

Quenching of the total luminescence of Ho^{3+} in HoLiF_4 crystals

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The luminescent-channel efficiency for Ho^{3+} ions in HoLiF_4 crystals was measured and compared with the case of Ho^{3+} as a low-concentration dopant (1.71%) in crystals of YLiF_4 . The $^5S_2 \rightarrow ^5I_7$, 5I_8 luminescent transitions are strongly quenched by two possible cross-relaxation processes: one with almost zero mismatch energy, favoring the population of the 5I_5 , 5I_6 , and 5I_7 levels, and the other, a laser transition $^5I_7 \rightarrow ^5I_8$ in the mid-infrared region. Also seen was a strong decrease of the total Ho^{3+} luminescence by approximately 6.6 times in HoLiF_4 crystals from 10 to 300 K. This quenching effect was attributed to an energy transfer from the Ho^{3+} excited 5I_6 and 5I_7 levels to traps present in the crystal.

I. INTRODUCTION

Laser emissions in the near-infrared region of various crystal hosts doped with rare-earth ions have attracted considerable attention in recent years as a result of a search for an eye-safe laser source with low atmospheric attenuation. In particular, the 2- μm laser line of Ho^{3+} turned out to be a potential source for tunable operational amplifiers,¹ range finders, and target illuminators. The 2- μm laser line is also applicable in medicine^{1,2} and in industrial processes.

A significant advantage of the Ho^{3+} ion for laser operation at 2 μm is its high gain cross section and the long lifetime of the 5I_7 upper laser level, which results in high energy-storage capability and efficient Q -switched operation.^{3,4} As a result, several studies of cw and pulsed holmium laser operation as well as spectroscopic studies of some Ho^{3+} -doped crystals, have been conducted and reported,⁵⁻⁷ with emphasis on YLiF_4 and yttrium aluminum garnet (YAG) doped with Ho^{3+} . It is well known that trivalent rare-earth ions can transfer energy from visible and near-visible transitions to near- and mid-infrared transitions by thermally assisted cross-relaxation processes⁸ in highly concentrated samples, changing the laser properties of the host crystals. In this paper we present a quantitative investigation of the efficiency of each holmium luminescent-channel in HoLiF_4 crystals when the 5G_6 state, well above the fluorescent 5S_2 level, is excited. This was done by measuring the luminescence with respect to the analog luminescent signals also measured for the diluted system $\text{Ho}^{3+}:\text{YLiF}_4$ at 1.71 at. % concentration. This study presents a very important approach to investigating the behavior of trivalent rare-earth ions as a light source in laser materials that are susceptible to contamination during synthesis or in the crystal growth process. Thus this investigation provides information for further development of laser crystals.

II. EXPERIMENT

The samples used in this investigation were single crystals of pure HoLiF_4 and doped YLiF_4 containing 1.71 at. % of Ho^{3+} ions. The starting materials for the crystal growth were synthesized from ultrapure rare-earth oxides by a conventional hydrofluorination procedure. The $\text{Ho}^{3+}:\text{YLiF}_4$ thus synthesized was grown by the conventional Czochralski method under argon atmosphere. The $\text{Ho}^{3+}:\text{YLiF}_4$ and HoLiF_4 boules were submitted to a thermal treatment prior to the sample preparation, to remove the stress originating from the crystal growth process. Samples were extracted from the boule after the appropriate choice of a region free of scattering defects.

From preliminary optical absorption spectra the most intense line of the 5G_6 multiplet (447 nm) was chosen for excitation, since it can populate the 5S_2 metastable state very efficiently, giving a wide range for the luminescence study. The electronic spectrum of the HoLiF_4 crystal at 300 K is shown in Fig. 1. Samples of 2 mm thickness were placed in a cold finger of a refrigerator cryostat, which allows luminescence measurements ranging from 10 to 300 K. A schematic arrangement of the experimental setup used for the luminescence measurements is described in Fig. 2. For quantitative purposes, all these measurements kept the same photon-collecting area of the sample surface by using a fixed excitation area.

The excitation at 447 nm was provided by a stabilized 150-W xenon lamp. The detection geometry was arranged into two opposite arms as shown in Fig. 2. All the emissions below 2450 nm were detected in arm *A* utilizing a system composed of a GG475 filter, a Kratos analyzer monochromator (0.25 m) with slits of 1 mm, and an S-20 (or S-1) extended-type photomultiplier detector for $\lambda < 1050$ nm and an InSb detector for $\lambda > 1050$ nm.

In arm *B* the integrated emission above 1050 nm was measured utilizing a silicon filter ($T=0.50$ at 1100 nm), a collecting mirror, and a Judson InSb detector model J-10

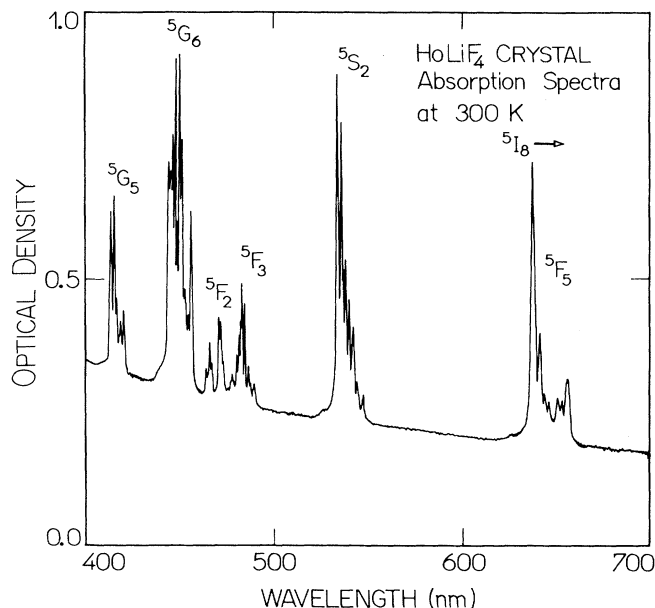


FIG. 1. Electronic absorption spectrum of a thin HoLiF_4 crystal sample ($d = 0.002$ cm) at 300 K.

