On the temperature dependence of transition intensities of rare-earth ions: A modified Judd-Ofelt theory

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Abstract: We report on a modification of the Judd-Ofelt theory accounting for thermal populations of Stark sub-levels of the multiplets involved in transitions in absorption and emission. The calculations require the data on the crystal-field splitting, the irreducible representations of Stark sub-levels and the selection rules for electric-dipole transitions. Simple formulas for absorption oscillator strengths and probabilities of radiative spontaneous transitions are obtained. The application of the proposed model allowed us to remove the contradiction between the transition intensities in absorption and emission ($^3H_6 \leftrightarrow {}^3F_4$) for Tm^{3+}-doped crystals. It was also used to explain the experimental temperature dependences of luminescence lifetimes of the $^3F_4$ Tm^{3+} manifold in two widely used laser crystals, $LiYF_4$ and $Y_3Al_5O_{12}$. The case of Yb^{3+} ions featuring a small number of crystal-field sub-levels is also considered.

Keywords: Judd-Ofelt theory; rare-earth ions; transition intensities; luminescence lifetime.

1. Introduction

The Judd-Ofelt theory [1,2] is a theory describing the intensity of electron transitions within the 4f shell of rare-earth ions (RE^{3+}). It was introduced independently in 1962 by B. R. Judd and G. S. Ofelt. Nowadays, it is widely used for describing experimental data on the intensities of transitions in absorption, as well as for calculating emission properties (radiative lifetimes and luminescence branching ratios) of RE^{3+} ions. Its attractiveness stems from the intrinsic simplicity of this theory, as the line strength of any electric dipole transition depends only on three variable parameters (called the intensity or Judd-Ofelt parameters, denoted Ω_k, k = 2, 4, 6). This small number of free parameters is dictated by several strict approximations under which this theory is derived. It is assumed that both the ground and excited configurations of the RE^{3+} ion are fully degenerated and the energy of multiplets is much lower than the energy gap to the excited configuration. Note that the latter condition is valid only for two rare-earth ions, namely Ce^{3+} and Yb^{3+}. Despite this, the Judd-Ofelt theory is commonly used for describing transition intensities of almost all the RE^{3+} ions (except Pr^{3+} and Eu^{3+}) yielding a reasonable agreement between the experimental and calculated data. This problem was discussed by Dunina *et al.* [3] and explained by the fact that strong spin-orbit interaction combines multiplets $^{2S+1}L_J$ with the same total angular momentum J into groups. The multiplets belonging to a given group (with the same J) are bounded to each other and the action of excited configurations to one of them is thus transferred to all the multiplets of this group. For rare-earth ions with a large total number of multiplets, such as Nd^{3+}, Sm^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+}, within such groups of multiplets, there always exists one with a strong interaction with excited configurations, and through this particular multiplet the influence of excited configurations is transferred to all the group members, even low-lying ones. As a result, it is difficult to determine the influence of configuration interaction on the oscillator strength of transitions in absorption terminating at a particular multiplet. In this case, the deviation from the Judd-Ofelt theory can be revealed by a joint analysis of transitions in absorption and emission. When analyzing the mutual influence of multiplets within a group with the same J, one needs to consider even multiplets lying in the energy range where intrinsic absorption of the host matrix occurs (in the energy continuum), as it was shown that bounded states may also exist in the continuum [4].

The trivalent thulium ions (Tm^{3+}, electronic configuration: [Xe]4f^{12}) and praseodymium ions (Pr^{3+}, [Xe]4f^{2}) possess a total of 13 multiplets. The spin-orbit interaction bounds the multiplets with the same total angular momentum J into the following groups: ($^3H_6$, $^1I_6$), ($^3H_4$, $^3F_4$, $^1D_4$), ($^3F_2$, $^3P_2$) and ($^3P_0$, $^1S_0$), listed in the order of decreasing J, Fig. 1. For three multiplets, namely $^3H_5$, $^3F_3$ and $^3P_1$, there are no partners with the same J momentum. Moreover, for Pr^{3+} ions, all the multiplets except for $^1S_0$ are usually lying within the energy range corresponding to the transparency window of dielectric host matrices. Because of this, the influence of excited configurations is easily detected. The deviation from the Judd-Ofelt theory for Pr^{3+} ions was detected in 1973 [5]. In the review paper [6], generalized equations accounting for the influence of excited configurations on the transition intensities in absorption and emission are given. In this work, it was assumed that the interaction of a given multiplet with the excited configuration depends on the energy gap between them. The proposed approximations have been widely used for describing the transition intensities of RE^{3+} ions.

