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J. Rubin, A. Brenier, R. Moncorge, C. Pedrini. $\text{Er}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer mechanisms at room temperature in YLiF_4 single crystals. Journal de Physique, 1987, 48 (10), pp.1761-1777. 10.1051/jphys:0198700480100176100 . jpa-00210618

HAL Id: jpa-00210618

<https://hal.science/jpa-00210618>

Submitted on 1 Jan 1987

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Classification
 Physics Abstracts
 78.55 — 42.70F

$\text{Er}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer mechanisms at room temperature in YLiF_4 single crystals

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(Reçu le 30 avril 1987, accepté le 24 juin 1987)

Résumé. — On présente une analyse détaillée des processus de transfert d'énergie entre les ions sensibilisateurs Er^{3+} et activateurs Ho^{3+} dans des monocristaux $\text{YLiF}_4 : \text{Er}^{3+}, \text{Ho}^{3+}$. Cette étude est réalisée à température ambiante sur des matériaux diversement concentrés en ions Ho^{3+} et utilisant différentes excitations laser dans les états excités de Er^{3+} situés dans les domaines optiques visible et proche infra-rouge. L'accent est mis sur l'importance relative des principales voies d'excitation du niveau $^5\text{I}_7$ de Ho^{3+} qui constitue l'état initial de la transition $^5\text{I}_7 \rightarrow ^5\text{I}_8$ intéressante pour l'émission laser caractéristique vers $2 \mu\text{m}$.

Abstract. — A detailed analysis of the energy transfer processes between Er^{3+} sensitizer ions and Ho^{3+} activator ions in $\text{YLiF}_4 : \text{Er}^{3+}, \text{Ho}^{3+}$ single crystals is reported. This study is carried out at room temperature on materials having different Ho^{3+} concentrations and for various selective laser excitations in the excited states of Er^{3+} in the visible and in the infrared optical regions. Emphasis is laid on the relative importance of the main channels of excitation of the $^5\text{I}_7$ level of Ho^{3+} which is the initial state of the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transition of interest for the characteristic $2 \mu\text{m}$ laser emission.

1. Introduction.

This paper reports part of a series of optical studies we have carried out on fluorescence dynamics in the so-called $\alpha\beta$ $\text{YLiF}_4 : \text{Ho}^{3+}$ laser material in which the infra-red laser emission of Ho^{3+} activator ions around $2 \mu\text{m}$ is sensitized by Er^{3+} and Tm^{3+} ions. Such a system has been extensively studied in the past ten years but comparatively only few and often short papers have come out on this subject: the most significant ones are indicated in references [1-6]. However, to optimize the laser material, it is necessary to have a complete knowledge of all the fluorescence processes which strongly depend on the range of excitation and on the impurity ion concentrations.

Our first study was devoted to the optical processes occurring in Er^{3+} single doped and fully concentrated systems [7]. The present optical investigation mainly focuses on the study of the energy transfer mechanisms occurring at room temperature between Er^{3+} sensitizer ions and Ho^{3+} activator ions in co-doped $\text{YLiF}_4 : 50 \% \text{Er}^{3+} : x \% \text{Ho}^{3+}$ ($x = 0.5 ; 2 ; 5$) compounds. The excited state dynamics is studied

within both types of impurities by selective excitation in the various energy levels of Er^{3+} ions. The study consists in recording and analysing the experimental time-dependences of emitting level fluorescences in the infra-red and visible ranges. The optical processes are described in terms of rate equations which apply because fast diffusion is generally involved between the Er^{3+} sensitizers. A special attention is drawn on the different excitation channels by which the $^5\text{I}_7$ lowest excited state of Ho^{3+} is populated, owing to the prime interest of this level which acts as the initial state of the $2 \mu\text{m}$ infra-red laser transition $^5\text{I}_7 \rightarrow ^5\text{I}_8$. Section 3 is devoted to the description and the interpretation of the fluorescence dynamics within the Ho^{3+} ions only and section 4 to the analysis of the various Er^{3+} to Ho^{3+} energy transfers. Concluding remarks are added in section 5.

2. Experimental.

The crystals were grown by the Czochralski method by J. Y. Henry at the L.E.T.I. Laboratory (Grenoble, France). The optical techniques used for

this work are the same as those described in a previous paper [7]. The only change is in the way of recording the infra-red fluorescence decays. Rather than using a P.A.R. Model 162/165 Boxcar Averager, we have most often used either a sampling oscilloscope model 19 860A from Hewlett Packard or a digital oscilloscope model NIC 320 from Nicolet Instruments.

3. Direct excitation and fluorescence dynamics of the Ho^{3+} centres.

3.1 EXPERIMENTAL RESULTS.

3.1.1 $\text{YLiF}_4 : 1\% \text{Ho}^{3+}$. — Figure 1 shows the decay modes and the characteristic time constants of the fluorescences coming from the various energy levels of Ho^{3+} centres following pulsed excitation in the ($^5\text{S}_2$, $^5\text{F}_4$) excited states. It is to be noted that only the $^5\text{I}_4$ state does not emit, because of a probably weak radiative oscillator strength and a rapid multiphonon relaxation. The decays are purely exponential and are preceded by a rise time when the emitting levels are indirectly excited.

Fig. 1. — Time-dependence of the main fluorescences observed in $\text{YLiF}_4 : 1\% \text{Ho}^{3+}$ by excitation of the ($^5\text{S}_2$; $^5\text{F}_4$) level at room temperature.

