



Magnetic circular dichroism of $^5I_8 \rightarrow ^5F_3$, 5F_2 and 3K_8 transitions in $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ single crystal

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ABSTRACT

We measured optical absorption and magnetic circular dichroism spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ single crystal in the region of $^5I_8 \rightarrow ^5F_3$, 5F_2 and 3K_8 transitions in Ho^{3+} ion at 90 K and room temperature. Paramagnetic magneto-optical activities (MOA) of the transitions were found for these two temperatures and compared with the theory based on the nature of $f-f$ transitions allowance. It was shown that nature of allowance of three considered transitions is different. The MCD spectra were also analyzed in approximation of the $|J, \pm M_J\rangle$ wave functions of the free atom and using concept of the crystal quantum number. Using this concept and experimental paramagnetic MOA, we found that $M_{J\text{eff}} = 2.1$ for the initial state of the $^5I_8 \rightarrow ^5F_3$ transition.

1. Introduction

The $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ solid solution crystallizes in a modified structure of fluorite, in which Na^+ and Ho^{3+} cations occupy mixed 4a Wyckoff positions for $Fm\bar{3}m$ space group. These crystals are disordered and their structure is considered from the point of view of clusters. A model of a defect structure of this type crystals suggests that cations and interstitial fluorine anions, which arise due to different charges of cations and are required for electrostatic compensation, are grouped into hypothetical cuboctahedral complexes $\{(\text{Na}_{0.5}\text{Ho}_{0.5})_8[\text{Ho}_6\text{F}_{37}]\text{F}_{32}\}$ [1,2]. These structural fragments are based on the so-called octahedral $\text{R}_6\text{F}_{36-37}$ -type cluster of defects (Fig. 1) [3,4]. The coordination polyhedron for the rare-earth ion in this $\text{R}_6\text{F}_{36-37}$ cluster is tetragonal antiprism (Thompson cube). This cluster formed by fluoride ligands (with a coordination number equal to 8) and its internal cavity has cuboctahedral shape. Therefore, the local symmetry of the rare-earth ion environment is tetragonal C_{4v} [5]. (Fig. 1). The $\text{R}_6\text{F}_{36-37}$ cluster can be naturally coherently embedded in the cubic lattice of fluorite without distorting the cation packing motif with the retention of long-range order and the appearance of strong local deformations only in the anion sublattice.

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 rare earth (RE) ions are rather broad due to the inhomogeneous broadening. Broad lines in absorption spectra ensure the stability of the absorbed pumping energy, while broad lines in emission spectra of rare-earth ions make it possible

to retune the generation wavelength within tens of nanometers. Crystals with a high concentration of rare-earth ions are of great interest for the use in solid-state lasers and optical converters. They have also magneto-optical applications [6]. Spectroscopic investigations were carried out in crystals of such kind containing a number of different RE ions: Ho^{3+} [7], Er^{3+} [8–10], Nd^{3+} [11], Pr^{3+} [12,13] and Tm^{3+} [14].

In particular, optical absorption spectra of the Ho^{3+} containing crystal were studied at 11 K and at room temperature in Ref. [7]. The Judd-Ofelt parameters were determined there and the probabilities of the radiative transitions, the radiative lifetimes, and the branching ratios were calculated. The luminescence decay kinetics from excited holmium levels has been studied upon selective excitation in the range of 490 nm, and the lifetimes of these levels have been experimentally determined. With respect to all their radiative characteristics, the authors concluded that such crystals can be considered as potential active media for solid state continuously tunable lasers in the IR and visible ranges. Similar investigations were carried out in the crystals containing other RE ions [8–14].

We present first study of magnetic circular dichroism (MCD) of $f-f$ transitions in the crystal of the discussed type. Earlier MCD of $f-f$ transitions in Ho^{3+} ion was studied in trigonal crystals $\text{HoAl}_3(\text{BO}_3)_4$ and $\text{HoFe}_3(\text{BO}_3)_4$ [15,16]. In $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal the Ho^{3+} ions are located in the tetragonal C_{4v} positions. Such crystal field substantially changes electron structure and properties of the Ho^{3+} ion wave functions. MCD gives important information about nature of electron states and about

