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ORIGINAL PAPER

Dielectric and Magnetic Anomalies in α-MnS Single Crystals at Applied Magnetic Fields

G. Abramova[1] · A. Freydman[1] · E. Eremin[1] · E. Pogoreltcev[1] · D. Velikanov[1]

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Abstract
Temperature and magnetic field dependences of the magnetic susceptibility and dielectric permittivity of the α-MnS single crystal with NaCl structure are first investigated at around Neel temperature and at 4.2 K and H up to 70 kOe. A relation between the investigated properties was established. The founded phenomena can be due to the magnetostriction or magnetoelastic mechanism and the spin-dependent dipole moment.

Keywords Correlated electron systems · Magnetic fields · Magnetic and dielectric properties · Sulfide of 3d-elements

1 Introduction

α-MnS belongs to MnO-type substances (the transition-metal monoxides MnO, FeO, CoO, and NiO) with the strong electron correlations [1]. In the paramagnetic phase, these compounds crystallized in the centrosymmetric rock salt NaCl structure with space group Fm-3 m (O^5_h) and below their respective Neel temperatures exhibit an antiferromagnetic ordering which is usually denoted as AFM II [2, 3]. In MnO the magnetic phase transition goes along with a structural distortion which reduces the symmetry of the crystal from rock salt structure to a rhombohedral structure, the cubic lattices of MnO is trigonaly distorted along the [111] direction. This structure transition for MnO was observed by the IR spectroscopy [4] and the study results of the dielectric response [5]. Similar structure change was found for the isostructural alfa-MnS (α-MnS) [6–8]. The investigation of α-MnS by the IR and Raman methods [9] show no any transformations of the transverse and longitude modes in the range of 4.2–300 K, but found the low-energy mode, which can be connected with the magnetic transition. The anomaly of thermal expansion coefficient for α-MnS single crystal was found around the Neel temperature [10]. Additional data indicated non-centrosymmetric structure of alfa MnS in the antiferromagnetic state obtained by the Mossbauer method [11, 12].

As the study of the dielectric response of a solids provides valuable information about its electronic properties and lattice dynamics, in this paper we report new results of the experimental investigations of magnetic susceptibility and dielectric properties of the α-MnS single crystal with NaCl structure near its magnetic ordering temperature and low temperatures at applied magnetic fields up to 70 kOe.

2 Experimental

Previously, we reported the details of synthesis of α-MnS and $Fe_XMn_{1-X}S$ single crystals for these materials [13]. The crystal structure of the α-MnS samples was determined on a D8 ADVANCE X-ray powder diffractometer (Bruker). It was confirmed that the structure is cubic space group Fm-3 m and has NaCl-type with the measured lattice constants $a = 5224$ Å at 300 K and $a = 5.211$ (4) Å at 80 K, which are good agreement with those reported in JCPDS Card No. 72–1534. Microstructures and chemical compositions of α-MnS single crystals were investigated by scanning electron microscopy (SEM) using a JEOL JSM-7001F equipped with an energy-dispersive X-ray spectrometer (Oxford Instruments). The investigations of the chemical compositions of different surfaces α-MnS single crystal indicated that its real chemical composition correspond to S = 50.54 ± 0.21, Mn = 49.46 ± 0.21. Additional magnetic impurity was not found. The magnetic properties of

✉ G. Abramova
agm@iph.krasn.ru

[1] Kirensky Institute of Physics, Federal Research Center KSC, Siberian Branch Russian Academy of Sciences, Krasnoyarsk 660036, Russia

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the α-MnS crystal were studied using an MPMS SQUID magnetometer (QuantumDesign) in magnetic fields up to 50 kOe at temperatures of 2–400 K. The dielectric properties of the α-MnS samples were determined on an Agilent E4980ALCR-meter in the frequency range from 20 Hz to 2 MHz. The investigated samples were the single crystals with $S = 25.1$ mm^2, $d = 1.5$ mm and $S = 10.23$ mm^2, $d = 0.62$ mm in size. The electrodes were formed from a silver paste deposited onto the largest faces of the single crystal that coincide with the cubic (100) planes.

