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High-Resolution Spectroscopy of $\text{HoFe}_3(\text{BO}_3)_4$ Crystal: a Study of Phase Transitions

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Abstract—The transmission spectra of $\text{HoFe}_3(\text{BO}_3)_4$ multiferroic single crystals are studied by optical Fourier-transform spectroscopy at temperatures of 1.7–423 K in polarized light in the spectral range 500–10 000 cm^{-1} with a resolution up to 0.1 cm^{-1} . A new first-order structural phase transition close to the second-order transition is recorded at $T_c = 360$ K by the appearance of a new phonon mode at 976 cm^{-1} . The reasons for considerable differences in T_c for different samples of holmium ferroboration are discussed. By temperature variations in the spectra of the f – f transitions in the Ho^{3+} ion, we studied two magnetic phase transitions, namely, magnetic ordering into an easy-plane structure as a second-order phase transition at $T_N = 39$ K and spin reorientation from the ab plane to the c axis as a first-order phase transition at $T_{SR} = 4.7 \pm 0.2$ K. It is shown that erbium impurity in a concentration of 1 at % decreases the spin-reorientation transition temperature to $T_{SR} = 4.0$ K.

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INTRODUCTION

Complex study of magnetic, magnetoelectric, and magnetoelastic properties of holmium ferroboration $\text{HoFe}_3(\text{BO}_3)_4$ [1] made it possible to assign this compound to multiferroics, to which also many other rare-earth (RE) ferroboration $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Y}, \text{La}, \text{Pr} - \text{Er}$) belong. Multiferroics are defined as materials in which at least two of several order parameters (electric, magnetic, elastic, etc.) coexist. The interaction between different subsystems makes it possible to control, for example, the magnetic properties of multiferroics using an electric field and vice versa, which is of interest for applications. RE ferroboration exhibit a variety of magnetic, magnetoelectric, magnetodielectric, and structural properties depending on the R element in the $R\text{Fe}_3(\text{BO}_3)_4$ formula. It is obvious that, to explain these properties, it is important to know the electronic structure of the RE ion in the ferroboration crystal field and, first of all, the structure of the ground state. In our previous studies, we determined by spectroscopic data the energies of the Stark levels of RE ions and used them to find the physically justified sets of crystal field parameters for neodymium [2], praseodymium [3], samarium [4], and terbium [5] ferroboration, which provided the complete information on the RE subsystem and was already used in works [6, 7] to develop the quantum theory of magnetoelectric phenomena. The first three mentioned compounds have no structural transition, which facilitates the

interpretation of optical spectra. Terbium ferroboration undergoes a structural phase transition, but its spectrum is rather simple. Holmium ferroboration, which is the object of this study, is characterized by three phase transitions and a very rich and complex spectrum. Therefore, it seems reasonable to perform stepwise investigations of its spectroscopic properties. In this work, we present for the first time the high-resolution spectra in the region of f – f transitions in the $\text{HoFe}_3(\text{BO}_3)_4$ crystal and study their changes upon phase transitions. These investigations, in combination with the study of the infrared (IR) vibrational absorption spectra, made it possible to perform a comprehensive spectroscopic study of phase transitions in $\text{HoFe}_3(\text{BO}_3)_4$.

STRUCTURE AND PROPERTIES OF HOLMIUM FERROBORATE

RE ferroboration crystallize in the trigonal syngony (space group $R32$), and their properties are to a large extent determined by the RE ion. A characteristic feature of the crystal structure of $R\text{Fe}_3(\text{BO}_3)_4$ compounds is the existence of mutually independent spiral chains of plane-sharing FeO_6 octahedra, which are oriented along the c axis. The $R\text{Fe}_3(\text{BO}_3)_4$ ferroboration in which the radius of the R^{3+} ion is smaller than the Sm^{3+} ion radius undergo a structural phase transition at temperatures T_c from 88 ($R = \text{Eu}$) to ~ 445 K ($R = \text{Y}$) [8].

