Time-resolved fluorescence line narrowing in Yb^{3+}-doped fluoroindate glasses

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Fluorescence line narrowing measurements have been carried out between the lowest Stark components of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions in fluoroindate glasses. At low concentration (0.15 mol % of Yb^{3+}) the luminescence spectrum consists in a narrow band which repeats the exciting profile, so the migration processes between Yb^{3+} ions are not important at this concentration. However, at higher concentrations (0.75 or 2.25 mol %) the luminescence spectrum contains moreover a broad band produced by other ions nonexcited initially (background fluorescence). A model is proposed to describe the temporal evolution of the narrow band fluorescence and the shape of the background fluorescence. A very good agreement with the experimental results is found taking into account a dipole-quadrupole ($S=8$) nonradiative energy transfer process assisted by a phonon. [S0163-1829(98)03406-7]

I. INTRODUCTION

The conversion from infrared to visible light (upconversion) has been extensively investigated over the last two decades. In these processes the most efficient and therefore the most important schemes have been obtained in fluoride compounds involving successive transfer from Yb^{3+} to activator ions (Er^{3+}, Ho^{3+}, or Tm^{3+}).[1–4] Fluoroindate glasses are now emerging as a promising group for efficient upconversion processes because of their low phonon energies in comparison with other fluoride glasses.[5–9] On the other hand, the upconversion efficiency is largely influenced by the energy transfer between Yb^{3+} ions, so the knowledge of these migration processes is essential in order to obtain systems with high upconversion efficiency. In this way, the time resolved fluorescence line narrowing (TRFLN) technique has proven to be a powerful tool to analyze these migration processes between ions.

In the TRFLN technique an inhomogeneously broadened absorption band is excited with a monochromatic pulsed light. Initially, a narrow line emission spectrum coming from ions that were excited by the incident light is observed. However, as time passes broad background fluorescence can be observed coming from ions excited by energy transfer. The analysis of the fluorescence spectrum evolution in these experiments allows us to obtain information of the microscopic transfer processes between ions, the different sites occupied by the ions in the matrix, the homogeneous widths of the transitions, etc.

The Yb^{3+} ions are especially interesting for TRFLN measurements because these ions present a simple level structure. They have only two levels with a gap between them of about 10 000 cm^{-1} and the Stark components are well resolved at low temperature. Moreover, the relatively long lifetime (about 1.66 ms in fluoroindate glasses[10]) allows us to follow the temporal evolution of the fluorescence without difficulty.

However, there are only a few works dealing with the TRFLN of Yb^{3+} in glasses and, in particular, analyzing the background fluorescence evolution such as Refs. 11 and 12. It is found that a theoretical model which explains the spectral diffusion in glasses is needed.

In this work, the energy transfer between different sites occupied by Yb^{3+} ions in fluoroindate glasses is investigated by TRFLN as a function of concentration in the range 0.15–2.25 mol %. Theoretical expressions for the evolution of the fluorescence are obtained in order to analyze these experimental results.

II. EXPERIMENTAL

The samples used in this study were prepared with the following composition in mol %: (40-x) InF$_3$, 20ZnF$_2$, 20SrF$_2$, 20BaF$_2$ and x YbF$_3$, with x equal to 0.15, 0.75, or 2.25. Broad band emission spectra were obtained by exciting the samples with light from a 250 W incandescent lamp passed through a 0.25 m monochromator. Fluorescence was detected through a 0.25 m double monochromator with a silicon avalanche photodiode.

For TRFLN spectra a tunable jet dye laser was used as excitation source. This laser was pumped by the 532 nm pulsed light from a doubled Nd-YAG laser. The time resolved fluorescence was recorded using a digital storage oscilloscope controlled by a personal computer. For low-temperature measurements a helium continuous flow cryostat was utilized in the range from 12 to 50 K.

III. THEORETICAL REVIEW

In TRFLN experiments the temporal evolution of the fluorescence can be analyzed by using a formalism based on rate equations for the set of functions $\{P_n(t)\}$,[13–18] where $P_n(t)$ is the probability that ion n is excited at time t:

$$\frac{dP_n(t)}{dt} = -\left(\frac{1}{\tau_n} + X_n + \sum_{n \neq n'} W_{nn'}\right) P_n(t)$$

$$+ \sum_{n' \neq n} W_{n'n} P_{n'}(t), \tag{1}$$

where τ_n is the lifetime of ion n, X_n is the transfer rate from ion n to all the traps in the system, and $W_{nn'}$ is the transfer rate from ion n to ion n'.

