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Fluorescence quenching of Nd\(^{3+}\) in LaF\(_3\) studied by direct measurements on pairs (+)

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Résumé. — L'auto-extinction de la fluorescence infrarouge du Nd\(^{3+}\) dans LaF\(_3\) a été étudiée par la mesure directe de son efficacité pour plusieurs catégories de paires d'ions Nd\(^{3+}\). En utilisant des cristaux très dilués, les paires sont isolées et le comportement observé est intrinsèque. Les résultats obtenus à 1,2 K sont utilisés pour prédire les propriétés de cristaux concentrés. A partir de la différence entre les prédictions et les résultats expérimentaux publiés par ailleurs, le rôle important de la migration de l'excitation parmi les donneurs est mis en évidence. Cette situation, inhabituelle à basse température, est discutée. D'autres résultats, comme l'existence d'une interaction à courte portée, la valeur des taux de transferts pour des paires (Nd, Pr) ou l'efficacité des processus à trois ions sont commentés.

Abstract. — The self-quenching of the Nd\(^{3+}\) infrared fluorescence in LaF\(_3\) has been studied by the direct measurement of the transfer rates for various classes of Nd\(^{3+}\) pairs. Using weakly doped samples, the pairs are isolated and their behaviour is intrinsic. The results obtained at 1.2 K are used to predict the properties of concentrated crystals. From the difference between the predicted behaviour and the experimental results reported by others, it is concluded that migration of the excitation among the donors plays a prominent part. This situation, unusual at low temperatures, is discussed. Other results as existence of a short range interaction, transfer rates inside (Pr, Nd) pairs, efficiency of three ions processes are also discussed.

1. Introduction.

The experimental study of excitation transfers in disordered systems has been revived with the use of dye lasers. By a selective excitation of an ion class within the inhomogeneous width of optical lines it has been possible to study the spectral transfer. Spatial transfer resulting from resonant transfer and connected to delocalization of the excitation has also been studied with tunable lasers. In a recent book, edited by Yen and Selzer [1], excellent review papers have been written by specialists of these fields, as well for a theoretical than for an experimental survey. Among the studied systems, rare earth ions in inorganic crystals have yielded a lot of interesting results which are reviewed in a book which will shortly appear [2]. The general references can be found in these books and will not be repeated here.

In a series of experiments of LaF\(_3\) : Pr\(^{3+}\), a system considered as a model system [2], the problem of transfers has been handled with a new approach. Instead of studying the donor fluorescence in strongly doped crystals as a function of concentration, the transfer between two ions associated as a pair has been directly studied [3]. This has been possible due to the mutual perturbation that each ion induces at the site of its neighbour which shifts the energy levels and thus produces satellites of the optical lines. A narrow laser can then selectively excite a given class of pairs. Using weakly doped crystals, the pairs are isolated and their intrinsic behaviour can be observed. The coupling between the two ions of some strongly coupled pairs has also been measured with a two lasers technique [4]. It must be pointed out that with this approach the microscopic parameters of the coupling are directly measured whereas they can be deduced from macroscopic properties of concentrated crystals only by supposing a single interaction mechanism.

This method has been applied to study the quenching of the \(^3P_0\) level in LaF\(_3\) : Pr\(^{3+}\) [5]. From the measurements on pairs, it has been possible to predict the behaviour of concentrated crystals. The comparison of this prediction with experimental results obtained by others [6] has led to a new interpretation of these results which proves the existence of a short range interaction [5].
The present work is an application of the above experimental method to the study of the I.R. fluorescence quenching of Nd\(^{3+}\) in two systems: LaF\(_3\) : Nd\(^{3+}\) and LaF\(_3\) : Nd\(^{3+}\) : Pr\(^{3+}\). The choice of Nd\(^{3+}\) was made for its great importance in laser materials but also because a very extensive experimental study of the quenching was done by Voronko et al. [7] after the conflicting results of Asawa and Robinson [8] and Vasil’ev et al. [9]. It was thought interesting to compare the observed behaviour of concentrated LaF\(_3\) : Nd\(^{3+}\) crystals with that predicted from direct measurements on pairs in dilute crystals.

