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Study of the magnetic properties of neodymium and samarium iron borates by the method of erbium spectroscopic probe

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Iron borates $\text{NdFe}_3(\text{BO}_3)_4$ and $\text{SmFe}_3(\text{BO}_3)_4$ activated with 1% erbium, with a huntite structure (space symmetry group $R32$) were investigated by the method of erbium spectroscopic probe. From an analysis of the temperature dependence of the transmission spectra in the region of the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition in the Er^{3+} ion, it was found that both studied compounds order antiferromagnetically at $T_N \approx 33$ K into an easy-plane magnetic structure. No other phase transitions were found.

Keywords: Multiferroics, optical spectroscopy, crystals with rare earths, Kramers ions.

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Introduction

The erbium spectroscopic probe method (see, for example, [1,2]) was developed by M.N. Popova's group and successfully applied to study magnetic phase transitions and types of magnetic structures in several families of isostructural oxide compounds, namely in „blue“ $R_2\text{Cu}_2\text{O}_5$ [3,4] and „green“ $R_2\text{BaCuO}_5$ [5–7] accompanying phases of high-temperature superconductors of type 1-2-3, in nickelates $R_2\text{BaNiO}_5$ [8–11] (here R is rare-earth (RE) element or yttrium). In papers [12–14] this method was also used to study compounds $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Pr}, \text{Eu}–\text{Er}, \text{Y}$) of the family of rare-earth iron borates with the huntite structure, and information about the types of magnetic structures formed in them is obtained. This information was later confirmed by the results of neutron experiments. Erbium probe studies for neodymium and samarium iron borates ($\text{NdFe}_3(\text{BO}_3)_4$ and $\text{SmFe}_3(\text{BO}_3)_4$) were not yet carried out. They are carried out in the present paper.

Information about the structure and properties of $\text{NdFe}_3(\text{BO}_3)_4$ and $\text{SmFe}_3(\text{BO}_3)_4$

Neodymium and samarium iron borates crystallize in the rhombohedral system with space group of symmetry $R32$. $\text{SmFe}_3(\text{BO}_3)_4$ crystal is antiferromagnetically ordered at the temperature of $T_N = 32 \pm 1$ K [15–17]. Complex studies of magnetic, magnetoelastic, and magnetoelectric properties [17,18] and spectroscopic study of oriented $\text{SmFe}_3(\text{BO}_3)_4$ single crystals [15] showed that below the Neel temperature T_N the moments of Fe^{3+} ions are ordered in ab plane perpendicular to c axis of the crystal. The easy-plane nature of the antiferromagnetic structure was

confirmed in neutron scattering experiments [19]. The magnetic properties of samarium iron borate were explained on the basis of the parameters of the crystal field and the parameters of the exchange interaction between RE ions and iron ions [20]. The parameters were obtained from an experimental and theoretical study of the Stark structure of multiplets of Sm^{3+} ion in $\text{SmFe}_3(\text{BO}_3)_4$ crystals in paramagnetic and magnetically ordered phases [20].

The study of the temperature dependence of the magnetic susceptibility of $\text{NdFe}_3(\text{BO}_3)_4$ crystal, carried out in paper [21], showed the presence of a maximum at 32 K, associated with the antiferromagnetic ordering of the subsystem of iron ions, and singularity at 6 K. The authors supposed that the low-temperature singularity is associated with three-dimensional antiferromagnetic ordering both in Fe^{3+} sublattice and in Nd^{3+} sublattice. Later, in a spectroscopic study of $\text{NdFe}_3(\text{BO}_3)_4$ [22], a magnetic ordering was established at 33 K, and the singularity at 6 K is related to the redistribution of the populations of the split Kramers doublets of Nd^{3+} ion. In the paper [23] the study of the magnetic and thermodynamic properties of $\text{NdFe}_3(\text{BO}_3)_4$ single crystal, taking into account spectroscopic data, shown that the low-temperature singularity at 6 K on the temperature dependence of the magnetic susceptibility and the Schottky anomaly at 4 K on the temperature dependence of the heat capacity are associated not with the magnetic ordering of the RE subsystem, but with the redistribution of the populations of the Kramers doublet components of Nd^{3+} ion, split by the exchange interaction. Based on the analysis of the temperature behavior of wide-range transmission spectra in linearly polarized light in the region of transitions in the Nd^{3+} ion in $\text{NdFe}_3(\text{BO}_3)_4$ crystal the calculation was carried out according to the crystal field (CF) theory [24]. From the calculation, in particular,

