

# Magnetic and Electrical Properties of Cation-Substituted Sulfides $Me_xMn_{1-x}S$ ( $Me = Co, Gd$ )

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**Abstract**—The temperature dependences of the specific magnetization  $\sigma$  and the electrical resistivity  $\rho$  of  $Me_xMn_{1-x}S$  single crystals ( $Me = Co, Gd$ ;  $x = 0.05$ ) have been studied in the temperature range  $80\text{ K} < T < 1000\text{ K}$ . The samples under study have revealed the presence of a spontaneous magnetic moment below the Néel temperature ( $T_N$ ) and ferromagnetic clusters in  $Gd_{0.05}Mn_{0.95}S$  in the temperature range  $146\text{ K} < T < 680\text{ K}$ . Substitution of gadolinium for manganese initiates a transition from  $p$ -type to  $n$ -type conduction. The change in the conduction type is accompanied by an increase in the electrical resistivity at 300 K by approximately one order of magnitude and, accordingly, by a decrease in the activation energy. The magnetic and electrical properties of the crystals under study have been interpreted in terms of the cluster model with temperature-dependent ferromagnetic exchange and an electron localized in this cluster.

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## 1. INTRODUCTION

Materials with intimately interrelated magnetic and electrical properties have attracted interest in connection with their possible application in devices intended for spintronics [1, 2]. Disordered systems revealing metal–insulator (MI) transitions and colossal magnetoresistance (CMR) belong in this class [3–7]. The cation-substituted sulfides  $Me_xMn_{1-x}S$  ( $Me = Cr, Fe, Co$ ) synthesized on the basis of  $\alpha$ -MnS hold promise as subjects for investigation of the metal–insulator transition and CMR effects [8–11].

The  $\alpha$ -MnS monosulfide is an antiferromagnet ( $T_N = 150\text{ K}$ ) with a NaCl-type FCC lattice. Its magnetic structure exhibits ferromagnetic ordering of magnetic moments of manganese ions in the (111)-type plane and antiferromagnetic ordering between planes [12, 13]. Band structure calculations of  $\alpha$ -MnS performed within the density functional theory [14] suggest partial filling of the upper Hubbard  $t_{2g}$  and  $e_g$  bands resulting from  $p$ – $d$  hybridization of sulfur and manganese ions. The conduction mediated by electrons located below the Fermi level in the  $t_{2g}$  and  $e_g$  bands is of the hole nature, which is confirmed by thermopower

and Hall effect measurements [15]. Calculations [16] reveal the existence in  $\alpha$ -MnS of a charge-density wave which can become pinned when manganese cations are replaced by other transition metals, for instance, by the divalent cobalt cation  $Co^{2+}$  whose  $t_{2g}$  shell lacks one electron to complete filling, a situation that can be visualized with one hole. Coulomb orbital interaction can give rise at some temperature to charge–orbital ordering.

Insertion of one electron into the  $t_{2g}$  shell in the  $5d$  level can shift the lower Hubbard band toward the conduction band as a result of  $sd$  interaction and initiate ferromagnetic exchange in a local region, i.e., the ferron (according to the terminology used by Nagaev [17]). The orbital splitting induces lattice distortion, which is a dynamic nature and results in the hopping integrals becoming dependent on electron–phonon coupling.

These effects can become probable when the manganese cations are replaced by the rare-earth gadolinium ion. A comparison of the electronic terms of the  $Mn^+Gd^{3+}$  and  $Mn^{2+}Gd^{2+}$  pairs in ionization energy, which for the  $Mn^+$  and  $Mn^{2+}$  ions is  $E = 15.6$  and  $33.7\text{ eV}$ , and for  $Gd^{2+}$  and  $Gd^{3+}$ ,  $E = 20.6$  and  $4.0\text{ eV}$ ,

respectively, suggests preferential formation of divalent gadolinium cations with the  $4f^1, 5d^1$  term configuration.

Our purpose was to study the effect exerted on the magnetic and electrical properties of  $Me_xMn_{1-x}S$  crystals ( $Me = Co, Gd; x = 0.05$ ) by hole and electron doping produced by cation substitution of cobalt and gadolinium for the manganese.

