Upconversion in LaF$_3$:Tm^{3+}

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When excited by the 6471-Å line from a krypton laser, blue and uv fluorescence has been observed in LaF$_3$:Tm^{3+} at room temperature. The main emission features have been identified as originating from the $^1D_2$ and $^1G_4$ levels, reached by a stepwise excitation process. A set of accurate Judd-Ofelt Ω parameters for LaF$_3$:Tm^{3+} has been derived from the measured lifetime of the $^1D_2$, $^1G_4$, $^3H_4$, and $^3F_4$ levels.

I. INTRODUCTION

The energy-level schemes of the Tm^{3+} and Pr^{3+} ions in LaF$_3$ are very similar, but much less work has been done in Tm^{3+} than in Pr^{3+}. Carnall *et al.*[1] have measured the absorption spectrum and identified the Stark components of most states in LaF$_3$:Tm^{3+}. The reduced matrix elements $U^{(\lambda)}$ between any two states have been calculated by Pappalardo.[2] The Ω parameters have also been reported by some authors.[2,3] However, the Ω values deviate among the authors and the radiative lifetimes calculated from these parameters also differ from the measured values.

The Tm^{3+} ion is particularly suitable for upconversion studies because of its energy-level structure and long lifetimes of the low-lying excited states. Upconversion processes for Tm^{3+} in a series of fluorides and in CaWO$_4$ were observed by Esterowitz *et al.*,[4] when exciting with a broad-band light source. Multiple-quanta stepwise processes have been observed in a Yb^{3+}-Tm^{3+} system, with the Yb^{3+} ions being the energy donors (sensitizers) and the Tm^{3+} ions the acceptors in multiple energy transfers.[5–8]

With a monochromatic, intense laser source the intensity of the upconverted fluorescence increases and the routes by which upconversion takes place are limited by energy conservation, resulting in simpler spectra that are easier to interpret. Unlike the mixed systems of sensitizer-activator, we deal in the present work only with transitions within a single type of ions. This enables us to extract level lifetimes directly from the rise and decay of the fluorescence. In addition, levels such as $^1I_6$ and $^3F_4$, which are difficult to excite directly by conventional laser sources, become populated in the upconversion processes. The measurement of their lifetimes contributes to the accurate determination of the Ω intensity parameters of Tm^{3+} in LaF$_3$.

II. EXPERIMENTAL DETAILS

The samples used in this experiment were grown by Optovac, and had nominal concentrations of 1,

0.3, and 0.1 at. % Tm^{3+} in LaF$_3$. A coherent radiation CR 3000K cw laser, with 2.5-W output at 6471 Å, was used as the pumping source. The short-wavelength emission background of the laser was cut off by a 2-60 Corning filter. The fluorescence from the sample was focused onto a Spex 1-m single monochromator and was detected by an RCA C31034 photomultiplier tube. Laser pulses were obtained by using a conventional chopping wheel. The rise and decay of the fluorescence was analyzed with a PAR 162 boxcar integrator.

III. RESULTS AND DISCUSSION

A. Fluorescence characterization

The radiative transition scheme for a Tm^{3+} ion in LaF$_3$ is shown in Fig. 1(a). A 6471-Å photon excites a Tm ion from its ground state, $^3H_6$ to $^3F_2$. Owing to the nearby levels $^3F_3$ and $^3H_4$, the $^3F_2$ ions quickly relax nonradiatively to the $^3H_4$ state, which is relatively long lived. Absorption of a second photon will promote an electron from $^3H_4$ to the $^1D_2$ level. The ions at $^3H_4$ decay radiatively either to the $^3H_6$ ground state or to the $^3F_4$ state. A second photon may also excite the electrons on $^3F_4$ to the $^1G_4$ state, while a third photon can promote an electron at $^1G_4$ to $^3P_2$. The latter relaxes nonradiatively to the long-lived state $^1I_6$. Radiative transitions from $^1I_6$, $^1D_2$, and $^1G_4$ are observed in the fluorescence spectrum, as shown in Fig. 2. The four emission groups labeled A to D, are due to transitions from $^1I_6$ to $^3F_4$, $^1D_2$ to $^3H_6$, $^1D_2$ to $^3F_4$, and $^1G_4$ to $^3H_6$, respectively. At room temperature the fluorescence intensity of groups B, C, and D shows a quadratic dependence on the laser power, while group A shows a cubic dependence, indicating two-photon processes for groups B, C, and D, and three-photon process for group A fluorescence. A justification of this assignment and of the upconversion schemes is supported by a study of the rise and decay of the observed fluorescence.

