Colossal magnetoresistance of $Fe_xMn_{1-x}S$ magnetic semiconductors

G. A. Petrakovskiĭ,*) L. I. Ryabinkina, N. I. Kiselev, D. A. Velikanov, and A. F. Bovina

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

G. M. Abramova

Krasnoyarsk State University, 660041 Krasnoyarsk, Russia

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The magnetic, electric, magnetoresistive, and structural properties are investigated in the sulfide solid solutions $Fe_xMn_{1-x}S$, which are based on the antiferromagnetic semiconductor α-MnS (the fcc NaCl lattice). Colossal negative magnetoresistance ($\delta_H \sim -83\%$ at 160 K for $x \sim 0.29$), comparable to that observed in La–Ca–Mn–O polycrystals and films ($\delta_H \sim -90\%$ at 100 K and 40 kOe), is observed in compounds with intermediate concentrations $0.26 < x < 0.4$, corresponding to the region of incipient ferromagnetism. © *1999 American Institute of Physics.* [S0021-3640(99)01212-8]

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The compounds $Re_{1-x}Me_xMnO_3$ with perovskite structure, where Re are trivalent La, Pr, Y, Nd, and other ions, and Me are divalent Pb, Sr, Ca, and Ba ions, are under intensive investigation.[1] The interest in these materials is due to the observation of colossal magnetoresistance (CMR) in them under certain technological conditions and doping levels. The practical significance of this effect and the importance of studying its mechanism are stimulating the search for new compounds with CMR and the experimental investigation of the transport properties in materials of different structural types.

It is known[2] that manganese monosulfide α-MnS, similarly to $LaMnO_3$ (cubic perovskite structure), has a peculiar antiferromagnetic order with a characteristic ferromagnetic orientation of the spins in alternating planes and a lattice distortion wherein the cubic lattice is protracted along one of the diagonals of the cube.[2,3] In α-MnS, in contrast to $LaMnO_3$ ($T_s \sim 900$ K, $T_N \sim 140$ K), the structural transition temperature T_s is comparable to the Néel temperature ($T_N \sim 148$ K). The band structure and the nonactivational conductivity for high values of the resistivity ($\sim 10^8\ \Omega \cdot$cm) at $T < T_N$ in α-MnS,[4] just as in $LaMnO_3$,[5] are characteristic for a band insulator. In the paramagnetic state $LaMnO_3$ and α-MnS are semiconductors. Just as in $LaMnO_3$-based systems,[1] concentration transitions from an antiferromagnetic semiconductor state into a ferromagnetic metallic state are produced in cation-substituted manganese sulfides $Me_xMn_{1-x}S$ as the dopant concen-

tration changes.[4,6] It is important to clarify the possibility of CMR in materials based on manganese monosulfide.

We report in the present letter the results of an investigation of the structural, electric, magnetic, and magnetoresistive properties of sulfide compounds of the system $Fe_xMn_{1-x}S$ synthesized on the basis of α-MnS.

Polycrystalline samples of $Fe_xMn_{1-x}S$ ($0<x\leqslant 0.5$) were obtained from pure iron, manganese, and sulfur by the ampul method.[6,7] Investigations of the physical properties were performed as a function of concentration x, temperature T, and magnetic field H. The resistivity measurements were performed by the potentiometric method using dc current in a zero magnetic field and in transverse magnetic fields up to 10 kOe in the temperature range 77–300 K. A SQUID was used to measure the magnetic properties of the samples in the temperature range 4.2–300 K in fields up to 100 Oe. X-ray diffraction analysis (XDA) was performed with a DRON-2.0 diffractometer and monochromatized CuK_α radiation in the temperature range 77–300 K.

The XDA data showed the synthesized $Fe_xMn_{1-x}S$ samples at room temperature to be single-phase solid solutions with the fcc NaCl lattice that is characteristic for manganese monosulfide. As the degree x of cationic substitution increases, the cubic cell is compressed and the lattice parameter decreases from 5.222 Å ($x=0$) to 5.165 Å ($x\sim 0.5$). Near the Néel temperature the $Fe_xMn_{1-x}S$ samples possess a structural distortion similar to the orthorhombic distortion of the lattice in α-MnS at $T_N=148$ K.[3]

The SQUID data show that as the iron concentration in $Fe_xMn_{1-x}S$ increases, the antiferromagnetic transition temperature increases from 148 K ($x=0$) to 196 K ($x=0.25$). A concentration transition from an antiferromagnetic to a ferromagnetic state is observed in the concentration range $0.25<x<0.29$. The transition is accompanied by a sharp (two orders of magnitude) increase in the magnetic susceptibility from $\chi_{4.2\,\mathrm{K}}=8.56\times 10^{-5}$ cm^3/g ($x\sim 0.25$) to $\chi_{4.2\,\mathrm{K}}=2.43\times 10^{-3}$ cm^3/g ($x\sim 0.29$) (Fig. 1) and a field dependence of the magnetization that is characteristic of a ferromagnet.[6] The Curie temperature of the ferromagnetic samples is $T_C\sim 800$ K. As an illustration, the temperature dependence of the magnetization for the composition $x=0.3$ is displayed in the inset in Fig. 1. Anomalous behavior of the susceptibility was observed in the experimental samples in weak fields ($H\sim 100$ Oe) at low temperatures ($T\sim 30$–40 K).

