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Effect of Electron and Hole Doping on the Transport Characteristics of Chalcogenide Systems

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Abstract—The electrical properties of the $Ag_{0.01}Mn_{0.99}S$ and $Tm_{0.01}Mn_{0.99}S$ semiconductor compounds and the Hall effect in them have been investigated in the temperature range of 80–400 K in a magnetic field of 12 kOe. Using the I–V characteristics, the conductivity mechanism depending on the doping type and concentration has been established. Upon substitution of silver for manganese, the Mott-type conductivity has been found, while substitution of thulium causes the ohmic conductivity. The mobility and type of carriers have been determined from the Hall constant data.

Keywords: semiconductors, conductivity, Hall constant, mobility

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1. INTRODUCTION

Study of the electronic phenomena and conductivity mechanism in disordered systems holds a central position in physics of condensed matter. This is, as a rule, due to both the application potential of such systems and the intrinsic logic of the development of physics. At present, europium chalcogenides [1, 2], selenides $CdCr_2Se_4$ and $HgCr_2Se_4$ [3–5], topological insulators Bi_2X_3 (X = Se, Te) [6], and manganese sulfides Me_XMn_{1-X} (Me = 3*d* and 4*f* elements) based on manganese monosulfide [7–9] have been intensively investigated, in which the effect of magnetic order and doping on the transport properties is reflected in the magnetoresistive and galvanomagnetic effects and the metal–insulator transition.

Nonstoichiometry in the α-MnS magnetic semiconductor induces a significant change in the transport and electrical properties. Manganese monosulfide is an antiferromagnet with the type-II ordering on a face-centered cubic (fcc) lattice with a Néel temperature of $T_N = 150$ K, which is characterized by the semiconductor conductivity [10]. According to the Hall effect measurements, in the temperature range of $T < 450$ K, carriers are low-mobility holes (the *p*-type conductivity) localized at the 3*d* levels of the manganese ion [11, 12]. Interest in manganese monosulfide has increased due to the discovery of the magnetoresistive effect with a value of ~12% observed in the α-MnS(111) plane, while in the (100) plane the positive magnetoresistance prevails at temperatures above T_N in a magnetic field of 10 kOe [13]. The value of the magnetoresistive effect significantly increased upon doping of this system with 3*d* metals and rare-earth elements [14, 15].

In electrically inhomogeneous semiconductors, the conductivity is determined by scattering of carriers on charged impurities in a matrix and by hopping over the impurity states. At sufficiently high concentrations, when the thickness of the potential barrier between high-mobility regions is comparable with the average carrier path, the conductivity is implemented along two channels and has a nonlinear character [16]. In the $Me_XMn_{1-X}S$ system with a concentration of $X = 0.01$, substitution of a trivalent thulium ion for manganese will lead to electron doping of the t_{2g} shell and substitution of a monovalent silver ion, to hole doping with the formation of trivalent manganese ions and the degeneracy of the t_{2g} and e_g orbitals, which induces the local Jahn–Teller effects. At low concentrations, an additional contribution to the carrier scattering by local lattice strains will arise and, consequently, the conductivity type and mobility character will change.

In view of the aforesaid, the aim of this study was to establish the effect of the correlation of impurity states on the conductivity mechanism, mobility, and carrier type in the manganese monosulfide system upon electron and hole doping.

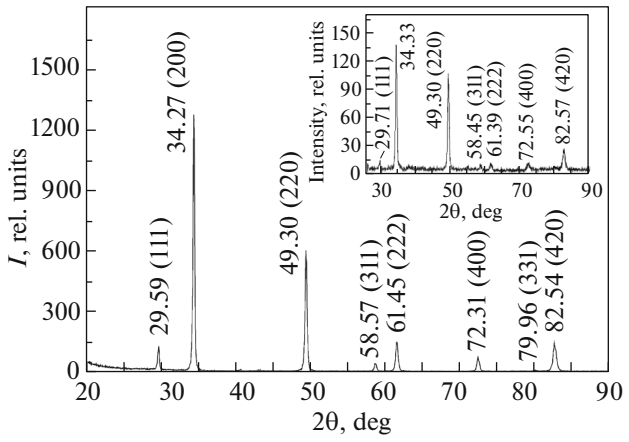

Fig. 1. X-ray diffraction data on the $Ag_{0.01}Mn_{0.99}S$ solid solutions at 300 K. Inset: X-ray diffraction pattern for the $Tm_{0.01}Mn_{0.99}S$ sample.

