Metal–Insulator Transition in $Fe_xMn_{1-x}S$ Crystals

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Results of an experimental study of MnS, FeS, and $Fe_xMn_{1-x}S$ single crystals are presented. The phase composition, the lattice parameters, and the state of paramagnetic ions in $Fe_xMn_{1-x}S$ have been determined by x-ray diffraction analysis and Mössbauer spectroscopy. A sequence of transitions have been found in iron manganese sulfide with $x = 0.29$ at temperatures $T_1 \approx 25$–50 K, $T_2 \approx 125$ K, and $T_3 \approx 190$ K with a change in kinetic properties and the formation of a metallic state at low temperatures $T \approx 2$ K. The possibility of a Mott–Hubbard transition in $Fe_xMn_{1-x}S$ sulfides with variation of the composition and the temperature is discussed.

1. INTRODUCTION

Interest in manganese monosulfide MnS and its cation-substituted solid solutions is associated with the detection of colossal magnetoresistance for a series of polycrystalline sulfides of the $Fe_xMn_{1-x}S$ system [1, 2]. The starting manganese monosulfide matrix of iron manganese sulfides $Fe_xMn_{1-x}S$ [3], as well as NiO and $LaMnO_3$ oxides, belongs to the class of Mott–Hubbard insulators (MHIs) [4], in which electron correlations play an important role in the formation of structural, magnetic, and electrical properties. It is known that the phase diagram of MHIs is complicated and, depending on the concentration of free electrons, suggests the formation of states with different magnetic and electrical properties. It was noted by Mott [4] that special attention should be paid to disordered systems with a small Hubbard gap, when, in addition to correlation effects, processes of the Anderson localization of charge carriers are exhibited in the substances. In this case, a comparison of physical properties of polycrystals and single crystals of the same composition can provide important information on the mechanism of kinetic processes and on the ground electron state of the substance. This work presents the results of an experimental study of single crystals of iron manganese sulfides $Fe_xMn_{1-x}S$.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The technology of single-crystal synthesis was described in [5]. The x-ray diffraction analysis of $Fe_xMn_{1-x}S$ samples was performed on a DRON dif-

fractometer in $CuK\alpha$ radiation at 110 and 300 K. Mössbauer studies were performed with powders obtained by grinding single crystals on a spectrometer with a $Co^{57}(Cr)$ source at 300 K. Resonance studies were performed at a frequency of 9.4 GHz. Temperature studies were performed with MnS and FeS single crystals and with three single-crystalline $Fe_xMn_{1-x}S$ samples of the same composition $x = 0.29$ (nos. 1, 2, and 3). Magnetic properties were studied in the temperature range 4.2–300 K on a SQUID magnetometer. The electrical resistance was measured by the four-contact method using a direct current in the temperature range 2–350 K. The Seebeck coefficients were measured on a special device in the range 2–350 K. The reflection spectra were measured in the middle IR range using an FT/IR-610 (JASCO) spectrometer and an IR microscope with an FFM detector.

3. RESULTS AND DISCUSSION

3.1. Room Temperature

According to x-ray diffraction data, $Fe_xMn_{1-x}S$ crystals at 300 K, similarly to the α-phase of manganese monosulfide, have a face-centered cubic (fcc) structure of the NaCl type. The substitution of iron ions for manganese ions in $Fe_xMn_{1-x}S$ leads to a decrease in the lattice parameter from 5.22 Å ($x = 0$) to 5.15 Å ($x = 0.29$). The found parameter of the cubic face-centered unit cell at 300 K $a = 5.15$–5.16 Å (depending on the quality of the $Fe_{0.29}Mn_{0.71}S$ samples) corresponds to the value observed for MnS under a pressure ≈ 4–5 GPa [6]. Hence, cation substitution in the $Fe_xMn_{1-x}S$ system at
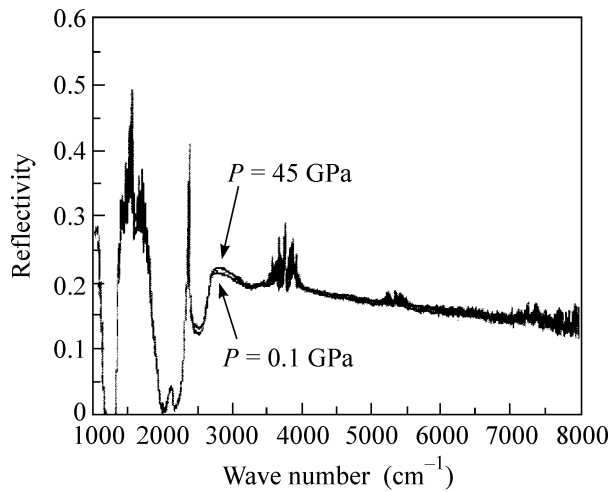
Fig. 1. Optical reflection spectrum of $Fe_{0.25}Mn_{0.75}S$ at 300 K. A contribution from the diamond anvil is observed in the region of small wave numbers.

