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Magnetic properties of the warwickite $MnMgBO_4$

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ABSTRACT

Magnetic properties of a new single crystal $MnMgBO_4$ have been studied. It was determined that below 16 K antiferromagnet spin order was observed with the axis of easy magnetization along the *c* axis crystal. The short antiferromagnetic range order was observed below 100 K. The Curie–Weiss temperature has been determined in single crystal $MnMgBO_4$ as $\theta_{CW} = -98$ K and the frustration parameter has been estimated as 6.125.

1. Introduction

A low-dimensional materials exhibit excellent physical properties which are differed from the three-dimensional compounds. A large number of exotic phases, unusual phase transitions and sensitivity to external influences which associated with strong the degeneration of the ground state attract the attention of researchers. A rich phase diagram is demonstrated by compounds with manganese [1], such as manganites $RMnO_3$, where R is rare earth element. Another system with interesting magnetic properties is a warwickite.

The system of the warwickite is a mixed borate with the general formula $M1^{2+}M2^{3+}BO_4$ with a linear structure in the form of a ribbons, which located along the *c* axis, where M1 and M2 are metal ions. The ribbons consist from four octahedra columns which were formed by oxygen atoms, and two or trivalent metal ions located in the center. These structural features provide a low-dimensional properties of warwickite. The warwickite Mn_2BO_4 structure in the projection along [001] has been presented on Fig. 1 of the article [2]. Another feature of these structures is the random distribution of 2+ and 3+ valence ions in ribbon. As a result, in addition to the quasi-one-dimensional spin nature, this system still has a disperse of exchange integral values between neighbor spins in the ribbon.

The different atoms can be cations including the metals with variable valence such as Fe, Mn, Co in $M1^{2+}M2^{3+}BO_4$. The exchange interaction between spins is realized both within quasi-one-dimensional ribbons and between ribbons, which increases geometric frustration. The magnitudes of the isotropic exchange interaction between spins of manganese ions have been calculated in Ref. [2] for Mn_2BO_4: $J_1 = -4.03$ K; $J_2 = -1.44$ K; $J_3 = -6.83$ K; $J_4 = -5.21$ K; $J_6 = -5.03$ K; $J_5 = -5.03$ K using the model of virtual charge transfer. The interactions between the spins of manganese from neighboring ribbons are weaker and are equal $J_7 = -2.41$ K; $J_8 = -0.47$ K; $J_9 = -0.65$ K that show the presence of frustration in the triangular structure of the competing exchange interaction of warwickite. The additional interest of these compounds has been caused with the practical point of view: mixed oxiborite turned out to be promising anodes for lithium-ion accumulators. According to the work of L. Xu [3] modification anode Mn_2BO_4 in Li-ion batteries have a capacity of 1172 mAh/g at a current of 100 mA/g and 724 mAh/g after 120 recharge cycles.

The magnetic properties of $MgFeBO_4$, $Mg_{0.5}Co_{0.5}FeBO_4$ and $CoFeBO_4$ compounds were studied in Ref. [4]. Analysis of magnetization and heat capacity data showed that in these compounds there is a transition to the spin glass state at $T_{sg} = 10$; 20 and 22 K, respectively. Analyzing the temperature dependence of the magnetic susceptibility in AC current, it was found that low-dimensional magnetic behavior above T_{sg} is described by a model of Heisenberg antiferromagnetic chain with random exchange where $\chi(T) \approx T^{-\alpha}$ [4] below $T_f \approx 130$ K. The α value has been varied in the range from 0.4 to 0.6, that proves the existence of random singlet phase in this temperature region. The spin glass order is explained by the disordering substitution of Mg, Fe and Co in two possible crystallographic positions. The cobalt substitution causes uniaxial anisotropy along the *b* axis, increasing absolute magnetization and increasing the transition temperature in the spin glass state.

