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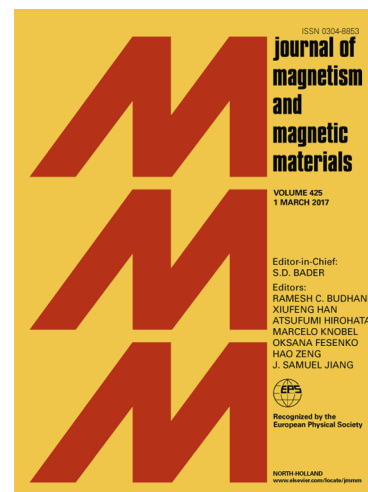
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# Chemical Disorder Reinforces Magnetic Order in Ludwigite (Ni,Mn)<sub>3</sub>BO<sub>5</sub> with Mn<sup>4+</sup> Inclusion

Svetlana Sofronova<sup>a</sup>, Evgeniya Moshkina<sup>a,b</sup>, Ilya Nazarenko<sup>a</sup>, Alexey Veligzhanin<sup>c</sup>, Maxim Molokeev<sup>d</sup>, Evgeniy Eremin<sup>a,d</sup>, Leonard Bezmaternykh<sup>a</sup>

<sup>a</sup> L.V. Kirensky Institute of Physics SB RAS, 660036 Krasnoyarsk, Russia

<sup>b</sup> Siberian State Aerospace University named after Academician M.F. Reshetnev, 660037 Krasnoyarsk, Russia

<sup>c</sup> National Research Centre "Kurchatov Institute", 123182 Moscow, Russia

<sup>d</sup> Siberian Federal University, 660041 Krasnoyarsk, Russia

## Abstract

Crystals of ludwigite Ni<sub>2.14</sub>Mn<sub>0.86</sub>BO<sub>5</sub> were synthesized by flux growth technique. We show in the paper that it contains Mn<sup>3+</sup> and Mn<sup>4+</sup>. A possible mechanism of the manganese valence states stabilization has been proposed. The structural and magnetic characterization of the synthesized samples has been carried out in detail. The cations composition and Mn valence states of the crystal were determined using X-ray diffraction and EXAFS technique. The comparative analysis was carried out between the studied crystal and Ni<sub>2</sub>MnBO<sub>5</sub> synthesized previously. Magnetic susceptibility measurements were carried out. The magnetic transition in the studied composition occurs at the 100 K that is higher than in Ni<sub>2</sub>MnBO<sub>5</sub> although the studied composition is more disordered. The calculations of the exchange integrals in the frameworks of indirect coupling model revealed strong antiferromagnetic interactions. The several magnetic subsystems existence hypothesis was supposed. The possible magnetic structure was suggested from the energies estimation for different ordering variants.

## Keywords

oxide, oxyborate, magnetism, crystal growth, EXAFS

## Introduction

Oxiborates Ni<sub>3-x</sub>Mn<sub>x</sub>BO<sub>5</sub> belong to the family of ludwigites [1]. The peculiarity of these compounds is the presence of quasi-low-dimensional elements in the structure - three-legged ladders, as well as triangular groups, which in some cases leads to very interesting physical properties. In addition to this, there are different valence metal ions in the structure; they can be di- and tri- [2, 3], as well as di- and tetravalent ions [4, 5, 6].

There are monometallic ludwigites: Fe<sub>3</sub>BO<sub>5</sub> and Co<sub>3</sub>BO<sub>5</sub>, in which Fe (Co) ions are represented in the di- and trivalent state. Both compounds exhibit interesting physical properties.

In Fe<sub>3</sub>BO<sub>5</sub> at high temperatures, the Fe<sup>3+</sup> ions with spin 5/2, are localized in one of the two 3LL (3-legged ladder) formed by Fe<sup>3+</sup>-Fe<sup>2+</sup>-Fe<sup>3+</sup> ions, and one additional electron is smeared out between three ions. With increasing temperature, this additional electron is localized in one of the pairs, as a result, a dimer is formed, and a structural phase transition occurs with an increase in the crystalline cell by the factor of two. In addition, a singularity is also observed on the magnetization curves. Magnetic ordering occurs at lower temperatures in two stages: at 112 K and 74 K, while the two subsystems are ordered mutually orthogonally. [3]

In Co<sub>3</sub>BO<sub>5</sub>, charge ordering arises immediately at high temperatures, and unlike iron ludwigite, magnetic ordering occurs in one stage at 42 K. However, the Co<sup>3+</sup> ion is in the low-spin state, and its spin is zero.

Apparently, the transition to the low-spin state of the  $\text{Co}^{3+}$  ion and the mutual orthogonal orientation of the two magnetic subsystems in  $\text{Fe}_3\text{BO}_5$  arises to reduce frustrations in the system [3, 7].

It is interesting to prepare other compounds in which a magnetic ion would be present in different valence states. The manganese ion is found in compounds in di-, tri-, and tetravalent states.

It is known that there is a  $\text{Ni}_2\text{MnBO}_5$  compound, where the manganese ion is in the tetravalent state. We have obtained and investigated the compound  $\text{Ni}_2\text{MnBO}_5$ , where the manganese ion is in the trivalent state [8]. In this paper, we present an attempt to obtain the ludwigite  $\text{Ni}_{3-x}\text{Mn}_x\text{BO}_5$ , in which the manganese ion would be represented in the tri- and tetravalent state. We also investigate the effect of a tetravalent manganese ion presence on physical properties.

## 1. Synthesis

The physical properties of ludwigites are very sensitive to the changes in the composition, even within the small limits. Therefore, in the synthesis of such compounds, a special role is played by controlling the valence state of the metallic cations. The synthesis of ludwigites with a certain composition involves the development of a growing technique that will allow us to determine the factors that affect the conversion of the transition metals cations valence states, especially Mn cations.

Initially, the hypothesis of the Mn-heterovalent (containing  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ , and maybe  $\text{Mn}^{2+}$ ) ludwigite  $\text{Ni}_{3-x}\text{Mn}_x\text{BO}_5$  existence was made on the basis of the criterion presented in [9], which consists in a certain ratio of the radius of the tetra- / trivalent cation to the divalent radius.

### 1.1. Flux Growth Technique

$\text{Mn}_{0.86}\text{Ni}_{2.14}\text{BO}_5$  single crystals were synthesized from the flux with an initial molar ratio of the components  $\text{Bi}_2\text{Mo}_3\text{O}_{12} : 1.6\text{B}_2\text{O}_3 : 0.84\text{Na}_2\text{O} : 0.94\text{NiO} : 0.178\text{Mn}_2\text{O}_3$ .

The flux in a mass of 67 g was prepared from initial oxides  $\text{Mn}_2\text{O}_3$  and  $\text{NiO}$  in combination with sodium carbonate at the temperature  $T = 1100^\circ\text{C}$  in a platinum crucible with the volume  $V = 100\text{ cm}^3$  by sequential melting of powder mixtures, first  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ , and  $\text{B}_2\text{O}_3$ , then  $\text{Mn}_2\text{O}_3$  and  $\text{NiO}$ ; finally,  $\text{Na}_2\text{CO}_3$  was added in portions.

In the prepared flux, the phase crystallizing within a sufficiently wide (about  $40^\circ\text{C}$ ) high-temperature range was  $\text{Mn}_{3-x}\text{Ni}_x\text{BO}_5$  with the ludwigite structure. The saturation temperature of the flux was  $T_{\text{sat}} = 920^\circ\text{C}$ .

