Uniaxial magnetic anisotropy in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ compared to Co$_3$O$_2$BO$_3$ and Fe$_3$O$_2$BO Ludwигites

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Magnetic and Mössbauer spectroscopy (MS) measurements have been performed on a single crystal of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ with Ludwígite structure. Two magnetic transitions ($T_N$ = 115 K and $T_C$ = 70 K) were traced from the ac susceptibility temperature dependence. The MS spectra as a function of temperature clearly show the onset of magnetic ordering below 115 K. Magnetization measurements on the parent Co$_3$O$_2$BO$_3$ and Fe$_3$O$_2$BO$_3$ compounds have been done for comparison. In Fe$_2$O$_2$BO$_3$, the anisotropy of the different phases has been determined, showing that the anisotropy axis changes from the $a$ to the $b$ axis in the low-temperature antiferromagnetic phase. High magnetic uniaxial anisotropy has been detected for both Co$_3$O$_2$BO$_3$ and Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$. From the angle-dependent magnetization measurements it is found that in both compounds the easy axis of magnetization is the $b$ [010] axis, where an antiferromagnetic component is superimposed on the main ferromagnetic component. In the $c$ direction the behavior is purely antiferromagnetic. In Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$, a strong reduction of the remanent magnetization and a very strong increase in coercive field along the $b$ axis with respect to those found in Co$_3$O$_2$BO$_3$ were observed from magnetic hysteresis cycles measured below $T_C$. The increase of coercive field is caused by the increase of defects upon Co substitution by Fe.

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I. INTRODUCTION

Homometallic and heterometallic oxyborates with one or several transition metal ions have been intensively investigated owing to their interesting magnetic and structural properties. These materials crystallize in several structures. Oxyborates with a Ludwígite crystal structure (space group $Pbnm$, $Z = 4$) are of the general formula $M_2'M'(BO_3)O_2$ where $M$ acts as a divalent ion and $M'$ is trivalent. Both types of ion occupy the four nonequivalent crystallographic positions (Fig. 1).

In Wyckoff notation these positions are $2a$, $2d$, $4g$, and $4h$ and we number them as $1$, $2$, $3$, and $4$ correspondingly. The probability of occupation by a $d$- or trivalent ion is different for each position. The Ludwígite crystal structure consists of low-dimensional subunits: two three-leg ladders (3LLs) of different types. The columns of edge-sharing octahedra form zigzag walls spreading along the crystallographic $c$ axis. Mixed valence, complex distribution of magnetic ions among crystallographic positions, and strong electron correlations allow a variety of magnetic structures, charge ordering, and structural and electronic transitions to appear. The heterometallic compounds, where $M$ and $M'$ are ions of different sorts, have been so far the object of different studies.1–4

The ions in the 4–2–4 positions form so-called triads arranged as the rungs of a three-leg ladder of type I, which constitutes the main element of the Ludwígite crystal structure. The distance between the transition ions in the sites 2 and 4 is the shortest and allows direct overlap of their electron orbitals. In addition, the ions in the 1 and 3 positions form a three-leg ladder of type II. [Note: we adhere to the notation given in Ref. 5 for the Fe sites and triads (see Fig. 1).]

These series have attracted much interest after the observation of a phase transition in Fe$_2$O$_2$BO$_3$ at $T_{CD}$ = 283 K due to excitonic instability.6,7 Short and long Fe–Fe bonds are formed in the 4–2–4 triads in the direction perpendicular to the axis of the ladder, with a doubling of the cell parameter on the $c$ axis that affects the magnetic properties of the material. In this work the magnetic properties of the substitutional compound Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ are studied and compared to those of the parent compounds Co$_3$O$_2$BO$_3$ and Fe$_3$O$_2$BO$_3$—the two homometallic oxyborates with Ludwígite structure available now.

At present there exist quite some experimental data for Fe$_3$O$_2$BO$_3$: x-ray diffraction,5,6,8 neutron powder diffraction (NPD),5,9 magnetic measurements,6,10 Mössbauer spectroscopy (MS),5,10–14 electron paramagnetic resonance,15 and theoretical works.7,16 The properties of this compound are summarized as follows:

(a) Four phase transitions in Fe$_3$O$_2$BO$_3$ with preferable occupation of nonequivalent crystallographic positions by Fe ions in varying valence states have been observed. Early MS experiments5 have shown that the sites 1 and 3 are occupied by Fe$^{3+}$ ions, while sites 2 and 4 were apparently occupied by Fe$^{3+}$ ions. (1) It undergoes a structural transition at $T_{CD}$ = 283 K, when being cooled, in the form of a subtle dimerization of iron ion pairs along 3LLs type I and charge localization,6,11 while the Fe$^{2+}$ (sites 1 and 3) play no role in this transition.11 Above $T_{CD}$ the ions in the sites 2 and 4 are occupied by Fe$^{3+}$ cations with one additional electron per rung, while below $T_{CD}$ mixed-valence ion pairs are formed.15 The magnetic state is paramagnetic (PM). (2) At $T_N$ = 112 K, there is an antiferromagnetic transition (AFM1) where the Fe$_2$ and Fe$_4$ moments become ordered, and they
share one electron in a mixed-valence state. Otherwise, Fe\textsubscript{1} and Fe\textsubscript{3} sublattices are disordered, although Fe\textsubscript{3} is subject to a transferred weak hyperfine field from the already ordered Fe\textsubscript{2} and Fe\textsubscript{4} sublattices. (3) On further cooling, a new transition at $T_{N2} = 74$ K is observed where Fe\textsubscript{1} and Fe\textsubscript{3} also become ordered, and all other Fe moments reorient giving rise to a canted weak ferromagnetic (F) phase. Mixed-valence pairs in the Fe\textsubscript{2}-Fe\textsubscript{2}-Fe\textsubscript{4} rungs were clearly observed. (4) Below $T_{N3} = 50$ K there is charge order in the mixed-valent pair and the extra electron is localized at Fe\textsubscript{2}.\textsuperscript{10,11} The low-temperature phase was reported as antiferromagnetic (AFM\textsubscript{2}).\textsuperscript{14} In all these results an electron hopping mechanism of the extra electron within the rung and between rungs is invoked to explain the different transitions.