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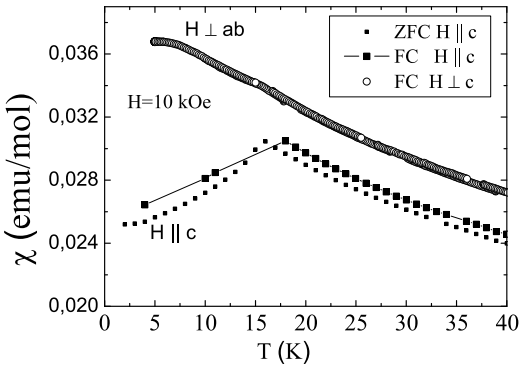

Fig. 1. Temperature dependencies of magnetic susceptibility for single crystal $MnMgBO_4$ below 40 K.

The X-ray diffraction analysis was performed on the compound Mn_2BO_4 in Ref. [2]. It was obtained that symmetry group is $P2_1/n$ with a = 9.2934(5)Å, b = 9.5413(5) Å, c = 3.2475(2) Å and β = 90.7510(10)°. The slightly different parameters were obtained in Ref. [5] for the identical compound: a = 9.490(1) Å; b = 9.422(1) Å; c = 3.2189(4) Å; β = 90.757(7)°. The X-ray diffraction analysis was performed on the compound $MgScOBO_3$ [6]. It has been received: symmetry group is *Pnma*; a = 9.490(1) Å; b = 9.422(1) Å; c = 3.2189(4) Å.

If one ion from $M1^{2+}$ $M2^{3+}$ BO_4 is nonmagnetic, then the new exchange pattern interactions in the ribbon is formed, and, as a result, the symmetry is modified unit cell. In the literature, it is absent data relating to the study of the magnetic properties of the warwickite compounds where the valence of the magnetic metal manganese does not change and when the second metal is non-magnetic. The detailed studies of these compounds will allow to establish a picture of the exchange interactions between the identical spins of manganese ions. The purpose of this work is the study of magnetic properties new single crystals of $MgMnBO_4$ by magnetometry methods.

2. Experiment and discussion

The single crystals $MnMgBO_4$ have been obtained by flux method: crystal forming oxides (Mn_2O_3, MgO and B_2O_3) have been dissolved in the mixture $Bi_2Mo_3O_{12}$ − −B_2O_3–Na $_2O$. Microstructure and the elemental composition of the samples have been studied by scanning electron microscope EVO 50 XVP (SEM) and dispersion by X–ray spectroscopy (EDX, Oxford, Inca Energy 350, equipped with a scanning electron microscope). We calculated a relative errors and the concentration of elements in the sample on the basis of four points. The content of magnesium atoms was taken as 1 when calculating of the chemical formula due to the smallest relative error concentration of magnesium ions. From the electrical neutrality of the sample it has been obtained that the oxygen content was equal 4.42. It was found that the our crystal has composition $Mn_{1.07}MgB_{1.21}O_{4.42}$ ($MnMgBO_4$).

The measurements of the temperature dependence of the magnetic susceptibility, magnetization and the molar heat capacity were conducted on a vibration magnetometer PPMS in the temperature range 2–300 K. The measurements of magnetization on the applied external magnetic field at a temperature of 5 K in the range from −1 T to 1 T were carried out. The hysteresis loop is not observed. The external magnetic field has been applied parallel and perpendicular to the *c* axis of the crystal. The temperature dependencies of the magnetic susceptibility for $MnMgBO_4$ were shown in Fig. 1 in two regimes: FC – field cooling, ZFC – zero field cooling. As can see from the picture the peak in the temperature dependence of the magnetic susceptibility was identified when the orientation of external the magnetic field is parallel to the *c* axis of the crystal at 16 K. The peak was absent with orientations of the external magnetic field perpendicular to the *c* axis of the crystal

