

Crystal Structure and EPR Spectra of $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$

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Abstract—Results are presented from investigating the structure of $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ via powder neutron diffraction. Crystals of ludwigite $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ are grown by flux method using a $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ -based solvent diluted with Na_2CO_3 carbonate. Boric acid H_3BO_3 is used as the boron-containing reagent. Powder neutron diffraction measurements are made at a temperature of 100 K on powder prepared by grinding grown single crystals. Rietveld studies show that the grown $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ crystals belong to *Pbam* space group. Crystallographic sites occupied by cobalt and manganese ions are identified by analyzing powder neutron diffractograms. A bottleneck regime is observed in the temperature dependence of the EPR spectra.

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INTRODUCTION

The field of spintronics—which studies magnetic phenomena in solids caused by intrinsic and orbital magnetic moments of ions and the creation information processing devices based on them—is developing rapidly. The scientific community is actively searching for new exotic spin states in previously unknown newly-grown low-dimensional magnets.

Oxyborates with the general chemical formula $(\text{MeMe}')_3\text{BO}_5$ mostly have a ludwigite crystal structure and belong to the *Pbam* (55) space group [1, 2]. Oxyborates with ludwigite-type structures (structural formula $\text{M}'_2\text{M}''\text{BO}_5$, where M' and M'' are metal ions with 2+ and 3+ valences, respectively) have highly unusual magnetic properties, due to the random distribution of magnetic ions, mixed valences, and strong electronic correlations. These properties are due to zigzag walls in the crystal structure formed by metal ions of different valences. Another reason is the presence of four nonequivalent structural sites, which can be occupied by up to twelve magnetic ions per unit cell. The chemical formula and condition of electrical neutrality for ludwigite suggest a 2 to 1 ratio between di- and trivalent elements, which can occupy four possible sites at the center of a distorted octahedron.

According to the condition of electrical neutrality, Me and Me' metal ions have different valences. Metal ions can be either one ion with different valences (homometallic) [1–6] or different ions (heterometallic) [2, 5, 7–19]. Metal divalent, trivalent, tetravalent, and even pentavalent ions lie at the centers of oxygen coordination octahedra with common edges. Boron

ions lie at the centers of coordination triangles, each angle of which is the angle of a different octahedron. The ludwigite structure contains separate structural elements known as triads. The first triad has metal ions in sites 4-2-4, with octahedra connected by the edges of the base. Ions in sites 1 and 3 in the octahedral environment are connected by vertices and form triads of the second type. The ludwigite structure is shown in Fig. 1.

Different spin states of the same ions can form in ludwigites, due to the variety of possible ions at sites 1,

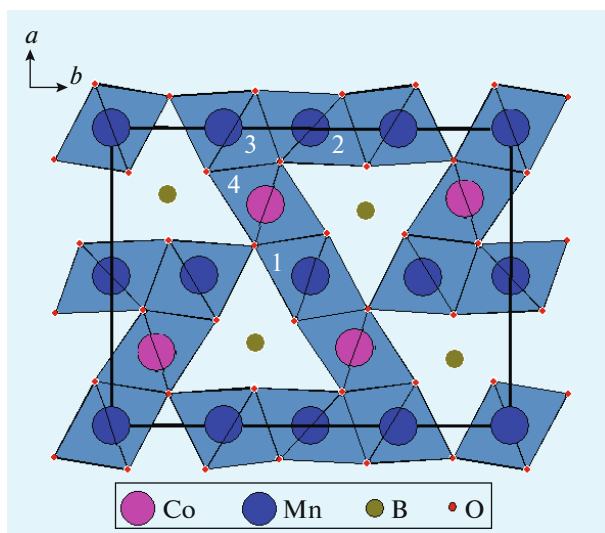


Fig. 1. Ludwigite structure.

