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Triad spectroscopy via ultraviolet up-conversion in Pr^{3+}:LaF_3

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The first observation of isolated isoionic triads in solids is reported. A three-ion energy transfer according to ${}^1D_2+{}^1D_2+{}^1D_2\rightarrow{}^1S_0+{}^3H_4+{}^3H_4$ was observed in dilute Pr^{3+}:LaF_3 where triads of random distributed impurities can be considered as isolated. The ultraviolet luminescence following this process allows the spectroscopic observation of different kinds of triads.

I. INTRODUCTION

The optical properties of rare-earth (RE) doped crystals have been the subject of intensive research in recent years.[1] The small oscillator strength for intraconfigurational transitions is responsible for the existence of long-lived excited states with decay times ranging from microseconds to milliseconds. Thus the excited RE ions in a crystal can be seen as an excitation storage whose energy is available during the lifetime of the excited state. The relaxation of this stored energy has motivated a great number of works where different nonradiative mechanisms have been demonstrated. An important relaxation channel appearing when increasing the RE concentration in the crystal is due to the possibility of energy transfer between RE impurities.[1,2] This energy transfer can be resonant or nonresonant with phonon emission or absorption, compensating the energy mismatch. An example of an energy transfer process is the "cross relaxation"[3] in which an excited ion transfers part of its energy to a neighboring impurity in the ground state in such a way that after the transfer both impurities are excited. This process can be generalized in order to involve any number of ions in any excitation state. In particular, we can consider a group of excited ions, all of them in the same excited state, relaxing by energy transfer to a final state where the energy has been redistributed between all the impurities in such a way that the excitation state is no longer the same for all ions. If this occurs with little energy lost by phonon emission, we have after this process some ions in higher excited states than before the energy transfer. By such a process, the energy stored in the group of excited ions can be partially "accumulated" in one or several of them. This is an important mechanism for generation of up-converted emission.

The first observation of this kind of process in Pr^{3+}:LaF_3 is due to Zalucha *et al.*;[4] afterwards it was extensively studied by Vial *et al.*[5,6] In that case two Pr^{3+} ions are excited into the ${}^1D_2$ state ($16\,897\ cm^{-1}$) and the energy redistribution takes place according to

$$ {}^1D_2+{}^1D_2\rightarrow{}^3P_0+{}^1G_4+\text{phonons}\ , \qquad (1)$$

afterwards an intense blue emission is observed to arise from the ${}^3P_0$ state.

The first observation of this kind of energy transfer involving three ions is due to Lee *et al.*[7] They observed in PrF_3 and highly concentrated Pr^{3+}:LaF_3 ($[Pr^{3+}]>10$ at. %), an uv emission after excitation of the ${}^3P_0$ state of Pr^{3+} ($20\,930\ cm^{-1}$). This emission was interpreted as due to the following energy transfer process:

$$ {}^3P_0+{}^3P_0+{}^3P_0\rightarrow{}^1S_0+{}^3F_2+{}^1G_4+\text{phonons}\ , \qquad (2)$$

although other alternative mechanisms were suggested.

In this paper we report the first observation of three-ions up-conversion by energy transfer in dilute Pr^{3+}:LaF_3, where triads of Pr^{3+} ions can be considered as isolated. The observed effect corresponds to the process described by

$$ {}^1D_2+{}^1D_2+{}^1D_2\rightarrow{}^1S_0+{}^3H_4+{}^3H_4+\text{phonons}\ . \qquad (3)$$

The luminescence arising from state ${}^1S_0$ ($46\,986\ cm^{-1}$) allows the selective spectroscopic study of triads of Pr^{3+} impurities.

The distribution of Pr ions in the LaF_3 crystal lattice is generally accepted to be random. At low dopant concentrations most of the impurities are isolated. However, a small fraction of them can be close enough to interact. We can consider as a "cluster" a group of random distributed impurities contained in the same sphere of influence of M sites (the choice of M is arbitrary and must be based on an estimation of the range of the interactions between RE ions).

