Paramagnetic magneto-optical activity of *f-f* transitions in HoFe$_3$(BO$_3$)$_4$ and HoAl$_3$(BO$_3$)$_4$ single crystals

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A B S T R A C T

Absorption and magnetic circular dichroism (MCD) spectra of HoFe$_3$(BO$_3$)$_4$ and HoAl$_3$(BO$_3$)$_4$ single crystals were measured as a function of temperature in the range of 90–293 K. Based on integrals of *f-f* absorption and MCD bands, temperature dependences of the paramagnetic magneto-optical activity (MOA) of *f-f* transitions were obtained for the first time. It was revealed that MOA of the same *f-f* transitions in the studied crystals were substantially different and their temperature dependences did not follow the Curie-Weiss law in contrast to the properties of allowed transitions. The observed phenomena were accounted for as a consequence of the nature of *f-f* transitions allowance. In temperature dependences of the MOA of two transitions the singularities were revealed, which indicated to some local structural distortions in the corresponding excited states.

1. Introduction

HoAl$_3$(BO$_3$)$_4$ and HoFe$_3$(BO$_3$)$_4$ crystals have huntite-like structure. HoAl$_3$(BO$_3$)$_4$ has $R32$ space symmetry at all temperatures. HoFe$_3$(BO$_3$)$_4$ crystal undergoes the structural phase transition from $R32$ to $P3_121$ (D_3^4) symmetry. At this transition the local symmetry of Ho decreases from D_3 to C_2 one. Temperature of the transition depends strongly on the method of crystal growing: it is 427 K for the powder samples obtained by the solid-state synthesis [1] and 360 K for single crystals grown from a solution-melt [2].

Ho^{3+} is the active ion widely used in solid state lasers with the emissions in the infrared and visible spectral ranges. Optical properties of Ho^{3+} ion were studied in many materials (e. g. Refs. [3–10]). The visible and near-infrared luminescence in Ho:YAl$_3$(BO$_3$)$_4$ crystal was investigated by Koporulina et al. [11]. The huntite-like structure has no center of inversion. Therefore, crystals of this type are used also as nonlinear active media [12,13]. Spectroscopic properties of the HoAl$_3$(BO$_3$)$_4$ crystal were studied in Ref. [14]. The first study of optical absorption spectra of HoFe$_3$(BO$_3$)$_4$ single crystal in the infrared region (500–10000 cm^{-1}) was presented in Ref. [2]. The detailed spectroscopic study of *f-f* transitions in HoFe$_3$(BO$_3$)$_4$ in the region of 8500–24500 cm^{-1} in the temperature range including the spin-reorientation temperature was carried out in Ref. [15] and as a function of magnetic field in Ref. [16].

Investigations of magnetic and magneto-electric properties of the HoFe$_3$(BO$_3$)$_4$ single crystal showed that it referred to multiferroics [17,18], i. e., it possessed magnetic and electric polarizations simultaneously. It should be noted that the giant magnetoelectric polarization in magnetic field was also detected in alumoborate of holmium HoAl$_3$(BO$_3$)$_4$ at the absence of magnetic ordering [19–21]. Both crystals have highly anisotropic magnetic properties at low temperatures [20,22,23]. HoFe$_3$(BO$_3$)$_4$ crystal transfers from the paramagnetic to the magnetically ordered state at temperatures below $T_N = 38$ K [22].

Magnetic circular dichroism (MCD) of *f-f* transitions in solids is widely studied. It is worth mentioning only some of them related to the Ho^{3+} ion in different compounds [24–26]. Usually the MCD spectra of *f-f* transitions were measured only at one or several temperatures. These spectra were decomposed on the diamagnetic and paramagnetic parts, but the nature of the MCD was not analyzed. At the same time, just the temperature dependence of the MCD of the parity forbidden *f-f* transitions reveals peculiar behavior and can give information also about the nature of the *f-f* transitions allowance [27]. In the present work we measured temperature dependences of the integral paramagnetic magneto-optical activity (MOA) of *f-f* absorption bands in the Ho-Fe$_3$(BO$_3$)$_4$ and HoAl$_3$(BO$_3$)$_4$ single crystals. Nature of the observations is analyzed and accounted for. Investigation of the magneto-optical properties of the crystals with the very close structure carried out in the present work gives useful information about the nature of the *f-f* transitions MOA.

