Optical spectroscopy of $ErFe_3(BO_3)_4$: detection of phase transitions and crystal-field levels of the Er^{3+} ground multiplet

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Abstract. High-resolution spectra of oriented $ErFe_3(BO_3)_4$ single crystals are registered in the spectral range 500 – 8000 cm^{-1} at various temperatures (4 – 470 K). The temperature behaviour of the phonon mode at 976 cm^{-1} allowed us to register a structural phase transition at T_S=431 K. The energies of crystal-field levels of the ground $^4I_{15/2}$ and the first excited $^4I_{13/2}$ multiplets of the Er^{3+} ion are determined in the paramagnetic state of $ErFe_3(BO_3)_4$. The exchange splitting of the ground Kramers doublet in the magnetically ordered state was found to be Δ_0=6.3±1 cm^{-1}. The interference occurring due to birefringence in the single crystals was also registered. The temperature dependence of the position of the maximum of the interference band demonstrates two anomalies, at T_N and T_S, associated with the phase transitions in $ErFe_3(BO_3)_4$.

1 Introduction

$ErFe_3(BO_3)_4$ belongs to the family of rare-earth (RE) iron borates $RFe_3(BO_3)_4$ (R = Y, La – Lu) that have the same structure as a natural mineral huntite (*R32* space symmetry group). These compounds possess a number of fascinating properties. First of all, a magnetoelectric (ME) effect was discovered, which made it possible to classify them as multiferroics. Among the iron borates, the highest values of the electric polarization induced by a magnetic field were observed in $NdFe_3(BO_3)_4$ and $SmFe_3(BO_3)_4$, 400 and 500 $\mu C/m^2$, respectively [1, 2]. Below the Neel temperature, both these compounds order antiferromagnetically into an easy-plane structure. $ErFe_3(BO_3)_4$ also is an easy-plane antiferromagnet, therefore it was expected to have a large value of the induced polarization as well. In fact, its value is negligible [3]. The magnetic properties of iron borates are interesting also due to the presence of two magnetic subsystems, *f*- and *d*- ones, and their mutual interaction. The differences between the magnetic and ME properties of RE iron borates result from differences in crystal-field (CF) levels of the RE ion and RE-Fe exchange interaction. The data on CF levels and exchange interactions can be obtained from spectroscopic measurements and further theoretical calculations based on them. In this work, we present the first results on the temperature dependences of polarized optical spectra of $ErFe_3(BO_3)_4$ crystals. We demonstrate spectral signatures of the phase transitions in $ErFe_3(BO_3)_4$ and report the values of CF energies of the ground $^4I_{15/2}$ and the first excited $^4I_{13/2}$ multiplets of the Er^{3+} ion.

2 Structure and properties

In the trigonal crystal structure *R32,* the main elements are MO_6 octahedra forming quasi-one-dimensional helicoidal chains along the crystallographic axis *c*. Distorted ErO_6 prisms and triangular BO_3 groups unite the chains into a three-dimensional structure. Raman spectra measurements for $RFe_3(BO_3)_4$ revealed a structural phase transition at T_S=155, 198, 340, and 350 K for R = Gd, Tb, Er, and Y, respectively [4]. According to a single-crystal x-ray structural study of $GdFe_3(BO_3)_4$ [5], this transition corresponds to the crystal symmetry lowering from the *R32* space group to the $P3_121$ one. The first order structural phase transition to lower symmetry occurred in $ErFe_3(BO_3)_4$ was determined by excess heat capacity in the work [6]. The value T_S = 433 K was registered during cooling measurements, and 439 K – during heating measurements. Also in the work [6] the research provided absorption, magnetic circular dichroism and natural circular dichroism spectra of $ErFe_3(BO_3)_4$ as a function of temperature in the range of 90-293 K. As far as we know, there are no other works devoted to the spectroscopic study of $ErFe_3(BO_3)_4$ single crystals.