The X-ray diffraction analysis of the low-temperature $\text{GdFe}_3(\text{BO}_3)_4$ phase showed that it is characterized by the trigonal space group $P3_121$ [9]. For iron atoms, there appear two nonequivalent sites (Fe(2) with the point symmetry group C_2 (as at $T > T_c$) and Fe(1) with the symmetry C_1), while the site symmetry for holmium ions decreases from D_3 to C_2 [9]. Subsequent comparative study [10] of the Raman scattering spectra of $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Gd}, \text{Tb}, \text{Er}, \text{Y}$) allowed the authors to conclude that all these compounds undergo the structural phase transition $R32 \rightarrow P3_121$ [10]. The study of Raman spectra of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals [11, 12] showed that the $R32 \rightarrow P3_121$ structural phase transition takes place in this compound as well. Temperature of this transition $T_c \approx 366$ K was determined from the temperature dependence of the frequency of the quasi-soft mode, which, as well as in other ferroborates with a phase structural transition [10, 13], appears at temperatures below T_c . This value of T_c significantly differs from $T_c = 427$ K determined in [8] from the measured thermal conductivity of holmium ferroborate powder samples fabricated by solid-phase synthesis. The authors of [11] note that the reason for this distinction is not clear. In study [14] on the IR absorption spectra of powdered $\text{HoFe}_3(\text{BO}_3)_4$ single crystals pressed into pellets together with KBr [14], the appearance was reported of a new 976-cm^{-1} phonon mode at a temperature below 355 K, but the T_c value is not given. One of the aims of the present work is to determine the structural phase transition temperature in the $\text{HoFe}_3(\text{BO}_3)_4$ single crystal by another spectroscopic method.

In the temperature range from 22 (for $R = \text{La}$) to 40 K (for $R = \text{Er}$), the three-dimensional antiferromagnetic ordering of the Fe-subsystem of ferroborates occurs [8, 15]. This magnetizes the RE subsystem due to the f - d interaction. Depending on the single-ion anisotropy of the R^{3+} ion, the magnetic moments of iron are either oriented along the crystallographic axis c or lie in the ab plane of the crystal [16]. Antiferromagnetic ordering of holmium ferroborate into the easy-plane magnetic structure occurs at $T_N \approx 39$ K [15, 17, 18]. According to [15, 18], further decrease in temperature to ~ 5 K leads to reorientation of the iron magnetic moments from the ab plane to the c axis, i.e., to the first-order spin-reorientation phase transition. Note that a spin-reorientation transition was also observed in one more RE ferroborate, namely, in $\text{GdFe}_3(\text{BO}_3)_4$ at $T_{SR} = 9$ K [13, 19].

Study of the magnetoelectric properties of holmium ferroborate [1, 20] showed that the electric polarization reaches significant values, in particular, 200 ($\mathbf{H} \parallel a$)–300 ($\mathbf{H} \parallel b$) $\mu\text{C}/\text{m}^2$ in magnetic fields stronger than 100 kOe [1], which, nevertheless, is noticeably lower than in neodymium (400 $\mu\text{C}/\text{m}^2$ [21]) and samarium (500 $\mu\text{C}/\text{m}^2$ [22]) ferroborates. This points to a dependence of magnetoelectric effects

on the electronic structure of the RE ion [1]. It is interesting that holmium alumoborate $\text{HoAl}_3(\text{BO}_3)_4$, which is isostructural with holmium ferroborate but has no magnetic ordering at least to a temperature of 1.7 K, exhibits a record-high (for multiferroics) electric polarization of ~ 3600 $\mu\text{C}/\text{m}^2$ at a temperature of 5 K in a field of 70 kOe [23].

The spontaneous polarization of holmium and samarium ferroborates is an order of magnitude higher than that of the other ferroborates—namely, 60–90 $\mu\text{C}/\text{m}^2$ depending on the direction in the crystal [20, 24]. In contrast to $\text{SmFe}_3(\text{BO}_3)_4$, in which the spontaneous polarization is recorded beginning from the magnetic phase transition temperature, the spontaneous polarization in $\text{HoFe}_3(\text{BO}_3)_4$ appears at the considerably lower temperature $T \approx 25$ K [20, 24].

Holmium ferroborate exhibits a giant spontaneous magnetodielectric effect in the temperature range $T_{SR} < T < T_N$ [20]. While the maximum change in dielectric constant ϵ_a at temperatures below T_N (with respect to the permittivity at T_N) is $\sim 0.7\%$ for $\text{GdFe}_3(\text{BO}_3)_4$ [10, 25] and 2.5% for $\text{TbFe}_3(\text{BO}_3)_4$ [26], this value for $\text{HoFe}_3(\text{BO}_3)_4$ is almost 100% [20]. Thus, the spin–lattice interaction in holmium ferroborate is two orders of magnitude stronger than in gadolinium and terbium ferroborates.