The condition for easy application of the quantum theory of the angular momentum is the assumption of equal populations of crystal-field (Stark) components of multiplets. Under this assumption, the summation over the Stark sub-levels of the two multiplets involved in the transition $J \rightarrow J'$ can be performed analytically and the corresponding expressions for the transition intensities (e.g., line strengths) are relatively simple and contain just a few free parameters. The total Stark splitting of multiplets strongly depends on the host matrix and the way the RE^{3+} ion is incorporated within it (i.e., the site symmetry, the multi-ligands, etc.). It can exceed a few hundred cm^{-1}. Even at room temperature (~293 K), a significant variation in the thermal populations of different components of the same multiplet will be evident. One of the first attempts to account for the crystal-field splitting of the ground-state on the intensities of transitions in absorption was reported for Er^{3+} ions in the $Y_3Al_5O_{12}$ garnet crystal [7]. The authors did not consider the actual Stark splitting of the Er^{3+} ground-state ($^4I_{15/2}$) in their modification of the Judd-Ofelt theory, but instead represented this multiplet by two degenerated sub-levels. From the point of view of prediction of temperature dependence of spectroscopic properties of rare-earth ions based on the temperature-dependent populations of the crystal-field sub-levels, one needs to mention the recent study of Püschel *et al.* [8]. The authors have measured the luminescence lifetime of the excited-state of Yb^{3+} ions ($^2F_{5/2}$) in the $LiYF_4$ fluoride crystal over a broad temperature range of 17 – 440 K and proposed an equation for describing this dependence. This equation is based on the Boltzmann distribution to calculate the thermal population of Stark sub-levels of the $^2F_{5/2}$ emitting state.

In the present work, we aimed to modify the main expressions of the standard Judd-Ofelt theory to account for thermal populations of Stark sub-levels of the ground- and excited-states of rare-earth ions, and to apply this approach for describing and predicting the temperature dependence of spectroscopic parameters of RE^{3+} ions.

2. Judd-Ofelt theory accounting for thermal populations of Stark sub-levels

Here and below, we will denote the multiplets by the total angular momentum J. One of the most important parameters of a multiplet J for optical spectroscopy is the radiative lifetime which is calculated based on the probabilities of radiative spontaneous transitions $A_{JJ'}$:

$$\tau_J = \frac{1}{\sum_{J'} A_{JJ'}}. \tag{1}$$

The $A_{JJ'}$ probabilities are often expressed via the transition oscillator strengths $f_{JJ'}$:

$$A_{JJ'} = \frac{8\pi^2 e^2 n^2 \sigma_{JJ'}^2}{mc} f_{JJ'} \tag{2}$$

Here, e and m are the electron charge and mass, respectively, n is the refractive index of the host medium, $\sigma_{JJ'}$ is the mean energy (wavenumber) of the transition expressed in cm^{-1}, and c is the speed of light.

The oscillator strengths $f_{JJ'}$ are dimensionless quantities and they are related to the line strengths of transitions $S_{JJ'}$ as following:

$$f_{JJ'} = \frac{8\pi^2 mc\sigma_{JJ'}}{3\left(2J+1\right)he^2}\left[\frac{(n^2+2)^2}{9n}S^{ed}_{JJ'} + nS^{md}_{JJ'}\right]. \tag{3}$$

The line strengths of magnetic dipole (MD) transitions $S^{md}_{JJ'}$ are weakly dependent on the host matrix and are determined by the following expression:

$$S^{md}_{JJ'} = \frac{e^2h^2}{16\pi^2 m^2 c^2}\left\langle \gamma[LS]J\left\|\vec{L}+2\vec{S}\right\|\gamma'[L'S']J'\right\rangle^2 . \tag{4}$$