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2. Experimental details

HoAl$_3$(BO$_3$)$_4$ crystals were grown from the melt solution based on bismuth trimolybdate and lithium molybdates using the technique described in Ref. [28]. HoFe$_3$(BO$_3$)$_4$ single crystals were grown from a bismuth trimolibdate solution-melt with a nonstoichiometric composition of the crystal forming oxides. The technology was described in detail in Ref. [15].

Both crystals belong to the trigonal symmetry. The lattice constants of the HoAl$_3$(BO$_3$)$_4$ are: a = 9.293(3) Å, c = 7.240(3) Å [29] and those of HoFe$_3$(BO$_3$)$_4$ are a = 9.53067(5) Å, c = 7.55527(6) Å [22]. The unit cell contains three formula units. Trivalent rare-earth (RE) ions occupy positions of only one type. In HoAl$_3$(BO$_3$)$_4$ they are located at the center of trigonal prisms made up of six crystallographically equivalent oxygen ions. The triangles formed by the oxygen ions in the neighboring basal planes are not superimposed on each other but are twisted by a certain angle. Owing to this distortion, the symmetry D$_{3h}$ of the ideal prism is reduced to the symmetry D$_3$. In HoFe$_3$(BO$_3$)$_4$ the prisms are deformed along one of the C$_2$ axes. The FeO$_6$ and AlO$_6$ octahedrons share edges in such a way that they form helicoidal chains, which run parallel to the C_3 axis and are mutually independent.

The absorption spectra were measured by the two beam technique, using an automated spectrophotometer designed on the basis of the diffraction monochromator MDR-2. The spectra were obtained for the light propagating along the C_3 axis (α spectrum). Optical slit with (spectral resolution) was 0.2 nm in the region of 300–600 nm and 0.4 nm in the region of 600–1100 nm.

The MCD spectra, the same as the absorption spectra, were recorded with the light propagating along the C_3 axis of the crystals. The magnetic field of 5 kOe was also directed along the C_3 axis. The circular dichroism was measured using the modulation of the light wave polarization with the piezoelectric modulator (details see in Ref. [30]). The MCD was obtained as a half difference of the circular dichroisms at opposite magnetic fields. The natural circular dichroism is excluded in this case. The sensitivity in measuring of the circular dichroism was 10^{-4}, and the spectral resolution was the same as that at the absorption spectra measuring. The sample was put in a nitrogen gas flow cryostat. Accuracy of the temperature measuring was $\sim$ 1 K. Thickness of the HoAl$_3$(BO$_3$)$_4$ sample was 0.25 mm and that of the HoFe$_3$(BO$_3$)$_4$ sample was 0.19 mm.

3. Results and discussion

The absorption and MCD spectra of the HoAl$_3$(BO$_3$)$_4$ crystal were measured in the spectral range of 10500–25000 cm^{-1} (Figs. 1 and 2). The identification of f-f absorption bands was made according to Kaminskii [31]. The absorption and MCD spectra of the HoFe$_3$(BO$_3$)$_4$ crystal were measured in the range of 11000–22700 cm^{-1} (Figs. 3 and 4). The MCD spectra of one of the absorption bands are shown as an

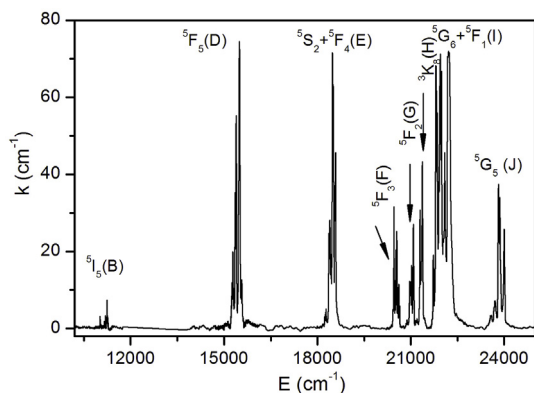**Fig. 2.** MCD spectrum (Δk) of HoAl$_3$(BO$_3$)$_4$ at 90 K.

Fig. 3. Absorption spectrum (k) of HoFe$_3$(BO$_3$)$_4$ at 90 K.

