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Energy up-conversion in the visible to ultraviolet range in LaF_3:(Pr^{3+},Nd^{3+})

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We report the observation, at low temperature, of ultraviolet fluorescence arising from state $^4D_{3/2}$ of Nd^{3+}, in LaF_3 containing impurities of Pr and Nd, following the irradiation of the sample by a laser pulse resonant with the $^3H_4$ to $^1D_2$ Pr^{3+} transition. The mechanism responsible for the up-conversion effect is shown to be photon addition by energy transfer, within a Pr^{3+}-Pr^{3+}-Nd^{3+} triad. The up-conversion process is observed in a (1 at. % Pr+0.5 at. % Nd)—doped sample and in a 0.1 at. % Nd—doped crystal where Pr impurities are present as unintentional traces. The different behaviors obtained from the two samples are discussed.

I. INTRODUCTION

Energy up-conversion processes have been the object of great interest in recent years.[1,2] The generation of coherent light at short wavelength—green to violet visible frequencies and ultraviolet (uv)—is still an important goal and the development of broad tunable laser sources in this spectral region is of considerable interest. Among the different mechanisms allowing light generation at these frequencies, up-conversion by energy transfer between electronic centers in solids has proven to be one of the most efficient.[1] Due to the well-established spectroscopic properties of the trivalent rare-earth (RE) ions in solids, crystals, and glasses doped with these elements have often been chosen as model systems for the research in this domain. An important number of these works are concerned with LaF_3 doped with Pr and/or Nd, and several up-conversion processes have been reported where visible or uv light emission follows the excitation of the system by a visible dye laser.[3-8]

From a different point of view, up-conversion processes involving the interaction between a limited number of ionic impurities has proven to be a useful spectroscopic tool for the study of groups of ionic impurities. The detection of up-converted emission produced by energy transfer within these clusters allows the selective observation of the impurity group avoiding the saturation of the detection by the emission from isolated ions. Also the observations of the temporal dynamics of the up-converted emission provides important information on the nature and the strength of the coupling between the RE impurities. This technique has been particularly successful for the study of clusters in crystals where charge compensation exists and where the impurity distribution is not random.[2,9]

In this paper, we present a new up-conversion process involving energy transfer between Pr^{3+} and Nd^{3+} ions in LaF_3. After excitation of the crystal, at low temperature, by a dye laser pulse resonant with the transition $^3H_4(1)$ to $^1D_2(2)$ of Pr^{3+} (16 896 cm^{-1}), uv fluorescence is observed corresponding to transitions arising from level $L(^4D_{3/2})$ of Nd^{3+} (Fig. 1). As will be discussed below, this up-conversion effect can be understood in terms of energy transfer within a triad of impurities composed by two Pr ions and a Nd ion. The present effect appears to be strong in a 1 at. % Pr—doped sample but is also unusually intense in samples where Pr ions are only present as unintentional traces resulting from the crystal preparation. Up-conversion effects involving RE impurity traces have already been reported.[4] This is, however, the first case where a three-ion mechanism is involved.

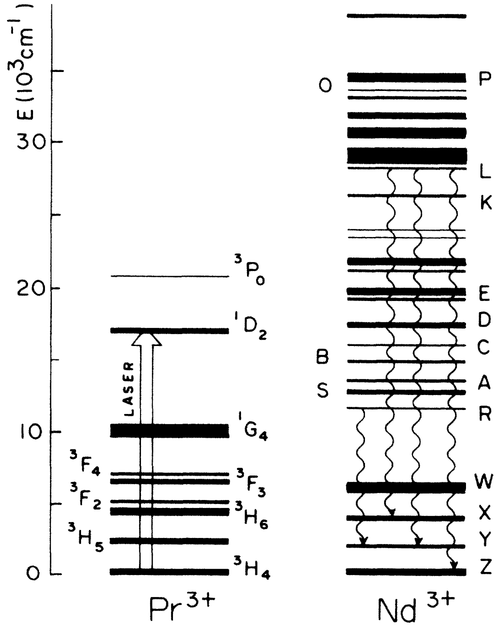

FIG. 1. Energy levels of Pr^{3+} and Nd^{3+} in LaF_3. The excitation transition and the observed fluorescences are indicated.

