Research articles

Magnetic linear dichroism and features of the local magnetic structure of HoFe$_3$(BO$_3$)$_4$ single crystal in $^5F_2$ and $^5F_3$ excited states of Ho^{3+} ion

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ABSTRACT

We measured spectra of magnetic linear dichroism (MLD) of $^5I_8 \rightarrow {}^5F_2$, $^5F_3$ transitions in the basal plane of the HoFe$_3$(BO$_3$)$_4$ single crystal in the light propagated along the trigonal *c*-axis at temperature 2 K as a function of magnetic field 0 – 65 kOe directed along *a* and *b* axes. The substantial anisotropy of the MLD in the basal plane was revealed. The anisotropy of the MLD is strongly different for different electron transitions, that is, the MLD is mainly connected with the excited electron states. Transformations of the MLD spectra permitted us to retrace variations of the Ho ion magnetic moment orientation in different excited electron states as a function of the magnetic field. It was shown that in the excited states the local Ho magnetic moments do not reveal reorientation transitions synchronously with that of the Fe-sublattice. A small splitting of the ground doublet of the Ho^{3+} ion was observed during certain electron transitions. This means that during these electron transitions the local crystal field can change not only in the excited but in the ground state as well.

1. Introduction

Rare-earth ferroborates RFe$_3$(BO$_3$)$_4$ (where R is a rare earth element) with trigonal huntite-like crystal structure demonstrate a wide variety of magnetic properties and multiferroic effects [1–3]. Most of the ferroborates are antiferromagnets with ordering temperatures in the range of 30–40 K. Their magnetic ordering is conditioned predominantly by exchange interaction within the Fe subsystem; the rare-earth subsystem acquires magnetic order due to the *f-d* exchange interaction with Fe ions. Multifarious magnetic properties of rare-earth ions give rise to a large variety of magnetic structures of the ferroborates.

Among the members of the RFe$_3$(BO$_3$)$_4$ family, holmium ferroborate HoFe$_3$(BO$_3$)$_4$ attracts an interest due to rather non-trivial magnetic properties. The crystal orders antiferromagnetically at $T_N \approx$ 38–39 K [4–7], forming easy-plane magnetic structure. At lowering temperature to T_{SR} = 4.7 K, a spontaneous spin-reorientation phase transition to easy-axis magnetic state occurs [5,6]. In both phases, the magnetic structure deviates from the collinear one. So, in the easy-axis state ($T < T_{SR}$) magnetic moments of Fe^{3+} are strictly collinear to the trigonal *c*-axis, while Ho^{3+} moments have also a component parallel to the basal plane and these components form a basal plane spiral propagating along the trigonal axis [5]. At $T > T_{SR}$, in the easy-plane state, the Fe sublattice

moment has a non-zero component along the trigonal *c*-axis [5]. Applying magnetic field along any of the main crystallographic directions at $T < T_{SR}$ leads to reorientation of the magnetic moments to the basal plane [5,6,8,9]. 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 [6]. The dielectric and magnetoelectric experiments on HoFe$_3$(BO$_3$)$_4$ reveal giant magnetodielectric effect and the existence of a spontaneous polarization below the Neel temperature which suddenly drops to zero at T_{SR} [8]. This effect has not been observed before in rare earth iron borates.

The holmium ferroborate crystallizes in trigonal structure with the space group $R32$, and, as many of the ferroborate crystals, undergoes a symmetry reducing phase transition to $P3_121$ (D_3^4) with the lowering temperature. The temperature of the structural phase transition in HoFe$_3$(BO$_3$)$_4$ is about 360 K for single crystals grown from a solution-melt [10,11] and 427 K for the powder samples obtained by the solid-state synthesis [12]. Ho^{3+} ions occupy a single type positions with the symmetry D_3 in the $R32$ phase and C_2 in the low-temperature $P3_121$ phase.

There are three main kinds of optical investigations of crystals: absorption spectra, magnetic circular dichroism and magnetic linear dichroism spectra. The study of the HoFe$_3$(BO$_3$)$_4$ absorption in the infrared

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spectral region using the high-resolution spectroscopy method [11] allowed authors to refine the temperature of the structural phase transition and a character of magnetic spontaneous phase transformations in the crystal. The spectroscopic study of $HoFe_3(BO_3)_4$ [13] has shown that the spontaneous magnetic phase transition at T_{SR} and the field-induced spin-reorientation phase transitions result in very similar changes in the optical absorption spectra. The study of optical absorption spectra in the external magnetic field [9] revealed a number of peculiar local properties of the crystal in the vicinity of the optically excited $^5F_5$ state of Ho^{3+} ions. For example it was shown, that in some excited states of Ho^{3+} ion its magnetic moment is perpendicular to the Fe^{3+} magnetic moment.

Investigation of magnetic circular dichroism (MCD) and absorption spectra of $HoFe_3(BO_3)_4$ [14] allowed authors to determine the Zeeman splitting of *f-f* transitions and to reveal influence of crystal field on these splitting. Temperature dependences of paramagnetic MCD [15] made it possible to explain the nature of *f-f* transitions allowance.

Magnetic linear dichroism (MLD) is of great interest itself as one more parameter, characterizing *f-f* transitions. Additionally, MLD is the sensitive tool for studying of magnetic structure evolution with temperature or magnetic field [16] and, in particular, in the optically excited states. For example, recent study of neodymium ferroborate [17] revealed a very strong linear dichroism at one of the Nd^{3+} Kramers doublets which appeared in the basal plane of the crystal in magnetic field $H \perp C_3$. Non-trivial field dependences of intensities of the polarized doublet components reflected the change of magnetic moments directions in the ground and excited states of Nd^{3+} ion.