Fig. 4. MCD spectrum (Δk) of HoFe$_3$(BO$_3$)$_4$ at 90 K.

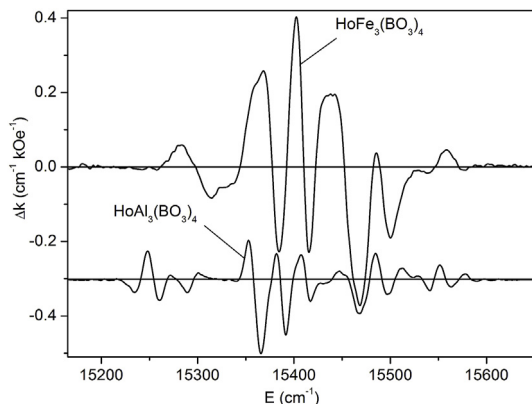**Fig. 1.** Absorption spectrum (k) of HoAl$_3$(BO$_3$)$_4$ at 90 K.

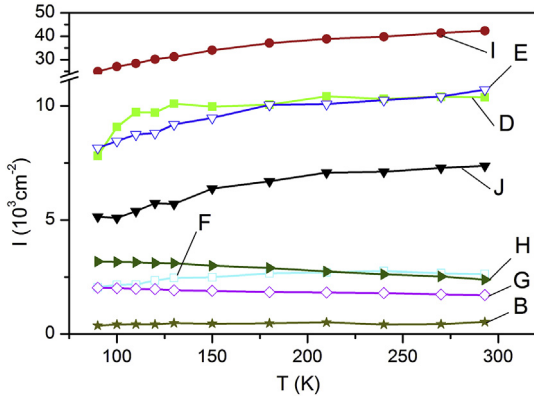**Fig. 5.** MCD spectra (Δk) of $^5I_8 \rightarrow {}^5F_5$ transition (D-band) at 90 K.

Fig. 6. Temperature dependences of intensities (I) of absorption bands in $HoAl_3(BO_3)_4$.

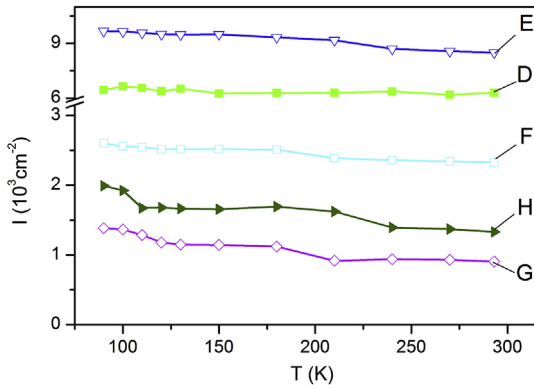**Fig. 7.** Temperature dependences of intensities (I) of absorption bands in $HoFe_3(BO_3)_4$.

example in Fig. 5. Detailed analysis of the absorption and MCD spectra fine structure will be done elsewhere later. All spectra were measured as a function of temperature in the interval 90–293 K. The absorption spectrum of the $HoFe_3(BO_3)_4$ crystal (Fig. 3) consists of narrow bands corresponding to f-f transitions in Ho^{3+} ions and of wide bands due to d-d transitions in Fe^{3+} ions ($^6A_1 \to ^4T_1$ and $^6A_1 \to ^4T_2$ in the cubic crystal field notation). At $E \sim 22900\,cm^{-1}$ there is also a comparatively strong d-d transition $^6A_1 \to ^4A_1{}^4E$ and at $E \sim 25000\,cm^{-1}$ the edge of the strong absorption occurs, which is due to the interatomic Fe–Fe (Mott-Hubbard) transitions [32]. These strong transitions overlap the f-f transitions at higher energies. We approximated d-d absorption bands by the Gauss functions and subtracted them from the total spectra. So we obtained f-f absorption spectra. MCD of the d-d transitions was too small to be observed (Fig. 4). All f-f spectra were measured as a function of temperature from 90 till 293 K. Integral intensities of f-f absorption bands did not reveal substantial dependence on temperature (Figs. 6 and 7).