Single crystals of the ludwigites were synthesized by spontaneous nucleation. After homogenization of the flux at  $T = 1100^\circ\text{C}$  for 3 h, the temperature was first rapidly reduced to  $(T_{\text{sat}} - 10)^\circ\text{C}$  and then slowly reduced with a rate of  $4^\circ\text{C}/\text{day}$ . In 3 days, the growth was completed, the crucible was withdrawn from the furnace, and the flux was poured out. The grown single crystals in the form of orthogonal prisms with a length of 6 mm and a transverse size of about 0.3 mm were etched in a 20% water solution of nitric acid to remove the flux remainder.

### 1.2. Manganese Valence State Conversion Mechanism

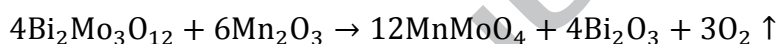
The synthesis of the single crystals containing the multiple-valence cations of the same element is a complex problem since the relative content of such cations cannot be often controlled due to valence conversion at the high temperatures. In the synthesis of heterovalent oxyborates with a ludwigite structure, the mechanism for stabilizing valence states of transition metal cations is not clearly defined for many systems in particular, and moreover, there is no universal technique.

Depending on the type of cation, several methods of heterovalent oxyborates single crystal synthesis are known. In the framework of these methods, the stabilization of valence states was carried out by maintaining the atmosphere of argon [10] or oxygen [11], with the help of the Fe metal chips additives when growing ludwigite  $\text{Fe}_3\text{BO}_5$  [12, 13], under high-pressure conditions [12]. Many methods for growing such single crystals involve the use of the borax  $\text{Na}_2\text{B}_4\text{O}_7$  [14, 15] or boric acid  $\text{H}_3\text{BO}_3$  [16, 15],

the effect of these components on the stabilization of valence states of transition metal cations has not been reported. In a number of cases, the combined crystallization of ludwigites and oxides ( $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ) was observed [10, 17, 2].

As was shown in the previous section, the operating temperature of alloying the initial components of the solution-melt is  $1100^\circ\text{C}$ . This temperature is higher than the decomposition temperature of the oxide  $6\text{Mn}_2\text{O}_3 \xrightarrow{1080^\circ\text{C}} 4\text{Mn}_3\text{O}_4 + \text{O}_2$ , as a result of which the valence of manganese partially changes and an uncertainty arises over the composition of the flux. In the synthesis of Mn-heterovalent ludwigite  $\text{Ni}_{3-x}\text{Mn}_x\text{BO}_5$  at  $x > 2$  (with the presence of the  $\text{Mn}^{4+}$  cation) with the help of the flux method, it is assumed in this paper that the components of the  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  and  $\text{Na}_2\text{CO}_3$  solvent play a special role in the stabilization of manganese in the divalent and trivalent state, respectively, at the temperature of the flux.

When the initial components are fused, it is assumed that the hierarchy of chemical bonds is such that due to the interaction between  $\text{Mn}_2\text{O}_3$  manganese trioxide and  $\text{MoO}_3$  molybdenum trioxide, which is released from  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ , the following reaction occurs with the formation of  $\text{Mn}^{2+}\text{MoO}_4$  intermediate bonds, which keep manganese in a state with valence  $2+$ :

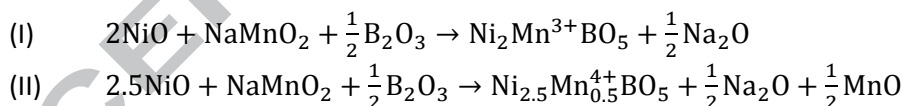


It is also assumed that due to the interaction of manganese trioxide  $\text{Mn}_2\text{O}_3$  and sodium carbonate  $\text{Na}_2\text{CO}_3$ , the following reaction occurs:



As a result of this reaction, intermediate bonds of the Delafossite type  $\text{NaMn}^{3+}\text{O}_2$  are formed in the solution-melt, which makes it possible to retain manganese in a trivalent state.

Thus, in  $\text{NiO}$  and  $\text{Mn}_2\text{O}_3$  solutions in  $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  melts diluted with  $\text{Na}_2\text{CO}_3$  and  $\text{MoO}_3$ , it is possible to stabilize  $\text{Mn}^{2+}$  by a  $\text{Mn}^{2+}\text{MoO}_4$  bond and  $\text{Mn}^{3+}$  by a bond of  $\text{NaMn}^{3+}\text{O}_2$  types. As shown by our experiments, the connection of the second type prevails. Therefore, in molten solutions with a large ratio of  $\text{NiO}$  to  $\text{NaMn}^{3+}\text{O}_2$ , the crystallization of the ludwigite phase  $\text{Ni}_{2+x}^{2+}\text{Mn}_{1-2x}^{3+}\text{Mn}_x^{4+}\text{BO}_5$  ( $0 \leq x \leq 0.5$ ) is determined by two processes:



It is the second process that is responsible for the conversion of  $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ .

Using this technique, a number of compounds with different contents of nickel and manganese was obtained.

## 2. Crystal Structure

The powder diffraction data of  $(\text{Ni,Mn})_3\text{BO}_5$  for Rietveld analysis was collected at room temperature with a Bruker D8 ADVANCE powder diffractometer ( $\text{Cu-K}\alpha$  radiation) and linear VANTEC detector. The step size of  $2\theta$  was  $0.016^\circ$ , and the counting time was 3 s per step. The  $2\theta$  range of  $5-70^\circ$  was measured with 0.6 mm divergence slit, but the  $2\theta$  range of  $70-140^\circ$  was measured with 2 mm divergence slit. The reason of these experimental conditions can be read in another our manuscript [18].

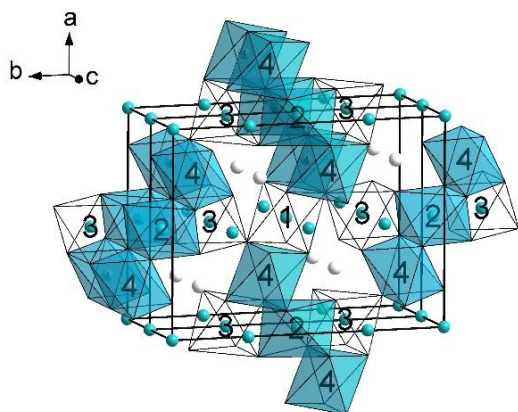


Figure 1. The structure of the studied crystal. The site 4 is occupied randomly by Mn and Ni ions. Crystallographic positions are 1 – 2a, 2 – 2d, 3 – 4g, 4 – 4h.

Rietveld refinement was performed by using TOPAS 4.2 [19] which accounts esd's of each point by a special weight scheme. All peaks were indexed by orthorhombic cell (*Pbam*). The unit cell contains two formula units (Figure 1). Metallic ions occupy four positions, in Figure 1, they are indicated by the numbers 1-4. In most ludwigites, positions 1-3 are often occupied by divalent cations, while the position 4 is occupied by trivalent cations (alternatively tetravalent and divalent in the ratio 1:1). The crystal structure of  $\text{Mn}_{0.5}\text{Ni}_{2.5}\text{BO}_5$  [20] was taken as starting model for Rietveld refinement. Within the framework of this method, it is difficult to clarify the composition and population of atoms by positions. So, we assumed that the occupation of the Mn and Ni sites follows a ratio 0.25/0.75, according to the chemical formula of  $\text{Mn}_{0.5}\text{Ni}_{2.5}\text{BO}_5$  by Mn and Ni ions with fixed occupations. In order to reduce the number of refined parameters, only one thermal parameter was refined for all O atoms. Refinement was stable and gives low R-factors (Table 1, Figure 1). Coordinates of atoms and main bond lengths are in Table 2. For comparison in Table 1, the lattice parameters for the  $\text{Ni}_2\text{MnBO}_5$  [21] compound are also given, which we will need later in our discussion.

