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To cite this version:
J. Rubin, A. Brenier, R. Moncorge, C. Pedrini. Er3+ → Ho3+ energy transfer mechanisms at room temperature in YLiF4 single crystals. Journal de Physique, 1987, 48 (10), pp.1761-1777. <10.1051/jphys:0198700480100176100>. <jpa-00210618>
Er$^{3+} \rightarrow$ 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 YLiF$_4$: Er$^{3+}$, 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 $^5I_7$ de Ho$^{3+}$ qui constitue l’état initial de la transition $^5I_7 \rightarrow ^5I_8$ intéressante pour l’émission laser caractéristique vers 2 $\mu$m.

Abstract. — A detailed analysis of the energy transfer processes between Er$^{3+}$ sensitizer ions and Ho$^{3+}$ activator ions in YLiF$_4$: Er$^{3+}$, 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 $^5I_7$ level of Ho$^{3+}$ which is the initial state of the $^5I_7 \rightarrow ^5I_8$ transition of interest for the characteristic 2 $\mu$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 $\alpha\beta$ YLiF$_4$: Ho$^{3+}$ laser material in which the infra-red laser emission of Ho$^{3+}$ activator ions around 2 $\mu$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 YLiF$_4$: 50 % Er$^{3+}$ : $x$ % 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 $^5I_7$ 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 $\mu$m infra-red laser transition $^5I_7 \rightarrow ^5I_8$. 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

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:0198700480100176100
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 \( \text{Ho}^{3+} \) 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 \( \text{Ho}^{3+} \) centres following pulsed excitation in the \( (5\ S_2 , 5\ F_4) \) excited states. It is to be noted that only the \( 5I_4 \) 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.

\[ \begin{array}{c|c|c|c} \text{x}\% & 0.5 & 2 & 5 \\ \hline \tau_{2} & 125\ ms & 125\ ms & 1\ ms \\ \tau_{4} & 13\ ms & 16\ ms & 19\ ms \\ \eta_{T} & 37\% & 26\% & 20\% \end{array} \]

Fig. 2. — Time constant of the directly excited infrared fluorescence decays of \( \text{Ho}^{3+} \) 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 \( \tau \) then represents the lifetime of this level. In this way the lifetimes of \( (5\ S_2 , 5\ F_4) \) in \( \text{YLiF}_4 : 1 \% \text{Ho}^{3+} \) and of \( 5I_6 \) and \( 5I_7 \) 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 \( \tau' \) is proportional to \( \exp(-t/\tau) - \exp(-t/\tau') \) if \( \tau' \ll \tau \). The lifetimes of \( 5F_5 \), \( 5I_6 \) and \( 5I_7 \) in \( \text{YLiF}_4 : 1 \% \text{Ho}^{3+} \) are deduced accordingly and are indicated in figure 1. The \( 5I_7 \) excited level is very short lived \( (< 2\ \mu s) \); its fluorescence decay is exactly the same as that of level \( 5F_7 \) and level \( 5F_6 \) feeds level \( 5I_7 \) via \( 5I_6 \) by rapid multiphonon relaxations. The increase of the observed \( 5I_7 \) fluorescence lifetime in \( \text{YLiF}_4 : 50 \% \text{Er}^{3+} : x \% \text{Ho}^{3+} \) with \( \text{Ho}^{3+} \) concentration \( x \), may be tentatively explained by the occurrence of radiative energy transfers among the \( \text{Ho}^{3+} \) ions: the fluorescence emitted by one centre at around 2 \( \mu m \) 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:

\[
\frac{1}{\tau} = \frac{1}{\tau^0} - KN
\]

where \( \tau^0 \) is the emission rate without transfer, \( N \) represents the total number of \( \text{Ho}^{3+} \) 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 $Ho^{3+}$ concentration. Then the observed radiative emission rate can be written as:

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

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 $4I_{6}$ obtained in the same co-doped crystals in which the $Ho^{3+}$ ions are either directly or indirectly — via $Er^{3+} \rightarrow Ho^{3+}$ energy transfer — excited: indeed, under direct excitation of level $4I_{6}$ of $Ho^{3+}$, the $5I_{6}$ fluorescence lifetime $\tau$ equals 1.25, 1.25 and 1 ms in YLiF$_{4}$: 50 % $Er^{3+}$; $x$ % $Ho^{3+}$ with $x = 0.5, 2$ and 5 respectively (see the Tab. in Fig. 2), whereas, by exciting the $Er^{3+}$ ions, the $4I_{6}$ fluorescence lifetime $\tau_1$ takes the values 2.1, 1.75 and 1.3 ms (see Tab. 1). We also note that the 2 ms value which is found in the 1 % $Ho^{3+}$ doped crystal agrees well with the $Ho^{3+}$ 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 $Er^{3+}$ 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 $Ho^{3+}$ to $Er^{3+}$ starts from levels $4I_{6}$ and $4I_{15/2}$. It can be a transfer of type $4I_{6} \rightarrow 4I_{15/2}$, $4I_{15/2} \rightarrow 4I_{13/2}$ and the smaller the number of $Er^{3+}$ ions in their excited state, the stronger the transfer process. If $\tau$ stands for the $4I_{6}$ fluorescence lifetime in the presence of $N_0 Er^{3+}$ ions in their ground state $4I_{15/2}$ (Tab. associated to Fig. 2) and $\tau_2$ the $5I_{6}$ lifetime when level $4I_{15/2}$ is partly depopulated or when there is no $Er^{3+}$ 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 $\eta_T$. $\eta_T$ is given by

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

The $\eta_T$ values are given in the table of figure 2.

4. $Er^{3+} \rightarrow Ho^{3+}$ energy transfers in co-doped YLiF$_{4}$.

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 $Ho^{3+}$ and $Er^{3+}$ and detected for different $Er^{3+}$ excitations. The various decay modes are strongly influenced by the way of pumping, in particular by the up-conversion processes occurring in the $Er^{3+}$ centres and that we have analysed in details before [7]. Excitations in the low energy infrared levels of $Er^{3+}$ give rise to anti-Stokes fluorescences originating from upper levels with long-lived behaviours. Direct excitations in these upper levels of $Er^{3+}$ 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 $Er^{3+}$ ions.

Table I gathers all the lifetimes of the excited states of interest in YLiF$_{4}$: 50 % $Er^{3+}$; $x$ % $Ho^{3+}$ ($x = 0.5, 2, 5$) and used in the models. Quantum efficiencies of energy transfers:

(i) $\eta_{1_1}$: $4I_{13/2} \rightarrow 4I_{15/2}$; $5I_{6}$

(ii) $\eta_{1_2}$: $4I_{11/2} \rightarrow 4I_{15/2}$; $5I_{6}$ via excitation in $4I_{6/2}$ of $Er^{3+}$.

(iii) $\eta_{1_1}^*$: $4I_{11/2} \rightarrow 4I_{15/2}$; $5I_{6}$ via excitation in $4I_{11/2}$ of $Er^{3+}$.