(b) In a recent recent x-ray and NPD study\textsuperscript{8} it is stated that (1) below $T_{CD}$ the magnetic phase is paramagnetic. (2) Below $T_{N1} = 112$ K the high-temperature antiferromagnetic (AFM\textsubscript{1}) phase consists of Fe\textsubscript{2}-Fe\textsubscript{2}-Fe\textsubscript{4} AFM chains ferromagnetically coupled along the rungs of the 3LLs of type I, with the moments oriented in the $b$ direction, and with practically identical moment value between the three Fe cations. In contrast, the Fe\textsubscript{1} and Fe\textsubscript{3} in 3LLs of type II support no magnetic moment. (3) Below $T_{N2} = 74$ K, (F) phase, the magnetic cell unit is doubled ($Z = 8$), the Fe\textsubscript{1} and Fe\textsubscript{2} belonging to 3LLs of type II develop a nonzero magnetic moment in the $a$ direction, and order as ferromagnetic chains coupled antiferromagnetically along the $c$ axis. It is reported that the Fe\textsubscript{1} and Fe\textsubscript{3} moments are different and opposed, giving rise to a net moment in the $a$ direction of 2.36 $\mu_B$/f.u. Thus, there are some conflicting results between the MS and NPD studies. Of course, MS is a local probe, while NPD is a bulk one, so some differences may be expected. Notwithstanding this fact, the differences are that (1) the WF phase is rather a ferrimagnetically ordered magnetic phase according to NPD and (2) the AFM\textsubscript{2} phase is not observed in NPD.

In the case of the homometallic Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3}, there is scarce information available, because high-quality and large enough crystals were obtained only recently.\textsuperscript{17-20} At first, it seemed reasonable to assume the properties of Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} to be analogous to those of Fe\textsubscript{3}O\textsubscript{2}BO\textsubscript{3}. However, the extensive study of the structural, magnetic, and thermodynamic properties of Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} showed that, in contrast,

(a) there is no structural transition in this compound;
(b) there is no partial magnetic ordering.

The investigations of Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} are not completed up to now, and its magnetic structure is not precisely defined. However, a magnetic and thermodynamic study, carried out in Ref.\textsuperscript{20}, clearly showed only one magnetic transition near $T_N = 42$ K. Below this temperature the magnetic order is of ferrimagnetic or weak ferromagnetic type with an $ab$ easy plane anisotropy.\textsuperscript{18} The picture of magnetic ordering is much simpler for Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} than for Fe\textsubscript{3}O\textsubscript{2}BO\textsubscript{3}.

So, surprisingly, the structural and magnetic properties of Fe\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} and Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} appear to be quite different. This unexpected difference has led to renewed interest in the mixed Co-Fe ludwigites. In this paper, we have partially substituted Co by Fe ions and synthesized single-crystals of Co\textsubscript{3-x}Fe\textsubscript{x}O\textsubscript{2}BO\textsubscript{3} to study their magnetic properties in comparison with the parent compounds. We reconsidered first the two pure compounds to determine their anisotropic behavior, so that a detailed comparison could be established. In Ref.\textsuperscript{21}, devoted to the mixed compound Co\textsubscript{2}Fe\textsubscript{O}BO\textsubscript{3}, it was established that the magnetic properties of this ludwigeite are close to those of Fe\textsubscript{3}O\textsubscript{2}BO\textsubscript{3} and not to Co\textsubscript{3}O\textsubscript{2}BO\textsubscript{3}. However, for $x = 0.75$, there is no evidence of the structural transition which takes place in Fe\textsubscript{3}O\textsubscript{2}BO\textsubscript{3}.

## II. EXPERIMENTAL TECHNIQUES

Single crystals of Co\textsubscript{3-x}Fe\textsubscript{x}O\textsubscript{2}BO\textsubscript{3} were grown by the flux method in the system Co\textsubscript{3}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}/B\textsubscript{2}O\textsubscript{3}/PbO-PbF\textsubscript{2}. The relative content of Co and Fe ions in the prepared compounds was first estimated from the mass ratio of the initial components, Fe\textsubscript{2}O\textsubscript{3}/(Fe\textsubscript{3}O\textsubscript{4} + Co\textsubscript{3}O\textsubscript{4}), and was later checked by X-ray and Mössbauer measurements. At relatively high Co:Fe ratio in the solution (>$2.5$) we have succeeded in preparing high-quality single crystals of Co\textsubscript{3-x}Fe\textsubscript{x}O\textsubscript{2}BO\textsubscript{3} with ludwigeite structure and maximal substitution ($x$ value) near 1. All the samples were of needle shape up to 4 mm long. The maximal sample mass was about 1.2 mg. By lowering the Co:Fe concentration ratio in the solution a tendency to the synthesis of the warwickite phase appears in our synthetic process. At equal concentrations of cobalt and iron ions in the solution, single crystals of warwickite structure with lattice parameters $a = 3.134(2)$, $b = 9.269(7)$, and $c = 9.430(7)$ were grown.

The x-ray diffraction measurements were performed with a SMART APEX II diffractometer (Mo $K\alpha$ radiation, CCD detector). The scanning angle $2\theta = 5.4^\circ-58^\circ$ ($R1 = 1.40\%$, $wR2 = 3.31\%$).

The $^{57}$Fe Mössbauer spectra were recorded at temperatures between 80 and 300 K in transmission geometry with a standard spectrometer operating in the constant acceleration regime. A nitrogen flow cryostat was used for the
low-temperature measurements. The γ-ray source $^{57}\text{Co}(\text{Rh})$ was at room temperature, and the isomer shifts were measured relative to the metal $\alpha$-Fe at room temperature. The number of channels used was 1024. The spectrometer linewidth with a standard $\alpha$-Fe absorber and the NaI(Tl) detector is $<0.25$ mm/s. The spectra were fitted with the UNIVEMMS program.

ac susceptibility measurements were performed in a superconducting quantum interference device (SQUID) magnetometer with ac option, in the frequency range $10 < f < 937$ Hz, with an exciting field of 4 Oe. The angle-dependent magnetization $M(\theta, H, T)$ on oriented single crystals was measured with a rotating sample holder option in the SQUID magnetometer up to 50 kOe and with a vibrating sample magnetometer up to a bias field of 90 kOe. The temperature ranges are shown in Sec. IV.

The samples are highly anisotropic, so they were oriented and placed in the sample holder along the desired axis with a four-circle x-ray diffractometer. They were positioned using vacuum grease and fixed with glue to prevent them from falling. For the sake of comparison with Co$_3$O$_2$BO$_3$ and Fe$_3$O$_2$BO$_3$, their magnetic properties which are not available in the literature, like hysteresis cycles of an oriented single crystal, were measured.

III. X-RAY DIFFRACTION AND MÖSSBAUER EFFECT

The crystallographic structures of the single crystals Co$_3$O$_2$BO$_3$ and Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ was solved in detail by means of single-crystal x-ray diffraction, and the results were given in Ref. 22. For both compounds the space group is $Pbam$. The lattice parameters of the parent compound Co$_3$O$_2$BO$_3$ are in good agreement with those published earlier. For the solid solution ludwigite Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ the lattice parameters are $a = 9.282$, $b = 12.231$, and $c = 3.029$ Å. According to the x-ray diffraction data there is a pronounced preference in the occupation of distinct crystallographic sites by iron ions. Site 4 is the most preferable (similar data were obtained in Ref. 21 for Co$_2$FeO$_2$BO$_3$), with site 2 the next preferred.

