



## Research articles

Magnetic field induced local structural transformations in the optically excited states  ${}^5F_2$  and  ${}^5F_3$  of  $\text{HoFe}_3(\text{BO}_3)_4$  single crystalA.V. Malakhovskii<sup>a,\*</sup>, S.L. Gnatchenko<sup>b</sup>, I.S. Kachur<sup>b</sup>, V.G. Piryatinskaya<sup>b</sup>, I.A. Gudim<sup>a</sup><sup>a</sup> Kirensky Institute of Physics, 660036 Krasnoyarsk, Russian Federation<sup>b</sup> B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, 61103 Kharkov, Ukraine

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## ABSTRACT

We measured absorption spectra of transitions  ${}^5I_8 \rightarrow {}^5F_2, {}^5F_3$  in  $\text{Ho}^{3+}$  ion in the  $\text{HoFe}_3(\text{BO}_3)_4$  single crystal at temperature 2 K as a function of magnetic field 0–65 kOe directed along *a* and *c* axes. The spectra were decomposed to the Lorentz shape components and magnetic field dependences of their parameters: position, intensity and line width, were obtained. Substantial difference between dependences of the energy and intensity of the transitions on magnetic field was revealed. So, the abrupt changes of the electron transition energies were mainly observed at the reorientation magnetic phase transitions in the crystal. A number of singularities in the magnetic field dependences of the electron transition intensities were revealed both at the reorientation transitions and outside of them. The singularities in the average intensities of transitions into multiplets at the reorientation magnetic transitions are due to the changes of the odd part of the crystal field, responsible for the allowance of *f-f* transitions, and also are due to the changes of the magnetic state. The singularities in behavior of intensity of each separate transition are due to the local even distortions in the excited states, which mix the electron states.

## 1. Introduction

Investigation of the local crystal properties in the vicinity of optically excited atoms becomes important in recent years, especially in view of the possible applications in quantum information processing. The electronic excitation can substantially change interaction of the atom with the environment and so can change the local properties of the crystal [1,2]. In this sense the optically excited atom is similar to an impurity. Investigation of the parity-forbidden optical transitions, such as *f-f* transitions in rare earth (RE) ions, can provide information about the local structural distortions in crystals, as well as about variations of the magnetic moments orientation. Recent studies of the optical properties of trigonal borates  $\text{RFe}_3(\text{BO}_3)_4$  (R is RE element) revealed a number of phenomena related to the local changes of magnetic and structural properties in the vicinity of optically excited states [3–8].

Holmium ferroboration  $\text{HoFe}_3(\text{BO}_3)_4$  is distinguished among the RE ferroboration by well pronounced multiferroic effects [9–11], by a number of phase transitions (magnetic and structural), by non-trivial magnetic moments arrangement and by rather complicated energy spectrum of RE ion. At high temperatures it has huntite-like trigonal structure with the space group  $R\bar{3}2$ , and at about 360 K a structural phase transition reducing the space symmetry to  $P3_121$  ( $D_3^4$ ) occurs

[12–15].  $\text{Ho}^{3+}$  ions occupy a single type positions with the symmetry  $D_3$  in the high-temperature phase and  $C_2$  in the low-temperature phase. At  $T_N = 38$ – $39$  K antiferromagnetic ordering of the crystal takes place [16–18]; strong polarization effect of the iron sublattice on the holmium one leads to simultaneous ordering of both magnetic subsystems. At lowering temperature to  $T_{SR} = 4.7$  K, a spontaneous spin-reorientation phase transition from the easy-plane to the easy-axis state occurs in the crystal as the result of competition of the different sign anisotropies of  $\text{Fe}^{3+}$  and  $\text{Ho}^{3+}$  ions [17,18]. According to the neutron diffraction and X-ray scattering data [17,19] the magnetic structure deviates slightly from the collinear one in both magnetic phases. At  $T < T_{SR}$ , applying the external magnetic field both along the *c* axis and perpendicular to it leads to spin-reorientation phase transitions from the easy-axis to easy-plane state [9,17,18]. The critical fields of the reorientation transitions are about 5.7 kOe for  $H||c$  and about 9.2 kOe for  $H \perp c$  at the temperature 2 K [18].

The spectroscopic study of *f-f* transitions in  $\text{HoFe}_3(\text{BO}_3)_4$  in the region of 8500–24,500  $\text{cm}^{-1}$  in a wide temperature range was carried out by the authors [20]. It was found out that in most of the absorption bands the splitting of the  $\text{Ho}^{3+}$  states and change of the transitions polarizations, corresponding to the symmetry reduction from the  $D_3$  to  $C_2$ , was not observed. Moreover, spectra of some transitions correspond

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to the cubic crystal field splitting. The studying of the spontaneous and the field-induced spin-reorientation phase transitions revealed that the changes of the absorption spectra in both cases are very similar [20,21].

