EAST EUROPEAN JOURNAL OF PHYSICS. **4.** 341-348 (2024)
DOI:10.26565/2312-4334-2024-4-39 ISSN 2312-4334

MAGNETO-OPTICS FEATURES OF RADIATION TRANSITIONS OF NON-KRAMERS Tm^{3+} ION IN YTTRIUM-ALUMINUM GARNET CRYSTALS

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Received August 18, 2024; revised October 21, 2024; accepted November 4, 2024

The spectra of luminescence and magnetic circular polarization of a single crystal of thulium-yttrium garnet-aluminate Tm^{3+}:YAG have been studied within the visible spectral range at a temperature of 90 and 300 K in a magnetic field of 10 kOe. Based on the analysis of optical and magneto-optical data, the presence of "quasi-degenerate" states of excited multiplets $^1D_2$, $^3F_4$,$^3G_4$ and the ground multiplet $^3H_6$ of the Tm^{3+} RE ion in garnet-aluminate YAG at the radiative transitions $^1G_4 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_4$ and $^1D_2 \rightarrow {}^3F_3$ has been determined. The effect of quantum mechanical "mixing" plays a significant role in the occurrence of magneto-optical effects on luminescence bands caused by "forbidden" 4f→4f transitions in the non-Kramers Tm^{3+} ion having a "quasi-doublet" structure in the energy spectra.
Keywords: *Thulium-yttrium garnet; Rare-earth ions; Magneto-optical properties; Luminescence; Energy levels; Magnetic circular polarization*
PACS: 71.70.Ej; 78.20.Ls

INTRODUCTION

Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) doped with trivalent rare-earth (RE) ions R^{3+} is well known as a material used for creation of solid-state lasers [1-3]. This circumstance has contributed to the intensive study of the optical and magneto-optical properties and energy levels of a number of rare-earth ions R^{3+} in the garnet crystalline cell, replacing the yttrium ions Y^{3+} located in the dodecahedral positions of the garnet structure [4]. But among all these garnets with RE ions as impurities, the similar properties (in particular, magneto-optical ones) of Tm^{3+}:YAG garnet have been studied comparatively insufficiently. Therefore, at present, the magneto-optical properties of Tm^{3+} RE ions in garnet crystals are studied systematically [5-6], and this circumstance has become one of the motivating factors for this study to be conducted.

On the other hand, the presence of a large number of emission transitions observed within the wide spectral range from near infrared (IR) to ultraviolet (UV) shows that Tm^{3+}:YAG is a good material for lasers operating within the near IR range [7-9]. An effective process in the same region is emission due to the up-conversion pumping [10]; in this case also promising matrices are garnet-structure crystals for further activation by trivalent thulium ions. Another new possible application of the Tm^{3+}:YAG RE compound is its use in information display systems operating within the spectral range from 460 nm to 470 nm because of proximity of the $^1D_2 \rightarrow {}^3F_4$ emission transition to optimal operating wavelengths of video-displays in this spectral range. Therefore, the study of this transition is still of great interest, since an in-detail consideration of the spectroscopic properties of this transition to be aimed at obtaining information on mechanisms of excitation of the radiative states of Tm^{3+} ions and hence obtaining efficient generation is currently of paramount importance.

The crystalline electrostatic field (CF) created by the low-symmetry environment of the RE ion in the garnet lattice leads to a partial or almost complete "removal" of the quantum degeneracy from the Stark sublevels in the multiplets belonging to the ground $4f^{(n)}$ configuration of the ion. Further removal of degeneracy from the Stark sublevels of the RE ion with the help of the Zeeman splitting of their states by an outer magnetic field H leads to emerging induced circular anisotropy of the optical absorption and luminescence bands, which manifests itself both in magnetic circular dichroism (MCD) observed during light absorption [11] and in magnetic circular polarization of luminescence (MCPL) recorded during light radiation emission [12]. The study of the MCD and MCPL phenomena (being differential in essence) in non-Kramers RE ions (i.e. with an even number of electrons in the unfilled $4f^{(n)}$ shell) provides a fundamental opportunity to determine a symmetry of the wave functions of the Stark sublevels (including the so-called "quasi-degenerate" sublevels that cannot be resolved directly in optical experiments), from which (or to which) the optical 4f→4f transitions occur (forbidden in the electrodipole (ED) approximation) [13].

At the same time, it is well known that the main source of MCPL (or MCD) phenomena in non-Kramers RE ions is the Van Vleck "mixing" (by an outer magnetic field) of the wave functions of neighboring non-degenerate Stark sublevels combining in the optical transition. This circumstance makes it possible to reliably position the "quasi-degenerate" states in the energy spectrum of the non-Kramers RE ion. According to the results of experimental and theoretical studies of YAG (or YGaG) garnets activated by Ho^{3+} [14] and Tb^{3+} [15] RE ions, in the low-symmetry CP of the garnet a set of the "quasi-doublet" states are formed in the energy spectra of the ground and excited multiplets of non-Kramers ions [16], while no "quasi-doublets" were detected in the multiplets of Tm^{3+} ions in the similar garnets. The absorption and

