

Magnetic properties of $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ single crystals

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Orthorhombic $\text{Me}_3\text{B}_2\text{O}_6$ (Me = Co, Ni) single crystals of the kotoite family are grown from the fluxes based on a mixture of bismuth trimolybdate and sodium oxide upon spontaneous nucleation. The field and temperature dependences of magnetization of the single crystals with the magnetic field oriented along the principal crystallographic directions are obtained.

Unlike $\text{Ni}_3\text{B}_2\text{O}_6$, $\text{Co}_3\text{B}_2\text{O}_6$ exhibits strong anisotropy of the magnetic properties. At the temperature $T = 10$ K, the magnetization curves of $\text{Co}_3\text{B}_2\text{O}_6$ reveal an anomaly attributed to the spin-reorientation transition. Strong anisotropy of the magnetic properties of $\text{Co}_3\text{B}_2\text{O}_6$ is also confirmed by the calculation of the exchange interactions within a simple indirect coupling model.

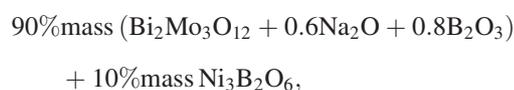
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1 Introduction In recent years, close attention has been focused on the compounds with geometric magnetic frustrations, because these materials can exhibit intriguing magnetic properties and magnetic states (spin glass, spin liquid, and spin ice) [1–4]. A characteristic feature of these compounds is the presence of triangular or tetrahedral groups in the structure that form chains and ribbons. Oxyborates $\text{Me}_3\text{B}_2\text{O}_6$ (Me = Co, Ni, or Mn) with the kotoite structure [5, 6] contain structural elements necessary for the occurrence of the fascinating magnetic peculiarities: there are triangular groups in their structure and all metal ions are localized inside an oxygen octahedron. Manganese, cobalt, and nickel oxyborates were obtained for the first time in the 1960s. All the three compounds are antiferromagnets and, despite the fact that they are isostructural, their magnetic properties are different [6]. Pioneering investigations were carried out on powder samples. It was found that $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ undergo one magnetic phase transition at 49 and 30 K, respectively, whereas $\text{Mn}_3\text{B}_2\text{O}_6$ is apparently characterized by two magnetic transitions at 55 and 35 K. The magnetic structures of $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ were studied in Refs. [5, 6]. It was established that their magnetic cell is larger than the crystallographic one by a factor of four. The authors, however, were not fully convinced in their conclusions. An interesting feature of $\text{Ni}_3\text{B}_2\text{O}_6$ is the closeness of

its paramagnetic Curie temperature (5 K) to zero, which may point out the competition between the ferromagnetic and antiferromagnetic interactions, while the paramagnetic Curie temperature of $\text{Co}_3\text{B}_2\text{O}_6$ is quite typical of an antiferromagnet (63 K). The paramagnetic Curie temperature of $\text{Mn}_3\text{B}_2\text{O}_6$ exceeds the Neel temperature by a factor of six, which may indicate the presence of strong frustrations in the system. However, the data reported in Refs. [5, 6] are insufficient to clarify the magnetic structure and understand the origin of the magnetic order in the investigated compounds.

In this study, we report a developed technique of growing high-quality $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ single crystals from fluxes and the results of magnetic measurements performed in different crystallographic directions. Using a group-theoretical analysis and a simple indirect coupling model, we determined possible magnetic structure of both compounds and estimated indirect exchange interactions.

2 Preparation of the samples $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ single crystals were grown by the flux method. The following fluxes were used:



55%mass ($\text{Bi}_2\text{Mo}_3\text{O}_{12} + 0.7\text{Na}_2\text{O} + 2.1\text{B}_2\text{O}_3$)
+ 45%mass $\text{Co}_3\text{B}_2\text{O}_6$.

The calculated mass of each flux was 80 g. The fluxes were prepared in platinum crucibles with a volume of 100 cm^3 by successive melting of B_2O_3 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, Na_2CO_3 , and NiO (or Co_2O_3) at a temperature of $1100\text{ }^\circ\text{C}$. At this stage, Na_2CO_3 and Co_2O_3 decompose:



and CO_2 and O volatilize.