The specific heat data for $ErFe_3(BO_3)_4$ exhibit a lambda-type anomaly at 38 K, which matches closely the Neel temperature, and the Schottky anomaly [7]. A modeling of the latter allowed the authors of Ref. [7] to calculate the ground-state exchange splitting of Er^{3+} ions: 7.5 K [7]. The magnetic ordering as a second-order phase transition into an easy-plane magnetic structure at T_N = 39 K was detected by the erbium spectroscopic probe method [8]. The work also provided experimental data on the splitting of the Er^{3+} ground Kramers doublet, which equals 7.3 cm^{-1} at 5 K. The temperature dependences of magnetic susceptibility and

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magnetization of $ErFe_3(BO_3)_4$ along and perpendicular to the c-axis at low temperatures demonstrate a contribution of the ground Kramers doublet of the Er^{3+} ion, which possesses a significant anisotropy of the g-tensor [3]. The compound also shows a spontaneous magnetic polarization in the magnetically ordered state [3].

3 Experimental methods

Transparent green single crystals of $ErFe_3(BO_3)_4$ of good optical quality were grown by a solution-melt method with a flux based on $Bi_2Mo_3O_{12}$ in the Kirensky Institute of Physics, Krasnoyarsk, Russia [9]. The growth details will be given elsewhere. The single crystals were oriented (by habitus and polarization method using a polarization microscope Olympus SZX7), cut, and polished. The result was several samples of different thickness, cut along (π- and σ-polarizations) and perpendicular (α-polarization) to the crystallographic axis *c*. Transmission spectra were recorded on a high-resolution Fourier spectrometer Bruker IFS 125HR in the spectral range 500-8000 cm^{-1} with a spectral resolution up to 0.1 cm^{-1}. Temperature measurements were carried out in the range 4–470 K using a Cryomech ST403 closed-cycle cryostat and a Bruker 2216e heating device.

To study the birefringence, a sample cut parallel to the crystallographic axis *c* of the crystal was placed into a cryostat between two crossed identical polarizers, so that the plane of polarization was at an angle of 45° to the *c* axis. As a result, interference of the ordinary and extraordinary rays was observed.

4 Results and discussion

4.1 Structural phase transition

Structural changes in a crystal are unambiguously detected in the temperature behavior of phonon modes. We were able to measure a phonon mode at 976 cm^{-1}, which is the E mode corresponding to internal oscillations ν_4 of the BO_3 group [4]. The mode appears only in the low-symmetry $P3_121$ phase of $RFe_3(BO_3)_4$ [4]. The temperature dependence of the mode's integral intensity allowed us to determine the temperature of the transition $T_S = 431$ K (fig.1). The influence of the phase transition on the spectral lines corresponding to the *f-f* optical transitions of Er^{3+} is difficult to interpret, due to significant broadening of these lines at high temperatures. The difference in the values of T_S obtained by different research groups [4, 6] is associated with the entrance of impurities from the flux into the crystal in the course of growth, which depends on technology [10]. The powder samples synthesized by the solid-phase synthesis method do not contain such impurities. However, there are no temperature data on T_S for the $ErFe_3(BO_3)_4$ powder samples. But the approximation of the dependence of T_S on the ionic radius of the RE ion provides a value of about 430 K [11]. The fact that the value of T_S obtained in the present work is close to the one for powder samples proves a good quality of our samples. This gives us hope that the data we obtained are reliable.

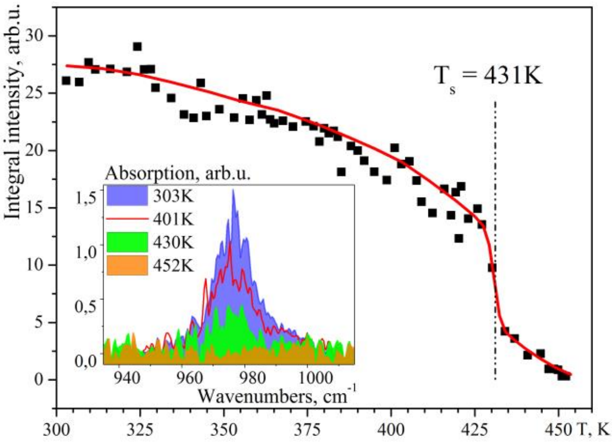

Fig.1. Temperature dependence of the integral intensity of the 976 cm^{-1} phonon appearing below structural phase transition temperature T_S in $ErFe_3(BO_3)_4$. The inset shows this phonon in the π-polarized absorption spectra at different temperatures.

