

Investigation of the iron borates $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ by the method of Er^{3+} spectroscopic probe

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Abstract

Temperature-dependent high-resolution optical spectra of the Er^{3+} probe ion in $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ are reported. The data provide the temperature of magnetic ordering and direction of the Fe^{3+} magnetic moments. Both compounds order magnetically at $T_N = 39 \pm 1$ K. The magnetic structure of $\text{DyFe}_3(\text{BO}_3)_4$ is of the easy-axis type, while that of $\text{HoFe}_3(\text{BO}_3)_4$ is of the easy-plane type. The role of anisotropic interactions between the iron and the rare-earth subsystems is discussed.

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1. Introduction

Compounds with the general formula $RM_3(\text{BO}_3)_4$ ($R = \text{Y}$, La–Tm, $M = \text{Al}$, Cr, Ga, Fe, Sc) crystallize in a trigonal structure and belong to the $R32$ (D_3^7) space symmetry group [1]. Aluminates from this family manifest good luminescent and non-linear optical properties and are used in self-frequency summing and self-frequency doubling lasers [2]. The absence of the concentration quenching of luminescence makes aluminates appropriate for medium power minilasers [2]. The compounds with the magnetic Fe^{3+} ions possess a number of new interesting properties. In particular, the magnetoelectric effect has been recently discovered in some iron borates [3]. This gives a possibility to control the dielectric polarization by the magnetic field (and vice versa) and makes iron borates to be promising materials for optoelectronic applications. From the other hand, iron borates are interesting for magnetism, as they contain two magnetic subsystems, namely, rare-earth and iron ones, the latter being quasi-one-dimensional.

The investigation of iron borates on powder samples [4] has shown that all these compounds undergo the antiferromagnetic (AF) ordering at temperatures that linearly depend on rare-earth ion radius r_{Ln} and vary from 22 K for $\text{LaFe}_3(\text{BO}_3)_4$ to 40 K for $\text{TbFe}_3(\text{BO}_3)_4$. For compounds with $R = \text{Eu}$ –Ho, Y a structural phase transition at higher temperatures was observed [4,5]. X-ray structural study on the single crystal of $\text{GdFe}_3(\text{BO}_3)_4$ has shown that in the course of this phase transition the symmetry of the crystal lowers from $R32$ to $P3_121$ and the site symmetry for a single position of the R^{3+} ion lowers from D_3 to C_2 [6]. Complex studies of Ref. [7] on gadolinium iron borate have revealed a spin-reorientation phase transition at $T_R = 9$ K (1% Er doped samples of $\text{GdFe}_3(\text{BO}_3)_4$ have demonstrated a lowering of T_R [8,9]). Above T_R , magnetic moments form the easy-plane collinear AF structure while below T_R they are arranged antiferromagnetically along the c -axis of the crystal [7,10]. In other iron borates ($R \neq \text{Gd}$) spin-reorientation phase transition was not observed.

Application of the Er^{3+} spectroscopic probe method enabled us to investigate magnetic phase transitions and to determine magnetic structures in the single crystals of yttrium, terbium, and erbium iron borates [8,9]. In the present work, we

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continue our study of the rare-earth iron borates by the Er^{3+} spectroscopic probe method and focus on $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$.

2. Experiment

Single crystals of $\text{DyFe}_3(\text{BO}_3)_4$ doped with Er (0.3 at%) and of $\text{HoFe}_3(\text{BO}_3)_4$ doped with Er (1 at%) were grown using the bismuth trimolibdate $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ based flux [11]. Non-oriented plates of 2 mm thickness were cut and polished for optical measurements. Transmission spectra were registered using a Fourier-transform spectrometer Bruker 125 HR with an InSb nitrogen-cooled detector in wide spectral [4000–10 000 cm^{-1}] and temperature [4.2–300 K] regions. The samples were in an optical helium-vapor cryostat. The temperature was stabilized within ± 0.15 K.