Fig. 2. Concentration dependences of the electrical resistivity at 300 and 350 K in the $Fe_xMn_{1-x}S$ system ($x = 0$, 0.29, 1). Inset: temperature dependences of the electrical resistivity of $Fe_{0.29}Mn_{0.71}S$ and FeS single crystals.

300 K changes the parameter of the cubic unit cell of MnS similar to hydrostatic pressure.

It is known that a compression of the lattice leads, as a rule, to a transition of a Mott–Hubbard insulator to a metallic state [4] by virtue of a change in the overlap integrals and the overlap of two Hubbard bands. For manganese monosulfide MnS [6], a decrease in the optical gap and a transition to a metallic state are observed at room temperature under a pressure $P \approx 23$–26 GPa. With the aim of revealing an optical gap, studies of IR reflection spectra were performed for $Fe_{0.25}Mn_{0.75}S$ crystals at 300 K and various pressures. The results (Fig. 1) show that the observed reflection spectrum of the $Fe_{0.25}Mn_{0.75}S$ solid solution is close to the MnS spectrum at $P = 25$ GPa, which points to a decrease in the optical gap with an increase in the degree of cation substitution in $Fe_xMn_{1-x}S$ and to an increase in the concentration of charge carriers.

Figure 2 presents electrical resistivities at 300 and 350 K found for MnS, $Fe_{0.29}Mn_{0.71}S$, and FeS crystals. The inset in Fig. 2 shows temperature dependences of the electrical resistivity of $Fe_{0.29}Mn_{0.71}S$ and FeS crystals in the range 187–350 K. The electrical resistivity at room temperature $\rho(300\ K)$ for MnS equals $1.18 \times 10^4\ \Omega$ cm and is close to the value obtained in [7]. For iron monosulfide FeS, the value $\rho(300\ K) = 1.052 \times 10^{-3}\ \Omega$ cm agrees with the data of [3]. The $Fe_{0.29}Mn_{0.71}S$ crystals at 300 K have values of $\rho(300\ K) = 0.18$–$0.32\ \Omega$ cm, which are six orders of magnitude lower than those for MnS. This is a consequence of a concentration transition of the dielectric to a metallic state. The activation energy of $Fe_{0.29}Mn_{0.71}S$ near room temperature comprises 10^{-2} eV. This allows the $Fe_{0.29}Mn_{0.71}S$ crystals to be assigned to a higher degree to degenerate semiconductors or to Mott–Hubbard insulators with a small Hubbard gap. Measurements of
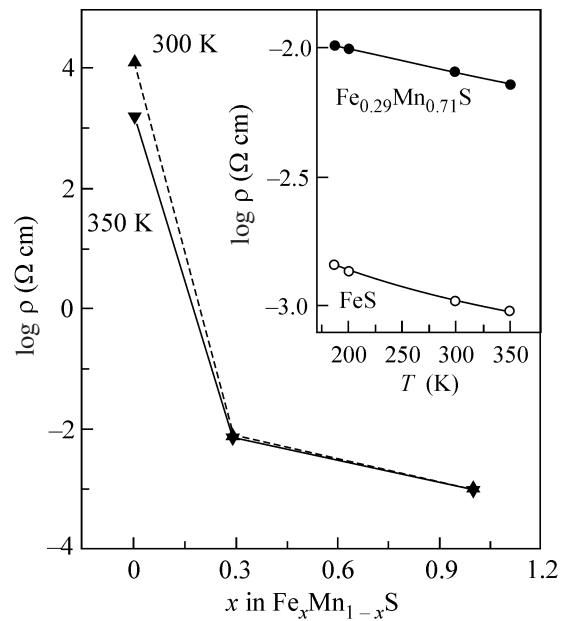
the Seebeck coefficient (S) of $Fe_{0.29}Mn_{0.71}S$ crystals showed that cation substitution at 300 K does not change the sign of S, which points to the p type of the conductivity of the solid solution. The value of S comprises 10.4 μV/K and is two orders of magnitude lower than that for MnS (517–900 μV/K) [8]. The significant decrease in the Seebeck coefficient in $Fe_{0.29}Mn_{0.71}S$ can be a consequence of both a decrease in the concentration of p charge carriers and an increase in the contribution of the electronic component of the conductivity, which was found in $Fe_xMn_{1-x}S$ polycrystals [7].