After homogenization at $T = 1100\text{ }^\circ\text{C}$ for 3 h, it was established that the high-temperature crystallizing phases are $\text{Ni}_3\text{B}_2\text{O}_6$ or $\text{Co}_3\text{B}_2\text{O}_6$ with the respective saturation temperatures $T_{\text{sat}} \approx 983 \pm 3\text{ }^\circ\text{C}$ and $960 \pm 3\text{ }^\circ\text{C}$. The temperature interval of crystallization of these phases is $40\text{ }^\circ\text{C}$.

After repeated homogenization, the flux was rapidly cooled down to $T_0 = T_{\text{sat}} - 10\text{ }^\circ\text{C}$ and then slowly cooled at a rate of $8\text{ }^\circ\text{C}/\text{day}$. In 3 days, the solution-melt was poured off. The crystals, 3–4 mm in size grown on the crucible walls, were released from the residue of the flux by etching in a 20% nitric acid in water solution.

3 Crystal structure The $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ crystals belong to the $Pn\bar{m}n(D_{2h}^{12})$ space group (kotoite structure) with the lattice parameters $a = 8.30\text{ \AA}$, $b = 4.46\text{ \AA}$, and $c = 5.40\text{ \AA}$ for $\text{Ni}_3\text{B}_2\text{O}_6$ and $a = 8.44\text{ \AA}$, $b = 4.53\text{ \AA}$, and $c = 5.46\text{ \AA}$ for $\text{Co}_3\text{B}_2\text{O}_6$. The unit cell involves two formula units. Magnetic atoms are Ni (Co) occupying two nonequivalent crystallographic positions 2a and 4f. Thus, there are six magnetic atoms in the unit cell. The kotoite structure is illustrated in Fig. 1. The bold lines indicate chains of the triangular groups in the ac planes.

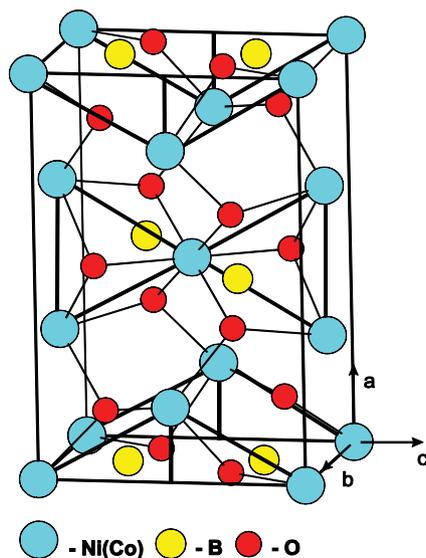


Figure 1 (online color at: www.pss-b.com) Unit cell of kotoite structure.

4 Technique Magnetic measurements were performed on PPMS and MPMS facilities (Quantum Design) at temperatures of 2–300 K in magnetic fields up to 90 kOe. Figures 2 and 3 present the temperature dependences of magnetization of $\text{Co}_3\text{B}_2\text{O}_6$ and $\text{Ni}_3\text{B}_2\text{O}_6$, respectively. The measurements were performed in the magnetic field oriented along the a -, b -, and c -axes. It can be seen that, at the temperatures $T_N = 46.3\text{ K}$ for $\text{Ni}_3\text{B}_2\text{O}_6$ and $T_N = 34\text{ K}$ for $\text{Co}_3\text{B}_2\text{O}_6$, the curve has a sharp kink, pointing out the occurrence of magnetic ordering. The temperature dependences of magnetization are characteristic of a collinear antiferromagnet with the easy magnetization axis directed along the a -axis for $\text{Ni}_3\text{B}_2\text{O}_6$ and along the c -axis for $\text{Co}_3\text{B}_2\text{O}_6$. In $\text{Co}_3\text{B}_2\text{O}_6$, in contrast to $\text{Ni}_3\text{B}_2\text{O}_6$, there is strong anisotropy of magnetization both above and below the temperature of the magnetic phase transition. Magnetization along the a - and b -axes decreases with a decrease in

