ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2019, Vol. 83, No. 7, pp. 792–794. © Allerton Press, Inc., 2019.
Russian Text © The Author(s), 2019, published in Izvestiya Rossiiskoi Akademii Nauk, Seriya Fizicheskaya, 2019, Vol. 83, No. 7, pp. 873–875.

Investigation of the Magnetic Properties of Warwickite $Mn_{0.89}Mg_{1.11}BO_4$

R. M. Eremina[a, *], E. M. Moshkina[c, d], T. P. Gavrilova[a], A. R. Muftakhutdinov[b], and I. F. Gilmutdinov[b]

[a] *Zavoisky Physical-Technical Institute, Kazan Scientific Center, Russian Academy of Sciences, Kazan, 420029 Russia*
[b] *Kazan Federal University, Kazan, 420008 Russia*
[c] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
[d] *Reshetnev Siberian State University of Science and Technology, Krasnoyarsk, 660037 Russia*
**e-mail: REremina@yandex.ru*

Received September 7, 2018; revised January 31, 2019; accepted March 27, 2019

Abstract—The temperature dependences of the magnetic susceptibility in magnetic fields applied parallel and perpendicular to axis *c* of a $Mn_{0.89}Mg_{1.11}BO_4$ single crystal were measured. Spin ordering typical of an antiferromagnetic with an easy magnetization axis was observed below 16 K. The Dzyaloshinskii–Moriya interaction between spins of manganese ions in $Mn_{0.89}Mg_{1.11}BO_4$ was estimated by analyzing the EPR linewidth.

DOI: 10.3103/S106287381907013X

INTRODUCTION

Warwickites are mixed borates with the general formula $M1^{2+}M2^{3+}BO_4$ (where M1 and M2 are metals) and a linear ribbon structure. Metal ions in warwickites occupy two crystallographically nonequivalent octahedral sites. Four octahedra with common faces form a row (M2–M1–M1–M2). Rows are combined into ribbons directed along axis *c*. The distribution of ions of di- and trivalent metals over nonequivalent sites may be random [1]. Several work on the synthesis and structure of Mg–Mn warwickites have already been published, but the magnetic properties of these compounds have not been studied systematically. The aim of this work was to examine the magnetic properties of $Mn_{0.89}Mg_{1.11}BO_4$ warwickite single crystals.

EXPERIMENTAL

$Mn_{2-x}Mg_xBO_4$ single crystals were synthesized at the Kirensky Institute of Physics (Krasnoyarsk) via solution-melt crystallization with crystal-forming Mn_2O_3, MgO, and B_2O_3 oxides dissolved in a $Bi_2Mo_3O_{12}$–B_2O_3–Na_2O mixture. These single crystals had the form of black prisms up to 5 mm long (along axis *c*) and with transverse sizes of up to 0.4 mm. Temperature dependences of their magnetic susceptibility and magnetization were measured in magnetic fields applied parallel and perpendicular to axis *c* with a PPMS-9 vibration magnetometer in the 2–300 K range.

Figure 1 shows the temperature dependences of the magnetic susceptibility of $Mn_{0.89}Mg_{1.11}BO_4$, measured in magnetic fields applied parallel and perpendicular to axis *c* in the modes of field cooling (FC) and field heating (FH): an external field was applied at room temperature, the sample was cooled, and the magnetization was then measured as the temperature

