Synthesis and magnetic properties of MnGeO$_3$ single crystals with orthorhombic structure

N V Sapronova$^1$, A D Balaev$^1$, K A Sablina$^1$, N V Volkov$^{1,2}$ and A D Vasilyev$^{1,2}$

$^1$Kirensky Institute of Physics SB RAS, 660036 Krasnoyarsk, Russia
$^2$Siberian Federal University, Department of Physics, 660041 Krasnoyarsk, Russia

natalisapronova@yandex.ru

Abstract. The current report is devoted to the study of magnetic properties of MnGeO$_3$ single crystals with orthorhombic symmetry Pbca. MnGeO$_3$ single crystals have been grown by a flux method. A new data of 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 a-axis. The exchange and anisotropy fields are determined.

1. Introduction

Among manganese oxides, there are compounds that exhibit magnetoelectricity. Magnetoelectric materials may be defined as the materials which reveal a linear correlation between electric field and magnetization, as well as between magnetic field and electric polarization. In particular, the formation of magnetoelectric domains in Mn$_{0.94}$Mg$_{0.06}$GeO$_3$ single crystals was reported [1]. Previously, the magnetoelectric effect in MnGeO$_3$ polycrystalline samples below $T_N$ was observed [2]. Recently, multiferroic properties of quite a number of pyroxene with the total composition ABSi$_2$O$_6$ (A is a mono- or divalent metal and B is a di- or trivalent metal) were found [3]. This fact enhances our interest especially for investigation of magnetic and magnetoelectrical properties of MnGeO$_3$.

The MnGeO$_3$ single crystals were grown by the flux method. These crystals are characterized by orthorhombic symmetry stable up to 900°C [4]. The Neel temperature of these crystals ($T_N=38$ K) appeared significantly higher than that reported in the literature [5, 6, 7] ($T_N\sim 10-16$ K). We shown that the magnetic characteristics are sensitive even to minor impurity amount and to the synthesis conditions. Apparently, this sensitivity is concerned with features of MnGeO$_3$ chain structure [8]

In the present paper the results of thorough magnetic measurements with the accurate orientation of magnetic field relative to the crystallographic axes of a sample are presented.

2. Experimental

Manganese germanate single crystals (s/c) were obtained by a flux growth method generally used for growing single crystals of high-melting oxide compounds by spontaneous crystallization. The details of technological process were presented in our previous study [4]. The MnGeO$_3$ single crystals were 0.6 x 0.2 x 0.2 cm$^3$ in maximum size, brown, transparent, and had a 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, the 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 the accurate orientation of 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 II (Bruker AXS) diffractometer.

3. Results and discussion

3.1. Crystal structure

The MnGeO₃ compound possesses of the pyroxene structure with space group Pbca and cell parameters a=19.25 Å, b=9.23 Å, 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 GeO₄, which are connected via common vertices into an infinite series. Two atoms of the oxygen tetrahedron appear common, while the two others can make bonds with manganese ions Mn²⁺. The manganese atoms, in their turn, are in octahedral surrounding of oxygen atoms (MnO₆) 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 (Fig. 1).

![Figure 1. Projections of the MnGeO₃ crystal structure onto the bc plane. Mn ions are in octahedrons](image)