Table 1. Main parameters of processing and refinement of the studied sample.

Compound	Studied sample	$\text{Ni}_2\text{MnBO}_5$ [22]
Sp.Gr.	<i>Pbam</i>	<i>Pbam</i>
a, Å	9.1650 (2)	9.176(1)
b, Å	12.2545 (3)	12.316(2)
c, Å	2.98895 (5)	2.9978(4)
V, Å <sup>3</sup>	335.69 (1)	338.78(8)
Z	4	4
2θ-interval, °	5-140	
R <sub>wp</sub> , %	1.92	
R <sub>p</sub> , %	1.57	
R <sub>exp</sub> , %	1.28	
χ <sup>2</sup>	1.50	
R <sub>B</sub> , %	1.53	

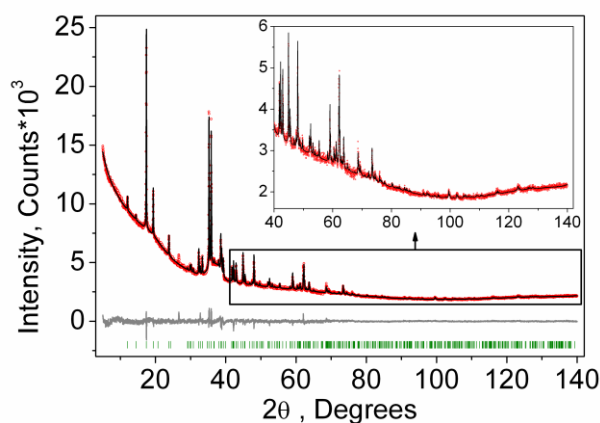


Figure 2. Difference Rietveld plot of the studied sample.

Table 2. Fractional atomic coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) of the studied sample.

	x	y	z	$B_{\text{iso}}$	Occ.
Mn1	0	1	0	3.2 (4)	0.25
Mn2	0	0.5	-0.5	3.0 (4)	0.25
Mn3	-0.002 (1)	0.7220 (3)	0	2.7 (4)	0.25
Mn4	0.2584 (7)	0.6180 (5)	-0.5	2.1 (4)	0.25
Ni1	0	1	0	3.2 (4)	0.75
Ni2	0	0.5	-0.5	3.0 (4)	0.75
Ni3	-0.002 (1)	0.7220 (3)	0	2.7 (4)	0.75
Ni4	0.2584 (7)	0.6180 (5)	-0.5	2.1 (4)	0.75
B	0.222 (5)	0.868 (4)	-0.5	3 (1)	1
O1	-0.107 (2)	0.860 (1)	0	2.6 (4)	1
O2	0.155 (2)	0.765 (2)	-0.5	2.6 (4)	1
O3	0.102 (2)	0.577 (1)	0	2.6 (4)	1
O4	-0.150 (2)	0.647 (2)	-0.5	2.6 (4)	1
O5	0.147 (2)	0.948 (1)	-0.5	2.6 (4)	1

## 2.1. EXAFS

The composition of the studied compound was refined by studying the XAS at the K-edge of manganese and nickel ions. X-ray absorption spectra were measured at the experimental station "Structural Material Science" of the Kurchatov synchrotron radiation source [23]. The experimental procedure and technique of processing and analyzing the results have been described in detail in the paper [24].

To compensate the decrease in the amplitude of the EXAFS oscillations with increasing energy, the exposure time  $T$  at the points after the absorption edge was increased according to the quadratic law ( $T = a \cdot n^2 + c$ ), depending on the number of the point  $n$ . The adjustment constants  $a$  and  $c$  of this expression were chosen so that the initial exposure of 1 second, while at the end of the measurement area was 4 seconds. Thus, each spectrum was measured for approximately 20 minutes. To improve the statistics, each sample was measured for 2-3 times, after which the spectrum was averaged.

The processing and analysis of the results were carried out using the IFEFFIT [25, 26] program version 1.2.11c. The measured XAFS data were first processed by the ATHENA program of this complex to adjust the background, normalize the spectra to a unity-height jump, and obtain the oscillating part of the spectrum. The fine structure of the X-ray absorption spectrum obtained in this manner after the  $K$ -jump was then used for the structural analysis.

The local structure of investigated compounds was determined by fitting the EXAFS spectra at Ni and Mn K-edge.

The number of coordination spheres was adjusted for each of the absorbing atoms separately and in the final model, two coordination spheres for the nickel atom and five coordination spheres for the manganese atom were used.

The fit determines following parameters of local structure: distances between absorbing and the neighboring atoms  $R_j$  and mean-square variation of the bond length  $\sigma_j^2$ .

The coordination numbers  $N_j$  were fixed accordingly to the crystal structure of the samples. The shift of Fermi energy  $\Delta E_0$  and the damping coefficient of the signal amplitude  $S_0^2$  were also included in the refinement (Table 3).

Table 3. Parameters of the nearest environment of Ni and Mn obtained by fitting EXAFS data.

Ion	$R_f, \%$	$k$ -range	$R$ -range	$S_0^2$	$E_0, \text{eV}$	The scattering path	$N$	$R, \text{\AA}$	$\sigma^2, \text{\AA}^2 \times 10^{-3}$
Mn	7.78	2.000 - 12.000	1.0 - 4.2	0.63 $\pm$ 0.18	0.39 $\pm$ 2.71	Mn-O1	4.0	1.91(3)	6 $\pm$ 3
						Mn-O2	2.0	2.11(6)	
						Mn-Mn1(Ni)	1.0	2.81(5)	5 $\pm$ 2
						Mn-Mn2(Ni)	6.0	3.05(1)	
						Mn-Mn3(Ni)	2.0	3.33(3)	
Ni	1.9	2.000 - 12.000	1.15 - 3.25	0.58 $\pm$ 0.06	1.65 $\pm$ 1.1	Ni-O	6.0	2.081(8)	4 $\pm$ 1
						Ni-Mn(Ni)	8.0	3.072(8)	8 $\pm$ 1
Ni	1.5	2.000 - 12.000	1.15 - 3.25	0.59 $\pm$ 0.06	2.15 $\pm$ 1.1	Ni-O	6.0	2.083(8)	4 $\pm$ 1
						Ni-Mn1(Ni)	6.0	3.055(9)	5 $\pm$ 1
						Ni-Mn2(Ni)	2.0	3.18(4)	5 $\pm$ 1

The local environment of nickel is characterized by a relatively small value of the parameter  $S_0^2$ , which may be due to some distortion of the octahedral environment. However, attempts to describe this distortion by adding an additional nonequivalent Ni-O distance does not improve the fit.

The results of fitting the Fourier transform and the oscillating part of the EXAFS spectra are shown in Figure 3, Figure 4.

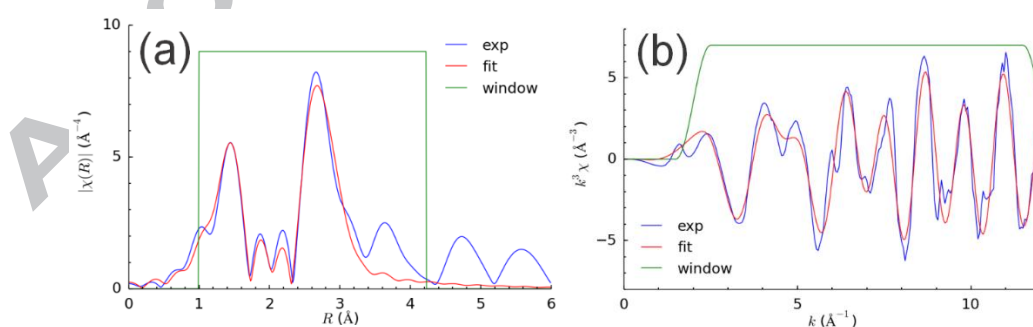


Figure 3. FT and an oscillating part of the manganese spectrum for the studied sample.