II. EXPERIMENT

Two samples are used for the experiments. The first one is a LaF_3 crystal doped with 1 at. % of Pr^{3+} and 0.5 at. % of Nd^{3+} purchased from Varian. As this sample contains an appreciable amount of Pr, it will be hereafter denoted as the concentrated sample, although such concentration is generally considered as low. The second sample is a 0.1 at. % Nd–doped LaF_3 crystal purchased from Optovac, Inc. As no specified Pr concentration is given for this sample, it will be called, in the following, the dilute sample. All the experiments were carried out at 20 K. The excitation laser pulse is obtained from a Nd:YAG pumped dye laser constructed in the grazing incidence configuration (YAG denotes yttrium aluminum garnet). The spectral linewidth of the laser emission is 0.2 cm^{-1}, its duration 8 ns, and its energy 0.2 mJ. The laser beam was focused into the sample with a 6-cm focal length lens and was linearly polarized perpendicular to the *c* axis of the crystal. The beam propagated through the sample in the vertical direction. The detection was performed along the crystal *c*-axis direction. The fluorescence light was collected through uv transmitting optics and sent into the vertical entrance slit of a 1.4-m double spectrometer. Since an optical image of the illuminated region of the sample was formed at the entrance slit of the spectrometer, a small hole situated at the slit allowed selective observation of different portions of the crystal. The visible and the uv emissions were observed with a 1P28 photomultiplier tube. The infrared (ir) light was detected with a cooled 150 CVP photomultiplier tube from AMPEREX. The electronic treatment of the signals was performed with a boxcar averager.

III. RESULTS

When the excitation dye laser is tuned at the $^3H_4(1)$ to $^1D_2(2)$ transition of the Pr^{3+} ion uv, fluorescence is observed arising from level $L(^4D_{3/2})$ of Nd^{3+}. The observed fluorescence spectrum is shown in Fig. 2, where the corresponding transitions are indicated. No fluorescence associated to emissions from other Nd^{3+} levels lying above level $^1D_2(2)$ of Pr^{3+} was detected. In the concentrated sample the time-integrated intensity of the uv emission corresponding to the $^4D_{3/2}(1) \rightarrow {}^4I_{11/2}(2)$ transition (380 nm), obtained after excitation at ω_0 [the frequency corresponding to the center of the isolated Pr ion $^1D_2(2)$ absorption line] was compared to the well-known blue emission at 479 nm, corresponding to the $^3P_0 \rightarrow {}^3H_4(2)$ transition of Pr^{3+}, obtained by pair up-conversion in the same excitation conditions.[3] The fluorescence from Nd ions is 50 times weaker than that arising from Pr ions. The dependence of the intensity of the uv fluorescence from Nd ions on the laser intensity was observed to be quadratic.

The excitation spectra of the fluorescence at 380 nm are shown in Figs. 3 and 4 for the dilute and the concentrated samples. In the dilute sample, the excitation spectrum is essentially composed at all time delays by a single peak centered at ω_0. However, the spectrum recorded with a 50 μs gate, positioned immediately after the excitation time, shows a number of rapidly evolving peaks. These peaks spread over a wide spectral region and are not distributed near the main excitation line as expected for pair satellites.[10,11] Some of these lines indicated in the spectrum can be attributed to two photon absorption transitions between levels $^4I_{9/2}$ and $^2D_{3/2}(2)$ of Nd^{3+}.[12] The origin of the remaining lines could not be identified and is presumably due to other impurities. The fact that the excitation spectrum is essentially composed by a single line at ω_0 contrasts with the behavior observed in the concentrated crystal. In this crystal, at short delays, the excitation spectrum shows a broad structure around the excitation frequency of the isolated Pr^{3+} ion [Fig. 4(a)]. This structure can be attributed to Pr ions in sites where the crystalline field is appreciably distorted by the presence of one or several neighboring impurities. Due to the strong interionic coupling, the luminescence from these sites presents a short temporal evolution. Similar structures have already been observed in other systems and has been