Investigation of weak *f-f* transitions in the optical region of dielectric crystals transparency gives element sensitive tool for study of the local crystal properties in the 4f excited states. Spectral measurements in the X-ray region (see, e. g., [18,19]), the same as spectra of *f-f* transitions in the optical region, are element sensitive, and they also give information about local properties of crystals in the excited but different states. It is necessary to emphasize, that investigation of the local properties of crystals in the excited states of atoms has become important in recent years in connection with the problem of the quantum information processing. In the present paper we have undertaken the first study of MLD in $HoFe_3(BO_3)_4$ crystal. The MLD gave us the unique opportunity to reveal peculiar transformations of the local magnetic structure of Ho ions in the optically excited states of these ions.

2. Experimental details.

The process of growing of holmium ferroborate single crystals was described in Ref. [13]. For the MLD measurements, we used the sample in the form of plane-parallel plate cut perpendicular to the trigonal axis c. The a-axis was directed along the second order axis of the crystal, the b-axis was perpendicular to it in the basal plane. The width of the sample in c-direction was 60 μm. The light wave vector k was directed along the c-axis; the external magnetic field was applied in the basal plane along a or b axis (Fig. 1). The MLD spectra were measured in the region of $^5I_8 \rightarrow$ $^5F_2, ^5F_3$ electron transitions as a difference of the absorption spectra for the light polarized parallel and perpendicular to the magnetic field.

For the recording of absorption spectra we used a DFS-13 diffraction spectrometer with linear dispersion 0.4 nm/mm and an optical multi-channel analyzer OMA 1450A with linear array of photodiodes. The spectral resolution was about 1.5 cm^{-1} in the investigated spectral range. A superconducting solenoid with Helmholtz-type coils was used to create a magnetic field. All spectra were measured at a temperature of 2 K, with the sample immersed in liquid helium.

3. Results and discussion

An absorbed photon excites only one Ho ion in only one sublattice, what can result in a change of magnetic state of the excited ion due to a change of its exchange interaction with the Fe ions and due to a change of the local crystallographic anisotropy of the Ho ion. The exchange
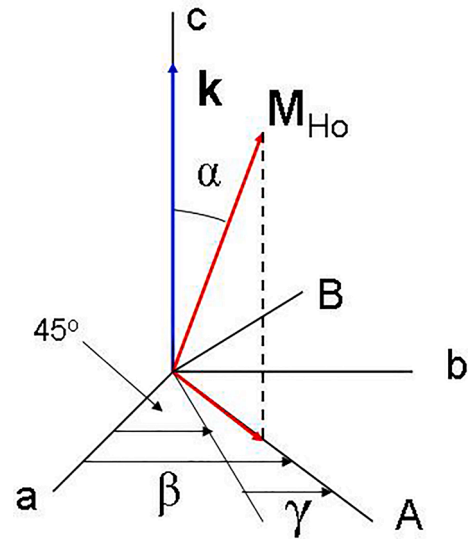

Fig. 1. Diagram of the experiment. The a-axis is directed along the second order axis of the crystal, the b-axis is perpendicular to the a-axis, the c-axis is the trigonal axis of the crystal, and ab plane is perpendicular to the c-axis. k is the light wave vector. α is the angle between magnetic moment of the Ho ion (M_{Ho}) and vector k. A and B are directions of the normal mode polarizations, which are parallel and perpendicular to the projection of M_{Ho} on the ab plane respectively. If the angle between normal mode A and a-axis is 45°, then the measured dichroism k_a-k_b is zero. Angle γ is a deviation of the normal mode (M_{Ho}) from this position.

interaction between Ho ions is very small and can be neglected. Thus magnetic moment M_{Ho} of one excited atom determines MLD of the transition, which can be written in a first approximation in the following way:

$$\Delta k_M = k_A - k_B = F(\omega)M_{Ho}^2 sin^2\alpha \tag{1}$$

Here k_A and k_B are absorption coefficients for normal waves polarized along (A) and perpendicular (B) to the projection of M_{Ho} on the ab plane, respectively (Fig. 1); $F(\omega)$ is the scale coefficient, which characterizes the MLD activity of the transition; α is the angle between the ion magnetic moment and the light wave vector k. Eq. (1) is valid for the light propagating along the optical axis of a crystal, when its MLD is not taken into account yet. M_{Ho} is, first of all, the magnetic moment of the Ho ion in the excited state. However, its magnetic moment in the ground state also can influence the MLD, since the ground state also takes part in the electron transition probability through the electric dipole matrix element between the ground and excited states of the transition. The MLD is an even effect relative to the magnetic moment (see (1)), therefore it is invariant relative to the antiferromagnetic Ho sublattices.