In systems where the spectral transfer leads to background fluorescence, the most appropriate quantitative measure of the transfer is the ratio of the intensity in the narrow band I_R, coming from ions excited resonantly, to the total intensity, which includes the background fluorescence I_B. This relation can be expressed as

$$R(t) = \frac{I_R}{I_R + I_B}. \tag{2}$$

If τ_n is equal for all the ions and the transfer to the traps is ignored, then $R(t)$ is identified with the function $P_0(t)$ which is the solution to Eq. (1) having excluded the contributions of the lifetime and the transfer rate to the traps, i.e.,

$$\frac{dP_n(t)}{dt} = -\sum_{n' \neq n} W_{nn'} P_n(t) + \sum_{n' \neq n} W_{n'n} P_{n'}(t), \tag{3}$$

with the initial conditions $P_0(0) = 1$ and $P_n(0) = 0$ for $n \neq 0$.

Exact solutions for $P_0(t)$ when the active ions form part of an arranged lattice and under certain restrictions are presented in Ref. 13. However, the calculation of the function $P_0(t)$ is very complicated when the ion array is disordered. When this happens it is necessary to compare $R(t)$ with the configurational average of $P_0(t)$. In this case a reasonable approximation to $R(t)$ for systems with asymmetric transfer rates and depending on the energy mismatch between ions was obtained by Huber and Ching.[15] Their results can be expressed by

$$R(t,E_0) = \prod_L \int dE_L p(E_L) \left\{ 1 + c \left[\frac{\exp(-W_{0L}t)}{W_{0L} + W_{L0}} \right. \right.$$
$$\left. \left. \times [W_{L0} \exp(W_{0L}t) + W_{0L} \exp(-W_{L0}t)] - 1 \right] \right\}, \tag{4}$$

where E_0 is the energy of ions excited by a pulse at $t = 0$, the index L refers to sites, $p(E)$ is the normalized inhomogeneous line shape, c is the probability that site L is occupied, and W_{0L} is the transfer rates between sites and they are related by the detailed balance equation

$$W_{0L} \exp(-E_0/KT) = W_{L0} \exp(-E_L/KT). \tag{5}$$

The background fluorescence spectra do no coincide with the inhomogeneous line shape when the transfer rates are asymmetric and energy dependent. Huber and Ching also analyzed the evolution of the background.[15] They obtained the following expression for the probability $f(t,E,E_0)$ that ions with energy E are excited at time t:

$$f(t,E,E_0) = \frac{[1 - R(t,E_0)]p(E)}{\ln R(t,E_0)}$$
$$\times \left[-C_A 4\pi \int_0^{R_V} R^2 dR \left(1 - \frac{1}{W_-} \right. \right.$$
$$\left. \left. - \frac{\exp(-W_{0R}W_+ t)}{W_+} \right) \right], \tag{6}$$

where $R(t,E_0)$ is given by Eq. (4).

IV. EVOLUTION OF THE FLUORESCENCE

A. Resonant fluorescence

In order to be compared with experimental results, Eq. (4) must be evaluated assuming an interaction mechanism for the energy transfer processes. A multipole interaction assisted by a phonon will be here considered.

The right-hand side of Eq. (4) may be written as the exponential of a sum of logarithms and expanding the logarithms to first order in c. If the transfer rate is treated as a continuous function of the separation and the sum on L is converted to an integral, then

$$R(t,E_0) = \exp\left[-C_A 4\pi \int_0^{R_V} R^2 dR \int \left(1 - \frac{1}{W_-} \right. \right.$$
$$\left. \left. - \frac{\exp(-W_{0R}W_+ t)}{W_+} \right) p(E) dE \right], \tag{7}$$

where R_v is the radius of a sphere of volume V that contains a high number of ions N so that N/V is the acceptor concentration C_A and the terms W_+ and W_- are given by

$$W_+ = 1 + \exp\left(\frac{E - E_0}{KT} \right), \tag{8}$$

$$W_- = 1 + \exp\left(-\frac{E - E_0}{KT} \right). \tag{9}$$

Considering a multipole interaction assisted by a phonon W_{0R} can be expressed by

