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Effect of uncontrolled impurities on the magnetic state of ferroborates $GdFe_3(BO_3)_4$

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A comparative analysis of magnetic properties of gadolinium ferroborates $GdFe_3(BO_3)_4$ grown from three different solvents: lithium tungstate [$GdFe_3(BO_3)_4$], trimolybdate-bismuth [$GdFe_3(BO_3)_4$:Bi] and potassium-molybdate [$GdFe_3(BO_3)_4$:Mo] melt solutions has been carried out. Phase diagrams of the magnetic state „temperature — magnetic field" of the investigated crystals have been constructed. It is shown that $GdFe_3(BO_3)_4$ does not contain uncontrolled impurities, whereas for $GdFe_3(BO_3)_4$:Bi the incorporation of uncontrolled Bi^{3+} impurities in small amounts (~ 6 at.%) is confirmed. For $GdFe_3(BO_3)_4$:Mo, it was assumed that both Mo ions (of valence higher than 3+) and potassium ions K^+ are present as uncontrolled impurities.

Keywords: antiferromagnetics, multiferroics, spin reorientation transition.

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1. Introduction

In recent years, rare earth ferroborates with the general formula $RFe_3(BO_3)_4$ ($R =$ Y, La-Lu) have attracted increased attention due to their unique physical properties. These compounds have a rhombohedral structure similar to the natural mineral huntite, described by space group R32 or $P3_121$. The noncentrosymmetric structure makes these materials promising candidates for optical applications due to their good luminescence and nonlinear optical properties. For $RFe_3(BO_3)_4$ ferroborates it has been established that they belong to a new class of multiferroics, where magnetic, electrical, and elastic order parameters coexist [1–7].

Magnetically, ferroborates are antiferromagnetic materials with two interacting magnetic subsystems (rare earth and iron subsystems). The iron subsystem is ordered at $T_N = 30-40$ K. The rare-earth subsystem is magnetized by the f-d interaction and essentially contributes to the magnetic anisotropy and orientation of magnetic moments.

Initially, for isostructural nonlinear optical crystals of $RFe_3(BO_3)_4$ trigonal ferroborates, a technique was developed to grow them from melt solutions based on $K_2Mo_3O_{10}-B_2O_3$ potassium trimolybdate [8]. Later, for growing single crystals of $RAl_3(BO_3)_4$ and $RFe_3(BO_3)_4$ new melt solutions based on $Bi_2Mo_3O_{12}-B_2O_3$ bismuth trimolybdate were proposed [9]. In these melt solutions, Bi_2O_3 and MoO_3 are bound stronger than K_2O_3 and MoO_3. Therefore, the substitution of bismuth and molybdenum in the grown crystal for the rare-earth element was assumed to be relatively weak [10]. However, as it was shown in [11] by chemical analysis and structural studies for the $GdFe_3(BO_3)_4$ ferroborate, Bi^{3+} ions replace the rare-earth ion in an amount up to 5% at., which is nevertheless smaller as compared to the introduction of potassium and molybdenum [10]. Later this fact was confirmed using magnetic studies [12]. In connection with the above, the lithium tungstate-based melt-solutions were proposed. It was assumed that in the latter case, ions from the solvent do not enter the crystal matrix.

This study is devoted to investigation of the effect of uncontrolled impurities on the magnetic properties of $GdFe_3(BO_3)_4$ ferroborates grown from three different solution-melts: based on $K_2Mo_3O_{10}-B_2O_3$ potassium trimolybdate, $Bi_2Mo_3O_{12}-B_2O_3$ bismuth trimolybdate, and Li_2WO_4- B_2O_3 lithium tungstate.

2. Preparation of samples and measurement procedure

Crystals of the $GdFe_3(BO_3)_4$ gadolinium ferroborate were grown from three solution-melt systems: based on $K_2Mo_3O_{10}-B_2O_3$ potassium trimolybdate described in detail in [8], based on $Bi_2Mo_3O_{12}-B_2O_3$ bismuth trimolybdate [9], and based on $Li_2WO_4-B_2O_3$ lithium tungstate [12].

