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Single crystals of Co$_3$O$_2$BO$_3$ with partial (4%) substitution of Co by Cu ions were synthesized by the flux technique. X-ray diffraction and magnetic studies were carried out. The x-ray diffraction measurements show clearly that Cu preferentially occupies only one of the four nonequivalent crystallographic positions, the one with the smallest electric field gradient. The ferrimagnetic ordering near $T_N = 43$ K and the high magnetic hardness in this magnetic phase are similar to those of Co$_3$O$_2$BO$_3$. Copper substitution causes a small reduction in the effective magnetic moment. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818633]

1. Introduction

Among the wide range of transition metal oxides, the oxyborates have long been of great interest because of a combination of mixed valence, low dimensionality, and a complex hierarchy of exchange interactions. These oxyborates can crystallize into a large variety of crystallographic structures named after natural minerals: calcite, hantite, pyroborate, cotoite, warwickite and ludwigite.[1–5] Over the last few years, the ludwigites have been of particular interest because of their extremely unusual magnetic properties.[6–10] For example, one of the two known homometallic ludwigites Fe$_3$O$_2$BO$_3$ seems to possess at least two magnetic sublattices with orthogonal ordering at temperatures of 110 and 70 K.[7,9] In our previous papers we have concentrated on the properties of the second homometallic ludwigite Co$_3$O$_2$BO$_3$ and the intermediate compounds Co$_{3-x}$Fe$_x$O$_2$BO$_3$ ($x \leq 1$).[5,9,10] Crystals of these materials with high quality and sufficient size have became available only recently.[5,6] The properties of iron-substituted Co-ludwigite can be summarized briefly as follows:

- Iron ions occupy one of four types of distinct crystallographic sites with a highly pronounced preference and form the magnetic sublattice, which tends to become ordered at the same temperature as in Fe$_3$O$_2$BO$_3$ (near 110 K). The type of magnetic ordering in this sublattice is antiferromagnetic;
- The Co-sublattice orders ferrimagnetically at 70 K. This point is also a characteristic temperature of Fe-, but not Co-ludwigite;

- High magnetic anisotropy occurs in the end members of pure Fe$_3$O$_2$BO$_3$ and Co$_3$O$_2$BO$_3$ as well as in the intermediate materials Co$_{3-x}$Fe$_x$O$_2$BO$_3$, with the crystallographic direction c being the hard axis of magnetization; and,
- The magnetic hardness is inherently high in Co$_3$O$_2$BO$_3$ and Co$_{3-x}$Fe$_x$O$_2$BO$_3$. In the latter material at low temperatures, the coercive field is extraordinary high.

This paper is devoted to a study of another member of ludwigite family: Co$_{3-x}$Cu$_x$O$_2$BO$_3$.

2. The samples and experimental techniques

Single crystals of Co$_{3-x}$Fe$_x$O$_2$BO$_3$ were grown by the flux method in a system Co$_3$O$_4$-CuO-B$_2$O$_3$-PbO-PbF$_2$. The relative amounts of Co and Cu ions in the prepared compound were later checked by x-ray diffraction. After mixing of the components, the composition was heated up to 1100 °C and kept at this temperature for about 3 h. Then the solution was subjected to two-step cooling. The first step was fast cooling to 930 °C. The second step was slow cooling by 12 °C a day over three days. During this time, spontaneously formed single crystals of Co$_{3-x}$Cu$_x$O$_2$BO$_3$ were grown. The crystals were then cleaned in a 20% water solution of nitric acid. The single crystals were needle shaped, up to 4 mm long, and black in color. The long axis of the needle in all known transition metal ludwigites coincides with the crystallographic c-direction.

X-ray diffraction measurements were made on one from the single crystals and the crystallographic structure was resolved in detail. A SMART APEX II (MoKα radiation, CCD detector) x-ray diffractometer was used. The site occupation factors determined for the different transition ions (Co and Cu) in the distinct crystallographic positions were used to calculate the relative amount of these elements in the material, so the chemical formula of our compound can be rewritten as $Co_{2.88}Cu_{0.12}O_2BO_3$.

