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MAGNETISM AND FERROELECTRICITY

Hall Effect in the $Fe_xMn_{1-x}S$ Magnetic Semiconductors

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Abstract—The electrical properties and the Hall effect in the $Fe_xMn_{1-x}S$ magnetic semiconductors ($0 < x \le 0.5$) have been experimentally studied in the range 77–300 K in magnetic fields of up to 15 kOe. The cation-substituted sulfides with $0.25 \le x \le 0.3$ possessing colossal magnetoresistance (CMR) were established to be narrow-gap semiconductors with carrier concentrations $n \sim 10^{11}$–10^{15} cm^{-3} and high carrier mobilities $\mu \sim 10^2$–10^4 cm^2 V^{-1} s^{-1}. It is believed that the CMR effect in these sulfides can be explained in terms of the model of magnetic and electron phase separation, which is analogous to the percolation theory in the case of heavily doped semiconductors. © *2004 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Despite an impressive number of experimental and theoretical studies into the colossal magnetoresistance effect (CMR) [1–5], clear understanding of its mechanism is still lacking and the criteria governing the realization of this effect in a substance are unknown. An efficient method to gain insight into the mechanisms of conduction is based on investigating the Hall effect; this approach makes it possible to determine the type, concentration, and mobility of charge carriers. Combined study of the Hall effect and the magnetoresistance may help us to understand the mechanism of CMR in magnetic semiconductors [6–8].

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The present communication reports on the results of a study on the electrical and galvanomagnetic properties of solid solutions in the $Fe_xMn_{1-x}S$ sulfide system ($0 < x \le 0.5$). The technology of synthesized polycrystalline $Fe_xMn_{1-x}S$ samples and the results of their x-ray characterization are described elsewhere [2, 3]. X-ray diffraction analysis showed the $Fe_xMn_{1-x}S$ samples prepared from α-MnS by cation substitution to have a NaCl-type fcc lattice deformed slightly in the region ~150 K. Experimental studies on the electrical and galvanomagnetic properties of the samples were carried out using the standard four-probe dc method at temperatures of 77 to 300 K in magnetic fields H = 5, 10, and 15 kOe oriented normal to the sample plane. To avoid possible side effects, the Hall voltages were measured for two field and current directions in a sample [9]. The samples prepared for measurements were 3 × 5 × 10 mm parallelepipeds pelletized from the starting powder material and annealed at 1000°C for 2 h.

3. EXPERIMENTAL RESULTS

At room temperature, manganese monosulfide is a *p*-type semiconductor with carrier concentration $n = 10^{18}$ cm^{-3} and carrier mobility $\mu = 0.065$ cm^2 V^{-1} s^{-1} [10]. When in the paramagnetic phase, the conduction activation energy of manganese monosulfide is 0.3 eV in the range 150–300 K. Below the Néel temperature ($T_N \sim 150$ K), conduction has a practically nonactivated character (similar to $LaMnO_3$ [1]).

Increasing the cation substitution x in the $Fe_xMn_{1-x}S$ sulfide compounds prepared from α-MnS changes the type of magnetic order from antiferromagnetic to ferromagnetic [2], as occurs in manganese oxide compounds synthesized from $LaMnO_3$ and possessing CMR [1]. Similar to the $LaMnO_3$-based cation-substituted systems, the $Fe_xMn_{1-x}S$ sulfides exhibit CMR for some concentrations x [2].

Figure 1 plots the temperature dependences of the electrical resistivity ρ of the cation-substituted $Fe_xMn_{1-x}S$ sulfides ($0 < x \le 0.5$) measured with no magnetic field applied. As the cation substitution x increases, the electrical resistivity of the $Fe_xMn_{1-x}S$ sulfides changes behavior with temperature in the range 77–300 K. One observes a decrease in the electrical resistivity and activation energy for conduction (the slope of the logρ vs. $1/T$ curves), a feature characteristic of the Anderson-type concentration transitions [11]. The critical concentration at which the $Fe_xMn_{1-x}S$ sulfides switch from the semiconductor to semimetal state is $x_c \sim 0.4$ [12].