<table>
<thead>
<tr>
<th>$Ho^{3+}$ concentration</th>
<th>0 %</th>
<th>0.5 %</th>
<th>2 %</th>
<th>5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_0 (4I_{13/2})$</td>
<td>6 ms</td>
<td>1.5 ms</td>
<td>400 $\mu$s</td>
<td>220 $\mu$s</td>
</tr>
<tr>
<td>$\tau_0 (4I_{11/2})$</td>
<td>3 ms</td>
<td>1.5 ms</td>
<td>800 $\mu$s</td>
<td>500 $\mu$s</td>
</tr>
<tr>
<td>$\tau_0 (4I_{15/2})$</td>
<td>10 ms</td>
<td>10 ms</td>
<td>10 ms</td>
<td>10 ms</td>
</tr>
<tr>
<td>$\tau_0 (4F_{9/2})$</td>
<td>/</td>
<td>20 $\mu$s</td>
<td>5 $\mu$s</td>
<td>5 $\mu$s</td>
</tr>
<tr>
<td>$\tau_0 (4S_{3/2})$</td>
<td>/</td>
<td>7 $\mu$s</td>
<td>7 $\mu$s</td>
<td>7 $\mu$s</td>
</tr>
<tr>
<td>$\tau_1 (5I_5)$</td>
<td>/</td>
<td>13 ms</td>
<td>16 ms</td>
<td>19 ms</td>
</tr>
<tr>
<td>$\tau_2 (5I_6)$</td>
<td>/</td>
<td>2.1 ms</td>
<td>1.75 ms</td>
<td>1.3 ms</td>
</tr>
<tr>
<td>$\eta_{1_1}$</td>
<td>0 %</td>
<td>75 %</td>
<td>93 %</td>
<td>96 %</td>
</tr>
<tr>
<td>$\eta_{1_2}$</td>
<td>0 %</td>
<td>50 %</td>
<td>73 %</td>
<td>83 %</td>
</tr>
<tr>
<td>$\eta_{1_1}^*$</td>
<td>0 %</td>
<td>24 %</td>
<td>38 %</td>
<td>50 %</td>
</tr>
</tbody>
</table>

4.2 $Er^{3+} \rightarrow Ho^{3+}$ energy transfers.

4.2.1 $4I_{13/2}; 5I_6 \rightarrow 4I_{15/2}; 5I_7$. — This transfer is pointed out by exciting in level $4I_{13/2}$ of $Er^{3+}$ and is depicted
Fig. 3. — Excitation of level $^4I_{13/2}$.

Fig. 4. — Excitation of level $^4I_{11/2}$.

Fig. 5. — Excitation of level $^4I_{9/2}$. 
in figure 8. The rate equation for the $^4I_{13/2}$ population density can be written:

$$\dot{N}_1 = -\frac{N_1}{\tau_1} - k_1 N_0' N_1$$

(4)

so

$$\dot{N}_1 = -\left[\frac{1}{\tau_1} + k_1 N_0'\right] N_1$$

(5)

where $k_1$ stands for the transfer constant and where $N_0'$, the $^3I_8$ population density of Ho$^{3+}$, is supposed to be constant. $\tau_1$ is the fluorescence lifetime of level $^4I_{13/2}$ of Er$^{3+}$ in the absence of Er $\rightarrow$ Ho energy transfer. The solution of equation (5) gives rise to an exponential decay with the time constant $\tau_1$ such as:

$$\frac{1}{\tau_1} = \frac{1}{\tau_1'} + k_1 N_0'$$

(6)

Expression (6) predicts a decrease of $\tau_1$, the fluorescence lifetime of level $^4I_{13/2}$ in case of Er $\rightarrow$ 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).
Using this expression gives the energy transfer quantum rate:

$$\eta_T = 1 - \frac{\tau_1}{\tau_1^0}.$$  

(7)

The value of \(\tau_1^0\) is deduced from curve (a) of figure 10 at \(N_0^t = 0\) and is used in expression (7) to estimate \(\eta_T\) (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 \(\text{Er}^{3+}\) the \(^3I_2 \rightarrow \, {}^5I_8\) radiative transition of \(\text{Ho}^{3+}\) around 2 \(\mu\)m is observed. The rate equation describing the population \(N_{T1}'\) of \(^5I_7\) is then:

$$N_{T1}' = -\frac{N_{T1}'}{\tau_1} + (k_1 N_0) N_1$$  

(8)

the solution of which is

$$N_{T1}' \approx \exp\left[-\frac{t}{\tau_1}\right] - \exp\left[-\frac{t}{\tau_1}\right].$$  

(9)

This expression (9) fits the experimental data (Fig. 11) quite well.
4.2.2 $^4I_{11/2}, \; ^5I_8 \rightarrow ^4I_{15/2}, \; ^3I_6$. — This energy transfer, easily observed by exciting in level $^4I_{9/2}$ of $Er^{3+}$, 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.

