

# Influence of magnetic ordering on electronic structure of $\text{Tb}^{3+}$ ion in $\text{TbFe}_3(\text{BO}_3)_4$ crystal

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**Abstract.** Optical absorption spectra of trigonal crystal  $\text{TbFe}_3(\text{BO}_3)_4$  have been studied in the region of  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$  transition in  $\text{Tb}^{3+}$  ion depending on temperature (2–220 K) and on magnetic field (0–60 kOe). Splitting of the  $\text{Tb}^{3+}$  excited states, both under the influence of the external magnetic field and effective exchange field of the Fe-sublattice, have been determined. Landé factors of the excited states have been found. Stepwise splitting of one of the absorption lines has been discovered in the region of the Fe-sublattice magnetic ordering temperature. This is shown to be due to the abrupt change of equilibrium geometry of the local  $\text{Tb}^{3+}$  ion environment only in the excited state of the  $\text{Tb}^{3+}$  ion. In general, the magnetic ordering is accompanied by temperature variations of the  $\text{Tb}^{3+}$  local environment in the excited states. The crystal field splitting components have been identified. In particular, it has been shown that the ground state (in  $D_3$  symmetry approximation) consists of two close singlet states of  $A_1$  and  $A_2$  type, which are split and magnetized by effective exchange field of the Fe-sublattice. Orientations of magnetic moments of the excited electronic states relative to that of the ground state have been experimentally determined in the magnetically ordered state of the crystal. A pronounced shift of one of absorption lines has been observed in the vicinity of the  $\text{TbFe}_3(\text{BO}_3)_4$  structural phase transition. The temperature interval of coexistence of the phases is about 3 K.

## 1 Introduction

Rare-earth ferrobates  $\text{REFe}_3(\text{BO}_3)_4$  attract attention due to variety of magnetic structures and phase transitions realized in them depending on a choice of a rare-earth (RE) ion R and owing to the interaction of two magnetic subsystems: Fe and RE elements [1]. Depending on the choice of RE ion, they can be easy-axis or easy-plane antiferromagnets, and a change of temperature results in orientation phase transitions in some compounds. For example, the antiferromagnetic ordering phase transition in  $\text{GdFe}_3(\text{BO}_3)_4$  occurs at 37 K. At  $T < 9$  K,  $\text{GdFe}_3(\text{BO}_3)_4$  crystal transforms from easy plane to easy axis antiferromagnet [2]. Spontaneous spin-reorientation transitions was also found in mixed ferrobates  $\text{Nd}_{1-x}\text{Dy}_x\text{Fe}_3(\text{BO}_3)_4$  [3,4]. Crystals of this type refer to multiferroics [5], which possess magnetic and electric order simultaneously. Magnetic field induced dielectric polarization was discovered in  $\text{GdFe}_3(\text{BO}_3)_4$  [6],  $\text{NdFe}_3(\text{BO}_3)_4$  [7] and  $\text{PrFe}_3(\text{BO}_3)_4$  [8]. In reference [8] it was mentioned that electric polarization is also observed in  $\text{TbFe}_3(\text{BO}_3)_4$ . The greatest dielectric polarization was

found in  $\text{NdFe}_3(\text{BO}_3)_4$ . Magnetoelectric effects provide the possibility to control the dielectric polarization by a magnetic field and vice versa, and makes such materials interesting for applications.

At room temperature, ferrobate  $\text{TbFe}_3(\text{BO}_3)_4$  has the huntite like structure with the space group  $R\bar{3}2$  ( $D_3^7$ ) [9]. Trivalent RE ions occupy only one type positions. RE ions are located at the center of trigonal prisms made up of six crystallography equivalent oxygen ions. Each oxygen ion in the environment of the RE ion belongs to its own borate group. The  $\text{FeO}_6$  octahedra share edges in such a way that they form helicoidal chains, which run parallel to the  $C_3$  axis and are mutually independent. A structural phase transition to the  $P\bar{3}_121$  ( $D_3^4$ ) phase was found in  $\text{TbFe}_3(\text{BO}_3)_4$  at  $T = 192$  K [9,10]. Correspondingly, the local symmetry of the  $\text{Tb}^{3+}$  environment reduces from  $D_3$  to  $C_2$  one. In this phase, two nonequivalent positions of the  $\text{Fe}^{3+}$  ions appear.

At  $T_N = 40$  K, antiferromagnetic ordering of the Fe-sublattice with magnetic moments along the trigonal  $C_3$  axis of the crystal arises [9,10]. Simultaneously, due to the interaction with the Fe-sublattice, antiferromagnetic ordering also appears in Tb-sublattice with magnetic moments parallel to the same axis [9,10]. The magnetic

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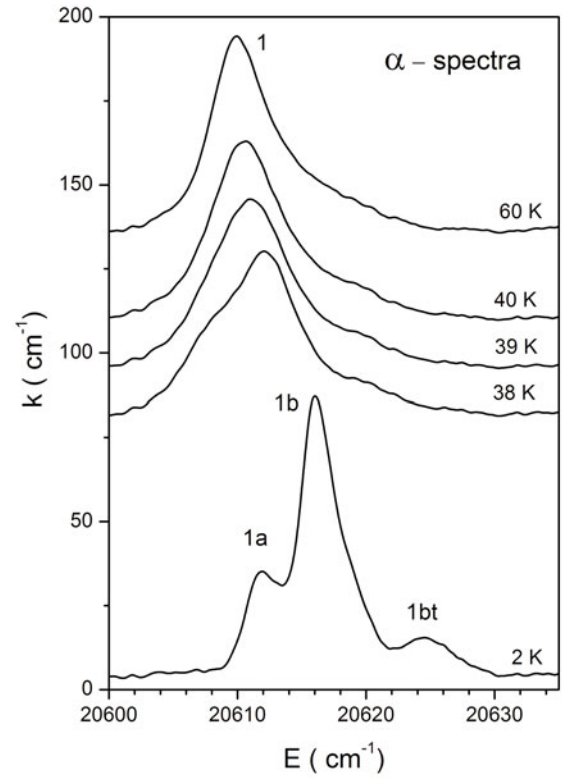
moment of the  $\text{Tb}^{3+}$  ground state at  $T = 2$  K is  $8.6\mu_B$  [9], Landé factor for magnetic field along the trigonal axis  $g_c \approx 17.8$ , and that along  $a$ -axis:  $g_a \ll g_c$  [10]. Vasiliev et al. have found the Schottky-type anomaly in the temperature dependence of heat capacity in the magnetically ordered state of the crystal [11], which is due to splitting of the ground state of about  $19.5 \text{ cm}^{-1}$ .