After a description of the systems, the fluorescence lifetime results obtained at temperatures ranging from 1.2 K to 30 K for various pairs are given in section 2 as well as the quenching rates which can be deduced. Section 3 begins with a short review of theoretical works related to the fluorescence dynamics in presence of migration among the donors. Then, previous experimental works on LaF\(_3\) : Nd\(^{3+}\) are summarized. The results obtained here for pairs are then used to predict the behaviour of concentrated crystals. The difference between predictions and previously obtained results is discussed and explained by the existence of processes other than the two ion quenching ones. Studies of up-conversion in LaF\(_3\) : Nd\(^{3+}\), also connected with pair interaction, are reported in a companion paper [10].

2. Experimental results.

The energy levels of Nd\(^{3+}\) and Pr\(^{3+}\) in LaF\(_3\) are shown in figure 1. Energy values have been taken from the very fruitful report of Carnall et al. [11] on spectroscopy of rare earth ions in LaF\(_3\). On this figure are shown the transitions excited by the laser and the observed fluorescence. Lifetimes for isolated ions in some metastable states are also given.

For a weakly doped crystal the optical lines are narrow and the satellites associated with various classes of pairs are clearly visible in the wings of these lines. Figure 2a shows the absorption spectrum of a 0.1 % doped LaF\(_3\) : Nd\(^{3+}\) crystal near the transition \(^{4}I_{9/2}(1)\rightarrow^{4}G_{5/2}(1)\) and \(^{4}I_{9/2}(1)\rightarrow^{4}G_{5/2}(2)\) (numbers 1 and 2 inside parentheses recall these levels are the lowest or the first excited within the multiplet). This spectrum has been obtained with a high resolution (0.1 cm\(^{-1}\)) THR Jobin-Yvon monochromator. The linewidths are also \(\sim 0.1\) cm\(^{-1}\). The lifetimes of the pumped levels \(^{4}G_{5/2}(1)\) and \(^{4}G_{5/2}(2)\) are very short, \(\sim 100\) ns, due to a strong multphonon relaxation. Excited ions reach the metastable \(^{4}F_{3/2}(1)\) in less than 1 \(\mu\)s. An excitation spectrum of the I.R. fluorescence emitted from this level is shown in figure 2b. The laser we used is a modified SOPRA dye laser pumped by a home made N\(_2\) laser. It produces 5 ns pulses having a spectral width of \(\sim 0.1\) cm\(^{-1}\). The fluorescence is simply detected.

![Fig. 1. — Energy levels of Nd\(^{3+}\) and Pr\(^{3+}\) in LaF\(_3\). The widths of the lines show the crystal field splitting of each multiplet. Arrows show the transition excited by the laser and the fluorescence observed. Numbers inside brackets give the lifetime of some metastable states in \(\mu\)s.](image-url)

![Fig. 2. — Absorption spectrum (a) and excitation spectrum of the \(^{4}F_{3/2}\) fluorescence (b) for a 0.1 % doped LaF\(_3\) : Nd\(^{3+}\) crystal at 1.2 K around transitions \(^{4}I_{9/2}(1)\rightarrow^{4}G_{5/2}(1)\) and \(^{4}I_{9/2}(1)\rightarrow^{4}G_{5/2}(2)\). Satellites of the former transitions have been numbered.](image-url)
by a photomultiplier through a filter which absorbs the diffuse laser light and unwanted fluorescences. It can be seen that satellites are as well resolved in the excitation spectrum as in the absorption spectrum, the signal to noise ratio being even better. The relative intensities of the satellites are correct but, due to a strong absorption and the resulting saturation effects, the intensities of the main lines are not representative. Since this study mainly concerns satellites and since excitation spectra are easily obtained, they are generally used to adjust the laser wavelength for selective excitation experiments.

Figure 3 shows the absorption spectra around the transition $^4I_{9/2}(1) \rightarrow ^4G_{5/2}(1)$ for a 0.1 % LaF$_3$: Nd$^{3+}$ crystal and for a LaF$_3$ crystal doped with 0.1 % Nd$^{3+}$ and 0.1 % Pr$^{3+}$. New satellites, attributed to (Nd-Pr) pairs, are clearly visible: one near satellite 3, another in coincidence with satellite 4, two others in the wings of satellites 5, 6. Dynamical experiments described below have revealed other satellites hidden in the main line.