The shortening of the $^4I_{11/2}$ fluorescence decay when the $Ho^{3+}$ concentration is increased (Fig. 5) can be interpreted according to the notations of figure 12 by using the following rate equations:

\[
N_3 = N_3^0 \exp(-t/\tau_3)
\]
\[
N_2 = -\frac{N_2}{\tau_2} - \left( k_2 N_0' \right) N_2 + A_{32} N_3
\]

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

If we set
\[
\frac{1}{\tau_2} = \frac{1}{\tau_0} + k_2 N_0'
\]

the solution of equation (11) is then:

\[
N_2 \approx \exp\left[-\frac{t}{\tau_2}\right] - \exp\left[-\frac{t}{\tau_3}\right]
\]

The linear dependence of $1/\tau_2$ 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 $\eta_T$ of the present transfer labeled $T_2$ by using the relation:

\[
\eta_T = 1 - \frac{\tau_2}{\tau_0}
\]

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 $^5I_8$ of $Ho^{3+}$ has been studied and will be presented and discussed subsequently (subsection 4.3.2).

4.2.3 $^4F_{9/2}, \; ^5I_8 \rightarrow ^4I_{15/2}, \; ^3F_5$. — This transfer is obtained by exciting in level $^4F_{9/2}$ of $Er^{3+}$ as indicated in figure 13. Both red emissions, the one $^4F_{9/2} \rightarrow ^4I_{15/2}$ occurring in $Er^{3+}$ centres and the other $^3F_5 \rightarrow ^5I_8$ in $Ho^{3+}$ ions, have exactly the same time-dependence (Fig. 6). This indicates that levels $^3F_5$ 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 $Er^{3+}$ (Fig. 7), these red emissions have again the same time-dependence, confirming the above thermalization process.

4.2.4 $^4S_{3/2}, \; ^5I_8 \rightarrow ^4I_{15/2}, \; ^3F_4$. — Excitation in level $^2H_{11/2}$ of $Er^{3+}$ 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 $Ho^{3+}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ of $Er^{3+}$ are identical, thus indicating
4.3 DISCUSSION. — The best laser systems will be those which give rise to the most efficient infra-red emission $5I_{17} \rightarrow 5I_{18}$ near 2 μm. It is therefore particularly interesting to know about the main deexcitation channels which populate the $5I_{17}$ metastable state of $\text{Ho}^{3+}$ when $\text{Er}^{3+}$ excitation is used.

The 2 μm infra-red fluorescence occurring after various excitations of $\text{Er}^{3+}$ 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 $\text{Er}^{3+}$ are excited because of one-centre energy relaxations and the RED channel is efficient even if the lower excited states of $\text{Er}^{3+}$ are excited due to up-conversion mechanisms in these ions [7]. However the relative probability of these three channels strongly depends on the $\text{Er}^{3+}$ 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 $\text{Er}^{3+}$ 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
already derived (Expr. (10) and (13), respectively), while the rate equation for level \( ^4I_{13/2} \) is:

\[
\dot{N}_1 = -\frac{N_1}{\tau_1} + A_{31} N_3 + A_{21} N_2
\]

(15)

where \( A_{31} N_3 \) and \( A_{21} N_2 \) represent the channels \( \alpha \) and \( \beta \), 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 \( ^4I_{13/2} \) 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 \( \alpha \) is supposed to occur via a transfer \( ^4I_{9/2}, ^4I_{15/2} \rightarrow ^4I_{13/2}, ^4I_{13/2} \) in co-doped crystals containing 50% \( \text{Er}^{3+} \) whereas this transfer was found to be quite negligible in single-doped material containing only 1% \( \text{Er}^{3+} \) [7]. On the other hand, its efficiency was found to be so high in \( \text{ErLiF}_4 \) that the channel \( \beta \) which likely occurs via multiphonon relaxation was completely negligible. The co-doped crystals with 50% \( \text{Er}^{3+} \) ions lead to the intermediate case where both channels coexist.