We measured absorption coefficients of waves polarized along a and b axes of the crystal and corresponding dichroism $\Delta k_H = k_a$-k_b. This dichroism depends on the mutual orientation of axes a, b and A, B, which depends on the magnetic moment orientation and, consequently, on the magnetic field. The wave polarized along a-axis is decomposed to normal waves polarized along A and B axes and intensities of these waves are summarized on the outlet from the crystal. Thereby for k_a we obtain:

$$k_a = \frac{1}{d}ln\frac{I_0}{I_A + I_B} = \frac{1}{d}ln\frac{1}{cos^2\beta exp(-k_A d) + sin^2\beta exp(-k_B d)}, \tag{2}$$

where d is the width of the sample along the light propagation. Similar formula is obtained for k_b and at last:

$$\Delta k_H = k_a - k_b = \frac{1}{d}ln\frac{sin^2\beta + cos^2\beta exp(\Delta k_M d)}{cos^2\beta + sin^2\beta exp(\Delta k_M d)}. \tag{3}$$

If $\Delta k_M d \ll 1$, or $2.3\ \Delta k_M d \ll 1$ for decimal logarithm, $\qquad$ (4)

then equation (3) transforms into the following form (see also Fig. 1):

$$\Delta k_H = \Delta k_M (cos^2\beta - sin^2\beta) = \Delta k_M cos2\beta = \Delta k_M cos\left(\frac{\pi}{2} + 2\gamma\right) = -\Delta k_M sin2\gamma,\ \text{and at last:}$$

$$\Delta k_H = - F(\omega)M_{Ho}^2 sin^2\alpha sin2\gamma. \qquad (5)$$

Formulas (3) and (5) both give evident results at the extreme situations: $\Delta k_H = \pm \Delta k_M$ at $\gamma = \mp\pi/4$ and $\Delta k_H = 0$ at $\gamma = 0$. The angle α certainly depends on the magnetic field and the angle γ can also depend on the magnetic field. MLD activity of the transition $F(\omega)$ can depend on the magnetic field at least due to the dependence of the transition intensity on the magnetic field.

Both Fe and Ho magnetic moments are collinear to the *c* axis in the zero magnetic field at $T < T_{SR}$ according to Ref. [20]. However, the neutron diffraction study of the $HoFe_3(BO_3)_4$ single crystal in the zero external magnetic field at $T = 2$ K shows [5], that the Fe magnetic moments are indeed strictly parallel to the *c*-axis, while the *ab* components of the Ho magnetic moments exist and have an angle of $60°$ to each other, going from one *ab* plane to the neighboring one. These *ab* components are rather large: about 40% from the *c*-component [5]. The magnetic cell contains six Ho ions, but it is possible to consider only three directions in every $120°$, since all the rest ones are antiferromagnetically equivalent. For the simplicity we shall call such mutual orientation of the Fe and Ho sublattices as collinear one, since average magnetic moment of such three Ho ions is collinear with magnetic moment of the Fe ion, if the *c*-projections of the Ho ions moments are identical. Let us suppose that orientation of one of the Ho magnetic moments is characterized by the angle γ (Fig. 1). Then the measured MLD from ions with two other essentially different magnetic moments orientations according to (5) will be:

$$\Delta k_H = - \Delta k_M sin2\left(\gamma \pm \frac{2\pi}{3}\right) = - \Delta k_M \left(-\frac{1}{2}sin2\gamma \mp \frac{\sqrt{3}}{2}cos2\gamma\right) \qquad (6)$$

Consequently, the average MLD from ions with three considered magnetic moment directions is zero. Thus, the MLD from these three kinds of ions compensate each other, if there is equal number of the Ho ions in the magnetically identical states. This result is evident, if we introduce concept of the average magnetic moment M_{Ho1} of the mentioned three Ho ions. If these three moments have the same *c*-projection, but *ab* components have an angle of $120°$ to each other, than their average magnetic moment M_{Ho1} is parallel to k, and MLD in zero magnetic field is zero according to (1). In what follows we shall use the average magnetic moment M_{Ho1} of three mentioned Ho ions from one sublattice instead of magnetic moment M_{Ho} of a single atom.

Fe ions are positioned in two sites, but their magnetic moments have identical antiferromagnetic directions at $T < T_{SR}$ [5]. We shall designate average Fe magnetic moments in these directions as M_{Fe1} and M_{Fe2} (see also [20]).

3.1. $^5I_8 \rightarrow {}^5F_3$ (F) absorption band

At conversion from a free atom to that in octahedron and further to the D_3 and C_2 symmetry positions the $^5F_3$ state of the Ho^{3+} ion is transformed like this:

$$J = 3 \rightarrow A_2 + T_1 + T_2 \rightarrow A_2 + (A_2 + E) + (A_1 + E) \rightarrow A_2(F1) + (A_2 + A_1 + A_2)$$
$$(F2) + (A_1 + A_1 + A_2)(F3). \qquad (7)$$

F1, F2 and F3 are notations of bands in the absorption [13] and MLD spectra. The transition F1 observed in the absorption spectra at 20474 cm^{-1} [13] is very weak and is not seen in the MLD spectra. Splitting of the ground *E*-state of the D_3 symmetry due to the decrease of the symmetry to the C_2 one was not revealed earlier, and therefore it was not taken into account in the splitting of absorption spectrum in a first

approximation. Figs. 2-5 demonstrate transformation of the MLD spectra in magnetic fields $H||a, b$ at $T = 2$ K. Already in the small magnetic field $H = 2$ kOe, which is much below the field of the reorientation transition H_{SR}, there is an appreciable anisotropy of MLD (Fig. 2). It will increase with the field increasing. It is worth noting, that MLD is not changed within the limit of the experimental error with the change of the field sign. This means that Ho magnetic moments change only signs but not orientation.

If the Ho magnetic moment orientation follows that of Fe, than the angle α between the magnetic moment M_{Ho1} and k in the field $H||a$ (Fig. 6a) below H_{SR} is small and should increase as a function of magnetic field. According to (1), MLD also should increase, that corresponds to the experimental behavior of MLD in $H||a$ (compare Figs. 2 and 3). Projection of M_{Fe1} on *ab* plane is directed along *a* or *b* axis according to the field direction (Fig. 6a). Projection of M_{Ho1} was supposed to have the same directions (Fig. 6a). Shape of the MLD spectrum in the field below H_{SR} changes a little (compare Figs. 2 and 3), that testifies to some dependence of coefficient $F(\omega)$ in (1) on magnetic field.

