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MAGNETISM AND FERROELECTRICITY

Magnetic Properties of $Fe_xMn_{1-x}S$ Sulfides Exhibiting the Magnetoresistive Effect

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Abstract—The magnetic, electrical, and thermal (derived from DTA data) properties of $Fe_xMn_{1-x}S$ polycrystalline sulfides ($0 \le x \le 0.38$) synthesized based on α-MnS (NaCl cubic lattice) and exhibiting colossal magnetoresistance were studied. The studies were conducted at temperatures from 77 to 1000 K and magnetic fields of up to 30 kOe. As the degree of cation substitution in the $Fe_xMn_{1-x}S$ system was increased, the magnetic order was found to change from antiferromagnetic to ferromagnetic. In the high-temperature domain (550–850 K), the samples undergo two phase transitions with critical temperatures T_{c_1} and T_{c_2}, which are accompanied by reversible anomalies in the magnetization and thermal (DTA) properties and by a semiconductor–metal transition. *© 2002 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

The colossal magnetoresistance (CMR) remains an intriguing problem, because a clear understanding of the mechanism of this phenomenon is still lacking. The CMR effect has been revealed recently [1, 2] in new, NaCl-type cubic fcc compounds synthesized on the basis of manganese monosulfide. Materials with a NaCl lattice exhibiting CMR can be exemplified by cation-substituted systems based on europium oxide and chalcogenides [3]. In these compounds, CMR is observed to occur at low temperatures, ≤40 K. In the $Fe_xMn_{1-x}S$ sulfides, negative colossal magnetoresistance is found at temperatures $T \le 200$ K. A possible origin of the CMR is the magnetic and electronic separation of crystallographically similar compounds [2, 3].

2. EXPERIMENTAL TECHNIQUES

The present communication reports on a study of the electrical, magnetic, and thermal (derived from DTA measurements) properties of polycrystalline sulfides $Fe_xMn_{1-x}S$ with compositions $0 \le x \le 0.38$ at temperatures from 77 to 1000 K in magnetic fields of up to 30 kOe. The techniques used to prepare the compounds and to measure their electrical properties are described elsewhere [1, 2]. The magnetic measurements in the range 100–1000 K and in fields of up to 10 kOe were performed using the Faraday method on samples placed in evacuated quartz ampoules. Measurements of the magnetic properties within the 77- to 300-K temperature interval and in fields up to 30 kOe were made in a vibrating-sample, superconducting-coil magnetometer.

X-ray structural measurements of the $Fe_xMn_{1-x}S$ samples thus synthesized ($0 \le x \le 0.38$) showed them to be solid solutions with a NaCl-type structure typical of manganese monosulfide [1, 2]. The fcc lattice parameter decreases as the degree of cation substitution (x) increases, which agrees with the data from [4].

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 displays temperature dependences of the magnetization (measured in a field of 8.6 kOe) of single-crystal α-MnS (curve *1*) and polycrystalline α-MnS (curve *2*). The magnetic susceptibility of the polycrystalline manganese monosulfide, $\chi_{300\,K} = 6.9 \times 10^{-5}$ cm^3/g, is in agreement with the data from [5, 6] and is higher than that of the single-crystal compound. In the region of the Néel temperature $T_N \sim 150$ K, the temperature-dependent magnetization exhibits a maximum which signals an antiferromagnetic transition. Above the Néel temperature, the inverse magnetic susceptibility $\chi^{-1}(T)$ of the manganese monosulfide follows the Curie–Weiss relation, with the paramagnetic temperature Θ and Curie constant C equal to –450 K and 4.32, respectively. At temperatures above ~450 K, the inverse magnetic susceptibility is seen to deviate from the Curie–Weiss law. According to [7], in this temperature interval, the charge carriers in α-MnS reverse sign. For $T < 450$ K, the manganese monosulfide behaves as a *p*-type semiconductor, with the carrier mobility being $\mu \sim 0.065$ cm^2 V^{-1} s^{-1}. For $T > 450$ K, the carriers are electrons and their mobility increases by an