3.2. Magnetic properties

Figure 2 presents temperature dependences of susceptibility $\chi_a$, $\chi_b$, and $\chi_c$ for the MnGeO₃ single crystal in three directions of magnetic field $H=1$ kOe applied along crystallographic axes. Below $T_N=36$ K pronounced anisotropy of the susceptibility is observed, with $\chi_a (T)$ tended to zero and $\chi_b (T), \chi_c (T)$ increased at temperature decreasing. It is obvious that there is a spontaneous antiferromagnetic vector along a-axis, in other words $\chi_a$ is $\chi ||$ and $\chi_b(T), \chi_c(T)$ are $\chi \perp$. As is seen from the fig. 2 the Curie-Weiss law is obeyed in the range temperature 60-300 K. The Curie-Weiss constants $C_{a,b}, C_c$ and Curie paramagnetic temperatures $\theta_{a,b}, \theta_c$ were obtained. They are 4.26 cm$^{-1}$/K/mole, 4.37 cm$^{-1}$/K/mole and -107 K, -102 K, respectively. The effective magnetic moment values $\mu_{\text{eff} \ a,b}=5.84 \mu_B$ and $\mu_{\text{eff} \ c}=5.91 \mu_B$. The obtained values $\mu_{\text{eff} \ a,b,c}$ for the three directions of sample are agreement with value $\mu_{\text{eff}}$ for Mn$^{2+}$ ion with $S=5/2$. The visible anisotropy of paramagnetic susceptibility apparently is concerned with exchange anisotropy as indicated by the different values of 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 $T_N$. In spite of the fact that the reason of such behaviour requires the specific investigation, nevertheless, at this stage of research we are taking the risk to suggest that there is some contribution of “loose” spins to $\chi_b$ and $\chi_c$. The availability of “loose” spins can be explained by frustrating interactions in magnetic structure MnGeO$_3$ described in detail in our previous work [4].

In figure 3 the field dependences of magnetization for $a$-direction are shown. It is seen that at 4.2 K in the magnetic field $H_{sf}=35$ kOe spin-flop occurs. The critical fields $H_{sf}$ for the different isotherms were defined by maximum value of derivatives $(\partial \mu_a / \partial H)_{T=\text{const}}$. As temperature increases the value $H_{sf}$ increases in the range of antiferromagnetic ordering (see insert in fig.3).
Above $H_{sf}$ the field dependences of magnetization have a linear character. A slight hysteresis observed at spin-flop transition (does not show in figure) indicates that this transition is the first order magnetic phase transition. As is seen from fig. 3 the spin-flop transition vanishes at $T=34$ K. Using all these experimental results we estimated exchange fields at 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 Mn$^{2+}$ ion [9, 10]. They are $2H_{ea}=822$ kOe, $2H_{eb}=826$ kOe and $2H_{ec}=827$ kOe. From the relation $H_{sf}^2=2H_eH_a$ the anisotropic field $H_a$ was estimated to be 0.75 kOe in ac-plane. The presence of the small values $\mu_{0c}=\mu_{0a}\approx 7*10^{-3}\mu_B$/f.u (see fig. 3, 4, 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 the accurate orientation of magnetic field relative to the crystallographic axes of a sample are presented. The magnetic data confirmed that our samples are antiferromagnets with $T_N=36$ K in contrast to the literature data for polycrystalline samples and single crystals. For the first time the pronounced pin-flop transition along the $a$-axis is observed in the field $H_{sf}=35$ kOe and $T=4.2$ K. The exchange and anisotropic field values are $2H_e=825$ kOe and $H_a=0.75$ kOe, respectively. The study of the magnetoelectric properties of MnGeO$_3$ is being continued.

References

[1] Brown P J, Forsyth J B, Tasset F 2005 Solid State Science 7 682
[2] Gorodetsky G 1972 Phys.Letters 39A 155
[3] Jodlauk S, Becker P, Mydosh J A, Ikhomskii D, Lorenz T, Streltsov S V, Hezel D C and Bohaty L 2007 J. Phys.: Condens. Matter 19 432201
[4] Sapronova N V, Volkov N V, Sabrina K A, Petkovskii G A, Bayukov O A, Vorotynov A M, Velikanov D A, Bovina A F, Vasilyev A D, and Bondarenko G V 2009 Phys. Stat. Sol(b) 246 206
[5] Herpin P and Whuler A 1971 Phys. Stat. Sol. (b) 44 71
[6] Sawaoaka A, Miyahaka S, and Akimoto S 1968 J. Phys. Soc. Japan 25 1253
[7] Holmes L M, Uitert L G 1972 Sol. St. Comm. 10 85
[8] Bregg U and Klaringbull G 1967 Crystal structures of minerals (Moscow: Mir)
[9] Turov E A, Kolchanov A V, Men’shenin V V, Miraev I F, Nikolaev V V 2001 Symmetry and physical properties of antiferromagnetics (Moscow: PhysMatLit)
[10] Nagamiya T, Yosida K, Kudo R 1955 Adv. Phys. 4 1