

# Polarized Absorption Spectra and Spectroscopic Parameters of $\text{Tm}^{3+}$ in the $\text{TmAl}_3(\text{BO}_3)_4$ Single Crystal

A. V. Malakhovskii<sup>a</sup>, A. É. Sokolov<sup>a</sup>, V. L. Temerov<sup>a</sup>, L. N. Bezmaternykh<sup>a</sup>, A. L. Sukhachev<sup>a</sup>,  
V. A. Seredkin<sup>a</sup>, S. L. Gnatchenko<sup>b</sup>, I. S. Kachur<sup>b</sup>, and V. G. Piryatinskaya<sup>b</sup>

<sup>a</sup> Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia

e-mail: malakha@iph.krasn.ru

<sup>b</sup> Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine,  
pr. Lenina 47, Kharkov, 61103 Ukraine

Received December 10, 2007

**Abstract**—High-optical-quality single crystals of the  $\text{TmAl}_3(\text{BO}_3)_4$  compound were synthesized from a solution in the melt. The absorption spectra in the  $\sigma$  and  $\pi$  polarizations for the  ${}^3H_6 \rightarrow {}^3F_4$ ,  ${}^3H_6 \rightarrow {}^3H_5$ ,  ${}^3H_6 \rightarrow {}^3H_4$ ,  ${}^3H_6 \rightarrow {}^3F_3$ ,  ${}^3H_6 \rightarrow {}^3F_2$ ,  ${}^3H_6 \rightarrow {}^1G_4$ , and  ${}^3H_6 \rightarrow {}^1D_2$  transitions in the  $\text{Tm}^{3+}$  ion were recorded at room temperature. The transition intensities were analyzed in the framework of the Judd–Ofelt theory generalized to the case of anisotropic crystals, and the following parameters of the theory were obtained:  $\Omega_2 = 6.14 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 3.09 \times 10^{-20} \text{ cm}^2$ , and  $\Omega_6 = 2.04 \times 10^{-20} \text{ cm}^2$ . The lifetimes and the branching ratios were determined for all possible transitions.

PACS numbers: 78.20.-e, 78.40.Ha

DOI: 10.1134/S1063783408070159

## 1. INTRODUCTION

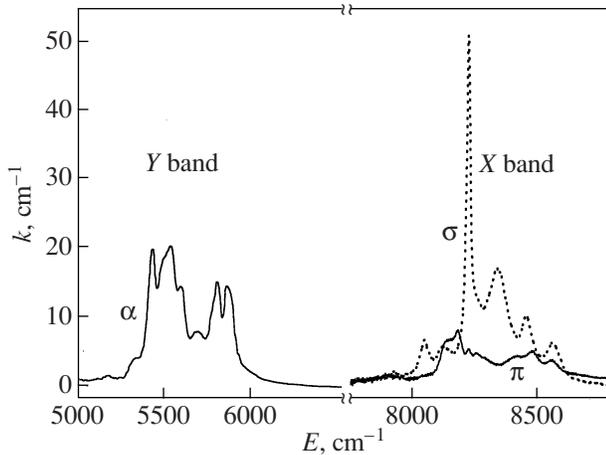
In recent years, considerable attention has been focused on materials (crystals, glasses) doped with  $\text{Tm}^{3+}$  ions [1, 2] due to the wide spectral range of their emission [3]. In particular, Caird et al. [4] and Johnson et al. [5] achieved the lasing on the  $f$ – $f$  transitions of  $\text{Tm}^{3+}$  ions in yttrium aluminum garnet and  $\text{YAlO}_3$  crystals at wavelengths of 2.0 and 2.3  $\mu\text{m}$ . The emission of the  ${}^3F_4 \rightarrow {}^3H_6$  transition at approximately 1.9  $\mu\text{m}$  has been used in medicine and remote probing systems [6]. The upconversion process on the  ${}^1D_2 \rightarrow {}^3F_4$  transition in the  $\text{Tm}^{3+}$  ion was observed in yttrium scandium aluminum garnet at a wavelength of 450 nm [7]. The  ${}^3H_6 \rightarrow {}^3H_4$  transition in the  $\text{Tm}^{3+}$  ions in the  $\text{YVO}_4$  and  $\text{Y}_2\text{O}_3$  compounds at approximately 800 nm turned out to be promising for pumping of commercial GaAlAs lasers [8]. Media with a high concentration of active rare-earth ions are necessary for miniature solid-state lasers. Rare-earth aluminoborate crystals with a huntite structure characterized by a one-position distribution of cations are ideal materials for these purposes, because this structure makes it possible to introduce rare-earth (including  $\text{Tm}^{3+}$ ) ions at high concentrations up to the stoichiometric composition.