physically substantiated CF parameters were obtained, as well as wave functions and g -factors for the Stark levels of the Nd^{3+} ion. The calculation results indicate the primary role of the magnetic anisotropy of RE ions in establishing one or another type of magnetic structure [24].

Regarding the studies of the magnetic structure of $\text{NdFe}_3(\text{BO}_3)_4$, there are conflicting data in published articles. In the paper [25] measurements of the magnetic susceptibility and thermal capacity, X-ray diffraction studies and experiments on the diffraction of unpolarized neutrons on powder and single-crystal samples of neodymium iron borate were carried out. It was determined that at 1.6 K the magnetic moment of Fe^{3+} ions subsystem is $4.9 \mu\text{B}$, which is close to the moment of free iron ions. The magnetic moment of Nd^{3+} ions subsystem seems to be saturated due to the effects of the crystal field, reaching $2.7 \mu\text{B}$. Magnetic measurements indicate antiferromagnetic ordering at Neel temperature of 30.5 K. Paper [25] also found a sharp increasing of the magnetic moment of Nd^{3+} ions subsystem at approximately 15 K, which was presumably associated with a phase transition from a commensurate to an incommensurate phase. In the paper [26] single crystal $\text{NdFe}_3(^{11}\text{BO}_3)_4$ was studied using neutronography and spherical neutron polarimetry. The results of neutron diffraction show that below $T_N = 30$ K the magnetic moments of Fe^{3+} and Nd^{3+} lie in the ab plane, are ordered ferromagnetically in one plane and antiferromagnetically in adjacent planes along c axis. It is clarified in the paper [26] that below the temperature of $T_{IC} = 13.5$ K the magnetic structure transforms into the incommensurate antiferromagnetic spiral along c axis with a period of about 1140 \AA .

Experiment

$\text{NdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) single crystals studied in this paper were grown by the solution-melt method using $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ based flux [27]. Growth was carried out in a group mode on seeds obtained preliminary in the spontaneous nucleation mode regime. A crystal holder with four seeds was lowered immersed into a crucible with a solution-melt and rotated at a given frequency of 30 rpm. Thus, the growth process lasted from 10 to 15 days, while the solution-melt temperature decreased at an increasing rate of 0.04–0.125 K/h, so that the crystal growth rate did not exceed 1 mm per day. By same method but based on Li_2WO_4 flux $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) single crystals were obtained. The grown single crystals had a good optical quality and a green color characteristic for iron borates. From them, non-oriented plates 2.2 mm and 4.42 mm thick for $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) and $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%), respectively, were cut and polished.

Absorption spectra were recorded on Bruker IFS 125 HR Fourier spectrometer in the spectral region from 5000 to 10000 cm^{-1} and with a spectral resolution up to 0.1 cm^{-1} . Temperature was measured using both an optical helium-

vapor cryostat and Cryomech ST 403 closed cycle cryostat in the temperature range from 4 to 300 K. The temperature of the sample in the cryostat was monitored and stabilized through a two-channel thermal controller Scientific Instruments 9700.

Results and discussion

Figure 1 shows the transmission spectra of crystal $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}^{3+}$ (1 at.%) in the region of transitions from the Stark levels of the ground multiplet $^4I_{15/2}$ of Er^{3+} ion into the Stark levels of the excited multiplet $^4I_{13/2}$ at four temperatures (50, 31, 20, and 5 K).