4.2 Crystal-field levels and the exchange splittings

In the high-temperature structural phase (*R32*) of $ErFe_3(BO_3)_4$, the CF levels of Er^{3+} ion are the Γ_4 and Γ_{56} Kramers doublets of the D_3 point symmetry group. In the low-temperature phase, all of them are described by the Γ_{34} irreducible representations of the C_2 point group. At temperatures below the Neel temperature, the Er^{3+} Kramers doublets split in two in the effective magnetic field created by the ordered iron magnetic subsystem, and the corresponding spectral lines split generally into four components (fig.2).

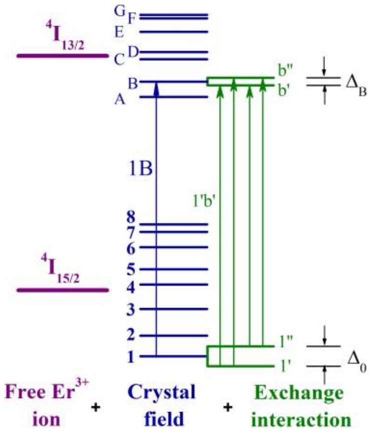

Fig.2. CF and exchange splittings of energy levels of the free Er^{3+} ion caused by the crystal-field and exchange interations in the magnetically ordered state of $ErFe_3(BO_3)_4$.

Fig.3 represents the spectra illustrated by the scheme on fig.2. A comparison of the spectra at different temperatures and polarizations allowed us to determine the energies of CF levels of the ground $^4I_{15/2}$ and the excited $^4I_{13/2}$ multiplets of Er^{3+} ion in $ErFe_3(BO_3)_4$. More lines appear at higher temperatures, due to population of higher levels according to the Boltzmann distribution. Seven lines that remain at low temperatures represent the structure of the CF levels of the excited multiplet $^4I_{13/2}$ (fig.3a). Further identification of the CF levels with energies higher than that of the level 3 (see fig.2) over high-temperature spectra is not possible. That is due to substantial broadening of the spectral lines at temperatures above 150 K. To increase the absorption of the spectral lines corresponding to the transitions from the excited levels of the ground multiplet, we measured the spectra of a much thicker sample (fig.3b). The analysis of these spectra at different temperatures allowed us to determine the energies of all the eight levels of the ground multiplet $^4I_{15/2}$. Table 1 presents the data on the CF levels of the two lowest multiplets of Er^{3+} in $ErFe_3(BO_3)_4$.