Angle α is $90°$ for the Fe magnetic moments immediately above H_{SR} (Fig. 6b). Then, if M_{Ho1} would follow the M_{Fe1}, a strong jump of the MLD value should be observed at H_{SR} according to (5) and the MLD should decrease with the magnetic field increasing. However the opposite behavior is observed (compare Figs. 2, 3, 4). Thus, we have to suppose that the average holmium magnetic moment M_{Ho1} remains at a small angle α to the *c*-axis just above H_{SR} (Fig. 6b), and this angle increases with the magnetic field increasing. When $H||a$ is larger than H_{SR}, position of the M_{Ho1} projection on the *ab* plane (Fig. 6b) is different in different excited states and certainly depends on the magnetic field. This follows from the qualitative changes of the MLD spectra in the field $H||a$ (Figs. 3, 4). In particular, MLD of F2a and F2b lines in the field $H||a$ change sign between 20 and 40 kOe (Fig. 4) that corresponds to the change of the angle γ sign in (5), characterizing position of the M_{Ho1} projection on the *ab* plane (Figs. 1, 6b) in the F2a and F2b states. Similar situation occurs in the F3a,b states between 12 and 20 kOe (Fig. 4). In the field $H||b$ (Fig. 5) components of the F2 and F3 bands do not change signs of MLD in contrast to that in the field $H||a$. All this demonstrates a substantial anisotropy of the MLD in the basal plane, which is also different for different transitions. The latter also testifies to the different local magnetic properties of Ho ions in different excited *4f* states, which also differ from those in the ground state. Similar phenomena were observed in $Ho_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ crystal in the X-ray excited states [19].
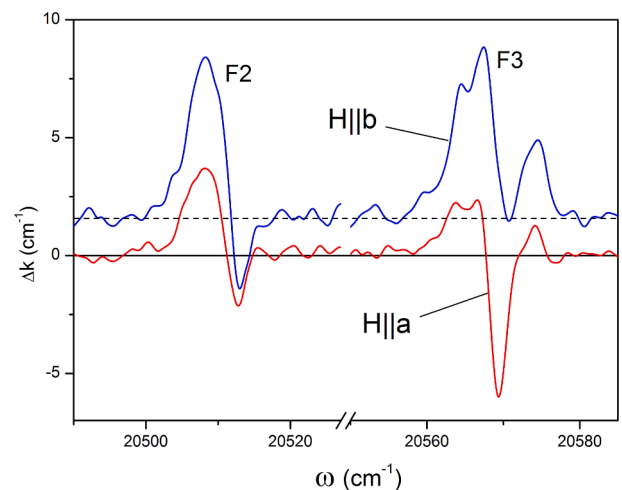

Fig. 2. MLD spectra of $^5I_8 \rightarrow {}^5F_3$ (F) absorption band at $T = 2$ K in the magnetic field $H = 2$ kOe much below the reorientation transition, which was applied along crystallographic directions *a* and *b*. F2 and F3 – are components of the F-band splitting in the D_3 symmetry. $\Delta k = k_{||} - k_\perp$, where $k_{||}$ and $k_\perp$ are absorption coefficients for waves polarized parallel and perpendicular to the magnetic field, respectively.
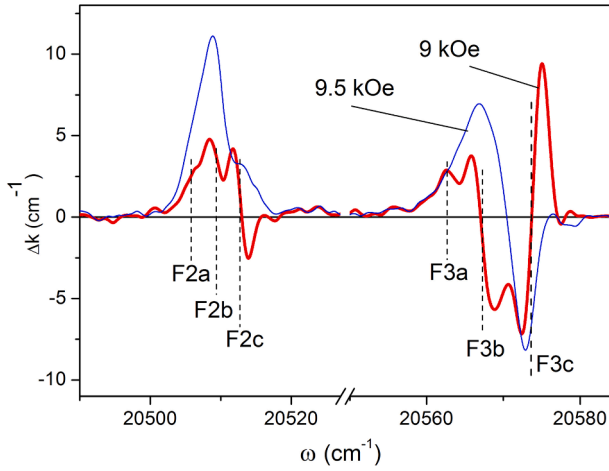
Fig. 3. MLD spectra of $^5I_8 \rightarrow {}^5F_3$ (F) absorption band at $T = 2$ K in the magnetic field $H \| a$ below (9 kOe) and above (9.5 kOe) the reorientation transition. F2 and F3 – are components of the F-band splitting in the D_3 symmetry. F2a, F2b, F2c and F3a, F3b, F3c are components of the F2 and F3 bands splitting in the C_2 symmetry.
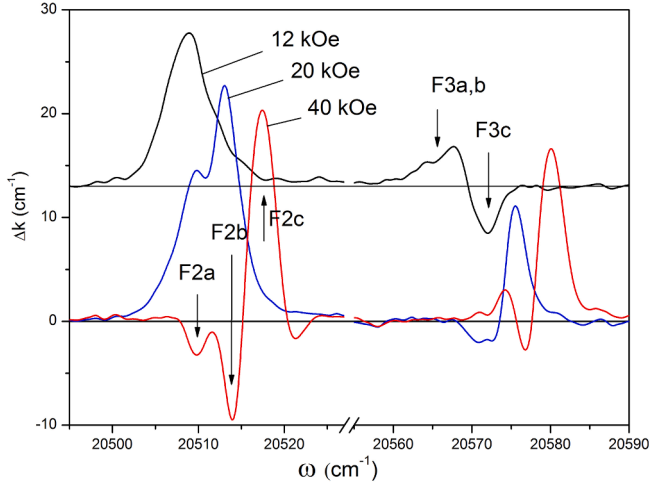

