

# Ludwigites: From natural mineral to modern solid solutions

S. Sofronova\*\* and I. Nazarenko\*

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Ludwigites is a type of oxyborates compounds with  $\text{BO}_3$  groups, which have low-dimensional elements: stairs, zigzag walls, tapes. Such structural features influence on the physical properties of the compounds and cause charge ordering, the existence of two magnetic subsystems, ordered at different temperatures in the perpendicular direction, the quasi-one-dimensional magnetism, spin-glass state. In this survey, we have summarized all known experimental and theoretical studies and analyzed the proposed by the authors mechanisms of phase transitions in the ludwigite structure oxyborates.

## 1 Introduction

Oxyborates is a family of waterless compounds with  $\text{BO}_3$  groups in its composition. Currently, there are more than ten already known structural types of oxyborates: warwickites, ludwigites, kotoites, huntites, calcite, pyroborates, etc. [1–7]. Oxyborates' main feature is a presence of low-dimensional elements: stairs, zigzag walls, tapes, etc. [8] in the structure. These structural features have a great influence on the physical properties of the compounds. The amazing variety of physical properties depending on the composition is shown by ludwigite oxyborates [9–12]: charge ordering, the existence of two magnetic subsystems, ordered at different temperatures in the perpendicular direction, the quasi-one-dimensional magnetism, spin-glass state.

Despite the fact that the ludwigite structure oxyborates are being actively investigated, a lot of questions remains still without an answer. Why have two magnetic subsystems arranged at different temperatures in the perpendicular directions in  $\text{Fe}_3\text{BO}_5$  [9, 12]? Why does the replacing non-magnetic ion of titanium by stannum in  $\text{Co}_5\text{Ti}(\text{BO}_5)_2$  and  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  lead to a fundamental change in the magnetic properties [11, 13]? In this paper, we have tried to summarize all known experimental and theoretical studies and analyze the mechanisms of phase transitions in the ludwigite structure oxyborates proposed by the authors.

## 2 Crystal structure

Ludwigite crystal structure belongs to the space group  $Pbam$  (55) [9]. The general chemical formula is  $\text{Me}^{+3}\text{Me}^{+2}_2\text{BO}_5$ . Metal ions can be present as one ion with a different valence (homometallic) [9, 12, 14], and various ions (heterometallic) [10, 11, 13–25]. Metal ions (bivalent - Mg, Ni, Zn, Co, Fe, trivalent - Al, V, Cr, Mn, Fe, Ga, Co, tetravalent - Mn, Sn, Ge, Zr, Ti, and even pentavalent - Sb, Nb) are located in the center of the oxygen octahedral coordination with common edges. Boron ions are in the centers of coordination triangles; each triangle's corner is formed by different octahedrons' corners. Connected octahedrons structure looks like the zigzag walls (figure 1). In figure 1, numbers 1–4 designate non-equivalent positions of the metal ion. As seen from Table 1 taken from [26], in all compounds  $M^{+3}$ ,  $M^{+4}$ ,  $M^{+5}$  prefer to occupy the 4<sup>th</sup> position, and at least the 2<sup>nd</sup> one.

In ludwigite structure, it can be distinguished that the individual structural elements are triads. Triad of the first type is formed by metal ions in positions 4-2-4. Distances between the metal ions in the 2<sup>nd</sup> and 4<sup>th</sup> positions are minimal in all known ludwigites, besides their octahedrons are joined by base edges as well as the triads 4-2-4 in neighboring cells (along the  $c$  axis) as a result the structure resembling a ladder with three legs is formed. Ions in positions 1 and 3 form the second type triad: 3-1-3, these ions octahedrons are connected by vertices, and the distance between ions is the greatest here. The second type triads connecting along  $c$  axis also form a three leg ladder.

Currently, a large number of compounds with the ludwigite structure is derived, their chemical composition, crystallographic parameters are largely studied. However, the physical properties of most ludwigites are not widely studied, a little work has been devoted to the theoretical study of ludwigites properties.

\* Corresponding author: e-mail ilnz007@live.ru

\*\* e-mail ssn@iph.krasn.ru

L.V. Kirensky Institute of Physics, Siberian Branch of Russian Academy of Science, 660036 Krasnoyarsk, Russia

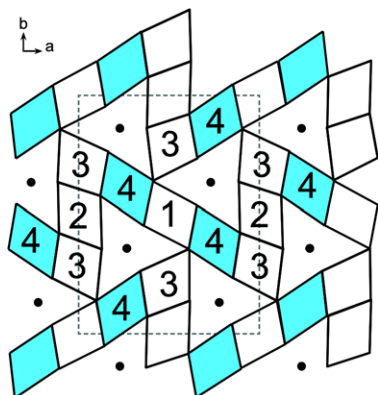


Fig. 1 The schematic ludwigite structure projected along the *c* axis. The points in the triangles are B ions [10].

### 3 Natural mineral ludwigite

Natural mineral  $Mg_2FeBO_5$  is the ancestor of the ludwigites family and received its name in honor of Ernst Ludwig, the first who analyzed this mineral in 1874. In modern times, this compound is also actively investigated, the results are given in [2, 15, 32, 37–39].

Ludwigite  $Mg_2FeBO_5$  contains only one magnetic ion -  $Fe^{3+}$ , which occupies position 4 and forms linear chains separated from each other by nonmagnetic  $Mg^{2+}$  ions. These chains can be viewed as a quasi-one-dimensional Heisenberg system with a strong short intra-sublattice antiferromagnetic superexchange interactions ( $\sim -15$  K [15]) in which a local short-range antiferromagnetic ordering of spins progressively appears.

The interchain exchange interaction can be realized by the super-superexchange of Fe-O-B-O-Fe. As the temperature decreases, these small but not negligible interchain interactions give a rise to frustrations and freezing of spin dynamics. The characteristic for the spin-glass state behavior of the properties was observed in this compound below 10 K by neutron diffraction and Mössbauer spectroscopy [9, 16, 17].

Thus,  $Mg_2FeBO_5$  is an interesting model system in which a quasi-one-dimensional magnetism and a spin glass state exist in different temperature ranges.

### 4 Homometallic ludwigites

#### 4.1 Iron ludwigite

Currently, the most studied compound is  $Fe_3BO_5$  ludwigite, which occupies a special position among all studied ludwigites. A unique  $Fe_3BO_5$  feature is the presence of structural transition, charge ordering and two magnetic

Table 1 Occupation of octahedral positions.

| Compound   | Occupation (%) for $M^{2+}$ |       |       |       |
|--|-----------------------------|-------|-------|-------|
|  | M1                          | M2    | M3    | M4    |
| $Mg_{2.11}Al_{0.31}Fe_{0.53}Ti_{0.05}Sb_{0.01}BO_5$ [27] | 42.5                        | 73.8  | 87.2  | 87.2  |
| $Mg_{1.92}Ti_{0.02}Fe_{0.65}Al_{0.41}BO_5$ [1]           | 0.0                         | 83.5  | 100.0 | 100.0 |
| $Mg_{1.988}Ti_{0.21}Fe_{0.702}Al_{0.10}BO_5$ [28]        | 15.0                        | 67.6  | 100.0 | 100.0 |
| $Mg_{1.76}Fe_{1.22}Al_{0.02}BO_5$ [29]                   | 0.0                         | 44.3  | 99.0  | 99.0  |
| $Mg_{1.98}Mn_{0.78}Fe_{0.22}Al_{0.02}BO_5$ [30]          | 0.0                         | 92.0  | 100.0 | 100.0 |
| $Mg_{1.93}Mn_{1.07}BO_5$ [31]                            | 27.4                        | 65.4  | 90.2  | 86.0  |
| $Mg_2FeBO_5$ [32]  | 0.0                         | 100.0 | 100.0 | 100.0 |
| $Mg_2InBO_5$ [26]  | 21.4                        | 80.8  | 92.0  | 92.4  |
| $Mg_{2.5}Ti_{0.5}BO_5$ [33]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Co_{2.1}Al_{0.9}BO_5$ [21]                              | 54.4                        | 59.2  | 85.0  | 78.8  |
| $Co_2FeBO_5$ [10]  | 0.0                         | 100.0 | 100.0 | 100.0 |
| $Co_{2.5}Mn_{0.5}BO_5$ [34]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Co_{2.5}Sn_{0.5}BO_5$ [34]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Co_{2.5}Ti_{0.5}BO_5$ [11]                              | 52.0                        | 100.0 | 100.0 | 70.0  |
| $Zn_{2.5}Mn_{0.5}BO_5$ [35]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Ni_{2.5}Ti_{0.5}BO_5$ [23]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Ni_{2.5}Mn_{0.5}BO_5$ [25]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Ni_{2.5}Ge_{0.5}BO_5$ [24]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Ni_{2.5}Zr_{0.5}BO_5$ [24]                              | 50.0                        | 100.0 | 100.0 | 100.0 |
| $Ni_2GaBO_5$ [20]  | 0.0                         | 100.0 | 100.0 | 100.0 |
| $Ni_2FeBO_5$ [36]  | 38.1                        | 61.5  | 85.6  | 91.2  |
| $Ni_2AlBO_5$ [21]  | 35.8                        | 65.2  | 89.0  | 85.2  |
| $Ni_2CrBO_5$ [22]  | 12.0                        | 89.0  | 94.0  | 100.0 |
| $Ni_2VBO_5$ [22]   | 25.0                        | 90.0  | 94.0  | 72.0  |

subsystems, which arrange at different temperatures in perpendicular directions.

At temperatures above 293 K,  $Fe_3BO_5$  has ludwigite crystal structure and belongs to the space group  $Pbam$  (55) [9]. In the high-temperature phase heterovalent iron ions ( $Fe^{+2}$  and  $Fe^{+3}$ ) are not localized in certain positions, except  $Fe^{+2}$  ion in positions 1 and 3. The first type triad 4-2-4 consists of three localized  $Fe^{+3}$  ions with spin 5/2, which divide one extra electron [40].

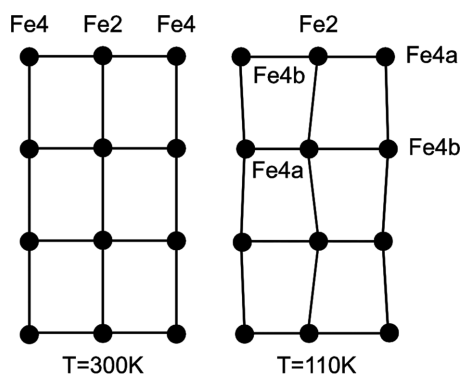


Fig. 2 The structural ordering of the Fe(4)-Fe(2)-Fe(4) ladders above and below the structural phase transition in  $\text{Fe}_3\text{BO}_5$  [9].

The structural change observed at 283 K is associated with the localization of an additional electron in one of the pairs of Fe(2)-Fe(4), which leads to distortion of the three leg ladders and doubling the crystal cell along the  $c$  axis (figure 2) [9]. The structural transition is accompanied by magnetization anomaly and the resistivity slope change, and apparently, it has the electronic origin associated with the formation of dimers, i.e. this is Peierls' and spin-Peierls' instability. A theoretical study carried out in [41] showed that in the three leg ladders charge density wave may arise leading to similar distortions of the lattice.

