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Crystal structure and magnetic properties of Mn substituted ludwigite $Co_3O_2BO_3$

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ABSTRACT

The needle shape single crystals Co_{3-x} $Mn_xO_2BO_3$ with ludwigite structure have been prepared. According to the X-ray diffraction data the preferable character of distinct crystallographic positions occupation by Mn ions is established. Magnetization field and temperature dependencies are measured. Paramagnetic Curie temperature value $\Theta = -100$ K points out the predominance of antiferromagnetic interactions. Spin-glass magnetic ordering takes the onset at $T_N = 41$ K. The crystallographic and magnetic properties of $Co_3O_2BO_3$:Mn are compared with the same for the isostructural analogs $Co_3O_2BO_3$ and CoO_2BO_3:Fe.

1. Introduction

The wide family of transition metal oxyborates is actively investigated during the last few years. These materials attract attention due to a large variety of crystallographic structures formed by oxygen octahedral surrounded transition ions and the trigonal BO_3-groups. Among these compounds namely the oxyborates with the ludwigite structure have attracted the most interest [1–6] due to their unusual and very substantial physical behavior. These materials are characterized by the nonuniform occupation of the distinct crystallographic positions by the transition ions in the different valence state [7], structural transition under varying temperature accompanied by the charge ordering [7] and brightly pronounced magnetic anisotropy [8]. The most intriguing problem concerning the homometallic ludwigites $Co_3O_2BO_3$ and $Fe_3O_2BO_5$ consists of following: 1) there is a temperature structural transition doubling the elementary cell in $Fe_3O_2BO_3$, but there is not in isostructural $Co_3O_2BO_3$ [5]; 2) there are two magnetic subsystems in $Fe_3O_2BO_3$, ordering independently at different temperatures and in the orthogonal directions [9], but there seems to be only one magnetic system in $Co_3O_2BO_3$ ordering ferrimagnetically at $T_N = 42$ K [5]; 3) the mixed compounds $Co_{2.25}Fe_{0.75}BO_5$ [10] and Co_2FeBO_5 [6] demonstrate the properties closer to the parent $Fe_3O_2BO_3$, but not to $Co_3O_2BO_3$ contrary to high cobalt content. In the present work we choose another transition ion (Mn instead Fe) for the cobalt substitution in $Co_3O_2BO_3$ aimed to shed some light to these intriguing aspects of transition metal ludwigite physical behavior. The single crystals $Co_{1-x}Mn_xO_2BO_3$ have never been synthesized before, so we did not find any information about them in the literature. The tasks of the present investigation were to understand: 1) the occupation of the distinct crystallographic positions preferable by Mn as it is in the case of Fe or they are filled randomly and 2) how the Mn substitution has influence on the magnetic properties of cobalt ludwigite.

2. The crystal synthesis and the measurements technique

The single crystals $Co_3O_2BO_3$ and $Co_{3-x}Mn_xO_2BO_3$ have been grown by the solution method. For the first compound the chemical components were taken in the next molar relation:

$$Bi_2Mo_3O_{12}:B_2O_3:CoO:Na_2O:Co_2O_3 = 3:1:2:2:2$$

Then the part of cobalt oxide Co_2O_3 was substituted by Mn_2O_3. For the total solution and homogenization the composition was heated to 1100 °C. After 3 h the solution underwent two steps cooling. The first step: fast cooling to 930 °C. The second step: slow cooling by 12 °C a day during the three days. During these three days the spontaneously formed single crystals $Co_{3-x}Mn_x$ O_2BO_3 were grown. Then the crystals were cleaned by 20% water solution of nitric acid. The single crystals were of the needle form

