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# Magnetic properties of $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ crystals with the ludwigites structure

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The studied solid solutions $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ are ferrimagnets with magnetic transition temperatures of 46 and 48 K, respectively. Substitution of nickel ions for divalent cobalt ions in ludwigite $Co_3BO_5$ has virtually no effect on the magnetic properties: temperature, magnetic crystallization, and the same characteristics, temperature dependences, and field dependences of magnetization, corresponding to the cm$^{-1}$ behavior of magnetization in $Co_3BO_5$, are identical. Trivalent cobalt ions likely remain in a low-spin state, and the nature of the exchange interactions of magnetic ions remains unchanged.

**Keywords:** ludwigites, magnetic phase transition, indirect exchange interactions.

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## 1. Introduction

Ludwigite $Co_3BO_5$ is isolated among other ludwigites by the fact that first of all cobalt ions in it are in two valence states — bivalent and trivalent, while, secondly, the trivalent cobalt ion is in a low-spin state with a zero spin. Of four nonequivalent positions, the three positions (*1, 2* and *3* in Figure 1) are occupied by $Co^{2+}$, while one position (*4* in Figure 1) is occupied by $Co^{3+}$. A crystal structure and distribution of magnetic and nonmagnetic cobalt ions are such that the compound can be presented as consisting of magnetic planes that contain the ions $Co^{2+}$ separated by nonmagnetic planes formed by the ions $Co^{3+}$. Despite this, the magnetic system is ordered at 42 K [1–3]. A magnetic structure of $Co_3BO_5$ was determined by a neutron diffraction method [1] and it was shown that magnetic moments of the ions were oriented almost parallel to the axis $b$ and slightly biased towards the axis $a$. It was found that the magnetic moments of the ions $Co^{2+}$ in the positions *1–3* are $(3.1-3.8)\mu_B$, which corresponds to a high-spin state of the ions $Co^{2+}$, whereas the magnetic moment of the ions $Co^{3+}$ in the position *4* is just $0.5\mu_B$ (Figure 1).

Currently, there are a lot of known heterovalent ludwigites based on $Co_3BO_5$. There have been studies of compounds, in which the cobalt ions are substituted with aliovalent ions with a nonzero spin, such as manganese, copper, iron [4,5], and with zero spins in the ground state — gallium, tin, titanium, magnesium [6–11]. Almost all the said compounds had substitution in the trivalent subsystem.

In the compound $Co_{1.7}Mn_{1.3}BO_5$, both the magnetic ions (cobalt and manganese) can be both in the bivalent and the trivalent state. Despite the fact that almost a half of the cobalt ions is substituted by the manganese ions, the magnetic transition into a spin-glass state is observed in $Co_{1.7}Mn_{1.3}BO_5$ at 41 K. The manganese ions are distributed along all the positions in the different valence states, but the position *4* is preferable [5]. Probably, presence of the magnetic ion in the position *4* enhances

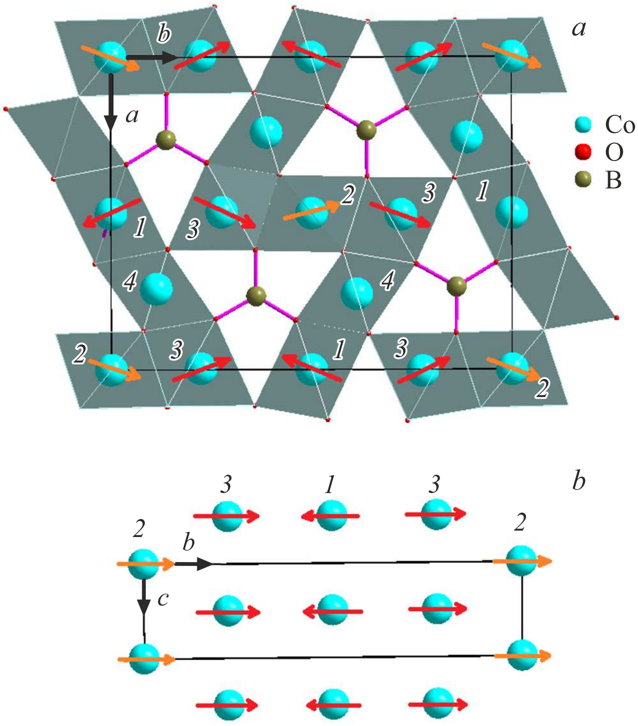

**Figure 1.** *a* — the magnetic structure of $Co_3BO_5$; *b* — magnetic ordering in the plane that is formed by the bivalent cobalt ions which occupy the positions *1, 2* and *3* [1].

competition of exchange interactions, thereby preventing establishment of a long-range magnetic order.

