Structure and magnetism of copper substituted cobalt ludwigite Co$_3$O$_2$BO$_3$

N.B. Ivanova[1,2], N.V. Kazak[2], Yu.V. Knyazev[1], D.A. Velikanov[1,2], A.D. Vasiliev[1,2], L.N. Bezmaternykh[2], and M.S. Platunov[2]

[1]*Siberian Federal University, 26 Kirensky Str., Krasnoyarsk 660074, Russia*

[2]*L.V. Kirensky Institute of Physics, SB of RAS, Akademgorodok, Krasnoyarsk 660036, Russia*
E-mail: nat@iph.krasn.ru

The single crystals 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 properties investigations were carried out. The x-ray diffraction measurements have shown that Cu clearly prefers only one from four nonequivalent crystallographic positions with the smallest electric field gradient. The ferrimagnetic ordering near $T_N = 43$ K and high magnetic hardness in this magnetic phase are similar to Co$_3$O$_2$BO$_3$. The small reduction of the effective magnetic moment was revealed under copper substitution.

1. Introduction

Among the wide raw of transition metal oxides the oxyborates family during a long time attracts the grate attention due to combination of mixed valence, low dimensionality and complex hierarchy of exchange interactions. These oxyborates may crystallize into a large variety of crystallographic structures named after the natural minerals: calcite, hantite, pyroborate, cotoite, warwickite and ludwigite [1–5]. The latter compounds known as ludwigites at last few years forced the high wave of interest due to their extremely unusual magnetic properties [6–10]. For example, one from two known homometallic ludwigites Fe$_3$O$_2$BO$_3$ seems to possess at least two magnetic sublattices, which order orthogonally at temperatures 110 and 70 K [7,9]. In our previous works we have concentrated on the properties of the second homometallic ludwigite Co$_3$O$_2$BO$_3$ and intermediate compounds Co$_{3-x}$Fe$_x$O$_2$BO$_3$ ($x \leq 1$) [5,9,10]. The high quality and large enough crystals of these materials became available not long ago [5,6]. Shortly the properties of iron substituted Co-ludwigite may be summarized as follows:

— Iron ions occupy one from four distinct crystallographic sites with brightly pronounced preference and form the magnetic sublattice, which tends to order 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 also is a characteristic temperature of Fe-, but not Co-ludwigite;

— High magnetic anisotropy occurs as in the end members of the raw Fe$_3$O$_2$BO$_3$ and Co$_3$O$_2$BO$_3$ as in the intermediate materials Co$_{3-x}$Fe$_x$O$_2$BO$_3$, the crystallographic direction c being the hard axis of magnetization;

— The high magnetic hardness is inherent for 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.

The present work is devoted to the investigation of the other member of ludwigite family — Co$_{3-x}$Cu$_x$O$_2$BO$_3$.

2. The samples and experimental techniques

The single crystals of Co$_{3-x}$Fe$_x$O$_2$BO$_3$ were grown by the flux method in the system Co$_3$O$_4$–CuO–B$_2$O$_3$–PbO–PbF$_2$. The relative content of Co and Cu ions in the mixed compound was later checked by the means of x-ray diffraction. After mixing of the components the composition was heated up to 1100 °C and contained at this temperature about

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3 hours. Then the solution underwent two-step cooling. The first step was the fast cooling to 930 °C. The second step was slow cooling by 12 °C a day during three days. By these days the spontaneously formed single crystals $Co_{3-x}Cu_xO_2BO_3$ were grown. Then the crystals were cleaned by the 20% water solution of nitric acid. The single crystals obtained were of the needle shape up to 4 mm long and black color. The long side of the needle in all known transition metal ludwigites coincides with crystallographic *c*-direction.

The x-ray diffraction measurements were carried out for one from the single crystals and the crystallographic structure was solved in detail. The x-ray diffractometer SMART APEX II (MoKα radiation, CCD detector) have been used. Site occupation factors defined for different transition ions (Co and Cu) in the distinct crystallographic positions allowed to calculate the relative content 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 MPMS-XL SQUID-magnetometer Quantum Design. The dc magnetization measurements were carried out in the temperature interval 2–300 K. The magnetization curves $M(H)$ were measured in the magnetic field up to 50 kOe. Before the magnetic measurements the accurate weighting of the single crystal was carried out using the microscales DV 215 CD. Usually the needle crystals of transition metal ludwigites obtained by the flux method are very thin and their weight is small. In the case of parent $Co_3O_2BO_3$ the samples mass was up to 1 mg. The $Co_{2.88}Cu_{0.12}O_2BO_3$ sample chosen for the magnetic measurements weighted only 0.26 mg.