EXPERIMENTAL METHODS

$\text{HoFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) single crystals were grown by the solution–melt method described in [27]. The grown single crystals with dimensions of about $3 \times 3 \times 1$ mm³ had a good optical quality, a green color typical for ferroborates, and natural facets. From these crystals, oriented plates were cut, ground to a thickness of 0.1 mm, and polished. The crystals were oriented by the habit and by the polarization method. The transmission spectra of oriented $\text{HoFe}_3(\text{BO}_3)_4$ single crystals were recorded on a Bruker IFS 125HR high-resolution Fourier-transform spectrometer in the spectral range of 500–10 000 cm^{-1} with a spectral resolution up to 0.1 cm^{-1} . The measurements were performed in unpolarized light on plates with a normal parallel to the c axis ($\mathbf{k} \parallel c$, $\mathbf{E}, \mathbf{H} \perp c$ (α polarization)) and in linearly polarized light on samples with a plane containing the c axis ($\mathbf{k} \perp c$) in two possible configurations: $\mathbf{E} \parallel c$ (π polarization) and $\mathbf{E} \perp c$ (σ -polarization). The sample was placed into a Cryomech ST403 closed-cycle cryostat at temperatures from 4 to 300 K or in a helium-filled optical cryostat with helium vapor evacuation at temperatures down to 1.7 K. For measurements in the temperature range of 300–423 K, we used a special Bruker 2216e heating attachment. The temperature was stabilized using a Scientific Instruments 9700 temperature controller with an accuracy of ± 0.05 K at temperatures below 70 K and ± 0.1 K at temperatures above 70 K.

Heating of samples to temperatures higher than room temperature was performed in a continuous regime. The transmission spectra of $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) single crystals in the region of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions were recorded at temperatures from 1.7 to 5 K.

RESULTS AND DISCUSSION

1. Structural Phase Transition

Structural changes in crystals are indicated first of all by the temperature behavior of phonon modes. According to the group-theoretical analysis performed in [10], the new phonon mode at 976 cm^{-1} , which appears below T_c in the IR spectra [14], is the E mode corresponding to internal vibrations ν_4 of BO_3 groups. As follows from X-ray diffraction data [9], the largest shifts of atoms upon structural phase transitions are observed just in BO_3 triangles. Figure 1 shows the temperature dependence of this mode intensity. As is seen from Fig. 1, the structural phase transition temperature in the $\text{HoFe}_3(\text{BO}_3)_4$ crystal is $T_c = 360\text{ K}$. The difference in T_c for the solid-phase synthesized powder samples and the single crystals grown by the solution–melt method is obviously caused by the entrance of bismuth and molybdenum from the $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ flux into the crystal [28]. The large radius of the bismuth ion increases the lattice constant, and T_c decreases because, as was experimentally proven, the transition temperature is inversely proportional to lattice constant [8]. This effect should be especially pronounced

for RE ferrobates with small ionic radii, such as $\text{HoFe}_3(\text{BO}_3)_4$.

The character of the temperature dependence in Fig. 1 indicates that the structural transition in $\text{HoFe}_3(\text{BO}_3)_4$ is a first-order phase transition close to the second-order transition [10]. We failed to find a hysteresis in the temperature dependence of the 976-cm^{-1} phonon intensity upon heating and cooling of the sample. This most probably indicates that the hysteresis is small (at least smaller than 0.2 K). For comparison, the hysteresis is 0.35 K for $\text{GdFe}_3(\text{BO}_3)_4$ and 0.2 K for $\text{TbFe}_3(\text{BO}_3)_4$ [10]. It should also be noted that the structural transition in holmium ferrobate is stretched by $\sim 10\text{ K}$ in contrast to gadolinium and terbium ferrobates, in which this stretch is < 0.02 and $\sim 0.2\text{ K}$, respectively. Obviously, these differences are related to the inhomogeneous incorporation of impurities from the flux into the crystals.