3. Results and discussion

The lowest-frequency optical transition ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ in the Er^{3+} ion is the only one that lies in the infrared transparency window of iron borates. Other optical transitions could not be used for our investigation because of an overlap between them and broad absorption bands due to the Fe^{3+} ions [8,12]. Fig. 1 shows transmission spectra of Gd, Dy, and Ho iron borates at $T = 50$ K in the region of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition in Er^{3+} . Close positions of all spectral lines in these crystals point to a similarity of their crystal fields. In the crystal field (CF) with a symmetry lower than a cubic one energy levels of a free ion with an odd number of electrons (e.g. of Er^{3+}), are split into $(2J + 1)/2$ Kramers doublets, where J is a total angular momentum of electrons. As the site symmetry of a rare-earth ion in all iron borates is not higher than D_3 , the ${}^4I_{15/2}$ energy level splits into 8 sublevels and the ${}^4I_{13/2}$ one splits into 7 sublevels, according to the scheme on Fig. 2. A decrease of the temperature leads to an increase of the ground-state population. Hence, the intensities of the spectral lines corresponding to transitions from the ground state to the CF levels of the ${}^4I_{13/2}$ multiplet

also increase. On the contrary, the intensities of the spectral lines due to transitions from the excited levels of the ${}^4I_{15/2}$ multiplet decrease with decreasing the temperature. From the analysis of the growing and freezing spectral lines and of the distances between them, we determine the positions of the CF levels of the ${}^4I_{13/2}$ multiplet. Using the Stark structure of the ${}^4I_{13/2}$ multiplet and the data from Ref. [9] we calculate the center of gravity E_0 of this multiplet in different iron borates $R\text{Fe}_3(\text{BO}_3)_4$, $R = \text{Gd}-\text{Er}$. Fig. 3 demonstrates that E_0 linearly depends on the ionic radius of the R^{3+} ion. A reduction of the ionic radius of R^{3+} leads to a reduction of $R-\text{O}$ distances and, thus, to an increase in overlap between wave-functions of the Er^{3+} ion and neighboring ligands. In its turn, this causes a decrease in E_0 (so-called nepheloxetic shift [14]).

Unless placed in the magnetic field, CF sublevels remain doubly degenerate. An emergence of the magnetic field lifts

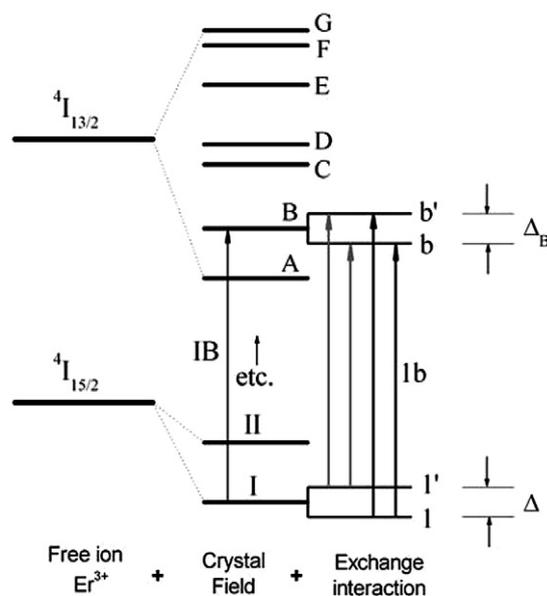


Fig. 2. Scheme of the crystal-field and exchange splittings for the levels of the Er^{3+} ion in a magnetic crystal.

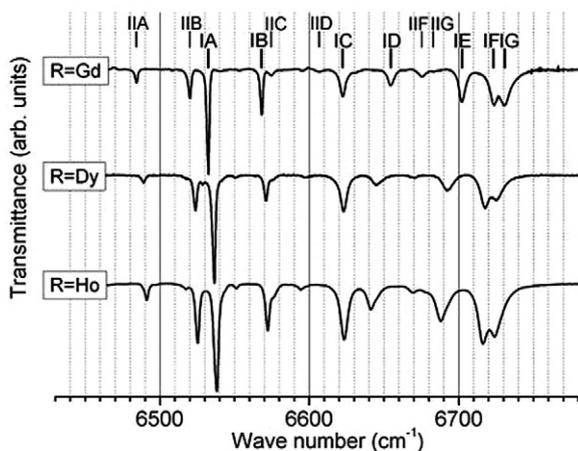


Fig. 1. Transmission spectra of $R\text{Fe}_3(\text{BO}_3)_4$, $R = \text{Gd}$, Dy , and Ho , in the region of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ optical transition in the Er^{3+} probe ion at $T = 50$ K (in the paramagnetic state).

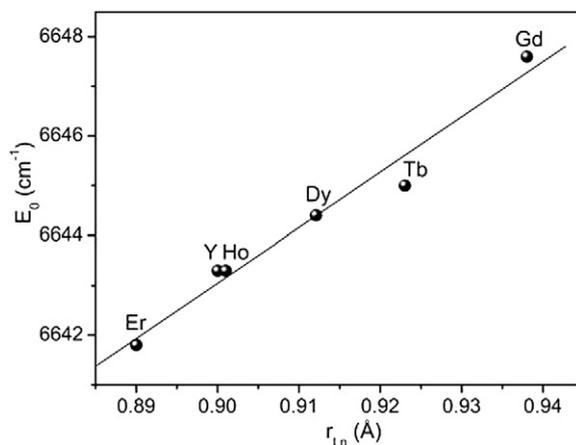


Fig. 3. The relation between the center of gravity E_0 of the ${}^4I_{13/2}$ multiplet of Er^{3+} in $R\text{Fe}_3(\text{BO}_3)_4:\text{Er}$ and the ionic radius of the R^{3+} ion. The data on the ionic radii were taken from Ref. [13].

