

ORDER, DISORDER, AND PHASE TRANSITION
IN CONDENSED SYSTEM

Crystal Structure and Magnetic Anisotropy
of Ludwigite $\text{Co}_2\text{FeO}_2\text{BO}_3$

N. B. Ivanova^{a,b}, N. V. Kazak^{c,*}, Yu. V. Knyazev^a, D. A. Velikanov^{a,c}, L. N. Bezmaternykh^c,
S. G. Ovchinnikov^{a,c,d}, A. D. Vasiliev^{a,c}, M. S. Platunov^{c,d}, J. Bartolomé^e, and G. S. Patrin^{a,c}

^aSiberian Federal University, pr. Svobodnyi 79, Krasnoyarsk, 660074 Russia

^bKrasnoyarsk State Agrarian University, Krasnoyarsk, 660200 Russia

^cKirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia

*E-mail: nat@iph.krasn.ru

^dSiberian Aerospace Academy, Krasnoyarsk, 660123 Russia

^eInstituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza and Departamento de Física de la Materia Condensada, Zaragoza, 50009 Spain

Received December 16, 2010

Abstract— $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ single crystals with a ludwigite structure are fabricated, and their crystal structure and magnetic properties are studied in detail. Substituted ludwigite $\text{Co}_2\text{FeO}_2\text{BO}_3$ undergoes two-stage magnetic ordering at the temperatures characteristic of $\text{Fe}_3\text{O}_2\text{BO}_3$ ($T_{N1} \approx 110$ K, $T_{N2} \approx 70$ K) rather than $\text{Co}_3\text{O}_2\text{BO}_3$ ($T_N = 42$ K). This effect is explained in terms of preferred occupation of nonequivalent crystallographic positions by iron, which was detected by X-ray diffraction. Both materials exhibit a pronounced uniaxial magnetic anisotropy. Crystallographic direction b is an easy magnetization axis. Upon iron substitution, the cobalt ludwigite acquires a very high magnetic hardness.

DOI: 10.1134/S1063776111140172

1. INTRODUCTION

The unusual properties of the oxyborates of transition metals with a ludwigite structure have recently attracted particular attention [1–5]. On the whole, the class of oxyborates is an attractive subject of inquiry due to the variety of their crystal structures, which include low-dimensional elements in the form of zigzag walls in ludwigites [6] or ribbons in pyroborates [7] and warwickites [8]. The presence of low-dimensional substructures makes various positions of transition ions nonequivalent. These positions in oxyborates can be occupied by ions of different valences. As a result, the internal structure of oxyborates is very diverse, which determines their rich physical properties.

In this work, we concentrate on studying oxyborates with a ludwigite structure. It is known that metal ions in these materials can occupy four nonequivalent positions and show a pronounced preference depending on the valence. The crystal structure of ludwigite is schematically shown in Fig. 1. Numerals 1–4 indicate the nonequivalent crystallographic positions of a metallic ion. The number of positions 3 and 4 is twice as large as that of positions 1 and 2. Every metallic ion is inside an oxygen octahedron, and the distortions of octahedra are different depending on the position. The metal–oxygen distances are also shown in Fig. 1 for various directions for the nonequivalent positions. Ions on positions 2 and 4 form first-type 4–2–4 triads (as will be shown below, they are most important for a

magnetic order). Ions on positions 1 and 3 form second-type 3–1–3 triads. The zigzag walls formed by these triads are located along crystallographic direction c .

Only two homometallic ludwigites are known, namely, $\text{Fe}_3\text{O}_2\text{BO}_3$ [3–5] and $\text{Co}_3\text{O}_2\text{BO}_3$ [1, 3]. Ludwigites have an orthorhombic structure and space group $Pbam$. Mössbauer spectroscopy [9, 10] and X-ray diffraction [3] data indicate that positions 4 in ludwigites are occupied by trivalent ions and that the other positions are occupied by divalent ions. (This fact is thought to be reliable for $\text{Fe}_3\text{O}_2\text{BO}_3$, where the iron ion valence was determined from Mössbauer data and is thought to be questionable for $\text{Co}_3\text{O}_2\text{BO}_3$, where the ion valences were determined from the valence bond lengths [3]. The point is that the possible valence bond lengths for di- and trivalent cobalt in various compounds have a wide overlapping region.) Mixed iron–cobalt ludwigites $\text{Co}_{3-x}\text{Fe}_x\text{O}_2\text{BO}_3$ are being extensively studied as well [1, 11, 12]. Great interest in these materials is mainly caused by the following three factors.

(1) The physical behavior of the first parent compound ($\text{Fe}_3\text{O}_2\text{BO}_3$) is full of substance. When the temperature decreases below $T = 283$ K, this material undergoes a smooth structural dimerization transition, which manifests itself in a change in the bond lengths in triad Fe(4)–Fe(2)–Fe(4) so that the central ion occupying position 2 shifts alternately toward one

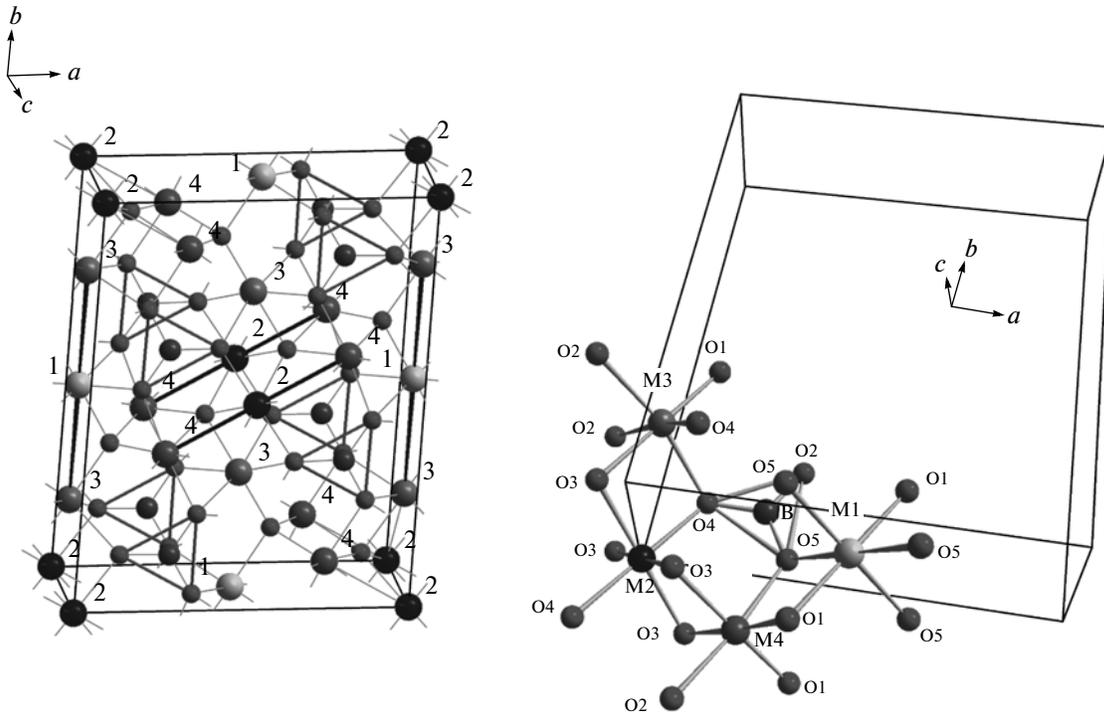


Fig. 1. (on the left) Crystal structure of ludwigite: (large circles) transition cobalt or iron ions, (medium circles) boron ions, and (small circles) oxygen ions. Numerals indicate the nonequivalent positions of transition ions. Boron and oxygen ions form triangular BO_3 groups. (on the right) Coordination of metallic M ions in the nonequivalent crystallographic positions.