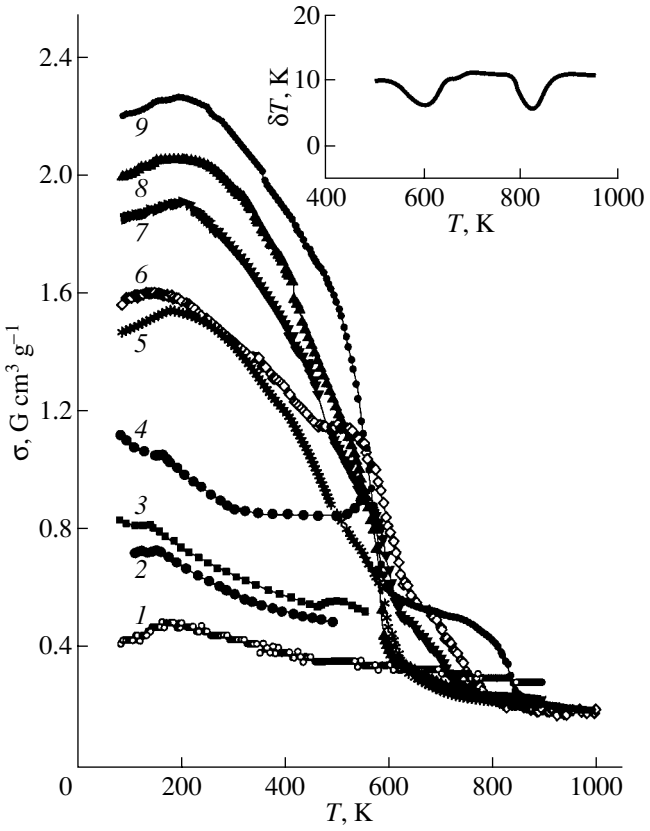

Fig. 1. Temperature dependences of the magnetization of the $Fe_xMn_{1-x}S$ system measured in a field $H = 8.6$ kOe for different compositions x: (*1*) 0, α-MnS single crystal; (*2*) 0, polycrystalline α-MnS; (*3*) 0.05; (*4*) 0.15; (*5*) 0.25; (*6*) 0.29; (*7*) 0.27; (*8*) 0.32; and (*9*) 0.38. Inset: differential thermal analysis data for $x \sim 0.35$.

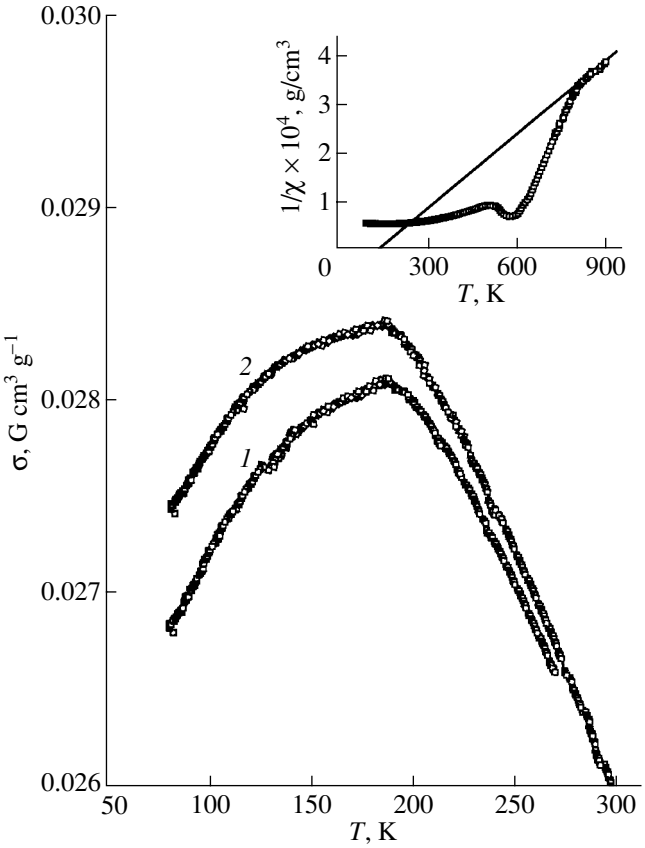

Fig. 2. Temperature dependence of the magnetization of $Fe_{0.2}Mn_{0.8}S$ cooled (*1*) in a zero magnetic field and (*2*) in a field $H = 2$ kOe. Inset: temperature dependence of inverse magnetic susceptibility for $Fe_{0.25}Mn_{0.75}S$.