In our earlier work [9], we measured the absorption spectra for all observable  $f$ – $f$  transitions in  $\text{TmAl}_3(\text{BO}_3)_4$  single crystals over a wide range of tem-

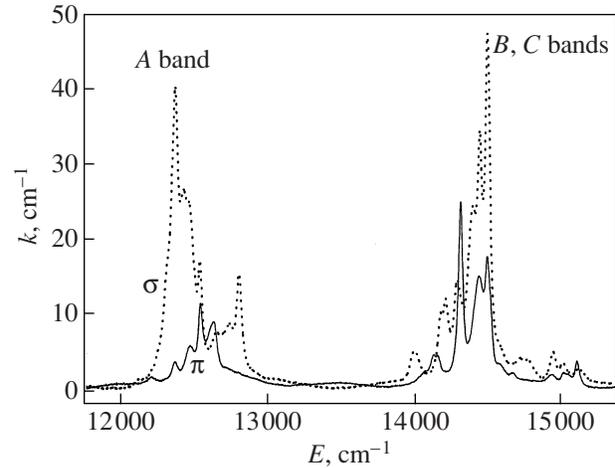
peratures. However, the absorption spectra allow one to determine the probabilities of transitions only to the ground state. In order to estimate the probabilities of all  $f$ – $f$  transitions and the branching ratios, it is common practice to use the Judd–Ofelt theory. These estimates for  $\text{TmAl}_3(\text{BO}_3)_4$  crystals were made by Guohua Jia et al. [10] from the analysis of unpolarized spectra that considerably reduced the reliability of the results of processing with the use of this theory. Moreover, the strong absorption band for the crystals synthesized in [10] was observed beginning with an energy of 25000  $\text{cm}^{-1}$  in contrast to 35000  $\text{cm}^{-1}$  for our crystal samples, which indicates a lower quality of the former crystals. As a consequence, the transition to the  ${}^1D_2$  state in [10] was poorly observed against the background of the strong absorption edge, which could also affect the results of processing in [10]. All the above factors have given impetus to the performance of new investigations of the spectroscopic parameters of  $\text{TmAl}_3(\text{BO}_3)_4$  crystals with the use of the Judd–Ofelt theory.

## 2. OBJECTS OF INVESTIGATION

Single crystals of the  $\text{TmAl}_3(\text{BO}_3)_4$  compound were grown from a melt solution (the growth procedure is described in detail in [11, 12]). The lattice constants of the grown crystals were determined using x-ray diffraction:  $a = 9.280(1) \text{ \AA}$  and  $c = 7.211(1) \text{ \AA}$ . The samples



**Fig. 1.** Absorption spectra measured in the  $\alpha$  polarization for the  ${}^3H_6 \rightarrow {}^3F_4$  transition (the Y band) and in the  $\pi$  and  $\sigma$  polarizations for the  ${}^3H_6 \rightarrow {}^3H_5$  transition (the X band).



**Fig. 2.** Absorption spectra measured in the  $\pi$  and  $\sigma$  polarizations for the transitions  ${}^3H_6 \rightarrow {}^3H_4$  (the A band),  ${}^3H_6 \rightarrow {}^3F_3$  (the B band), and  ${}^3H_6 \rightarrow {}^3F_2$  (the C band).

for measurements were prepared in the form of polished plane-parallel plates oriented perpendicular or parallel to the crystallographic threefold axis.

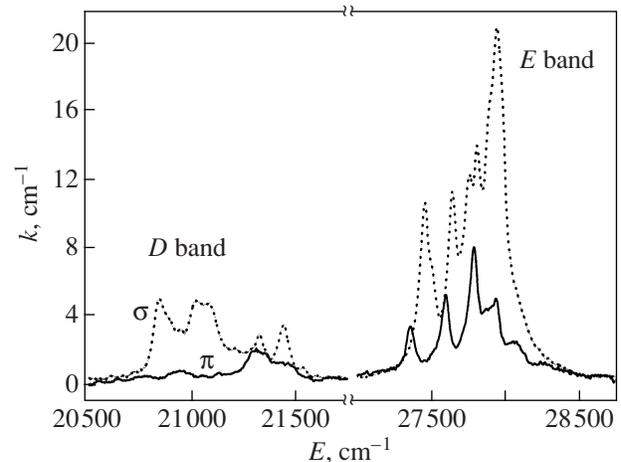
### 3. EXPERIMENTAL RESULTS AND DISCUSSION

At room temperature, the crystals have trigonal symmetry with space group  $R32$  (no. 155, International Tables for X-ray Crystallography). The unit cell contains three formula units ( $Z = 3$ ). Trivalent rare-earth ions occupy only one type of positions with symmetry  $D_3$  (this substantially simplifies the interpretation of spectral information). These ions are located at the center of a trigonal prism formed by six crystallographically equivalent oxygen ions. Each oxygen ion in the environment of the rare-earth ion belongs to its own borate group. The triangles formed by the oxygen ions in the neighboring basal planes are not superimposed on each other but are twisted through a particular angle. Owing to this distortion, the symmetry  $D_{3h}$  of the ideal prism is reduced to the symmetry  $D_3$  [13].

