

Mössbauer Studies of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ Single Crystals

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Abstract—Single crystals of iron manganese sulfides $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($0.25 \leq x \leq 0.29$) are experimentally investigated using Mössbauer spectroscopy and x-ray diffraction. The Mössbauer spectra measured at 300 K exhibit a single broadened line characteristic of paramagnets. The isomer shift of this line is equal to 0.92–0.94 mm/s, which is typical of Fe^{2+} ions in the octahedral position. The quadrupole splitting (0.18–0.21 mm/s) suggests a distortion of the coordination polyhedron of iron ions in the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ compounds.

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1. INTRODUCTION

Monosulfides of 3d elements located midway in the series (CrS, MnS, FeS) are known to be semiconducting antiferromagnets [1]. Their antiferromagnetic properties originate from ferromagnetic ordering of the magnetic moments of atoms in the metal layers separated by sulfur layers and from their interlayer antiferromagnetic ordering. The Néel temperature for ionic MnS with a NaCl-type face-centered cubic lattice and an electrical resistivity $\rho(300 \text{ K}) = 10^5 \text{ } \Omega \text{ cm}$ is $T_N = 147 \text{ K}$, whereas for more covalent FeS with $\rho(300 \text{ K}) = 0.6 \text{ } \Omega \text{ cm}$ and a hexagonal NiAs-type structure, it increases to $T_N = 590 \text{ K}$. Stoichiometric manganese monosulfide (the gamma phase) can also have a hexagonal structure (wurtzite) at 300 K [2]. This phase also exhibits antiferromagnetic ordering ($T_N = 100 \text{ K}$).

Among all the known cation-substituted systems [3–7] based on manganese monosulfide ($\text{Me}_x\text{Mn}_{1-x}\text{S}$, where $\text{Me} = \text{V}, \text{Fe}, \text{Cr}, \text{or Co}$), only the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solution system was found to exhibit ferromagnetism at 300 K [6, 7]. Ferromagnetic polycrystalline samples of this system possess colossal magnetoresistance [8, 9]. The conditions favoring the onset of colossal magnetoresistance and its mechanism, as well as the nature of ferromagnetic ordering in iron–manganese sulfides, remain the subjects of debate.

This paper presents the first results of x-ray structural and Mössbauer studies of iron–manganese sulfide single crystals $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ ($0.25 \leq x \leq 0.29$).

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

To prepare $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystals, we first synthesized sulfides in a powder form by sulfidization of the required amounts of mixtures of metal oxides and metallic iron (Fe, FeO, Fe_2O_3 , MnO_2) in a horizontal quartz reactor, with glassy carbon boats used as containers. The mixtures of metal oxides were heated to 700–800°C by quartz halogen lamps. The sulfidizing agents were gaseous products of thermolysis of ammonium thiocyanate NH_4SCN transported by helium as an inert carrier gas. This procedure was interrupted twice to thoroughly grind the samples for their homogenization. The completeness of sulfidization was checked by weighing the samples. The powder sulfides thus obtained were crystallized from melt in sulfur vapor in glassy carbon containers, which were heated by drawing them through a one-coil rf inductor with a velocity of 5–10 mm/h (the vertical version). The studies were carried out for samples with compositions $x = 0.25, 0.27, \text{ and } 0.29$. The samples with $x = 0.29$ were compounds prepared in different runs, 1 and 2, but with the same program. The x-ray measurements were performed on a DRON diffractometer with CuK_α radiation. The Mössbauer investigation was carried out on a spectrometer with a Co^{57} (Cr) source. The studies were performed with powder samples prepared by grinding single crystals.

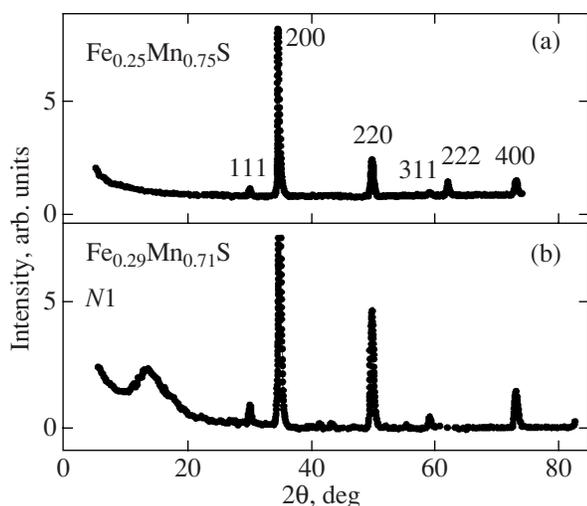


Fig. 1. X-ray diffraction patterns of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solutions.