D cooled to 77 K. The responsivities of the detectors, in V W^{-1} , were determined using an electrically calibrated pyroelectric radiometer (model RS-5900 from Laser Precision) as a reference. The transmission bandpass of the monochromator was always tuned to the maximum of the emission wavelength for each multiplet in order to integrate its intensity.

The lifetimes of excited Ho^{3+} ions were measured using a pulsed laser excitation (10 ns) from a dye-pumped nitrogen laser tuned at 450 nm. The time-dependent signal was detected by faster detectors and analyzed using a signal-processing boxcar averager (PAR 4402).

III. RESULTS

The integrated luminescence signals were always corrected for the band-pass transmission of the analyzer monochromator, using a factor $\Gamma = P/Q$, where P is the integrated area below the multiplet emission band and Q

is the corrected one. P and Q are defined by the following expressions:

$$P = \sum [S_i \delta(\lambda_i)] , \quad (1)$$

$$Q = \sum [S_i \delta(\lambda_i) T_i] , \quad (2)$$

where S_i is the luminescence signal at the wavelength λ_i , T_i is the monochromator transmission, and $\delta(\lambda_i)$ is a constant-wavelength width of 2 nm at λ_i . The bandpass of the monochromator always has a Gaussian shape and a full width at half maximum of approximately 10 nm.

We obtained the integrated luminescence of each channel using the following expressions:

$$S = \frac{S_I g f_1}{RT} \text{ for } \text{YLiF}_4:\text{Ho}(1.71\%) , \quad (3)$$

$$S = \frac{S_I g G}{RT f_2} \text{ for } \text{HoLiF}_4 , \quad (4)$$

where S_I is the measured integrated luminescence signal. The g factor is the ratio between the total solid angle 4π and the one used in arm A (or B). R is the detector responsivity. The f_1 factor is the ratio between the two absorbed powers at two different temperatures (300 and 12 K) for $\text{Ho}^{3+}:\text{YLiF}_4$. The factor f_2 is the ratio between the absorbed power in HoLiF_4 and that absorbed in $\text{Ho}^{3+}:\text{YLiF}_4$, when exciting the $^5I_8 \rightarrow ^5G_6$ transition. T is the optical transmission of the GG475 filter ($T = 99\%$) used to measure all the channels below 1050 nm in arm A . For all the channels with $\lambda > 1050$ nm we used a silicon filter ($T = 50\%$) in arm B .

The estimated f_1 and f_2 values with temperature are the following.

	300 K	250 K	200 K	150 K	100 K	50 K	12 K
$f_1 =$	1.00	1.03	1.09	1.12	1.25	1.45	1.65
$f_2 =$	2.33	2.41	2.53	2.62	2.91	3.39	3.87

Table I shows the detector responsivities, the maximum transmission, and the bandpass width of the optical channels used to integrate the luminescence.

We found the equivalent power of each luminescent channel for both crystals using expressions (3) and (4). Dividing the power of each luminescent channel by its

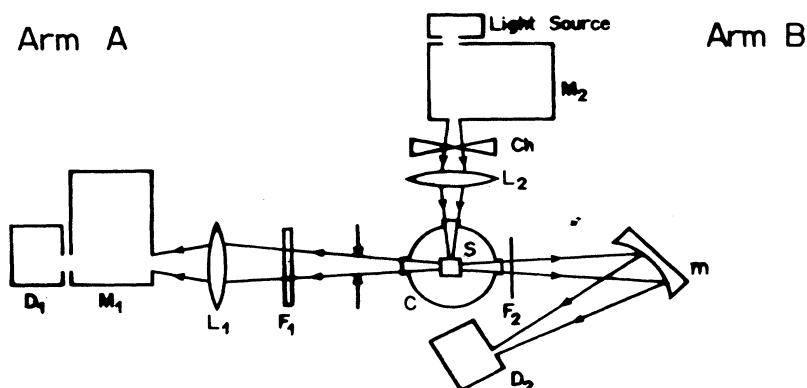


FIG. 2. Schematic arrangement of the experimental setup used to measure the integrated luminescence. M_2 is the monochromator used for excitation and M_1 the one used for luminescence analysis. Ch is the chopper for excitation light and L_1 and L_2 are lenses. D_1 is the extended S-20 cathode (or S-1) photomultiplier tube. D_2 is the InSb detector cooled to 77 K. S is the sample and C the refrigerator cryostat working from 10 to 300 K. m is the concave mirror of 10 cm diameter and 15 cm focal length. F_1 is the optical filter GG476 and F_2 is a thin silicon filter.

TABLE I. Measured values of the detector responsivities R and the maximum optical transmission T_i for each luminescent channel and its total width H .

λ_i (nm)	H (nm)	R (10^9 V/W)	T_i (%)
490	26	0.8468	4.10
540	22	0.5852	1.11
650	24	0.4631	12.50
745	24	0.6443	30.80
790	24	0.037	39.20
900	25	2.60×10^{-4}	58.30
978	25	1.93×10^{-4}	64.20
≥ 1050		4.26×10^{-7}	50.00

average photon energy, one gets the number of emitted photons per second for each luminescent channel.

Table II shows the emitted photons per second measured for each luminescent channel in the $\text{Ho}^{3+}:\text{YLiF}_4$ crystal at several temperatures. Table III shows the same quantities for the HoLiF_4 crystal. The transitions that effectively contribute to the integrated luminescence signal for the $\lambda \geq 1050$ nm channels in the HoLiF_4 crystal and their respective contributions are the $^5I_6 \rightarrow ^5I_8$ (1208 nm) and $^5I_7 \rightarrow ^5I_8$ (2066 nm) transitions with 7% and 93% contributions at 300 K and 1.1% and 98.9% contributions at 12 K, respectively, with an average photon energy of 1.043×10^{-19} J.