In crystal field the energy levels of a free RE ion generally split into $(2J + 1)$ Stark levels (J is total moment of the system). Er^{3+} ($4f^{11}$) ion is Kramers ion, and its energy levels remain doubly degenerate in the absence of a magnetic field. At the Neel temperature $T_N = 33$ K, the $\text{NdFe}_3(\text{BO}_3)_4$ crystal is magnetically ordered due to exchange Fe–Fe interactions. In this case, the Kramers degenerations are removed in the resulting effective magnetic field, and each Stark level of the erbium ion splits into two sublevels. Figure 2 shows the diagram of Stark splittings of ground $^4I_{15/2}$ and the first excited $^4I_{13/2}$ levels of the free ion Er^{3+} in crystal field, as well as the splitting of Kramers doublets due to the exchange Er–Fe interaction at $T < T_N$. The Stark levels of the ground multiplet $^4I_{15/2}$ are denoted by Arabic digits, and of the excited ones by capital Latin letters.

The diagram (Figure 2) shows the transition 1A from the Stark level 1 of $^4I_{15/2}$ multiplet to the level A of $^4I_{13/2}$ multiplet. With magnetic ordering the Kramers degeneration of the doublets is removed: the level 1 splits into Kramers sublevels 1' and 1'', and the level A —

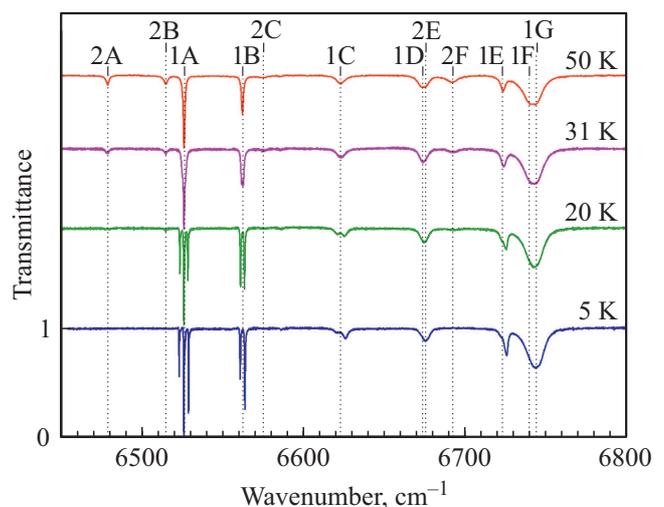


Figure 1. Transmission spectra of crystal $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}^{3+}$ (1 at.%) in the transition region $^4I_{15/2} \rightarrow ^4I_{13/2}$ in Er^{3+} ion. The spectra at different temperatures are shifted vertically relative to each other. The designations of the spectral lines are given in accordance with the diagram in Figure 2.

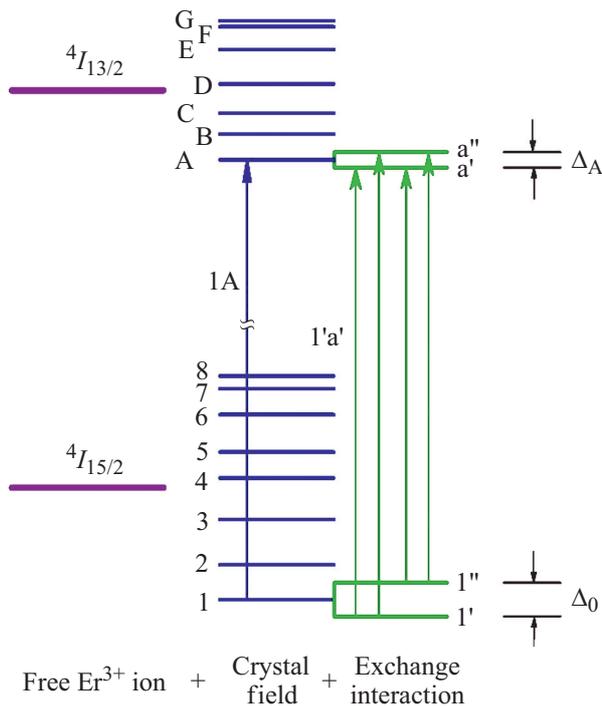


Figure 2. Diagram of Stark levels of the ground ${}^4I_{15/2}$ and excited ${}^4I_{13/2}$ multiplets of the Er³⁺ ion in the crystal field and exchange splittings of Kramer's doublets in the magnetically ordered state of the crystal.