Magnetic ordering in  $\text{Fe}_3\text{BO}_5$  occurs in two stages: firstly, at 112 K, the ordering of the Fe moments in distorted ladders formed by triads of the 1<sup>st</sup> type - subsystem 1, then at 74 K - the ordering in the triads of the 2<sup>nd</sup> type - subsystem 2. In the temperature dependence of the specific heat (figure 3), there are two anomalies: the first in the region of 112 K is small and blurred, which also certifies the partial ordering of the magnetic moments, the second anomaly near 74 K has a classic  $\lambda$ -shape indicating a transition to a fully magnetically ordered state [42]. As research by neutron diffraction has shown, the ordering of the magnetic moments in the subsystem 1 and 2 is orthogonal.

In the temperature dependence of the magnetization in the region of 112 K, there is a small anomaly only when the field is applied in the direction of the  $b$  axis, which is due to the antiferromagnetic ordering in the subsystem 1 according to the authors [43]. Below the temperature of the second transition (74 K) when subsystem 2 is ordering ferrimagnetically, there is a significant increase of the magnetization when a field is applied along the  $a$  axis. Applying the field along  $b$  axis also causes a weak anomaly (figure 4). On the field dependence of magnetization (figure 5) below 74 K for the field application along

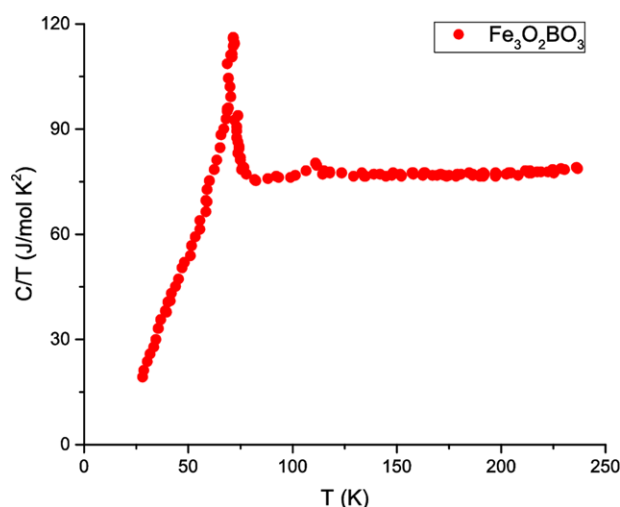


Fig. 3 Specific heat as a function of temperature for Fe ludwigite. In the Fe system, 2 magnetic transitions are observed. These transitions appear as anomalies on the Specific heat curve [14].

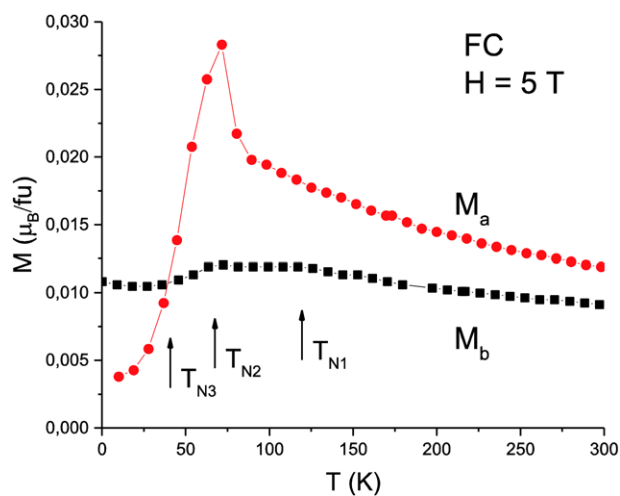


Fig. 4  $M_a(T)$  and  $M_b(T)$  measurements for  $\text{Fe}_3\text{BO}_5$  [43].

the  $a$  axis, hysteresis loops are observed, and disappear below 30 K [43].

On the Mössbauer spectra at 50 K, changes related to the localization of an additional electron in the position 2 are observed, which according to the authors [40, 44] below 50 K (30 K [43]) are due to the fact that  $\text{Fe}_3\text{BO}_5$  becomes again antiferromagnetic that is evidenced by the hysteresis loops vanishing.

Studies of the magnetic structure by neutron diffraction were carried out by two different groups [9, 12]. The studies were carried out at 5 K [12], 10 K and 82 K [9]. In [9] it was shown that at 112 K the magnetic moments ordering of subsystem 1 is really going on, and at 74 K, ordering of the magnetic moments in the subsystem 2 is

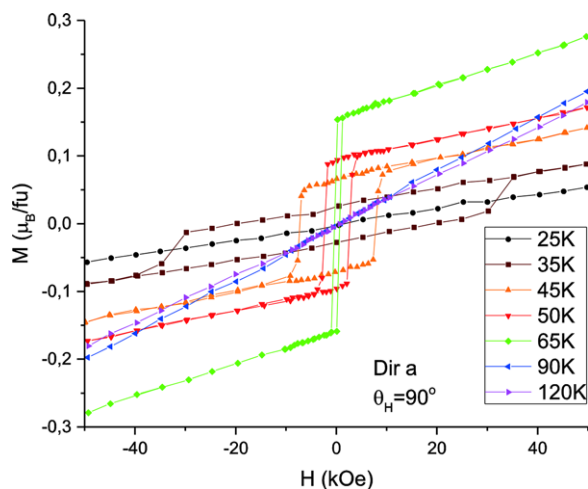


Fig. 5  $\text{Fe}_3\text{BO}_5$  sample hysteresis loops at different temperatures, and H parallel to  $a$  axis [43].

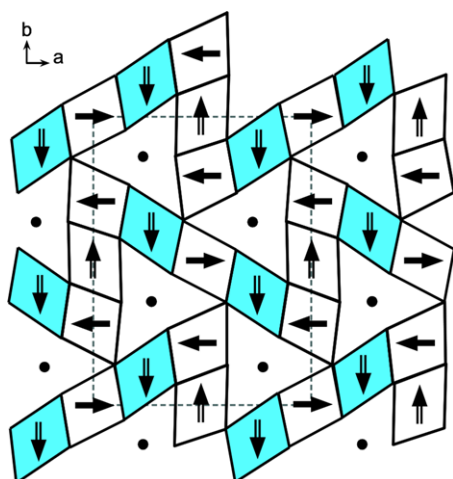


Fig. 6 View in the  $(0\ 0\ 1)$  direction at  $\text{Fe}_3\text{BO}_5$  structure with  $\text{FeO}_6$  octahedra located in the planes  $z = 0$  (positions of Fe(1) and Fe(3)) /  $z = 1/2$  (Fe(2) and Fe(4)), magnetic moments are directed along the axes  $a$  and  $b$ , solid / double-line arrows indicate the ferromagnetic / antiferromagnetic chains parallel to  $[0\ 0\ 1]$  [12].

taking place. Both groups confirmed that the subsystem 1 and 2 magnetic moments ordering takes place in the direction of the crystallographic  $b$  and  $a$  axis, respectively. The subsystem 2 magnetic moments are ordered ferromagnetically along the  $c$  axis, and there is an uncompensated magnetic moment. The ordering of the magnetic moments in the subsystem 1 along the  $c$  axis is antiferromagnetic, but the relative orientation of the magnetic moments in the triad 4-2-4 in [12] and [9] is different, it is antiferromagnetic (figure 6) and ferromagnetic (figure 7) respectively. Ascertain the true

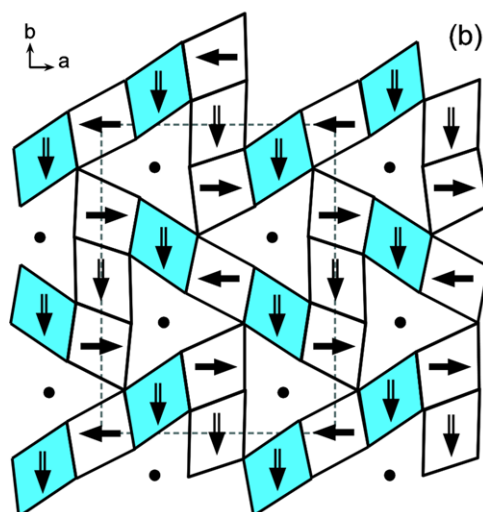
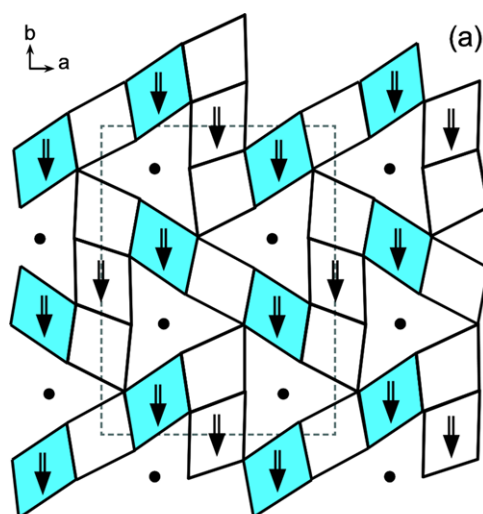


Fig. 7 The  $\text{Fe}_3\text{BO}_5$  magnetic structure at 82 K (a) and 10 K (b). At 82 K, moments on the Fe(1) and Fe(3) are absent. Solid / double-line arrows indicate the ferromagnetic / antiferromagnetic chains parallel to  $[0\ 0\ 1]$  [9].

orientation of the magnetic moments in the triad is impossible by other methods.

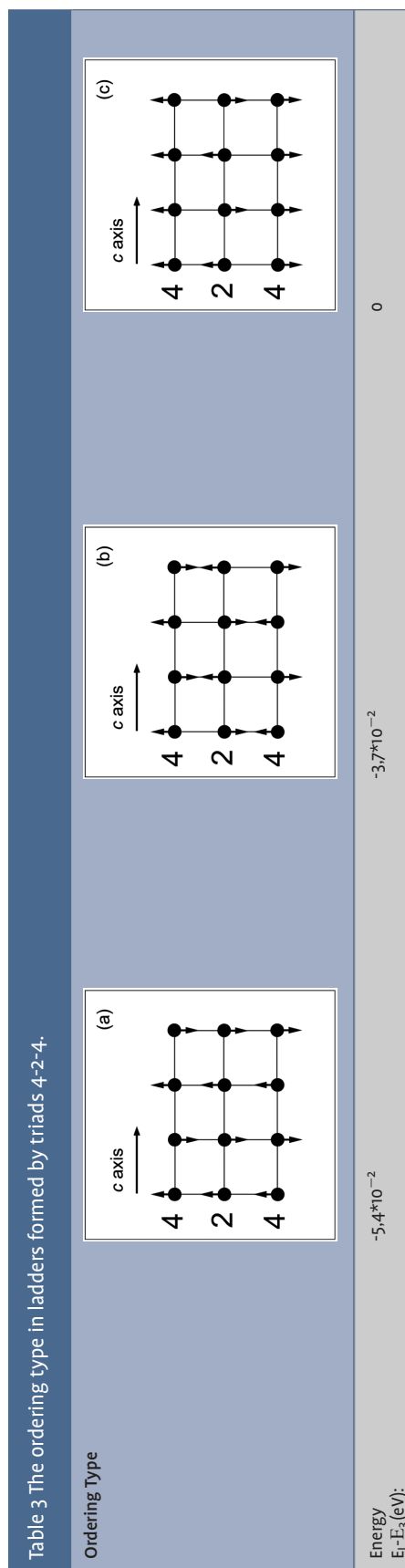
The group-theoretic analysis performed for the  $k = 0$  case of  $\text{Fe}_3\text{BO}_5$  low-temperature phase with space group  $Pbnm$  (62) showed that the ordering in subsystems 1 and 2 is related to different irreducible representations:  $\tau_5$  and  $\tau_8$ . The basis vectors for these irreducible representations and the corresponding magnetic ions are given in Table 2. It should be noted that despite the differences in the experimental data the ordering in the first type triads in both cases corresponds to one irreducible representation -  $\tau_5$ . This is due to the fact that the first triad is constituted by three types of ions, each of which