3.1.2 $\text{YLiF}_4 : 50\% \text{Er}^{3+} : x\% \text{Ho}^{3+}$ ($x = 0.5 ; 2 ; 5$). — In figure 2 are indicated the time-constants of the fluorescences emitted by $^5\text{I}_6$ and $^5\text{I}_7$ when they are directly excited. The decays are purely exponential without any measurable rise time.

x%	0.5	2	5
τ	1.25 ms	1.25 ms	1 ms
τ'	13 ms	16 ms	19 ms
η_T	37%	26%	20%

Fig. 2. — Time constant of the directly excited infrared fluorescence decays of Ho^{3+} observed in $\text{YLiF}_4 : 50\% \text{Er}^{3+} : x\% \text{Ho}^{3+}$ ($x = 0.5, 2, 5$) at room temperature.

3.2 KINETICS OF FLUORESCENCE. — When a level is directly excited, it gives rise to a fluorescence which is proportional to $\exp(-t/\tau)$ and τ then represents the lifetime of this level. In this way the lifetimes of ($^5\text{S}_2$, $^5\text{F}_4$) in $\text{YLiF}_4 : 1\% \text{Ho}^{3+}$ and of $^5\text{I}_6$ and $^5\text{I}_7$ in $\text{YLiF}_4 : 50\% \text{Er}^{3+} : x\% \text{Ho}^{3+}$ were deduced, as indicated in figures 1 and 2, respectively. On the other hand, such a directly excited level feeds that lying just below it so that the fluorescence of the latter with a lifetime τ' is proportional to $\exp(-t/\tau) - \exp(-t/\tau')$ if $\tau' < \tau$. The lifetimes of $^5\text{F}_5$, $^5\text{I}_6$ and $^5\text{I}_7$ in $\text{YLiF}_4 : 1\% \text{Ho}^{3+}$ are deduced accordingly and are indicated in figure 1. The $^5\text{I}_5$ excited level is very short lived ($< 2\mu\text{s}$); its fluorescence decay is exactly the same as that of level $^5\text{F}_5$ and level $^5\text{F}_5$ feeds level $^5\text{I}_5$ via $^5\text{I}_4$ by rapid multiphonon relaxations. The increase of the observed $^5\text{I}_7$ fluorescence lifetime in $\text{YLiF}_4 : 50\% \text{Er}^{3+} : x\% \text{Ho}^{3+}$ with Ho^{3+} concentration x , may be tentatively explained by the occurrence of radiative energy transfers among the Ho^{3+} ions : the fluorescence emitted by one centre at around $2\mu\text{m}$ is absorbed by another centre within a photon travel distance. Indeed, it can be expected that the observed radiative emission rate decreases according to a relation of the type :

$$\frac{1}{\tau_1} = \frac{1}{\tau^0} - KN$$

where τ^0 is the emission rate without transfer, N represents the total number of Ho^{3+} ions in each sample and K a transfer rate which depends on their

particular geometry. As we have worked with crystals having about the same geometric characteristics (shape and volume), the product KN can be considered as proportional to x , the Ho³⁺ concentration. Then the observed radiative emission rate can be written as :

$$\frac{1}{\tau_1'} = \frac{1}{\tau_0} - kx \quad (1)$$

an expression which fits the data reported in the table associated to figure 2 well.

A discussion is also necessary concerning the different lifetimes of level ⁵I₆ obtained in the same co-doped crystals in which the Ho³⁺ ions are either directly or indirectly — *via* Er³⁺ → Ho³⁺ energy transfer — excited : indeed, under direct excitation of level ⁵I₆ of Ho³⁺, the ⁵I₆ fluorescence lifetime τ equals 1.25, 1.25 and 1 ms in YLiF₄ : 50 % Er³⁺ ; x % Ho³⁺ with $x = 0.5, 2$ and 5 respectively (see the Tab. in Fig. 2), whereas, by exciting the Er³⁺ ions, the ⁵I₆ fluorescence lifetime τ_2' takes the values 2.1, 1.75 and 1.3 ms (see Tab. I). We also note that the

2 ms value which is found in the 1 % Ho³⁺ doped crystal agrees well with the Ho³⁺ concentration dependence indicated by these last results. This can be explained as follows. The only difference between the above two situations is that in one case all the Er³⁺ ions are in their ground state while, in the other case, some of them have been brought in their excited states. It can be considered that an energy transfer process from Ho³⁺ to Er³⁺ starts from levels ⁵I₆ and ⁴I_{15/2}. It can be a transfer of type ⁵I₆, ⁴I_{15/2} → ⁵I₈, ⁴I_{13/2} and the smaller the number of Er³⁺ ions in their excited state, the stronger the transfer process. If τ stands for the ⁵I₆ fluorescence lifetime in the presence of N_0 Er³⁺ ions in their ground state ⁴I_{15/2} (Tab. associated to Fig. 2) and τ_2' the ⁵I₆ lifetime when level ⁵I_{15/2} is partly depopulated or when there is no Er³⁺ ion at all, one can write :

$$\frac{1}{\tau} = \frac{1}{\tau_2'} + kN_0 \quad (2)$$

so that $\tau < \tau_2'$.

This transfer occurs with a rather strong efficiency that we label η_T . η_T is given by

$$\eta_T = 1 - \frac{\tau}{\tau_2'} \quad (3)$$

The η_T values are given in the table of figure 2.