The IR2 deexcitation channel populates level \( ^5I_6 \) of \( \text{Ho}^{3+} \) according to the equation:

\[
\dot{N}^*_2 = -\frac{N^*_2}{\tau_2} + (k_2 N^*_6) N_2
\]

(16)

Its solution is compared with the experimental time-dependence of the fluorescence \( ^5I_6 \rightarrow ^5I_8 \) (Fig. 17). For the \( \text{Ho}^{3+} \) higher concentration (5%) the fit is quite good (curve c) because the transfer \( ^4I_{13/2} \rightarrow ^5I_6 \) is very efficient, while for the other \( \text{Ho}^{3+} \) concentra-

![Fig. 16. — Time dependence of \( \text{Er}^{3+} \) emission from level \( ^4I_{13/2} \) in case of \( ^4I_{13/2} \) excitation in \( \text{YLiF}_4 \): 50% \( \text{Er}^{3+} : x \% \text{Ho}^{3+} \) 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 \( \alpha \) channel or \( \beta \) channel or both channels (\( \alpha + \beta \)) is (are) involved.](image1)

![Fig. 17. — Time dependence of \( \text{Ho}^{3+} \) emission from level \( ^4I_6 \) in case of \( ^4I_{9/2} \) excitation of \( \text{Er}^{3+} \) in \( \text{YLiF}_4 \): 50% \( \text{Er}^{3+} : x \% \text{Ho}^{3+} \) 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).](image2)
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 $^{5}I_{6}$.

Level $^{3}I_{1}$ can be populated by both IR1 and IR2 deexcitation channels. The corresponding rate equation for level $^{3}I_{1}$ 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 $^{5}I_{7}$ 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 $^{5}I_{7}$ level.

* Excitation of level $^{3}H_{11/2}$. — First of all we have ruled out the two feeding processes of level $^{5}I_{6}$ of Ho$^{3+}$ which borrows the so-called RED channel as follows (Fig. 15):

$$^{2}H_{11/2} \rightarrow ^{4}F_{9/2} \rightarrow \text{RED Channel}$$
$$^{2}H_{11/2} \rightarrow ^{5}S_{2} \rightarrow \text{RED Channel}.$$ 

Indeed, in this way, the $^{5}I_{6}$ population density is governed by the rate equation:

$$\dot{N}_{4} = -\frac{N_{4}}{\tau_{2}} + A_{42} N_{4} \quad (18)$$

where $A_{42}$ is the probability of relaxation between levels $^{5}F_{3}$ and $^{5}I_{6}$. $\tau_{2}$ is given in table I. When use is made of the experimental fluorescence decay of level $^{5}F_{3}$ or $^{5}I_{6}$ (since they are the same) for $N_{4}$ the solution of equation (18) cannot fit correctly the $^{5}I_{6}$ fluorescence data for all the Ho$^{3+}$ concentrations (Fig. 19). Here is to be noted that the fluorescence decay of levels ($^{5}S_{2} - ^{4}S_{3/2}$) following pulsed excitation of level $^{2}H_{11/2}$ 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 $^{4}F_{9/2}$ state is short-circuited in case of $^{2}H_{11/2}$ excitation by cross-relaxation processes in Er$^{3+}$ indicated in figure 15 and already pointed out [7]:

$$^{4}S_{3/2}, ^{4}I_{15/2} \rightarrow ^{4}I_{9/2}, ^{4}I_{13/2}$$
$$^{4}S_{3/2}, ^{4}I_{15/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{9/2}.$$ 

These mechanisms give rise to the IR2 channel which then populates level $^{5}I_{6}$ according to the system of equations:

$$N_{5} \approx \exp \left[-\frac{t}{\tau_{5}} \right]$$
$$\dot{N}_{3} = -\frac{N_{3}}{\tau_{3}} + A_{35} N_{5}$$
$$\dot{N}_{2} = -\frac{N_{2}}{\tau_{2}} + A_{32} N_{3}$$
$$\dot{N}_{2} = -\frac{N_{2}}{\tau_{2}} + (k_{2} N_{0}) N_{2} \quad (19)$$