Figures 1–3 show the absorption spectra (decimal absorption coefficient) measured at room temperature for seven  $f$ - $f$  transitions in the range from 5000 to 35000  $\text{cm}^{-1}$ , in which a strong absorption occurs. We used the identification of the states of the  $\text{Tm}^{3+}$  ion that has been universally accepted in recent years [14]. This identification differs from that initially proposed in [15] by the mutual arrangement of the  ${}^3F_4$  and  ${}^3H_4$  states due to their strong mixing by the spin-orbit interaction. The shorthand notation of the transitions is taken from [16]. The absorption spectra were measured with the light propagating normal to the  $C_3$  axis of the crystal for the light wave vector  $\mathbf{E}$  parallel (the  $\pi$  spectrum) and perpendicular (the  $\sigma$  spectrum) to the  $C_3$  axis and the light

propagating along the  $C_3$  axis (the  $\alpha$  spectrum). The spectral resolution was approximately equal to 10  $\text{cm}^{-1}$ .

The absorption spectra measured in the  $\sigma$  and  $\alpha$  polarizations coincide with each other. This implies that the absorption occurs through the electric dipole mechanism. The shape and integrated intensities of the  $\pi$  and  $\sigma$  spectra differ substantially; i.e., there is a dichroism (Figs. 1–3, Table 1). In particular, the intensities of the  $\sigma$  spectra are higher than those of the  $\pi$  spectra by a factor of 2.5–3.8. The maximum values of the  $\sigma$  absorption cross sections  $K_1 = K/N_0$  [where  $K$  is the absorption coefficient ( $\text{cm}^{-1}$ ) and  $N_0$  is the concentration of  $\text{Tm}^{3+}$  ions per cubic centimeter] are observed at the following wavelengths: 1810 nm ( $K_1 = 0.37 \times$



**Fig. 3.** Absorption spectra measured in the  $\pi$  and  $\sigma$  polarizations for the transitions  ${}^3H_6 \rightarrow {}^1G_4$  (the D band) and  ${}^3H_6 \rightarrow {}^1D_2$  (the E band).

**Table 1.** Parameters  $\Gamma_\lambda^2$  in formula (1), average wave numbers  $k_{av}$ , integrated intensities  $I$ , oscillator strengths  $f$ , and transition strengths  $s_{if}$ 

Transition	Excited state	$\Gamma_2^2$	$\Gamma_4^2$	$\Gamma_6^2$	$k_{av}, \text{cm}^{-1}$	$I, \text{cm}^{-2} \text{mol}^{-1}$		$f, 10^{-7}$	$s_{if}, 10^{-20} \text{cm}^2$	
						$\pi$	$\sigma$		experiment	calculation
<i>Y</i>	$^3F_4$	0.5589	0.7462	0.2574	5600		867			6.27
<i>X</i>	$^3H_5$	0.1074	0.2313	0.6382	8300	179	560	18.7	2.70	2.68
<i>A</i>	$^3H_4$	0.2187	0.0944	0.5758	12500	225	884	28.7	2.75	2.81
<i>B</i>	$^3F_3$	0	0.3163	0.8409	14400	453	882	31.9	2.66	2.69
<i>C</i>	$^3F_2$	0	0	0.2591	15000	38	59	2.24	0.18	0.53
<i>D</i>	$^1G_4$	0.0452	0.0694	0.0122	21150	78	298	9.69	0.55	0.52
<i>E</i>	$^1D_2$	0	0.3144	0.0916	27800	247	786	26.2	1.13	1.16

$10^{-20} \text{cm}^2$ ), 1217 nm ( $K_1 = 0.89 \times 10^{-20} \text{cm}^2$ ), 808 nm ( $K_1 = 0.73 \times 10^{-20} \text{cm}^2$ ), 690 nm ( $K_1 = 0.83 \times 10^{-20} \text{cm}^2$ ), 669 nm ( $K_1 = 0.08 \times 10^{-20} \text{cm}^2$ ), 480 nm ( $K_1 = 0.09 \times 10^{-20} \text{cm}^2$ ), and 358 nm ( $K_1 = 0.37 \times 10^{-20} \text{cm}^2$ ).