The branching ratios (β_i) were defined as $N(i)/\sum N(i)$, where $N(i)$ is the number of emitted photons per second

TABLE II. Total number of emitted photons per second per luminescent channel for the $\text{YLiF}_4:\text{Ho}$ (1.71%) crystal at several temperatures. $g_A = 1790$ for all measurements with the exception of $\lambda \geq 1050$ nm where $g_B = 64$. A dash indicates that the transition is out of the luminescence detectivity limit of 3×10^5 photons/s. A typical error of 5% must be considered in the values presented in the table.

Transition λ_i (nm)	(10 ¹¹ photons/s)						
	300	250	200	150	100	50	12
	(K)						
$^5F_3 \rightarrow ^5I_8$ (490)	1.66	4.2	4.5	3.8	3.5	3.0	5.9
$^5S_2 \rightarrow ^5I_8$ (540)	417	442	352	316	253	281	232
$^5F_5 \rightarrow ^5I_8$ (650)	101	100	103	114	105	75	79
$^5S_2 \rightarrow ^5I_7$ (749)	604	662	548	676	648	656	1067
$^5I_4 \rightarrow ^5I_8$ (790)	—	—	—	—	—	—	—
$^5I_5 \rightarrow ^5I_8$ (900)	13.8	72	34	44	46	47	31
$^5F_5 \rightarrow ^5I_7$ (1000)	134	152	144	132	134	112	86
$\lambda \geq 1050$	1859	1952	1859	2057	1909	1955	1772
Total	3130	3384	3045	3343	3099	3129	3273

TABLE III. Total number of emitted photons per second per luminescent channel for the HoLiF_4 crystal at several temperatures. The data were normalized for comparison with the low-concentration crystal using the factor f_2 . $g_A = 1790$ for all measurements with the exception of $\lambda \geq 1050$ nm where $g_B = 64$. A dash indicates that the transition is out of the luminescence detectivity limit of 3×10^5 photons/s. A typical error of 5% must be considered in the values presented in the table.

Transition λ_i (nm)	(10 ¹¹ photons/s)						
	300	250	200	150	100	50	12
	(K)						
$^5F_3 \rightarrow ^5I_8$ (490)	—	—	—	—	—	—	—
$^5S_2 \rightarrow ^5I_8$ (540)	—	—	—	—	—	—	—
$^5F_5 \rightarrow ^5I_8$ (650)	0.35	17.5	19.5	22.0	78	237	204
$^5S_2 \rightarrow ^5I_7$ (749)	—	—	—	—	—	—	—
$^5I_4 \rightarrow ^5I_8$ (790)	0.46	0.87	14.4	31.5	61	23.6	23.4
$^5I_5 \rightarrow ^5I_8$ (900)	—	—	—	—	—	—	—
(978)	100	213	343	350	331	241	151
$^5F_5 \rightarrow ^5I_7$ (1000)	100	107	126	140	248	149	100
$\lambda \geq 1050$	276	413	427	474	807	1416	1644
Total	477	751	930	1018	1525	2067	2122

in the i^{th} channel and $\sum$ is a sum over all channels. In the low-concentration crystal, ($\text{Ho}^{3+}:\text{YLiF}_4$) the total number of emitted photons of excited Ho^{3+} ions (obtained by adding all channel contributions) remains constant with decreasing temperature from 300 K to 12 K. The branching ratios (β_i) of the luminescent channels suffer slight modifications with temperature as seen in Table IV. This effect is an indication that the oscillator strengths for all the respective optical transitions have approximate values. An opposite effect occurs in the case of Ho^{3+} in HoLiF_4 crystal. In this case, the total number of emitted photons per second (Table III) is drastically reduced by a factor of 6.6 at 300 K and by a factor of 1.5 at 12 K, the lowest investigated temperature, when compared to the low-concentration system. The branching ratios also suffer greater modifications with temperature as seen in Table IV.

The results for the HoLiF_4 crystal show that there is a total quenching of the luminescent channels at 490, 540 and 749, and 900 nm, starting from the levels 5F_3 , 5S_2 , and 5I_5 , respectively. This partial luminescence quenching is independent of the temperature, indicating that there is some energy transfer between neighboring excited Ho^{3+} (Ho^*) ions with mismatch energies $\Delta E \approx 0$. These processes are responsible for the conversion of visible and near-infrared transitions into the mid-infrared transitions.

When investigating the schematic energy level diagram of the Ho^{3+} ions in the HoLiF_4 crystal, two resonant cross-relaxation processes, were found, P_1 and P_3

TABLE IV. Experimental branching ratios of the luminescent channels for $\text{YLiF}_4\text{:Ho}$ (1.71%) and HoLiF_4 crystals at 300 K and 12 K.