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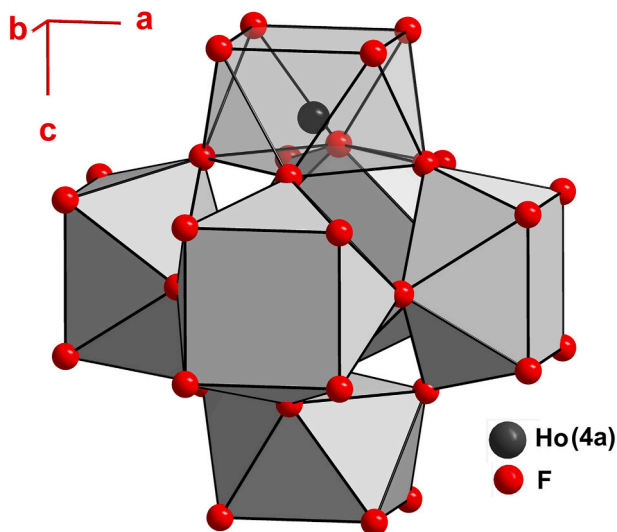


Fig. 1. Octahedral R_6F_{36-37} ($R = \text{Ho}$) cluster of defects.

influence of the crystal environment.

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 method in a graphite heating unit using multicellular graphite crucibles. The growth technique was reported in Refs. [17,18]. NaF and HoF_3 powders (99.99%, LANHIT) melted in a fluorinating atmosphere were used as the initial charge. The fluorinating agent was CF_4 . The $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystals up to 15 mm in diameter and 50 mm long without light-scattering inclusions were obtained. Crystal density was measured by hydrostatic weighing to be $\rho = 5.910(5) \text{ g/cm}^3$ at $T = 300 \text{ K}$. Samples for measurements with a thickness 2–5 mm were cut from the central part of crystalline boules and polished (Fig. 2, inset). The refractive index for $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal was measured by refractometric method for $\lambda = 0.589 \mu\text{m}$ and was equal to $n_D = 1.4817(2)$ at room temperature.

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

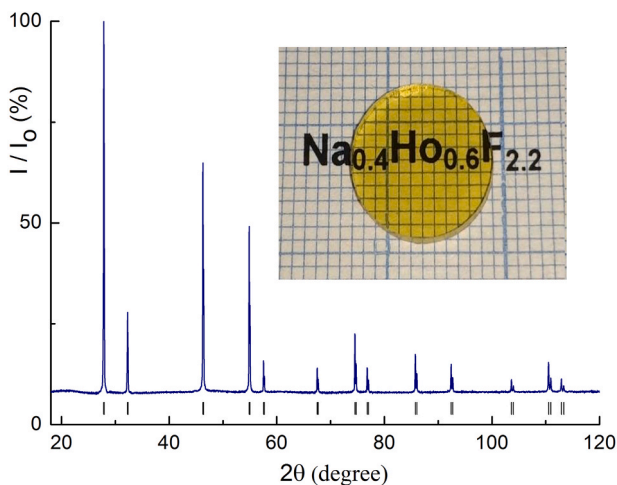


Fig. 2. The XRD patterns of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ solid solution single crystal. Vertical bars denote the Bragg reflection positions corresponding to the cubic phase with $Fm\bar{3}m$ space group and lattice parameter $a = 5.5154(1) \text{ \AA}$. Inset: The $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal sample appearance.

range of diffraction angles $2\theta = 10^\circ\text{--}120^\circ$). Phases were interpreted using the ICDD PDF database. The lattice parameter was calculated using the Jana2006 software, which allows full-profile analysis of diffraction patterns by the Le Bail method within the $Fm\bar{3}m$ space symmetry group. The XRD data confirmed the fluorite structure type ($Fm\bar{3}m$ space group) of the grown crystals (Fig. 2). The samples were single-phase, and had a cubic lattice parameter $a = 5.5154(1) \text{ \AA}$.

The absorption spectra were measured in unpolarized light by the two beam technique, using an automated spectrophotometer designed on the basis of the diffraction monochromator DFS-8. Optical slit width (spectral resolution) was 0.8 \AA . The MCD spectra were recorded in magnetic field of 5 kOe directed along the light beam. The circular dichroism was measured using the modulation of the light wave polarization with the piezoelectric modulator (details see in Ref. [19]). 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 $\sim 1 \text{ K}$. Thickness of the sample was 0.5 mm .