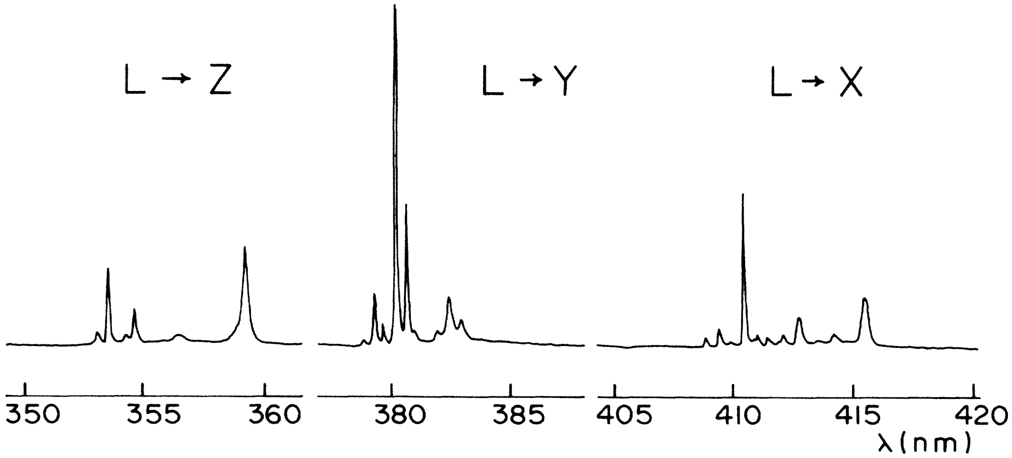

FIG. 2. Fluorescence spectrum of the uv up-conversion emission from the (1 at. % Pr + 0.5 at. % Nd)–doped LaF_3 sample at 20 K. The corresponding Nd^{3+} transitions are indicated.

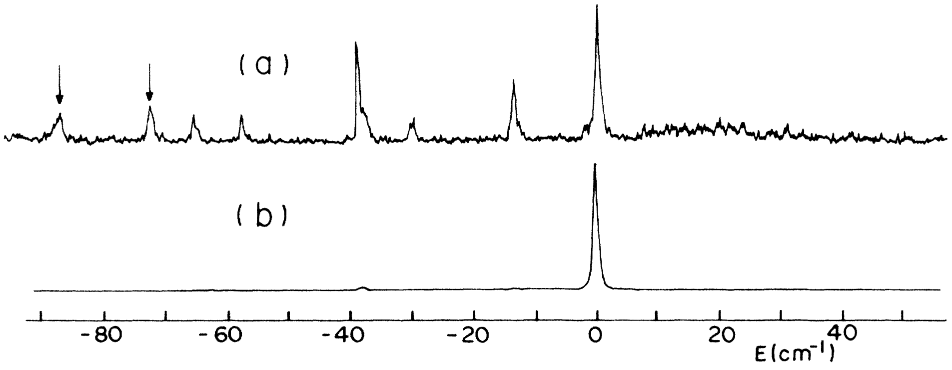

FIG. 3. Excitation spectrum of the 380 nm fluorescence arising from the 0.1 at. % Nd—doped LaF_3 crystal at 20 K. Spectrum (a) was recorded using a 50 μs detection gate positioned immediately after the laser pulse. Spectrum (b) is the time-integrated spectrum. The origin of the energy scale corresponds to the Pr^{3+} ion $^3H_4(1)$ to $^1D_2(2)$ excitation frequency. The lines indicated by the arrows are probably due to two photon absorption transitions.

attributed to the excitation frequencies of pairs of triads of impurities.[8,10] At longer delays, the excitation spectrum is dominated by frequency ω_0 which correspond to quasi-isolated ions (ions weakly coupled with other impurities), but the contribution of the perturbed sites is still observable in the asymmetric shape of the line. The relative contribution of the central line to the spectra of the dilute and concentrated samples is different. However, if a random distribution of the impurities is assumed, the relative number of impurity clusters (with the same number of ions) in the different crystal site configurations is independent of concentration at low concentration. As no evidence for nonrandom impurity distribution has been given in these materials, we interpret the different weight of the central line in the two samples as due to variations of the penetration of the excitation beam in the two crystals. In fact, we observe that for Pr concentrations as low as 0.1% the penetration of the excitation beam into the crystal is greatly diminished at the central line frequency.[13] Figure 4 shows the influence of this effect on the excitation spectrum of the uv emission when the light is collected from a portion of the concentrated sample lying at a distance of 1.5 mm from the laser beam incidence surface. So the concentrated sample is optically thick at the central frequency and thin at other frequencies, whereas the dilute sample is optically thin at all frequencies. Since the quasi-isolated ions are the most abundant, their contribution is predominant in the dilute sample. The fact that no satellite line is observed in this crystal around the main line is probably due to the low signal intensity collected when the detection is performed during a short time interval after the laser pulse.