The lifetime of the $^4F_{3/2}$ level of the various pairs has been measured by selective excitation of the satellites. This lifetime $\tau_i$ is shorter than the lifetime $\tau_0$ of the isolated ions associated with the main line due to the quenching induced on the excited ion of the pair by its unexcited neighbour. The quenching rate, for pair $i$, is easily deduced:

$$W_{0i} = \frac{1}{\tau_i} - \frac{1}{\tau_0}$$

by supposing the radiative lifetime of the ions associated as pairs is the same than that of the isolated ions, i.e. by supposing the crystalline perturbation induced by one ion at the site of its neighbour does not significantly change the oscillator strengths of the transitions.

Measurement of $\tau$ is easy for the well resolved satellites but is less precise for those which are in the wings of the main line and for which the contribution of nearly isolated ions must be subtracted from the signal. This measurement is impossible for satellites hidden in the main line whose existence is however proven by up-conversion experiments [7]. Measurements have thus been done only for satellites 1 to 7 of figure 3. The values of $\tau_i$ measured with a 0.2 % doped sample are given in table I with the corresponding $W_{0i}$ values. The precision of these values is better than $\pm 5$ % for lines 1, 2, 3, 4 and 7, $\pm 10$ % for line 5 and 6. Values of $\tau_i$ measured with a 0.1 % doped sample are nearly the same but, due to the smaller signal, the precision is not so good.

When temperature is increased, all lines broaden and the measurement of $\tau$ becomes more difficult, even impossible for satellites which are too near the central line. Figure 4 shows the results obtained at 7 K for satellites 1, 2, 3, 4, 5, 6 and 7 and at temperatures ranging from 7 to 30 K for satellites 1, 2, 3 and 7. $W$'s values are deduced from the $\tau$'s as above.

<table>
<thead>
<tr>
<th>$N_i$</th>
<th>1</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>3</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_i$ (µs$^{-1}$)</td>
<td>780</td>
<td>500</td>
<td>500</td>
<td>370</td>
<td>570</td>
<td>750</td>
<td>350</td>
</tr>
<tr>
<td>$W_{0i}$ (ms$^{-1}$)</td>
<td>0.72</td>
<td>0.72</td>
<td>1.42</td>
<td>0.47</td>
<td>0.05</td>
<td>1.58</td>
<td>0.41</td>
</tr>
</tbody>
</table>

For doubly doped samples, two types of measurements have been done. Firstly, lifetimes of satellites attributed to (Nd, Nd) pairs have been measured, except for satellite 6 whose proximity to the central line reduced too much the precision. Table II gives values of $\tau_i$ measured with a 0.1 % Nd$^{3+}$ + 0.1 % Pr$^{3+}$ and recalls $\tau_i$ values obtained with a singly doped sample. It must be emphasized that to make these variations meaningful, the experiments have been made by gluing a singly doped crystal and a doubly doped crystal on the same holder. The decay fluorescence curves are then successively obtained and analysed with a multichannel analyser by irradiating...
Fig. 4. — Variation of the lifetimes $\tau_i$ for satellites of the $^4I_{9/2}(1) \rightarrow ^4G_{5/2}(1)$ transition. The index of the satellite is recalled at the left ($0$ refers to the central line). Due to the proximity of the central line, the measurement for satellites 4, 5 and 6 was not possible at high temperatures.

one crystal then the other without modifying the parameters of the experiment. From the $\tau_i$ and $\tau'_i$ of table II, the quenching rate $W'_i = \frac{1}{\tau'_i} - \frac{1}{\tau_i}$ induced by the Pr$^{3+}$ ions can be calculated. As this value results from the difference between two measured quantities, the precision is not good, of the order of 20%.