The solution for $N_{4}$ is fitted to the time-dependence of the fluorescence $^{3}I_{6} \rightarrow ^{5}I_{6}$ (Fig. 20). The agreement between the model and the experimental data is
Fig. 19. — Time dependence of \( \text{Ho}^{3+} \) emission from level \( ^{3}I_{6} \) in case of \( ^{2}H_{1/2} \) excitation of \( \text{Er}^{3+} \) in \( \text{YLiF}_{4} \) : 50 % \( \text{Er}^{3+} : x \% \text{Ho}^{3+} \) 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 \( \text{Ho}^{3+} \) emission from level \( ^{3}I_{6} \) in case of \( ^{2}H_{1/2} \) excitation of \( \text{Er}^{3+} \) in \( \text{YLiF}_{4} \) : 50 % \( \text{Er}^{3+} : x \% \text{Ho}^{3+} \) 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 \( \text{Ho}^{3+} \) 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 \( ^{3}I_{6} \) fluorescence. At this time we have no simple explanation to propose.

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

\[
\dot{N}_{1} = - \frac{N_{1}}{\tau_{1}} + A_{31} N_{3} + A_{31} N_{3} + A_{21} N_{2}.
\]

However, the best fits of the solution of equation (20) to the experimental time-dependence of the \( ^{4}I_{13/2} \) fluorescence are given in figure 21 in the following three cases: (i) the cross-relaxation process is only involved (ii) the \( \alpha \) and \( \beta \) channels only occur and in the same relative proportions as those deduced when the \( \text{Er}^{3+} \) ions are excited in level \( ^{4}I_{9/2} \) and (iii) the cross-relaxation and \( \alpha \) and \( \beta \) channels occur simultaneously. It is clear that the best fits are obtained in the last case.
Let us consider now the $^5I_7$ level of Ho$^{3+}$. It is populated via the IR1 and IR2 channels and its rate equation may be written as:

$$\dot{N}_i = -\frac{N_i}{\tau_i} + A_{IR1}^i N_{IR1}^i + (k_1 N_{IR2}^0) N_i$$  \hspace{1cm} (21)

the solution of which is fitted to the experimental $^5I_7$ 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 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 $^5I_7$ population process.

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

---

**Fig. 21.** — Time dependence of Er$^{3+}$ emission from level $^4I_{13/2}$ in case of $^2H_{11/2}$ 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 $\alpha$ and $\beta$ channels ($\alpha + \beta$) (iii) the cross-relaxation and $\alpha$ and $\beta$ channels (C.R. $+$ $\alpha + \beta$).

**Fig. 22.** — Time dependence of Ho$^{3+}$ emission from level $^1I_7$, in case of $^2H_{11/2}$ 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 IR$_1$, channel IR$_2$ or both channels (IR$_1$ + IR$_2$) is (are) involved.
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 $^{4}I_{11/2}$ is:

$$
\dot{N}_2 = - \frac{N_2}{\tau_2^0} - (k_2 N_0) N_2 - kN_2^2 .
$$

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 $\tau_2^0$ and $k_2 N_0 = \frac{1}{\tau_2^0} - \frac{1}{\tau_2}$ 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 $^{4}I_{11/2}$ population.

The IR2 channel transfers energy into level $^{5}I_6$ of Ho$^{3+}$ with a quantum efficiency:

$$
\eta_T = \frac{1}{N_2^0} \int_0^{\infty} k_2 N_0 N_2 \, dt
$$

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

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

The population density of level $^{5}I_6$ verifies the equation:

$$
\dot{N}_2 = - \frac{N_2}{\tau_5} + (k_2 N_0) N_2 .
$$

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

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

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

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

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

The $^{5}I_7$ population density of $^{5}I_7$ is governed by the IR1 and IR2 channels according to the equation:

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

It appears again that the fits to the time-dependence
Fig. 24. — Time dependence of Ho\(^{3+}\) emission from \(^5\)I\(_8\) level in case of \(^4\)I\(_{13/2}\) 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 (24).