One of the optical transitions of the  $\text{Ho}^{3+}$  ion ( $^5I_8 \rightarrow ^5F_5$ ) in  $\text{HoFe}_3(\text{BO}_3)_4$  was studied at applying external magnetic fields 0–60 kOe along three main crystallographic directions at  $T = 2$  K [21]. A number of specific features which testify to changes of the local properties in the  $\text{Ho}^{3+}$  excited states were found out. So, an appearance of non-equivalent positions of the  $\text{Ho}^{3+}$  ion was found in some excited states that was explained by the local decrease of the space symmetry to the  $C_2$  one. It was revealed that in some excited states the  $\text{Ho}^{3+}$  ion is in the easy-plane state while the total crystal is in the easy-axis state and vice versa. This means that magnetic moment of the  $\text{Ho}^{3+}$  ion in such excited states is perpendicular to the  $\text{Fe}^{3+}$  magnetic moment. Such phenomenon points out the existence of the antisymmetric Fe-Ho exchange interaction in the  $\text{Ho}^{3+}$  excited states. The present paper is devoted to the detailed study of the spectroscopic effects induced by the magnetic field, which are related to changes of the local properties in some excited  $\text{Ho}^{3+}$  states.

## 2. Experimental details

$\text{HoFe}_3(\text{BO}_3)_4$  single crystals were grown from a bismuth trimolibdate solution melt with a nonstoichiometric composition of the crystal forming oxides (details see in Ref. [20]). The sample for optical measurements was 85  $\mu\text{m}$  thick plate cut parallel to the  $bc$  plane; so, the light propagated along the crystallographic axis  $a$  (see Fig. 1). The absorption spectra were measured using linearly polarized light with the electric vector  $E$  parallel (the  $\pi$  spectrum) or perpendicular (the  $\sigma$  spectrum) to the trigonal axis  $c$ . The spectra were registered using a diffraction spectrometer DFS-13 with diffraction grating 600 lines/mm and linear dispersion 0.4 nm/mm. The light intensity at the exit of the spectrometer was measured by linear photodiode array of the optical multichannel analyzer (OMA, model 1450A). The spectral resolution in the studied spectral range was about  $1.5 \text{ cm}^{-1}$ . Magnetic field was applied along  $a$  and  $c$  axes of the crystal. It was created by a superconducting solenoid with the Helmholtz type coils. The superconducting solenoid with the sample was placed in the liquid helium and all measurements in the magnetic field were fulfilled at  $T = 2$  K.

## 3. Results and discussion

There are two main characteristics of  $f-f$  transitions: energy and intensity (probability). The energies of  $4f$  states are defined by the

eigenfunctions of the Hamiltonian [22]:

$$\hat{H}_i(\text{Ho}) = \hat{H}_{CF}^i - g_J \mu_B \vec{J}_i \cdot (\vec{H} + \lambda_{fd} \vec{M}_i) \quad (1)$$

Here  $i$  is the number of sublattice,  $\hat{H}_{CF}^i$  is the crystal field (CF) Hamiltonian, whose form is determined by the symmetry of the local environment of a Ho ion,  $g_J$  is the Landé factor and  $\vec{J}_i$  is the angular momentum operator of the Ho ion,  $\lambda_{fd} < 0$  is the molecular constant of the antiferromagnetic interaction Ho-Fe,  $\vec{M}_i$  is the magnetic moment of the Fe ion. The intensities of electron transitions are defined by non diagonal matrix elements of the electric dipole operator between initial and final states. Parity forbidden  $f-f$  transitions possess additional features. They are allowed due to the mixing of  $4f$  states with the states of the opposite parity by the odd components of the CF, while energies of  $4f$  states are mainly defined by the even part of the CF and also by the  $4f$  ion magnetic moment orientation. Thus, energies and intensities of  $f-f$  transitions provide substantially different information about electron states and about  $4f$  ions environment. As a consequence, the reaction of the energy and intensity of  $f-f$  transitions on the structural and magnetic transformations in crystals can be substantially different. We decomposed the measured absorption spectra into the Lorentz-type components and obtained their parameters (frequency, intensity and line-width) in function of the magnetic field.