3 Results and Discussion

Temperature dependences of the magnetic susceptibility for the α-MnS single crystal (fcc NaCl) measured at H along cubic [100] crystal axes in a magnetic field H from 500 Oe to 50 kOe are presented in Fig. 1. The temperature of the magnetic ordering $T_N = 150 \pm 2$ K is determined by the jump of the derivative $d\chi/dT$ at $H = 500$ Oe. The Neel temperature is close to the data reported in [6, 7]. The additional maximum of the magnetic susceptibility appeared at the temperature around 130 ± 5 K as the magnetic field increases up to 5 kOe, and this maximum anomaly increases with growing of the magnetic field up to 50 kOe (Fig. 1). Above 200 K the magnetic susceptibility at all magnetic fields follows the Curie–Weiss law with the paramagnetic Curie temperature -520 ± 10 K and magnetic moment $5.7 \pm 0.1\ \mu_B$, $J^{180} = -4.196 \pm 0.5$ K, $J^{90} = -6.28 \pm 1$ K, which are close to [14]. Field dependences of the magnetization of α-MnS single crystal that were measured at temperatures of 4.2 K, 130 K, 160 K, and 300 K have linearly behavior. For comparison on insert of Fig. 1 presented the temperature dependences of the relative magnetization for the powder sample α-MnS with 3% Fe-substitution obtained from the neutron investigation data [10]. It has been fitted by a power-law $M(T) = A(T_N - T)^{\beta}/T_N$ with $A = 1.0464 \pm 0.01$, $T_N = 162.81 \pm 0.9$ K, $\beta = 0.278 \pm 0.017$. The magnetic structure of the powder sample is similar to the antiferromagnetic structure II-type [3] with spin vector propagation $k = (1/2, 1/2, 1/2)$, but the critical exponent β is smaller than for a 3D Heisenberg model. According to [10] at $H = 0$ the temperature behavior of the magnetization of the powder sample is typical for the two sublattices collinear II-type antiferromagnet. Below Neel temperature T_N, α-MnS exhibit the antiferromagnetic order with ferromagnetic (FM) sheets of the (111) planes antiferromagnetically

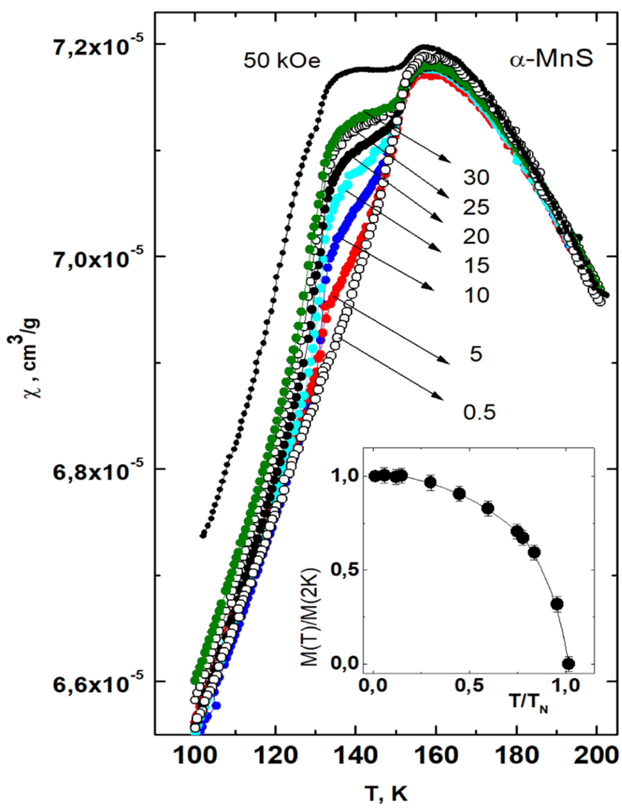

Fig. 1 (color online) Temperature dependences of the magnetic susceptibility for α-MnS single crystal at different magnetic fields. The insert presented the temperature dependences of the relative magnetization for the powder sample α-MnS with 3% Fe-substitution obtained from the neutron investigation data [10]