The room temperature (RT) Mössbauer data of Ref. 22 have shown that iron enters into the ludwigite structure mostly in a trivalent state and nonuniformly distributed in the lattice. According to the RT MS, site 4 possesses the highest occupation factor for Fe ions (0.78), site 2 is the next (0.18), and for sites 1 and 3 the iron occupation factors are small (0.1 and $<0.01$, respectively). Thus, according to the investigations described in Ref. 21 and our previous work, iron ions clearly prefer the positions inside the type-I triads.

In the present work we investigated the temperature evolution of the MS spectra in the temperature interval 80–300 K. The spectra were obtained for a powder of crushed Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ single crystals (see Fig. 2). The most evident feature is the pronounced temperature evolution upon cooling which begins near 110 K, where the splitting of quadrupole doublets into sextets by hyperfine interaction becomes observable. Remarkably, magnetic ordering in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ appears near the same temperature as in Fe$_3$O$_2$BO$_3$, while Co$_3$O$_2$BO$_3$, much closer in cobalt content to our Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$, does not show such a transition.

In analyzing the MS spectra we proceeded from the assumption that iron ions occupy a discrete set of crystallographic sites, as is previously shown in Refs. 21 and 22, but are not randomly distributed in the lattice. In the paramagnetic region at temperatures between 120 and 300 K, the MS spectra can be well described by four quadrupole doublets $D_1$, $D_2$, $D_3$, and $D_4$. As shown in Fig. 3, the isomer shift values $\delta$ for three doublets $D_2$, $D_3$, and $D_4$ are in the range of 0.28–0.47 mm/s (at 130 K) which is typical of iron ions in the trivalent Fe$^{3+}$ high-spin state. The isomer shift for doublet $D_1$ is much higher ($\approx 0.85$ mm/s) and its value is close to that for iron ions in the intermediate (Fe$^{2.5+}$–Fe$^{2+}$) valence state.

FIG. 2. Representative Mössbauer spectra of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ at selected temperatures.
We found that the temperature dependences of the isomer shift values in the paramagnetic state (see Fig. 3) are close to those for Fe$_2$O$_2$BO$_3$,\textsuperscript{13} and in general they follow the Doppler second-order (temperature) shift.

The doublet $D_4$ clearly dominates in area, and it seems reasonable to assign it to the Fe$^{3+}$ in site 4. Between 110 and 120 K magnetic splitting of the doublets begins and below 110 K the MS spectra may be described by four sextets and one low-area doublet with $\delta = 0.75$ mm/s and quadruple splitting $\Delta_1 = 1.25$ mm/s. In the paramagnetic state this doublet belongs to the $D_1$ component in Fig. 3.

The MS spectra of the parent Fe$_3$O$_2$BO$_3$ between 70 and 115 K have also been described by some sextets and one doublet.\textsuperscript{13,14} The doublet was assigned to the Fe$^{2+}$ ions in site 1, and it was supposed\textsuperscript{14} that these ions are magnetically disordered in Fe$_3$O$_2$BO$_3$ down to $T = 70$ K. Fe$^{2+}$ in site 3 was also considered as disordered, though a weak hyperfine field of transferred origin was observed. The Fe$_2$ and Fe$_4$ ions are magnetically ordered near $T = 110$ K.

Most probably, the doublet $D_1$ in our sample also corresponds to the paramagnetic Fe$^{2+}$ (or/and Fe$^{2.5+}$) ions, but due to the small doublet area (about 5% of the total iron area) its relative contribution to magnetic properties is negligible.

Below $T = 110$ K, the isomer shift and quadruple splitting values for the Fe$^{3+}$ iron in the dominant site 4 are temperature independent ($\delta = 0.46$ mm/s, $\Delta = 1.0$ mm/s), while the magnetic hyperfine field at iron nuclei, $B_{hf}$, increases as the temperature decreases (Fig. 4).

Comparing our MS data for Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ with the same obtained for the parent compound Fe$_3$O$_2$BO$_3$,\textsuperscript{13} one can conclude that the picture has a pronounced similarity in both cases, mainly consisting in the evidence of magnetic ordering near 110 K. Also in both considered ludwigites there is a fraction of the magnetic ions remaining disordered down to 70 K. Probably they are Fe$^{2+}$ ions in crystallographic sites 1, but in our case of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ their contribution is small.

In this section the results obtained from rotating angle $M(\theta_H,T)$ and $M(H)$ measurements for the parent compounds Co$_2$O$_2$BO$_3$ and Fe$_2$O$_2$BO are presented first. This facilitates the understanding of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ magnetic properties. It is known that in both Co and Fe pure compounds the $c$ axis is a hard magnetization direction,\textsuperscript{18} therefore only the anisotropy in the $ab$ plane has been studied below.

A. Co$_3$O$_2$BO$_3$

This compound has just one magnetic phase transition to a ferromagnetic phase at $T_C = 42$ K.\textsuperscript{20} In $M(\theta_H,T)$ measurements we could determine that the easy magnetization direction (EMD) in the ordered phase is the $b$ axis (not shown). In Fig. 5 the hysteresis cycles for the compound Co$_3$O$_2$BO$_3$, measured below $T_C$ on a single crystal along its $b$ axis, are given. Although the remanent magnetization $M_r$ remains practically constant, the coercive field $H_c$ increases as

![FIG. 5. (Color online) Hysteresis cycles of a Co$_3$O$_2$BO$_3$ sample as a function of $T(T < T_N)$. $H$ parallel to $b$ axis.](image)
TABLE I. Collected magnetic transition temperature data for Co$_{3-x}$Fe$_x$O$_2$BO$_3$ from $\chi_m$ or $M(T)$ (rows 1–3), easy magnetization direction at $T<T_C$ (row 4), and data extracted from high-$T$ susceptibility (rows 5–8) and from hysteresis cycles (rows 9 and 10). The references to other work are indicated by superscripts. By the asterisk we mark the values calculated by us using the data presented in the corresponding reference. The present work results are shown in bold.

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<td>b</td>
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<td>0.029(3)</td>
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the temperature is lowered. The small slope of $M(H)$ at high fields indicates the existence of a small superimposed antiferromagnetic susceptibility, with the value $\chi_{AFM} = 0.024(1)$ (emu/mol) (see Table I). Additionally, in the hysteresis cycles measured at fixed temperature $T = 2$ K, Fig. 6, the coercive field increases when the angle $\theta_H$ between the applied field and the $b$ axis increases, following a $1/\cos\theta_H$ dependence.