According to the resistivity measurements, the increase in the magnetic susceptibility of samples with $0.25\leqslant x\leqslant 0.29$ due to the appearance of ferromagnetic order is accompanied by a decrease in the resistivity measured in a zero magnetic field. For example, $\rho_{77\,\mathrm{K}}=49.5\times 10^6\ \Omega\cdot$cm for samples with $x\sim 0.25$, while $\rho_{77\,\mathrm{K}}=32.1\times 10^2\ \Omega\cdot$cm for $x\sim 0.29$. As x is increased further, a semiconductor–semimetal concentration transition is observed (Fig. 2), and $\rho_{77\,\mathrm{K}}=8.88\ \Omega\cdot$cm for $x=0.4$.

Investigations of the magnetoresistive properties established that samples with $x\leqslant 0.25$, being antiferromagnetic semiconductors, and do not show a strong magnetic field dependence of the resistivity in the temperature range 77–300 K in magnetic fields up to 10 kOe.

In $Fe_xMn_{1-x}S$ samples with intermediate concentration $0.25<x<0.4$ the temperature dependence and the magnitude and sign of the magnetoresistance were found to depend on the magnetic field. It is seen in Fig. 3a, which shows the temperature dependence of the magnetoresistance in fields of 5 and 10 kOe for composition $x\sim 0.29$, that

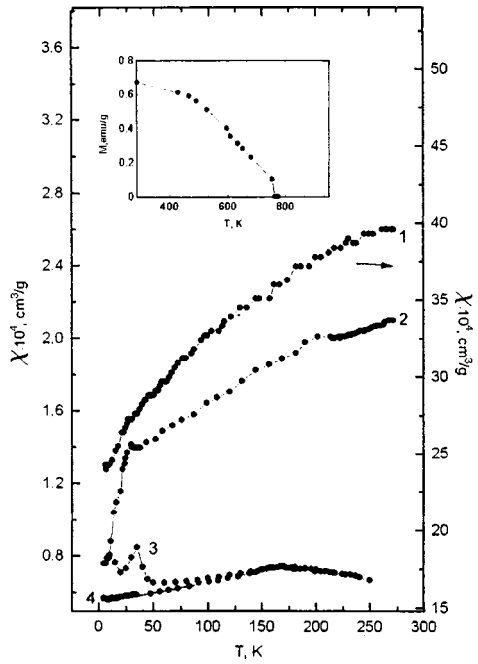

FIG. 1. Temperature dependences of the magnetic susceptibility of the sulfides $Fe_xMn_{1-x}S$ in the range 4.2–300 K for compositions x: 0.29 (*1*), 0.25 (*2*), 0.05 (*3*), and 0 (*4*). Inset: Temperature dependence of the magnetization of $Fe_xMn_{1-x}S$ with $x \sim 0.3$ in the temperature range 300–800 K in a field $H = 700$ Oe.

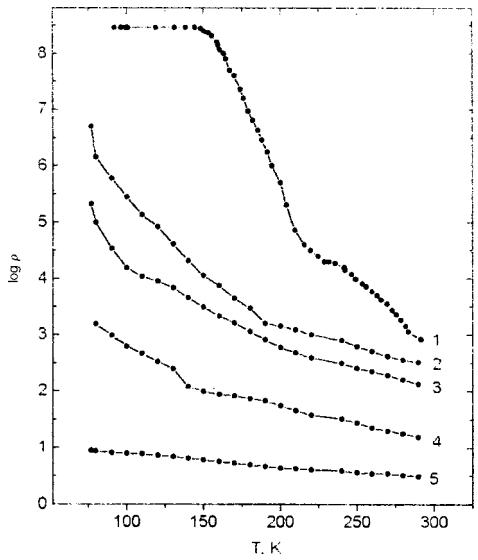

FIG. 2. Temperature dependences of the resistivity of the sulfides $Fe_xMn_{1-x}S$ for compositions $x = 0$ (*1*), 0.15 (*2*), 0.25 (*3*), 0.29 (*4*), and 0.4 (*5*).

