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SEMICONDUCTORS

Galvanomagnetic Properties of Polycrystalline Manganese Selenide $Gd_{0.2}Mn_{0.8}Se$

O. B. Romanova[a, b, *], S. S. Aplesnin[a, b], A. M. Khar'kov[b], A. N. Masyugin[b], and K. I. Yanushkevich[c]

[a] *Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, 660036 Russia*
[b] *Siberian State Aerospace University, Krasnoyarsk, 660014 Russia*
[c] *Scientific and Practical Materials Research Center, National Academy of Sciences of Belarus, Minsk, 220072 Belarus*
**e-mail: rob@iph.krasn.ru*

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Abstract—The electrical and galvanomagnetic properties of the $Gd_{0.2}Mn_{0.8}Se$ solid solutions are investigated in zero magnetic field and in a field of 13 kOe in the temperature range of 80–400 K. The negative magnetoresistance below room temperature and hysteresis of the $I–V$ characteristics are found. The change in the magnetoresistance sign and thermopower with increasing temperature is established. The carrier type is determined from the Hall constant; the difference between the thermopower and Hall coefficient signs at high temperatures is established. The experimental data are explained using the model of orbital ordering and spin-orbit interaction.

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1. INTRODUCTION

The development of magnetic semiconductors is interesting both for fundamental research and application in microelectronic, including spintronic, elements operating in a wide temperature range. The operation of spintronic devices is based on the magnetoresistive effect. Transition metal chalcogenides and their solid solutions were found to be excellent model objects for studying this effect. The investigations of manganese monosulfide and solid solutions synthesized on its basis using cation substitution of 3*d* (Fe, Cr, Co, etc.) [1] and 4*f* (Gd, Yb, Sm, etc.) elements [2, 3] disclosed the magnetoresistive effect and metal–dielectric transition upon variation in the substitution concentration, magnetic field, and temperature.

In the $Gd_xMn_{1-x}S$ manganese sulfides, the change of the magnetoresistance sign from positive to negative was observed and the magnetoresistance maximum in the region of the transition to the magnetically ordered state for two compositions at a percolation concentration of about $x_c = 0.16$ was found [4]. The permittivity growth and magnetocapacitive effect were established [5]. Upon anion substitution of manganese selenide, the negative magnetoresistance above the Neel temperature up to room temperatures was observed [6]. In view of the aforesaid, synthesis of a new chalcogenide compound using cation substitution of gadolinium for manganese in the MnSe system will make it possible to clarify the effect of the anion system by studying its transport and galvanomagnetic properties at a concentration of $x = 0.2$ in the region of percolation of gadolinium ions through the lattice.

The initial manganese monoselenide is an antiferromagnetic *p*-type semiconductor with a face-centered cubic (fcc) lattice and a cubic unit cell [7, 8]. Complex investigations of the electrical and optical properties showed that the MnSe band gap can be $E_g = 2.30$ eV [9]. Upon cooling and heating of MnSe, the temperature dependence of its resistivity has a hysteresis in the temperature range of $125\ \text{K} < T < 260\ \text{K}$, which is caused by the coexistence of the cubic and hexagonal modifications. The temperature of the magnetic phase transition determined from the neutron diffraction data [10] is $T_N = 135$ K for the MnSe cubic modification; in the hexagonal NiAs phase, it coincides with a temperature of $T_s = 272$ K of the structural transition. In MnSe [11], the resistivity decreases with increasing external magnetic field.

Gadolinium selenide is widely used in the production of radioisotope energy sources. The GdSe compound is characterized by the metal-type conductivity and at low temperatures (50 K) transforms to the magnetically ordered (antiferromagnetic) state [12]. The compound crystallizes in the NaCl-type cubic structure with a unit-cell parameter of 0.5775 nm. Substitution of rare-earth element ions for manganese cations leads to electron doping and formation of additional exchange ferromagnetic interactions between manganese ions as a result of the *s–d* kinetic interaction. One can expect the change of the magnetic structure,

intensification of the ferromagnetic properties, change in the conductivity type, and the magnetoresistive effect.

The aim of this study was to establish the effect of the anion subsystem on the galvanomagnetic properties of the substituted selenides, including the transport properties in magnetic field, in the region of the rare-earth ion percolation concentration.