### B. Fe$_2$O$_2$BO$_3$

This compound is known to undergo a charge ordering transition at $T_{CD} = 283$ K, and three successive magnetic transitions as the temperature is lowered (PM-AF flux-AFM2). The transition temperatures we have measured are $T_{N1} = 110.7(5)$ K, $T_{N2} = 70.0(5)$ K, and $T_N = 30.0(5)$ K, in reasonable agreement with previous findings.$^{10}$ It is convenient to remember in the discussion, as determined from NPD measurements,$^8$ that in all ordered phases the Fe$_2$ and Fe$_3$ sublattice magnetizations are parallel to the $b$ axis, while only in the F phase do the Fe$_3$ and Fe$_4$ sublattice magnetizations bear a nonzero moment along the $a$ axis. Although the AFM2 phase could not be discerned from NPD, MS gave evidence of this low-temperature phase when the angle $\theta$ between $B_H$ and $V_{zz}$ (electric field gradient) for the different Fe sites became different from those in the AFM1 or F phase.$^{10,11,14}$

Surprisingly, the detailed magnetization anisotropy directions of the different phases in this much studied compound have not been unambiguously determined up to date, since the measurements were performed on randomly oriented powders or small collections of crystals. To unravel this question the same methodology of rotating sample magnetometry around the $c$ axis has been applied to a Fe$_2$O$_2$BO$_3$ single crystal. In Fig. 7, where the $M(\theta,T)$ data measured at 50 kOe are shown, it is evidenced that the antiferromagnetic phase AFM1 ($T_{N1} > T > T_{N2}$) is anisotropic, with the $a$ axis as EMD at $H = 50$ kOe. Below $T_{N2}$, the ferromagnetic phase F is strongly anisotropic, with the $a$ axis as the EMD. The observed magnetization reversal process is characteristic for a system of anisotropy field much higher than the coercive field (see below).

In Fig. 8 the hysteresis cycles measured along the $a$ direction at different temperatures are depicted. As the compound is cooled from room temperature, at $T_{N2}$ in the F phase the cycle opens, as expected for a ferrimagnetic phase. The coercive field increases with decreasing temperature and the remanence $M_r$ decreases. At $T = 30$ K there is no coercivity and $M_r$ becomes zero, as the system transforms into the AFM2 phase (see Fig. 8 inset). This temperature is 10 K lower than $T_{N2}$ reported earlier.$^{10}$ In stark discrepancy with the value of $M_r = 2.36 \mu_B$/f.u. deduced from the NPD, we find that $M_r(T_{N2}) \approx 0.16 \mu_B$/f.u., which, on the other hand, is in good agreement with the value given in Ref. 10 for a collection of crystals ($\approx 0.1 \mu_B$/f.u.). Additionally, in NPD it was found that the Fe$_3$ and Fe$_1$ magnetic sublattices give rise to the ferrimagnetic character since they have opposite contributions to the magnetization in the $a$ direction.$^8$ Therefore, the reduction of $M_r$ indicates that there is a compensation process of the Fe$_3$ and Fe$_3$ sublattice magnetization as the temperature decreases below $T_{N2}$.

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FIG. 6. (Color online) Hysteresis cycles of a Co$_2$O$_2$BO$_3$ single crystal at $T = 2$ K, as a function of rotation around the $c$ axis. The extreme values of $\theta_H$ are indicated. The inset shows the variation of $H_C$ as a function of $\theta_H$. The fit to a $1/\cos\theta_H$ function is also shown.
The high-field slope of the hysteresis curves allows us to determine the subjacent antiferromagnetic susceptibility $\chi_{AFM}(T)$ (see Fig. 8 inset). It has the temperature dependence of an antiferromagnetic system measured along the parallel direction, with ordering temperature at the point of maximum slope below the maximum, which corresponds nicely to the $T_{N2}$ temperature. Since only below this temperature do Fe$_1$ and Fe$_3$ sublattice moments become nonzero, as observed by NPD, it can be stated that these sublattices are at the origin of the AFM subjacent susceptibility along the $a$ axis. This interpretation also agrees with the conclusion reached from MS that Fe$_1$ and Fe$_3$ sublattices do not order at $T_{N1}$, although some polarization from the transferred field of the ordered sublattices is present on Fe$_3$. Thus, the Fe$_1$ and Fe$_3$ sublattices only order below $T_{N2}$.\cite{14}

$M_a(T)$ and $M_b(T)$, measured at 50 kOe along the $a$ and $b$ axes, respectively, illustrate this compensation behavior clearly (Fig. 9). The transition at $T_{N1}$ gives rise to a change of slope in $M_b$ only, while the transition to the ferrimagnetic ordered phase at $T_{N2}$ shows as a peak in both $M_a(T)$ and $M_b(T)$, as could be expected for the establishment of ferrimagnetism.\cite{10}

Below $T_{N2}$ there is a decrease in $M_a(T)$ as a consequence of the progressive compensation of the Fe$_1$ and Fe$_3$ sublattice magnetization. In fact, at $T \approx 40$ K $M_a(T) = M_b(T)$ and the anisotropy is planar within the $ab$ plane. Below this temperature, $b$ is the EMD of the anisotropic AFM$_2$ phase; i.e., orthogonal to that in the AMF$_1$ or F phase.

**C. Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$**

First, the evidence for the presence and character of the magnetic phase transitions in this compound is obtained from the temperature-dependent susceptibility and magnetization measurements, and later the anisotropy of the single crystal is analyzed by means of the angle-dependent magnetization and hysteresis cycle data.

**1. Magnetization temperature dependence**

Field-cooled (FC) and zero-field-cooled (ZFC) dc magnetization measurements were performed with applied fields of 100 and 600 Oe on a single crystal. As is seen in Fig. 10 there is a sharp increase of the FC and ZFC magnetization near $T = 70$ K; then the FC value decreases on cooling and the ZFC value drops to zero, being peaklike. Comparing the present data for Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ with the same obtained in Ref. \cite{21} for Co$_2$FeO$_2$BO$_3$, one can see that they are very similar. The shape of the magnetization temperature dependence is closer to that of Fe$_3$O$_2$BO$_3$,\cite{10} and it is rather different from the same for Co$_3$O$_2$BO$_3$\cite{18,20}.

There is no sign of the magnetic ordering...
UNIAXIAL MAGNETIC ANISOTROPY IN Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$

at 42 K, the characteristic magnetic transition temperature of Co$_3$O$_2$BO$_3$, indicating the absence of any spurious fraction of the pure compound in the sample; i.e., the sample is homogeneous.