or the other neighbor when passing from one to another row. The magnetic ordering in $\text{Fe}_3\text{O}_2\text{BO}_3$ proceeds in two stages. As follows from Mössbauer spectroscopy [9, 10] and heat capacity [3] data, the first phase transition occurs near $T_{N1} = 110$ K. Neutron scattering data [4] demonstrate that the magnetic moments of the ions in first-type triads 4–2–4 undergo ferromagnetic ordering at this temperature: these moments are ordered along the crystallographic b axis. The magnetic moments of the neighboring rows formed by triads 4–2–4 are directed antiferromagnetically with respect to each other. Thus, the magnetic moment in the b direction in $\text{Fe}_3\text{O}_2\text{BO}_3$ is fully compensated. At $T_{N2} = 70$ K, the magnetic moments of second-type 3–1–3 triads are ordered: ordering takes place along the a axis, the ordering inside the triads is antiferromagnetic, and the magnetic moments of the ions are incompletely compensated. These triads are coupled ferromagnetically. Thus, as follows from the neutron scattering data, $\text{Fe}_3\text{O}_2\text{BO}_3$ has two magnetic subsystems, which are ordered mutually perpendicularly at different temperatures.

(2) Unexpectedly, the properties of the related ludwigites $\text{Fe}_3\text{O}_2\text{BO}_3$ and $\text{Co}_3\text{O}_2\text{BO}_3$ are substantially different. $\text{Co}_3\text{O}_2\text{BO}_3$ does not undergo a structural transition when the temperature changes [3]. At first glance, the magnetic ordering of this material seems to be much simpler: it is likely to have a ferrimagnetic

character, occurs in one stage [3], and has an ordering temperature of 42 K.

(3) There exist some conflicting data and unclear points regarding both the initial compounds ($\text{Fe}_3\text{O}_2\text{BO}_3$, $\text{Co}_3\text{O}_2\text{BO}_3$) and mixed iron–cobalt ludwigites. First, Mössbauer spectroscopy and neutron scattering data unambiguously indicate that the magnetic ordering in $\text{Fe}_3\text{O}_2\text{BO}_3$ begins in the vicinity of $T = 110$ K [4, 9, 10]. The heat capacity of $\text{Fe}_3\text{O}_2\text{BO}_3$ also has a peak at this temperature [3]. However, the measurements of the magnetic susceptibility in this temperature range detected only a weak anomaly, which is almost invisible in the $\chi(T)$ curve [5, 10]. The same is true of mixed compound $\text{Co}_2\text{FeO}_2\text{BO}_3$ [11]. Second, the mechanical properties of mixed compounds $\text{Co}_{3-x}\text{Fe}_x\text{O}_2\text{BO}_3$ unexpectedly resemble those of $\text{Fe}_3\text{O}_2\text{BO}_3$ and differ sharply from those of $\text{Co}_3\text{O}_2\text{BO}_3$. For example, the mixed $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ composition exhibits two magnetic transitions near $T = 70$ and 110 K [12], which are characteristic of $\text{Fe}_3\text{O}_2\text{BO}_3$, in spite of the fact that the number of cobalt ions in this mixed composition is threefold that of iron ions. Third, the substitution of iron for cobalt leads to a substantial decrease in the magnetic moment in a magnetically ordered state: under the same conditions ($T \approx 4.2$ K, cooling in a magnetic field $H = 1$ kOe), the magnetic moment of $\text{Co}_3\text{O}_2\text{BO}_3$ is $\mu \approx 0.8$ [3], the magnetic moment of $\text{Co}_2\text{FeO}_2\text{BO}_3$ is $\mu \approx 0.5$ [11], and that of $\text{Fe}_3\text{O}_2\text{BO}_3$ is $\mu = 0.15\mu_B$ per

formula unit [5]. With allowance for the spin magnetic moments of the ions ($\text{Co}^{2+} : S = 3/2$, $\text{Co}^{3+} : S = 2$, $\text{Fe}^{2+} : S = 2$, $\text{Fe}^{3+} : S = 5/2$), this drop in the magnetic moment is unexpected.

Although iron- and cobalt-based ludwigites are known to be materials with a high magnetic anisotropy [1, 13], the problem of studying the magnetic anisotropy in the ab crystallographic plane of a crystal has not been formulated for more than a decade of their investigation. Most measurements in the cited works were performed on powders or single crystals randomly oriented in a magnetic field.

This is an incomplete list of the intriguing aspects of the behavior of both initial and mixed iron- and cobalt-based ludwigites. The purpose of this work is to elucidate the unclear points of the physics of the oxyborates of transition metals with a ludwigite structure described above. We are going to answer the following two questions: (i) Why do the mixed compositions exhibit the scenario of magnetic ordering characteristic of $\text{Fe}_3\text{O}_2\text{BO}_3$ rather than $\text{Co}_3\text{O}_2\text{BO}_3$ despite a lower iron content as compared to cobalt? (ii) Why does the magnetic order that appears at $T_M \approx 110$ K according to neutron scattering, Mössbauer spectroscopy, and thermodynamic data weakly manifest itself in magnetic behavior? To answer these questions, we studied the structure and magnetic properties of mixed compound $\text{Co}_2\text{FeO}_2\text{BO}_3$ in comparison with initial compound $\text{Co}_3\text{O}_2\text{BO}_3$. Prominence was given to magnetic susceptibility. This work is a logical continuation of our works [12, 14], where the structure and magnetic behavior of mixed ludwigite $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ with a Co : Fe ratio of 3 : 2 were considered.