The Co-ludwigite samples are highly anisotropic [9], so the magnetic measurements have be done in magnetic field directed along different crystallographic axes. In our experiment the sample was oriented by the x-ray diffractometer and then attached to the plexiglas cube by glue. During the measurements the cube was fixed by the way providing the necessary magnetic field direction relative to the sample and magnetization values in *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 the space group *Pbam*. The lattice parameters together with other x-ray diffraction data are presented in Table 1. The unit cell parameters are comparable with the same for $Co_3O_2BO_3$. There are four distinct crystallographic sites of the metal ion in the ludwigite structure. According to Wyckoff notation [11] we have numbered these sites as it is shown in the Table 2. Schematically the ludwigite crystallographic structure including the numbering of distinct crystallographic sites is shown in Fig. 1.

Table 1. The x-ray diffraction data for $Co_{3-x}Cu_xO_2BO_3$

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	Orthorombic
Space group	*Pbam*
Unit cell parameters, Å	
a	9.2986
b	11.9625
c	2.9890
Volume, Å^3	332.48
Density (calculated), mg/mm^3	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	
*R*1	0.0186
*wR*2	0.0426

Table 2. The accordance between Wyckoff and present distinct sites numbering

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

Every metal ion is placed in the center of the distorted oxygen octahedral, the distortion type and degree being different for each nonequivalent site. The edge-shearing octahedra form zig-zag walls spreading along the *c*-axis. More detail description of cobalt ludwigite crystallographic structure one can find in our work [10]. The selected inter-ion distances in $Co_{2.88}Cu_{0.12}O_2BO_3$ are presented in the 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 in the positions 2 and 4 and is smaller than 3 Å. It is the common feature of transition metal ludwigites.

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

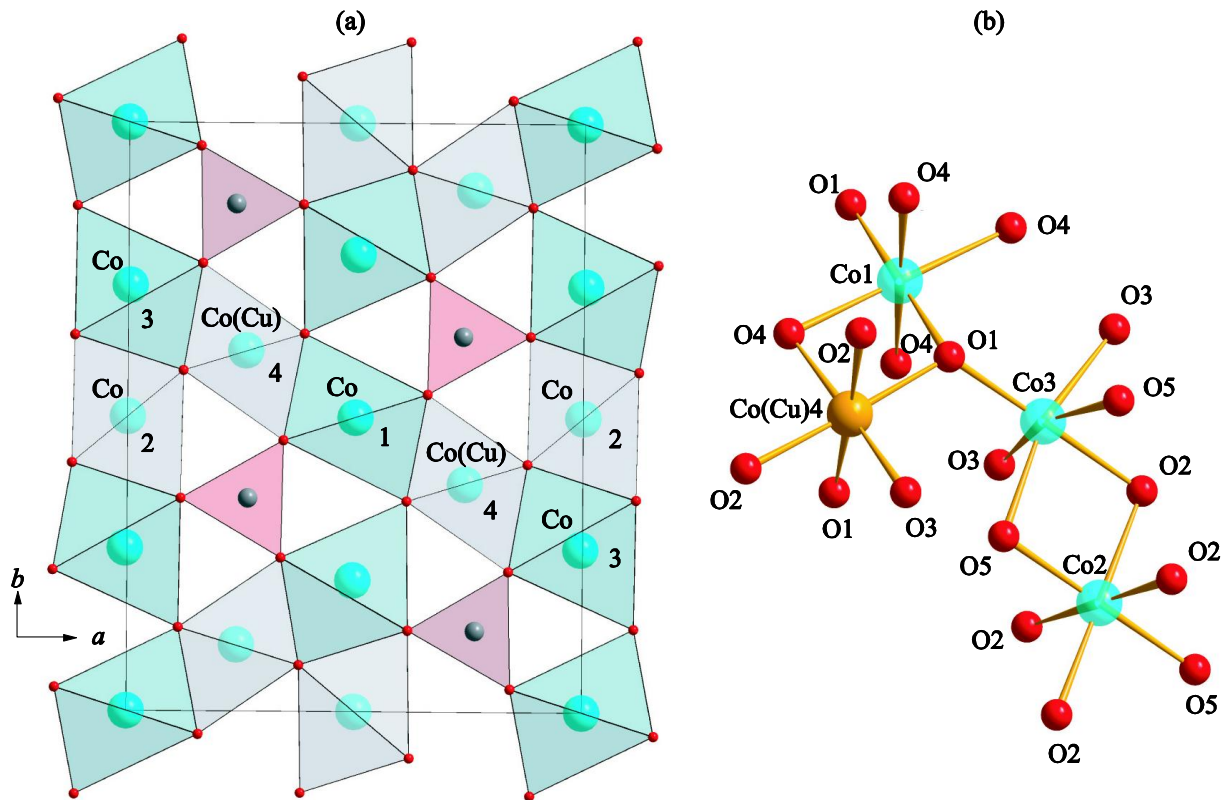|			
Co1–O1	1.9986 (0.0020)	Co(Cu)4–O1	1.9418 (0.0014)
Co1–O4	2.1478 (0.0015)	Co(Cu)4–O2	2.0080 (0.0014)
Co2–O2	2.0988 (0.0015)	Co(Cu)4–O3	1.9849 (0.0021)
Co2–O5	1.9794 (0.0019)	Co(Cu)4–O4	1.9800 (0.0017)
Co3–O1	1.9456 (0.0020)	B–O3	1.3868 (0.0038)
Co3–O2	2.0428 (0.0022)	B–O4	1.3814 (0.0036)
Co3–O3	2.1470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