In order for a transition to be allowed, the representation of the transition operator  $\Gamma_t = \Gamma_i \Gamma_f$  (where  $\Gamma_i$  and  $\Gamma_f$  are the representations of the initial and final states, respectively) should contain the representation of the electric dipole moment. In particular, in the group  $D_3$ , this is the representation  $A_2$  for the  $\pi$  polarization and the representation  $E$  for the  $\sigma$  polarization [17, 18]. In our previous works [9, 19], the symmetry of transitions was analyzed using the tables taken from [20]. However, it turned out that they involve errors, which led us to the assumption regarding distortions of the local symmetry of the thulium ion to the symmetry  $C_3$  even at room temperature [9, 19]. The tables presented in [17, 18] do not permit us to make this assumption. According to these tables, unlike the tables taken from [20], the electric dipole transitions in the symmetry  $D_3$ , as in the symmetry  $C_3$ , are allowed for any polarization. However, the number of the absorption bands observed at liquid-helium temperatures and their polarization properties suggest a lowering of the local symmetry to  $C_1$  with a decrease in the temperature [9, 19].

In the framework of the Judd–Ofelt theory, the strength of an  $f$ – $f$  transition in an ion in a crystal field is described by the relationship [21–23]

$$s_{IF} = \sum_{\lambda} \Omega_{\lambda} \Gamma_{\lambda}^2(I, F). \quad (1)$$

Here,  $s_{IF} = \frac{1}{2} \sum_{if} |\mathbf{D}_{if}|^2$ ,  $i \in I$ ,  $f \in F$ , and  $\Gamma_{\lambda}^2 =$

$\langle I || U^{(\lambda)} || F \rangle^2$  are theoretically calculated coefficients. The sets  $I$  and  $F$  of states are  $J$  multiplets. The index  $\lambda$  for the  $f$ – $f$  transitions has three values, namely, 2, 4, and 6. Therefore, it is sufficient to find experimentally the

strengths of any three transitions in order to determine three parameters  $\Omega_{\lambda}$  and to calculate the strengths of all the other transitions. The transitions under consideration in a free  $\text{Tm}^{3+}$  ion are forbidden in the electric dipole approximation not only by the parity, but the majority of these transitions are forbidden by the total momentum in accordance with the selection rule  $\Delta J = 0, \pm 1$ . According to the Judd–Ofelt theory, when transitions are allowed by the parity selection rule due to the odd components of the crystal field, they can occur at  $\Delta J \leq \lambda$ , where  $\lambda = 2, 4$ , and 6 for the  $f$ – $f$  transitions. Therefore, within this approximation, all  $f$ – $f$  transitions in the  $\text{Tm}^{3+}$  ion are allowed. The transition strength and the oscillator strength are related by the expression [24]

$$s_{IF} = \frac{3hg_I}{8\pi^2 mck_{IF}} f_{IF}, \quad (2)$$

where  $g_I$  is the degree of degeneracy of the ground state and  $k_{IF}$  is the average wave number of the absorption band.

Relationships (1) and (2) describe the properties of the atom in a local electromagnetic field. The influence of the electric polarization of the medium manifests itself when the oscillator strength and the transition strength are determined from the experimental absorption spectrum. In experiments, one measures the natural or decimal absorption coefficient

$$K^{(e)} = \frac{1}{d} \ln \frac{I_0}{I} \quad \text{or} \quad K^{(10)} = \frac{1}{d} \log \frac{I_0}{I}. \quad (3)$$

Here,  $I_0$  and  $I$  are the intensities of the incident and transmitted fluxes, respectively. The plane wave can be represented in the form

$$E = E_0 \exp\left(i \frac{\omega}{c} nx - i\omega t\right), \quad (4)$$

where  $n = n' + in''$  is the complex refractive index, which is related to the permittivity through the expres-

sion  $n = \sqrt{\varepsilon}$  when only the electric dipole interaction is taken into account. By using the definition of the permittivity

$$\varepsilon = 1 + 4\pi\alpha, \quad (5)$$

where  $\alpha$  is the polarizability of the material per unit volume, we can find

$$n'' = 2\pi\alpha''/n'. \quad (6)$$

From expressions (3), (4), and (6), with due regard for the relationship  $I \sim E^2$ , we find

$$K^{(e)} = \frac{4\pi\omega\alpha''}{c n'}. \quad (7)$$

According to the definition, the electric dipole moment of the material per unit volume is given by the formula

$$\begin{aligned} P &= \alpha E = N\alpha_1 E_{\text{loc}} = N\alpha_1(E + L_1 P) \\ &= N\alpha_1 E(1 + L_1\alpha). \end{aligned} \quad (8)$$