$$W_{0R} = \frac{C_{DA}^{(S)}}{R^S} W(E - E_0), \tag{10}$$

where $S = 6, 8, 10, \ldots$, depending on the interaction character (dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, etc.), R is the donor-acceptor distance, $C_{DA}^{(S)}$ is the donor-acceptor energy transfer parameter, and $W(E - E_0)$ is the probability of emission or absorption of a phonon with energy $|E - E_0|$ and can be expressed as[19]

$$W(E - E_0)$$
$$= \begin{cases} |E - E_0| \left[\dfrac{1}{\exp[|E - E_0|/KT] - 1} + 1 \right] & E \leq E_0, \\ |E - E_0| \left[\dfrac{1}{\exp[|E - E_0|/KT] - 1} \right] & E \geq E_0. \end{cases} \tag{11}$$
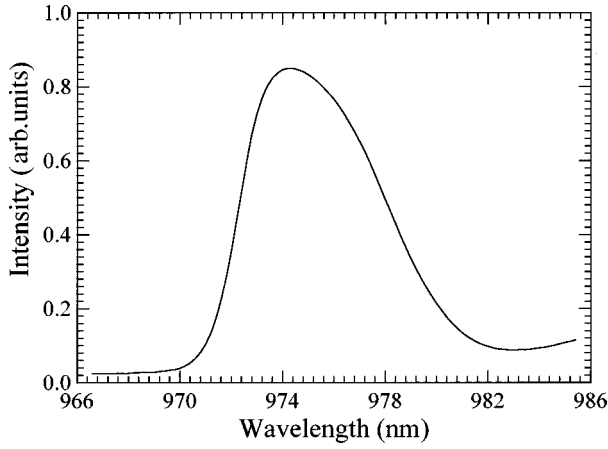
FIG. 1. Inhomogeneous emission line shape between the lowest Stark components of the transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ in fluoroindate glass with 0.75 mol % of Yb^{3+} at 12 K. The excitation wavelength was 920 nm.

Evaluating Eq. (7) in the limit $R_v \rightarrow \infty$, finally

$$R(t,E_0) = \exp[-\beta t^{3/S}], \qquad (12)$$

with

$$\beta = C_A \frac{4\pi}{3} (C_{DA}^{(S)})^{3/S} \Gamma(1-3/S)$$

$$\times \int W(E-E_0)^{3/S} W_+^{3/S-1} p(E) dE. \qquad (13)$$

As a particular case, if the transfer rate is symmetric and independent of the energy mismatch between ions, then the expression proposed in Ref. 13 is obtained, i.e.,

$$R(t,E_0) = \exp\left[-C_A \frac{4\pi}{3} (C_{DA}^{(S)})^{3/S} \Gamma(1-3/S) 2^{3/S-1} t^{3/S}\right]. \qquad (14)$$

It must be emphasized that Eq. (14) has the same functional dependence on t that Eq. (12) does.
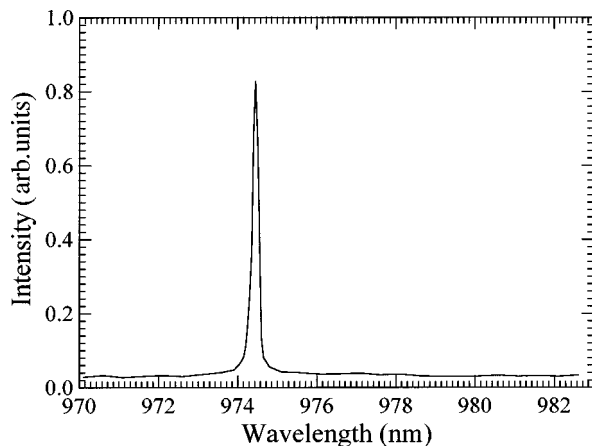

FIG. 2. TRFLN measurement in fluoroindate glass with 0.15 mol % of Yb^{3+} at 12 K with a delay of 3 ms after laser excitation at 974.6 nm.
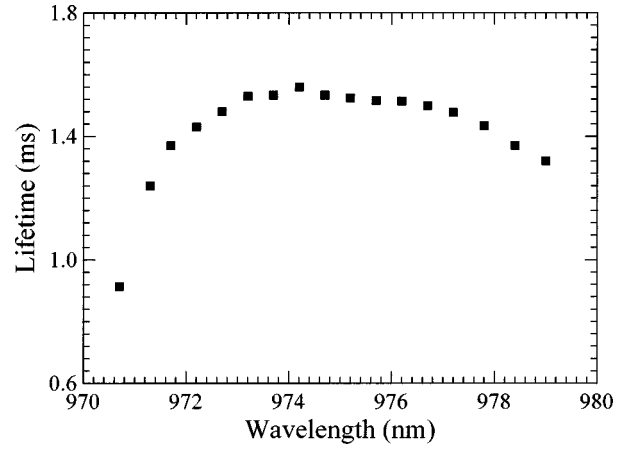

FIG. 3. Lifetime as a function of excitation wavelength for fluoroindate glass with 0.15 mol % of Yb^{3+} at 12 K.