2. EXPERIMENTAL, RESULTS, AND DISCUSSION

The $Gd_xMn_{1-x}Se$ ($x = 0.2$) solid solutions were prepared from powders of the initial compounds by the solid-state reaction [13] in evacuated quartz ampoules placed in a one-zone resistance furnace.

Phase composition and crystal structure of the $Gd_xMn_{1-x}Se$ samples were determined at 300 K on a DRON-3 X-ray facility (CuK_α radiation). According to the X-ray diffraction (XRD) data, the synthesized compounds have a NaCl-type fcc structure typical of manganese monoselenide. As the degree of cation substitution (x) increases, the unit-cell parameter a grows from $a = 0.5440$ nm for MnSe to $a = 0.5520$ nm for $Gd_{0.2}Mn_{0.8}Se$ in accordance with the growth of the substitute ionic radius ($r = 0.83$ Å for Mn and 0.94 Å for Gd). The investigated compounds with a substitution concentration of $x = 0.2$ are antiferromagnets with a Neel temperature of $T_N = 80$ K and a negative paramagnetic Curie temperature Θ with the absolute value decreasing relative to the initial compound (from -350 K at $x = 0$ to -86 K at $x = 0.2$), which is indicative of the increase in the ferromagnetic correlations with increasing gadolinium concentration [13]. The enhancement of the ferromagnetic correlations is confirmed by the changes in the behavior of the resistivity, magnetoresistance, and Hall effect.

The resistivity measurements were performed by a four-probe technique in zero magnetic field and in a field of 13 kOe directed perpendicular to the current. The results of the electric measurements are presented in Fig. 1. The temperature dependence of the resistivity for the $Gd_{0.2}Mn_{0.8}Se$ sample is indicative of the semiconductor conductivity type, analogously to MnSe [11, 14]. The band gap ΔE determined from the slope of the straight portion of the dependence $\log\rho(1/T)$ is ~0.3 eV; in a magnetic field, this value remains invariable. The ρ value of the $Gd_{0.2}Mn_{0.8}Se$ samples is lower than in the initial manganese monoselenide. The similar behavior was observed upon substitution of gadolinium ions for manganese in the MnS system [15]. It should be noted that at $T = 250$ K, the resistivity is nearly temperature-independent. As the temperature further increases, the resistivity drops in accordance with the exponential law. The magnetoresistance $\delta_R = (R(H) - R(0))/R(0)$ in the Gd–Mn–Se system with a substitution concentration of $x = 0.2$ changes its sign at $T = 320$ K with increasing temperature. At this temperature, the Hall constant sharply decreases, the I–V characteristic has a wide hysteresis, and there is the maximum in the temperature dependence of the thermopower.

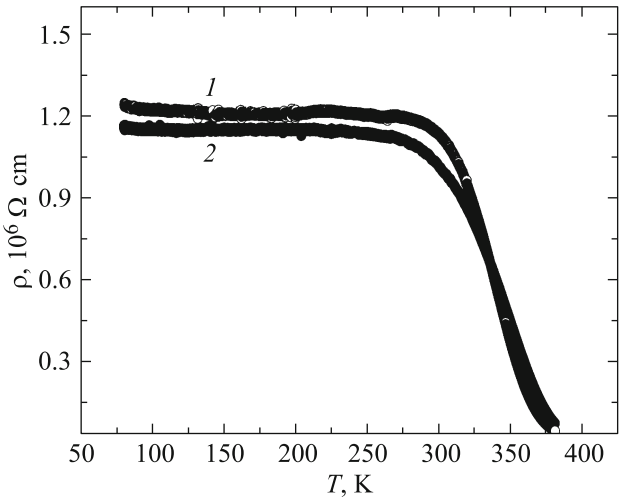

Fig. 1. Temperature dependences of the resistivity for the $Gd_xMn_{1-x}Se$ ($x = 0.2$) system (*1*) in zero magnetic field and (*2*) in a field of 13 kOe.