The magnetic study was carried out on a PPMS Quantum Design (research equipment sharing center of the Federal Research Center of KSC SB RAS) in the temperature range of 4.2–300 K and magnetic fields of up to 90 kOe.

3. Results and discussion

Due to the fact that in [11,12] it was shown that with the use of bismuth trimolybdate as a solvent the Bi^{3+} ions are present in the crystal as an impurity (replacing the Gd^{3+} ions), so in the following text crystals grown

Magnetic parameters of the crystals

	T_N (K)	$\theta \parallel$ (K)	$\theta \perp$ (K)	μ_{eff} (μ_B)
$GdFe_3(BO_3)4$	37.2	−44.5	−43.8	12.96
$GdFe_3(BO_3)_4$: Bi	36.4	−43.9	−43.2	12.81
$GdFe_3(BO_3)_4$: Mo	36.6	−43.9	−42.7	12.66

from this solution-melt are denoted as $GdFe_3(BO_3)_4$: Bi, whereas crystals grown from the solution-melt based on lithium tungstate are denoted as $GdFe_3(BO_3)_4$, because it is assumed that with this sort of solvent there must not be uncontrolled impurities. As for the crystals of $GdFe_3(BO_3)_4$ grown from a solvent based on potassium trimolybdate, in [10] it was shown by spectroscopic methods that Mo^{3+} molybdenum ions replace Fe^{3+} iron ions. Therefore, crystals grown from this solvent in the following text are denoted as $GdFe_3(BO_3)_4$: Mo.

Basically, the magnetic properties were studied only on the ferroborate grown on the basis of $GdFe_3(BO_3)_4$: Bi bismuth trimolybdate [13–15]. Unfortunately, determining the magnetic structure in holmium ferroborate by neutron diffraction methods is difficult due to the strong absorption of neutrons by Gd^{3+} ions. Therefore, there are discrepant data in the literature regarding the magnetic structure of gadolinium ferroborate.

To date, the most plausible is the magnetic behavior described in [15]. It was shown on the basis of antiferromagnetic resonance investigation, that the magnetic phase transformation of the Fe^{3+} ions subsystem occurring at the Neel point T_N corresponds to the two-sublattice spin ordering of easy plane type. With a decrease in temperature below T_S, under the effect of interaction between iron and gadolinium subsystems a spin-flip transition from the easy-plane state to the easy-axis state takes place.

Magnetic studies of all three samples qualitatively confirm this model. The temperature dependences of $M_{\parallel}$ and $M_{\perp}$ magnetizations were measured in a magnetic field of 1 kOe directed along the crystallographic *c*-axis (the third order axis) and in the basal plane along the *a*-axis (the second-order axis), respectively.

Figure 1 shows such magnetization dependences. It can be seen from the figure that with a decrease in temperature in the region of 37K̇ (see the table) a peak is observed for all compounds, indicating the antiferromagnetic ordering. The sharp knick in the magnetization curves in the region of 10 K indicates a spin-flip transition of the „easy plane“-„easy axis“ type. It can be seen from the graphs in the insets that the presence of an impurity results in a decrease in the transition temperature.

It is important to note two factors here. First, for the direction of **H** $\parallel$ **c**, both the Bi^{3+} and Mo^{3+} impurities leads to approximately the same result (Figure 1, *a*) — decrease in the temperature of the spin-flip transition by approximately 2 K. Whereas for the direction of **H**$\perp$ the Bi^{3+} ions have a stronger effect on the transition temperature than the Mo^{3+} ions (Figure 1, *b*). Second, it is clearly seen that the temperature range of the spin-flip transition for the $GdFe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$: Bi is comparatively small, whereas the same interval for the $GdFe_3(BO_3)_4$: Mo is more diffuse in temperature, which is especially clearly visible in the insert to Figure 1, *b*.