Transition λ_i (nm)	β_i $T=300\text{ K}$ (Ho^{3+})		$T=12\text{ K}$ (Ho^{3+})	
	1%	100%	1%	100%
$^5F_3 \rightarrow ^5I_8$ (490)	0.0005		0.0018	
$^5S_2 \rightarrow ^5I_8$ (540)	0.131		0.072	
$^5F_5 \rightarrow ^5I_8$ (650)	0.032	0.0007	0.025	0.096
$^5S_2 \rightarrow ^5I_7$ (749)	0.189		0.330	
$^5I_4 \rightarrow ^5I_8$ (790)		0.0009		0.011
$^5I_5 \rightarrow ^5I_8$ (900)	0.0044		0.0097	
$^5F_5 \rightarrow ^5I_7$ (978)		0.209		0.071
$^5F_5 \rightarrow ^5I_7$ (1000)	0.0419	0.209	0.0269	0.047
$\lambda \geq 1050$	0.581	0.579	0.554	0.775

($\Delta E \approx 0$), and a nonresonant one P_2 with $\Delta E > 0$, involving two nearest-neighbor Ho^{3+} ions. In Fig. 3, the three possible cross-relaxation processes (P_1 , P_2 , and P_3) are indicated by dark arrows. These processes are represented generically by the sequence $[\text{Ho}^*(1), \text{Ho}(2)] \rightarrow [\text{Ho}^*(1), \text{Ho}^*(2)]$, respectively,

$$P_1: (^5F_3, ^5I_8) \rightarrow (^5F_5, ^5I_7) \text{ resonant } \Delta E \approx 0,$$

$$P_2: (^5S_2, ^5I_8) \rightarrow (^5I_6, ^5I_6)$$

$$\text{energy mismatch } \Delta E = 1047 \text{ cm}^{-1},$$

$$P_3: (^5I_4, ^5I_8) \rightarrow (^5I_6, ^5I_7) \text{ resonant } \Delta E \approx 0.$$

The P_1 process was identified by measuring the excitation spectrum of the 655-nm emission from the 5F_5 level, showing peaks following the absorption band in the violet and blue, due to the $^5I_8 \rightarrow ^5G_6, ^5F_2, ^5F_3$ transitions. No excitation in the green, due to the $^5I_8 \rightarrow ^5S_2$ transition, was observed for the investigated temperature range. So P_1 and P_2 must quench the green emission from the 5S_2 level. Clearly, the P_1 process short-circuits the 5S_2 state and populates the 5F_5 level, besides quenching the 490-nm fluorescence. The population of the 5F_5 level is modulated by the P_1 process, which competes with W_0 , a multiphonon process with $p=6$ at 300 K.

The lifetime of the very weak 490-nm emission was measured at 12 K by using a strong pulsed laser excitation at 447 nm. The measured lifetime τ_0 was 43 μs showing that $(W_0 + P_1) = \tau_0^{-1}$ is $2.33 \times 10^4 \text{ s}^{-1}$ at 12 K. At this temperature the transition P_1 is more probable than W_0 ($P_1 = 13.95 W_0$), according to the rate-equation model presented in the Discussion. P_1 should be temperature independent as expected for a resonant process. As

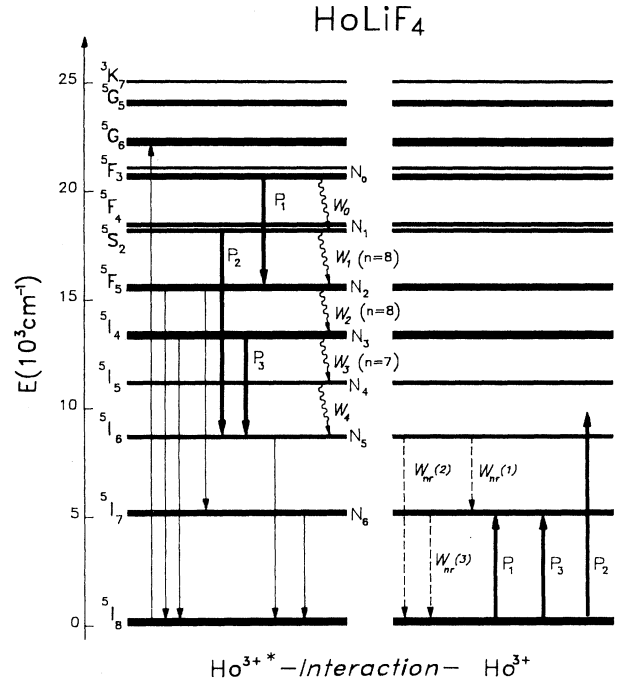


FIG. 3. The energy level diagram of Ho^{3+} ions in YLiF_4 crystals. At the left are indicated the intracenter processes (optical and multiphonon transitions) and at the right the inter-center cross-relaxation processes (1–3) involving two neighboring Ho ions. The processes P_1 and P_3 are resonant and P_2 is nonresonant involving a mismatch energy of 1047 cm^{-1} .

a consequence, the 5F_5 level population decreases with increase of temperature (when $W_0 \approx P_1$).

The value of the cross-relaxation process P_2 was obtained from the measured lifetime (τ_1) of the 5S_2 level at 300 K, considering that $P_2 = \tau_1^{-1} - \tau_{r1}^{-1}$, where $\tau_1 = 6.5 \mu\text{s}$ (at 300 K) and $\tau_{r1} = 0.45 \text{ ms}$. The estimated value of P_2 is $1.5 \times 10^5 \text{ s}^{-1}$ and it is temperature dependent (a nonresonant process with $\Delta E = 1047 \text{ cm}^{-1}$). The 5I_5 state is short-circuited by the cross-relaxation process P_3 that dominates the deexcitation level 5I_4 in the low-temperature range from 12 to 50 K. At higher temperatures W_3 dominates the deexcitation of the 5I_4 level. W_3 is a multiphonon process of 7th order at 300 K, which populates the 5I_5 level efficiently. On the other hand, the P_2 process, which is more effective at higher temperatures, also short-circuits the 5I_5 level. Considering these two short-circuiting processes (P_2 and P_3), the population of the 5I_5 level should decrease at all temperatures and the 900-nm emission should not be observed, as was confirmed experimentally.

The population of 5I_6 and 5I_7 levels is highly favored due to these three cross-relaxation processes. In spite of that, we observed that the 1208-nm emission from the 5I_6 levels is very weak and constant with temperature. The emission at 2064 nm from the 5I_7 level is temperature dependent, with an increase in intensity by a factor of 10 when going from 300 to 12 K. It is evident from these results that both emissions are strongly (1208 nm) and par-

tially (2064 nm) quenched by some mechanism of energy transfer.