In the compound $Co_5Ti(BO5)_2$ the cobalt ions are only in the bivalent state. The position *4* is almost equally occupied by the ions of titanium and cobalt in a disordered way. The position *1* is also occupied by the ions of titanium and cobalt in a proportion 0.075 : 0.175 [6]. At the temperature of 19 K the system transits into the spin glass state. In this compound, the bivalent cobalt ions, which occupy the position *4*, also enhance competition, thereby preventing establishment of the long-range order.

Unlike the other compositions, in $Co_{2.4}Ga_{0.6}BO_5$ the magnetic transition's temperature is reduced to 37 K, but the long-range magnetic order is preserved. The gallium ions have valence of $3^+$ and preferably occupy the position *4*, substituting the trivalent cobalt ions. The magnetic moment of the cobalt ions is within the plane $ab$. Since in $Co_3BO_5$ the trivalent cobalt ions are in the low-spin state and their magnetic moment is zero, their substitution with nonmagnetic gallium apparently does not significantly affect the magnetic structure [7].

Magnetization was studied in the solid solutions $Co_{3-x}Cr_xBO_5$ to show that substitution of the cobalt ions with the chromium ions sharply increases the magnetic transition's temperature from 42 K an undoped compound to 115 K for the compound with the maximum Cr concentration ($x = 0.9$) [12]. The last value is the highest temperature of long-range magnetic ordering, which has been recorded up to now for the ludwigites based on $Co_3BO_5$. The substitution changes the main magnetic structure of the compound, transiting from a ferrimagnetic state (at the low Cr concentrations) into an antiferromagnetic state (at the high Cr concentrations). Besides, with the concentration of the Cr ions, which exceeds 0.5, $Co^{3+}$ transits from the low-spin state into the high-spin state.

Substitution in the bivalent subsystem of the ludwigites base on $Co_3BO_5$ is almost unstudied. It is known that the compound $Co_{2.88}Cu_{0.12}BO_5$ exists [4], in which the temperature of magnetic ordering insignificantly varies from 42 to 43 K. The authors assumed that copper substituted the trivalent cobalt ions in the position *4* and had a trivalent state. However, it should be noted that the trivalent state ($3^+$) is absolutely untypical for copper in dielectrics. It is most probable that copper is included in the composition $Co_{2.88}Cu_{0.12}BO_5$ in the bivalent state and since little copper is included in the composition $Co_{2.88}Cu_{0.12}BO_5$, the magnetic system is ordered in the same way as in $Co_3BO_5$.

In our study, we investigate the influence of substitution of the cobalt ions with the nickel ions in the bivalent subsystem on the magnetic properties of the compounds $Co_{3-x}Ni_xBO_5$. Nickel occurs in the bivalent state in oxyborates and, moreover, nickel and cobalt are neighboring elements in the Mendeleev periodic table and have similar ionic radii. We know the systems, for example, kotoite-structure solid solutions $Co_xNi_{3-x}B_2O_6$, where the nickel ions are isostructurally substituted with cobalt. And since these ions have different single-ion anisotropy, then, for example, in the kotoites a direction of the light magnetization axis is changed [13]. It is interesting to trace evolution of the magnetic properties in the ludwigites $Co_{3-x}Ni_xBO_5$ when substituting the cobalt ions with nickel: whether the trivalent cobalt ions will remain in the low-spin state, how will the magnetic moments of the ions be oriented.

We have previously performed growth experiments in order to obtain a series of the solid solutions $Co_{3-x}Ni_xBO_5$ and obtained two compositions when $x = 0.33$ and $x = 0.66$ [14]. In this paper, we present a detailed study of the magnetic properties of the obtained compounds.

## 2. Composition and the crystal structure

The two compositions $Co^{3+}Ni^{2+}_{2-x}Co^{2+}_xBO_5$ with the ludwigite structure were produced by spontaneous generation from a solution-melt system based on $Bi_2Mo_3O_{12}-B_2O_3$, diluted with a carbonate $Na_2CO_3$ [15]. The synthesized crystals have a black color with a needle-like shape. A method of energy-dispersive microscopy was used to refine the composition of the two studied solid solutions $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$, to determine the crystal structure $Pbam$ (55) and the lattice parameters ($a = 9.2855(7)$ Å, $b = 11.9893(9)$ Å, $c = 2.9908(2)$ Å and $a = 9.244(5)$ Å, $b = 12.049(5)$ Å, $c = 2.9966(14)$ Å, respectively for $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$). It was shown within the framework of ab initio calculation of energies of various cation-ordered configurations that the nickel ions preferred to substitute the cobalt ions in the positions $2a$ and $4g$ [14].