The structural phase transition also affects the electronic spectrum of the $f-f$ transitions in the Ho^{3+} ion due to a change of the crystal field, which leads to a shift and/or splitting of Stark levels. In the temperature range $T > T_c$, the Ho^{3+} ion site symmetry is described by the D_3 point group; the crystal field of this symmetry splits the $(2J + 1)$ -fold degenerate $2S+1L_J$ levels of free ions with an even number of electrons (Ho^{3+} , Eu^{3+} , Tb^{3+} , Pr^{3+}) into the Γ_1 and Γ_2 singlets and the Γ_3 doublets. At $T < T_c$, the Ho^{3+} site symmetry decreases to C_2 , and the doublets split. The corresponding splitting of spectral lines at $T_c = 59\text{ K}$ was recorded in the optical spectra of the $\text{EuFe}_3(\text{BO}_3)_4$

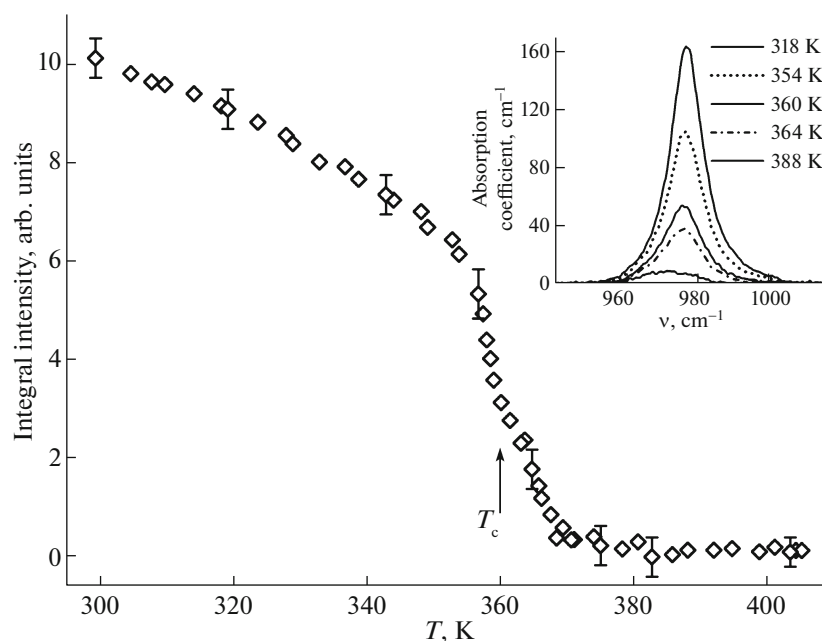


Fig. 1. Temperature dependence of the intensity of the 976 cm^{-1} phonon appearing below structural phase transition temperature T_c . The inset shows this phonon in the π -polarized absorption spectra at different temperatures.

crystal [29]. The structural phase transition in $\text{TbFe}_3(\text{BO}_3)_4$ at $T_c = 192$ K was detected by a shift of the spectral line of the $f-f$ transition [5]. Since temperature T_c for $\text{HoFe}_3(\text{BO}_3)_4$ is higher than room temperature, the spectral lines are strongly broadened and neighboring lines in the extremely rich spectrum overlap with each other. Because of this, although abrupt changes in the positions and intensities of lines in the optical spectrum of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal are indeed observed upon its heating above room temperature, these changes are difficult to interpret unambiguously. Nevertheless, high-resolution optical spectra provide information on low-temperature magnetic phase transitions.