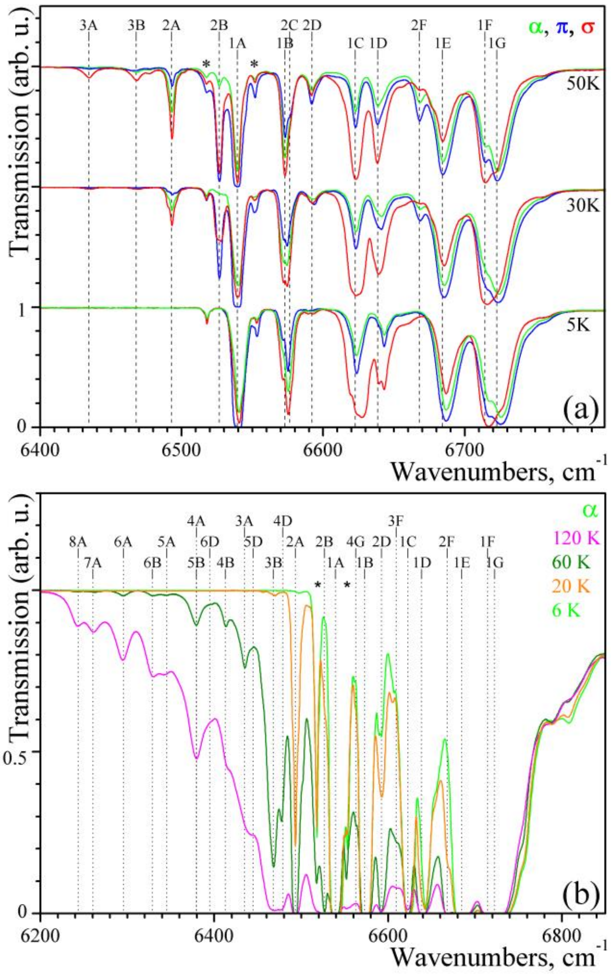

Fig.3. Transmisson spectra of $ErFe_3(BO_3)_4$ in the region of the $^4I_{15/2}\rightarrow{}^4I_{13/2}$ optical transition at different temperatures and polarizations for a sample with the thickness d=0.15mm (a) and for an α-polarized sample with d=2.016mm (b). The symbol $*$ denotes the spectral lines related to the absorption of an impurity.

Table 1. Energies of CF levels of the Er^{3+} ion in the paramagnetic state of $ErFe_3(BO_3)_4$ (cm^{-1}).

$^4I_{15/2}$	0	46	105	160	194	244	279	296
$^4I_{13/2}$	6539	6573	6623	6639	6684	6714	6723	

The fact that in the low-temperature phase a polarization dependence is still present in the spectra, indicates that deviations from the D_3 local symmetry are small. At temperatures below T_N, the spectral lines split. The splitting of the spectral line 1B into four components (fig.4) allowed us to determine the exchange splitting of the ground level, according to the scheme of fig.2: Δ_0 = 6.3±1 cm^{-1}. The obtained data within the error limit agree with the heat capacity data [7] and the estimate given in Ref. [8] from the spectral data on nonoriented $ErFe_3(BO_3)_4$ samples of a poor quality.

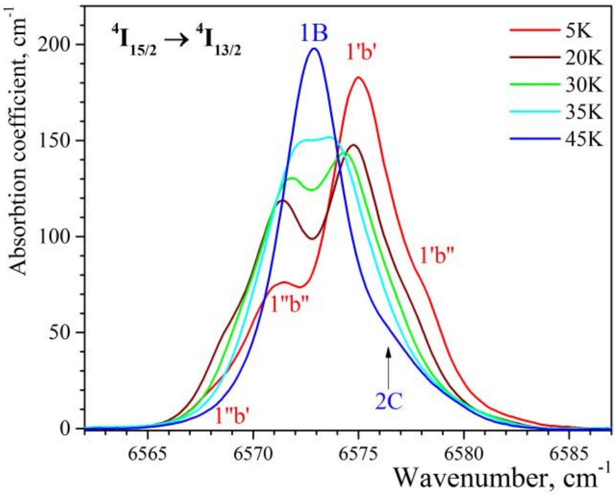

Fig.4. The absorption spectrum of $ErFe_3(BO_3)_4$ in the region of the 1B spectral line of the $^4I_{15/2}\rightarrow{}^4I_{13/2}$ optical transition at several temperatures.

The exchange splitting of the excited level B of the multiplet $^4I_{13/2}$ at T = 5 K is Δ_B = 2.7 ± 1 cm^{-1} (fig.4). Through the analysis of the temperature dependence of the transmission spectra of the thick sample (fig.3b), it was possible to determine the splitting of the first excited Kramers doublet of the ground multiplet $^4I_{15/2}$ (level 2 on fig.2): Δ_2 = 1.7 ± 1 cm^{-1} at T = 5 K. This value was established under the assumption that the nature of the temperature dependences of the exchange splittings is similar for the spectral lines 1B (fig.4), 2A and 2B fig.3b). The obtained data can be used for the explanation of the anomalies in the temperature dependences of the specific heat and magnetic susceptibility of $ErFe_3(BO_3)_4$.