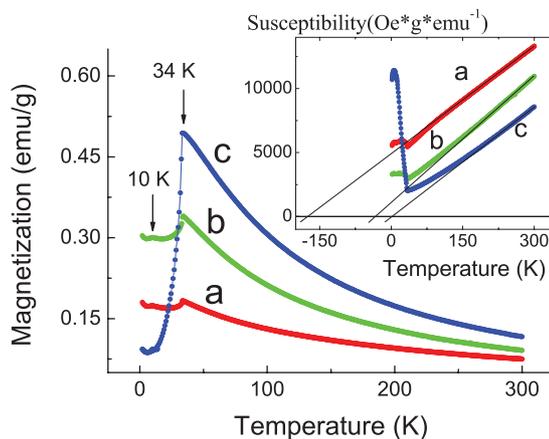


Figure 2 (online color at: www.pss-b.com) Temperature dependences of magnetization of $\text{Co}_3\text{B}_2\text{O}_6$ along the a -, b -, and c -axes at a field of 1 kOe. The insert shows the temperature dependences of inverse magnetic susceptibility.

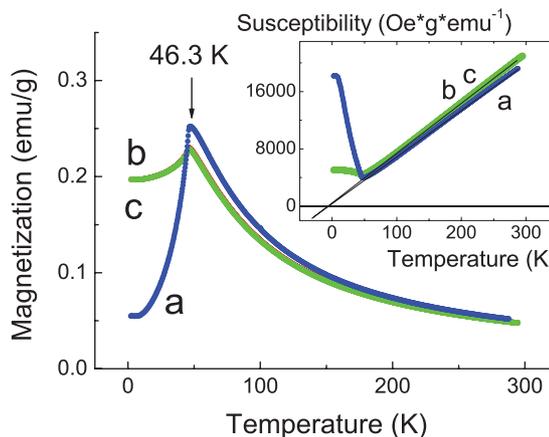


Figure 3 (online color at: www.pss-b.com) Temperature dependences of magnetization of $\text{Ni}_3\text{B}_2\text{O}_6$ along the a -, b -, and c -axes at a field of 1 kOe. The insert shows the temperature dependences of inverse magnetic susceptibility.

temperature below T_N , in contrast to the case of a classical two-sublattice antiferromagnet whose magnetization does not change during the measurements perpendicular to the easy axis. One should also note that the magnetization measured along the c -axis does not tend to zero monotonically with decreasing temperature, but has a kink and weakly grows below 5 K. In addition, in the temperature dependences of magnetization of Co₃B₂O₆, there is an abnormal peak at $T^* = 10$ K, which can be related to the change in the magnetic structure of the crystal (a spin-reorientation phase transition).

The inserts in Figs. 2 and 3 show the temperature dependences of inverse magnetic susceptibility for the three preferential directions in the crystals. In the case of the Ni₃B₂O₆ crystal, the susceptibility follows the Curie–Weiss law from the high-temperature side, up to $T \sim 100$ K. The paramagnetic Curie temperature of this compound $\theta = -7.5$ K is independent of direction. Such a small value of θ as compared to T_N indicates, most likely, the existence of the competition between the antiferromagnetic and ferromagnetic exchange interactions in the system.

In the case of the Co₃B₂O₆ crystal, the Curie–Weiss law is also followed up to $T \sim 100$ K in the direction along the a -axis; for the two other preferential directions, starting from $T \sim 150$ K, deviation from this law is observed. The paramagnetic Curie temperature of the Co₃B₂O₆ crystal strongly depends on direction ($\theta_a = -174$ K, $\theta_b = -38$ K), being positive for the c direction ($\theta_c = 7$ K).

Figure 4 presents the field dependences of magnetization obtained at different temperatures. It can be seen that at $T = 50$ K the dependences are linear, as expected for a paramagnet. In the ordered region, at temperatures of 2 and 30 K along the axes perpendicular to the easy magnetization axis, magnetization linearly grows with magnetic field, as one could expect in the case of a classical two-sublattice antiferromagnet. For the latter, the field dependence along the easy magnetization axis should also be linear with a typical magnetization jump corresponding to the spin-flop field. No spin-flop is observed in our case, which indicates either a large value of the uniaxial anisotropy constant or a complex magnetic structure.