Fig. 1. Ludwigite crystal structure in *ab* crystallographic plane. The four distinct metal positions in the zig-zag walls are shown. Oxygen octahedra are sharing edges. BO_3 groups look as the triangles (a); The Co–O bonds for cobalt (copper) ions in the distinct crystallographic sites (b).

As can be seen from the Table 3, the interion distances are the shortest for BO_3 triangle, the most strongly coupled group of ions in the oxyborates.

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

Table 4. Fractional coordinates, site occupation factor (SOF) and isotropic displacement parameter 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

The degree of the oxygen octahedral distortion can be characterized by the electric field gradient tensor. For the qualitative analysis it is sufficient to define only 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 tensor direction and oxygen anion radius-vector, r is the the M–O bond length, e is the elementary charge. The values of V_{zz} were calculated accounting the bond lengths presented in the Table 3. The data obtained for the four nonequivalent crystallographic positions are shown in the Table 5. One can see that the oxygen octahedral for the site 4 is less distorted comparing the others. It is interesting to note that namely this position is the most preferable for occupation in the cases of different substitution ions: Fe [6,10], Mn [12] and Cu (present work).

Table 5. The main component of electric field gradient tensor 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

4. Magnetism

The temperature dc magnetization dependencies have been measured at two different values of magnetic field: 0.6 and 50 kOe. Figure 2 presents FC and ZFC magnetization behavior in the field 0.6 kOe. The magnetization data have demonstrated that $Co_{2.88}Cu_{0.12}O_2BO_3$ ludwigite sample possess a high magnetic anisotropy. The magnetic moment values measured in the field directed along a and c crystallographic axes appeared to be about 100 times smaller than the same for b one. They are near the limit of magnetometer accuracy. Moreover in the magnetometer used it is impossible to provide the ideal coincidence of magnetic field direction with any crystallographic axis. So a small projection of lying along b magnetic moment can contribute to signal measured for a- and c-directions. By these reasons we didn't take a and c data into account and concentrated on the M values measured in magnetic field directed along b-axis. According them the magnetic transition occurs near $T = 43$ K, the same critical temperature as for unsubstituted $Co_3O_2BO_3$. In the parent compound $Co_3O_2BO_3$ the magnetic transition is followed by the pronounced λ-anomaly of the heat capacity confirming its first order character. In $Co_{2.88}Cu_{0.12}O_2BO_3$ the magnetic transition in the field 0.6 kOe is sharp by temperature leading to proposal about its similarity to one in $Co_3O_2BO_3$. FC and ZFC dependencies for $H = 0.6$ kOe are very different at low temperatures. They sharply diverge at $T_{div} = 21$ K — considerably below the temperature of magnetic transition. This isn't usually the case 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 $Co_3O_2BO_3$ FC and ZFC curves divergence is called by the motion of domain walls but not the magnetic moments freezing.

