

Nature of magnetic circular dichroism and absorption spectra of f - f transitions in $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ single crystal

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ABSTRACT

We present first study of magnetic circular dichroism (MCD) spectra of Ho^{3+} ion in C_{4v} local symmetry, which it has in fluorite $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$. Optical absorption and MCD spectra were studied in this single crystal in the region of $^5I_8 \rightarrow ^5F_3$, 5F_2 , 3K_8 and 5G_5 transitions in the temperature range 3.6—90 K. It was revealed, that number of transitions observed in the MCD and absorption spectra coincides with the number of transitions only from the doublet E state to singlet excited states. The E - E type transitions are not active in MCD, but they are not observed in the absorption spectra either. Paramagnetic magneto-optical activities (MOA) of the absorption bands and their temperature dependences were measured and interpreted with the help of the theory based on the nature of f - f transitions allowance. The MCD spectra were also analyzed in approximation of the $|J, \pm M_J\rangle$ wave functions of the free atom. It was shown in particular, that the lowest initial state of the transitions observed at $T > 10$ K had $M_J = 7$, but this is not the lowest state of the holmium ion in the crystal. A little lower there is a quasi-doublet with $M_J = 8$ and, accordingly, with a higher magneto-optical activity of transitions from it. However, the intensity of transitions from this state is low.

1. Introduction

The $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ solid solution crystallizes in a modified structure of fluorite. Na^+ and Ho^{3+} cations occupy mixed 4a Wyckoff positions within the $Fm\bar{3}m$ space group. Such crystals are partly disordered. Their structure is considered from the point of view of clusters [1,2]. These structural fragments are based on the octahedral $\text{R}_6\text{F}_{36-37}$ -type cluster of defects (Fig. 1) [3,4]. The rare-earth ions are in tetragonal C_{4v} positions [5]. (Fig. 1).

Absorption lines of f - f transitions in crystals with the general formula $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{RE}^{3+}$ with high concentration of RE ions are rather broad due to the inhomogeneous broadening. This ensure the stability of the absorbed pumping energy. Broad lines of the rare-earth ions emission provide a possibility to retune the generation wavelength. Thus, crystals of such kind can be used in solid-state lasers and optical converters. They have magneto-optical applications as well [6]. There are a number of spectroscopic investigations devoted to crystals with the discussed structure, containing different RE ions: Ho^{3+} [7], Er^{3+} [8,9,10], Nd^{3+} [11], Pr^{3+} [12,13] and Tm^{3+} [14]. Magnetic properties of fluorides containing the rare earth containing fluorides were studied in Ref. [15].

Magnetic circular dichroism (MCD) of f - f transitions in Ho^{3+} ion was

earlier studied in trigonal crystals $\text{HoAl}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ [16,17], where Ho^{3+} ions are located in D_3 и C_2 positions respectively. In $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal the Ho^{3+} ions are in the tetragonal C_{4v} positions. Therefore, we can expect substantial changes of electron structure and of the Ho^{3+} ion wave functions. Preliminary results of MCD measurements in the $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal at 90 K and at room temperature were given in Ref. [18]. In the present work we carried out measurements of MCD and absorption spectra of a number of absorption bands as a function of temperature beginning from 3.6 K. This study made it possible to clarify the identification of absorption spectra and to determine the nature of MCD and f - f transition allowance in the crystal.

2. Experimental details

$\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ solid solution single crystals were grown from melt by the Bridgman technique in a two-zone resistive setup with a graphite heating unit in a fluorinating atmosphere using graphite crucibles [18,19,20]. The crystals up to 15 mm in diameter and 50 mm long without cracks and light-scattering inclusions were grown.

X-ray diffraction (XRD) analysis of the crystals was performed on the X-ray powder diffractometer Rigaku MiniFlex 600 (radiation $\text{CuK}\alpha$,