2, 3, and 4. The magnetic structure of Co_3BO_5 was thus solved in [20] via neutron diffraction. It was found that the magnetic moments of Co^{2+} ions at sites 1–3 are 3.1–3.8 μ_B , which corresponds to the high-spin state of Co^{2+} ions. The magnetic moment of Co^{3+} ions at site 4 is only 0.5 μ_B , from which the authors of [20] concluded that Co^{3+} ions are in a low spin state. A magnetic transition occurs near 42 K with ferromagnetic bonds between planes (*ab*) and in the plane between cobalt ions. The magnetic moments of the ions are oriented almost parallel to axis *b* and are slightly skewed in the direction of axis *a*.

Neutron diffraction studies of Fe_3BO_5 magnetic structure have been made by two different groups [1, 6]. The magnetic moments of subsystems 1 and 2 are ordered in the directions of crystallographic axis *b* and *a*, respectively.

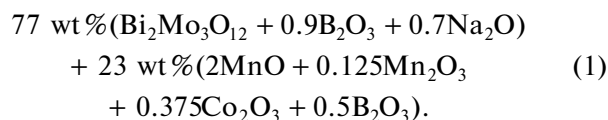
Theoretical and experimental research in the field of low-dimensional magnetism has recently been associated with such new ideas as the spin liquid in the Kitaev model, i.e., quantum spin ice [21] for the $\text{Na}_3\text{Co}_2\text{SbO}_6$ compound, which contains cobalt ions.

Low-dimensional magnets are therefore actively studied systems in which researchers continue to find new phenomena. Due to the complex structure of magnetic interactions in ludwigites, neutron diffraction is a powerful tool for determining the structure of heterometallic and homometallic ludwigites.

The aim of this work was to synthesize new oxyborate single crystals with general chemical formula $\text{Mn}_{3-x}\text{Co}_x\text{BO}_5$ and study their properties by means of neutron diffraction methods.

EXPERIMENTAL

$\text{Mn}_{2.25}\text{Co}_{0.75}^{11}\text{BO}_5$ single crystals were grown using the flux method. The flux system system had the form



It was assumed that the divalent subsystem included only manganese cations, and adding cobalt oxide produces Co^{3+} cations in the crystal.

A flux with $m = 81$ g was prepared by sequentially melting mixtures Bi_2O_3 – MoO_3 – B_2O_3 powders in a platinum crucible ($V = 100$ cm³) at $T = 1100^\circ\text{C}$. Portions of Mn_2O_3 , Co_2O_3 , and Na_2CO_3 powders were then added. The thermal decomposition of carbonate occurs upon heating and is accompanied by the release of carbon dioxide: $\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2$.

We used chemical reagent $\text{H}_3^{11}\text{BO}_3$ with boron isotope ^{11}B to prepare system (1). The thermal decomposition of boric acid $\text{H}_3^{11}\text{BO}_3$ into boron oxide B_2O_3 and water H_2O occurs upon heating, with the subsequent

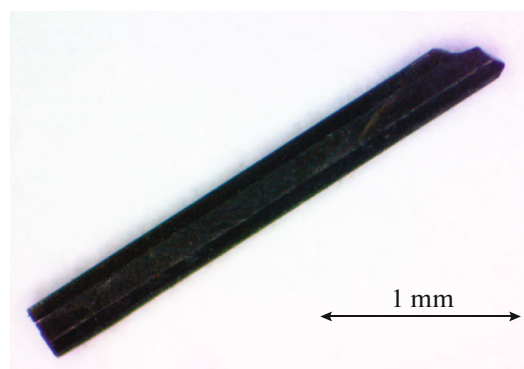


Fig. 2. Obtained ludwigite single crystal $\text{Mn}_{2.25}\text{Co}_{0.75}^{11}\text{BO}_5$.

evaporation of water. Expression (1) is therefore true when using boric acid as an initial component of a flux. Phases were probed and flux parameters were determined after homogenizing for 3 h at $T = 1100^\circ\text{C}$. The synthesis procedure was described in more detail in [22].