2. SYNTHESIS AND SAMPLES

Cobalt ($\text{Co}_3\text{O}_2\text{BO}_3$) and mixed ($\text{Co}_2\text{FeO}_2\text{BO}_3$) ludwigite single crystals were grown from a molten solution. In the first case, the initial reagents of a total mass of 50 g were taken in the molar ratios

$$\text{Bi}_2\text{Mo}_3\text{O}_{12} : \text{B}_2\text{O}_3 : \text{CoO} : \text{Na}_2\text{CO}_3 : \text{Co}_2\text{O}_3 \\ = 3 : 2 : 4 : 3 : 3.$$

To form the mixed composition, we substituted iron oxide Fe_2O_3 for part of cobalt oxide Co_2O_3 . The molten solution was prepared in a 50-mm³ platinum crucible by sequential smelting at 900–1000°C. The crucible was placed in a solidification furnace with a nonuniform temperature field so that the vertical component of the temperature gradient in the molten solution was at most 1 K/cm at 900°C. The composition was held at 1100°C for 3 h to ensure complete dissolution and homogenization. The molten solution was then subjected to two-stage cooling: first stage, rapid cooling to $T = 960^\circ\text{C}$; second stage, slow cooling at a rate of 12 K/day for three days. At the second stage, spontaneously formed $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_3\text{O}_2\text{BO}_3\text{:Fe}$ single crystals grew. The molten solution was then poured. The single crystals grown on the

Table 1. Atom coordinates and site occupation factors (SOF) in $\text{Co}_2\text{FeO}_2\text{BO}_3$

	x/a	y/b	z/c	SOF
Co1	0.50000	0.00000	0.50000	0.25000
Co2	0.00000	0.00000	0.00000	0.16262
Fe2	0.00000	0.00000	0.00000	0.08738
Co3	0.00069	0.22049	0.50000	0.50000
Co4	0.23777	0.38432	0.00000	0.10448
Fe4	0.23777	0.38432	0.00000	0.39552
O1	0.10700	0.35662	0.50000	0.50000
O2	0.34533	0.23645	0.00000	0.50000
O3	0.38483	0.42280	0.50000	0.50000
O4	0.12425	0.14000	0.00000	0.50000
O5	0.34760	0.04221	0.00000	0.50000
B	0.27257	0.13845	0.00000	0.50000

crucible walls were cleaned from the molten solution retained on them by etching in a 20% aqueous solution of nitric acid. As a result, we prepared single crystals in the form of rectangular parallelepipeds strongly extended along the c axis.

The monocobalt ludwigite crystals were up to 5-mm-long needles, and the cross-sectional area was smaller than 0.5×0.5 mm. This shape of the crystals made it possible to easily orient them in a magnetic field so that it coincided with or was normal to the c axis. However, it was difficult to orient the crystals with respect to the magnetic field direction in the ab plane of the cross section of the crystals.

The mixed ludwigite single crystals represented thin brittle plates. The crystallographic b direction was normal to the plate plane. This shape of the single crystals made it easy to orient them with respect to the magnetic field direction.

3. X-RAY DIFFRACTION

The crystal structure of ludwigite is rather complex. The presence of low-dimensional substructures determines the hierarchy of exchange interactions in such materials. Therefore, we comprehensively describe the results of crystallographic examination of $\text{Co}_2\text{FeO}_2\text{BO}_3$.

The crystal structure of cobalt ludwigite $\text{Co}_3\text{O}_2\text{BO}_3$ was characterized in [3], and we omit the structural data obtained in our work for this composition. In Table 2, we only give the distances between transition ions in nonequivalent positions. The X-ray diffraction (XRD) investigation of mixed ludwigite $\text{Co}_2\text{FeO}_2\text{BO}_3$ was performed on a single crystal at room temperature. The crystal structure of the crystals was clearly resolved. We used a SMART APEX II X-ray diffractometer (MoK_α -radiation, CCD detector).

Table 2. Minimum distances between the transition ions in nonequivalent positions

Compound	d_{13} , Å	d_{23} , Å	d_{34} , Å	d_{14} , Å	d_{24} , Å
$\text{Co}_3\text{O}_2\text{BO}_3$	3.2979	3.0512	3.0847	3.0045	2.7473
$\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$	3.4177	3.0939	3.1355	3.0280	2.8141
$\text{Co}_2\text{FeO}_2\text{BO}_3$	3.4504	3.1219	3.1674	3.0582	2.8446

Table 3. Interionic distances in $\text{Co}_2\text{FeO}_2\text{BO}_3$

Co1–O1, Å	2.0375 (0.0018)	Co3–O1, Å	1.9608 (0.0014)
Co1–O5, Å	2.1571 (0.0013)	Co3–O2, Å	2.1696 (0.0013)
		Co3–O3, Å	2.0693 (0.0021)
		Co3–O4, Å	2.1676 (0.0014)
		Co(Fe)4–O1, Å	1.9899 (0.0014)
Co(Fe)2–O3, Å	2.1008 (0.0014)		
Co(Fe)2–O4, Å	2.0846 (0.0019)	Co(Fe)4–O2, Å	2.0858 (0.0021)
		Co(Fe)4–O3, Å	2.1135 (0.0014)
		Co(Fe)4–O5, Å	2.1072 (0.0020)
B–O2, Å			1.3891 (0.0037)
B–O4, Å			1.3916 (0.0037)
B–O5, Å			1.3809 (0.0034)
Co(Fe)4–Co(Fe)2, Å			2.8446 (0.0005)

As follows from the XRD data, $\text{Co}_2\text{FeO}_2\text{BO}_3$ has a ludwigite structure; orthorhombic structure type; space group *Pbam*; lattice parameters $a = 9.3818$ Å, $b = 12.3445$ Å, and $c = 3.0578$ Å; and the unit cell volume $V = 354.13$ Å³.

Each of the three lattice parameters of the unit cell is slightly larger than that obtained for the same compound in [11]. The same is true of unit cell volume V , which is larger than that in [11] by 1.9%. The unit cell volume increases with the iron content. For composition $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ with the ratio Co : Fe = 3, we have $V = 343.92$ Å³ [12]; for $\text{Co}_2\text{FeO}_2\text{BO}_3$ with the ratio Co : Fe = 2, this volume is larger by 3%.

Table 1 gives the atom coordinates and site occupation factors for iron and cobalt ions. As follows from these data, iron ions occupy the nonequivalent positions in the ludwigite structure with a pronounced preference. Position 4 is the most preferred position, as was found in [11, 12]. Noticeable substitution of iron for cobalt is detected for position 2, in contrast to [11] but in agreement with [12]. Positions 1 and 3 are occupied by cobalt. Thus, the XRD data demonstrate that all iron ions in compound $\text{Co}_2\text{FeO}_2\text{BO}_3$ enter into first-type 4–2–4 triads and only cobalt ions occupy the positions of second-type 3–1–3 triads.

The interionic distances for the transition ions in ludwigite $\text{Co}_2\text{FeO}_2\text{BO}_3$, which are about 3 Å, are given in Table 2 in comparison with initial $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ synthesized in [12]. The distance between the cobalt and iron ions inside the first-type triads is minimal (2.8446 Å). As the iron content increases, the average distances between the transition ions in all nonequivalent positions increase irrespective of whether these ions belong to sublattice 4–2–4, which is mainly filled with iron, or 3–1–3, which contains only cobalt.