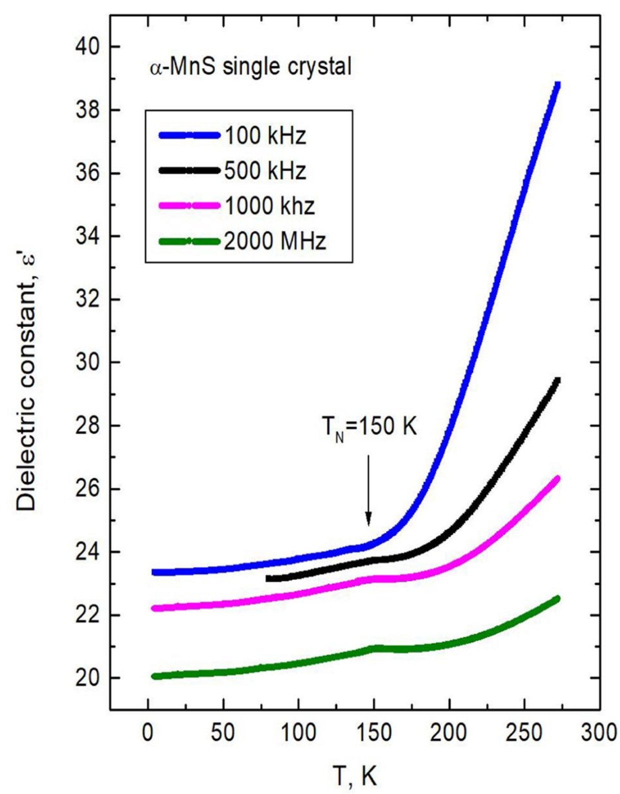

Fig. 2 (color online) Temperature dependences of the real ε′ part for the αMnS single crystal at H = 0 at different frequency

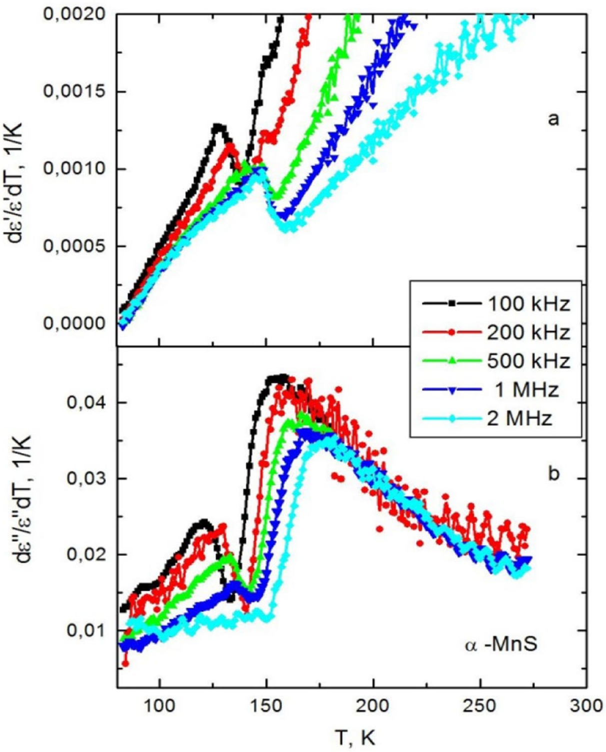

Fig. 3 (color online) The temperature coefficients dε′/ ε′dT and dε″/ε″dT of the ε′ and ε″ for the α-MnS single crystal at different temperatures and H = 0

stacked along the [111] direction. The spins of Mn^{2+} ions are along a cubic < 110 > direction. The authors [6, 15] at the investigation of α-MnS single crystal sample found the linear optical anisotropy, domain structure, and two antiferromagnetic phase transition (130 K and ~ 150 K). According to [11, 15] the multi-axis spin structure can be appeared in alfa-MnS below 130 K. Taking into account the anomaly $\alpha = (1/L)dL/dT$ (thermal expansion coefficient) [10] and the local distortion of the octahedral positions of Mn^{2+} ions, and the domain structure around the Neel temperature [11, 15] we can conclude that the observed temperature dependences of susceptibility at applied magnetic fields can be the attribute of the exchange striction and the shift of the domain boundaries in the antiferromagnetic state of α-MnS.