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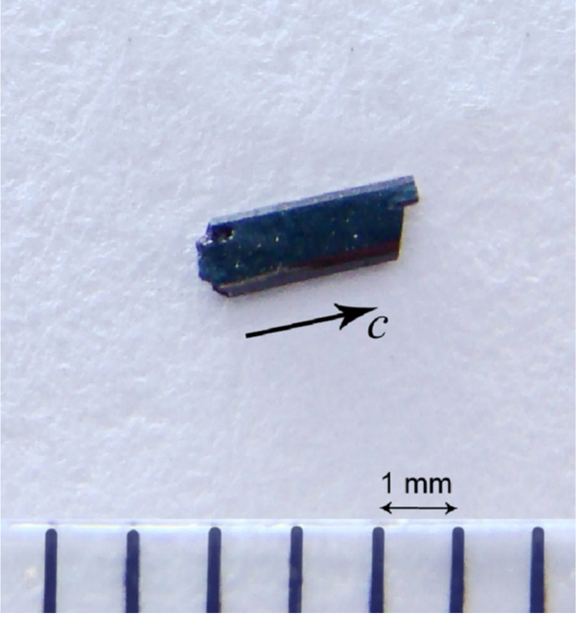

Fig. 1. Mixed $Co_{3-x}Mn_xO_2BO_3$ ludwigite single crystal.

up to 3 mm long similar to their prototype $Co_3O_2BO_3$ (Fig. 1). The long side of the needle in $Co_3O_2BO_3$, $Co_{3-x}Fe_xO_2BO_3$ [5,6,8,10] and $Co_{3-x}Mn_xO_2BO_3$ coincides with crystallographic *c*-direction.

The X-ray diffraction measurements were carried out for one of the single crystals and the crystallographic structure is solved in detail. The X-ray diffractometer SMART APEX II (MoKα radiation, CCD detector) has been used. Site occupation factors defined for different transition ions (Co and Mn) 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 $Co_{1.7}Mn_{1.3}O_2BO_3$.

For the magnetic measurements we have used MPMS-XL SQID-magnetometer Quantum Design. The *dc* magnetization measurements were carried out in the temperature interval 2–300 K. The magnetization curves *M*(*H*) are measured in the magnetic field value up to 50 kOe. Before the magnetic measurements the accurate weighing of the single crystal was carried out using the microscales DV 215 CD. The sample mass was 0.36 mg. The magnetization measurements are carried out at the arbitrary direction of magnetic field in the *ab* plane perpendicular to the needle. The maximal error value for the magnetic data does not exceed 2%.

3. The crystal structure

The crystal structure of parent compound $Co_3O_2BO_3$ was investigated in the previous works in detail [5,8], and the orthorhombic structure (symmetry group *Pbam*) was found. Nevertheless it seems useful to present the main crystal parameters for the $Co_3O_2BO_3$ crystal obtained in the same technological process as the mixed $Co_{1.7}Mn_{1.3}O_2BO_3$. They were: $a=9.2800(9)$, $b=11.9278(11)$, $c=2.9660(3)$ Å, unit cell volume $V=328.31(6)$Å^3.

The most remarkable feature of the ludwigite crystallographic structure consists in the low-dimension subunits in the form of three leg ladders (3LL). The zigzag walls formed by 3LL substructures spread along crystallographic *c*-direction. The transition ion can occupy the four nonequivalent crystallographic sites (Fig. 2), which can be combined as two types of the triads. The type I triads are formed by the ions in the positions 4–2–4; the type II triads consist of the ions in the positions 3–1–3.

