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Magnetic properties and the metal–insulator transition in $Gd_XMn_{1-X}S$ solid solutions

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ABSTRACT

The structural, magnetic, electrical, and thermoelectric properties of $Gd_XMn_{1-X}S$ ($0.01 \leq X \leq 0.3$) solid solutions synthesized for the first time on the basis of α-MnS have been studied experimentally in the temperature range 77–1000 K in magnetic fields up to 10 kOe. The synthesized samples are antiferromagnetic semiconductors with an NaCl-type cubic lattice typical of α-MnS. Both concentration ($X_c = 0.3$) and temperature ($T_c = 450$ K) metal–insulator phase transitions have been observed. The concentration metal–insulator transition is accompanied by a decrease in resistivity and thermopower by twelve and two orders of magnitude, respectively, with the change in conductivity from p-type to n-type.

1. Introduction

Recently, close attention has been given to multiferroics, i.e., substances with the coexistence of at least two of the three order parameters (magnetic, electrical, and crystallographic) [1,2]. The magnetic properties of these materials can be controlled by an electric field and, conversely, the electrical properties can be modulated by a magnetic field. The correlation between the electric and magnetic subsystems in these materials manifests itself in a number of interesting effects, such as various phase transitions and the magnetoelectric effect [3,4]. The creation of novel materials possessing these properties makes it possible to solve urgent problems of sensing, magnetic storage, and microelectronics including its new field, spintronics [5,6]. Among the substances with the strong correlation between the magnetic and electrical properties, there are the disordered systems revealing metal–insulator phase transitions and colossal magnetoresistance. The promising materials for studying these effects are cation-substituted sulfides Me_XMn_{1-XS} (Me is a 3d metal) synthesized on the basis of the antiferromagnetic semiconductor α-MnS [7–9]. The interest in the α-MnS-based sulfides is caused by possible observation of the metal–insulator transition and colossal magnetoresistance upon substitution of rare-earth gadolinium ions for manganese cations. In view of this, it appears important to synthesize new cation-substituted $Gd_XMn_{1-X}S$ ($0.01 \leq X \leq 0.3$) sulfides with a rare-earth element and to study their crystal structure and magnetic, electrical, and thermoelectric properties.

2. Synthesis and measurements

For the first time the synthesized $Gd_XMn_{1-X}S$ crystals were grown in a quartz reactor from a melt of polycrystalline powders of sulfides. The reactor, with its charge in glass–carbon crucibles, was pulled through a single-turn inductor of a high-frequency facility. As an inert medium, high-purity argon was used [10].

The phase composition and the crystal structure of the $Gd_XMn_{1-X}S$ samples were determined with a DRON-3 X-ray diffractometer using Cu K_α radiation at 300 K. The specific magnetization and magnetic susceptibility were measured in vacuum by a ponderomotive method in the temperature range 100–800 K in a magnetic field of 8.6 kOe [11]. The magnetization of the samples at 4.2–300 K in the field $H = 0.5$ kOe was measured using a SQUID magnetometer with a superconducting solenoid. The resistivity and thermopower were determined by a four-probe compensation method in dc current at 80–1000 K. The thermopower coefficient was measured relative to copper with the device described in detail in [12].

3. Experimental results and discussion

The X-ray diffraction analysis shows that the synthesized $Gd_XMn_{1-X}S$ samples are single phase with an NaCl-type cubic lattice typical of α-MnS. With an increase in concentration X of

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the cation substitution, parameter a of the unit cell grows from 0.5225 nm for α-MnS to 0.5315 nm for $Gd_{0.3}Mn_{0.7}S$ as the ionic radius of the substituent increases.