Measurements of absorption spectra caused by transitions inside  $4f$  shell of RE ions ( $f$ - $f$  transitions) were used for study of magnetic properties of the ferroborates in a number of works [12–15]. In particular, the Néel temperature of  $\text{TbFe}_3(\text{BO}_3)_4$  was estimated as being  $41 \pm 1$  K [12,15]. As a result of infrared absorption measurements in the region of  ${}^7F_6 \rightarrow {}^7F_2$  transition of  $\text{Tb}^{3+}$  ion in the  $\text{TbFe}_3(\text{BO}_3)_4$ , the splitting of two absorption lines at  $T < T_N$  were observed [12] ( $32 \text{ cm}^{-1}$  at 5 K for one of them). The authors ascribed this value to splitting of the lowest quasi doublet of the  $\text{Tb}^{3+}$  ion ground state in the effective field of the magnetically ordered Fe-sublattice. However, investigation of  $f$ - $f$  transitions has independent importance. These transitions are electric dipole allowed only due to non-centrosymmetrical components of crystal field (CF), and, consequently, their properties are very sensitive to changes in the environment of  $4f$  ions. Therefore,  $f$ - $f$  transitions are an effective tool for detection of the local structure variations. Besides that, properties of electron transitions reflect properties of a substance not only in the ground state but also in the electronically excited states. This paper is devoted to the detailed study of temperature and field dependences of  $\text{TbFe}_3(\text{BO}_3)_4$  absorption spectrum in the region of  ${}^7F_6 \rightarrow {}^5D_4$   $f$ - $f$  transition in the  $\text{Tb}^{3+}$  ion. The goal of the study is to obtain additional information about processes accompanying the magnetic ordering of the crystal, in particular, in the electronically excited states.

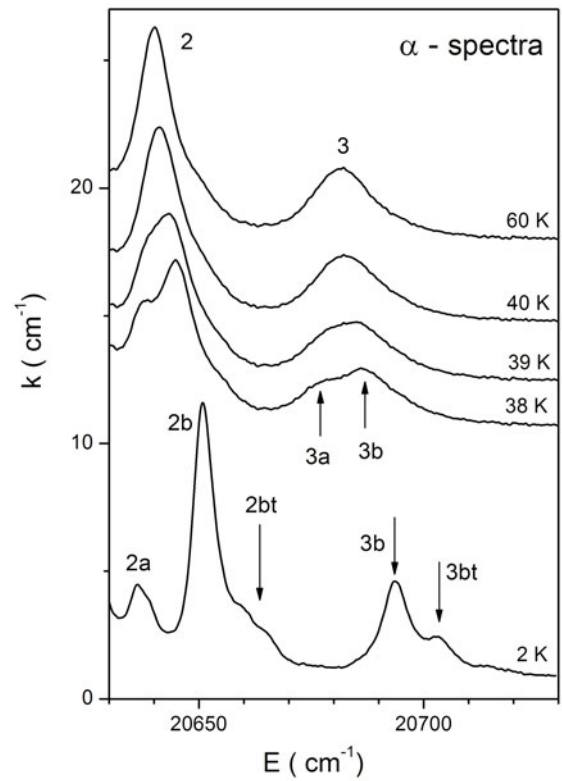
## 2 Results and discussion

Single crystals of  $\text{TbFe}_3(\text{BO}_3)_4$  were grown by a group method using a  $\text{K}_2\text{Mo}_3\text{O}_{10}$ -based flux, as described in reference [16]. The samples prepared for optical measurements were 0.11–2.5 mm-thick plane-parallel polished plates oriented perpendicular and parallel to the threefold crystallographic axis  $C_3$ . Absorption spectra were measured using a diffraction spectrometer and optical multi-channel analyzer (spectral resolution was  $\sim 0.34 \text{ cm}^{-1}$ ). The magnetic field was created by a superconducting solenoid. At temperatures  $\leq 4.2$  K the sample was in liquid helium. At higher temperatures the sample was situated in a volume filled by gaseous helium. The temperature was measured with accuracy around 0.3 K.

Figures 1–3 present  $\alpha$ - and  $\pi$ -polarized absorption spectra of  $\text{TbFe}_3(\text{BO}_3)_4$  in the region of  ${}^7F_6 \rightarrow {}^5D_4$   $f$ - $f$  transition at different temperatures in units of the natural absorption coefficient.  $\alpha$ - and  $\sigma$ -spectra were practically identical ( $\alpha$ -light wave vector  $\vec{k}$  is parallel to  $C_3$  axis of the crystal and electric vector  $\vec{E}$  of light is perpendicular to  $C_3$  axis;  $\pi - \vec{k} \perp C_3$ ,  $\vec{E} \parallel C_3$ ;  $\sigma - \vec{k} \perp C_3$ ,  $\vec{E} \perp C_3$ ).

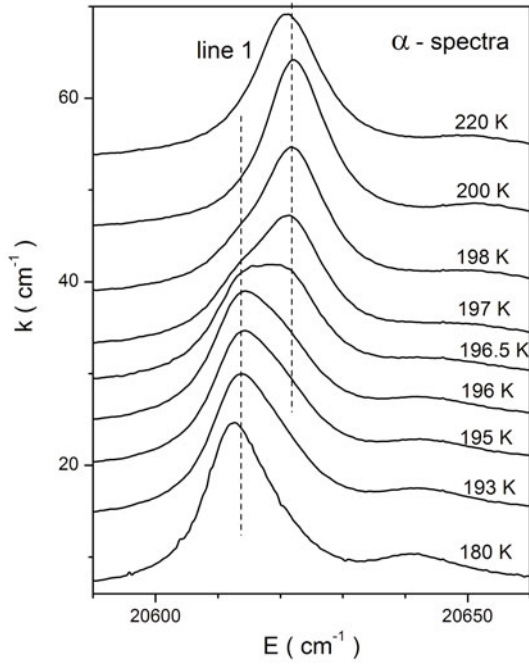


(a)



(b)

**Fig. 1.** Absorption spectra of  $\text{TbFe}_3(\text{BO}_3)_4$  in the region of  ${}^7F_6 \rightarrow {}^5D_4$  transition in  $\text{Tb}^{3+}$  ion in  $\alpha$ -polarization at different temperatures and in zero external magnetic field.