According to the occupation factors given in Table 2, the ratio of the number of cobalt ions to the number of iron ions in our $\text{Co}_2\text{FeO}_2\text{BO}_3$ samples is 2.11, which is slightly higher than the value corresponding to the chemical formula (2). However, our compound is closer to nominal composition $\text{Co}_2\text{FeO}_2\text{BO}_3$ as compared to the samples from [11], where this Co : Fe ratio was 2.29.

The character and distortion of the oxygen octahedra surrounding every nonequivalent site can be estimated from the data in Table 3, which contains the metallic ion–oxygen distances.

With the data in Table 3, we can calculate the electric field gradient (EFG) of the oxygen octahedron surrounding a metallic ion in every nonequivalent

position. The calculations were carried out using the formula

$$V_{zz} = \sum 2e \frac{3 \cos^2 \theta - 1}{r^3}$$

with allowance for the first coordination shell. Here, V_{zz} is the electric field gradient along the major axis of the oxygen octahedron, θ is the angle between this axis and the direction to the neighboring oxygen ion, e is the electron charge, and r is the metallic ion–oxygen distance. The calculation results are given in Table 4; they indicate that positions 2 and 4, which are occupied by $d^5 \text{Fe}^{3+}$ ions with a half-filled electron shell, have the most symmetrical oxygen surrounding. In [12], we obtained a similar result for mixed ludwigite $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$.

4. MAGNETIC MEASUREMENTS

The magnetic measurements were performed on an MPMS Quantum Design SQUID magnetometer. The static magnetization was measured in the temperature range 2–300 K, and magnetization curves were recorded in magnetic fields up to 50 kOe. Before magnetic measurements, we precisely weighed a single crystal with a DV 215 CD microbalance. The single crystal was oriented with an X-ray diffractometer and fixed on an acrylic plastic holder so that a magnetic field was alternately directed along each of the crystallographic axes. For each direction, we measured the temperature and field dependences of the magnetization. The signal generated by the holder was at most $2.7 \times 10^{-4} \text{ G cm}^3$ in a magnetic field of 50 kOe. The temperature dependence of the holder signal was obtained individually and subtracted from the integral signal. When performing measurements in the b direction, we estimated the demagnetization effect caused by the sample shape. At the maximum magnetization, the demagnetizing field was about 150 Oe, which was only 0.3% of the measuring field (50 kOe). The total error in determining the sample magnetization did not exceed 5% with allowance for all errors introduced by weighing, the subtraction of the holder signal, and measurement.

The magnetic measurement results are shown in Figs. 2–8. To determine the magnetic ordering temperature of $\text{Co}_3\text{O}_2\text{BO}_3$, we recorded the temperature dependences of the magnetization of a sample on its cooling in a weak magnetic field $H = 20 \text{ Oe}$ (FC curves) and without a magnetic field (ZFC curves). The measurements were carried out in a magnetic field directed along the b direction. For the other two directions, the signal obtained in the weak magnetic field is too low to be measured. These dependences are shown in Fig. 2, where one magnetic transition is seen in the vicinity of $T = 42 \text{ K}$, in accordance with the reported data.

Table 4. Major EFG tensor component and the occupancy of the metal nonequivalent positions by iron ions

Position	1	2	3	4
$V_{zz}, \text{e}/\text{\AA}^3$	0.186	0.040	0.234	−0.060
Occupancy, %	≈0	34.8	≈0	79.1

Hysteresis loops are observed at a temperature below T_N in magnetization direction b (Fig. 3). At temperatures below 30 K, these loops have a pronounced saturation and an almost rectangular shape. The coercive force increases strongly with decreasing temperature. The remanent magnetization and the saturation magnetization are close to each other, about $3.4\mu_B$ per formula unit ($1.13\mu_B$ per magnetic ion). Based on the loop shape and the magnetic moment, we assume that the ordering in the b direction is ferrimagnetic. For a field directed along crystallographic axes a and c , the magnetization is low and linear in field, exhibiting antiferromagnetic behavior. Thus, the magnetic anisotropy of $\text{Co}_3\text{O}_2\text{BO}_3$ is well pronounced and crystallographic direction b coincides with the easy magnetization axis.

In the paramagnetic range, the temperature dependence of the reciprocal magnetic susceptibility of a $\text{Co}_3\text{O}_2\text{BO}_3$ single crystal obeys the standard Curie–Weiss law (Fig. 4). The difference between the Weiss θ temperatures obtained for fields along the b and c axes is seen to be substantial. In the former direction, we have $\theta_b = 1.2 \text{ K}$, which is close to zero. In the latter direction, the Weiss temperature has a high modulus and a negative value ($\theta_c = -153.8 \text{ K}$), which indicates predominant antiferromagnetic interactions. This “anisotropy” of the Weiss temperature points to the

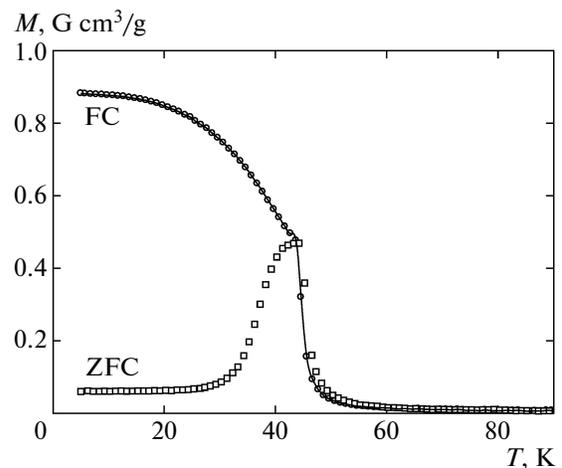


Fig. 2. Temperature dependences of the magnetization of $\text{Co}_3\text{O}_2\text{BO}_3$ measured in cooling in a weak magnetic field $H = 20 \text{ Oe}$ (FC) and a zero magnetic field (ZFC). The magnetic field is directed along the b axis.