This quantitative luminescence analysis shows that there is a quenching of the total luminescence of Ho^{3+} in the HoLiF_4 crystal not mentioned before in the literature to our knowledge for holmium-doped systems. In Table V the total luminescence efficiencies (η_T) for Ho^{3+} ions in both crystals are shown; for example, $\eta_T=0.34$ for $\text{Ho}^{3+}:\text{YLiF}_4$ and $\eta_T=0.052$ for HoLiF_4 at 300 K. η_T was calculated using the expression

$$\eta_T = \frac{\sum N(i)}{U_0},$$

where U_0 is the number of excited Ho^{3+} ions per second for the ${}^5I_8 \rightarrow {}^5G_6$ transition in $\text{Ho}^{3+}:\text{YLiF}_4$. The quenching mentioned is due to a nonradiative deexcitation process from the two most populated excited states (5I_6 and 5I_7), by the three identified cross-relaxation processes.

IV. DISCUSSION

This quantitative luminescence analysis allowed us to write rate equations at equilibrium conditions for the HoLiF_4 crystal under continuous pumping (${}^5I_8 \rightarrow {}^5G_6$) including all the luminescent levels. A typical rate equation of the j th excited level is represented by the expression

$$N_{j-1}W_{j-1} + N_{j'(j'<j)}P_K + N(i) + N_{j-1}W_{\text{NR}}(l-1) \\ = N_j W_j + N_j \tau_{rj}^{-1} + N_j P_{K'(K' \neq K)} + N_j W_{\text{NR}}(l),$$

where on the left side of the equation we have a sum over all population rate terms and the right side represents the sum over all the deexcitation rate terms. We note the following.

(i) $j=0, 1, 2, 3, 4, 5$, and 6 correspond to the 5F_3 , 5S_2 , 5F_5 , 5I_4 , 5I_5 , 5I_6 , and 5I_7 levels, respectively.

(ii) The equilibrium population of the j th level will be given by

$$N_j = f_2 \tau_{rj} \sum_i N(i),$$

where $N(i)$ is the number of photons per second of the i th channel that contributes to the fluorescent level j and the τ_{rj} were obtained from Ref. 9.

(iii) W_j is the multiphonon deexcitation probability (in s^{-1}) of the j th level (as indicated in Fig. 3). It can be estimated using the well-known expression

$$W_j(T) = \frac{W(0)\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^p},$$

where $W(0) = N(S_0^p/p!)\exp(-S_0)$, $\hbar\omega = 331 \text{ cm}^{-1}$, p is the number of local phonons created in the transition, S_0 is the Huang-Rhys factor (≈ 0.25), and $N = 10^{13} \text{ s}^{-1}$ (Ref. 10).

(iv) $P_{K'}$ and P_K represent the cross-relaxation probabilities (in s^{-1}) starting from the levels j' and j , respectively (see Fig. 3 to identify all the possible processes P_1 , P_2 , and P_3).

(v) $N(i)$ is the number of emitted photons per second from a particular channel (i), which contributes to the population rate of level j .

(vi) τ_{rj}^{-1} is the radiative deexcitation probability (in s^{-1}) for level j .

(vii) $W_{\text{NR}}(l-1)$, $W_{\text{NR}}(l)$, ... are the nonradiative down transitions in the $(j-1)$ and j levels, induced by the effect of impurities in the host (see Fig. 3 for identification of these processes).

(viii) The total lifetime of level j is related to all these processes by the following expression for HoLiF_4 :

$$\frac{1}{\tau_j} = \frac{1}{\tau_{rj}} + W_j + P_K + W_{\text{NR}}(l).$$

Evidently for the highest excited luminescent level (5F_3) the population rate will be equal to the excitation rate U , which is equal to $2.13 \times 10^{15} \text{ s}^{-1}$. U is the number of the excited Ho^{3+} ions per second in HoLiF_4 and it is constant with temperature because the absorbed power of the excitation beam in the ${}^5I_8 \rightarrow {}^5G_6$ transition is always the same, since the effective absorption coefficient (α) is very large. This value was obtained considering $U = 2.33 U_0$, where U_0 is the excitation rate of the Ho^{3+} ions in the low-concentration system at 300 K. U_0 was calculated from the rate equation of the 5S_2 level. In that system U_0 is given by

$$U_0 = \frac{\tau_{r1}}{\tau_1} \sum N({}^5S_2),$$

where τ_1 is the measured lifetime ($54 \mu\text{s}$) at 300 K and $\sum$ is the sum of all the luminescent transitions from the 5S_2 level in the $\text{Ho}^{3+}:\text{YLiF}_4$ crystal (1.71%).

The rate equations for the HoLiF_4 crystal at 12 K are as follows.

$${}^5F_3: U = N_0(W_0 + P_1) = N_0\tau_0^{-1}, \quad (5)$$

$${}^5S_2: N_0W_0 = N_1(W_1 + P_2) \cong N_1P_2, \quad (6)$$

$${}^5F_5: N_1W_1 + N_0P_1 \cong N_0P_1 = N_2(W_2 + \tau_{r2}^{-1}), \quad (7)$$

$${}^5I_4: N_2W_2 = N_3P_3, \quad P_3 \gg W_3, \quad (8)$$

$${}^5I_6: N_4W_4 + 2N_1P_2 + N_3P_3 \cong 2N_1P_1 + N_3P_3 \\ = N_5W_{\text{NR}}(1), \quad (9)$$

$${}^5I_7: N_0P_1 + N_3P_3 + N(1000) + N_5W_{\text{NR}}(1) \\ = N_6[\tau_{r6}^{-1} + W_{\text{NR}}(3)]. \quad (10)$$

The rate equation for the 5I_5 level was neglected because P_3 short-circuits this level, making its population negli-

TABLE V. Total luminescence efficiency (η_T) of Ho^{3+} measured at several temperatures for YLiF_4 crystals with 1.71% and 100% $[\text{Ho}^{3+}]$ concentrations.