2. ac magnetic susceptibility

The F transition can be clearly observed in the ac magnetic susceptibility temperature dependence at $T_C = 70$ K. For these measurements a single crystal was not large enough to give a good signal-to-noise ratio, so the collective signal for several samples was measured. The temperature behavior of the real $\chi'$ and imaginary $\chi''$ components of the magnetic susceptibility is shown in Fig. 11, where a large peak at 70 K and a small anomaly near 115 K are visible. The latter is reminiscent of the AFM1 transition in Fe$_3$O$_2$BO$_3$ and corresponds to the anomaly near 115 K. The arrows indicate the magnetic transitions: a large peak near 70 K and a small anomaly near 115 K.

FIG. 10. (Color online) The magnetization temperature dependence of a Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ single crystal.

These ac susceptibility data are also very similar to those for Co$_3$Fe$_2$O$_5$BO$_3$. The analysis of the $\chi''$(ω) obtained with the ZFC measurements allows determination of the Curie constant $C$ and the Curie-Weiss temperature $\theta_C$. The results are given in Table I, together with the values for the end members of the row and Co$_3$Fe$_2$O$_5$BO$_3$. For all compounds the $\theta_C$ value is negative, pointing out the predominance of antiferromagnetic interactions. The modulus of $\theta_C$ increases with Fe content in a regular trend. Consequently, the AFM component of the exchange interaction values is higher for iron ions than for cobalt ions. Our results are on the whole consistent with those previously obtained except for the value of the effective magnetic moment in the paramagnetic phase, which in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ is closer to that of Co$_3$O$_2$BO$_3$ than that of Co$_3$Fe$_2$O$_5$BO$_3$, as shown below. Earlier, the authors of Refs. 20 and 21 defined the effective magnetic moment values averaged for one magnetic ion. In our Table I their results are recalculated as effective magnetic moments per formula unit. As for the effective magnetic moment of Fe$_3$O$_2$BO$_3$, defined in Ref. 6, we have calculated a value of $\mu_{eff} = 9.34 \mu_B$ per formula unit from their value for the Curie constant $C = 10.9$ emu K/mol Oe. This value is presented in Table I (row 5) for comparison. All the values calculated by us using the data of Refs. 6, 8, 20, and 21 are marked by an asterisk.

It is important to estimate the expected values of the effective moment per formula unit in the paramagnetic phase for the considered set of ludwigite compounds to understand whether the orbital moments of magnetic ions are quenched or not. To analyze this question, first, the orbital component of magnetic moment is neglected and the spin component of the effective moment is calculated according to the formula

\[
\mu_{eff} = \sqrt{\sum \mu_i^2},
\]

Orbital component. In this case

\[
\mu_{eff} = \sqrt{\sum \mu_i^2} = \sqrt{\sum g_i^2 S_i (S_i + 1)},
\]

Wall motion of the ferrimagnetic domains. This peak is slightly shifted to higher temperature as the frequency increases.

These ac susceptibility data are also very similar to those for Co$_3$Fe$_2$O$_5$BO$_3$. The analysis of the $\chi''$(ω) obtained with the ZFC measurements allows determination of the Curie constant $C$ and the Curie-Weiss temperature $\theta_C$. The results are given in Table I, together with the values for the end members of the row and Co$_3$Fe$_2$O$_5$BO$_3$. For all compounds the $\theta_C$ value is negative, pointing out the predominance of antiferromagnetic interactions. The modulus of $\theta_C$ increases with Fe content in a regular trend. Consequently, the AFM component of the exchange interaction values is higher for iron ions than for cobalt ions. Our results are on the whole consistent with those previously obtained except for the value of the effective magnetic moment in the paramagnetic phase, which in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ is closer to that of Co$_3$O$_2$BO$_3$ than that of Co$_3$Fe$_2$O$_5$BO$_3$, as shown below. Earlier, the authors of Refs. 20 and 21 defined the effective magnetic moment values averaged for one magnetic ion. In our Table I their results are recalculated as effective magnetic moments per formula unit. As for the effective magnetic moment of Fe$_3$O$_2$BO$_3$, defined in Ref. 6, we have calculated a value of $\mu_{eff} = 9.34 \mu_B$ per formula unit from their value for the Curie constant $C = 10.9$ emu K/mol Oe. This value is presented in Table I (row 5) for comparison. All the values calculated by us using the data of Refs. 6, 8, 20, and 21 are marked by an asterisk.

It is important to estimate the expected values of the effective moment per formula unit in the paramagnetic phase for the considered set of ludwigite compounds to understand whether the orbital moments of magnetic ions are quenched or not. To analyze this question, first, the orbital component of magnetic moment is neglected and the spin component of the effective moment is calculated according to the formula

\[
\mu_{eff} = \sqrt{\sum \mu_i^2} = \sqrt{\sum g_i^2 S_i (S_i + 1)},
\]

FIG. 11. (Color online) The real and imaginary components of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ magnetic susceptibility temperature dependences. The arrows indicate the magnetic transitions: a large peak near 70 K and a small anomaly near 115 K.
per formula unit, $\mu_J$, are in Table I (row 7). Comparing the calculated values of $\mu_S$ and $\mu_J$ with the experimental value $\mu_{\text{eff}}$, one can see that the spin value $\mu_S$ is closer to it than is $\mu_J$. So we can conclude that the orbital moments of Co and Fe ions are almost quenched.

3. Magnetic hysteresis

The main characteristic of Co$_{25}$Fe$_{75}$O$_2$BO$_3$ is its high anisotropy. Indeed, with the rotating sample holder option which allows us to measure the projection of the magnetization along the field direction it was found that the easy axis of magnetization is $b$, the [010] axis. This is evidenced in Fig. 12, where we show the projection of the magnetization of Co$_{25}$Fe$_{75}$O$_2$BO$_3$, $M(\theta_H,T)$ at $H = 50$ kOe, in the direction of the applied field upon rotation around the $c$ axis.