3. Results and discussion

Ho^{3+} ions are located in the C_{4v} symmetry positions in $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal. At the conversion from a free atom to that in octahedron and further to the C_{4v} symmetry position, the ground and discussed excited states of the Ho^{3+} ion are transformed in the following way:

$${}^5I_8, {}^3K_8(J=8) \rightarrow A_1 + 2E + 2T_1 + 2T_2 \rightarrow A_1 + 2(B_1 + B_2) + 2(B_2 + E_2) + 2(B_1 + E_1) \quad (1)$$

$${}^5F_2(J=2) \rightarrow E + T_2 \rightarrow (B_1 + B_2) + (A_1 + E_1) \quad (2)$$

$${}^5F_3(J=3) \rightarrow A_2 + T_1 + T_2 \rightarrow A_2 + (B_2 + E_2) + (B_1 + E_1) \quad (3)$$

Difference between states E_1 and E_2 will be understood later. An electric dipole transition is allowed, if the product of representations of the initial and final states contains the representation of the electric dipole. Using multiplication table [20] and the base functions (Table 1) for the C_{4v} group, we find the selection rules for the electric dipole transitions in the C_{4v} symmetry (Table 2). (Compare with selection rules in D_3 symmetry presented in Ref. [16].) The crystal is inhomogeneous. Therefore the splitting of states due to the C_{4v} symmetry according (1–3) is not observed (Fig. 3). The 3K_8 (H) band does not reveal the splitting even due to the cubic crystal field. The studied crystal is a paramagnetic one. Therefore the ground state must have the E symmetry. According to (2 and 3) and selection rules of Table 2, all lines resolved in the cubic approximation have at least σ polarization, and, consequently, they are active in MCD.

The MCD of a doublet in magnetic field directed along the light propagation is given by the equation:

$$\Delta k = k_{m+} \varphi(\omega, \omega_0 + \Delta\omega_0) - k_{m-} \varphi(\omega, \omega_0 - \Delta\omega_0) \quad (4)$$

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:

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

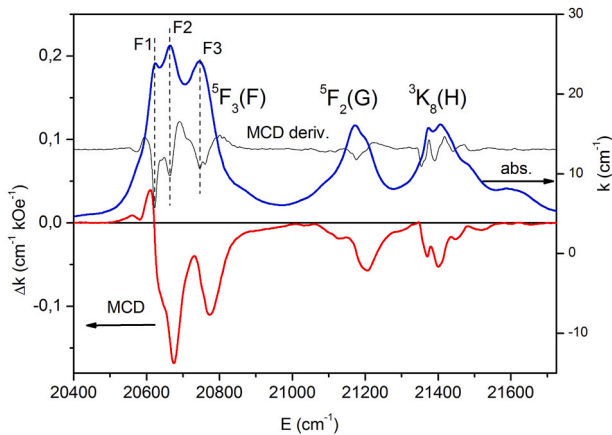


Fig. 3. Absorption (k), MCD (Δk) and derivative of MCD (arbitrary units) spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal at 90 K.

Table 3
Intensities ($\langle k \rangle_0$) and MOA (C) of transitions.

	$\langle k \rangle_0$ (90 K)	$\langle k \rangle_0$ (300 K)	C (90 K)	C (300 K)
F	4660	4580	-5.23	-5.49
G	1740	2180	-4.48	-4.16
H	2470	1740	-2.21	-3.59

$$\Delta k = k_m c \varphi(\omega, \omega_0) + k_m \Delta \omega_0 \partial \varphi(\omega, \omega_0) / \partial \omega_0 \quad (5)$$

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 (4) is the paramagnetic MCD and the second one is the 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 sign-changing fine structure of the diamagnetic effect usually predominates over the paramagnetic spectrum. However in the inhomogeneous crystal under study the space integration takes place, which diminishes the diamagnetic spectrum (Fig. 3). Diamagnetic MCD of the distinct lines is not always spectrally resolved. However, it is possible to define signs of the diamagnetic MCD ($\Delta \omega_0$) with the help of the first derivative of the MCD. For the MCD written in the form (4), it is possible to show [21] that signs of extremums of the function $\partial \Delta k / \partial \omega$ at positions of the absorption lines give signs of the diamagnetic effect ($\Delta \omega_0$). Thus we found from the experimental MCD spectra that diamagnetic MCD of F1, F2 and F3 lines is negative (Fig. 3).

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

$$M = \begin{matrix} 0 & \pm 1 & \pm 2 & \pm 3 & \pm 4 & \pm 5 & \pm 6 & \pm 7 & \pm 8 \end{matrix} \quad (8)$$

$$\mu = \begin{matrix} 0 & \pm 1 & 0 & \mu 1 & 0 & \pm 1 & 0 & \mu 1 & 0 \end{matrix} \quad (9)$$

$$A_1(A_2) \quad E_1 \quad B_1, B_2 \quad E_2 \quad A_1, A_2 \quad E_1 \quad B_1, B_2 \quad E_2 \quad A_1, A_2 \quad (10)$$

$$c = \frac{\langle \Delta k(\omega) \rangle_0}{\langle k(\omega) \rangle_0} = C \frac{\mu_B H}{k_B (T - \theta)} \quad (6)$$