Fig. 4. Transformation of the MLD spectra of $^5I_8 \rightarrow {}^5F_3$ (F) absorption band at $T = 2$ K in the magnetic field $H \| a$ above the reorientation transition. F2 and F3 – are components of the F-band splitting in the D_3 symmetry. F2a, F2b, F2c and F3a, F3b, F3c - are components of the F2 and F3 bands splitting in the C_2 symmetry.

In particular, it was shown that the spin-flop transitions observed in macroscopic magnetization curves were due to the Ho^{3+} but not to the Nd^{3+} magnetic moment reorientation.

Demidov and Volkov [20] suggested the following Hamiltonians for Ho and Fe ions of the *i*-sublattice ($i = 1,2$) in the $HoFe_3(BO_3)_4$ crystal in the presence of magnetic field:

$$\widehat{H}_i(Ho) = \widehat{H}_{CF}^i - g_J \mu_B \vec{J}_i \cdot \left(\vec{H} + \lambda_{fd} \vec{M}_i \right), \tag{8}$$

$$\widehat{H}_i(Fe) = -g_S \mu_B \vec{S}_i \cdot \left(\vec{H} + \lambda \vec{M}_j + \lambda_{fd} \vec{m}_i \right) \tag{9}$$

Here $\widehat{H}_{CF}^i$ is the crystal field Hamiltonian of the Ho ion. Its form corresponds to the symmetry of the local environment of a Ho ion in the ground electron state. $\vec{M}_i$ and $\vec{m}_i$ are the magnetic moments of the Fe and Ho ions, respectively. $\lambda_{fd} < 0$ is the constant of the antiferromagnetic interaction Ho-Fe. Only isotropic exchange is evidently taken into account in the Hamiltonians (8, 9). However, from the described above
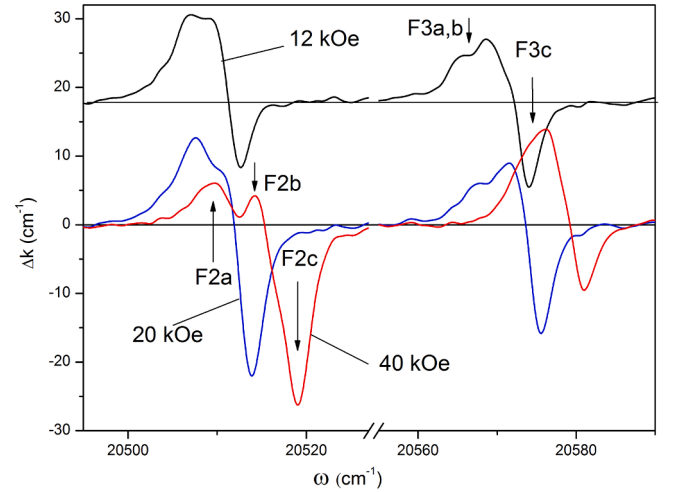

Fig. 5. Transformation of the MLD spectra of $^5I_8 \rightarrow {}^5F_3$ (F) absorption band at $T = 2$ K with the magnetic field $H \| b$ above the reorientation transition. F2 and F3 – are components of the F-band splitting in the D_3 symmetry. F2a, F2b, F2c and F3a, F3b, F3c - are components of the F2 and F3 bands splitting in the C_2 symmetry.
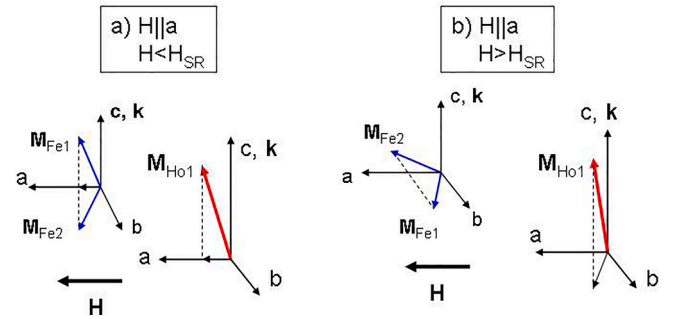

Fig. 6. Diagrams of the mutual orientations of magnetic moments of the Fe ions from two different antiferromagnetic sublattices $\boldsymbol{M}_{Fe1}$ and $\boldsymbol{M}_{Fe2}$ and of the average magnetic moment of the Ho ions from one sublattice in three neighboring planes $\boldsymbol{M}_{Ho1}$ in magnetic field $H \| a$ of different values: below (a) and above (b) the field-induced reorientation transition. $\boldsymbol{k}$ is the light wave vector.

phenomena we can infer that it is necessary to take into account also the antisymmetric exchange Fe-Ho:

$$\widehat{H} = \vec{D} \cdot \left[\vec{S}_i \times \vec{J}_i \right], \tag{10}$$

not only in the ground but in the excited states as well ($\vec{D}$ in eq. (10) is a constant vector). It can provide noncollinear (canted) orientation of magnetic moments of the Fe and Ho ions. Crystal field should be taken into account also in the Fe Hamiltonian, since it is the source of the Fe ion magnetic anisotropy. The spin-reorientation phase transition in $HoFe_3(BO_3)_4$ originates from competition of the iron and rare-earth subsystems contributions into the total magnetic anisotropy of the crystal [6] under the condition, that the exchange coupling Fe-Ho is large enough for the Fe and Ho magnetic moments to move synchronously in magnetic field. Thus, orientation of the Ho ion magnetic moment in the external magnetic field depends on the local crystal field and on the Ho-Fe exchange coupling. All these interactions strongly depend on the electron state of the Ho ion, and thus the Ho excited states are the source of the different Ho magnetic moment orientations and of the different MLD of different electron transitions.