order of magnitude. Measurements of the temperature dependence of the magnetization of the cation-substituted $Fe_xMn_{1-x}S$ samples revealed (Fig. 1) that, at low concentrations ($x \le 0.2$), sulfides (similar to manganese monosulfide) undergo an antiferromagnet–paramagnet transition at low temperatures, with the Néel temperature increasing from 150 K ($x = 0$) to 185 ± 5 K ($x \sim 0.2$). The behavior of the magnetization $\sigma(T)$ of samples with $x \sim 0.2$ depends on the way in which the sample was cooled, namely, in a nonzero or zero magnetic field (Fig. 2). At $T > T_N$, the magnetic properties of cation-substituted samples with compositions $0.05 \le x \le 0.2$ behave similarly to $\chi^{-1}(T)$ of manganese monosulfide. The temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$is described by the Curie–Weiss law, with the paramagnetic temperature Θ and the Curie constant C increasing to –400 and 10.8 K ($x \sim 0.2$), respectively. For temperatures $T > 450$ K, samples with $0.05 \le x \le 0.2$ exhibit a deviation from the Curie–Weiss relation. More specifically, the magnetization (Fig. 1) displays an anomaly at a temperature T_{c_1}, which grows from 500 for $x \sim 0.05$ to 580 K for $x \sim 0.2$. For compositions with $x \sim 0.25$, the behavior of the inverse magnetic susceptibility $\chi^{-1}(T)$ in the high-temperature domain is similar to that characteristic of ferrimagnets (see inset to Fig. 2) [8]. The paramagnetic Curie temperature assumes positive values (Θ ~ 106 K for $x \sim 0.25$). The Curie constant becomes smaller, which indicates a decrease in the effective paramagnetic moment (for $x \sim 0.25$, $C = 1.69$). As seen from Fig. 1, the temperature dependences of the magnetization measured on samples with $0.27 \le x \le 0.38$ in the range 100–1000 K in a field of 8.6 kOe are typical of ferromagnetic compounds. Below ~200 K, the magnetization of these samples decreases with decreasing temperature. In the high-temperature region, the $\sigma(T)$ curve exhibits two magnetization anomalies at the critical temperatures T_{c_1} and T_{c_2}, which are accompanied by anomalies in the thermal (DTA) properties (inset to Fig. 1), thus indicating the occurrence of two phase transitions. At $T_{c_1} \sim 550$–650 K, in the region of the reversible thermal (derived from DTA data) anomaly, there are anomalies in the electrical resistivity (Fig. 3) and in the fcc lattice parameter [9]. Below T_{c_1}, the resistivity behaves in a manner typical of the Fermi

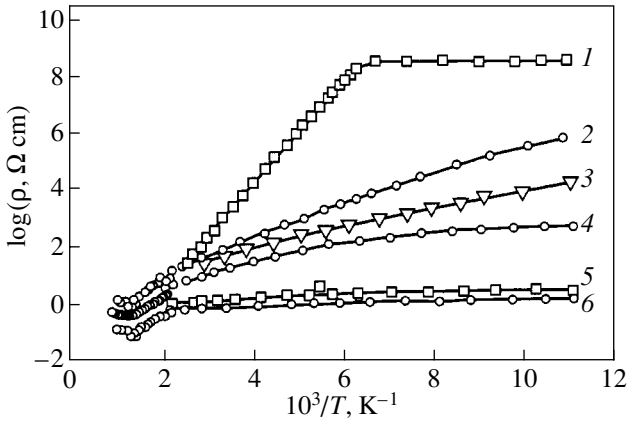

Fig. 3. Temperature dependences of the electrical resistivity of the $Fe_xMn_{1-x}S$ system for different compositions x: (*1*) 0, (*2*) 0.3, (*3*) 0.33, (*4*) 0.36, (*5*) 0.4, and (*6*) 0.5.

glass state and of systems with Anderson localization [10]. The temperature T_{c_2} is the Curie point of sulfides; this temperature increases with increasing concentration x from 730 ($x \sim 0.27$) to 860 K ($x \sim 0.38$). As seen from Fig. 1, the magnetization of the high-temperature paramagnetic phase ($T > T_{c_2}$) of the cation-substituted $Fe_xMn_{1-x}S$ samples is close to that of the paramagnetic phase of single-crystal α-MnS and, for compositions with $x \sim 0.27$, 0.29, and 0.38, virtually does not depend on temperature. According to electrical resistivity measurements, the ferromagnet–paramagnet transition near T_{c_2} is accompanied by a semiconductor–metal change in the conduction character (Fig. 3).