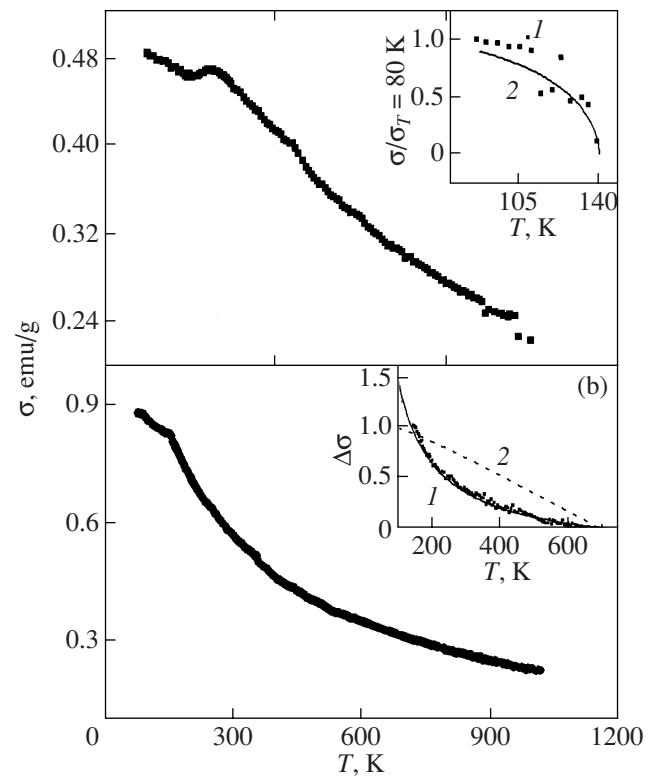
## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Samples of sulfides  $Me_xMn_{1-x}S$  ( $Me = Co, Gd; x = 0.05$ ) were synthesized from the following initial compounds: commercial oxides  $MnO_2$ ,  $CoO$ , and  $Gd_2O_3$  (purity no worse than 99.9%),  $NH_4CNS$  as a sulfurizing reagent, and high-purity argon as a carrier gas. The calculated mixture of the oxides was placed in a glassy-carbon boat into a quartz tube. After the air had been displaced by argon and the products of decomposition of ammonium rhodanide from a separate reactor, the furnace was switched on. The synthesis was performed in two steps, with the mixture heated to  $500^\circ C$  and kept at this temperature for 1 h, and after grinding, repeated sulfurizing for 3 h at  $750\text{--}800^\circ C$ . To make sulfurizing complete, the sulfide powder thus obtained was subjected to homogenization annealing for 30 h in sulfurizing atmosphere at  $800^\circ C$ , interrupted by repeated grinding. The completeness of the sulfurizing procedure was checked by X-ray diffraction analysis and weighing.

Crystallization from the sulfide melt was effected by high-frequency heating (with VChG-25-440 equipment) of a graphite crucible (10 mm in diameter) into which 6–7 g of the sulfide powder was placed. The quartz reactor with the crucible was drawn with a velocity of 0.5 to 1.0 cm/h through a one-turn inductor. The inert atmosphere in the reactor was supported by argon. To obtain a sulfide melt, one determined experimentally the parameters of the power fed into the reactor.

The crystal structure of the samples was studied on a DRON-3 diffractometer (monochromatic  $CuK_\alpha$  radiation) at room temperature. The electrical resistivity measurements were performed within the temperature interval 80–1000 K by the standard four-point probe dc compensation method in zero magnetic field. The thermopower was measured with a setup used to establish the conduction type. The magnetic measurements were performed in the temperature interval of 100–1000 K in a field of 8.6 kOe on samples placed in evacuated quartz ampules.

The X-ray diffraction analysis showed that the  $Me_xMn_{1-x}S$  single-crystal samples ( $Me = Co, Gd; x = 0.05$ ) have the NaCl-type fcc lattice characteristic of  $\alpha$ -MnS. In accordance with the ionic radii of the substituting elements, doping with cobalt reduces the lattice parameter  $a = 5.225 \text{ \AA}$  of  $\alpha$ -MnS to  $5.216 \text{ \AA}$  for  $Co_{0.05}Mn_{0.95}S$ , while doping with gadolinium increases it to  $5.274 \text{ \AA}$  for  $Gd_{0.05}Mn_{0.95}S$ . The diffraction patterns