## 3. Magnetic properties

The magnetic properties of the compounds were studied in a PPMS Quantum design installation within the temperature range 4–300 K at the value of magnetic strength −90 – +90 kOe. As mentioned above, the single-crystal samples were needle-like. The needles intensely grow along the shortest crystallographic direction. The crystallographic axis $c$ coincides with a needle direction, but transverse dimensions of the produced samples do not allow orienting them relative to the crystallographic directions $a$ and $b$. Temperature and field dependencies of magnetization were measured along two directions: along and perpendicular to the axis $c$. Figure 2 shows the temperature dependences of magnetization of the single crystals of the two compositions when applying the magnetic field along and perpendicular to the axis $c$ in the mode of field cooling (FC), field heating (FH) and zero-field cooling with subsequent heating in the nonzero field (ZFC) for the fields of 200 Oe and 1 kOe. As it is clear from Figure 2, the temperature of magnetic ordering increases with an increase of the nickel concentration. A type of the curves is very similar to the temperature dependences of magnetization of $Co_3BO_5$. At the same time, the

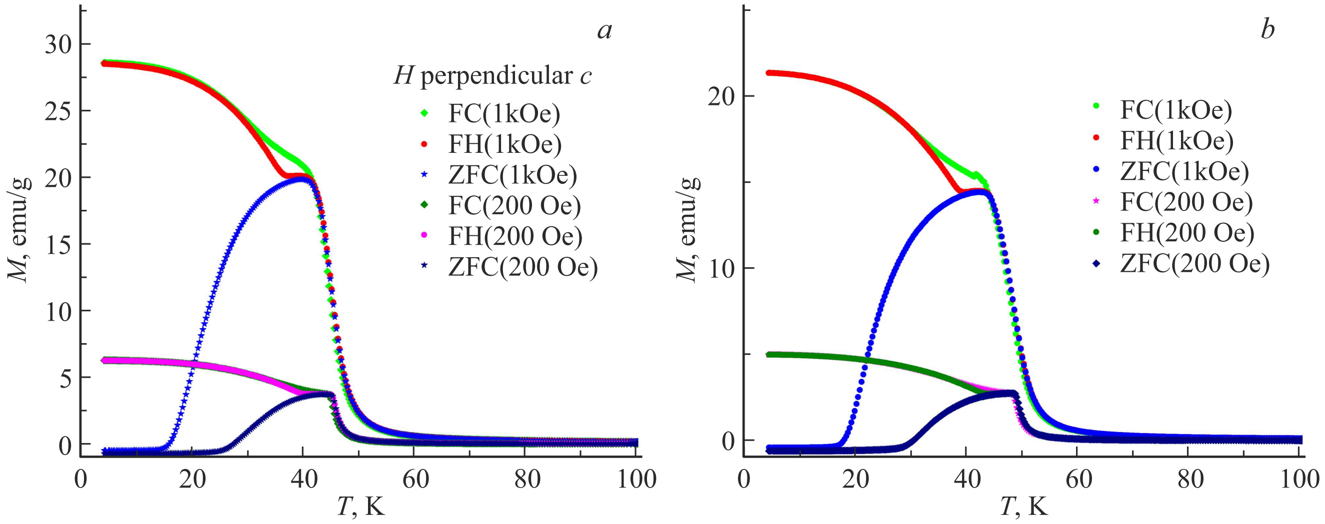

**Figure 2.** Temperature dependences of magnetization of the single crystals $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ (*a*) and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ (*b*) when applying the magnetic field perpendicular to the axis *c* in the mode of field cooling (FC), field heating (FH) and zero-field cooling and subsequent heating in the nonzero field (ZFC) for the fields of 200 Oe and 1 kOe.

temperature dependences of magnetization in the different modes are different in both the studied compositions in the same way as in $Co_3BO_5$. The curves measured in the mode of field cooling (FC) and field heating (FH) exhibit two specific features: in the composition $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ at 29 and 46 K, in the composition $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ at 30 and 48 K. In the same ways as in $Co_3BO_5$, the Curie–Weiss temperature is considerably different: when applying the magnetic field along the axis $c$ — $T_\theta = -508$ and $-616$ K, when applying the field perpendicular to the axis $c$ — $T_\theta = 7$ and $-8$ K for $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$, respectively.