2. High-Resolution Spectra in the Region of $f-f$ Transitions in $\text{HoFe}_3(\text{BO}_3)_4$

Figure 2 shows the α -polarized transmission spectra of the $\text{HoFe}_3(\text{BO}_3)_4$ single crystal at different temperatures $T < T_c$ (i.e., in the $P3_121$ structural phase) in the regions of the $^5I_8 \rightarrow ^5I_{7,6}$ transitions in Ho^{3+} . At decreasing temperature, the spectral lines become narrower. The intensities of lines corresponding to the transitions from the ground state increase with decreasing temperature, while the intensity of lines originating from the excited Stark levels of the ground 5I_8 multiplet decreases (in Fig. 2, these lines are marked by arrows). Above structural phase transition temperature T_c , in the $R32$ structural phase, the Ho^{3+} levels of our interest are split by the crystal field of the D_3 symmetry as follows: $^5I_8 = 3\Gamma_1 + 2\Gamma_2 + 6\Gamma_3$; $^5I_7 = 2\Gamma_1 + 3\Gamma_2 + 5\Gamma_3$; and $^5I_6 = 3\Gamma_1 + 2\Gamma_2 + 4\Gamma_3$. In the low-temperature $P3_121$ phase, degeneration is completely removed and a level with a given J splits into $2J + 1$ Stark sublevels. Thus, the spectrum of the $^5I_8 \rightarrow ^5I_7$ transition at a sufficiently low temperature should contain 15 lines, while the spectrum of the $^5I_8 \rightarrow ^5I_6$ transition should consist of 13 lines. The number of lines observed in Fig. 2 is considerably smaller. We can suggest that, first, the doublets Γ_3 of the high-temperature phase do not strongly split in the low-temperature phase and, second, some levels of different symmetries happen to be close to each other. Indeed, it is seen that some lines have a structure at a low temperature (6 K). Based on these considerations and taking into account the π - and σ -polarized spectra (which differ according to the selection rules [5]), we determined the positions of levels in the 5I_7 and 5I_6 Stark multiplets at $T = 6$ K. These positions are shown by short vertical lines in Fig. 2.

3. Magnetic Ordering and Spin-Reorientation Transition

Antiferromagnetic ordering into the easy-plane magnetic structure in the iron subsystem occurs at

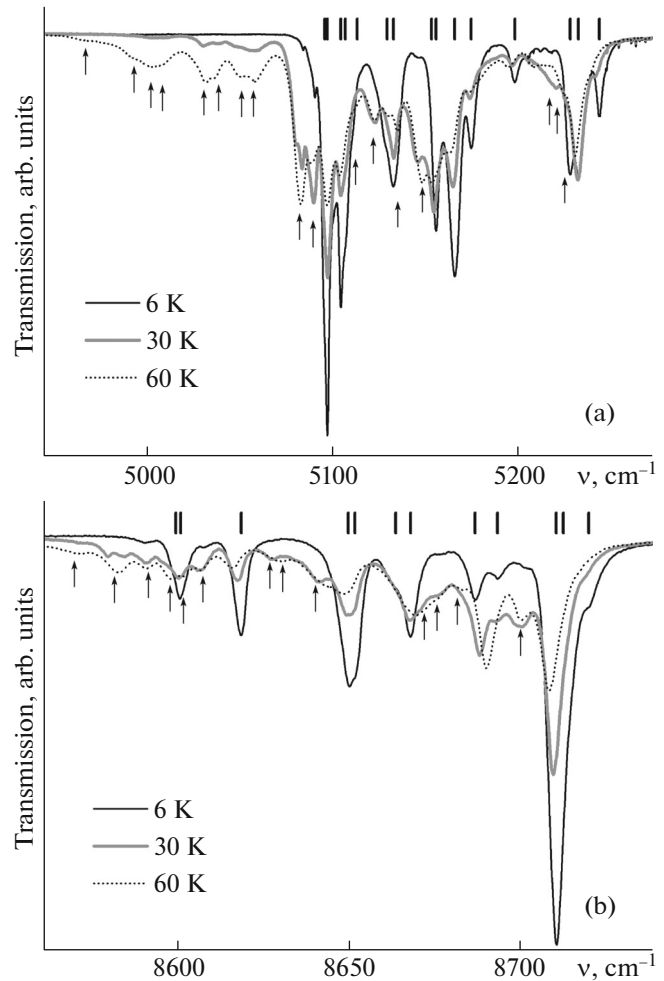


Fig. 2. α -polarized transmission spectra of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal at different temperatures in the regions of the (a) $^5I_8 \rightarrow ^5I_7$ and (b) $^5I_8 \rightarrow ^5I_6$ transitions. ν is the wave number. The short vertical lines show the positions of the spectral lines corresponding to the transitions from the ground level of the Ho^{3+} ion at temperature $T_N > 6$ K $> T_{SR}$. The arrows point to the lines belonging to the transitions from the excited Stark levels of the ground 5I_8 multiplet.

