and hole gas we have $n=p=n_i$ and from (20) we can receive

$$\Delta = C\cdot\frac{1+\beta}{m_n^*}\cdot n_i^{2/3} \qquad (21)$$

where $C = \frac{(3\pi^2)^{2/3}}{2}$, $\beta = \frac{m_n^*}{m_p^*}$ (22)

We guess, that Δ is a linear function of temperature T and m_n^* does not vary then we can receive an expression for intrinsic concentration of current carriers $n_i \sim T^{3/2}$.

Let's estimate Δ also its change with temperature for β- Ag_2S. Unknowns parameters, as n, m_n and β is entered

to the formula (21) . It is possible to define n_i by measuring of Hall effect. We shall assume, that $\beta = \frac{m_n^*}{m_p^*}$ has the same value as in α-Ag_2S, equal β =2.1/3.1. And we can define m_n^* by the measuring of Hall effect and thermo-emf. It permissible, that in β- Ag_2S takes place only degeneration of electronic gas . Thermo-emf for degenerate semiconductor with parabolic band expresses as

$$\alpha = -\frac{\pi^2}{3}(r+1)\cdot\frac{k_0^2 T}{qE_n} \qquad (24)$$

at a dispersion of current carriers on the ultrasonic oscillations of a lattice

$$\alpha = -\frac{\pi^2}{3}\cdot\frac{k_0}{q}\cdot\frac{k_0 T}{E_n} \qquad (25)$$

Let's substitute

$$E_n = C\cdot\frac{n^{2/3}}{m_n} \qquad (26)$$

from expression (25), for effective mass of electrons we can obtain

$$m_n^* = -\frac{3qC}{k_0^2}\cdot\frac{n^{2/3}}{T}\cdot\alpha = -A\cdot\frac{n^{2/3}}{T}\cdot\alpha \qquad (27)$$

The effective mass of charge carriers at 500 K was $m_n^* = 0.2\cdot m_o$. Having substituted this value in (21) and using fig.3 we can obtain the temperature dependence $\Delta \sim T$. The level of band overlap of β-Ag_2S is incremented with increasing of temperature.

Electron mobility of conductance have been designed from experimental dates of σ_e. For β-Ag_2S values of electron mobility was $\mu_n \sim 10^3 sm^2V^{-1}s^{-1}$. Electron mobility of β- Ag_2S , obtained in the work [9] was $\mu_n \sim 1.6\cdot10^2 sm^2V^{-1}s^{-1}$.

The relaxation time $\tau = 2m_n^*\mu_n^*/q$ and medial free path of electrons $l = \tau\sqrt{3kT/m^*}$ have an order of magnitude 10^{-14} and 10^2 Angstrom unit accordingly and are in the consent with the data of works [9, 10]. The relaxation time at constant value of temperature feebly varies with concentration.

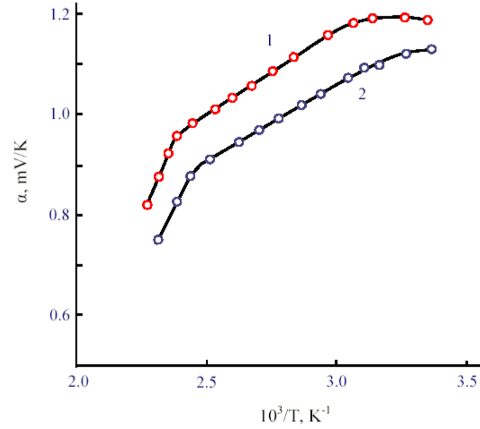

Fig. 3. Temperature dependences of thermo-emf of Ag2S 2-monocrystal, 1-polycrystal.

V. CONCLUSION

Summarizing above-stated data it is possible to say that in monocrystal silver sulphide at structural phase change from monoclinic to a cubic lattice the kinetic parameters change spasmodically. Energy bands of high-temperature β.Ag_2S are feebly overlapped. Engagement factor of overlapping is incremented with propagation of temperature. Character of change of the kinetic parameters in explored fields of temperature testifies to a dispersion of charge carriers in basic on acoustic phonons.

REFERENCES

1. *L. Motte, F. Billoudet, D. ThiaudiAre, A. Naudon and M.-P. Pileni* J. Phys. III France 7517-527
2. *Abdul-Zade N.N., Alekperova Sh.M., Mursakulov N.N.* “Transport phenomenas in a monocrystal of silver sulphide”, the Preprint №83 of the Institute of Physics of NASA, Baku - 1983, 14 pages (in Russian).
3. *Mustafayev F.M., Ismaylov F.I., Abbasov A.S.,* "Neorg. mat. ", v. II, № 9, 1975. (in Russian)
4. *R.N.Iskenderov, R.M.Sultanov, R.B.Shafizade.* The news of NASA .A series of physicotechnical and mathematical sciences 1975, №4, page 98. (in Russian)
5. *R.N.Iskenderov, I.R.Nuriev, R.M.Sultanov, R.B.Shafizade* The news of NASA .A series of physicotechnical and mathematical sciences, v. XXIX, I973, N 5, page I6. (in Russian)
6. *Askerov B.M.* "Kinetic effects in semiconductors" Leningrad. From – in “Science”, 1970, 303 pages. (in Russian)
7. *Kireev P.S.* Physics of semiconductors. Moscow. “Higher school”, 1974 (in Russian)
8. *Moss T.* Optical properties of semiconductors. Moscow. Publishing house “ IL “, 1961, 304 pages (in Russian)
9. *Junod P.* Helv. Phys. Acta, 1959, v32, N6/7, p.567-600.
10. *Astakhov O.P., Godyshev V.D., Sgibnev I.V.* Izv. AS of the USSR « Neorganicheskie materiali», 1973, v.9, №5, p. 841-842 (in Russian).