Figure 3 shows the field dependences of magnetization of both the compositions at the various temperatures when applying the magnetic field along and perpendicular to the axis *c*. A behavior of the field dependences of magnetization $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ is similar to a behavior of magnetization in $Co_3BO_5$: when applying the field perpendicular to the axis *c* hysteresis loops are observed and a value of a coercive filed varies from 17 to 25 kOe; when applying the field along the axis *c* magnetization is almost linear and within a region of magnetic ordering a curve slope does not change in a dependence on the temperature.

Figure 4 shows the temperature dependences of *ac* magnetization $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ when applying the variable magnetic field of a different frequency. As it is clear from Figure 4, unlike *dc* magnetization, the ac magnetization in both the compositions exhibit only one specific feature that is not shifted along the temperature in a dependence on a frequency of the applied field: at 48 and 46 K in $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$, respectively.

## 4. Discussion of results

The magnetic properties of the substituted compositions $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ are very similar to the properties of $Co_3BO_5$. The temperatures of magnetic ordering in the substituted compositions are somewhat higher (46–48 K) than in the pure compounds (42 K), i. e. implantation of the nickel ions still somewhat enhances the magnetic order. If proceeding from an assumption that the trivalent cobalt ions occupying the position *4* (see Figure 1) are in the low-spin state with the 0 spin (i. e. are nonmagnetic) and do not change their spin state when being substituted in the bivalent subsystem, then the magnetic ions that form the magnetic order will be only the bivalent ions of cobalt and nickel (in the substituted compositions).

In our previous studies, we evaluated the exchange interactions within the framework of indirect exchange coupling both for $Co_3BO_5$ [12] and for other compounds of the ludwigite structure, which contain the nickle ions in the positions *1, 2* and *3* (see Figure 1), for example, in the compound $Ni_2MnBO_5$ [16]. When the position *4* is occupied by the magnetic ion, it is possible to select 11 various exchange interactions in the ludwigite structure. In our considered compounds, the position *4* is occupied by the nonmagnetic ion. Thus, only 5 exchange interactions remain in the bivalent subsystem. These exchange interactions are listed in a table for the compounds $Co_3BO_5$ and $Ni_2MnBO_5$ [1,16]. We can use the exchange interactions calculated for the bivalent system $Ni_2MnBO_5$, considering the compound $Ni_2Co^{3+}BO_5$, since it was assumed in the calculations that the nickel ions occupied the positions *1–3*. For the experimental compositions, where the nickel content is $x = 0.33$ and $x = 0.59$, the compound $Ni_2Co^{3+}BO_5$ is a