The presence of the negative magnetoresistance is confirmed by the I–V characteristics (Fig. 2) of the polycrystalline $Gd_{0.2}Mn_{0.8}Se$ sample in magnetic fields of $H = 0$ and 13 kOe. In a magnetic field, the hysteresis weakens. Substitution of a trivalent gadolinium ion for a divalent manganese ion leads to the electron density redistribution between the Mn^{2+} and Gd^{3+} t_{2g} states and e_g states. Due to the strong electron correlations, the orbital ordering occurs on the nearest manganese ions and gadolinium ions. The latter percolate through the lattice and demonstrate the orbital ferromagnetic ordering divided in domains. There is the strong Rashba spin-orbit interaction at the Mn–Gd interface [16]. In the gadolinium subsystem, the orbital moment $\langle L^z \rangle$ on an ion polarizes conduction electron spins, which leads to splitting of the electron excitation spectrum at the interface by $2\lambda\langle L^z\rangle\sigma$, where λ is the parameter of the spin-orbit interaction of 5d electrons and σ is the conduction electron spin. In a magnetic field, domains with the orbital momentum oriented antiparallel to the field disappear and the density of domains with the angular momenta oriented along the field increases. This leads to an increase in the conduction current $U_{\delta\max} = 40$ V and $U(dI/dU = \max) = 50$ V at $T = 80$ K. Due to the Coulomb interaction, the external electric field leads to the change of the electron momentum, rotation of the magnetic moment vector, and domain coalescence. This process gives rise to the hysteresis of the I–V characteristic.

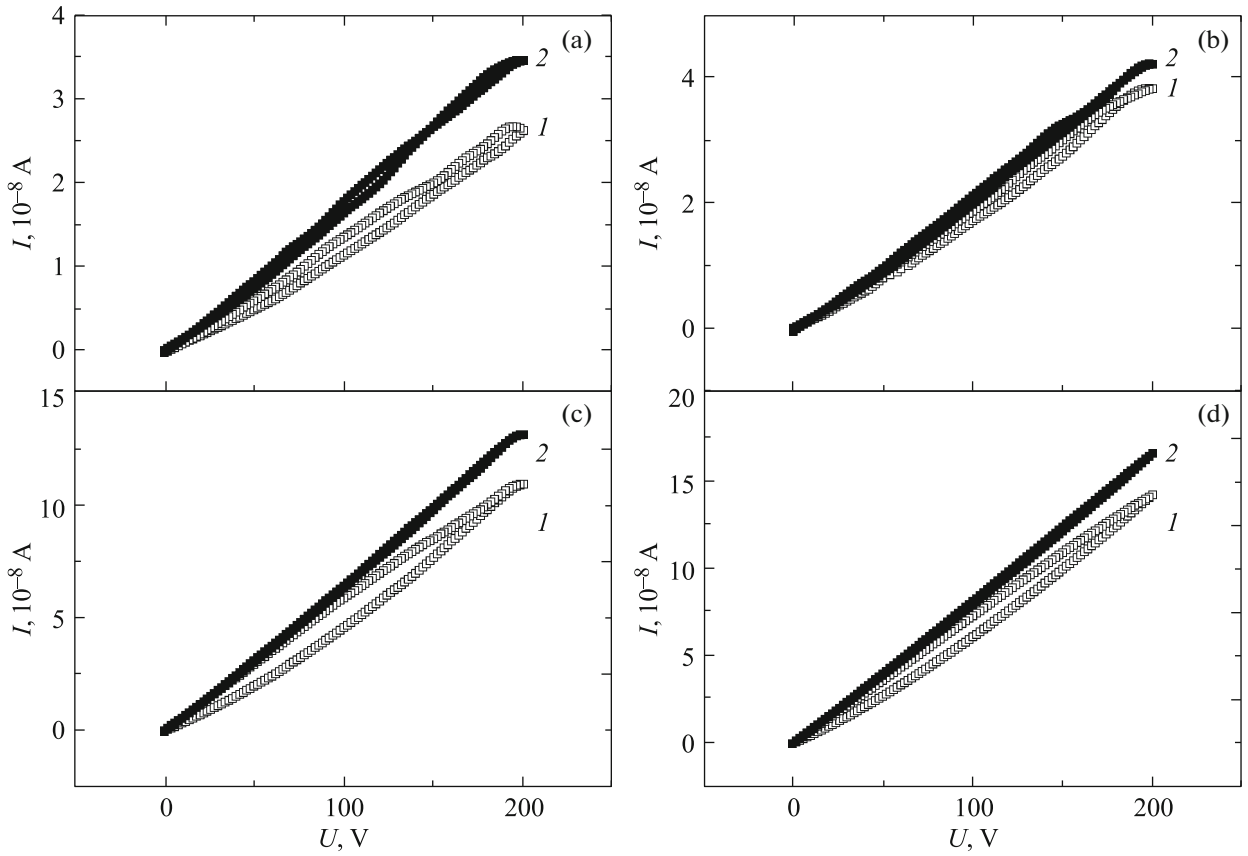

Fig. 2. *I–V* characteristics for the $Gd_{0.2}Mn_{0.8}Se$ sample (*1*) in zero magnetic field and (*2*) in a field of 13 kOe at T = (a) 80, (b) 160, (c) 200, and (d) 280 K.