Local symmetry of the Ho^{3+} ion in the $HoFe_3(BO_3)_4$ crystal is C_2 and therefore the F2 and F3 manifolds are split into three singlet states (7), which give corresponding absorption lines F2a, F2b, F2c and F3a, F3b,

F3c (Fig. 3). Shape of the MLD spectra corresponding to the F2b, F2c, F3b and F3c lines at $H||a = 9$ kOe (Fig. 3) testifies that these lines are additionally split into two close lines with the opposite linear polarizations. The excited states F2 and F3 can not be split into more than three states. However, the ground state is the doublet E-state in the D_3 symmetry approximation [13]. Its splitting in the C_2 local symmetry of the HoFe$_3$(BO$_3$)$_4$ was not earlier observed. The splitting of lines observed in Fig. 3 can be referred to the splitting of the ground E-state. The F2a and F3a lines are not split. This means, that the splitting of the ground state depends on the electron transition. Indeed, the electron transition occurs due to the mixing of the initial and final states by the electromagnetic excitation of light. As a result the initial state and its interaction with the environment are changed. The similar behavior of the MLD spectrum near the reorientation transition is observed also in the magnetic field $H||b$. The discussed splitting disappears above the reorientation transition (Fig. 3). Consequently, the observed phenomenon is connected also with the magnetic state of the crystal.

Electric dipole transition between states a and b is allowed, if the product of representations $\Gamma_a \times \Gamma_b$ contains irreducible representation of the corresponding component of the electric dipole. Using multiplication tables of the representations and basis functions of the irreducible representations corresponding to the electric dipole components, one can obtain selection rules in the D_3 local symmetry (Table 1). The selection rules in C_2 symmetry are obtained in the similar way (Table 2). Then, for the transition from the split ground state $E(A_1 + A_2) \rightarrow A_1$ we obtain $a + b$ polarized lines and for the transition $E(A_1 + A_2) \rightarrow A_2$ we obtain $b + a$ polarized lines. Thus, we obtain mutually perpendicular polarized components of the splitting, the very thing observed in the MLD spectra before the reorientation transitions (Fig. 3). Moreover, alternation of a and b polarizations in transitions into A_1 and A_2 states is opposite (Fig. 3) that corresponds to the theory. We should emphasize that existing of the magnetic order is not necessary for the creating of the discussed splitting. Influence of the magnetic order is revealed, when we compare the MLD spectra in magnetic fields of different values (Fig. 3). The discussed splitting disappears, if the splitting of the ground E state is zero, or if intensity of one of the lines $A_1 \rightarrow A_1$ or $A_2 \rightarrow A_1$ strongly prevails. This occurs mainly above the reorientation transition. If the splitting of the ground E state is zero, then all transitions are allowed both in a and b polarizations, but ratio of a and b intensities is not known a priori. This ratio is changed by the exchange and external magnetic fields, which mix the close states and so change polarizations of the transitions being the source of the MLD. The strong modification of the MLD spectra in the magnetic field shows, that magnetic order and magnetic field have a substantial influence on the electron states.

3.2. $^5I_8 \rightarrow {}^5F_2$ (G) absorption band

At the conversion from a free atom to that in octahedron and further to the D_3 and C_2 symmetry positions, the $^5F_2$ state of the Ho^{3+} ion is transformed like this:

$$J = 2 \rightarrow T_2 + E \rightarrow (A_1 + E) + E \rightarrow A_1(G1) + (A_1 + A_2)(G2) + (A_1 + A_2)(G3). \quad (11)$$

G1, G2 and G3 are notations of bands in spectra of the MLD and absorption (Fig. 7 and so on). Identification of the bands in the D_3 symmetry approximation was made earlier [13], based on the π and σ absorption spectra. MLD of the G2 band in the field $H||a$ reveals the

Table 1
Selection rules for electric dipole transitions in D_3 symmetry for ions with integer moment.

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

Table 2
Selection rules for electric dipole transitions in C_2 local symmetry for ions with integer moment. Polarizations are shown relative to the local C_2 axis. Polarizations relative to the trigonal axis of the total HoFe$_3$(BO$_3$)$_4$ crystal are shown in brackets.