For the magnetic measurements we have used a Quantum Design MPMS-XL SQUID-magnetometer. The dc magnetization measurements were made at temperatures of 2–300 K. The magnetization curves $M(H)$ were measured in the magnetic field up to 50 kOe. Before the magnetic measurements, the single crystal was weighed carefully using a DV 215 CD microbalance. Usually needle-shaped crystals of the transition metal ludwigites obtained by the flux method are very thin and their weight is low. In the case of the parent $Co_3O_2BO_3$ the sample mass was up to 1 mg. The $Co_{2.88}Cu_{0.12}O_2BO_3$ sample chosen for the magnetic measurements weighed only 0.26 mg.

The Co-ludwigite samples are highly anisotropic,[9] so that magnetic measurements have to be made in magnetic fields directed along the different crystallographic axes. In our experiment the sample orientation was determined using the x-ray diffractometer and the sample was glued to a plexiglas cube. During the measurements the cube was adjusted to provide the necessary magnetic field direction relative to the sample and the magnetizations in the a, b and c crystallographic directions were obtained.

3. X-ray diffraction

The x-ray diffraction measurements confirmed the ludwigite crystal structure of our compound with space group *Pbam*. The lattice parameters and other x-ray diffraction data are given in Table 1. The unit cell parameters are

TABLE 1. X-ray diffraction data for $Cu_{3-x}Cu_xO_2BO_3$.

Empirical formula	$Co_{2.88}Cu_{0.12}O_2BO_3$
Molar weight, g	268.1
Wavelength, Å	0.71073
Temperature, K	298
Crystal system	Orthorhombic
Space group	*Pbam*
Unit cell parameters, Å	
a	9.2986
b	11.9625
c	2.9890
Volume, Å³	332.48
Density (calculated), mg/mm³	4.577
$F(000)$	426.0
Absorption coefficient, mm⁻¹	16.69
Diffraction angle θ, deg	2.70–29.53
Absorption correction	Gaussian
Refinement method: Full-matrix least squares on F^2	
Data/restraints/parameters	534/0/59
Goodness-of-fit on F^2	1.177
Final R indices	
$R1$	0.0186
$wR2$	0.0426

TABLE 2. The correspondence between the Wyckoff notation and the notation used here for the distinct sites.

Wyckoff notation	Number
2 *a*	1
2 *d*	2
4 *g*	3
4 *h*	4

comparable with those of $Co_3O_2BO_3$. There are four distinct crystallographic sites for the metal ion in the ludwigite structure. We have numbered these sites as shown in Table 2, which lists the corresponding Wyckoff notation.[11] The ludwigite crystallographic structure with the numbers of the distinct crystallographic sites is illustrated in Fig. 1.

Every metal ion lies at the center of a distorted oxygen octahedron; the type and degree of distortion are different for each nonequivalent site. The edge-shearing octahedra form zig-zag walls spreading along the c-axis. A more detailed description of the cobalt ludwigite crystallographic structure is given elsewhere.[10] Selected inter-ion distances in $Co_{2.88}Cu_{0.12}O_2BO_3$ are listed in Table 3. The corresponding sites and bonds are shown in Fig. 1. The smallest distance between the metal ions in the present case corresponds to the metal ions at positions 2 and 4 and is less than 3 Å. This is a common feature of the transition metal ludwigites.

Table 3 shows that the inter-ion distances are the shortest for the BO_3 triangle, the most strongly coupled group of ions in the oxyborates.

Table 4 lists the ionic coordinates and site occupation factors of the distinct crystallographic sites. According to the x-ray diffraction data, copper occupies only the sites numbered 4.

The degree of distortion of the oxygen octahedron can be characterized by the electric field gradient tensor. For a qualitative analysis it is sufficient to determine just the main tensor component:

$$V_{ZZ} = 2e \sum \frac{3\cos^2\alpha - 1}{r^3},$$

where α is the angle between the main electric field direction and the radius-vector of the oxygen anion, r is the M-O bond length, and e is the elementary charge. V_{zz} was calculated using the bond lengths given in Table 3. The results for the four nonequivalent crystallographic positions are shown in Table 5. It is clear that the oxygen octahedron for the site 4 is less distorted than the others. It is interesting that this position is preferred for occupation by various substitution ions: Fe,[6,10] Mn,[12] and Cu (this paper).