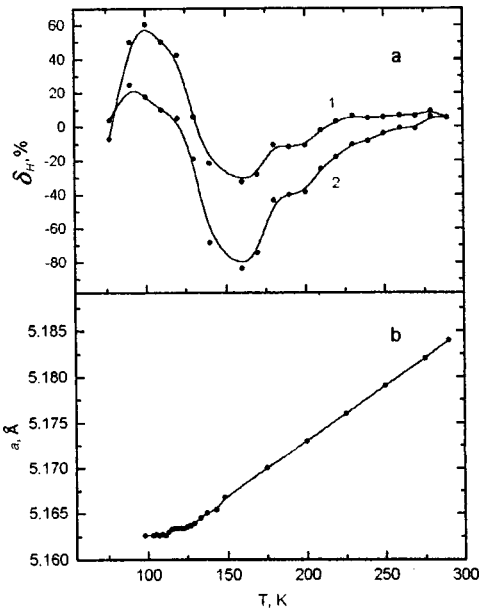

FIG. 3. Temperature dependence of the magnetoresistance δ_H (a) and lattice parameter (b) for $Fe_xMn_{1-x}S$ ($x \sim 0.29$); $H = 5$ kOe (*1*) and 10 kOe (*2*).

the negative CMR increases with decreasing temperature and reaches a maximum (for given temperature and field ranges) value $\delta_H = (\rho_H - \rho_0)/\rho_H = -83\%$ at $T \sim 160$ K in a 10 kOe field. Below ~ 150 K, in the region of the structural distortion (Fig. 3b), the magnetoresistance becomes positive and δ_H reaches $\sim 60\%$ at 90 K in a 5 kOe field and 20% in a 10 kOe field. As temperature decreases further, the positive magnetoresistance decreases, and δ_H once again becomes negative near liquid-nitrogen temperature.

As the iron concentration x increases, the negative magnetoresistance decreases, and $\delta_H = -40\%$ for $x \sim 0.3$ at 77 K in a 10 kOe field. In ferromagnetic samples with $x \geqslant 0.4$, corresponding to the semiconductor–semimetal concentration transition range, the negative magnetoresistance does not exceed 10%.

In summary, the results presented above attest to the presence of the CMR effect in materials based on manganese monosulfide.

In Nagaev's paper[1] it is conjectured that the CMR mechanism in lanthanides is due to the formation of the magnetically two-phase state and attendant electronic stratification with preservation of a homogeneous crystal lattice.

All of the currently available experimental results on the physical properties of the sulfides $Fe_xMn_{1-x}S$, specifically, calculations of the magnetic phase diagram, measurements of the magnetization in weak (up to 100 Oe) and strong (up to 20 kOe) fields,[6] and Mössbauer investigations[8] suggest that a possible mechanism for CMR in the magnetic semiconductors $Fe_xMn_{1-x}S$ could be magnetic and electronic phase separation. A characteristic feature of the sulfide compounds $Fe_xMn_{1-x}S$ investigated in the present work is their two-phase nature over a wide temperature range (at least in the range 77–300 K). According to Mössbauer data,[8] the ferromagnetic samples with $x \geqslant 0.3$ at room tempera-

ture consist of a collection of paramagnetic and ferromagnetic phases, and at 77 K the samples consist of two magnetically ordered phases. It can be concluded on the basis of these data that as the temperature decreases, the paramagnetic part of the material passes into a magnetically ordered state. One can see from Fig. 3 that the negative CMR increases with decreasing temperature (in the range 150–300 K). Since the magnetic state of the samples changes with decreasing temperature, it can be inferred that for effective magnetic and electronic percolation to appear a definite ratio of the volumes of the magnetic phases for a given magnetic field is required. The change in sign of the magnetoresistance at $T<150$ K is probably due to changes in the crystal lattice, since a structural distortion is observed in this temperature range.

In summary, new compounds $Fe_xMn_{1-x}S$ which have a colossal negative magnetoresistance and crystallize in the cubic NaCl structure have been found. The observed behavior of the magnetic and electric properties of the compounds $Fe_xMn_{1-x}S$ shows that it would be promising to study materials based on manganese monosulfide.

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*)e-mail: gap@cc.krascience.rssi.ru

[1] É. L. Nagaev, Usp. Fiz. Nauk **166**, 833 (1996).
[2] J. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963) [Russian original, Metallurgiya, Moscow, 1968].
[3] H. H. Heikens, G. A. Wiegers, and C. F. van Bruggen, Solid State Commun. **24**, 205 (1977).
[4] G. V. Loseva, S. G. Ovchinnikov, and L. I. Ryabinkina, Fiz. Tverd. Tela (Leningrad) **28**, 2048 (1986) [Sov. Phys. Solid State **28**, 1145 (1986)].
[5] L. P. Gor'kov, Usp. Fiz. Nauk **168**, 665 (1998).
[6] G. A. Petrakovskiĭ, S. S. Aplesnin, G. V. Loseva *et al.*, Fiz. Tverd. Tela (Leningrad) **33**, 406 (1991) [Sov. Phys. Solid State **33**, 233 (1991)].
[7] G. A. Petrakovskii, G. V. Loseva, L. I. Ryabinkina, and S. S. Aplesnin, J. Magn. Magn. Mater. **140–144**, 146 (1995).
[8] G. V. Loseva, L. I. Ryabinkina, S. G. Ovchinnikov, and O. A. Bayukov, Fiz. Tverd. Tela (Leningrad) **25**, 3717 (1983) [Sov. Phys. Solid State **25**, 2142 (1983)].

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