### 3.1. Transition $^5I_8 \rightarrow ^5F_2$ (G-band)

As mentioned in the introduction, the local symmetry of the  $\text{Ho}^{3+}$  ion in the crystal at low temperature is  $C_2$ . However, in Ref. [20] it was shown that in a first approximation, at least in the easy axis state, the splitting of the  $\text{Ho}^{3+}$  ion states and the absorption lines polarizations correspond to the  $D_3$  symmetry. At the conversion from a free atom to that in octahedron and further to the  $D_3$  symmetry position, the  $^5F_2$  state of the  $\text{Ho}^{3+}$  ion is transformed in the following way:

$$J = 2 \rightarrow E + T_2 \rightarrow E + (A_1 + E). \quad (2)$$

It was shown [20] that in the  $D_3$  symmetry approximation the ground state of  $\text{Ho}^{3+}$  ion has the  $E$  symmetry. The G1 line (Fig. 2) is observed only in the  $\sigma$ -polarization. Then, according to polarization of the rest of transitions presented in Fig. 2 and according to the selection rules for  $D_3$  symmetry (Table 1), the G1-state is the singlet ( $A_1$ ) and the G2 and G3 states are doublets ( $E$ ) in the  $D_3$  approximation. Therefore, the splitting of the G1 line observed even at  $H = 0$  (Fig. 2, inset) should be referred to the existence of two non-equivalent absorbing centers in the excited state, the same as it took place in the  $^5I_8 \rightarrow ^5F_5$  transition

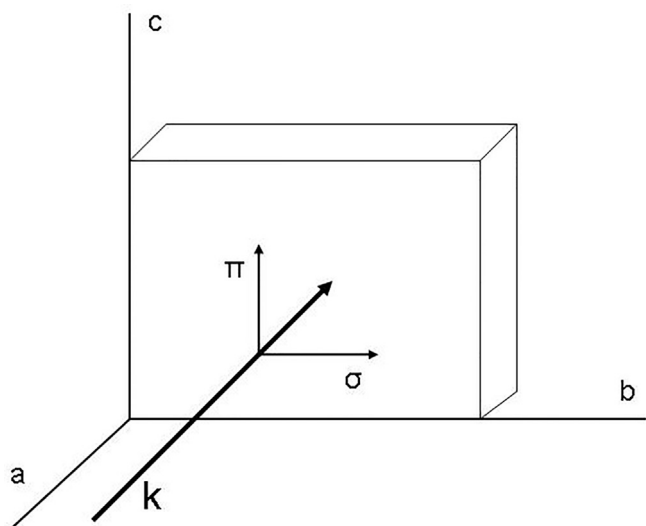


Fig. 1. Diagram of the experiment.

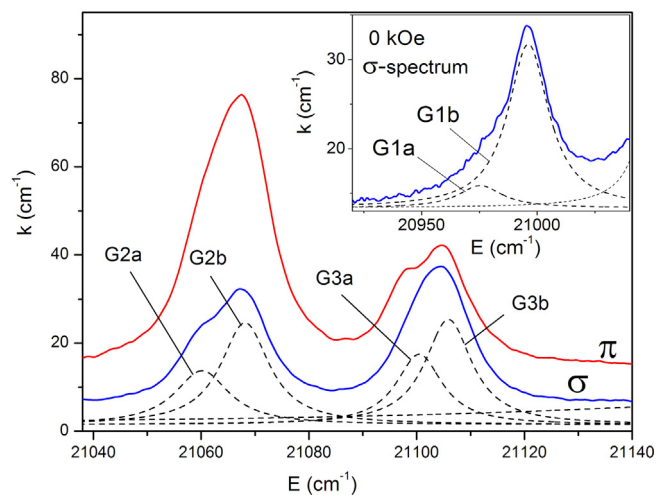


Fig. 2. Absorption spectra of the  $^5I_8 \rightarrow ^5F_2$  transition (G-band) in magnetic field 65 kOe parallel to  $a$ -axis of the crystal. Inset: spectra of G1a and G1b lines in the zero field.

**Table 1**  
Selection rules for electric dipole transitions in  $D_3$  symmetry.

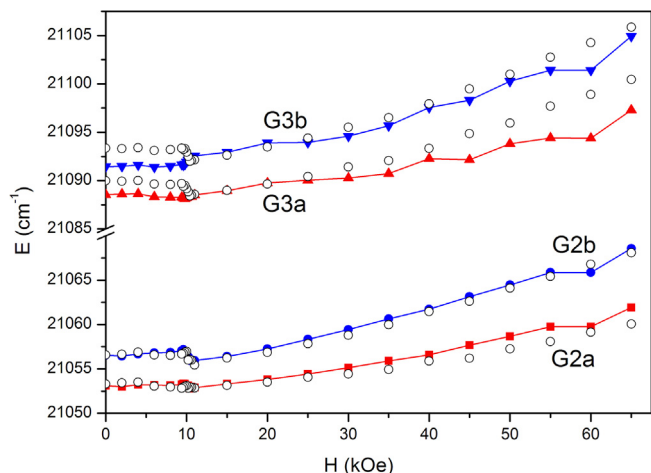
	$A_1$	$A_2$	E
$A_1$	–	$\pi$	$\sigma(\alpha)$
$A_2$	$\pi$	–	$\sigma(\alpha)$
E	$\sigma(\alpha)$	$\sigma(\alpha)$	$\pi, \sigma(\alpha)$

[21]. Small hysteresis in  $\text{HoFe}_3(\text{BO}_3)_4$  magnetization [18] as well as in absorption spectra [21] is observed only in the region of the reorientation transitions. This means that there are no distinct magnetic domains at other magnetic fields, and the splitting cannot be referred to domains. Therefore we can suppose that in the excited state the space symmetry locally decreases to  $C_2$  one. In this group the unit cell of the huntite structure is twice as large and it has four RE ions in  $C_1$  symmetry positions and two RE ions in  $C_2$  symmetry positions [23,24].