Cite as: F.K. Turotov, M.E. Malysheva, R.R. Vildanov, East Eur. J. Phys. 4, 341 (2024), https://doi.org/10.26565/2312-4334-2024-4-39

luminescence spectra of Tm^{3+}:YAG have been studied in detail within the visible and near infrared ranges at various temperatures (including low ones) by J.B.Gruber et al. [17]. For the emission spectra of the transitions from the $^1D_2$ state to the $^3H_6$, $^3F_4$, $^3F_3$ and $^3F_2$ multiplets to be studied, laser excitation of the optical transitions was used. Although these data provided information confirming the crystal-field splitting of the most multiplets (i.e. the *J,L,S*-states) belonging to the ground $4f^{(n)}$-configuration of the Tm^{3+} ion in the garnet structure, as well as information on the symmetry of the Stark sublevels of these multiplets, we believe that the previously obtained energy spectra of the Tm^{3+} ion in the garnet-aluminate structure should be supplemented by the corresponding "quasi-doublet" states that in turn can be detected and identified by magnetic circular polarization of luminescence methods in a wide range of wavelengths and temperatures [18]. Therefore, new studies of the emission spectra of Tm^{3+}:YAG by the differential magneto-optical methods would be very useful, since their application can help in positioning and determining a symmetry of the nearby (i.e. "quasi-degenerate") Stark sublevels in non-Kramers Tm^{3+} ions. On the other hand, the similar studies of the magneto-optical activity of emission transitions in thulium-yttrium garnets seems relevant due to a certain smallness of the Faraday rotation detected in these garnets within the visible spectral range as compared to the similar spectra observed in other rare-earth garnets [19], and their analysis led to contradictory results associated with the possible absence of "quasi-degenerate" ground states in non-Kramers Tm^{3+} ions in the garnet structure. The above-mentioned contradictions discovered during the study and interpretation of magneto-optical and magnetic properties of thulium garnet Tm:YAG were the motivating factors for this work to be carried out.

MATERIALS AND METHODS

A single crystal of thulium-yttrium garnet-aluminate Tm^{3+}:YAG grown by a spontaneous crystallization method from the "solution-melt" was provided by Prof. J. Heber (Physics Institute of the Technical University, Darmstadt, Germany). A sample under study containing ~1% Tm^{3+} ions was X-ray oriented and cut in the crystallographic planes of the (110) and (001); after that the sample surface was ground and polished with diamond pastes with a slowly thinning grain (down to ~1 μm). The luminescence spectra of Tm^{3+}:YAG were measured at temperatures T = 90K and 300K for the radiative 4f→4f transitions $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ within the spectral ranges of 452-462 nm and 484-488 nm with a resolution of ~ 1.5-2.0 cm^{-1}. The differential magneto-optical spectrum of Tm^{3+}:YAG, i.e. a spectrum of the MCPL degree $P = \frac{I_+ - I_-}{I_+ + I_-}$ (where $I_\pm$ is the intensity of orthogonal circularly polarized components of the luminescence line), was studied at a temperature of T = 300 K within the spectral range of 453-462 nm and 484-488 nm with a resolution of ~10 cm^{-1} and orientation of the outer magnetic field H = 10 kOe along the [110] axis of the garnet crystal. The MCPL degree spectra was recorded by a method of light radiation polarization modulation at a frequency of ~36 kHz with a photoelastic modulator with positive optical feedback [13]. The relative errors of the measured values (intensities of luminescence and degrees of circular light polarization) in all experiments did not exceed ~3-5%.

RESULTS AND DISCUSSION

The luminescence and MCPL spectra in single crystals of thulium-yttrium garnet-aluminate were studied for the radiative transitions $^1G_4 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3F_4$ within the wavelength range of 453-484 nm. The luminescence observed for the radiative transitions of the type: $^1G_4 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_4$, $^1D_2 \rightarrow {}^3F_3$, turns out to be the most intensive in the emission band caused by the radiative transition $^1D_2 \rightarrow {}^3F_4$ (Fig. 1).

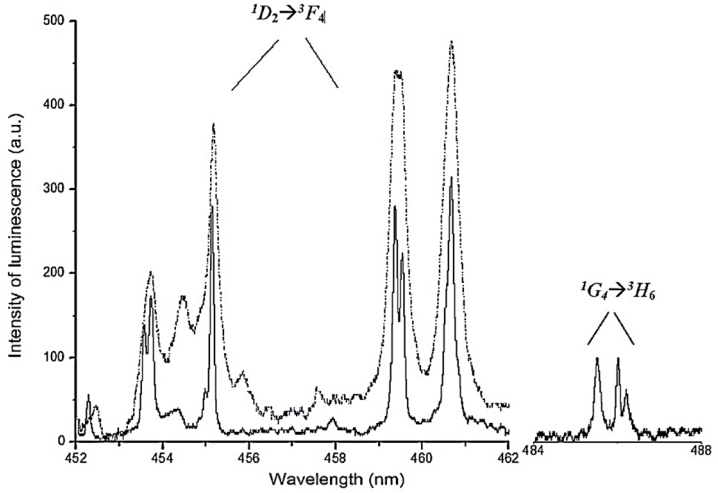

Figure 1. The luminescence spectrum of Tm^{3+}:YAG recorded in the emission band $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ at T=300K (blue dotted line) and at T=90K (black solid line)