Table 2 The basis vectors of irreducible representations  $\tau_5$  and  $\tau_8$ .

| Position | Basis Vectors  |
|----------|--|
| $\tau_8$ |  |
| 4a (1)   | $(u, v, w), (u, -v, -w), (u, -v, w), (u, v, -w)$   |
| 8d (3)   | $(u, v, w), (u, -v, -w), (u, -v, w), (u, v, -w), (u, v, w), (u, -v, -w), (u, -v, w), (u, v, -w)$ |
| $\tau_5$ |  |
| 4c (2)   | $(u_1, v_1, 0), (u_1, -v_1, 0), (-u_1, -v_1, 0), (-u_1, v_1, 0)$                                 |
| 4c (4a)  | $(u_2, v_2, 0), (u_2, -v_2, 0), (-u_2, -v_2, 0), (-u_2, v_2, 0)$                                 |
| 4c (4b)  | $(u_3, v_3, 0), (u_3, -v_3, 0), (-u_3, -v_3, 0), (-u_3, v_3, 0)$                                 |

occupies a symmetry positions 4c but these are three different 4c positions that exist in the low-temperature phase. Ion moments orientation in one position is determined by group-theoretic analysis, but the relative ions moments orientation in different positions can be parallel or antiparallel. Table 3 shows three possible ions magnetic moments orientations in the triad of the first type for the irreducible representation  $\tau_5$ . In all cases, the magnetic moments ordering along the c axis is antiferromagnetic and the total magnetic moment in the subsystem 1 is zero. However, in triad 4-2-4 three options are possible, two of which correspond to neutron diffraction experimental data, and the third option is consistent with the occurrence of spin dimers. Thus, the question of the magnetic moments ordering in the triad 4-2-4 is still open at the moment. We evaluated the difference in the crystal exchange energy for the three different types of the magnetic moments ordering in the ladders formed by triads 4-2-4, using the exchange interaction constant obtained through empirical calculation and the classical expression  $E = -1/2 \sum_{ij} s_i s_j J_{ij}$ . For the reference point, we have chosen the energy of the third order type, which was the maximum.

Ordering in the triad 4-2-4 is not the only issue where there is inconsistency in the experimental data. According to neutron diffraction [9, 12],  $\text{Fe}_3\text{BO}_5$  remains ferromagnetic down to the lowest temperatures, however, then it is not clear why below 30 K in the field dependences of the magnetization hysteresis loops disappear. Localization of an additional electron in position 2, which is observed at 50 K, may affect the magnetic order in the subsystem 1, however, this subsystem has no uncompensated magnetic moment. Ferrimagnetism is associated with the ordering of the subsystem 2, the magnetization decrease in direction of the crystallographic  $a$





axis at low temperatures may be due to the reversal of the triads 3-1-3 part in the opposite direction. Two pairs of triads 3-1-3 and 3'-1'-3' comprises in the  $\text{Fe}_3\text{BO}_5$  unit cell, which according to the neutron diffraction data coincides with the same magnetic cell at low temperatures. According to the group-theoretic analysis, the two triads 3-1-3 pairs ordering may be the same according to the representation  $\tau_8$ , and mutually antithetical according to the representation  $\tau_4$ . Triad 3-1-3 and 3'-1'-3' are linked to each other only via super-superexchange interaction through oxygen and boron ions, apparently, this connection is very weak, and it is possible that it contributes only when the temperature is lowered orienting triad 3-1-3 and 3'-1'-3' mutually antithetical, which leads to the disappearance of the magnetic moment.

In theory, the magnetic ordering in  $\text{Fe}_3\text{BO}_5$  was investigated both in individual subsystems: three leg ladders formed by triads 1 [45] and throughout the crystal [46, 47], the calculation results are only partially consistent with the experimental data. In [47], it was shown that the magnetic order in  $\text{Fe}_3\text{BO}_5$  at 15 K can be described as follows (figure 8): the triad of the first type consists of two almost independent elements: the ferromagnetically ordered dimer  $\text{Fe}4a\text{-Fe}2$  and weakly bound magnetic moment  $\mu_{\text{Fe}4b}$ . Significant magnetic moment  $\mu_{\text{Fe}4b}$  slant ( $78^\circ$ ) with regard to the magnetic moments of  $\text{Fe}2\text{-Fe}4a$  dimer arises from the  $\text{Fe}2\text{-Fe}4b$  pairs spin-spin interactions, which leads in turn to the sample magnetization decrease. Triads of the first type are antiferromagnetically ordered along the  $c$  axis. The second type triads ordering corresponds to the experimental data. The magnetic moments ordering in the three leg ladders formed by the first type triads obtained by the authors of [47] is almost the same as with other calculations, moreover in [45], it is mentioned that Bordet (one of the neutron diffraction studies author) in a private conversation assumed ordering in the triad 4-2-4 by type: ( $\uparrow\uparrow\rightarrow$ ), but in his published paper [9] the ferromagnetic ordering is proposed. As mentioned above, the irreducible representation  $\tau_5$  corresponds to another type of magnetic ordering, which is more consistent with the results of theoretical calculations. In light of the fact that the structural transition appears to be associated with the formation of dimers, and experimenters' opinion about the ordering of the magnetic moments in the triad 4-2-4 odds, it is possible that the third option of ordering in the triad can be realized, which is not contrary to group-theoretic analysis.

Thus, despite the fact that  $\text{Fe}_3\text{BO}_5$  is fairly well understood, there is no unambiguous and clear picture of magnetic ordering in the crystal, there are still contradictions between the experimental data which do not allow to

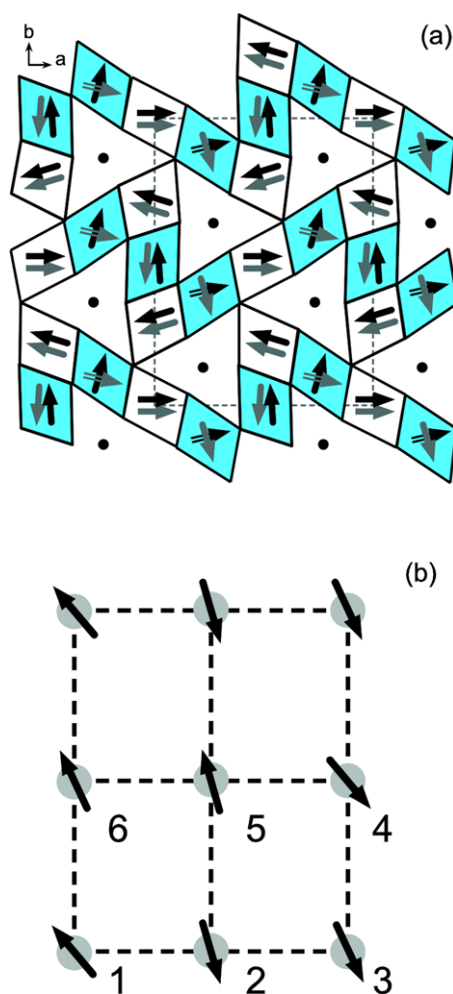


Fig. 8 The distribution of  $\text{Fe}_3\text{BO}_5$  magnetic moments in projection on  $ab$  plane. Double-line arrows: pos.  $4b$ ; black (gray) arrows: top (bottom) parts of the unit cell  $1 \times 1 \times 2$  (a) [47]; the ordering of the magnetic moments in the triad (b) [45].

establish and build a true model of magnetic phase transitions in the crystal and orientation of the magnetic moments.

#### 4.2 Cobalt ludwigite

Unlike  $\text{Fe}_3\text{BO}_5$ ,  $\text{Co}_3\text{BO}_5$  is less studied and primarily theoretically. It is known that in  $\text{Co}_3\text{BO}_5$  there is one magnetic transition at 42 K, when the whole sample becomes magnetically ordered [14, 18]. Magnetic measurements shown in figure 9 and figure 10 confirm the magnetic transition and determine the material as a weak ferromagnetic or ferrimagnetic with uncompensated magnetic moment directed along the  $b$  axis. The magnetic moment per formula unit in  $\text{Co}_3\text{BO}_5$  is significantly

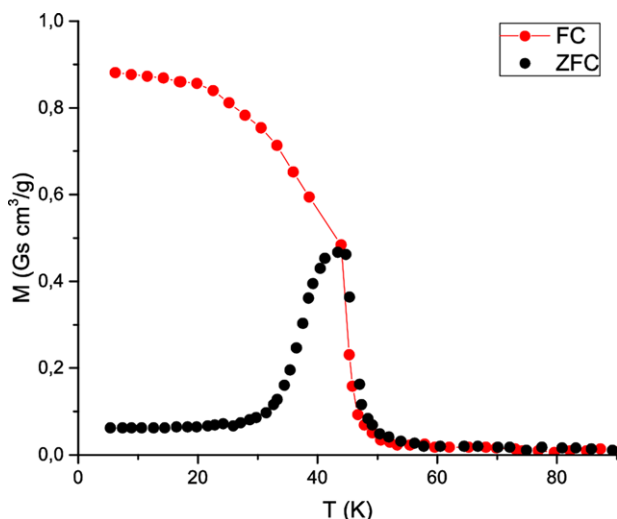


Fig. 9 The temperature dependence of  $\text{Co}_3\text{BO}_5$  magnetization measured under cooling in a weak magnetic field  $H = 2 \text{ Oe}$  (FC) and in the absence of the magnetic field (ZFC). The magnetic field is directed along the crystallographic  $b$  axis [18].

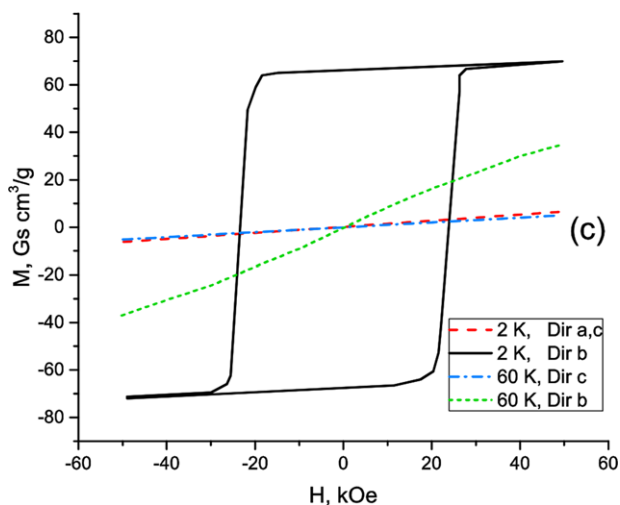


Fig. 10 The isotherms of the magnetization of the  $\text{Co}_3\text{BO}_5$  crystal [18].

higher than in  $\text{Fe}_3\text{BO}_5$  - 0.8 vs.  $0.15 \mu\text{B}$ . The Curie-Weiss temperature is significantly different: -485 K in  $\text{Fe}_3\text{BO}_5$  and 1 K for  $b$  direction and -158 K for  $a$  and  $c$  directions in  $\text{Co}_3\text{BO}_5$ . Close to zero Curie-Weiss temperature may indicate the presence of competition between ferromagnetic and antiferromagnetic exchange interactions in the system. Anisotropy of the inverse susceptibility in the paramagnetic region in  $\text{Co}_3\text{BO}_5$  apparently associated with the spin-orbital interaction. Despite the fact that in  $\text{Co}_3\text{BO}_5$  first type triads as in the  $\text{Fe}_3\text{BO}_5$ , di- and trivalent ions are present, an extra electron is localized in the position 2 (Table 4) and the structural phase transition

Table 4 Oxidation states of cobalt ions in  $\text{Co}_3\text{BO}_5$  obtained by the Wood and Palenik's method [48] in [14].

| Position | Oxidation State ( $Z_j$ ) |
|----------|---------------------------|
| Co(1)    | 1.913                     |
| Co(2)    | 2.056                     |
| Co(3)    | 1.977                     |
| Co(4)    | 2.725                     |

with dimers formation does not occur. It is possible that in  $\text{Co}_3\text{BO}_5$ , spin-orbital interaction acts as a destroyer of the Peierls transition preventing structural transition [14]. Perhaps, as noted in [14], chemical, electronic, and magnetic configuration in the ladders lead to the different mechanisms of magnetic interactions in  $\text{Fe}_3\text{BO}_5$  and  $\text{Co}_3\text{BO}_5$ . Apart from the usual super-exchange, mechanism of double exchange due to the additional electron transition polarization in the ladders formed by the first type triads plays an important role as well as exchange interactions competitions.