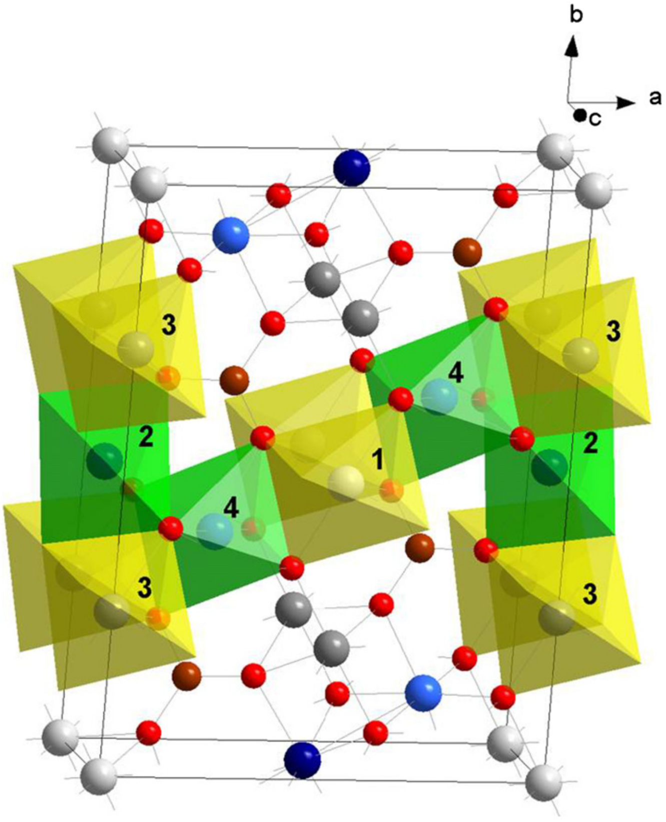

Fig. 2. Ludwigite crystal structure. The transition ions are octahedraly rounded by the oxygen anions, shown by the small circles. The nonequivalent crystallographic positions of the transition metal are numbered. The middle circles are the boron ions. Low dimensional substructures in the form of zigzag walls spread along crystallographic *c*-direction.

Table 1
X-ray diffraction data for the $Co_3O_2BO_3$:Mn single crystal.

Chemical formula	$Co_{1.7}Mn_{1.3}O_2BO_3$
Molar weight	262.48
Wave length, Å	0.71073
Temperature, K	296
Crystal structure	Orthorhombic
Symmetry group	*Pbam*
Unit cell parameters, Å	
A	9.2605
B	12.3278
C	3.0341
Unit cell volume, Å^3	346.38
Calculated density, g/cm^3	4.146
F(000)	402.0
Absorption coefficient, mm^{-1}	12.28
Diffraction angle θ, grad	$2.70\div29.78°$
Correction	Gaussian
The results of the least square method	
Data/absorption/parameters	554/0/62
Goodness-of-fit on F^2	1.183
Final *R* indexes	
*R*1	0.0243
*wR*2	0.0589

The X-ray diffraction data for $Co_{1.7}Mn_{1.3}O_2BO_3$ are presented in Table 1. The type of the crystal structure is the same as for the initial compound $Co_3O_2BO_3$—orthorhombic *Pbam*.

Table 2
Ionic coordinates, site occupation factors (SOF) and isotropic displacement parameter U_{eq} (Å^2) for $Co_{1.7}Mn_{1.3}O_2BO_3$.

	x/a	y/b	z/c	SOF	U_{eq}
Co1	0.50000	0.50000	0.00000	0.17416	0.00613
Mn1	0.50000	0.50000	0.00000	0.07584	0.00613
Co2	0.00000	0.50000	0.50000	0.17379	0.00662
Mn2	0.00000	0.50000	0.50000	0.07621	0.00662
Co3	−0.00182	0.27888	0.00000	0.33253	0.00630
Mn3	−0.00182	0.27888	0.00000	0.16747	0.00630
Co4	0.26016	0.38426	0.50000	0.17557	0.00566
Mn4	0.26016	0.38426	0.50000	0.32443	0.00566
O1	−0.10731	0.14281	0.00000	0.50000	0.01253
O2	0.12586	0.64094	0.50000	0.50000	0.00992
O3	0.34996	0.54236	0.50000	0.50000	0.01044
O4	0.14948	0.23574	0.50000	0.50000	0.01147
O5	0.11387	0.42005	0.00000	0.50000	0.01489
B	0.22468	0.13861	0.50000	0.50000	0.00855

According to the X-ray diffraction data the unit cell volume for the substituted compound exceeds the same for the parent $Co_3O_2BO_3$. The difference is about 5%. It is not surprising because the ionic radii of Mn ion are larger than the same for Co ion both in di- and trivalent states (the ionic radii values for high spin ions: Co^{2+}—0.65, Mn^{2+}—0.75, Co^{3+}—0.61 and Mn^{3+}—0.64 Å) [11].

The coordinates, site occupation factors (SOF) and isotropic displacement parameters for the different ions are shown in Table 2. The thermal parameters U_{eq} have physically reasonable values. The large values U_{eq} correspond to the oxygen ions as for $Co_3O_2BO_3$ [12].