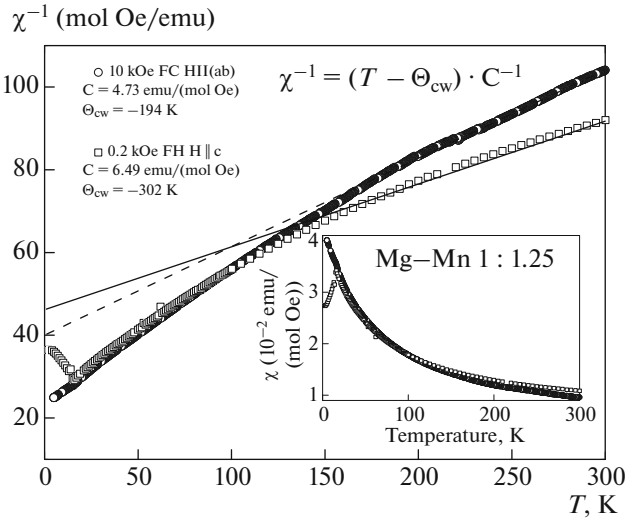

Fig. 1. Temperature dependence of the inverse magnetic susceptibility in a $Mn_{0.89}Mg_{1.11}BO_4$ single crystal. The solid line is the Curie–Weiss approximation.

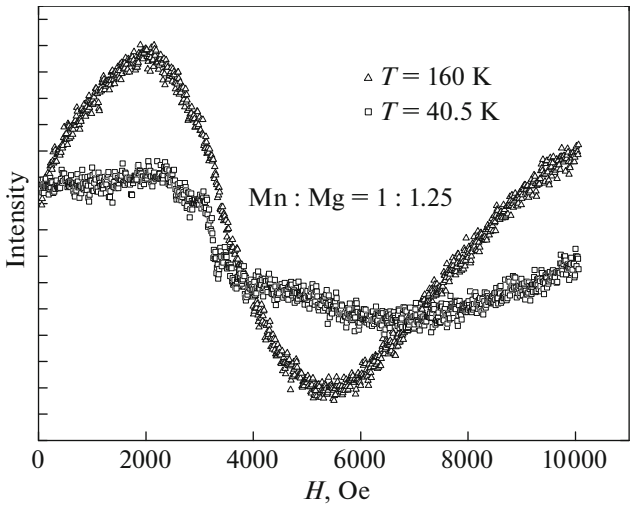

Fig. 2. EPR spectrum in a $Mn_{0.89}Mg_{1.11}BO_4$ single crystal at 40.5 and 160 K.

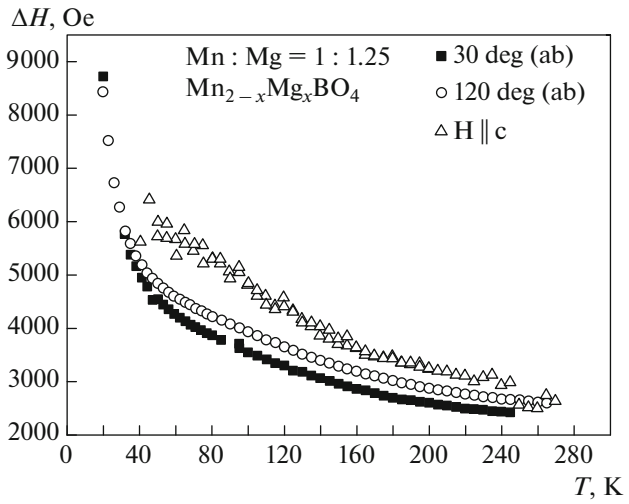

Fig. 3. Temperature dependences of the EPR linewidth in a $Mn_{0.89}Mg_{1.11}BO_4$ single crystal in three perpendicular directions.

increased. A well-marked peak is seen at 16 K in the dependence measured in an external field parallel to axis *c* of the crystal; when the field was perpendicular to this axis, the susceptibility curve increased at temperatures below 16 K. This behavior is indicative of the antiferromagnetic ordering of spins of manganese ions below 16 K. The solid line represents the Curie–Weiss law: $\chi = C/(T - \theta_{CW})$, where $\theta_{CW} = 194$ K. The molecular field approach allows us to estimate the isotropic Heisenberg exchange interaction using the formula for the Curie–Weiss temperature [2]: $\theta_{CW} = ZJS(S + 1)/3$, where Z is the number of nearest neighbors in a ribbon. If we assume that manganese ions occupy all positions in a ribbon with $Z = 6$ with equal probability and $S = 2$ for Mn^{3+}, it follows that $J = 16$ K.