In addition to the uv up-converted fluorescence, infrared fluorescence, corresponding to the $R(^4F_{3/2}) \rightarrow Y(^4I_{11/2})$ transition of Nd^{3+}, is observed after excitation at level $^1D_2(2)$ in the dilute sample. In the concentrated sample the observation of this Nd^{3+} fluorescence is difficult due to the higher intensity of the fluorescence

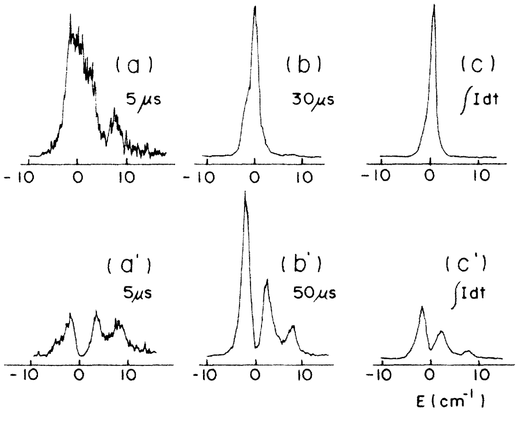

FIG. 4. Excitation spectrum of the 380-nm fluorescence arising from the (1 at. % Pr + 0.5 at. % Nd)—doped LaF_3 sample. The time gate used for the detection is indicated in each case. The spectra (a), (b), and (c) correspond to light emitted near the laser incidence crystal surface. The spectra (a'), (b'), and (c') correspond to light emitted 1.5 mm inside the crystal.

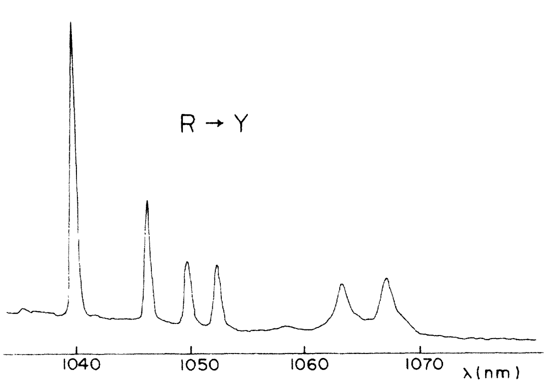

FIG. 5. Fluorescence spectrum of the R to Y Nd^{3+} transition observed after excitation of state $^1D_2(2)$ of Pr^{3+} in the 0.1 at. % Nd—doped crystal at 20 K.

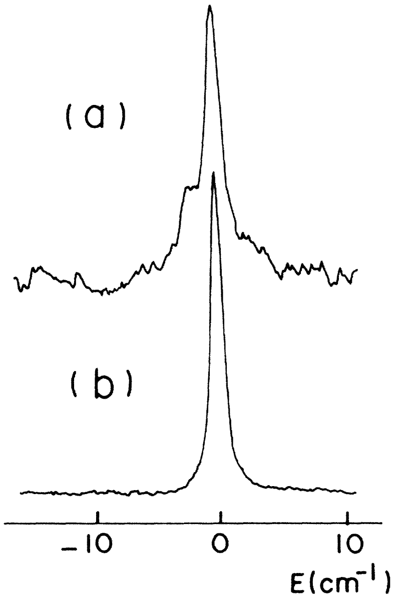

FIG. 6. Excitation spectrum of the 1040-nm Nd^{3+} emission from the 0.1 at. % Nd—doped crystal at 20 K. Spectrum (a) was recorded with a 50 μs gate after the laser pulse. Spectrum (b) is the time-integrated spectrum.

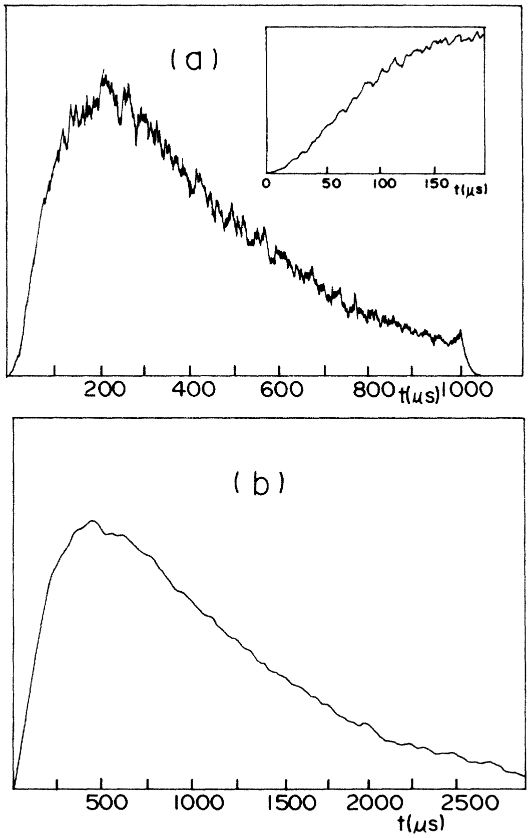

FIG. 7. Temporal evolutions of the 380-nm fluorescence (a) and of the 1040-nm fluorescence (b) obtained from the 0.1 at. % Nd—doped sample.

