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<sup>†</sup> In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

## High-temperature properties of $Mn_{0.75}Co_{2.25}BO_5$ compound

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Temperature-dependence measurements specific heat, thermoelectric power, conductivity, and electron paramagnetic resonance measurements were performed on  $Mn_{0.75}Co_{2.25}BO_5$  powder at temperatures above 290 K. Single crystals of  $Mn_{0.75}Co_{2.25}BO_5$  were grown by the flux method using Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>-based solvent diluted with Na<sub>2</sub>CO<sub>3</sub>. To investigate EPR and specific heat capacity, the single crystals were ground to powder. The temperature dependencies of the resistance, specific heat, Seebeck constant, and EPR spectra in the range from 290 K to 700 K were obtained. The transition from the dielectric state to the semiconductor state was detected at 348 K, consistent with the change in the fine structure of the EPR spectrum associated with S = 5/2 for the manganese ion Mn<sup>2+</sup>.

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#### 1. Introduction

Oxyborates with the ludwigite structure, represented by  $M_2MeBO_5$  (M and Me are metal ions with valences of 2+ and 3+, respectively), have unique magnetic properties due to the random distribution of magnetic ions, mixed valence, strong electronic correlations, and unusual charge ordering. These properties are attributed to the spatial structure of ludwigite, which contains four crystallographically non-equivalent positions for metal ions, each surrounded by an octahedral oxygen environment. These positions pair to form two sublattices in the shape of a three-legged ladder (3LL) [1]. Metal ions occupy four distinct sites-2a, 2b, 4g, and 4h-within the unit cell, usually designated as M1, M2, M3, and M4, respectively [2,3]. Ludwigites typically belong to the *Pbam* space group.

Several papers have been published reporting on the characteristics of the magnetic and transport properties of ludwigite in the temperature range above room temperature. Two consecutive sharp electronic transitions were observed at and 495 K in Co<sub>3</sub>BO<sub>5</sub> [4–6], which were accompanied by anomalies in the unit cell parameters [6]. The temperature dependence of the expansion coefficient was measured at 296, 403, 503, 603, and 703 K [4]. The authors observed that the thermal expansion coefficients along the *b* and *c* axes, as well as for the unit cell, show a nonmonotonic dependence on temperature, reaching a maximum around 500 K. According to the GGA + U approach, the average Co–O distances for Co1 and Co3 ions should be longer than those for Co2 and Co4 ions. The paper [6] points out that it is impossible to determine the specific spatial distribution of Co charge in the phase above 475–495 K. In addition, the Co<sub>3</sub>BO<sub>5</sub> compound showed a deviation from the phonon contribution to the specific heat at temperatures above 300 K. The best approximations of this deviation were two Gaussians centered at 526 K and 695 K, respectively. The first temperature is close to T = 500 K, at which the Co–O

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bonds in the octahedral environment of metal ions grow rapidly, indicating the presence of spin crossover [4].

In this study, we analyzed the high-temperature parameters of a new ludwigite  $Mn_{0.75}Co_{2.25}BO_5$  (Mn/Co=1/3).

#### 2. Sample preparation

Single crystals of  $Mn_{3-x}Co_xBO_5$  (x = 2.5) have been grown by flux method using Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> based solvent diluted by Na<sub>2</sub>CO<sub>3</sub>. The flux components in a ratio of Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> : 1.06B<sub>2</sub>O<sub>3</sub> : 0.7Na<sub>2</sub>O : 0.23Mn<sub>2</sub>O<sub>3</sub> : 0.23Co<sub>2</sub>O<sub>3</sub> : 1.85CoO were melted in a platinum crucible ( $V = 100 \text{ cm}^3$ ) at  $T = 1100^{\circ}$ C. The prepared flux was homogenized at this temperature for 3 hours. The saturation temperature  $T_{\text{sat}} = 970^{\circ}$ C and the growth cooling rate  $dT/dt = 3^{\circ}$ C/day have been determined at the research stage. For the growth process beginning, the flux was homogenized at  $T = 1100^{\circ}$ C again for 3 hours. After that, the temperature in the furnace was reduced rapidly with the rate of  $dT/dt = 200^{\circ}$ C/h down to  $T_{\text{start}} = 960^{\circ}$ C, and then slowly with the rate of  $dT/dt = 3^{\circ}$ C/day for 6 days. After 6 days the crucible has been extracted from the furnace and the flux has been poured out. The grown crystals with a shape of black elongated prisms were separated from the flux remainder by etching in 20% aqueous solution of nitric acid.