Table I. — Lifetimes τ assigned to the excited states of Er³⁺ and Ho³⁺ in YLiF₄ : 50 % Er³⁺ ; x % Ho³⁺ ($x = 0.5, 2, 5$) and used in the models. Quantum efficiencies of energy transfers :

- (i) η_{T_1} : ⁴I_{13/2}, ⁵I₈ → ⁴I_{15/2}, ⁵I₇.
- (ii) η_{T_2} : ⁴I_{11/2}, ⁵I₈ → ⁴I_{15/2}, ⁵I₆ via excitation in ⁴I_{9/2} of Er³⁺.
- (iii) $\eta_{T_2}^*$: ⁴I_{11/2}, ⁵I₈ → ⁴I_{15/2}, ⁵I₆ via excitation in ⁴I_{11/2} of Er³⁺.

Ho ³⁺ + concentration	0 %	0.5 %	2 %	5 %
$\tau_1(^4I_{13/2})$	6 ms	1.5 ms	400 μ s	220 μ s
$\tau_2(^4I_{11/2})$	3 ms	1.5 ms	800 μ s	500 μ s
$\tau_3(^4I_{9/2})$	10 μ s	10 μ s	10 μ s	10 μ s
$\tau_4(^4F_{9/2})$	/	20 μ s	5 μ s	5 μ s
$\tau_5(^4S_{3/2})$	/	7 μ s	7 μ s	7 μ s
$\tau_1'(^5I_7)$	/	13 ms	16 ms	19 ms
$\tau_2'(^5I_6)$	/	2.1 ms	1.75 ms	1.3 ms
η_{T_1}	0 %	75 %	93 %	96 %
η_{T_2}	0 %	50 %	73 %	83 %
$\eta_{T_2}^*$	0 %	24 %	38 %	50 %

4. Er³⁺ → Ho³⁺ energy transfers in co-doped YLiF₄.

4.1 GENERAL RESULTS. — In figures 3, 4, 5, 6, 7 are presented the time dependences of the visible and infrared fluorescences originating from the various energy levels of Ho³⁺ and Er³⁺ and detected for different Er³⁺ excitations. The various decay modes are strongly influenced by the way of pumping, in particular by the up-conversion processes occurring in the Er³⁺ centres and that we have analysed in details before [7]. Excitations in the low energy infrared levels of Er³⁺ give rise to anti-Stokes fluorescences originating from upper levels with long-lived behaviours. Direct excitations in these upper levels of Er³⁺ in the visible region induce similar long-lived visible fluorescences, but after a very short decay that is assigned to rapid radiative and non-radiative relaxations within the Er³⁺ ions.

Table I gathers all the lifetimes of the excited states of interest in YLiF₄ : 50 % Er³⁺ ; x % Ho³⁺. Explanations and comments are given in the subsequent Er³⁺ → Ho³⁺ energy transfer study.

4.2 Er³⁺ → Ho³⁺ ENERGY TRANSFERS.

4.2.1 ⁴I_{13/2}, ⁵I₈ → ⁴I_{15/2}, ⁵I₇. — This transfer is pointed out by exciting in level ⁴I_{13/2} of Er³⁺ and is depicted

Fig. 6. — Excitation of level $4F_{9/2}$ (and $5F_5$). Fig. 7. — Excitation of level $2H_{11/2}$.

Figs. 3-7. — Time dependence of the main fluorescences of Ho^{3+} and Er^{3+} in YLiF_4 : 50 % Er^{3+} ; x % Ho^{3+} ($x = 0.5, 2, 5$) at room temperature. The decays enclosed by a dashed line are plotted in a semi-log scale while the other ones are drawn in a linear scale. Double lines indicate laser excitations while single lines are related to observed emission transitions.

in figure 8. The rate equation for the $4I_{13/2}$ population density can be written :

$$\dot{N}_1 = -\frac{N_1}{\tau_1^0} - k_1 N_0' N_1 \quad (4)$$

so

$$\dot{N}_1 = -\left[\frac{1}{\tau_1^0} + k_1 N_0'\right] N_1 \quad (5)$$

where k_1 stands for the transfer constant and where N_0' , the $5I_8$ population density of Ho^{3+} , is supposed to be constant. τ_1^0 is the fluorescence lifetime of level

$4I_{13/2}$ of Er^{3+} in the absence of $\text{Er} \rightarrow \text{Ho}$ energy transfer. The solution of equation (5) gives rise to an exponential decay with the time constant τ_1 such as :

$$\frac{1}{\tau_1} = \frac{1}{\tau_1^0} + k_1 N_0' \quad (6)$$

Expression (6) predicts a decrease of τ_1 , the fluorescence lifetime of level $4I_{13/2}$ in case of $\text{Er} \rightarrow \text{Ho}$ energy transfer, when the Ho^{3+} activator concentration N_0' increases and this agrees well with the data (see Fig. 9 ; Fig. 10 curve (a) and Tab. I).

Fig. 8. — Energy transfer ${}^4I_{13/2}$, ${}^5I_8 \rightarrow {}^4I_{15/2}$, 5I_7 .

Fig. 9. — Experimental fluorescence decays from level ${}^4I_{13/2}$ of Er^{3+} for various Ho^{3+} concentrations in case of ${}^4I_{13/2}$ excitation.

Fig. 10. — Deexcitation probabilities of level ${}^4I_{13/2}$ (curve a) and level ${}^4I_{15/2}$ (curve b) via $\text{Er}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer at different Ho^{3+} concentrations.