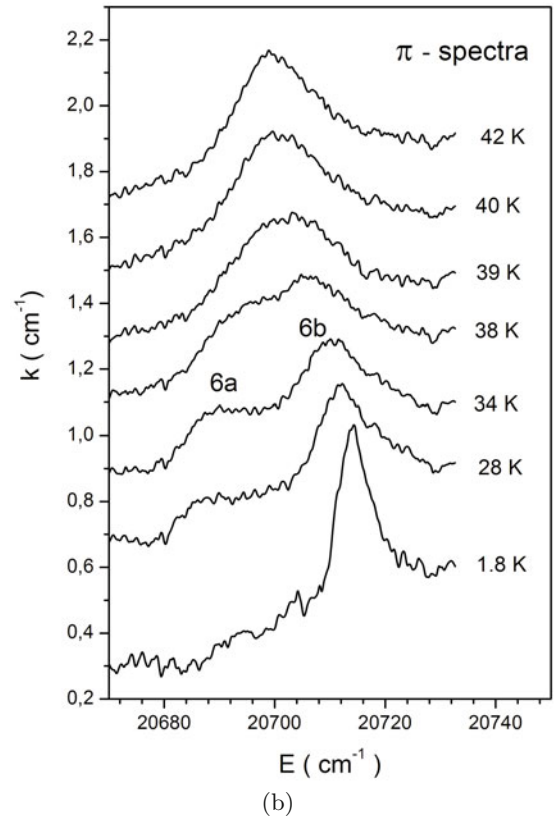
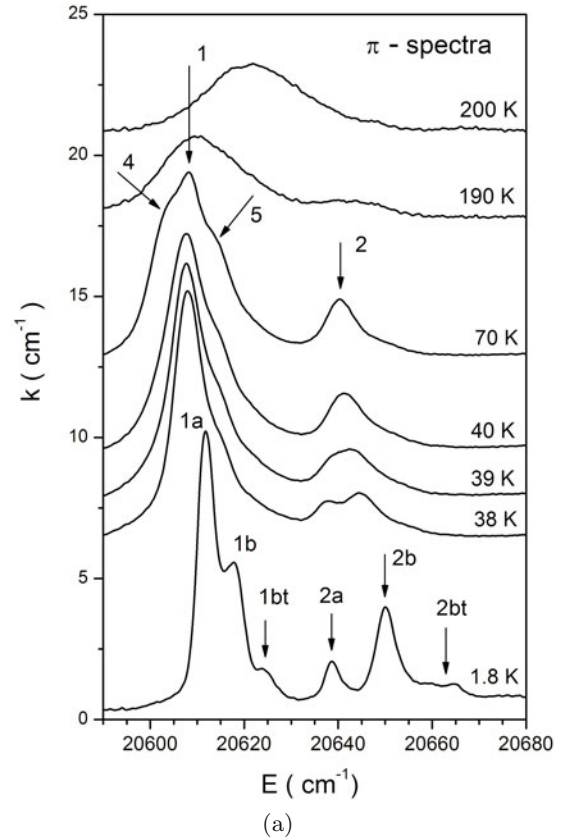


**Fig. 2.** Absorption spectra of  $\text{TbFe}_3(\text{BO}_3)_4$  in the region of line 1 of  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$  transition in  $\text{Tb}^{3+}$  ion in  $\alpha$ -polarization at different temperatures in the vicinity of the structural phase transition.

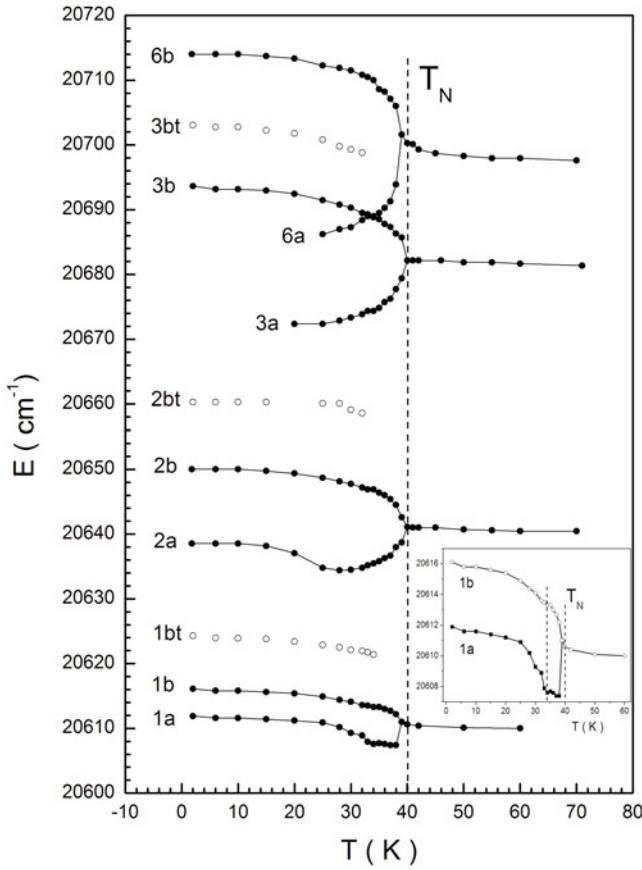
Figure 2 demonstrates transformation of the  $\text{Tb}^{3+}$  absorption spectrum in the temperature range of the structural phase transition. These spectra show that the transition proceeds between 195 and 198 K and at 196.5 K both phases exist in equal amounts.

We believe that the lines marked by index “t” in Figures 1 and 3 are phonon side bands of the corresponding electron absorption lines (without index “t”), which are formed by acoustic phonons. Temperature and field dependences of these lines positions are identical to those of the original, purely electron, lines (see below). With the temperature increase, these side bands significantly widen due to many phonon processes and are merging with the electron lines. The shape of the phonon sideband at  $T = 0$  K is the product of phonon density of states and the function of the corresponding Stokes losses. The acoustic phonon density of states in the Debye approximation is proportional to the square of the phonon frequency. The function of the Stokes losses is unknown, and therefore it is impossible to describe the shape of the observed phonon sidebands quantitatively. However, this shape is quite typical [17].

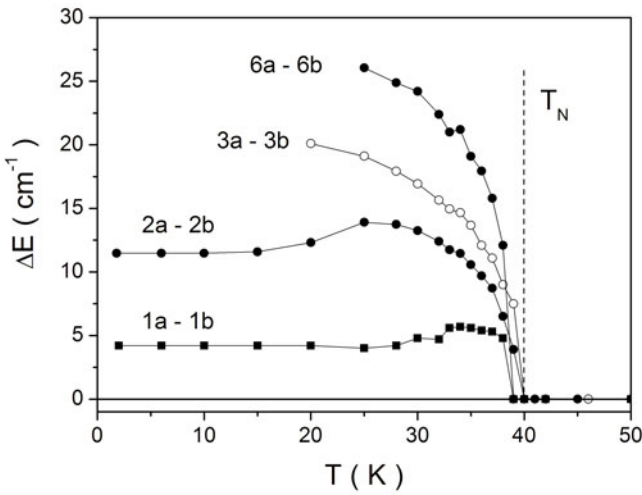
Lines 1, 2, 3 and 6 are split (Figs. 1 and 3) into two components at temperature lower than  $T_N = 40$  K. Figure 4a depicts the line positions and Figure 4b shows the line splitting: 1a-1b, 2a-2b, 3a-3b and 6a-6b as a function of temperature. Line 3 is not observed in  $\pi$ -polarization, while line 6 appears (see explanation below). Splitting of lines 1 and 2 at  $T = 2$  K in zero external magnetic field, which are equal to 4.2 and 11.6  $\text{cm}^{-1}$ , respectively (see Tab. 1), are the consequence of the excited states splitting,



**Fig. 3.** Absorption spectra of  $\text{TbFe}_3(\text{BO}_3)_4$  in the region of  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$  transition in  $\text{Tb}^{3+}$  ion in  $\pi$ -polarization at different temperatures and in zero external magnetic field.