EPR spectra were measured with a Bruker EMX spectrometer in temperature intervals of 100–320 K at a frequency of 9.4 GHz. The experimental EPR spectra for $Mn_{0.89}Mg_{1.11}BO_4$ at 40.5 and 160 K are shown in Fig. 2. These spectra were fitted with a Lorentzian line shape function. It can be seen that the EPR line at 160 K was fitted well by a single line; as the temperature fell, less intense lines attributable to the impurity phase emerged in the spectrum.

Temperature dependences of the EPR linewidth in three perpendicular directions (Fig. 3) were determined by analyzing the EPR spectra of ceramic $Mn_{0.89}Mg_{1.11}BO_4$ samples.

With strong exchange narrowing, the EPR linewidth can be approximated using the high-temperature approximation ($k_BT \gg J$):

$$\Delta H = \frac{\hbar M_2}{g\mu_B\omega_{ex}}, \quad (1)$$

where M_2 is the second line moment, expressed in terms of the microscopic parameters of the spin-system Hamiltonian as

$$M_2 = \frac{\left\langle \left[H_{an}, S^+\right]\left[S^-, H_{an}\right]\right\rangle}{\hbar^2\left\langle S^+S^-\right\rangle}. \quad (2)$$

The effective spin Hamiltonian is given by

$$H = J\mathbf{S_i}\mathbf{S_j} + D[S_i \times S_j], \quad (3)$$

where $J\mathbf{S_i}\mathbf{S_j}$ is the isotropic Heisenberg interaction between neighboring spins S_i and S_j, and D is the antisymmetric anisotropic exchange interaction in the local reference system with axis z parallel to an external magnetic field. The transformations below characterize the transition between crystallographic (a, b, c) and local (x, y, z) reference systems:

$$\begin{aligned} D_x &= D_a\cos\beta\cos\alpha + D_b\cos\beta\sin\alpha - D_c\sin\beta, \\ D_y &= D_a\cos\alpha - D_b\sin\alpha, \\ D_z &= D_a\sin\beta\cos\alpha + D_b\sin\beta\sin\alpha + D_c\cos\beta, \end{aligned} \quad (4)$$

where $\cos\alpha$ and $\cos\beta$ are defined by relations (13) in [3]. The second and the fourth moments for spins in a chain are written as

$$M_2 = \frac{2N}{3}\left[D_x^2 + D_y^2 + 2D_z^2\right], \quad (5)$$

where $N = S(S + 1)$. Using relations (1)–(5) and the obtained EPR linewidth at 250 K, we estimated the antisymmetric exchange interaction in $Mn_{0.89}Mg_{1.11}BO_4$: $D = 0.7$–1.0 K.

CONCLUSIONS

The magnetic properties of a new low-dimensional $Mn_{0.89}Mg_{1.11}BO_4$ crystal with antiferromagentic ordering below 16 K were studied. The average magnitude of the isotropic exchange interaction (J = 16 K) was determined. The antisymmetric isotropic exchange interaction between spins of manganese ions was estimated at 0.7–1.0 K by analyzing the EPR linewidth.

FUNDING

This work was supported by the Russian Foundation for Basic Research; the Administration of Krasnoyarsk Krai; and the Krasnoyarsk Krai Science Foundation, project no. 18-42-243007.

REFERENCES

1. Kazak, N.V., Platunov, M.S., Knyazev, Yu.V., et al., *J. Magn. Magn. Mater.*, 2015, vol. 393, p. 316.
2. Glazkov, V.N., *Vvedenie v fiziku magnitouporyadochennykh sistem* (Introduction to the Physics of Magnetically Ordered Systems), Moscow: Mosk. Fiziko-tekh. Inst., 2015.
3. Eremina, R.M., *Magn. Reson. Solids*, 2014, vol. 16, p. 14102.

Translated by D. Safin