At this field and $T = 5$ K the anisotropy along the $b$ axis is so strong that the magnetization remains oriented along that axis during a 180° revolution, and $M(\theta)$ is fitted with a cosine function superimposed onto a constant antiferromagnetic component. This proves without any ambiguity that the magnetic anisotropy of this crystal is uniaxial along the $b$ axis direction, and implies that at this field and temperature the crystal is saturated in the single-domain state. When the temperature rises, the anisotropy decreases, so that above a certain temperature the applied constant field is capable of inducing a magnetization reversal from the [010] direction to the [0\bar{1}0] direction (Fig. 13, for $T = 40$ K). The reversal of the magnetization is very abrupt, that is, the effect due to the field component perpendicular to the $b$ axis is reversible but very small, and remains so until the magnetization reversal, while the magnetization reorientation in the $b$ direction is irreversible. Therefore, the field component parallel to the $b$ axis produces the magnetization reversal when $H \cos \theta_H \approx H^b_C$, where $H^b_C$ is the coercive field in the $b$ direction. This behavior is characteristic for systems where the coercive field is much weaker than the anisotropy field. The magnetization reversal cannot occur in unison, but instead by curling or buckling, and the appearance and displacement of domain walls within the sample. It is noteworthy that the anisotropy remains visible above $T_C$ and $T_N$, up to the paramagnetic phase. The coercive fields at 20, 30, and 40 K could be determined by angular rotation of the applied field (Fig. 13, for $T = 40$ K).

We have obtained the following $H_C$ values: 44, 22, and 13 kOe at 20, 30, and 40 K, respectively. As we will see below, these values are similar to the values found from actual hysteresis loops.

Co$_{25}$Fe$_{75}$O$_2$BO$_3$ is highly anisotropic; therefore the $M(H)$ hysteresis cycles have been measured at several temperatures in the directions parallel to the $c$ axis and perpendicular to it ($b$ axis) on a single crystal (Fig. 14), in the temperature range $70 < T < 115$ K. In the $c$ direction the material behaves as a simple antiferromagnet with a linear magnetization curve at all measured temperatures. Thus the magnetic moments in the compound are fully compensated along the $c$ axis. In contrast, in the $b$ direction the hysteresis cycle below 115 K shows an increase in the magnetization which indicates that already noncompensation of the moments sets in below that temperature. Below $T_C$ the hysteresis cycle is open, thereby showing the existence of ferro- or ferrimagnetic ordering. Both curves tend to the same high-field limit, which indicates that the Co sublattice is already contributing to the magnetization in the region $T_C < T < T_N$, but since the Co sublattice is not yet magnetically ordered it is due to polarization of the Co moments by the Fe ordered sublattice.

The coercive field increases drastically as temperature is lowered (Fig. 15), with a measured maximum $H^c_C = 90$ kOe at 10 K. Below that temperature the coercive field becomes larger than the maximum applied field, 90 kOe, of our setup.
This is an extraordinarily high coercivity. Superimposed on this fascinating feature is an AFM component, expressed as the absence of saturation and linear dependence of the magnetization on the field at high fields. This behavior is characteristic for an uncompensated antiferromagnet, or a ferrimagnet. Thus, the high-field branches of $M(H)$ are not saturated, but have a positive slope $\chi_{\text{AFM}}$. The remanent magnetization $M_r$ and dc susceptibility values $\chi_{\text{AFM}}$ extracted from hysteresis loops are collected in Table I together with the data obtained earlier for Fe$_3$O$_2$BO$_3$, Co$_3$O$_2$BO$_3$, and Co$_2$FeO$_2$BO$_3$. The maximum values of $\chi_{\text{AFM}}$ obtained for our sample and those of Fe$_3$O$_2$BO$_3$, Co$_3$O$_2$BO$_3$, and Co$_2$FeO$_2$BO$_3$ are quite close to each other: $\chi_{\text{AFM}} \approx 0.03$ emu/mol. That is, there are several sublattices with AFM coupling but incomplete compensation in this material. It is found that $\chi_{\text{AFM}}$ is practically isotropic at a fixed temperature. In addition, the remanent magnetization $M_r$ is almost independent of $T$ at low temperatures, and at the coercive field the difference between the magnetization in the up and down orientations is $\Delta M = 2M_r$, which implies that the ferromagnetic component of the magnetization is saturated at a value $M = M_r$.

In Fig. 16 the $H_C(T)$ curves found for the three samples are compared along their corresponding EMDs. For Co$_3$O$_2$BO$_3$, $H_C(T)$ in the $b$ direction increases only below 10 K, while for Fe$_3$O$_2$BO$_3$ $H_C^b$ increases rapidly as the temperature decreases once the F phase is reached at $T_N$, and becomes zero below $T_N$. It becomes evident that there is a strong increase of $H_C^b(T)$ upon Fe substitution of Co, i.e., at $T = 10$ K the ratio of $H_C^b$ for Co$_2$Fe$_{0.75}$O$_2$BO$_3$ and Co$_3$O$_2$BO$_3$ is about 40.

The similarity of Co$_2$Fe$_{0.75}$O$_2$BO$_3$ and Fe$_3$O$_2$BO$_3$ in magnetic hardness increase with lower temperature explains the similarity in the FC and ZFC $M(T)$ curves of these two compounds, and, in turn, the rather different $M(T)$ in Co$_3$O$_2$BO$_3$, which only becomes magnetically hard at much lower temperature.

As can be seen for Co$_2$Fe$_{0.75}$O$_2$BO$_3$ (Fig. 17, inset), when an external field is applied at an angle $\theta_H$ from the $b$ direction, the coercive field increases approximately as $1/\cos \theta_H$ (Kondorsky law). The same dependence is found for Co$_3$O$_2$BO$_3$ (Fig. 6, inset). It is justified at low temperatures in view of the fact that the $M(\theta_H)$ curves can be fitted with the expression

$$M(\theta_H) = M_r \cos \theta_H + \chi_{\text{AFM}} H.$$

As mentioned above, the compliance with this $1/\cos \theta_H$ dependence of the angular dependence of the coercive field is characteristic of coercive fields smaller than the anisotropy field. The reason for this behavior may be stress anisotropy or defect pinning of domain walls. Since we are dealing with a single crystal we do not expect stress as the origin of anisotropy but, on the other hand, it is a substitutional system, where many defects in the crystal may be present; therefore, pinned domain walls may account for the coercive field. The coercive field in the $b$ direction due to this mechanism, with $180^\circ$ domain walls...
being created and propagated at the switching field gives a coercive field

$$H_C^{(0)}(\theta_H) = \frac{\gamma}{\cos \theta_H / |M_r|},$$

where $\gamma$ is the domain wall energy and $l$ is the average defect-defect distance. The temperature dependence of this coercive field enters via the dependence of the wall energy on the anisotropy constant $K_1$, $\gamma \propto \sqrt{AK_1}$, where $A$ is proportional to the exchange coupling.\(^{25}\) For comparison, at the same temperature $T = 10$ K, and $\theta_H = 0$ one obtains $H_C^{(0)}M_r = \gamma / l = 8.73 \times 10^6$ and $7.46 \times 10^5$ G\(^2\) for Co\(_{2.25}\)Fe\(_{0.75}\)O\(_2\)BO\(_3\) and Co\(_3\)O\(_2\)BO\(_3\), respectively, i.e., an order of magnitude increase upon the Co substitution by Fe. Since $T_C$ is larger and therefore $A$ is larger for Co\(_{2.25}\)Fe\(_{0.75}\)O\(_2\)BO\(_3\), but not enough to explain the observed increase, and $K_1$ may be similar in both compounds, it can be concluded that the main reason for the increase in coercivity field is the increase of the number of defects in the crystal upon the introduction of Fe, which in turn reduces strongly the average distance between defects, $l$.