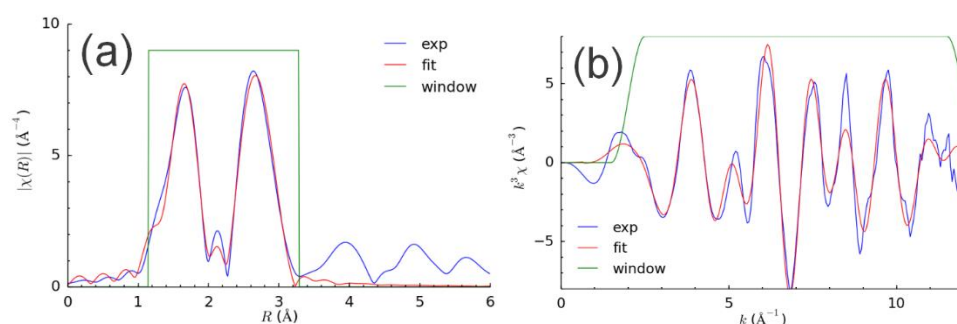


Figure 4. FT and the oscillating part of the nickel spectrum for the studied sample.

The composition of the compound was refined by the jump in the K-edge of the manganese and nickel absorption spectrum. As a result of the refinement, the following formula of the compound was obtained:  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$ . The obtained composition completely corresponds to the composition "by laying".

The valence of metal ions was studied by the fingerprint method. Comparison of the spectra of the K-edge of nickel with the NiO standard shows good agreement (Figure 5), in addition, it can be seen from the figure that the spectra of the composition of  $\text{Ni}_2\text{MnBO}_5$  and the composition under study also coincide. We conclude that the nickel in the ludwigites is present only in the divalent state.

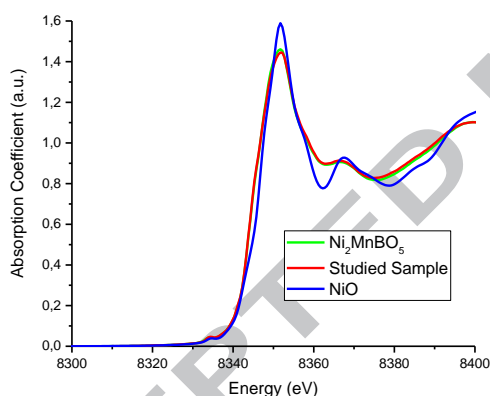


Figure 5. K-absorption edge of Ni for the studied sample.

For the manganese oxidation degree analysis, the XANES region of absorption spectrum and the first derivative of the spectrum were compared with corresponding spectra of well-characterized standards -  $\text{MnB}_2\text{O}_4$  (Mn II),  $\text{Mn}_{1-x}\text{Fe}_x\text{MoO}_4$  (Mn II),  $\text{Mn}_2\text{O}_4$  (Mn III) and  $\text{MnO}_2$  (Mn IV) (Figure 6).

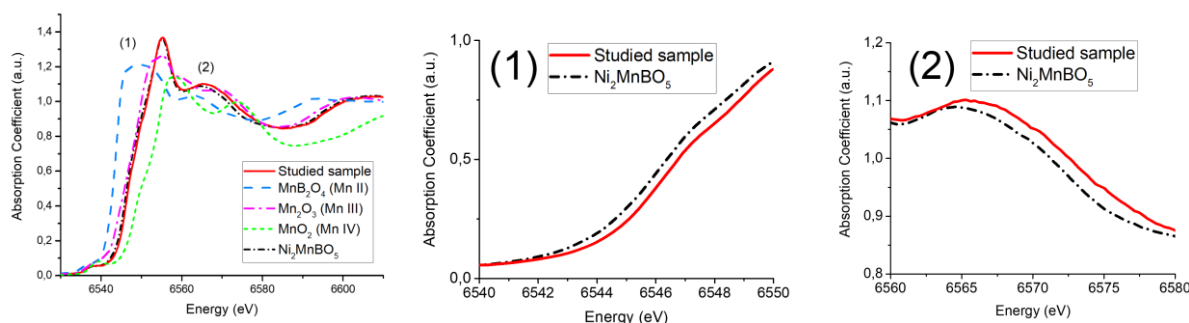


Figure 6. K-absorption edge of Mn and comparison insets of studied sample and  $\text{Ni}_2\text{MnBO}_5$ .

Mn K-edge absorption spectrum of the studied composition differs from the  $\text{Ni}_2\text{MnBO}_5$  spectrum, where manganese is supposedly included only in the trivalent state. There is a shift of the spectrum to the higher energy, which corresponds to some increase in the Mn valence. To maintain electroneutrality, when the divalent ion (Ni) content in the composition is greater than 2, the presence of tetravalent ion



is necessary. The composition and the displacement of the absorption spectrum of manganese K-edge indicate the presence of manganese in two valence states: 3- and 4-valent.

Table 4 shows the parameters of the local structure of the  $\text{Ni}_2\text{MnBO}_5$  crystal and the  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$  around Mn atoms, determined with the same initial model. The presence of the ion with a smaller ionic radius manifests itself by the substantial Mn-O bond decrease. Ni-O bonds are also shortened, but to a lesser extent, that is likely related to a decrease in the lattice parameters (Table 4). The Mn-O octahedron is quite distorted and has a local structure that can be described by two long and four short bonds, Ni-O octahedra are apparently more balanced, and the difference of Ni-O bonds as it is observed by X-ray diffraction cannot be resolved by EXAFS.

Thus, we have confirmed that we obtained a composition in which manganese is included in different valence states: tri- and tetravalent.

Table 4. The bond lengths obtained in the compositions of the nickel-manganese ludwigites.

Composition	Mn-O		Ni-O	
	4 bonds	2 bonds	6 bonds	6 bonds
$\text{Ni}_2\text{MnBO}_5$	1.95	2.17	2.087	2.091
$\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$	1.91	2.11	2.081	2.083

### 3. Magnetic Properties

Magnetic measurements of  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$  were performed using the physical properties measurements system PPMS-9 (Quantum Design) at temperature range  $T=3\div300$  K and magnetic fields up to 80 kOe. The studies were carried out on small single crystals, each of which was randomly oriented to obtain isotropic magnetization. The temperature dependence of the magnetization in the fields of 1, 5 and 10 kOe is shown in Figure 7. As can be seen from the figure, in the region of 100 K, an ordering of the magnetic moments occurs, the magnetization increases and decreases below 30 K, which is typical for the disordered systems. Temperature dependence of the inverse magnetic susceptibility  $1/\chi=B/M$  of ludwigite  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$  is shown in Figure 7b (inset).