side band of the Pr^{3+} ${}^1D_2 \rightarrow {}^3F_4$ transition. The fluorescence spectrum of the ir emission is shown in Fig. 5 and its excitation spectrum in Fig. 6. Once again, the excitation spectrum is essentially composed by a single line centered at ω_0. No emission could be detected arising from level R of Nd^{3+} when the laser was tuned a few linewidths off the center of the excitation line indicating that the population of level R by any process not involving Pr ions is negligible. The laser intensity dependence of the fluorescence arising from level R is linear.

The temporal evolutions of the intensities of the fluorescences corresponding to the transition from levels L to Y and R to Y of Nd^{3+} have been recorded in the dilute sample after excitation at ω_0 and are shown in Fig. 7. At long time delays both signals approach exponential decays. The corresponding decay times have been measured at $T_{d\text{uv}} = 320 \pm 20$ μs and $T_{d\text{ir}} = 820 \pm 60$ μs, respectively. Using these values, the temporal evolutions shown in Fig. 7 have been fitted using a standard minimal quadratic method to the expression

$$I(t) = A\left(e^{-t/T_d} - e^{-t/T_r}\right) . \tag{1}$$

From this fit we obtained $T_{r\text{uv}} = 145 \pm 10$ μs and $T_{r\text{ir}} = 310 \pm 20$ μs. The fit is reasonably good for the ir signal but less accurate for the uv signal. This is not surprising since, as shown in Fig. 7(a), the time derivative of the intensity of the uv fluorescence is zero at the origin, indicating that the expression (1) is not applicable in this case around $t = 0$ (see discussion below).

IV. DISCUSSION

The results above clearly indicate that the mechanism producing the up-converted uv emission from level L of Nd^{3+} involves the absorption of laser photons by Pr ions and subsequent energy transfer to Nd acceptors. The quadratic laser intensity dependence of the observed emission shows that we are concerned with a two-photon process.

Several mechanisms can be considered in order to explain the observed up-conversion effect. Figure 8 shows

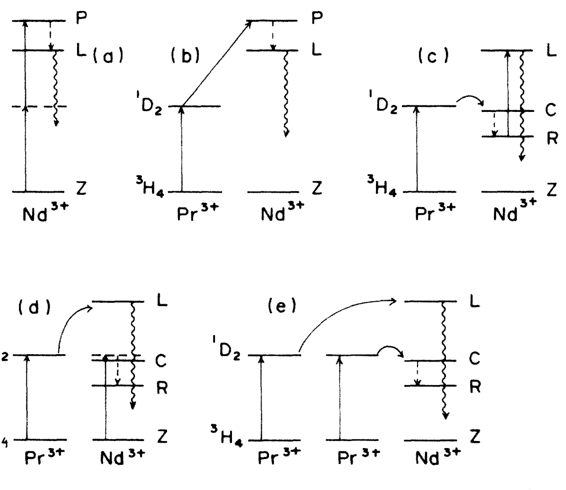

FIG. 8. Up-conversion mechanisms considered for the analysis of the observed effect (see text).

