

ORDER, DISORDER, AND PHASE TRANSITION
IN CONDENSED SYSTEM

Magnetic Properties of $\text{Co}_2^{2+}\text{Co}_{1-x}^{3+}\text{Fe}_x^{3+}\text{BO}_5$ ($x = 0.10$) Single Crystals with a Ludwigite Structure

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Abstract—The investigation of mixed Co–Fe ludwigite single crystals shows that their magnetic properties are close to the magnetic properties of Fe_3BO_5 despite the predominance of cobalt ions. The magnetic properties of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ single crystals with $x = 0.10$ are studied in detail. Magnetometric measurements demonstrate a strong magnetic anisotropy with easy magnetization axis b , and the orbital magnetic moment of cobalt is in a frozen state. The detected temperature dependence of the absorption of Mössbauer spectra allowed us to determine the magnetic ordering temperature, which agrees with the results of magnetization measurements ($T_C = 84$ K).

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1. INTRODUCTION

A sufficiently large body of data on the physical properties of the single crystals having a ludwigite structure and various chemical compositions has been accumulated to date [1–4]. Oxyborates with a ludwigite structure have the general formula $\text{M}_2^{2+}\text{M}'^{3+}\text{BO}_5$, where M and M' are transition metal ions (space group *Pbam* and the orthorhombic lattice type). The crystal structure of ludwigites contains four nonequivalent sites of metal ions, which have an octahedral oxygen environment and form low-dimensional elements in the form of zigzag walls. In turn, these walls are coupled by planar BO_3 groups [5]. A large number of synthesized ludwigites with various cation substitutions are known [1–3], and the ludwigites based on iron [6–8] and cobalt [9–11] have received much attention.

The magnetic ordering in $\text{Fe}_2^{2+}\text{Fe}^{3+}\text{BO}_5$ proceeds in two stages. According to the experimental data obtained by measuring the magnetization [6], the Mössbauer effect [7], and neutron diffraction [8], the magnetic structure of Fe_3BO_5 consists of two orthogonal subsystems, which are independently ordered at temperatures $T_{N1} = 112$ K and $T_{N2} = 70$ K. However, the ferrimagnetic ordering in another homometallic ludwigite (Co_3BO_5) was detected at $T_C = 42$ K [9, 10].

This sharp difference between the magnetic properties of two homometallic ludwigites, namely,

Fe_3BO_5 and Co_3BO_5 , provoked interest to mixed Co–Fe ludwigites. The properties of single crystals with the ion ratio Co : Fe = 2 : 1 and 3 : 1 were comprehensively studied in [12–15]. These studies showed that the magnetic properties of these ludwigites resembled the properties of Fe_3BO_5 (two magnetic transitions at temperatures of 70 and 115 K) and differed radically from the properties of Co_3BO_5 .

Therefore, the problem of further investigation of Co–Fe ludwigites consists in searching for the limiting iron concentration in a structure at which these ludwigites exhibit the magnetic properties that are close to the properties of Co_3BO_5 . To answer this question, we synthesized $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.0125, 0.025, 0.05, 0.10$) single crystals with a low iron content. The structural properties of these single crystals at room temperature were studied by powder X-ray diffraction and Mössbauer spectroscopy [16]. It was shown that iron was in the trivalent state and that the majority of iron substitutes for cobalt in two nonequivalent sites 2 and 4, which is also characteristic of other mixed Co–Fe ludwigites [9, 15]. To investigate the magnetic properties of the mixed ludwigites with a low iron content, we chose high-quality $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) single crystals.

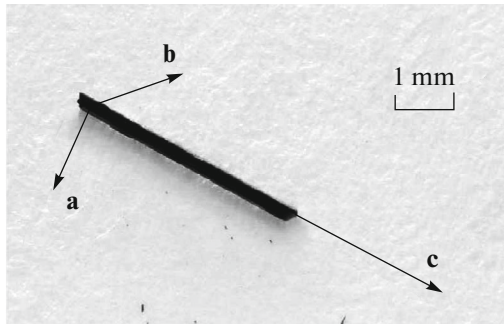


Fig. 1. $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) ludwigite single crystals. Arrows indicate the directions of the crystallographic axes.

2. EXPERIMENTAL

The $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) single crystals were grown at the Kirensky Institute of Physics by the solution–melt method. As a result of synthesis, single crystals with a typical (for ludwigites) shape and 3–4 mm long were formed. The results of X-ray diffraction analysis of the samples were presented in [16].