(Ho^{3+}) (%)	η_T						
	300	250	200	150	100	50	12
				(K)			
1.71	0.34	0.37	0.33	0.37	0.34	0.34	0.36
100	0.052	0.082	0.10	0.11	0.17	0.22	0.23

ble. As a consequence of that, $N_4 W_4$ is very small compared to other population rates in Eq. (9).

At 300 K we observed no change in Eqs. (5)–(7). In spite of that, the W_3 process became larger than P_3 at room temperature, altering all the other equilibrium equations as follows:

$${}^5I_4: N_2 W_2 = N_3 (W_3 + P_3) \cong N_3 P_3, \quad P_3 \ll W_3, \quad (11)$$

$${}^5I_5: N_3 W_3 = N_4 W_4, \quad (12)$$

$${}^5I_6: N_3 P_3 + 2N_1 P_2 + N_4 W_4 \cong 2N_1 P_2 + N_4 W_4 \\ = N_5 W_{\text{NR}}(2), \quad (13)$$

$${}^5I_7: N_0 P_1 + N(1000) = N_6 [\tau_{r6}^{-1} + W_{\text{NR}}(3)]. \quad (14)$$

The $(N_3 P_3)$ term was neglected since it is very small compared to the other population rates in Eq. (13). The $(N_1 W_1)$ term was also neglected at both temperatures since it is very small compared to the $(N_1 P_2)$ and $(N_0 P_1)$ deexcitation rates. The deexcitation rate $(N_2 W_2)$ has values $1.04 \times 10^{15} \text{ s}^{-1}$ at 300 K and $1.89 \times 10^{15} \text{ s}^{-1}$ at 12 K.

As the 5S_2 fluorescent level was completely quenched by the P_1 and P_2 cross-relaxation processes, it was not possible to calculate its population N_1 (which should be very small). In spite of that, it was possible to calculate the probabilities of the three cross-relaxation processes P_1 , P_2 , and P_3 and the probabilities of the nonradiative deexcitation $W_{\text{NR}}(1)$, $W_{\text{NR}}(2)$, and $W_{\text{NR}}(3)$, from the 5I_6 and 5I_7 levels, respectively.

The values of N_j are shown in Fig. 4 where it is seen that 5I_7 (N_6) is the most populated level. At 12 K, the resonant cross-relaxations (P_1 and P_3) are the most probable deexcitation processes compared to the intracenter relaxations, consequently, the 5I_7 population increases by 6.9 times.

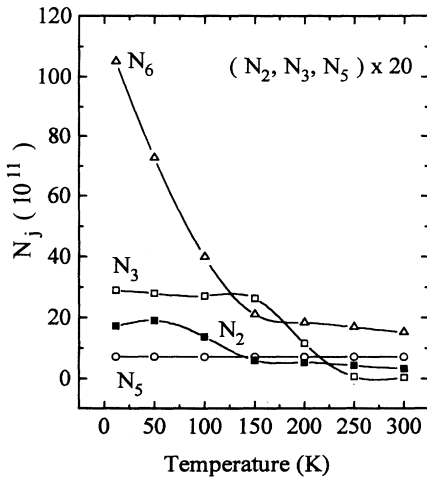


FIG. 4. Temperature dependence of the equilibrium population N_j of several fluorescent levels in the HoLiF_4 crystal, obtained from the experimental values of number of photons per luminescent channel and the radiative lifetimes. The solid line was used as a visual guideline.

P_1 was calculated using Eqs. (5) and (7) as follows:

$$P_1 = \frac{N_2}{U \tau_0} \left[W_2 + \frac{1}{\tau_{r2}} \right],$$

where U is the excitation rate, τ_0 is the measured lifetime of the 5F_3 level at 12 K, and τ_{r2} is the radiative lifetime of the 5F_5 level. The calculated value of P_1 is $2.17 \times 10^4 \text{ s}^{-1}$ and its rate is independent of the temperature. It is seen also that $P_1 = 13.95 W_0$ at 12 K and $P_1 \approx W_0$ at 300 K.

By using $p=6$, $\hbar\omega=331 \text{ cm}^{-1}$, and the value of $2.17 \times 10^4 \text{ s}^{-1}$ for the W_0 process at 300 K in the previous expression for a multiphonon process, we can obtain the S_0 value of 0.09 for the ${}^5F_3 \rightarrow ({}^5F_4, {}^5S_2)$ transition. This means that the expected value for W_0 at 12 K should be 6746 s^{-1} compared with the value of 1500 s^{-1} derived from the model. A seventh-order process would give a rate of 87 s^{-1} for this transition. We conclude that the W_0 process must be governed by a mixture of two multiphonon processes of sixth and seventh order (actually $p=6.76$) at lower temperature (12 K) in order to account for its estimated value from the present model.

From Eq. (8) we have

$$P_3 = \frac{(N_2 W_2)}{N_3} \quad \text{at 12 K},$$

where P_3 is a resonant process independent of the temperature. Its calculated value is $1.38 \times 10^4 \text{ s}^{-1}$.