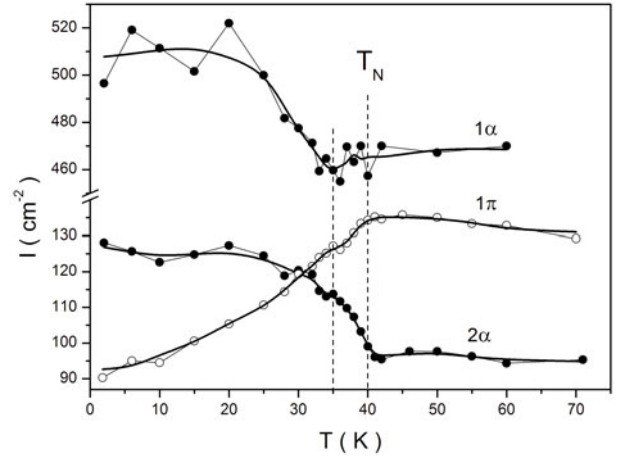
(a)



(b)

**Fig. 4.** Temperature dependencies of the absorption line positions (a) and of the line splitting (b) at  $H = 0$ .

since these lines are observed at low temperature  $T = 2$  K. Additionally, the splitting values are different and they differ from those observed in the  ${}^7F_6 \rightarrow {}^7F_2$  transition [12]. It is necessary to note the abrupt appearance of the line 1 splitting at temperature in the vicinity of  $T_N$  (Fig. 4). It is also easy to see the step-wise splitting directly in the spectra of Figure 1a.



**Fig. 5.**  $1\alpha$  and  $1\pi$  – integral intensities of the line 1 ( $1a + 1b$ ) in  $\alpha$ - and  $\pi$ -polarizations, respectively;  $2\alpha$  – integral intensity of the line 2 ( $2a + 2b$ ) in  $\alpha$ -polarization. The thick lines were obtained by smoothing procedure.

Frequency  $\omega_0$  of a transition at  $T = 2$  K is connected with the frequency  $\omega_N$  of the transition at  $T = T_N$  by the equation:

$$\omega_0 = \omega_N + \Delta_f - \Delta_i,$$

where  $\Delta_i$  is a shift of the initial level as a result of temperature changing from  $T_N$  to 2 K and  $\Delta_f$  is the same for the final state. We assumed that  $\Delta_i = -15.5 \text{ cm}^{-1}$ , i.e., half of the ground state splitting in the effective field of the Fe sublattice [10], and negative, since only transitions from the lowest level are observed at  $T = 2$  K. Then we can find shifts of the final states as a result of magnetic ordering (see Tab. 1). Assuming  $\Delta_i = -15.5 \text{ cm}^{-1}$ , we consider the exchange splitting of the ground state to be symmetrical. From Table 1 it can be seen that shifts of the excited states as a result of the magnetic ordering are asymmetrical. Shift and splitting of the state 6 is equal to zero within the experimental error, consequently, the state 6 is a singlet.

We have integrated  $\alpha$ - and  $\pi$ -polarized absorption spectra in the region of lines 1a and 1b and decomposed the  $\alpha$ -polarized absorption spectra at  $E > 20620 \text{ cm}^{-1}$  into Gaussian components. Obtained temperature dependences of the integrated intensities and of the summarized intensity of 2a and 2b lines are shown in Figure 5. These dependencies, as well as temperature variation of the line 1a position (Fig. 4a inset), have singularities not only at  $T = T_N$ , but also at 34–35 K. The shape of the above-mentioned functions of temperature, together with the asymmetric shifts of the excited states as a result of magnetic ordering, testifies to an appearance of the crystal distortions at  $T < T_N$ . The lattice distortions can be stimulated by the large magnetostriction appearing with the Fe-sublattice ordering. Thus, not only the Fe-sublattice ordering but also crystal distortions influence the excited states splitting observed at  $T = 2$  K in zero external magnetic field.

The question arises, is there the similar influence of crystal distortions on the ground state splitting of  $\text{Tb}^{3+}$  ion in the effective field of Fe-sublattice? For the

**Table 1.** Properties of absorption lines and states. All energies are in cm<sup>-1</sup>.

$M$	$(\pm 6)_{1,2}$	$\mp 5$	$\pm 4$	$(\pm 3)_{1,2}$	$\mp 2$	$\pm 1$	0
$\mu$	0	$\pm 1$	$\pm 1$	0	$\pm 1$	$\pm 1$	0
Symmetry of states in $D_3$ group.	$A_1, A_2$	$E$	$E$	$A_1, A_2$	$E$	$E$	$A_1$
Notations of lines.			1a 1b	4 5	2a 2b	3a 3b	6a 6b
Energies of transitions at 2 K	–		20 611.8 20 616	–	20 638.5 20 650.1	– 20 693.5	– 20 714
Energies of transitions at 70 K	–	$\sim 190$ [28]	20 610	20 603, 20 615	20 640	20 681	20 697
$g_c$ of states (theory)	$\sim 18$ (in large field)	15	12	$\sim 9$ (in large field)	6	3	0
Splitting of states $H = 35$ kOe (theory)	29.4	24.5	19.6	14.7	9.8	4.9	0
Splitting of states $H = 35$ kOe, $T = 2$ K (experiment)	29.1	–	+15.1 +18	–	–4.7 +4.5	+6	$\sim 0$
$g_c$ of states at $T = 2$ K (experiment)	17.8	–	9.2 11	–	2.9 2.75	– 3.7	$\sim 0$
Shift of states ( $T_N \rightarrow 2$ K)	–15.5 +15.5	–	–14.3 –10.1	–	–18.3 –6.7	– –4.4	$\sim 0$
Splitting of states $T = 2$ K, $H = 0$	31	–	4.2	–	11.6	–	$\sim 0$

beginning we suppose, that magnetization of Tb<sup>3+</sup> is determined only by the difference of populations of two components of the ground state splitting in the effective field of the Fe-sublattice. Then for Tb magnetization we obtain

$$M_{\text{Tb}} = M_{\text{Tb}}(0) \frac{1 - \exp(-D/kT)}{1 + \exp(-D/kT)} = M_{\text{Tb}}(0) \tanh\left(\frac{D}{2kT}\right), \quad (1)$$

$$D = D(0)M_{\text{Fe}}(T)/M_{\text{Fe}}(0). \quad (2)$$

Magnetizations  $M_{\text{Tb}}(0)$  and  $M_{\text{Fe}}(0)$  at  $T = 0$  K and function  $M_{\text{Fe}}(T)$  were taken from reference [9]. Splitting  $D(0) = 31$  cm<sup>-1</sup> of the Tb<sup>3+</sup> ground state in the effective field of the Fe-sublattice was taken from reference [10]. Then temperature dependence of Tb<sup>3+</sup> magnetization obtained from (1) exactly coincided with the experimental one [9]. This means, that splitting of the Tb<sup>3+</sup> ground state is determined only by the effective field of the Fe-sublattice, and lattice distortions take place only in the excited states of the Tb<sup>3+</sup> ion and are the local ones. Similar phenomena were observed, e.g., in references [18–22] and, in particular, in the crystal YbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, which has the same structure as the studied one [22]. Crystal structure directly depends on the electronic structure of atoms which the crystal comprises. Symmetry of huntite structure ferrobates is sensitive to change of rare earth atoms. Indeed, the temperature of the transition to lower symmetry increases with the increasing number of 4*f* electrons in rare earth ion [23]. Electronically excited atom is, actually, an impurity atom, and, therefore, geometry of its local environment can change. This statement does not mean that the atoms really change their positions during the electron transition, but rather that they are not in equilibrium positions for the excited state since the interaction of the rare