The MCD of a single line which is split on two components in the magnetic field directed along the light propagation is given by the equation:

$$\Delta k = k_{m+} \phi(\omega, \omega_0 + \Delta\omega_0) - k_{m-} \phi(\omega, \omega_0 - \Delta\omega_0) \qquad (1)$$

Here k_{m+} and k_{m-} are amplitudes of (+) and (−) circularly polarized lines; φ are form functions of (+) and (−) polarized lines. If the Zeeman splitting $\Delta\omega_0$ is much less than the line width then one obtains:

$$\Delta k = k_m c \phi(\omega, \omega_0) + k_m \Delta\omega_0 \partial\phi(\omega, \omega_0)/\partial\omega_0 \qquad (2)$$

Here $k_m = k_{m+} + k_{m-}$ is the amplitude of the line not split by the magnetic field, and $c = (k_{m+} - k_{m-})/k_m$. The first term in (2) is the paramagnetic MCD and the second one is the diamagnetic effect. The

integral over absorption band paramagnetic magneto-optical activity (MOA) is determined by the equation:

$$c = \frac{\langle \Delta k(\omega) \rangle_0}{\langle k(\omega) \rangle_0} = C \frac{\mu_B H}{k_B(T-\theta)} \qquad (3)$$

Here C is a dimensionless parameter of the MOA, k_B is the Boltzmann constant, θ is the Curie-Weiss constant. It is supposed in (3) that the MOA is proportional to the paramagnetic susceptibility according to Van Vleck and Hebb [33], and that both of them follow the Curie-Weiss law. equation (3) is valid both for a single line and for a complex band. From equation (2) we see that the diamagnetic effect gives zero as a result of integration over the absorption band. In this work we will consider only the paramagnetic MCD.

The zero moments of the MCD and absorption bands, presented in (3), were found from the corresponding spectra, and so the temperature dependences of the parameter c were obtained. In the studied temperature range the paramagnetic susceptibility of the $HoAl_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ crystals follows the Curie-Weiss law [20,22]. Using data of Refs. [20,22], we found the Curie-Weiss constants $\theta = +5.5$ and $-19\,K$ for the $HoAl_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ crystals, respectively, in the field $H||C_3$. Then, with the help of Eq. (3), we found parameter "C" of MOA of f-f transitions at all temperatures from the experimental temperature dependences of the parameter "c". If the MOA of the transition is proportional to the paramagnetic susceptibility, then the dimensionless parameter C of the MOA in (3) should be independent of temperature. However, on the contrary, the parameter "C" revealed substantial temperature dependence (Fig. 8 – 13). The MOA (C) of some transitions even changes sign with the temperature variation (Figs. 9, 10, 12 and 13). As noted above, the studied crystals have identical (huntite-like) structure and close lattice constants, however, the MOA of the same f-f transitions in these crystals substantially differ in value, sign and temperature dependence (Figs. 8–12).

As known, the MOA of allowed transitions obeys the Van Vleck and Hebb theory [33], i. e., the MOA is proportional to the paramagnetic susceptibility. Besides that, the MOA of allowed transitions is practically independent of the crystal structure. The obtained experimental results revealed that both of these statements are not valid for forbidden f-f transitions. MOA of the forbidden f-f transitions was theoretically considered previously in Ref. [27]. In short situation is the following.

f–f transitions become partially allowed since states of the opposite parity are admixed to $4f$ states by the static or dynamic odd components of the crystal field (CF). Let's suppose that such state J'_F is admixed to the excited $4f$ state. This state should also satisfy the selection rule:

$$|J'_F - J_I| \leq 1 \qquad (4)$$

where J_I is the total angular-momentum of the ground state. In particular, the f–f transitions from the $J_I = 8$ ($^5I_8$) ground state of the Ho^{3+} ion can become allowed due to an admixture of states with $J = 7$, 8 and 9 to the excited $4f$ states. The Judd-Ofelt theory gives one more selection rule for the parity forbidden f-f transitions, which are allowed by
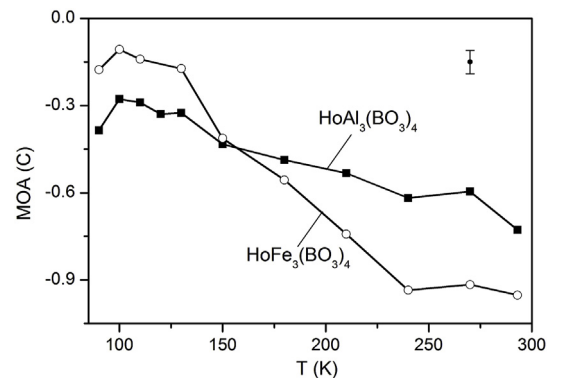