The second type of measurements concerns (Pr, Nd) pairs. However no measurement was possible for satellites (3') and (4') which do not produce a significant I.R. fluorescence as a comparison between spectra of figure 5 and 3b shows. In other words, due to the efficiency of the quenching induced by the neighbouring Pr$^{3+}$ ion, this I.R. fluorescence decays too fast to be measured with our time resolution. On the contrary, for some laser wavelengths labelled I to IV in figure 5, the fluorescence decay has the shape indicated on the left part of this figure. As these wavelengths are very near the centre of the spectrum, it is thought that they correspond to (Pr, Nd) satellites hidden in the central line and therefore undetectable in the absorption spectrum. It must be emphasized that the decay shape shown in figure 5 is not observed in a singly doped crystal glued on the same sample holder as the doubly doped crystal, the comparison between the decay shapes being done without changing the laser wavelength. It is possible to extract the fast decay times $\tau'_i$ of these satellites and to deduce the quenching rates $W'_i$. They are given in figure 5. The precision for these values is of the order of 20%. Attempts to observe in doubly doped crystals a $^1D_2$ fluorescence of Pr$^{3+}$ ions after pumping Nd$^{3+}$ ions in $^4G_{5/2}$ have given a negative result for any wavelength around the main line.

Before discussing all these results, it seems important to point out that, although the spectral width of the laser is comparable with the linewidths, a structure within the main line can be detected. The same observation has been done in up-conversion experiments [10].

Table II. — Decay times at 1.2 K for the central line ($i = 0$) and for the satellites as numbered in figure 2: $\tau_i$ are the values for a 0.2% Nd$^{3+}$ doped sample and $\tau'_i$ the values for a (0.1% Nd$^{3+}$ + 0.1% Pr$^{3+}$) doped sample. $W'_i$ values are calculated by $W'_i = \frac{1}{\tau'_i} - \frac{1}{\tau_i}$.

<table>
<thead>
<tr>
<th>$i$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_i$ [µs]</td>
<td>780</td>
<td>500</td>
<td>500</td>
<td>370</td>
<td>570</td>
<td>750</td>
<td>590</td>
</tr>
<tr>
<td>$\tau'_i$ [µs]</td>
<td>680</td>
<td>450</td>
<td>450</td>
<td>340</td>
<td>500</td>
<td>640</td>
<td>520</td>
</tr>
<tr>
<td>$W'_i$ [ms$^{-1}$]</td>
<td>0.19</td>
<td>0.22</td>
<td>0.22</td>
<td>0.24</td>
<td>0.25</td>
<td>0.23</td>
<td>0.23</td>
</tr>
</tbody>
</table>
3. Discussion.

3.1 INTRODUCTION. — The problem of the fluorescence dynamics of donors in presence of traps in disordered systems has recently been reviewed by Huber [12]. The general references concerning this problem can be found there but the pioneer works of Burshtein [13] and Sakun [14] can be mentioned. The conclusions are briefly summarized here.

In a system where donors and acceptors are randomly distributed, the dynamics of the donor fluorescence is given by

where $W_0$ is the decay rate for an isolated donor, $W_{0i}$ the transfer rate between a donor at site 0 and an acceptor at site $i$, $N_i$ the number of equivalent ion pairs $(0, i)$, $c$ is the concentration of acceptors. For the self quenching which will first be considered, donors and acceptors are the Nd$^{3+}$ themselves and $c$ their concentration. The well known result of Inokuti and Hirayama [15] can be deduced from (1) when $c \to 0$ by supposing a continuous distribution of the sites and choosing an interaction mechanism.

When the excitation can migrate among the donors, the problem becomes more complex. The limiting case for which the migration is very fast is however easy: the donors form a single system whose decay is exponential with the rate

For a slower migration, the decay is exponential only at long times with a rate which has been calculated by Huber [12] with three hypotheses: i) the donor-donor migration is hopping-like and not diffusive-like, ii) the sites are continuously distributed, iii) the transfer mechanism is dipole-dipole as well for donor-donor transfers than for donor-acceptor transfers. This rate is found to be:

where explicit expressions for $A$ and $B$ can be found in (12). Equation (3) gives the result (2) when the migration becomes very fast i.e. when the average value of the donor-donor transfer rate $\beta/R^6$ (where $R$ is the average donor-donor distance) is larger than the fastest donor-acceptor rate $\alpha/R_m^6$ ($R_m$ is the smallest donor-acceptor distance). Equation (3) then becomes