B. Background fluorescence

The evolution of the background fluorescence after the excitation pulse, given by Eq. (6), can also be evaluated assuming a multipole interaction mechanism assisted by a phonon. The obtained result can be expressed by

$$f(t,E,E_0) = \frac{[1-R(t,E_0)]p(E)}{\ln R(t,E_0)} \left[-C_A \frac{4\pi}{3} \Gamma(1-3/S) \right.$$

$$\left. \times (C_{DA}^{(S)} W(E-E_0)t)^{3/S} W_+^{3/S-1} \right], \qquad (15)$$

where $R(t,E_0)$ is now given by Eq. (12). As a particular case, if the transfer rate is symmetric and independent of the energy mismatch between ions, the expression proposed by Huber and Ching[15] can be obtained from Eq. (15).

V. EXPERIMENTAL RESULTS AND DISCUSSION

The inhomogeneous emission line shape corresponding to the transition between the lowest Stark components of the levels $^2F_{5/2}$ and $^2F_{7/2}$ of Yb^{3+} ions is presented in Fig. 1. This spectrum has been obtained exciting at 920 nm a fluor-
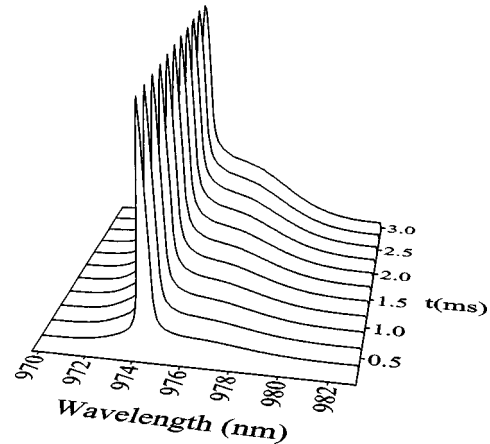

FIG. 4. TRFLN spectra obtained in fluoroindate glass with 0.75 mol % of Yb^{3+} at 12 K with increasing delay after laser pulse at 974.6 nm. Spectra have been normalized to the intensity of the narrow line emission.

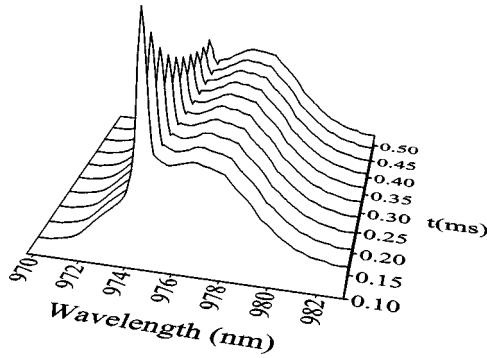FIG. 5. TRFLN spectra obtained in fluoroindate glass with 2.25 mol % of Yb^{3+} at 12 K with increasing delay after laser pulse at 974.6 nm. Spectra have been normalized to the intensity of the broad band emission.

oindate glass with 0.75 mol % of Yb^{3+} at 12 K. The emission spectrum changes when the Yb^{3+} concentration is enlarged due to efficient radiative energy transfer processes.[10] In the matrix in which these processes are not relevant,[12,20] a shift of the emission band towards higher wavelength when the Yb^{3+} concentration is enlarged, due to migration processes between Yb^{3+} ions, has been observed.

The TRFLN measurement with a delay of 3 ms after excitation in fluoroindate glass with 0.15 mol % of Yb^{3+} at 12 K is showed in Fig. 2. It is outstanding that, within the experimental resolution, only is observed emission coming from ions excited initially. This allows to conclude that for this concentration the transfer processes between different sites are negligible. The same conclusion was obtained in the analysis of the energy transfer processes between Yb^{3+} (donor) and Tm^{3+} or Ho^{3+} ions (acceptors) in fluoroindate glasses with low concentrations of Yb^{3+}.[10,21] In these codoped samples the luminescence decay curves of the Yb^{3+} ions were well fitted to the Inokuti model,[22] which does not take into account migration between donors.