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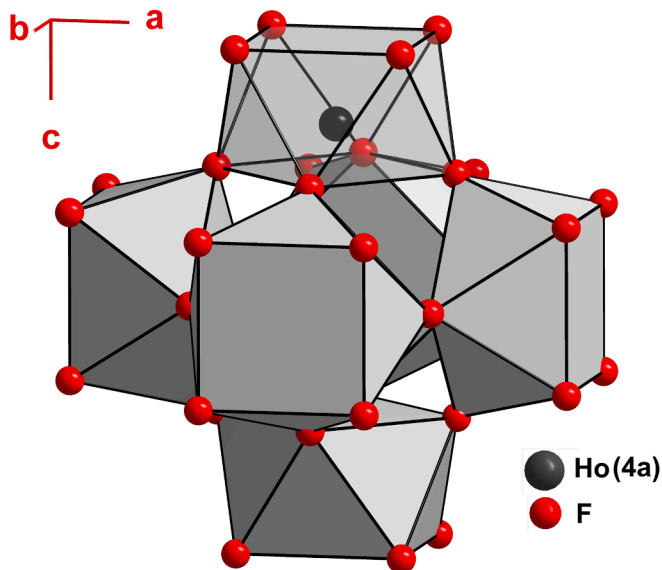


Fig. 1. Octahedral R_6F_{36-37} ($R = \text{Ho}$) cluster of defects.

range of diffraction angles $2\theta = 10^\circ\text{--}120^\circ$) [18]. The XRD data confirmed the fluorite structure type ($Fm\bar{3}m$ space group) of the grown crystals. The samples were single-phase, and had a cubic lattice parameter $a = 5.5154(1)$ Å.

Absorption and MCD spectra were measured with the help of spectrometer and dichrograph created on the basis of DFS-8 monochromator, using technique described in Ref. [21]. Optical slit width (spectral resolution) was 0.2 Å. The MCD spectra were recorded in magnetic field of 2 kOe. The sample was located into optical gas flow helium cryostat LH-320-MAG. Temperature adjustment and stabilization were performed by temperature controller LakeShore Model 325 using temperature sensor CX-1050-CU-HT-1.4L.

3. Results and discussion

As it was mentioned above, Ho^{3+} ions were in the C_{4v} symmetry positions in $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal. Using multiplication table [22] and the base functions of Table 1 for the C_{4v} group, we found the selection rules for the electric dipole transitions in the C_{4v} symmetry (Table 2) [18]. (Compare with selection rules in D_3 symmetry presented in [17].).

The studied crystal is a paramagnet [15]. Then the ground state should presumably be a doublet of the E symmetry. The MCD of a transition doublet \rightarrow singlet in case, when magnetic field is parallel to the light propagation, is evidently given by the equation:

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

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

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

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 paramagnetic

Table 1
Base functions of the C_{4v} point group.

| A_1 | $z, x^2 + y^2, z^2$ |
|-------|------------------------------|
| A_2 | R_z |
| B_1 | $x^2 - y^2$ |
| B_2 | xy |
| E | $(x, y) (R_x, R_y) (xz, yz)$ |

Table 2
Selection rules for electric dipole transitions in the C_{4v} symmetry.

| | A_1 | A_2 | B_1 | B_2 | E |
|-------|----------|----------|----------|----------|----------|
| A_1 | π | 0 | 0 | 0 | σ |
| A_2 | 0 | π | 0 | 0 | σ |
| B_1 | 0 | 0 | π | 0 | σ |
| B_2 | 0 | 0 | 0 | π | σ |
| E | σ | σ | σ | σ | π |

MCD, which depends on temperature and the second one is the temperature independent diamagnetic effect. Integral of the MCD spectrum over multiplet gives the integral paramagnetic MCD of the multiplet. Integral of the diamagnetic part is zero. The integral over absorption band paramagnetic magneto-optical activity (MOA) is described by the equation:

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

The equation (3) is valid both for a complex band and for a single line. Here C is the basic dimensionless parameter of the MOA, k_B is the Boltzmann constant, θ is the Curie-Weiss constant. For a transition doublet \rightarrow singlet in a free atom $C = g$, where g is the Lande factor of the ground state. It is supposed in (3), that according to Van Vleck and Hebb [23] the MOA is proportional to the paramagnetic susceptibility.