Temperature dependences of magnetization $\sigma(T)$ for the $Gd_XMn_{1-X}S$ samples with $X = 0.01$ (a) and 0.1 (b) are presented in Fig. 1(a), (b). In the $\sigma(T)$ curves, one can see the maxima corresponding to the Néel temperature T_N indicating the antiferromagnetic transition with a decrease in temperature. As the Gd concentration grows, the T_N value reduces from 160 K for $X = 0.01$ to 130 K for $X = 0.1$. In the magnetically ordered region below T_N for the sample with $X = 0.1$ one can observe the change in magnetization (see the inset in Fig. 1(b)) upon cooling the sample in zero magnetic field (ZFC(1)) and in the magnetic field $H = 0.5$ kOe (FC(2)). This can be reasoned from several facts. Firstly, the antiferromagnetic order possibly breaks down; as a result, the cations which are not exchange coupled reveal the paramagnetic properties. Consequently, the sharp maximum can disappear from the $\sigma(T)$ dependence (Fig. 1(b)) when the concentration of Gd ions in a magnetic cell increases. A similar situation occurs in CrSe and $Mn_{0.1}Cr_{0.9}Se$ [13]. Both experimental and theoretical data showed that smoothing of the minimum in the $1/\chi(T)$ dependence of these substances is caused by the fact that a certain number of the cations reveal paramagnetic properties. Secondly, in the $Gd_XMn_{1-X}S$ samples, a spontaneous magnetic moment probably appears. For the concentration $X = 0.01$ in the same magnetic field in the magnetically ordered region the ZFC and FC curves coincide (see the inset in Fig. 1). Above temperature T_N, the behavior of the $\sigma(T)$ curves of the $Gd_{0.01}Mn_{0.99}S$ composition follows the Curie–Weiss law, similar to the $\sigma(T)$ dependence of the α-MnS monosulfide [8]. The asymptotic paramagnetic temperature, Curie–Weiss constant, and effective magnetic moment determined from the temperature dependences of magnetic susceptibility at $X = 0.01$ are $\Theta_P = -346$ K, $C = 2.6$, and $\mu_{\ni\Phi\Phi} = 5.40\mu_B$, respectively. It was found that at temperatures from T_N to 700 K for the concentration $X = 0.1$ the dependences $10^{-2}/\chi = f(T)$ deviate from the Curie–Weiss law. As compared to the case $X = 0.01$, the $Gd_{0.1}Mn_{0.9}S$ sample has lower (in absolute value) asymptotic paramagnetic Curie temperature ($\Theta_P = -157$ K) and value $10^{-2}/\chi$. This behavior of magnetic susceptibility is typical of the chalcogenide systems containing ferromagnetically ordered clusters [10].

The change in Gd concentration within the range $X = 0.01$–0.3 substantially influences the electric and thermoelectric properties of the system, which are accompanied by the change in conductivity type and the value of resistivity.

Fig. 2 presents the temperature dependences of resistivity of the $Gd_XMn_{1-X}S$ ($0.01 \le X \le 0.3$) samples. The curves for $X = 0.01$ indicate semiconductivity within the range 80–300 K. The increase in gadolinium concentration to 0.3 leads to disappearance of the dielectric state in the system of the $Gd_XMn_{1-X}S$ solid solutions. At $X = 0.3$, the temperature behavior of resistivity is typical of semimetals; at 80 K, the resistivity decreases by about twelve orders of magnitude. The concentration $X = 0.3$ is critical for the system as at this concentration the conductivity changes from that of a semiconductor to that of a semimetal. The concentration behavior of the temperature dependence of resistivity for $Gd_XMn_{1-X}S$ with $0.01 \le X \le 0.3$ is characteristic of disordered systems with the Anderson metal–insulator transition ($X_c = 0.3$) [4,8].