To investigate the EPR and specific heat properties, the grown single crystals were ground to powder.

#### 3. Results

#### 3.1. Specific heat

High temperature specific heat was measured in a temperature range of  $300 \div 520$  K without an external magnetic field using a SETARAM C80 calorimeter .

The high-temperature specific heat measurement is shown in Fig. 1. The temperature at which the specific heat capacity reaches its maximum coincides with the temperature of the spin crossover for  $Co_3BO_5$  [4].



Figure 1. Temperature dependence of the specific heat of  $Mn_{0.75}Co_{2.25}BO_5$ .

#### 3.2. Seebeck coefficient

The Seebeck effect was measured on a homemade device in the temperature range of  $300 \div 573 \text{ K}$  for both heating and cooling of the sample with a temperature gradient of  $\Delta T = 30 \text{ K}$ . Resistance was also measured at the same temperatures using the same equipment.

The temperature dependence of the Seebeck coefficient is shown in Fig. 2. The Seebeck coefficient value was increased with temperature, reaching a maximum of 0.217 mV/K at 358 K, and then gradually was decreased to 0.128 mV/K at 294 K (Fig. 2). There is a slight difference between the values when the sample is heated and when it is cooled. There are at least two possible reasons for the abrupt change in the Seebeck coefficient around 358 K. The first reason may be related to a change in spin state. In this case, one would expect the Seebeck coefficient to change with the application of a magnetic field [7]. However, in our experiments in which the Seebeck coefficient was measured in a magnetic field, the value of the Seebeck constant was changed little. The second reason, most likely in our case, is a structural transition as in the  $Co_3BO_5$  ludwigite [4]. As discussed below, the EPR spectrum also undergoes a similar change at this temperature. It should be noted that the change at 358 K is also observed in the temperature dependence of the specific heat capacity (see Fig. 1). At this temperature, the temperature dependence of resistance also was changed, and it demonstrates changes its dielectric properties to semiconducting ones (see inset of Fig. 2).



Figure 2. Temperature dependence of Seebeck coefficient and resistance (inset). Black line are rescaled high-temperature specific heat of  $Mn_{0.75}Co_{2.25}BO_5$ . The temperature gradient between the two surfaces of the sample was 30 K.

#### 3.3. Conductivity

The temperature dependence of conductivity is shown in Fig. 3. The band gap was calculated from the approximate parameters using the formula for the model of small polaron jumps

$$\sigma \propto \frac{A}{T} \exp\left(-\frac{\Delta E}{k_{\rm B}T}\right),$$
(1)

where A is a constant,  $\Delta E$  is the band gap, and  $k_{\rm B}$  is Boltzmann's constant. The band gap value is 0.56(2) eV. A linear approximation of the 1/T dependence of  $\ln(T/\rho)$  is shown in Fig. 3.

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Figure 3. Temperature dependence of the resistivity of  $Mn_{0.75}Co_{2.25}BO_5$  and linear approximation (red line).

### 3.4. EPR

High-temperature EPR spectra were measured on a Varian E12 spectrometer in the X-band (9.36 GHz) in the temperature range  $294 \div 395 \text{ K}$ .

Several lines are observed in the magnetic resonance spectrum (Fig. 4).



Figure 4. EPR spectra of Mn<sub>0.75</sub>Co<sub>2.25</sub>BO<sub>5</sub>. Experimental data (scattering) and approximate (line).

