

## MAGNETISM AND FERROELECTRICITY

# Antiferromagnet–Ferromagnet Transition in $\alpha$ - $\text{Mn}_x\text{S}$ Manganese Sulfides

G. A. Petrakovskii\*, L. I. Ryabinkina\*, G. M. Abramova\*\*, D. A. Velikanov\*, and A. F. Bovina\*

\*Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia

\*\*Krasnoyarsk State University, Krasnoyarsk, 660041 Russia

e-mail: ovm@online.ru

Received July 19, 2000

**Abstract**—Off-stoichiometric manganese monosulfides  $\alpha$ - $\text{Mn}_x\text{S}$  ( $1 \leq x \leq 1.25$ ) are synthesized, and their crystal structure and magnetic properties are studied in the 4.2- to 300-K range. The compounds have a NaCl fcc lattice. Increasing the manganese ion concentration  $x$  in the antiferromagnetic semiconductors  $\alpha$ - $\text{Mn}_x\text{S}$  is found to result in concentration- ( $x_c \sim 1.05$ ) and temperature-driven ( $T_c \sim 50$  K) magnetic transitions from the antiferromagnetic to ferromagnetic state, with the cubic structure remaining unchanged. © 2001 MAIK “Nauka/Interperiodica”.

It is customarily assumed [1, 2] that manganese monosulfide, similar to MnO and NiO, is a classical second-type antiferromagnet, with the magnetic unit cell being a doubled crystallographic cell. The magnetic moments associated with the  $\text{Mn}^{2+}$  ions lie in the (111)-type planes and exhibit ferromagnetic in-plane and antiferromagnetic intraplane ordering. This magnetic structure is typical of rare-earth metal oxides with a  $\text{LaMnO}_3$ -type perovskite structure [3]. Interest in manganese monosulfide increased after the discovery in its solid solutions  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  of a colossal negative magnetoresistance [4], whose mechanism, as well as ferromagnetic nature, remains unclear. It thus appeared of interest to perform an integrated investigation of the physical properties of manganese monosulfide.

This paper presents the results of an investigation into the temperature behavior of the structure (100–300 K) and magnetic properties (4.2–300 K) of the  $\alpha$ - $\text{Mn}_x\text{S}$  sulfides ( $1.00 \leq x \leq 1.25$ ). The investigation was carried out on single-crystal ( $x = 1.00$ ) and polycrystalline ( $x = 1.00, 1.05, 1.15$ , and  $1.25$ ) samples. The technology used to prepare the polycrystals was described in [5]. The  $\alpha$ - $\text{Mn}_x\text{S}$  single crystal was obtained by sulfidization of molten metallic manganese. The x-ray characterization of the samples was performed on a DRON-2.0 diffractometer with  $\text{CuK}\alpha$  radiation within a grazing angle region of  $0^\circ$  to  $70^\circ$ . The magnetization of the samples was measured with a SQUID magnetometer in the temperature range from 4.2 to 300 K in a magnetic field of 100 Oe.

The x-ray diffraction measurements showed that at 300 K the samples have the fcc NaCl lattice typical of manganese monosulfide. The lattice parameter for the single crystal with  $x = 1.00$  is  $a = 5.216$  Å, and for the polycrystal,  $a = 5.222$  Å, which is close to the data

quoted in [2] ( $a = 5.22$  Å). At  $T \sim 166$  K, the lattice parameter exhibits an anomaly similar to the one observed at 150 K in [2], which indicates a rhombohedral distortion of the cubic lattice. The lattice parameter decreases with decreasing temperature (Fig. 1a); this decrease becomes sharper for  $T < 166$  K, but within the  $100 < T < 122$  K region, it is practically temperature-independent. The results of the structural study of the single crystal are corroborated by optical measurements made on the same crystal [6]. Optical measure-