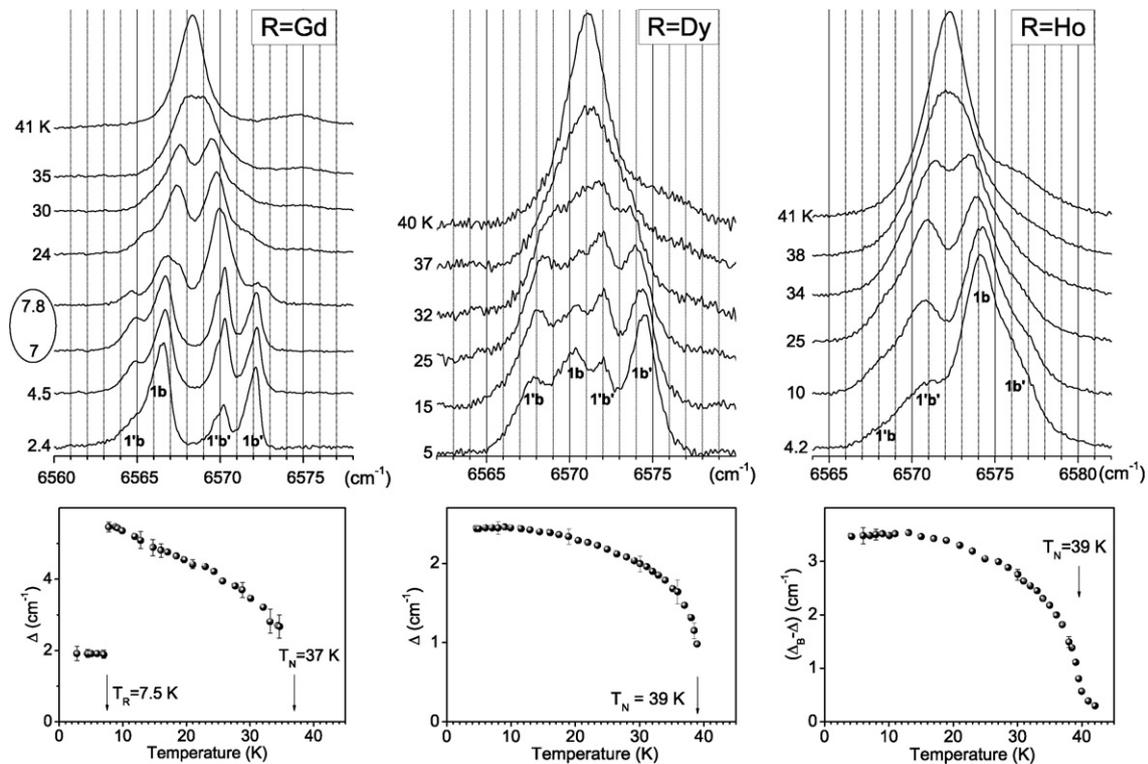


Fig. 4. The absorption line IB of the Er^{3+} probe in $R\text{Fe}_3(\text{BO}_3)_4$ (top) and the temperature dependence of its splitting (bottom).

the degeneracy, each of the Kramers doublets splits into two sublevels and the corresponding spectral line splits into four components (see Fig. 2). Such kind of spectral line splitting is a good indicator of an establishment of the magnetic order in a system.

Fig. 4 shows the absorption line IB of the Er^{3+} ion in the compounds under study. Let us consider, for example, $\text{DyFe}_3(\text{BO}_3)_4$. With decreasing the temperature, line IB splits into four components due to magnetic ordering of the Fe-subsystem. The intensity of transitions from the level $1'$ decreases with lowering the temperature, because of a depopulation of the level according to the Boltzmann distribution. The temperature dependence of spectral line splitting manifests magnetic ordering at $T_N = 39 \pm 1$ K. Spectral line IB in $\text{HoFe}_3(\text{BO}_3)_4$ splits in the same way, though because of the large inhomogeneous broadening four components are not clearly observed and we applied the method of spectral line decomposition into components. Another situation takes place in the case of $\text{GdFe}_3(\text{BO}_3)_4$. Below 37 K, line IB splits and the splitting grows with further lowering the temperature, but at 7.5 K distances between the split components and their mutual intensities change abruptly. It is connected with a spin-reorientation first-order phase transition.