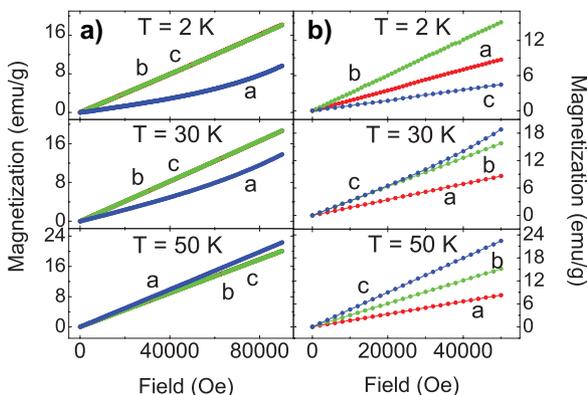


Figure 4 (online color at: www.pss-b.com) Field dependences of magnetization of (a) Ni₃B₂O₆ and (b) Co₃B₂O₆ for three directions at different temperatures.

5 Group-theoretical analysis of possible magnetic structures Possible magnetic structures were determined using the group-theoretical analysis [7]. The expansion of the magnetic representation by irreducible representations for the center of the Brillouin zone was obtained:

$$T(k=0) = 2\tau_1 + \tau_2 + 4\tau_3 + 2\tau_4 + 4\tau_5 + 2\tau_6 + 2\tau_7 + \tau_8.$$

The expansion of the magnetic representation by irreducible representations for atoms in the 2a position is

$$T_{2a}(k=0) = \tau_1 + 2\tau_3 + 2\tau_5 + \tau_7.$$

The expansion of the magnetic representation by irreducible representations for atoms in the 4f position is

$$T_{4f}(k=0) = \tau_1 + \tau_2 + 2\tau_3 + 2\tau_4 + 2\tau_5 + 2\tau_6 + \tau_7 + \tau_8.$$

According to the Landau theory, phase transitions are related, as a rule, to one irreducible representation; therefore, we considered possible magnetic structures related to the representations $\tau_1, \tau_3, \tau_5, \tau_7$ common to both sublattices. The directions of the magnetic moments for these representations are given in Table 1.

It follows from the experimental data obtained that, at low temperatures, both crystals, Ni₃B₂O₆ and Co₃B₂O₆ are antiferromagnets and the magnetic moments on ions are directed along the a - and c -axes, respectively. Since our experiments do not allow establishing a magnetic cell, we considered the simplest case when the magnetic cell coincides with the crystallographic one. As can be seen from Table 1, the magnetic structure in which all the magnetic moments are directed along the same axis is possible for two irreducible representations τ_1 and τ_7 , the magnetic structure corresponding to irreducible representation τ_1 is then antiferromagnetic. Regardless of the chosen crystallographic direction of the rhombic lattice (a, b, c) corresponding to the Z-axis, the direction of the magnetic moments indicated in Table 1 corresponds to representation τ_1 .

6 Indirect coupling model To analyze the magnetic structures and estimate the exchange interactions and Curie temperatures of the Ni₃B₂O₆ and Co₃B₂O₆ crystals, we applied a simple indirect coupling model [8, 9] based on

Table 1 Directions of the magnetic moments on ions for different irreducible representations of the center of the Brillouin zone.

irreducible representations	ions					
	A ₁ (2a)	A ₂ (2a)	A ₃ (4f)	A ₄ (4f)	A ₅ (4f)	A ₆ (4f)
τ_1	0,0,z	0,0,-z	0,0,z	0,0,-z	0,0,z	0,0,-z
τ_3	x,y,0	x,y,0	x,y,0	x,-y,0	x,y,0	x,-y,0
τ_5	x,y,0	-x,y,0	x,y,0	-x,y,0	x,y,0	-x,y,0
τ_7	0,0,z	0,0,z	0,0,z	0,0,z	0,0,z	0,0,z

the theory of the superexchange interaction of Anderson and Zavadskii [10] and Eremin [11].

Within the indirect coupling model, the structure of the crystals can be characterized by the following integrals of the indirect exchange coupling with regard to populations of individual cation orbitals and allowed symmetries of the lattice of indirect couplings J_{ij}^α , where i and j are the numbers of nonequivalent crystallographic positions for magnetic ions and α is the angle of the indirect coupling between magnetic ions.