From here, the behavior of magnetic susceptibly of α-MnS single crystal (Fig. 1) at magnetic field $H > 5$ kOe can be explained by the change of the trigonal distortion of the cubic lattice in the strong magnetic field, or transformed it due to change of the *S* and *T* domain structures, which are characteristic of AFM II state of MnO-type compounds [16, 17].

At room temperature α-MnS is a charge transfer insulator with semiconductor-type conductivity. In the range of Neel temperature the anomalous change of the energy activation and anisotropy of electrical resistivity are observed [18] for the single crystal.

Figure 2 shows the temperature dependences of real permittivity part, ε', measured at different frequencies on the α-MnS single crystal at the temperature range of 4.2–270 K. At all the frequencies, the values of the real ε' and imaginary ε'' permittivity parts grow with increasing of temperature. With an increase in the measuring frequency the anomalies of dielectric properties appeared around Neel temperature. More clearly these anomalies can be seen on the temperature dependences of the temperature coefficients $d\varepsilon'/\varepsilon' dT$ and $d\varepsilon''/\varepsilon'' dT$ (Fig. 3). The critical temperature T_S of these anomalies shift towards higher temperatures as the frequency (*f*) increases and changes from 130 ± 5 K and $f = 100$ kHz to 160 ± 5 K and $f = 2$ MHz. This temperature range corresponds to the temperature region of the magnetic susceptibility anomalies at $H > 5$ kOe, which are presented above. We measured the temperature dependences of ε' and ε'' at $H = 10$ kOe with the goal to clarify the magnetic field dependence of the dielectric properties of α-MnS and calculate the magnetoelectric coefficient MD used:

$$\mathrm{MD(H)} = (\varepsilon'(\mathrm{H}) - \varepsilon'(0))/\varepsilon'(0) \,{}^{*}100\% \quad (1)$$

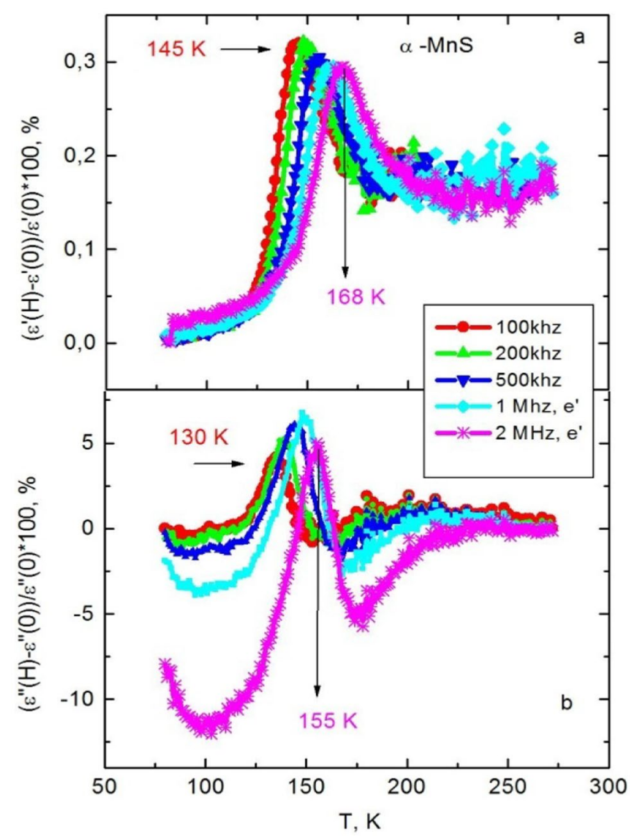

Fig. 4 (color online) Temperature dependences of the magnetoelectric coefficients MD of ε′ (a) and ε″ (b) for the α-MnS single crystal at H = 10 kOe around Neel temperature

$$MD(H) = (\varepsilon''(H) - \varepsilon''(0))/\varepsilon''(0) * 100\% \quad (2)$$