Using this expression gives the energy transfer quantum rate :

$$\eta_{T_1} = 1 - \frac{\tau_1}{\tau_1^0} \quad (7)$$

The value of τ_1^0 is deduced from curve (a) of

figure 10 at $N_0' = 0$ and is used in expression (7) to estimate η_{T_1} (Tab. I). Its large magnitude shows that this ${}^4I_{13/2}$, ${}^5I_8 \rightarrow {}^4I_{15/2}$, 5I_7 energy transfer is very efficient.

In addition to the emission of ${}^4I_{13/2}$ of Er^{3+} the ${}^5I_7 \rightarrow {}^5I_8$ radiative transition of Ho^{3+} around $2 \mu\text{m}$ is observed. The rate equation describing the population N_1' of 5I_7 is then :

$$\dot{N}_1' = -\frac{N_1'}{\tau_1'} + (k_1 N_0') N_1 \quad (8)$$

the solution of which is

$$N_1' \approx \exp\left[-\frac{t}{\tau_1'}\right] - \exp\left[-\frac{t}{\tau_1}\right] \quad (9)$$

This expression (9) fits the experimental data (Fig. 11) quite well.

Fig. 11. — Time dependence of Ho^{3+} emission from 5I_7 level in case of ${}^4I_{13/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) x = 0.5 ; (b) x = 2 ; (c) x = 5. Solid lines represent the best fits to experimental data obtained from the solution of expression (9).

4.2.2 $^4I_{11/2}$, $^5I_8 \rightarrow ^4I_{15/2}$, 5I_6 . — This energy transfer, easily observed by exciting in level $^4I_{9/2}$ of Er³⁺, is shown in figure 12. Direct excitation in level $^4I_{11/2}$ will be studied later because it leads to more complicated fluorescence dynamics (subsection 4.3.2). The present transfer can be analysed as before.

Fig. 12. — Energy transfer $^4I_{11/2}$, $^5I_8 \rightarrow ^4I_{15/2}$, 5I_6 .

The shortening of the $^4I_{11/2}$ fluorescence decay when the Ho³⁺ concentration is increased (Fig. 5) can be interpreted according to the notations of figure 12 by using the following rate equations :

$$N_3 = N_3^0 \exp(-t/\tau_3) \quad (10)$$

$$\dot{N}_2 = -\frac{N_2}{\tau_2} - (k_2 N_0') N_2 + A_{32} N_3 \quad (11)$$

where A_{32} is the non-radiative relaxation probability between levels $^4I_{9/2}$ and $^4I_{11/2}$.

If we set

$$\frac{1}{\tau_2} = \frac{1}{\tau_2^0} + k_2 N_0' \quad (12)$$

the solution of equation (11) is then :

$$N_2 \approx \exp\left[-\frac{t}{\tau_2}\right] - \exp\left[-\frac{t}{\tau_3}\right]. \quad (13)$$

The linear dependence of $\frac{1}{\tau_2}$ with N_0' predicted by expression (12) is experimentally verified in figure 10 curve b.

As in the previous case, one can calculate the

quantum efficiency η_{T_2} of the present transfer labelled T_2 by using the relation :

$$\eta_{T_2} = 1 - \frac{\tau_2}{\tau_2^0} \quad (14)$$

and the results are gathered in table I. One observes the same trend as for the previous transfer with efficiencies lightly weaker but still large enough to consider this energy transfer as a very important process.

The time-dependence of the infra-red fluorescence originating from level 5I_6 of Ho³⁺ has been studied and will be presented and discussed subsequently (subsection 4.3.2).

4.2.3 $^4F_{9/2}$, $^5I_8 \rightarrow ^4I_{15/2}$, 5F_5 . — This transfer is obtained by exciting in level $^4F_{9/2}$ of Er³⁺ as indicated in figure 13. Both red emissions, the one $^4F_{9/2} \rightarrow ^4I_{15/2}$ occurring in Er³⁺ centres and the other $^5F_5 \rightarrow ^5I_8$ in Ho³⁺ ions, have exactly the same time-dependence (Fig. 6). This indicates that levels 5F_5 and $^4F_{9/2}$ are thermalized by a transfer process which is efficient in the two directions because the levels have nearly the same energy. Furthermore when they are obtained by exciting in level $^2H_{11/2}$ of Er³⁺ (Fig. 7), these red emissions have again the same time-dependence, confirming the above thermalization process.

Fig. 13. — Energy transfer $^4F_{9/2}$, $^5I_8 \rightarrow ^4I_{15/2}$, 5F_5 .

4.2.4 $^4S_{3/2}$, $^5I_8 \rightarrow ^4I_{15/2}$, (2S_2 ; 5F_4). — Excitation in level $^2H_{11/2}$ of Er³⁺ followed by a rapid non-radiative relaxation to $^4S_{3/2}$ also gives rise to such a transfer (see in Fig. 14). Like before, the time-dependences of the green fluorescences $^5S_2 \rightarrow ^5I_8$ of Ho³⁺ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ of Er³⁺ are identical, thus indicating

Fig. 14. — Energy transfer ${}^4S_{3/2}$, ${}^5I_8 \rightarrow {}^4I_{15/2}$, (5S_2 ; 5F_4).

now a transfer induced thermalization of levels 5S_2 and ${}^4S_{3/2}$.

4.3 DISCUSSION. — The best laser systems will be those which give rise to the most efficient infra-red emission ${}^5I_7 \rightarrow {}^5I_8$ near $2\ \mu\text{m}$. It is therefore particularly interesting to know about the main deexcitation channels which populate the 5I_7 metastable state of Ho^{3+} when Er^{3+} excitation is used.