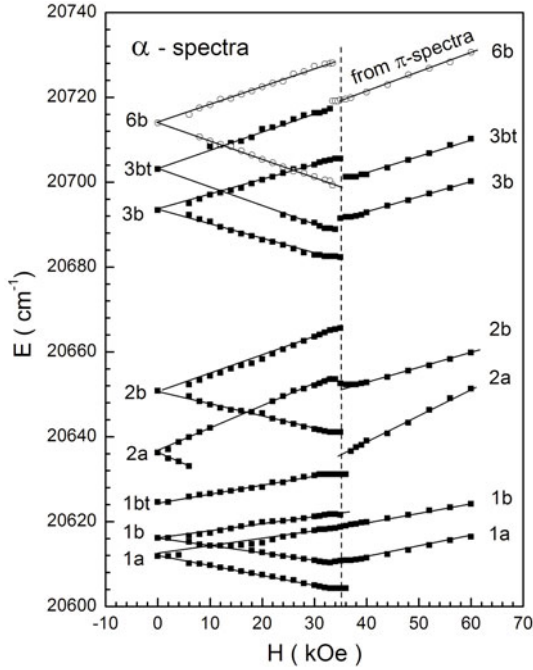
earth ion with ligands changes. The change of the positions (i.e. deviation from the adiabatic approximation) can also take place, but this can be revealed in luminescence [18]. Moreover, an electron transition is not an instant event, but a process, which occurs over some time. According to perturbation theory, electron transitions occur due to mixing of initial and final states by the time dependent perturbation caused by an electromagnetic wave. Therefore, during the electron transition, the initial state of the ion and its interaction with the environment also change.

Absorption spectra of TbFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> were also studied under the influence of the external magnetic field directed along and perpendicular to  $C_3$  axis of the crystal (magnetic easy axis) at  $T = 2$  K (Figs. 6 and 7). It is known from magnetic measurements [9,10], that at  $H||C_3$  spin-flop transition in the Fe-subsystem occurs at  $H_t = 35$  kOe. Simultaneously, magnetic moments of the both Tb-sublattices are directed along the magnetic field. In Figure 6, field dependences of the line positions at  $H||C_3$  are shown. We also retraced the field dependence of the integral intensity of part of the spectrum (Fig. 8). A feature found in the region of the spin-flop transition testifies to magnetostriction distortions accompanying the re-magnetization of the crystal (see also Ref. [24]).

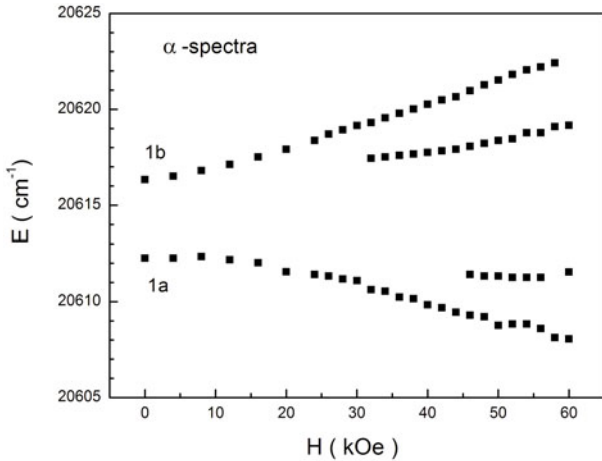
In the magnetic field along the  $C_3$  axis, the absorption lines are split linearly in the field value (Fig. 6). This splitting is caused by nonequivalence of Tb-sublattices at  $H < H_t$ . The splitting of the non-Kramers quasi doublet in magnetic field directed along the  $C_3$  axis of a crystal is represented in the form [10]:

$$\Delta = \mu_B g_c H, \quad (3)$$

where  $g_c$  is the effective Landé factor.

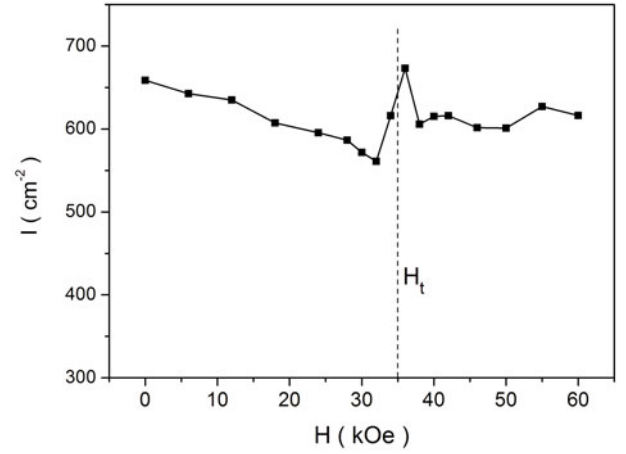


**Fig. 6.** Positions of  $\alpha$ - and  $\pi$ -polarized absorption lines as a function of external magnetic field  $\vec{H}||C_3$  at  $T = 2$  K.



**Fig. 7.** Positions of  $\alpha$ -polarized absorption lines at  $T = 2$  K as a function of external magnetic field  $\vec{H} \perp C_3$  axis.

Up to the spin-flop field, the exchange field, acting from Fe-sublattice on Tb-sublattice, does not change and the energies of Tb-sublattices are changed only by the external field. Using equation (3), we can find the energy difference between the ground states of opposite Tb sublattices in magnetic field 35 kOe of the spin-flop transition at  $T = 2$  K:  $\Delta_{gr} = 29.1 \text{ cm}^{-1}$ . Ritter et al. [9] supposed that a critical field  $H_t$ , needed to induce the metamagnetic transition, corresponds to the value of the Fe-sublattice exchange field acting on the Tb-sublattice. Indeed, Popova et al. [10] have estimated the splitting in this field as  $\Delta(T = 0 \text{ K}) \approx 31 \text{ cm}^{-1}$ , which is close to the splitting in the spin flop field. Splitting of lines 1a, 1b, 2a, 2b, 3b and 6b in the same field are: 14, 11, 33.8, 24.6,



**Fig. 8.** Integral intensity of the  $\alpha$ -polarized absorption in the interval  $20\,600\text{--}20\,670 \text{ cm}^{-1}$  as a function of external magnetic field  $\vec{H}||C_3$  at  $T = 2$  K.