Here, $|\gamma[LS]JM\rangle$ is the wavefunction of the rare-earth ion, $\vec{L}$ and $\vec{S}$ are the orbital momentum and spin of the rare-earth ion, respectively. The MD transitions obey the following selection rules:

$$|J-J'| = 0,\pm 1\text{, except of } 0 \leftrightarrow 0',\ \Delta L = 0,\ \Delta S = 0 \text{ and } \Delta l = 0. \tag{5}$$

The line strengths of electric dipole (ED) transitions strongly depend on the surrounding of the RE^{3+} ion and are calculated as:

$$S^{ed}_{JJ'} = \sum_{MM'}\left|\left\langle \gamma JM\left|\vec{D}\right|\gamma' J'M'\right\rangle\right|^2. \tag{6}$$

It should be pointed out that Eq. (4) and Eq. (6) for calculating the line strengths of electric-dipole and magnetic-dipole transitions, respectively, are valid only under the assumption of equal population of all Stark sub-levels of the multiplets involved in the transition.

The following derivations will be performed for electric-dipole transitions, while the resulting expression will be valid for magnetic-dipole ones as well (in fact, the derivations performed below do not depend on the nature of transition). After substituting Eq. (6) into Eq. (3), one obtains:

$$f_{JJ'} = \frac{8\pi^2 mc\sigma_{JJ'}}{3he^2}\frac{(n^2+2)^2}{9n}\underbrace{\frac{1}{(2J+1)}\sum_{MM'}\left|\left\langle \gamma JM\left|\vec{D}\right|\gamma' J'M'\right\rangle\right|^2}_{\bar{S}_{JJ'M'}} . \tag{7}$$

The parameter $\bar{S}_{JJ'M'}$ can be treated as a mean value of the transition line strength between the sub-levels of the excited multiplet J into one of the sub-levels $|J'M'>$ of the lower-lying multiplet. Here, it still assumed that all the sub-levels of the emitting multiplet $|JM>$ are equally populated.

In Fig. 2, we show the crystal-field splitting of the ground-state ($^3H_6$) and first excited-state ($^3F_4$) of Tm^{3+} ions in the $LiYF_4$ crystal [9], together with the irreducible representations of the Stark sub-levels (Γ_i). The thermal populations of Stark sub-levels can be calculated using the Boltzmann distribution:

$$W_i = \frac{g_i \cdot \exp\left(-\frac{\Delta E_i}{kT}\right)}{Z}, \tag{8}$$

Where, g_i is the degeneracy of the sub-level with an energy E_i, and Z indicates the partition functions:

$$Z = \sum_i g_i \cdot \exp\left(-\frac{\Delta E_i}{kT}\right). \tag{9}$$

The temperature dependence of Stark sub-level populations for the two above-mentioned multiplets is given in Fig. 3.

From the performed calculations, it is evident that the assumption of equal population of Stark sub-levels of the two considered multiplets is not valid even at room temperature. Figure 4 shows the fractional thermal populations of Stark sub-levels and their differences from the assumption of equally populated sub-levels (one of the basic assumptions in the standard Judd-Ofelt theory) for the ground-state, $^3H_6$, and first excited-state, $^3F_4$, of Tm^{3+} ions in the $LiYF_4$ crystal. Moreover, this assumption further breaks at low temperatures. To overcome this issue, in Eq. (7), one needs to perform averaging accounting for the Boltzmann distribution:

$$f_{JJ'} = \frac{8\pi^2 mc}{3he^2}\frac{(n^2+2)^2}{9n}\cdot\sum_j\sum_i \frac{SR\left(\Gamma_i,\Gamma'_j\right)\sigma_{\Gamma_i\Gamma'_j}\left|\left\langle\gamma J\Gamma_i\left|\vec{D}\right|\gamma' J'\Gamma'_j\right\rangle\right|^2 g(\Gamma_i)\cdot g(\Gamma'_j)\cdot\exp\left(-\frac{\Delta E_{\Gamma_i}}{kT}\right)}{Z}. \tag{10}$$