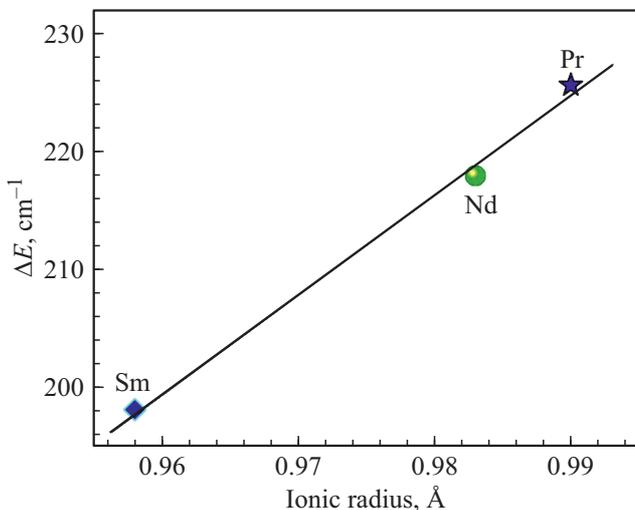


Figure 3. Dependence of ΔE splitting of ${}^4I_{13/2}$ multiplet of the Er³⁺ probe ion in $R\text{Fe}_3(\text{BO}_3)_4:\text{Er}^{3+}$ crystals ($R = \text{Pr}, \text{Nd}, \text{Sm}$, are shown in the figure) on the ionic radius of R^{3+} ion.

into a' and a'' . Then the spectral line corresponding to 1A transition is split in the general case into four components related to the transitions $1'a'$, $1'a''$, $1''a'$, and $1''a''$. Let us denote the exchange splitting of the ground level as Δ_0 , of excited level A — as Δ_A .

Figure 3 shows the dependence of splitting ΔE of multiplet ${}^4I_{13/2}$ of probe ion Er³⁺ on ionic radius R^{3+} for iron

borates $R\text{Fe}_3(\text{BO}_3)_4:\text{Er}^{3+}$, $R = \text{Sm}, \text{Nd}, \text{Pr}$ [28] having the structure $R32$. The dependence $\Delta E(T)$ is linear. The ionic radius decreasing leads to decreasing of the distances $R\text{--O}$ and, consequently, to increasing of the overlap of the wave functions of Er³⁺ ion and neighboring ligands. The strength of the crystal field increases, which causes an increase in the splitting of multiplets of Er³⁺ ion [29,30].

Next, let's review the spectra of the probe erbium ion in the magnetically ordered state of samarium and neodymium iron borates. Figure 4 shows spectral lines 1A and 1B in the region of transition ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ in Er³⁺ ion in $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}^{3+}$ and $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}^{3+}$ at various temperatures.

Below the Neel temperature of T_N the ordered magnetic moments of iron create an effective magnetic field on erbium ions, which leads to the degeneracy removal of the Stark levels (Kramers doublets) of Er³⁺ ion and splitting of the corresponding spectral lines in the studied compounds. The line 1A of Er³⁺ ion in the crystal field of neodymium iron borate splits into three components, which indicates the same values of splitting Δ_0 of the ground state and splitting Δ_A of the first excited level A of the multiplet ${}^4I_{13/2}$.

For the central component of line 1A of Er³⁺ ion in the crystal field $\text{SmFe}_3(\text{BO}_3)_4$ a weakly pronounced shoulder is observed, which allows the line to be divided into four components. The designations in Figure 4 correspond to the diagram in Figure 2. The analysis of the splitting of spectral lines 1A at different temperatures made it possible to determine the exchange splittings of the ground state Δ_0 of ${}^4I_{15/2}$ multiplet of Er³⁺ ion in $\text{SmFe}_3(\text{BO}_3)_4$ and $\text{NdFe}_3(\text{BO}_3)_4$. The results obtained in comparison with the data for $\text{PrFe}_3(\text{BO}_3)_4$ [28] are presented in the Table.