The  $\text{Co}_3\text{BO}_5$  magnetic structure is not solved therefore we can only suppose how the magnetic moments are ordered in the crystal. Based on the experimental data, it is likely that all the magnetic moments in  $\text{Co}_3\text{BO}_5$  are oriented in one direction. To determine the magnetic phase transition mechanisms, it is necessary to conduct further investigations.

## 5 Heterometallic ludwigites

The greatest properties diversity is found in heterometallic ludwigites, which may contain both magnetic and non-magnetic ions.

### 5.1 Cobalt-Iron, Nickel-Iron, and Copper-Iron ludwigites

Different compositions  $(\text{Co,Fe})_3\text{BO}_5$  ludwigites research can explain the difference between the  $\text{Fe}_3\text{BO}_5$  and  $\text{Co}_3\text{BO}_5$  properties. However, getting ludwigites with a specific ionic composition is quite a trivial challenge, and currently, compounds only with a great cobalt content,  $\text{Co}_{2.25}\text{Fe}_{0.75}\text{BO}_5$  and  $\text{Co}_2\text{FeBO}_5$ , were studied. Despite the fact that the cobalt content in these compounds is greater than iron both compositions as  $\text{Ni}_2\text{FeBO}_5$  and  $\text{Cu}_2\text{FeBO}_5$  have a significant magnetic properties similarity between each other and  $\text{Fe}_3\text{BO}_5$ .

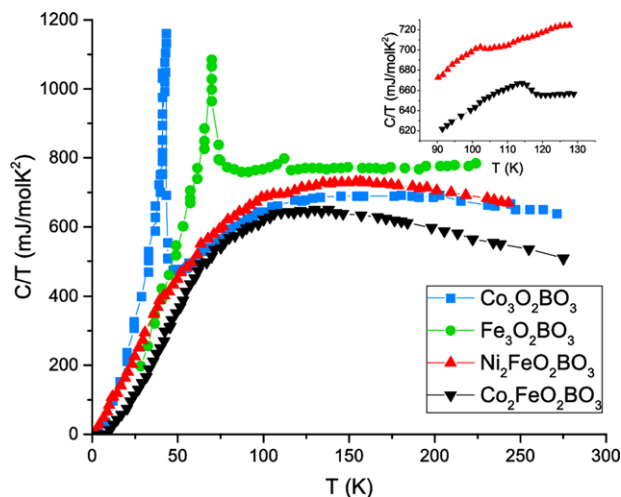


Fig. 11 The specific heat dependence versus temperature for ludwigites with different composition. The inset shows the specific heat curves showing in detail the peaks associated with the  $\text{Fe}^{3+}$  ions ordering [10].

In all compounds,  $\text{Fe}^{3+}$  ion prefers to take the position 4 occupying the edges of ladders formed by the first type triads [8, 18, 43, 49]. The specific heat, magnetization, and Mössbauer spectroscopy studies indicate that all three compounds have at least two transitions. The first transition (around 110 K in  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$ , 68 K in  $\text{Cu}_2\text{FeBO}_5$ ) is associated with the Fe ion magnetic moments ordering, which is confirmed by studies of Mossbauer spectroscopy [8, 10, 49], in the specific heat (figure 11), there is a small anomaly also on the magnetization curves (figure 12) of powder samples as in  $\text{Fe}_3\text{BO}_5$  there is no significant changes [10]. However,  $\text{Co}_2\text{FeBO}_5$  single crystal magnetization study (figure 13) has revealed that near 115 K under applied field along  $a$  axis as in  $\text{Fe}_3\text{BO}_5$  a sharp peak is observed although the magnetization magnitude with respect to the second anomaly is small enough [43].

The second transition in all three systems is observed in the region of 70, 46 and 38 K in  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$ ,  $\text{Cu}_2\text{FeBO}_5$  respectively. In the magnetization curves in all the compounds, a peak is clearly visible, in  $\text{Co}_2\text{FeBO}_5$ , in contrast to the transition at 115 K, this anomaly is the maximum in applied field along the  $b$  direction [18]. The second transition is associated with the ordering or freezing of divalent ions magnetic moments. In the second transition area, there are no any anomalies in the Mössbauer spectra, which indicates that the subsystem of divalent ions and iron subsystem is virtually connected to each other at these temperatures. The divalent ions magnetic moments freezing is evidenced by the absence of any specific heat features in the

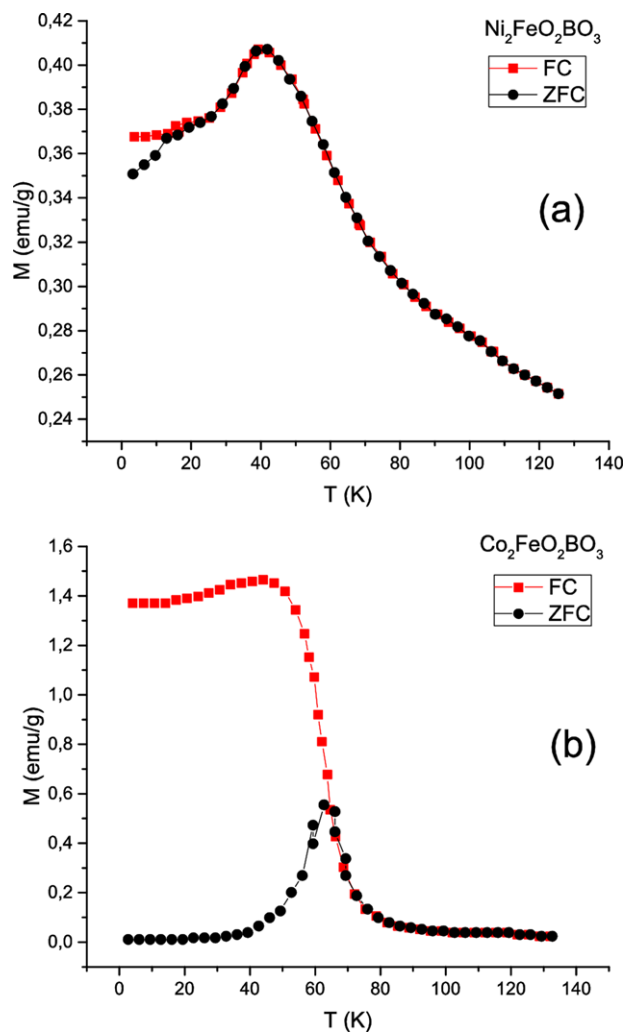
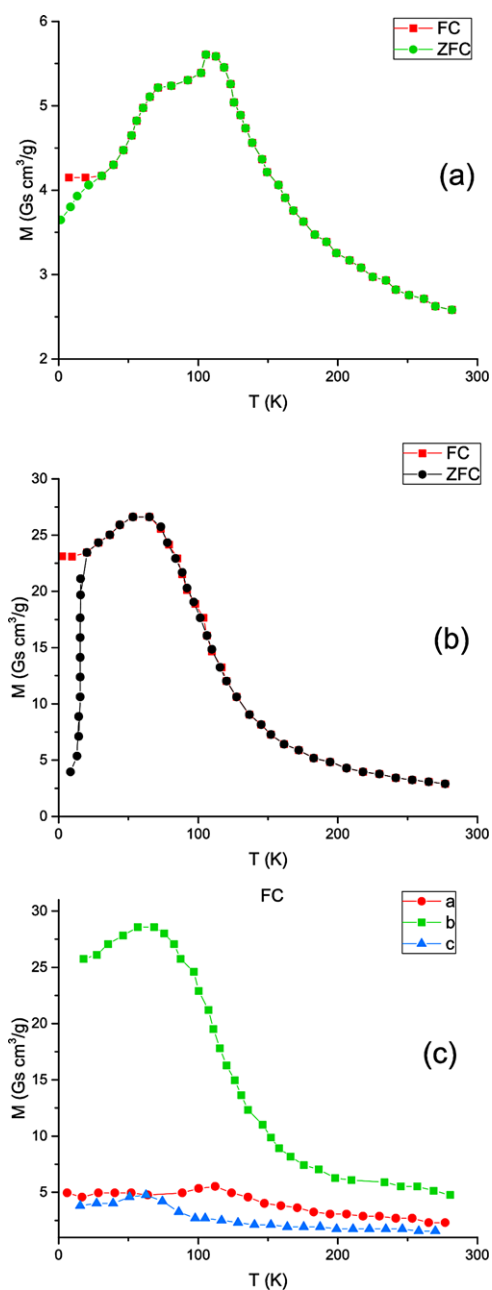


Fig. 12 The  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$  magnetization dependences versus the temperature for ZFC and FC regimes in the field of 0.1 T [10].

second transition area in the  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$  compounds, for  $\text{Co}_2\text{FeBO}_5$ , it is confirmed by a shift of the peak in the real part of the AC susceptibility under the field frequency change (figure 14). However, the peak position in the real part of the  $\text{Ni}_2\text{FeBO}_5$  AC susceptibility does not vary with frequency (figure 14), which excludes transition to the spin-glass state. The authors of [8] have suggested that the  $\text{Ni}_2\text{FeBO}_5$  nickel subsystem shows the behavior characteristic of the Heisenberg antiferromagnetic chains with random exchanges, and the iron subsystem is most likely in the spin glass state.