The spectroscopic study of these clusters in dilute samples where only groups of a few ions can be expected to be found is difficult to perform by conventional spectroscopy. They appear as small satellites near (and also within) the main line which is due to isolated ions. The observation of up-converted emission due to energy transfer between ions in a RE cluster provides the possibility of selective detection of cluster effects.[8] The discovery of process (1) by Zalucha *et al.*[4] provided a technique for a systematic study of Pr^{3+} pairs without any background from isolated ions. The detection of the blue fluorescence arising from state ${}^3P_0$ ensures that only pairs of ions are contributing to the signal. By scanning the excitation laser it is possible to selectively excite different types of pairs. This technique was very fruitfully used by Vial *et al.*[5,6,9] These workers identified up to 13 types of pairs with excitation frequencies varying over 12 cm^{-1}. They also measured the dynamics of the up-conversion transfer for different pairs. From their results it appears that the coupling between impurities is due to dipole-dipole interaction except for very close pairs (first- and second-nearest neighbors) where a short-range interaction has to be invoked. In this paper we present an extension of this technique for the study of triads.

II. EXPERIMENTAL DETAILS

The crystal used in the experiments were manufactured by Optovac. Three samples were used with 0.1, 0.5, and 1 at. % of Pr. The samples were cooled to 20 K. The excitation was achieved with a Nd:YAG (YAG denotes yttrium aluminum garnet) pumped dye laser producing 5-ns pulses of 0.15 mJ. The laser linewidth was 0.4 cm^{-1}. The excitation beam was focused into the sample with a 68-mm focal-length lens. The laser beam was linearly polarized parallel to the crystal *c* axis and propagated perpendicular to it. The emitted fluorescence was collected along the *c* axis direction, and analyzed in a 1.4-m double spectrometer equipped with a 1P28 photomultiplier tube. The signal was processed in a boxcar averager (PAR model No. 162/164). For a weak signal levels a digital photon counting was preferred. The counting was achieved with a home-modified digital photometer (Spex model No. DPC-2) during an aperture gate generated by the boxcar averager, and accumulated over 100 laser pulses.

III. RESULTS

Figure 1 shows some uv fluorescence lines observed when the sample is excited around the ${}^3H_4 \rightarrow {}^1D_2$ transition. These emissions correspond to the transition from the state ${}^1S_0$ to states ${}^3P_1 - {}^1I_6$ and ${}^1G_4$. The transitions to states ${}^1D_2$ and ${}^3F_4$ were also detected at very low signal level. The positions of the observed lines are in agreement with previous observations.[7,10,11] The laser intensity dependence of the uv fluorescence was measured to be $I_f \propto I_l^n$, with $n = 2.8 \pm 0.6$. At 30-kW laser peak the uv fluorescence was 5 orders of magnitude weaker than the blue emission due to pair up-conversion. With use of similar excitation conditions the fluorescence intensity was compared for three different samples. A 0.5-at. % doped crystal presents a uv fluorescence approximately 8 times weaker than that of a 1-at. % sample. In a 0.1-at. % doped sample the signal was weaker than the noise background. Both results are consistent with a cubic dependence on dopant concentration.

The excitation spectrum of the uv fluorescence is shown in Fig. 2, along with the excitation spectrum of the blue light produced by pair up-conversion. The comparison between both spectra presents some interesting features. When the emission is analyzed at short delays after the excitation pulse (a few microseconds) the blue spectrum is dominated by peaks which are shifted from the single-ion excitation frequency and correspond to close-neighbor Pr^{3+} pairs. For longer delays after excitation the contribution of peaks near the single-ion excitation frequency, corresponding to pairs of distant ions, becomes predominant. The pairs of distant ions also dominate the time-