After exploratory studies, the flux was again homogenized for 3 h at $T = 1100^\circ\text{C}$ in the growth stage. The temperature in the furnace was then lowered quickly to temperature $T_{\text{start}} = (T_{\text{sat}} - 5)$ ($T_{\text{sat}} = 965^\circ\text{C}$) at a rate of $dT/dt = 200^\circ\text{C/h}$, and then slowly at a rate of $dT/dt = 4^\circ\text{C/day}$. After 3 days, the crucible was removed from the furnace and the flux was drained. The grown crystals were separated from the flux residue via etching in a 20% aqueous solution of nitric acid. The resulting crystals were in the form of elongated prisms. (Single crystals are shown in Fig. 2.)

The structure of the grown crystals was determined via neutron diffraction using the DISK polycrystalline multidetector ring neutron diffractometer with a constant wavelength on the neutron beam of the IR-8 research reactor at National Research Center Kurchatov Institute; $\lambda = 2.438$ Å. Low temperature measurements (at 100 K) were made with a closed cycle cryostat. The temperature dependence of EPR spectra of $\text{Mn}_{2.25}\text{Co}_{0.75}^{11}\text{BO}_5$ powder was also measured on a Bruker ER 200 SRC (EMX/plus) spectrometer equipped with He and N_2 flow cryostats at a frequency of 9.4 GHz in the 100–260 K range of temperatures. EPR lines are shown in Fig. 3.

RESULTS AND DISCUSSION

Neutron diffraction spectra of $\text{Mn}_{2.25}\text{Co}_{0.75}^{11}\text{BO}_5$ powder were obtained at a temperature of 100 K. The resulting neutron diffraction pattern is shown in Fig. 4.

The MAUD (Materials Analysis Using Diffraction) v.2.992 program was used to analyze the diffraction pattern [23]. We used the ludwigite structure determined in 2019 [24] to adjust the crystallographic

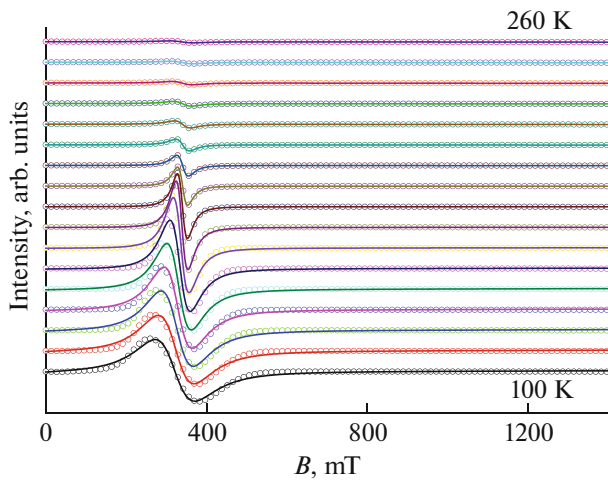


Fig. 3. Temperature dependence of $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ powder EPR spectra in the X-band (9.4 GHz). The spectra are presented in the range of 100–260 K with a step of 10 K. Experimental spectra are shown with white symbols; solid lines indicate an approximation according to formula (3).

parameters. The unit cell parameters and atomic positions were determined and space group $Pbam$ was confirmed. The occupation of oxygen and boron ion sites did not change when approximating neutron diffraction patterns. The diffraction pattern contained several unrecognized peaks at angles $2\theta = 12.7^\circ, 23.06^\circ, 32.4^\circ, 39.7^\circ$, due presumably to magnetic ordering. The intensity of these peaks was more than an order of magnitude below the intensity of the main ludwigite peaks, but they contributed to measuring errors. Fitting also did not consider hardware error, so some parameters of thermal fluctuations had negative values affecting those of errors. The quality of the fit parameter was nevertheless quite acceptable: $R_{wp}(\%) = 17.43$, where

$$R_{wp} = \sqrt{\frac{\sum_{i=1}^N [w_i (y_i(\text{ex}) - y_i(\text{calc}))]^2}{\sum_{i=1}^N [w_i y_i(\text{ex})]^2}}, \quad (2)$$

and $w_i = 1/\sqrt{y_i(\text{ex})}$; $y_i(\text{ex})$ is experimental intensity of neutron diffraction at point i , and $y_i(\text{calc})$ is the calculated intensity of the neutron diffraction pattern at point i .