At 300 K, the samples with $X = 0.01$ and 0.1 reveal anomalies related to the transition from the semiconductor state to the semimetal state. The anomaly at $T = 450$ K can be caused by either the temperature semimetal–semiconductor transition or the transition of weakly coupled 4d electrons from the impurity subband to the conductivity band. Above 670 K, anomalies are observed which are typical of the transitions from impurity conductivity to intrinsic conductivity (see the inset in Fig. 2),

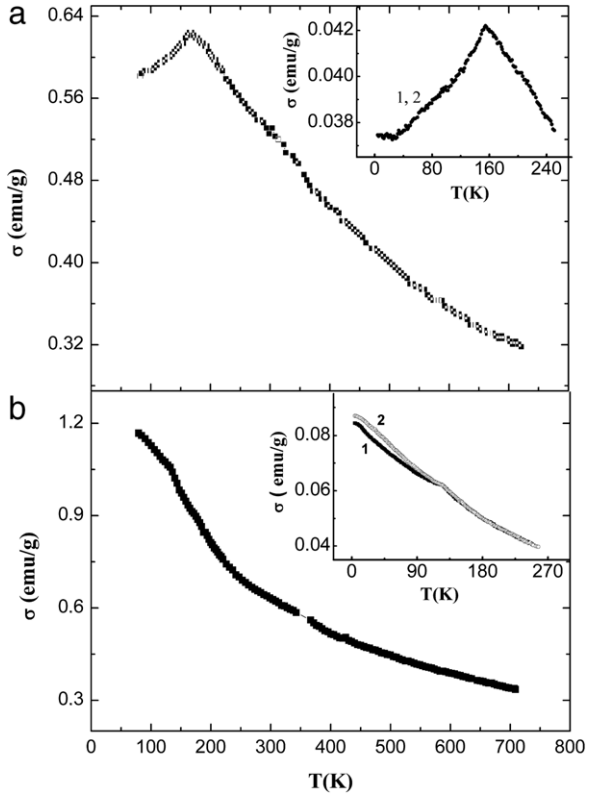

Fig. 1. Temperature dependences of the specific magnetization of $Gd_XMn_{1-X}S$ samples with $X = 0.01$ (a) and $X = 0.1$ (b) in magnetic field $H = 8.6$ kOe. In the insets: Temperature dependences of specific magnetization for $X = 0.01$ (a) and $X = 0.1$ (b) at cooling in zero magnetic field (1) and in the field $H = 0.5$ kOe (2).

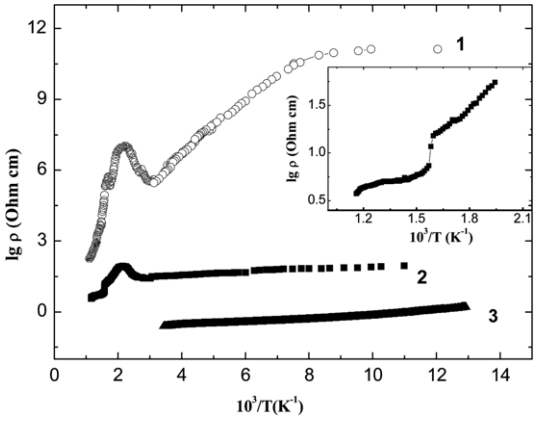

Fig. 2. Temperature dependences of resistivity of the $Gd_XMn_{1-X}S$ samples with $X = 0.01$ (1), $X = 0.1$ (2) and $X = 0.3$ (3). Inset: Temperature dependence of resistivity for $X = 0.1$ within the range 500–900 K.

similar to the case of α-MnS [14]. The value of the bandgap E_g determined from the slope of the linear portion of the $lgp(1/T)$ dependence reduces from 1.46 eV for α-MnS ($X = 0$) to 0.64 eV for $Gd_XMn_{1-X}S$ ($X = 0.1$).