We measured absorption and MCD spectra in the region of $^5I_8 \rightarrow ^5F_3$, 5F_2 , 3K_8 and 5G_5 transitions. When we come from a free atom to octahedron and further to the C_{4v} symmetry, the excited states of the Ho^{3+} ion are transformed as follows [24]:

$$F - \text{band}: ^5F_3(J = 3) \rightarrow T_1 + T_2 + A_2 \rightarrow A_2 + B_1 + B_2 + 2E \quad (4)$$

$$G - \text{band}: ^5F_2(J = 2) \rightarrow E + T_2 \rightarrow A_1 + B_1 + B_2 + E \quad (5)$$

$$H - \text{band}: ^3K_8(J = 8) \rightarrow A_1 + 2E + 2T_1 + 2T_2 \rightarrow A_1 + 4B_1 + 4B_2 + 4E \quad (6)$$

$$J - \text{band}: ^5G_5(J = 5) \rightarrow E + 2T_1 + T_2 \rightarrow A_1 + 2A_2 + B_1 + B_2 + 3E \quad (7)$$

According to the selection rules of Table 2 and expansions (4, 5 and 7), at low temperature the F and G bands should contain three and the J band five lines polarized perpendicular to the local C_4 axis (σ -polarized lines) during transitions from the E state to singlets, and it is these lines must be active in the MCD. This is indeed the case in the F, G and J bands (Figs. 2, 3). π -polarized lines (polarized parallel to the local C_4 axis) are not observed, although they could be present in the spectra due to the random orientation of the holmium clusters. In the H band a similar

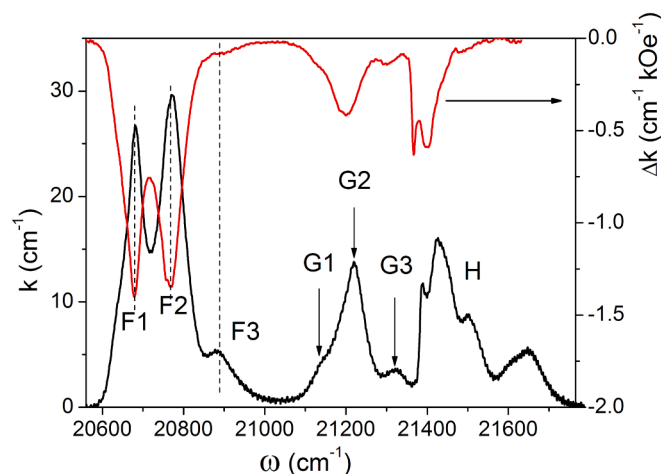


Fig. 2. Absorption (k) and MCD (Δk) spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal at 5 K in the region of $^5I_8 \rightarrow ^5F_3$, 5F_2 3K_8 transitions (F, G and H bands).

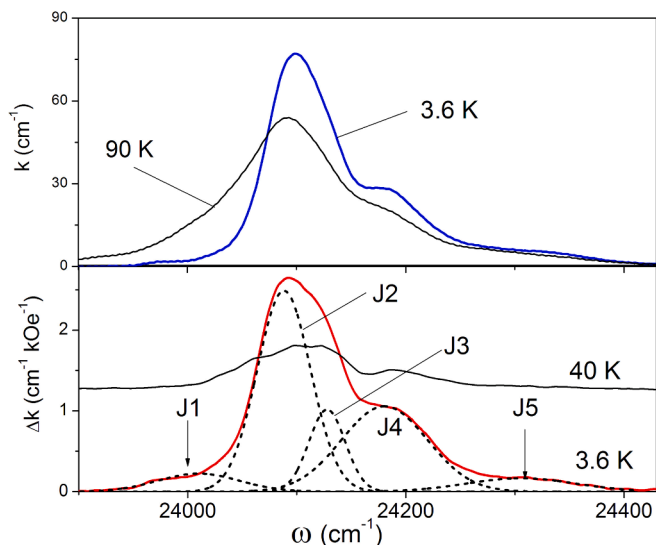


Fig. 3. Absorption (k) and MCD (Δk) spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal in the region of ${}^5I_8 \rightarrow {}^5G_5$ transition (J-band).

splitting according to (6) for transitions to singlets is not observed. Apparently, it is a consequence of space inhomogeneity of the crystal.

As a result of comparison of the F-band absorption spectra at 5 K and 90 K (Figs. 2 and 4) we infer, that line f1 is due to the transition from the excited sublevel of the ground multiplet at 47 cm^{-1} , occupied with the increasing temperature. It is worth noting, that decomposition of the absorption spectrum into the Gauss shape lines at 90 K failed and it was decomposed into the Lorentz shape lines. On the contrary, decomposition into the Gauss shape lines at 5 K was successful, that is, the inhomogeneous broadening is larger than the natural one at this temperature. Spectrum at room temperature (Fig. 4) permitted us to find two levels more in the ground multiplet at 312 and 389 cm^{-1} . Identification of transitions is seen in Fig. 4. These levels are occupied only with the increasing temperature.