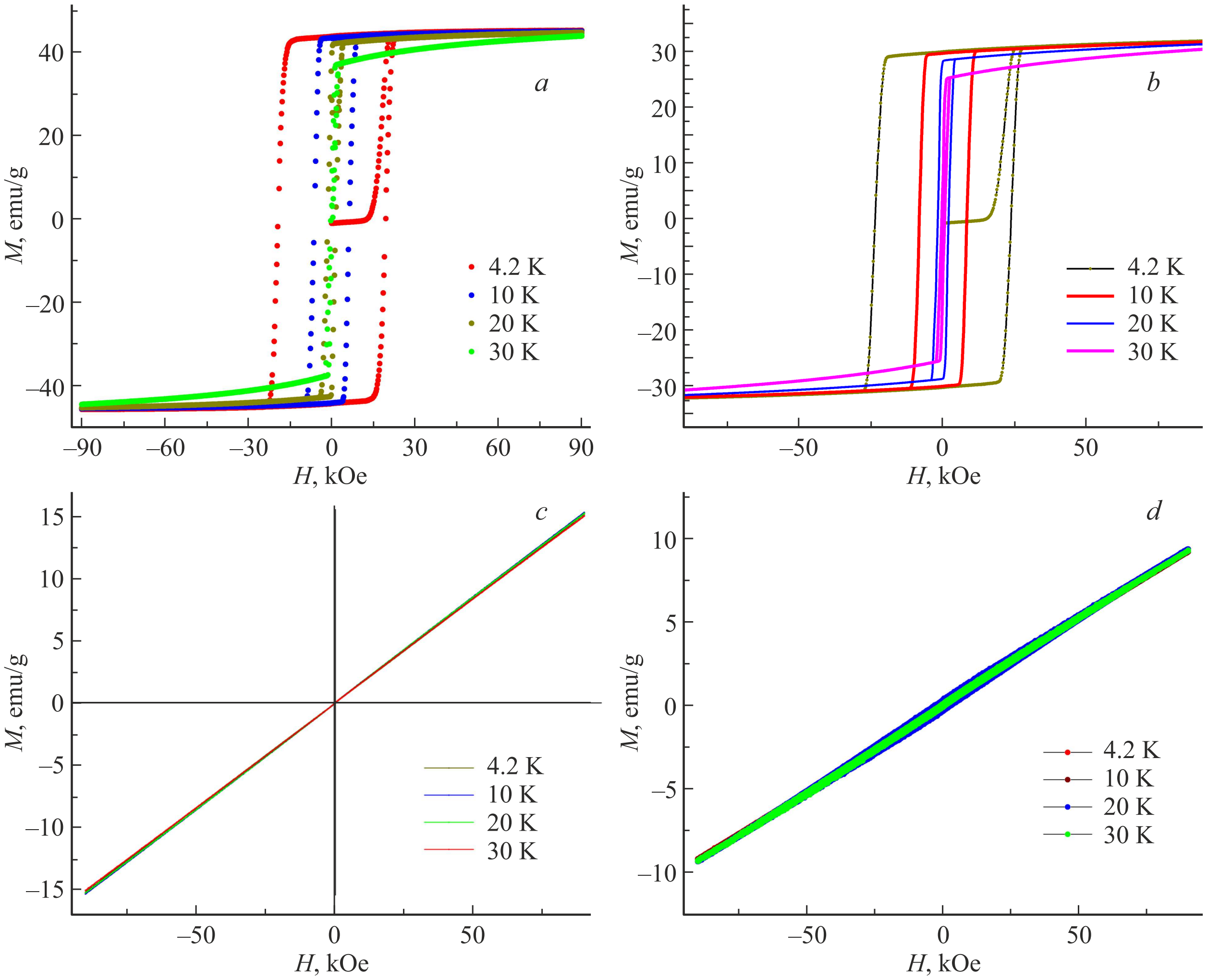

**Figure 3.** Field dependences of magnetization $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ (*a, c*) and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ (*b, d*) at the various temperatures when applying the magnetic field perpendicular to (*a, b*) and along (*c, d*) the axis *c*.

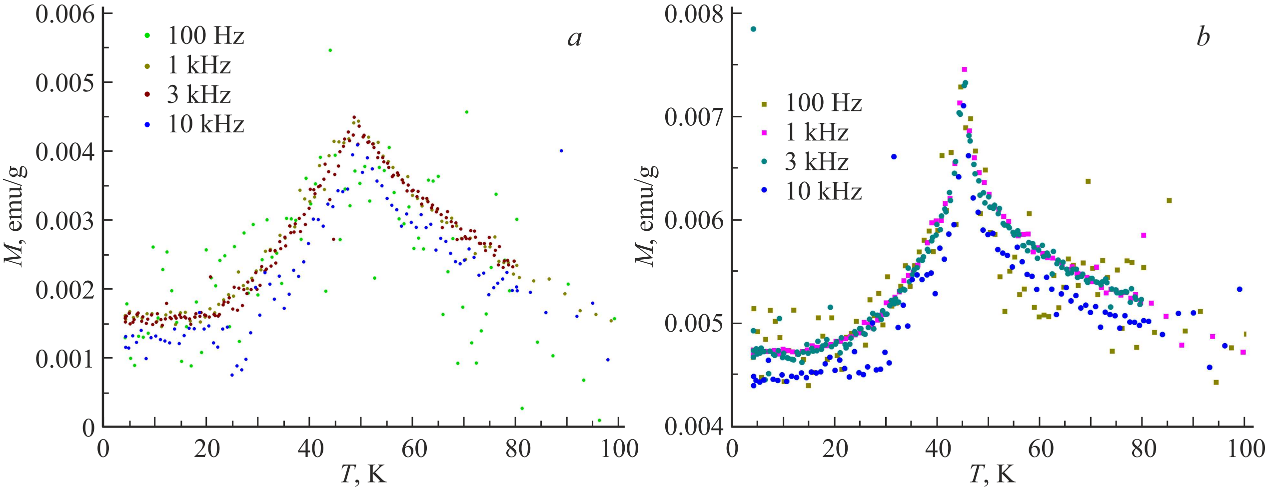

**Figure 4.** Temperature dependences of ac magnetization $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ (*a*) and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ (*b*) when applying the alternating magnetic field with the different frequencies.