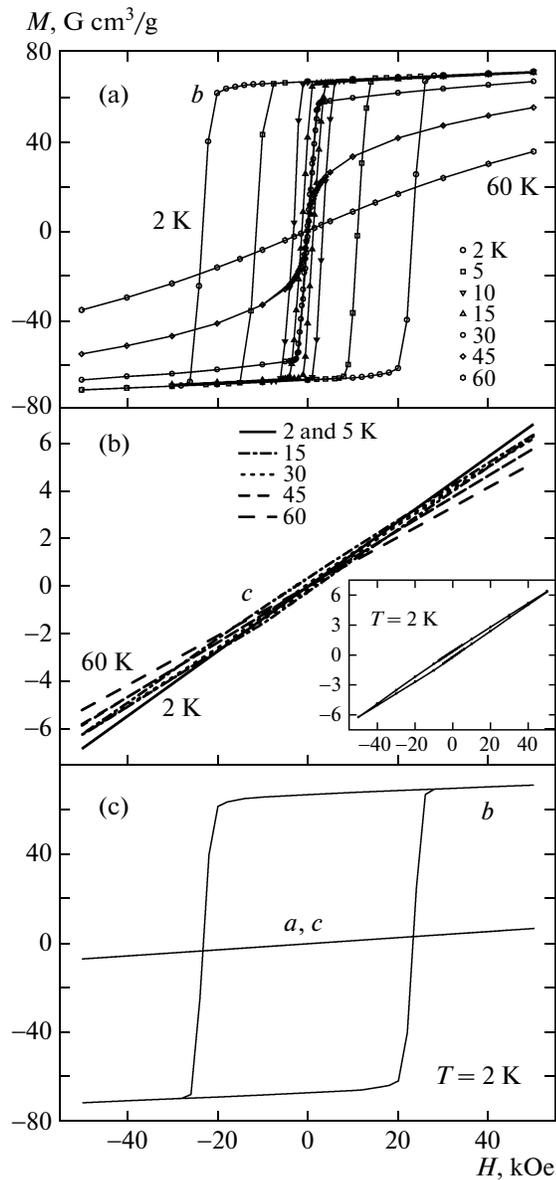


Fig. 3. Magnetization isotherms of a $\text{Co}_3\text{O}_2\text{BO}_3$ crystal: (a) magnetization in direction b ; (b) magnetization in direction c ; and (c) magnetization in directions a , b , and c at $T = 2$ K. The inset shows a weakly pronounced hysteresis in the magnetization curve in direction a at $T = 2$ K.

presence of several contributions to the susceptibility with molecular fields of different signs.

The effective magnetic moments μ_{eff} calculated for the paramagnetic phase in directions b and c are close to each other (the difference is about 6%). Moreover, the effective magnetic moment measured in magnetization-dominating direction b ($\mu_{\text{eff}} = 4.26\mu_{\text{B}}$) almost ideally coincides with the purely spin value ($\mu_{\text{eff}} = 4.24\mu_{\text{B}}$; see Table 5). This finding points to the absence of a significant orbital contribution to the magnetic moment of the cobalt ions in $\text{Co}_3\text{O}_2\text{BO}_3$.

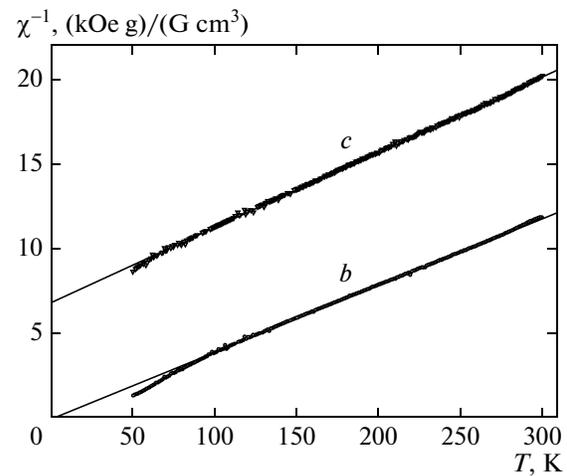


Fig. 4. Temperature dependences of the reciprocal magnetic susceptibility of a $\text{Co}_3\text{O}_2\text{BO}_3$ crystal in crystallographic directions b and c . The magnetic field is 50 kOe. (straight lines) Approximation of the high-temperature part according to the Curie–Weiss law.

The spin effective magnetic moment in $\text{Co}_2\text{FeO}_2\text{BO}_3$ ($4.65\mu_{\text{B}}$) was calculated on the assumption that all iron ions in this compound are trivalent ($S = 5/2$) and contribute to the total magnetic moment at a weight of $1/3$, according to the chemical formula. The cobalt ions are considered to be divalent ($S = 3/2$), their weight contribution is $2/3$, and the g factor was taken to be 2. Similar examples of calculating the effective magnetic moments in mixed iron–cobalt ludwigites are given in [12].

Figure 5 shows the temperature dependences of the magnetization of mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition in a high field ($H = 50$ kOe) for three crystallographic directions. It is clearly visible that the magnetization in the b direction is well above the other two magnetizations, as in the case of $\text{Co}_3\text{O}_2\text{BO}_3$. The magnetization in the b direction is approximately half the magnetization in initial $\text{Co}_3\text{O}_2\text{BO}_3$. The next interesting feature is a high magnetization peak at $T = 115$ K in the a direction. It was absolutely unclear earlier why this peak is almost invisible in the temperature dependences of the magnetization and magnetic susceptibility of $\text{Fe}_3\text{O}_2\text{BO}_3$ [5, 10] and $\text{Co}_2\text{FeO}_2\text{BO}_3$ [11] in spite of the fact that heat capacity, Mössbauer spectroscopy, and neutron diffraction data clearly indicate the beginning of magnetic ordering in the vicinity of $T = 110$ K. Our investigation performed on an oriented sample clearly demonstrates that the corresponding peak in the $M(T)$ dependence of $\text{Co}_2\text{FeO}_2\text{BO}_3$ can be reliably detected only upon measurements in a magnetic field directed along axis a rather than along any random direction in the ab plane, as was done earlier for $\text{Fe}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ [5, 10, 11].

The FC and ZFC dependences measured in the a direction almost coincide if we do not take into account a certain discrepancy at temperatures below

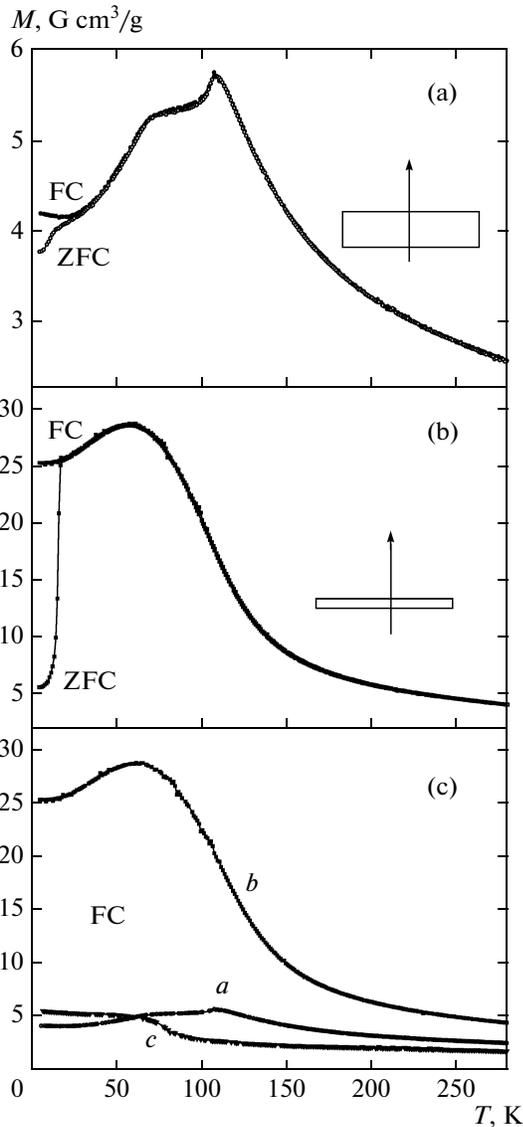


Fig. 5. Temperature dependences of the magnetization of $\text{Co}_2\text{FeO}_2\text{BO}_3$ in a magnetic field of 50 kOe: (a) magnetic field along direction a ; (b) magnetic field along direction b ; and (c) cooling in a magnetic field (FC curves) in crystallographic directions a , b , and c .