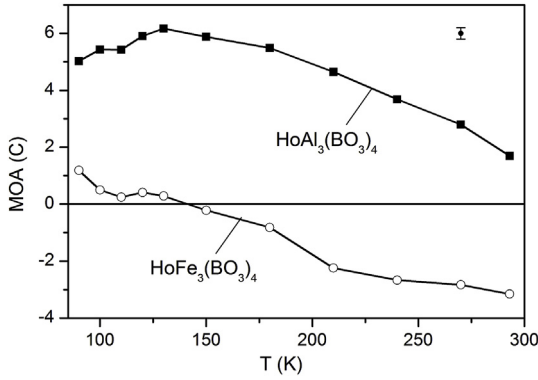**Fig. 8.** Temperature dependences of MOA of $^5I_8 \to ^5F_5$ transition (D-band).

Fig. 9. Temperature dependences of MOA of $^5I_8 \to {}^5S_2 + {}^5F_4$ transition (E-band).

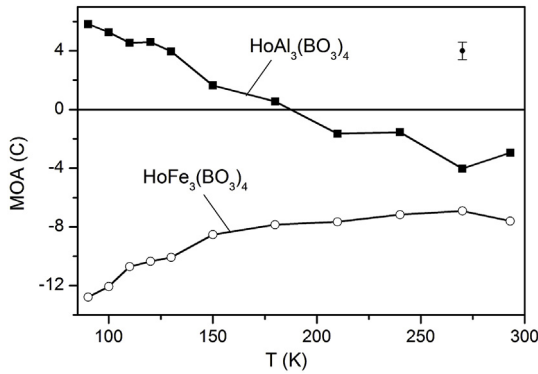**Fig. 10.** Temperature dependences of MOA of $^5I_8 \to {}^5F_3$ transition (F-band).

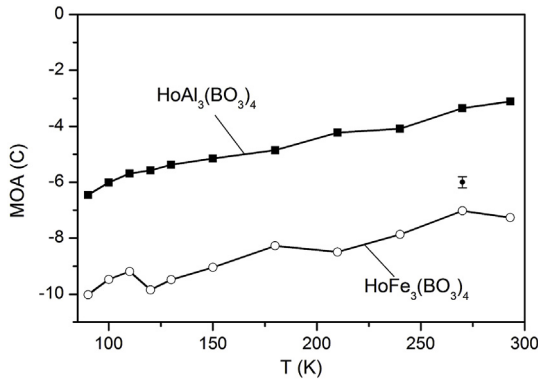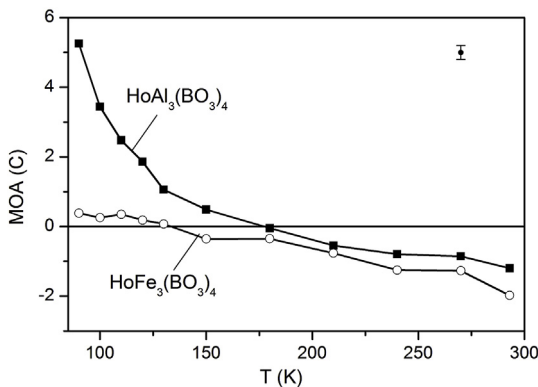**Fig. 11.** Temperature dependences of MOA of $^5I_8 \to {}^5F_2$ transition (G-band).

Fig. 12. Temperature dependences of MOA of $^5I_8 \to {}^3K_8$ transition (H-band).