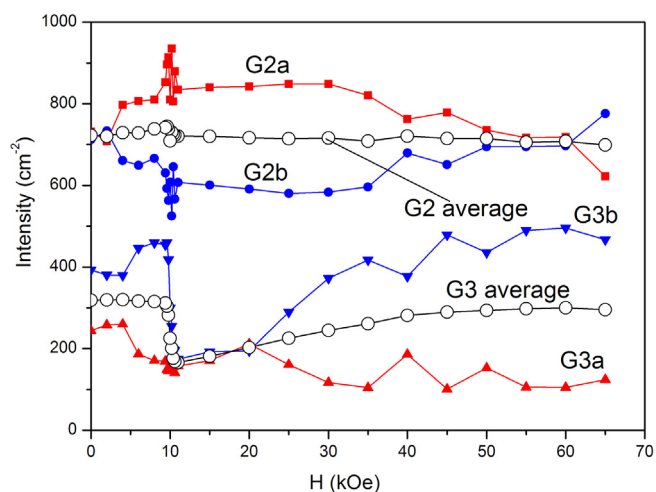
The doublets G2 and G3 can be split (Fig. 2) due to the decrease of the local symmetry of  $\text{Ho}^{3+}$  ion from the  $D_3$  to  $C_2$  one in the crystal, or by the exchange interaction with the Fe sublattice, or due to the appearance of two absorbing centers in the G2 and G3 states or due to all those together. Positions of G3a and G3b lines are different in  $\pi$  and  $\sigma$  polarizations (Fig. 3). This is possible, if in the G3 state there are two absorbing centers with  $C_1$  and  $C_2$  local symmetries, respectively, and if in both of them the doublets are split due to the decrease of the local symmetry or due to the exchange interaction with the Fe sublattice or due to both of them. There are actually four lines in the G3 spectrum (Fig. 3), but it is impossible to separate them totally. The splitting between G3a and G3b lines as a function of magnetic field does not change below the reorientation transition and only slightly changes after it and only in the  $\pi$ -polarization (Fig. 3). Consequently, orientation of the  $\text{Ho}^{3+}$  magnetic moment almost does not change in the considered excited states as a function of the magnetic field (excluding area of the reorientation transition). This testifies to the strong local magnetic anisotropy, connected with the local CF of the low symmetry, and therefore we can infer that the splitting of the G3 line is mainly due to the existence of two absorbing centers in the G3 excited state and due to the decrease of the local symmetry in both of them.

In contrast to the energy of lines, there is a strong changing of the G3a and G3b absorption intensities with the magnetization (Fig. 4), that testifies to a substantial changing of the 4f wave functions under the influence of the local deformations. Largest local deformations occur at the reorientation transition, but substantial deformations are also observed outside the transition (Fig. 4). Properties of these deformations will be discussed below.

Positions of the G2 lines in  $\pi$  and  $\sigma$  polarizations are identical in the



**Fig. 3.** Energies of  $\pi$ -polarized components of the  ${}^5I_8 \rightarrow {}^5F_2$  transition (G-band) as a function of magnetic field  $H||a$ . Circles refer to  $\sigma$ -polarization.



**Fig. 4.** Intensities of  $\pi$ -polarized components of the  ${}^5I_8 \rightarrow {}^5F_2$  transition (G-band) as a function of magnetic field  $H||a$ .

range of the experimental error (Fig. 3). Consequently, the splitting between G2a and G2b lines can be either due to the exchange interaction with the Fe sublattice or due to the decrease of the local symmetry or due to both of them. However the latter cause is preferable by the same reason as in the case of the G3 lines. Behavior of the G2 lines intensities shows (Fig. 4) that the local CF changes in the G2a and G2b states symmetrically in opposite directions. The largest local deformations in the G2 state also occur at the reorientation transition.

