

MAGNETISM  
AND FERROELECTRICITY

## Magnetic, Resonant, and Thermal Properties of $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$ Crystals

G. M. Abramova<sup>a,b</sup>, G. A. Petrakovskii<sup>a,b</sup>, M. Boem<sup>c</sup>, A. M. Vorotynov<sup>b</sup>, A. V. Kartashev<sup>b</sup>,  
D. A. Velikanov<sup>b</sup>, V. V. Sokolov<sup>d</sup>, and A. Yu. Pichugin<sup>d</sup>

<sup>a</sup> Siberian Federal University, Svobodnyĭ pr. 79, Krasnoyarsk, 660041 Russia  
e-mail: agm@iph.krasn.ru

<sup>b</sup> Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia

<sup>c</sup> Laue–Langevin Institute, Grenoble, France

<sup>d</sup> Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,  
ul. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

Received April 22, 2008

**Abstract**— $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  single crystals were studied. A magnetic transition is detected near 197 K, which is accompanied by anomalies of the thermal, electrical, and resonant properties.

PACS numbers: 75.50.Pp, 76.30.-v, 75.47.-m

DOI: 10.1134/S106378340902019X

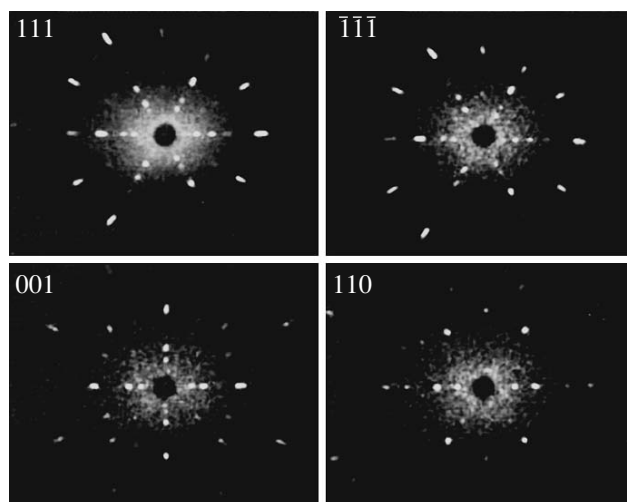
### 1. INTRODUCTION

Manganese monosulfide with an NaCl-type face-centered cubic lattice, as well as NiO and  $\text{LaMnO}_3$  oxides, is a Mott–Hubbard insulator [1], in which electron correlations play an important role in the formation of magnetic and electrical properties [2]. Studying Mott–Hubbard insulator solid solutions permits one to elucidate the possibility of controlling the physical properties of the materials by choosing a certain substitutional cation or anion that causes a change in the free-electron concentration. It was previously established [3–5] that substitution of iron ions for manganese ions in manganese monosulfide significantly decreases (by six orders of magnitude) the electrical resistivity at room temperature. In this work, we experimentally studied the magnetic, resonant, and thermal properties of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  single crystals.

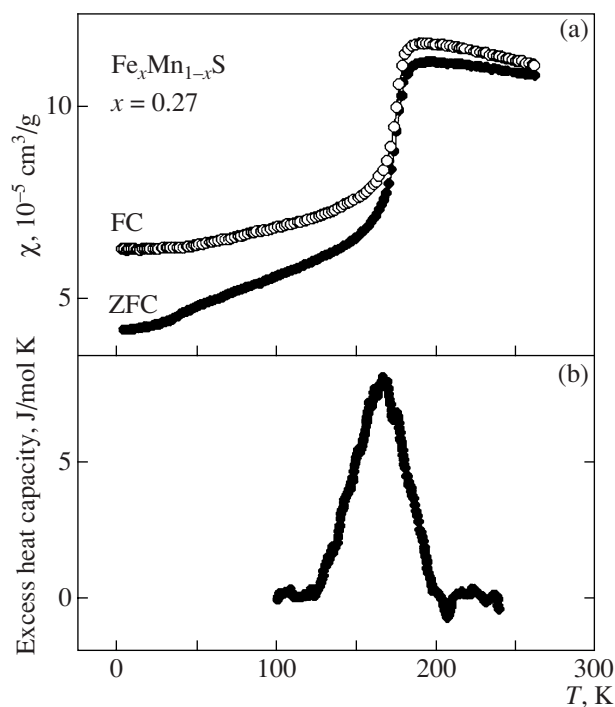
### 2. EXPERIMENTAL

Polycrystalline sulfide  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  with  $x = 0.27$  was synthesized by sulfidization from a mixture of oxides and elemental iron taken in the stoichiometric proportion. From the powders thus obtained, crystals 0.5–1.0 cm<sup>3</sup> in size were grown by spontaneous crystallization. According to X-ray diffraction data obtained using a DRON diffractometer with  $\text{CuK}_\alpha$  radiation, the synthesized  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  crystals have an NaCl-type fcc structure characteristic of manganese monosulfide. The cation substitution is accompanied by lattice compression and a decrease in the lattice parameter from 5.22 Å (at  $x = 0$ ) to 5.17 Å (at  $x = 0.27$ ) [6]. No attendant phases

were found to within the experimental error. Mössbauer studies [6] showed that pure iron is absent to within 1%. The  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  crystals have clear Laue X-ray diffraction patterns (Fig. 1) measured on a single-crystal Laue diffractometer (OrientExpress, ILL, France). The magnetic properties were measured using a SQUID magnetometer in the temperature range 4.2–275.0 K in a magnetic field of 100 Oe. The resonant properties were measured in the range 77–300 K in a magnetic field of 100 Oe at a frequency of 9.4 GHz on an EPR



**Fig. 1.** Magnetic Laue X-ray diffraction pattern of an  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  single crystal.