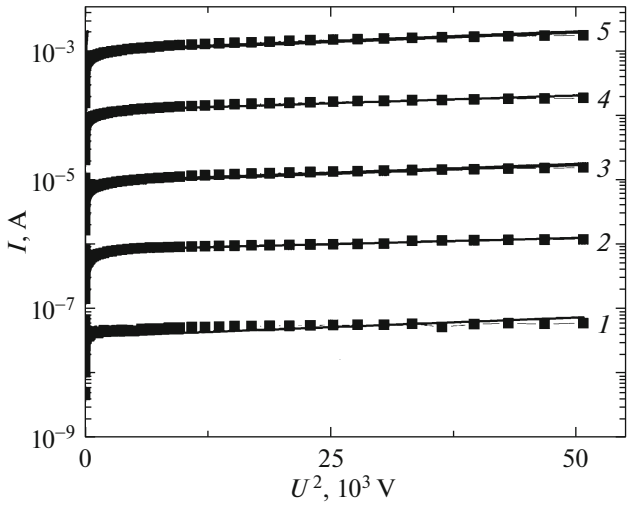

Fig. 2. *I–V* characteristics measured at T = (*1*) 100, (*2*) 140, (*3*) 200, (*4*) 280, and (*5*) 360 K for the $Ag_{0.01}Mn_{0.99}S$ sample.

2. MEASURING TECHNIQUE

The $Ag_{0.01}Mn_{0.99}S$ and $Tm_{0.01}Mn_{0.99}S$ solid solutions were synthesized in glassy carbon crucibles and a quartz reactor by crystallization of the obtained powder sulfides using the flux technique [16, 17]. The X-ray diffraction (XRD) study was carried out on a DRON-3 X-ray diffractometer (CuK_α radiation) at $T = 300$ K.

The effect of electron and hole doping on the transport characteristics was determined from the *I–V* characteristics measured at constant temperatures by a four-probe technique on parallelepiped samples with indium ohmic contacts. The dc Hall voltage measurements were performed in the temperature range of 100–400 K in a magnetic field of 12 kOe. During the measurements, the contributions of the spurious emf induced by side galvanomagnetic and thermomagnetic effects and the nonequipotentiality of the arrangement of Hall probes were taken into account by measuring in zero magnetic field.

3. RESULTS AND DISCUSSION

According to the XRD data, the $Ag_{0.01}Mn_{0.99}S$ and $Tm_{0.01}Mn_{0.99}S$ samples are single-phase polycrystalline compounds with a NaCl-type fcc structure characteristic of manganese monosulfide [18]. As the degree of cationic substitution X increases, the unit cell parameter a slightly grows with increasing ionic radius of the substituent (r = 0.083 nm for Mn, r = 0.113 nm for Ag, and r = 0.117 nm for Tm). The XRD data on these systems are presented in Fig. 1.

The *I–V* characteristics of the $Ag_{0.01}Mn_{0.99}S$ and $Tm_{0.01}Mn_{0.99}S$ samples were analyzed using the Poole–Frenkel and Mott mechanism and the Ohm's law. Figure 2 shows the dependences of current I on the squared voltage U at temperatures of 100, 140, 200, 280, and 360 K. From the slope of the $I(U^2)$ curves shown in Fig. 2, we established the presence of linear portions over the entire voltage range at temperatures above 100 K. The linearity of these dependences points out the dominant contribution of the space-charge-limited currents [19], which is described by the quadratic Mott law. The experimental *I–V* characteristics for the $Ag_{0.01}Mn_{0.99}$ system are satisfactorily described by Eq. (1) and the conductivity, by the Mott law [20]

$$j = 9/8\tau_\mu\sigma_0\mu U^2/L^3, \quad (1)$$

where j is the current density, τ_μ is the Maxwell relaxation time, σ_0 is the electrical conductivity in the bulk of the material in the absence of carrier injection, μ is the carrier mobility, U is the applied voltage, and L is the sample thickness. The conductivity mechanism in $Ag_XMn_{1-X}S$ depends on the substitution concentration. For example, at $x = 0.05$, the Ohm's law is satisfied and the *I–V* characteristic is linear [17].

Electron doping qualitatively changes the conductivity mechanism. Figure 3 shows the *I–V* characteristic of the $Tm_{0.01}Mn_{0.99}S$ solid solution on a logarithmic scale in the temperature range of 120–280 K. In this temperature range, the *I–V* characteristic is linear. Using the slope of the curves, which was no more than unity, we established the ohmic conductivity of this system. At the high concentrations $x > 0.05$ in the $Tm_XMn_{1-X}S$ system, the *I–V* characteristic is nonlinear [16]. The shapes of the *I–V* curves obtained at different temperatures does not significantly differ. An increase in the conductivity is caused by an increase in the concentration and mobility of carriers.