4. Magnetism

The dc magnetization has been measured as a function of temperature for two different values of magnetic field: 0.6 and 50 kOe. Figure 2 shows the FC and ZFC magnetization behavior for a 0.6 kOe field. The magnetization data show that the $Co_{2.88}Cu_{0.12}O_2BO_3$ ludwigite sample has a high magnetic anisotropy. The magnetic moment measured for a field directed along the a and c crystallographic axes was
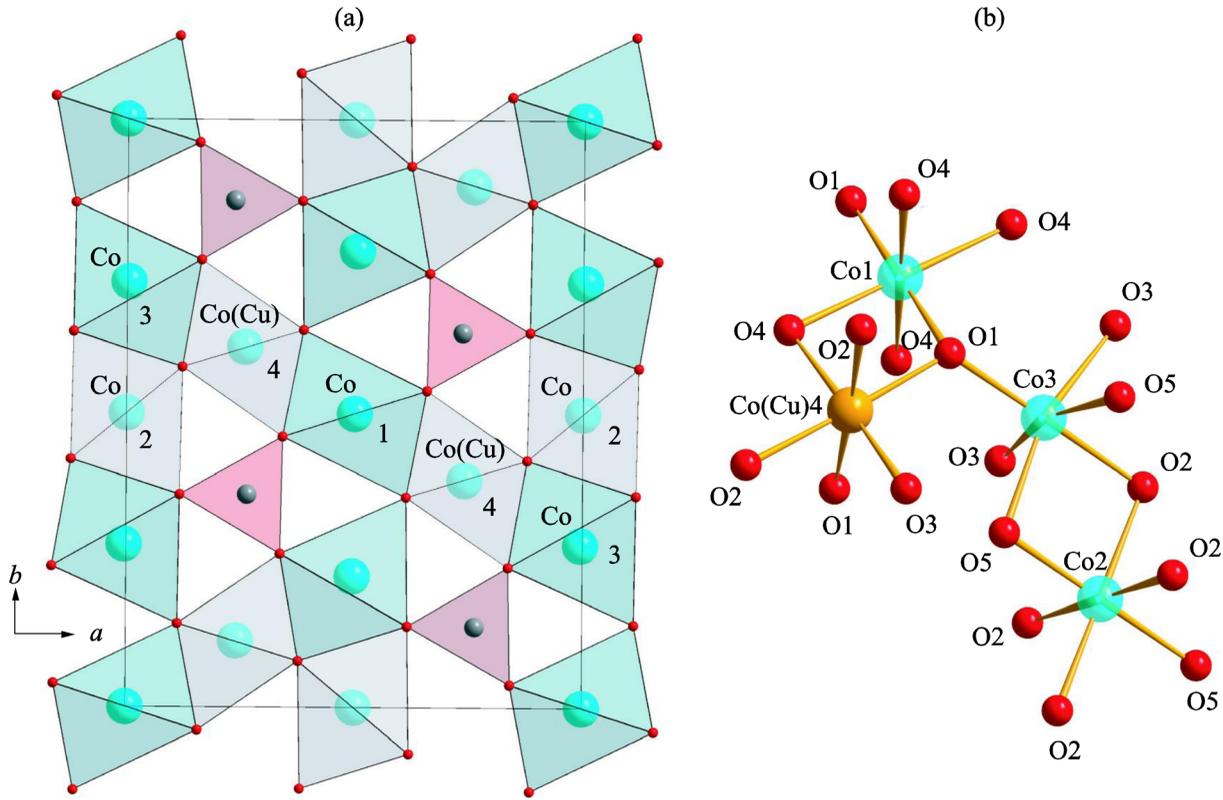
FIG. 1. Ludwigite crystal structure in the *ab* crystallographic plane. The four distinct metal positions in the zig-zag walls are shown. The oxygen octahedra share edges. The BO_3 groups look like triangles (a); the Co–O bonds for cobalt (copper) ions in the distinct crystallographic sites (b).