The calculated exchange integrals for $\text{Ni}_3\text{B}_2\text{O}_6$ are

$$\begin{aligned} J_{11} &= 0, \\ J_{12}^{95} &= J_{22}^{93} = \frac{4}{3}bcJ^{\text{in}} = +6.2 \text{ K}, \\ J_{12}^{114} &= \frac{2}{3}bcJ^{\text{in}} \sin 114^\circ = +2.8 \text{ K}, \\ J_{22}^{124} &= -\frac{8}{9}b^2U|\cos 124^\circ| = -6.2 \text{ K}. \end{aligned} \quad (1)$$

The calculated exchange integrals for $\text{Co}_3\text{B}_2\text{O}_6$ are

$$\begin{aligned} J_{11} &= 0, \\ J_{x12}^{95} &= \frac{1}{9} \left(\frac{16}{3}bcJ^{\text{in}} + 2c^2J^{\text{in}} \right) = +3.6 \text{ K}, \\ J_{y12}^{95} &= -\frac{1}{9} \left(\frac{32}{3}bcU \right) = -9.1 \text{ K}, \\ J_{22}^{88} &= \frac{1}{9} \left(\frac{16}{3}bcJ^{\text{in}} + 2c^2J^{\text{in}} \right) = +3.6 \text{ K}, \\ J_{12}^{110} &= \frac{1}{9} \left(\frac{8}{3}bcJ^{\text{in}} + c^2J^{\text{in}} \right) \sin 110^\circ = +3.3 \text{ K}, \\ J_{x22}^{125} &= \frac{1}{9} \left(-\frac{32}{9}b^2U + bcJ^{\text{in}} \right) |\cos 125^\circ| = -3.1 \text{ K}, \\ J_{y22}^{125} &= \frac{1}{9} \left(-\frac{32}{9}b^2U - 2c^2U \right) |\cos 125^\circ| = -3.9 \text{ K}. \end{aligned} \quad (2)$$

Here, b and c are the electron transfer parameters being squares of ligand–cation intermixing coefficients for the σ and π coupling, respectively (the values of these parameters are $b=0.02$ and $c=0.01$); $U(\text{Ni}^{2+})=2.7 \text{ eV}$; $U(\text{Co}^{2+})=3.3 \text{ eV}$ is the cation–ligand excitation energy; $J^{\text{in}}(\text{Ni}^{2+})=2 \text{ eV}$; and $J^{\text{in}}(\text{Co}^{2+})=2.2 \text{ eV}$ is the integral of the interatomic exchange interaction.

As can be seen from Eq. (2), exchange integrals J_{12}^{95} and J_{22}^{125} for $\text{Co}_3\text{B}_2\text{O}_6$ depend on the direction of the indirect coupling, which is not observed in $\text{Ni}_3\text{B}_2\text{O}_6$. In our calculation, it is related to the fact that, unlike the Ni^{2+} ion, the Co^{2+} ion have different populations of the xz and yz orbitals. First, let us consider the simplest case assuming that the magnetic cell coincides with the crystallographic one. Then, we have six magnetic sublattices coupled by the exchange interactions given in Tables 2 and 3 for the $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ crystals, respectively.

Arrows indicate the magnetic structure imposed by these couplings (see also Fig. 5). The frustrating (disordering) interactions in $\text{Ni}_3\text{B}_2\text{O}_6$ are shown in red. As can be seen from Fig. 6a for the $\text{Ni}_3\text{B}_2\text{O}_6$ crystal, in the chains of the triangular groups the magnetic moments are oriented similarly.

The direction of the magnetic moments of the chains relative to one another is determined by the competing exchange interactions $J_{22}^{124} = -6.2 \text{ K}$ and $J_{12}^{114} = +2.8 \text{ K}$ with the latter being frustrating. Competition of these interactions apparently explains the nearly zero paramagnetic Curie temperature. According to the data reported in Refs. [5, 6], the magnetic cell in this crystal is larger than the crystallographic one ($2a \times 2b \times c$) by a factor of more than four. Assuming that the directions of the magnetic moments in the chains of triangles are oriented as in Fig. 6, we will see that the magnetic order in the diagonal ($a, b, 0$) directions is determined by exchange interaction J_{22}^{124} and in the ($a, -b, 0$)

Table 2 Exchange interactions between sublattices in the $\text{Ni}_3\text{B}_2\text{O}_6$ crystal. The frustrating (disordering) interactions are shown in bold.