It is known that an octahedron is the main structural unit of the NaCl lattice of the ionic dielectric MnS. The manganese ion is located in the regular octahedral anionic environment (the quadrupole splitting $QS = 0.0$ mm/s, the isomeric shift $IS = 1.1$ mm/s [9], and the concentration of the ^{57}Fe isotope is no more than 0.5%). Figure 3 presents the results of studying Mössbauer and magnetic resonance spectra for $Fe_xMn_{1-x}S$ crystals ($0.05 \leq x \leq 0.29$) at room temperature. It is found that the replacement of manganese ions Mn^{2+} by iron ions Fe^{2+} is accompanied by the occurrence of a weak quadrupole splitting (Fig. 3a) pointing to a distortion of octahedra. The results are in good agreement with the magnetic resonance data (9.4 GHz). A deformation of the lattice of $Fe_xMn_{1-x}S$ sulfides explains the observed change in the resonance field (Fig. 3b). Changes in the intensity and shape of the EPR signal were observed with increasing degree of cation substitution, pointing to a metallization of the substance (more detailed results will be presented in a different
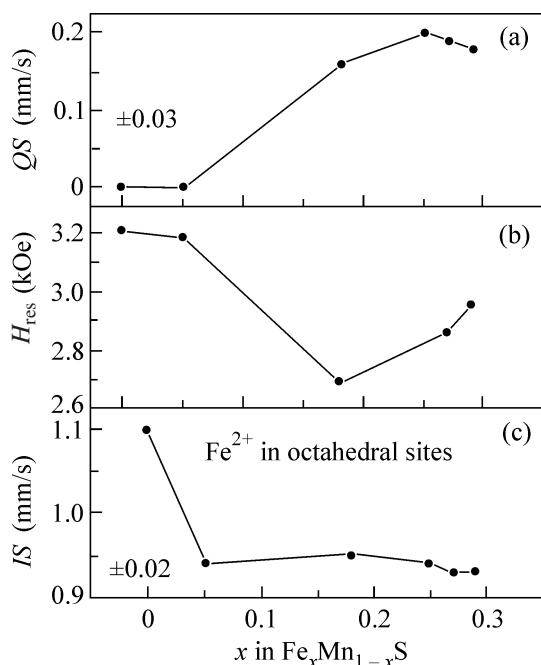
Fig. 3. Concentration dependences of (a) the quadrupole splitting, (b) the resonance field, and (c) the isomer shift for $Fe_xMn_{1-x}S$ crystals.
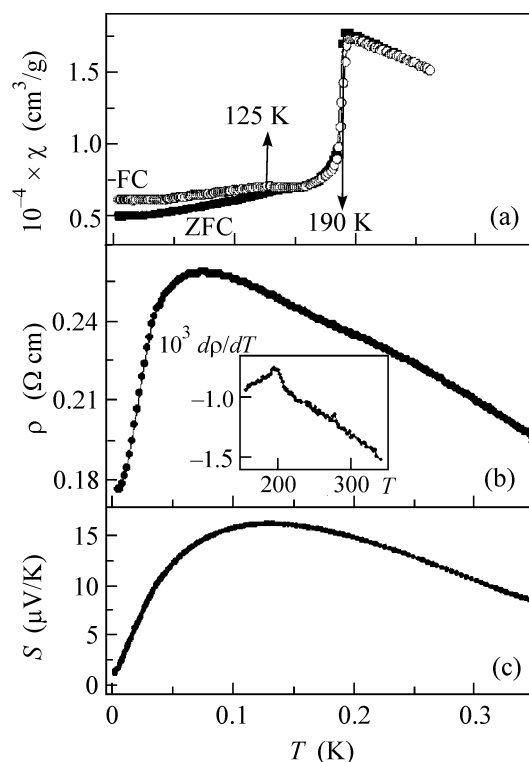