The line 1B splits into two components, which indicates that the splitting of level B of the ${}^4I_{13/2}$ multiplet is negligibly small. This is confirmed by the fact that splitting of the line 1B at 5 K is equal to the value Δ_0 .

Figure 5 shows the temperature dependence $\Delta_0(T)$ of the ground state splitting of Er³⁺ ion for the compounds under study. Approximation of this dependence to zero gives the magnetic ordering temperature $T_N = 33 \pm 1$ K both for $\text{SmFe}_3(\text{BO}_3)_4$, and for $\text{NdFe}_3(\text{BO}_3)_4$, which is in good agreement with the literature data. Comparison of spectroscopic results relating the ground state splitting of Er³⁺ probe ion with data of the magnetic moment of iron obtained from experiments on neutron scattering in $\text{SmFe}_3(\text{BO}_3)_4$ [19] and in $\text{NdFe}_3(\text{BO}_3)_4$ [26], also shown in Figure 5, confirms the hypothesis of the effective magnetic field on erbium ions proportional to the magnetic moment of iron M_{Fe} .

Thus, the applicability of the erbium spectroscopic probe method for studying magnetic phase transitions and types of magnetic structures in iron borates is substantiated. Compare the values of the exchange splitting Δ_0 of the ground Kramer's doublet of Er³⁺ ion at $T = 5$ K in the studied iron borates $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) and $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) given in the Table with the value $\Delta_0 = 1.46 \text{ cm}^{-1}$ for easy-axis magnetic $\text{PrFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) [28]. Note