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 (6) that the MOA is proportional to the paramagnetic susceptibility according to Van Vleck and Hebb [22], and that both of them follow the Curie-Weiss law. Equation (6) is valid both for a single line and for a complex band. The zero moments of the MCD and absorption bands, presented in (6), were found from the corresponding spectra, and parameter c was obtained. The studied crystal is a paramagnet. We supposed that $\theta = 0$. Then, with the help of Eq. (6), we found parameter “ C ” of MOA of $f-f$ transitions at two temperatures (Table 3). If the MOA of the transition is proportional to the paramagnetic susceptibility, then the dimensionless parameter C of the MOA in (6) should be independent of temperature. This is approximately valid for F and G bands, but certainly not for H band (Table 3).

$f-f$ 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: $|J_f - J_l| \leq 1$, where J_l is the total angular-momentum of the ground 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 paramagnetic MOA of the mentioned allowed transitions in free atom was found in Ref. [21]:

$$\begin{aligned} \text{for the transition } J \rightarrow (J-1): \quad C &= -g(J+1)/2, \\ \text{for the transition } J \rightarrow J: \quad C &= -g/2 \\ \text{for the transition } J \rightarrow (J+1): \quad C &= +gJ/2, \end{aligned} \quad (7)$$

where g is the Landé factor of the ground state. For the ground state $5I_8$ of Ho^{3+} ion $g = 1.25$. 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. The admixtures can exist separately and all together. If all components of the ground state split by CF are equally populated, the results (7) are valid for crystals for the integral over the $f-f$ absorption band paramagnetic MOA (C). At room temperature the mentioned condition of the equal population of the ground state sublevels is better fulfilled. In Table 3 the experimental MOA (C) are given at two temperatures. It is seen from Table 3 that the experimentally observed MOA of the F band is close to the theoretical prediction for the admixture $J = 7$ and practically does not depend on temperature. Absorption intensity of the band also almost does not depend on temperature (Table 3). All these means, that $f-f$ transitions from all components of the ground multiplet splitting are allowed by only one admixture. MOA of the G and H bands are less than the theoretical one (Table 3). Consequently, at least one more admixture takes part in the allowance of the transitions. Ratio of admixtures changes with the population of components of the ground multiplet splitting, what results in dependence of MOA and absorption of the bands on temperature (Table 3).

Selection rules of Table 2 make it possible to analyze linear polarizations of transitions, but not circular polarizations in magnetic field. Such possibility is given by the concept of the crystal quantum number μ suggested in [23] for electron states in crystals of the axial symmetry. Additionally, the electron states in the uniaxial crystals can be described in a first approximation by the $|J, \pm M_J\rangle$ wave functions of the free atom. Between values of μ , M_J and irreducible representations of states there is the following correspondence in the C_{4v} local symmetry [23]:

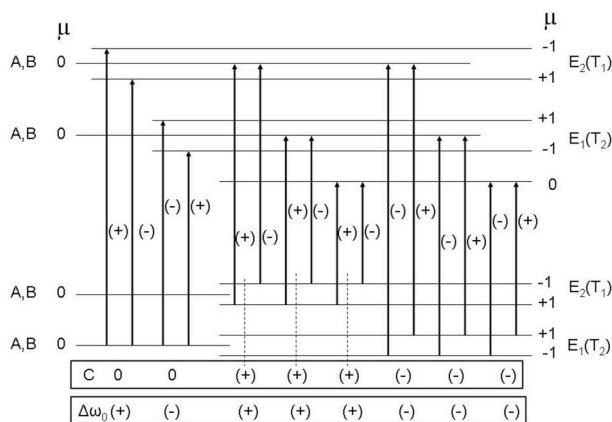


Fig. 4. Diagram of MCD of all types of transitions.

The doublets E_1 and E_2 differ by signs of μ . The projection M_J defines the splitting of the state in magnetic field. Correspondingly, the Landé factor g_{CM} of the $\pm M_J$ doublet in the $|J, \pm M_J\rangle$ wave functions approximation is:

$$g_{CM} = 2gM_J \quad (11)$$

where g is the Landé factor of the free atom. Selection rules for the number μ in crystals presented in [23] were similar to those for the number M_J in free atoms. In particular, for the electric dipole absorption:

$$\begin{aligned} \Delta\mu = \pm 1 & \text{ corresponds to } \mp \text{ circularly polarized and } \sigma - \text{ polarized waves,} \\ \Delta\mu = 0 & \text{ corresponds to } \pi - \text{ polarized waves.} \end{aligned} \quad (12)$$