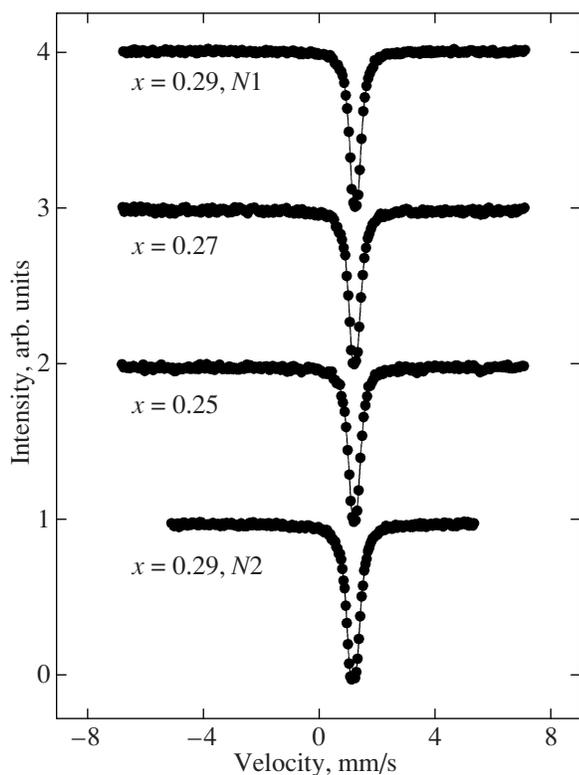


Fig. 2. Mössbauer spectra of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solutions.

3. EXPERIMENTAL RESULTS AND DISCUSSION

There are three known structural modifications of the manganese monosulfide [1]: the α phase (face-centered cubic, NaCl type), the β phase (sphalerite structure), and the γ phase (wurtzite structure). In the man-

ganese monosulfide with a NaCl-type face-centered cubic structure, the manganese and sulfur atoms form cubic sublattices in such a way that the cation and the anion are located in regular octahedra. The parameter of the NaCl-type face-centered cubic lattice of manganese monosulfide is $a_0 = 5.224 \text{ \AA}$ [1]. Application of pressure P at 300 K lowers the lattice symmetry of the α phase of the MnS monosulfide and narrows the dielectric gap in the electron energy spectrum of this compound [10, 11].

For illustration, Figs. 1a and 1b present the x-ray diffraction patterns of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ samples with compositions $x = 0.25$ and 0.29 (no. 1). The experimental diffraction patterns of samples with compositions $x = 0.25, 0.27,$ and 0.29 (no. 1) were found to correspond to the cubic structure of the α phase of manganese monosulfide, with no concomitant phases having been detected within measurement accuracy. The additional broad maximum at small angles, which is observed in the x-ray diffraction pattern of $\text{Fe}_{0.29}\text{Mn}_{0.71}\text{S}$, no. 1 and no. 2, is characteristic of the amorphous state as seen in x rays, and possibly reflects a disorder of the solid solution. At the same time, the crystal structure of the sample with $x = 0.29$ (no. 2) could be described by a combination of two crystalline phases of manganese monosulfide (the NaCl-type cubic and wurtzite-type hexagonal phases). The hexagonal and cubic phases were observed to coexist in manganese monosulfide as well [2]. The parameters of the face-centered cubic lattice of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ samples at 300 K were measured to be $a = 5.177 \text{ \AA}$ ($x = 0.25$), 5.174 \AA ($x = 0.27$), 5.151 \AA ($x = 0.29$, no. 1), and 5.160 \AA ($x = 0.29$, no. 2). Replacement of manganese by iron in the cation substitution of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ brings about compression of the NaCl cubic lattice, as observed in MnS at 300 K under pressure. The lattice parameter ratio $a(x)/a_0$ for the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystal with $x = 0.29$ is 0.986. The value of the $a(P)/a_0$ ratio, which is 0.990 for MnS, corresponds to a hydrostatic pressure $P = 26 \text{ kbar}$ [10]. Considering that the lattice compression in MnS is accompanied by a change in symmetry and that x-ray powder diffraction yields an averaged pattern, there were grounds to assume that the lattice in $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solutions is locally distorted.