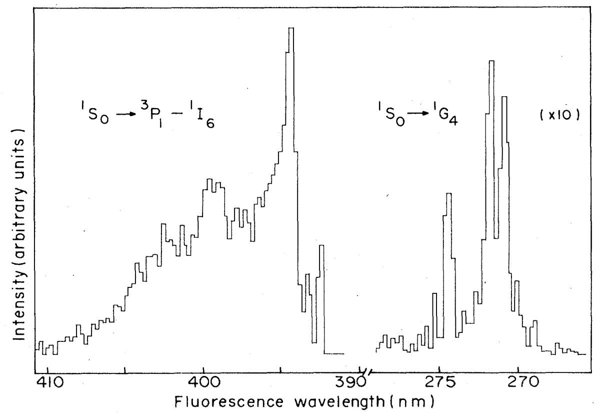

FIG. 1. Partial fluorescence spectrum of the observed uv emission, corresponding to transitions from state ${}^1S_0$ to states ${}^3P_1 - {}^1I_6$ and ${}^1G_4$. The excitation wavelength was in resonance with the transition ${}^3H_4 \rightarrow {}^1D_2(2)$.

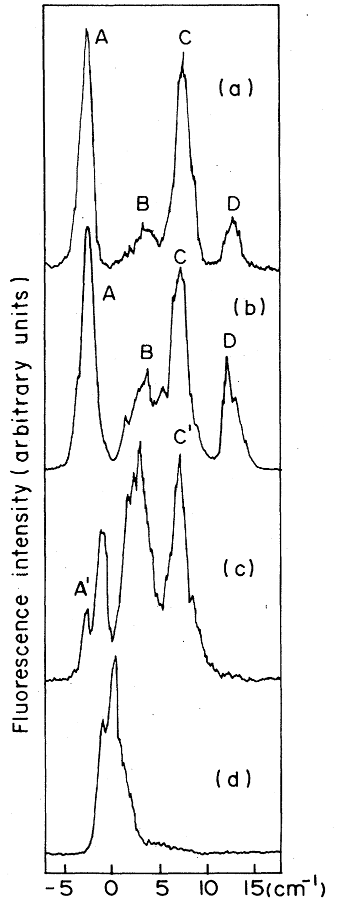

FIG. 2. Excitation spectra of the uv emission [(a) and (b)] and of the blue emission due to pair up-conversion [(c) and (d)]. The origin of the energy scale corresponds to the isolated ion excitation frequency for the transition ${}^3H_4(1) \rightarrow {}^1D_2(2)$. Spectrum (a) was recorded after a delay of 1 μs. Spectrum (b) is a time-integrated spectrum. The delays for spectra (c) and (d) were 3 and 300 μs, respectively.

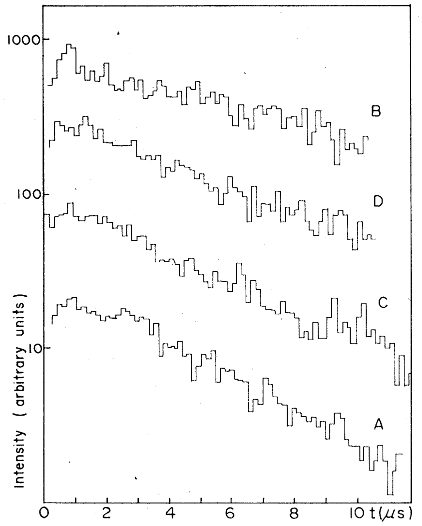

FIG. 3. Time evolution of the observed uv fluorescence. The letters refer to the excitation frequencies according to Fig. 2. The intensity units are arbitrary and different for each curve.

integrated excitation spectrum (not shown, see Ref. 6). The temporal variation of the uv spectrum is different as the peaks labeled *A*, *C*, and *D* dominate the spectrum at all delays after excitation. Peaks *A* and *C* of the uv spectrum seems to be correlated with the corresponding *A*′ and *C*′ of the blue spectrum. However, a small shift in their positions can be observed and their relative intensity is completely modified. In addition, peak *D* appearing in the uv has no equivalent in the blue excitation spectrum.