As it can be seen from the above data the position 4 is the most preferable for the Mn ions similarly to the case of Fe substitution [6,10]. This position is occupied by about 65% of Mn ions. Nevertheless this preference is not so brightly pronounced in $Co_{3-x}Mn_xO_2BO_3$ as in $Co_{3-x}Fe_xO_2BO_3$, where the SOFs for the positions 1 and 3 are very small [10]. There is a very significant amount of Mn not only in position 4, but also in the other three positions contrary to Fe-substituted compound. These last positions according to our X-ray data are filled by Mn without any preference, and there is about 30% Mn ions in each of them.

As it was mentioned above, the SOFs value for the distinct positions allow to define Co:Mn ratio in the compound, which appeared to be near 1.33. Taking into account the distribution of two types of ions among the four nonequivalent sites the chemical formula of compound $Co_{1.7}Mn_{1.3}O_2BO_3$ can approximately be rewritten as $(Co_{0.35}Mn_{0.15})^1$ $(Co_{0.35}Mn_{0.15})^2$ $(Co_{0.67}Mn_{0.33})^3$ $(Co_{0.35}Mn_{0.65})^4O_2BO_3$. It is known that both in $Fe_3O_2BO_3$ and $Co_3O_2BO_3$ the transition ions in the positions 1 and 3 are divalent [5,7]. The triad formed by the ions 4–2–4 consists of three trivalent ions with one extra electron per triad and may be formally considered as two trivalent ions in the position 4 and one divalent ion in the position 2. Applying this consideration to $Co_{1.7}Mn_{1.3}O_2BO_3$ and proposing that Mn^{2+} substitutes Co^{2+} and Mn^{3+} substitutes Co^{3+}, one can expect almost equal amount of di- and trivalent manganese ions in the investigated compound. So, the average oxidation number Z for Mn ions must be near +2.5. Below, this proposal is checked by the bond valence sum method and magnetic measurements.

Fig. 3 demonstrates the formula unit of $Co_{1.7}Mn_{1.3}O_2BO_3$ (one molecule). The inter-ion distances are presented in Table 3. The distances between the nearest transition ions situated in the distinct crystallographic sites inside one zig-zag wall are shown in Table 4 in comparison with $Co_3O_2BO_3$. These distances were found to be about 3 Å, which is typical for the ludwigites. The shortest distance in $Co_{1.7}Mn_{1.3}O_2BO_3$ is inside the triad 4–2–4 as in the parent $Co_3O_2BO_3$, but it is a little bit larger in the former compound.

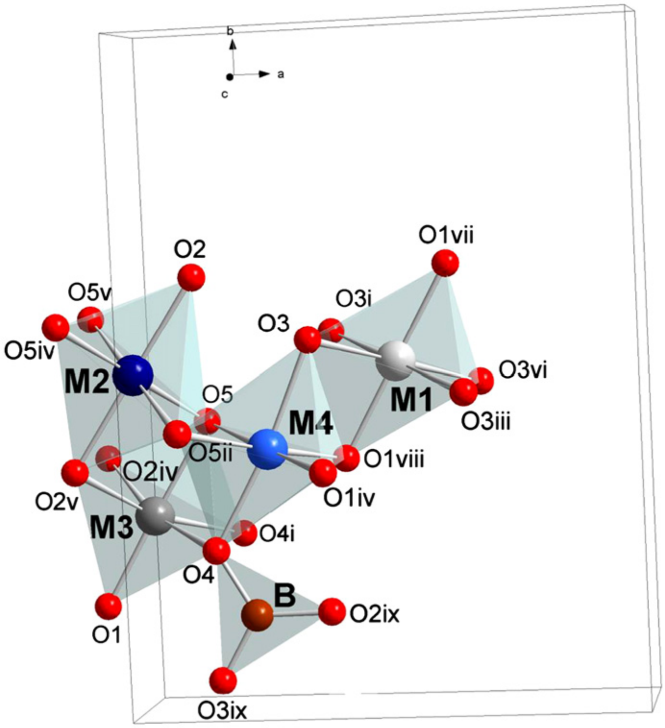

Fig. 3. Formula unit (molecule) of the mixed ludwigite $Co_{3-x}Mn_xO_2BO_3$. M—the transition ion (Co or Mn) in the distinct crystallographic positions. The distances between the ions inside the formula unit are presented in the Table 3. (i) $x, y, 1-z$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, z$; (iv) $-x, 1-y, 1+z$; (v) $-x, 1-y, z$; (vi) $1-x, 1-y, 1+z$; (vii) $0.5+x, 0.5+y, -z$; (viii) $0.5+x, 0.5-y, -z$; (ix) $0.5+x, 0.5-y, -z$; (x) $0.5-x, -0.5+y, 1-z$.