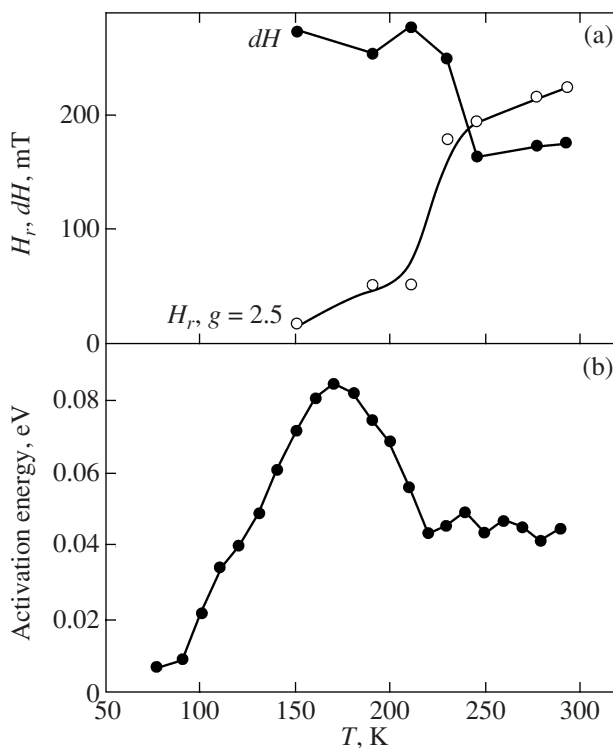


**Fig. 2.** Temperature dependences of (a) the magnetic susceptibility and (b) the excess heat capacity of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$ .

spectrometer. The thermal properties were measured by differential microcalorimetry. Neutron diffraction studies were carried out on powders prepared from single crystals using a DIA diffractometer (neutron wavelength, 1.91 Å) in the temperature range 2–250 K.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

Manganese monosulfide is well known to be an anti-ferromagnetic semiconductor with a Néel temperature of 147 K [1, 4]. Figure 2 presents the temperature dependences of the magnetic susceptibility and excess heat capacity for a  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  solid solution ( $x = 0.27$ ). A thermal anomaly was detected in the range 120–200 K with a maximum at  $T_i = 170$  K. The phase transition enthalpy is 184.97 J/mol, and the entropy change is  $\Delta S = 0.13087R$ , where  $R = 8.31$  J/K mol. A maximum of the magnetic susceptibility indicating the occurrence of a magnetic transition was observed near  $T_N = 190$  K. The critical temperature of the magnetic transition in the  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  ( $x = 0.27$ ) is  $\sim 50^\circ$  higher than the Néel temperature of manganese monosulfide. In contrast to MnS, the magnetic susceptibility of iron-substituted sulfide  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  ( $x = 0.27$ ) is changed stepwise near the magnetic transition and has an additional anomaly at low temperatures near  $T = 30$  K. Over the entire temperature range studied, the ZFC and FC magnetic susceptibilities measured on cooling in a zero and a non-



**Fig. 3.** Temperature dependences of (a) the resonance field  $H_r$  and the width  $dH$  of the first magnetic resonance line and (b) the activation energy of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$ .

zero magnetic field, respectively, differ in behavior. The difference between the ZFC and FC susceptibilities increases as the temperature decreases below  $T < 190$  K.

In manganese monosulfide,  $\text{Mn}^{2+}$  ions are in octahedral anion surroundings. The room-temperature magnetic resonance spectrum of the initial MnS contains one Lorentzian line with a  $g$  factor equal to 2 ( $S^6$  state). The resonance field of this line is practically independent of temperature in the range 160–300 K. According to Mössbauer studies [6],  $\text{Fe}^{2+}$  ions in  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  substitute for  $\text{Mn}^{2+}$  in the octahedral sites. Figure 3 presents the temperature dependences of the resonance field and the magnetic-resonance line width for  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$ . The magnetic resonance spectrum of the  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  solid solution is a wide line which can be described at 300 K by two Gaussians with resonance fields  $H_{r1} = 2.59$  kOe and  $H_{r2} = 1.15$  kOe. The  $g$  factor for the first Gaussian at room temperature is 2.5, which is significantly larger than that for the divalent manganese ion. As the temperature decreases, the resonance field decreases and the first Gaussian line narrows and transforms into a Lorentzian. Near the magnetic transition point, this line increases in width (Fig. 3) and the corresponding resonance field decreases sharply. The  $g$  factor for the second line exceeds the value typical of  $\text{Fe}^{2+}$  ( $g = 4.2$ ). Below the magnetic-transition tempera-