Table 1. $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ crystal cell parameters at a temperature of 100 K

$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$V, \text{\AA}^3$
9.2378 ± 0.0023	12.5603 ± 0.0031	3.0793 ± 0.0005	357.24

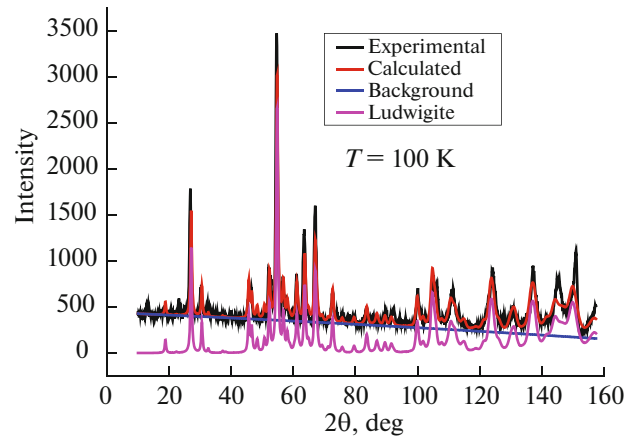


Fig. 4. Neutron diffraction patterns of $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ at a temperature of 100 K.

The obtained lattice parameters of $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ are given in Table 1.

It was found that manganese ions mostly occupied 2+ valence positions at Me1, Me2, and Me3 sites, while cobalt ions occupied 3+ valence positions at Me4 sites. We can see from Table 2 that the greatest thermal fluctuations were observed for the ions occupying site number 3 (which were probably Jahn–Teller ions of manganese and cobalt).

One exchange-narrowed line was observed in the EPR spectrum of the powder. Its shape was approximated by the equation

$$\frac{\partial P}{\partial B} = \frac{\partial}{\partial B} \left[\frac{\Delta B + \alpha(B - B_{\text{res}})}{(B - B_{\text{res}})^2 + \Delta B^2} + \frac{\Delta B + \alpha(B + B_{\text{res}})}{(B + B_{\text{res}})^2 + \Delta B^2} \right], \quad (3)$$

where B_{res} is the position of the resonant line, ΔB is the linewidth, and α is the parameter of line asymmetry. The values of the effective g-factor, linewidth, and characteristic intensity were obtained from the approximation of the EPR line shape using formula (3), the resulting temperature dependences of which are shown in Fig. 5.

We can see from Fig. 5 that the linewidth of the EPR line and the effective g-factor fell along with temperature, passed through a minimum at a temperature of approximately 175 K, and then began to grow. We associate this behavior with an exchange-coupled system of spins of manganese and cobalt ions Co^{3+} ($S = 2$),

Table 2. Crystallographic sites and atomic coordinates in $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ at a temperature of 100 K