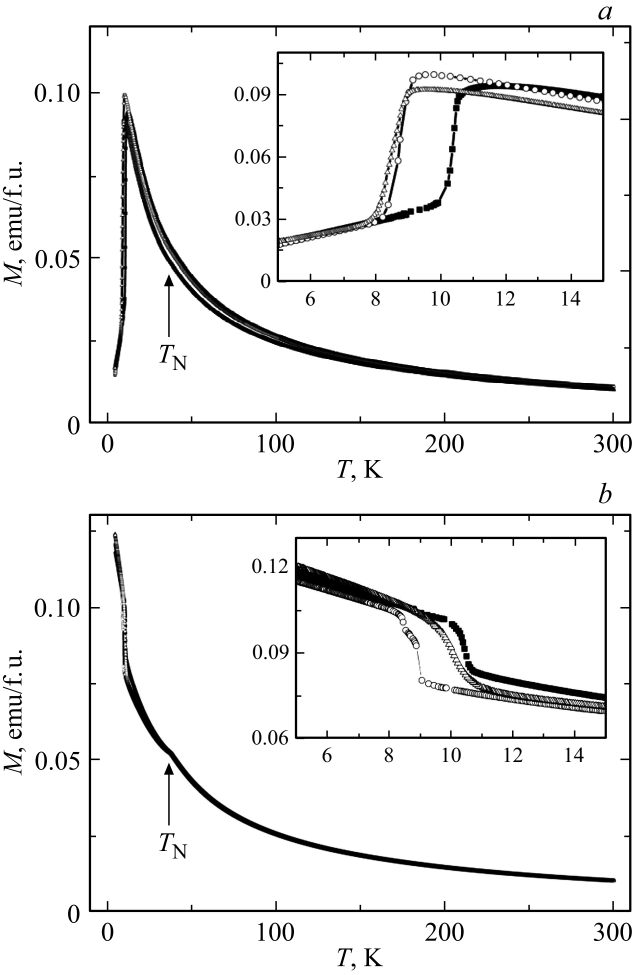

Figure 1. Temperature dependences of magnetization of $GdFe_3(BO_3)_4$ (squares), $GdFe_3(BO_3)_4$: Bi (circles) and $GdFe_3(BO_3)_4$: Mo (triangles) measured in a magnetic field of 1 kOe and in the geometry of **H** $\parallel$ **c** (*a*) and **H** $\perp$ **c** (*b*). The inserts show the same dependencies in a different scale.

The review of the temperature dependences of magnetization recorded at different magnetic field strengths shows that the temperature of the spin-flip transition shifts to the region of low temperatures with increasing magnetic field. As an example, Figure 2 shows this for the $GdFe_3(BO_3)_4$ compound. The behavior of other compounds is not qualitatively different.

In the paramagnetic region, the magnetization of both compounds is isotropic and obeys the Curie–Weiss law. The experimentally found paramagnetic Curie temperatures differ slightly and are also presented in the table. The negative sign of the paramagnetic Curie temperature θ indicates the