Here,  $\alpha_1$  is the atomic polarizability in the local field,  $N$  is the number of active atoms per unit volume,  $E_{\text{loc}} = E + L_1 P$  is the local electric field acting on the atom, and  $L_1$  is the Lorentz factor. By expressing the polarizability  $\alpha$  through the permittivity  $\varepsilon$  from relationship (5) and substituting it into the right-hand side of formula (8), we derive

$$\alpha = \alpha_1 N \left[ 1 + L_1 \frac{(\varepsilon - 1)}{4\pi} \right] \equiv LN\alpha_1, \quad (9)$$

where  $L$  is the Lorentz correction. For the cubic environment, we have  $L_1 = 4\pi/3$  [25] and, hence,  $L = (\varepsilon + 2)/3$ . If the transition is not strong, i.e., the inequality  $\varepsilon'' \ll \varepsilon'$  is satisfied in the resonance range, the quantity  $\varepsilon'$  in this range is governed by other transitions. As a consequence, we can set  $\varepsilon \approx \varepsilon'$ . However, by contrast, the quantities  $\alpha$  and  $\alpha_1$  should be associated only with the transition under consideration. In this case, from relationships (9) and (7), we obtain

$$K^{(e)} = 4\pi\omega LN\alpha_1''/cn', \quad n' \approx \sqrt{\varepsilon'}. \quad (10)$$

It is known from the quantum theory [24] that the atomic polarizability in the local field has the form

$$\alpha_1 = \frac{2e^2}{\hbar} \omega_{if} s_{if} \varphi(\omega) = \frac{e^2}{m} f_{if} \varphi(\omega). \quad (11)$$

Here,  $\varphi(\omega) = \varphi'(\omega) + i\varphi''(\omega)$  is the dispersion function for the real and imaginary polarizabilities in the framework of the classical electron theory. According to this theory, we can write

$$\varphi''(\omega) = \gamma\omega / \left[ (\omega_{if}^2 - \omega^2)^2 + \gamma^2\omega^2 \right]. \quad (12)$$

Here,  $\gamma$  (at  $\gamma^2 \ll \omega_{if}^2$ ) is approximately equal to the width at half-height of the resonance curve  $\varphi''(\omega)$ . In accordance with expressions (11) and (12), we have

$\alpha_{1\text{max}}'' = \frac{e^2}{m\gamma\omega_{if}} f_{if}$  at the absorption maximum ( $\omega = \omega_{if}$ ). Then, with the help of formula (10), we find

$$f_{if} = \frac{mc n'}{4\pi e^2 LN} \gamma K_{\text{max}}^{(e)} = \frac{mc}{4\pi e^2 N} \cdot \frac{3n'}{(n')^2 + 2} I_{if}, \quad (13)$$

where  $I_{if} = \gamma K_{\text{max}}^{(e)} \approx \int K^{(e)}(\omega) d\omega$ . The replacement of the natural absorption coefficient by the decimal absorption coefficient, the absorption coefficient by the molar extinction, and the frequency by the wave number ( $\omega = 2\pi kc$ ) results in the expression

$$\begin{aligned} f_{if} &= 10^3 \ln 10 \frac{mc^2}{2e^2 N_A} \cdot \frac{3n'}{(n')^2 + 2} I_{if} \\ &= 6.78 \times 10^{-9} \frac{3n'}{(n')^2 + 2} I_{if}. \end{aligned} \quad (14)$$

Here,  $N_A$  is the Avogadro number,  $I_{if} = \int \sigma^{(10)}(k) dk$ ,  $\sigma^{(10)} = K^{(10)}/C$  is the decimal molar extinction, and  $C$  is the molar concentration (mol/l). In expression (14), the numerical coefficient most frequently used (without justification) in the literature is equal to  $4.318 \times 10^{-9}$  [26], which is smaller by a factor of  $\pi/2$ . In order to avoid the loss of generality of the results, we will also use this coefficient.

Relationships (1), (2), (11), (13), and (14) correspond to the isotropic case. Therefore, we averaged the transition intensities over the polarizations:  $I = (2I_\sigma + I_\pi)/3$ . By using the data obtained in [1, 27], it is possible to demonstrate that both the birefringence and the change in the refractive index of crystals of the  $RAI_3(BO_3)_4$  type over the entire spectral range under investigation do not exceed 4% and, hence, can be treated as constant, so that the refractive index can be taken equal to an average value of the order of 1.75. In this situation, the correction in expression (14) due to the electric polarization of the medium is close to unity and will be ignored. The calculated values of the oscillator and transition strengths are listed in Table 1. The transition strengths were calculated from formula (2), in which the wave numbers corresponding to approximately the midpoint of the absorption bands under consideration were used as the quantities  $k_{if}$ .