The results are presented in Fig. 4. The positive anomaly MD(H) of ε′ is below 1% and has the critical temperature T_S increasing as the frequency (f) is increased. The positive magnetoelectric coefficients of ε″ approach to 5% and have similar frequency dependence. But at fixed temperature 80 K and 300 K the dependences of the dielectric properties of α-MnS single crystal from the magnetic field up to 10 kOe are not observed. The measured value of the dielectric constant and dielectric loss for α-MnS single crystal at room temperature and $H=0$ were close to the data [19].

To clarify above results we measured the dielectric properties of the α-MnS single crystal in the temperature range of 4.2–80 K at the magnetic field up to $H=70$ kOe. Field dependences of the magnetoelectric coefficients MD of ε′ for α-MnS, which are measured at $T=4.2$ K and 10 K, are presented in Fig. 5. The magnetoelectric coefficients MD for the real part of dielectric permittivity ε′ is below 1% and practically independent from the frequency. This effect is observed at increasing and decreasing of the magnetic field; the critical magnetic field is around 50 kOe. Low-temperature antiferromagnetic state of α-MnS single crystal at 4.2 K is dielectric with the dielectric loss below 10^{-3}. The value of ε′ at 4.2–80 K for $H=0$ changes from 23 ($f=1$–100 kHz) to 20 ($f=2$ MHz) and close to the low-frequency dielectric constant ($\varepsilon_0=20$) obtained from the optical investigation in [20].

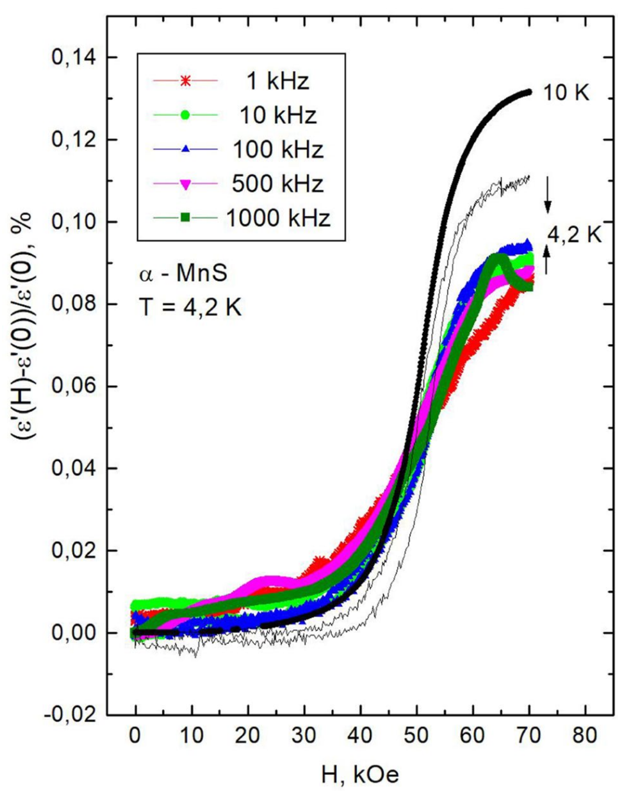

Fig. 5 (color online) Field dependences of the magnetoelectric coefficients MD of ε′ for α-MnS at H up to 70 kOe and at T = 4.2 K and 10 K