The spectra of blue luminescence bands recorded at T=300K and 90K are characterized by a large number of well-resolved emission lines associated with the radiative 4f→4f transitions between the sublevels of the $^1D_2$ and $^3F_4$ multiplets

in the Tm^{3+} ion. A decrease in the sample temperature from 300 to 90K is accompanied by a decrease in the luminescence brightness, with the intensities of the strongest emission lines at wavelengths of 455, 459, 460 nm, determined by the areas under the corresponding lines, decreasing to the same extent by approximately 1.5 times as compared to a more significant decrease in the intensity of the remaining emission lines. The redistribution of the luminescence line intensity is due to a sharp decrease in the populations of the excited Stark singlets of the $^3F_4$ and $^1D_2$ multiplet when the temperature drops. When the temperature is lowered to 90 K, it is clearly seen that the emission lines at wavelengths of 453.6 and 457 nm are doublet lines insufficiently resolved at T=78 K. The most intensive luminescence lines in the $^1D_2 \rightarrow {}^3F_4$ luminescence band originate from the ground quasi-doublet state of the excited $^1D_2$ multiplet of the ground $4f^{(12)}$ configuration of the Tm^{3+} ion in YAG garnet-aluminate. The remaining emission lines are apparently due to radiative transitions from excited singlet sublevels of the $^1D_2$ multiplet to Stark sublevels of the $^3F_4$ multiplet.

Comparison of experimentally observed energies of the ground $4f^{(12)}$ configuration of Tm^{3+} ions in the crystal field (CF) of D_2 symmetry with theoretical values makes it possible to carry out symmetry identification of the radiative 4f→4f transitions in the luminescence band of $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$. Symmetry identification of the radiative transitions observed in the luminescence band $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ was performed based on the data of [17] and according to the notation of [4]. Classification (in symmetry) of the Stark sublevels of the multiplets $^3F_4$, $^1G_4$, $^1D_2$ and $^3H_6$ was carried out using irreducible representations Γ_i (where i = 1,2,3,4) of the D_2 symmetry group; and the directions and notations of the axes of the local coordinate system corresponding to one of the crystallographically nonequivalent positions (the so-called c-sites) of the RE ion Tm^{3+} in the garnet structure coincide with those adopted in [4].

The spectra of the MCPL degree measured in a single crystal of thulium-yttrium garnet-aluminate on the luminescence line $^1D_2 \rightarrow {}^3F_4$ (Fig. 2, Fig. 3) and on the luminescence line $^1G_4 \rightarrow {}^3H_6$ (Fig. 4) at T=300 K and T=90 K in the outer magnetic field H = 10 kOe are presented in Fig. 2, Fig. 3 and Fig. 4.

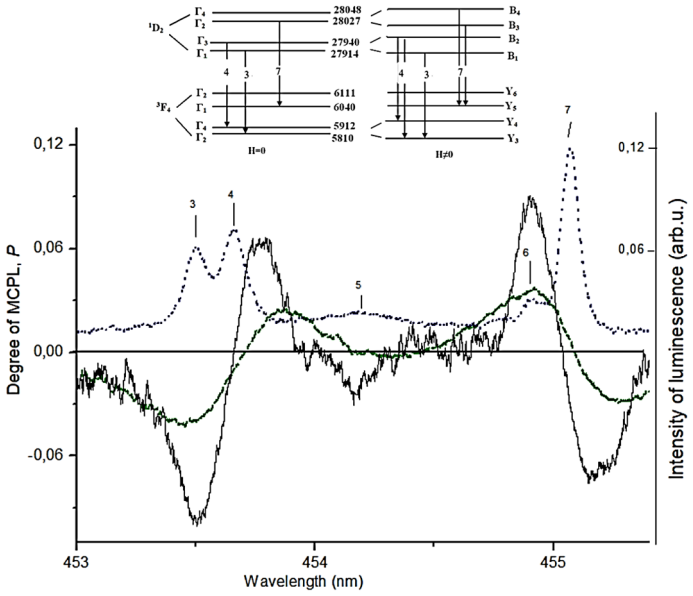

Figure 2. The spectra of the MCPL degree measured for the radiative transitions $^1D_2 \rightarrow {}^3F_4$ within the wavelength range 453-456 nm at T=90 K (black) and 300 K (green). The luminescence spectra (dots) were measured at 90 K. The inset shows a diagram of optical transitions between sublevels of the multiplets $^1D_2$ and $^3F_4$ of the Tm^{3+} in Tm^{3+}:YAG with no outer magnetic field and that of H=10 kOe