about 100 times smaller than that along the *b* axis. These values are near the sensitivity of the magnetometer. With the magnetometer used here, it is impossible to provide perfect coincidence of magnetic field direction with any crystallographic axis, so that a small projection of the magnetic moment along *b* could contribute to the measured signals for the *a*- and *c*-directions. For these reasons we ignore the *a* and *c* data and concentrate on the values of *M* measured with the magnetic field along the *b*-axis. These indicate that the magnetic transition occurs near $T = 43$ K, the same as the critical temperature for unsubstituted $Co_3O_2BO_3$. In the parent compound $Co_3O_2BO_3$ the magnetic transition is followed by a pronounced λ-anomaly in the heat capacity, which confirms its first order character. In $Co_{2.88}Cu_{0.12}O_2BO_3$ the magnetic transition in a 0.6 kOe field varies sharply with temperature which suggests that it is similar to the transition in $Co_3O_2BO_3$. The FC and ZFC dependences for $H = 0.6$ kOe are very different at low temperatures. They diverge sharply at $T_{div} = 21$ K, considerably below the magnetic transition temperature. This is not usually so in spin or cluster

spin glasses.[13] It seems that in the case of $Co_{2.88}Cu_{0.12}O_2BO_3$, by analogy with $Co_3O_2BO_3$, the divergence of the FC and ZFC curves is caused by the motion of domain walls, rather than by freezing of the magnetic moments.

On the other hand, the $M(T)$ measurements in a high (50 kOe) magnetic field indicate similar behavior of the FC and ZFC magnetizations (Fig. 3). In the paramagnetic phase at $T > 150$ K the inverse magnetic susceptibility temperature dependence (the inset to Fig. 3) obeys the Curie-Weiss law, $\chi = C/(T - \theta)$, quite well. The effective magnetic moment $\mu_{eff} = 3.83\,\mu_B$ calculated from the Curie constant *C* is slightly lower than that for $Co_3O_2BO_3$. The paramagnetic Curie temperature $\theta = -12.6$ K indicates a weak predominance of antiferromagnetic interactions. Between 43 and 150 K, magnetic correlations cause the deviations from Curie-Weiss behavior.

TABLE 4. Fractional coordinates, site occupation factors (SOF) and isotropic displacement parameters U (Å^2) for $Co_{2.88}Cu_{0.12}O_2BO_3$.

	x/a	*y/b*	*z/c*	SOF	*U*
Co1	0.00000	0.00000	0.00000	0.25000	0.00593
Co2	0.50000	0.00000	0.50000	0.25000	0.00577
Co3	−0.00444	0.27680	0.00000	0.50000	0.00565
Co4	0.24089	0.11307	0.50000	0.43930	0.00470
Cu4	0.24089	0.11307	0.50000	0.06070	0.00470
O1	0.11292	0.14216	0.00000	0.50000	0.00852
O2	−0.12177	0.42118	0.00000	0.50000	0.01183
O3	−0.16286	0.23883	0.50000	0.50000	0.00907
O4	0.15797	−0.03939	0.50000	0.50000	0.01106
O5	0.11674	0.36164	0.50000	0.50000	0.01279
B	0.26417	0.36226	0.50000	0.50000	0.00374

TABLE 3. Selected bond lengths for $Co_{2.88}Cu_{0.12}O_2BO_3$ (Å).

Co1–O1	1.9986 (0.0020)	Co(Cu)4–O1	1.9418 (0.0014)
Co1–O4	2.1478 (0.0015)	Co(Cu)4–O2	2.0080 (0.0014)
Co2–O2	2.0988 (0.0015)	Co(Cu)4–O3	1.9849 (0.0021)
Co2–O5	1.9794 (0.0019)	Co(Cu)4–O4	1.9800 (0.0017)
Co3–O1	1.9456 (0.0020)	B–O3	1.3868 (0.0038)
Co3–O2	2.0428 (0.0022)	B–O4	1.3814 (0.0036)
Co3–O3	2.1470 (0.0015)	B–O5	1.3709 (0.0039)
Co3–O5	2.1291 (0.0014)		
Co2–Co(Cu)4		2.7631 (0.0004)	

TABLE 5. The main component of electric field gradient G and copper content for the distinct crystallographic sites.

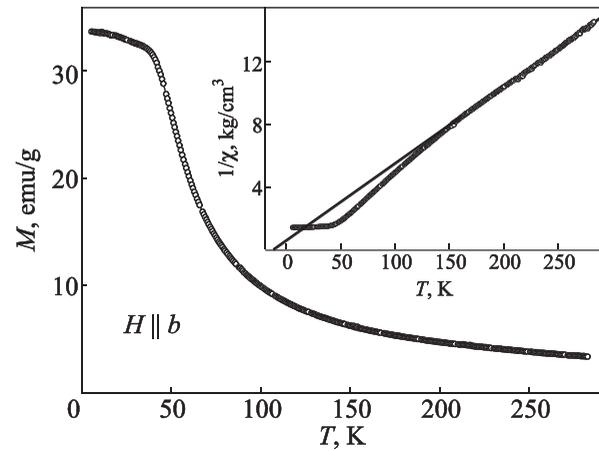| Position	1	2	3	4
G, e/Å^3	0.2666	0.18362	0.21608	−0.0214
Copper content, %	0	0	0	12

