# Magnetostriction of $Fe_xMn_{1-x}S$ ($x = 0.27$) Crystals

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The magnetostriction of $Fe_xMn_{1-x}S$ ($x = 0.27$) single crystals in strong magnetic fields up to 120 kOe has been investigated. It has been found that the magnetostriction reaches colossal values ($\pm 3 \times 10^{-4}$) atypical of compounds of 3$d$ elements. It has been found that the magnetostriction changes sign when varying temperature and magnetic field; this behavior indicates an important role of the spin–phonon interactions in the formation of the magnetic order in solid solutions of iron–manganese sulfides.

## 1. INTRODUCTION

Solid solutions of oxide and sulfide manganese compounds are actively studied in view of the discovery of the colossal magnetoresistance and phase separation in them. Classical representatives of the compounds with colossal magnetoresistance are substances based on the $LaMnO_3$ antiferromagnet (perovskite cubic structure). Recent investigations show that the states of orbital ordering, phase magnetic separation, and metal–insulator transitions, which change under the action of the magnetic field, appear in these substances in dependence on the cation substitution degree and the choice of the substitution cation. One of the possible mechanisms responsible for the relation of the magnetic and electric properties in these substances is the strong spin–phonon interaction manifesting, in particular, in giant magnetostriction values. The detection of the giant magnetostriction [1–4] in compounds with colossal magnetoresistance, on one hand, opens new fields of the application of these substances and, on the other hand, allows for the refinement of the colossal magnetoresistance mechanism. It is assumed that negative magnetoresistance values correspond to negative magnetostriction values [5].

Solid solutions of manganese monosulfide constitute another class of compounds with related magnetic and electric properties. In $Fe_xMn_{1-x}S$ sulfides synthesized on the basis of MnS, the magnetic transition temperature increases from 147 K ($x = 0$) to 200 K ($x = 0.29$) and the negative magnetoresistance found in polycrystals is observed in the temperature range of

50–150 K [6]. A concentration electron transition with a variation of the composition at 300 K and a sequence of magnetic transitions accompanied by a change in the conduction type with decreasing temperature were observed in $Fe_xMn_{1-x}S$ single crystals [7–9]. The mechanism of the magnetoresistance and the relation between the magnetic and transport properties, as well as their significant dependence on the technology of obtaining $Fe_xMn_{1-x}S$, remain to be discussed.

It is known that the magnetostriction in compounds of 3$d$ elements is low ($\approx 10^{-6}$ [10]) owing to the absence of a pronounced spin–orbit interaction. This fact likely explains the absence of published results of such investigations. In any case, the analysis of the available published data indicates that the magnetostriction of sulfides of 3$d$ elements and their solid solutions has not yet been studied. In this work, we report the results of the experimental investigation of the magnetostriction of $Fe_xMn_{1-x}S$ ($x = 0.27$) single crystals in magnetic fields up to 120 kOe. The aim of this investigation was to obtain new information and to determine the mechanism of the relation between the magnetic and transport properties of iron–manganese sulfides.

## 2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The technology of the synthesis of $Fe_xMn_{1-x}S$ single crystals and results of the X-ray diffraction and Mössbauer analysis were described in [9]. The

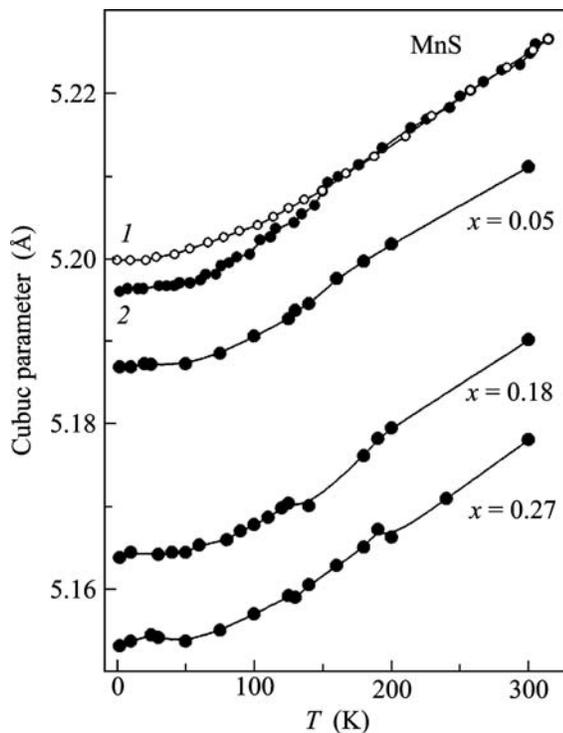**Fig. 1.** Temperature dependences of the unit cell parameter of $Fe_xMn_{1-x}S$. For comparison, the experimental data for MnS from [13] are given: (*1*) disregarding rhombohedral distortion and (*2*) experiment.