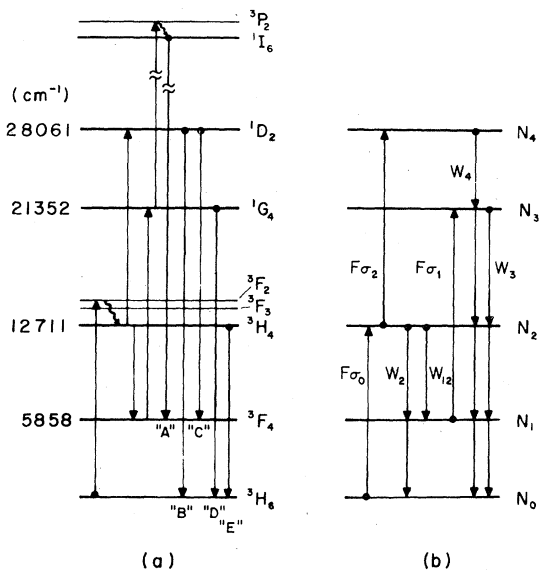By chopping the laser beam at an appropriate

FIG. 1. Schematics for the energy levels in $LaF_3:Tm^{3+}$. In (a) the routes for the upconversion process are indicated. The relevant fluorescence levels are marked with heavy dots. The groups of transitions observed are labeled from A to E in accordance with the notations in Fig. 2. In (b) the absorption cross sections and transition probabilities between relevant energy levels are shown.

FIG. 2. Fluorescence spectrum at room temperature from 1 at. % $Tm^{3+}:LaF_3$. The four dominant groups are labeled by A to D, and the identification of the pertinent transitions is discussed in the text.

speed, a series of rise and decay curves have been measured for the fluorescence resulting from upconversion. All the decays and the rises of fluorescence show exponential character at room temperature; the corresponding time constants for various energy levels are tabulated in Table I. The almost identical rise times of the emission originating from both $^1D_2$ and $^3H_4$ indicate a link between these levels, while a dif-
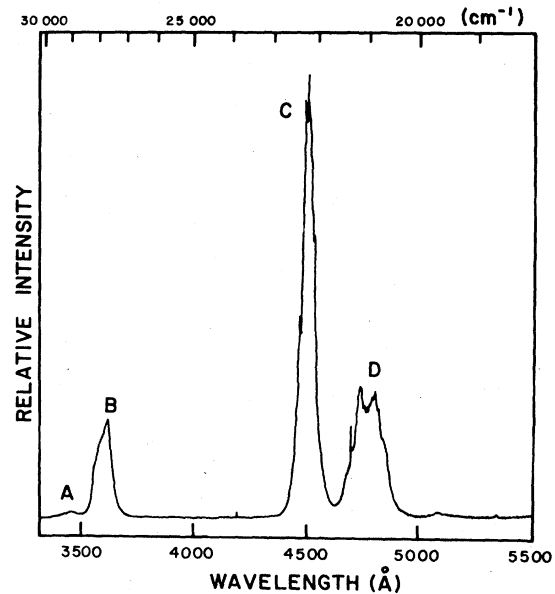
ferent origin of the $^1G_4$ fluorescence is shown by its much slower rise time.

Since nonradiative relaxation process is dominant for those levels with closely lying lower-energy states,[9] we can safely approximate the excitation from ground state $^3H_6$ to $^3F_2$, then relaxing to $^3H_4$, with an equivalence of a pumping from $^3H_6$ to $^3H_4$ as indicated in Fig. 1(b). The transient dynamics of different groups of fluorescence at unsaturated pumping re-

TABLE I. The rise and decay time constants (μ sec) measured for various groups of fluorescence lines; A ($^1I_6$), B and C ($^1D_2$), D ($^1G_4$), and E ($^3H_4$) as indicated in Fig. 1(a).

