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MAGNETISM AND FERROELECTRICITY

Low-Field Magnetization of Ludwigites $Co_3O_2BO_3$ and $Co_{3-x}Fe_xO_2BO_3$ ($x \approx 0.14$)

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Abstract—Ludwigite single crystals of compositions $Co_3O_2BO_3$ and $Co_{3-x}Fe_xO_2BO_3$ ($x \approx 0.14$) have been synthesized. The crystal structure is investigated at room temperature, and the magnetization is studied in the temperature range $T = 4.2$–100 K in magnetic fields of up to 600 Oe. The orthorhombic symmetry is revealed, and the unit cell parameters are determined. A number of features are established for the temperature dependence of the magnetization. In unsubstituted $Co_3O_2BO_3$, two magnetic transitions are found at $T_{C1} = 43$ K and $T_{C2} = 15$ K. At temperatures below 40 K, spin-glass state is revealed. Substitution of iron ions for cobalt ions leads to a noticeable shift in the magnetic transitions toward the high-temperature range: $T_{C1} = 83$ K and $T_{C2} = 74$ K. A ferromagnetic ordering of the *P* type is found in the $Co_{3-x}Fe_xO_2BO_3$ ($x \approx 0.14$) compound.

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1. INTRODUCTION

Oxyborates with the general formula $M_2^{2+}M'^{3+}O_2BO_3$ (M^{2+} = Mg, Fe, Co, Ni, Cu; M'^{3+} = Co, Cr, V, Fe, Mn) belong to the ludwigite family. The unit cell contains four formula units. The metal ions are situated in an oxygen octahedral environment. The edge-sharing octahedra form an ensemble of zigzag walls. Boron is located at the center of the BO_3^{-3} trigonal group joining the walls. Divalent and trivalent ions occupy four nonequivalent positions (Fig. 1). The mixed valence, random distribution of magnetic ions, and strong electron correlations make it possible to observe a variety of magnetic states, charge ordering, structural and magnetic transitions.

Heterometallic compounds with $M \neq M'$, for example, $Ni_2CrO_2BO_3$ [1], $Ni_2VO_2BO_3$ [1], $Ni_2FeO_2BO_3$ [2], $Cu_2FeO_2BO_3$ [3], $Mg_2FeO_2BO_3$ [4], and $Li_{0.93}V_{2.07}O_2BO_3$ [5], have been most extensively investigated, whereas studies of homometallic ludwigites have been predominantly focused on the $Fe_3O_2BO_3$ compound [6–8]. The Mössbauer and magnetization studies of the $Fe_3O_2BO_3$ ludwigite have demonstrated that part of the iron ions are antiferromagnetically ordered at $T = 114$ K. Below $T \approx 75$ K, the entire sample becomes magnetically ordered and exhibits a weak ferromagnetism. At a temperature $T = 50$ K, the transition to a three-dimensional antiferromagnetic state occurs and charge ordering is observed for the divalent and trivalent iron ions. Above this temperature, the thermally activated hops of electrons result in a uniform charge distribution in the *ab* plane. At temperatures $T >$ 150 K, there arise electron hops along the *c* axis, which leads to a fast charge delocalization.

The works devoted to investigation of cobalt ludwigites are limited in number. The first studies of the crystal structure of $Co_3O_2BO_3$ and substituted $Co_{2.1}Al_{0.9}O_2BO_3$ were carried out in [9] and [10], respectively. Investigation of the magnetic susceptibility of the $Co_3O_2BO_3$ compound demonstrated that, at $T \approx 40$ K, the material undergoes a transition to a magnetically ordered state. Our preliminary studies of the magnetic and electrical properties of the $Co_3O_2BO_3$ compound revealed a nontrivial behavior of the magnetization and the electrical resistance [11]. The present paper reports on a more detailed investigation of the magnetic properties of the homometallic cobalt oxyborate $Co_3O_2BO_3$ and the crystal structure and magnetic properties of partially substituted ludwigite $Co_{3-x}Fe_xO_2BO_3$ ($x \approx 0.14$).

