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Magnetic properties of MnGeO$_3$ single crystals with orthorhombic structure

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Abstract
The current report is devoted to the further study of magnetic properties of MnGeO$_3$ single crystals with orthorhombic symmetry $Pbca$. New data from magnetic measurements in magnetic fields up to 80 kOe are presented. A spin flop transition is observed at $H_{sf} = 35$ kOe and $T = 4.2$ K along the a-axis. The exchange and anisotropy fields are determined. The magnetic structure of MnGeO$_3$ with $T_N \approx 36$ K is qualitatively described using a two-sublattice model.

1. Introduction

MnGeO$_3$ is of interest as a magnetoelectric material [1, 2] that reveals a linear correlation between electric field and magnetization, as well as between magnetic field and electric polarization. This compound is a magnetic analogue of the natural mineral enstatite MgSiO$_3$ with pyroxene structure. Recently, multiferroic properties were found for quite a number of pyroxenes with the total composition ABSi$_2$O$_6$ (A is a monovalent or divalent metal and B is a divalent or trivalent metal) [3]. This increases our interest, especially with regards to further investigation of magnetic and magnetoelectrical properties of MnGeO$_3$.

In the previous work [4], we reported the first data on magnetic measurements of orthorhombic MnGeO$_3$ single crystals. The MnGeO$_3$ single crystals were grown by a flux method. The Néel temperature of these crystals ($T_N = 38$ K) appeared significantly higher than those reported in the literature [5–7] ($T_N \sim 10$–16 K). We showed that the magnetic characteristics are sensitive even to minor impurity amounts and to the synthesis conditions. Apparently, this sensitivity is concerned with features of the MnGeO$_3$ chain structure [8].

To clarify the origin of the magnetoelectric properties we have continued the investigation of magnetic properties of MnGeO$_3$ single crystals. In the present paper the results of thorough magnetic measurements with accurate orientation of the magnetic field relative to the crystallographic axes of a sample are presented.

2. Experimental details

Manganese germanate single crystals (sc) were obtained by a flux growth method generally used for growing single crystals of high melting temperature oxide compounds by spontaneous crystallization. The details of the technological process were presented in our previous study [4]. The MnGeO$_3$ single crystals were $0.6 \times 0.2 \times 0.2$ cm^3 in maximum size, brown, transparent, and had the form of needles extended along the c-axis.

The crystal structure of the samples obtained was determined with an x-ray DRON-2 facility for powder samples and a SMART APEX (Bruker AXS) diffractometer for single crystals. All the x-ray patterns taken at room temperature show that all samples have a pyroxene-type structure without any impurity phase. According to the results of polarization microscopy, twinning of crystals is absent.

The magnetic properties were measured with a vibrating sample magnetometer of original construction in the temperature range 4.2–300 K in magnetic fields up to 80 kOe. The magnetic measurements were carried out with accurate orientation of the magnetic field relative to the crystallographic axes of the sample. The directions of the crystallographic axes in the measured sample were determined with a single-crystal SMART APEX ll (Bruker AXS) diffractometer.
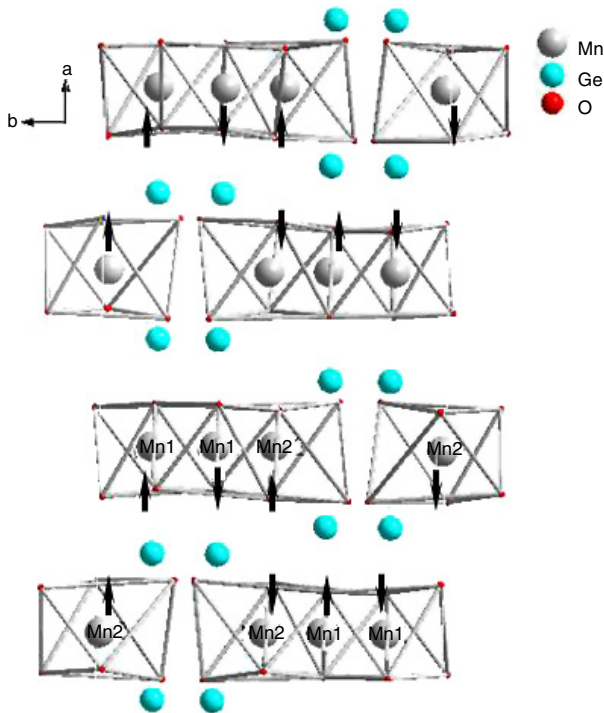
Figure 1. Projections of the MnGeO$_3$ crystal structure onto the **ab** plane. The arrows show the spin structure in zero magnetic field. (This figure is in colour only in the electronic version)