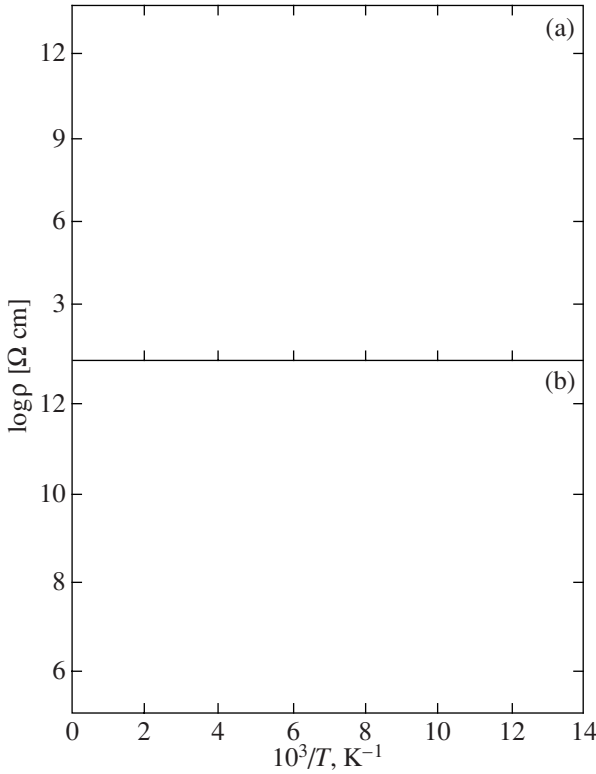


**Fig. 1.** Temperature dependences of the magnetization in the field  $H = 8.6$  kOe for the (a)  $Co_{0.05}Mn_{0.95}S$  and (b)  $Gd_{0.05}Mn_{0.95}S$  samples. Inset (a) shows the temperature dependence of the normalized magnetization  $\sigma/\sigma_{T=80\text{ K}}$  for  $Co_{0.05}Mn_{0.95}S$  according to (1) experiment and (2) theory. Inset (b) shows the temperature dependence of the normalized magnetization  $\Delta\sigma = (\sigma_{Gd} - \sigma_{Mn})(T)/(\sigma_{Gd} - \sigma_{Mn})(T = T_N)$  for  $Gd_{0.05}Mn_{0.95}S$ : (1) normalized magnetization for  $\lambda \approx 0.5$ ,  $\omega_f = 305$  K and (2) probability of observation of a ferromagnetically ordered cluster with an electron localized in it.

of the sulfides under study were measured on powders obtained by grinding the crystals.

Figure 1 plots the behavior with temperature of the magnetization of  $Me_xMn_{1-x}S$  samples ( $Me = Co, Gd; x = 0.05$ ). In the region of  $T_N \sim 180$  K for  $Co_{0.05}Mn_{0.95}S$  and  $T_N \sim 146$  K for  $Gd_{0.05}Mn_{0.95}S$ , maxima appear in the temperature dependence of the magnetization  $\sigma(T)$ , which are signatures of the antiferromagnetic transition in the compounds under study. Above  $T_N$ , the pattern of the temperature dependence of magnetization for  $Co_{0.05}Mn_{0.95}S$  is described by the Curie–Weiss law, while for  $Gd_{0.05}Mn_{0.95}S$  a deviation from this law is observed.

Figure 2 illustrates measurements of the electrical resistivity of the  $Me_{0.05}Mn_{0.95}S$  sulfides ( $Me = Co, Gd$ ) performed in the temperature range 80–1000 K. The temperature dependences  $\log\rho(10^3/T)$  for these samples suggest semiconducting behavior, with the electrical resistivity of  $Gd_{0.05}Mn_{0.95}S$  an order of magnitude being larger ( $\rho_{300\text{ K}} \sim 10^6 \text{ \Omega cm}$ ) than that of the  $Co_{0.05}Mn_{0.95}S$  composition. In the Néel temperature



**Fig. 2.** Temperature dependences of the electrical resistivity for the (a)  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  and (b)  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  samples.

region ( $T_N$ ) for both samples one observes an insulator–semiconductor-type anomaly in the  $\log \rho(10^3/T)$  dependences. Below  $T_N$ , the activation energy  $\Delta E \sim 0.01$  eV. For  $T > T_N$ , the activation energy varies from 0.46 eV for  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  to 0.26 eV for the  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  composition. Above 600 K, intrinsic conduction sets in the  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  sample. The band gap width was found to be  $\Delta E \sim 0.17$  eV. Thermopower measurements suggest transition of conduction in the compositions under study from  $p$  type for  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  to  $n$  type for  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$ .