Magnetization measurements in magnetic fields up to 600 Oe were performed on single crystals oriented with respect to crystallographic axes using a SQUID magnetometer in the temperature range 4–250 K (Fig. 1) [17]. Before the magnetic measurements, the single crystals were weighed with a DV 215 CD microbalance, oriented, and fixed to a substrate. The magnetization was measured during field cooling (FC) and zero-field cooling (ZFC). The total error of measuring the magnetization did not exceed 5% with allowance for all errors introduced upon weighing, the subtraction of a holder signal during measurements, and the demagnetizing factor.

The Mössbauer effect was measured on a pressed powder made of single crystals about 8 mg/cm^2 thick using an MS1104-Em spectrometer in the geometry of γ radiation ($\text{Co}^{57}(\text{Cr})$ source) transmission in the temperature range 40–290 K. The low-temperature measurements were carried out with a Kriotreid cryorefrigerator.

3. ANALYSIS OF THE MAGNETIZATION DATA

The FC and ZFC temperature dependences of the magnetization of the $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ sample ($x = 0.10$) for crystallographic direction **b** are shown in Fig. 2a. The inset to Fig. 2a depicts the magnetization in direction **c**, which is seen to have a significantly lower value. The magnetization in direction **a** turned to be two orders of magnitude lower than that along the easy magnetization axis, which indicates a strong easy axis magnetic anisotropy with easy magnetization axis **b**. It should be noted that the anisotropy is also significant at temperatures above the temperature of magnetic transition. The type of magnetic anisotropy and the easy magnetization axis in the sample do not change in comparison with Co_3BO_5 [9].

According to magnetic data, the magnetic transition temperature is $84 \pm 4 \text{ K}$ with allowance for the measurement error. This temperature is twice as large as the magnetic ordering temperature in Co_3BO_5 ($T_C = 42 \text{ K}$) [9]. The FC and ZFC magnetizations diverge below 75 K. This behavior is characteristic of homometallic Co_3BO_5 [18] and a copper substitution sample ($\text{Co}_{2.88}\text{Cu}_{0.12}\text{BO}_5$) [19]. The magnitude of magnetic moment of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) at $T = 4 \text{ K}$ along direction **b** is $2.3\mu_B/\text{formula unit}$ (Fig. 2a). This value is almost twice as large as that in Co_3BO_5 under analogous conditions, which had $1.2\mu_B$ per for-

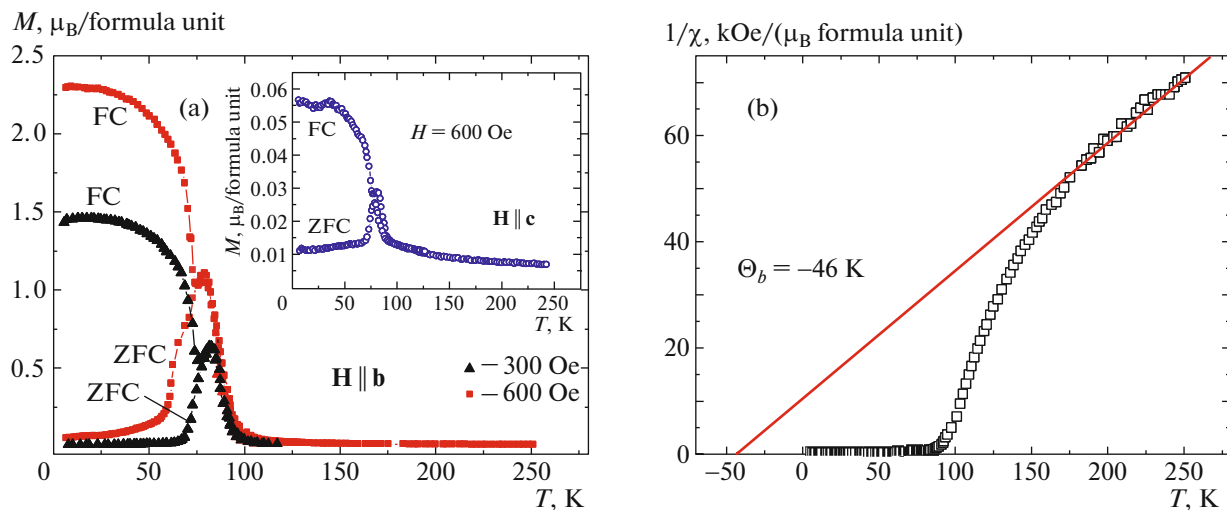


Fig. 2. (Color online) Temperature dependences of (a) magnetization and (b) inverse magnetic susceptibility of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) in a magnetic field parallel to the **b** axis. The inset shows the temperature dependence of magnetization along the **c** axis.