Fig. 4. Temperature dependences of (a) the magnetic susceptibility, (b) the electrical resistivity, and (c) the Seebeck coefficient for $Fe_{0.29}Mn_{0.71}S$ single crystals.

paper). The experimental values of isomer shifts (Fig. 3c) observed in $Fe_{0.29}Mn_{0.71}S$ are close to those observed in the covalent FeS sulfide [10]. This result indicates that the character of chemical bonding changes upon cation substitution, which leads to a decrease in chemical shift values.

Thus, the results of Mössbauer and resonance studies and measurements of the electrical resistivity and the Seebeck coefficient performed at 300 K allow the conclusion that the *d*-electron subsystem of the $Fe_{0.29}Mn_{0.71}S$ compound is to a great extent similar to covalent FeS. According to [11], correlation effects in iron monosulfide are less pronounced in comparison with manganese monosulfide. This leads to a decrease in the Hubbard gap and to lower values of the electrical resistivity in FeS. With regard to this fact and to a compression of the lattice and a decrease in the optical gap upon cation substitution in the $Fe_xMn_{1-x}S$ system, it can be suggested that the mechanism of the change in the electrical resistivity and the mechanism of the concentration electronic transition at 300 K in iron manganese sulfides are related not only to the formation of the impurity Fe band [3] but also to a decrease in the Hubbard gap in the electronic spectrum of the substance.

3.2. Low Temperatures

Experimental studies showed that a compression of the lattice and a decrease in the unit cell parameter to $a = 5.14$ Å are observed in $Fe_{0.29}Mn_{0.71}S$ samples with decreasing temperature from 300 to 100 K. No marked differences were observed in the x-ray diffraction patterns of the substance measured at 300 and 110 K.

Figure 4a presents temperature dependences of the magnetic susceptibility of a $Fe_{0.29}Mn_{0.71}S$ single crystal in the range 4.2–260 K. The magnetic susceptibility at 300 K and $H = 100$ Oe comprises 1.52×10^{-4} cm³/g (3.05×10^{-4} cm³/g for a block crystal). It is two orders of magnitude higher than that for manganese monosulfide, which agrees with the data obtained in studying polycrystalline $Fe_{0.29}Mn_{0.71}S$ samples [1, 2]. As distinct from polycrystals [1], a stepwise decrease in the magnetic susceptibility is observed in $Fe_{0.29}Mn_{0.71}S$ single crystals with decreasing temperature in the region of $T_1 = 190$ K. The magnetic transition temperature $T_1 = 190$ K is close to the Néel temperature of manganese monosulfide under pressure [12]. This allows the magnetic anomaly observed in $Fe_{0.29}Mn_{0.71}S$ at $T_1 = 190$ K to be identified as the establishment of antiferromagnetic order. The second magnetic anomaly manifested as a weakly pronounced maximum of susceptibility is observed in the region of $T_2 = 125$ K. According to [13], an additional magnetic transition is observed in manganese monosulfide at 123 K. Its nature has been poorly understood. A difference in the behavior of the magnetic susceptibility measured upon cooling in zero (ZFC) and specified FC magnetic fields is observed in $Fe_{0.29}Mn_{0.71}S$ single crystals at temperatures in the