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Single crystals of the $Co_3O_2BO_3$ and $Co_{3-x}Fe_xO_2BO_3$ ($x \approx 0.14$) compounds were grown through solution–melt crystallization in the Co_3O_4–

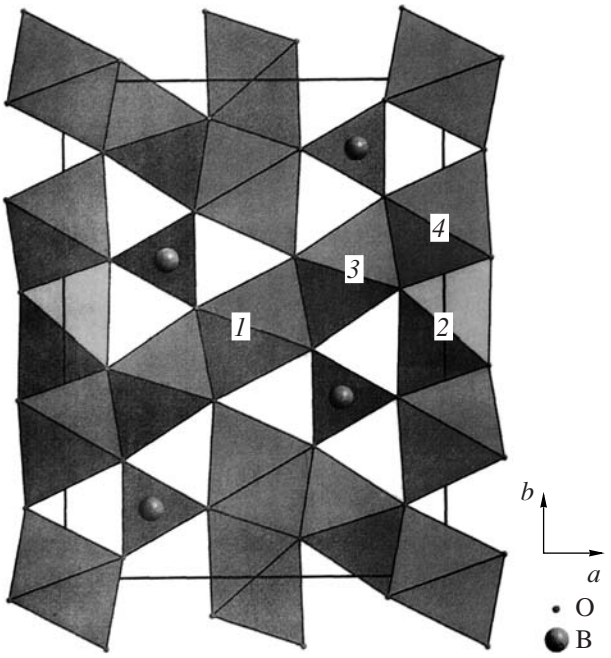

Fig. 1. Structure of ludwigite in the *ab* plane. Numerals *1–4* indicate different crystallographic positions occupied by the divalent and trivalent metal ions. Trigonal BO_3 groups are also shown.

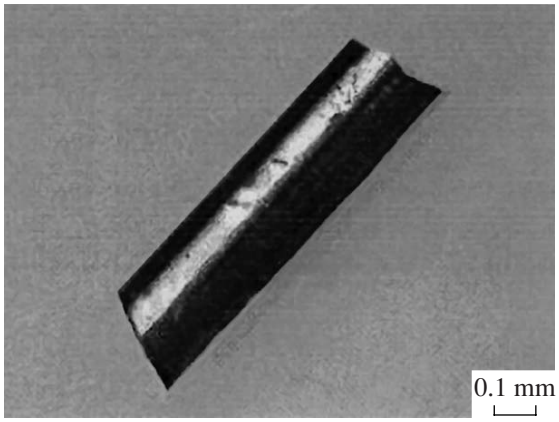

Fig. 2. A $Co_3O_2BO_3$ single crystal.

Fe_2O_3–B_2O_3–PbO–PbF_2 system with intermediate cooling from 1000 to 880°C. The oxide components were taken in the ratio $Fe_2O_3/(Fe_2O_3 + Co_3O_4) = 5\%$, which resulted in a substitution ratio $x \approx 0.14$. The prepared samples crystallized in the form of needles $0.2 \times 0.2 \times 4.0$ mm in size with a shiny surface (Fig. 2). The crystal structure was investigated at room temperature on a SMART APEX II automated diffractometer equipped with a CCD detector (MoK_α radiation, $\lambda = 0.7107$ Å, $2\theta = 5.4°$–$58.0°$). The temperature dependences of the magnetization were measured on a SQUID magnetometer in the temperature range $T = 4.2$–100 K in magnetic fields up to 600 Oe.

3. RESULTS

X-ray diffraction measurements revealed the orthorhombic structure (space group P_{bam}) for both compounds. We determined the unit cell parameters that are presented in the table together with the data from other sources. One can see that the partial substitution of iron ions with larger radius for cobalt ions leads to an increase in the lattice parameters and the unit cell volume, which agrees with the data for the $Fe_3O_2BO_3$ ludwigite [12].

The measurements showed a considerable anisotropy of the magnetization. With a sample magnetized along the *c* axis (i.e., along the needle), the magnetic moment is one order of magnitude smaller than that in the *ab* plane. The present work reports on the results of magnetic measurements in the *ab* plane.