their corresponding scheme. Process (a) consists of a two-photon absorption between the ground state and state $P[^2H_{9/2}(1)]$ of a Nd^{3+} impurity followed by relaxation of the excitation down to level L and fluorescence. As no Nd^{3+} line is known in the spectral region covered by the excitation laser, no sharp line is expected for this process when the excitation frequency reaches ω_0. In addition, the temporal evolution of the fluorescence arising from level L after this process would be completely different of that observed in Fig. 7(a). The rise time of the emission should be of the order of the relaxation time between levels P and L. This time can be estimated to be a few microseconds.[14] Also the decay time of the uv fluorescence would be associated to the lifetime of level L which is 35 μs.[7] In view of these arguments, this process cannot explain our results. Process (b) consists of the excitation into state $^1D_2$ of a Pr ion belonging to a Pr^{3+},Nd^{3+} pair followed by laser-assisted energy transfer between the Pr and the Nd ions.[15] The cross section of this process is expected to be small compared to other competing processes such as process (a). Also the expected temporal evolution of the up-converted fluorescence would be the same as for process (a). Consequently process (b) is not consistent with our observations. In process (c), after the excitation of state $^1D_2$ of a Pr ion belonging to a Pr^{3+},Nd^{3+} pair, the absorbed energy is transferred to the nearby Nd ion, and, after relaxation to level R, a second photon is absorbed by the Nd impurity which is then excited into level L. The energy mismatch between the donor and the acceptor energy levels involved in the energy transfer mentioned above is 700 cm^{-1} and can be compensated by phonon emission. As a consequence, this energy transfer is expected to be a rather efficient mechanism. However, this process also has to be ruled out in view of the observed temporal behavior. No rise time is expected to be observable for the fluorescence arising from level L after process (c) since this level would be populated during the excitation pulse. In fact, the population transferred to level R of Nd^{3+} during the laser pulse is negligibly small. However, in a continuous excitation experiment, the contribution of this process to energy up-conversion should be considerable. In process (d) a photon resonant with the $^3H_4 \rightarrow {}^1D_2$ transition is absorbed by a Pr ion while a second photon is absorbed by a Nd neighbor. The latter absorption taking place at the high-energy side of the absorption lines corresponding to level $C[^2H_{11/2}(2)]$ of Nd^{3+}. Following this two-photon absorption the Nd ion relaxes to level R and energy transfer takes place between the two impurities leaving the Nd ion in level L. Although the nonresonant absorption necessary to this process is allowed by vibronic coupling, the fact that no emission is observed from level R when the laser is tuned out of the $^1D_2(2)$ line indicates that its probability is very small. Once again, the expected temporal evolution of the fluorescence following this process provides additional arguments leading to the conclusion that this mechanism cannot explain our observations; the expected rise time of the uv emission following process (d) should not be longer than the lifetime of level L which is much shorter than the observed one. Our results are consistent with process (e). This is a three-ion process where two Pr impurities are excited into state $^1D_2$ and then the energy is transferred to the Nd neighbor in two steps. In the first one, the energy from one of the Pr ions is transferred to the Nd ion following the path described for process (c), and in the second step the remaining excited Pr ion transfers its energy leaving the Nd ion in level L. This double transfer benefits from long lifetimes of state $^1D_2$ of Pr^{3+} (500 μs) and state R of Nd^{3+} ($\sim$800 μs) and is doubly resonant within the energy interval allowing phonon-assisted energy transfers. Such mechanism of stepwise excitation addition was first observed by Auzel[16] and denoted as APTE ("Addition de Photons par Transfert d'Energie").

The fact that a three-ion process involving two Pr ions is observed in a sample where this element is only present as unintentional traces is surprising. Although processes concerning two-ion mechanisms and involving traces of impurities in systems similar to the one considered here have already been reported,[3] this is to our knowledge the first case where traces of impurities appear to play a significant role via a three-ion mechanism. The purity of the chemicals used for the growth of our sample by the manufacturer is specified as 99.99%. In consequence, the expected Pr traces concentration is of the order of 10^{-4}. In order to check this value, we have recorded the transmission spectra of the two crystals. As seen in Fig. 9(a) the absorption line at the wavelength corresponding to the Pr^{3+} transition $^3H_4(1) \rightarrow {}^1D_2(2)$ is observable in the dilute sample. By comparing the relative absorption at this wavelength in the two crystals the concentration of Pr in the dilute sample can be estimated to be (2×10^{-2})–(3×10^{-2}) times the concentration in the concentrated sample. By assuming that the manufacturer specification of 1 at. % Pr^{3+} concentration in the latter sample is correct, then the concentration of Pr^{3+} in the dilute sample is (2×10^{-4})–(3×10^{-4}). The relative concentration of Nd in both crystals was checked following the same procedure and agrees with the manufacturer specifications within 20%. Assuming a quadratic Pr^{3+} concentration dependence of the effect (as expected for a process involving two Pr^{3+} impurities) the observed signal in the dilute sample should be (2×10^{-4})–(9×10^{-4}) times the signal observed in the concentrated sample. The actual intensity of the signal from the dilute sample is 10^{-3} times the intensity of the signal from the concentrated one. In the dilute sample, the principal contribution to the up-conversion process is given by triads of quasi-isolated ions, that is, triads where the constituents are relatively far from each other and consequently the energy levels are not appreciably shifted from those of isolated ions. This is also surprising in view of previous results where the contribution of quasi-isolated ions to pair or triad processes is not so important.[9,10] As already pointed out, we believe that the difference between the present and the previous observations can be explained by the strong absorption at the central lines in samples with Pr concentrations of the order of 0.1% or more.