$z_{ij}J_{ij}$ (K)	A_1 (2a)↓	A_2 (2a)↑	A_3 (4f)↓	A_4 (4f)↑	A_5 (4f)↓	A_6 (4f)↑
A_1 (2a)↓	0	0	+12.4	+5.6	+12.4	+5.6
A_2 (2a)↑	0	0	+5.6	+12.4	+5.6	+12.4
A_3 (4f)↓	+12.4	+5.6	0	-24.8	+6.2	0
A_4 (4f)↑	+5.6	+12.4	-24.8	0	0	+6.2
A_5 (4f)↓	+12.4	+5.6	+6.2	0	0	-24.8
A_6 (4f)↑	+5.6	+12.4	0	+6.2	-24.8	0

Table 3 Exchange interactions between sublattices in the $\text{Co}_3\text{B}_2\text{O}_6$ crystal.

$z_{ij}J_{ij}$ (K)	A_1 (2a)↑	A_2 (2a)↓	A_3 (4f)↓	A_4 (4f)↑	A_5 (4f)↓	A_6 (4f)↑
A_1 (2a)↑	0	0	-5.5	+3.3	-5.5	+3.3
A_2 (2a)↓	0	0	+3.3	-5.5	+3.3	-5.5
A_3 (4f)↓	-5.5	+3.3	0	-14.2	+3.6	0
A_4 (4f)↑	+3.3	-5.5	-14.2	0	0	+3.6
A_5 (4f)↓	-5.5	+3.3	+3.6	0	0	-14.2
A_6 (4f)↑	+3.3	-5.5	0	+3.6	-14.2	0

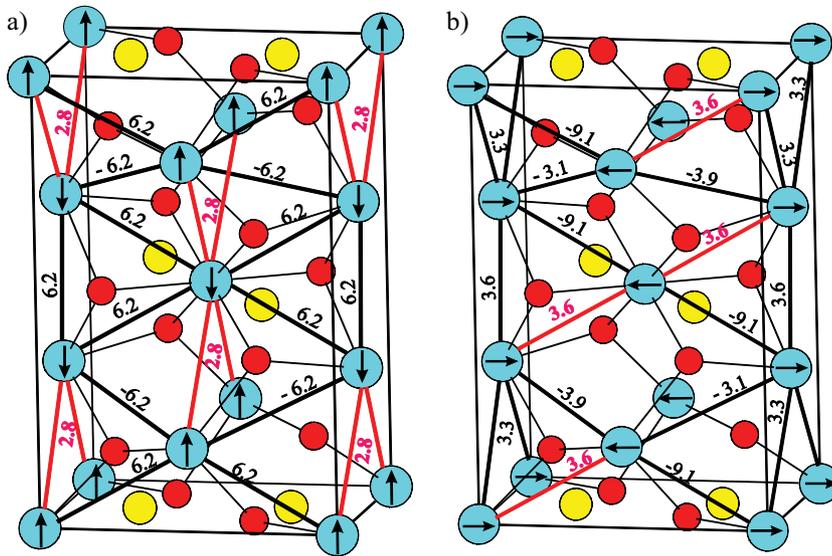


Figure 5 (online color at: www.pss-b.com) Possible magnetic structure of (a) $\text{Ni}_3\text{B}_2\text{O}_6$ and (b) $\text{Co}_3\text{B}_2\text{O}_6$. Arrows indicate the direction of the magnetic moments. The calculated exchange integrals between magnetic ions are shown in bold, frustrating (disordering) interactions are shown in red.

directions, by J_{12}^{14} . The magnetic cell, in this case, coincides with that obtained experimentally [5, 6].

When choosing the magnetic cell coinciding with the crystallographic cell in $\text{Co}_3\text{B}_2\text{O}_6$, we do not take into account that the exchange integrals depend on the direction of the indirect coupling, since, at such a choice, due to summation over the nearest neighbors, these interactions are averaged. As the magnetic exchange interactions in the $\text{Co}_3\text{B}_2\text{O}_6$ compound depend on the coupling direction (Fig. 5b), six magnetic sublattices are apparently insufficient for a correct description of the magnetic structure. Adequate choices of the magnetic cell and construction of the magnetic structure of $\text{Co}_3\text{B}_2\text{O}_6$ appear rather difficult,

because, except for magnetic exchange interaction J_{12}^{95} , all the others are comparable in value and, due to the features of the crystal structure, the magnetic moments cannot be oriented such that no competing exchange interactions would occur.