Thus, the concentration dependence of the quenching rate $W_Q = (W - W_0)$ is linear for a fast migration and quadratic for a slow migration. For fixed values of $\alpha$ and $\beta$, there exists a critical concentration $c^*$ between these two extreme cases defined as

3.2 PREVIOUS EXPERIMENTAL RESULTS. — The LaF$_3$ : Nd$^{3+}$ system has been studied by Asawa and Robinson as soon as 1966 (8). They have measured the 4F$^{3/2}$ lifetime for concentrations ranging from 0.1 % to 100 % at various temperatures between 4.2 K and 300 K. Of course, the excitation was broadband and all types of ions were excited. No mention of non-exponential decay is made. The observed quenching whose efficiency increases with the temperature is attributed to the following cross-relaxation between two Nd$^{3+}$ ions:

Vasil'ev et al. [9] have also studied the variation of the 4F$^{3/2}$ lifetime with temperature and concentration and have concluded that migration of the excitation among the donors played a major role. After these contradictory conclusions, Voronko et al. [7] have undertaken a very detailed experimental study and have made an elaborate analysis using recently published theoretical results [14]. In figure 6 are shown the observed variations of the 4F$^{3/2}$ lifetime with temperature and concentration. The measurements have been made after pumping the ions into the *4G$_{5/2}$ level by a laser, as in the present work, but the spectral width of the laser was large and no selective excitation was achieved. The more striking results are the following: i) there exists a plateau between 0 and 12 K for all the concentrations, ii) for $T > 12$ K, the lifetime decreases continuously when the concentration increases, iii) for $12$ K $< T < 150$ K, the decrease of $\tau$ when the temperature increases is larger for large concentrations. The shape of the fluorescence decay is said to be exponential except for weak concentrations and high temperatures. Finally, the type of variation of the quenching rate with the concentration has been summarized in figure 7 which shows the $(T, c)$ plane.

Two quenching processes are considered by Voronko et al. The first is the one described by (5). Since, as seen from the energy levels of figure 1, it needs the adsorption of a 40 cm$^{-1}$ phonon, its efficiency is very small at very low temperatures but increases
Fig. 6. — Experimental results reported by Voronko et al. [7] giving the $^4F_{3/2}$ fluorescence lifetime as a function of temperature for various concentrations. Curves 1 to 8 refer respectively to concentrations: 0.3, 2, 3, 5, 10, 30, 50, 100 % rapidly with $T$. The second process is described by

$$[^4F_{3/2}(1), ^4I_{9/2}(1)] \rightarrow [^4I_{13/2}(i), ^4I_{15/2}(j)].$$

Depending on the numbers $i$ and $j$, an energy between 760 cm$^{-1}$ and 1900 cm$^{-1}$ is emitted as phonons. Although its efficiency can be thought to be small since many phonons must be created, this process is dominant at very low temperatures and is responsible for the quenching up to 12 K, temperature at which process, (5) becomes efficient.

Using the above presented theoretical results, Voronko et al. [7] have interpreted their results for $T > 40$ K. Indeed, since the signal is exponential and since the concentration dependence of $W_Q$ is quadratic for $c \leq 0.05$ linear for $c > 0.1$, the migration plays a major rôle, the critical concentration $c^*$ being approximately 0.1. That implies $\alpha/\beta \sim 10^{-2}$ validating the choice of the hopping model [12]. From the shape of the non-exponential decay, Voronko et al. obtained the value of $\alpha$ and its temperature dependence for $T > 90$ K.

The very low temperature results for which (cf. Fig. 7) $W_Q \propto c$ for $c \ll 1$ and $W_Q \propto c^3$ for $c > 0.1$ are not interpreted.

![Fig. 7. — Type of dependence of the quenching rate $W_Q$ versus concentration $c$. The hachured region corresponds to a non exponential decay of the $^4F_{3/2}$ fluorescence.](image)

3.3 USE OF PAIR MEASUREMENTS. — The shape of the fluorescence decay given by (1) can be obtained as soon as the $W_{Qi}$ and the $N_i$ are known. The direct measurements on the pairs reported in section 2 gives the $W_{Qi}$ (cf. Table I). The determination of the $N_i$, i.e. the number of equivalent pairs which contribute to each satellite is not easy. As already explained (5), it is the weakness of the method since it has not yet been possible to know what are the pairs associated with each satellite. From the LaF$_3$ structure [16], it is possible to list the classes of pairs by giving for each the $(R, N)$ couple, $R$ being the distance in Å between the two ions, $N$ the number of equivalent pairs. This list is the following:

(4.10, 4), (4.25, 2), (4.30, 2), (4.42, 4), (6.0, 4), (6.14, 2)...