The temperature dependences of the thermopower coefficient for the $Gd_XMn_{1-X}S$ solid solutions (Fig. 3) show that at $X = 0.01$ the thermopower coefficient is positive within 80–670 K, which implies hole conductivity in this temperature range. The increase in coefficient α in the $Gd_{0.01}Mn_{0.99}S$ solid solution within the range 400–600 K is possibly related to the reduction of the number of charge carriers when injection of electrons to the conduction band at the expense of the impurity centers stops,

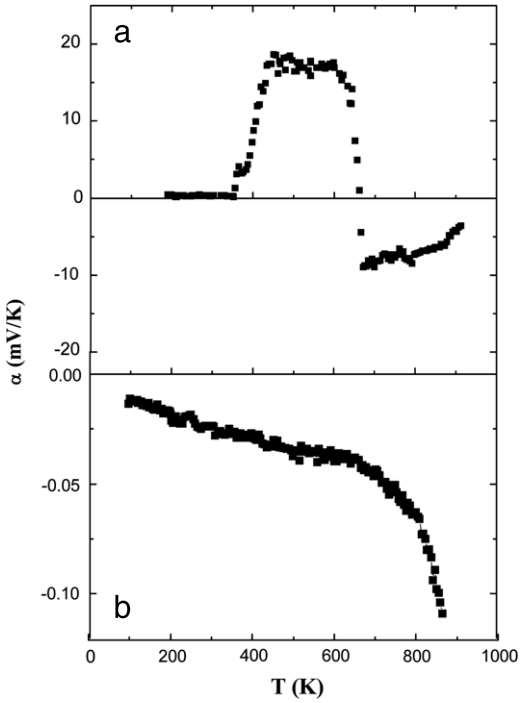

Fig. 3. Temperature dependences of the thermopower coefficient for $Gd_XMn_{1-X}S$ with $X = 0.01$ (a) and $X = 0.1$ (b).

whereas the interband transition of electrons has not started yet. The transition of impurity conductivity to intrinsic conductivity at about 670 K in the sample with $X = 0.01$ is accompanied by a decrease in thermopower coefficient. In the temperature range $670 < T < 900$ K, the curve $\alpha = f(T)$ is in the negative range of values of the thermopower coefficient. The change in the sign of the thermopower coefficient evidences predominance of electron, not hole, conductivity. This is caused, first of all, by higher mobility of electrons as compared to that of holes. With an increase in gadolinium concentration to $X = 0.1$, the thermopower coefficient noticeably decreases and becomes negative in the entire temperature range (Fig. 3(b)). A similar situation is observed in the sample with $X = 0.3$. Reduction of the thermopower coefficient α with an increase in gadolinium concentration in the α-MnS lattice indicates that gadolinium acts as a donor impurity. The increase in the number of electrons related to an increase in concentration of the gadolinium cations embedded into the lattice leads to the state of a highly doped semiconductor. Electron conductivity starts to be predominant and the thermopower coefficient becomes negative.

4. Conclusions

In this study, the effect of electron doping on the structural, magnetic, electric, and thermoelectric properties of the α-MnS-based $Gd_XMn_{1-X}S$ solid solutions have been considered. The anomalies in the temperature dependences of the magnetic characteristics can be attributed to the appearance of the spontaneous magnetic moment in the magnetically ordered region and the existence of clusters with ferromagnetic ordering within the temperature range $130 < T < 700$ K, as well as to the distortion of the indirect exchange interaction at cation substitution of gadolinium for manganese in the solid solutions. The break of the exchange interactions should naturally weaken the bonds of the 4d electrons with the frame; thus, gadolinium becomes a donor of electrons, the magnitudes of resistivity and thermopower of the $Gd_XMn_{1-X}S$ solid solutions changes, and a certain fraction of the magnetically active ions become paramagnetic. According to the data on resistivity and thermopower, in the system of the $Gd_XMn_{1-X}S$ solid solutions ($0.01 \leq X \leq 0.3$) both concentration and temperature metal–insulator transitions occur, accompanied by the change in conductivity from p-type to n-type. The results obtained are of importance for further investigation of the magnetoelectric and dielectric properties of the system and the prediction of novel materials with properties typical of multiferroics.

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