Transformation of the HoFe$_3$(BO$_3$)$_4$ absorption spectra at reorientation magnetic transitions and local properties in the excited $^5F_5$ states of the Ho^{3+} ion

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Polarized absorption spectra of the $^5I_8 \rightarrow {}^5F_5$ transition of the Ho^{3+} ion in the HoFe$_3$(BO$_3$)$_4$ single crystal were measured at $T = 2$ K as a function of magnetic field 0–60 kOe directed along the a, b, and c axes of the crystal. The spin-reorientation transitions were observed in the field $H\|c$ at 5.35 kOe, in the field $H\|a$ at 10.25 kOe, and in the field $H\|b$ at 9.1 kOe. We also observed a small hysteresis of the transitions. We found that the optical properties of the crystal change as a function of the magnetic field orientation in the basal plane in spite of the nominally axial symmetry of the crystal. We found a number of specific local properties in the Ho^{3+} excited states. Nonequivalent positions of the Ho^{3+} ion appear in some excited states. It was shown that during one of the electron transitions the local symmetry changes not only in the excited state but in the ground state as well. We observed local metamagnetic transitions in some Ho^{3+} excited states. In some excited states, the 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 the magnetic moments of the Fe^{3+} and Ho^{3+} ions in these excited states of the Ho^{3+} ions are mutually perpendicular. Such phenomenon testifies to the existence of the antisymmetric Fe-Ho exchange interaction in the Ho^{3+} excited states.

I. INTRODUCTION

Among the family of rare-earth trigonal ferroborates RFe$_3$(BO$_3$)$_4$ (where R is the rare-earth element), holmium ferroborate attracts an interest due to its strongly pronounced multiferroic properties. It implies the simultaneous existence of at least two different ordering parameters—magnetic, electric, or elastic ones. The HoFe$_3$(BO$_3$)$_4$ crystal demonstrates a large spontaneous electric polarization arising below the temperature of magnetic ordering and a giant magnetodielectric effect—change of dielectric constant in an external magnetic field [1–3]. These properties open the perspectives for manifold applications of the compound.

The HoFe$_3$(BO$_3$)$_4$ crystal, as well as other rare-earth ferroborates, has a trigonal huntitelike structure. It crystallizes in $R32$ space group structure and then, with lowering temperature, around 360–366 K (for powder samples 427 K), undergoes a structural phase transition, reducing its symmetry to the $P3_121$ (D_3^4) space group [4–7]. In both phases, there is a single type position for the rare-earth ion, but the local symmetry of this position reduces from the D_3 to C_2 one at the transition from the $R32$ to $P3_121$ space symmetry.

Besides the structural transformation, the holmium ferroborate possesses two magnetic phase transitions. At $T_N = 38 - 39$ K, a simultaneous ordering of iron and rare-earth magnetic subsystems takes place, forming the easy-plane magnetic structure [8–10]. Further, at $T_{SR} = 4.7$ K, the competition between the Fe^{3+} and Ho^{3+} anisotropies results in a spontaneous spin-reorientation phase transition from the easy-plane to the easy-axis state [9,10]. The neutron diffraction measurements [9] indicated that the magnetic structure deviates from the collinear one in both phases. The x-ray scattering studies [11] allowed the authors to suppose that the Ho magnetic moments

form an ab-plane spin spiral propagating along the c axis in the easy-plane phase. At $T < T_{SR}$, in an external magnetic field applied both along the trigonal axis c and perpendicular to it, a spin-reorientation phase transition from the easy-axis to the easy-plane state occurs [1,9,10]. The critical fields of the reorientation phase transition were found to be about 5.7 kOe for $H\|c$ and about 9.2 kOe for $H\perp c$ at 2 K [10]. In Ref. [12], a theoretical analysis of the HoFe$_3$(BO$_3$)$_4$ magnetic properties was made in the molecular field approximation and the parameters of crystal field and exchange interaction were calculated.

The first study of optical absorption spectra of HoFe$_3$(BO$_3$)$_4$ single crystals in the infrared region (500–10 000 cm^{-1}) was presented in Ref. [7]. Using the high-resolution spectroscopy method, the authors studied the magnetic and structural phase transformations. Particularly, an abrupt change of the doublet line splitting of Ho^{3+} at the spontaneous spin-reorientation phase transition was revealed.

A detailed spectroscopic study of the ff transitions of HoFe$_3$(BO$_3$)$_4$ in the region of $8500-24\,500$ cm^{-1} in the temperature range including T_{SR} was carried out in Ref. [13]. It was found that both the spontaneous and the field-induced spin-reorientation transitions result in identical changes of the absorption spectra. It was also found that the crystal-field splitting of the states, corresponding to symmetry reduction from D_3 to C_2, is practically not observed in the spectra.

All properties of crystals directly depend on the electronic structure of atoms which the crystal consists of. An electronically excited atom is, actually, an impurity atom, and, consequently, the local properties of its environment and of the atom itself can change. In particular, our spectroscopic study of the Nd$_{0.5}$Gd$_{0.5}$Fe$_3$(BO$_3$)$_4$ single crystal [14–16] has shown that the local magnetic properties of the crystal in the optically excited states of the Nd^{3+} ion substantially differ from those in the ground state. The investigation of the local properties of crystals in the optically excited

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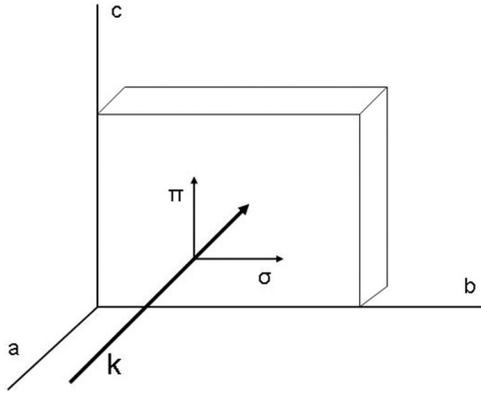
FIG. 1. Diagram of the experiment.

states becomes important in connection with the problem of quantum information processing. In the present work, we have undertaken a spectroscopic study of the $HoFe_3(BO_3)_4$ single crystal in the region of the optical transition $^5I_8 \rightarrow {}^5F_5$ in the Ho^{3+} ion in an external magnetic field in order to find the local properties of the crystal in the excited states of the Ho^{3+} ion.