Tm^{3+} (at. %)	Concentrations	$^1I_6$	$^1D_2$	$^1G_4$	$^3H_4$
0.1	Rise		2080	11 000	2060
	Decay		91.8	1 007	2070
0.3	Rise		1880	13 380	1890
	Decay		85	912	1790
1	Rise	10 400	1790	11 030	1760
	Decay	89	78	738	1670

gime are governed by the set of rate equations:

$$\frac{dN_1}{dt} = W_{21}N_2 - W_1N_1 \ , \tag{1}$$

$$\frac{dN_2}{dt} \simeq F\sigma_0 N_0 - W_2 N_2 \ , \tag{2}$$

$$\frac{dN_3}{dt} = F\sigma_1 N_1 - W_3 N_3 \ , \tag{3}$$

$$\frac{dN_4}{dt} = F\sigma_2 N_2 - W_4 N_4 \ , \tag{4}$$

where $N_i (i = 0, \ldots, 4)$ denote the population of levels $^3H_6$, $^3F_4$, $^3H_4$, $^1G_4$, and $^1D_2$, respectively; W_i is the radiative transition rate of the ith level; W_{12} is the transition rate between level 1 and 2 ; F denotes the laser-photon density at 6471 Å; and σ_i are the absorption cross sections. These quantities are represented schematically in Fig. 1(b). We use the approximations $W_4 \gg W_2$, $W_3 > W_2 \gg W_1$, which can be justified later by the calculated values. The rise characteristics of the N_i populations are obtained by solving Eqs. (1)–(4). We have

$$N_1 \simeq \frac{W_{21}}{W_1 W_2} F\sigma_0 N_0 (1 - e^{-W_1 t}) \ , \tag{5}$$

$$N_2 = \frac{F\sigma_0 N_0}{W_2} (1 - e^{-W_2 t}) \ , \tag{6}$$

$$N_3 \simeq \frac{W_{21}F^2\sigma_0\sigma_1 N_0}{W_1 W_2 W_3} (1 - e^{-W_1 t}) \ , \tag{7}$$

$$N_4 \simeq \frac{F^2\sigma_0\sigma_2 N_0}{W_2 W_4} (1 - e^{-W_2 t}) \ , \tag{8}$$

indicating that the rise characteristics are adequately described by simple exponentials. Starting from

steady-state equilibrium, the decay goes like

$$N_1 \simeq \frac{W_{21}}{W_1 W_2} F\sigma_0 N_0 e^{-W_1 t} \ , \tag{9}$$

$$N_2 = \frac{F\sigma_0 N_0}{W_2} e^{-W_2 t} \ , \tag{10}$$

$$N_3 \simeq \frac{W_{21}F^2\sigma_0\sigma_1}{W_1 W_2 W_3} N_0 e^{-W_3 t} \ , \tag{11}$$

$$N_4 \simeq \frac{F^2\sigma_0\sigma_2}{W_2 W_4} N_0 e^{-W_4 t} \ . \tag{12}$$

The lifetime of the $^3F_4$ state can be inferred from the $^1G_4$ rise curve.

Hence the lifetimes of the $^3F_4$, $^3H_4$, $^1G_4$, and $^1D_2$ states can be measured directly from the rise and decay portions of the emission curves obtained under excitation with a single krypton line 6471 Å. This is possible owing to the phonon broadening at room temperature of the absorption linewidth, and the presence of strong phonon sidebands, as in the transitions from $^3H_6 \rightarrow {}^3F_2 \rightarrow {}^3H_4$. Fluorescence from sample with different Tm^{3+} concentrations has also been studied. The corresponding lifetime constants are listed in Table I. The concentration quenching effect on all energy states is noted. However, such an effect does not produce nonexponential decay characteristics owing to rapid energy transfer at elevated temperatures.[10]

B. Intensity parameters Ω

The successful prediction of fluorescence intensity from Nd^{3+} and Pr^{3+} ions was first put forward by Judd[11] and Ofelt.[12] These calculations were later ex-

TABLE II. The radiative transition rates (sec^{-1}) from $^1I_6$, $^1D_2$, $^1G_4$, $^3H_4$, and $^3F_4$ to all lower levels. The Ω parameters used in the calculation are $\Omega_2 = 0.71 \times 10^{-20}$ cm^2, $\Omega_4 = 1.62 \times 10^{-20}$ cm^2, and $\Omega_6 = 0.62 \times 10^{-20}$ cm^2. The cumulative entry in the last row (W_R) denotes the inverted radiative lifetime of the emitting level.

	$^1I_6$	$^1D_2$	$^1G_4$	$^3H_4$	$^3F_4$
$^3H_6$	785.5	6422.6	452.5	396.3	86.6
$^3F_4$	5762.3	3285.8	97.6	53.6	
$^3H_5$	48.8	53.2	332.6	24.9	
$^3H_4$	1440.1	467.8	85.6		
$^3F_3$	17.1	361.2	30.0		
$^3F_2$	482.2	649.2	9.5		
$^1G_4$	1269.8	62.9			
$^1D_2$	37.8				
W_R	9843.6	11 302.7	1007.8	474.8	86.6

TABLE III. The Ω parameters $(10^{-20}\ \mathrm{cm}^2)$ and the calculated lifetimes (μsec).