At low temperatures, when paramagnetic MCD strongly increases, practically only it remains, and its spectrum almost coincides with the absorption spectrum (Fig. 2). On the contrary, at higher temperatures the diamagnetic spectrum begins to prevail (Fig. 5 - transition f1 and Fig. 4 inset - transition f3). We came to the conclusion above, that excited states of transitions F1, F2 и F3 are singlet. Then lines f1 and f3

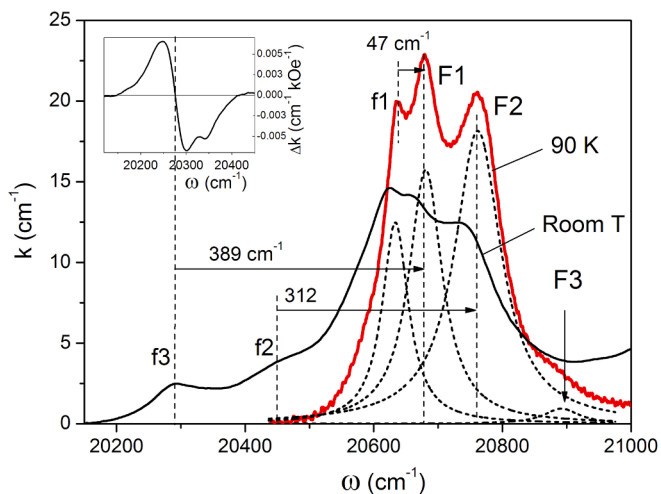


Fig. 4. Absorption spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal in the region of ${}^5I_8 \rightarrow {}^5F_3$ transition (F-band) at two temperatures. Insert: MCD of the f3 line at room temperature.

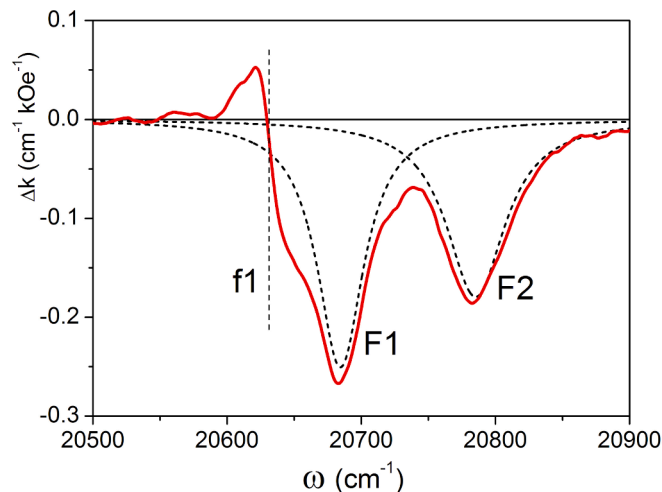


Fig. 5. MCD spectrum of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal in the region of ${}^5I_8 \rightarrow {}^5F_3$ transition (F-band) at 90 K.

(Fig. 4) are due to transitions from excited doublets, since only in this case σ polarization (Table 2) and consequently MCD are possible.

At 90 K (and above), the MCD of the F1 and F2 transitions from the ground state preserves its paramagnetic shape (Fig. 5), but the diamagnetic effect already dominates in the spectrum of the f1 transition from the excited state. The diamagnetic effect is also observed during the f3 transition from the excited state (Fig. 4 inset). The absence of a diamagnetic component in the spectrum of the MCD transitions F1 and F2 from the ground state can be explained by the spatial integration of the MCD spectrum due to the spatial inhomogeneity of the crystal. Then it is possible to draw a conclusion, that the spatial inhomogeneity has a weaker effect on transitions from excited states.

It can be seen from (2) that splitting $\Delta\omega_0$ is the coefficient of proportionality between diamagnetic MCD spectrum and derivative by ω_0 of absorption spectrum. The derivative by ω_0 differs from the derivative by ω only by a sign. Thus, with the help of absorption and MCD spectra at 90 K (Figs. 4 and 5), we determined the Zeeman splitting of the f1 line: $2\Delta\omega_0 = -0.555 \text{ cm}^{-1} \text{ kOe}^{-1}$. This is simultaneously the value of the initial level Zeeman splitting, since excited state is singlet.