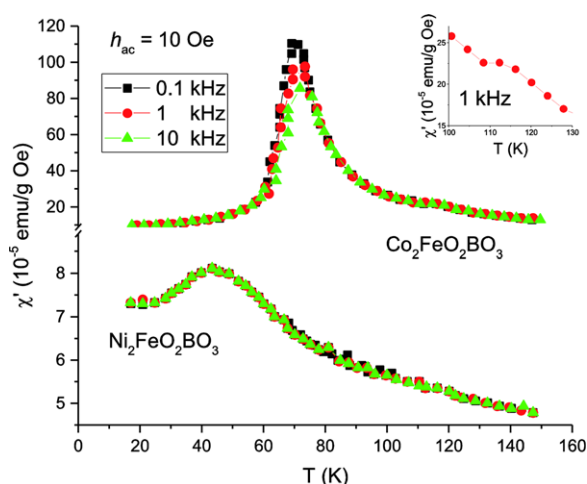
Another common feature of  $\text{Co}_2\text{FeBO}_5$ ,  $\text{Ni}_2\text{FeBO}_5$ , and  $\text{Cu}_2\text{FeBO}_5$  is big enough Weiss temperature: -387 K (for the  $b$  direction), -442 K -178 K, respectively. This usually indicates the predominance of antiferromagnetic interactions or the presence of frustration in the system,





**Fig. 13** The  $\text{Co}_2\text{FeBO}_5$  magnetization dependence versus temperature in a magnetic field of 50 kOe: a - the magnetic field in the direction of a; b - the magnetic field in the direction b; c - magnetization dependence versus temperature obtained by cooling in a magnetic field (FC-curves) for three crystallographic direction a, b and c [18].

which is characteristic of the spin-glass state [43, 49]. The oriented single crystals magnetization studies confirm the presence of a strong anisotropy in  $\text{Co}_3\text{BO}_5$  and  $\text{Co}_2\text{FeBO}_5$ . The anisotropy in cobalt compounds may be associated with strong spin-orbital coupling, which is



**Fig. 14** The real part of the  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$  susceptibility versus temperature at different frequencies. The inset shows  $\text{Co}_2\text{FeBO}_5$  susceptibility near the magnetic phase transition [10].

typical for bivalent cobalt in an octahedral environment. Strong anisotropy, which is likely due to the  $\text{Cu}^{+2}$  ions Jahn-Teller's effect and leads to the severe distortion of the octahedrons and the symmetry lowering to monoclinic [49], is also found in  $\text{Cu}_2\text{FeBO}_5$ .

It is noted that in the  $\text{Co}_2\text{FeBO}_5$ ,  $\text{Ni}_2\text{FeBO}_5$ , and  $\text{Cu}_2\text{FeBO}_5$  compounds, there is no virtual relationship of the iron subsystem with the divalent metal subsystem. Only at the temperatures of about 20 K in the Mössbauer spectra, features associated by the authors with the relationship between the sub-systems establishment [8, 10, 49] appear, however, other experimental methods do not confirm it. According to the Goodenough rule [50] the  $\text{Cu}^{+2} - \text{Fe}^{+3}$  exchange interaction is negligible, it is possible that one of the sublattices does not order and freezes in a disordered state.

In Table 5, we present calculated indirect exchange interaction values between  $\text{Fe}^{+3}$  ion in position 4 with surrounding divalent ions using the method of [51–53]. As can be seen from the table the Cu-Fe interaction is really very weak whereas, in the case of nickel and cobalt, it seems to be that frustrations have more influence.

Another evidence of frustration or disorder in  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$  is a linear dependence of the specific heat at low temperatures (figure 15). Since these compounds are dielectrics, the linear behavior of the specific heat near the 0 K cannot be associated with the conductivity and very likely due to the presence of disorder in the system [10].

The heterovalent ludwigites magnetic structure studies would help to expand the magnetic phase transitions mechanisms understanding in these compounds,

Table 5 Calculated indirect exchange interaction for iron-containing ludwigites.  $i, j$  - ions position,  $\alpha, \beta$  - the angles between ions  $i, j$  through O ion, exchanges values are listed in K.

| $i$ | $j$ | $\alpha$         | $\beta$         | $\text{Co}_2\text{FeBO}_5$ | $\text{Ni}_2\text{FeBO}_5$ | $\text{Cu}_2\text{FeBO}_5$ |
|-----|-----|------------------|-----------------|----------------------------|----------------------------|----------------------------|
| 2a  | 2a  | $\sim 90^\circ$  |                 | 3.6                        | 5.6                        | 3.1                        |
| 2d  | 2d  | $\sim 90^\circ$  |                 | 3.6                        | 5.6                        | 3.1                        |
| 2d  | 4h  | $\sim 180^\circ$ |                 | -3.8                       | -5.4                       | -0.5                       |
| 4g  | 2a  | $\sim 125^\circ$ |                 | -3.7                       | -1.8                       | -1.6                       |
| 4g  | 2d  | $\sim 90^\circ$  | $\sim 90^\circ$ | 1.0                        | 5.5                        | 7.7                        |
| 4g  | 4g  | $\sim 90^\circ$  | $\sim 90^\circ$ | 3.6                        | 5.6                        | 3.1                        |
| 4h  | 2a  | $\sim 90^\circ$  | $\sim 90^\circ$ | -6.1                       | -3.0                       | -2.1                       |
| 4h  | 2d  | $\sim 90^\circ$  |                 | -2.7                       | -3.0                       | 0.9                        |
| 4h  | 4g  | $\sim 125^\circ$ |                 | -1.9                       | -2.0                       | -3.1                       |
| 4h  | 4g  | $\sim 90^\circ$  | $\sim 90^\circ$ | -6.0                       | -3.0                       | -2.1                       |
| 4h  | 4h  | $\sim 90^\circ$  | $\sim 90^\circ$ | -5.3                       | -5.3                       | -5.3                       |

however, the magnetic structure has been solved only for  $\text{Fe}_3\text{BO}_5$ . In  $\text{Co}_2\text{FeBO}_5$ , X-ray absorption spectra (XAS) and X-ray magnetic circular dichroism (XMCD) measurements near the  $L$ -absorption edge of Co and Fe [54] were carried out, which also gives some insight into the process of magnetic ordering in this compound. The XMCD Co and Fe signal signs are opposite indicating the antiparallel orientation of these ions moments,

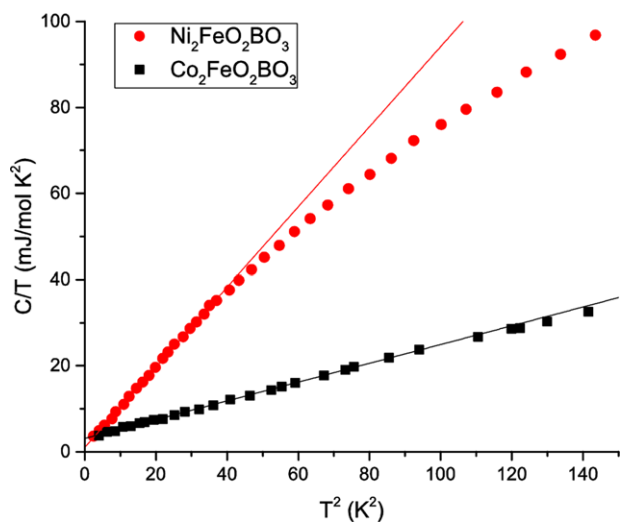


Fig. 15 The specific heat as a function of  $C/T$  versus  $T^2$ . Linearization parameters are given in Table VIII as  $C/T = \gamma + \beta T^2$  in [10].

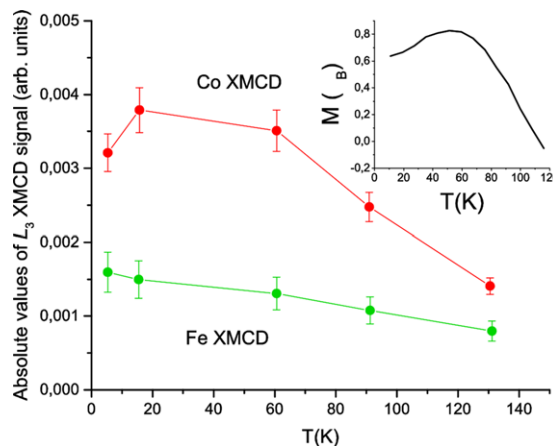


Fig. 16 The temperature dependence of the XMCD signal absolute value at  $L_3$ -edge of Co and Fe. Inset: the temperature dependence of magnetization in a field  $H = 50$  kOe [54].

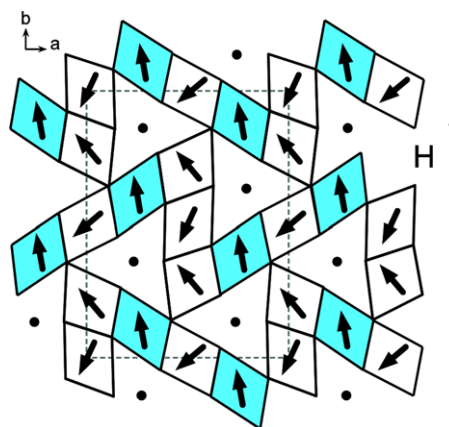


Fig. 17 The Co (white octahedrons) and Fe (blue octahedrons) magnetic moments direction for each position [54].

and the XMCD Co signal temperature dependence (figure 16) qualitatively repeats the dependence of magnetization. Field element-selective curves indicate that the iron is in a state of saturation, and Co is in a pronounced paraprocess indicating the not compensated moment-rotation in the direction of the external field. As a result of data analysis, the magnetic structure is proposed (figure 17): the iron ions magnetic moments are oriented mainly along the  $b$  axis whereas the Co magnetic moments are along  $a$  axis. In some ways, the proposed magnetic structure is similar to the  $\text{Fe}_3\text{BO}_5$  magnetic structure. Perhaps, splitting into two subsystems, and these subsystems orthogonal orientation relative to each other are common for all ludwigites due to the geometric characteristics of the crystal.

The  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$ ,  $\text{Cu}_2\text{FeBO}_5$  compounds experimental studies show that the presence of the  $\text{Fe}^{+3}$

ion in position 4 has a greater influence on the compound magnetic properties than the type of divalent cation: for all compounds two-step appearance of the magnetic order is typical, and as in  $\text{Fe}_3\text{BO}_5$  first magnetic order occurs in the subsystem associated with the  $\text{Fe}^{+3}$ , and then in divalent subsystem when the temperature is lowered. Apparently, Fe-Fe exchange interactions are the greatest, and decisive role is played by the interaction Fe-Fe, which makes  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$ ,  $\text{Cu}_2\text{FeBO}_5$  magnetic properties similar. The  $\text{Mg}_2\text{FeBO}_5$  magnetic behavior is indicating in favor of this version [15]. Firstly, Fe-Fe interactions lead to the emergence of the Heisenberg antiferromagnetic chains, and then at 10 K, weak Fe-O-B-O-Fe superexchange interactions become sufficient to form a spin glass state. In the case where Mg is replaced by a magnetic ion, long-range order occurs, however, divalent subsystem has less influence on the magnetic properties either due to weak exchange interactions or frustrations. Additional evidence for the key role of  $\text{Fe}^{+3}$  is that e.g. in the mono cobalt ludwigite and various solid solutions based on it and containing no Fe, there is a significant difference in the magnetic properties caused by cobalt ions substitution.

## 5.2 Solid solutions based on cobalt ludwigite

Currently several solid solutions based on  $\text{Co}_3\text{BO}_5$  were received and investigated. Substitution of Co was produced by magnetic ions of Mn, Cu [55, 56] and nonmagnetic - Ga, Ti, Mg, Sn [10, 11, 13, 14, 18, 19, 34, 54–57].

Replacement ion greatly influences the magnetic properties of the compounds, even replacing various nonmagnetic ions gives rise to different magnetic phases or spin glass magnetic ordering.