The comparison of $M_r$ of Co\(_{2.25}\)Fe\(_{0.75}\)O\(_2\)BO\(_3\) with that of Co\(_3\)O\(_2\)BO\(_3\) may now be done with the present measurements of the hysteresis cycles of the single crystal of the latter compound, since in Ref.\(^{18}\) it could not be discerned whether the $M_r$ data corresponded to a single crystal or a collection of crystals with different orientations. The value found is $M_r = 3.4(1) \mu_B$/f.u., i.e., much larger than the previously published result, most probably because of the fact that our measurement was on an oriented single crystal. Additionally, in the present work the remanent magnetization in the Fe\(_3\)O\(_2\)BO\(_3\) a direction was found in the F phase to be $M_r(T = 65$ K) = 0.16 $\mu_B$/f.u., similar to the average value previously published of 0.1 $\mu_B$ at 70 K,\(^{10}\) and drastically different from the powder neutron diffraction value\(^{6}\) 2.36 $\mu_B$/f.u. On the other hand, the value given for Co\(_{2.25}\)Fe\(_{0.75}\)O\(_2\)BO\(_3\) (0.48 $\mu_B$/f.u.) is half that found for Co\(_{2.25}\)Fe\(_{0.75}\)O\(_2\)BO\(_3\) (0.9 $\mu_B$/f.u.), although we explain this difference in the former compound as due to possible misorientation of the crystal in that paper. From this comparison a very puzzling conclusion is drawn. The effect of substitution of 25% of Co atoms by Fe is a dramatic decrease of $M_r$, which cannot be explained by the Co moments ($\mu_{cCo} = 7.2 \mu_B$) being substituted by Fe moments ($\mu_{cFe} = 8.01 \mu_B$).

One striking result of this work is the drastic reduction of magnetic moment in the $b$ direction with respect to the Co\(_3\)O\(_2\)BO\(_3\) compound. A naive accounting of the magnetic moment per Co in Co\(_3\)O\(_2\)BO\(_3\) yields $m_{Co\text{atom}} = M_r / 3 = 1.15 \mu_B$/Co along the $b$ direction; therefore in Co\(_{2.25}\)Fe\(_{0.75}\)O\(_2\)BO\(_3\) the Co sublattice should account for $m_{Co\text{sublattice}} = 2.58 \mu_B$, while the observed $M_r = 0.9 \mu_B$. The difference can be conjectured to be caused by the Fe moments being oriented with a component of the Fe sublattice $m_{Fe} = -1.68 \mu_B$ ($m_{Fe\text{atom}} = 2.24 \mu_B$/Fe); i.e., opposing the net moment of the Co sublattice. Indeed, if the Fe moments order similarly as in Fe\(_3\)O\(_2\)BO\(_3\), the moments at sites 2 and 4 will be oriented in the $b$ direction and will tend to compensate one another, and will also oppose the Co magnetic moment in that direction. There should be an interplay of compensation of Co moments in the diluted compound and probably Fe-Co antiferromagnetic interactions to account for the reduction of $M_r$.

In Ref.\(^{22}\) a simplified model of Fe substitution is proposed to study the effect of Fe-Co interactions, where only position 4 is assumed to be occupied by Fe. The superexchange interactions between Co-Co and Co-Fe ions are estimated, and the conclusion reached is that the Co$_3$,Fe$_x$ exchange interaction tends to orient the Fe$_4$ magnetic moment in the opposite direction from that of the Co$_4$ moment it has substituted. Although other interactions may be present, this gives us a clue as to the reason for the strong reduction in magnetic moment that we have observed in the $b$ direction.

Another possibility is that Co$^{3+}$ transforms from high-spin to intermediate- or low-spin states upon reduction of cell volume when Co is substituted by Fe. Obviously, the magnetic structure of Co$_3$O$_2$BO$_3$ is not yet known; therefore it is not possible to go further into the analysis of this puzzling result.

V. DISCUSSION AND CONCLUSIONS

The x-ray data obtained in the present work have shown that there are some difficulties in the synthesis of the solid solution Co$_{3-x}$Fe$_x$O$_2$BO$_3$ oxycobaltites with the ludwigite structure with high iron content. When the $x$ value exceeds 1 the material tends to crystallize in the warwickite structure. The unit cell volume of the mixed ludwigites exceeds the values expected from Vegard’s law.

This work provides information on single crystals that clarifies the magnetic properties of the pure compounds along their crystallographic axes. In Co$_3$O$_2$BO$_3$ it has been established that the $b$ axis is the EMD in the ferromagnetic phase and the dependence of $H_c$ with temperature has been found.

In Fe$_3$O$_2$BO$_3$ the $a$ axis is the EMD down to $T_{N3}$, below which it is the $b$ axis. The Fe$_2$ and Fe$_4$ sublattices order antiferromagnetically at $T_{N1}$, and the Fe$_1$ and Fe$_3$ sublattices order as a ferrimagnetic at $T_{N2}$ with their moments parallel to the $a$ direction. The subjacent antiferromagnetic ordering of these sublattices, once the ferrimagnetism is saturated by the
field, is clearly seen to set in at that temperature (Fig. 8 inset). The AFM2 phase is reached continuously at approximately $T_{N2}$, as the temperature decreases from the F phase, by compensation of the Fe and Fe$_3$ oppositely oriented sublattice magnetizations.

In the solid solution Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ the paramagnetic effective magnetic moment per formula unit at high temperatures is slightly higher than for Co$_3$O$_2$BO$_3$, as expected. The spin-only values of the effective magnetic moments in Co-Fe ludwigites appear to be closer to the experimental values than the total one, calculated using $J$ and $g$ values obtained in Ref. 23. This indicates that the orbital moment of magnetic ions in these compounds is quenched to a high degree.