Figure 2 displays the temperature dependences of the electrical resistivity measured for the compositions with $x \sim 0.29$ and ~0.3 in magnetic fields of up to 30 kOe. The variation in the electrical resistivity in the temperature interval from 4.2 to 300 K with magnetic field (for a given composition x) is similar in character

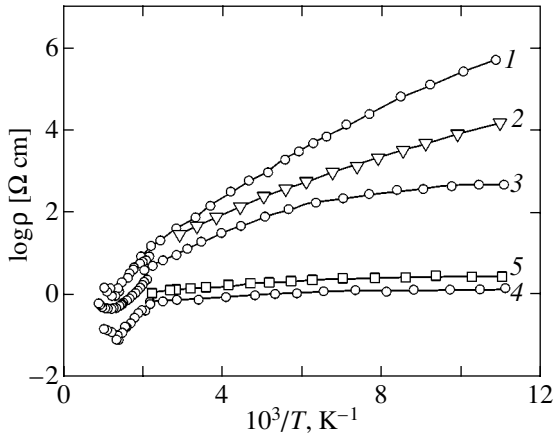

Fig. 1. Temperature dependences of the electrical resistivity of samples of the $Fe_xMn_{1-x}S$ sulfide system obtained for compositions with (*1*) $x = 0.3$, (*2*) 0.33, (*3*) 0.36, (*4*) 0.4, and (*5*) 0.5 in zero magnetic field.

to the variation in $\rho(T)$ observed in $Fe_xMn_{1-x}S$ with increasing cation substitution x without a magnetic field; in other words, application of a magnetic field brings about a simultaneous decrease in the electrical resistivity and conduction activation energy, as is seen as the substitution concentration x increases. Negative magnetoresistance $\delta_H = (R(H \neq 0) - R(H = 0))/R(H \neq 0) \times 100\%$ is observed in the $Fe_xMn_{1-x}S$ sulfide system in ferromagnetic compositions in the range $0.25 \leq x \leq 0.4$. The value of the magnetoresistance depends on the concentration x and reaches a maximum for the composition $x \sim 0.29$ ($\delta_H = -450\%$ in a magnetic field of 30 kOe at a temperature of 50 K) [2, 3]).

Figure 3 shows temperature dependences of the Hall constant, carrier concentration, and mobility obtained for $x \sim 0.25$ in a magnetic field of 10 kOe. The Hall constant R_H grows with decreasing temperature and is positive. When measured at temperature $T = 110$ K in a field of 10 kOe, the carrier concentration and mobility for $x \sim 0.25$ are $n = 0.32 \times 10^{11}$ cm^{-3} and $\mu = 1.2 \times 10^4$ cm^2 V^{-1} s^{-1}.

Figure 4 presents graphs of the temperature dependences of the Hall constant, carrier mobility, and concentration measured in different magnetic fields on the $Fe_xMn_{1-x}S$ sulfide with $x \sim 0.29$, the composition with maximum magnetoresistance. In magnetic fields $H = 5$ and 10 kOe at temperatures of 77–300 K, our sulfide samples with $x \sim 0.29$ are *p*-type semiconductors, which is illustrated by the positive sign of the Hall constant R_H (Fig. 4a). The Hall constant changed in sign to negative in a magnetic field of 15 kOe for $T < 180$ K, with electrons becoming the majority carriers in this temperature region. For a given field $H = 5$ kOe, the mobility of the *p*-type carriers in this sample increases and their concentration decreases with decreasing temperature, similar to the way this occurs in the $x \sim 0.25$ composition in a field of 10 kOe. An increase in mag-