Figure 3 presents the temperature dependences of the magnetization of the $Co_3O_2BO_3$ compound in fields of 200 and 600 Oe. At $T_f \approx 45$ K, the magnetization sharply increases and reaches a value of 0.6 μ_B per formula unit ($H = 600$ Oe). Below T_f, there is a difference between the zero-field cooling (ZFC) curves $M(T)$ and the field-cooling (FC) curves $M(T)$. This magnetization behavior is characteristic of the spin glass state. In the temperature range $T < 30$ K, the FC curve indicates an increase in the magnetic moment. The temperatures of magnetic transitions determined from the temperatures dependence of the derivative $\partial M/\partial T$ yield the values $T_{C1} = 43.5 \pm 0.5$ K and $T_{C2} = 15.5 \pm 0.5$ K. The results obtained are in good agreement with data on the dynamic magnetic susceptibility, according to which the $Co_3O_2BO_3$ compound undergoes a magnetic transition at a temperature of $T_C \approx 40$ K [12]. One can see that, as the applied magnetic field increases, the maximum at T_{C2} shifts toward the low-temperature range,

Unit cell parameters of ludwigites ($T = 296$ K)

Ludwigite	*a*, Å	*b*, Å	*c*, Å	*V*, Å	References
$Co_3O_2BO_3$	9.302	11.957	2.972	330.58	
$Co_3O_2BO_3$	9.275	12.146	3.026	340.95	[9]
$Co_{2.86}Fe_{0.14}O_2BO_3$	9.440	12.340	3.057	356.11	
$Fe_3O_2BO_3$	9.453	12.296	3.072	357.07	[12]

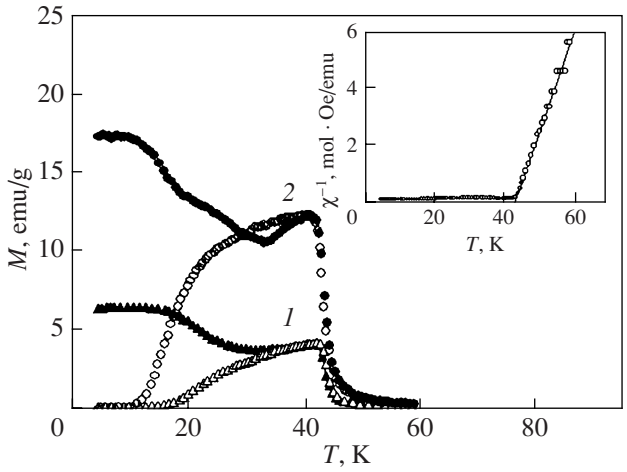

Fig. 3. Temperature dependences of the magnetization of the $Co_3O_2BO_3$ ludwigite in magnetic fields of (*1*) 200 and (*2*) 600 Oe. Open and closed symbols correspond to zero-field cooling (ZFC) and field-cooling (FC) with a magnetic field strength H, respectively. The inset shows the temperature dependence of the inverse magnetic susceptibility at $H = 600$ Oe.

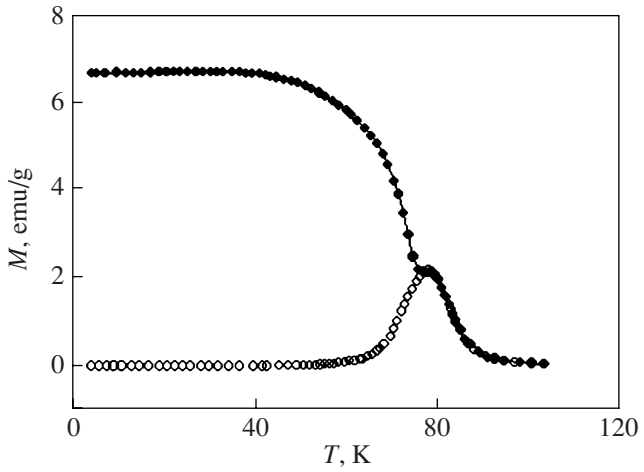

Fig. 4. Temperature dependence of the magnetization of the $Co_{3-x}Fe_xO_2BO_3$ ludwigite with $x \approx 0.14$ at the magnetic field strength $H = 200$ Oe. Open and closed symbols correspond to zero-field cooling (ZFC) and field-cooling (FC) with a magnetic field strength H, respectively.