Table 3
Inter-ion distances in $Co_{1.7}Mn_{1.3}O_2BO_3$ (Å).

Co(Mn)1–O1(vii)	2.0217 (0.0022)	Co(Mn)3–O1	1.9412 (0.0023)
Co(Mn)1–O1(viii)	2.0217 (0.0022)	Co(Mn)3–O2(iv)	2.1443(0.0016)
Co(Mn)1–O3	2.1224 (0.0015)	Co(Mn)3–O2(v)	2.1443(0.0016)
Co(Mn)1–O3(iii)	2.1224 (0.0015)	Co(Mn)3–O4(i)	2.1324 (0.0015)
Co(Mn)1–O3(vi)	2.1224 (0.0015)	Co(Mn)3–O4	2.1324 (0.0015)
Co(Mn)1–O3(i)	2.1224 (0.0015)	Co(Mn)3–O5	2.0436(0.0026)
Co(Mn)2–O2	2.0922 (0.0022)	Co(Mn)4–O1(ix)	1.9796(0.0016)
Co(Mn)2–O2(v)	2.0922 (0.0022)	Co(Mn)4–O1(viii)	1.9796(0.0016)
Co(Mn)2–O5	2.0940 (0.0017)	Co(Mn)4–O3	2.1191 (0.0023)
Co(Mn)2–O5(ii)	2.0940 (0.0017)	Co(Mn)4–O4	2.0982(0.0023)
Co(Mn)2–O5(iv)	2.0940 (0.0017)	Co(Mn)4–O5	2.0812(0.0016)
Co(Mn)2–O3(v)	2.0940 (0.0017)	Co(Mn)4–O5(ii)	2.0812(0.0016)
B–O2(x)	1.3843 (0.0044)		
B–O3(x)	1.3732(0.0040)		
B–O4	1.3853 (0.0044)		
Co(Mn)4–Co(Mn)2	2.8000(0.0005)		

Table 4
The shortest distances between the transition ions in the distinct crystallographic positions for $Co_{1.7}Mn_{1.3}O_2BO_3$ (Å).

	d_{13}	d_{23}	d_{34}	d_{14}	d_{24}
$Co_3O_2BO_3$	3.2979	3.0512	3.0847	3.0045	2.7473
$Co_{1.7}Mn_{1.3}O_2BO_3$	3.4380	3.1197	3.1424	3.0447	2.8000

In order to estimate the valence state of the manganese ions in $Co_{1.7}Mn_{1.3}O_2BO_3$ we have calculated the bond valence sum and obtained the oxidation numbers $Z=\sum_i s_{ij}$ for each of the distinct position. Here s_{ij}—the bond valence between i and j ions: $s_{ij}=\exp[(R_0-r_{ij})/b]$, R_0—the parameter dependent on the nature of ions forming the ij-pair, b—the constant value 0.37 Å, r_{ij}—ij-pair bond length [5,13,14]. The average bond valence sum for Mn ions appeared to be +2.65, slightly higher than the expected value +2.5. Thus, both di- and trivalent Mn ions are presented in approximately equal amount in $Co_{1.7}Mn_{1.3}O_2BO_3$ contrary to the case of $Co_{3-x}Fe_xO_2BO_3$, where only trivalent Fe ions appeared to enter the ludwigite structure [10].