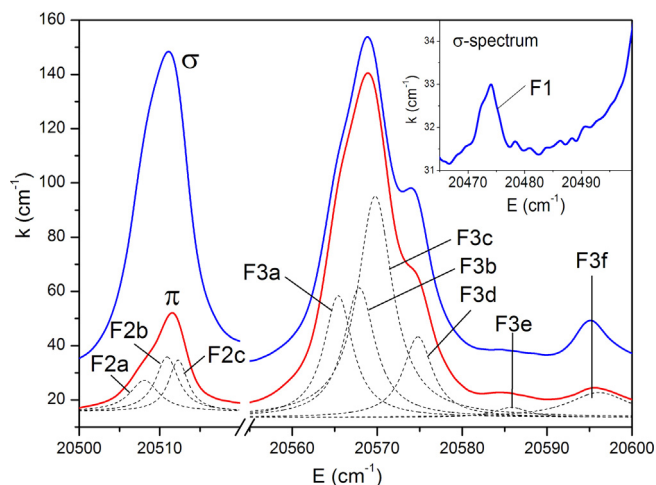
Behavior of the G2a, G2b, G3a and G3b lines positions and intensities in the field  $H||c$  is similar to that in the field  $H||a$ . This testifies that orientation of the  $\text{Ho}^{3+}$  magnetic moments in these cases is also similar. In particular, it is almost independent of the magnetic field. The weak influence of the external magnetic field on the states energy shows that magnetic anisotropy connected with the crystal field is strong in these states.

### 3.2. Transition ${}^5I_8 \rightarrow {}^5F_3$ (F-band)

At the conversion from a free atom to that in octahedron and further to the  $D_3$  symmetry position, the  ${}^5F_3$  state of the  $\text{Ho}^{3+}$  ion is transformed like this:

$$J = 3 \rightarrow A_2 + T_1 + T_2 \rightarrow A_2 + (A_2 + E) + (A_1 + E). \quad (3)$$

The transition F1 (Fig. 5, inset) is mainly  $\sigma$ -polarized. Then according to selection rules of Table 1, the F1 state is the singlet  $A_2$  in the



**Fig. 5.** Absorption spectra of the  ${}^5I_8 \rightarrow {}^5F_3$  (F-band) in the zero magnetic field.

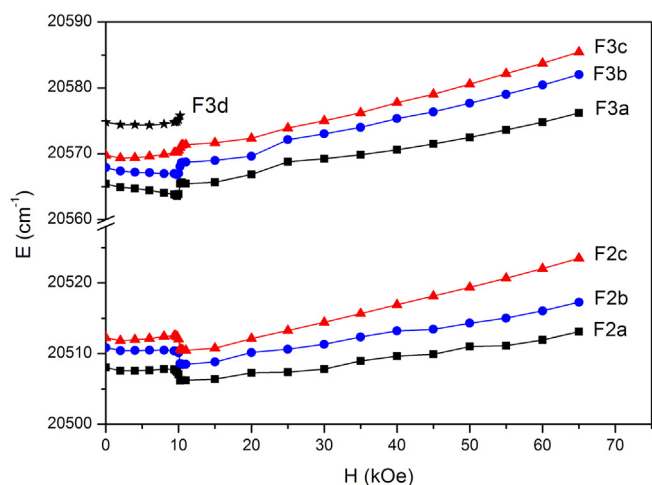


Fig. 6. Energies of  $\pi$ -polarized components of the  ${}^5I_8 \rightarrow {}^5F_3$  transition (F-band) as a function of magnetic field  $H||a$ .

$D_3$  symmetry approximation, while other singlet states, which also should be purely  $\sigma$ -polarized in the  $D_3$  symmetry, cannot be identified in this symmetry approximation. Consequently, this symmetry approximation is not suitable for interpretation of the rest spectrum. However the F2 and F3 manifolds (second and third terms in (3)) are three fold degenerated and can be split into three states with the symmetry decrease to the  $C_2$  one (Fig. 5).

For the beginning, we shall consider behavior of F2 and F3 bands in magnetic fields  $H||a$ . The energies of multiplets F2 and F3 as a function of the magnetic field  $H||a$  (Fig. 6) are identical in both polarizations within the limit of the experimental error. Consequently, we can suppose that the splitting are not connected with the different absorbing centers. One of the components in F2 and F3 manifolds is singlet already in the  $D_3$  symmetry. Another two components of F2 and F3 manifolds are caused by the splitting of the  $E$ -type states due to the decrease of the local symmetry or due to the exchange interaction with the Fe-sublattice. In the  $C_2$  symmetry all transitions are active both in  $\pi$  and  $\sigma$  polarizations according to the selection rules of Table 2 and according to the transformation of the ground state:  $E \rightarrow A_1 + A_2$  at the decrease of the symmetry. (However the real splitting of the ground state was not proved.) Thus, it is difficult to identify states, which were singlet  $A_1$  and  $A_2$  in the  $D_3$  symmetry. With some probability it is possible to suppose that they are F2c and F3c states, since their energies almost have no features in dependence on the magnetic field (Fig. 6). The F3e and F3f lines (Fig. 5) were earlier identified as vibrational repetitions of the F2 electron transition [20]. Nature of the F3d transition is not clear. It is only possible to suppose that the F3d line is connected with the low frequency vibrations appeared in the  $P3_121$  symmetry [25]. Its strong dependence on magnetization testifies to a strong coupling between the lattice and magnetic degrees of freedom. In particular, the F3d line disappears at the reorientation transition and above it in the field  $H||a$  (Fig. 7).