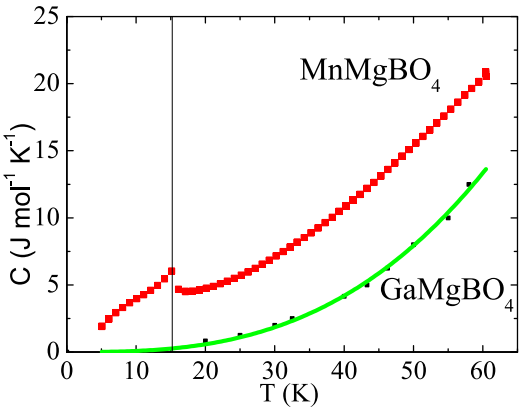

Fig. 2. Temperature dependencies of molar heat capacity in zero magnetic field for $MnMgBO_4$; solid green curve data is polynomial fitting for isomorphic compound $GaMgBO_4$ from Ref. [7]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and, in this case, the temperature dependence of magnetic susceptibility was increased below 16 K. This behavior indicates that the antiferromagnetic order of manganese ion spins was observed below 16 K, but these dependencies can be interpreted as the spin glass system.

The confirmation of antiferromagnetic phase transition proves the observation of the lambda point at the same temperature in the temperature dependence of the molar heat capacity, which is shown in Fig. 2. The experimental values of temperature dependence of molar heat capacity are presented by squares in Fig. 2. In order to determine the magnetic contribution in the molar heat capacity, we subtracted the molar heat capacity for the isomorphic diamagnetic crystal $GaMgBO_4$ [7] from the our experimental values. The magnetic contribution to the molar heat capacity of the crystal $MnMgBO_4$ is shown in Fig. 3. As can see from Fig. 3 in addition to the lambda point at 16 K a wide maximum at T ≈ 53 K is observed in the temperature dependence of the molar heat capacity. A similar maximum was observed in Ref. [8] at 45 K for single crystal $FeMgBO_4$. The authors of [8] believe that an additional contribution to the heat capacity is due to the presence of variable valence ions in the chain and delocalization of the electron, which generate optical phonon.

The temperature dependence of the inverse magnetic susceptibility is shown in Fig. 4 in external magnetic field 10 kOe, parallel to the *c* axis of the crystal. The solid line was conducted in according the Curie-Weiss law $\chi = C/(T-\theta_{CW})$, where $\theta_{CW} = -98$ K. Using the constant *C*, we estimated the effective magnetic moment per mole as $\mu_{exp} = 5.01 \pm 0.02\mu_B$.

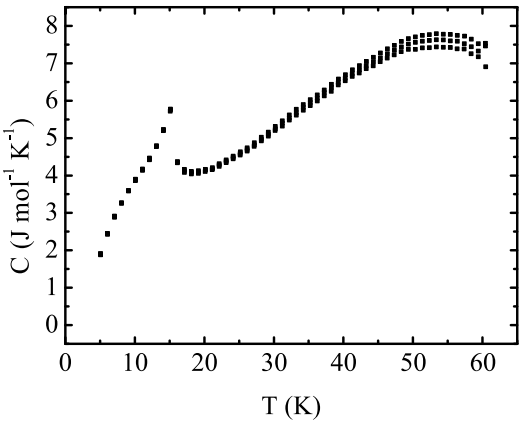

Fig. 3. The temperature dependence of the magnetic part of the molar heat capacity for crystal $MnMgBO_4$.

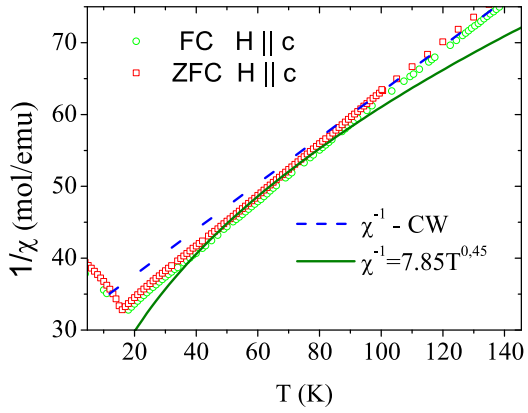

Fig. 4. The temperature dependence of the inverse magnetic susceptibility, in magnetic field 10 kOe, external magnetic field parallel to the *c* axis of the $MnMgBO_4$ crystal. Dotted line – Curie - Weiss law, solid line – antiferromagnetic chain model with random Heisenberg exchange.