The $M(T)$ measurements in the high (50 kOe) magnetic field contrary gave the similar behavior of FC and ZFC
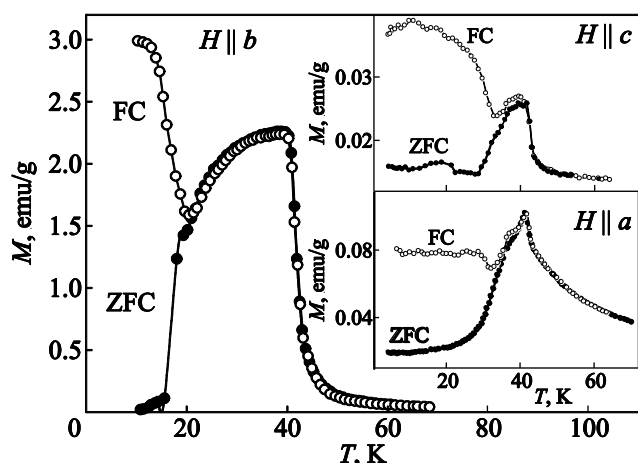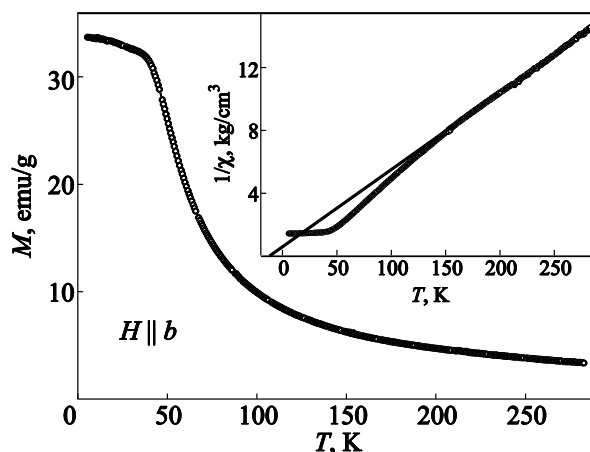
Fig. 3. Temperature dependences of high field (50 kOe) FC and ZFC magnetization and the inverse magnetic susceptibility for $Co_{2.88}Cu_{0.12}O_2BO_3$. The solid line shows Curie–Weiss law fitting.

magnetizations (Fig. 3). In the paramagnetic phase at $T > 150$ K the inverse magnetic susceptibility temperature dependence (the inset to Fig. 3) well obeys the Curie–Weiss law: $\chi = C/(T - \theta)$. The effective magnetic moment $\mu_{eff} = 3.83$ μ_B calculated from Curie constant C is slightly lower than that for $Co_3O_2BO_3$. The paramagnetic Curie temperature $\theta = -12.6$ K points out the weak predominance of antiferromagnetic interactions. Between 43 and 150 K the magnetic correlations cause the deviations from Curie–Weiss behavior.

In magnetically ordered phase the magnetizations curves look as hysteresis loops (Fig. 4). The loops are of parallelogram form, symmetric, with no any shift relative the coordinate origin. A coercive field is almost 40 kOe at 2 K and remnant magnetization near 20 emu/g, which cor-
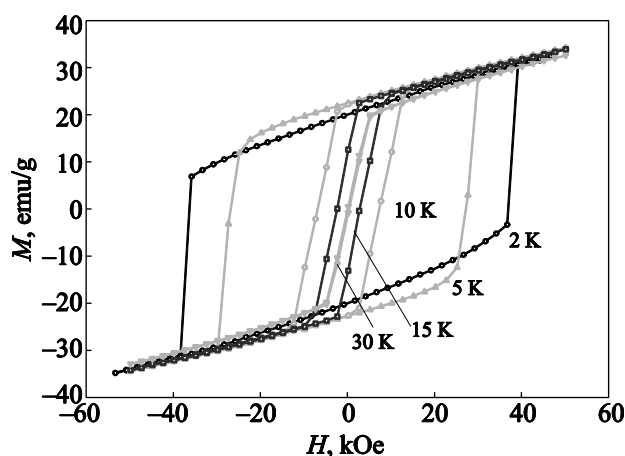
Fig. 2. FC and ZFC magnetization temperature dependencies of $Co_{2.88}Cu_{0.12}O_2BO_3$ single crystal measured in magnetic field directed along three crystallographic directions. $H = 0.6$ kOe.

Fig. 4. The hysteresis loops corresponding to magnetization isotherms of $Co_{2.88}Cu_{0.12}O_2BO_3$ single crystal. The magnetic field applied in b crystallographic axis.

responds to 0.32 μ_B per magnetic ion. The maximal magnetization value obtained in the magnetic field 50 kOe is near 35 emu/g (0.56 μ_B/ion), when the theoretical magnetic moment (only spin) value for $Co_3O_2BO_3$ consists 1.67 μ_B/ion. So the experimental magnetic moment is far from maximal possible value, leading to proposal about its partial compensation. The magnetization doesn't saturate up to $H = 50$ kOe for all the temperatures. The high field branches of the loops are close to linear pointing out the possible antiferromagnetic contribution to the magnetic moment. The observed $M(H)$ behavior is very similar to the parent $Co_3O_2BO_3$ [9]. It seems that in both compounds the magnetic ordering at 43 K is of ferrimagnetic character.