Here, $SR\left(\Gamma_i,\Gamma'_j\right)$ is the matrix of selection rules of radiative transitions, $\sigma_{\Gamma_i\Gamma'_j}$ is the wavenumber of transition from the Stark component with an irreducible representation Γ_i of the multiplet J to the component with an irreducible representation Γ'_j of the multiplet J', $\Delta E_{\Gamma_i} = E_{\Gamma_i} - E_{\Gamma_1}$ is the energy of the Stark sub-level with an irreducible representation Γ_i within the multiplet J with respect to the lowest sub-level of this multiplet, and k is the Boltzmann constant.

The main difficulty consists of calculating the squared moduli of dipole moment $\left|\left\langle\gamma J\Gamma_i\left|\vec{D}\right|\gamma' J'\Gamma'_j\right\rangle\right|^2$ between the multiplet components with the irreducible representations Γ_i and Γ'_j. We are aware of only a few such derivations [10,11]. To simplify Eq. (10) and connect it to the results of analyzing the experimental data on the oscillator strengths by means of the Judd-Ofelt formalism, we will perform the following derivations. In Eq. (7), we will replace the squared reduced matrix elements $\left|\left\langle\gamma JM\left|\vec{D}\right|\gamma' J'M'\right\rangle\right|^2$ by an average value $\left\langle\left|\left\langle\gamma JM\left|\vec{D}\right|\gamma' J'M'\right\rangle\right|^2\right\rangle = Const$:

$$f_{JJ'}^{J-O} = \frac{8\pi^2 mc\sigma_{JJ'}}{3he^2}\frac{(n^2+2)^2}{9n}\cdot(2J'+1)\cdot\left\langle\left|\left\langle\gamma JM\left|\vec{D}\right|\gamma' J'M'\right\rangle\right|^2\right\rangle. \tag{11}$$

In a similar way, in Eq. (10), we replace $\left|\left\langle\gamma J\Gamma_i\left|\vec{D}\right|\gamma' J'\Gamma'_j\right\rangle\right|^2$ by the average value $\left\langle\left|\left\langle\gamma J\Gamma_i\left|\vec{D}\right|\gamma' J'\Gamma'_j\right\rangle\right|^2\right\rangle = Const$:

$$f_{JJ'} = \frac{8\pi^2 mc}{3he^2}\frac{(n^2+2)^2}{9n} \cdot \left\langle \left| \left\langle \gamma J\Gamma_i \middle| \vec{D} \middle| \gamma' J'\Gamma'_j \right\rangle \right|^2 \right\rangle \cdot \sum_j \sum_i \frac{SR\left(\Gamma_i,\Gamma'_j\right)\sigma_{\Gamma_i\Gamma'_j}\, g(\Gamma_i)\cdot g(\Gamma'_j)\cdot \exp\left(-\frac{\Delta E_{\Gamma_i}}{kT}\right)}{Z}. \quad (12)$$

Assuming that the average values are equal, i.e., $\left\langle \left| \left\langle \gamma JM \middle| \vec{D} \middle| \gamma' J'M' \right\rangle \right|^2 \right\rangle = \left\langle \left| \left\langle \gamma J\Gamma_i \middle| \vec{D} \middle| \gamma' J'\Gamma'_j \right\rangle \right|^2 \right\rangle = Const$, one obtains:

$$f_{JJ'} = \frac{f_{JJ'}^{J-O}}{\sigma_{JJ'}\cdot(2J'+1)} \cdot \sum_j \sum_i \frac{SR\left(\Gamma_i,\Gamma'_j\right)\sigma_{\Gamma_i\Gamma'_j}\, g(\Gamma_i)\cdot g(\Gamma'_j)\cdot \exp\left(-\frac{\Delta E_{\Gamma_i}}{kT}\right)}{Z}. \quad (13)$$

For the oscillator strength $f_{JJ'}^{J-O}$, one can use the value calculated using the standard Judd-Ofelt theory or the experimental value $f_{JJ'}^{Expt}$.