It seems necessary to mention here that we did not succeed in growing the oxyborates $Co_{3-x}Fe_xO_2BO_3$ with ludwigite structure at $x>1$. All the attempts have led to obtaining the crystals $Co_{2-x}Fe_xBO_4$ with warwickite structure. As for $Co_{3-x}Fe_xO_2BO_3$ the crystal growing problems begin near the point where iron totally fill the position 4 specific for the trivalent ions. So, probably, the compound $Co^{2+}_{2-x}Fe^{2+}_xFe^{3+}O_2BO_3$ is unstable and the ludwigite $Co^{2+}_2Fe^{3+}O_2BO_3$ lies at the border of two phases: ludwigite and warwickite. Contrary, in $Co_{3-x}Mn_xO_2BO_3$ the manganese easily enters the ludwigite structure both in divalent and trivalent states.

The degree of the oxygen octahedral distortion can be characterized by the electric field gradient tensor [15]. In the common case this tensor is nonsymmetrical. Nevertheless 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—the bond M—O length, e—elementary charge. The values of V_{zz} for the four nonequivalent crystallographic positions are presented in Table 5, which shows that the oxygen octahedra around the sites 2 and 4 are less distorted when compared to the octahedra around the site 1 and especially 3. The comparison of the site occupation data for Mn^{2+} and Mn^{3+} ions with the EFG values for each sites did not reveal any direct correlation between them, as it was in the case of $Co_{3-x}Fe_xO_2BO_3$ [10].

4. The magnetic behavior

The results of magnetic measurements are presented in the Figs. 4–6. Fig. 4 shows the ZFC and FC temperature magnetization behavior $M(T)$ in the fields 1 and 50 kOe. The first that catches the eye is the magnetic transition near $T_N=41$ K, very close to the one similar in $Co_3O_2BO_3$. The next is the brightly pronounced splitting of ZFC and FC $M(T)$ dependencies below T_N. Despite the closeness of magnetic ordering temperatures in $Co_3O_2BO_3$ and $Co_{1.7}Mn_{1.3}O_2BO_3$ the type of magnetic ordering in these two compounds is obviously different. If the parent $Co_3O_2BO_3$ demonstrates the ferrimagnetic behavior [5], in the latter compound the most probable type of magnetic ordering is the spin-glass freezing. The magnetization curves $M(H)$ also provide evidence in favor of this proposal. In the ordered state $M(H)$ dependencies look as slightly open hysteresis loops with low remnant magnetization values (Fig. 5).

At temperatures above the magnetic transition $Co_{1.7}Mn_{1.3}O_2BO_3$ demonstrates the typical paramagnetic behavior. The inverse magnetic susceptibility temperature running well obeys Curie–Weiss law at the temperatures higher than 100 K (Fig. 6). The paramagnetic Curie temperature $\Theta=-100$ K is negative pointing out the predominance of antiferromagnetic interactions. The effective average magnetic moment per one magnetic ion is $\mu_{eff}=4.83\ \mu_B$.

Table 5
The main component of electric field gradient tensor and manganese content in the distinct crystallographic sites of $Co_{1.7}Mn_{1.3}O_2BO_3$.

Position	1	2	3	4
V_{zz}, e/Å^3	0.16	0.02	0.23	−0.05
Mn content, %	30.3	30.5	33.5	64.9

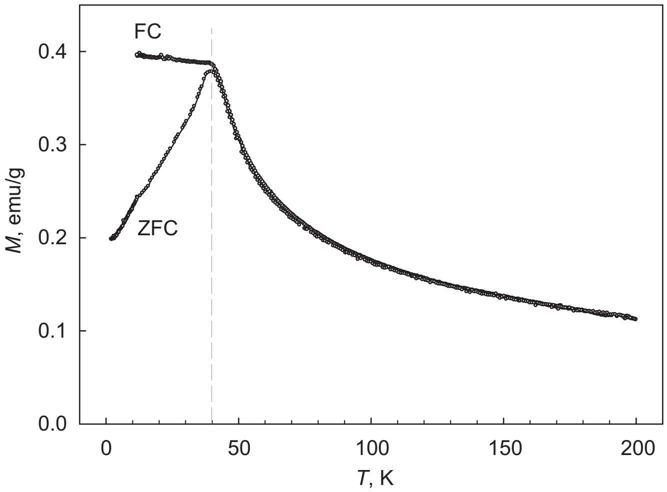

Fig. 4. Field cooled (FC) and zero field cooled (ZFC) temperature magnetization dependences of $Co_{1.7}Mn_{1.3}O_2BO_3$ single crystal in the magnetic field $H=1$ kOe. The onset of the magnetic ordering is near 41 K.