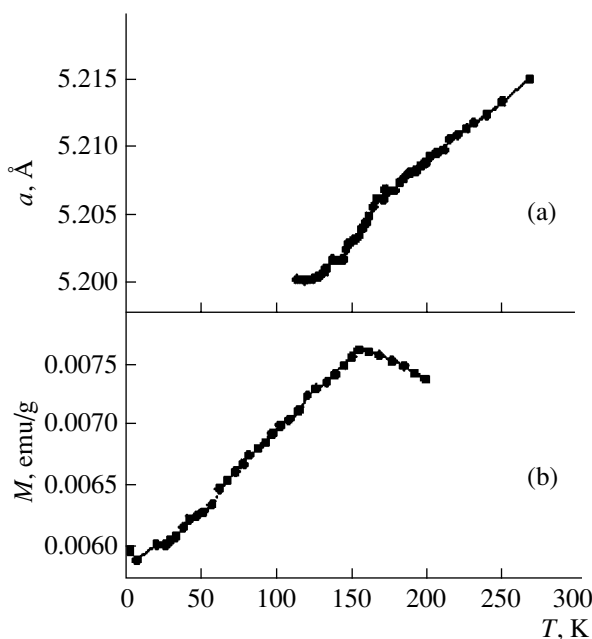
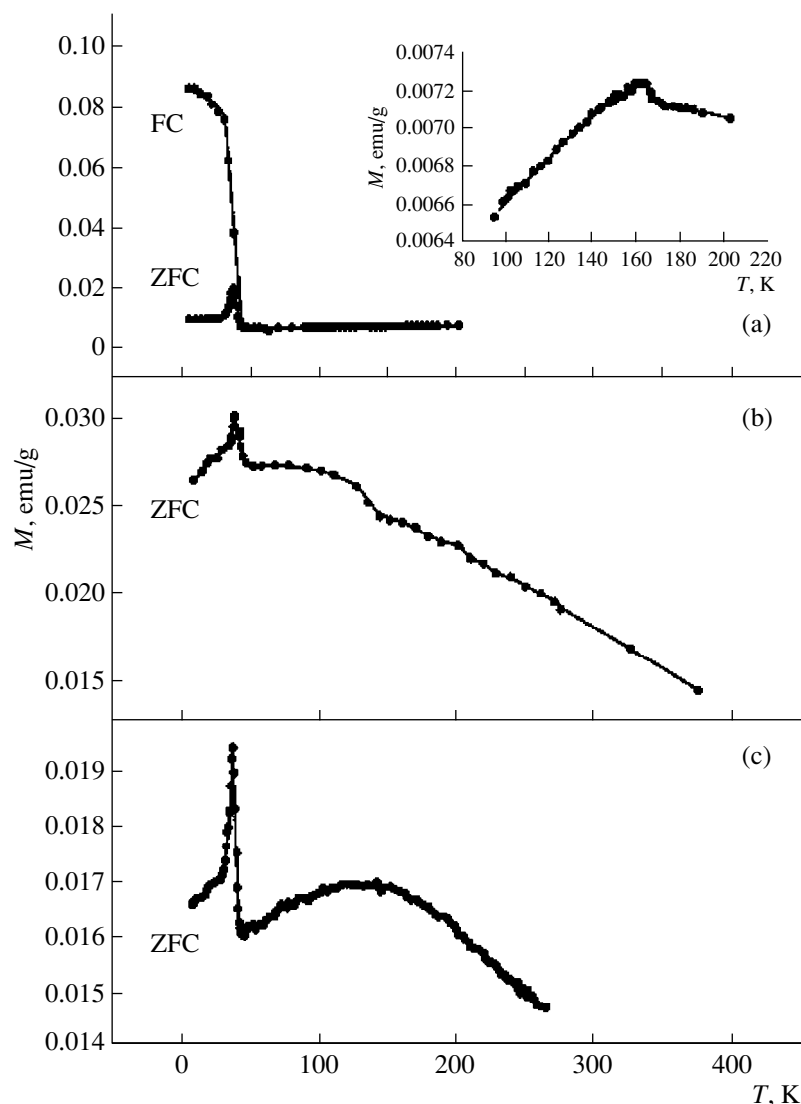


Fig. 1. Temperature dependences of (a) the lattice parameter and (b) magnetization of  $\alpha$ - $\text{MnS}$ .



**Fig. 2.** Temperature dependences of the magnetization of  $\alpha\text{-Mn}_x\text{S}$  with compositions ( $x$ ): (a) 1.05, (b) 1.15, and (c) 1.25. The inset to Fig. 2a shows the temperature dependence of magnetization obtained for  $x = 1.05$  in the 100- to 200-K region.

ments and a calculation of the temperature coefficient of expansion yield  $T_s = 162 \pm 2$  K for the temperature of the structural transition in single-crystal manganese monosulfide. As the manganese concentration in  $\text{Mn}_x\text{S}$  ( $1.00 \leq x \leq 1.25$ ) increases at 300 K, the cubic cell parameter of the polycrystalline sample varies from 5.222 Å ( $x = 1.00$ ) to 5.218 Å ( $x = 1.25$ ).

Figure 1b shows the temperature dependence of the magnetization of single-crystal  $\alpha\text{-MnS}$  measured in a magnetic field perpendicular to the (100) plane. This dependence is similar to the one reported in [2] and passes through a maximum at  $T_N = 157$  K, which is evidence of a transition from the paramagnetic to antiferromagnetic state. Similarly to the  $\alpha\text{-MnS}$  single crystal studied in [2], in our crystal, the antiferromagnetic transition is observed to occur in the region of existence of the distorted NaCl structure. The magnetic

susceptibility of  $\alpha\text{-MnS}$  at  $T_N$  is  $76.2 \times 10^{-6} \text{ cm}^3/\text{g}$  ( $66.28 \times 10^{-4} \text{ cm}^3/\text{mol}$ ), which is in accord with available data ( $63.5 \times 10^{-4} \text{ cm}^3/\text{mol}$  [2]). In the 200–400-K region, the magnetic susceptibility obeys the Curie–Weiss law with a paramagnetic Curie temperature of  $\sim -600$  K.