Magnetic parameters of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) in comparison with those of Co_3BO_5 , $\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$, and Co_2FeBO_5

	Axis	Θ , K	μ_{eff} , $\mu_{\text{B}}/\text{ion}$	$\mu_{\text{eff}}^{\text{theor}}$, $\mu_{\text{B}}/\text{ion}$	T_{C} , T_{N}	Reference
Co_3BO_5	b	1.2	4.26	4.24	42	[9]
	a, c	-153.8	4.01			
$\text{Co}_{2.90}\text{Fe}_{0.10}\text{BO}_5$	a	-140	4.61	4.28	84 ± 4	this work
	b	-46	4.53			
$\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$	b	-69	4.20	4.55	70, 115	[15]
Co_2FeBO_5	b	12.4	4.29	4.65	70, 115	[9]

mula unit [18]. In the paramagnetic region at $T > 150$ K, the temperature dependence of the inverse magnetic susceptibility obeys the Curie–Weiss law (Fig. 2b). At temperatures below 150 K, the dependence of the inverse magnetic susceptibility deviates from the linear Curie–Weiss law, which is related to enhanced spin correlations. The paramagnetic Curie temperature is negative for all directions and is $\Theta_b = -46$ K (see table) for the easy magnetization axis, whereas this temperature for Co_3BO_5 is positive ($\Theta_b = 1.2$ K) [9]. This Θ_b dynamics points to an increase in the role of the antiferromagnetic interactions induced by Fe^{3+} ions in chains 4–2–4 (where the iron content is maximal) in the crystal [16].

The effective magnetic moments μ_{eff} of the $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) compound that were obtained in the paramagnetic phase for all crystallographic directions are given in the table. The theoretical value of effective magnetic moment $\mu_{\text{eff}}^{\text{theor}}$ was determined with allowance for the fact that all iron ions in this compound are trivalent (spin $S = 5/2$) and contribute to the total magnetic moment according to their weight in the chemical formula ($x = 0.10$). The number of divalent cobalt ions (spin $S = 3/2$) accounts for two-thirds of the total number of cobalt ions, the number of trivalent cobalt ions (spin $S = 2$) decreases because of the appearance of iron, and its quantitative contribution is $(1/3) - x$ (where x is the weight fraction of iron cations). The g factor was taken to be $g = 2$. Thus, the theoretical magnetic moment of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) is $4.28\mu_{\text{B}}$ per magnetic ion and is close to the experimental value ($4.53\mu_{\text{B}}/\text{ion}$), which indicates a frozen orbital moment of cobalt ions in the $\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$ and Co_2FeBO_5 samples.

4. MÖSSBAUER SPECTROSCOPY RESULTS

Figure 3 shows the Mössbauer spectra measured in the paramagnetic and magnetically ordered states. The distribution of iron ions in $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ludwigites at room temperature was comprehensively studied by Mössbauer spectroscopy in [16]: trivalent iron ions were shown to mainly occupy nonequivalent sites 2 and 4. The processing of the Mössbauer spectrum

recorded in this work at room temperature supports this character of trivalent iron ion distribution. Information on the magnetic state of iron in ludwigite was obtained upon low-temperature measurements of the Mössbauer effect.

The distribution of hyperfine field probabilities in the spectrum at a temperature of 40 K suggests that this spectrum consists of four sextets. According to the probability distribution, the hyperfine field at iron nuclei lies in the range 440–520 kOe, which is higher than the values characteristic of $\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$ (350–480 kOe) [15]. As a result, effective magnetic moment μ_{eff} of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) is slightly higher than that of $\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$ (see table).

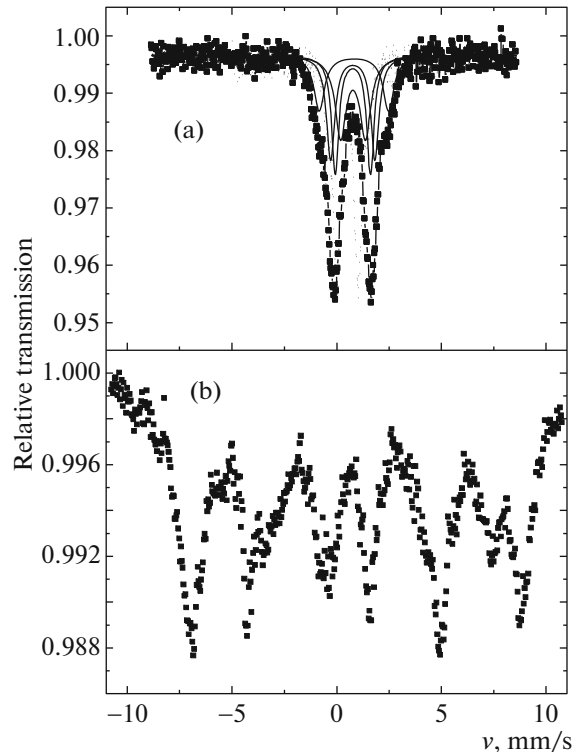


Fig. 3. Mössbauer spectra of the $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) compound at a temperature of (a) 290 and (b) 40 K.