23.1 and  $29.4 \text{ cm}^{-1}$ , respectively. Splitting of absorption lines ( $\Delta$ ) are equal to the differences between corresponding energy splitting obtained by the Tb-sublattices in the ground ( $\Delta_{gr}$ ) and excited ( $\Delta_{ex}$ ) states:

$$\Delta = \Delta_{gr} - \Delta_{ex}. \quad (4)$$

Then, we find excited states splitting to be  $\Delta_{ex} = 15.1, 18, -4.7, 4.5, 6$  and  $\sim 0 \text{ cm}^{-1}$  and their Landé factors:  $g_c = 9.2, 11, 2.9, 2.75, 3.7$  and  $\sim 0$ , respectively (see also Tab. 1). The zero Landé factor again indicates that the state No. 6 is a singlet. The same followed above from the zero shift of this state as a result of magnetic ordering. The negative value of  $\Delta_{ex}$  for the state No. 2a (which is the lower component of the state No. 2 splitting at  $T < T_N$ ) means that the magnetic moment of this state is directed opposite to the magnetic moment of the ground state. A similar situation, probably, takes place also for the state No. 3. The magnetic moments of the both components of the state No. 1 are oriented in the same direction as that of the ground state, though the splitting is somehow connected with the antiferromagnetic ordering in the Fe-sublattice. The intensity of the 2a line both in  $\alpha$  and  $\pi$ -polarizations at  $T = 2$  K is smaller than intensity of 2b line (see Figs. 1 and 3). Line 3a at  $T = 2$  K is not observed at all. (Lines 1a and 1b will be discussed separately). This becomes understandable, if we take into account that the former lines at  $T = 2$  K are due to transitions which occur from the lower component of the ground state with the change of the magnetic moment to the opposite direction.

We mentioned above that the field  $H_t$  of the spin-flop transition is considered to be equal to the Fe-sublattice effective field acting on the Tb-sublattice [9]. Thus, after the spin-flop transition these fields substitute each other, since magnetic moments of the Fe-sublattice are perpendicular to those of Tb-sublattice and therefore effective field acting from Fe to Tb-sublattice is equal to zero. If the effective field was identical for the ground and excited states, then positions of the absorption lines immediately after the spin-flop would coincide with those at  $H = 0$ .

**Table 2.** Selection rules for electric dipole transitions in  $D_3$  symmetry.

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

**Table 3.** Selection rules for electric dipole transitions in  $C_2$  symmetry. Polarizations are shown relative to the local  $C_2$  axis.

	$A_1$	$A_2$
$A_1$	$\pi$	$\sigma$
$A_2$	$\sigma$	$\pi$

But the effective field of Fe-sublattice has an exchange nature [9,10] and depends on the Tb electron state (Tab. 1). Nevertheless, the energy of the transition No. 6 into the singlet state in zero magnetic field and just above 35 kOe should coincide with this logic. However, this is not so (see Fig. 6). Magnetostriction at the spin-flop transition, and change of the crystal field connected with it, can be a source of the discrepancy. The dipole-dipole interaction can be an additional source of the discrepancy. Thus, positions of lines after spin-flop can not be predicted.

Considering the splitting of  ${}^7F_6$  ( $J = 6$ ) and  ${}^5D_4$  ( $J = 4$ ) states successively in cubic  $O$  and trigonal  $D_3$  CF, we obtain [25]:

$${}^7F_6(J = 6) \rightarrow A_1 + A_2 + E + T_1 + 2T_2 \rightarrow A_1 + A_2 + E + (A_2 + E) + 2(A_1 + E), \quad (5)$$

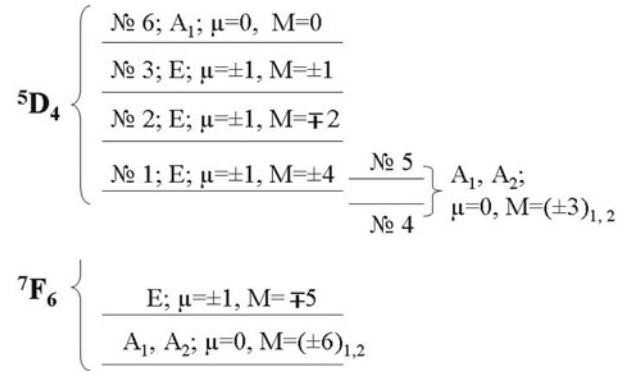
$${}^5D_4(J = 4) \rightarrow A_1 + E + T_1 + T_2 \rightarrow A_1 + E + (A_2 + E) + (A_1 + E). \quad (6)$$

Here  $A_1$  and  $A_2$  are singlets,  $E$  is doublet,  $T_1$  and  $T_2$  are triplets. It was noted in reference [12], that splitting connected with the symmetry lowering from  $D_3$  to  $C_2$  one are very small in the TbFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> crystal and are not observed. Symmetry selection rules in  $D_3$  and  $C_2$  CF are described by Tables 2 and 3.  $f$ - $f$  transitions are formally allowed by parity, since these CF have no center of inversion and wave functions have no definite parity. In reality, the forbiddenness by the parity selection rule is removed because the non-centrosymmetric CF intermixes odd and even atomic wave functions.

There is one more approach to the classification of states in CF. In a homogeneous electric field ( $C_{\infty v}$  symmetry), atomic states are split according to the absolute value of magnetic quantum number  $M$ . If the atom is also in a magnetic field, each of these states with the quantum number  $M$  is split. The value of the splitting is

$$\Delta_H = 2g\mu_B MH, \quad (7)$$

under the condition, that this splitting is much less than the splitting in the electric field. Here  $g$  is the Landé factor of the free atom ( $g = 1.5$  in our case). According to definition (3) of the splitting of quasi doublets in a magnetic field, for  $M = 6$  we obtain  $g_c = 2gM = 18$ , that almost exactly coincides with the experimental value  $g_c = 17.8$ .