A comparison of the spectra of the MCPL degree P and luminescence (fluorescence) indicates the obvious fact that despite the relatively complicated structure of the observed spectrum P, for some emission lines the dispersion of the MCPL degree spectrum can be explained in a fairly simple way. For example, on lines 4, 7 (Fig. 2), 12 (Fig. 3) and 14 (Fig. 4), within the luminescence line the spectral dependence of the MCPL degree can be approximated by inclined linear dependences for which an effect magnitude is symmetrical (or asymmetrical) relative to zero (when the effect sign changes in the "centers of gravity" of the corresponding line). Moreover, from the schemes of radiative transitions shown in Fig. 2 and Fig. 3 it follows that the lines 4 and 12 are associated with allowed (in symmetry in the D_2 group) forced optical transitions occurring from the $B_2(\Gamma_3)$ sublevel of the $^1D_2$ multiplet to the nearby Stark sublevels $Y_4(\Gamma_4)$, $Y_3(\Gamma_2)$ for the line 4 and to the $Y_8(\Gamma_4)$, $Y_7(\Gamma_1)$ sublevels for the line 12 of the $^3F_4$ multiplet. At the same time, the line 7 in Fig. 2 is caused by permitted (in symmetry) optical transitions occurring from the B_2 Stark sublevel of the $^1D_2$ multiplet with Γ_3 symmetry to the nearby $Y_8(\Gamma_4)$ and $Y_7(\Gamma_1)$ Stark sublevels of the $^3F_4$ multiplet. Besides, the special feature of the spectral dependence of the MCPL degree on the line 7 (Fig. 2) is caused by the permitted (in symmetry) optical transitions occurring from the nearby Stark sublevels $B_4(\Gamma_4)$ and $B_3(\Gamma_2)$ of the $^1D_2$ multiplet to the $Y_5(\Gamma_1)$ sublevel of the $^3F_4$ multiplet.

The scheme of optical transitions between sublevels of multiplets $^1D_2$ and $^3F_4$ of the Tm^{3+} ion in Tm^{3+}:YAG is shown in the insets to Fig. 2 and Fig. 3. On the emission line 12, the spectral dependence $P(\nu)$ is an inclined linear dependence

within the luminescence line with a change in the sign of the effect in its center. According to the general theory (see [18]), a value of the spectrum slope - P (A is the term of the MCPL degree) is due to the Zeeman splitting of the sublevels of the final and initial states combining in the optical transition; in this case, to the Zeeman splitting of the quasi-doublet state of the $^5D_1$ multiplet in the magneto-optically active transition "singlet → quasi-doublet". In the outer magnetic field, the wave functions of nearby singlets and singlets from multiplets combining in radiative transitions begin to "mix" with each other; and magnetic dipole and electric dipole transitions begin to occur between them. Using the available selection rules (in symmetry) for the matrix elements of the components of the electric and magnetic dipole moments of the RE ion from the expression for the A term of the MCPL degree, it is easy to establish the symmetry of one of the combining states in the magneto-optical transition if the symmetry of the other is known [12].

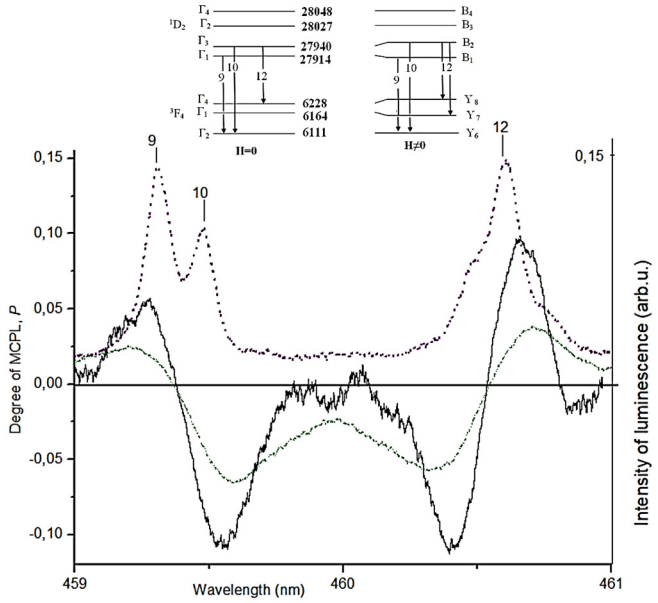

Figure 3. The spectra of the MCPL degree measured for the radiative transitions $^1D_2 \rightarrow {}^3F_4$ within the wavelength range 459-461 nm at T=90 K (black) and 300 K (green). The luminescence spectra (dots) were measured at 90 K. The inset shows a diagram of optical transitions between sublevels of the multiplets $^1D_2$ and $^3F_4$ of the Tm^{3+} ion in Tm^{3+}:YAG with no outer magnetic field and that of H=10 kOe.

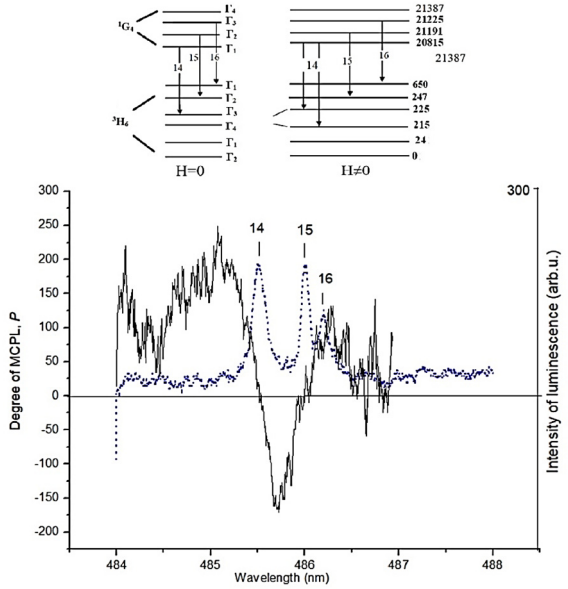

Figure 4. The MCPL degree spectra measured on radiative transitions $^1G_4 \rightarrow {}^3H_6$ within the wavelength range 483-488 nm at T=90 K (black) and 300 K (green). The luminescence spectra (dots) were measured at 90 K. The inset shows a diagram of optical transitions between sublevels of the $^1D_2$ and $^3F_4$ multiplets of the Tm^{3+} ion in Tm^{3+}:YAG in the absence of an external magnetic field and at H=10 kOe