3. Results and discussion

3.1. Crystal structure

The MnGeO$_3$ compound possesses the pyroxene structure with space group $Pbca$ and cell parameters $a = 19.25, b = 9.23, c = 5.46$ Å. The structure is characterized by germanium chains of the following type: germanium atoms surrounded by four oxygen atoms form oxygen tetrahedra GeO$_4$, which are connected via common vertices into an infinite series. Two atoms of the oxygen tetrahedron appear common, while the other two can make bonds with manganese ions Mn^{2+}. The manganese atoms, in their turn, are in octahedral surroundings of oxygen atoms (MnO$_6$) in two non-equivalent positions: Mn1 and Mn2. The octahedra create zigzag two-step ladders (strips) extended along the c-axis and alternated along the a-axis. Thus, Mn ions form the a-plane (figure 1).

3.2. Magnetic properties

Figure 2 presents temperature dependences of the susceptibility χ_a, χ_b and χ_c for the MnGeO$_3$ single crystal in three directions of the magnetic field $H = 1$ kOe applied along the crystallographic axes.

Below $T_N \approx 36$ K, pronounced anisotropy of the susceptibility is observed, with $\chi_a(T)$ tending to zero and $\chi_b(T)$, $\chi_c(T)$ increasing with temperature decreasing. It is obvious that there is a spontaneous antiferromagnetic vector along the a-axis; in other words, χ_a is $\chi_\parallel$ and $\chi_b(T)$, $\chi_c(T)$ are $\chi_\perp$. As is seen from figure 2, the Curie–Weiss law is obeyed in the range of temperature 60–300 K. The Curie–Weiss constants
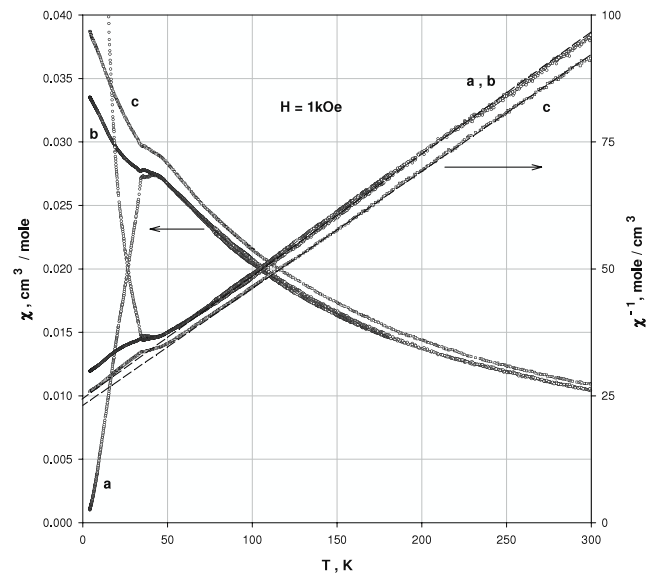
Figure 2. The temperature dependences of the susceptibility and inverse susceptibility for orthorhombic axes of MnGeO$_3$.

$C_{a,b}$, C_c and Curie paramagnetic temperatures $\theta_{a,b}$, θ_c were obtained. They are 4.26 cm^3 K mol^{-1}, 4.37 cm^3 K mol^{-1} and -107 K, -102 K, respectively. The effective magnetic moment values are $\mu_{\text{eff } a,b} = 5.84\ \mu_B$ and $\mu_{\text{eff } c} = 5.91\ \mu_B$. The values $\mu_{\text{eff } a,b,c}$ obtained for the three directions of the sample are in agreement with the value μ_{eff} for Mn^{2+} ions with $S = 5/2$. The visible anisotropy of the paramagnetic susceptibility apparently involves exchange anisotropy, as indicated by the different values of the g-factors [4].