We compared the obtained value with theoretical estimation, according the formula:

$$\mu_{theor} = g \cdot \mu_B \cdot \sqrt{Z_{Mn^{3+}} S_{Mn^{3+}} \left(S_{Mn^{3+}} + 1\right)}, \quad (1)$$

where μ_B – the Bohr magneton, g – factor Lande, Z – number of magnetic ions in a unit cell, S – spin of the ion. According to the element analysis, the Mn content is 1.07, the valence is 3+, in this case [9] spin value for Mn^{3+} is $S = 2$. Using this data, the effective magnetic moment per mole of the substance was calculated $\mu_{theor} = 5.07 \pm 0.62\mu_B$. The theoretically calculated and experimental values of the effective magnetic moment practically coincide, which confirms the valence of the manganese ion. Note that the filling of the bivalent cation positions in a unit cell by the diamagnetic ion Mg^{2+} instead of magnetic Mn^{2+} led to decrease the Neel temperature from 25 K [2] to 16 K.

We used the theory of the molecular field for estimation the value of the isotropic Heisenberg exchange from Curie-Weiss temperature using the formula from Ref. [10]: $\theta_{CW} = Z \cdot J \cdot S(S + 1)/3k_B$. In ideal case we assume that the manganese ions are equally probable can occupy all positions in the ribbon, in this case Z = 6, and taking into account that $\theta_{CW} = -98$ K, then $J = 8.17$ K.

This estimation was agreement with the order of theoretical value of exchange interaction between spins of the manganese ions from Ref. [2], where the maximum value of the exchange interaction is - 6.83 K. The degree of frustration we estimated using the ratio $|\theta_{CW}|/T_N = 98/16 = 6.125$.

As can be seen from Fig. 4 below 100 K the temperature dependence of magnetic susceptibility are not described by Curie - Weiss law. We assumed that below 100 K the magnetic system of spins of manganese ions crosse from the paramagnetic region in the antiferromagnetic short range order state. Antiferromagnetic short range order were observed at higher as Neel temperatures in other low dimensional compound $LiCu_2O_2$ [11]. The temperature dependence of the magnetic susceptibility can be described using the Heisenberg antiferromagnetic chains model with random exchange at temperatures below 100 K up to 40 K. As a result of the approximation of the inverse temperature dependence of the magnetic susceptibility using the formula $\chi(T) \propto T^{-\alpha}$ [12], in the magnetic fields 200 and 10000 Oe, which were applied parallel to the *c* axis of the crystal, the value of the parameter $\alpha = 0.45 \pm 0.03$ was obtained. As can be seen from Figs. 1 and 4 below 40 K the range associated with quasi-one-dimensional short range order is destroyed and the three-dimensional interactions in the spin system become predominant. The resulting value α is almost equal the parameter $\alpha = 0.54$ that was determined for the $MgFeBO_4$ warwickite in the temperature range below 100 K [13].

3. Conclusions

We note that antiferromagnetic ordering below 16 K was observed in new low-dimensional crystal $MnMgBO_4$. From analysis of effective magnetic moments it is established that ions manganese have the 3+ valence. Using the theory of mean field the average isotropic exchange interaction $J = 8.17$ K was estimated from Curie - Weiss temperature $\theta_{CW} = -98$ K. The frustration parameter was carried out as the ratio of Curie - Weiss temperature to Neel temperature. The short range antiferromagnetic order was observed below 100 K, where the temperature dependence of the magnetic susceptibility has been described by the model of the antiferromagnetic chain with random Heisenberg exchange, where $\alpha = 0.45 \pm 0.03$.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ssc.2018.12.019.

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