Indeed, in accordance with the formula for the ratio of the paramagnetic term C' of the magneto-optical activity (MOA) and the diamagnetic A' term of the MOA to the dipole strength of the D transition:

$$\frac{C'}{D_1} = \frac{2\,Im\{\langle a|\hat{\mu}_z|b\rangle \cdot (\langle a|\hat{P}_x|j\rangle \cdot \langle j|\hat{P}_y|b\rangle - \langle a|\hat{P}_y|j\rangle \cdot \langle j|\hat{P}_x|b\rangle)\}}{\left[\left|\langle a|\hat{P}_x|j\rangle\right|^2 + \left|\langle j|\hat{P}_y|b\rangle\right|^2\right]}$$

$$\frac{A'}{D_2} = \frac{2\,Im\{\langle j|\hat{\mu}_z|k\rangle \cdot (\langle a|\hat{P}_x|j\rangle \cdot \langle j|\hat{P}_y|b\rangle - \langle a|\hat{P}_y|j\rangle \cdot \langle j|\hat{P}_x|b\rangle)\}}{\left[\left|\langle a|\hat{P}_x|j\rangle\right|^2 + \left|\langle k|\hat{P}_y|a\rangle\right|^2\right]} \quad (1)$$

where $\hat{\mu}_z$ is the z-projection operator of the ion magnetic moment (in units of μ_B); $|a\rangle$ and $|b\rangle$ are the wave functions of two closely located Stark singlets of the ion ground state; $|j\rangle$,$|k\rangle$ are the wave functions of two closely located Stark singlets of the excited state; $\hat{P}_{x,y}$ are the components of the ion dipole moment operator; D_1 and D_2 are the dipole "transition strengths" for the "quasi-doublet–isolated singlet" and "isolated singlet–quasi-doublet" transitions, we obtain a unique opportunity to unambiguously determine a symmetry of the Stark sublevels of the ground and excited multiplets of the non-Kramers RE ion in the garnet structure according to the selection rules in symmetry. It is easy to see that if the symmetry of the quasi-doublet states is described by the irreducible representations Γ_2 and Γ_4, then for a "diamagnetic" contribution to the MCPL to exist, it is necessary that the possible symmetry of the singlet $|a\rangle$ be described by the irreducible representation Γ_1 (or Γ_3). If this condition is met the transitions from the level $|a\rangle$ to the levels $|j\rangle$ and $|k\rangle$ will be permitted (see formula (1)). Similarly, for the existence of a "paramagnetic" contribution to the MCPL at the "quasi-doublet–singlet" transition, the singlet symmetry is to be described by irreducible representations Γ_1 (or Γ_3), in accordance with the selection rules (see (1)).

In accordance with formula (1) and the data of crystal-field calculations in Table 1, the symmetry of the Stark sublevels of the Γ_4, Γ_1 quasidoublet of the ^{3}F$_4$ multiplet is directly dictated by the symmetry of the Γ_3 Stark sublevel of the ^{1}D$_2$ multiplet combining in the "singlet → quasidoublet" transition.

Table 1. Theoretically calculated energies and wave functions of the Stark sublevels of the ^{3}H$_6$, ^{3}F$_4$ and ^{1}G$_4$ multiplets of the Tm^{3+} ion in Tm^{3+}:YAG