5. Discussion

In the present work we have succeed in growing of new single crystal transition metal oxyborate with ludwigite structure $Co_{2.88}Cu_{0.12}O_2BO_3$. The copper content in the material happened to be much smaller than in the solution of the initial chemical components. It points out the hard copper entering to the $Co_3O_2BO_3$.

The detail x-ray diffraction data analysis has shown that Cu ions clearly prefer only one from four nonequivalent crystallographic positions. It is the same position 4 (4h) as in the case of iron [10] or manganese [12] ions. The interion distances were defined and the calculations of electric field gradient created by the distorted oxygen octahedral have been made. As the result of these calculations one can see that namely in the case of 4 (4h) crystallographic position the electric field gradient is minimal. By the other words, this metal position possesses the most symmetric oxygen surrounding. Probably it is the reason of metal ion type indifference in it.

For the understanding of magnetic and other phenomena in the oxyborates with complex crystallographic structure the question about the valence state of metal ion is very important. In the previous investigations of $Co_3O_2BO_3$, $Co_3O_2BO_3$:Fe and $Co_3O_2BO_3$:Mn ludwigites by the means of Mössbauer spectroscopy and bond valence sum method it was revealed that Co ions in the positions 1–3 are divalent and Co, Fe, Mn ions in the position 4 are trivalent. It seems reasonable to conclude that the position 4 is preferable for the trivalent ions. But, by the other side, the trivalent state isn't typical for the copper ions in different compounds. Now we have no the experimental data allowing to distinguish between the different valence states of copper in $Co_{2.88}Cu_{0.12}O_2BO_3$. This question remains open until following investigations.

The previous investigations of the substituted cobalt ludwigites ($Co_{3-x}Mn_xO_2BO_3$ [12] and $CoGaMgO_2BO_3$ [14]) have shown the destroying of long magnetic order and spin-glass state in both the cases. In the present work we have shown that 4% substitution Co by Cu in ludwigite $Co_3O_2BO_3$ doesn't lead to any dramatic changes in magnetic behavior of this compound. The reason obviously is a low copper content. The type of magnetic ordering in $Co_{2.88}Cu_{0.12}O_2BO_3$ seems being ferrimagnetic, the critical temperature $T_N = 43$ K similar to the parent compound $Co_3O_2BO_3$. Nevertheless the effective magnetic moment μ_{eff} in $Co_{2.88}Cu_{0.12}O_2BO_3$ is less smaller than in $Co_3O_2BO_3$ (3.8 against 4.2 [9]). The matter probably is in the spin value S of copper and cobalt ions. We don't know the oxidation state of copper in the mixed compound but in all the cases the charge equilibrium have remain unchanged under substitution. At both possible scenarios 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 value have to considerably decrease.

For the transition metal ludwigites their unusual magnetic properties are the direct consequence of their crystallographic structure in view of complex hierarchy of superexchange interactions. A detail crystallographic data allow estimating the relative values of the exchange energies in the ludwigite structure. For $Co_3O_2BO_3$ the corresponding analysis have been done in our work [10] and revealed the strong frustration contribution. Calculating the superexchange integrals through the oxygen anions we have based on the model proposed in [15]. There the interaction of two half filled electron orbitals is considered as antiferromagnetic, the interaction between empty or totally filled and half filled orbitals is considered as ferromagnetic. The ions $Co^{2+,3+}$ and $Cu^{2+,3+}$ have no empty 4d-orbitals. As for totally filled orbitals, their number is higher for copper comparing cobalt ions. So the substitution of cobalt by copper may call the tendency to ferromagnetic ordering. To confirm this proposal we need to synthesize the samples with higher copper content which will be done in the nearest future.

6. Conclusion

The single crystals of cobalt ludwigite with partial Cu substitution have been grown. By the means of x-ray diffraction it was shown that copper clearly prefers only one among four distinct crystallographic sites in the ludwigite structure. It is the position with the smallest electric field gradient created by oxygen octahedral. Copper content in compound $Co_{2.88}Cu_{0.12}O_2BO_3$ appeared being low to call any pronounced change in magnetic behavior comparing the parent material $Co_3O_2BO_3$. Both the compounds seem to be ferrimagnets with T_N near 43 K and high coercive field. Nevertheless the effective magnetic moment decreases under copper substitution according the lower spin value of copper comparing cobalt ions.

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