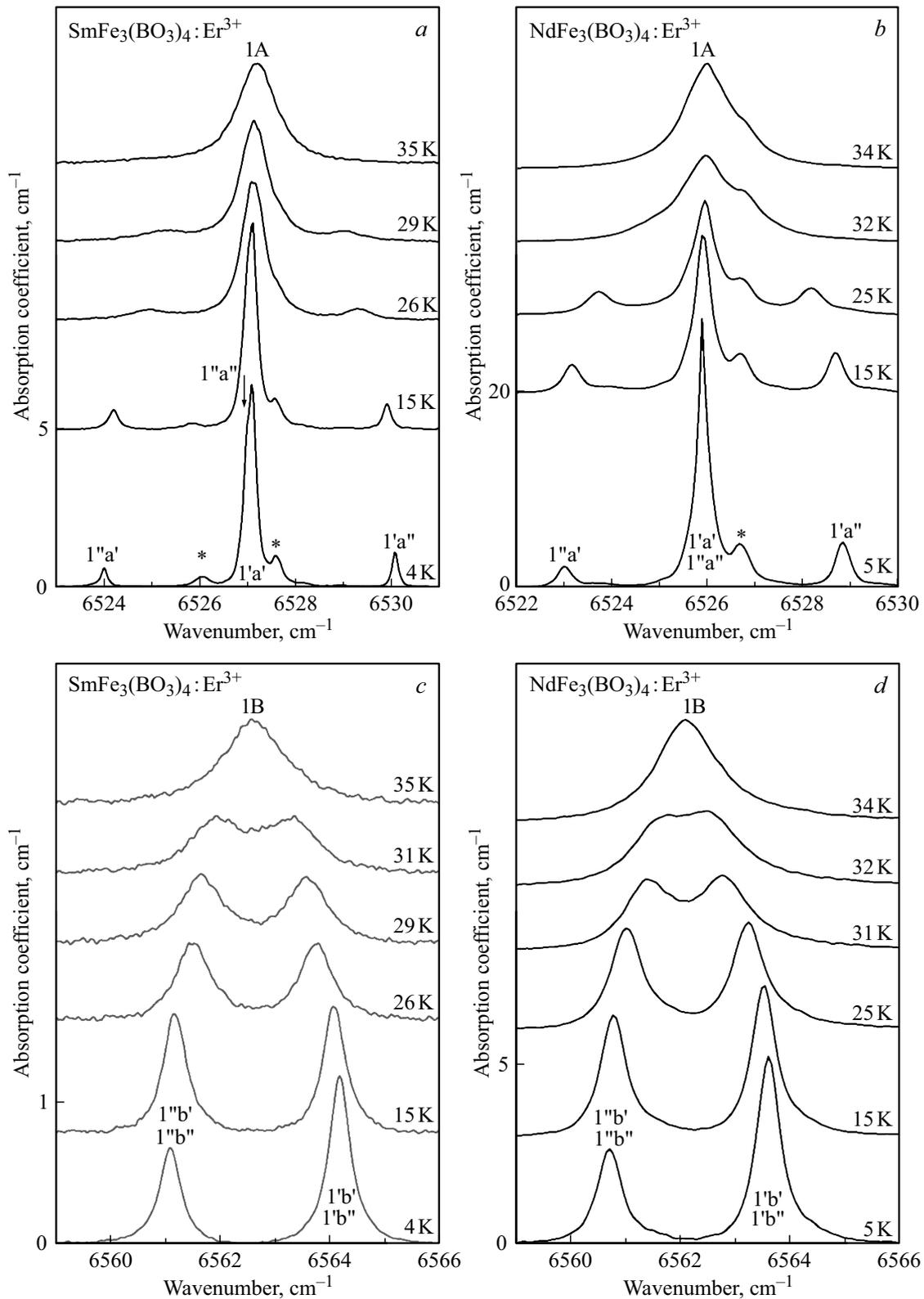


Figure 4. Absorption lines 1A (a, b) and 1B (c, d) in the transition region $^4I_{15/2} \rightarrow ^4I_{13/2}$ in Er³⁺ ions in crystals SmFe₃(BO₃)₄:Er (1 at.%) (a, c) and NdFe₃(BO₃)₄:Er (1 at.%) (b, d). The spectra at different temperatures are shifted vertically relative to each other. The asterisk (*) denotes impurity lines.

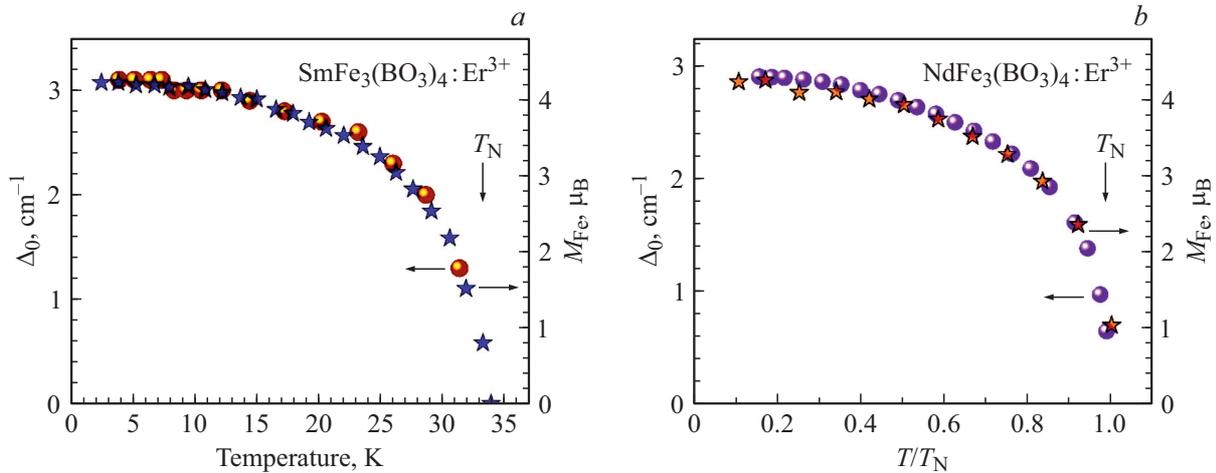


Figure 5. Temperature dependences of the exchange splitting of the ground Kramers doublet Δ_0 of Er^{3+} ion (circles) in $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) (a) and in $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) (b) and magnetic moments M_{Fe} of Fe^{3+} ions (stars) according to measurements of neutron scattering in $\text{SmFe}_3(\text{BO}_3)_4$ (a) [19] and in $\text{NdFe}_3(\text{BO}_3)_4$ (b) [26].