Since the energy transfer processes are negligible for concentrations of 0.15 mol %, it is possible to obtain the Yb^{3+} lifetime for each site exciting with a narrow line and mea-

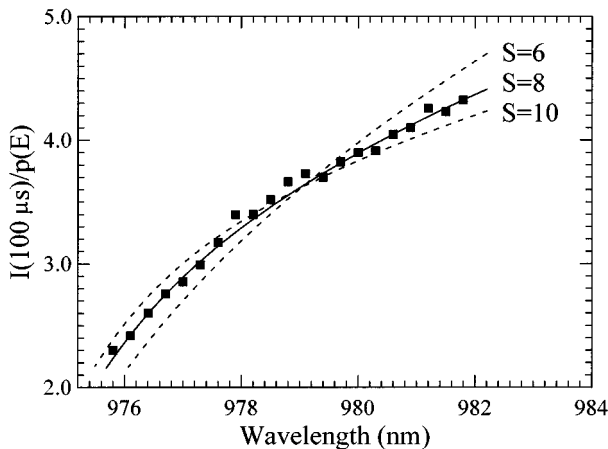FIG. 6. Ratio between the TRFLN spectrum obtained with a delay of 100 μs in fluoroindate glass with 2.25 mol % of Yb^{3+} and the inhomogeneous band (Fig. 1). The lines correspond to the ratios calculated from Eq. (15) with different values for S.
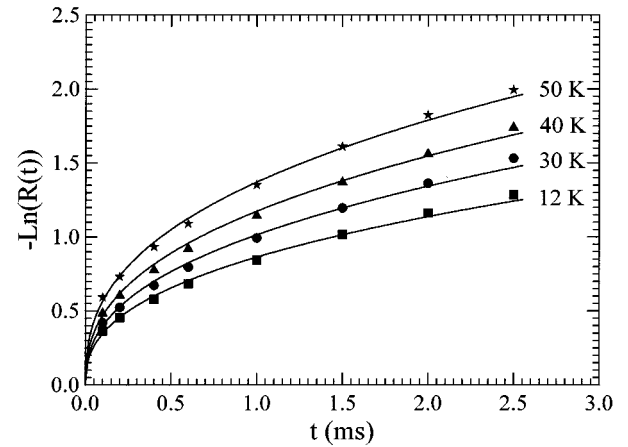

FIG. 7. Values obtained for $R(t)$ as a function of delay time with laser excitation at 974.6 nm at different temperatures in fluoroindate glass with 0.75 mol % of Yb^{3+}. The solid lines correspond to the fits to Eq. (12).

suring the fluorescence temporal evolution. The decays are well fitted by exponential curves in the central zone of the band, but the fits worse in the tails while the lifetime decreases. In Fig. 3 the obtained lifetime is presented as a function of excitation wavelength at 12 K. A similar dependence of the lifetime has also been observed in other matrices.[12,23,24] The nonexponential behavior of the decays observed in the tails of the inhomogeneous band, according to Savostyanov et al.[12] in phosphate glasses, could be due to the existence of centers with the same energy but with different lifetime.

TRFLN spectra obtained in fluoroindate glasses with 0.75 and 2.25 mol % of Yb^{3+} are presented in Figs. 4 and 5, respectively. These spectra have been obtained at 12 K with increasing delays after laser pulse at 974.6 nm. It is noteworthy that for these concentrations the background fluorescence at long times becomes important, especially in the sample with 2.25 mol % of Yb^{3+} and in the low-energy side.

In order to analyze the dependence of the transfer rate on the energy mismatch, TRFLN spectra have been obtained exciting at different positions in the inhomogeneous band. The background fluorescence observed in these measurements depends on the excitation wavelength. The ratio between the TRFLN spectrum obtained with a delay of 100 μs and the inhomogeneous band (Fig. 1) is presented in Fig. 6. This ratio can be also calculated from Eq. (15) considering a probability $W(E-E_0)$ given by Eq. (11). The results are presented in Fig. 6 for different values of S. As it can be

TABLE I. Values obtained for S and β at different temperatures in fluoroindate glass with 0.75 mol % of Yb^{3+} and laser excitation at 974.6 nm.