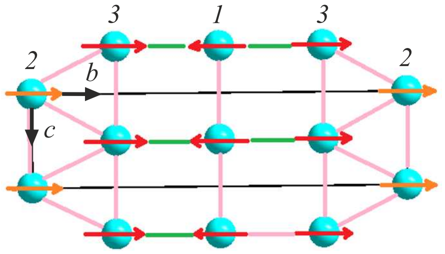

**Figure 5.** Magnetic disordering in the plane *bc*. Antiferromagnetic (the green lines) and ferromagnetic (the pink lines) superexchange interactions.

Exchange interactions of the ions in the positions $k$ and $l$ ($J_{k-l}$) in the bivalent subsystem of the ludwigites $Co_3BO_5$ and $Ni_2MnBO_5$ [1,16]

| J(K) | $J_{1-1}$ | $J_{2-2}$ | $J_{3-3}$ | $J_{1-3}$ | $J_{2-3}$ |
|---|---|---|---|---|---|
| $Co_3BO_5$ | 3.5 | 3.5 | 3.5 | −2.9 | 1.8 |
| $Ni_2MnBO_5$ | 5.5 | 5.5 | 5.5 | −1.8 | 5.5 |

limit case of substitution of the cobalt ions with the nickel ions in the bivalent subsystem.

As it is clear from Table, full substitution of the cobalt ions with the nickel ions in the bivalent subsystem does not change a nature of the exchange interactions: ferromagnetic interactions are still ferromagnetic and enhance, and although antiferromagnetic interactions between the ions in the positions *1* and *3* are somewhat attenuated, they are still antiferromagnetic ones.

Thus, even with full substitution of the bivalent subsystem one may expect that the magnetic order will be still the same as in $Co_3BO_5$, if the trivalent cobalt ions remain in the low-spin state. However, a direction of the magnetic moments can change as it is observed in the isostructural kotoites $Ni_3B_2O_6$ and $Co_3B_2O_6$, in which the ions of nickel and cobalt are also in the bivalent state, since spin-orbit interaction of the ions of nickel and cobalt is different. However, the sample dimension did not allow us to make orientation measurements, separating the directions $b$ and $a$. We can not determine how orientation of the magnetic moments in the plane $ab$ changed.

Since a magnetic cell of $Co_3BO_5$ coincides with the crystallographic one and the magnetic ions occupy the three nonequivalent positions, then by omitting a bias of the magnetic moments relative to the axis $b$ it is possible to evaluate the temperature of magnetic ordering within the framework of a three-sublattice ferrimagnetic both for $Co_3BO_5$ and for $Ni_2Co^{3+}BO_5$, if assuming that magnetic ordering does not change when substituting cobalt with the nickel ions [17]. For evaluation, we used the exchange interactions from Table. For the three-sublattice ferrimagnetic, the cubic equation for determining $T_c$ provides three roots: $T_c = 34.8$, 17.5 and 0.2 K for $Co_3BO_5$ and $T_c = 38.6$, 7.3 and $-1.0$ K for $Ni_2Co^{3+}BO_5$. One of the roots for $Co_3BO_5$ ($T_c = 34.8$ K) is close to the observed magnetic transition's temperature of 42 K. In the same way as in the experiment, where with the increase of the nickel concentration $T_c$ increases, in the compound $Ni_2Co^{3+}BO_5$ $T_c$ increases to 38.6 K.

## 5. Conclusion

The magnetic properties of the solid solutions $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ were studied to show that substitution of the bivalent cobalt ions with the nickel ions has almost no effect on the magnetic properties, the behavior of the temperature and field dependences of magnetization is similar to the behavior of magnetization in $Co_3BO_5$. The magnetic transition's temperature in the substituted compositions $Co^{3+}Ni^{2+}_{0.33}Co^{2+}_{1.67}BO_5$ and $Co^{3+}Ni^{2+}_{0.59}Co^{2+}_{1.41}BO_5$ increases to 46 and 48 K, respectively. Evaluation of the magnetic transition's temperature within the framework of the three-sublattice ferrimagnetic using exchange interactions obtained within the framework of the semi-empirical indirect exchange coupling model qualitatively agrees with the experimental data: enhancement of the ferromagnetic interactions $J_{1-1}$, $J_{2-2}$, $J_{3-3}$ and $J_{2-3}$ when substituting the cobalt ions with the nickel ions results in a slight increase of the magnetic transition's temperature in spite of weakening of the antiferromagnetic interactions $J_{1-3}$.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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