In the uniaxial crystals, electron states can be described by the $|J, \pm M_J\rangle$ wave functions of an atom in a first approximation. In the C_{4v} local symmetry, between values of M_J and irreducible representations of states there is the correspondence [24]:

| M_J | 0 | ± 1 | ± 2 | ± 3 | ± 4 | ± 5 | ± 6 | ± 7 | ± 8 | (8) |
|-------|------------|---------|------------|---------|------------|---------|------------|---------|------------|-----|
| = | $A_1(A_2)$ | E | B_1, B_2 | E | A_1, A_2 | E | B_1, B_2 | E | A_1, A_2 | (9) |

First state in (9) is A_1 if J is even number. The projection M_J defines the splitting of doublets $\pm M_J$ in magnetic field in approximation of $|J, \pm M_J\rangle$ functions: $\Delta E = 2g\mu_B M_J H$. Taking into account that the Zeeman splitting of initial state of the f1 transition is: $2\Delta\omega_0 = \Delta E = 2g\mu_B M_J H = -0.555 \text{ cm}^{-1} \text{ kOe}^{-1}$ and $g = 1.25$ for the ground 5I_8 multiplet, we find, that the initial state has $M_J = 4.72$. This value approximately corresponds to E type state $M_J = \pm 5$ in the $J = 8$ multiplet (see (8) and (9)).

The zero moments of absorption bands and of their MCD spectra (Figs. 2, 3) and corresponding parameter c presented in (3) was obtained as a function of temperature. The Curie-Weiss constant of the crystal $\theta = -11 \text{ K}$ was determined from magnetic measurements [15]. Then, parameter "C" of MOA of absorption bands was found as a function of temperature with the help of Eq (3) (Fig. 6). The dimensionless parameter C of the MOA in (3) should be independent of temperature, if the MOA of a transition follows (3). This statement is approximately valid for the studied bands (Fig. 6).

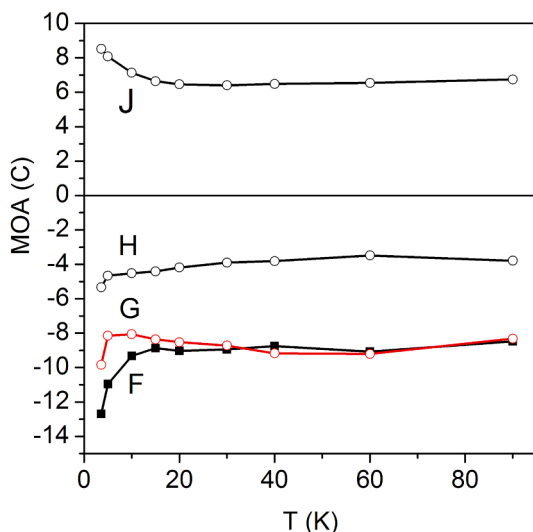


Fig. 6. Integral magneto-optical activity of the $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal absorption bands.

Properties of f - f transitions MOA was considered in Ref. [25]. Parity forbidden f - f transitions become partially allowed because odd components of the crystal field admix states of the opposite parity to $4f$ states. If such state J_f is admixed to the excited $4f$ state, it should also satisfy the selection rule: $|J_f - J_I| \leq 1$, where J_I is the ground state total angular-momentum. Allowed transitions from the ground state to the admixed states are sources of absorption intensity and MOA of the f - f transition. In Ref. [25] the paramagnetic MOA of the mentioned allowed transitions between multiplets in free atom was found:

$$\text{for the transition } J \rightarrow (J-1) : C = -g(J+1)/2 \quad (10)$$

$$\text{for the transition } J \rightarrow J : C = -g/2 \quad (11)$$

$$\text{for the transition } J \rightarrow (J+1) : C = +gJ/2 \quad (12)$$

where g is the ground state Landé factor. The ground state 5I_8 of Ho^{3+} ion has $g = 1.25$. Then from (10–12) we find possible MOA (C) of f - f transitions in Ho^{3+} ion: -5.625 , -0.625 and 5 . They correspond to states with $J = 7$, 8 and 9 , respectively, admixed to excited states. The admixtures can exist separately and all together.

Experimental value of the J-band MOA at $T > 15$ is close to the theoretical one at mechanism of allowance (12) (Fig. 6). Absolute value of the H-band MOA is less than the theoretical one (10). This means that at least one more admixture J_f allows the absorption band. Ratio of admixtures can change due to change of population of the ground multiplet splitting components with temperature. This can result in dependence of parameter C of the band on temperature (Fig. 6).