The splitting of the ground state of the  $Tm^{3+}$  ion in the crystal field of the  $TmAl_3(BO_3)_4$  crystal is approximately equal to  $465 \text{ cm}^{-1}$  [9]. This circumstance makes the application of the Judd–Ofelt theory unrigorous. Actually, one of the main postulates of the theory, namely, the equal population of all components of the

**Table 2.** Average wave numbers of transitions  $k_{av}$ , transition strengths  $s_{ij}$ , transition probabilities  $A$ , branching ratios  $\beta$ , and excited state lifetimes  $\tau$ 

Transition	Initial level	Final level	$k_{av}$ , $\text{cm}^{-1}$	$s_{ij}$ , $10^{-20} \text{ cm}^2$	$A$ , $\text{s}^{-1}$	$\beta$	$\tau$ , ms
<i>E</i>	$^1D_2$	$^1G_4$	6650	1.7	126	0.006	0.05
		$^3F_2$	12800	1.35	716	0.036	
		$^3F_3$	13400	1.23	747	0.038	
		$^3H_4$	15300	1.22	1104	0.056	
		$^3H_5$	19500	0.039	73.5	0.004	
		$^3F_4$	22200	3.9	10790	0.543	
		$^3H_6$	27800	1.16	6310	0.329	
<i>D</i>	$^1G_4$	$^3F_2$	6150	0.33	10.8	0.007	0.69
		$^3F_3$	6750	0.87	38.5	0.026	
		$^3H_4$	8650	1.71	156	0.107	
		$^3H_5$	12850	1.50	450	0.308	
		$^3F_4$	15550	0.214	113	0.078	
		$^3H_6$	21150	0.517	688	0.475	
<i>B</i>	$^3F_3$	$^3H_4$	1900	2.21	2.73	0.002	0.59
		$^3H_5$	6100	4.93	203	0.12	
		$^3F_4$	8800	0.359	43.8	0.026	
		$^3H_6$	14400	2.69	1450	0.856	
<i>A</i>	$^3H_4$	$^3H_5$	4200	1.57	16.4	0.019	1.16
		$^3F_4$	6900	1.62	74.7	0.087	
		$^3H_6$	12500	2.81	772	0.895	
<i>X</i>	$^3H_5$	$^3F_4$	2700	1.075	2.43	0.014	5.6
		$^3H_6$	8300	2.67	177	0.990	
<i>Y</i>	$^3F_4$	$^3H_6$	5600	6.26	154	1	6.46

splitting of the ground state in the crystal field, is not satisfied. Nonetheless, the Judd–Ofelt theory is applied to both glasses [14] (where the splitting is masked by the spatial inhomogeneity of the crystal field) and crystals [28]. The parameters  $\Gamma_\lambda^2$  in relationship (1) for the  $\text{Tm}^{3+}$  ion were determined in several works (see, for example, [14, 28–30]). We used the parameters obtained by Spector et al. [14] (Table 1). The parameters  $\Omega_\lambda$  were calculated by the least-squares method with the use of two sets of transitions: the set of *X*, *A*, *B*, *C*, *D*, and *E* transitions and the same set without the *C* band. The least root-mean-square deviations of the experimental transition strengths (except for the *C* band) from those calculated from relationship (1) were obtained with the use of the parameters  $\Omega_\lambda$  derived for the second set of transitions:  $\Omega_2 = 6.14 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 3.09 \times 10^{-20} \text{ cm}^2$ , and  $\Omega_6 = 2.04 \times 10^{-20} \text{ cm}^2$ . None of the variants of the calculation of the intensity of the transition *C* ( $^3H_6 \rightarrow ^3F_2$ ) is consistent with the Judd–Ofelt theory, even though this transition seemingly leads directly to the parameter  $\Omega_6 = 0.68 \times 10^{-20} \text{ cm}^2$  ( $\Gamma_2 = \Gamma_4 = 0$ ). When determining the parameters  $\Omega_2$  and

$\Omega_4$  with the use of this value of  $\Omega_6$  and the other transitions (except for the transition *C*), the obtained approximation turns out to be substantially worse than those considered above.

Apart from the basic assumptions underlying the Judd–Ofelt theory, there are other circumstances that reduce the accuracy of its application. The wave numbers  $k_{IF}$  in expression (2) are rather approximate and uncertain quantities for broad absorption bands, and they differ for absorption and emission because the adiabatic potentials are different in different electronic states. It is also important that the equilibrium configuration of atoms can be different in different electronic states and, therefore, the crystal field modifying the electron wave functions can also be different. This is most significant for the electronic transitions forbidden by the parity, because they become allowed as a result of small odd distortions of the crystal field. Furthermore, the system in the excited state can relax to a new equilibrium configuration due to the long lifetime. As a result, the matrix elements of the electric dipole moment can depend on the transition direction (upward or downward). Therefore, the change in the atomic configuration during the electronic transition can be one of

the reasons that some transitions do not obey the Judd–Ofelt theory.