II. EXPERIMENTAL DETAILS

$HoFe_3(BO_3)_4$ single crystals were grown from a bismuth trimolibdate solution melt with a nonstoichiometric composition of the crystal forming oxides (for details see Ref. [13]). The sample was cut in the bc plane and a magnetic field was applied in three directions: a, b, and c (Fig. 1). The absorption spectra were measured with the light propagating normally to the c axis of the crystal for the light electric vector $\vec{E}$ parallel (the π spectrum) and perpendicular (the σ spectrum) to the c axis. The spectra were registered using a diffraction spectrometer with linear dispersion 0.2 nm/mm. The spectral resolution in the studied spectral range was about $1 \, \text{cm}^{-1}$. A magnetic field was created by a superconducting solenoid with the Helmholtz-type coils. A superconducting solenoid with the sample was placed in the liquid helium and all measurements in the magnetic field were fulfilled at $T = 2 \, \text{K}$.

III. RESULTS AND DISCUSSION

Polarized absorption spectra of the $^5I_8 \rightarrow {}^5F_5$ transition (D band) of the Ho^{3+} ion in the $HoFe_3(BO_3)_4$ single crystal were measured at $T = 2 \, \text{K}$ as a function of magnetic field 0–60 kOe directed along the a, b, and c axes of the crystal. The spectra were decomposed to the Lorentz shape components and the field dependences of their parameters were obtained.

As mentioned in Introduction, the local symmetry of the Ho^{3+} ion in the crystal at low temperature is C_2. However, in Ref. [13], it was shown that in a first approximation, at least in the easy-axis state, the splitting of the Ho^{3+} ion states and the change of the absorption lines polarizations corresponding to the transition from the D_3 to the C_2 local symmetry were not observed. Figure 2 presents the total spectra of the $^5I_8 \rightarrow {}^5F_5$ transition (D band) in zero magnetic field and after the reorientation phase transition in the field $H \| b$. The changes of the line intensities are the consequence of the magnetic linear
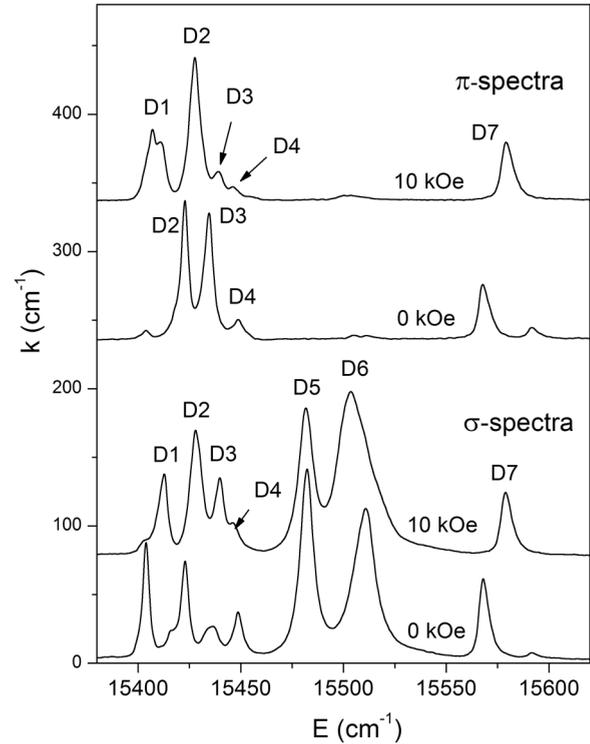
FIG. 2. Absorption spectra of the $^5I_8 \rightarrow {}^5F_5$ band in zero magnetic field and after the reorientation phase transition in the magnetic field $H \| b$ at $T = 2 \, \text{K}$.

dichroism, and they are the result of the change of the mutual orientation of the light polarization and magnetization.

The identification of electron states in the easy-axis state of the crystal in the D_3 symmetry approximation goes as follows [13]: the ground state has the E symmetry and

$$D1 - A, \quad D2 - E, \quad D3 - E, \quad D4 - E,$$
$$D5 - A, \quad D6 - A, \quad D7 - E. \tag{1}$$

This identification was obtained with the help of the selection rules of Table I and is based on the line polarizations (Fig. 2). Since all measurements were fulfilled at $T = 2 \, \text{K}$, the crystal in the zero magnetic field is in the easy-axis state. Therefore we will consider the spectra measured in zero magnetic field in the D_3 local symmetry approximation. In Ref. [13], it was also shown that the Ho^{3+} ion in the ground state has $M_J = 4$ in the $|J, \pm M_J\rangle$ wave function approximation and an exchange splitting $\Delta E = 11.7 \, \text{cm}^{-1}$. Such value of the exchange splitting permits us to consider that at $T = 2 \, \text{K}$, only transitions from the lower component of the ground state doublet are observed. According to Ref. [12],

TABLE I. Selection rules for electric dipole transitions in D_3 symmetry.

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

TABLE II. 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	$\sigma\,(\pi,\sigma)$	$\pi\,(\sigma)$

immediately after the reorientation transitions in a magnetic field, the Fe^{3+} moments are approximately in the basal plane, same as after the temperature induced reorientation transition [9]. Therefore, immediately after these transitions, the absorption spectra of the Ho^{3+} ions exchange coupled with the Fe^{3+} ions mainly coincide [13].

A. Transitions into singlet states

According to (1), we should consider transitions into D1, D5, and D6 states. In the D_3 symmetry, these transitions should be σ-polarized (Table I). The D1 line demonstrates unique behavior as compared with other transitions in the singlet states: after the field-induced or spontaneous transitions into the easy-plane state, the D1 line (and only D1 line) appears in the π-polarization (see Fig. 2 and Ref. [13]). (A small absorption in the π polarization in the easy-axis state can be due to a small deviation of the Ho^{3+} local symmetry from the D_3 one, since nominally should be the C_2 symmetry.) Transitions D1, D5, and D6 have identical initial and final states, and the final states are singlet; however, only the D1 transition changes polarization after the reorientation magnetic transitions. This is possible only if the local symmetry in the initial state of the D1 transition changes. Indeed, only after a transformation of the ground state: $E \rightarrow A_1 + A_2$ at the decrease of the local symmetry from the D_3 to C_2 one, the π polarization of the considered transition is possible according to the selection rules of Table II. Such decrease of the local symmetry in the ground state during the electron transition is possible since according to the perturbation theory, electron transitions occur due to mixing of initial and final states by perturbation caused by the electromagnetic wave. Therefore, during the electron transition, the initial state of the ion and its interaction with the environment also change. In particular, the local symmetry in the ground state decreases, and the transition becomes allowed in the π polarization. Such behavior of the D1 line permitted us to retrace the process of the magnetic phase transitions (Fig. 3). The spin-reorientation transition in the field $H\|c$ was observed at 5.35 kOe at 2 K. The value of the field of the spin-reorientation transition at $H\perp c$ was found to depend on the orientation of the external field in the basal plane. In particular, it is 10.25 kOe when $H\|a$ and 9.1 kOe when $H\|b$. We also observed a small hysteresis: 0.15 kOe in the field $H\|a$ and 0.20 kOe in the field $H\|b$. The smallest hysteresis (<0.1 kOe) was observed at $H\|c$.