The $2\ \mu\text{m}$ infra-red fluorescence occurring after

various excitations of Er^{3+} ions can be explained by considering three main deexcitation channels that we call IR1, IR2 and RED by taking into account the energy transfers previously described (Fig. 15). Two remarks can be made: (i) The transfer ${}^4S_{3/2} \rightarrow {}^5S_2$ does not give rise to an efficient « green » channel to level 5I_7 , as it will be seen later (ii) the above three channels always coexist: the IR1 and IR2 channels occur even if the upper levels of Er^{3+} are excited because of one-centre energy relaxations and the RED channel is efficient even if the lower excited states of Er^{3+} are excited due to up-conversion mechanisms in these ions [7]. However the relative probability of these three channels strongly depends on the Er^{3+} sensitizer energy level which is directly excited.

4.3.1 IR1 deexcitation channel. — This channel is strongly efficient mostly after direct excitation of ${}^4I_{13/2}$, as it has been seen previously and in most cases it occurs alone.

4.3.2 Competition between the IR1 and IR2 channels. — The excitation energy goes through simultaneously both IR1 and IR2 channels when ${}^4I_{11/2}$, ${}^4I_{9/2}$ or ${}^2H_{11/2}$ are directly excited.

*** Excitation of level ${}^4I_{9/2}$.** — The excitation energy relaxes in Er^{3+} ions by the following two possible channels called α and β . Channel α leads to the only IR1 whereas channel β feeds both IR1 and IR2. The solutions of the rate equations for levels ${}^4I_{9/2}$ (#3) and ${}^4I_{11/2}$ (#2) (see Figs. 12 and 15) have been

Fig. 15. — Main channels of Ho^{3+} excitation via $\text{Er}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer and self-quenching mechanisms within Er^{3+} ions.

already derived (Expr. (10) and (13), respectively), while the rate equation for level ${}^4\text{I}_{13/2}$ (# 1) is :

$$\dot{N}_1 = -\frac{N_1}{\tau_1} + A_{31} N_3 + A_{21} N_2 \quad (15)$$

where $A_{31} N_3$ and $A_{21} N_2$ represent the channels α and β , respectively. The solutions of equation (15) are represented in figure 16 by taking into account only one or both channel(s) of deexcitation. It is clear that the experimental ${}^4\text{I}_{13/2}$ fluorescence decays are well fitted by the solution of equation (15) only when both channels are considered. It is to be noted that the channel α is supposed to occur *via* a transfer ${}^4\text{I}_{9/2}, {}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{13/2}, {}^4\text{I}_{13/2}$ in co-doped crystals contain-

ing 50 % Er^{3+} whereas this transfer was found to be quite negligible in single-doped material containing only 1 % Er^{3+} [7]. On the other hand, its efficiency was found to be so high in ErLiF_4 that the channel β which likely occurs *via* multiphonon relaxation was completely negligible. The co-doped crystals with 50 % Er^{3+} ions lead to the intermediate case where both channels coexist.

The IR2 deexcitation channel populates level ${}^5\text{I}_6$ of Ho^{3+} according to the equation :

$$\dot{N}'_2 = -\frac{N'_2}{\tau_2} + (k_2 N'_0) N_2. \quad (16)$$

Its solution is compared with the experimental time-dependence of the fluorescence ${}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ (Fig. 17). For the Ho^{3+} higher concentration (5 %) the fit is quite good (curve c) because the transfer ${}^4\text{I}_{11/2} \rightarrow {}^5\text{I}_6$ is very efficient, while for the other Ho^{3+} concentra-

Fig. 16. — Time dependence of Er^{3+} emission from level ${}^4\text{I}_{13/2}$ in case of ${}^4\text{I}_{13/2}$ excitation in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (15) when α channel or β channel or both channels ($\alpha + \beta$) is (are) involved.

Fig. 17. — Time dependence of Ho^{3+} emission from level ${}^5\text{I}_6$ in case of ${}^4\text{I}_{9/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (16).

tions (2 and 0.5 %) for which this transfer is weaker, the agreement is less satisfying (curves b and c). Probably the RED channel is activated by up-conversion processes within the Er^{3+} ions and may partially contribute to the feeding of level $^5\text{I}_6$.

Level $^5\text{I}_7$ can be populated by both IR1 and IR2 deexcitation channels. The corresponding rate equation for level $^5\text{I}_7$ is given by :

$$\dot{N}'_1 = -\frac{N'_1}{\tau'_1} + A'_{21} N'_2 + (k_1 N'_0) N_1. \quad (17)$$

The numerical solution fits the data for the $^5\text{I}_7$

Fig. 18. — Time dependence of Ho^{3+} emission from level $^5\text{I}_7$ in case of $^4\text{I}_{9/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} ; x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (17) when IR₁ channel or IR₂ channel or both channels (IR₁ + IR₂) is (are) involved.

fluorescence very well only when both channels are involved (Fig. 18). So the IR1 and IR2 channels are predominant and both active in the feeding of the $^5\text{I}_7$ level.