The hyperfine field splitting of the quadrupole doublets into sextets (Fig. 2) and a small anomaly in the magnetic susceptibility near $T_N$ = 115 K (Fig. 11) have been observed, which hint at an antiferromagnetic transition of the 3LL type-I sublattice. Indeed, in Ref. 8, devoted to Fe$_2$O$_3$BO$_3$ it was shown that at this temperature the 3LL type-I sublattice orders while the 3LL type-II sublattice remains without long-range magnetic ordering. The definite clue for the long-range ordering of the 3LL type-I sublattice was the detection of a peak at $T_N$ in the heat capacity of Fe$_3$O$_2$BO$_3$. Such a peak was also detected in Co$_2$Fe$_2$O$_5$BO$_3$, which has the same ac susceptibility bump near 110 K as we have observed in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$. Moreover, in Fig. 14 it is demonstrated that there is a magnetic moment developing in the b direction at 80 K, albeit the compound is not yet magnetically ordered. We conclude that the transition from the PM to the AFM1 phase takes place already at a dilution fraction of Co:Fe of 3:1. So, in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ we deal with partial magnetic ordering as in Fe$_3$O$_2$BO$_3$ in the intermediate region $T_C < T < T_N$, in contrast to absence of this intermediate phase in Co$_3$O$_2$BO$_3$.

The large susceptibility peak at $T_C$ = 70 K and the open hysteresis cycles below this temperature show that Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ orders ferrimagnetically. The frequency dependence of this susceptibility peak may be explained as due to the magnetic domain motion of the ferrimagnetic domains. Ferrimagnetism rather than weak ferromagnetism is preferable to describe this transition since the net moment originates from magnetic moments of different modulus and orientation, rather than from identical moments with near but not complete antiferromagnetic compensation by orientation; however, there is some ambiguity in naming this transition in the literature. The same type of transition is described in Fe$_3$O$_2$BO$_3$ in Ref. 10; its authors propose that this peak shows additional ordering of the ions in the positions 1. More recently, in Ref. 8 it is shown by neutron diffraction that the Fe moments at positions 1 and 3 develop each a different net magnetization, oppositely oriented, giving rise to a ferrimagnetic ordering. So, on one hand, by similarity with Fe$_3$O$_2$BO$_3$, one would expect the few Fe moments entering into sites 1 in the 3LL type-II sublattice to contribute to the net moment in the a direction; however, we observe no net moment in this direction. On the other hand, the compensation of Co and Fe moments in the 3LL type-I sublattice should give a second contribution to the ferrimagnetic moment below $T_C$. The net effect observed is a strong reduction in the ferrimagnetic moment in the b direction and compensated antiferromagnetism in the c direction. In our opinion the frequency dependence of ac susceptibility peak near 70 K in the mixed ludwigites originates rather from the motion of ferrimagnetic domain walls than from partial spin-glass freezing.

It is surprising that in our magnetic data there is no sign of a magnetic phase transition at 42 K, the $T_N$ of Co$_3$O$_2$BO$_3$. Our magnetic results are very similar to those obtained in Ref. 21 for Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$. In that paper, partial magnetic ordering of some of the magnetic ions near 117 K and a spin-glass freezing of the remainder near 70 K is proposed.

The magnetic ordering of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ below $T_N$ has a predominant ferromagnetic moment on the b axis, just as in Co$_3$O$_2$BO$_3$, and antiferromagnetic components in all directions, the contribution being nearly isotropic. The ground state seems to be ferrimagnetic. The remanent magnetization of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ is much lower compared to Co$_3$O$_2$BO$_3$, but the coercive field is much higher. The 1/$\cos \theta$ law followed by the coercive field angle dependence indicates that we are dealing with the case of a very large crystalline anisotropy field, larger than the coercive field. $H_C$ depends essentially on the number of defects in the crystal, while the temperature dependence of $H_C$ is driven by the increase of the anisotropy constant $K_1$ with decreasing temperature.

The anisotropy in the b direction is the same as that in Co$_3$O$_2$BO$_3$ and different from that in the ferrimagnetic phase of Fe$_3$O$_2$BO$_3$, where the EMD is the a axis, according to the present work and neutron diffraction results. For this reason, it is impossible at this stage to conjecture what is the orientation of the Fe inserted moments, except that they compensate strongly the net moment of the Co sublattice, giving rise to a strong decrease of $M_r$. It has been proposed from a simplified model that the Fe$_2$-Co$_3$ superexchange interaction tends to orient the Fe moment in the opposite direction to that of the Co$_3$BO$_3$ that it has substituted, thus explaining partially the strong reduction in $M_r$ observed.

Obviously, neutron diffraction experiments on Co$_3$O$_2$BO$_3$, as reference, and on Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ are needed to clarify this question. An open question is the fact that the anisotropy is very high, as argued in Sec. IV, the orbital moment is highly quenched. The origin of the anisotropy, therefore, has to be related to exchange interactions between the Co and Fe moments.

The magnetic behavior of Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ may also be compared to that of the heterometalic ludwigites with different transition metals Ni and Cu. These compounds undergo three successive magnetic phase transitions at $T_{N1} > T_{N2} > T_{N3}$. In Ni$_2$Fe$_2$O$_2$BO$_3$, $T_{N1}$ = 106 K, $T_{N2}$ = 46 K, and $T_{N3}$ = 14 K, while in Cu$_2$Fe$_2$O$_2$BO$_3$, $T_{N1}$ = 63 K, $T_{N2}$ = 38 K, and $T_{N3}$ = 20 K. They are explained in terms of a hierarchy of interactions such that at $T_{N1}$ only the Fe sublattice orders partially, at $T_{N2}$ the transition metal sublattice orders independently, and only at $T_{N3}$ do the two sublattices couple and give rise to the reentrant AFM2 phase. It may be concluded that in the three cases the substitution of the transition metal by Fe induces the ordering of the Fe sublattice at $T_{N1}$ ($T_N$ in our case), an indication of the strong Fe-Fe interaction. However, in Co$_{2.25}$Fe$_{0.75}$O$_2$BO$_3$ we have shown in Fig. 14 that below $T_{N1}$ the Co sublattice already gives an important contribution to the magnetization in the b direction, probably through polarization.
by the Fe sublattice; therefore the Fe-Co coupling is already effective below $T_{N1}$. In addition, the phase below $T_{N2}$ ($T_C$ in the Co case) is ferromagnetic in the Co compound, while in the Ni and Cu cases it is antiferromagnetic, on one hand, and does not undergo any reentrant transition, on the other. It can be concluded that the Fe-Co coupling is stronger than that for Ni or Cu, probably due to the lower magnetic moment of these atoms with respect to Co.

In this work we showed unambiguously that Fe substitution induces an extraordinarily high uniaxial anisotropy along the [010] axis in the Co$_3$O$_2$BO$_3$ compound, and a strong decrease in the net ferromagnetic moment. For further understanding of the competing roles of Fe and Co in this structure, the magnetic structure determination of Co$_3$O$_2$BO$_3$ with neutron diffraction would be of paramount importance.

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