Figures 4–8 demonstrate the transformation of the D1 transition spectrum and the change of the component energies in magnetic fields $H\|a$, $H\|b$, and $H\|c$. The absorption spectra in the fields $H\|a$ and $H\|b$ are appreciably different (Fig. 4). In the conditions of the experiment (Fig. 1), the
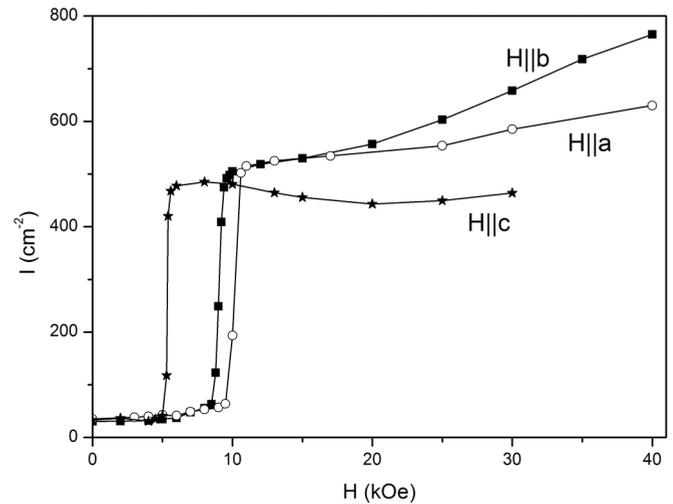
FIG. 3. Intensity of the D1 transition in π polarization at $T = 2$ K as a function of magnetic field of different orientations. All three dependencies were measured at increasing field.

magnetic-dependent part of the dielectric tensor rotates by $90°$ relative to the light beam direction, when the magnetic field rotates from a to b direction. Therefore the absorption spectra should change due to magnetic linear dichroism, even if there is no magnetic anisotropy in the basal plane and the magnetic parts of the dielectric tensor are identical for $H\|a$ and $H\|b$. However, Figs. 5 and 6 show that not only the intensities but also the energies of the D1 transitions in magnetic fields
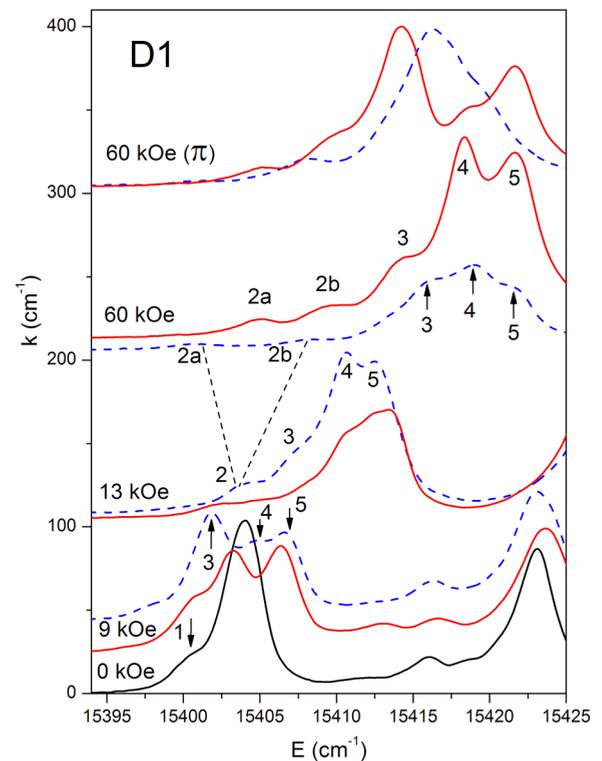
FIG. 4. σ-polarized absorption spectra of the D1 transition at $T = 2$ K in magnetic field $H\|b$ (solid lines) and $H\|a$ (dash lines). At 60 kOe π-polarized spectra are also shown.
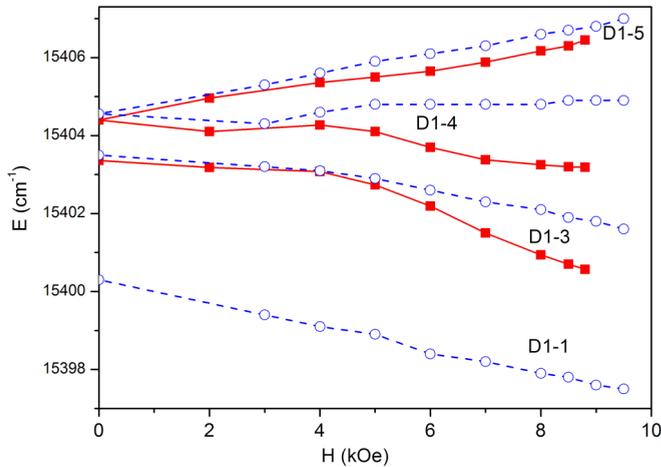
FIG. 5. Energies of the σ-polarized absorption lines in the D1 transition as a function of magnetic field $H \| b$ (solid lines) and $H \| a$ (dash lines) below the reorientation phase transition.

$H \| a$ and $H \| b$ reveal different behavior. In contrast to the line intensities, the energies of electron transitions cannot change depending on the orientation of the magnetization in the basal plane if there is no magnetic anisotropy in the basal plane. Consequently, magnetic anisotropy in the basal plane exists. Additionally, the π-polarized spectra would be identical for $H \| a$ and $H \| b$, if there were no magnetic anisotropy in the basal plane (see diagram of the experiment in Fig. 1). However, these spectra are substantially different (Fig. 4). The magnetic anisotropy can be connected with the anisotropy of magnetostriction and with the corresponding deformations of the crystal, depending on the direction of the magnetic field. However, the main feature of the discussed spectra is the splitting of the D1 line in spite of the singlet character of the excited state [see (1)]. It is necessary to emphasize that in spite of the splitting, the spectra remain σ-polarized in the easy-axis state till the magnetic transitions, i.e., the local mainly trigonal symmetry does not change.