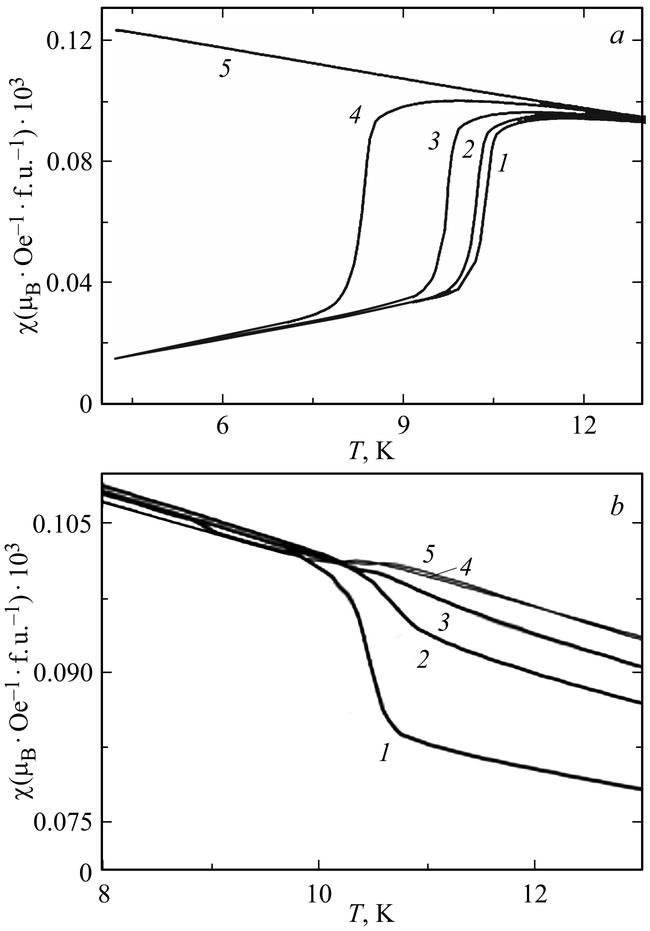

Figure 2. Temperature dependences of magnetization of $GdFe_3(BO_3)_4$ measured in different magnetic fields: *1* — 1 kOe, *2* — 2 kOe, *3* — 3 kOe, *4* — 5 kOe, *5* — 10 kOe.

presence of antiferromagnetic exchange interaction in the magnetic system, which is typical for all ferroborates with the huntite structure. It can be seen that θ has the lowest value (in absolute terms) for the $GdFe_3(BO_3)_4$:Mo. The value for the $GdFe_3(BO_3)_4$:Bi is not much higher, and the highest value is for the $GdFe_3(BO_3)_4$. From this it can be conclude that non-magnetic impurities are present in the first two crystal structures.

The effective magnetic moment of one structural unit was calculated for all compounds and presented in the table. It can be seen that the experimental value for the $GdFe_3(BO_3)_4$ turned out to be equal to $\mu_{\text{eff}} = 12.96\,\mu_B$, which is exactly equal to the theoretical value of μ_{eff} defined as:

$$\mu_{\text{eff}} = \sqrt{3 \cdot g_S^2 \cdot \langle S_{\text{Fe}} \rangle^2 \cdot \mu_B^2 + g_J^2 \cdot \langle J_{\text{Gd}} \rangle^2 \cdot \mu_B^2}, \qquad (1)$$

where $g_S = 2$ is g-factor taking into account only the spin magnetic moment, $g_J = 2$ is Lande factor for the Gd^{3+} ion, $\langle S_{\text{Fe}} \rangle^2 = S \cdot (S + 1)$ is square of the iron ion spin moment operator ($S = 5/2$ for Fe^{3+}), $\langle S_{\text{Gd}} \rangle^2 = J \cdot (J + 1)$ is square of the total moment operator of the gadolinium ion ($J = 7/2$ for Gd^{3+}).

Based on the data presented above, it is hard to escape a conclusion that the gadolinium ferroborate grown from a lithium tungsten solvent does not contain impurities.

The gadolinium ferroborate grown from a bismuth-molybdate solvent has an effective magnetic moment of one structural unit equal to $\mu_{\text{eff}} = 12.81\,\mu_B$, which is slightly less than the theoretically found value of μ_{eff}. Assuming that Gd^{3+} ions are replaced by Bi^{3+} ions and using the difference in values of μ_{eff} for $GdFe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$:Bi, the impurity of Bi^{3+} can be estimated. In our case it appears that in $GdFe_3(BO_3)_4$:Bi there are Bi^{3+} ions in an amount of 6% at.

As for the gadolinium ferroborate grown from a potassium-molybdate solvent, the situation is not so unambiguous. If the result of [10] is used, where it was shown by spectroscopic methods that Mo^{3+} molybdenum ions replace Fe^{3+} iron ions, then in the case of the experimentally observed effective moment $\mu_{\text{eff}} = 12.66\,\mu_B$ an assumption should be made that Mo^{3+} molybdenum ions replace