At room temperature, the manganese monosulfide α-MnS is in the paramagnetic state, in which the σ(H) relation is linear (Fig. 4). The σ(H) relations for the cation-substituted $Fe_xMn_{1-x}S$ solid solutions ($0.05 \le x \le 0.2$) measured at room temperature become nonlinear [6], with no hysteresis in the field dependence of the magnetization. As the degree of cation substitution x increases, the ferromagnetic contribution to magnetization increases and samples with $x > 0.2$ exhibit a magnetization hysteresis (Fig. 4), with the coercive force H_c increasing from 0.8 ($x = 0.25$) to 1.2 kOe ($x = 0.29$). The magnetization isotherms σ(H) measured for samples with $0.25 \le x \le 0.27$ at temperatures of 77 and 300 K do not exhibit saturation. As seen from Fig. 4, which displays hysteresis loops, hysteresis is no longer seen in comparatively weak magnetic fields ($H \sim$ 3–5 kOe), but the magnetization does not saturate and continues to grow as the field increase. Such a situation is observed, for instance, in the gadolinium ferrite garnets and can be attributed to the positive component of magnetostriction appearing in strong fields [8]. The magnetization curves obtained on samples with $x \sim 0.29$ are typical of ferromagnets, which is supported by the presence

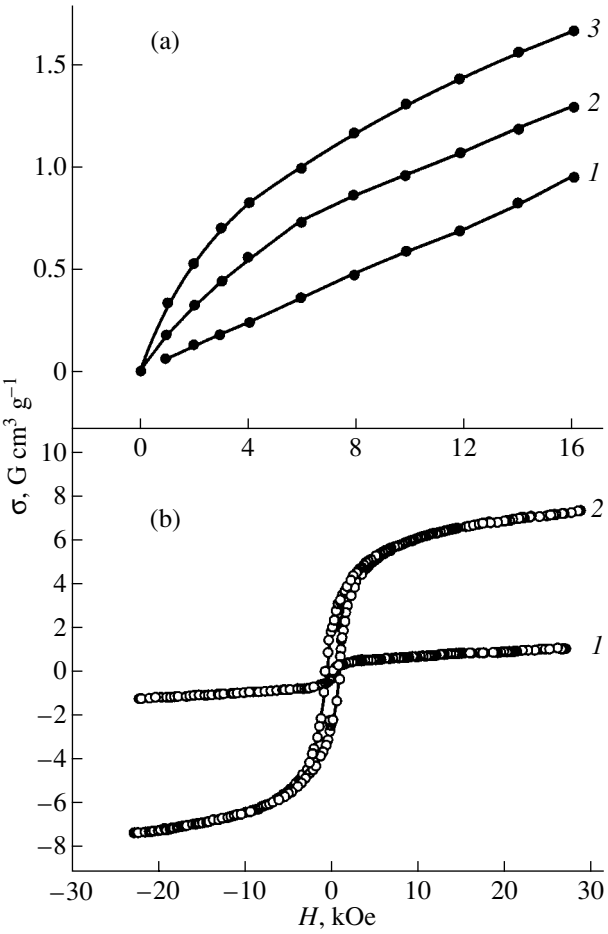

Fig. 4. Field dependences of the magnetization of the $Fe_xMn_{1-x}S$ system for different compositions x (a) at 300 K: (*1*) 0, (*2*) 0.05, and (*3*) 0.2; and (b) at 77 K: (*1*) 0.27 and (*2*) 0.29.

of a hysteresis loop. The same compositions exhibit the maximum colossal magnetoresistance ($\sigma_H \sim$ –450% in a field of 30 kOe at 50 K) [2].

4. CONCLUSION

Thus, studies of the magnetic, electrical, and thermal properties of the $Fe_xMn_{1-x}S$ solid solutions have revealed a sequence of phase transitions (at T_{c_1} and T_{c_2}) in the compositions of the above sulfides exhibiting colossal magnetoresistance. The high-temperature phase ($T > T_{c_2}$) is a paramagnetic metal. At $T \sim T_{c_2}$, a transition to the ferromagnetic state takes place, with the conduction character changing from metallic to semiconducting. The phase transition at T_{c_1}, associated possibly with lattice distortion, is accompanied by a strong increase in the magnetization and by a change in the conduction character of the semiconducting phase.

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