FIG. 7. σ-polarized absorption spectra of the D1 transition in magnetic field $H \| c$.

There are two main observations for discussion: (1) the total number of absorption lines, corresponding to transitions into the nominally singlet states, and (2) the magnetic field dependencies of the splitting of some absorption lines. Five lines are observed in the D1 transition (see Figs. 4–8): three strong lines D1-3, 4, 5 and two weak lines D1-1, 2. We suppose that the weak lines are connected with the crystal defects. However, in the field $H \| c$, these lines are strongly increased in the easy-plane state of the crystal (Fig. 7). The strong lines

FIG. 6. Energies of absorption lines in the D1 transition as a function of magnetic field $H \| b$ (solid lines) and $H \| a$ (dash lines) above the reorientation phase transition.
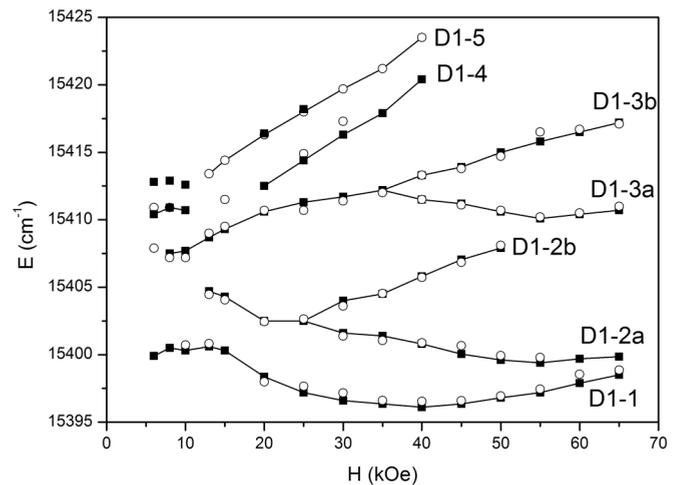
FIG. 8. Energies of the π-polarized (circles) and the σ-polarized (squares) absorption lines in the D1 transition as a function of magnetic field $H \| c$.

are, most probably, due to nonequivalent absorbing centers. There are possible at least two kinds of such centers: (1) those connected with the magnetic anisotropy in the basal plane and (2) centers connected with the local decrease of the space symmetry in the excited states to the $C2$ symmetry [17]. In a number of alumoborates such modification of the crystals was revealed experimentally in the ground electron state [18]. In the former case, in the unit cell of the $P3_121$ space symmetry, there are three equivalent positions of the rare-earth (RE) ion with three directions of the C_2 axis. If the magnetic field is directed along one of a axes (C_2 axes), then there are two nonequivalent positions: the a axis parallel and not parallel to the field. If the magnetic field is directed along one of the b axes, then there are three nonequivalent positions. On the contrary to the $P3_121$ space symmetry, the unit cell of the huntite structure in the $C2$ space symmetry is twice as large and it has four RE ions in C_1 symmetry positions and two RE ions in C_2 symmetry positions [17,18]. From Figs. 5 and 6, it is seen that the number of strong components does not depend on the field orientation in the basal plane. Therefore the latter assumption is more presumable.

The behavior of the D1 line energies in magnetic fields $H\|a$ and $H\|b$ below the spin-reorientation transition (Fig. 5) shows that the RE ions in one of the nonequivalent positions (C_1 or C_2) have magnetic moments in the excited state induced by the exchange field of the iron sublattice (Van-Vleck magnetism). These magnetic moments are oriented antiferromagnetically in the exchange field of the iron. An external magnetic field removes the sublattice degeneration. Below, it will be seen that the D1-4 and D1-5 lines refer to one position and the D1-3 line corresponds to another position of the Ho^{3+} ion in which the field of anisotropy is large. In zero magnetic field, the energies of the Ho^{3+} ion in the D1 state in these positions are different (Fig. 5).

In magnetic fields below the reorientation transitions, i.e., in the easy-axis state of the crystal in the ground electron state, the electron transitions should split linearly in the field $H\|c$ and very weak and nonlinearly in the field $H\perp c$ (see, e.g., Ref. [19]). The D1 transition in the first position (D1-4 and D1-5 lines) reveals opposite behavior, typical for an easy-plane state (Figs. 4, 5, and 7), i.e., it is not split in the field $H\|c$ and splits in the field $H\perp c$. Additionally, the behavior of the splitting in the fields $H\|a$ and $H\|b$ is appreciably different due to anisotropy in the basal plane (Fig. 5). Consequently, the Ho^{3+} ion in the D1 electron state (the first position) is locally in the easy-plane state in spite of the easy-axis state of the total crystal in the ground electron state of the Ho^{3+} ion. Thus the magnetic moments of the Fe and Ho ions are mutually perpendicular.

In Ref. [12], for the HoFe$_3$(BO$_3$)$_4$ crystal, the authors suggested the following Hamiltonians of Ho and Fe ions from the ith sublattice ($i = 1,2$) in the presence of a magnetic field:

$$\hat{H}_i(\text{Ho}) = \hat{H}_{\text{CF}}^i - g_J\mu_B\vec{J}_i \cdot (\vec{H} + \lambda_{fd}\vec{M}_i), \qquad (2)$$

$$\hat{H}_i(\text{Fe}) = -g_S\mu_B\vec{S}_i \cdot (\vec{H} + \lambda\vec{M}_j + \lambda_{fd}\vec{m}_i). \qquad (3)$$

Here, $\hat{H}_{\text{CF}}^i$ is the crystal field Hamiltonian, whose form is determined by the symmetry of the local environment of a Ho ion in the ground state, g_J is the Landé factor, and

$\vec{J}_i$ is the operator of the angular momentum of the Ho ion, $g_S = 2$ is the Landé factor and $\vec{S}_i$ is the operator of the spin moment of an iron atom, $\lambda_{fd} < 0$ is the molecular constant of the antiferromagnetic interaction Ho-Fe, and λ (including $\lambda_1 < 0$ and $\lambda_2 < 0$) are the constants of the Fe-Fe intrachain and interchain antiferromagnetic interactions, respectively, $\vec{M}_i$ and $\vec{m}_i$ are the magnetic moments of the Fe and Ho ions, respectively. The interaction inside the RE subsystem is not taken into account, since it is negligibly small.