The dynamics of the excitation within a doubly excited Pr-Pr-Nd triad during process (e) can be analyzed with the help of the rate equations describing the evolution of the population of the triad states involved in the process.

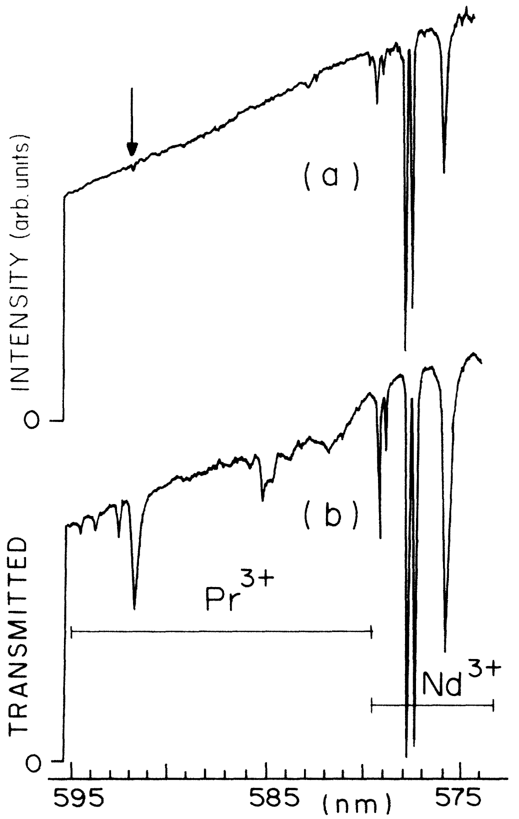

FIG. 9. Transmission spectra at 20 K of the 0.1 at. % Nd—doped LaF_3 sample (a) (thickness: 4.87 mm) and of the (0.5 at. % Nd + 1 at. % Pr)—doped sample (b) (thickness: 3.25 mm). The absorption lines corresponding to transitions ${}^3H_4 \rightarrow {}^1D_2$ in Pr^{3+} and $Z \rightarrow D$ in Nd^{3+} are indicated. The arrow indicates the ${}^3H_4(1) \rightarrow {}^1D_2(2)$ transition. The monotonic intensity background corresponds to the power spectrum of the incandescent lamp used as light source.

Let $|\alpha\rangle$ be the initial state of the triad, $|\beta_1\rangle$ the state where a Pr ion is excited, the other is in the ground state, and the Nd ion is in state R, $|\beta_2\rangle$ the state obtained from $|\beta_1\rangle$ by exchanging the excitation between the two Pr ions, and $|\gamma\rangle$ the state where both Pr ions are in the ground state and the Nd ion is in state L. The corresponding rate equations for the populations of these states are

$$\dot{n}_\alpha = -(2W_1 + 2W_t)n_\alpha \,, \tag{2}$$

$$\dot{n}_\gamma = W_u n_{\beta_1} + W_u n_{\beta_2} - W_3 n_\gamma \,, \tag{3}$$

$$\dot{n}_{\beta_1} = W_t n_\alpha - (W_2 + W_1 + W_e + W_u) n_{\beta_1} + W_e n_{\beta_2} \,, \tag{4}$$

$$\dot{n}_{\beta_2} = W_t n_\alpha - (W_2 + W_1 + W_2 + W_u) n_{\beta_2} + W_e n_{\beta_1} \,, \tag{5}$$

where W_1, W_2, and W_3 are the radiative relaxation rates of states ${}^1D_2$ of Pr^{3+}, R and L of Nd^{3+}, respectively. W_t is the energy transfer rate from state ${}^1D_2$ of Pr^{3+} to state R of Nd^{3+}. It is assumed to be the same for the two Pr ions of the triad. W_u is the energy transfer rate from state ${}^1D_2$ of Pr^{3+} to an already excited Nd ion leaving it in state L. It is also assumed to be the same for the two Pr ions. W_e is the resonant energy-transfer rate between the two Pr ions. The total population of states $|\beta_1\rangle$ and $|\beta_2\rangle$ can be described in a single equation leading to