* Excitation of level $^2\text{H}_{11/2}$. — First of all we have ruled out the two feeding processes of level $^5\text{I}_6$ of Ho^{3+} which borrows the so-called RED channel as follows (Fig. 15)

Indeed, in this way, the $^5\text{I}_6$ population density is governed by the rate equation :

$$\dot{N}'_2 = -\frac{N'_2}{\tau'_2} + A'_{42} N'_4 \quad (18)$$

where A'_{42} is the probability of relaxation between levels $^5\text{F}_5$ and $^5\text{I}_6$. τ'_2 is given in table I. When use is made of the experimental fluorescence decay of level $^5\text{F}_5$ or $^5\text{I}_5$ (since they are the same) for N'_4 the solution of equation (18) cannot fit correctly the $^5\text{I}_6$ fluorescence data for all the Ho^{3+} concentrations (Fig. 19). Here is to be noted that the fluorescence decay of levels ($^5\text{S}_2 - ^4\text{S}_{3/2}$) following pulsed excitation of level $^2\text{H}_{11/2}$ of Er^{3+} is very complex and consists first of a very short decay correlated with the short lifetime of the thermalized coupled levels, followed by a risetime behaviour and a long time decay due to refeeding of the levels by up-conversion mechanisms which were shown to be very efficient in Er^{3+} [7]. The conclusion is that the $^4\text{F}_{9/2}$ state is short-circuited in case of $^2\text{H}_{11/2}$ excitation by cross-relaxation processes in Er^{3+} indicated in figure 15 and already pointed out [7] :

These mechanisms give rise to the IR2 channel which then populates level $^5\text{I}_6$ according to the system of equations :

$$\begin{aligned} N_5 &\approx \exp\left[-\frac{t}{\tau_s}\right] \\ \dot{N}_3 &= -\frac{N_3}{\tau_3} + A_{53} N_5 \\ \dot{N}_2 &= -\frac{N_2}{\tau_2} + A_{32} N_3 \\ \dot{N}'_2 &= -\frac{N'_2}{\tau'_2} + (k_2 N'_0) N_2 . \end{aligned} \quad (19)$$

The solution for N'_2 is fitted to the time-dependence of the fluorescence $^5\text{I}_6 \rightarrow ^5\text{I}_8$ (Fig. 20). The agreement between the model and the experimental data is

Fig. 19. — Time dependence of Ho^{3+} emission from level $^5\text{I}_6$ in case of $^2\text{H}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (18).

Fig. 20. — Time dependence of Ho^{3+} emission from level $^5\text{I}_6$ in case of $^2\text{H}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expressions (19).

rather good for higher Ho^{3+} concentrations (5 and 2 %) (curves c and b, respectively), but rather bad for the low concentration (0.5 %), although the description of the risetime is appreciably improved (curve a). This means that for such low concentration, the cross-relaxation is not so dominant. It is evident however from figures 19 and 20, curves (a), that a superposition of the two models is still unable to interpret the rapid risetime of the $^5\text{I}_6$ fluorescence. At this time we have no simple explanation to propose.

As a matter of fact, the $^4\text{I}_{13/2}$ level of Er^{3+} is likely populated by three fluxes : one is due to the above mentioned cross-relaxation processes and the two other ones are the α and β channels, so that the rate equation for this state is :

$$\dot{N}_1 = -\frac{N_1}{\tau_1} + \underset{\text{cross relaxation}}{A_{51} N_5} + \underset{\alpha \text{ channel}}{A_{31} N_3} + \underset{\beta \text{ channel}}{A_{21} N_2} \quad (20)$$

The best fits of the solution of equation (20) to the experimental time-dependence of the $^4\text{I}_{13/2}$ fluorescence are given in figure 21 in the following three cases : (i) the cross-relaxation process is only involved (ii) the α and β channels only occur and in the same relative proportions as those deduced when the Er^{3+} ions are excited in level $^4\text{I}_{9/2}$ and (iii) the cross-relaxation and α and β channels occur simultaneously. It is clear that the best fits are obtained in the last case.

Fig. 21. — Time dependence of Er^{3+} emission from level $^4\text{I}_{13/2}$ in case of $^2\text{H}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} ; x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (20) when is (are) involved: (i) only the cross-relaxation (C.R.) process (ii) only both α and β channels ($\alpha + \beta$) (iii) the cross-relaxation and α and β channels (C.R. + $\alpha + \beta$).

Let us consider now the $^5\text{I}_7$ level of Ho^{3+} . It is populated *via* the IR1 and IR2 channels and its rate equation may be written as:

$$\dot{N}'_1 = -\frac{N'_1}{\tau'_1} + A'_{21} N'_2 + (k_1 N'_0) N_1 \quad (21)$$

the solution of which is fitted to the experimental $^5\text{I}_7$ fluorescence time-dependence in the three following cases (i) the IR1 channel occurs alone (ii) the IR2 channel occurs alone (iii) IR1 and IR2 occur

Fig. 22. — Time dependence of Ho^{3+} emission from level $^5\text{I}_7$ in case of $^2\text{H}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} ; x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (21) when channel IR₁, channel IR₂ or both channels (IR₁ + IR₂) is (are) involved.

simultaneously (Fig. 22). It is shown that for high Ho^{3+} concentrations (2 and 5 %, curves b and c) both channels are efficient whereas for 0.5 % (curve a) IR1 dominates in the $^5\text{I}_7$ population process.