However, it is important that the Hamiltonians (2) and (3) do not take into account the anisotropic and antisymmetric exchange, which can be the reasons of the peculiar magnetic properties of the Ho ion in the excited states. In particular, antisymmetric exchange Fe-Ho,

$$\hat{H} = \vec{D} \cdot [\vec{S}_i \times \vec{J}_i] \qquad (4)$$

can provide the mutually perpendicular orientation of the magnetic moments of Fe and Nd ions that is really observed in the D1 and in some other excited states (see below). $\vec{D}$ in Eq. (4) is a constant vector. It is necessary to note that some manifestations of the antisymmetric exchange occur in the ground state as well. The neutron diffraction measurements [9] have shown that in the easy-axis state there are significant components of the Ho magnetic moments in the a directions, while Fe magnetic moments are strictly in the c direction.

In the easy-plane state of the crystal, the energies of the D1-3, 4, 5 lines change appreciably differently in $H\|a$ and $H\|b$ (Fig. 6) due to the magnetic anisotropy in the basal plane, but they change qualitatively as if a and b were the hard directions. According to Fig. 8, the c axis is also the hard direction for transitions D1-4, 5. The shapes of the line energy dependencies on the magnetic field are defined by the competition between the magnetic field, the exchange field Fe-Ho (H_E), and the anisotropy field (H_A). If $H_A \geqslant H_E$, then the spin-flop transition does not occur. However, when the external magnetic field $H \geqslant H_A$, the antiferromagnetic states of the excited Ho^{3+} ions transform into the ferromagnetic one in the magnetic field. This form of transition is known as a metamagnetic transition [20]. In the field $H\|c$, the local metamagnetic phase transition in the D1-3 state occurs at approximately 35 kOe (Fig. 8). Such phenomena were earlier observed in Nd$_{0.5}$Gd$_{0.5}$Fe$_3$(BO$_3$)$_4$ single crystals [16]. The splitting of the D1-3 line testifies that it was indeed not split before because of the large field of anisotropy and that it refers to another absorbing center than lines D1-4 and D1-5 refer.

The D1-2 line connected with defects appears only in the easy-plane state of the crystal and reveals a magnetic field dependent splitting in magnetic fields $H\|a, H\|b$, and $H\|c$ (Figs. 4, 6, 7, and 8). The D1-2 state demonstrates a metamagnetic phase transition in the field $H\|c$ at 25 kOe (Figs. 7 and 8). If we express the splitting through the effective Landé factor, $\Delta E = \mu_B g H$, then we obtain $g_c = 7.1$ for the D1-2 state and $g_c = 6$ for the D1-3 state in the field $H\|c$. The D1-2 state starts to split in the field $H\|a$ immediately after the reorientation transition (Fig. 6). This means that the field of anisotropy is weak, but increases with the magnetic field, that reveals in a nonlinear dependence of the splitting on the magnetic field. Thus the a axis is indeed the easy axis in the D1-2 state.
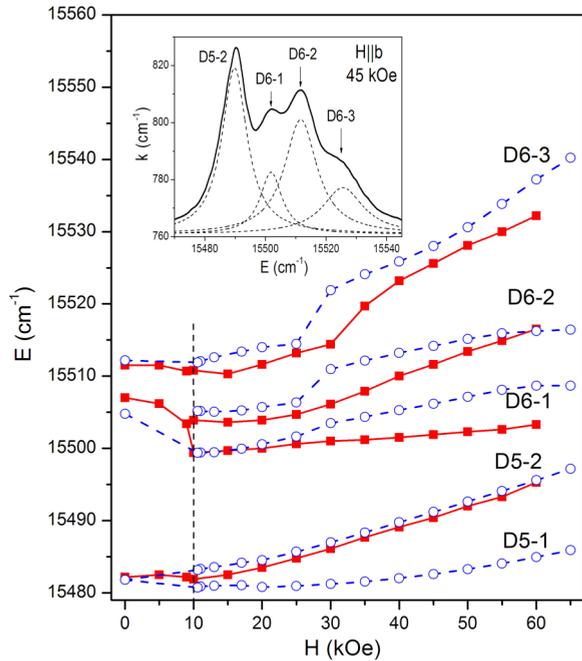
FIG. 9. Energies of the σ-polarized absorption lines in the D5 and D6 transitions as a function of magnetic field $H\|a$ (circles) and $H\|b$ (squares). Inset: Absorption spectrum of the σ-polarized D5 and D6 lines in the magnetic field $H\|b$ at 45 kOe.

The properties of transitions D5 and D6 into singlet states substantially differ from those of the D1 transition. They do not appear in the π polarization after magnetic transitions with increasing temperature or magnetic field (Ref. [13] and Fig. 2). Consequently, a substantial deviation from the D_3 symmetry during D5 and D6 electron transitions does not take place in all magnetic states. Nevertheless, a splitting of the states occurs (Figs. 9 and 10). The splitting of the D5 state in the zero field is very small, if any. The D5 state does not split in the field $H\|b$, but splits in the fields $H\|a$ and $H\|c$ after the spin-reorientation transitions (Figs. 9 and 10). Taking into account the above, we conclude that the D5 state acquires a magnetic moment in
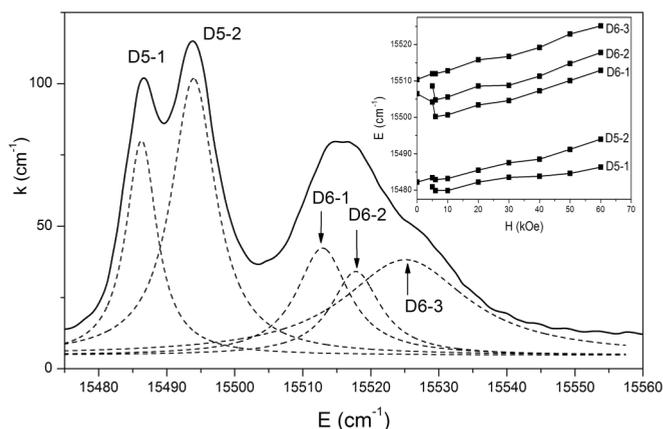
FIG. 10. Absorption spectrum of the σ-polarized D5 and D6 lines in the magnetic field $H\|c$ at 60 kOe. Inset: Energies of the σ-polarized absorption lines in the D5 and D6 transitions as a function of magnetic field $H\|c$.

the fields $H\|a$ and $H\|c$ after the reorientation transitions, but does not acquire it in the field $H\|b$. However, in both cases, the absorption refers to the identical centers, i.e., the local space symmetry in the D5 state does not change. The splitting between D5-1 and D5-2 states depends on $H\|a$ not linearly (Fig. 9). The linear part of the splitting corresponds to $g_a = 6.3$. The field depending splitting between D5-1 and D5-2 states in the field $H\|c$ (Fig. 10) approximately corresponds to $g_c = 2.7$. It means that after transition of the crystal into the easy-plane state in the ground electron state, the local anisotropy of the Ho^{3+} ion in the D5 excited state is not strictly of the easy-plane type.