4.3 Temperature dependences of the birefringence

The temperature dependence of the position of the maximum in the interference pattern $\nu_{max}(T)$ reveal two anomalies (see fig.5). The first one is a step-like shift at the temperature of the structural phase transition T_S. A further smooth decrease of ν_{max} with lowering the temperature changes to its growth at about 100 K with a saturation at the lowest temperatures. The low-temperature part of the dependence has an inflection point near T_N. This behavior is evidently associated with a magnetic contribution. An analogous dependence for $ErAl_3(BO_3)_4$, known to have no phase transitions in the studied temperature range, has a practically linear character without pronounced anomalies.

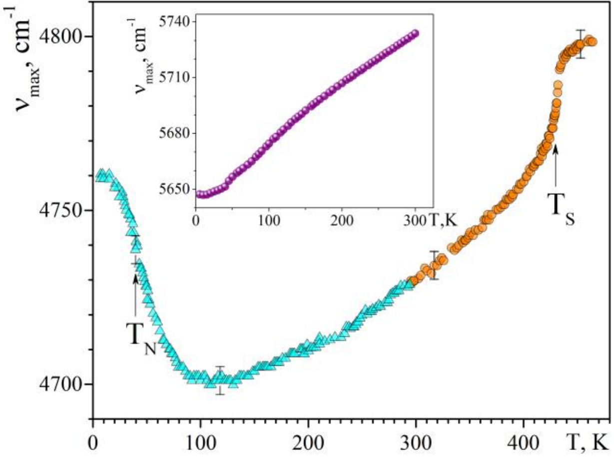

Fig.5. Temperature dependence of the position of one of the maxima in the interference between ordinary and extraordinary rays in $ErFe_3(BO_3)_4$ and $ErAl_3(BO_3)_4$ (inset).

The shift of the interference band is caused both by the temperature change in the refractive index (dielectric constant) of the compound and by its thermal expansion. The work [3] presents data on thermal expansion $\Delta L_a(T)/L_a$ for $RFe_3(BO_3)_4$ crystals (R = Eu, Gd, Tb). For $ErFe_3(BO_3)_4$ these data are not available. We assume that for isostructural compounds the behavior of $\Delta L_a(T)/L_a$ is similar. The maximum change in $\Delta L_a(T)/L_a$ caused by phase transitions is of the order of 10^{-4}. This is two orders of magnitude smaller than the observed relative shift of the maximum of the interference band $\nu_{max}(T)$. Thus, the temperature shift of the interference band is determined mainly by the change in the difference of refractive indices $\Delta n(T) = n_o(T) - n_e(T)$. The change in $\Delta n(T)$ is due to magnetic and lattice contributions. The magnetic contribution is proportional to the average value of the squared magnetization of the sublattices [12]. The lattice contribution consists of a change in birefringence due to the regular thermal expansion and to spontaneous magnetostriction. The spontaneous polarization in $ErFe_3(BO_3)_4$ is also providing a contribution into $\Delta n(T)$ below T_N. The structural phase transition in $RFe_3(BO_3)_4$ is accompanied by anomalies of the dielectric properties associated with the antiferroelectric phase transition. They are naturally related to the anomalies observed in fig.5.

Conclusion

In this work, we have presented the data on the energies of the CF levels of the ground and the first excited multiplets of the Er^{3+} ion in the paramagnetic state of $ErFe_3(BO_3)_4$. The exchange splitting of the ground Kramers doublet was found to be $\Delta_0 = 6.3\pm1$ cm^{-1}. The obtained results are important for the interpretation of thermodynamic and magnetic properties of $ErFe_3(BO_3)_4$. The temperature dependence of the interference occurring due to birefringence in the $ErFe_3(BO_3)_4$ single crystals was investigated. It demonstrates two anomalies near the temperatures of the phase transitions T_N and T_S. Possible contributions into the anomalies were discussed.

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