20 K. The sharp magnetization peak at T_{NI} indicates an antiferromagnetic order, which is supported by the shape of the magnetization curve (it is close to linear at all temperatures; see Fig. 6a). Figures 6b and 6c show the magnetization curves in directions b and c . The b -axis magnetization is seen to be predominant, which supports the finding that the b direction is an easy magnetization axis. Along the c direction, the magnetization curves are linear at $T = 130$ and 90 K. At lower temperatures, an inflection point is seen in the magnetization curve, which is likely to be related to a small deviation from an exact sample orientation from the magnetic field direction.

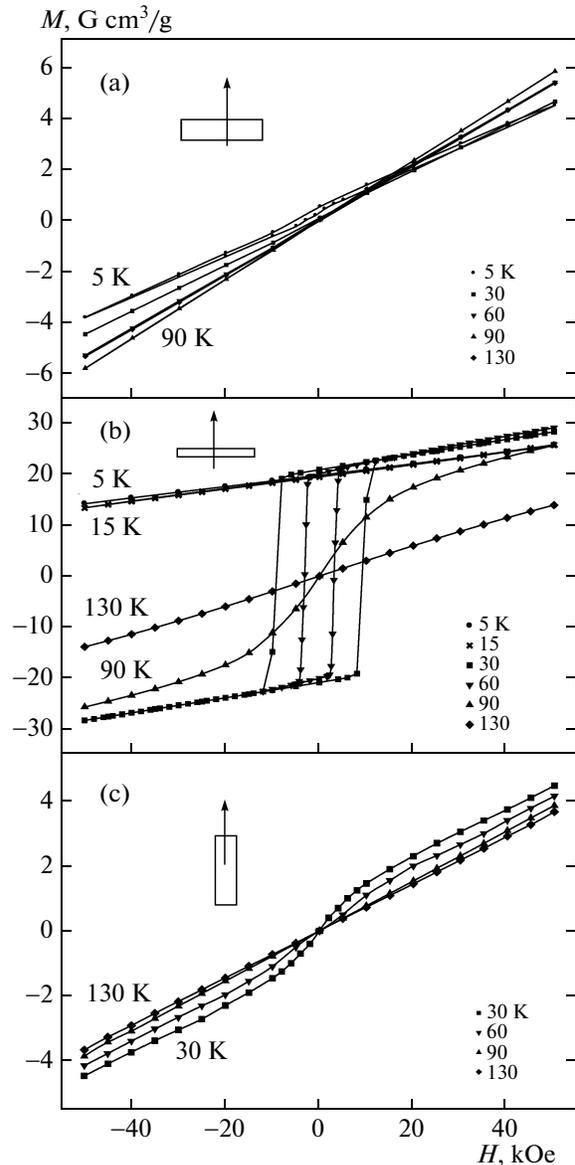


Fig. 6. Magnetization isotherms of $\text{Co}_2\text{FeO}_2\text{BO}_3$: (a) magnetic field along axis a , (b) magnetic field along axis b , and (c) magnetic field along axis c .

We can compare the magnetic parameters of $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ in the magnetically ordered state using the data from Table 6. It is seen that the magnetic moment decreases significantly when iron ions substitute for part of the cobalt ions and that the magnetization in both compounds represents the superposition of ferromagnetic and linear-in-field (antiferromagnetic) components. The b direction is the easy magnetization axis of the ferromagnetic component. The antiferromagnetic component is likely to be isotropic. The corresponding antiferromagnetic susceptibility is $\chi_{AF} \approx 0.1$ (G cm^3)/(kOe g). Mixed ludwigite $\text{Co}_2\text{FeO}_2\text{BO}_3$ is unusually magnetically hard: at temperatures below 15 K, the maximum field of

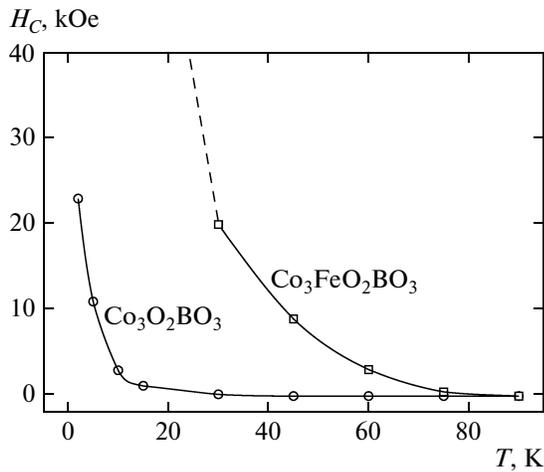


Fig. 7. Temperature dependences of the coercive field. The coercive field of $\text{Co}_2\text{FeO}_2\text{BO}_3$ exceeds 50 kOe at $T = 15$ K or below (see dashed line).

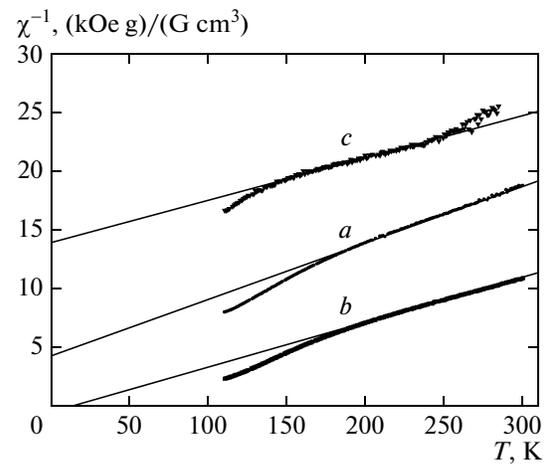


Fig. 8. Temperature dependences of the reciprocal magnetic susceptibility of a $\text{Co}_2\text{FeO}_2\text{BO}_3$ crystal in crystallographic directions a , b , and c . The magnetic field is 50 kOe. (straight lines) Approximation of the high-temperature part according to the Curie–Weiss law.

50 kOe was insufficient to achieve magnetization reversal of the sample (upper straight lines in Fig. 6 obtained at $T = 5$ and 15 K). In Fig. 7, we compare the temperature dependences of the coercive field for the initial and mixed ludwigites.

In the paramagnetic state, mixed composition $\text{Co}_2\text{FeO}_2\text{BO}_3$ exhibits a sharp difference in the Weiss temperatures as a function of the magnetization direction, as in the case of its prototype $\text{Co}_3\text{O}_2\text{BO}_3$ (Fig. 8). This temperature is positive for direction b and negative for directions a and c . In direction c , the Weiss temperature has a very high modulus ($\theta_c = -387$ K), which indicates strong antiferromagnetic interactions.