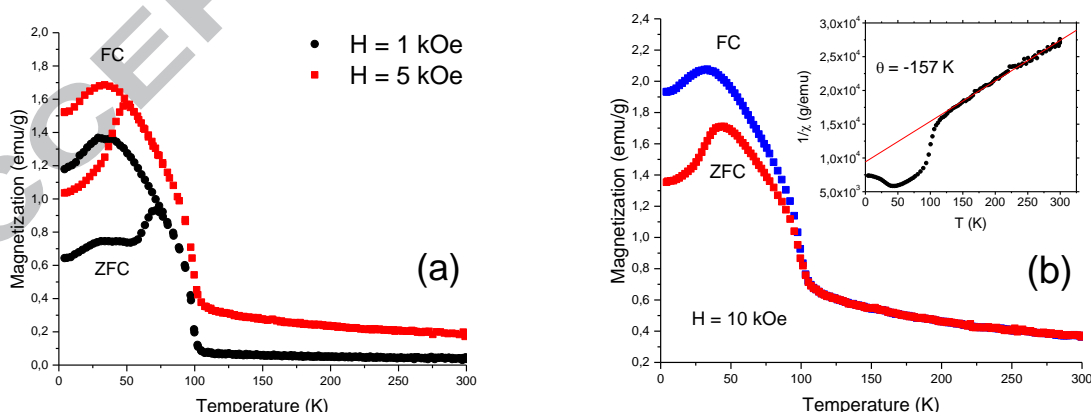


Figure 7. (a) - magnetization versus temperature for the studied composition in the fields 1 and 5 kOe; (b) - magnetization versus temperature for the studied composition in a field of 10 kOe, the inset shows the inverse susceptibility versus temperature for the studied compound.

It should be noted that the magnetic ordering temperature for the studied composition is 15 K higher than  $\text{Ni}_2\text{MnBO}_5$  composition. However, as in  $\text{Ni}_2\text{MnBO}_5$ , there is a feature on the magnetization curves at 60 K. [21]

The effective magnetic moment and the Curie-Weiss temperature were determined using the modified Curie-Weiss law:  $\chi = \chi_0 + \frac{C}{T-\theta}$ , where  $\chi_0$  – diamagnetic contribution from completely filled shells and Van Vleck paramagnetism,  $\theta$  – Curie-Weiss temperature,  $C$  – Curie constant.

Adjustment of the magnetic susceptibility temperature dependence was carried out in the paramagnetic phase in the temperature range of 200-300 K. As a result, the following values of the parameters were obtained:  $\chi_0 \approx 0.22 \cdot 10^{-4}$  emu/mol,  $\theta = -157$  K,  $C \approx 4.4$  emu · K/mol. The negative Curie-Weiss temperature indicates strong antiferromagnetic interactions in the crystal.

The experimental  $\mu_{eff}^{exp} = 5.93 \mu_B/\text{mol}$  value was determined by the formula  $\mu_{eff}^{exp2} = 8C$ .

The theoretical  $\mu_{eff}^{theor}$  value was determined as  $\mu_{eff}^{theor} = \sum (Ng^2S(S+1)\mu_B^2)^{1/2}$ , where  $N$  – amount of ion in formula unit,  $g$  – g-factor  $\text{Mn}^{3+}$  ( $g=2$  [27]),  $\text{Mn}^{4+}$  ( $g=1.96$  [28]) and  $\text{Ni}^{2+}$  ( $g=2.08$  [29]). We take into account only the spin component contribution to the effective magnetic moment and consider the high-spin states  $S(\text{Ni}^{2+})=1$ ,  $S(\text{Mn}^{3+})=2$ ,  $S(\text{Mn}^{4+})=3/2$ . Obtained experimental and theoretical  $\mu_{eff}$  values are in a good agreement:  $\mu_{eff}^{theor} \approx 6.19 \mu_B/\text{mol}$ ,  $\mu_{eff}^{exp} \approx 5.93 \mu_B/\text{mol}$ .

Residual magnetization in the studied composition is  $0.021 \mu_B/\text{mol}$ , and in  $\text{Ni}_2\text{MnBO}_5$  [21], it is 0.079, 0.069,  $0.025 \mu_B/\text{mol}$  at 3, 20, 50 K, respectively.

Below the magnetic transition temperature, unlike  $\text{Ni}_2\text{MnBO}_5$ , remanence does not vary, though it is smaller than  $\text{Ni}_2\text{MnBO}_5$ . Apparently, the  $\text{Mn}^{4+}$  appearance in the composition reduces exchanges competition in the system and helps to stabilize the magnetic structure at higher temperature than in  $\text{Ni}_2\text{MnBO}_5$ .

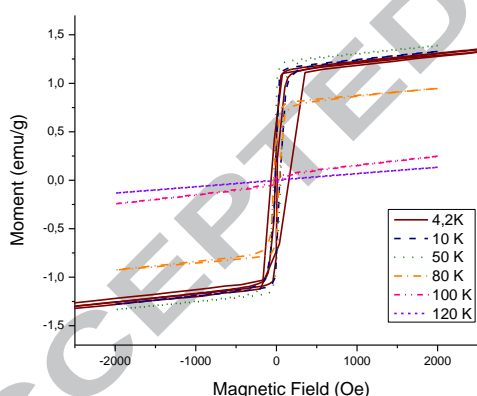


Figure 8. The studied sample field dependencies of the magnetization.

### 3.1. Calculation of the Exchange Interactions

We tried to analyze the exchange interactions in  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$  in the framework of the Andersen-Zawadsky's indirect exchange model [30] to understand the possible reasons for increasing the magnetic ordering temperature. Model parameters were taken from [31]. The results of the calculation and comparison with  $\text{Ni}_2\text{MnBO}_5$  are shown in Table 5.

We assume that the position 4 is occupied by 0.14 of  $\text{Ni}^{2+}$ , 0.14 of  $\text{Mn}^{4+}$  and 0.72 of  $\text{Mn}^{3+}$ , in the third column, there are average values of the indirect exchange interaction, and in the last column, there are values for each type of ions.

Table 5. Comparison of the exchange interaction values for both compositions of nickel-manganese ludwigites.