As it has been shown earlier [15], in compounds containing both f- and d-magnetic subsystems the splitting of a Kramers doublet of the f-ion (R^{3+}) is mainly due to the exchange interaction with neighboring d-ions (Fe^{3+}). The f–f interactions are much weaker. In iron borates, RO_6 prisms are mutually independent and do not have common oxygen ions; thus f–f interactions are especially weak. The splitting of the Er^{3+} ground state (extracted from the analysis of the spectra) changes abruptly at

Table 1

Temperatures of the magnetic ordering and the ground-state splittings of the Er^{3+} probe ion in different iron borates $R\text{Fe}_3(\text{BO}_3)_4$

| R | T_N , K | | Δ , cm^{-1} | |
|-----|--------------|-----|-----------------------------|------|
| | Present work | [4] | 5 K | 10 K |
| Gd | 37 ± 1 | 37 | 1.9 | 5.5 |
| Dy | 39 ± 1 | 39 | 2.5 | 2.4 |
| Ho | 39 ± 1 | 39 | 5.9 | 5.9 |

the spin-reorientation phase transition (see Fig. 4). This makes the Er^{3+} ion to be a proper probe of the magnetic structure of the Fe-subsystem in iron borates.

Table 1 lists the ground-state exchange splitting of Er^{3+} probe in different iron borates. The temperatures of magnetic ordering are also indicated there. Knowing the magnetic structure of $\text{GdFe}_3(\text{BO}_3)_4$ we compared the exchange splitting of Er^{3+} probe in $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ with those in $\text{GdFe}_3(\text{BO}_3)_4$ and suggested the following types of magnetic structures: easy-axis one in $\text{DyFe}_3(\text{BO}_3)_4$ and easy-plane one in $\text{HoFe}_3(\text{BO}_3)_4$.

The influence of the single-ion anisotropy of the R^{3+} ion on the establishment of a magnetic structure was mentioned in Refs. [8,9]. In $\text{YFe}_3(\text{BO}_3)_4$, where Y is a non-magnetic ion, the iron subsystem is the only magnetic subsystem and, thus, its anisotropy imposes the ordering of Fe^{3+} moments in the ab -plane. It worth noting, that Fe^{3+} , being an S-ion, has zero orbital moment ($L = 0$) and, thus, its single-ion anisotropy should be weak. In the case of $\text{TbFe}_3(\text{BO}_3)_4$, where Tb^{3+} is an Ising ion (that is, $g_{\parallel} \gg g_{\perp}$, where g is the magnetic g -factor), the strong single-ion anisotropy of the terbium sub-

system results in the arrangement of Fe^{3+} magnetic moments along the c -axis [9]. Obviously, the easy-axis magnetic structure of $\text{DyFe}_3(\text{BO}_3)_4$ is due to the single-ion anisotropy of the Dy^{3+} ion. In $\text{GdFe}_3(\text{BO}_3)_4$, Gd^{3+} , like Fe^{3+} , is also an S-ion and has a weak single-ion anisotropy. The competition between weak anisotropies of the iron and gadolinium subsystems leads to a spin-reorientation phase transition [10]. On the contrary, the anisotropies of the Er^{3+} and Ho^{3+} ions stabilize the easy-plane magnetic structure of erbium and holmium iron borates, respectively. To verify the assumptions mentioned above, it is necessary to have data on the magnetic anisotropy of different R^{3+} ions in the crystal field of $R\text{Fe}_3(\text{BO}_3)_4$. Such data can be obtained from the optical spectroscopy of the R^{3+} ions in $R\text{Fe}_3(\text{BO}_3)_4$ ($R = \text{Tb}–\text{Er}$) and further calculations based on the CF theory. It should be mentioned that calculations using the CF parameters for the isostructural aluminate $\text{DyAl}_3(\text{BO}_3)_4$ predict the orientation of iron magnetic moments just along the trigonal c -axis in $\text{DyFe}_3(\text{BO}_3)_4$ [16], which supports our assumptions.

Note added in proof

Magnetic measurements on the oriented single crystals of $\text{DyFe}_3(\text{BO}_3)_4$ performed recently by two independent groups have revealed the antiferromagnetic ordering of $\text{DyFe}_3(\text{BO}_3)_4$ into the easy-axis magnetic structure (E.A. Popova, I.A. Gudim, private communications).

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