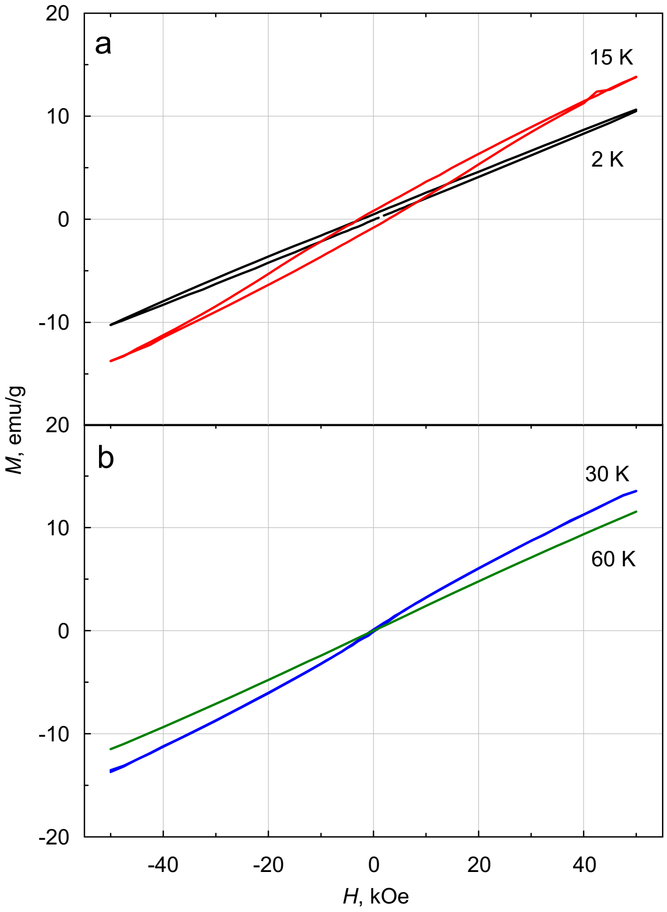

Fig. 5. Magnetization isotherms of $Co_{1.7}Mn_{1.3}O_2BO_3$.

5. Discussion and conclusion

The crystallographic investigation of the mixed oxyborate $Co_{1.7}Mn_{1.3}O_2BO_3$ has shown that the crystal structure is similar

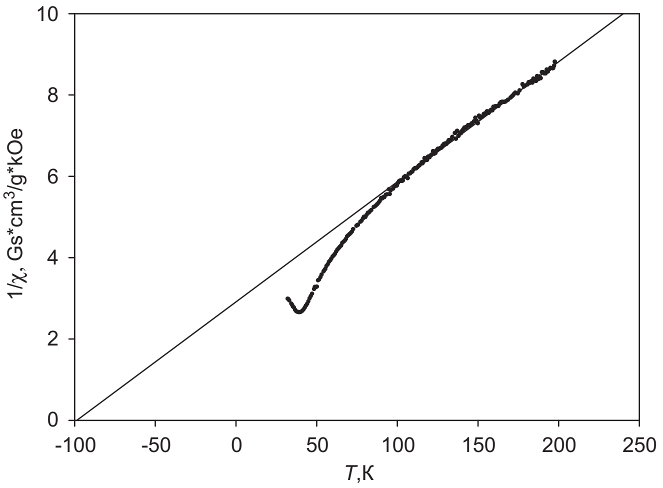

Fig. 6. Inverse magnetic susceptibility temperature dependence for $Co_{1.7}Mn_{1.3}O_2BO_3$ in the field $H=1$ kOe. The solid line corresponds to Curie–Weiss law approximation.

Table 6
Electron configurations and the spin values of the Mn and Co transition ions.

Ion	Co^{2+}	Co^{3+}	Mn^{2+}	Mn^{3+}
Configuration	d^7	d^6	d^5	d^4
S	3/2	2	5/2	2

the parent $Co_3O_2BO_3$ excluding small increase of the unit cell volume and lattice parameters.