$T_N = 39$ K [17, 18], and the spectral lines of the probe erbium ion in $\text{HoFe}_3(\text{BO}_3)_4$ split due to lifting of the Kramers degeneracy [17]. In the case of the non-Kramers holmium ion in C_2 symmetry site (structural phase $P3_121$, $T < T_c$), the internal magnetic field arising upon magnetic ordering in the crystal splits the occasional quasi-doublets and shifts the singlet levels (Fig. 2). An example of splitting of a quasi-doublet consisting of two close singlet levels Γ_1 and Γ_2 can be the temperature behavior of the line at 8690.7 cm^{-1} (it is the line position at $T = 60$ K, when the doublet splitting is not yet resolved, see Fig. 2b), which is demonstrated in Fig. 3a. As is seen from Fig. 3a, the

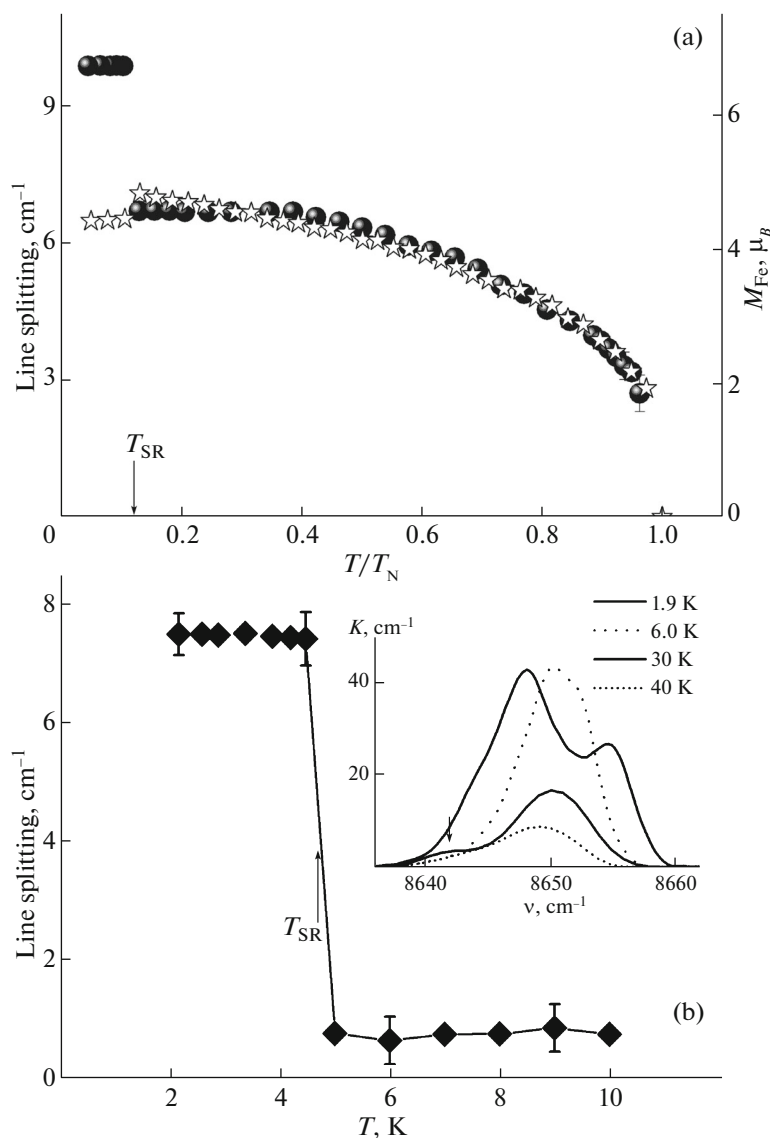


Fig. 3. (a) Temperature dependences of the splitting of quasi-doublets in the $\text{HoFe}_3(\text{BO}_3)_4$ crystal. (a) Splitting of the 8690.7 cm^{-1} line (spheres). For comparison, stars show the temperature dependence of magnetic moments of Fe^{3+} ions according to the neutron data of [18]. The abscissa is normalized temperature T/T_N ($T_N = 38 \text{ K}$ [18]; $T_N = 39 \text{ K}$ according to our data). (b) Splitting of the quasi-doublet at $\sim 8649 \text{ cm}^{-1}$ in the temperature region near the spin-reorientation transition. The inset shows this line at different temperatures. K is the absorption coefficient. The short arrow points to the line corresponding to the transition from the first excited Stark level of the ground 5I_8 multiplet.