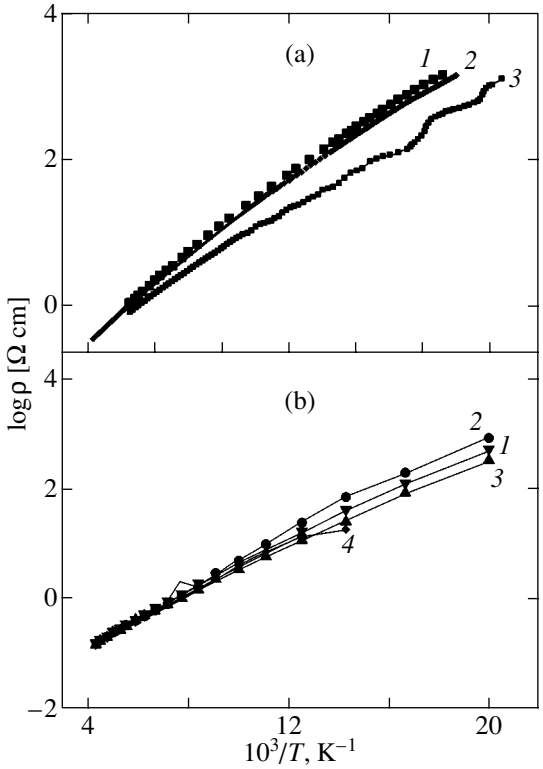

Fig. 2. Temperature dependences of the electrical resistivity of $Fe_xMn_{1-x}S$ samples obtained in different magnetic fields: (a) $x \sim 0.29$ and (*1*) $H = 0$, (*2*) 5, and (*3*) 30 kOe; (b) $x \sim 0.3$ and (*1*) $H = 3$, (*2*) 7, (*3*) 8, and (*4*) 14 kOe.

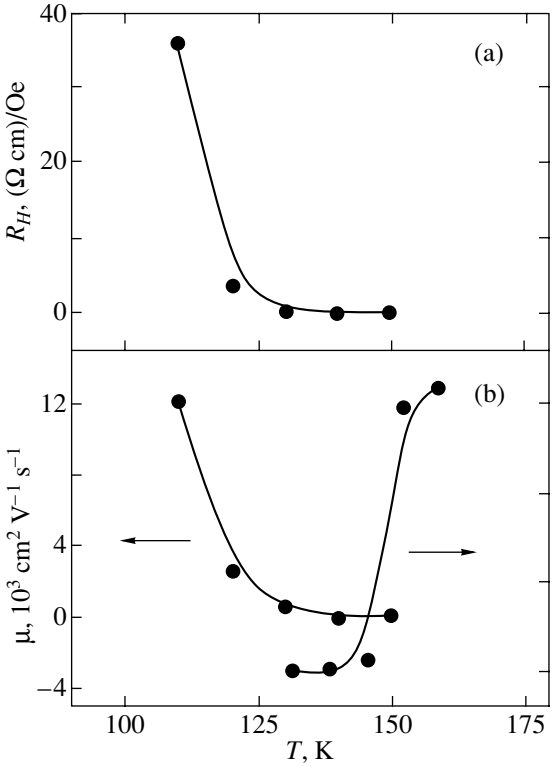

Fig. 3. Temperature dependences of (a) the Hall constant and (b) carrier concentration and mobility for $Fe_xMn_{1-x}S$ ($x \sim 0.25$) obtained in a field $H = 10$ kOe.