5. DISCUSSION OF RESULTS

Our XRD data obtained for $\text{Co}_2\text{FeO}_2\text{BO}_3$ support the earlier data on its crystal structure and strongly preferred iron occupation of the positions inside the first-type triads formed by ions in positions 4–2–4 [11, 12]. The second-type triads formed by ions in positions 3–1–3 are occupied by cobalt.

The distances between the metallic ions in triads 4–2–4 are minimal; therefore, the exchange interactions inside these triads are strongest. The Mössbauer

spectroscopy [9, 10] and neutron diffraction [4] data obtained for related composition $\text{Fe}_3\text{O}_2\text{BO}_3$ demonstrate that the magnetic moments of the iron ions in triads 4–2–4 are first ordered at $T_{M1} \approx 110$ K. In the case of the substituted $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition, iron enters into the positions belonging to 4–2–4 triads, and the temperature of the first magnetic transition almost coincides with that of $\text{Fe}_3\text{O}_2\text{BO}_3$. This finding suggests that we again deal with the stage-by-stage scenario of magnetic ordering that takes place in the $\text{Fe}_3\text{O}_2\text{BO}_3$ compound, which is caused by the pronounced preference in the iron occupation of triads 4–2–4 with the minimum interionic distance. However, there exists an important difference between our magnetic data obtained for $\text{Co}_2\text{FeO}_2\text{BO}_3$ and the neutron diffraction data obtained for $\text{Fe}_3\text{O}_2\text{BO}_3$ in [4]. Both experiments exhibit the beginning of the first magnetic transition in both materials near $T = 110$ K. However, according to [4], the magnetic moments of triads 4–2–4 in $\text{Fe}_3\text{O}_2\text{BO}_3$ are ordered at $T = 110$ K along the crystallographic b direction. As follows from the magnetic data obtained in this work, the magnetic ordering in mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ occurs along the a direction. In both cases, the magnetic ordering at $T = 110$ K is antiferromagnetic.

Table 5. Magnetic transition temperatures and the effective magnetic moments for $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$

Compound	Direction	$\mu_{\text{eff}}, \mu_{\text{B}}/\text{ion}$	$\mu_{\text{eff}}(\text{spin value}), \mu_{\text{B}}/\text{ion}$	$T_{\text{C}}, T_{\text{N}}$
$\text{Co}_3\text{O}_2\text{BO}_3$	b	4.26	4.24	42
	c	4.01		
$\text{Co}_2\text{FeO}_2\text{BO}_3$	a	3.83	4.65	70, 115
	b	4.29		
	c	4.43		

Table 6. Magnetic parameters of $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ crystals in the magnetically ordered state

Compound	Direction	M_0 , μ_B/ion	$H_C(2\text{ K})$, kOe	$\chi_{AF}(2\text{ K})$, $(\text{G cm}^3)/(\text{kOe g})$
$\text{Co}_3\text{O}_2\text{BO}_3$	b	0.91	23	0.07
	c	—	—	0.12
$\text{Co}_2\text{FeO}_2\text{BO}_3$	a	—	—	0.11
	b	0.19	>90	0.07
	c	—	—	0.10

The effective magnetic moment of the cobalt ions in $\text{Co}_3\text{O}_2\text{BO}_3$ is very close to the purely spin value, which suggests that the spin component mainly contributes to the total magnetic moment of the cobalt ions in $\text{Co}_3\text{O}_2\text{BO}_3$. The average effective magnetic moment per ion for the mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition is slightly higher than that of the plain composition. This result is expected, since trivalent cobalt with $S = 2$ is substituted by trivalent iron with $S = 5/2$.

The main result of our magnetic measurements indicates that the materials under study are extremely anisotropic. A magnetic anisotropy manifests itself clearly in the paramagnetic state, which is obvious from the sharp difference in the Weiss temperatures as a function of the magnetic field direction. In the substituted $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition, the deviations from the Curie–Weiss law manifest themselves well above the magnetic ordering temperature $T_{N1} = 110\text{ K}$ (Fig. 8), which indicates that the contribution of magnetic correlations and the tendency toward magnetic ordering in the mixed composition appear at a temperature above 200 K. The magnetizations measured in the b direction in both the magnetically ordered and paramagnetic states exceed the values obtained in the a and c directions in initial $\text{Co}_3\text{O}_2\text{BO}_3$ and substituted $\text{Co}_2\text{FeO}_2\text{BO}_3$.

As follows from the magnetic data, the initial $\text{Co}_3\text{O}_2\text{BO}_3$ composition below $T_N = 42\text{ K}$ is a ferrimagnet with an uncompensated magnetic moment lying in the b direction. The $\text{Co}_3\text{O}_2\text{BO}_3$ formula unit contains two divalent cobalt ions and one trivalent ion. This should give $10\mu_B$ during ferromagnetic ordering in saturation against $3.4\mu_B$ detected in our samples. Based on the XRD data, we can state that the 3–1–3 triads in the mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ material are occupied by cobalt and find an approximately twofold decrease in the magnetic moment in the b direction in the substituted composition as compared to the initial one (Figs. 3, 7). Therefore, we assume that the magnetic sublattices formed by the 3–1–3 triads in $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ are similar.

The presence of two magnetic transitions in the mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition at $T = 70$ and 110 K inevitably brings up the question about the processes that proceed in the magnetic system of this composition at these temperatures. Do we deal with sequential ordering of two magnetic systems in different crystal-

lographic directions or with reorientation transitions when the temperature changes? The comprehensive experimental results obtained for the $\text{Fe}_3\text{O}_2\text{BO}_3$ composition support the first version. This is evidenced by the Mössbauer spectroscopy data [9, 10], which demonstrate that the magnetic moments of triads 3–1–3 in the temperature range 70–110 K are not ordered and that a long-range order magnetic order takes place throughout a sample only below $T = 70\text{ K}$. The neutron diffraction results obtained for $\text{Fe}_3\text{O}_2\text{BO}_3$ [4] also indicate stage-by-stage ordering in this material, where orthogonal magnetic moments are ordered at $T = 110$ and 70 K . Therefore, we assume that a similar scenario of the magnetic behavior is most likely to take place in the mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition: the magnetic system mainly formed by iron ions in triads 4–2–4 are antiferromagnetically ordered along direction a at $T_{N1} = 110\text{ K}$, and the magnetic system of cobalt ions is ferrimagnetically ordered along direction b at $T_{N2} = 70\text{ K}$.