distance between the doublet components is approximately proportional to magnetic moment of iron ions M_{Fe} [18]. The ordered magnetic subsystem of iron creates an effective magnetic field proportional to M_{Fe} , which affects Ho^{3+} ions and causes the Zeeman splitting of the quasi-doublet. Previously [5, 16], we observed similar splitting of the ground quasi-doublet of Tb^{3+} ions in $\text{TbFe}_3(\text{BO}_3)_4$. The fact that not all the lines in the transmission spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ split at $T < T_N$ testifies that the ground state of the Ho^{3+} ion in $\text{HoFe}_3(\text{BO}_3)_4$ is singlet.

Further decrease in the $\text{HoFe}_3(\text{BO}_3)_4$ crystal temperature from T_N to T_{SR} leads to an additional first-order magnetic phase transition, at which the magnetic moments of iron ions reorient from the ab plane to the c axis [18]. In a narrow temperature range, one observes an abrupt change in the characteristics of the spectral lines of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal, in particular, a sharp change in the value of splitting of quasi-doublets (Fig. 3). From this, the spin-reorientation transition temperature is determined with a high accuracy as $T_{SR} = 4.7 \pm 0.2 \text{ K}$, which agrees with the data of [18].

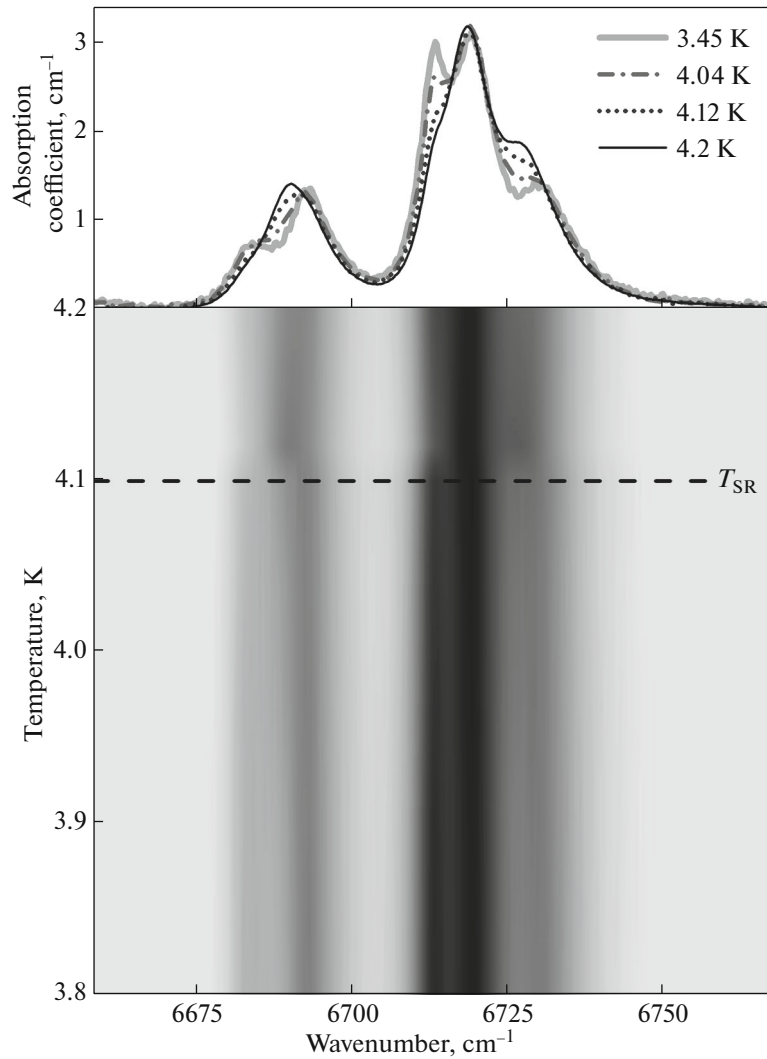


Fig. 4. Absorption spectra of the $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) crystal in the region of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions at several temperatures near T_{SR} and the same dependence in the form of an intensity map in wavenumber–temperature coordinates.