**Fig. 9.** Diagram of states at  $T > T_N$  in  $D_3$  symmetry notations.

However in the crystal electric field, atomic states are classified according to the crystal quantum number  $\mu$ . This quantum number is an analog of  $M$  in a free atom. In a trigonal CF,  $\mu$  can acquire three values: 0,  $\pm 1$  [26]. States with  $M = \mu \pm 3n$  (where  $n = 0, 1, 2, \dots$ ) correspond to each  $\mu$  in the trigonal symmetry [26]. As a result, the following set of states is obtained [26]:

$$\begin{array}{ccccccc} M = 0 & \pm 1 & \mp 2 & (\pm 3)_{1,2} & \pm 4 & \mp 5 & (\pm 6)_{1,2} \\ \mu = 0 & \pm 1 & \pm 1 & 0 & \pm 1 & \pm 1 & 0. \end{array} \quad (8)$$

These states are also shown in Table 1 and preliminary identification of the observed transitions and states is made, taking into account that energy of states in CF is determined in the first approximation by the absolute value of  $M$  (see also Fig. 9). States with  $|M| = 0-6$  belong to the ground state and states with  $|M| = 0-4$  belong to the excited state. In the same Table, symmetries of these states in the  $D_3$  group are shown [26]. The number and types of states, naturally, coincide with those in (5) and (6), but the classification of states with the help of quantum numbers  $\mu$  and  $M$  permits us to estimate succession of the states according to their energies. The states  $A_1$  and  $A_2$  with  $|M| = 6$  are, evidently, the lowest ones in the ground manifold. They are of the type  $(\langle M_+ | \pm \langle M_- |)$  and the splitting between them is very small. In particular, in the crystal TbAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> (with the same symmetry as the studied one at high temperatures) the splitting is less than  $1 \text{ cm}^{-1}$  [27]. Already in a small effective field of the Fe-sublattice these states are mixed and are transformed into almost pure states  $\langle M = \pm 6 |$  with the mentioned consequence for the value of  $g_c$ .

Splitting of the states (8) is described by equation (7), where  $M$ , in the first approximation, is defined by (8). Then we can find theoretical values of  $g_c$  and splitting of the states in the field 35 kOe of the spin-flop transition. Results are shown in Table 1. They differ from the experimental ones, since states (8) are approximate. In reality, in (7) instead of  $M$  should be  $M_{eff}$ , because states (8) contain, besides shown  $M$ , admixtures of states with another  $M$ . It is so because the matrix of CF in the basis of free atom functions is not diagonal over  $M$  already in trigonal symmetry, but we have  $C_2$  distortions. Experimental  $g_c$  values differ from the theoretical ones, however,

they confirm identification of states 1, 2 and 3 as doublets and of state 6 as the singlet in  $D_3$  symmetry (see Tab. 1 and Fig. 9).

In crystals, selection rules for the polarized light absorption are governed by the number  $\mu$  and coincide with those for the number  $M$  in a free atom [26]:

$$\begin{aligned} \Delta\mu = \pm 1 & \text{ corresponds to } \mp \text{ circularly polarized} \\ & \text{and } \sigma\text{-polarized waves,} \\ \Delta\mu = 0 & \text{ corresponds to } \pi\text{-polarized waves.} \end{aligned} \quad (9)$$

Referring to Table 1, we obtain in  $D_3$  symmetry (at  $T > T_N$ ) only three spectrally resolved transitions allowed in  $\alpha$  ( $\sigma$ ) polarization. Selection rules (9) are valid for the considered transitions only because functions (8) are approximate and contain admixtures of functions with another  $M$ . Indeed, selection rules of the form (9) are strict only for magnetic quantum number  $M$  of a free atom. For instance, in order to allow the transition No. 1:  $M = \pm 6 \rightarrow M = \pm 4$  in  $\alpha$  ( $\sigma$ ) polarization, it is necessary to admix the state  $M = \pm 5$  to the ground state  $M = \pm 6$ . According to reference [28], this state is  $190 \text{ cm}^{-1}$  higher than the ground one. Now it is understandable why intensity of transitions decreases in the sequence 1, 2, 3. Selection rules (9) certainly coincide with those for irreducible representations (Tab. 2). However selection rules (9) permit to judge about relative intensities of transitions.

Transitions Nos. 1, 2 and 3, according to (9) and Table 2, are allowed in  $D_3$  symmetry only for  $\alpha$  ( $\sigma$ ) polarization. This is just the case in  $\text{TbAl}_3(\text{BO}_3)_4$  [27], where the local symmetry of  $\text{Tb}^{3+}$  ion is  $D_3$ . We observe transitions Nos. 1 and 2 also in  $\pi$ -polarization (Fig. 3), since the local symmetry of  $\text{Tb}^{3+}$  ion in the studied crystal is  $C_2$ . In this symmetry,  $E$ -states are split:  $E \rightarrow A_1 + A_2$ . The splitting at  $T > T_N$  is too small to be observed, but deviation from  $D_3$  symmetry appeared to be enough to allow transitions Nos. 1 and 2, but not enough to allow transition No. 3 (this transition is not observed in  $\pi$ -polarization). Polarizations and selection rules in  $C_2$  symmetry (Tab. 3) are defined relative to the two-fold  $C_2$  axis of the Tb position. Below temperature of the structural phase transition (192 K) the local  $C_2$  axis coincides with one of three  $C_2$  axes of the whole trigonal crystal, which are perpendicular to the  $C_3$  axis of the crystal. There are three equivalent but differently oriented (along the different  $C_2$  axes of the crystal) Tb centers with the  $C_2$  symmetry. In this case  $\pi$ -polarization relative to  $C_3$  axis of the crystal is  $\sigma$ -polarization relative to the local  $C_2$  axis. Then transitions  $A_1 \leftrightarrow A_2$  in  $\pi$ -polarization relative to  $C_3$  axis of the crystal are allowed (Tab. 3) and, consequently, become partially allowed  $\pi$ -polarized transitions  $A_1, A_2 \rightarrow E$  in  $D_3$  designations.

In  $\pi$ -spectra (Fig. 3) three additional, relative to  $\alpha$ -spectra, lines (4, 5 and 6) are observed. They are due to transitions in two states  $\mu = 0, M = \pm 3$  ( $A_1, A_2$ ) and in the state  $\mu = 0, M = 0$  ( $A_1$ ), respectively (Fig. 9), which are allowed only in  $\pi$ -polarization in  $D_3$  symmetry (see Eq. (9) and Tab. 2). The latter identification is confirmed by the zero Landé factor of this state and the zero shift due to magnetic ordering found experimentally (Tab. 1).