range 4.2–125 K. In the region of 25–30 K, an additional, weakly pronounced anomaly is observed in the temperature dependences of the magnetic susceptibility. This anomaly is most pronounced in the temperature dependence of the AC magnetization. The magnetic susceptibility of $Fe_{0.29}Mn_{0.71}S$ at 4.2 K is close to the value characteristic of the antiferromagnetic phase of manganese monosulfide. It should be noted that the value and behavior of the magnetic susceptibility in the region of temperatures below 200 K substantially depend on the quality of the $Fe_{0.29}Mn_{0.71}S$ crystal. For block crystals, the anomaly in the region of 200 K becomes smeared, and a broad smeared maximum rather than a jump is observed in the magnetic susceptibility similar to that observed in polycrystals [1].

Figure 4b presents a typical temperature dependence of the electrical resistivity $\rho(T)$ observed for three block $Fe_{0.29}Mn_{0.71}S$ crystals. The measurements were performed in the range 2–350 K. The electrical resistivity increases with decreasing temperature with a weakly pronounced break in the region of 190 K. At temperatures below 50 K, a rather sharp decrease by a factor of 1.3 is observed in the electrical resistivity. The occurrence of phase changes in the electronic system at $T = 195$ K and $T = 25$ K is indicated by the anomalies of the temperature coefficient of the resistivity $d\rho/dT$ (for illustration, its anomaly at 190 K is shown in the inset in Fig. 4b). Based on the experimental data for $\rho(T)$, temperature dependences of the activation energy of the conductivity $E_a(T)$ were calculated. The results show that the activation energy of $Fe_{0.29}Mn_{0.71}S$ in the range of room temperatures equals $E_a = 0.012$–0.016 eV, depending on the quality of the crystal. With decreasing temperature, $E_a(T)$ decreases with a break in the region of the magnetic transition $T_1 = 190$ K and changes its sign to negative at temperatures below 75 K. Because the activation energy itself is always positive, the change of the sign of E_a indicates that a transition to a metallic state is observed in $Fe_{0.29}Mn_{0.71}S$ with decreasing temperature.

Additional information on the state of charge carriers and the behavior of the activation energy of the conductivity can be obtained from the results of studying the Seebeck coefficient. The experimental dependence of the Seebeck coefficient $S(T)$ for an $Fe_{0.29}Mn_{0.71}S$ single crystal is presented in Fig. 4c. With decreasing temperature, $S(T)$ increases (which is typical of semiconductors) and exhibits a maximum in the region of $T_2 = 125$ K. The absence of an anomaly of the Seebeck coefficient in the region of the magnetic transition at $T_1 = 190$ K indicates that no substantial changes occur in the concentration of charge carriers of the p type upon the establishment of AF order. At temperatures $T < T_2 = 125$ K, the Seebeck coefficient of $Fe_{0.29}Mn_{0.71}S$ decreases and becomes equal to 1.18 μV/K at 2 K. With regard to the results of [14] and to a decrease in $S(T)$ and $\rho(T)$ of $Fe_{0.29}Mn_{0.71}S$ with decreasing temperature,

it can be suggested that the temperature region of the maximum of $S(T)$ corresponds to the region of the crossover from activation to metallic conductivity of the Mott–Hubbard insulator.

From a comparison of the obtained results, it follows that the $Fe_{0.29}Mn_{0.71}S$ substance with decreasing temperature exhibits a sequence of phase transitions in the regions of $T_1 = 25$–50 K, $T_2 = 125$ K, and $T_3 = 190$ K in a zero magnetic field, as a result of which the type of conductivity changes. At low temperatures, the substance exhibits metallic properties. To reveal the detailed mechanism of the observed sequence of phase transitions and of the change in the type of conductivity, additional experimental studies are necessary.

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