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Uniaxial anisotropy and low-temperature antiferromagnetism of Mn_2BO_4 single crystal

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ABSTRACT

The Mn_2BO_4 single crystals have been grown by the flux technique. A careful study of the crystal structure and magnetic properties have been carried out. The antiferromagnetic transition at $T_N = 26$ K has been traced through the *dc* magnetization and specific heat temperature dependences. Magnetic uniaxial anisotropy has been found with easy axis magnetization lying in the ab-plane. The obtained value of effective magnetic moment is assigned to the non-quenched orbital moment of Jahn–Teller Mn^{3+} ions. The discussion of magnetic properties is based on the superexchange interaction calculations.

1. Introduction

It is well known that low dimensionality in crystal and magnetic structure plays an important role in the physics of magnetic crystals. The experimental and theoretical investigations have revealed properties of the materials with low dimensionality to be quite different from their bulk analogs. This difference results in the rich variety of phases and phase transitions caused by high degree of degeneration and extraordinary sensitivity to external influences. From this point of view the borates of transition and rare-earth metals with quasi-low dimension crystal structure and unique magnetic and optic properties are the perspective objects for the fundamental and practical investigations. These materials form a wide class of narrow-band oxide semiconductors intensely studied recently [1–5].

The oxyborates $M^{2+}M^{3+}BO_4$ with the warwickite structure attract attention due to a large number of isomorphic substitutions. There is a large variety of natural and synthetic warwickites containing rare-earth, alkaline earth and transition metal ions (M^{2+} = Mg, Co, Mn, Fe, and Ni, and M^{3+} = Ti, V, Cr, Fe, Mn, In, Lu, Yb, and Tm) [6–8]. The metal ions occupy two structurally distinct octahedral sites usually labeled as 1 and 2. Four octahedra linked by sharing edges form the *row* of 2-1-1-2. The *rows* are connected by sharing edges forming quasi low-dimensional *ribbons* extending along crystalline *c*-axis. The heterometallic warwickites ($M^{2+} \neq M^{3+}$) are naturally disordered materials since each cation site may be occupied by any one of the two metals. Most heterometallic warwickites show typical spin-glass transition [6,9].

Recently, we have performed the crystal structure, magnetic and electronic studies of $Mg_{1-x}Co_xBO_4$ ($x = 0.0$, 0.5, and 1.0) single crystals [10–13]. Mössbauer and magnetization studies have shown spin-glass behavior and quantum entanglement behavior $\chi(T) \infty T^{-\alpha(T)}$ above T_{SG}. The Co induced magnetocrystaline anisotropy increases the magnetic viscosity of the magnetic lattice, by freezing magnetic fluctuations below T_{SG}. On the contrary, the introduction of Cobalt does not alter transport properties radically.

Only two homometallic warwickites ($M^{2+} = M^{3+}$) are available now: Fe_2BO_4 and Mn_2BO_4 [14,15]. Both compounds display charge ordering (CO). The nature of CO in the warwickites is the subject of hot discussions. The temperature dependence of CO in Fe_2BO_4 was extensively investigated by resistivity and differential scanning

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calorimetry measurements, Mössbauer spectroscopy, synchrotron x-ray scattering, transmission electron microscopy, and electronic-structure calculations [16–19]. It has been proposed that the low-temperature phase ($T_{CCO} < 280$ K) is a commensurately charge ordered with integer iron valence separation Fe^{2+} and Fe^{3+} alternating in the *a*-axis direction. The intermediate temperature range ($T_{CCO} < T < T_{CO}$, where $T_{CO}=340$ K) is characterized by the onset of the temperature-dependent lattice incommensurate CO accompanied by coexisting mobile and immobile carriers. There is a valence fluctuating state (Fe^{2+}–Fe^{3+} electron hopping) in the high-temperature interval ($T > T_{CO}$) where the structural transformation from monoclinic→orthorhombic symmetry takes place. In Mn_2BO_4 the CO appears to be related to the strong Jahn–Teller distortion of the $Mn1O_6$ octahedra. CO of the $Mn^{2+}(2)$–$Mn^{3+}(1)$–$Mn^{3+}(1)$–$Mn^{2+}(2)$ kind and relevant orbital ordering ($d_z{}^2$) occurs. From the magnetic point of view the Fe_2BO_4 was found to be a *L*-type ferrimagnet with the transition temperature $T_N=155$ K [20]. As for the Mn_2BO_4, the situation is more intriguing. Nowadays this compound is known in three forms: single crystals [15], powder polycrystals [21–23], and necklace-like nanofibres [24]. The magnetic characterization has been carried out for the two first forms of Mn_2BO_4 and the results obtained are dramatically controversial. On one hand, magnetization, specific heat, and ESR studies of polycrystalline samples have revealed an antiferromagnetic transition at $T_N=104$ K and weak ferromagnetism below 70 K. Recent neutron diffraction data have shown the occurrence of the long-range antiferromagnetic order only below 26 K [23], while the ferrimagnetic transition at 42 K was found from magnetization measurements. On the other hand, a weak anomaly at ~25 K was observed from the magnetic susceptibility measurements performed on single crystals. The reason of this dramatic disagreement probably lies in the samples quality. The authors of [21–23] marked the presence of magnetic impurities in the form of Mn_2O_3 and Mn_3O_4 oxides.