### 3. DISCUSSION OF THE RESULTS

To determine the contribution of cobalt and gadolinium ions to magnetization, we subtract from the temperature dependence of the magnetization measured on  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  and  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  samples in an external magnetic field the magnetization of  $\text{MnS}$ . Obviously enough, in the samples under study one observes for  $T < T_N$  formation of a spontaneous magnetic moment. The inset in Fig. 1a shows the normalized magnetization as a function of temperature and the approximation of the experimental data with the Brillouin function  $\sigma = B_S(X)$ , where  $X = 2S^2zJgM/k_B T$ ,  $M$  is the reduced magnetization,  $g = 2$  is the spectroscopic splitting factor,  $T$  is the temperature,  $J$  is the exchange interaction parameter,  $z$  is the number of nearest neighbors, and  $S$  is the spin. A molecular field with isotropic exchange

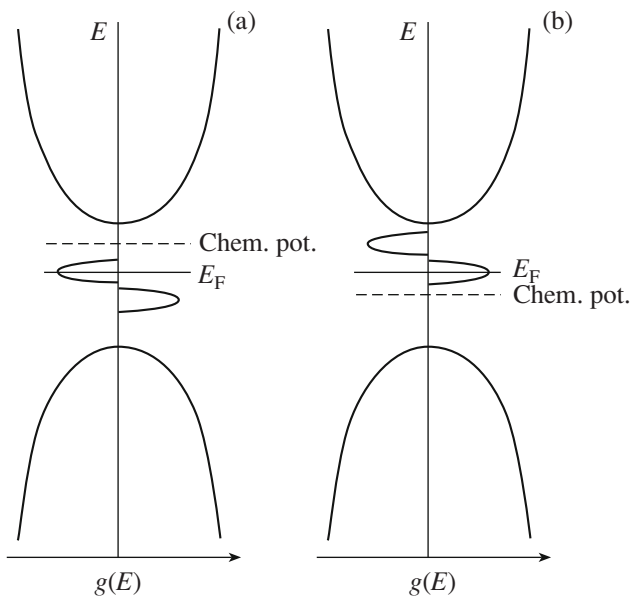
interaction for  $S = 1/2$  and  $S = 4$  does not provide even a qualitative fit to the temperature dependence of the magnetization. Approximation of the normalized magnetization with a power-law function  $\sigma = A(1 - T/T_c)^\beta$  in the temperature interval of  $0 < 1 - T/T_c < 0.2$  yields  $\beta = 0.12$ , which suggests quasi-two-dimensional behavior of the magnet with Ising-like anisotropy. The mechanism responsible for such a strong anisotropy can involve ordering of the  $t_{2g}$  orbitals on manganese ions located in the nearest environment of the  $\text{Co}^{2+}$  ion. Because of the manganese and cobalt ions having different electronegativities, the electronic density on two nearest  $\text{Mn}^{2+}$  ions can change, just as the Co–S–Mn covalent bond length, which should be assigned to hybridization of the  $d_{zx}-p_z-d_{zx}$  and  $d_{zy}-p_z-d_{zy}$  orbitals.

The situation initiated by replacement of manganese by gadolinium is slightly different. Hybridization of the  $5d^1$  state of the gadolinium ion with the  $4s$  state of the manganese ions makes possible spin polarization of the nearest environment of manganese ions through kinetic exchange. As a result, the electron becomes localized in a cluster with ferromagnetic spin ordering. A moving electron interacts with elastic lattice vibrations and undergoes scattering, which can change its spin polarization associated with the change in the wave function  $\psi(\mathbf{k}, \sigma) \rightarrow \psi(-\mathbf{k}, \sigma')$ . In second order of perturbation theory, the electron scattering probability  $\sim q^2 n_f / (\omega_f t)$ , where  $q$  is the electron–phonon coupling constant,  $\omega_f$  is the frequency of the lattice vibrational mode, for which one can choose the acoustic or optical mode,  $t$  is the hopping integral, and  $n_f = 1/(\exp(h\omega_f/k_B T) - 1)$  is the average concentration of phonons. Invoking the dimensionless electron–phonon coupling parameter  $\lambda = q^2 / (\omega_f t)$ , the density of nonscattered electrons in a ferromagnetically ordered cluster can be written as  $N(T) = (1 - \lambda n_f) = 1 - \lambda / (\exp(h\omega_f/k_B T) - 1)$ .