In the magnetically ordered phase, the magnetization curves have the appearance of hysteresis loops (Fig. 4). The loops are in the form of parallelograms, symmetric, with no shift relative the coordinate origin. The coercive field is almost 40 kOe at 2 K and the remnant magnetization is close to 20 emu/g, which corresponds to 0.32 μ_B per magnetic ion. The maximum value of the magnetization for a magnetic field of 50 kOe is near 35 emu/g (0.56 μ_B/ion), while the theoretical magnetic moment (spin only) value for $Co_3O_2BO_3$ is 1.67 μ_B/ion. Thus, the experimental magnetic moment is far from the maximum possible value, which suggests partial compensation. The magnetization does not saturate up to $H = 50$ kOe at any temperature. The high field branches of the loops are nearly linear, which indicates a possible antiferromagnetic contribution to the magnetic moment. The observed behavior of $M(H)$ is very similar to that in the parent $Co_3O_2BO_3$.[9] It seems that in both compounds the magnetic ordering at 43 K is ferrimagnetic.

5. Discussion

We have grown a new single-crystal transition metal oxyborate with a ludwigite structure, $Co_{2.88}Cu_{0.12}O_2BO_3$. The copper content in this material turns out to be much lower than in the initial solution of the chemical components. This indicates that it is difficult for copper to enter the $Co_3O_2BO_3$.
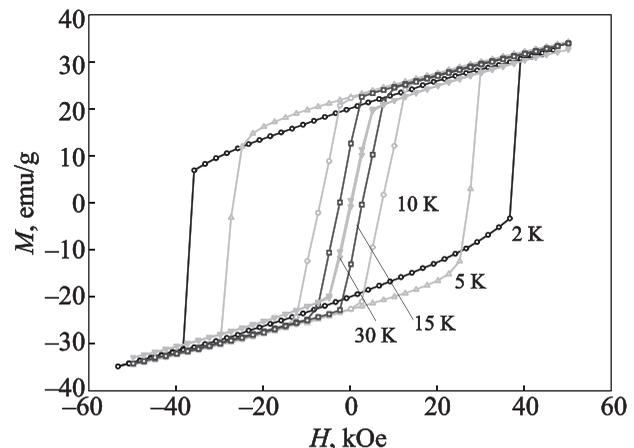
A detailed analysis of x-ray diffraction data shows that Cu ions clearly prefer only one of the four nonequivalent crystallographic positions, the same position 4 (4 h) as in the case of iron[10] or manganese[12] ions. The inter-ion distances were determined and the electric field gradient created by the distorted oxygen octahedron have been calculated. These calculations show that the electric field gradient is minimal
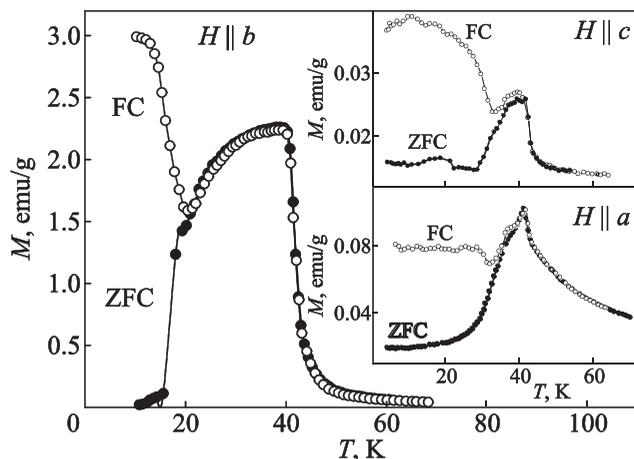
FIG. 3. Temperature dependences of the high field (50 kOe) FC and ZFC magnetization and the inverse magnetic susceptibility for $Co_{2.88}Cu_{0.12}O_2BO_3$. The solid line shows a fit to the Curie–Weiss law.

for the 4 (4 h) crystallographic position. In other words, this metal position has the most symmetric oxygen environment. This is probably why this site is indifferent to the type of metal ion.