Pos.	Angles	Expression	Occ.	J(studied sample)	J(Ni <sub>2</sub> MnBO <sub>5</sub> )
4-4	$\alpha = 93^\circ$ $\beta = 99^\circ$	$\frac{2c}{27}(4bJ_{Mn^{4+}} - 3cU_{Mn^{4+}})(\sin \alpha + \sin \beta) = -0,085 K$	0.020	-2.437	-1.815
		$\frac{c}{3}(3cJ_{Ni^{2+}} - 4b(U_{Mn^{4+}} + U_{Ni^{2+}}))(\sin \alpha + \sin \beta) = -7,805 K$	0.040		
		$\frac{2}{3}bcJ_{Ni^{2+}}(\sin \alpha + \sin \beta) = 5,527 K$	0.020		
		$\frac{2c}{48}(3bJ_{Mn^{3+}} - (3c + 2b)U_{Mn^{3+}})(\sin \alpha + \sin \beta) = -1,826 K$	0.518		
		$\frac{c}{36}(b(4J_{Mn^{3+}} + 3J_{Mn^{4+}}) - (3c + b)(U_{Mn^{4+}} + U_{Mn^{3+}}))(\sin \alpha + \sin \beta) = -1,314 K$	0.202		
		$\frac{c}{24}((3c + b)J_{Mn^{3+}} - 4b(U_{Ni^{2+}} + U_{Mn^{3+}})) \sin \alpha = -5,156 K$	0.202		
3-3	$\alpha = 90.4^\circ$ $\beta = 91^\circ$	$\frac{8}{3}bcJ_{Ni}(\sin \alpha + \sin \beta)$	1	5.570	5.570
2-2	$\alpha = \beta = 92^\circ$		1	5.564	5.564
1-1	$\alpha = \beta = 91^\circ$		1	5.568	5.568
4-2	$\alpha = 84^\circ$	$\frac{c}{9}(3cJ_{Ni^{2+}} - 4b(U_{Mn^{4+}} + U_{Ni^{2+}})) \sin \alpha = -7,828 K$	0.140	-4.020	-5.139
		$\frac{2}{3}bcJ_{Ni^{2+}} \sin \alpha = 5,543 K$	0.140		
		$\frac{c}{24}(3(2c + b)J_{Ni^{2+}} - 8b(U_{Mn^{3+}} + U_{Ni^{2+}})) \sin \alpha = -5,139 K$	0.720		
3-4	$\alpha = 95^\circ$ $\beta = 99^\circ$	$\frac{bc}{3}2J_{Ni^{2+}}(\sin \alpha + \sin \beta) = 5,522 K$	0.140	-3.630	-4.599
		$\frac{c}{18}[(3cJ_{Ni^{2+}} - 4b(U_{Ni^{2+}} + U_{Mn^{4+}})) \sin \alpha + (3cJ_{Ni^{2+}} - 8bU_{Ni^{2+}}) \sin \beta] = -7,797 K$	0.140		
		$\frac{c}{24}[(3c + 4b)J_{Ni^{2+}} - 4b(U_{Ni^{2+}} + U_{Mn^{3+}})) \sin \alpha + ((3c + b)J_{Ni^{2+}} - 4b(U_{Ni^{2+}} + U_{Mn^{3+}})) \sin \beta] = -4,599 K$	0.720		
4-1	$\alpha = 92^\circ$ $\beta = 98^\circ$	$\frac{c}{18}(3cJ_{Ni^{2+}} - 4b(U_{Mn^{4+}} + U_{Ni^{2+}}))(\sin \alpha + \sin \beta) = -7,820 K$	0.140	-3.644	-4.618
		$\frac{2}{3}bcJ_{Ni^{2+}}(\sin \alpha + \sin \beta) = 5,538 K$	0.140		
		$\frac{c}{24}[(3c + b)J_{Ni^{2+}} - 4b(U_{Mn^{3+}} + U_{Ni^{2+}})) \sin \alpha + ((3c + 4b)J_{Ni^{2+}} - 4b(U_{Mn^{4+}} + U_{Ni^{2+}})) \sin \beta] = -4,618 K$	0.720		
3-4	$\alpha = 117^\circ$	$\frac{1}{9}b[3cJ_{Ni^{2+}} \sin \alpha - 4bU_{Ni^{2+}} \cos \alpha ] = -1,432 K$	0.140	-1.061	-1.010
		$\frac{1}{108}[3c(3cJ_{Ni^{2+}} - 4b(U_{Ni^{2+}} + U_{Mn^{4+}})) \sin \alpha + 2(9c^2J_{Ni^{2+}} + 8b^2J_{Mn^{4+}}) \cos \alpha ] = -0,948 K$	0.140		
		$\frac{c}{48}((b + 3c)J_{Ni^{2+}} - b(U_{Ni^{2+}} + U_{Mn^{3+}}))(\sin \alpha +  \cos \alpha ) = -1,010 K$	0.720		

3-1	$\alpha = 121^\circ$	$\frac{4}{3}b \left( cJ_{Ni} \sin \alpha - \frac{4}{3}b^2 U_{Ni} \cos \alpha \right)$	1	-1.794	-1.794
4-2	$\alpha = 165^\circ$	$\frac{1}{27}(8b^2 J_{Mn^{4+}} + 9c^2 J_{Ni^{2+}}) \cos \alpha  = 3,293 K$	0.140	-0.682	0.558
		$-\frac{8}{9}b^2 U_{Ni^{2+}} \cos \alpha  = -11,037 K$	0.140		
		$\frac{1}{36}(9c^2 J_{Ni^{2+}} + 2b^2(3J_{Mn^{3+}} - U_{Mn^{3+}} - U_{Ni^{2+}})) \cos \alpha  = 0,558 K$	0.720		

As can be seen from Table 5, the average interaction 4-4 is strengthened, when 4-3 and 4-1 are weakened.

In ludwigite structure, one can distinguish two main structural elements consisting of two types of ladders (3LL). The first 3LL is formed by ions in the positions 4-2-4 (blue octahedra in Figure 1), the second 3LL is 3-1-3 (white octahedra in Figure 1). The exchange interaction 4-3 and 4h-2a are responsible for the interaction between the 4-2-4 and 3-1-3 three-legged ladders. The magnetic structure studies of the Fe [2, 3], Co [7], Cu-Mn ludwigite showed that the magnetic structure is divided into two subsystems formed by 3LLs. In the Fe ludwigite, the magnetic moments in the subsystems are mutually orthogonal, in the Cu-Mn ludwigite, the angle between the magnetic moments of the subsystems is  $60^\circ$ . In the Co ludwigite, the trivalent cobalt passes into the low-spin state to reduce frustrations. For other known ludwigites, the magnetic structure has not been studied, but there is an indirect evidence that there are two magnetic subsystems. Apparently, such decomposition is the result of the crystal structure geometry. The exchange paths between two 3LLs form numerous triangular groups (Figure 9a, b) and if the interaction is antiferromagnetic, it leads to a frustration in the system. A striking example is Fe ludwigite, the exchange interactions between the 3LLs are compensated, which probably leads to mutually orthogonal orientation of the magnetic moments in the subsystems [2]. It seems that in the studied ludwigite, the weakening of the exchange coupling between the subsystems increases the ordering temperature, which may be indirect evidence that the magnetic system is also divided into two subsystems. In comparison in the  $Ni_2MnBO_5$ , remanence is decreased.

When comparing these two compounds, one can see that there is no change in the 3-1-3 subsystem, since this system is formed by  $Ni^{2+}$  ions, both in one and the other compounds. All changes take place in subsystem 4-2-4.

Ions of tri- and tetravalent manganese, like bivalent nickel, occupy position 4, position 2 is occupied mainly by nickel ions. A disordered arrangement of ions in the three-legged ladders was modeled, and exchange interactions in this subsystem were considered.

The Figure 9 (a, b) shows the ions 3 and 1 neighboring triad 4-2-4, as can be seen from the Figure 10, the nickel ions in position 4h have a strong exchange interaction with its neighbors, two of which are opposite in sign to the exchange with manganese ions.

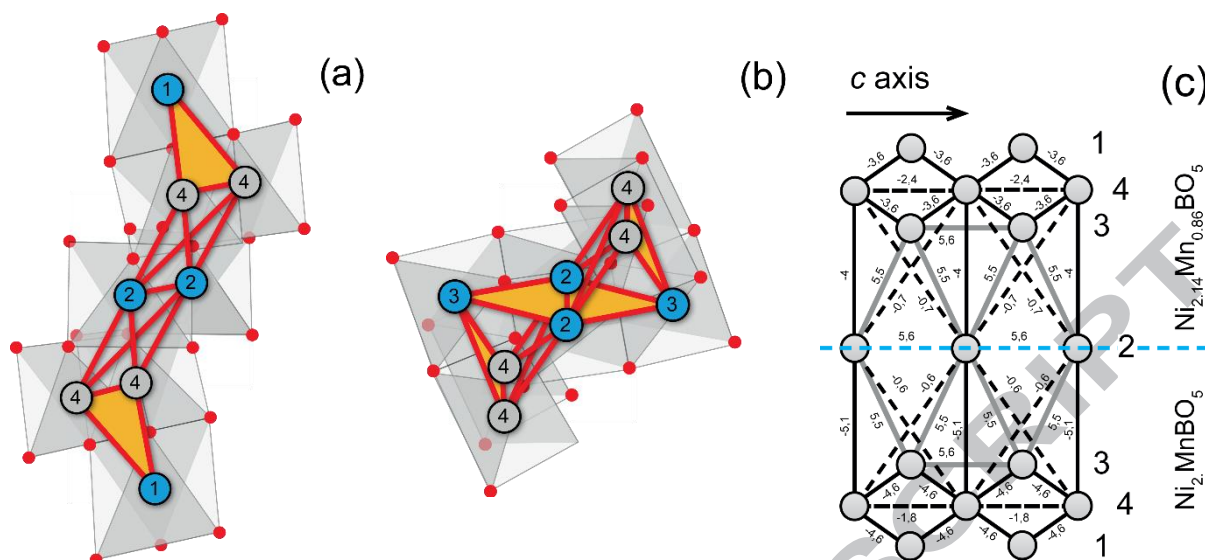


Figure 9. a, b - the triangular groups connecting the 3LL of triads 4-2-4 and 3-1-3; c - comparison of the exchanges in the triangular groups for the two compositions.