The inset to Fig. 1b plots the temperature dependence of normalized magnetization  $\Delta \sigma = (\sigma_{\text{Gd}} - \sigma_{\text{Mn}})(T) / (\sigma_{\text{Gd}} - \sigma_{\text{Mn}})(T = T_N)$ , which is defined as the difference between the magnetizations of  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  and  $\text{MnS}$  at a temperature  $T$  referenced to that at the Néel temperature  $T_N$ . In the paramagnetic state,  $\sigma = \chi H$ , where  $\chi = g_{\text{eff}}^2 \mu_B S(S + 1) / T$ ; now the normalized magnetization due to clusters with localized electron reduces to the following expression:  $\Delta \sigma = N(T) T_N / T = (1 - \lambda / [\exp(h\omega_f/k_B T) - 1]) T_N / T$ . A good agreement with experiment is reached for  $\lambda \approx 0.5$ ,  $\omega_f = 305$  K (inset in Fig. 1b). The expression for the frequency  $\omega_f$  corresponds to the optical vibrational mode of manganese sulfide. The probability to observe a cluster with ferromagnetic order and an electron localized in it decreases with increasing temperature to disappear altogether at  $T \sim 680$  K, as is evident from the inset to Fig. 1b.

The transport properties allow qualitative interpretation in terms of the electronic structure model proposed to account for the magnetic properties. Figure 3 pre-





**Fig. 3.** Diagram of the density of states for the (a)  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  and (b)  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  samples.

sents a diagram of the density of states for  $\text{Co}_x\text{Mn}_{1-x}\text{S}$  and  $\text{Gd}_x\text{Mn}_{1-x}\text{S}$ . For  $\text{Co}_x\text{Mn}_{1-x}\text{S}$ , the chemical potential lies close to the top of the upper Hubbard band, and the activation energy is 0.46 eV. Hybridization of the  $5d$  and  $4s$  orbitals in  $\text{Gd}_x\text{Mn}_{1-x}\text{S}$  accounts for the upward displacement of the  $d$  band above the chemical potential; it is associated with partial filling of the lower Hubbard band. As a result, the conduction type changes from the  $p$ - to  $n$ -type, with  $\Delta E = 0.26$  eV. The activation energy decreases, and the electrical resistivity at 300 K rises by an order of magnitude. This should be possibly assigned to polarization of the conduction spin. Indeed, the current density  $j = e v(n_{\downarrow} + n_{\uparrow})$ , where  $n_{\downarrow}$  and  $n_{\uparrow}$  are the spin-down and spin-up electron concentrations. Electrons with spins parallel to those of the Gd pass through the Gd clusters, and those with an opposite spin direction are scattered. Thus, this is equivalent to a decrease in the effective carrier concentration by an order of magnitude.

#### 4. CONCLUSIONS

We have studied the effect of electron and hole doping on the magnetic and electrical properties of the  $\text{Me}_x\text{Mn}_{1-x}\text{S}$  solid solutions ( $\text{Me} = \text{Co}, \text{Gd}$ ). We have detected a spontaneous magnetic moment in the magnetically ordered region of the samples under study and a deviation from the Curie–Weiss law for  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  at temperatures of  $146 \text{ K} < T < 680 \text{ K}$ . A good agreement of theory with experiment was reached in the model involving an electron localized in a cluster with ferromagnetically ordered localized spins whose probability decreases with increasing temperature as a result of electron scattering from optical phonons. The increase in the resistivity of  $\text{Gd}_{0.05}\text{Mn}_{0.95}\text{S}$  which has a lower activation energy than  $\text{Co}_{0.05}\text{Mn}_{0.95}\text{S}$  can result

from a change in the spin polarization of the scattered electron.

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