$Fe_xMn_{1-x}S$ samples under investigation have an fcc NaCl-type structure at room temperature. Neutron diffraction studies of the samples were performed on a D1A setup in the range of 2–240 K by the powder neutron diffraction method. The magnetostriction was measured using the differential capacitance method [11]. A copper measuring cell is a flat capacitor whose one electrode is fixed and the second electrode is displaced due to the magnetostriction of a sample. A change in the capacitance of the capacitor caused by magnetostriction processes is detected by a supersensitive Andeen–Hagerling AH 2550A bridge. The sample is a single crystal plate oriented so that the plate plane corresponds to the (100) plane. The longitudinal magnetostriction $\lambda_{\parallel}$ is measured in the direction of the applied magnetic field, which is perpendicular to the sample surface. The sample thickness is 0.7 mm. The measuring cell is placed into a superconducting solenoid (Cryogenic Ltd.), which allows for measurements in magnetic fields up to 12 T. The cell temperature in the field measurements of the magnetostriction is maintained constant; the sample is aged at a chosen temperature for 3–4 h for thermostabilization. The field measurements at a given temperature are multiply repeated.

## 3. RESULTS AND DISCUSSION

It is known [12–16] that MnS manganese monosulfide and MnO, FeO, and NiO isostructural oxides (fcc NaCl-type structure, space group *Fm−3m*) are Heisenberg antiferromagnets with a prevailing 180° superexchange interaction (Mn–S–Mn type) in the cube edge direction. The antiferromagnetic order in these substances is determined by the ferromagnetic ordering of the magnetic moments of bivalent 3*d* ions in the planes of the (111) type of the cubic NaCl lattice and their antiferromagnetic ordering between neighboring planes. For the ideal cubic NaCl structure, four equivalent directions of the [111] type can be specified. In this case, the angles between the atoms in the (111) plane are 60°. The feature of the indicated substances is that the formation of the antiferromagnetic order due to the exchange striction processes is accompanied by the rhombohedral distortion of the fcc NaCl lattice [12–16], which leads to a weak change in the distance between the (111) planes and the angle between magnetic atoms in these planes. The magnetic structure of MnS and isostructural oxides is considered in the representation of a magnetic cell with a period that is the doubled period of the crystallographic cell; the propagation vector is $Q = (1/2, 1/2, 1/2)$.

Figure 1 shows the temperature dependences of the unit cell parameter for $Fe_xMn_{1-x}S$ solid solutions in comparison with the known experimental data [13] for manganese monosulfide. The behavior of the $Fe_xMn_{1-x}S$ lattice parameter for a small content of $x = 0.05$ is similar to that observed for MnS. An additional anomaly is found for iron–manganese sulfides with $x > 0.18$ at low temperatures near ~25 K. We emphasize that this result was obtained by the neutron diffraction method when studying powders prepared from single crystals.