№	$^{2S+1}L_J$	Energy (cm^{-1})	Major components of the Stark sublevels wavefunctions of Tm^{3+} ion ground ^{3}H$_6$, ^{3}F$_4$ and ^{1}G$_4$ multiplets in the CF of D$_2$ symmetry
1	$^3H_6$	9.09	$/\Psi_1(\Gamma_2) >= -0.661(/\,^3H_6,+1> - /\,^3H_6,-1>) - 0.2379(/\,^3H_6,+5> - /\,^3H_6,-5>)$
2		17.47	$/\Psi_2(\Gamma_1) >= 0.8338/\,^3H_6,0> -0.3649(/\,^3H_6,+2> + /\,^3H_6,-2>)$
3		211.84	$/\Psi_3(\Gamma_4) >= -0.3088(/\,^3H_6,+1> + /\,^3H_6,-1>) - 0.3176(/\,^3H_6,+3> + /\,^3H_6,-3>)$ $-0.5461(/\,^3H_6,+5> + /\,^3H_6,-5>)$
4		233.24	$/\Psi_4(\Gamma_3) >= -0.4534(/\,^3H_6,+2> - /\,^3H_6,-2>) + 0.4407(/\,^3H_6,+4> - /\,^3H_6,-4>)$ $+0.3062(/\,^3H_6,+6> - /\,^3H_6,-6>)$
5		260.23	$/\Psi_5(\Gamma_1) >= -0.2555/\,^3H_6,0> -0.3676(/\,^3H_6,+2> + /\,^3H_6,-2>)$ $-0.4787(/\,^3H_6,+4> + /\,^3H_6,-4>) - 0.3104(/\,^3H_6,+6> + /\,^3H_6,-6>)$
6		265.93	$/\Psi_6(\Gamma_2) >= 0.1542(/\,^3H_6,+1> - /\,^3H_6,-1>) - 0.4671(/\,^3H_6,+3> - /\,^3H_6,-3>)$ $-0.5031(/\,^3H_6,+5> - /\,^3H_6,-5>)$
7		500.4	$/\Psi_7(\Gamma_4) >= 0.621(/\,^3H_6,+1> + /\,^3H_6,-1>) - 0.2599(/\,^3H_6,+3> + /\,^3H_6,-3>)$ $-0.2013(/\,^3H_6,+5> + /\,^3H_6,-5>)$
8		614.83	$/\Psi_8(\Gamma_3) >= -0.5257(/\,^3H_6,+2> - /\,^3H_6,-2>) + 0.448(/\,^3H_6,+4> - /\,^3H_6,-4>)$ $+0.1337(/\,^3H_6,+6> - /\,^3H_6,-6>)$
9		638.91	$/\Psi_9(\Gamma_1) >= 0.4645/\,^3H_6,0> +0.4692(/\,^3H_6,+2> + /\,^3H_6,-2>)$ $-0.3585(/\,^3H_6,+4> + /\,^3H_6,-4>) - 0.1936(/\,^3H_6,+6> + /\,^3H_6,-6>)$
10		691.13	$/\Psi_{10}(\Gamma_2) >= 0.1542(/\,^3H_6,+1> - /\,^3H_6,-1>) - 0.4671(/\,^3H_6,+3> - /\,^3H_6,-3>)$ $-0.5031(/\,^3H_6,+5> - /\,^3H_6,-5>)$
11		696.5	$/\Psi_{11}(\Gamma_4) >= 0.1106(/\,^3H_6,+1> + /\,^3H_6,-1>) - 0.5717(/\,^3H_6,+3> + /\,^3H_6,-3>)$ $-0.3945(/\,^3H_6,+5> + /\,^3H_6,-5>)$
12		772.68	$/\Psi_{12}(\Gamma_3) >= -0.1119(/\,^3H_6,+2> - \,^3H_6,-2>) - 0.3151(/\,^3H_6,+4> - /\,^3H_6,-4>)$ $+0.6186(/\,^3H_6,+6> - /\,^3H_6,-6>)$
13		784.29	$/\Psi_{13}(\Gamma_1) >= 0.1961/\,^3H_6,0> -0.355(/\,^3H_6,+4> + /\,^3H_6,-4>)$ $+0.597(/\,^3H_6,+6> + /\,^3H_6,-6>)$
14	$^3F_4$	5817.13	$/\Psi_{16}(\Gamma_1) >= 0.1402(/\,^3F_4,3> - /\,^3F_4,-3>) + \quad 0.5330(/\,^3F_4,-1> - /\,^3F_4,1>) +$ $+0.3708(/\,^1G_4,+1> - /\,^1G_4,+1>) + 0.1975(/\,^3H_2,+1> - /\,^3H_2,-1>)$
15		5918.01	$/\Psi_{17}(\Gamma_1) >= 0.4344(/\,^3F_4,3> + /\,^3F_4,-3>) - \quad 0.1502(/\,^3H_4,3> + /\,^3H_4,-3>) -$ $-0.1267(/\,^3H_4,1> + /\,^3H_4,-1>) + 0.3496(/\,^3F_4,1> + /\,^3F_4,-1>) + 0.2920(/\,^1G_4,-3> +$ $+/\,^1G_4,+3>) + 0.2404(/\,^1G_4,1> + /\,^1G_4,-4>)$
16		6043.83	$/\Psi_{18}(\Gamma_1) >= 0.1238(/\,^3H_4,4> + /\,^3H_4,-4>) - \quad 0.3741(/\,^3F_4,4> + /\,^3F_4,-4>) -$ $-0.2459(/\,^3G_4,4> + +/\,^3G_4,-4>) + 0.1402(/\,^3F_4,2> + /\,^3F_4,-2>) -$ $-0.5637/\,^3F_4,0> -0.3782/\,^1G_4,0> +0.1957/H_4,0>$