7 Discussion of the results The measurements of temperature and field dependences of magnetization of the $\text{Ni}_3\text{B}_2\text{O}_6$ and $\text{Co}_3\text{B}_2\text{O}_6$ crystals showed that, unlike $\text{Ni}_3\text{B}_2\text{O}_6$, $\text{Co}_3\text{B}_2\text{O}_6$ exhibits strong anisotropy of the magnetic properties depending on the crystallographic direction. In addition, the directions of the easy magnetization axis are different: in $\text{Ni}_3\text{B}_2\text{O}_6$ it coincides with the a -axis, while in $\text{Co}_3\text{B}_2\text{O}_6$, with the c -axis. Also, there is a minor feature on the magnetization curves of the $\text{Co}_3\text{B}_2\text{O}_6$ crystal at 10 K, which was not observed previously [5]. We attribute this anomaly to the spin-reorientation phase; however, to verify our hypothesis, further investigations of specific heat and the magnetic structure of the $\text{Co}_3\text{B}_2\text{O}_6$ crystal are required.

According to the results of our calculation, the strongest exchange interactions in $\text{Co}_3\text{B}_2\text{O}_6$, *i.e.*, J_{y12}^{95} , occur in the ac plane (Fig. 5b). Since these interactions are ferromagnetic, in the chains of the triangular groups (Fig. 1) exchange interactions J_{x12}^{95} and J_{22}^{88} compete with one another and, as they have the same value, orientation of the magnetic moments will be affected also by the other exchange interactions. The hypothesis on the competition of exchange interactions J_{x12}^{95} and J_{22}^{88} can be confirmed by the value of the paramagnetic Curie temperature in the c direction that is very close to zero. Since in $\text{Co}_3\text{B}_2\text{O}_6$ all the exchange interactions, except for one, are nearly identical, we may suggest that the magnetic structure is determined by the fine balance between these interactions and, with decreasing temperature, the Co–O–B–O–Co indirect exchange interactions may be important. Consequently, a spin-reorientation phase transition at 10 K may occur.

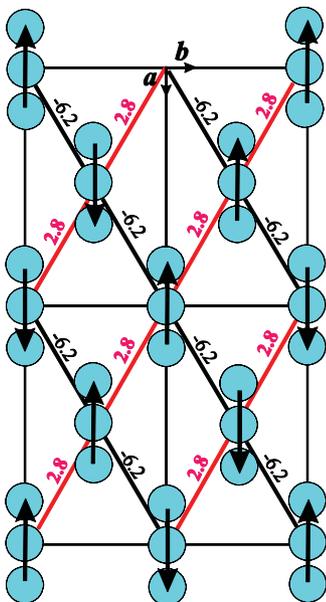


Figure 6 (online color at: www.pss-b.com) Magnetic cell of $\text{Ni}_3\text{B}_2\text{O}_6$. Arrows indicate the magnetic moments in the chains.

To establish the magnetic structure and mechanisms of the phase transition, additional experimental magnetic studies at different temperatures and investigations of specific heat are required.

8 Conclusions For the first time, we grew $\text{Me}_3\text{B}_2\text{O}_6$ ($\text{Me} = \text{Co}, \text{Ni}$) crystals with the kotoite structure by the melt-solution method upon spontaneous nucleation. We measured the field and temperature dependences of magnetization of the samples obtained in the magnetic field oriented along the a , b , and c crystallographic axes. We observed an anomaly on the magnetization curves of $\text{Co}_3\text{B}_2\text{O}_6$ at $T = 10 \text{ K}$ and attributed it to the possible spin-reorientation transition.

The calculation of the exchange interactions within a simple indirect coupling model shows that in both compounds there is the competition between the ferromagnetic and antiferromagnetic exchange interactions. In the $\text{Co}_3\text{B}_2\text{O}_6$ crystal, strong anisotropy of the magnetic properties is observed. However, the available experimental and theoretical data are still insufficient to establish the magnetic structure of the compounds under study and to describe all the features, in particular, the strong anisotropy in the paramagnetic phase and the magnetization growth below 5 K. Clarification of the magnetic structure and mechanisms of the phase transitions in these compounds requires additional neutron studies.

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