The full list shows that a class of pairs contains 2, 4 or 6 pairs. Some classes can be very similar and their corresponding satellites unresolved. By a comparison of the satellite areas in the absorption spectrum of figure 3a, one could associate 2, 2, 4, 6, 4, 6 pairs respectively with satellites 1, 2, 3, 4, 5, 7 by supposing one satellite is associated with one class of pairs. While that supposition was correct for LaF$_3$ : Pr$^{3+}$ (5), it is probably incorrect here because Nd$^{3+}$ is a Kramers ion. As discussed in more detail in [10], the 8-fold degeneracy of the singly excited state and the 4-fold degeneracy of the ground state of the pair between which the optical transition occurs can be lifted. Many optical lines can thus be associated with one pair. The experiments where up-conversion is induced by two lasers [10] suggest that different satellites could be associated with the same pair. It is the case for satellites 4 and 7 and satellites 3 and 6. The equality, within the experimental accuracy, of the quenching rates for satellites 1 and 2 given in table I, also suggests that these satellites belong to the same pair.
As discussed in [10] this seems compatible with the behaviour of the corresponding up-conversion excitation line when a magnetic field is applied. In evaluating (1), it is then equivalent to associate 1, 1, 2, 3, 2, 3 pairs respectively with satellites 1 to 7. It must once more be clearly stated that this choice of \( N_i \), given in Table I and used below is the weakness of the analysis. Only a complete (and very difficult) spectroscopy of pairs could give a definitive answer.

With the \( W_{0i} \) and the \( N_i \) of Table I, the shape of the fluorescence decay can be calculated by (1). A plot of this calculated shape on a semi-log diagram shows that a non exponential decay appears for a 2 \( \% \) doped sample if a two decade variation is considered (which is possible for an experimental signal with a very good signal/noise ratio). With a 5 \( \% \) doped sample, a one decade variation shows unambiguously the non exponential character of the signal. Since Voronko et al. [7] clearly observed an exponential signal over a two decade variation for any concentration at \( T < 10 \text{ K} \), migration of the excitation must be considered. In addition, the linear dependence of \( W_Q \) at low temperatures (cf. Fig. 7) shows that the migration is fast and that (2) can be used to calculate the quenching rate. With the values of Table I, one finds

\[
W_Q = c \sum_i N_i W_{0i} = c \times 10^4 \text{ s}^{-1}.
\]

The use of only 7 classes of pairs in calculating the above sum introduces a small error because for other pairs, whose associated lines are hidden within the central line, the \( W_{0i} \) values are weak (the contribution of \( N_5 W_{05} \) to (8) is already quite small).

The result is shown by the continuous straight line in figure 8, the points being the experimental values of \( W_Q \) deduced from Voronko's results by

\[
W_Q = \frac{1}{\tau} - W_0.
\]

The broken straight line in this figure shows the linear dependence of \( W_Q \) versus \( c \) at low concentrations. The difference between the slopes of the two straight lines can be thought as resulting from the use of (2) valid in the extreme case of very fast migration. If the migration is « only fast », \( W_Q \) can be slightly smaller keeping its linear dependence versus the concentration. It can be pointed out that keeping the first group of values for the \( N_i \)'s would have given a twice larger value for \( W_Q \). The disagreement with the experimental result would have then been larger and difficult to explain : how processes observed on pairs could be quenched in concentrated crystals? Thus, our choice of the \( N_i \) numbers is confirmed by the consistency of the results.