Considering Eqs. (5), (6), and (8)–(10) and Eqs. (5)–(7) and (12)–(14), we calculated the values of $W_{\text{NR}}(1)$ and $W_{\text{NR}}(3)$ at 12 K and $W_{\text{NR}}(2)$ and $W_{\text{NR}}(3)$ at 300 K using the following expressions. At 12 K,

$$W_{\text{NR}}(1) = \frac{2U - N_2 W_2}{N_5} - \frac{1}{\tau_{r5}},$$

$$W_{\text{NR}}(2) \cong 0,$$

$$W_{\text{NR}}(3) = \frac{2U + N(1000) + N_2 W_2}{N_6} - \frac{1}{\tau_{r6}};$$

at 300 K,

$$W_{\text{NR}}(1) \cong 0,$$

$$W_{\text{NR}}(2) = \frac{2U - N_2 W_2}{N_5} - \frac{1}{\tau_{r5}},$$

$$W_{\text{NR}}(3) = \frac{N(1000) + N_2 W_2}{N_6} - \frac{1}{\tau_{r6}}.$$

The calculated values for $W_{\text{NR}}(l)$ are shown in Table VI.

Finally, based on the rate equations (5)–(14) and taking into account the observation that the time to populate any fluorescent level is always shorter than the corresponding decay time, in the HoLiF_4 crystal it was possible to determine the decay time of the states using the expressions

$${}^5F_3: \tau_0^{-1} = W_0 + P_1,$$

$${}^5S_2: \tau_1^{-1} = W_1 + P_2,$$

TABLE VI. Nonradiative probabilities for Ho^{3+} deexcitation derived from the present model for the HoLiF_4 crystal. $W_{\text{NR}}(l)$ represents the nonradiative decay rate induced in the 5I_6 and 5I_7 energy levels due to the presence of the acceptor molecules.

Process	Nonradiative rates (s^{-1})	
	300 K	12 K
P_1	2.17×10^4	2.17×10^4
P_2	1.51×10^5	
P_3	1.38×10^4	1.38×10^4
W_0	2.17×10^4	1.5×10^3
W_2	6.11×10^4	2.20×10^4
N_2	0.17×10^{11}	0.859×10^{11}
$N_2 W_2$	1.039×10^{15}	1.89×10^{15}
W_3	6.23×10^5	$< 1 \times 10^4$
$W_{\text{NR}}(1)^a$	≈ 0	6.25×10^4
$W_{\text{NR}}(2)^b$	8.86×10^4	≈ 0
$W_{\text{NR}}(3)^c$	635.6	566.9

^a $\text{Ho}^{3+}(^5I_6) \rightarrow (0 \rightarrow 1) \text{Mg}^{2+}[(\text{OH})^-]_2$.

^b $\text{Ho}^{3+}(^5I_6) \rightarrow (0 \rightarrow 1 \rightarrow 2) \text{Mg}^{2+}[(\text{OH})^-]_2$.

^c $\text{Ho}^{3+}(^5I_7) \rightarrow (0 \rightarrow 2) \text{HCO}^-$.

$$^5F_5: \tau_2^{-1} = W_2 + \tau_{r2}^{-1},$$

$$^5I_4: \tau_3^{-1} = W_3 + P_3 + \tau_{r3}^{-1},$$

$$^5I_5: \tau_4^{-1} = W_4,$$

$$^5I_6: \tau_5^{-1} = W_{\text{NR}}(1) + W_{\text{NR}}(2) + \tau_{r5}^{-1},$$

$$^5I_7: \tau_6^{-1} = W_{\text{NR}}(3) + \tau_{r6}^{-1}.$$

In Table VII we show the lifetime values (τ_j) calculated from the present model and the measured values for comparison.

Another physical parameter that can be derived from this model, is the population efficiency η_p for the j th fluorescent level defined as

$$\eta_p = \frac{\text{population rate of } j\text{th level}}{\text{excitation rate}}.$$

The population rate of the j th level is given by the left

TABLE VII. Theoretical lifetimes (μs) determined from the present model are compared to the experimental values obtained for the HoLiF_4 crystal at 300 and 12 K. These values were compared to the ones measured for the low-concentration system. A dash indicates that the emission was not observed.

$\text{Ho}^{3+}:\text{YLiF}_4$ (level)	τ (μs)			
	100%		1.71%	
	300 K	12 K	300 K	12 K
	theor	(expt.)	theor	(expt.)
5F_3	23	—	(43)	—
5S_2	—	(6.5)	—	(54)
5F_5	—	(16)	(43)	(100)
5I_4	1.6	—	72	—
5I_6	11.3	—	16	—
5I_7	1400	(1600)	1600	(1400)

part of the corresponding rate equation. The excitation rate is given by U , as defined before. It was very important to calculate η_p for the two lowest excited levels 5I_6 and 5I_7 since they are laser active at 2940 and 2065 nm. Their behavior is represented in Fig. 5 where it is seen that the 5I_7 level is populated more efficiently at 12 K while 5I_6 population is favored at a higher temperature (300 K). It is also shown that the population efficiency value for the 5I_6 level is always higher than unity. There is an increase in η_p from 0.47 to 3.25 for the 5I_7 level when the temperature is lowered to 12 K. When these efficiencies are higher than unity it means that the cross-relaxation probabilities for the energy transfer between Ho ion pairs ($\text{Ho}^*\text{-Ho}$) are more effective than the intra-center relaxations (multiphonon and radiative decays). Each excited Ho^* ion can excite other Ho ions in the ground state. It is important to bear in mind that the excitation energy of the 5F_3 level can be converted into four excitation energies of the 5I_7 level by considering all the energies involved.

The experimental values of η_p (5I_7) can be obtained independently of the rate-equation model by using the relation

$$\eta_p(\text{expt}) = \frac{N_6}{\tau_6 U}, \quad (15)$$

where N_6 is the equilibrium population of 5I_7 level, τ_6 its fluorescent lifetime, and U the excitation rate. The values of $\eta_p(\text{expt})$ as a function of temperature are plotted in Fig. 5 for comparison with the theoretical values from the model. A good agreement is obtained between theoretical and experimental values.