Relatively small cobalt substitution by copper [55] leads to a considerable increase of the anisotropy, the magnetic moment along the  $b$  axis is 100 times greater than along the  $c$  and  $a$ . Although the magnetic transition temperature varies slightly from 42 to 43 K. The effective magnetic moment reduced from 4.26 to 3.83. The Curie temperature along the  $b$  direction in both compounds decrease from 1 K to -12 K suggests the presence of competing exchanges. The  $\text{Co}_{2.88}\text{Cu}_{0.12}\text{BO}_5$  specific heat has not been investigated but since copper is present not so much, the authors of [55] has suggested that as well as  $\text{Co}_3\text{BO}_5$ ,  $\text{Co}_{2.88}\text{Cu}_{0.12}\text{BO}_5$  ordered ferrimagnetically. In the paper, the suggestion was made that copper, which is located mainly in positions 4 and replaces trivalent Co there, also has a trivalent state, but the valence state of  $3+$  is not typical for copper. Most likely, that copper is in the bivalent state as well as in  $\text{Cu}_2\text{FeBO}_5$ . Further research is

needed to clarify the valence state of the copper and the composition of the crystal.

Unlike copper, manganese is present in all positions although it prefers to take a position 4 [56]. In the  $\text{Co}_{1.7}\text{Mn}_{1.3}\text{BO}_5$  compound, the magnetic transition temperature is also close to the  $\text{Co}_3\text{BO}_5$  temperature of 41 K. However, the system magnetic state below the transition is spin glass. Assuming that in the compound manganese is present in the bi- and trivalent state, the effective magnetic moment has been estimated, which almost coincided with the experimentally calculated value of 4.83 and 4.71  $\mu_B$ , respectively. However, in ludwigites, manganese can be in the tetravalent state, e.g. in  $\text{Ni}_5\text{Mn}(\text{BO}_5)_2$  [25]. And probably in  $\text{Co}_{1.7}\text{Mn}_{1.3}\text{BO}_5$  compound, cobalt and manganese ions are present in different valence states, in different positions, which makes long-range magnetic order occurrence impossible in the system.

Just as in the previous case, it would be interesting to investigate the valence state of Mn and its distribution among the positions.

### 5.2.1 Cobalt-Titanium and Cobalt-Magnesium ludwigite

In the compound  $\text{Co}_5\text{TiBO}_5$ , nonmagnetic titanium with an almost equal probability of bivalent cobalt occupies the position 4, a small amount of titanium is also present in the position 1 [11]. At 19 K, the system goes into a spin glass state as evidenced by the frequency dependence of the AC susceptibility real part, a strong magnetization dependence on the sample history (significant difference between ZFC and FC regimes), the lack of features on the specific heat and its linear dependence in the zero region. The magnetization field dependences behavior is different from most ludwigites (figure 18) - on the curves, steps are clearly visible. Such behavior of the field and temperature dependences is observed in  $\text{CoMgGaBO}_5$  [57] where there is a spin glass state near 20 K. Authors [11] explain the abrupt behavior of the magnetization field dependencies as the memory effect characteristic of spin glasses.

In most cases, the addition of both magnetic and nonmagnetic impurities leads to the destruction of long-range magnetic order. However, in some cases, this question remains open. By substituting cobalt ion by gallium ions, gallium ions occupy preferably position 4, and to some extent position 2 [19]. On the magnetization curves in ZFC mode (figure 19) in a very weak field, a rise is visible in the 37 K area, such behavior is somewhat different from the rest ludwigites in which after lifting in the transition area a magnetization reduces in ZFC mode.

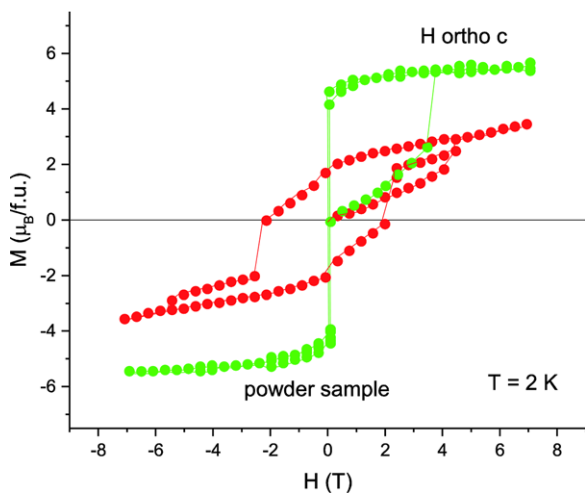


Fig. 18 The  $\text{Co}_5\text{Ti}(\text{BO}_5)_2$  magnetization curves versus the applied field at 2 K for a single crystal and a powder sample [11].

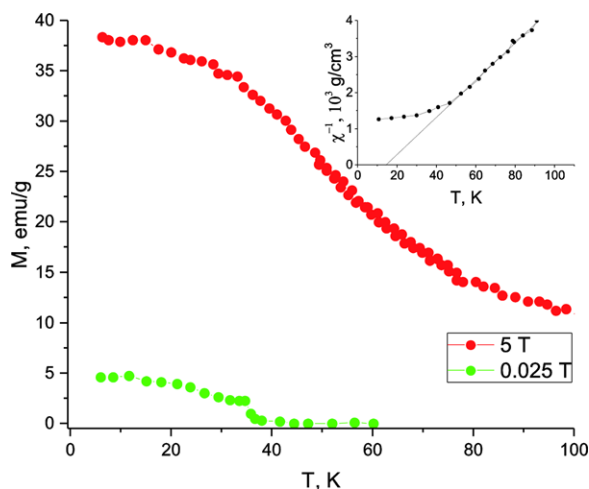


Fig. 20 The  $\text{Co}_{2.4}\text{Ga}_{0.6}\text{BO}_5$  crystal magnetization versus temperature obtained in ZFC-mode. Heating was carried out in two magnetic fields. The field is directed along the crystallographic axis. The inset shows the temperature dependence of the inverse magnetic susceptibility, corresponding to the  $M(H)$  curve, measured in a field  $H = 5$  T. The straight line is the approximation of the Curie-Weiss [19].

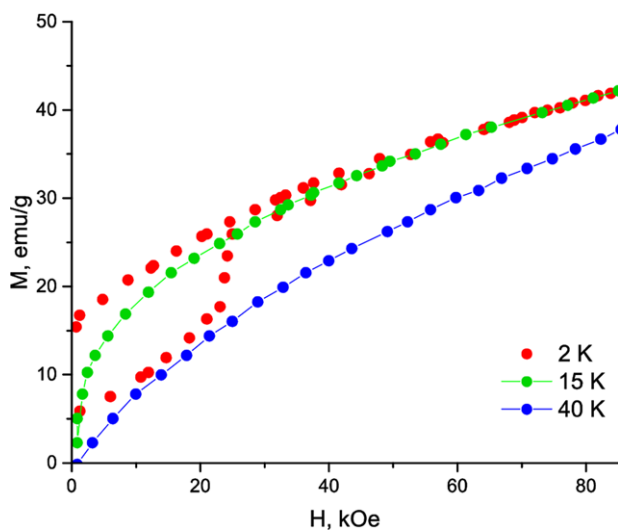


Fig. 19 The  $\text{CoMgGaBO}_5$  magnetization isotherms above and below the magnetic transition [57].

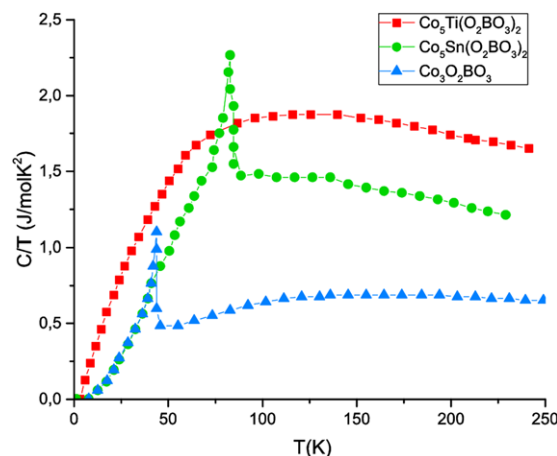


Fig. 21 The specific heat versus temperature comparison for different ludwigites [11, 13, 14].

With increasing field, the behavior character persists but the transition is blurred. The magnetic moment, unlike  $\text{Co}_3\text{BO}_5$  lies in the  $ab$  plane. The residual magnetization calculated from the field dependence at 1.8 K is 24% of the maximum possible value for this composition. Paramagnetic  $\text{Co}_{2.4}\text{Ga}_{0.6}\text{BO}_5$  Curie temperature in the  $a$  axis direction (9 Å) is 14 K whereas in  $\text{Co}_3\text{BO}_5$  it is 20 K. The introduction of gallium ions has weakened antiferromagnetic interactions prevailing in  $\text{Co}_3\text{BO}_5$ , which probably affected the behavior of the magnetization in ZFC mode. The  $\text{Co}_{2.4}\text{Ga}_{0.6}\text{BO}_5$  magnetic properties significantly differ from other solid solutions based on Co, and in greater extent correspond to the ferrimagnetic state transition (figure 20).

Among all the solid solutions based on  $\text{Co}_3\text{BO}_5$ , the most significant one is  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  [13]. Sn prefers position 4 like most tetravalent ions. In this position, it is practically disordered with divalent cobalt ions in the ratio 1:1. In all solid solutions based on  $\text{Co}_3\text{BO}_5$ , critical temperature is not more than 43 K, but in this compound the magnetic order occurs at 82 K, which is confirmed by a peak on the magnetization and the specific heat curves (figure 21), a feature on the specific heat curve is very similar to the homometallic ludwigites feature. The peak shift in the AC-magnetization is not more than 0.2 K,

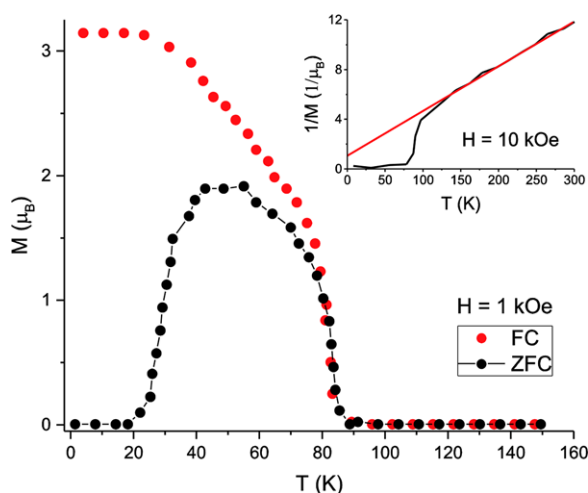


Fig. 22 The  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  magnetization versus temperature in a field of 0.1 T in both modes: field cooling (FC) and zero field cooling (ZFC). Inset: reverse ZFC-magnetization in a field of 1 T [13].

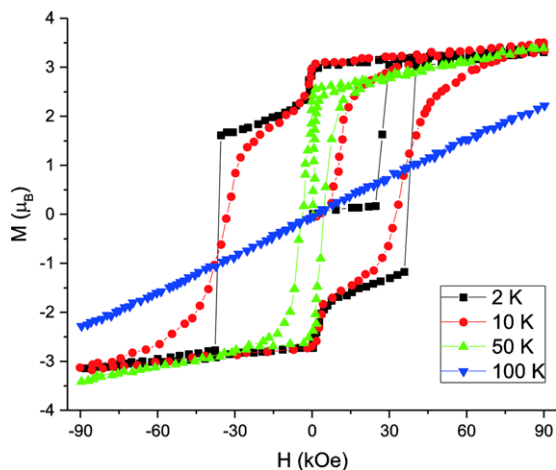


Fig. 23 The  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  magnetization versus field at 1, 10, 50 and 100 K [13].

which also favors the appearance of the magnetically ordered state. The significant difference between ZFC and FC regimes (figure 22) is explained by the authors [13] as division into domains. The AC susceptibility imaginary part frequency dependence is possible due to the domain walls formation. Interestingly, the  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  field dependence of magnetization (figure 23) behaves as well as in  $\text{CoMgGaBO}_5$  and  $\text{Co}_5\text{TiBO}_5$ . However, in this case, it is impossible to explain the spin-glass state, by the authors of [13], it was suggested that the magnetization jumps can be associated with a change in the magnetic configuration leading to a competition between the Zeeman's energy and magnetic anisotropy. At the low temperatures, specific heat curve is linear, unlike for  $\text{Co}_3\text{BO}_5$ , it does not depend on the magnetic field

which indicates a weak frustration of the sample. It is possible that the magnetically ordered state mechanisms in  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  are easier than in other ludwigite.