The situation found here is quite different from that of Nd\( ^{3+} \) doped pentaphosphate considered by Broer et al. [17]. For this compound, an exponential decay was observed, suggesting a migration of the excitation among the donors whereas FLN experiments showed that spectral diffusion was absent. Broer et al. [17], calculated the shape of the fluorescence decay using (1) with values of \( W_{0i} \) deduced from the room temperature quenching rate within the dipole-dipole interaction model. The exponential shape they got for any concentration was justified as resulting from the inequality \( \tau_0^{-1} > W_{01} \), where \( \tau_0^{-1} = 2.93 \times 10^3 \text{ s}^{-1} \) is the radiative decay rate and \( W_{01} = 1.1 \times 10^3 \) the quenching rate for two ions in first neighbour position. Thus, the exponential shape could not be used as an indication of migration. Nevertheless, the controversy on the existence of migration at low temperatures is perhaps not finished since four wave mixing experiments showing a migration at 10 K have recently been reported [18]. For the LaF\(_3\) : Nd\( ^{3+} \) case studied here, the values of the radiative decay rate \( \tau_0^{-1} = 1.2 \times 10^3 \text{ s}^{-1} \) and of the fastest measured quenching rate \( W_{06} = 1.58 \times 10^3 \text{ s}^{-1} \) (see Table I) are such that \( \tau_0^{-1} < W_{06} \), making, as mentioned above, the calculated signal non-exponential for concentrations larger than 5 \( \% \). That means that the observed exponential decay can really be used as an argument in favour of the existence of migration. It must be pointed out that the measurements reported here bring more confidence to this existence by the relatively good agreement between the quenching rate
deduced from the experiments of Voronko et al. [7] and that predicted from the pair measurements and given in (8).

A similar comparison between predictions based on the measurements on pairs and the observed behaviour of concentrated crystals has already been done for LaF$_3$ : Pr$^{3+}$ [5]. But since migration was absent at low temperatures in this system, the signals were not exponential and their slope at $t = 0$ was used for the comparison. The agreement was excellent for $c < 0.3$ but for $c > 0.3$ three ion processes were considered to explain that the observed efficiency of the quenching was greater than predicted. The quasi quadratic dependence of $W_Q$ versus $c$ observed by Voronko et al. for $c > 0.1$ (cf. Fig. 7) can also be attributed to three ion processes which can be phenomenologically represented in (2) by an additional term of the form

$$c^2 \sum_{ij} W_{0ij}$$

where $i$ and $j$ are the sites of the ions with which the central ion can exchange energy. The appearance of these three ion processes at a concentration lower for Nd$^{3+}$ than for Pr$^{3+}$ is certainly due to the weakness of the two ions quenching in LaF$_3$ : Nd$^{3+}$ at low temperatures. This weakness also explains why the migration is so efficient at low temperatures. It is known that, due to the inhomogeneous broadening induced by random strains, donor-donor transfer is usually weak at low temperatures and becomes noticeable when the lines are broadened by relaxation effects. That was clearly proved in LaF$_3$ : Pr$^{3+}$ [19]. But as the criterium for migration is a comparison between donor-donor and donor-acceptor transfer efficiencies, the former can dominate, even if it is small, when the latter is particularly weak. In addition, since these efficiencies change with temperature, the situation can be different at high temperatures. Indeed, Voronko et al. [7] have observed for small $c$'s, a non exponential decay at high temperatures, an indication that the migration rate has been less increased than the donor-acceptor transfer rate.

Finally, the measured $W_{0ij}$ values can be compared with the value of $\alpha$ found by Voronko et al. at low temperatures supposing a dipole-dipole interaction. If this hypothesis were correct, one could deduce the $W_{0ij}$ for pairs in first neighbour position. With $\alpha = 2.3 \times 10^{-42} \text{ s}^{-1} \text{ cm}^6$ [7] one should find $W_{01} = 480 \text{ s}^{-1}$ for $R = 4.1 \text{ Å}$. The greatest value in table I, which can be associated with pairs in first neighbour position is $1600 \text{ s}^{-1}$. Once more, it seems that a short range interaction does exist between nearest ions.