Calculations performed with Eq. (13) will be more adequate for describing the experimental data on the absorption oscillator strengths of transitions between two multiplets with a relatively large number of Stark sub-levels (e.g., for Tm^{3+} ions). In this case, the averaging $\left\langle \left| \left\langle \gamma J\Gamma_i \middle| \vec{D} \middle| \gamma' J'\Gamma'_j \right\rangle \right|^2 \right\rangle = Const$ represents a good approximation. When considering transitions between multiplets with only a few sub-levels (e.g., for Yb^{3+} ions), this equation must be modified to account for transition properties from each of these sub-levels (see below).

Equation (2) for calculating the probabilities of spontaneous radiative transitions from the multiplet *J* to the multiplet *J'* can be modified to account for thermal populations of the Stark sub-levels, using the oscillator strength given by Eq. (13):

$$A_{JJ'} = \frac{8\pi^2 e^2 n^2}{mc}\frac{f_{JJ'}^{J-O}}{\sigma_{JJ'}\cdot(2J'+1)} \cdot \sum_j \sum_i \frac{SR\left(\Gamma_i,\Gamma'_j\right)\sigma^3_{\Gamma_i\Gamma'_j}\, g(\Gamma_i)\cdot g(\Gamma'_j)\cdot \exp\left(-\frac{\Delta E_{\Gamma_i}}{kT}\right)}{Z}. \quad (14)$$

In Eq. (13) and Eq. (14), one finds the mean wavenumber $\sigma_{JJ'}$ and the wavenumber of transitions between particular Stark sub-levels $\sigma_{\Gamma_i\Gamma'_j}$. If the splitting of the multiplets *J* and *J'* by the crystal-field is much smaller than the energy gap between the multiplets, without losing precision of calculations, one can assume $\sigma_{\Gamma_i\Gamma'_j} = \sigma_{JJ'}$.

3. Validation of the modified Judd-Ofelt model

3.1. Temperature dependence of absorption oscillator strengths

Let us consider Tm^{3+} ions in the $LiYF_4$ crystal as a reference system for revealing the effect of thermal populations of Stark sub-levels of the ground-state $^3H_6$ on the absorption oscillator strength for the transition $^3H_6 \rightarrow {}^3F_4$. For this, we will use Eq. (13), the energies of Stark sub-levels given in Fig. 2 and the selection rules for S_4 symmetry sites [9] provided in Table 1. At room temperature, one obtains:

$$\frac{f^{J-O}_{{}^3H_6\rightarrow{}^3F_4}}{f_{{}^3H_6\rightarrow{}^3F_4}}=1.14\,. \qquad (15)$$

By applying the condition $\sigma_{\Gamma_i\Gamma_j^{'}}=\sigma_{JJ'}$ to simplify the calculations as explained above, one arrives to a very close result:

$$\frac{f^{J-O}_{{}^3H_6\rightarrow{}^3F_4}}{f_{{}^3H_6\rightarrow{}^3F_4}}=1.17\text{ , assuming } \sigma_{\Gamma_i\Gamma_j^{'}}=\sigma_{JJ'}\,. \qquad (16)$$

Consequently, the absorption oscillator strengths for the $^3H_6 \rightarrow {}^3F_4$ transition of Tm^{3+} ions in $LiYF_4$ calculated using the standard Judd-Ofelt theory are higher than those accounting for thermal populations of the Stark sub-levels of the ground-state. When searching for the optimum intensity parameters $\Omega_k\,(k=2,4,6)$ by the least square method, this error in the Judd-Ofelt theory will be compensated and the precision of fitting the experimental absorption oscillator strengths will not be notably reduced. However, the intensity parameters determined based on the experimental absorption oscillator strength do not account for the thermal populations of the Stark sub-levels of the *excited-state*, for example, $^3F_4$, and the radiative lifetime of the excited-state calculated using such “standard” intensity parameters can be much shorter than the intrinsic luminescence lifetime (measured for very low doping levels assuming negligible energy-transfer processes for the states featuring negligible non-radiative path).