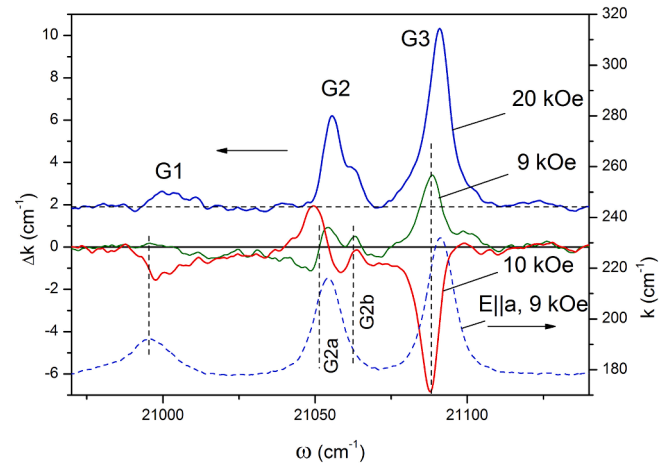|	A_1	A_2
A_1	z (a)	x,y (b,c)
A_2	x,y (b,c)	z (a)

Fig. 7. MLD spectra of $^5I_8 \rightarrow {}^5F_2$ (G) absorption band at different values of the magnetic field $H||a$: below (9 kOe) and above (10 and 20 kOe) the reorientation transition. Dashed curve: absorption spectrum at $H = 9$ kOe in the polarization $E||a$. G1, G2 and G3 – are components of the G-band splitting in the D_3 symmetry. G2a and G2b – are components of the G2-band splitting in the C_2 symmetry.

splitting of the excited doublet (Fig. 7). In addition, the splitting of the ground doublet at the transition G2a is observed, the same as it is in the F band (Fig. 3), but both before and after the reorientation transition. Succession of a and b polarizations changes at the reorientation transition. In the field $H||b$ the splitting of the ground state is not observed (Fig. 8).

Transformation of the MLD spectrum of the G3 band in $H||a,b$ is seen in Figs. 7 and 8. The spectrum has a particular behavior: it does not
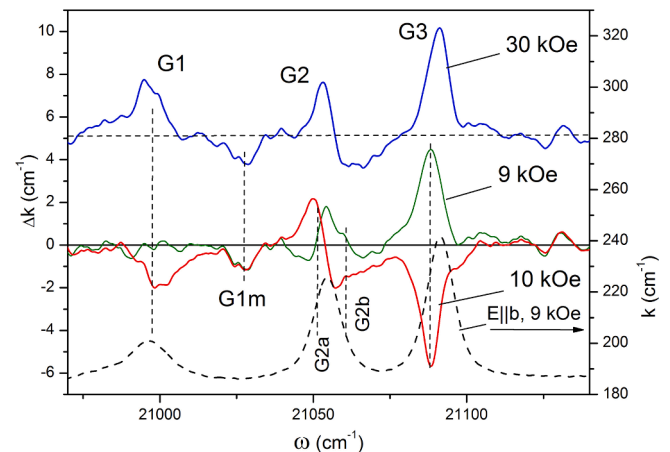

Fig. 8. MLD spectra of $^5I_8 \rightarrow {}^5F_2$ (G) absorption band at different values of the magnetic field $H||b$: below (9 kOe) and above (10 and 30 kOe) the reorientation transition. Dashed curve is absorption spectrum at $H = 9$ kOe in the polarization $E||b$. G1, G2 and G3 – are components of the G-band splitting in the D_3 symmetry. G2a and G2b – are components of the G2 band splitting in the C_2 symmetry. G1m line is associated with the exciton-magnon transition.

reveal a splitting of the doublet G3. This can be explained in the following way. MLD of the left component of the splitting (G3a) strongly predominates that of the right component (G3b), that is seen from the comparison of the MLD and absorption spectra in Figs. 7 and 8. Fig. 9 demonstrates positions of the components of the G3 splitting obtained from the absorption spectra [21], and position of the MLD extremum as a function of the magnetic field. Fig. 9 reflects the mentioned ratio of the MLD values of the components of the G3 splitting.

Fig. 10 shows integral MLD of the G1 and G3 lines as a function of magnetic field $H||a,b$, which allows us to retrace the rotation of the M_{Ho} projection on the ab plane. At $H < H_{SR}$ in the field $H||a(b)$ the MLD of the G3 line is small and increases (Fig. 10). This corresponds to M_{Ho1}, which is approximately collinear to M_{Fe1}, and corresponds to a small and increasing angle α between k and magnetic moment (Fig. 6a). If after H_{SR} the M_{Ho1} also followed M_{Fe1} then the MLD would increase stepwise since $\alpha = 90°$ (M_{Fe} is in ab plane according to Fig. 6b). In reality, at $H = H_{SR}$ the MLD change sign, but absolute value remains approximately the same (Fig. 10). This means that the angle α between M_{Ho1} and k remains the same as before the transition (Fig. 6b), that is, there is no reorientation of M_{Ho1} to the ab plane, but the angle γ, characterizing position of M_{Ho1} in the ab plane, changes sign. Before H_{SR} the M_{Ho1} projection on the ab plane is directed along $H||a(b)$ if M_{Ho1} is approximately parallel to M_{Fe1} (Fig. 6a). Just above H_{SR} the M_{Fe1} is approximately parallel to the b (a)-axis (Fig. 6b). If M_{Ho1} projection on the ab plane follows that of the M_{Fe1}, this results in rotation of M_{Ho1} projection on the ab plane to the b-direction and results in the change of the γ and MLD signs observed in Figs. 7, 8 and 10. With the increasing $H||a(b)$ the M_{Ho1} projection on the ab plane rotates from the $b(a)$ to $a(b)$ axis. This results in the one more change of the γ and MLD sign (Fig. 10). In particular, the MLD of the G3 line in the field $H||a$ changes sign between 12 and 15 kOe, and this is reflected in the G3 MLD peak position (Fig. 9). From Figs. 7, 8 and 10 we see that there is an appreciable anisotropy of the *f-f* transitions MLD in the basal plane in spite of the very small magnetic anisotropy of $HoFe_3(BO_3)_4$ in the ground electron state.