A number of exchange interactions are likely to occur in the magnetic system of iron–cobalt ludwigites. First, this is a direct exchange interaction between the transition ions in positions 2 and 4, which are located at a distance smaller than 3 \AA . Second, this is double exchange inside triads 4–2–4 at the expense of an “excess” electron, since these triads are formed by two trivalent ions and one divalent ion. Third, this is an indirect exchange through oxygen ions. Fourth, this is an exchange interaction between low-dimensional structures, namely, the rows formed by the two types of triads. The hierarchy of these exchange interactions is now unknown. The simplified calculation of the indirect exchange interactions in ludwigites performed by us in [12] showed the presence of contributions of opposite signs and, which is more important, disordering frustrating components. According to [12], these frustrating interactions are most pronounced for the ions on positions 4, which can cause the detected tendency toward ordering in different magnetic sublattices in mutually perpendicular directions.

The extraordinary increase in the magnetic hardness of the substituted $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition as compared to the initial $\text{Co}_3\text{O}_2\text{BO}_3$ composition is of particular interest. This effect can be caused by an increase in the concentration of pinning centers of domain walls and possible noncollinear magnetiza-

tions of different magnetic subsystems in $\text{Co}_2\text{FeO}_2\text{BO}_3$.

6. CONCLUSIONS

We showed that single-crystal ludwigites $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ are materials with a high degree of magnetic anisotropy. Earlier, the magnetic measurements were carried out on crystals with a random magnetic field orientation in the ab plane or on powder samples. As a result, the transition into an antiferromagnetic state at $T_{\text{NI}} \approx 110$ K, which is clearly visible from Mössbauer spectroscopy and neutron diffraction results, only weakly manifested itself in magnetic measurements. This problem has not been solved for years. In this work, we studied oriented samples and revealed a significant anisotropy in the ab plane in $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$. Crystallographic direction b is an easy magnetization axis. The magnetic ordering in this direction in both $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_2\text{FeO}_2\text{BO}_3$ is likely to be ferrimagnetic.

Mixed composition $\text{Co}_2\text{FeO}_2\text{BO}_3$ has the two magnetic ordering temperatures characteristic of $\text{Fe}_3\text{O}_2\text{BO}_3$ rather than $\text{Co}_3\text{O}_2\text{BO}_3$ despite a higher cobalt concentration as compared to iron. The temperature of the first magnetic transition is about 110 K. Mössbauer spectroscopy and neutron diffraction data for $\text{Fe}_3\text{O}_2\text{BO}_3$ demonstrated that the magnetic moments of the ions in triads 4–2–4 are ordered at this temperature. In addition, the X-ray diffraction data obtained in this work show that the iron ions in the mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition mainly occupy these positions, which explains similar magnetic behavior of $\text{Co}_2\text{FeO}_2\text{BO}_3$ and $\text{Fe}_3\text{O}_2\text{BO}_3$.

The nature of the magnetic transitions in $\text{Co}_2\text{FeO}_2\text{BO}_3$ is still incompletely clear. According to the neutron diffraction data in [4], the magnetic moments of the ions in triads 4–2–4 and 3–1–3 in $\text{Fe}_3\text{O}_2\text{BO}_3$ are orthogonally ordered at temperatures of 110 and 70 K, respectively. This finding may lead to the assumption that the scenario of magnetic ordering in the mixed $\text{Co}_2\text{FeO}_2\text{BO}_3$ composition is the same. However, our data demonstrate that the antiferromagnetic ordering in $\text{Co}_2\text{FeO}_2\text{BO}_3$ at $T = 110$ K takes place in crystallographic direction a rather than b , as in the initial $\text{Fe}_3\text{O}_2\text{BO}_3$ composition. Moreover, spin-reorientation transitions can also occur.

Thus, the picture of magnetic interactions in iron–cobalt ludwigites is very complex and still incompletely clear. For further progress in understanding the magnetic structure of the unsubstituted and mixed compositions, we need neutron diffraction data at various temperatures.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 09-02-00171-a), the Russian Science Foundation (President project no. MK-5632.2010.2), and the program of the Division of Physical Sciences of the Russian Academy of Sciences “Strong Electronic Correlations.”

REFERENCES

1. N. V. Kazak, N. B. Ivanova, V. V. Rudenko, S. G. Ovchinnikov, A. D. Vasil'ev, and Yu. V. Knyazev, *Solid State Phenom.* **152–153**, 104 (2009).
2. G. A. Petrakovskii, L. N. Bezmaternykh, D. A. Velikanov, M. S. Malokeev, O. A. Bayukov, A. M. Vortynov, and R. Szymchak, *Phys. Solid State* **51** (12), 2486 (2009).
3. D. C. Freitas, M. A. Continentino, R. B. Guimaraes, J. C. Fernandes, J. Ellena, and L. Ghivelder, *Phys. Rev. B: Condens. Matter* **77**, 184422 (2008).
4. F. Bordet and E. Suard, *Phys. Rev. B: Condens. Matter* **79**, 144408 (2009).
5. R. B. Guimaraes, M. Mir, J. C. Fernandes, M. A. Continentino, H. A. Borges, G. Cernicchiaro, M. B. Fontes, D. R. S. Candela, and E. Baggio-Saitovitch, *Phys. Rev. B: Condens. Matter* **60**, 6617 (1999).
6. R. Norrestam, M. Kritikos, K. Nielsen, I. Şçotofte, and N. Thorup, *J. Solid State Chem.* **111**, 217 (1994).
7. F. S. Sarrat, R. B. Guimaraes, M. A. Continentino, J. C. Fernandes, A. C. Doriguetto, and J. Ellena, *Phys. Rev. B: Condens. Matter* **71**, 224413 (2005).
8. R. Norrestam, *Z. Kristallogr.* **189**, 1 (1989).
9. J. J. Larrea, D. R. Sanchez, F. J. Litterst, and E. M. Baggio-Saitovitch, *Hyperfine Interact.* **161**, 237 (2005).
10. A. P. Douvalis, A. Moukarika, T. Bakas, G. Kallias, and V. Papaefthymiou, *J. Phys.: Condens. Matter* **14**, 3303 (2002).
11. D. C. Freitas, M. A. Continentino, R. B. Guimaraes, J. C. Fernandes, E. P. Oliveira, R. E. Santelli, J. Ellena, G. G. Eslava, and L. Ghivelder, *Phys. Rev. B: Condens. Matter* **79**, 134437 (2009).
12. N. V. Kazak, N. B. Ivanova, O. A. Bayukov, S. G. Ovchinnikov, A. D. Vasiliev, V. V. Rudenko, J. Bartolomé, A. Arauzo, and Yu. V. Knyazev, *J. Magn. Magn. Mater.* **323**, 521 (2011).
13. N. B. Ivanova, A. D. Vasil'ev, D. A. Velikanov, N. V. Kazak, S. G. Ovchinnikov, G. A. Petrakovskii, and V. V. Rudenko, *Phys. Solid State* **49** (4), 651 (2007).
14. J. Bartolomé, A. Arauzo, N. V. Kazak, N. B. Ivanova, S. G. Ovchinnikov, Yu. V. Knyazev, and I. S. Lyubutin, *Phys. Rev. B: Condens. Matter* **83**, 144426 (2011).

Translated by K. Shakhlevich