3.2. Temperature dependence of lifetime: $^3F_4$ Tm^{3+} state in $LiYF_4$

According to Fig. 2, the crystal-field splitting of the $^3F_4$ manifold of Tm^{3+} ions in $LiYF_4$ is relatively large and amounts to 372 cm^{-1}, and the energy gaps between the adjacent Stark sub-levels are far from being equal. The largest energy gap of 155 cm^{-1} separates the two lower-lying sub-levels. This type of splitting leads to a strong non-uniformity of fractional populations of Stark sub-levels even at room temperature, cf. Fig. 3(b). Thus, one can expect a strong temperature dependence of emission characteristics of the $^3F_4$ manifold. In the previous study [12], it was determined that on increasing the crystal temperature from 80 to 300 K, the luminescence lifetime of this manifold is reduced from 18 to 15.5 ms. Note that due to the low maximum phonon energy of $LiYF_4$ and a large energy gap between the $^3F_4$ and $^3H_6$ Tm^{3+} states, the multiphonon non-radiative relaxation from the $^3F_4$ state is negligible.

Based on the crystal-field splitting given in Fig. 2 and the selection rules for S_4 symmetry sites [9], cf. Table 1, using Eq. (14), we calculated the probability of spontaneous radiative transition $^3F_4 \rightarrow {}^3H_6$, and, accordingly, the radiative lifetime of the $^3F_4$ state. The paper [12] does not contain the information about the absorption oscillator strengths. In the present work, the absorption oscillator strength $f^{J-O}_{JJ'}$ in Eq. (14) was selected to be 1.244×10^{-6}, as it yields the radiative lifetime of the $^3F_4$ manifold of 15.5 ms (at room temperature), which is in line with the experimental study. The results of calculations are shown in Fig. 5.

According to our calculation, when the crystal temperature is raised from 50 to 300 K, the luminescence lifetime is reduced from 18.5 to 15.5 ms which agrees with the experimental data.

Note that our calculations do not account for the possible effect of reabsorption on the measured luminescence lifetimes which is common for bulk crystals.

3.3. Temperature dependence of lifetime: $^3F_4$ Tm^{3+} state in $Lu_3Al_5O_{12}$ and $Y_3Al_5O_{12}$

The crystal-field splitting for Tm^{3+} ions, the irreducible representations for the Stark components, as well as the selection rules for electric dipole transitions for cubic garnets $Lu_3Al_5O_{12}$ and $Y_3Al_5O_{12}$ are well documented [13,14]. In particular, Fig. 6 shows the crystal-field splitting of the ground-state ($^3H_6$) and first excited-state ($^3F_4$) of Tm^{3+} ions in $Y_3Al_5O_{12}$ (D_2 site symmetry). The structure of the $^3F_4$ and $^3H_6$ multiplets of Tm^{3+} ions in these crystals somehow resembles that for $LiYF_4$. Thus, one can expect a strong temperature dependence of transition intensities for these crystals as well.

The spectroscopic properties of Tm^{3+} ions in $Lu_3Al_5O_{12}$ were studied in Ref. [15]. The experimental absorption oscillator strengths were analyzed using another modification of the Judd-Ofelt theory accounting for weak configuration interaction. Based on this approach, the radiative lifetime τ_{rad} of the $^3F_4$ manifold was calculated yielding 6.46 ms (the corresponding experimental absorption oscillator strength $f^{Expt}_{{}^3H_6\to{}^3F_4} = 1.45\times10^{-6}$). This value of the radiative lifetime is significantly shorter than the measured reabsorption-free luminescence lifetime, τ_{lum} = 9.68 ms. This disagreement between the transition intensities in absorption and emission is removed if one uses Eq. (14) for calculating τ_{rad}. Indeed, at room temperature, using $f^{J-O}_{JJ'} = f^{Expt}_{{}^3H_6\to{}^3F_4} = 1.45\times10^{-6}$, one obtains τ_{rad} = 10.87 ms, which does not contradict with the measured value of τ_{lum} considering possible luminescence quenching.