Attention is drawn to the fact that the unusual temperature behavior of $\chi_b(T)$ and $\chi_c(T)$ takes place below T_N. The reason for such behavior requires specific investigation; nevertheless, at this stage of research we are taking the risk of suggesting that there is some contribution from 'loose' spins to χ_b and χ_c. The availability of 'loose' spins can be explained by there being frustrating interactions in the magnetic structure MnGeO$_3$, described in detail in our previous work [4].
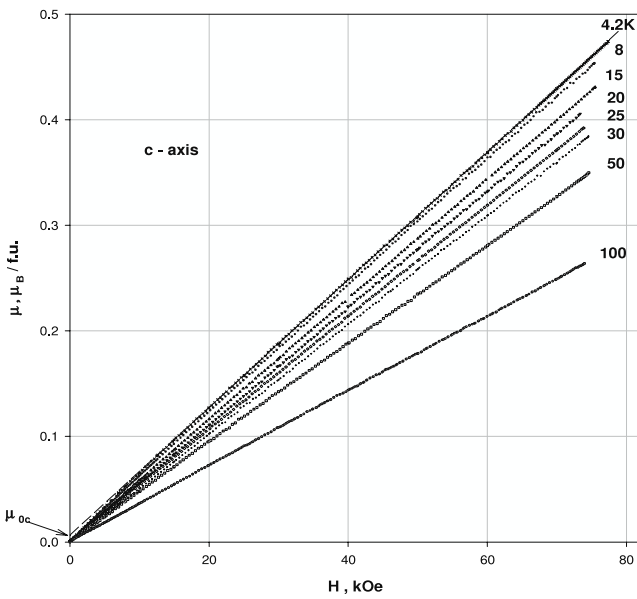
In figure 3 the field dependences of the magnetization for the a-direction are shown. It is seen that at 4.2 K in the magnetic field $H_{\text{sf}} = 35$ kOe, a spin flop occurs. The critical fields H_{sf} for the different isotherms were defined via maximum values of the derivatives $(\partial \mu_a / \partial H)_{T=\text{const}}$. As temperature increases, the value of H_{sf} increases in the range of antiferromagnetic ordering (see the inset in figure 3). In the range of antiferromagnetic ordering at low temperatures the magnetization increases slightly with increasing magnetic field; for $H \ll H_{\text{sf}}$ at $T = 4.2$ K, $\chi_a \approx 1.6 \times 10^{-3}$ cm^3 mol^{-1}.

Above H_{sf} the field dependences of the magnetization have a linear character. A slight hysteresis observed at the spin flop transition (which does not show in the figure) indicates that this transition is a first-order magnetic phase transition. As is seen from figure 3, the spin flop transition vanishes at $T = 34$ K.

The field dependences of the magnetization for the c-axis are linear in the temperature range 4.2–100 K (figure 4).
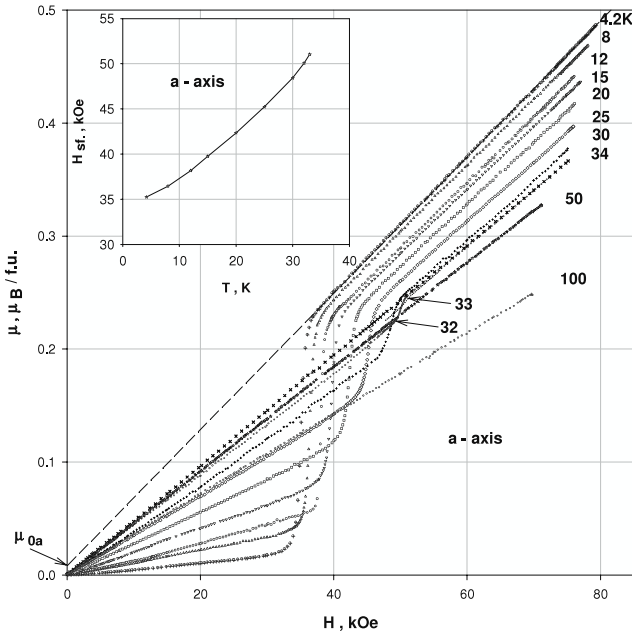
Figure 3. The field dependences of the magnetization for the *a*-axis of MnGeO$_3$. The inset shows the temperature dependence of H_{sf}.
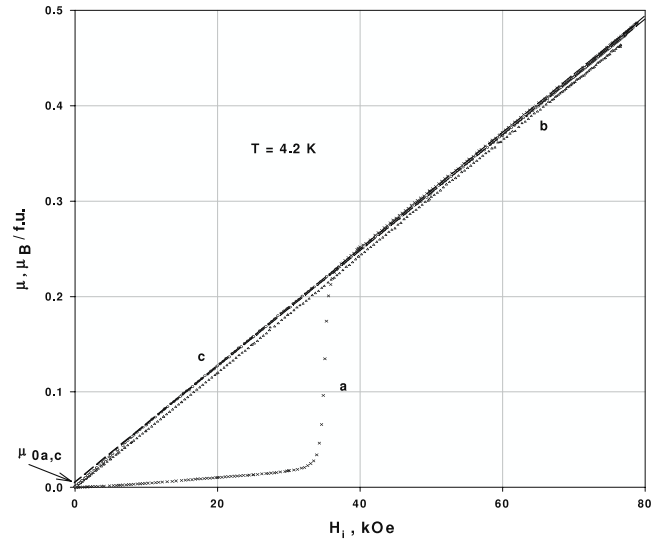