It was demonstrated that the present deexcitation model for Ho^{3+} in the HoLiF_4 crystal needs the inclusion of three nonradiative processes for the deexcitation of the

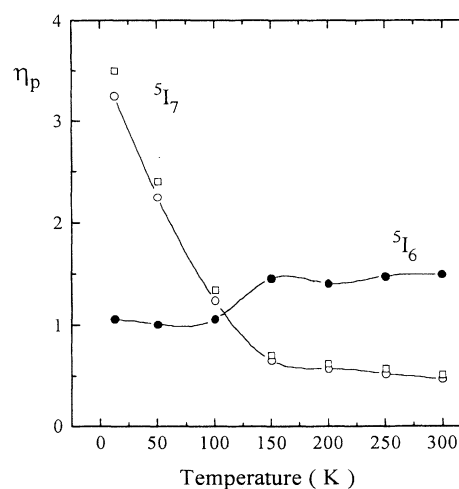


FIG. 5. Temperature dependence of the population efficiency η_p for the 5I_6 and 5I_7 fluorescent levels of the HoLiF_4 crystal derived from the presented model ($\bullet$, $\circ$). The solid line was used as a visual guideline. Experimental values of η_p (5I_7) were obtained from Eq. (15) and plotted for comparison ($\square$).

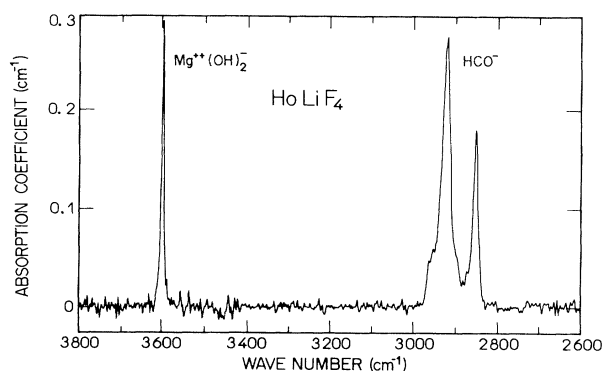


FIG. 6. Infrared spectrum of HoLiF_4 crystals at 300 K. The peak at 3610 cm^{-1} is attributed to the absorption of $\text{Mg}^{2+}[(\text{OH})^-]_2$ complexes. The absorption peaks at 2920 and 2850 cm^{-1} are attributed to HCO^- molecules present in the host in tenths of ppm.

5I_6 and 5I_7 levels, which cannot be justified by any intra-center multiphonon transition (since the energy gap is too large, involving creation of more than 16 local phonons). Clearly the migrating excitation energy from the 5I_6 and 5I_7 levels due to (Ho^*-Ho) exchange is trapped at some convenient Ho^{3+} site, from where it can be efficiently transferred to a nearby acceptor center able to absorb such energy in a quiresonant way. This center should be a particular type of molecular defect having fundamental and overtone absorptions very close to the energy transitions $^5I_6 \rightarrow ^5I_7$ and $^5I_7 \rightarrow ^5I_8$ of Ho^{3+} .

This particular type of molecular defect must have a permanent electric dipole and fundamental absorption between 3650 and 2800 cm^{-1} in order to allow the energy transfer from the Ho^* excited state via an induced (dipole-dipole) interaction. Taking into account the characteristics of such a molecular defect, one must conclude that this particular type of defect acting as an impurity trap in the host HoLiF_4 crystal must contain the OH^- radical. In order to find any trace of molecular impurities which may work like acceptor centers absorbing the energy of the two lowest excited states of the excited Ho^{3+} ions in the HoLiF_4 crystal, we investigated the absorption spectrum of this crystal in the range from 4000 to 1800 cm^{-1} at 300 K.

The infrared spectrum is exhibited in Fig. 6 where several unexpected absorption peaks at 3610, 2920, and

2850 cm^{-1} are seen. The first one, at 3610 cm^{-1} , is attributed to the absorption of $\text{Mg}^{2+}[(\text{OH})^-]_2$ complexes¹¹ and the two others to the HCO^- molecules.¹²⁻¹⁴ These molecular impurities are very commonly introduced in YLiF_4 , LiF , and gadolinium gallium garnet (GGG) laser crystals by contamination during the material preparation and crystal growth process. The fundamental absorption at 3610 cm^{-1} due to $\text{Mg}^{2+}[(\text{OH})^-]_2$ indicates the presence of acceptor impurity centers may trap the migrating energy from the 5I_6 excited level of Ho^{3+} . The calculated induced nonradiative deexcitation rate from the 5I_6 level was $W_{\text{NR}}(1) = 8.86 \times 10^4\text{ s}^{-1}$ at 300 K.

The HCO^- impurity center also observed in the host could be responsible for the partial quenching of the 5I_7 luminescent level since the observed value of this nonradiative probability is two orders of magnitude smaller than for the 5I_6 deexcitation [$W_{\text{NR}}(3) = 635.6\text{ s}^{-1}$ at 300 K].

V. CONCLUSIONS

Considering the evidence shown before, the only reasonable explanation for the observed quenching of the total Ho^{3+} luminescence in the HoLiF_4 crystal begins with the cross-relaxation processes P_1 , P_2 , and P_3 . These processes transfer most of the excited population to the 5I_6 and 5I_7 states, which at the end must efficiently transfer their excitation to acceptor impurity centers. This excitation energy from the 5I_6 and 5I_7 levels migrates through the crystal lattice by (Ho^*-Ho) exchange. It then becomes trapped at some distant Ho^{3+} ion and is modified by a nearby impurity center that dissipates this excitation into the lattice.

Direct involvement of these two types of molecules in the quenching effects of the 5I_6 and 5I_7 levels of Ho^{3+} in YLiF_4 crystals is under investigation at our laboratory. This will provide information on the role of these impurities as quenching centers for rare-earth ions emitting in the mid-infrared.

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