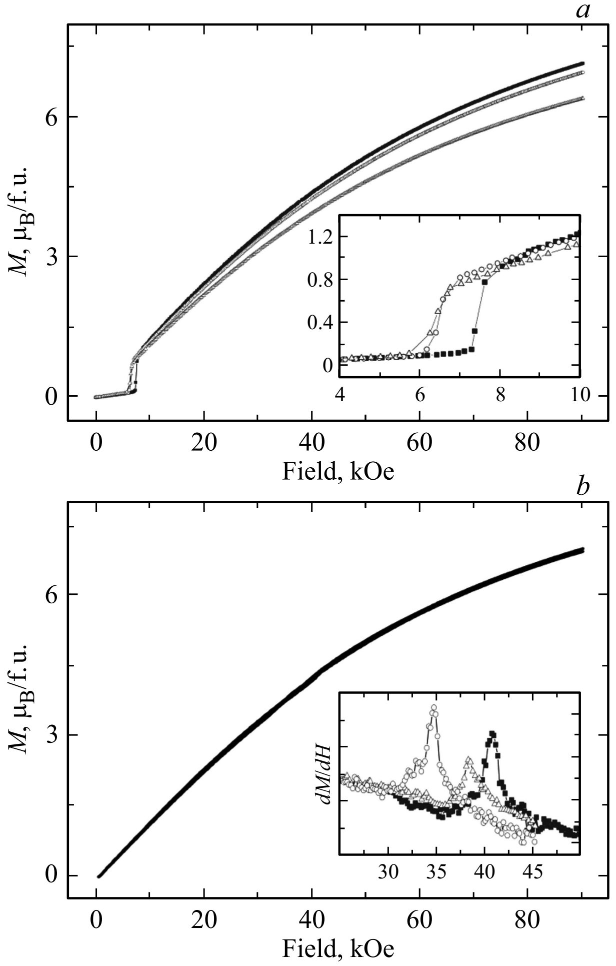

Figure 3. Field dependences of magnetization of $GdFe_3(BO_3)_4$ (squares), $GdFe_3(BO_3)_4$:Bi (circles), and $GdFe_3(BO_3)_4$:Mo (triangles) measured at a temperature of 4.2 K and in the geometry of $\mathbf{H} \parallel \mathbf{c}$ (*a*) and $\mathbf{H} \perp \mathbf{c}$ (*b*). The inserts show the same dependencies in a different scale.

iron ions in the amount of 2 at.% (provided that the spin mechanical moment of the Mo^{3+} ions is equal to $3/2$ and g-factor is $g_S = 2$). This result looks rather controversial, because, for example, the Curie temperature T_N and the paramagnetic Curie temperature θ are not very different for all compounds. Therefore, it can be assumed that the subsystem of iron ions, which is responsible for the establishment of long-range magnetic order, does not undergo a significant change. It is important to note that in [10] there is no any analysis of the incorporation of K^{1+} potassium ions into the crystal matrix. In this context, it can be assumed that the growth of the gadolinium ferroborates from a potassium-molybdate solvent leads to the inclusion of impurities of molybdenum ions instead of iron ions and potassium ions instead of gadolinium ions. At the same time, in order to maintain electrical neutrality, we must allow the presence of molybdenum ions with a valency greater than 3+. Unfortunately, it is not possible to determine the quantitative and qualitative composition of the impurity from magnetic measurements for $GdFe_3(BO_3)_4$:Mo due to the large variability of possible combinations. The only statement that can be made is that the quality of these compounds is not very high, which is clearly visible, for example, in a relatively wide temperature range of the spin-flip transition (Figure 1).