Figures 2 and 3 show, respectively, the field and temperature dependences of the magnetostriction for the oriented $Fe_xMn_{1-x}S$ single crystal with $x = 0.27$, which has the NaCl fcc structure with the lattice parameter $a = 5.178$ Å at room temperature. Figure 3b shows the temperature dependence of the magnetization of sublattices measured by the neutron diffraction method for the single crystal. The antiferromagnetic-transition temperature is $T_N = 197$ K. The investigations of the magnetostriction show that a positive longitudinal magnetostriction is observed near the magnetic transition temperature (see Fig. 2a); its magnitude in a magnetic field of 120 kOe is $6.3 \times 10^{-5}$. This magnetostriction value is higher than, e.g., that in the antiferromagnetic rare-earth manganese lanthanide $LaMnO_3$ at $H = 200$ kOe [1], which has weak longitudinal ferromagnetism. The field dependence of $\lambda_{\parallel}$ at 200 K for the $Fe_xMn_{1-x}S$ crystal with $x = 0.27$ can be described by a quadratic function $\lambda_{\parallel} \approx AH^2$, which is typical of the magnetostriction of a paraprocess [10].
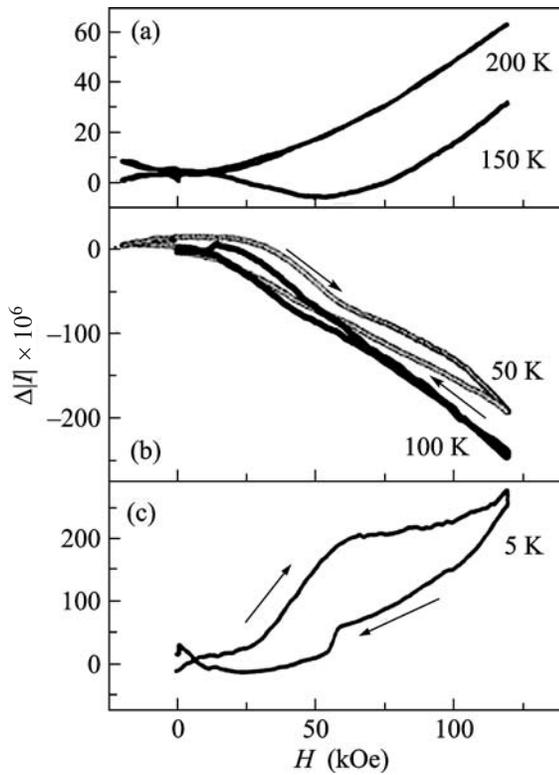
**Fig. 2.** Field dependences of the magnetostriction for the $Fe_xMn_{1-x}S$ single crystal with $x = 0.27$ measured at various temperatures.
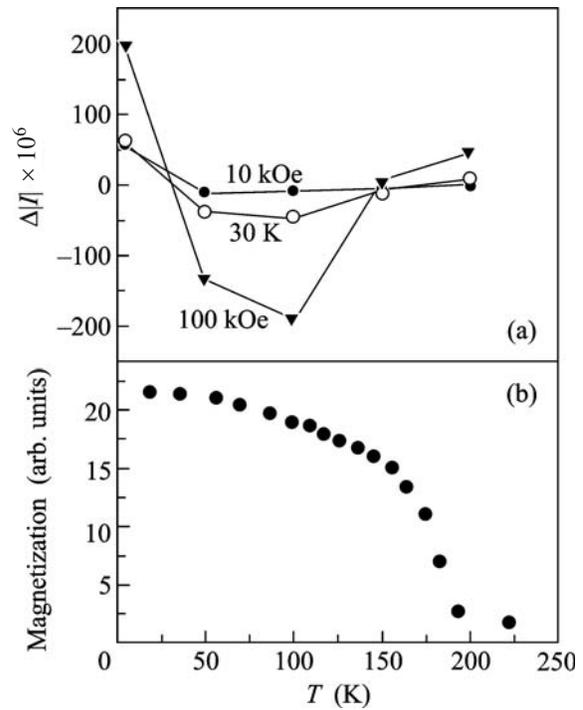


**Fig. 3.** Temperature dependences of the (a) magnetostriction in various magnetic fields and (b) magnetization measured by the neutron diffraction method for the $Fe_xMn_{1-x}S$ single crystal with $x = 0.27$.

A decrease in the temperature and the formation of the magnetic order in $Fe_xMn_{1-x}S$ with $x = 0.27$ are accompanied by the appearance of a negative contribution to the longitudinal magnetostriction (see Fig. 2b), which becomes dominant in strong magnetic fields (see Fig. 3) for the temperature range of 50–100 K, where negative magnetoresistance was previously observed in polycrystals [6]. The negative magnetostriction at 100 K increases almost linearly with the field, reaching a colossal value of $-2.4 \times 10^{-4}$ at $H = 120$ kOe. The saturation of the magnetostriction is not observed. The linear field dependence of the magnetostriction is characteristic of exchange striction processes [10] and indicates the dependence of exchange interactions on the interatomic distance. Taking into account this fact and the significant pressure dependence of the Neél temperature of the pure manganese monosulfide with a coefficient of $\approx 6.38$ K/GPa [17], it can be expected that one of the magnetostriction mechanisms in iron–manganese sulfides is the exchange mechanism associated with the dependence of the exchange integral on the interatomic distances.