As one can see, the substitution of Co in  $\text{Co}_3\text{BO}_5$  by both magnetic and nonmagnetic ions in most cases leads to a decrease of the magnetic transition temperature, magnetic ordering destruction, and the spin glass state rise, however, there are exceptions, such as  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$ , its magnetic behavior is different from other compounds. The magnetic structure of the  $\text{Co}_3\text{BO}_5$  and solid solutions based on it has not been investigated, theoretical calculations have not been carried out, so further research is needed, and at the moment, the magnetic ordering model based on experimental studies of the magnetization can be only assumed.

### 5.3 Solid solutions with a high content of nickel

Despite the fact that mono nickel ludwigite does not exist, there are many solid solutions containing nickel and other metals in ludwigite structure. However, the physical properties of most of these compounds, including magnetic, are still little understood. The  $\text{Ni}_2\text{FeBO}_5$  ludwigite has been already discussed by us, further, we will look at two compounds whose magnetic properties at the moment have been already investigated -  $\text{Ni}_5\text{Ge}(\text{BO}_5)_2$  and  $\text{Ni}_{3-x}\text{Mn}_x\text{BO}_5$ .

#### 5.3.1 Nickel-Germanium ludwigite

Unlike most cobalt ludwigites, nickel ludwigite have quite high temperatures of magnetic phase transitions (90 K). Despite the fact that apparently in  $\text{Ni}_5\text{Ge}(\text{BO}_5)_2$  there is no completely ordered magnetic state, the magnetic properties of this compound have a number of interesting features. On the field dependence of the magnetization in a fairly narrow range of temperatures, hysteresis loops exchange bias is observed (figure 24). Usually, hysteresis loops exchange bias is observed below the Neel temperature down to low temperatures [58]. Perhaps, in this case, the exchange bias disappearance is due to the change in the system's magnetic order. On the temperature dependence of the magnetization in a field of 25 kOe in the 46 K area, a small feature is observed, but at lower fields, the magnetization decreases with decreasing temperature. The field dependence of the magnetization has a "plateau" or "jumps" when the field is along the  $b$  axis. Similar behavior has been observed in some cobalt ludwigites:  $\text{Co}_5\text{TiBO}_5$ ,  $\text{CoMgGaBO}_5$ , the authors [11, 57] has attributed this behavior to the



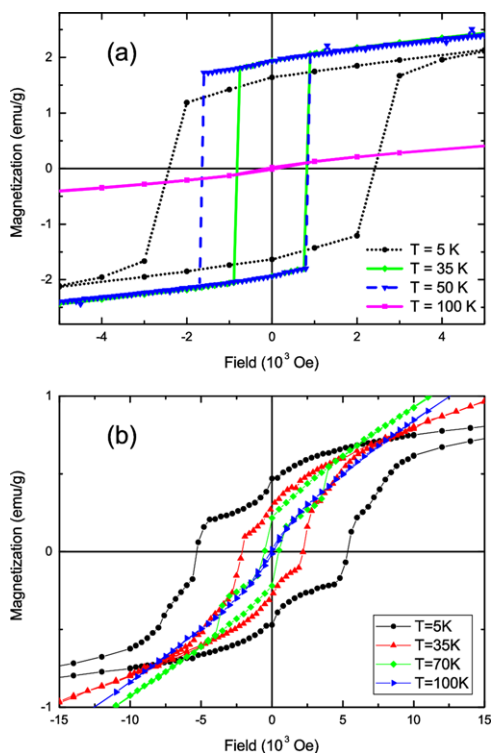


Fig. 24 Ferromagnetic and antiferromagnetic ordering areas in the ladder of type 1. Dark circles - Ni ions. Empty circles - Ge ions. The gray solid lines show ferromagnetic super exchanges. The black solid lines show antiferromagnetic super exchanges. Dotted lines indicate the frustrated interactions [59].

spin-glass magnetic order, but  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  [13], in which such hysteresis loops behavior is observed, enters the magnetically ordered state at 82 K. In the case of nickel-germanium ludwigite, such behavior is observed in a field in the only one direction, and possibly due to the partial reorientation of the sublattices [59].

Exchange interactions calculations have shown that in the system there is a competition between ferromagnetic and antiferromagnetic exchanges, and many frustrating interactions (figure 25). The presence of a non-magnetic germanium in one of the positions, its disordered distribution as well as the competition of exchange interactions can lead to the formation of ferromagnetically ordered regions (saturated with germanium) and antiferromagnetically ordered regions (saturated with nickel). Another interesting feature is the anisotropy in the paramagnetic region, which is not typical for compounds containing  $\text{Ni}^{2+}$  in the octahedral environment.

As we have noted above, the  $\text{Co}_5\text{Ti}(\text{BO}_5)_2$  and  $\text{Co}_5\text{Sn}(\text{BO}_5)_2$  properties vary greatly. It is known about the existence of  $\text{Ni}_5\text{Sn}(\text{BO}_5)_2$  and  $\text{Ni}_5\text{Ti}(\text{BO}_5)_2$  ludwigites,

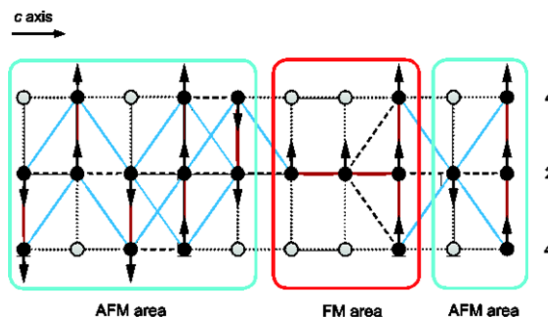


Fig. 25 The  $\text{Ni}_5\text{Ge}(\text{BO}_5)_2$  magnetization isotherms along the axes *a* and *b* [59].

however, the magnetic properties of these ludwigites are not investigated. It is interesting to determine whether there is such a strong dependence of the magnetic ordering temperature in nickel ludwigites as in solid solutions based on cobalt.

### 5.3.2 Nickel-Manganese ludwigites

Nickel-manganese ludwigites are interesting because manganese ions may be present in the ludwigite compound structure with different valence: 2+, 3+, 4+. One can assume that as in  $\text{Fe}_3\text{BO}_5$  in nickel-manganese ludwigite effects associated with charge ordering may spring up.

In the Institute of Physics RAS SB, a number of  $\text{Ni}_{3-x}\text{Mn}_x\text{BO}_5$  crystals with different composition were grown. However, clarification of the ions valence state within the crystal is not an easy task as it seems at first glance. The composition and the valence state of the metal ions study was carried out using synchrotron radiation for the two compounds  $\text{Ni}_{3-x}\text{Mn}_x\text{BO}_5$  containing Ni:Mn ions in the ratios 1:1 and 3:1 in the tab solution. The EXAFS spectra at the *K*-edges of the nickel and manganese absorption were studied. Composition refinement according to the *K*-edge absorption jump has shown that despite the substantial difference in the melt compositions: 1:1 and 3:1, crystal content of manganese and nickel ions was close to 2:1 and 2.5:1. The oxidation level analysis was carried out by the “fingerprint”, i.e. the comparison of the ion *K*-edge absorption position and well-studied standards for different levels of oxidation. The valence state of the nickel was very close to two. The valence state of manganese ion in both compositions was close to three. For the 2:1 composition, the manganese, and nickel valence state corresponds to the crystal electrical neutrality condition, but in the second case a few manganese ions should be present

in the tetravalent state. The K-edge absorption position comparison of these two compounds shows that in the second case there is a slight shift towards a greater degree of oxidation, which probably indicates a small inclusion of tetravalent manganese.

Magnetic ordering in nickel-manganese ludwigite as in  $\text{Ni}_5\text{Ge}(\text{BO}_5)_2$  occurs at high temperatures about 90 K. Also in  $\text{Ni}_2\text{MnBO}_5$  at 68 K, there is a point of inflection, and steps on the hysteresis loops, as in  $\text{Ni}_5\text{Ge}(\text{BO}_5)_2$ . Most likely, this is due to the ordering of another magnetic subsystem. The  $\text{Ni}_2\text{MnBO}_5$  magnetization increases with decreasing temperature and does not reach saturation, it is possible that one of the subsystems remains disordered down to low temperatures.

As we have noted, the composition Ni and Mn ratio 2.5:1 should include tetravalent manganese, therefore, the chemical disorder is increased, however, in spite of this the magnetic ordering temperature is increased as compared with the composition  $\text{Ni}_2\text{MnBO}_5$ . A possible reason for this behavior is the reduction of frustration or competition due to the  $\text{Mn}^{4+}$  and  $\text{Ni}^{2+}$  ions emergence in the 4h position.

#### 5.4 Copper-Manganese ludwigites

Copper-manganese ludwigites are interesting because of the Jahn-Teller ions -  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$  - content. Depending on the composition, bi- and tetravalent manganese may be also included. The currently being studied in some detail composition is  $\text{Cu}_2\text{MnBO}_5$ . We have been able to grow sufficiently large  $\text{Cu}_2\text{MnBO}_5$  ludwigite single crystals of  $10 \times 1 \times 2$  mm size. The  $\text{Cu}_2\text{MnBO}_5$  structure is highly distorted due to the Jahn-Teller effect of ions included in the compound. The composition and valence state are determined by the manganese and copper ions K-edge absorption jump. Comparisons with the standards:  $\text{CaO}$ ,  $\text{MnB}_2\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ , has shown that copper is in the bivalent state, and manganese is in the trivalent state. In this crystal, manganese occupies the fourth crystallographic position, copper occupies the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>; the positional distribution is typical of most ludwigites (see Table 1).

The authors [59] suggested that in  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_2\text{FeBO}_5$  ludwigites the magnetic moments are “frozen” in some positions.

The magnetic structure of this compound has been solved. It is interesting that the magnetic moments of the ions lie in one plane, but if in  $\text{Fe}_3\text{BO}_5$  it is the plane formed by the *a* and *b* axes, then in  $\text{Cu}_2\text{MnBO}_5$  it is the *bc* plane (figure 26). Although the magnetic structure was solved only for these two compounds with the

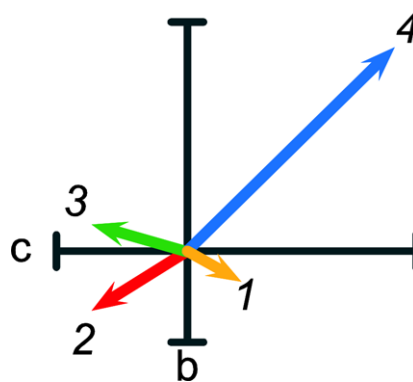


Fig. 26 Directions of the magnetic moments in  $\text{Cu}_2\text{MnBO}_5$  for different positions in the *ab* plane:  $0.2 \mu_B$  (pos. 1),  $0.57 \mu_B$  (pos. 2),  $0.94 \mu_B$  (pos. 3),  $2.65 \mu_B$  (pos. 4).