* Excitation of level $^4\text{I}_{11/2}$. — The large initial population of $^4\text{I}_{11/2}$ makes dominant the up-conversion process previously described in [7]: $^4\text{I}_{11/2}$, $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2}$ (*via* $^2\text{H}_{11/2}$) (Fig. 15). Consequently the fluorescence decay of the transition $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$

is not exponential while the same fluorescence is found to decay exponentially for other excitations when up-conversion is actually negligible (Figs. 5-6-7). The rate equation for level ⁴I_{11/2} is :

$$\dot{N}_2 = -\frac{N_2}{\tau_2^0} - (k_2 N_0') N_2 - k N_2^2. \quad (22)$$

The solution fits the experimental data very well (Fig. 23). Two remarks can be made. First, the only fitting parameter in equation (22) is k since τ_2^0 and $k_2 N_0' = \frac{1}{\tau_2} - \frac{1}{\tau_2^0}$ are deduced from figure 10, curve b. Second, we have shown in a previous paper [7] that an excited state absorption mechanism

occurs in addition to up-conversion and can be included in the last term of expression (22) since both processes depend on the square of the ⁴I_{11/2} population.

The IR2 channel transfers energy into level ⁵I₆ of Ho³⁺ with a quantum efficiency :

$$\eta_{T_2}^* = \frac{1}{N_2^0} \int_0^\infty k_2 N_0' N_2 dt \quad (23)$$

where N_2^0 stands for the initial ($t = 0$) ⁴I_{11/2} population density.

Calculated values of $\eta_{T_2}^*$ are reported in table I. As expected, $\eta_{T_2}^*$ is much weaker than η_{T_2} found by excitation of level ⁴I_{9/2} : the difference represents the part of the energy carried away by up-conversion.

The population density of level ⁵I₆ verifies the equation :

$$\dot{N}_2' = -\frac{N_2'}{\tau_2'} + (k_2 N_0') N_2. \quad (24)$$

One can see in figure 24 that the best fits obtained with the solution N_2' of equation (24) are rather satisfactory but not so good as those we have obtained in the previous cases.

As outlined above, the excitation of level ⁴I_{11/2} induces an absorption of the laser pulse in the ⁴I_{11/2} excited state which populates level ⁴S_{3/2}. It follows that level ⁴I_{13/2} can be fed by the same cross-relaxation process in Er³⁺ as in the case of ²H_{11/2} excitation. The ⁴I_{13/2} population is then governed by the rate equation :

$$\dot{N}_1 = -\frac{N_1}{\tau_1} + A_{21} N_2 + A_{51} N_5 \quad (25)$$

with $N_5 = N_5^0 \exp\left(-\frac{t}{\tau_5}\right)$.

The solution is compared to the time-dependence of the fluorescence ⁴I_{13/2} → ⁴I_{15/2} in figure 25.

It is evident that the contribution of level ⁴S_{3/2} (via excited state absorption and cross-relaxation) to the population of level ⁴I_{13/2} is needful to explain the relatively fast rise-time of the fluorescence. Indeed if the ⁴I_{11/2} excitation is considered as the only population source for level ⁴I_{13/2}, the calculated risetime is much too slow. If both ⁴I_{11/2} and ⁴S_{3/2} levels are taken into account, then the agreement with the experimental data is very good.

The ⁵I₇ population density of ⁵I₇ is governed by the IR1 and IR2 channels according to the equation :

$$\dot{N}_1' = -\frac{N_1'}{\tau_1'} + (k_1 N_0') N_1 + A_{21}' N_2'. \quad (26)$$

It appears again that the fits to the time-dependence

Fig. 23. — Time dependence of Er³⁺ emission from level ⁴I_{13/2} in case of ⁴I_{11/2} excitation of Er³⁺ in YLiF₄ : 50 % Er³⁺ : x % Ho³⁺ for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (22).

Fig. 24. — Time dependence of Ho^{3+} emission from $^5\text{I}_6$ level in case of $^4\text{I}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (24).

of the fluorescence $^5\text{I}_7 \rightarrow ^5\text{I}_8$ are really good only when both channels occur simultaneously (Fig. 26).

4.3.3 Competition between RED and IR1 channels. — These two channels compete only in the case of $^4\text{F}_{9/2}$ excitation.

The excited state dynamics in Er^{3+} is quite similar to what was already observed for excitation of level $^4\text{I}_{9/2}$. The energy gradually falls down according to the two main ways :

The analysis of the decays of the various Er^{3+} energy levels does not bring more information about the fluorescence dynamics than before.

Fig. 25. — Time dependence of Er^{3+} emission from level $^4\text{I}_{13/2}$ in case of $^4\text{I}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (25) when only $^4\text{I}_{11/2}$ or $^4\text{S}_{3/2}$ or both levels ($^4\text{I}_{11/2} + ^4\text{S}_{3/2}$) take(s) part in the fluorescence process.

In Ho^{3+} , it is described by the set of rate equations :

$$N_4' \approx \exp\left(-\frac{t}{\tau_4}\right) \quad (27)$$

$$\dot{N}_2' = -\frac{N_2'}{\tau_2} + \underbrace{A_{42}' N_4'}_{\text{RED channel}} + \underbrace{(k_2 N_0') N_2}_{\text{IR2 channel}} \quad (28)$$

$$\dot{N}_1' = -\frac{N_1'}{\tau_1} + \underbrace{A_{21}' N_2'}_{\text{RED channel}} + \underbrace{(k_1 N_0') N_1}_{\text{IR1 channel}} + \underbrace{\quad}_{\text{IR2 channel}} \quad (29)$$

Fig. 26. — Time dependence of Ho^{3+} emission from level $^5\text{I}_7$ in case of $^4\text{I}_{11/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (26) when only IR_1 channel or IR_2 channel or both channels ($\text{IR}_1 + \text{IR}_2$) is (are) involved.