MLD of the G1 line reveals peculiar properties: below the reorientation transition it is zero in the magnetic field $H||a,b$ (Figs. 7, 8), but it is not zero above H_{SR}. The most probable reason of this phenomenon may be the singlet nature of the G1 state already in the D_3 symmetry, and we can infer that the exchange field of the iron induces magnetic moment in the G1 state not in any Fe-sublattice orientation. Components of the G2 and G3 states splitting are also singlet, but they are singlet only in the C_2 symmetry.

In the field $H||b$ both below and above H_{SR} a line G1m is observed in the MLD spectra (Fig. 8). It is practically not seen in the absorption
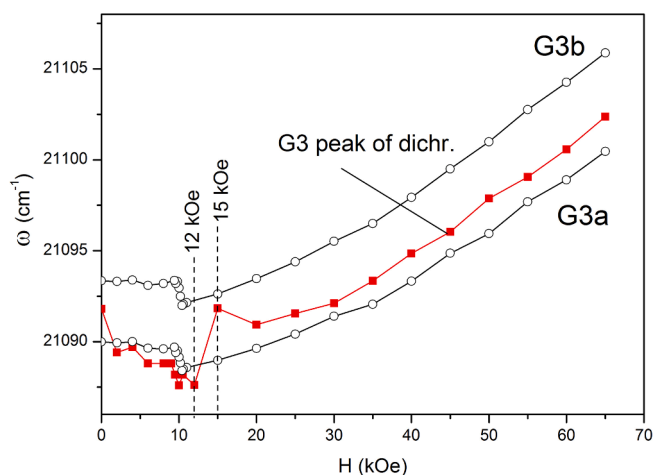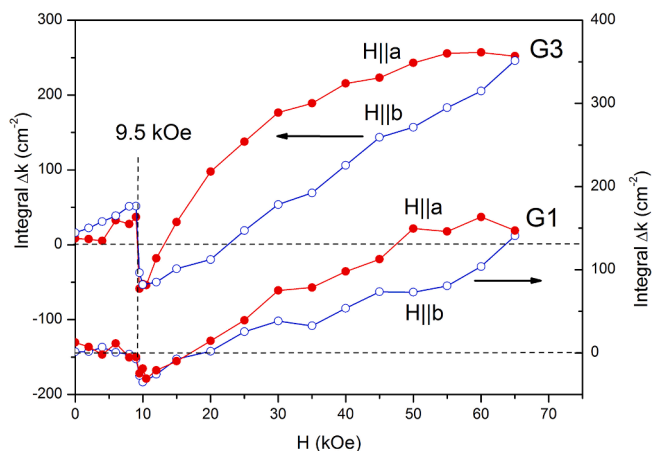

Fig. 10. Integral MLD of the G1 and G3 bands of $^5I_8 \rightarrow ^5F_2$ transition in the magnetic fields $H||a$ and $H||b$. G1 and G3 – are components of the transition splitting in the D_3 symmetry.

spectra and therefore it is possible to say that this line is totally polarized parallel to *a*-axis when $H||b$. The G1m line is observed only when $H||b$, and its intensity and position almost do not depend on the magnetic field value in the wide interval. Its distance from the G1 line (~28 cm^{-1}) also does not depend on the magnetic field value. In Ref. [22] a peak of the two-magnon Raman scattering was observed at approximately 55 cm^{-1} in $GdFe_3(BO_3)_4$. The Neel temperatures of $GdFe_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ are close (37–39 K). Thus, we can suppose that observed absorption line G1m is caused by the exciton-magnon transition: the optical excitation is in the Ho sublattice and the magnetic excitation is in the Fe sublattice.

4. Summary

We measured spectra of magnetic linear dichroism of $^5I_8 \rightarrow ^5F_2$, $^5F_3$ transitions in the basal plane of the $HoFe_3(BO_3)_4$ single crystal in the light propagated along the trigonal *c*-axis at temperature 2 K as a function of magnetic field 0 – 65 kOe directed along *a* and *b* axes. The substantial anisotropy of the MLD in the basal plane was revealed. The anisotropy of the MLD is strongly different for different electron transitions, that is, the MLD is mainly connected with the excited electron states. Transformations of the MLD spectra permitted us to retrace variations of the Ho ion magnetic moment orientation as a function of magnetic field in different excited electron states.

Assumption that the average magnetic moment of three Ho ions forming spiral is approximately collinear to the Fe moment both in the ground and excited states of the Ho^{3+} ion has led to the contradiction with the experiment. On the contrary, the assumption, that they are not collinear in the Ho excited electron states, permitted us to explain results of the experiments. In particular, in the excited states the local Ho magnetic moments do not reveal reorientation transitions synchronously with that of the Fe-sublattice. This is accounted for by the different Ho-Fe exchange interaction and by the different local Ho magnetic anisotropy in the different Ho excited states.

The splitting of the excited states in the C_2 symmetry was revealed due to the MLD. Additionally, the small splitting of the ground doublet of the Ho^{3+} ion was observed, but during only certain electron transitions. This means that during electron transitions the local crystal field can change not only in the excited but also in the ground state. The experiment showed that this phenomenon depended not only on the transition but also on the magnetic state of the crystal.

Declaration of Competing Interest

The authors declare that they have no known competing financial

Fig. 9. Positions of the G3a and G3b components of the G3 band (the $^5I_8 \rightarrow ^5F_2$ transition) splitting in the C_2 symmetry, obtained from the absorption spectra [21], and position of the peak of the G3 MLD band spectrum in the field $H||a$.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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