

Investigation of the Magnetic Properties of Ludwigites

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Abstract—Single crystals of Cu_2AlBO_5 and Cu_2GaBO_5 copper oxyborates are synthesized via solution–melt crystallization and subjected to X-ray diffraction analysis. Parameters of the crystal lattice and the positions of atoms in a unit cell are determined. Copper ions form a structural chain along axis a in Cu_2AlBO_5 and Cu_2GaBO_5 . Temperature dependences of the magnetic susceptibility are measured. The obtained curves feature kinks at $T = 2.4$ (Cu_2AlBO_5) and 4.1 K (Cu_2GaBO_5).

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INTRODUCTION

Different quantum effects become apparent in low-dimensional magnetic compounds at relatively high temperatures. When two magnetic subsystems are present, the pattern of exchange interactions and charge ordering becomes considerably more complex. The magnetic structure of such objects can therefore manifest itself in the form of spin ladders, ribbons, or zigzag walls. Oxyborates with ludwigite structure are a fine example of such systems. Their general formula is $\text{M1}_2^{2+}\text{M2}^{3+}\text{BO}_5$, where M1 and M2 are ions of the iron group. The results from detailed studies of the magnetic properties of $\text{Co}_{2-x}\text{Fe}_x\text{BO}_5$ single crystals with low iron concentrations were presented in [1]. It was shown that the ordering temperature grows considerably at iron concentration $x = 0.10$, but the magnetic behavior and direction of the easy magnetization axis typical of Co_3BO_5 are retained. Ludwigites feature a fairly complex pattern of exchange interactions between heterovalent ions. Data on the magnetic properties of ludwigites with one nonmagnetic metal ion would be of use in analyzing the dynamics of variation in magnetic properties.

EXPERIMENTAL

Single crystals of $\text{Cu}_2^{2+}\text{Me}^{3+}\text{BO}_5$ ludwigites, where Me is a trivalent metal (nonmagnetic Al or Ga), were studied in this work. Cu_2GaBO_5 and Cu_2AlBO_5 single crystals were synthesized via solution–melt crystallization. The melt for Cu_2GaBO_5 was prepared through

the successive melting of the solution–melt system components at $T_{\text{prep}} = 1100^\circ\text{C}$ in a platinum crucible ($V = 100 \text{ cm}^3$). Borax $\text{Na}_2\text{B}_4\text{O}_7$ (in the form of glass prepared beforehand at $T = 1100^\circ\text{C}$ from sodium tetraborate decahydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ powder) was melted first; portions of mixed B_2O_3 , Bi_2O_3 , and MoO_3 oxide powders were then added; Ga_2O_3 was introduced portionwise; and CuO powder was added last. The prepared solution–melt was homogenized over 4 h at $T_{\text{hom}} = 1100^\circ\text{C}$. At this stage, a platinum crystal support in the form of a rod was introduced into the crucible. The furnace temperature was then reduced rapidly ($100^\circ\text{C}/\text{h}$) to $T = (T_{\text{sat}} - 10^\circ\text{C}) = 865^\circ\text{C}$. Further cooling proceeded slowly at a rate of $2^\circ\text{C}/\text{d}$. The duration of growth was 6 days. When the process was complete, the crystal support was removed from the solution–melt, and the resulting crystals (dark green prisms up to $15 \times 4 \times 3 \text{ mm}$ in size; see Fig. 1a) were separated from the support and cleansed of solution–melt residue by etching in an aqueous solution of HNO_3 (20%). Cu_2AlBO_5 crystals were grown in a similar way and had the shape of elongated dark green prisms up to $1 \times 1 \times 10 \text{ mm}^3$ in size (Fig. 1b).

X-ray diffraction (XRD) analysis of these crystals was performed using a RigakuSmartLab diffractometer with a tube containing a Cu anode in the discrete mode with a pitch of 0.04° . XRD data confirmed that all of our Cu_2AlBO_5 and Cu_2GaBO_5 samples had ludwigite structure (space group $P2_1/c$). The XRD patterns for Cu_2AlBO_5 and Cu_2GaBO_5 are shown in Fig. 2. The lattice parameters of Cu_2AlBO_5 and