Thus, there is no clear understanding of either the type of magnetic order or the temperature of magnetic phase transition in Mn_2BO_4. This paper reports first magnetization and specific heat measurements carried out on the Mn_2BO_4 single crystals. The experimental observation of magnetic phase transition at $T_N=26$ K strongly supports the neutron diffraction results [23]. Long-range antiferromagnetic order occurs below T_N. The magnetic measurements performed for two directions of the applied field with respect to the crystalline *c*-axis allowed to reveal uniaxial anisotropy. Based on the superexchange interactions analysis the magnetic behavior is explained and possible spin configuration for the ordered state of Mn_2BO_4 is offered.

2. Experimental procedure

The solid state reaction method was found to give rise to difficulties in the preparing of pure samples [21–23]. The main synthetic problems relate to the existence of concurring phases with different crystal structures. This problem has been discussed in detail in the well known systematic work by Capponi [7], where it has been shown that attempts to grow oxyborates $Co^{2+}Ga^{3+}BO_4$, $Co^{2+}Cr^{3+}BO_4$, and $Co^{2+}Sc^{3+}BO_4$ with the warwickite structure have lead to concomitant ludwigite phases $Co^{2+}_2Ga^{3+}BO_5$, $Co^{2+}_2Cr^{3+}BO_5$, and $Co^{2+}_2Sc^{3+}BO_5$ respectively. Due to this reason the exact parameters of growing process are of great importance for the successful preparation of single-phase material. At present work these parameters were defined after some probe reactions and X-ray diffraction control.

The solution has been made by the step by step melting of B_2O_3 oxide (6.9 g), $Bi_2Mo_3O_{12}$ (51 g), Mn_2O_3 (17.7 g) and Na_2CO_3 (4.1 g) at $T_1=1100°$ C during 3 hours. Then the temperature was rapidly lowered to $T_2=970°$ C followed by a slow cooling at a rate of 4 °C a day. In two days the crucible was pulled out from the furnace and the solution was removed. Single crystals spontaneously formed on the walls of the crucible were rinsed with the aqueous nitric acid at room temperature. The crystals were in the form of black needles up to 12 mm long, and the cross sectional area was smaller than 1.0×0.5 mm^2.

The room temperature X-ray diffraction measurements were carried out using an X-ray diffractometer SMART APEX II (MoKα radiation, CCD detector).

The magnetization in a field was measured using the hand-made vibrating samples magnetometer (VSM) at the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland). The *dc* magnetization has been measured as function of the temperature and applied magnetic field up to 140 kOe. The temperature interval was 1.8–300 K. The measurements were carried out for two directions of the external magnetic field relative to the crystallographic *c*-axis, which coincides with the needle's axis. The holder contribution was subtracted from the integral signal and the corrections associated with form anisotropy were taken into account.

The specific heat measurements have been done by the relaxation method on commercial PPMS Quantum Design platform in Shared Facility Centre of Lebedev Physical Institute of RAS in the entire temperature interval ($T=2$–300 K). The experimental error did not exceed 1% for all temperatures.

3. Experimental results

3.1. X-ray diffraction and normal coordinates calculation

In this section, we present some crystallographic data, which are relevant for the theoretical discussion below. The Mn_2BO_4 has a monoclinic unit cell ($P2_1/n$ space group), with the angle $\beta \approx 90.751°$ slightly different from 90° (Table 1). No impurity phases have been detected by means of X-ray diffraction. All parameters are in good agreement with those reported earlier [15,23]. The metal ions have two distinct positions labeled as 1 and 2, which are at the general 4*e* Wyckoff positions, oxygen atoms have four distinct positions and boron has only one position. The atomic coordinates, isotropic displacement parameters, selected bond lengths and angles are listed in the Supplemental materials (SM) Tables SM1–SM3 [25].

The $Mn1O_6$ octahedron is considerably smaller that the $Mn2O_6$ one as deduced from the average ⟨M–O⟩ bond length (2.065 instead 2.210 Å). The smaller ⟨M–O⟩ distances lead to an increasing oxidation state and can indicate that the Mn^{3+} ions prefer the $M1O_6$ octahedra, while Mn^{2+} occupies the $M2O_6$ ones. As it was expected, the shortest distances (less than 1.5 Å) are B–O inside the BO_3 triangle, which is the most tightly bound group in oxyborate structures.

The Mn^{2+} and Mn^{3+} distribution over the metallic sites can be studied by means of bond valences sums (BVS) calculation [26]. These empirical estimations predict atomic charges of 3.20/2.95 for Mn1 and 2.01/1.85 for Mn2, when bond valence parameters are related to Mn^{2+}/Mn^{3+}. So, there is a clear propensity of Mn^{3+} to occupy the site 1 with atomic charge 2.95, while for Mn^{2+} it is the site 2 with atomic charge 2.01. The obtained values are in agreement with the BVS calculation results reported by Norrestam [15] confirming that Mn_2BO_4 is a transition metal oxyborate with the explicit charge ordering. The BVS value for the boron atom was found to be 2.96 close to the formal valence 3+.

Both $Mn1O_6$ and $Mn2O_6$ octahedra are distorted. The distortions of the coordination octahedra can be described by the normal coordinates Q_α ($\alpha=1, 2, \ldots 3N$-3; N – number of ligands), which are linear combinations of the Cartesian coordinates of