As can be seen from the Figure 10, in 3LL 4-2-4, the strong AFM interactions Ni-Ni ( $165^\circ$ ) and Ni-Mn<sup>4+</sup> have appeared, however,  $90^\circ$  interactions Ni-Ni is FM. After averaging,  $90^\circ$  interactions are weakening, and  $180^\circ$  interaction changes its sign but remains weak. AFM interaction 4-4 enhances, however it can be not enough to double magnetic cell along  $c$  axis because all other exchanges – 2-2, 3-3, 1-1 – are FM and strong.

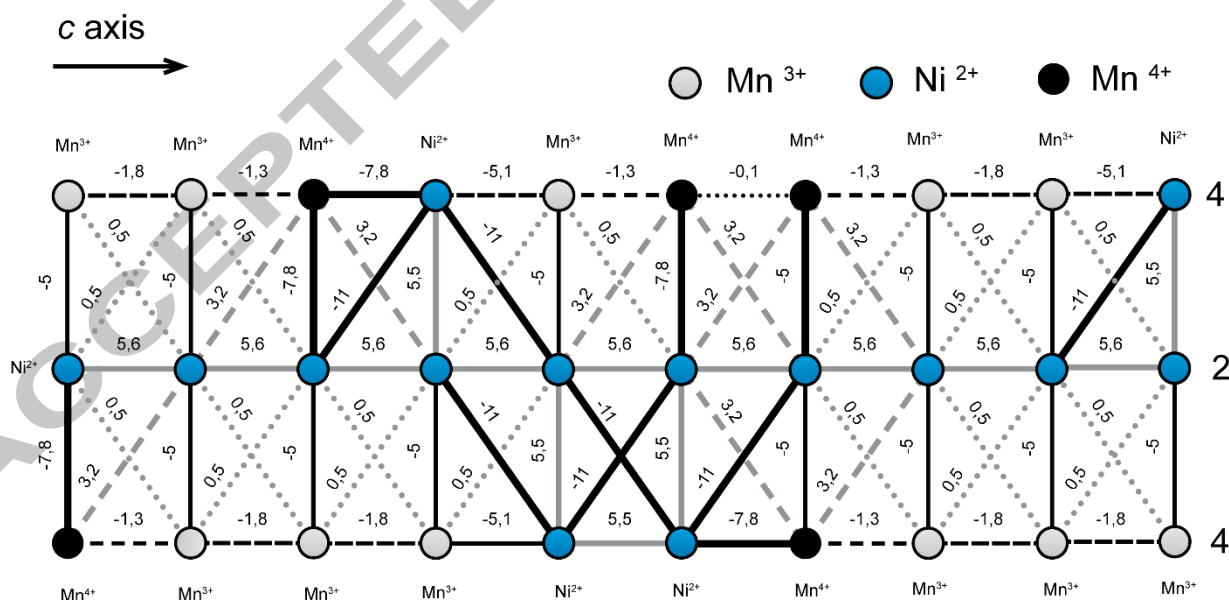


Figure 10. The 3LL of triads 4-2-4 with the designation of the exchange interactions between the ions of different types.

As we noted above, the structure geometry is formed by triangle groups of 4-1 and 4-3 bonds (Figure 9 a, b), and one can see in Figure 9c that exchange interactions in the studied compound become close in magnitude, leading to frustration enhancement and most likely, to the rotation of the 4-2 subsystems magnetic moments with respect to the 3-1 moments.

In the paper [21], we have assumed that the magnetic moments in the position 4 are antiferromagnetic to the moments in the position 2. The strong AFM interaction of Ni-Ni ( $165^\circ$ ) and Ni-Mn<sup>4+</sup> ( $90^\circ$ ) stabilize the orientation of the magnetic moments of the respective ions.

However, the question of the magnetic moments orientation along the  $c$  axis remains, the position 2 imposes an FM ordering, the position 4 imposes the AFM ordering. In one and the other case, there are frustrating interactions.

### 3.2. Energies Estimation

Next, we analyzed the magnetic order by averaging the contributions to the exchange interaction of the various ions in 4h position. Figure 11 shows 3LL 4-2-4 and its surrounding ions in the positions 3 and 1.

From the Figure 9c and Table 5, it is clear, that 4-4 antiferromagnetic interaction is enhanced, in addition to  $180^\circ$  exchange 4-2 which changes sign, although remains very weak.

Ions in the positions 1 and 3 are forming the triangular groups relative to the ion in position 4.

In the studied compound, exchanges in triangular groups are closer in magnitude and increase the frustration that likely leads to the orientation of the spins in the subsystems 3-1-3 and 4-2-4 forming an angle relative to each other, as in  $\text{Fe}_3\text{BO}_5$  and  $\text{Cu}_2\text{MnBO}_5$ .

To understand what type of ordering along the  $c$  axis is favorable, we estimate the energy of possible magnetically ordered structures:

$$E = - \sum_{ij} J_{ij} S_i S_j$$

The results of the calculation for both the studied compound and for the  $\text{Ni}_2\text{MnBO}_5$  for three cases are shown in Table 6. In the first case we have assumed that all the magnetic moments are oriented collinearly, in the second case, we have assumed that the magnetic moments in the 3LLs 4-2-4 are oriented at an angle of  $60^\circ$  with respect to those of 3-1-3, and in the third case, the magnetic moments in sublattices are oriented orthogonally to each other. As can be seen from the Table 6, in the first and second case, the energy of ferrimagnetic structure for both compositions has the lowest value. In the first case, in the studied compound and the  $\text{Ni}_2\text{MnBO}_5$ , the energy is virtually identical. In the second case, when the magnetic moments in the subsystems 4-2 and 3-1 oriented at 60 degrees to each other, the energy of the ferrimagnetic structure in the studied compound is slightly lower than the  $\text{Ni}_2\text{MnBO}_5$ , which is consistent with experimental data, according to which the studied compound magnetic order is set at a higher temperature than in  $\text{Ni}_2\text{MnBO}_5$ . In the third case, when the magnetic moments in subsystems 4-2 and 3-1 are oriented orthogonally, the antiferromagnetic magnetic structure has the lowest energy, which in the first and in the second case is close in energy to the ferromagnetic case. Just as in the latter case, the energy in the studied compound is slightly larger than in the  $\text{Ni}_2\text{MnBO}_5$ . Since we do not consider any other exchange interactions but superexchange, we cannot say what kind of structure is realized, but the growth of the energy in this compound, with the approach of the orientation of magnetic moment in subsystems to orthogonal can be seen in the calculation. As we have noted, in  $\text{Cu}_2\text{MnBO}_5$  and  $\text{Fe}_3\text{BO}_5$ , magnetic moments in the subsystems are deployed in relation to each other, frustrations are also presented in triangular groups 3-4-3 and 1-4-1 in the studied compound, and they are amplified in comparison with the  $\text{Ni}_2\text{MnBO}_5$ , that may lead to reversal of the magnetic moments in the sublattices.

Table 6. Energies of the different magnetic structures for two compounds.