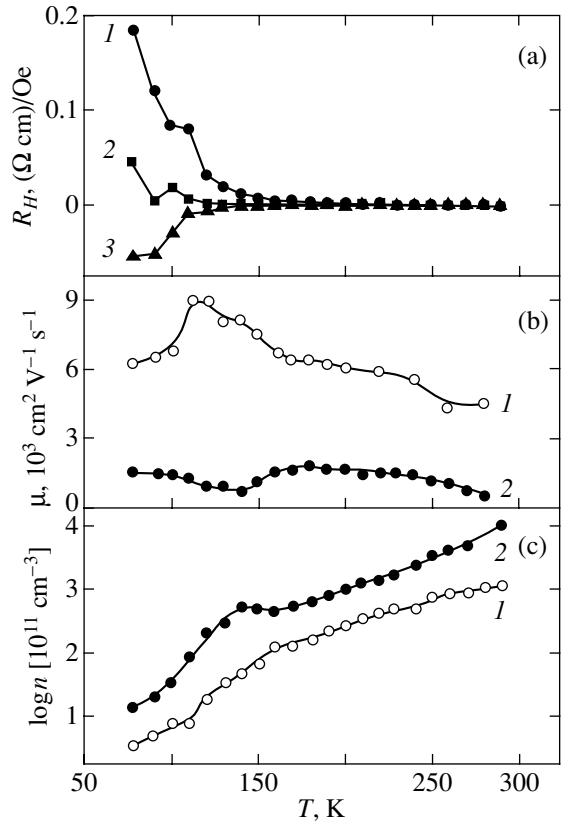

Fig. 4. Temperature dependences of (a) the Hall constant and (b) carrier mobility and (c) concentration for $Fe_xMn_{1-x}S$ ($x \sim 0.29$) obtained in different magnetic fields H: (*1*) 5, (*2*) 10, and (*3*) 15 kOe.

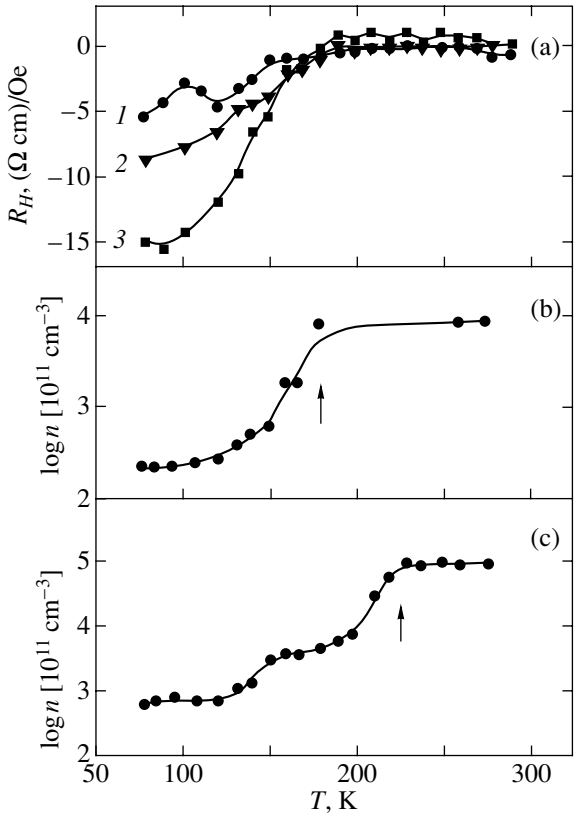

Fig. 5. Temperature dependences (a) of the Hall constant in magnetic fields H (*1*) 5, (*2*) 10, and (*3*) 15 kOe and (b, c) of the carrier concentration in magnetic fields H (b) 5 and (c) 15 kOe for $Fe_xMn_{1-x}S$ ($x \sim 0.3$).

netic field (up to 10 kOe) brings about a decrease in the mobility of p carriers and lead to a weak temperature dependence in the sample with $x \sim 0.29$ (Fig. 4b). The p-carrier concentration increases (Fig. 4c). For T = 110 K and H = 10 kOe, the carrier concentrations and mobilities in the sample with $x \sim 0.29$ are $n = 8.6 \times 10^{12}$ cm^{-3} and $\mu = 1.3 \times 10^3$ cm^2 V^{-1} s^{-1}.

Figure 5 illustrates the temperature behavior of the Hall constant and carrier concentration in different magnetic fields studied for the composition with $x \sim 0.3$. The majority carriers in this sulfide are negatively charged particles, electrons. In a magnetic field of 5 kOe, the temperature dependence of $n(T)$ is similar to that for the $x \sim 0.25$ composition (Fig. 3b), with the temperature at which $n(T)$ undergoes a sharp change shifting toward high temperatures with increasing field. At T = 110 K and H = 10 kOe, the carrier concentration and mobility for the sample with $x \sim 0.3$ are $n = 6.94 \times 10^{13}$ cm^{-3} and $\mu = 1.92 \times 10^2$ cm^2 V^{-1} s^{-1}. As the magnetic field is increased to 15 kOe, the carrier concentration increases to $n \sim 10^{15}$ cm^{-3}. The carrier mobility for this composition depends only weakly on temperature and was measured to be ~10^2 cm^2 V^{-1} s^{-1}.