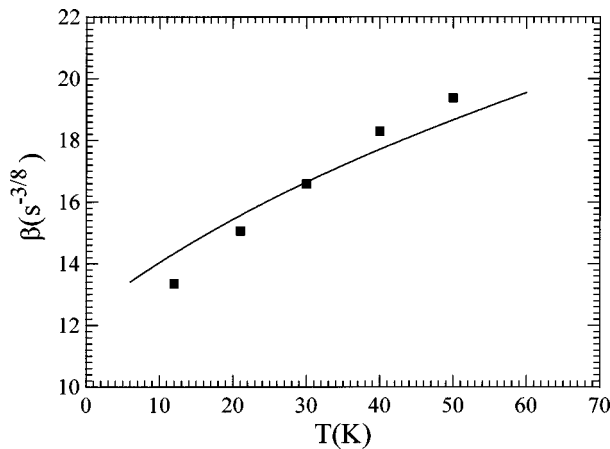| T(K)	S	$\beta(s^{-3/8})$
12	7.6	13.4
21	7.5	15.1
30	7.4	16.6
40	7.6	18.3
50	7.8	19.4

FIG. 8. Temperature dependence of β (■) in fluoroindate glass with 0.75 mol % of Yb^{3+} with laser excitation at 974.6 nm. The solid line corresponds to the fit to Eq. (13).

observed, a good fitting is obtained with $S=8$ indicating that the transfer toward different sites has dipole-quadrupole character and is assisted by a phonon.

This mixed character of the quasiresonant transfer between Yb^{3+} ions can result surprising but it can be understood with the following considerations. An expression for W_{OR} more general than Eq. (10) would include a sum over terms with different values of S. The dominant term in this sum depends on the values of the parameters $C_{DA}^{(S)}$ and on the mean distance between ions. Therefore, it depends on the dipole and quadrupole transition probabilities for an isolated ion and on the concentration of ions. For long distances, the dipole-dipole term is dominant but when the distance between ions is decreased, the other contributions to W_{OR} can be higher.

The energy of the phonons involved in the transfer corresponds to the difference of energy $E-E_0$ between donor and acceptor. From the inhomogeneous profile in Fig. 5, it is concluded that this energy is lower than 80 cm^{-1}.

The ratio $R(t)$, given by Eq. (2), has been calculated from TRFLN measurements. The values obtained for this param-

eter with laser excitation at 974.6 nm are presented in Fig. 7 as a function of delay time for different temperatures in fluoroindate glass with 0.75 mol % of Yb^{3+}. The fits to Eq. (12) are also included in this figure.

The values calculated for S and β from the fits presented in Fig. 7 are included in Table I. From these results a mean value of 7.6 is obtained for S. Moreover, in a sample with 2.25 mol % of Yb^{3+} a value of 7.7 for S has been obtained at 12 K with laser excitation at 974.6 nm. If the excitation is carried out at 973.4 nm the values obtained for S at 12 K are 7.5 and 8.8 in samples with 0.75 and 2.25 mol % of Yb^{3+}, respectively. In conclusion, all the values obtained for S are closed to 8, independent of the concentration, the temperature of the sample, or the excitation wavelength. This result is in agreement with the value obtained above from the analysis of the background fluorescence evolution.

The temperature dependence of β in the range from 12 to 50 K is presented in Fig. 8. A similar behavior was found for the diffusion parameter analyzing the energy transfer processes in fluoroindate glasses codoped with Yb^{3+} and Tm^{3+} or Ho^{3+}.[21] The fit to Eq. (13), considering $S=8$, $W(E-E_0)$ given by Eq. (11) and the inhomogeneous line shape $p(E)$ given by the inhomogeneous emission presented in Fig. 1, is also included in Fig. 8. The agreement can be considered reasonably good within the approximations involved in the theoretical model. A value of 2.4×10^{-54} cm^8 s^{-1} for the transfer parameter $C_{DA}^{(8)}$ is obtained from the fitting.

VI. CONCLUSIONS

Theoretical expressions for the evolution of the narrow band emission and the background fluorescence in TRFLN experiments in glasses have been obtained. An asymmetric and energy dependent transfer mechanism, based on a phonon assisted multipole interaction, was considered. Very good agreement with experimental results in Yb^{3+} doped fluoroindate glasses is found. The interaction between Yb^{3+} ions would have dipole-quadrupole character in these glasses.

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