Figure 4. The field dependences of the magnetization for the *c*-axis of MnGeO$_3$.

The field dependences for the *b*- and *c*-axes are similar. Figure 5 shows this similarity at 4.2 K, as an example.

As we can see from figure 5, at $H > H_{sf}$ the antiferromagnetic vector turns to the *c*-axis because the field dependences of the magnetizations μ_a and μ_c actually coincide; the turning of the antiferromagnetic vector took place in the *ac*-plane.

Using all these experimental results, we estimated the exchange fields in the 4.2 K state in fields up to 80 kOe for all crystallographic directions as $2H_e = \chi^{-1}(H)\mu_s$, where $\mu_s = 5\mu_B$ for the Mn^{2+} ion [9, 10]. They are $2H_{ea} = 822$ kOe,

Figure 5. The field dependences of the magnetization of MnGeO$_3$ at $T = 4.2$ K.

$2H_{eb} = 826$ kOe and $2H_{ec} = 827$ kOe. From the relation $H_{sf}^2 = 2H_e H_a$, the anisotropic field H_a was estimated to be 0.75 kOe in the *ac*-plane.

Thus, from the results presented here and [4] it can be concluded that MnGeO$_3$ with orthorhombic symmetry is antiferromagnetic, with $T_N \approx 36$ K. In the first approximation the magnetic structure of MnGeO$_3$ can be described in the framework of the two-sublattice model. The unit cell contains 16 Mn^{2+} ions occupying two non-equivalent positions: Mn1 and Mn2 (figure 1). At coincidence of the structural and magnetic unit cells and in the absence of the longitudinal magnetic moment, these 16 ions can be divided into 4 sublattices with spins oppositely directed: 4Mn1↑ + 4Mn1↓ + 4Mn2↑ + 4Mn2↓. Thus, if we combine 4Mn1↑ with 4Mn2↑ and 4Mn1↓ with 4Mn2↓, we can arrive at a two-sublattice model (figure 1).

The presence of the small values $\mu_{0c} = \mu_{0a} \approx 7 \times 10^{-3} \mu_B$/f.u. (see figures 3–5) is not analyzed in our present work. The fact that $\mu_{0b(H=0)} = 0$ suggests that there is no foreign impurity in our samples.

4. Conclusion

The results of thorough magnetic measurements carried out on MnGeO$_3$ single crystals of space group *Pbca* with accurate orientation of the magnetic field relative to the crystallographic axes of a sample are presented. The magnetic data confirmed that our samples are antiferromagnets with $T_N \approx 36$ K, in contrast to the literature data for polycrystalline samples and single crystals. For the first time, a pronounced spin flop transition along the *a*-axis is observed in the field $H_{sf} = 35$ kOe and for $T = 4.2$ K. The exchange and anisotropic field values are $2H_e \approx 825$ kOe and $H_a \approx 0.75$ kOe, respectively. The MnGeO$_3$ magnetic structure is considered in the framework of a two-sublattice model with the antiferromagnetic easy axis along the *a*-axis direction. The study of the magnetoelectric properties of MnGeO$_3$ is being continued.

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