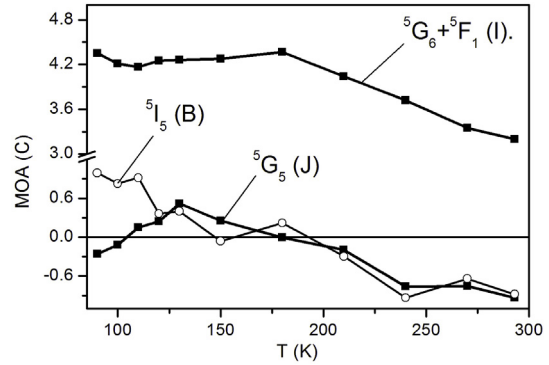**Fig. 13.** Temperature dependences of MOA of $^5I_8 \to {}^5I_5$, $^5G_5$, $^5G_6 + {}^5F_1$ transitions in $HoAl_3(BO_3)_4$.

odd components of the CF [34]:

$$|J_F - J_I| \le l \tag{5}$$

Here J_F is the total angular-momentum of the excited state and $l = 2$, 4 and 6 for the $4f$ shell. All considered excited states of Ho^{3+} ion satisfy this condition at least at one value of the parameter l. From equations (4) and (5) it also follows:

$$|J_F - J'_F| \le l - 1 \tag{6}$$

All excited states of Ho^{3+} ion under consideration satisfy condition (6) at least at one value of the parameter l and with at least one admixed state.

Allowed transitions from the ground state to the admixed states provide both the absorption intensity and the MOA of the f-f transition. The MOA of the mentioned allowed transitions in free atom was found in Ref. [27]:

for the transition $J \to (J-1)$: $C = - g (J+1)/2$,

for the transition $J \to J$: $C = - g / 2$, $\qquad\qquad\qquad$ (7)

for the transition $J \to (J+1)$: $C = + g J/2$.

For the ground state $^5I_8$ of Ho^{3+} ion the Landé factor $g = 1.25$. Then possible MOA (C) of f-f transitions in Ho^{3+} ion are found: -5.625, -0.625 and 5. They correspond to admixtures of states with $J = 7$, 8 and 9, respectively to excited states. If all components of the ground state split by CF are equally populated, the results (7) are valid for the integral over the f-f absorption band paramagnetic MOA (C) in crystals. In Table 1 the experimental MOA (C) are given at highest (room) temperature, when the mentioned condition of the equal population of the ground state sublevels is better fulfilled. It is seen from Table 1 that the maximum experimentally observed MOA of f-f transitions are close to the theoretical predictions. Comparison of the experimental data (Table 1) with the theoretical values permits us to infer, what of the admixtures allows the concrete f-f transition and creates its MCD. In particular, the transitions $\to {}^5F_3$ (F-band) and $\to {}^5F_2$ (G-band) in the $HoFe_3(BO_3)_4$ are allowed by the admixture only of the state with $J = 7$ to the excited state, while transitions $\to {}^5I_5$ (B-band), $\to {}^5F_5$ (D-band)

Table 1
The MOA values obtained from the experiment at room temperature.

Symbol	$^5I_8 \downarrow$	E (cm^{-1})	C exper $HoFe_3(BO_3)_4$	C exper $HoAl_3(BO_3)_4$
B	$^5I_5$	11110		-0.77
D	$^5F_5$	15300	-0.95	-0.73
E	$^5S_2 + {}^5F_4$	18500	-3.16	1.69
F	$^5F_3$	20500	-7.60	-2.94
G	$^5F_2$	21050	-7.26	-3.11
H	$^3K_8$	21300	-1.98	-1.2
I	$^5G_6 + {}^5F_1$	22000		3.2
J	$^5G_5$	23900		-0.93

and $\rightarrow^3K_8$ (H-band) in the $HoAl_3(BO_3)_4$ are allowed by the admixture of the $J = 8$ state or several states simultaneously.

The possibility of several contributions into the MOA with different ratios can result in the different MOA of the same *f-f* transition in different compounds. The ratio is very sensitive to value of the odd component of the CF. Indeed, in spite of the same structure and close parameters of the unit sells of the studied crystals, the MOA of the same *f-f* transitions are substantially different and even signs of the MOA are different in some cases (see Figs. 9 and 10 and Table 1). Thus we can infer that the odd distortions of the local environment of the Ho^{3+} ion, which allow the *f-f* transitions, are different in the crystals $HoFe_3(BO_3)_4$ and $HoAl_3(BO_3)_4$ both in the ground and in the excited states.