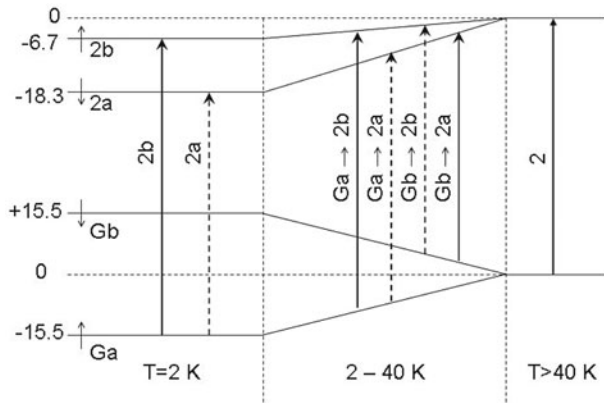
The former two transitions in  $\text{TbAl}_3(\text{BO}_3)_4$  [27] are also close to the strongest transition in  $E$ -state (in  $D_3$  symmetry). In  $\text{TbFe}_3(\text{BO}_3)_4$  these transitions are not observed at temperature  $T < T_N$  separately from components of the line 1 splitting caused by the magnetic ordering. First, it is due to overlapping of the close absorption lines with the close intensities (lines Nos. 4 and 5 are allowed but lines 1a and 1b are forbidden in  $\pi$ -polarization in  $D_3$  approximation). Therefore it is not reliable to use  $\pi$ -spectra for analysis of field and temperature dependences of the lines 1a and 1b positions. It is more reliable to use  $\alpha$ -spectra, where transitions 1a and 1b are allowed and transitions Nos. 4 and 5 are forbidden in  $D_3$  symmetry. However, there is also a more essential influence of the 4 and 5 states. They are  $A_1$  and  $A_2$  singlet states already in  $D_3$  symmetry. The states 1a and 1b have the same symmetry. They appeared as a result of splitting of  $E$  state (in  $D_3$  symmetry approximation) under the influence of the crystal distortions and the effective field of the Fe sublattice. States with the identical symmetry are effectively mixed by these perturbations, and two accidentally nearly doubly degenerated in  $C_2$  symmetry states are formed instead of four states. Indeed, in magnetic field  $H \perp C_3$ , which reduces symmetry of the crystal, these states are split (see Fig. 7). The total splitting ( $\Delta$ ) of the close crystal field split components ( $\Delta_{CF}$ ) in the magnetic field is described by the equation:

$$\Delta = (\Delta_{CF}^2 + \mu_B^2 g_{\perp}^2 H_{\perp}^2)^{1/2}. \quad (10)$$

When magnetic energy is much less or commensurable with the crystal field energy, the formula (10) is the non-linear function of magnetic field in agreement with the experiment (Fig. 7). It is also worth noting, that the splitting of the 1a state in magnetic field along  $C_3$  axis is close to the theoretical splitting in the magnetic field between states Nos. 4 and 5 (see Tab. 1). The particular nature of states in the considered energy interval is, probably, a cause of some phenomena, observed in this region: (1) ratio of intensities of the 1a and 1b lines is opposite in  $\alpha$ - and  $\pi$ -polarizations (Figs. 1a and 3a), (2) at temperature near  $T_N$  an abrupt shift of the 1a line occurs (Fig. 4a) that testifies to a change of the local distortions in the 1a state, (3) magnetic moment orientation in the states 1a and 1b is the same (Tab. 1), though splitting between them is caused by antiferromagnetic ordering in the Fe subsystem.

Now it is possible to consider the nature of lines 2a, 3a, 6a and the nature of temperature dependences of their positions and intensities. The diagram of transitions between sublevels of the ground state ( $G$ ) and the No. 2 state is shown in Figure 10. Similar diagram is supposed to be valid for the transitions to sublevels of the state No. 3. At  $T = 2 \text{ K}$  only transitions from the lower sublevel of the ground state are observed: more strong transition  $G_a \rightarrow 2b$  (without overturn of the magnetic moment) and less strong transition  $G_a \rightarrow 2a$  (with overturn of the magnetic moment) labeled as 2b and 2a in the spectra, respectively. At temperature near  $T_N$ , when both sublevels of the ground state are populated, four transitions are possible (Fig. 10): the same two transitions from the





**Fig. 10.** Diagram of transitions between sublevels of the ground state ( $G$ ) and the No. 2 state.

lower component of the ground state splitting and two transitions from the upper component (the more strong transition  $G_b \rightarrow 2a$  and the less strong one  $G_b \rightarrow 2b$ ). Thus, near  $T_N$ , the absorption line labeled as  $2a$  in the spectra is, actually, a superposition of three transitions (Fig. 10). The strongest of them,  $G_b \rightarrow 2a$ , has the lowest frequency. With the temperature decrease the population of the sublevel  $G_b$  decreases and transitions  $G_b \rightarrow 2a$  and  $G_b \rightarrow 2b$  disappear. Therefore, the frequency of the absorption line  $2a$  increases, approaching the frequency of the  $G_a \rightarrow 2a$  transition (Figs. 10 and 4a). The state No. 6 is the singlet and is not split in the exchange field. Therefore, the line  $6a$  is the pure  $G_b \rightarrow 6$  transition from the upper component of the ground state. The line  $3a$  (Figs. 1b and 4) is practically the pure  $G_b \rightarrow 3a$  transition in the whole temperature range, since transitions with the overturn of the magnetic moment ( $G_a \rightarrow 3a$  and  $G_b \rightarrow 3b$ ) appeared to be too weak, as it was inferred above from the low temperature spectra. At the same time, transition  $G_b \rightarrow 3a$  occurs from the upper sublevel of the ground state and, therefore, corresponding absorption line disappears with the temperature decrease.

### 3 Summary

Optical absorption spectra of trigonal crystal  $TbFe_3(BO_3)_4$  were studied in the region of  ${}^7F_6 \rightarrow {}^5D_4$  transition in  $Tb^{3+}$  ion. The splitting of  $Tb^{3+}$  absorption lines observed at  $T = 2\text{ K}$  in zero external magnetic field result from the splitting of the excited states connected with the magnetic ordering, while the splitting observed near the Néel temperature are mainly due to the ground state splitting. Measured splitting of the absorption lines in magnetic field permitted us to obtain the corresponding splitting of states and their Landé factors. The negative sign of the state splitting indicates that the orientation of the state magnetic moment is opposite to that of the ground state. In particular, this takes place for the low energy component of the exchange splitting of one of the  $Tb^{3+}$  excited states. Determined orientations of the excited states magnetic moments permitted us to explain the ratio of the intensities of

components of the lines splitting in the exchange field of the Fe-sublattice: stronger transitions occur without overturn of the magnetic moment. In the vicinity of the spin-flop transition of Fe-sublattice a distortion of  $Tb^{3+}$  ion environment takes place.

Step-wise splitting of one of the absorption lines ( $\sim 20615\text{ cm}^{-1}$ ) was discovered in the region of the Néel temperature. This is shown to be due to step-wise change of equilibrium geometry of the local  $Tb^{3+}$  ion environment only in the excited state of the  $Tb^{3+}$  ion. Asymmetric shifts of the excited states at cooling from  $T_N$  to  $2\text{ K}$  and the character of the temperature dependences of  $f-f$  transitions intensity indicates that the magnetic ordering is accompanied by temperature variations of the  $Tb^{3+}$  local environment in the excited states. A pronounced shift of one of the absorption lines has been observed in the vicinity of the  $TbFe_3(BO_3)_4$  structural phase transition. Temperature interval of the phase coexistence is  $\sim 3\text{ K}$ .

Crystal field splitting components have been identified according to crystal quantum number  $\mu$  and according to irreducible representations. The identification is consistent with the experimental results. In particular, the ground state (in  $D_3$  symmetry approximation) consists of two close singlets  $\mu = 0$  ( $M = \pm 6$ ) (or  $A_1$  and  $A_2$  in symbols of irreducible representations) which are split and magnetized by effective exchange field of the Fe-sublattice. The identification allowed us to explain the ratio of intensities of the crystal field splitting components.

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