Positions				Type	$0^\circ$			$60^\circ$		$90^\circ$	
1	2	3	4		$E(\text{st.sam.}), \text{K}$	$E(\text{Ni}_2\text{MnBO}_5), \text{K}$	$\mu/\text{mol}$	$E(\text{st.sam.})/\text{u.c.}, \text{K}$	$E(\text{Ni}_2\text{MnBO}_5), \text{K}$	$E(\text{st.sam.})/\text{u.c.}, \text{K}$	$E(\text{Ni}_2\text{MnBO}_5), \text{K}$
$\downarrow\downarrow$	$\downarrow\downarrow$	$\downarrow\downarrow\downarrow\downarrow$	$\uparrow\uparrow\uparrow\uparrow$	FIM	-252	-253	-0.42	-155	-149	-58	-45



↓↑	↑↓	↑↑↓↓	↓↓↑↑	AFM	-228	-235	0	-150	-147	<b>-72</b>	<b>-59</b>
↓↑	↓↓	↓↓↓↓	↑↑↑↑	FIM	-194	-186	0.58	-129	-119	-65	-52
↓↑	↑↓	↓↑↓↓	↑↓↑↑	AFM	-168	-170	0.79	-107	-104	-47	-37
↓↑	↑↓	↓↑↓↓	↓↓↑↑	FIM	-179	-180	-1	-124	-118	-69	-56
↓↑	↓↓	↓↑↓↓	↑↓↑↑	FIM	-168	-170	-0.21	-107	-104	-47	-37
↓↓	↓↑	↓↓↓↓	↑↑↑↑	FIM	-165	-172	0.58	-90	-90	-15	-8
↓↑	↓↓	↓↓↓↓	↓↑↑↑	FIM	-163	-160	-1.21	-103	-97	-44	-34
↓↓	↓↓	↓↓↓↑	↑↑↑↓	FIM	-160	-163	-1.21	-100	-97	-40	-30
↓↓	↓↓	↓↓↓↓	↑↑↑↑	FIM	-156	-153	-2.21	-96	-90	-37	-27

In Table 6, we show just the calculation results for some types of magnetic configurations, namely those that are more favorable in energy, though the calculation was performed for all possible ordering variants in the unit cell and the cell doubled along the shortest axis. The doubling of the magnetic cell is not profitable, despite the fact that the antiferromagnetic exchange between the ions in the position along the *c* axis increases.

It should be noted that several types of ordering are close enough in energy for all cases of the sublattices magnetic moments orientation relative to each other, the temperature dependence of the magnetization has a bend near the 70 K. According to the estimate from the hysteresis loop, the residual magnetization is  $0.021 \mu_B$ . In Table 6, we have given the saturation magnetization for the different type of ordering at the collinear orientation. As can be seen from the table, the calculated values are larger than the experimental values. We assume that the test compound is either canted antiferromagnetic or ferrimagnet. Since we consider only superexchange interaction and do not consider the direct exchange and super-superexchange interactions through boron ions, the energy of the ferromagnetic and antiferromagnetic states are very close.

## Conclusion

In the course of the study, we managed to obtain a compound with a ludwigite structure, in which manganese enters in two different valence states: tri- and tetravalent states. The composition of the studied compound was refined considering the jump on the absorption of manganese and nickel ions K-edge, the chemical formula of the compound obtained:  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$ . Despite the fact that in the studied compound due to the presence of manganese in the different valence states, the degree of disorder is higher than in the  $\text{Ni}_2\text{MnBO}_5$ , the magnetic order transition temperature in the studied compound is 15 K higher. Exchange interactions analysis held within the empirical model of Anderson-Zawadsky showed that frustrations appear due to all AFM interactions in triangular groups 3-4-3 and 1-4-1. The non-collinear orientation of magnetic moments in the sublattices 4-2-4 and 3-1-3 can appear to reduce frustrations. In the case where magnetic moments in the sublattices 4-2-4 and 3-1-3 are oriented at an angle of  $60^\circ$  and  $90^\circ$ , the energy of the studied compound is lower than that in the  $\text{Ni}_2\text{MnBO}_5$  (Figure 11). This conclusion is consistent with experimental data, according to which magnetic ordering is observed in the studied compound at a higher temperature. Energies of several magnetically ordered states are close enough.



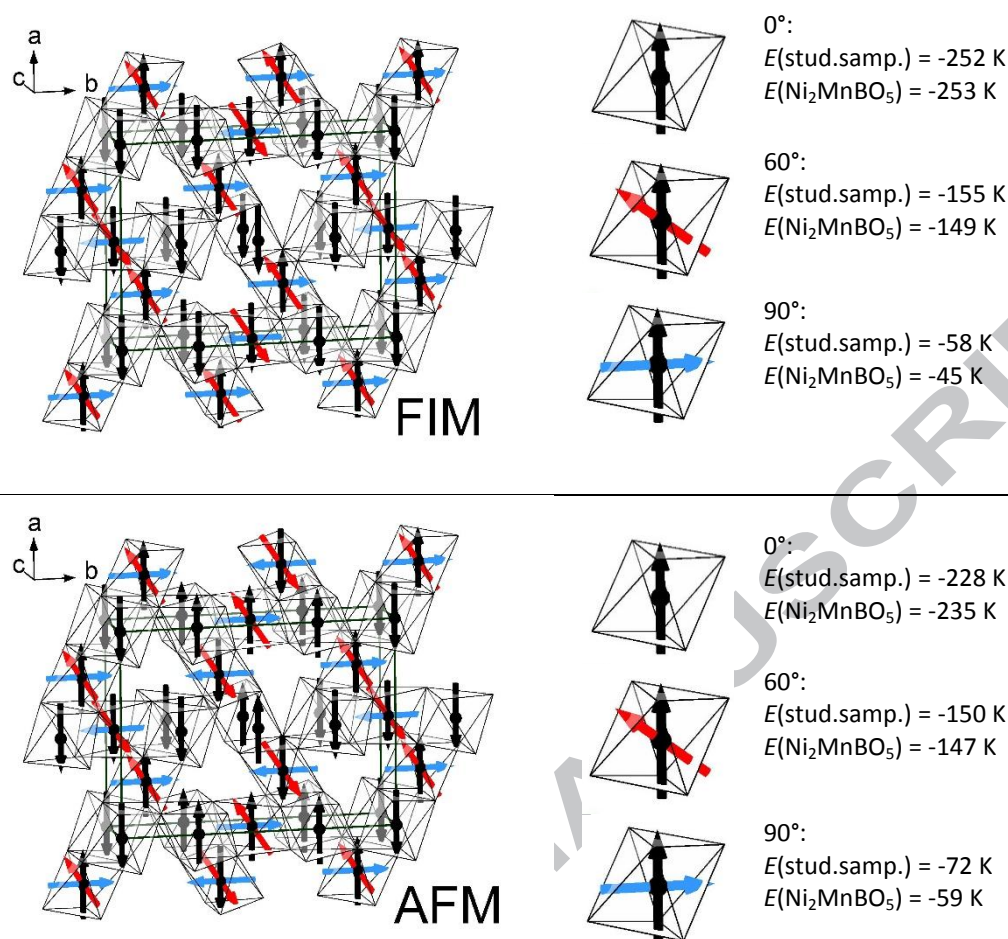


Figure 11. The energetically preferable magnetic structures with energy values for both compositions. Note that only one color arrow in the octahedron is applicable for the selected configuration.

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## Highlights

Single crystals of ludwigite  $\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$  were synthesized.

Structural characterization was carried out by X-ray diffraction and EXAFS technique.

Cations composition was determined by X-ray diffraction and EXAFS technique.

Magnetic properties were measured.

$\text{Ni}_{2.14}\text{Mn}_{0.86}\text{BO}_5$  magnetic behavior was analyzed within the indirect coupling model.