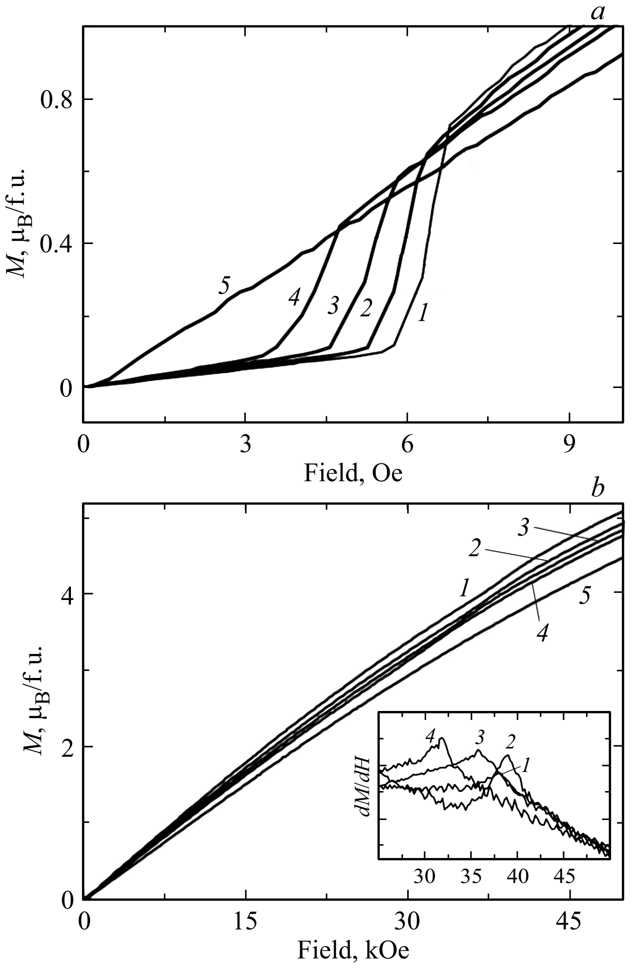

Figure 4. Field dependences of magnetization of the $GdFe_3(BO_3)_4$:Mo recorded at different temperatures: *1* — 4.2 K, *2* — 5 K, *3* — 6 K, *4* — 7 K, *5* — 10 K in the geometries of $\mathbf{H} \parallel \mathbf{c}$ (*a*) and $\mathbf{H} \perp \mathbf{c}$ (*b*). The insert to the figure *b* shows the derivative of magnetization.

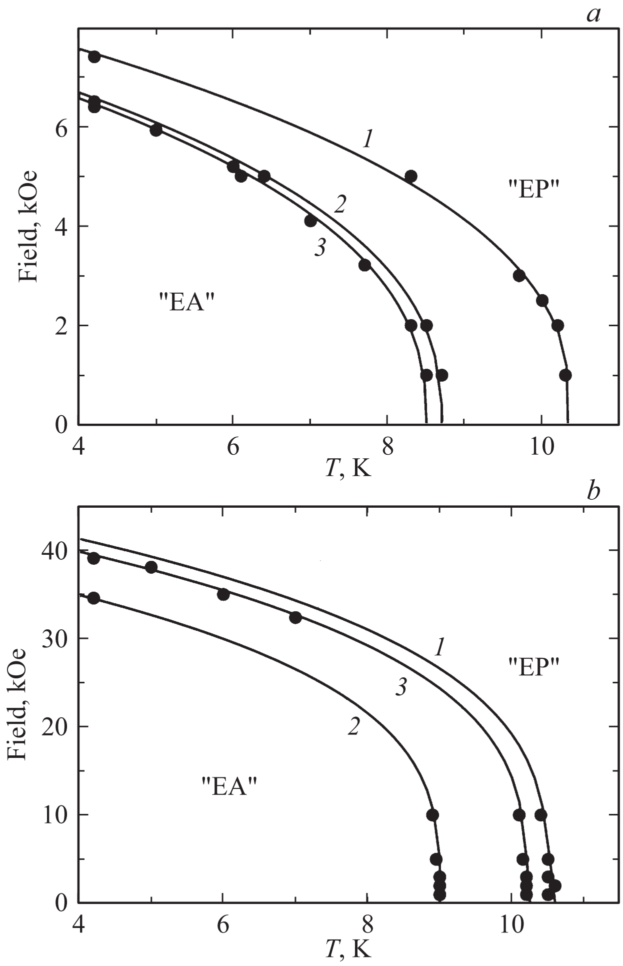

Figure 5. Phase diagram of the magnetic state of the gadolinium ferroborates *1* — $GdFe_3(BO_3)_4$, *2* — $GdFe_3(BO_3)_4$:Bi, *3* — $GdFe_3(BO_3)_4$:Mo in the geometry of $\mathbf{H} \parallel \mathbf{c}$ (*a*) and $\mathbf{H} \perp \mathbf{c}$ (*b*). EA — region of „easy axis“ type state, EP — region of „easy plane“ type state.