Fig. 25. — Time dependence of Er\(^{3+}\) emission from level \(^4\)I\(_{13/2}\) in case of \(^4\)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 \(^4\)I\(_{11/2}\) or \(^4\)S\(_{3/2}\) or both levels (\(^4\)I\(_{11/2} + ^4\)S\(_{3/2}\)) take(s) part in the fluorescence process.

of the fluorescence \(^5\)I\(_7\) \(\rightarrow^5\)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 \(^4\)F\(_{9/2}\) excitation.

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

\[
\begin{align*}
{^5F}_{9/2} & \rightarrow {^4I}_{9/2} \xrightarrow{\text{channel } A} {^4I}_{13/2} \\
{^4F}_{9/2} & \rightarrow {^4I}_{9/2} \xrightarrow{\text{channel } B} {^4I}_{11/2} \xrightarrow{\text{channel } \beta} {^4I}_{13/2}.
\end{align*}
\]

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

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

\[
\begin{align*}
N'_1 &= \exp \left( -\frac{t}{\tau_1} \right) \\
\dot{N}'_2 &= -\frac{N'_2}{\tau_2} + A'_{42} N'_2 + (k_2 N'_0) N_2 \\
\dot{N}'_3 &= -\frac{N'_3}{\tau_3} + A'_{21} N'_2 + (k_1 N'_0) N_1.
\end{align*}
\]
In figure 27, the solution of expression (28) is compared with the time-dependence of the \( ^5I_6 \rightarrow ^5I_8 \) fluorescence. It is remarkable that the RED channel is largely predominant in the feeding process of \(^5I_6\). 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 \( ^5I_7 \rightarrow ^5I_8 \) emission. The fits clearly show that both RED and IR1 channels occur to feed \(^5I_7\).

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 µm \(^5I_7 \rightarrow ^5I_8\) laser transition of Ho\(^{3+}\), we want to summarize now on the respective contributions of each excitation chan-
The dependence of Ho$^{3+}$ emission from level $5^1I_7$ in case of $4F_{9/2}$ 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 (IR$_1$ + RED) is (are) involved.

Table II. — Relative contribution of each channel of excitation to the $5^1I_7$ level of Ho$^{3+}$ as a function of the Er$^{3+}$ excitation level.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Ho$^{3+}$ concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5%</td>
</tr>
<tr>
<td>$4I_{13/2}$</td>
<td>IR$_1$</td>
</tr>
<tr>
<td></td>
<td>100%</td>
</tr>
<tr>
<td>$4I_{11/2}$</td>
<td>IR$_1$ + IR$_2$</td>
</tr>
<tr>
<td></td>
<td>57%</td>
</tr>
<tr>
<td>$4I_{9/2}$</td>
<td>IR$_1$ + IR$_2$</td>
</tr>
<tr>
<td></td>
<td>92%</td>
</tr>
<tr>
<td>$4F_{9/2}$</td>
<td>IR$_1$ + RED</td>
</tr>
<tr>
<td></td>
<td>?</td>
</tr>
<tr>
<td>$3H_{11/2}$</td>
<td>IR$_1$</td>
</tr>
<tr>
<td></td>
<td>100%</td>
</tr>
</tbody>
</table>

are those for which the relative efficiency of the IR1 channel is as large as possible. From this point of view, of course, excitation of level $4I_{13/2}$ is very suitable but powerful infra-red light sources around 1.5µm are not easily available for optical pumping. Excitations of levels $4I_{11/2}$ and $4I_{9/2}$ also have to be considered, depending on the Ho$^{3+}$ concentration. In the visible range, there is no doubt that green excitation of $2H_{11/2}$ 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 $2H_{11/2}$ or $2F_{9/2}$ gives very similar results: the IR1 channel relative efficiency remains strong at the highest 5% Ho$^{3+}$ concentration. This does not apply in the case of the $4I_{9/2}$ or $4F_{9/2}$ 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 $2H_{11/2}$ with the 532 nm second-harmonic radiation of a YAG: 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.
References