Figure 6 shows field dependences of the electrical resistivity, carrier concentration, and magnetization for the $x \sim 0.29$ composition measured at 160 K. We see that the decrease in the electrical resistivity and the growth in the magnetization are related to the increasing carrier concentration.

4. DISCUSSION OF THE RESULTS

The CMR effect was first discovered in NaCl-type fcc magnetic semiconductors (such as europium chalcogenides EuSe [13]), which are isostructural to manganese monosulfide. Just as in the europium chalcogenides, the magnetic transition from the paramagnetic to antiferromagnetic state in manganese monosulfide is accompanied by a rhombohedral-type lattice deformation caused by the exchange–striction mechanisms [14]. The antiferromagnetic transition in the cation-substituted sulfides $Fe_xMn_{1-x}S$ is apparently of the same nature. As the cation substitution in $Fe_xMn_{1-x}S$ increases from x = 0 to ~0.3, the Néel temperature increases from 150 K (x = 0) to 230 K ($x \sim 0.3$) [2, 3], which indicates expansion of the temperature region in which the antiferromagnetic state exists. As follows from Hall effect data, the concentration of the p carriers

decreases and their mobility increases. This suggests that the nature of the antiferromagnetic transition in the $Fe_xMn_{1-x}S$ solid solutions is related to a decrease in the *p*-carrier concentration and an increase in their mobility.

Many researchers relate the origin of the CMR in magnetic semiconductors (for instance, in EuSe, $CdCr_2Se_4$, $HgCr_2Se_4$) to a red shift of the conduction band bottom and carrier localization in ferron-type impurity states [6]. The dependence of the carrier concentration and mobility on magnetic field observed in these compounds is assigned to the delocalization of electrons in the ferron states, which gives rise to a reversal of the carrier sign and an increase in the electron concentration and mobility.

The above results obtained in an experimental study of the galvanomagnetic properties of the $Fe_xMn_{1-x}S$ sulfides permit us to conclude that, in magnetic fields $H \le 10$ kOe at temperatures from 77 to 300 K, the $Fe_xMn_{1-x}S$ sulfides ($x \le 0.29$) are *p*-type semiconductors, similar to manganese monosulfide. As x is increased from 0 to ~0.29, the *p*-carrier concentration decreases by five orders of magnitude and their mobility rises by the same factor (relative to α-MnS, $x = 0$). In the composition region of $x \sim 0.3$, the carriers reverse sign, with *n*-type carriers becoming the majority species. The conduction activation energy $E_a \sim 10^{-1}$ eV, the carrier concentration $n \sim 10^{11}$–10^{15} cm^{-3}, and the mobility $\mu \sim 10^3$ cm^2 V^{-1} s^{-1} found for the $Fe_xMn_{1-x}S$ sulfides in the range $0.25 \le x \le 0.3$ are typical of semiconductors with narrow-band gaps and small ($m^*/m \sim 10^{-2}$) effective carrier masses (for instance, PbS, Ge, Si) [11].