Obtained high-temperature EPR lines were approximated with a formula

$$\frac{dP}{dH} = \frac{d}{dH} \left( \frac{\Delta H + \alpha (H - H_{\rm res})}{(H - H_{\rm res})^2 + \Delta H^2} + \frac{\Delta H + \alpha (H + H_{\rm res})}{(H + H_{\rm res})^2 + \Delta H^2} \right),\tag{2}$$

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Figure 5. Temperature dependencies of ESR linewidths for Mn<sub>0.75</sub>Co<sub>2.25</sub>BO<sub>5</sub>.



Figure 6. Temperature dependencies of ESR line g-factors for Mn<sub>0.75</sub>Co<sub>2.25</sub>BO<sub>5</sub>.

where  $H_{\rm res}$  is the position of the resonance line,  $\Delta H$  is the linewidth, and  $\alpha$  is the asymmetry parameter [8]. The experiment data and the approximation of the EPR lines are shown in Fig. 4. Six EPR lines were used to approximation the specta. The approximation parameters are linewidth (Fig. 5), g-factor (Fig. 6), and intensity (Fig. 7) were obtained. As can be seen from these figures, the linewidth of line 6 is several times larger than the linewidths of the remaining lines. We assume that line 6 is observed from regions where Mn ions were connected exchange interactions, whereas lines 1-5 refer to fine structure ESR lines. It must be noted, that the width of the skin layer is much bigger, than the size of the compound powder particles at all studied temperatures, therefore, the effects of the skin layer on the EPR measurements' results are negligible.



Figure 7. Temperature dependencies of ESR intensity for  $Mn_{0.75}Co_{2.25}BO_5$ .

The EPR parameters changed in all temperature regions, but the most significant change was observed at about  $T \approx 340$  K.

The obtained resonant field values were analyzed to obtain of the crystal field parameters D and E for Mn<sup>2+</sup>. Using the spin Hamiltonian [9]:

$$H = g_{\parallel} \mu_{\rm B} H_z S_z + g_{\perp} \mu_{\rm B} (H_x S_x + H_y S_y) + DS_z^2 + E(S_x^2 - S_y^2), \tag{3}$$

 $D = 0.062 \,\mathrm{K}$  and  $E = 0.02 \,\mathrm{K}$  with  $g_{\parallel} = g_{\perp} = 2$  were obtained at a temperature ~ 290 K. As the resonance position changes with temperature growth, the crystal field parameters also change. At temperatures ~ 390 K the parameters are  $D = 0.064 \,\mathrm{K}$  and  $E = 0.02 \,\mathrm{K}$ . These values are close to those obtained in studies for Mn ions. According to [10] parameter Dhas a value of  $0.0553 \,\mathrm{cm}^{-1}$  at 300 K for  $\mathrm{Mn}^{2+}$  for  $(\mathrm{MnO}_6)^{10-}$  octahedral clusters in MnCO<sub>3</sub>. However, according to [11] the crystal field parameter of  $\mathrm{Zn}_{1-x}\mathrm{Mn}_x$  for the same Mn ions is  $D = 236.2 \cdot 10^{-4} \,\mathrm{cm}^{-1}$  at the same temperature.

#### 4. Conclusion

The single crystals of  $Mn_{0.75}Co_{2.25}BO_5$  ludwigite were synthesized by the flux method. The sample was studied by means specific heat, thermoelectricity, and EPR methods at temperatures above 290 K. Specific heat curves are similar to the curves for Co<sub>3</sub>BO<sub>5</sub>, indicating possible presence of the spin-crossover in the sample. For Mn ions, the crystal-field parameters were obtained according to EPR measurements and are equal to D = 0.062 K, E = 0.02 K at  $T \approx 290$  K and D = 0.064 K, E = 0.02 K at  $T \approx 390$  K. The Seebeck-coefficient behavior reflects the specific-heat features at the same temperature range. The value of the Seebeck coefficient displays a sharp increase from ~ 0 mV/K to ~ 0.275 mV/K between 300 and 350 K and then drops gradually down to ~0.15 mV/K at 550 K. The calculated band gap of the compound is  $\Delta E = 0.56(2)$  eV. The EPR spectra exhibit the presence of fine structure for Mn<sup>2+</sup> in the range of  $T = 295 \div 395$  K.

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