Exchange splittings (cm^{-1}) of the ground state Δ_0 and levels A and B of the first excited multiplet $^4I_{13/2}$ of Er^{3+} ion, Δ_A , and Δ_B , respectively, in the crystal fields of neodymium, samarium, and praseodymium iron borates

Exchange splitting of level	$\text{NdFe}(\text{BO}_3)_4$	$\text{SmFe}(\text{BO}_3)_4$	$\text{PrFe}(\text{BO}_3)_4$ [28]
Δ_0	2.9	3.08	1.49
Δ_A	2.9	3.01	3.9
Δ_B	~ 0.0	~ 0.0	—

that all three compounds have $R32$ crystal structure. The value of Δ_0 for easy-plane neodymium and samarium iron borates is approximately by 2 times greater than for easy-axis praseodymium iron borate. In earlier investigations of the magnetic structures types by the erbium spectroscopic probe method of iron borates with $P3_121$ structure, such a relation for Δ_0 in compounds with easy-plane and easy-axis magnetic structure is approximately preserved, but the absolute values are different [14], which can be explained by a different symmetry of RE center (D_3 for compounds with space group $R32$ and C_2 — with group $P3_121$). In contrast to the previously studied RE iron borates with $P3_121$ structure, in the case of compounds $\text{SmFe}_3(\text{BO}_3)_4$ and $\text{NdFe}_3(\text{BO}_3)_4$ having $R32$ structure there are no magnetically non-equivalent positions for RE ions at temperatures below T_N . In this regard, the spectral lines corresponding to absorption in Er^{3+} ions are narrower than similar lines in the spectra of magnetically ordered iron borates with $P3_121$ structure.

Since in the paper [26] on neutrons scattering in $\text{NdFe}_3(\text{BO}_3)_4$ it was said about the phase transition to the incommensurate phase at the temperature of $T_{IC} = 13.5$ K,

it was of interest to conduct a detailed study of the temperature dependences of the spectral line characteristics to search for features that could indicate additional phase transitions. We plotted shift vs. temperature and half-width vs. temperature dependences for the low-frequency component of the line 1B of Er^{3+} ion in $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) and $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%). They are shown in Figure 6. In plots there are no any features in the temperature range of 13–15 K for both $\text{SmFe}_3(\text{BO}_3)_4$, and for $\text{NdFe}_3(\text{BO}_3)_4$. Thus, the spectra of the erbium probe in neodymium and samarium iron borates do not make it possible to detect any additional phase transitions in these compounds.

Conclusion

The temperature dependences of the absorption spectra in the region of the transition $^4I_{15/2} \rightarrow ^4I_{13/2}$ in Er^{3+} ion in iron borates $\text{NdFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) and $\text{SmFe}_3(\text{BO}_3)_4:\text{Er}$ (1 at.%) were studied, their crystal structure is described by the $R32$ space group regardless of temperature. Both of these compounds exhibit antiferromagnetic ordering at $T_N = 33 \pm 1$ K. No other phase transitions were registered. A comparison was made with the data of the easy-axis magnetic $\text{PrFe}(\text{BO}_3)_4$, previously studied by the erbium spectroscopic probe method. It is shown that the method can be successfully applied to distinguish between easy-axis and easy-plane types of magnetic ordering in iron borates with $R32$ structure (previously, this conclusion was made for iron borates with the structure $P3_121$ [12–14]).