The filling of nonequivalent crystallographic positions by manganese in the mixed ludwigite is nonuniform. According to the X-ray diffraction data the crystallographic position 4 is filled in a most degree, the last three positions are filled randomly. In the present investigation we did not reveal the clear correlation between the site occupation factor and electric field gradient, as it was in the case of cobalt–iron mixed ludwigite [10]. Apparently we need to recognize that the mechanism of the any crystallographic position preference is based on the valence state of transition ion, and not on only electric field gradient value. The bond valence sum calculations have shown that in $Co_{1.7}Mn_{1.3}O_2BO_3$ the position 4 is preferable for the trivalent ions and the other three positions for divalent ions. Nevertheless this question needs further careful investigation.

The magnetic measurements carried out for $Co_{1.7}Mn_{1.3}O_2BO_3$ single crystal have lead to the two main results. The first consists in the increasing of the effective magnetic moment in paramagnetic phase compared to nonsubstituted $Co_3O_2BO_3$. The effective magnetic moment per magnetic ion calculated from the paramagnetic data is close to 4.2 μ_B in $Co_3O_2BO_3$ [8], and grows up to $\mu_{eff}=4.83$ μ_B in the Mn-substituted sample. This higher value can be explained by the contribution of Mn^{2+} and Mn^{3+} magnetic moments. Taking into account that for $Co_3O_2BO_3$ the effective magnetic moment is very close to the only spin value, let us estimate the average μ_{eff} in the mixed ludwigite also neglected by orbital contribution (Table 6) and taking g-factor value 2. One can see that the spin value of the divalent manganese ion is higher than the spin of the divalent cobalt ion. For the trivalent ions the spin values are equal.

Assuming that the position 4 belongs to the trivalent ions and taking into account site occupation factors (Table 2), one can write the valence formula of our mixed ludwigite as $Co^{2+}_{1.37}Mn^{2+}_{0.63}Co^{3+}_{0.35}Mn^{3+}_{0.65}(O_2BO_3)^{7-}$. Then the average effective magnetic moment per one transition ion can be calculated as

$$\mu_{eff}=g\sqrt{\frac{n^{2+}_{Co}\times\frac{3}{2}\times\frac{5}{2}+n^{2+}_{Mn}\times\frac{5}{2}\times\frac{7}{2}+(n^{3+}_{Co}+n^{3+}_{Mn})2\times 3}{n}}.$$

Here n is a total number of magnetic ions in the formula unit. Accounting $n^{2+}_{Co}=1.37$; $n^{2+}_{Mn}=0.63$; $(n^{3+}_{Co}+n^{3+}_{Mn})=1$; $n=3$, we get $\mu_{eff}=4.71$ μ_B in a good agreement with the experimental value. So, the magnetic data confirm the proposal about the closeness of Mn^{2+} and Mn^{3+} concentrations in our compound.

The second important result of the magnetic measurements consists in $Co_3O_2BO_3$ and $Co_{1.7}Mn_{1.3}O_2BO_3$ having close magnetic ordering temperatures but principally different type of magnetic order. Contrary to the ferrimagnetic ordering in $Co_3O_2BO_3$ for $Co_{1.7}Mn_{1.3}O_2BO_3$ there is only a spin-glass freezing. The close values of the Neel temperature allow proposing the closeness of the average exchange interaction strength. It is not surprising because the inter-ion distances are very similar in both the compounds.

As it is shown in [10], where the simplified calculations of the exchange interactions in $Co_3O_2BO_3$ magnetic system have been done, even in this pure compound some of the magnetic interactions are frustrating, brining a high degree of disorder. It is obvious that the mixed compound $Co_{1.7}Mn_{1.3}O_2BO_3$ is an intrinsically disordered system, because even in each crystallographic sublattice 1, 2, 3 and 4 the distribution of manganese ions is chaotic. So the substitution of Co ions by Mn ions brings the additional disordering interactions to the magnetic system. It seems that namely high degree of disorder is the reason of spin-glass freezing in the mixed ludwigite $Co_{1.7}Mn_{1.3}O_2BO_3$.

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