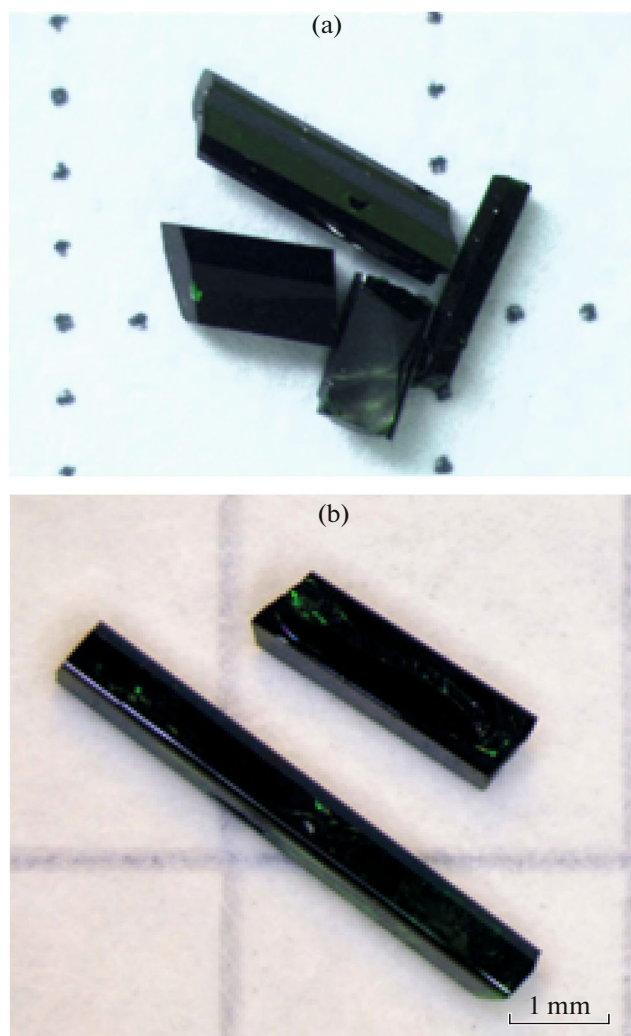


Fig. 1. Single crystals of (a) Cu_2GaBO_5 and (b) Cu_2AlBO_5 with ludwigite structure.

Cu_2GaBO_5 are listed in Table 1. Data were analyzed according to the standard Rietveld technique [2]. It was found that the atomic positions virtually coincided in the studied single crystals. A diagram of the Cu_2GaBO_5 oxyborate with ludwigite structure in plane (ac) is presented in Fig. 3. It can be seen that chains of copper ions form along axis a . The temperature dependences of magnetization were measured in

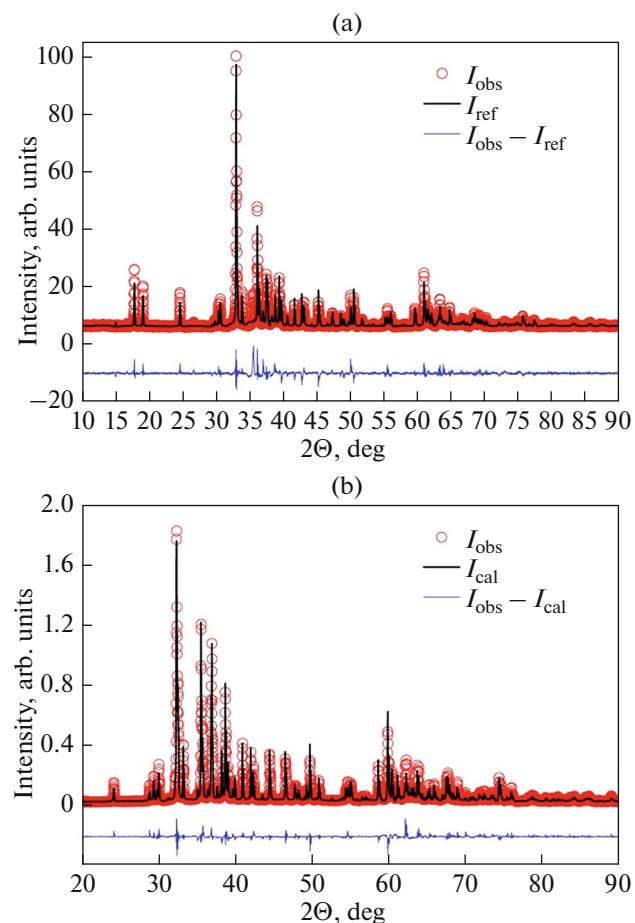


Fig. 2. X-ray diffraction patterns of (a) Cu_2AlBO_5 and (b) Cu_2GaBO_5 with ludwigite structure at room temperature.

magnetic fields applied parallel and perpendicular to axis a with a PPMS-9 vibration magnetometer in the 2–300 K range. Figure 4 shows the temperature dependences of the magnetic susceptibility of Cu_2AlBO_5 and Cu_2GaBO_5 , measured in magnetic fields applied parallel and perpendicular to axis a in two regions: FC (cooling in the magnetic field) and ZFC (cooling in a zero field). The obtained curves feature kinks at $T_N = 2.4$ (Cu_2AlBO_5) and 4.1 K (Cu_2GaBO_5). It should be noted that although the unit cell of the Cu_2AlBO_5 single crystal is smaller than that of