According to the reported temperature dependence of the luminescence lifetime of the $^3F_4$ manifold of Tm^{3+} ions in $Y_3Al_5O_{12}$ [16], on increasing the temperature from 50 to 300 K, the luminescence lifetime is shortened in the range of 15 – 12.8 ms. The authors of this study did not provide the absorption oscillator strengths, and in the present study, we have used a value of $f^{J-O}_{JJ'} = 1.233\times10^{-6}$, so that at room temperature, one arrives to τ_{rad} = 12.8 ms. The results of calculations are shown in Fig. 7. They agree well with the experimental data from Ref. [16].

3.4. Temperature dependence of lifetime: $^2F_{5/2}$ Yb^{3+} state in $LiYF_4$

Ytterbium ions (Yb^{3+}) possess an electronic configuration of $[Xe]4f^{13}$ and only two multiplets $^2F_{7/2}$ (ground-state) and $^2F_{5/2}$ (excited-state). In the crystal-field of symmetry S_4, the ground-state $^2F_{7/2}$ is split into 4 sub-levels and the excited-state $^2F_{5/2}$ – into 3 sub-levels [8] as shown in Fig. 8. All these sub-levels are double degenerated. The energy spectrum of Stark sub-levels of the ground- and excited-states of Yb^{3+} ions in $LiYF_4$ differs from that for Tm^{3+} ions in the same crystal by the number of sub-levels and their relative position in the energy-level diagram. Thus, it is not surprising that the experimental temperature dependence of the luminescence lifetime of the $^2F_{5/2}$ Yb^{3+} state notably differs from that for the $^3F_4$ Tm^{3+} one: with increasing the crystal temperature from 17 to 300 K, the lifetime *increases* from 1.93 to 2.20 ms [8].

Equation (13) can be used for calculating the temperature dependence of the $^2F_{5/2}$ Yb^{3+} state after small modification. Because of the small number of Stark components of the excited manifold, averaging is not fully valid. Consequently, to arrive to the proper *shape* of the temperature dependence of the luminescence lifetime, one needs to use correction coefficients *Kc*:

$$A_{JJ'} = \frac{8\pi^2 e^2 n^2}{mc} \frac{f_{JJ'}^{J-O}}{\sigma_{JJ'} \cdot (2J'+1)} \sum_j \sum_i \frac{Kc(\Gamma_i) SR\left(\Gamma_i, \Gamma'_j\right) \sigma^3_{\Gamma_i \Gamma'_j} g(\Gamma_i) g(\Gamma'_j) \cdot \exp\left(-\frac{\Delta E_{\Gamma_i}}{kT}\right)}{Z}. \qquad (17)$$

The authors of [8] did not report on the absorption oscillator strength $f^{Expt}_{^2F_{7/2} \to ^2F_{5/2}}$, so that we used the following value for calculations: $f_{JJ'}^{J-O} = 2.722 \times 10^{-6}$ and the correction coefficients *Kc*(1) = 1, *Kc*(2) = 0.585, *Kc*(3) = 0.898. This set of calculation parameters allowed us to obtain the calculated luminescence lifetime of 1.93 ms at 17 K (matching the measured one), as well as to reproduce the proper shape of the temperature dependence of the luminescence lifetime, as shown in Fig. 9. At a high temperature of 400 K, the luminescence lifetime is 2.22 ms, which again agrees with the experimental result.

Equation (7) from Ref. [8] can be obtained from our more general formula by summation over the sub-levels of the ground-state and performing additional operations connecting the radiative lifetime and the oscillator strength.

4. Conclusions

To conclude, we report on a modification of the Judd-Ofelt theory accounting for thermal populations of the Stark sub-levels of the ground- and excited-states involved in transitions in absorption and emission. The calculations using this approach require the data on the crystal-field splitting of the involved multiplets, the irreducible representations of Stark sub-levels and the selection rules for electric-dipole transitions. To simplify the calculations, we replaced the squared reduced matrix elements of electric- and magnetic-dipole moments by their average values. This allowed us to obtain simple formulas for calculating the oscillator strengths and probabilities of radiative spontaneous transitions from the excited multiplet, accounting for the Boltzmann distribution. As the main free parameter in our approach, we use the experimental absorption oscillator strength or that calculated using the standard Judd-Ofelt theory.