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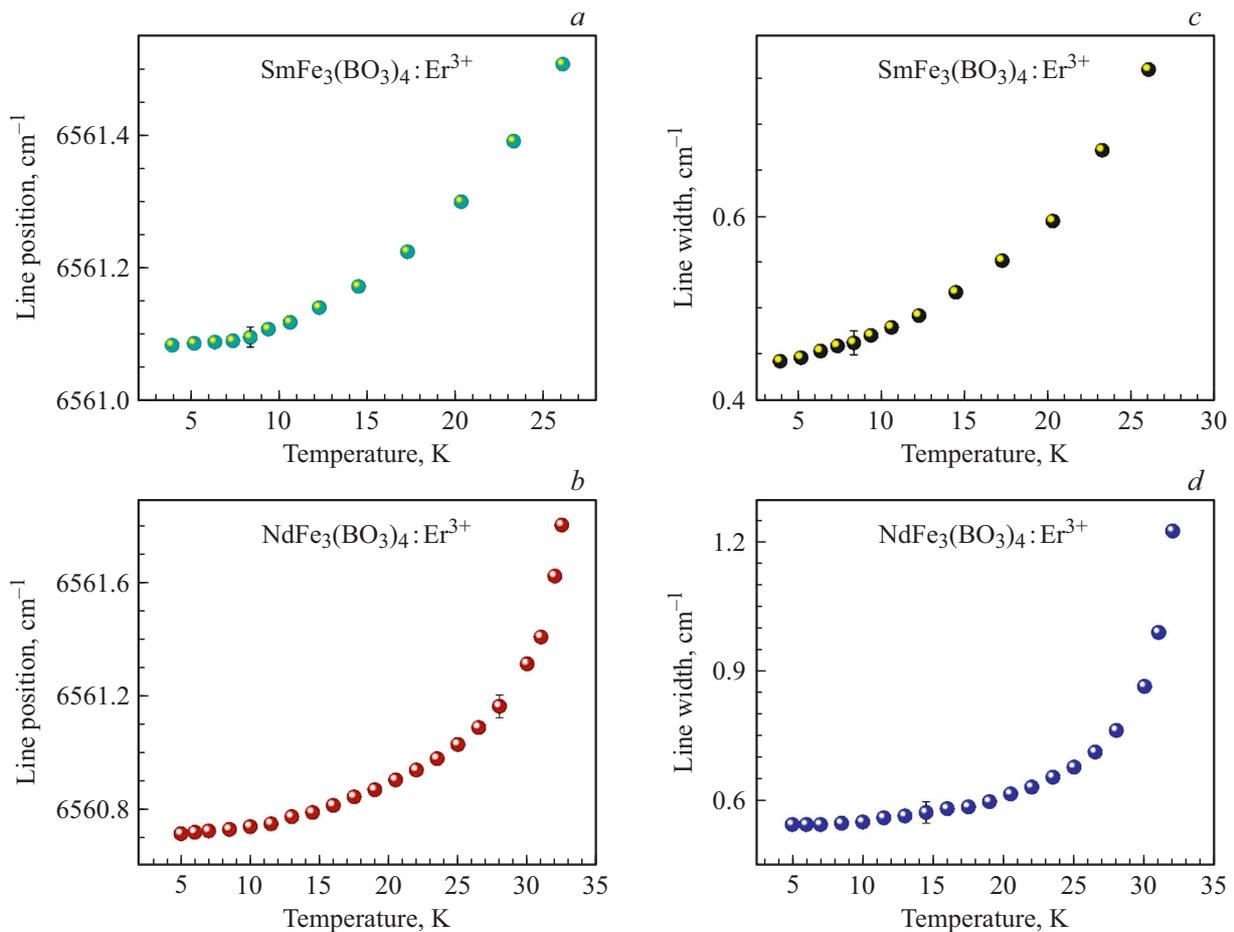


Figure 6. Temperature dependences of position (a, b) and half-width (c, d) of the low-frequency component of line 1B of the Er³⁺ ion in the crystal field SmFe₃(BO₃)₄:Er (1 at.%) (a, c) and NdFe₃(BO₃)₄:Er (1 at.%) (b, d).

resolution wide-range spectroscopy“ (USU MHRWRS ISAS), <http://www.ckp-rf.ru/usu/508571/>.

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Conflict of interest

The authors declare that they have no conflict of interest.

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