Figure 3 shows the temporal evolution of the uv fluorescence for excitation at peaks *A*, *B*, *C*, and *D*. This temporal evolution was recorded scanning an integration gate of 0.5 μs. In each case a risetime of the order of 1 μs was observed afterwards; the decay was exponential within the experimental uncertainty due to the low signal level. We observed (4.3±0.5)-, (7±1)-, (4.5±0.6)-, and (5.5±0.8)-μs exponential decay times for peaks *A*, *B*, *C*, and *D*, respectively.

IV. DISCUSSION

Three different processes can be considered in order to explain the population of the $^1S_0$ level after laser excitation of state $^1D_2$. Figure 4 shows the corresponding mechanisms involving, respectively, isolated ions, pairs, and triads. Process (a) is a three-photon excitation of an isolated Pr ion with an intermediate real state ($^1D_2$). This process can be seen as a transition within the 4*f* configuration followed by a two-photon transition between the 4*f* and 4*f* 5*d* configurations with no real intermediate state. The latter transition is parity forbidden and expected to have a small cross section. The excitation spectrum of such a process would present a main peak at the single-ion excitation frequency. This would be in complete disagreement with our spectra where such a peak is not observed. In addition, the concentration dependence for this process should be linear. Consequently, this process cannot explain our observations.

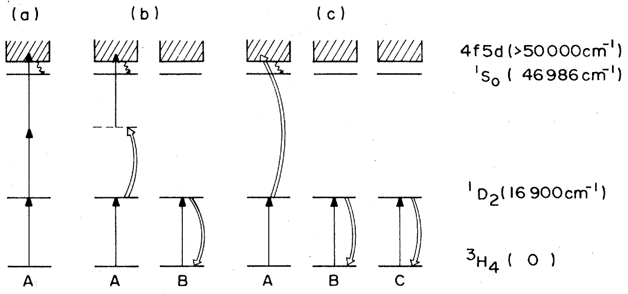

FIG. 4. Considered mechanisms for populating the state $^1S_0$ after laser excitation around the $^3H_4 \rightarrow {}^1D_2$ transition. Process (a) is a single-ion three-photon absorption. Process (b) is a two-ion excitation followed by a cooperative absorption. Process (c) is a three-ion excitation followed by up-conversion due to energy transfer.

Process (b) is a two-ion process where after excitation of both ions in the $^1D_2$ state a cooperative absorption of a third photon takes place according to

$$^1D_2 + {}^1D_2 + h\nu \rightarrow 4f5d + {}^3H_4 + \text{phonons} , \qquad (4)$$

followed by a rapid relaxation from the 4*f* 5*d* band to state $^1S_0$. This cooperative absorption is expected to be weak and its excitation spectrum must be that of Pr^{3+} pairs; that is, it should present the same structure of that of the blue emission due to the process corresponding to Eq. (1). In addition, the concentration dependence should be quadratic for this process. As those requirements are not satisfied, we also have to rule out this possibility.

Our results are consistent with process (c). In that process energy is stored in a triad of Pr^{3+} ions, all of them excited in the $^1D_2$ state; afterwards an energy transfer takes place, "concentrating" the excitation in one of the ions. The possible energy transfer channels are

$$^1D_2 + {}^1D_2 + {}^1D_2 \rightarrow {}^1S_0 + {}^3H_4 + {}^3H_5 + \text{phonons} \qquad (5)$$