Results of the high temperature measurements on pairs can also be used to predict the behaviour of concentrated crystals. The impossibility to measure the lifetime of satellites 4 and 6 (see Fig. 4) is not perturbing since, from the above discussion, these satellites have the same dynamics as respectively satellites 7 and 3. Figure 9 shows for a 3% doped crystal the value of the quenching rate $W_Q$ calculated from (2) with the $W_{0ij}$ deduced from the measured lifetimes in the temperature range 1.2 to 30 K. This figure also shows the $W_Q$ values deduced from the Voronko et al. [7] experiments. There is a strong disagreement which is confirmed when the concentration dependence (not shown here) is considered. Both these disagreements show that observed decay times are shorter that the ones predicted from pair measurements, i.e. that processes other than pair processes do exist at high temperatures. Again three ion processes can be considered, the quenching by unknown traps with so high an efficiency being ruled out.

3.4 (Nd, Pr) Pairs. — From figure 5, it appears that at low temperatures the quenching for (Nd, Pr) pairs is more efficient than for (Nd, Nd) pairs. The quenching rate for the more strongly coupled pairs has not been measured since the I.R. fluorescence does not exist for these pairs. The results for satellites I to IV have then to be compared with the rates for pairs in 2d or 3th neighbour position, i.e. satellites (1,2) or 7 of table I. The quenching rate is thus approximately 30 times greater for (Nd, Pr) pairs than for (Nd, Nd) pairs.

This greater efficiency results from the energy levels positions of the two ions. From figure 1, it can be seen that the following processes

$$[\text{Nd}(^{4}F_{3/2}), \text{Pr}(^{3}H_{4})] \rightarrow [\text{Nd}(^{4}I_{15/2}), \text{Pr}(^{3}F_{7})]$$

$$[\text{Nd}(^{4}F_{3/2}), \text{Pr}(^{3}H_{4})] \rightarrow [\text{Nd}(^{4}I_{13/2}), \text{Pr}(^{3}F_{4})]$$

Fig. 9. — Temperature variation of the quenching rate $W_Q$ for a 3% doped sample. Full circles are experimental values deduced from Voronko et al. [7] results, open circles are predicted values from pair measurements.
are possible for many levels of the multiplets with emission of phonons of energy ranging from 1 to 290 cm\(^{-1}\).

The quenching rates of the fluorescence indicated in table 2 show, within their accuracy, that the efficiency for isolated Nd\(^{3+}\) and for (Nd, Nd) pairs is the same. It then results from Pr\(^{3+}\) ions which are not too near these ions or these pairs. A correlation between the rates given in figure 5 and those of table 2 is difficult because, once more, it is yet impossible to associate each satellite with a specific pair. Finally, one may wonder why one observes a single exponential decay when Pr\(^{3+}\) is shortening the Nd\(^{3+}\) lifetimes (Table II): in this case, from the random distribution of Pr\(^{3+}\) ions, one would expect a non-exponential decay. The answer is that, with our selective excitation technique, we only observe the Nd\(^{3+}\) ions or pairs which have no Pr\(^{3+}\) as close neighbours (Nd\(^{3+}\) ions or pairs with close Pr\(^{3+}\) disturbers yield significantly shifted absorption transitions).

4. Conclusion.

The comparison between the quenching observed with concentrated samples and the predictions from direct measurements on pairs in dilute crystals had shown a good agreement for LaF\(_3\) : Pr\(^{3+}\), thus validating the recently developed new approach of the transfer problem. Applied here to the LaF\(_3\) : Nd\(^{3+}\) system, it has led to the conclusion that the migration of the excitation among the donors dominates even at low temperatures. This conclusion is based: i) on the fact that the predicted fluorescence decay shape is clearly non exponential whereas the previously reported experimental shape was exponential and ii) on the linear dependence of the quenching rate versus the concentration. This rather unusual situation results from a very weak efficiency of the donor-acceptor transfer which can thus be dominated by the donor-donor transfer even if this latter has a weak efficiency. Therefore, LaF\(_3\) : Nd\(^{3+}\) seems to be an interesting system to study resonant or quasi-resonant transfers.

Other conclusions can be drawn from the direct measurements on pairs. Firstly, they once more have shown the existence of a short range interaction which dominates the dipole-dipole interaction for very near ions. Secondly, they have shown that quenching rates of the Nd\(^{3+}\) fluorescence are about 30 times larger for (Nd, Pr) pairs than for (Nd, Nd) pairs. Finally, they have given evidence of the efficiency of three ion processes.

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