$$\dot{n}_\beta = 2W_t n_\alpha - (W_2 + W_1 + W_u) n_\beta \,, \tag{6}$$

$$\dot{n}_\gamma = W_u n_\beta - W_3 n_\gamma \,. \tag{7}$$

Assuming that, at $t = 0$, $n_\alpha = N$ and $n_\beta = n_\gamma = 0$, the solutions of these rate equations are

$$n_\alpha = N e^{-W_r t} \,, \tag{8}$$

$$n_\beta = \frac{2NW_t}{(W_r - W_d)} (e^{-W_d t} - e^{-W_r t}) \,, \tag{9}$$

$$n_\gamma = \frac{2NW_t W_u [(W_3 - W_d)e^{-W_r t} + (W_r - W_3)e^{-W_d t} + (W_d - W_r)e^{-W_3 t}]}{(W_r - W_d)(W_r - W_3)(W_3 - W_r)} \,, \tag{10}$$

where $W_r = 2W_1 + 2W_t$ and $W_d = W_1 + W_2 + W_u$. The evolution of the observed up-converted uv emission is proportional to n_γ. As seen in Eq. (7) the slope of the intensity as a function of time is zero at $t = 0$ in agreement with the observed behavior. As we are concerned with weakly interacting triads, the transfer rates involved in the process are small (typically smaller than the radiative relaxation rates) so we can assume that W_r is of the order of $2W_1$ and W_d is of the order of $W_1 + W_2$. In addition, $W_3 \gg W_r > W_d$. With these assumptions, Eq. (10) becomes, for $t > 0$,

$$n_\gamma \simeq B(e^{-W_d t} - e^{-W_r t}) \,, \tag{11}$$

where B is a constant. Since Eq. (11) has the same structure as expression (1), the observed values of $T_{d_{uv}}$ and $T_{r_{uv}}$ can be identified to W_d^{-1} and W_r^{-1}, respectively. The value obtained for W_r is 6.9 ms^{-1} which is larger than $2W_1 = 4.0$ ms^{-1}. This gives $W_t = 1.5$ ms^{-1} for the energy-transfer rate. Energy-transfer rates of the same order of magnitude have already been measured between two Pr ions when the interionic distance is of the order of 10 Å.[10] The observed value of $W_d = 3.2$ ms^{-1} coincides with the expected value for $W_1 + W_2$ indicating that W_u is small as previously assumed.

The previous description can be checked by confrontation with the dynamics of the emission from the intermediate level R of Nd^{3+}. The population of this level is essentially due to a two-ion process where an excited Pr ion transfers its energy to a Nd neighbor. The temporal evolution of the population n_r of level R can be easily obtained and is given by

$$n_R = \frac{N W_t}{(W'_r - W_2)} (e^{-W_2 t} - e^{-W'_r t}) , \qquad (12)$$

with $W'_r = W_1 + W_t$. The measured value of $T_{d\mathrm{ir}} = W_2^{-1}$ is close to already reported values.[17] The observed value of $(W'_r)^{-1} = T_{r\mathrm{ir}}$ is 310±20 μs. The relation $W_r = 2W'_r$ is verified within the experimental error confirming the validity of the model considered for the up-conversion process.

Finally, it is necessary to consider whether the previous analysis, involving constant transfer and emission rates, is convenient for the description of the dynamics of the actual fluorescence signal which is due to the average contribution of different kinds of triads having different radial distances. It is well known that in this case the temporal behavior can be nonexponential. In the present case, however, we are just concerned with triads of weakly coupled ions for which the energy-transfer rates are small. In this case, as seen in Eqs. (11) and (12) the decay rate is essentially governed by the radiative lifetimes which are independent of the triad configuration. As a consequence, the signal decay should be exponential at long times as observed. This is no more the case for the rise of the emission as the energy-transfer rate W_t can vary from one triad to another. Consequently the given value of W_t has to be considered as an average value over all the triads of weakly coupled ions participating to the observed process.

V. CONCLUSION

A new up-conversion process allowing the emission of uv radiation after excitation by yellow light has been demonstrated in LaF_3:(Pr^{3+},Nd^{3+}). The mechanism responsible for the up-conversion has been shown to be APTE within a Pr^{3+}-Pr^{3+}-Nd^{3+} triad. The observation of this effect in crystals with extremely low Pr concentration, shows, for the first time, that impurity traces can influence considerably the luminescence properties of RE-doped crystals even via three-ion processes. This influence is enhanced by the deeper penetration of the excitation beam at the line center frequency in highly dilute samples.

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