while the maximum at T_{C1} becomes more pronounced and does not change its position. The inset to Fig. 3 shows the inverse magnetic susceptibility as a function of the temperature in the paramagnetic range. The linear behavior of the curve $\chi^{-1}(T)$ in the temperature range $T = 45$–60 K is in agreement with the Curie–Weiss law. The processing of the experimental data yielded the following values of the effective magnetic moment and the paramagnetic Curie temperature: $\mu_{eff} = 4.83\mu_B$ and $\Theta = 42.6$ K. The positive value of Θ indicates the ferromagnetic interaction between the cobalt ions. It should be noted that, for the $Fe_3O_2BO_3$ compound, the paramagnetic Curie temperature ($\Theta = -485$ K) is one order of magnitude higher than that for the studied $Co_3O_2BO_3$ sample and has a negative value, which indicates a strong antiferromagnetic interaction between the iron ions [13]. It is interesting that, for the $CO_3O_2BO_3$ compound, the paramagnetic Curie temperature Θ is very close to the experimentally observed temperature T_C, while the paramagnetic Curie temperature for the $Fe_3O_2BO_3$ compound is considerably higher than the experimentally obtained temperature $T_C = 70$ K. Based on the aforementioned observations, Mir et al. [13] drew the conclusion that this system has a low dimension. It is interesting to compare the experimental value of the effective magnetic moment with the theoretical value calculated per formula unit $Co_3O_2BO_3$. The value of $\mu_{eff} = 4.83\mu_B$ is substantially less than the expected value of $7.35\mu_B$ (considering only the spin component of the magnetic moment) but is very close to the value of $4.9\mu_B$ for the Co^{3+} ion.

Figure 4 shows the temperature dependences of the magnetization for the substituted ludwigite $Co_{3-x}Fe_xO_2BO_3$ ($x \approx 0.14$) upon zero-field cooling and field-cooling at 200 Oe. The magnetization behavior is seen to differ substantially from that of the $Co_3O_2BO_3$ compound. There are two magnetic transitions in the temperature range $T = 70$–85 K. With decreasing temperature, the magnetization is growing gradually to reach a broad maximum near the temperature $T = 30$ K. This specific feature in the curve $M(T)$ is characteristic of the *P*-type ferromagnetic ordering, which was observed earlier in studying the $Fe_{1.91}V_{0.09}BO_4$ varvicite [14]. The temperatures of the magnetic transitions are $T_{C1} = 83.0 \pm 0.5$ K and $T_{C2} = 74.0 \pm 0.5$ K. It is seen from Fig. 4 that the magnetization depends strongly on the prehistory of the sample. At a temperature $T \approx 80$ K, the ZFC curve has a maximum, after which the magnetization drops sharply, and at temperatures $T < 55$ K, its value is less than that in the paramagnetic range. When part of the cobalt ions are substituted for by iron ions, the magnetic moment at $T = 4.2$ K increases by 6%.

4. DISCUSSION OF THE RESULTS

Investigations of iron-containing ludwigites of the composition $M_2^{2+}FeO_2BO_3$ (M^{2+} = Mg, Cu, Ni, Fe) have revealed the following general feature in the magnetic behavior [3, 15–17]. With decreasing temperature, sequential ordering takes place in the two magnetic sublattices: the sublattice of Fe^{3+} ions at T_{N1} and the sublattice of M^{2+} ions at T_{N2}. This hierarchy of magnetic interactions is associated with the Fe^{3+} ions predominantly occupying two crystallographic positions, thus creating a triad Fe(3)–Fe(2)–Fe(3) inside which the interatomic distance is less than 3 Å. This distribution can cause the direct exchange and strong correlation in the sublattice of iron ions. Up to temperatures

T = 10–20 K, two sublattices are not coupled and the system is in the spin glass state.

For the initial $Co_3O_2BO_3$ compound, X-ray diffraction revealed a considerable amount of Co^{3+} cobalt ions in the $M(3)$ and $M(2)$ positions [9]. One can assume that, just like in the case of iron-based ludwigites, the magnetic structure of the $Co_3O_2BO_3$ compound contains two sublattices, one of which is a chain of three Co^{3+} ions expanding along the c axis. Possibly, the magnetic transition at $T \approx 43$ K is associated with ordering of this sublattice.

The partial substitution of cobalt ions with iron ions with a greater magnetic moment leads to the enhanced magnetization at low temperatures. The magnetic transitions shift toward the high-temperature range. The complicated behavior of the $M(T)$ dependence at low temperatures can be associated with the existence of the nonequivalent magnetic sublattices that have different absolute values of magnetization and are characterized by different temperature dependences.

Based on the low-field magnetization data obtained in the present work, it is difficult to draw an unambiguous conclusion regarding the attribution of the magnetic transitions to the ordering of a particular sublattice. In the magnetic fields up to 600 Oe, there is, possibly, an effect of domains, which has ignored in the analysis of the experimental data. Nevertheless, the results presented provide important qualitative information about the magnetic properties of ludwigites and pave the way for further research.

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