The character of the field dependence of the magnetostriction of $Fe_xMn_{1-x}S$ with $x = 0.27$ changes at a temperature of 50 K owing to the appearance of pronounced hysteresis effects (see Fig. 2). The magneto-

striction again changes sign in the temperature range from 50 to 5 K (see Figs. 2, 3). Figure 2c shows the field dependence of the magnetostriction measured at a temperature of $T = 5$ K. The low-temperature magnetostriction is positive and increases stepwise with the magnetic field. The magnitude of the positive magnetostriction in a magnetic field of $H = 120$ kOe is $+2.5 \times 10^{-4}$ and is close in absolute value to the negative magnetostriction observed at 100 K. The magnetostriction process at a temperature of $T = 5$ K is accompanied by a significant field hysteresis, which may indicate both the formation of a domain structure and the presence of structure and magnetic transitions in this sulfide in the magnetic field.

It is known that isostructural MnS and FeO compounds are uniaxial antiferromagnets [12, 16] with different orientations of the magnetic moments of $3d$ ions. The magnetic moments of the $Mn^{2+}$ ions in manganese monosulfide below the Neél temperature are oriented along the $\langle 110 \rangle$ direction, whereas the magnetic moments of $Fe^{2+}$ in FeO are oriented along the $\langle 111 \rangle$ tetragonal axis. The spectroscopic state of a free manganese ion, $^6S_{5/2}$, and its magnetic moment are determined by the pure spin contribution. Five $d$ electrons of a bivalent manganese ion determine the spin $S = 5/2$. The spectroscopic state of a bivalent iron ion is $^5D_4$. The $^5D_4$ state in the cubic-symmetry field is split

into two levels, one of which is doubly degenerate and the other is triply degenerate. The triplet state of $Fe^{2+}$ ($d^6$, $S = 4/2$) at the octahedral position has lower energy and is nonmagnetic if the splitting by a crystal field is large. To explain the antiferromagnetic order and rhombohedral distortion of the cubic cell in FeO, Kugel and Carabatov [16] assumed that the magnetic moment of $Fe^{2+}$ is determined by both the spin and orbital contributions $2S + 1/2L$.

According to the Mössbauer data, the bivalent manganese and iron ions in $Fe_xMn_{1-x}S$ sulfides occupy the octahedral positions [9], similar to MnS and FeO. The replacement of the manganese ions by iron ions in $Fe_xMn_{1-x}S$ with $x > 0.15$ is accompanied by the appearance of weak quadrupole splitting of the singlet Mössbauer spectrum at room temperature, which indicates the local deformation of octahedra. The above features of $Fe^{2+}$ and $Mn^{2+}$ ions (different multiplet states and the prevailing orientation of the magnetic moment in the NaCl cubic lattice), as well as the formation of nonequivalent states of cations under the structure deformation in MnS [18], allow one to expect the formation of the nonuniform distribution of nonequivalent low-symmetry states of magnetic ions with different local anisotropies of each of them over the volume of the $Fe_xMn_{1-x}S$ sample, which contribute the magnetostriction process. Ising rare-earth magnets [10], in which the exchange magnetostriction has a strong field dependence, are among such substances. Owing to the spin–orbit interaction, which has different orientations for the iron and manganese subsystems of the $Fe_xMn_{1-x}S$ crystal, it is not excluded that the orientations of the magnetic moments of the $Fe^{2+}$ and $Mn^{2+}$ ions in strong magnetic fields are different.

To summarize, it has been found that iron–manganese sulfides have high magnetostriction values, which indicate the important role of the spin–phonon interactions. It has been shown that the longitudinal magnetostriction changes sign when the temperature and magnetic field are varied. The revealed features of the magnetostriction of $Fe_xMn_{1-x}S$ ($x = 0.27$) imply the necessity of additional investigations, including the study of the bulk magnetostriction, as well as the magnetic structure and magnetic properties in strong magnetic fields on samples with different contents $x$.

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