Mössbauer spectroscopy is known to be an efficient method for study of the local coordination distortion in a substance [12]. If a local environment of a metal ion does not have ideal cubic symmetry, the Mössbauer spectrum reveals a quadrupole splitting whose magnitude reflects the extent of distortion of the coordination polyhedron.

The results of the experimental investigation of the Mössbauer spectra are presented in Figs. 2 and 3 and in the table. The Mössbauer spectrum of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystal (Fig. 2) represents actually a single broadened absorption line characteristic of the paramagnetic state. The assignment of the spectra was effected in two stages. In the first stage, the distribution

function of quadrupole splittings $P(QS)$ was found by fitting the chemical shift, which is common for the whole group of doublets (Fig. 2). In the second stage, the model spectrum was constructed as the sum of doublets corresponding to the maxima of the $P(QS)$ function and this spectrum was fitted to experimental data by varying the whole set of hyperfine structure parameters. The results of the assignment are listed in the table.

It has been established that the major contribution to the spectrum of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ samples with compositions $x = 0.25, 0.27,$ and 0.29 (no. 1) is due to the positions with a chemical shift of $0.92\text{--}0.94$ mm/s, which is characteristic of the high-spin Fe^{2+} cation octahedrally coordinated by anions (sulfur). The chemical shifts measured are typical, for instance, of the synthetic troilite $\text{Fe}_{1.125}\text{S}$ with divalent iron ions occupying octahedral positions of the sulfur hexagonal lattice [13] (isomer shift, 0.92 mm/s; quadrupole splitting, 0.10 mm/s; $H_{\text{eff}} = 313$ kOe). The quadrupole splitting QS at iron positions in $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystals ($0.18\text{--}0.21$ mm/s) is less than the width of the absorption line, which implies a certain distortion of the coordination octahedra. A comparison of the quadrupole splittings for $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ and $\text{Fe}_{1.125}\text{S}$ suggests that the octahedral distortion in iron–manganese sulfides is stronger pronounced. As x in $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ increases (samples with $x = 0.25; 0.27; 0.29$, no. 1), the quadrupole splitting and the linewidth decrease. This result suggests that the coordination octahedra (or the local environment) become more symmetric with increasing extent of cation substitution and that the crystal structure is more ordered.

As seen from the table and Fig. 3, the $P(QS)$ function for the $\text{Fe}_{0.29}\text{Mn}_{0.71}\text{S}$ single crystal (no. 2) has four distinct maxima, which implies possible existence of four nonequivalent iron positions or states, three of which are significant. The main contribution of 87% comes from positions with a chemical shift of 0.92 mm/s characteristic of the octahedrally coordinated high-spin Fe^{2+} cation, similar to what is observed in the $\text{Fe}_{0.29}\text{Mn}_{0.71}\text{S}$ crystal (no. 1). Lattice deformation in crystal no. 2 is more clearly pronounced, which is evidenced by the larger quadrupole splitting (see table). The less frequently occupied positions (7 and 6%, see table) in the Mössbauer spectrum of the $\text{Fe}_{0.29}\text{Mn}_{0.71}\text{S}$ sample (no. 2) are probably associated with iron having different numbers of Mn^{2+} cations and/or vacancies as nearest neighbors. These positions are identified with a smaller chemical shift (0.89 and 0.84 mm/s) or a larger electron density at the iron nucleus, i.e., the cations in these positions have a larger degree of covalent bonding with the nearest neighbors than those in positions of the host matrix. The quadrupole splittings for the “covalent” positions are fairly large, 0.53 and 0.98 mm/s. This suggests a substantial distortion of the local environment. The experimental values of QS are close to those observed [14] in the $\text{ZnS} : \text{Fe}$ wurtzite (quadrupole splitting, $0.56\text{--}0.80$ mm/s; isomer shift, 0.64--