Fig. 27. — Time dependence of Ho^{3+} emission from level $^5\text{I}_6$ in case of $^4\text{F}_{9/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} : x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (28) when RED or IR_2 channel is involved.

In figure 27, the solution of expression (28) is compared with the time-dependence of the $^5\text{I}_6 \rightarrow ^5\text{I}_8$ fluorescence. It is remarkable that the RED channel is largely predominant in the feeding process of $^5\text{I}_6$. Therefore, the solution of (29) is obtained by neglecting the third term in (28) and is compared in figure 28 with the time-dependence of the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ emission. The fits clearly show that both RED and IR_1 channels occur to feed $^5\text{I}_7$.

5. Concluding remarks.

From the numerous results obtained through this systematic study, important information can be extracted about the excited state dynamics in the Er^{3+} and Ho^{3+} doped YLiF_4 laser system. Since we are mainly interested in the $2\text{ }\mu\text{m}$ $^5\text{I}_7 \rightarrow ^5\text{I}_8$ laser transition of Ho^{3+} , we want to summarize now on the respective contributions of each excitation chan-

Fig. 28. — The dependence of Ho^{3+} emission from level $^5\text{I}_7$ in case of $^4\text{F}_{9/2}$ excitation of Er^{3+} in YLiF_4 : 50 % Er^{3+} ; x % Ho^{3+} for (a) $x = 0.5$; (b) $x = 2$; (c) $x = 5$. Solid lines represent the best fits to experimental data obtained from the solution of expression (29) in which IR_2 channel is neglected and when IR_1 channel or RED channel or both channels ($\text{IR}_1 + \text{RED}$) is (are) involved.

nel to the population of the $^5\text{I}_7$ level. Thus we have calculated the relative efficiency of each channel for various excitations of the Er^{3+} ions, and the values are gathered in table II. They have been obtained from the fits of appropriate models to the time-dependent intensity of the $^5\text{I}_7 \rightarrow ^5\text{I}_8$ fluorescence (Figs. 11, 18, 22, 26, 28). These results show that the so-called IR_1 channel strongly dominates excepted in the case of excitation of the $^4\text{F}_{9/2}$ level for crystal containing 5 % Ho^{3+} ions. Fortunately this channel is the most desirable one since it gives the shortest risetime on $^5\text{I}_7$ which is the initial state of the laser transition $^5\text{I}_7 \rightarrow ^5\text{I}_8$. It is clear that for a given Ho^{3+} concentration, the most favourable excitations

Table II. — Relative contribution of each channel of excitation to the $^5\text{I}_7$ level of Ho^{3+} as a function of the Er^{3+} excitation level.

Excitation	Ho^{3+} concentration			
	0.5 %	2 %	5 %	
$^4\text{I}_{13/2}$	IR_1 100 %	IR_1 100 %	IR_1 100 %	
$^4\text{I}_{11/2}$	$\text{IR}_1 + \text{IR}_2$ 57 % 43 %	$\text{IR}_1 + \text{IR}_2$ 79 % 21 %	$\text{IR}_1 + \text{IR}_2$ 94 % 6 %	
$^4\text{I}_{9/2}$	$\text{IR}_1 + \text{IR}_2$ 92 % 8 %	$\text{IR}_1 + \text{IR}_2$ 82 % 18 %	$\text{IR}_1 + \text{IR}_2$ 66 % 34 %	
$^4\text{F}_{9/2}$	$\text{IR}_1 + \text{RED}$? ?	$\text{IR}_1 + \text{RED}$ 88 % 12 %	$\text{IR}_1 + \text{RED}$ 26 % 74 %	
$^2\text{H}_{11/2}$	IR_1 100 %	$\text{IR}_1 + \text{IR}_2$ 72 % 28 %	$\text{IR}_1 + \text{IR}_2$ 88 % 12 %	

are those for which the relative efficiency of the IR_1 channel is as large as possible. From this point of view, of course, excitation of level $^4\text{I}_{13/2}$ is very suitable but powerful infra-red light sources around $1.5 \mu\text{m}$ are not easily available for optical pumping. Excitations of levels $^4\text{I}_{11/2}$ and $^4\text{I}_{9/2}$ also have to be considered, depending on the Ho^{3+} concentration. In the visible range, there is no doubt that green excitation of $^2\text{H}_{11/2}$ level is very favourable whatever the Ho^{3+} concentration. This result is very important because it is well-known that in this range of excitation, many powerful light sources (lasers and lamps) are available. Finally, one notes that because of efficient excited-state absorption and up-conversion phenomena, excitation of level $^4\text{I}_{11/2}$ or $^2\text{H}_{11/2}$ gives very similar results: the IR_1 channel relative efficiency remains strong at the highest 5 % Ho^{3+} concentration. This does not apply in the case of the $^4\text{I}_{9/2}$ or $^4\text{F}_{9/2}$ excitation. Also, in view of the pump sources to be considered, a 5 % Ho^{3+} concentration seems to be reasonable when the system is to be pumped for example in level $^2\text{H}_{11/2}$ with the 532 nm second-harmonic radiation of a $\text{YAG} : \text{Nd}^{3+}$ laser. On the other hand, a compromise i.e. a lower Ho^{3+} concentration might be more suitable in case of broad band flash lamp excitation. This will be clarified in a subsequent work with direct measurements of excitation quantum efficiencies.

Acknowledgments.

This work was supported by the DRET grant # 84/071. The authors wish to thank M. J. Y. Henry from the L.E.T.I. Laboratory (Grenoble, France) who grew the single crystals.

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