Table 1. Lattice parameters of Cu_2AlBO_5 and Cu_2GaBO_5 , where α , β , and γ are the angles between axes b and c , a and c , and a and b , respectively

	a , Å	b , Å	c , Å	α	β	γ
Cu_2GaBO_5	3.11379	11.92720	9.47700	90.00	97.86	90.00
Cu_2AlBO_5	3.06606	11.76790	9.36590	90.00	97.74	90.00

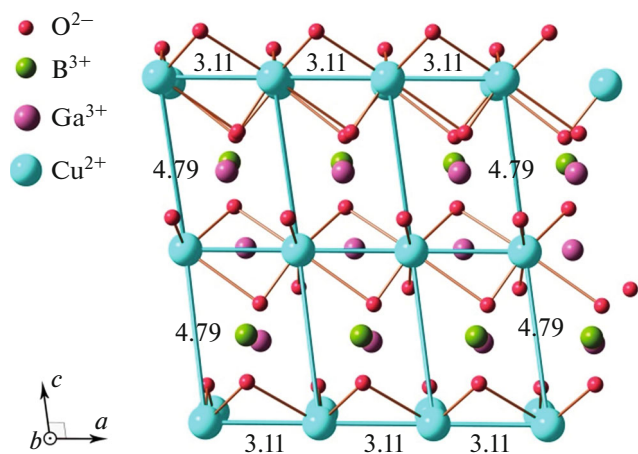


Fig. 3. Structure of the Cu_2GaBO_5 oxyborate with ludwigite structure in plane (ac).

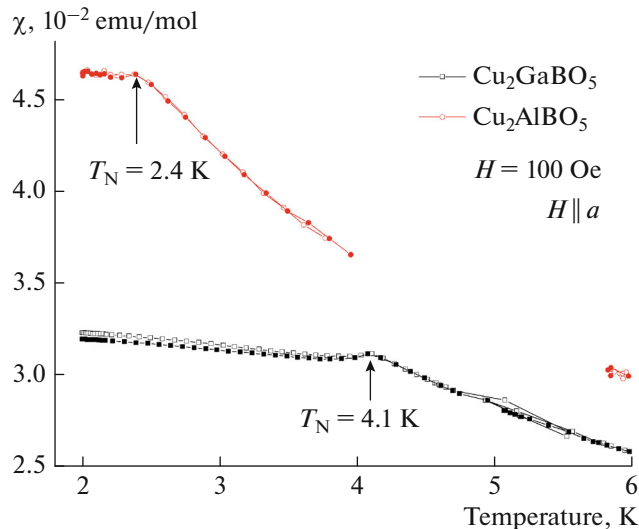


Fig. 4. Temperature dependences of the magnetic susceptibility of Cu_2AlBO_5 (circles) and Cu_2GaBO_5 (squares) oxyborates with ludwigite structure in the FC (white symbols) and ZFC (colored symbols) modes. The partially filled dots represent the data for Cu_2AlBO_5 in a magnetic field perpendicular to axis a .

Cu_2GaBO_5 , the ordering temperature of spins of copper ions in Cu_2AlBO_5 is lower. This is attributable to

the nature of the indirect isotropic exchange interaction (virtual charge transport through oxygen ligands) between spins of copper ions in a chain. The temperature dependences of the molar heat capacity of Cu_2AlBO_5 and Cu_2GaBO_5 also feature kinks at $T_N = 2.4$ and 4.1 K. It appears that the spin glass ordering transition occurs in Cu_2AlBO_5 and Cu_2GaBO_5 single crystals at $T_N = 2.4$ and 4.1 K, respectively. The complex nature of exchange interactions is corroborated by the results from estimating superexchange interactions with the indirect exchange model developed in [3–5]. The structure of ludwigite with space group $P2_1/c$ is characterized in the indirect exchange theory by 16 possible integrals of the indirect exchange coupling of Cu–O–Cu interactions. The formulas for calculating these exchange interaction integrals and their values were determined in [6] by assuming that copper ions can occupy any of the four metallic crystallographic sites. One site in Cu_2AlBO_5 and Cu_2GaBO_5 is occupied by a nonmagnetic ion, and six exchange interaction integrals remain. One of these is nearly zero, and the other exchange interactions form exchange couplings along axis a . Their maximum value is $J = 7.9$ K.

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