	<i>X</i>	<i>Y</i>	<i>Z</i>	Occupation	<i>B</i> _{iso}
Me1 Mn(2+)	0	0	0.5	0.10 ± 0.1	24 ± 20
Me1 Co(2+)	0	0	0.5	0.90 ± 0.1	24 ± 20
Me2 Mn(2+)	0.5000	0	0	0.95 ± 0.05	−1.86 ± 1.31
Me2 Co(2+)	0.5000	0	0	0.05 ± 0.05	−1.86 ± 1.31
Me3 Mn(2+)	0 ± 0.09	0.02 ± 0.18	0.5	0.98 − 0.53	94.34 ± 44.38
Me3 Co(2+)	0 ± 0.09	0.02 ± 0.18	0.5	0.02 + 0.53	94.34 ± 44.38
Me4 Mn(3+)	0.589 ± 0.008	0.167 ± 0.006	0	0.02 + 0.24	−3.61 ± 1.23
Me4 Co(3+)	0.589 ± 0.008	0.167 ± 0.006	0	0.98 − 0.24	−3.61 ± 1.23
O1	0.1102 ± 0.0027	0.1233 ± 0.0024	0.5	1.0000	−2.17 ± 0.58
O2	0.3916 ± 0.0024	0.0671 ± 0.0018	0.5	1.0000	−3.16 ± 0.59
O3	0.3617 ± 0.0024	0.2763 ± 0.0015	0	1.0000	−4.61 ± 0.52
O4	0.1374 ± 0.0066	0.9627 ± 0.0052	0	1.0000	6.75 ± 1.81
O5	0.1498 ± 0.0036	0.3692 ± 0.0042	0	1.0000	1.98 ± 1.29
B	0.2990 ± 0.0018	0.3777 ± 0.0019	0	1.0000	−6.40 ± 0.43

Co^{2+} ($S = 3/2$), Mn^{3+} ($S = 2$), Mn^{2+} ($S = 5/2$). The temperature dependence of the inverse characteristic intensity crosses axis *x* (Fig. 5d) at a temperature of 160 K.

As the temperature rose, the magnetic resonance linewidth fell, passed through a minimum, and then began to grow. As the temperature rose, the resonant value of the magnetic field grew, passed through a maximum, and then fell slightly. This behavior of the temperature dependence of the EPR linewidth and the effective *g*-factor resembles the so-called bottleneck effect for the EPR of localized moments. In our case, we would expect the spins of manganese ions to be strongly coupled with the spins of cobalt ions through

exchange interaction. If the rate of the cobalt spin system's relaxation into the lattice were much lower than that of Mn spins during the direct relaxation of manganese ions into the lattice, the spin relaxation of the cobalt system directly into the lattice would be ineffective, and a result similar to the bottleneck effect would be observed. Similar behavior was studied by B.I. Koche-laev et al. [25].

CONCLUSIONS

The structure of ludwigite $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$ was studied at $T = 100$ K via powder neutron diffraction. Powder samples were prepared from single crystals obtained with flux method using a solvent based on bismuth trimolybdate $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, diluted with sodium carbonate Na_2CO_3 and boric acid H_3BO_3 as the boron-containing component.

Neutron diffraction studies allowed us to determine true cationic composition of the obtained ludwigite $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$. The temperature dependences of the linewidth and effective *g*-factor indicated strong exchange interaction between the spins of manganese and cobalt ions.

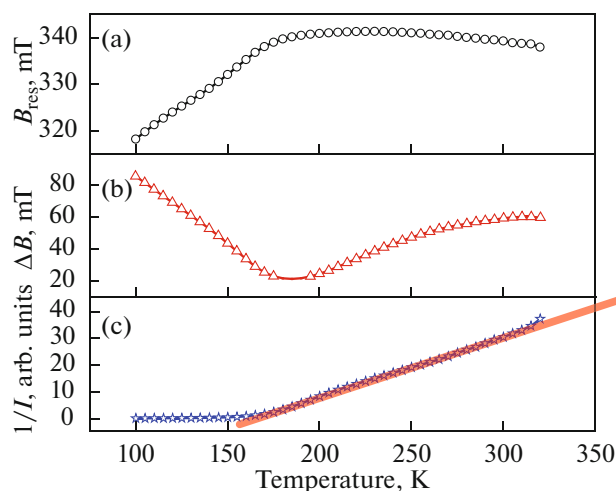


Fig. 5. Temperature dependences of (a) resonant magnetic field; (b) linewidth and (c) inverse integrated intensity of the EPR line in $\text{Mn}_{2.25}\text{Co}_{0.75}\text{BO}_5$.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