The magnetoresistance $\delta_R = (R(H) - R(0))/R(0)$ depends on the external electric field; the maxima of the absolute value of the magnetoresistance are observed up to 200 K. The δ_R values for some temperatures are presented in Fig. 3. The voltages at which the magnetoresistance and derivative dI/dU attain their maxima are similar. In particular, we have $U_{\delta max}$ = 40 V and $U(dI/dU = max) = 50$ V at $T = 80$ K, $U_{\delta max}$ = 88 V and $U(dI/dU = max) = 74$ V at $T = 160$ K, and $U_{\delta max}$= 184 V and $U(dI/dU = max) = 184$ V at T = 200 K. The maximum values are attained upon domain structure variation. In the magnetically ordered region, the resistance drop in a magnetic field attains 30–40%. This is related to the formation of ferromagnetic regions (ferrons) in the antiferromagnetic matrix. In a magnetic field, the ferron size increases, the potential barrier between ferrons narrows, and the carrier mobility grows. The change in the magnetoresistance sign at T = 320 K is caused by degeneracy elimination in the electron momentum and spin direction; i.e., spin splitting in the electron excitation spectrum in the Rashba model is comparable with the heat energy. The resistance growth in a magnetic field is related to a decrease in the carrier mobility in the gadolinium ion subsystem due to the orbital electron ordering [17].

The carrier type in the cation-substituted $Gd_xMn_{1-x}Se$ solid solutions was determined from the Hall-effect measurements. Figure 4a shows temperature dependences of the Hall coefficient for the $Gd_{0.2}Mn_{0.8}Se$ sample. The dc Hall-effect measurements were performed in the temperature range of 80–400 K. During the measurements, we took into account the contributions of the spurious voltages caused by side galvanomagnetic and thermomagnetic effects and the asymmetry of contacts. Upon substitution of gadolinium for manganese, the carrier type changes from holes (typical of manganese monoselenide [18]) to electrons (typical of $Gd_{0.2}Mn_{0.8}Se$). The temperature dependence of the R_H contains a portion where the Hall constant takes positive values at T = 195–275 K (Fig. 4a). The occurrence of portions with the positive R_H value in the temperature dependence of the Hall constant is related, first, to the presence of carriers of different signs in the $Gd_xMn_{1-x}Se$ solid solutions, second, to an increase or decrease in their number at different temperatures, and, third, to the carrier mobility.

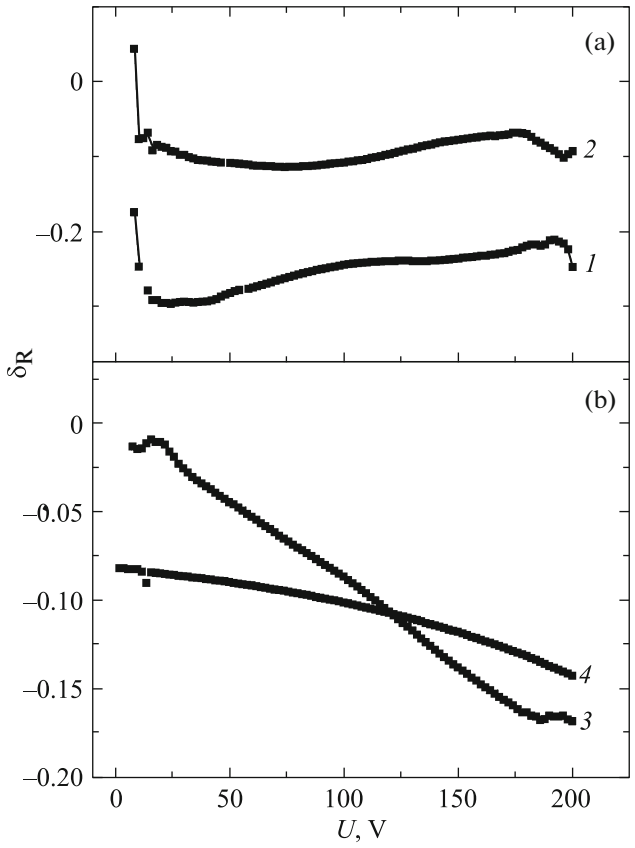

Fig. 3. Voltage dependence of magnetoresistance for the $Gd_{0.2}Mn_{0.8}Se$ sample at $T =$ (*1*) 80, (*2*) 160, (*3*) 200, and (*4*) 280 K.