In contrast to the energies of the transitions their intensities change substantially and sometimes not monotonically as a function of magnetic field not only in the region of the reorientation transition, but in the whole field interval (Figs. 7, 8). This testifies to the local distortions

Table 2

Selection rules for electric dipole transitions in  $C_2$  symmetry. Polarizations are shown relative to the local  $C_2$  axis. Polarizations relative to the trigonal axis of the crystal are shown in brackets.

	$A_1$	$A_2$
$A_1$	$\pi$ ( $\sigma$ )	$\sigma$ ( $\pi, \sigma$ )
$A_2$	$\sigma$ ( $\pi, \sigma$ )	$\pi$ ( $\sigma$ )

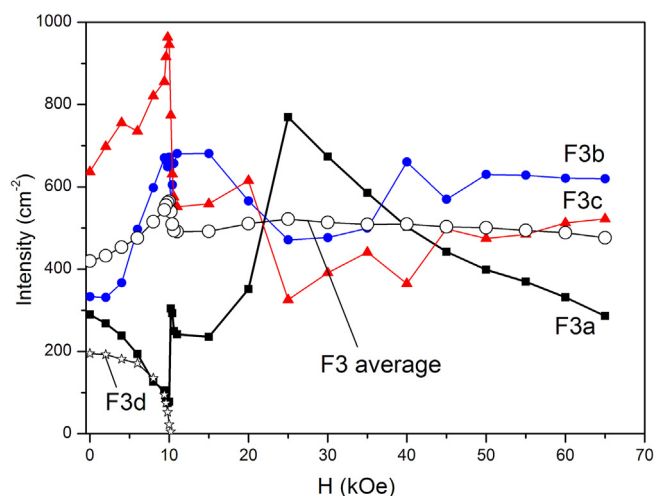


Fig. 7. Intensities of  $\pi$ -polarized components of the F3 manifold as a function of magnetic field  $H||a$ .

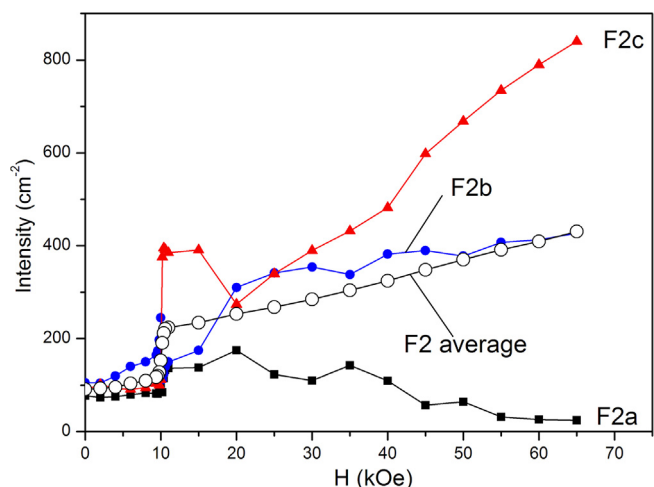


Fig. 8. Intensities of  $\pi$ -polarized components of the F2 manifold as a function of magnetic field  $H||a$ .

as a function of magnetization. A strong singularity in the field dependence of the F3a line intensity at 25 kOe (Fig. 7) testifies to the singularity in the CF dependence in the corresponding excited state. In the same magnetic field a small singularity is observed also in the F3a and F3b energy dependences (Fig. 6). Pronounced field dependences of the line widths are also observed (Fig. 9). These dependences rather good correlate with those of the line intensities (Fig. 7), that testifies to the mainly homogeneous broadening of the lines.

Positions and intensities of the lines as a function of magnetic field  $H||c$  are shown in Figs. 10–12. There is a singularity in the field dependence of intensity of the F2a and F2c lines at 20 kOe (Fig. 11). Only a small feature is observed at this field in the dependence of the energy of the F2a line (Fig. 10). The line F3d, which disappeared above the reorientation transition, appeared again above 40 kOe (Fig. 12). Pronounced features in the F3a, F3b and F3c intensities behavior are observed in the region of 15 kOe (Fig. 12). Some features are observed in the same field in the energy of the lines F3a and F3b, but not F3c (Fig. 10). Most strong singularities are observed in the behavior of the F3a and F3c lines intensity at 40 kOe (Fig. 12). Between 40 and 45 kOe the abrupt change of the F3a line intensity occurs. The corresponding abrupt change of the spectrum is demonstrated in Fig. 13. It is interesting to note that the abrupt change of the energy is revealed in the F3b line (Fig. 10), but not in the lines F3a and F3c, which demonstrate the strong change of intensity. Apparently, the change of the energy is