The valence state of the metal ion is very important for understanding magnetic and other phenomena in the oxyborates with complex crystallographic structures. In previous studies of $Co_3O_2BO_3$, $Co_3O_2BO_3$:Fe and $Co_3O_2BO_3$:Mn ludwigites by Mössbauer spectroscopy and the bond valence sum method it was found that Co ions in positions 1-3 are divalent, while Co, Fe, and Mn ions in position 4 are trivalent. It seems reasonable to conclude that position 4 is preferable for the trivalent ions. On the other hand, the trivalent state is not typical of copper ions in different compounds. At present, we have no experimental data that could be used to distinguish between the different valence states of copper in $Co_{2.88}Cu_{0.12}O_2BO_3$. This question requires further study.

Previous studies of the substituted cobalt ludwigites ($Co_{3-x}Mn_xO_2BO_3$ [Ref. 12] and $CoGaMgO_2BO_3$ [Ref. 14]) have revealed the destruction of long-range magnetic order and the spin-glass state in cases. Here we have shown that 4% substitution Co by Cu in ludwigite $Co_3O_2BO_3$ does not lead to any dramatic changes in magnetic behavior of this compound. The reason is obviously a low copper content.

FIG. 2. FC and ZFC magnetization temperature dependences of single-crystal $Co_{2.88}Cu_{0.12}O_2BO_3$ measured in magnetic fields directed along three crystallographic directions. $H = 0.6$ kOe.

FIG. 4. The hysteresis loops corresponding to the magnetization isotherms of single-crystal $Co_{2.88}Cu_{0.12}O_2BO_3$. The magnetic field is parallel to the b crystallographic axis.

The type of magnetic ordering in $Co_{2.88}Cu_{0.12}O_2BO_3$ seems to be ferrimagnetic, and the critical temperature $T_N = 43$ K is similar to that of the parent compound $Co_3O_2BO_3$. Nevertheless the effective magnetic moment μ_{eff} of $Co_{2.88}Cu_{0.12}O_2BO_3$ is smaller than that of $Co_3O_2BO_3$ (3.8 as opposed to 4.2 [Ref. 9]). The difference probably originates in the spin S of the copper and cobalt ions. We do not know the oxidation state of copper in the mixed compound, but in all the cases the charge equilibrium is the same after substitution. In both of the possible scenarios, i.e. when Cu^{3+} (d^8, $S = 1$) substitutes Co^{3+} (d^6, $S = 2$) or (more probable) when Cu^{2+} (d^9, $S = 1/2$) substitutes Co^{2+} (d^7, $S = 3/2$), the average spin must decrease substantially.

The unusual magnetic properties of the transition metal ludwigites are a direct consequence of their crystallographic structure, given the complex hierarchy of superexchange interactions. Detailed crystallographic data make it possible to estimate the relative values of the exchange energies in the ludwigite structures. We have done this analysis for $Co_3O_2BO_3$ [Ref. 10] and discovered a strong contribution from frustration. We calculated the superexchange integrals through the oxygen anions using the model proposed in Ref. 15. There the interaction of two half-filled electron orbitals is considered to be antiferromagnetic; the interaction between empty or totally-filled and half-filled orbitals is considered to be ferromagnetic. The $Co^{2+,3+}$ and $Cu^{2+,3+}$ ions have no empty 4d-orbitals. The number of totally-filled orbitals is higher for copper than for cobalt ions, so that substitution of cobalt by copper may favor the tendency to ferromagnetic ordering. To confirm this theory, we need to synthesize samples with higher copper contents; this will be done in the near future.

6. Conclusion

Single crystals of cobalt ludwigite have been grown with partial Cu substitution. X-ray diffraction studies show that copper preferentially occupies only one of the four distinct crystallographic sites in the ludwigite structure, the position with the lowest electric field gradient created by the oxygen octahedron. The amount of copper in $Co_{2.88}Cu_{0.12}O_2BO_3$ appears to be too low to cause any pronounced change in magnetic behavior compared to the parent material $Co_3O_2BO_3$. Both compounds seem to be ferrimagnets with T_N near 43 K and a high coercive field. Nevertheless, the effective magnetic moment decreases when copper is substituted because of the lower spin of copper compared to cobalt ions.

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