The D6 state splits both in magnetic field and without it (Figs. 9 and 10). In the zero field it splits into two components, but after magnetic transitions, it splits into three components. The splitting before the reorientation transitions is due to the two absorbing centers. Additional splitting of the D6 line above the reorientation transitions both in the fields $H\|a$ and $H\|b$ (Fig. 9) means that one of the centers acquires a magnetic moment. The difference between the energy dependencies in fields $H\|a$ and $H\|b$ (Fig. 9) testifies to the magnetic anisotropy in the basal plane. The dependencies of the D6 component energies on the magnetic field $H\|c$ after the reorientation transition (Fig. 10, inset) show that in the D6 excited state, first, there are two nonequivalent absorbing centers, second, one of the centers acquires a magnetic moment and, third, there is a strong easy-plane anisotropy ($g_c = 0$) the same as it takes place in the ground state of the crystal.

B. Transitions into doublet states.

States D2, D3, D4, and D7 are doublets [see Eq. (1)]. The absorption spectra, energies, and intensities of absorption lines as a function of magnetic fields $H\|a$, $H\|b$, and $H\|c$ are shown in Figs. 11–16. First of all, it is necessary to note that the same as in the case of the singlet states, not only the intensities, but also the energies of transitions substantially depend on the orientation of the external magnetic field in the basal plane (Figs. 11–13). The electron transitions into doublets can be split into two components in the exchange and in the external magnetic fields if the Landé factor of the state is not zero. However, some transitions are split into more than two components (Figs. 12, 13, 15, and 16). Consequently, in some excited states, the nonequivalent absorbing centers appear.

In the D4 state, the Ho^{3+} ion is in the easy-plane state according to the dependences of the line energies on magnetic fields $H\|a$ and $H\|b$ below the spin-reorientation transitions (Figs. 12 and 13), when the whole crystal is in the easy-axis state. However, in the field $H\|b$ (Fig. 13), the components of the splitting D4-1 and D4-2 appear only near the spin-reorientation transition and an additional independent on magnetic field component D4 appears which is probably due to another absorbing center. Till $H = 2\,\mathrm{kOe}$ in the c direction (Fig. 15, inset), the Ho^{3+} ion in the D4 state is in the easy-plane state. At $H_c = 2\,\mathrm{kOe}$, a local metamagnetic transition to the easy-axis ferromagnetic state with $g_c = 14.6$ occurs.

After the reorientation transitions in the fields $H\|a$ and $H\|b$, the D4 state is not split (Figs. 12 and 13). This means that the Landé factor $g_\perp = 0$ and a nonequivalent absorbing
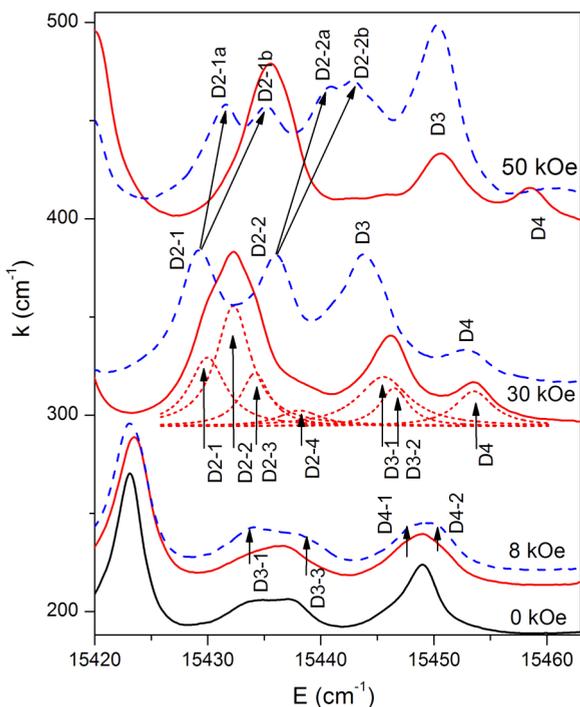
FIG. 11. σ-polarized absorption spectra of the D2, D3, and D4 transitions in magnetic field $H\|b$ (solid lines) and $H\|a$ (dash lines).

FIG. 13. Energies of the σ-polarized absorption lines in the D2, D3, and D4 transitions as a function of magnetic field $H\|b$. Inset: Intensities of the σ-polarized absorption lines in the D2 transition as a function of magnetic field $H\|b$.

center does not appear in the D4 excited state in these fields. Additionally, $g_\perp = 0$ shows that a and b are hard directions for the Ho^{3+} ion in this electron state, while the whole crystal is in the easy-plane state. In the field $H\|c$, the D4 state is split after the reorientation transition (Figs. 14 and 15). This splitting almost does not depend on the field till 35 kOe. Therefore we can suppose that the additional line is due to the exchange splitting of the D4 state into states with magnetic moments lying in the basal plane with the strong easy-plane anisotropy. In $H_c > 40$ kOe, the D4-1 line disappears. However, the linear extrapolation of the D4-1 state energy to higher fields

shows that in $H_c > 40$ kOe a field-dependent splitting appears, which approximately corresponds to $g_c = 4.6$. In this field, the magnetic energy starts to exceed the energy of the anisotropy and a metamagnetic transition to the ferromagnetic state along the c axis occurs.