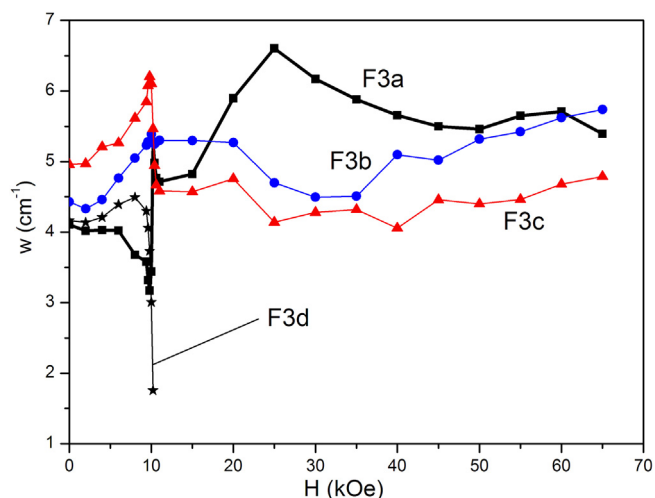


Fig. 9. Line widths of  $\pi$ -polarized components of the F3 manifold as a function of magnetic field  $H||a$ .

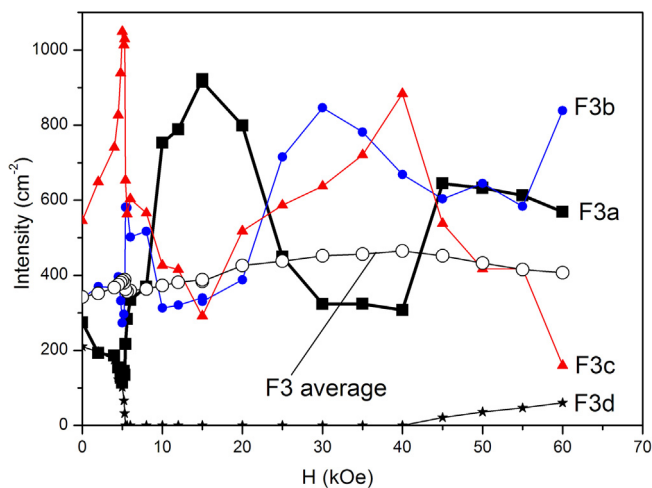


Fig. 12. Intensities of  $\pi$ -polarized components of the F3 manifold as a function of magnetic field  $H||c$ .

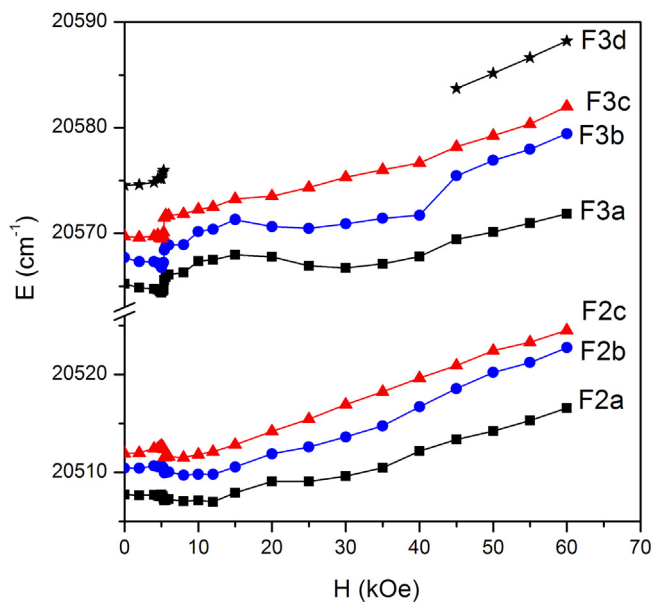


Fig. 10. Energies of  $\pi$ -polarized components of the  ${}^5I_8 \rightarrow {}^5F_3$  transition (F-band) as a function of magnetic field  $H||c$ .

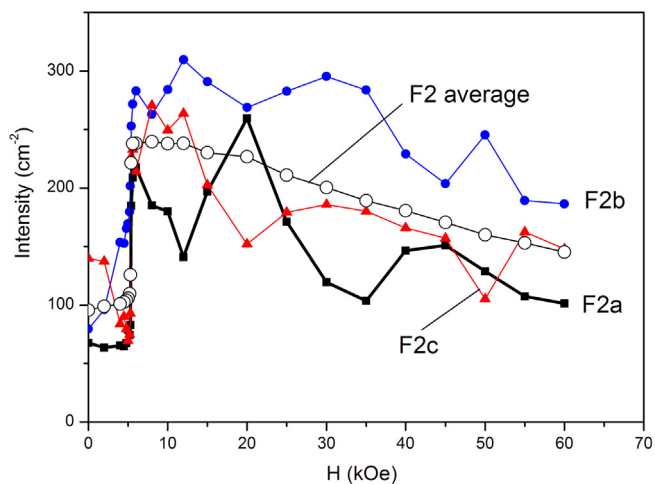


Fig. 11. Intensities of  $\pi$ -polarized components of the F2 manifold as a function of magnetic field  $H||c$ .