The transitions in the  $\text{Tm}^{3+}$  ion were investigated in a large number of crystals, glasses, and solutions (see, for example, [1–3, 14, 31–34]). The intensities of the  $f$ – $f$  transitions and, correspondingly, the parameters  $\Omega_\lambda$  can vary over a very wide range. No correlation of the intensities of the  $f$ – $f$  transitions and the parameters  $\Omega_\lambda$  with the structure of the environment of rare-earth ions has been revealed to date. Therefore, the properties of the  $f$ – $f$  transitions cannot be predicted from the structure of the material, and the spectroscopic properties of each new compound should be investigated experimentally. The parameters  $\Omega_\lambda$  obtained in our work for the  $\text{TmAl}_3(\text{BO}_3)_4$  crystal are very close to those for the thulium acetate in the solution [33], rather close to the corresponding parameters for the dilute crystal  $\text{GdAl}_3(\text{BO}_3)_4 : \text{Tm}^{3+}$  [1], and, as we expected, differ substantially from the parameters for the nominally identical crystal studied in [10].

The possibility of generating stimulated emission for a specific emission channel is characterized by the multiplet luminescence branching ratio

$$\beta_{IF} = \frac{A_{IF}}{\sum_F A_{IF}}, \quad (15)$$

where

$$A_{IF} = \frac{64\pi^4 e^2 k_{IF}^3 n(k_{IF})}{3hg_I} S_{IF} \quad (16)$$

is the probability of a spontaneous dipole transition between degenerate levels in a condensed material [35, 36],  $g_I$  is the degree of degeneracy of the initial level, and  $n(k_{IF})$  is the refractive index at the transition frequency (as was noted above, it is taken equal to 1.75). The absorption spectra enable us to determine the probabilities of spontaneous transitions only to the ground state. The Judd–Ofelt theory provides a means for theoretically evaluating the probabilities of all the  $f$ – $f$  transitions and, correspondingly, the branching ratios. The calculated values of the transition strengths, the spontaneous emission probabilities, the branching ratios  $\beta$ , and the excited state lifetimes  $\tau_I = 1/\sum_F A_{IF}$  are presented in Table 2. The transitions from the  ${}^3F_2$  state are omitted, because the  $C$  transition is inconsistent with the Judd–Ofelt theory. The transitions to the  ${}^3F_2$  state make an insignificant contribution to the lifetimes and branching ratios for the transitions from all the other states (Table 2). It follows from relationships (15), (16), and (1) that the branching ratios depend on the ratio of the Judd–Ofelt parameters rather than on their magnitude and, hence, depend on the ratio of the transition intensities. Therefore, any uncertainties in the measure-

ment of the magnitudes of the transition intensities do not affect the branching ratios.

#### 4. CONCLUSIONS

High-optical-quality single crystals of the  $\text{TmAl}_3(\text{BO}_3)_4$  compound were synthesized from a solution in the melt. The absorption spectra of the  $\text{TmAl}_3(\text{BO}_3)_4$  single crystals in the  $\sigma$  and  $\pi$  polarizations for the  $f$ – $f$  transitions in the range 5000–35000  $\text{cm}^{-1}$  were recorded at room temperature. The transition intensities were analyzed in terms of the Judd–Ofelt theory generalized to the case of anisotropic crystals, and the following parameters of the theory were obtained:  $\Omega_2 = 6.14 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 3.09 \times 10^{-20} \text{ cm}^2$ , and  $\Omega_6 = 2.04 \times 10^{-20} \text{ cm}^2$ . The strengths, spontaneous emission probabilities, branching ratios, and excited state lifetimes were calculated for all possible transitions. It was demonstrated that the branching ratios are large not only for the low-lying levels. This circumstance is important for the lasing in the visible and ultraviolet ranges. The large branching ratios for the  ${}^1D_2 \rightarrow {}^3F_4$ ,  ${}^1G_4 \rightarrow {}^3H_5$ , and  ${}^3F_2 \rightarrow {}^3F_4$  transitions indicate that upconversion processes can occur with the participation of these transitions.

#### ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 07-02-00704) and the Siberian Branch of the Russian Academy of Sciences (Integration Project no. 3.7). A.L. Sukhachev acknowledges the support of the Russian Science Support Foundation.