In our previous work [17], we studied the magnetic structure of holmium ferroborate by the method of erbium spectroscopic probe by the splitting of the Kramers doublets of the Er^{3+} ion introduced into the $\text{HoFe}_3(\text{BO}_3)_4$ crystal in the concentration of 1 at %. By measuring the spectra of the $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) crystal at temperatures of 4.2–300 K, we have found that ordering into the easy-plane magnetic structure occurs at a temperature of 39 K, but detected no spin-reorientation transition. To clarify the reason for this state of affairs, in the present work we studied the spectra of the $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) crystal at temperatures below 4.2 K. Figure 4 shows the absorption lines in the high-frequency region of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions at temperatures below 4.2 K. From Fig. 4, one can see a sharp change in the shape of lines in the narrow temperature range from 4.2 to

3.45 K, as well as a superposition of the spectra of the high-temperature and low-temperature magnetic phases in the temperature range $4.0 < T < 4.2$ K. The coexistence of two phases is characteristic for the first-order spin-reorientation transitions [30]. Analysis of the erbium spectrum in $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) ferroborate [16, 17] made it possible to determine the splittings of the ground state of the Er^{3+} ion in the high- and low-temperature magnetic phases (see table). The comparison with the corresponding values for gadolinium ferroborate [16, 17] shows the formation of the easy-axis structure below the temperature $T_{\text{SR}} = 4.0$ K. Thus, the spin-reorientation transition temperature in the $\text{HoFe}_3(\text{BO}_3)_4$ crystal with addition of 1 at % of erbium decreases to $T_{\text{SR}} = 4.0$ K (compared to 4.7 K in the pure crystal). For comparison, the spin-reorientation transition temperature in

Magnetic ordering (T_N) and spin-reorientation transition (T_{SR}) temperatures and values of the ground state exchange splitting (Δ_0) of the Er^{3+} probe ion in $\text{GdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) and in $\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %)

Ferroborate	T , K		Δ_0 , cm^{-1}	
	T_N	T_{SR}	$T > T_{SR}$	$T < T_{SR}$
$\text{GdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %)	37 [16]	7.5 [16]	5.5 [16]	1.9 [16]
$\text{HoFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %)	39 [17]	4.0	5.9 [17]	2.5

$\text{GdFe}_3(\text{BO}_3)_4$ decreases from $T_{SR} = 9$ K in pure crystals [13, 19] to $T_{SR} = 7.5$ K in $\text{GdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at %) [17]. This is caused by the anisotropy of the erbium ion. As is seen from the table, the ground state energy of Er^{3+} in the easy-plane phase of ferroborates is lower than in the easy-axis phase.

CONCLUSIONS

In this work, the high-resolution (up to 0.1 cm^{-1}) spectra of $\text{HoFe}_3(\text{BO}_3)_4$ multiferroic single crystals in the region of f - f transitions of the Ho^{3+} ions are recorded for the first time in a wide temperature range (1.7–423 K). From the splitting of the quasi-doublets in the holmium spectra, two magnetic phase transitions are recorded—namely, magnetic ordering into the easy-plane structure as a second-order phase transition at $T_N = 39$ K and the spin-reorientation transition from the ab plane to the c axis as a first-order phase transition at $T_{SR} = 4.7 \pm 0.2$ K. It is shown that addition of erbium in a concentration of 1 at % decreases the spin-reorientation transition temperature to $T_{SR} = 4.0$ K because the single-ion anisotropy of Er^{3+} facilitates the magnetic ordering in the ab plane.

From the change of the spectrum in the region of internal vibrations ν_4 of BO_3 groups, a first-order phase transition close to a second-order transition is recorded at $T_c = 360$ K. Note that the X-ray diffraction data [9] point to the largest shifts of atoms upon the structural transition just in BO_3 groups. The studies performed with different holmium ferroborate samples reported considerably different values of T_c for powder samples obtained by solid-phase synthesis ($T_c = 427$ K) and for single crystals grown by the solution–melt method ($T_c = 360$ – 366 K). In our opinion, the natural explanation of this situation is the incorporation of impurities from the flux into the crystal during its growth, which depends on the technology. In this work, we described the mechanism of the change in T_c .

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