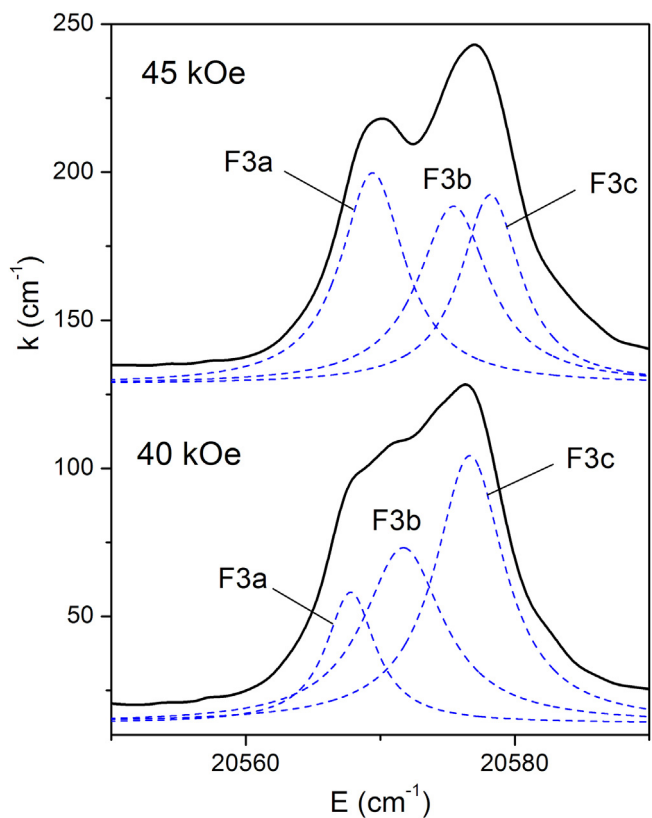


Fig. 13. Absorption spectra of the F3 manifold in magnetic field  $H||c$ .

connected with the change of the local magnetic state in the F3b electron state.

Now it is necessary to pay attention to one feature which is common for all transitions: average intensities of the G2, G3, F2 and F3 transitions have steps only at the reorientation phase transitions (Figs. 4, 7, 8, 11, 12). Consequently, only in this moment the odd part of the CF, responsible for the allowance of  $f-f$  transitions, abruptly changes due to the magnetostriction. Additionally, the electron transition probability can depend on the magnetic moment reorientation due to the magnetic dichroism. Then the question arises: what is the nature of the observed large changes of intensities of components of the G2, G3, F2 and F3 transitions in the magnetic fields outside the reorientation transitions? The splitting of the considered states in the zero magnetic field are very

small:  $3\text{--}6\text{ cm}^{-1}$ . Therefore a weak perturbation is enough for the mixing of the close states and for the redistribution of probabilities of the corresponding transitions. It is evident that such perturbation should be even, since functions of the same parity are mixed. Already the magnetic field itself could be such perturbation. However, the magnetic field changes uniformly. Thus, we can infer that the structural deformations due to the magneto-striction occur in the corresponding excited states.

#### 4. Summary

Absorption spectra of transitions  $^5I_8 \rightarrow ^5F_2$ ,  $^5F_3$  in  $\text{Ho}^{3+}$  ion in the  $\text{HoFe}_3(\text{BO}_3)_4$  single crystal were measured at temperature 2 K in magnetic fields 0–65 kOe directed along  $a$  and  $c$  axes. The spectra were decomposed to the Lorentz shape components and magnetic field dependences of their parameters: position, intensity and line width, were obtained. Substantial difference between dependences of the energy and intensity of the transitions on magnetic field was revealed. The energies of  $4f$  states are defined by the eigenfunctions of the  $\text{Ho}^{3+}$  ion Hamiltonian. Crystal field is the main part of this Hamiltonian, but changes of the states energy as a function of magnetic field are also due to changes of magnetic system. So, the abrupt changes of the transitions energy were observed at the reorientation transitions. However, the abrupt change of the energy of one of the states in the  $^5F_3$  manifold was also revealed in the field  $H||c$  between 40 and 45 kOe that testified to the local change of the magnetic state in this electron state. A number of singularities in the magnetic field dependences of the transition intensities were revealed. The singularities in the average intensities of transitions into multiplets at the reorientation magnetic transitions are due to the changes of the odd part of the crystal field, responsible for the allowance of  $f\text{--}f$  transitions, and also are due to the changes of the magnetic state. The singularities in behavior of intensity of each separate transition are due to the local even distortions in the excited states, which mix the electron states.

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