The selection rules (12) permitted us to create the diagram of MCD of all types of transitions (see Fig. 4). The very small splitting of the states in C_{4v} symmetry relative to that in the cubic symmetry was taken into account. Only circularly polarized transitions were shown in the diagram. From diagram of Fig. 4 it is seen, that for the linearly polarized (circularly polarized) waves, selection rules (12) coincide with those of Table 2 in contrast to the situation observed in the D_3 symmetry [16]. Indeed, transitions $E \leftrightarrow A, B$ have σ -polarization (Table 2) and circular polarizations (Fig. 4), while $E \leftrightarrow E$ transitions have π -polarization (Table 2) and, consequently, are not observed in the circular polarization.

We see from diagram of Fig. 4 that observed three lines with negative paramagnetic MOA can exist, if the initial state is of the E_1 type. This state is not obligatory the lowest one, since MOA of some other absorption bands in the crystal has positive MOA. Transitions from the singlet states, being part of the triplet T_2 , make a contribution into the diamagnetic effect but not into the paramagnetic one (Fig. 4). Lines f1 and f2 (Fig. 5) are due to the transitions from the excited singlet states into the state of the E_1 type, since they have purely diamagnetic MCD of negative sign (see Figs. 4 and 5).

Absorption spectra of the F band at 90 K and room temperature (Figs. 3 and 5) show that the spectra are mainly due to only one transition from the low lying level of the ground multiplet. Indeed, absorption lines due to transitions from the excited sublevels of the ground multiplet appear only at room temperature (Figs. 3 and 5). The same, naturally, refers to the MOA. Then we can find $M_{J_{eff}}$ of the initial state of the transition. Indeed, it is evident, that parameter C from (6) for one transition from doublet to singlet in the $|J, \pm M_J\rangle$ function approximation is: $C = 2gM_{J_{eff}}$, where $g = 1.25$ - the Landé factor of the ground multiplet. Then using $C = 5.23$ at 90 K (Table 3), we find $M_{J_{eff}} = 2.1$. Comparing this value with (8-10), we infer that the initial state is a mixture of the E_1 states due to the not strong axial anisotropy.

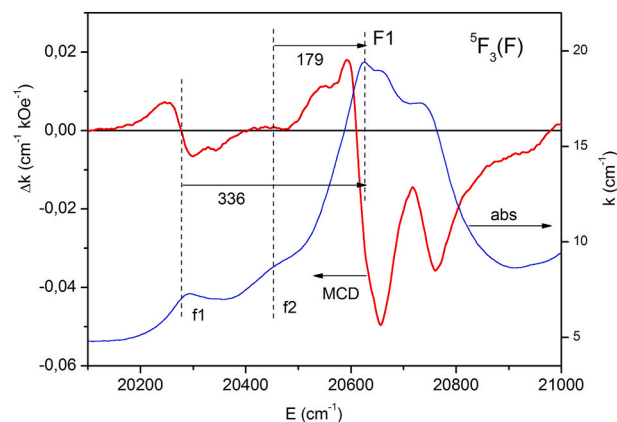


Fig. 5. Absorption (k) and MCD (Δk) spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ crystal in the region of ${}^5I_8 \rightarrow {}^5F_3$ transition at room temperature.

4. Summary

We measured optical absorption and magnetic circular dichroism spectra of $\text{Na}_{0.4}\text{Ho}_{0.6}\text{F}_{2.2}$ single crystal in the region of ${}^5I_8 \rightarrow {}^5F_3$, 5F_2 and 3K_8 transitions in Ho^{3+} ion at 90 K and room temperature. The diamagnetic component of MCD was substantially quenched by the space integration due to space inhomogeneity of the crystal. The visible splitting of the spectra correspond to the cubic crystal field. On the basis of the optical and MCD spectra we calculated paramagnetic magneto-optical activities of the transitions at these two temperatures and compared them with the theory based on the nature of $f-f$ transitions allowance. In particular, three contributions into allowance are possible, and they appeared to be different for the studied transitions. Selection rules for linear polarized waves in C_{4v} symmetry were obtained. The MCD spectra were also analyzed in approximation of the $|J, \pm M_J\rangle$ wave functions of the free atom and using concept of the crystal quantum number. Using this concept and experimental paramagnetic MOA, we found that $M_{J_{eff}} = 2.1$ for the initial state of the ${}^5I_8 \rightarrow {}^5F_3$ transition.

Author agreement

A.V. Malakhovskii: theoretical analysis.
V.V. Sokolov: experiment.
D.N. Karimov: synthesis and structure of the crystal.

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.

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