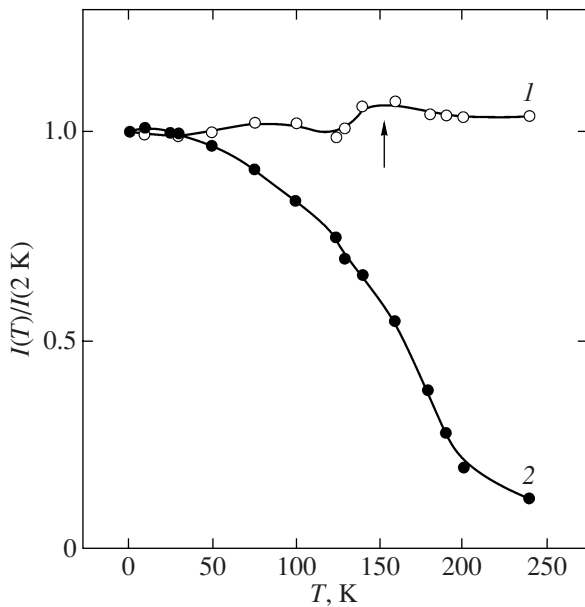


Fig. 4. Temperature dependences of the relative intensity of (1) the nuclear and (2) magnetic reflections of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  measured by neutron diffraction.

ture, the magnetic resonance lines decrease in intensity and, at  $T < 150$  K, no lines are observed, which indicates that a long-range magnetic order arose. Since the resistivity decreases sharply in the concentration range under study (for  $x = 0.29$ , the resistivity is  $0.18 \Omega \text{ cm}$  [5]), we can assume that, at room temperature, the material is a mixture of atoms with delocalized and localized electrons. The resistivity of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  crystals at room temperature is measured to be  $3.6 \text{ k}\Omega \text{ cm}$ , which is two orders of magnitude lower than that of manganese monosulfide. Figure 3b displays the temperature dependence of the conduction activation energy  $E_a$ . In the range 210–300 K, the activation energy is 0.045 eV. Near the magnetic transition point (170–210 K), the activation energy increases fairly sharply and then, below 170 K, it decreases.

Figure 4 presents the results of the neutron powder diffraction study of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  (the powder was prepared from a block single crystal), namely, the intensity variations of the nuclear (curve 1) and magnetic (curve 2) reflections. Near the thermal anomaly, the nuclear reflection intensity is changed indicating a lattice distortion. The magnetic-transition temperature as determined from the neutron diffraction data is 197 K. The

propagation vector of the magnetic structure is  $2\pi(1/2, 1/2, 1/2)$ . We also detected an attendant magnetic phase with a propagation vector  $2\pi(1/3, 1/3, 0)$ . The origin of this phase is not yet clear.

#### 4. CONCLUSIONS

Thus, the experimental studies of  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  single crystals have shown that the cation substitution in the  $\text{Fe}_x\text{Mn}_{1-x}\text{S}$  system substantially increases the magnetic-transition temperature compared to that of undoped manganese monosulfide. The magnetic transition is accompanied by an anomaly in the conduction activation energy and a thermal anomaly observed over a wide temperature range (down to 100 K). The substantial changes in the resonance field and the nuclear-reflection intensity in  $\text{Fe}_{0.27}\text{Mn}_{0.73}\text{S}$  observed with decreasing temperature are likely due to lattice distortions in this material, which can be caused, e.g., by magnetostriction.

#### ACKNOWLEDGMENTS

This work was supported in part by SB RAS–INTAS, grant no. 06-1000013-9002.

#### REFERENCES

1. G. V. Loseva, S. V. Ovchinnikov, and G. A. Petrakovskii, *Metal–Insulator Transition in 3d-Metal Sulfides* (Nauka, Novosibirsk, 1983) [in Russian].
2. N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979; Mir, Moscow, 1982).
3. G. V. Loseva, L. I. Ryabinkina, and S. V. Ovchinnikov, *Fiz. Tverd. Tela (Leningrad)* **33** (11), 3420 (1991) [*Sov. Phys. Solid State* **33** (11), 1929 (1991)].
4. G. M. Abramova and G. A. Petrakovskii, *Fiz. Nizk. Temp.* **32** (8/9), 954 (2006) [*Low Temp. Phys.* **32** (8/9), 725 (2006)].
5. G. M. Abramova, N. V. Volkov, G. A. Petrakovskii, E. Mita, O. A. Bayukov, D. A. Velikanov, A. M. Vorotynov, V. V. Sokolov, and A. F. Bovina, *Pis'ma Zh. Éksp. Teor. Fiz.* **86** (6), 427 (2007) [*JETP Lett.* **86** (6), 371 (2007)].
6. G. M. Abramova, G. A. Petrakovskii, O. A. Bayukov, V. A. Varnek, V. V. Sokolov, and A. F. Bovina, *Fiz. Tverd. Tela (St. Petersburg)* **50** (2), 229 (2008) [*Phys. Solid State* **50** (2), 237 (2008)].

Translated by Yu. Ryzhkov