- Bordet, P. and Suard, E., *Phys. Rev. B*, 2009, vol. 79, p. 144408.
- Bluhm, K. and Müller-Buschbaum, H., *Z. Anorg. Allg. Chem.*, 1989, vol. 579, p. 111.
- Li, H.K., Wang, L., Cai, G.M., et al., *J. Alloys Compd.*, 2013, vol. 575, p. 104.
- Norrestam, R., Dahl, S., and Bovin, J.-O., *Z. Crystallogr.*, 1989, vol. 187, p. 201.
- Freitas, D.C., Continentino, M.A., Guimarães, R.B., et al., *Phys. Rev. B*, 2008, vol. 77, p. 184422.
- Attfield, J.P., Clarke, J.F., and Perkins, D.A., *J. Phys. B*, 1992, vols. 180–181, p. 581.
- Neuendorf, H. and Gunßer, W., *J. Magn. Magn. Mater.*, 1997, vol. 173, nos. 1–2, p. 117.
- Bezmaternykh, L.N., Kolesnikova, E.M., Eremin, E.V., et al., *J. Magn. Magn. Mater.*, 2014, vol. 364, p. 55.
- Bezmaternykh, L., Moshkina, E., Eremin, E., et al., *Solid State Phenom.*, 2015, vols. 233–234, p. 133.
- Freitas, D.C., Continentino, M.A., Guimarães, R.B., et al., *Phys. Rev. B*, 2009, vol. 79, no. 13, p. 134437.
- Freitas, D.C., Guimarães, R.B., Sanchez, D.R., et al., *Phys. Rev. B*, 2010, vol. 81, p. 024432.
- Medrano, C.P.C., Freitas, D.C., Sanchez, D.R., et al., *Phys. Rev. B*, 2015, vol. 91, p. 054402.
- Ivanova, N.B., Kazak, N.V., Knyazev, Y.V., et al., *J. Exp. Theor. Phys.*, 2011, vol. 113, no. 6, p. 1015.
- Ivanova, N.B., Platunov, M.S., Knyazev, Y.V., et al., *Phys. Solid State*, 2012, vol. 54, no. 11, p. 2212.
- Eremina, R.M., Moshkina, E.M., Gavrilova, T.P., et al., *Bull. Russ. Acad. Sci.: Phys.*, 2019, vol. 83, no. 7, p. 912.
- Zamkova, N.G., Zhanduna, V.S., and Ovchinnikov, S.G., *JETP Lett.*, 2023, vol. 118, no. 5, p. 321.
- Kazak, N.V., Belskaya, N.A., Moshkina, E.M., et al., *JETP Lett.*, 2021, vol. 114, no. 2, p. 92.
- Stenger, C.G., Verschoor, G.C., and Ijdo, D.J., *Mater. Res. Bull.*, 1973, vol. 8, no. 11, p. 1285.
- Bluhm, K. and Müller-Buschbaum, H., *J. Less-Common Met.*, 1989, vol. 147, no. 1, p. 133.
- Freitas, D.C., Medrano, C.P.C., Sanchez, D.R., et al., *Phys. Rev. B*, 2016, vol. 94, p. 174409.
- Vavilova, E., Vasilchikova, T., Vasiliev, A., et al., *Phys. Rev. B*, 2023, vol. 107, no. 5, p. 054411.
- Moshkina, E., Bovina, A., Molokeyev, M., et al., *CrystEngComm*, 2021, vol. 23, p. 5624.
- Lutterotti, L., *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2010, vol. 268, p. 334.
- Popov, D.V., Gavrilova, T.P., Gilmutdinov, I.F., et al., *J. Phys. Chem. Solids*, 2021, vol. 148, p. 109695.
- Kochelaev, B.I., Kan, L., Elschner, B., et al., *Phys. Rev. B*, 1994, vol. 49, no. 18, p. 13106.

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