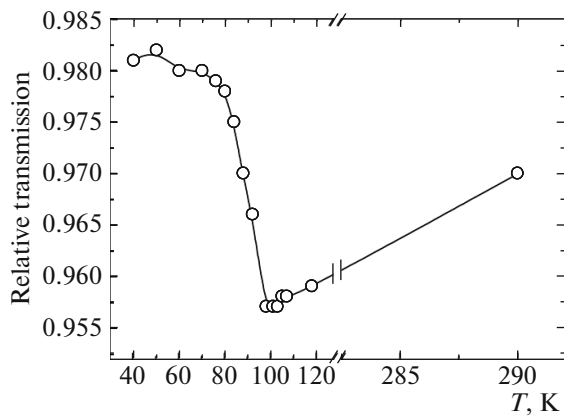


Fig. 4. Temperature dependence of the absorption in Mössbauer spectra.

In the case of magnetic transition, the spectra have the Zeeman splitting, and the relative absorption becomes minimal at low velocities, where the absorptions of the doublet and the sextet differ sharply. Using this phenomenon, we determined the magnetic transition temperature. In our case, the transition temperature lies in the range of the temperature dependence of the absorption spectra with the sharpest change in the relative absorption in the spectra, which corresponds to the temperature range 82–98 K (Fig. 4). In this range, the lines of the paramagnetic doublet broaden due to the hyperfine interaction of the magnetic moment of the iron nucleus and its electron shell. Because of a nonuniform iron distribution over the sample, the magnetic transition temperature is taken to be the center of the temperature range. Then, we have $T_C = 90 \pm 2$ K with allowance for the measurement error. This temperature agrees with the data of magnetic measurements, and the small discrepancy can be related to the characteristic time of the excited state of iron nuclei in the Mössbauer effect experiment. The monotonic increase in the absorption at temperatures above the magnetic transition temperature is associated with the temperature shift and an increase in the amplitude of elastic vibrations in the sample.

5. DISCUSSION

When some cobalt cations are substituted in $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$), the major part of iron ions occupy nonequivalent sites 2 and 4 [16]. The strong bonding of iron ions at these sites [12] leads to an increase in the antiferromagnetic interactions, which brings about a change in the paramagnetic Curie temperature. A low iron ion concentration in the crystal structure doubles the transition temperature ($T_C = 84$ K) as compared to this temperature in Co_3BO_5 , and the ferrimagnetic type of ordering and the direction of the easy axis (axis **b**) are retained.

The effective magnetic moment of $\text{Co}_{3-x}\text{Fe}_x\text{BO}_5$ ($x = 0.10$) is close to the theoretical value, which supports the fact that the orbital moment of cobalt is frozen. The decrease in the effective magnetic moment with increasing Fe^{3+} ion concentration (in the row from $\text{Co}_{2.90}\text{Fe}_{0.10}\text{BO}_5$ to Co_2FeBO_5) seems to be paradoxical. Several examples of this behavior are known (e.g., $\text{Fe}_x\text{Si}_{1-x}$ alloys) [20]. This nonstandard behavior is explained by the decisive role of interactions in the second coordination shell [21]. The mechanism of influence of the second coordination shell in ludwigites can be actualized through planar BO_3 groups. These groups represent a connecting link for zigzag walls through the iron ions located at nonequivalent sites 2 and 4. The effect of this mechanism can be significant at a low content of the kind of cations to be doped in the ludwigite structure. It was shown that a small copper addition led to a low magnetic moment in $\text{Co}_{2.88}\text{Cu}_{0.12}\text{BO}_5$ [19].

A triangular arrangement of magnetic cations in the ludwigite structure was detected in [9, 15]. The appearance of additional antiferromagnetic interactions at the expense of Fe^{3+} in this configuration of magnetic ions inevitably increases the level of frustrations in the magnetic structure. However, because of a low Fe^{3+} content, the level of frustrations is too low for the magnetic system to be divided into two independent magnetic sublattices, as in the case of samples with a significantly higher iron ion content, namely, Co_2FeBO_5 [9] and $\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$ [15].

6. CONCLUSIONS

The magnetic properties of single-crystal Co–Fe ludwigites with a low iron content were studied. The low content of iron ($x = 0.10$) was shown to cause a sharp increase in the transition temperature, and the magnetic transition, the easy magnetization direction typical of Co_3BO_5 were retained in this case. It was shown that the magnetic transition temperature can be determined by analyzing the change in the absorption during the Zeeman splitting of Mössbauer spectra.

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