The question arises, why MOA of F and G bands are larger in absolute value than the theoretical one -5.625 according to (10). It is seen from Figs. 2 and 4 that the main intensity of F-band even at high temperatures is due to the transitions only from a low state. According to [25], if f - f transition is allowed by mechanism (10), then MOA of the transition from state M_J of the J multiplet is:

$$C_M = \frac{-gM_J^2(2J-1)}{J^2 - J + M_J^2} \quad (13)$$

From Fig. 6 we obtain average value $C_M = -8.8$ for F and G bands in the region above 15 K. Then from (13) we obtain $M_J = 7.04$. According to (8) and (9) it is indeed state of the E -type.

Attention is drawn to the anomalous behavior of the absorption bands MOA at temperatures below 10 K (Fig. 6): they increase in absolute value with the temperature decrease. Another anomaly in the

same temperature range is observed in the intensity behavior of absorption bands: they decrease with decreasing temperature (Fig. 7). This is possible, if the observed transitions occur not from the lowest level, and the transitions from the lowest level are weak. At the same time, the MOA of transitions from the lowest level must be greater than that of the main observed transitions in order for the resulting MOA to grow. This condition is satisfied by the quasi-doublet $M_J = \pm 8$ (see (8) and (9)).

4. Summary

Optical absorption and magnetic circular dichroism (MCD) spectra of Ho^{3+} ion in $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ single crystal were measured in the region of $^5I_8 \rightarrow ^5F_3$, 5F_2 , 3K_8 and 5G_5 transitions (F, G, H and J bands) in Ho^{3+} ion as a function of temperature from 3.6 till 90 K. The crystal has cubic symmetry, but local symmetry of Ho ion is C_{4v} . However, a splitting of transitions according to this symmetry was not observed till 3.6 K. It was revealed, that number of transitions observed in the MCD and absorption spectra corresponds to the number of transitions from the doublet E -state only to singlet excited states. Transitions of the E - E type are not active in MCD, but they are not observed in absorption either, although they could be observed due to the random orientation of the clusters. Positions of three sublevels of the ground multiplet were found at 47, 312 and 389 cm^{-1} . With the help of absorption and MCD spectra the temperature dependences of paramagnetic magneto-optical activities (MOA) of the absorption bands were obtained and compared with the theory based on the nature of f - f transitions allowance. It appeared that nature of allowance of considered transitions is different. In particular, it was shown that $^5I_8 \rightarrow ^5F_3$ and 5F_2 bands are allowed due to admixture of the state with $J = 7$ and opposite parity to the excited multiplets. In the allowance of the $^5I_8 \rightarrow ^3K_8$ band another admixture additionally takes part. $^5I_8 \rightarrow ^5G_5$ band is allowed due to admixture of the state with $J = 9$. The MCD spectra were also analyzed in approximation of the $|J, \pm M_J\rangle$ wave functions of the free atom. It was shown that the initial state of transitions observed at $T > 5$ K has $M_J = 7$. However, this is not the lowest state. A little lower there is a quasi-doublet with $M_J = 8$ and, accordingly, with a higher magneto-optical activity of transitions from it. The intensity of transitions from this state is low.

Declaration of competing interest

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.

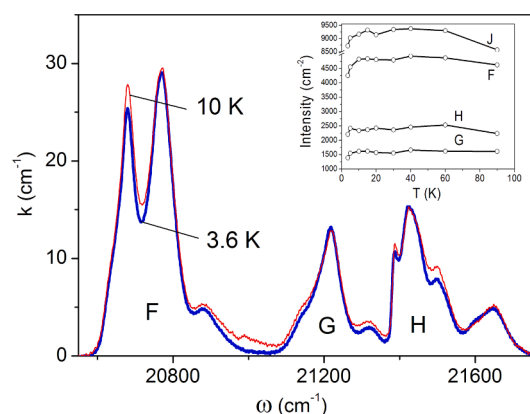


Fig. 7. Low temperature change of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal absorption spectrum in the region of $^5I_8 \rightarrow ^5F_3$, 5F_2 , 3K_8 transitions (F, G and H bands). Inset: temperature dependences of the integral intensities of F, G, H and J bands.

Data availability

No data was used for the research described in the article.

Acknowledgments

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