and

$$^1D_2 + {}^1D_2 + {}^1D_2 \rightarrow 4f5d + {}^3H_4 + {}^3H_4 , \qquad (6)$$

followed by interconfigurational relaxation between the 4*f* 5*d* band and the $^1S_0$ state. The former channel requires the emission of phonons with total energy between 560 and 1450 cm^{-1}. The latter seems to be more probable as it is resonant and takes advantage of the large density of states of the 4*f* 5*d* band. The cubic concentration dependence of the observed signal is in agreement with this interpretation. The excitation spectrum of the emission arising from $^1S_0$ after an energy transfer by a three-ion process is, as expected, different from the single-ion and pair excitation spectra. The observed excitation spectrum can be considered as characteristic of Pr^{3+} triads in LaF_3. The different peaks observed are due to different kinds of triads in the crystal. This is to our knowledge the first spectroscopic observation of isolated triads of impurities in solids. The reduced number of sharp peaks (mainly three: A, C, and D) and the absence of them in the neighborhood of the isolated ion frequency suggest that the peaks mentioned above correspond to triads composed by near-neighbor ions. It is interesting to point out that with first-nearest neighbor Pr^{3+} ions it is possible to have three classes of triads: one class having a D_3 symmetry and a F^- ion in its center, a second class of C_3 symmetry with a F^- ion on the C_3 axis but out of the Pr^{3+} plane, and a third class of C_2 symmetry.[12] It is probable that a connection could be made between the three observed peaks and the three classes of first-neighbor triads. The fact, that near-neighbor triads dominate the spectrum at all delays after excitation, is probably due to the rapid decrease of the strength of the coupling between the ions of the triads when the distance between them is increased. This decrease is rapid enough to compensate the larger number of possible triads when the separation between ions is increased.

The temporal evolution after excitation, of the populations of the initial state of the triad (that is, the state directly pumped by the laser) and of its final fluorescent state (one ion in the $^1S_0$ state and two ions in the ground state), can be described by

$$\dot{n}_0 = -(W_0 + W_t) n_0 \ , \tag{7}$$

$$\dot{n}_1 = W_t n_0 - W_1 n_1 \ , \tag{8}$$

where n_0 and n_1 are the populations of the triad states $|0\rangle = |{}^1D_2 + {}^1D_2 + {}^1D_2\rangle$ and $|1\rangle = |{}^1S_0 + {}^3H_4 + {}^3H_4\rangle$, respectively; W_0 is the relaxation rate of the state $|0\rangle$ due to all possible mechanisms except the transfer to state $|1\rangle$. W_t is the energy transfer rate from state $|0\rangle$ to state $|1\rangle$ and W_1 is the total radiative emission rate from the $^1S_0$ state. The solutions for these equations are

$$n_0 = N_0 e^{-(W_0 + W_t)t} \ , \tag{9}$$

$$n_1 = \frac{N_0 W_t}{W_r - W_d} (e^{-W_d t} - e^{-W_r t}) \ . \tag{10}$$

N_0 is the population of $|0\rangle$ at $t=0$, and W_r is the larger of the two transfer rates $(W_0 + W_t)$ and W_1, W_d is the smaller. According to Eq. (10), for long times the fluorescence signal decays exponentially with one exponential decay time equal to W_d^{-1}.

We observe decay times of the order of 4 μs which are longer than the lifetime of the $^1S_0$ state (0.7 μs).[13] Consequently, the decay time W_d cannot be identified as W_1. Thus we must have $W_d = W_0 + W_t$. We can assume that $W_0 \gg W_t$ as the transfer to state $|1\rangle$ is less probable than other competing relaxation processes. The observed value to W_0 is higher than the expected radiative decay rate for state $|0\rangle$ which is $3\tau^{-1}$. (τ is the lifetime of state $^1D_2$ for isolated ions, $\tau \simeq 500$ μs.) Consequently, W_0 is mainly due to nonradiative relaxation mechanisms. One possible mechanism is energy transfer between two of the three ions following the process described by Eq. (1). The observed lifetimes have the same order of magnitude of previous measurements[3] of the transfer rate for the process of Eq. (1) in the case of close neighbors. The observed risetime can be attributed to the $^1S_0$ state lifetime.

V. CONCLUSIONS

We have shown that up-conversion via energy transfer can take place in isolated triads of excited Pr^{3+} ions in LaF_3. As a result of this process the energy of the excited ions is almost all concentrated into the $^1S_0$ state of one of the ions of the triad (only 7% of the adsorbed energy is lost during the transfer). The observation of subsequent emission from the $^1S_0$ state provides a way of observing triads of impurities with no background for isolated ions or pairs. The excitation spectra of these triads show a reduced number of peaks, suggesting that first-nearest neighbor triads are predominant.

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