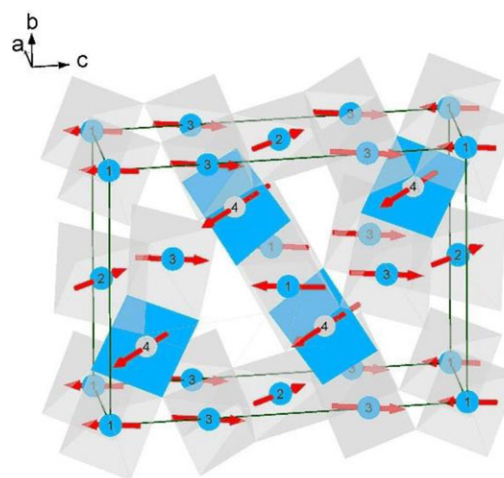


Fig. 27 The  $\text{Cu}_2\text{MnBO}_5$  magnetic structure. The magnetic moments values:  $0.2 \mu_B$  (pos. 1),  $0.57 \mu_B$  (pos. 2),  $0.94 \mu_B$  (pos. 3),  $2.65 \mu_B$  (pos. 4) [60].

ludwigite structure, from the  $\text{Co}_2\text{FeBO}_5$  and  $\text{Ni}_5\text{GeB}_2\text{O}_{10}$  crystal orientation magnetization studies it is known that the magnetic moments are oriented in the *ab* plane as in  $\text{Fe}_3\text{BO}_5$ . Probably in  $\text{Cu}_2\text{MnBO}_5$ , the other magnetic moments direction is also associated with the Jahn-Teller effect due to which the octahedrons surrounding the metal ions are strongly distorted [59]. Another  $\text{Fe}_3\text{BO}_5$  and  $\text{Cu}_2\text{MnBO}_5$  common feature is the magnetic system partition into two subsystems of three leg ladders formed by triads 4-2-4 and 3-1-3. The magnetic moments in each subsystem are parallel, and the angle between the magnetic moments of various subsystems is  $90^\circ$  in  $\text{Fe}_3\text{BO}_5$  and  $60^\circ$  in  $\text{Cu}_2\text{MnBO}_5$  (figure 27). Unlike  $\text{Fe}_3\text{BO}_5$ , in  $\text{Cu}_2\text{MnBO}_5$  magnetic ordering occurs in a single phase transition, however, on the temperature dependences of the magnetization there is a feature in

the area of 75 K, and a hysteresis in ZFC and FC regimes, also at low temperatures, there is a significant difference in ZFC and FC regimes. According to neutron diffraction, ions magnetic moment in position 1 is twice less than in positions 2 and 3, which are also occupied by copper. This may indicate that the magnetic moments in the position 1 are not arranged entirely after the transition. Such behavior has been observed previously in other ludwigites [9] and it is associated with the presence of frustration, or poor bonding between the sublattices.

Splitting into two subsystems apparently is also a characteristic feature of ludwigites and it is connected with the features of the structure.

If we consider ludwigite structure taking into account the known experimental data, it is possible to pay attention to the following features: in the compounds majority, the ions magnetic moments ordering primarily occurs in the so-called three leg ladders formed triads 4-2-4 (subsystem 1). In the majority of the compounds, position 4 is mainly occupied by trivalent ion (see Table 1), the distance between the ions in the positions 4 and 2 is the minimal and octahedrons around them are connected by base edges. Ions in positions 1 and 3 also form three leg ladders, the distance between the ions in positions 1 and 3 is contrary the maximum and the octahedra around them are connected by vertices. This subsystem is either ordered at a low temperature or has not been fully ordered, and it is frozen in this state.

Why is ludwigites magnetic system divided into the two subsystems? Maybe it is the ludwigite structure. If we consider the exchange interaction of two subsystems, we can pay attention to the following geometric feature of the ludwigite structure: ions at position 3 have two neighbors in position 4 and two neighbors in the position 2 (figure 1). Ion in position 1 also has 2 neighbors in position 4. These bonds form triangular groups. If antiferromagnetic exchange interactions are comparable in magnitude, then there is a strongly frustrated system. Apparently, this is what happens in  $\text{Fe}_3\text{BO}_5$ . From the indirect exchange interactions estimations in the Anderson-Sawadsky model, it follows that the exchange interaction between the ions in the positions 4 and 4, 4 and 3, 4 and 1, 2 and 3 are very close and equal to  $\sim -5$  K.

It turns out that in the ordering of three leg ladders formed by triads 4-2-4 at 114 K in  $\text{Fe}_3\text{BO}_5$  much-frustrated bonds 4-3, 2-3 and 4-1 occur. In order to reduce the frustration, the magnetic moments in positions 1 and 3 rotate perpendicularly to the magnetic moments in positions 2 and 4. The 3-1, 3-3, 1-1 exchange interactions are weaker (Table 6), and ordering of this subsystem occurs at a lower temperature (figure 28).

Table 6 Calculated indirect exchange interaction for  $\text{Fe}_3\text{BO}_5$  and  $\text{Cu}_2\text{MnBO}_5$  ludwigites.  $i, j$  - ions position,  $\alpha, \beta$  - the angle between ions  $i, j$  through O ion, exchanges values are listed in K. For  $\text{Cu}_2\text{MnBO}_5$ , exchanges specified by “/” correspond to different angles distorted by the structure geometry and approximately equal to  $\alpha, \beta$ .

| $i$ | $j$ | $\alpha$         | $\beta$ ;       | $\text{Fe}_3\text{BO}_5$ | $\text{Cu}_2\text{MnBO}_5$ |
|-----|-----|------------------|-----------------|--------------------------|----------------------------|
| 2a  | 2a  | $\sim 90^\circ$  |                 | 1.2                      | 7.9                        |
| 2d  | 2d  | $\sim 90^\circ$  |                 | 1.2                      | 7.9                        |
| 2d  | 4h  | $\sim 180^\circ$ |                 | -3.6                     | -8.3 / -1.8                |
| 4g  | 2a  | $\sim 125^\circ$ |                 | -2.6                     | -0.4                       |
| 4g  | 2d  | $\sim 90^\circ$  | $\sim 90^\circ$ | -5.7                     | 17.7 / 7.9                 |
| 4g  | 4g  | $\sim 90^\circ$  | $\sim 90^\circ$ | 1.2                      | 7.9                        |
| 4h  | 2a  | $\sim 90^\circ$  | $\sim 90^\circ$ | -5.4                     | 0.1 / -6.0                 |
| 4h  | 2d  | $\sim 90^\circ$  |                 | -2.3                     | 0.0                        |
| 4h  | 4g  | $\sim 125^\circ$ |                 | -2.6                     | -3.1 / -1.0                |
| 4h  | 4g  | $\sim 90^\circ$  | $\sim 90^\circ$ | -5.5                     | -5.0 / -0.8                |
| 4h  | 4h  | $\sim 90^\circ$  | $\sim 90^\circ$ | -5.3                     | -5.5                       |

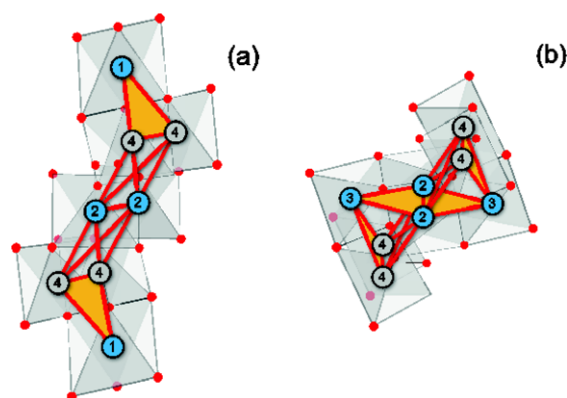


Fig. 28 The triad 4-2-4 surroundings by positions 1 and 3. Red circles - oxygen ions, gray/blue circles -  $\text{M}^{3+}/\text{M}^{2+}$  ions.

A similar situation appears in  $\text{Cu}_2\text{MnBO}_5$ , with the difference that a part of the exchange interaction, in this case, is close to 0 (in accordance with Goodenough's rule).

Taking into account the ludwigite structure geometric features, it can be assumed that the division into two subsystems formed by triads 4-2-4 and 3-1-3 is typical for ludwigites, however, this pattern can be confirmed only by the crystals magnetic structure study.

## 6 Conclusions

Oxyborates with the ludwigite structure are being widely studied in recent years. Due to the structure, which allows fairly wide cationic substitution and contains low-dimensional elements - zigzag walls and tapes - there are various and very unusual physical properties in these compounds. However, at the moment, the explanations for most of the observed features is not found. Virtually, there are no studies of the magnetic structure, there are few theoretical calculations, which does not allow to construct a reasonable physical model of phase transitions in crystals with a ludwigite structure and explain the observed properties.

In most studied compounds, the formation of magnetic ordering begins in three leg ladders formed by triads 4-2-4. Distances between the ions in these three leg ladders are the smallest and octahedrons surrounding the ions are connected by edges, which leads to the rise of strong exchange interactions. As noted earlier, the structure geometry is such that the ions in positions 1 and 3 form the three leg ladders of the 1<sup>st</sup> type with the triangular groups which often (in the case of antiferromagnetic interaction) leads to the appearance of frustration. For some ions (e.g. copper) the interactions between the 1<sup>st</sup> type triad ions and position 3 are close to 0 (according to the Goodenough rule) which is also related to the crystal geometry. As a result, the 3-1-3 ions form a triad of the 2<sup>nd</sup> type, the exchange bonds 3-1 are weaker due to the large distances and octahedrons connections, which surround the metal ion by vertices. The magnetic ordering formation in the second triad can occur later at lower temperatures and in both neutron diffraction compounds studies, magnetic moments in three leg ladders of the 2<sup>nd</sup> type are oriented at a substantial angle to the magnetic moments of ions in the three leg ladders of the 1<sup>st</sup> type - 90° (Fe<sub>3</sub>BO<sub>5</sub>) and 60° (Cu<sub>2</sub>MnBO<sub>5</sub>). Apparently, such orientation reduces frustration in the system.

One of the most interesting ludwigites mystery is the non-magnetic ion replacement impact on Co-containing ludwigites properties. It is unclear why there is a significant difference between the magnetic ground state and magnetic transition temperature: Co<sub>5</sub>TiBO<sub>5</sub> - spin glass,  $T_N = 20$  K, and Co<sub>5</sub>Sn(BO<sub>5</sub>)<sub>2</sub>,  $T = 82$  K - ferrimagnetic. Non-magnetic Ti and Sn ions have a significant difference in the ionic radii:  $R_{Ti} = 0.88$  Å,  $R_{Sn} = 0.69$  Å. The authors [13] wrote that the Zeeman energy contributes significantly and causes the difference in the Co<sub>5</sub>TiBO<sub>5</sub> and Co<sub>5</sub>Sn(BO<sub>5</sub>)<sub>2</sub> properties. If it is so, the question appears - whether this repeats in other compounds with magnetic ions, e.g. nickel.

In addition to the existing ludwigites study, the creation of new previously unknown oxyborates with ludwigite structure is possible. Compounds of this family have interesting properties: 2 positions ordering in different directions, the charge ordering, etc. Of course, it is important to receive and investigate new formulations as well as to establish mechanisms of magnetic transitions in the known compositions.

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**Key words.** ludwigites, ferrimagnetic, antiferromagnetic, spin-glass, oxyborates.

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