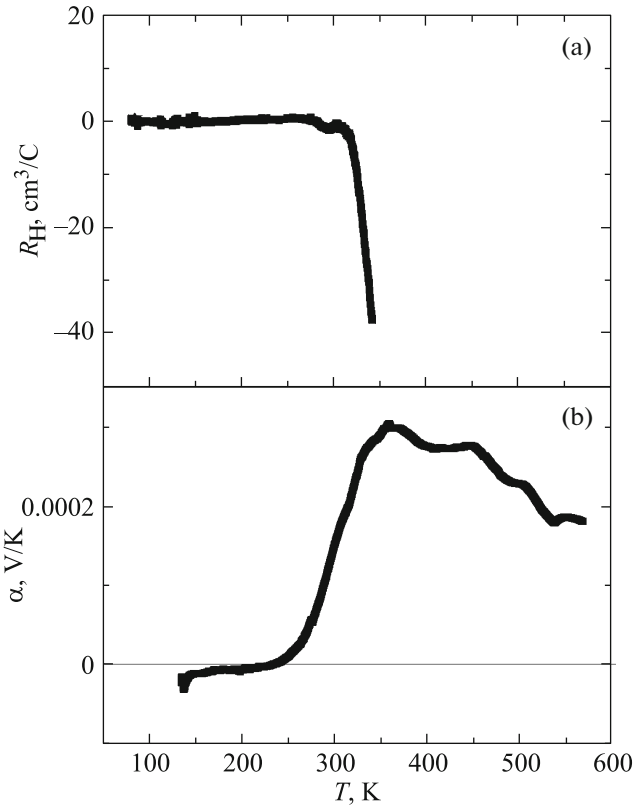

Fig. 4. Temperature dependences of (a) the Hall constant and (b) thermopower for the $Gd_{0.2}Mn_{0.8}Se$.

According to the literature data [12], the results of investigations of the differential thermopower of monochalcogenides of trivalent rare-earth elements showed that its sign, in most cases, is different from the Hall constant sign and its temperature dependence is complex. Figure 4b shows temperature dependences of the thermopower of the $Gd_xMn_{1-x}Se$ ($x = 0.2$) solid solutions. As is known, the thermopower is the most sensitive kinetic electron property of a metal. The temperature growth leads to the change in the thermopower sign from negative to positive at $T = 240$ K and, at $T = 350$ K, the thermopower attains its maximum values. The different signs of the Hall constant and thermopower above 275 K can be caused by electron drag by phonons. As a rule, the presence of the orbital ordering leads to the strong electron-phonon interaction.

Our data on the kinetic properties of the chalcogenide system showed that the $Gd_{0.2}Mn_{0.8}Se$ system contains two types of carriers: holes and electrons. According to the temperature dependences of the Hall constant, at high temperatures the majority carriers are electrons.

4. CONCLUSIONS

In the $Gd_xMn_{1-x}Se$ ($x = 0.2$) solid solutions based on manganese selenide, the resistivity drop in magnetic fields below 320 K was observed, similar to the case of the anion tellurium substitution. At high temperatures, the resistivity increased in a magnetic field. The experimental data are explained by the formation of orbital ordering and spin–orbit interaction in the Rashba model at the gadolinium and manganese ion interface. The I–V hysteresis induced by orbital magnetic domains and the dependence of the electron momentum on spin polarization was established.

In the temperature range of the negative magnetoresistance, there are two carrier types, electrons and holes, while in the region of the positive magnetoresistance electrons prevail. The presence of two carrier types is confirmed by the thermopower data. The difference between the Hall coefficients and thermopower above room temperature was found and attributed to electron drag by phonons as a result of the electron-phonon interaction.

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