The type of carriers and their mobility upon electron (Tm) and hole (Ag) doping was determined by

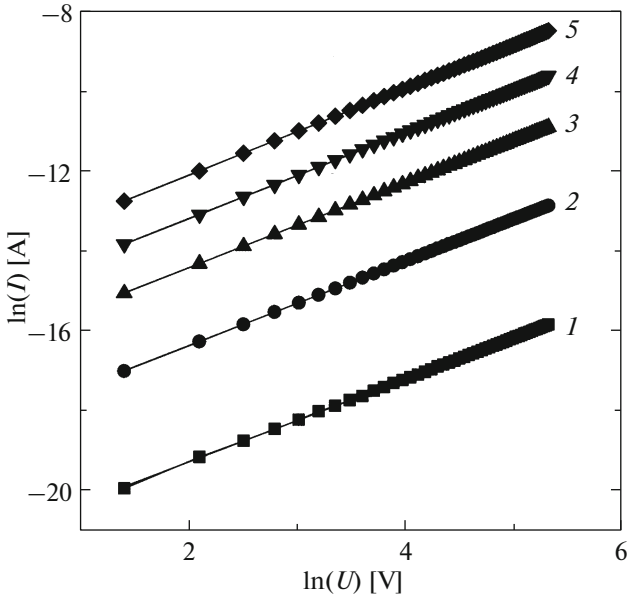

Fig. 3. Logarithmic I–V characteristics measured at T = (*1*) 120, (*2*) 160, (*3*) 200, (*4*) 240, and (*5*) 280 K for the $Tm_{0.01}Mn_{0.99}S$ sample.

studying the galvanomagnetic properties. At T < 450 K, the majority carriers in manganese monosulfide are holes with a mobility of 0.065 $cm^2\ V^{-1}\ s^{-1}$ at T = 435 K [11]. Above 450 K, electrons become carriers. Figures 4a and 4b show temperature dependences of the Hall constant R_H for $Ag_{0.01}Mn_{0.99}S$ and $Tm_{0.01}Mn_{0.99}S$, respectively. The shape of the $R_H(T)$ curves depends on the type of a substituent. In the investigated systems, as in the initial manganese monosulfide, the sign of majority carriers changes with temperature. At low temperatures (at T < 95 K for the $Ag_{0.01}Mn_{0.99}S$ system and at T < 100 K for $Tm_{0.01}Mn_{0.99}S$), the majority carriers are holes. According to the literature [21], in this temperature range, the lattice contraction of the initial manganese monosulfide matrix is observed, which is accompanied by rhombohedral distortion, according to the data on the lattice thermal expansion coefficient.

In the $Ag_{0.01}Mn_{0.99}S$ system, upon substitution of silver for manganese, R_H changes its sign in the temperature range of 95–125 K and above 350 K and has a broad maximum in the range of 240–300 K (Fig. 4a). It can be seen in Fig. 5a that, above 200 K, the mobility of the hole-type majority carriers sharply increases and, at 250 K, passes through a maximum.

In $Tm_{0.01}Mn_{0.99}S$, a decrease in the Hall constant by two orders of magnitude in comparison with $Ag_{0.01}Mn_{0.99}S$ as a result of electron doping was detected (Fig. 4b). In the region of the magnetic phase transition (T_N = 172 K) in $Tm_{0.01}Mn_{0.99}S$, the Hall constant takes negative values and the carrier mobility slightly increases (Fig. 5b). Upon heating above