In zero field and in the fields of all orientations before the reorientation transitions, the D3 state is split into three sublevels (Figs. 12, 13, and 15). Two of them can be referred to the exchange splitting of the state of one absorbing center, and the third sublevel can be referred to the state of another absorbing center, which is not split by the exchange interaction. A strong field of anisotropy quenches almost any changes of the magnetic state in magnetic fields of all orientations below the reorientation transitions. After the reorientation transition, the D3 state is not split in the field $H\|a$ (Fig. 12), but is split in the field $H\|b$ (Figs. 11 and 13). The splitting in $H\|b$ is apparently due to two absorbing centers appearing in the D3

FIG. 12. Energies of the π-polarized (triangles) and the σ-polarized (squares) absorption lines in the D2, D3, and D4 transitions as a function of magnetic field $H\|a$.
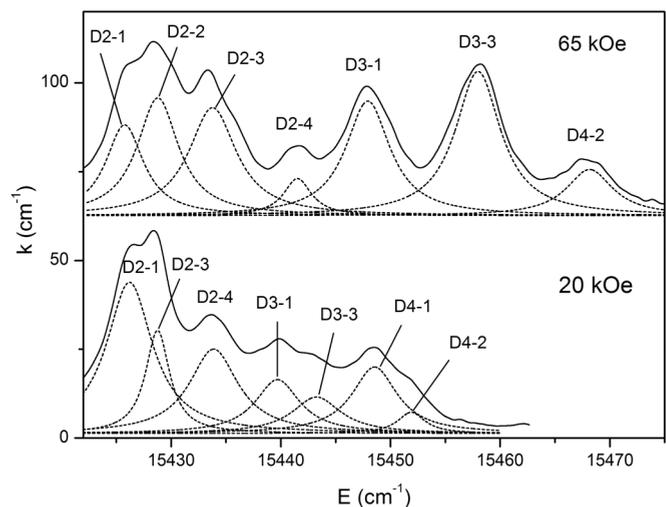
FIG. 14. σ-polarized absorption spectra of the D2, D3, and D4 transitions in magnetic field $H\|c$.
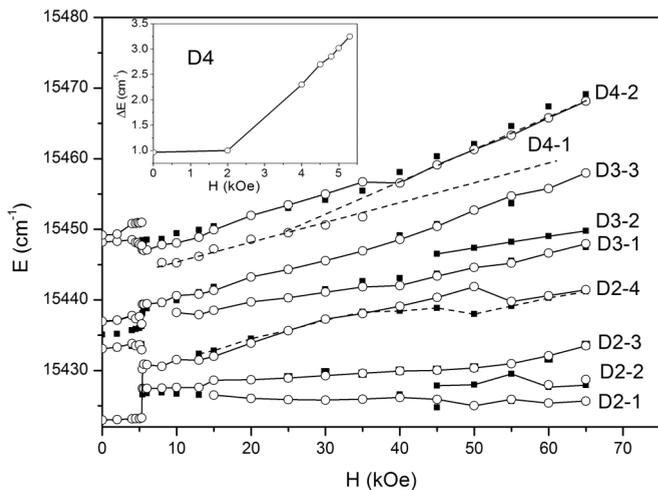
FIG. 15. Energies of the σ-polarized (circles) and π-polarized (squires) absorption lines in the D2, D3, and D4 transitions as a function of magnetic field $H\parallel c$. Inset: splitting of D4 line as a function of magnetic field below the reorientation transition.

state or due to the exchange splitting. In both cases $g_\perp \approx 0$. The D3-1 and D3-3 lines in the field $H\parallel c$ (Fig. 15) can be considered as a splitting of the E-type state of one of the centers with $g_c = 3.4$. The difference of g_c from zero and $g_\perp \approx 0$ means that the Ho^{3+} ion in this excited state is in the easy-axis state opposite to the whole crystal. The D3-2 line that appears in π-polarization above 45 kOe can be referred to the state of another absorbing center with $g_c = 0$.

The D2 transition in magnetic fields of all orientations is not split before the reorientation transitions (Figs. 12, 13, and 15). Above the reorientation transition, the D2 line is split into four components. However, the behavior of the components as a function of magnetic field and their nature are substantially different at different orientations of the field. In the field $H\parallel b$ (Fig. 13), the D2-1,2,3 components are mutually dependent (see intensities in Fig. 13 inset), while the line D2-4 is independent and weak. Therefore we can conclude that lines
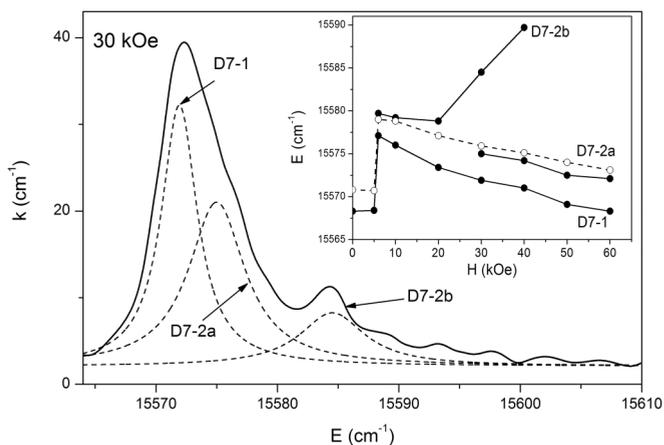
FIG. 16. σ-polarized absorption spectrum of the D7 transition in magnetic field $H\parallel c$. Inset: Energies of the σ-polarized (circles) and π-polarized (open circles) absorption lines in the D7 transition as a function of magnetic field $H\parallel c$.

D2-1,2,3 refer to two nonequivalent centers in one unit cell, while the D4 line refers to the defect centers. However, at $H = 25$ kOe, in all centers in the D2 state, a local distortion of the lattice occurs (see Fig. 13 inset). We can suppose that the state of one center in the $C2$ unit cell is split by the exchange field after the reorientation transition in the field $H\parallel b$, but the state of another center is not split and so we obtain three lines (Figs. 11 and 13). The influence of the increasing external field $H\parallel b$ is quenched by the increasing field of anisotropy induced by the magnetostriction (Fig. 13).

We suppose that in the field $H\parallel a$ the D2-1 and D2-2 lines (Figs. 11 and 12) refer to two nonequivalent centers. The linear in the field $H\parallel a$ splitting of D2-1 and D2-2 states (Fig. 12) begins from 30 and 40 kOe, respectively. This splitting testifies to the local metamagnetic transitions to a ferromagnetic state in the corresponding electron states. The splitting corresponds to $g_a = 4.3$ and 4.9, respectively.