The absorption oscillator strengths for the $^3H_6 \to {}^3F_4$ transition of Tm^{3+} ions in $LiYF_4$ calculated using the modified theory accounting for thermal populations of the Stark sub-levels of the ground-state are lower than those obtained using the standard Judd-Ofelt theory. However, when searching for the optimum intensity parameters Ω_k ($k = 2, 4, 6$) by the least square method, this error in the Judd-Ofelt theory will be compensated and the precision of fitting the experimental absorption oscillator strengths will not be notably reduced.

It is known [15] that the radiative lifetime of the $^3F_4$ Tm^{3+} state in cubic garnets, calculated using the Judd-Ofelt theory based on the experimental absorption oscillator strength, is much shorter than the measured luminescence lifetime. By applying the proposed model accounting for the Boltzmann distribution, this contradiction between the transition intensities in absorption and emission is removed.

The modified theory accounting for the Boltzmann distribution is successfully utilized to explain the experimental temperature dependences of luminescence lifetimes of the $^3F_4$ Tm^{3+} manifold in commonly used laser crystals, $LiYF_4$ and $Y_3Al_5O_{12}$.

To explain the previously observed experimental temperature dependence of the luminescence lifetime of the $^2F_{5/2}$ Yb^{3+} state in $LiYF_4$, an addition modification of the general approach is implemented. This is because of the small number of Stark sub-levels for Yb^{3+} multiplets, $^2F_{5/2}$ and $^2F_{7/2}$, namely 3 and 4, respectively. An excellent agreement with the experimental data (both on the absolute values of the luminescence lifetime and the shape of its temperature dependence) is reached when introducing correction coefficients for each of the Stark sub-levels of the $^2F_{5/2}$ excited-state.

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Figure 1. Energy level diagrams for Pr^{3+} and Tm^{3+} ions showing groups of bounded multiplets $^{2S+1}L_J$ with the same total angular momentum $J = 0, 2, 4$, and 6.

Figure 2. Crystal-field splitting of the ground-state ($^3H_6$) and first excited-state ($^3F_4$) of Tm^{3+} ions in the $LiYF_4$ crystal (S_4 site symmetry) [9], Γ_i - irreducible representations.

Figure 3. Temperature dependence of fraction populations of Stark sub-levels of (a) the ground-state, $^3H_6$, and (b) first excited-state, $^3F_4$, for Tm^{3+} ions in the $LiYF_4$ crystal. The numbers of sub-levels and their energies are given in Fig. 2.

Figure 4. Fractional thermal populations of Stark sub-levels and their differences from the assumption of equally populated sub-levels (one of the assumptions in the standard Judd-Ofelt theory) for (a) the ground-state, $^3H_6$, and (b) first excited-state, $^3F_4$, for Tm^{3+} ions in the $LiYF_4$ crystal. Room temperature (293 K). Γ_i – irreducible representations.

Figure 5. Temperature dependence of luminescence lifetime of the $^3F_4$ state of Tm^{3+} ions in the $LiYF_4$ crystal. *Circles* – experimental data from [12] and this work, *curve* - calculation using Eq. (14) (this work).

Figure 6. Crystal-field splitting of the ground-state ($^3H_6$) and first excited-state ($^3F_4$) of Tm^{3+} ions in the $Y_3Al_5O_{12}$ crystal (D_2 site symmetry) [14], Γ_i - irreducible representations.

Figure 7. Temperature dependence of luminescence lifetime of the $^3F_4$ state of Tm^{3+} ions in the $Y_3Al_5O_{12}$ crystal. *Circles* – experimental data from [16], *curve* - calculation using Eq. (14) (this work).

Figure 8. Crystal-field splitting of the ground-state ($^2F_{7/2}$) and first excited-state ($^2F_{5/2}$) of Yb^{3+} ions in the $LiYF_4$ crystal (S_4 site symmetry) [8], Γ_i - irreducible representations.

Figure 9. Temperature dependence of luminescence lifetime of the $^2F_{5/2}$ state of Yb^{3+} ions in the $LiYF_4$ crystal. *Circles* – experimental data from [8], *curve* - calculation using Eq. (17) (this work).