According to the said above, equation (7) are well applied to description of MCD of *f-f* transitions, if all sublevels of the ground state are almost equally populated. However this condition is usually not fulfilled for rare earth ions. Indeed, the crystal field splitting of the Ho^{3+} ground state is $283\,cm^{-1}$ (407 K) in $HoAl_3(BO_3)_4$ [6] and $354\,cm^{-1}$ (509 K) in $HoFe_3(BO_3)_4$ [35]. Therefore, if several contributions (7) into the MOA occur, the ratio of these contributions can change with the temperature variation. Therefore the deviation of the MOA temperature dependence from that of the paramagnetic susceptibility can occur, and the parameter C becomes to depend on temperature (Figs. 8–13). There are sharp bends on the temperature dependences of the MOA of the E and J bands at T = 130 K (Figs. 9 and 13) and of I band at T = 180 K (Fig. 13) in $HoAl_3(BO_3)_4$. These features can be due to the local deformations in the excited states, which change the odd part of the CF. The deformations occur just in the excited states, since such features are observed only on the corresponding transitions and are not observed in the crystal properties in the ground electron state.

It is worth paying attention that intensities of absorption bands weakly depend on temperature (Figs. 6 and 7) in contrast to those of the MOA (Figs. 8–13). This occurs because contributions into the *f-f* absorption intensity are summing up with the positive signs, while contributions into the MOA have different signs according to (7). Due to the latter reason temperature dependences of the MOA are more sensitive to the temperature changes of the local environment in the excited states.

Absolute values of the MOA of some transitions exceed theoretical values (7) at low or even at room temperature (Figs. 10 and 11). How can we explain this? In a first approximation, electronic states in the trigonal electric field are split according to absolute values of projection of the total moment M_J of the atom, the same as it takes place in the homogeneous electric field. Therefore, the ground state can have $|M_J| = J$. MOA of transitions from such state was found in Ref. [27]:

for the transition $J \rightarrow (J-1)$: $C_M = -gJ$,

for the transition $J \rightarrow J$: $C_M = -gJ$, (8)

for the transition $J \rightarrow (J+1)$: $C_M \approx +gJ$.

These values are twice as large those of Eq. (7). Thus, large values of the MOA testify that probability of transition from the state $|M_J| = J$ prevails.

Some contribution of the temperature independent B-term into the paramagnetic MOA is possible [36–38]. Such effect can exist only in crystals [37,38]. If electron states have integer moments, as in our case, the crystal field can create states, which have no magnetic moment. Magnetic field induces magnetic moment in such states due to the mixing of states and so creates MCD with the paramagnetic dispersion, which does not depend on temperature. Taking into account B-term, we obtain instead of (3): $c = \frac{\langle \Delta k(\omega) \rangle_0}{\langle k(\omega) \rangle_0} = C \frac{\mu_B H}{k_B(T-\theta)} + B$, or in a different way:

$$c \frac{k_B(T-\theta)}{\mu_B H} = C + B \frac{k_B(T-\theta)}{\mu_B H} \equiv C_{eff} \qquad (9)$$

Here C_{eff} is the measured parameter of MOA. Thus, contribution of the B-term into the measured C_{eff} should increase with the increasing

temperature, but it is difficult to separate it. However we can suppose that this contribution is small since order of values of the measured MOA are close to the theoretical parameters "C".

4. Summary

We measured absorption and magnetic circular dichroism spectra of the $HoFe_3(BO_3)_4$ and $HoAl_3(BO_3)_4$ single crystals as a function of temperature in the range of 90–293 K. With the help of these data we obtained the temperature dependences of the paramagnetic MOA of *f-f* transitions in the crystals for the first time. It was revealed, that the MOA of the same *f-f* transitions in the studied ferroborate and alumoborate were substantially different in value, sign and temperature dependence. This testifies to the substantial difference of the odd part of the local crystal field, which allows *f-f* transitions. Additionally, in contrast to the allowed transitions, their temperature dependences did not follow the Curie-Weiss law. It was shown that the observed phenomena were due to the existence of several contributions into the allowance of *f-f* transitions and of the corresponding contributions into the MCD with the different signs. In temperature dependences of the MOA of two transitions the singularities were revealed, which indicated to some local structural distortions in the corresponding excited states. The MOA values permitted us to show that the transitions $^5I_8 \rightarrow ^5F_3$ (F-band) and $\rightarrow^5F_2$ (G-band) in the $HoFe_3(BO_3)_4$ are allowed by the admixture only of the state with $J = 7$ to the excited states.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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