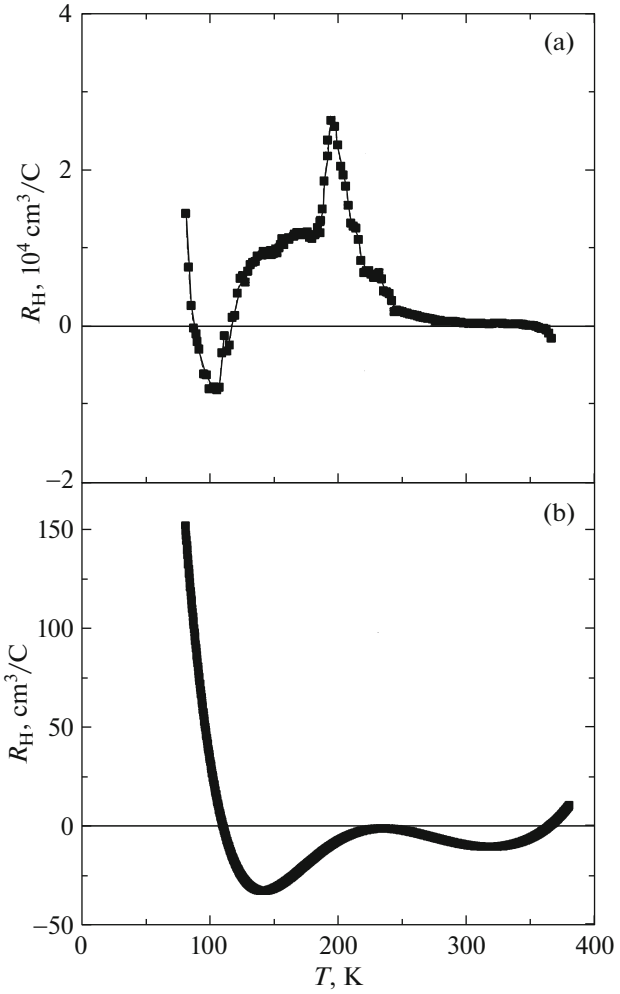

Fig. 4. Temperature dependences of the Hall constant for (a) $Ag_{0.01}Mn_{0.99}S$ and (b) $Tm_{0.01}Mn_{0.99}S$.

200 K, the mobility increases and attains its maximum value above room temperature. Another change in the R_H sign from negative to positive is observed around 360 K.

The study of the galvanomagnetic properties of the $Tm_{0.01}Mn_{0.99}S$ and $Ag_{0.01}Mn_{0.99}S$ solid solutions showed that the replacement of Mn^{+2} cations by Ag^{+1} and Tm^{+3} ions leads to the occurrence of both types of carriers (holes and electrons) in these substances. These compounds can be classified as mixed-type semiconductors. The ratio between the hole and electron densities determines the type of carriers, which changes with temperature and depends on the type of a substituent.

4. CONCLUSIONS

It was found that the conductivity mechanism in the $Me_XMn_{1-X}S$ chalcogenide systems depends on the concentration and type of a substituent. The conductivity of $Ag_{0.01}Mn_{0.99}S$ is described by the Mott law

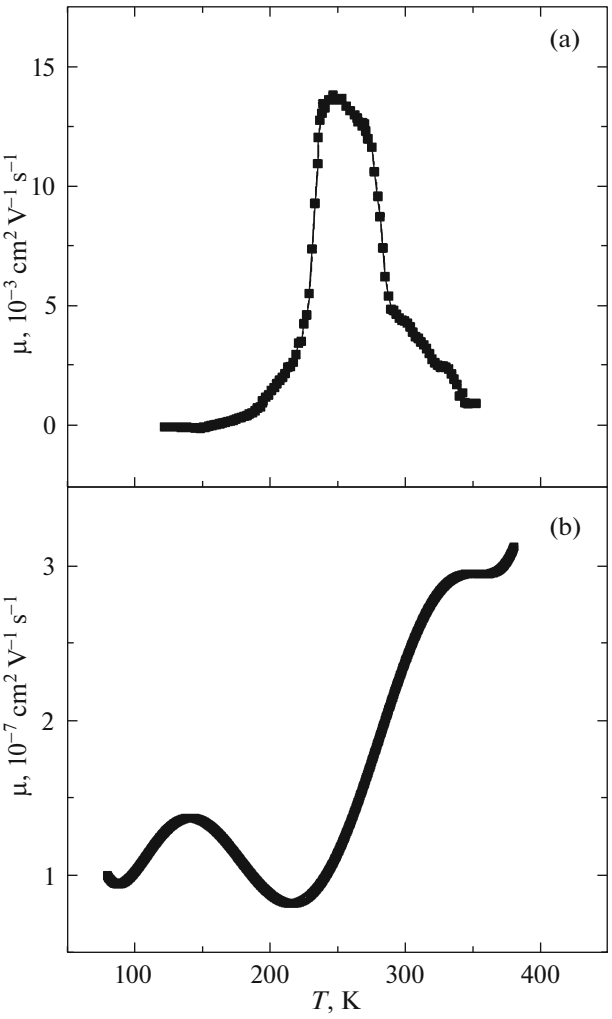

Fig. 5. Temperature dependences of the carrier mobility for (a) the $Ag_{0.01}Mn_{0.99}S$ and (b) $Tm_{0.01}Mn_{0.99}S$ samples.

and the conductivity of $Tm_{0.01}Mn_{0.99}S$, by the Ohm's law in a wide temperature range. Using the Hall measurements, the temperature regions of the change in the type of carriers and an anomalous behavior of their mobility were determined.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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