#### REFERENCES

1. G. H. Jia, C. Y. Tu, J. F. Li, Z. J. Zhu, Z. Y. You, Y. Wang, and B. C. Wu, *J. Appl. Phys.* **96**, 6262 (2004).
2. X. Chen and Z. Luo, *J. Phys.: Condens. Matter* **9**, 7981 (1997).
3. W. Ryba-Romanowski, S. Golab, I. Sokolska, G. Dominiak-Dzik, J. Zawadzka, M. Berkowski, J. Fink-Finowicki, and M. Baba, *Appl. Phys. B: Lasers Opt.* **68**, 199 (1999).
4. J. A. Caird, L. J. DeShazer, and J. Nella, *IEEE J. Quantum Electron.* **11**, 874 (1975).
5. L. F. Johnson, J. E. Geusic, and L. G. Van Uitert, *Appl. Phys. Lett.* **7**, 127 (1965).
6. T. S. Kubo and T. J. Kame, *IEEE J. Quantum Electron.* **28**, 1033 (1992).
7. J. B. Gruber, M. D. Seltzer, M. E. Hills, S. B. Stevens, and C. A. Morrison, *J. Appl. Phys.* **73**, 1929 (1993).
8. F. S. Ermeneux, C. Goutaudier, R. Moncorge, M. T. Cohen-Adad, M. Bettinelli, and E. Cavalli, *Opt. Mater.* **8**, 83 (1997).
9. A. V. Malakhovskii, I. S. Edelman, A. E. Sokolov, V. L. Temerov, S. L. Gnatchenko, I. S. Kachur, and V. G. Piryatinskaya, *J. Alloys Compd.* **459**, 87 (2008).

10. Guohua Jia, Chaoyang Tu, Jianfu Li, Zhenyu You, Zhaojie Zhu, and Baichang Wu, *Inorg. Chem.* **45**, 9326 (2006).
11. L. N. Bezmaternykh, V. L. Temerov, I. A. Gudim, and N. A. Stolbovaya, *Crystallogr. Rep.* **50** (Suppl. 1), 97 (2005).
12. A. V. Malakhovskii, A. É. Sokolov, A. L. Sukhachev, V. L. Temerov, N. A. Stolbovaya, and I. S. Edelman, *Fiz. Tverd. Tela (St. Petersburg)* **49** (1), 32 (2007) [*Phys. Solid State* **49** (1), 34 (2007)].
13. I. Couwenberg, K. Binnemans, H. De Leebeeck, and C. Gorller-Walrand, *J. Alloys Compd.* **274**, 157 (1998).
14. N. Spector, R. Reisfeld, and L. Boehm, *Chem. Phys. Lett.* **49**, 49 (1977).
15. J. B. Gruber and J. G. Conway, *J. Chem. Phys.* **32**, 1178 (1960).
16. J. B. Gruber, W. F. Krupke, and J. M. Poindexter, *J. Chem. Phys.* **41**, 3363 (1964).
17. I. G. Kaplan, *Symmetry of Many-Electron Systems* (Nauka, Moscow, 1969; Academic, New York, 1975).
18. H. Poulet and J.-P. Mathieu, *Spectres de vibration et symétrie des cristaux* (Gordon and Breach, Paris, 1970; Mir, Moscow, 1973) [in French and in Russian].
19. A. V. Malakhovskii, I. S. Edelman, A. E. Sokolov, V. L. Temerov, S. L. Gnatchenko, I. S. Kachur, and V. G. Piryatinskaya, *Phys. Lett. A* **371**, 254 (2007).
20. G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty Two Point Groups* (MIT Press, Cambridge, MA, Unites States, 1963).
21. B. R. Judd, *Phys. Rev.* **127**, 750 (1962).
22. G. S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).
23. R. D. Peacock, *Struct. Bonding (Berlin)* **22**, 83 (1975).
24. I. I. Sobel'man, *Introduction to the Theory of Atomic Spectra* (Pergamon, Oxford, 1972; Nauka, Moscow, 1977).
25. C. Kittel, *Introduction to the Solid State Physics* (Wiley and Sons, New York, 1976; Nauka, Moscow, 1978).
26. J. Hormadaly and R. Reisfeld, *J. Non-Cryst. Solids* **30**, 337 (1979).
27. B. Lu, J. Wang, H. Pan, and M. Jiang, *J. Appl. Phys.* **66**, 6052 (1989).
28. W. F. Krupke and J. P. Gruber, *Phys. Rev. A* **139**, 2008 (1965).
29. W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.* **49**, 4424 (1968).
30. W. F. Krupke, *Phys. Rev.* **145**, 325 (1966).
31. M. J. Weber, *Phys. Rev. B: Solid State* **8**, 47 (1973).
32. K. Ohta, H. Saito, and M. Obara, *J. Appl. Phys.* **73**, 3149 (1993).
33. A. Mondry and K. Bukietynska, *Mol. Phys.* **101**, 923 (2003).
34. F. Guell, J. Gavalda, R. Sole, M. Aguilo, F. Diaz, M. Galan, and J. Masons, *J. Appl. Phys.* **95**, 919 (2004).
35. V. L. Ginzburg, *Theoretical Physics and Astrophysics* (Nauka, Moscow, 1975; Pergamon, Oxford, 1979).
36. L. K. Aminov, A. A. Kaminskiĭ, and B. Z. Malkin, *Physics and Spectroscopy of Laser Crystals* (Nauka, Moscow, 1986), p. 84 [in Russian].

*Translated by O. Borovik-Romanova*