№	$^{2S+1}L_J$	Energy (cm^{-1})	Major components of the Stark sublevels wavefunctions of Tm^{3+} ion ground $^3H_6$, $^3F_4$ and $^1G_4$ multiplets in the CF of D_2 symmetry
17		6116.24	$/\Psi_{19}(\Gamma_2) >= -0.1454(/\ ^3F_4,+1> -/\ ^3F_4,-1>) - 0.3596(/\ ^1G_4,+3> -/\ ^1G_4,-3>)$ $+0.1801(/\ ^3H_4,+3> -/\ ^3H_4,-3>) - 0.5504(/\ ^3F_4,+3> -\ ^3F_4,-3>)$
18		6162.15	$/\Psi_{20}(\Gamma_1) >= -0.1841/\ ^3H_4,0> +0.5384/\ ^3F_4,0> +0.3591/\ ^1G_4,0>$ $+0.2914(/\ ^3F_4,+2> +/\ ^3F_4,-2>) + 0.1955(/\ ^1G_4,+4> +/\ ^1G_4,-4>)$ $-0.2989(/\ ^3F_4,+4> +/\ ^3F_4,-4>)$
19		6227.68	$/\Psi_{18}(\Gamma_4) >= >\ 0.4546(/\ ^3F_4,2> -/\ ^3F_4,-2>) +\ \ 0.3414(/\ ^3F_4,-4> +/\ ^3F_4,4>) +$ $+0.3010(/\ ^1G_4,2> -/\ ^3G_4,-2>) + 0.1518(/\ ^3H_4,-2> -/\ ^3F_4,2>) +$ $+0.4546(/\ ^3F_4,2> -/\ ^3F_4,-2>) + 0.3010(/\ ^1G_4,2> -/\ ^1G_4,-2>)$
20	$^1D_2$	27876.89	$/\Psi_{64}(\Gamma_1) >= 0.1152/\ ^3P_2,0> +/0.455(/\ ^3P_2,+2> +\ ^3P,-2>) + 0.295(/\ ^3F_2,+2$ $> +/\ ^3F_2,-2>)$ $+0.4382(/\ ^1D_2,+2> +/\ ^1D_2,-2>)$
21		27913.63	$/\Psi_{65}(\Gamma_3) >= 0.4437(/\ ^3P_2,+2> -/\ ^3P_2,-2>) - 0.3209(/\ ^3F_2,+2> -/\ ^3F_2,-2>)$ $+0.4459(/\ ^1D_2,+2> -/\ ^1D_2,-2>)$
22		28043.75	$/\Psi_{66}(\Gamma_2) >=\ 0.4624(/\ ^3P_2,1> -/\ ^3P_2,-1>) +\ \ 0.4455(/\ ^1D_2,1> +/\ ^1D_2,-1>) +$ $+0.2944\ (/\ ^3F_2,1> -/\ ^3F_2,-1>)$
23	$^1G_4$	28043.75	$/\Psi_{67}(\Gamma_1) >= 0.3604(/\ ^3H_4,+2> +/\ ^3H_4,-2>) + 0.4464(/\ ^1G_4,-2> +/\ ^1G_4,+2>) +$ $+ + 0.2429(/\ ^3G_4,-4> +/\ ^1G_4,-4>) + 0.1984(//\ ^3H_4,-4> +/\ ^3H_4,+4>) -$ $-0.1840(\ ^3F_4,2> +/\ ^3F_4,-2>$
24		21191.68	$/\Psi_{56}(\Gamma_2) >= 0.3932(/\ ^3H_4,-1> -/\ ^3H_4,+1>) +\ \ 0.5208(/\ ^1G_4,-1> -/\ ^1G_4,+1>) +$ $+0.2180(/\ ^3F_4,1> -/\ ^3F_4,-1>) + 0.1192(/\ ^1G_4,+3> -/\ ^1G_4,-3>)$
		21225.58	$/\Psi_{57}(\Gamma_3) >= 0.3969(/\ ^1G_4,-4> -/\ ^1G_4,+4>) + 0.3518(/\ ^1G_4,-2> -/\ ^1G_4,+2>) +$ $+0.3102(/\ ^3H_4,-4> -/\ ^3H_4,+4>) +\ \ 0.2713(/\ ^3H_4,-2> -/\ ^3H_4,+2>) +$ $+0.1626(/\ ^3F_4,+4> -/\ ^3F_4,-4>) + 0.1458(/\ ^3F_4,+2> -/\ ^3F_4,-2>)$

The peculiarity of the MCPL degree spectrum on line 4 in Fig. 2 is caused by the permitted (in symmetry) optical transitions occurring from the $B_2(\Gamma_3)$ sublevel of the $^1D_2$ multiplet to the nearby $Y_4(\Gamma_4)$ and $Y_3(\Gamma_2)$ Stark sublevels of the $^3F_4$ multiplet. The *C*-term of the MCPL degree on line 4 is due to the transition from the singlet sublevel to the quasi-doublet state. A similar analysis of the MCPL degree spectrum in Fig. 4 showed that on the luminescence line 14 in a magnetic field there is a magneto-optical transition caused by the transition between the sublevel Γ_1 (20815 cm^{-1}) of the $^1G_4$ multiplet to the nearby Stark sublevels Γ_3 (225 cm^{-1}), Γ_4 (215 cm^{-1}).

The inclined linear dependence within the luminescence line (with a change in the sign of the effect in its center) indicates the manifestation of the *A* - term of the MCPL degree on the line 14. In the approximation of the Gaussian contour of the luminescence band, the expression for the MCPL degree *P* of a non-Kramers ion:

$$P = \frac{1}{2}\mu_B H\left[\frac{(\nu-\nu_0)}{\Gamma^2}\cdot\{\frac{A'}{D_2}+\frac{C'}{D_1}\}+\frac{1}{kT}\cdot\frac{C'}{D_1}\right] \quad (2)$$

is an inclined linear dependence shifted relative to zero, the center of the radiation line, by a value of the temperature-dependent "addition" (proportional to the amplitude of the C'- term of the MCPL degree). The first and second terms in (2) determine the contributions of the "diamagnetic" (A'-term) and temperature-dependent "paramagnetic" (C'- term) mechanisms of the MCPL of a non-Kramers RE ion, respectively; ν is the wave number (in cm^{-1}).