Ω_2	Ω_4	Ω_6	$^1I_6$	$^1D_2$	$^1G_4$	$^3H_4$	$^3F_4$	Ref.
0.52	0.59	0.22		137	1560			3
0.12	1.77	4.78	38.2	52.0	280	467	7735	2
1.2	1.77	0.0	106	69.0	1186	2635	9336	2
0.71	1.62	0.62[a]	102	88.4	993	2103	11 540	Present work
	τ_{measured}		89[b]	91.8[c]	1007[c]	2070[c]	11 000[c]	

[a] By four lifetimes $(^1D_2, {}^1G_4, {}^3H_4, {}^3F_4)$ fit. [c] Measured in 0.1 at.% Tm^{3+}:LaF_3.
[b] Measured in 1 at.% Tm^{3+}:LaF_3.

tended to account for other lanthanide ions in solutions. The spontaneous emission rate between two states in the $4f$ configurations, with ground state (0) and excited state (i), is given by

$$W_{i0} = \frac{64\pi^4 e^2 v_{i0}^3}{3h(2J_1+1)}\ \frac{n(n^2+2)^2}{9}\ \sum_{\lambda=2,4,6} \Omega_\lambda (U_{i0}^{(\lambda)})^2\ ,$$

(13)

where all notations are defined in Ref. 11. The transition rate can then be related to the integrated absorption strength between such levels. Alternatively, the Ω parameters can also be deduced from lifetime measurements. In such a case all energy levels j below level i are summed over, and the lifetime for level i is

$$\frac{1}{\tau_i} = \sum_j W_{ij} = \sum_{\lambda=2,4,6} \Omega_\lambda \sum_j C_{ij}(U_{ij}^{(\lambda)})^2\ .$$

(14)

The prerequisite for the valid application of this approach is that the level i must be predominantly radiative. The large energy gaps separating the $^3F_4$, $^3H_4$, $^1G_4$, and $^1D_2$ levels of Tm^{3+} make such levels suitable candidates.

The measured lifetimes of the four levels $^3F_4$, $^3H_4$, $^1G_4$, and $^1D_2$ are used to determine the intensity parameters Ω. Least-squares analysis is performed for Eq. (14) with equal weights for all τ_i. The $U_s^{(\lambda)}$ are taken from Pappalardo's calculation,[2] energy-level positions are from Carnall et al.[1] and the refractive index n is taken from Ref. 13. The Ω's with the best fit are (in cm^2)

$$\Omega_2 = 0.71 \times 10^{-20}\ ,$$

$$\Omega_4 = 1.62 \times 10^{-20}\ ,$$

$$\Omega_6 = 0.62 \times 10^{-20}\ .$$

Using this set of parameters, the transition rates between pairs of $4f$ energy levels in Tm^{3+} are calculated and are listed in Table II. To minimize the effect of concentration quenching, we only consider τ measured from the 0.1 at.% concentration sample. The root-mean-square deviation is 5.4% between the measured and calculated lifetimes for the four levels used in calculation. Using the Ω parameters derived from absorption measurements,[2,3] the lifetimes of relevant energy levels were calculated. These values are listed in Table III for comparison.

The more accurate predictions with our Ω parameters over those derived from absorption measurements result from the fact that the lifetime measurements are intrinsically more accurate, compared with the process of extracting oscillator strength from absorption spectra. To test the accuracy of our set of Ω parameters, we calculate the lifetime of the $^1I_6$ state to be 102 μsec, compared with the measured 89 μsec in the 1 at.% Tm^{3+} sample. The concentration quenching effect in this sample may account for the downward deviation from the calculated value. The measurement of the $^1I_6$ fluorescence from the samples with 0.1 and 0.3 at.% Tm was attempted, but the intensity was far too weak to give reliable results.

In summary, we have investigated the uv and blue upconverted fluorescence induced by the 6471-Å krypton laser line. Using the measured lifetimes, a set of accurate intensity parameters Ω for Tm^{3+} in LaF_3 has been deduced. The calculated lifetime, based on this set of parameters shows excellent agreement with the measurements.

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