Figure 2a presents the temperature dependence of magnetization for the  $\alpha\text{-Mn}_x\text{S}$  sulfide with  $x = 1.05$  measured in a field of 100 Oe. The magnetization of this sample measured within the 45–270-K region behaves similarly to  $\alpha\text{-MnS}$  manganese monosulfide. At  $T_N = 155$  K, one observes a maximum indicating the transition from the paramagnetic to antiferromagnetic state. At the Néel temperature, the magnetic susceptibility for  $x = 1.05$  is close to that found for  $x = 1.00$ . At  $T_c \sim 40$  K, a second magnetic transition similar to that observed in the  $\text{Cr}_{0.5}\text{Mn}_{0.5}\text{S}$  solid solution [7] was dis-

covered. The temperature dependence of magnetization measured on a ZFC sample exhibits a sharp peak at  $T_c$  (the Hopkinson effect) (Fig. 2a). The FC magnetization measured at  $H = 100$  Oe is characteristic of ferromagnets and is evidence of a transition from the antiferromagnetic to ferromagnetic state. The ZFC magnetization measured on this sample ( $x = 1.05$ ) at 4.2 K is  $95.3 \times 10^{-4}$  emu/g.

Figure 2b displays the temperature dependence of ZFC magnetization for the  $x = 1.15$  sulfide. The magnetization of this sample within the 4.2–50-K interval behaves as it does in the sample with  $x = 1.05$  (Fig. 2a). The transition point to the low-temperature ferromagnetic phase in this sulfide is  $T_c = 45$  K. For  $T > T_c$ , the magnetization of the sulfide with  $x = 1.15$  differs in behavior from that observed in the previously mentioned samples. As the temperature increases, the magnetization drops to 370 K, with an anomaly seen at  $T = 133$  K. In the 133- to 370-K interval, the sample with  $x = 1.15$  does not obey the Curie–Weiss law characteristic of the manganese monosulfide ( $x = 1.00$ ) in the paramagnetic region. The magnetization measured at 4.2 K in a field of 100 Oe is  $266.7 \times 10^{-4}$  emu/g, which is an order of magnitude higher than that of samples with lower manganese contents. The temperature dependence of the magnetization of the sulfide with  $x = 1.25$  is shown in Fig. 2c; it is similar to that observed in the  $x = 1.05$  sample.

On comparing our results with the available data on the conductivity of off-stoichiometric manganese sulfides [5], we note that the increase in magnetization observed to occur in the  $Mn_xS$  system at 300 K is accompanied by metallization of the samples, with the electrical resistivity  $\rho$  at 300 K decreasing by two orders of magnitude as  $x$  varies from 1.00 to 1.05. The temperature dependence of the electrical resistivity of off-stoichiometric manganese sulfides at 77–300 K behaves similarly to  $\rho(T)$  for the monosulfide with  $x = 1.00$  and exhibits a sharp break at the points of structural and antiferromagnetic transitions.

Thus, we have found that manganese monosulfide undergoes concentration- and temperature-driven magnetic transitions. At room temperature, lattice compression occurring with increasing manganese concentration is accompanied by an increase in the magnetization by an order of magnitude and a decrease in the electrical resistivity by two orders of magnitude. A similar situation is observed to occur in the cation-substituted sulfides  $Me_xMn_{1-x}S$  ( $Me = Cr, Fe$ ) [7]. The similarity between the concentration dependences of the lattice parameter, magnetization, and electrical resistivity suggests that ferromagnetism in the  $Mn_xS$  and  $Me_xMn_{1-x}S$  sulfides may set in by similar mechanisms.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, grant no. 00-02-81059 Bel 2000a.

#### REFERENCES

1. É. L. Nagaev, *Physics of Magnetic Semiconductors* (Nauka, Moscow, 1979).
2. H. H. Heikens, G. A. Wiegers, and C. F. van Bruggen, *Solid State Commun.* **24** (3), 205 (1977).
3. É. L. Nagaev, *Usp. Fiz. Nauk* **166** (8), 833 (1996) [*Phys. Usp.* **39**, 781 (1996)].
4. G. A. Petrakovskii, L. I. Ryabinkina, G. M. Abramova, *et al.*, *Pis'ma Zh. Éksp. Teor. Fiz.* **69** (12), 895 (1999) [*JETP Lett.* **69**, 949 (1999)].
5. G. V. Loseva, L. I. Ryabinkina, L. S. Emel'yanova, and A. V. Baranov, *Fiz. Tverd. Tela (Leningrad)* **22** (12), 3698 (1980) [*Sov. Phys. Solid State* **22**, 2165 (1980)].
6. A. V. Malakhovskii, T. P. Morozova, V. N. Zabluda, and L. I. Ryabinkina, *Fiz. Tverd. Tela (Leningrad)* **32** (4), 1012 (1990) [*Sov. Phys. Solid State* **32**, 596 (1990)].
7. G. A. Petrakovskii, L. I. Ryabinkina, D. A. Velikanov, *et al.*, *Fiz. Tverd. Tela (St. Petersburg)* **41** (9), 1660 (1999) [*Phys. Solid State* **41**, 1520 (1999)].

*Translated by G. Skrebtsov*