The dependences of the D2 components energies on the field $H\parallel c$ resemble to some extent those in the field $H\parallel b$ (compare Figs. 15 and 13). However, there is no splitting between states D2-1, 2, 3 in the field $H\parallel c$ at the reorientation transition, but there is a linear in the field splitting between states D2-1 and D2-3 corresponding to $g_c = 2.3$, i.e., the ion in the D2 electron state is not in the easy-plane state in contrast to the crystal in the ground electron state.

The absorption spectrum of the D7 line does not change in fields $H\parallel a$ and $H\parallel b$, but changes and splits in the field $H\parallel c$ (Fig. 16). The splitting observed in the zero field and just after the reorientation transition of the crystal in the field $H\parallel c$ (Fig. 16, inset) apparently corresponds to two absorbing centers. In the field $H\parallel c$, the D7-2 state, which refers to one of the centers of the Ho^{3+} ion, reveals a metamagnetic transition at $H \sim 20$ kOe (Fig. 16, inset) to the ferromagnetic state along the c axis with $g_c = 13.9$.

Till now, we classified electron states in terms of irreducible representations of the D_3 point group. However, in crystals with the axial symmetry, there is one more approach to the classification of states. Electron states in such crystals are characterized by the crystal quantum number μ. In trigonal crystals it has values: $\mu = 0, +1, -1$ for states with the integer momentum [21]. Additionally, in the uniaxial crystals, the electron states can be described in a first approximation by the $|J, \pm M_J\rangle$ wave functions of the free atom. Between the values of μ and M_J there is a correspondence [21], presented in Table III. The irreducible representations of the states are also given in Table III. The Landé factor in the c direction in the $|J, \pm M_J\rangle$ wave functions approximation is $g_{cM} = 2gM_J$, where $g = 1.4$ is the Landé factor of the free atom in the studied $^5F_5$ state (see Table III). The states A_1 and A_2 with $|M| = 3$ are of the type $(\langle M_+| \pm \langle M_-|)$ and the splitting between them is very small in crystals with strong uniaxial anisotropy [19]. The studied crystal certainly does not have strong uniaxial anisotropy. In particular, the large values of $g_\perp$ in some excited states testify to this. Nevertheless, the data for the Landé factors presented in Table III show that there is some correlation between theoretical and experimental Landé factors of excited states in the c direction. It is necessary to note that the majority of the Landé factors g_c were measured in fields above the transition of the crystal to the easy-plane state, when the Fe magnetic moments are in the basal plane. At the

TABLE III. Identification of states in irreducible representations (Γ) and in the $|J,\pm M_J\rangle$ function approximation. μ is the crystal quantum number, g_{cM} is the theoretical Landé factor in the c direction in the $|J,\pm M_J\rangle$ function approximation, and g_c is the experimental Landé factor in the c direction. The two values of g_c for the D4 state correspond to the easy-axis and easy-plane states of the crystal, respectively. The two values of g_a for the D2 state and the two values of g_c for the D1 state correspond to two absorbing centers.

μ	0	± 1	∓ 1	0	0	± 1	∓ 1
M_J	0	± 1	± 2	± 3	± 3	± 4	± 5
Γ	A_2	E	E	A_1	A_2	E	E
g_{cM}	0	2.8	5.6	8.4	8.4	11.2	14
g_c	0	2.3	3.4	6, 7.1	2.7	14.6, 4.6	13.9
g_a	$\neq 0$	4.3, 4.9			6.3		
states	D6	D2	D3	D1	D5	D4	D7

same time, g_c of the Ho^{3+} ions corresponds to an orientation of their moments along the c axis after the local metamagnetic transition. In these conditions the Heisenberg exchange Fe-Ho is equal to zero.

IV. SUMMARY AND CONCLUSIONS

Polarized absorption spectra of the $^5I_8 \rightarrow {}^5F_5$ transition (D band) of the Ho^{3+} ion in the HoFe$_3$(BO$_3$)$_4$ single crystal were measured at $T = 2$ K as a function of magnetic field 0–60 kOe directed along the a, b, and c axes of the crystal. The spectra were decomposed into the Lorentz shape components and the field dependencies of their parameters were obtained.

One of the absorption lines in the studied band appears in the π-polarization, when the crystal transfers from the easy-axis to the easy-plane state. Such behavior of the line permitted us to retrace the process of the magnetic phase transitions at $T = 2$ K. The spin-reorientation transition in the field $H\|c$ was observed at 5.35 kOe. The value of the field of the spin-reorientation transition at $H\perp c$ was found to depend on the orientation of the field in the basal plane. In particular, it is 10.25 kOe when $H\|a$ and 9.1 kOe when $H\|b$. We also observed a small hysteresis: 0.15 kOe in the field $H\|a$, 0.20 kOe in the field $H\|b$, and < 0.1 kOe at $H\|c$.

The observed appearance of one of the $E\rightarrow A$ transitions in the π polarization is possible, if during this transition the local symmetry changes not only in the excited state but in the ground state as well. Such decrease of the local symmetry in the ground state during the electron transition is possible since according to the perturbation theory electron transitions occur due to mixing of the initial and final states by perturbation caused by the electromagnetic wave. Therefore, during the electron transition, the initial state of the ion and its interaction with the environment also change.

Not only the intensities but also the energies of the absorption lines and their field dependencies change as a function of the magnetic field orientation in the basal plane in spite of the nominally axial symmetry of the crystal. This can be accounted for by magnetic anisotropy caused by anisotropy of magnetostriction.

The transitions $E\rightarrow A$ into the singlet states are split into several lines in zero external magnetic field and as a function of magnetic field. Weak lines were referred to the crystal defects and the strong ones were referred to two nonequivalent positions of the Ho^{3+} ion in the unit cell of the $C2$ space group, which locally appears in the considered excited states. Similar nonequivalent positions appear also in the doublet E states.

The exchange field of the Fe sublattice induces magnetic moments in the singlet states of the Ho^{3+} ions and orientates them. An external magnetic field removes the sublattice degeneration and splits absorption lines. The local metamagnetic transitions were observed in some A and E excited states.

In some excited states, the 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 the magnetic moments of the Fe^{3+} and Ho^{3+} ions in these excited states of the Ho^{3+} ions are mutually perpendicular. Such phenomenon testifies to the existence of the antisymmetric Fe-Ho exchange interaction.

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