The Hall resistivity in magnetic semiconductors is defined as $\rho_H = R_0B + R_sM$, where R_0 and R_s are the normal and anomalous (spontaneous) Hall coefficients, B is the induction in the sample, and M is the magnetization. For a sample geometry with a demagnetizing factor of unity, we have $B = H$. Studies of the Hall effect in manganese monosulfide [10] showed that the Hall constant R_0 in the range 77–300 K is so small that it lies within the experimental error. Our studies demonstrated a similar situation to exist in a $Fe_xMn_{1-x}S$ sample with $x \sim 0.25$ at temperatures of ~200–300 K. Below 200 K, the Hall constant in the antiferromagnetic phase grows sharply (Fig. 3a). In ferromagnetic samples with $x \sim 0.29$ and ~0.3, the Hall effect is observed throughout the temperature range 77–300 K. It may be conjectured that the Hall constant observed in the interval from 200 to 300 K is actually the anomalous component R_s. It has positive sign for the composition $x \sim 0.29$ and negative sign for $x \sim 0.3$. The reversal of the carrier sign from the hole to the electronic sign in manganese monosulfide ($x = 0$) is observed to occur above ~480 K [10]. In view of this observation and the results of studies into the Hall effect in cation-substituted sulfides, the compounds investigated by us could be assigned to semiconductors with mixed conduction character, where both holes and electrons act as carriers. The ratio of the electron to hole concentrations determines the type of the carrier, which varies depending on the temperature and composition. A magnetic field apparently exerts a similar impact on the $x \sim 0.29$ composition in the range 77–200 K, where CMR and the coexistence of the antiferromagnetic and ferromagnetic phases are observed [15]. The sharp rise in the *p*-type carrier mobility as the degree of cation substitution x in the $Fe_xMn_{1-x}S$ sulfides is increased compared to the starting manganese monosulfide indicates either the formation of a light-carrier impurity band or a weakening of the polaron or ferron effects, as is the case with the magnetic semiconductors $La_{1-x}Sr_xMnO_3$ and $HgCr_2Se_4$ [6–8].

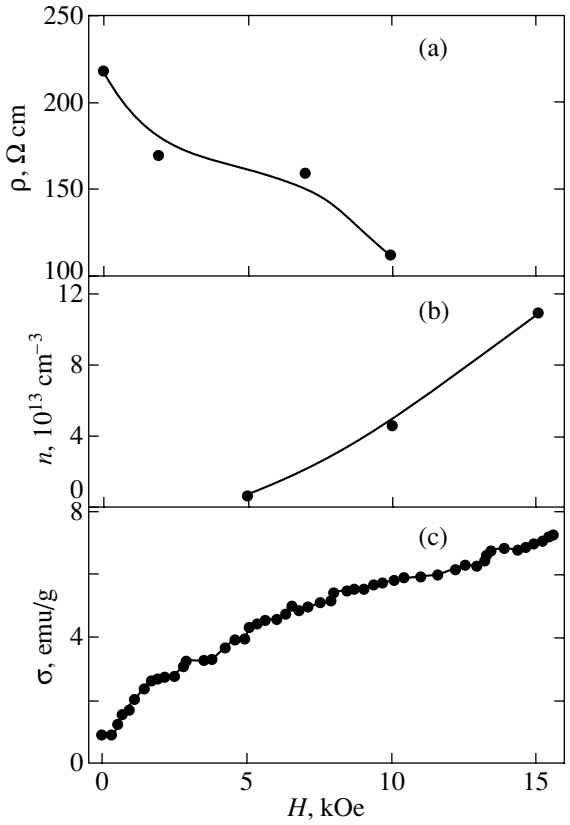

Fig. 6. Magnetic field dependences of (a) the electrical resistivity, (b) carrier concentration, and (c) magnetization for the $x \sim 0.29$ composition measured at $T = 160$ K.

To explain the concentration-driven transition from an antiferromagnetic semiconductor to a ferromagnetic metal occurring in $Fe_xMn_{1-x}S$ for zero magnetic field, an electronic level diagram was proposed, which includes a *p–d* hybridized valence band E_1 and a narrow impurity band E_2 [16]. It was shown that as x is increased, an Anderson transition takes place in $Fe_xMn_{1-x}S$ through a shift of the mobility edge E_c and crossing of the Fermi level E_F. The similarity observed in the behavior of the electrical resistivity as a function

of concentration x (Fig. 1) and of magnetic field H (Fig. 2) suggests that the mechanism of the concentration transition and the decrease in the electrical resistivity in a magnetic field (the negative CMR effect) have the same (percolation) character. This conjecture fits the model of electronic and magnetic phase separation [1], which is analogous to the theory of percolation in heavily doped semiconductors [17].

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