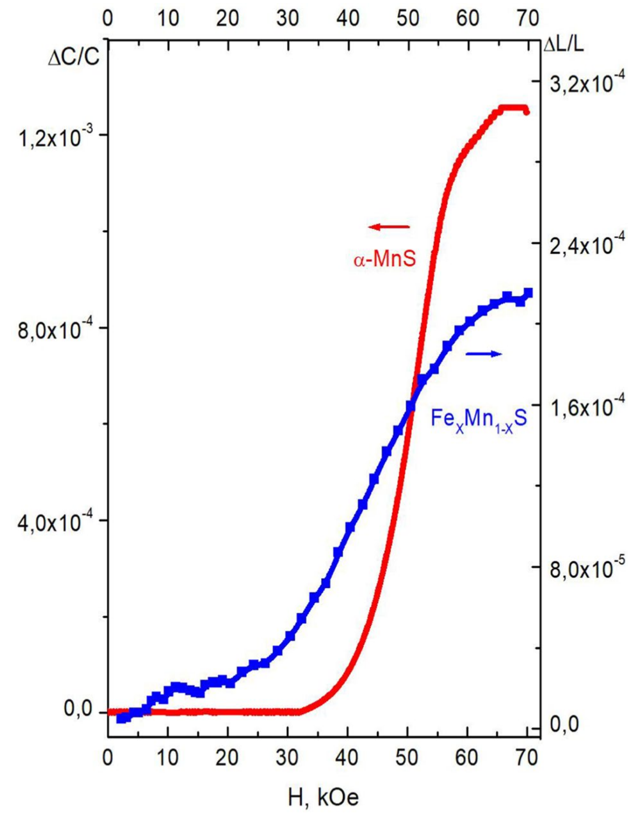

Fig. 6 (color online) Field dependences of the relation capacitance ΔCd/Cd for α-MnS and magnetostriction of FeXMn1 − XS at T = 4.2 K and H up to 70 kOe

Figure 6 shows the magnetic field dependence capacitance C_d of α-MnS single crystal at 4.2 K; it presented as $(C_d(H) - C_d(0)/C_d(0)) = \Delta Cd/Cd$. This figure also shows the change of magnetostriction $\Delta L/L\|$ at applied magnetic field up to 70 kOe, which is observed early for the $Fe_X Mn_{1-X}S$ solid solution synthesized on the base of α-MnS [21]. The comparison of these data allows us to propose that the anomaly behavior of the capacitance of α-MnS in the magnetic field from 30 to 70 kOe at 4.2 K can be the magnitostriction or magnetoelastic mechanism. The effective spin depended electric dipole moment in α-MnS can appear due to the magnon sideband that arises from the simultaneous creation of the exiton and magnon, as first calculated for α-MnS in [22].

4 Conclusions

Magnetic and dielectric properties of α-MnS single crystals with NaCl structure first were investigated at wide temperature and magnetic field ranges. The paramagnetic state of α-MnS is the semiconductor with the frequency dependences of the real ε' and imaginary ε'' dielectric permittivity parts and the Curie–Weiss magnetic susceptibility. The Neel temperature $T_N = 150 \pm 2$ K is practically independent on the magnetic field. The new broad maximum of susceptibility, as found here, appeared at $H \geq 5$ kOe at around $T_S = 130$ K. This temperature T_S depended from the frequency of sound diapason and appeared in the dielectric properties of α-MnS single crystals. The anomalies of ε' and ε'' permittivities were found in within the temperature ranges of 130–160 K at magnetic field up to 10 kOe. This confirms the correlation between the dielectric and magnetic subsystems in the α-MnS crystal near its magnetic ordering temperature. It was found that the antiferromagnetic phase of α-MnS at low temperature ($T = 4.2$ K) is the dielectric with the dielectric loss below 10^{-3}. The value of the real part of dielectric permittivities practical independent from the frequency (up to 1 MHz) and increases with increasing of the magnetic field up to 70 kOe. The magnetoelectric coefficients MD of the real dielectric permittivity part ′ at 4.2 K and $H = 70$ kOe is below 1% for α-MnS. Additional research of α-MnS is needed to clarify the details of the magnetic structure in applied magnetic fields.

Declarations

Conflict of Interest The authors declare no competing interests.

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