Considering that the magnetic moments μ_g of the corresponding quasidoublets combining in radiative transitions are determined by the values of the ratios C'/D_1 and A'/D_2 (in units μ_B), then from the experimental data (Fig. 2, Fig. 3, Fig. 4), it is easy to find the "effective" Zeeman splittings $\Delta E_{zeem}^{ef} = \mu_g H$ of the quasidoublet states combining in magneto-optically active radiative transitions. In this case, the "effective" Zeeman splittings of the corresponding quasi-doublet states $\Delta E_{zeem}^{ef} = \frac{A'}{D_2}\mu_B H$ in the $^3F_4$ multiplet can be easily found from the doubled products of the slopes of the MCPL degree spectra $\Delta P/_{\Delta\nu}$ on the lines 4 and 12 and the squares of their half-widths Γ^2 (Fig. 1). The Zeeman splittings responsible for the emergence of the A'- terms of the MCPL degree turn out to be relatively small and equal to $\Delta E_{zeem}^{ef} = 0.16\ cm^{-1}$ and $\Delta E_{zeem}^{ef} = 1.01\ cm^{-1}$ for the emission lines 4 and 12, respectively, and $\Delta E_{zeem}^{ef} = 0.23\ cm^{-1}$ for the line 14 for the quasi-doublet states of the $^3H_6$ multiplet in the outer field H = 9.5 kOe. In this case, the value of the "effective" splitting $\Delta E_{zeem}^{ef} = \frac{C'}{D_1}\mu_B H$ of the quasi-doublet state of the $^1D_2$ multiplet for the radiative transitions "quasi-doublet–isolated singlet" on the emission line 7 can be determined similarly to how this was done above for the lines 4 and 2 . From what was found in this way (for the line 7, it is equal to $\Delta E_{zeem}^{ef} = 0.6\ cm^{-1}$), it follows that the features of the MCPL degree spectra on them are apparently associated with radiative transitions occurring from the same quasi-doublet state located in the lower part of the $^1D_2$ multiplet. However, the asymmetry of

the MCPL degree spectrum observed on these lines cannot be explained only by a contribution of the MCPL C'-term caused by the above-found value of the "effective" Zeeman splitting of the quasidoublet in the $^1D_2$ multiplet (see also formula (1)) because of the smallness of the splitting itself. Therefore, the features in the behavior of the spectral dependence of magnetically polarized luminescence on the emission lines 4 and 8 are formed mainly by a mechanism of Van Vleck "mixing" of this quasi-doublet state with the states of nearby Stark singlets in the $^1D_2$ multiplet.

CONCLUSIONS

Based on the analysis of the spectral dependences of magneto-optical (MCPL) and optical (luminescence) effects in a single crystal of thulium-yttrium garnet-aluminate Tm^{3+}:YAG, it has been established that there are "quasi-degenerate" states of excited multiplets $^1D_2$, $^3F_4$,$^3G_4$ and the ground multiplet $^3H_6$ of the RE ion Tm^{3+} in the garnet-aluminate YAG in the luminescence band $^1G_4 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_4$ and $^1D_2 \rightarrow {}^3F_3$.

Analysis of optical and magneto-optical studies show that the quantum-mechanical "mixing" plays a significant role in the mechanism of occurrence of magneto-optical effects on luminescence bands caused by "forbidden" 4f→4f transitions in the non-Kramers Tm^{3+} ion that has a "quasi-doublet" structure in the energy spectra. The results of symmetry identification of the found 4f→4f transitions are confirmed by the data of the magneto-optical studies.

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МАГНІТООПТИЧНІ ОСОБЛИВОСТІ РАДІАЦІЙНИХ ПЕРЕХОДІВ НЕКРАМЕРСЬКОГО ІОНУ Tm^{3+} В КРИСТАЛАХ ІТРІЄВО-АЛЮМІНІЄВОГО ГРАНАТУ

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Досліджено спектри люмінесценції та магнітної кругової поляризації монокристалу тулій-ітрієвого гранат-алюмінату Tm^{3+}:YAG у видимій області спектру за температури 90 та 300 К у магнітному полі 10 кЕ. На основі аналізу оптичних та магнітооптичних даних встановлено наявність «квазівироджених» станів збуджених мультиплетів $^1D_2$, $^3F_4$,$^3G_4$ та основного мультиплета $^3H_6$ іона Tm^{3+} RE в гранат-алюмінатному YAG на випромінювальних переходах $^1G_4 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_4$ та $^1D_2 \rightarrow {}^3F_3$. Ефект квантово-механічного “перемішування” відіграє значну роль у виникненні магнітооптичних ефектів на смугах люмінесценції, зумовлених “забороненими” переходами 4f→4f в некрамерсовському іоні Tm^{3+}, що має “квазідублетну” структуру енергії спектри.

Ключові слова: *тулій-ітрієвий гранат; рідкоземельні іони; магнітооптичні властивості; люмінесценція; рівні енергії; магнітна кругова поляризація*