Figure 3 shows the field dependences of magnetization at $T = 4.2$ K. The spin-flip transition is observed for both magnetic field directions: $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \parallel \mathbf{c}$. And it can also be noted that the $GdFe_3(BO_3)_4$ compound has the greatest value, whereas the presence of an impurity results in a shift of the transition to the region of low fields.

With increasing temperature, the spin-flip transition in the field dependences for all compounds is shifted to the region of lower temperatures and at temperatures above ~ 10 K it is not observed at all. As an example, such dependences are presented for $GdFe_3(BO_3)_4$:Mo in Figure 4.

Using the data of temperature and field dependencies of magnetization, it is possible to plot „temperature magnetic field“ phase diagrams of the magnetic state for all compounds. Such diagrams are presented in Figure 5. The transition temperature was determined from the knick point of the $M(T)$ and $M(H)$ curves.

An explanation of the magnetic behavior of gadolinium ferroborate was given in [15]. It was shown there that the magnetic state is determined by the sign of the uniaxial anisotropy constant, the contribution to which is made by subsystems of iron and gadolinium ions, with different signs.

The behavior of the $\mathrm{GdFe_3(BO_3)_4}$:Bi ferroborate fits into the logic of this model. Thus, the replacement of $\mathrm{Gd^{3+}}$ gadolinium ions with $\mathrm{Bi^{3+}}$ bismuth ions leads to a decrease in the contribution to the rare-earth subsystem, and as a result, to a decrease in the total uniaxial anisotropy constant. This results in a shift of the boundary of existence of the uniaxial state towards lower temperatures and fields.

For the $\mathrm{GdFe_3(BO_3)_4}$:Mo ferroborate the situation should be the opposite (assuming that only $\mathrm{Mo^{3+}}$ ions can be the impurity, which replace the $\mathrm{Fe^{3+}}$ iron ions. If we accept the assumption made earlier about the presence of potassium ions as an impurity along with molybdenum ions, then the shift of the boundary of the existence of a uniaxial (or easy-axis) state towards lower temperatures and fields for the $\mathrm{GdFe_3(BO_3)_4}$:Mo ferroborate seems logical.

4. Conclusion

A comparative analysis was carried out for the magnetic properties of the $\mathrm{GdFe_3(BO_3)_4}$ gadolinium ferroborates grown from three different solvents: tungstate-lithium, trimolybdate-bismuth, and molybdate-potassium solution-melts.

From the magnetic studies it follows that the $\mathrm{GdFe_3(BO_3)_4}$ ferroborate does not contain uncontrolled impurities, and, therefore, is the purest compound. For the $\mathrm{GdFe_3(BO_3)_4}$:Bi, the presence of uncontrolled impurities of $\mathrm{Bi^{3+}}$ in small quantities is confirmed, ~ 6 at%. For the $\mathrm{GdFe_3(BO_3)_4}$:Mo the situation looks the most complicated. It has been suggested that both Mo ions (with a valence greater than 3+) and $\mathrm{K^+}$ potassium ions are present as an uncontrolled impurity. At the same time, it is not possible to determine the quantitative and qualitative composition of the impurity due to the large variability of possible combinations.

„Temperature — magnetic field“ phase diagrams of the magnetic state for the crystals under study are plotted. It is shown that the behavior of the $\mathrm{GdFe_3(BO_3)_4}$:Bi is explained within the framework of a simple model that takes into account antiferromagnetic interactions within the iron subsystem and between the iron and gadolinium subsystems. The behavior of the $\mathrm{GdFe_3(BO_3)_4}$:Mo ferroborate within the same model can be explained only by assuming the presence of uncontrolled impurities of both molybdenum ions and potassium ions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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