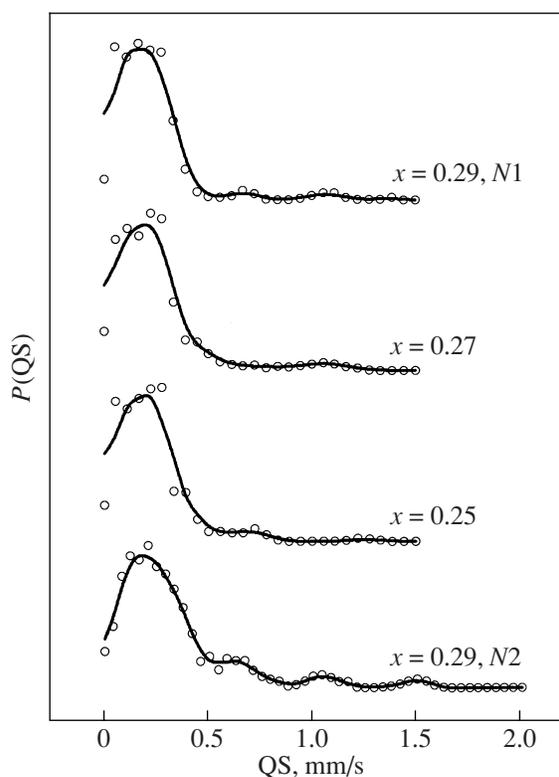


Fig. 3. Probability distribution functions of the quadrupole splitting for the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solutions.

0.66 mm/s). In the $\text{ZnS} : \text{Fe}$ wurtzite lattice, which is isostructural to one of the MnS polymorphic forms (the γ phase), atoms of the metal and sulfur are arranged tetrahedrally.

A comparison of the data obtained in a study of the Mössbauer and Debye spectra of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ samples of the same composition, $x = 0.29$ (nos. 1 and 2), permits the conclusion that the inherent structural characteristics of the $\text{Fe}_{0.29}\text{Mn}_{0.71}\text{S}$ solid solution (symmetry,

Mössbauer parameters of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystals

x	No.	IS, mm/s	QS, mm/s	W , mm/s	S
0.29, no. 2	1	0.92	0.21	0.30	0.87
	2	0.89	0.53	0.23	0.07
	3	0.84	0.98	0.38	0.06
	4	0.94	1.58	0.20	0.002
0.25	1	0.94	0.20	0.33	1
0.27	1	0.93	0.19	0.33	1
0.29, no. 1	1	0.93	0.18	0.32	1

Note: Designations: IS is the isomer (chemical) shift with respect to $\alpha\text{-Fe}$ (± 0.02 mm/s), QS is the quadrupole splitting (± 0.03 mm/s), W is the width of the absorption line at half-height (± 0.03 mm/s), and S is the relative occupancy of the position (± 0.03).

lattice parameters, local cation environment) are determined by the technology of synthesis employed.

It is known [12] that the isomer shift in the Mössbauer spectrum can be considered as a degree of electron delocalization (for metallic iron, it is zero). Iron sulfides belonging to different crystal structures exhibit a close-to-linear increase in the isomer shift with increasing Fe–S distance [14]. For each 0.1-Å increment in increasing Fe–S bond length, the isomer shift increases by 0.25 mm/s. For FeS monosulfide, the Fe–S bond length is 2.5 Å, whereas for MnS, the Mn–S distance is 2.6 Å. The closeness of the isomer shifts in FeS and $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ suggests a similar closeness in the degree of covalence between the *d* electron subsystems of these two compounds. This suggestion conforms to the measurements of the electrical resistivity of $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ polycrystals (see, e.g., review [15]). The more covalent character of the conductivity of the iron monosulfide as compared to that of the manganese monosulfide is attributed [16] to the direct *d*–*d* interaction of iron atoms and weak correlation effects.

Unlike MnS, iron sulfides at 300 K are in a magnetically ordered state, which accounts for the characteristic six-component Mössbauer spectrum of these substances. Our present Mössbauer studies of the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ iron–manganese sulfide solid solutions permit the conclusion that, at 300 K, these single crystals do not reveal, within experimental error (1%), any contribution due to local magnetic fields, which would argue for the existence of a magnetically ordered structure at room temperature.

4. CONCLUSIONS

Thus, $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ single crystals with compositions $x = 0.25, 0.27,$ and 0.29 were studied using x-ray diffraction and Mössbauer spectroscopy. It was shown that the cation substitution favors the formation of compounds with a NaCl-type cubic lattice. Iron ions in the $\text{Fe}_x\text{Mn}_{1-x}\text{S}$ solid solution reside in the high-spin Fe^{2+} state ($3d^64s^2$). Synthesis of iron–manganese sulfides can bring about the occupation of nonequivalent positions by cations in distorted octahedra of the cubic lattice. The cation substitution is accompanied by a slight lattice deformation and a change in the character of chemical bonding of the solid solution.

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