PHYSICAL REVIEW B VOLUME 33, NUMBER 7 1 APRIL 1986

Site-selective spectroscopy via energy up-conversion in CaF_2:Pr^{3+}

Arturo Lezama, Marcos Oriá, and Cid B. de Araujo
Departamento de Fisica, Universidade Federal de Pernambuco, 50000 Recife, Pernambuco, Brazil

(Received 9 August 1985)

Two up-conversion processes, described by ${}^1D_2+{}^1D_2\rightarrow{}^3P_0+{}^1G_4$ and ${}^1D_2+{}^1D_2+{}^1D_2\rightarrow{}^1S_0+{}^3H_4+{}^3H_4$, are observed in CaF_2:Pr^{3+}. The analysis of the excitation and fluorescence spectra of the emissions following these processes allows the selective observation of various impurity groups. Ten different impurity sites were detected. The temporal evolution of the up-converted emission arising from these sites provides qualitative information on the interionic coupling strength. In addition to the observation of strongly coupled clusters, the first evidence of intercluster interaction is reported.

I. INTRODUCTION

During the past twenty years, the actual distribution of trivalent rare-earth (RE) impurity ions in alkaline-earth fluoride crystals, has been a challenge for solid-state physicists.[1,2] The RE impurities enter into the crystal lattice, substituting divalent alkaline-earth ions. The necessary charge compensation is then realized by the presence of an interstitial F^- ion.[3] Since the early works it has appeared that this substitution can take place in several spatial configurations depending on the relative positions of the charge compensator and the RE ion in the lattice. In addition, it was demonstrated that even at low concentration, clusters containing several impurities and charge compensators are present.[4] A wide spectrum of multi-ion clusters has been suggested ranging from single-impurity-compensator pairs (hereafter also called single-impurity clusters) to clusters containing six or more impurities.[5] The relative concentrations of these clusters depend on the nature of the crystal host and the RE impurity, and on the crystal thermal history. The present paper focuses on CaF_2, the most studied host.

A great number of approaches have been tried to elucidate the nature and the statistical distribution of impurity clusters in CaF_2. Several theoretical calculations have been performed with this goal.[6–10] Extensive work in this area is due to Catlow and co-workers.[8–10] Using a defect simulation based on the Mott-Littleton approach, they have studied the formation and stability of impurity clusters. As a result of these calculations, they suggested[9] the variation of the sizes of the formed clusters with the ionic radius of the concerned impurity; for heavy RE ions, large clusters containing as much as six ions are shown to be predominant, while for light RE ions, small and large clusters are predicted. Recent experimental support has been given to these predictions.[11]

Several experimental techniques were used to study this problem, such as thermoluminescence,[12] ionic conductivity measurements,[13] ionic thermal current,[14] EPR,[1,15,16] NMR,[17] optical spectroscopy,[4,18–32] microwave spectroscopy,[33] and extended x-ray-absorption fine structure.[11] Although complementary information has been provided by these techniques, in this paper we concern ourselves with the area of laser spectroscopy. The most important contribution to this area has been made by Wright and collaborators. A large amount of information has been collected concerning mainly CaF_2:Er^{3+}, but also other RE's have been studied.[19–25] These works demonstrate the usefulness of laser spectroscopy for the prospection of the different impurity configurations into the crystal. As RE ions having different surroundings have slightly different energy levels, it is possible, with a narrow-band dye laser, to selectively excite the ions belonging to each single-site configuration. The analysis of the fluorescence and excitation spectra characteristic of such sites allows their identification. Up to 20 different sites have been identified in CaF_2:Er^{3+} (Ref. 20) but only five of them correspond to single-impurity clusters.

In contrast to these observations, the available data on CaF_2:Pr^{3+} (Refs. 26–32) depict a much simpler situation. Duran and co-workers[30–32] have studied this system by laser exciting the ${}^1D_2$ multiplet and observing the fluorescence from this level to the lower ${}^3F_2$ level. They showed that just four different sites were responsible for the observed emission. In addition, and with just one exception, the hypothesis of multi-impurity clusters was not necessary to explain their results. In view of these facts, it can be questioned whether the observation of the fluorescence arising directly from level ${}^1D_2$ is able to reveal the presence of multi-ion sites. Brown *et al.* have demonstrated[34] the quenching of the emission from this Pr^{3+} level (in LaF_3) due to cross relaxation involving the excited ion and an impurity neighbor in the ground state. This cross-relaxation quenching, if present in CaF_2, would prevent the observation of multi-ion clusters by this technique.

The observation of up-converted emission, originated from two- or three-ion energy-transfer processes, has proved to be an interesting way of observing multi-ion clusters.[20,24,35] In this case, just the clusters containing at least the ions necessary to accomplish the up-conversion process contribute to the signal. In addition, the temporal evolution of the up-converted emission provides useful information about the coupling between impurities into a cluster. If a long-range interaction acts between impurities, the observation of emission arising from up-conversion can be used to detect intercluster interaction. In this paper we present the first evidence for such intercluster energy transfer in CaF_2.

Although no systematic cluster study via up-conversion emission has been reported in the past concerning $CaF_2:Pr^{3+}$, up-conversion effects involving Pr ions have already been observed in other materials. In particular, two up-conversion processes have been observed in $LaF_2:Pr^{3+}$ after excitation of state $^1D_2$. The first one[36] corresponds to a two-ion process described by

$$^1D_2 + {}^1D_2 \rightarrow {}^3P_0 + {}^1G_4 \ . \tag{1}$$

This energy transfer is followed by blue emission corresponding to the transition from level $^3P_0$ to the ground state. According to process (1), only pairs of ions having their energy levels within the excitation laser bandwidth can participate in the emission. Recently,[37] a three-ion up-conversion process has been observed according to

$$^1D_2 + {}^1D_2 + {}^1D_2 \rightarrow {}^1S_0 + {}^3H_4 + {}^3H_4 \ . \tag{2}$$

As a consequence of this process, uv emission is observed from state $^1S_0$ to lower state. This up-conversion mechanism, clearly weaker than the previous one, corresponds to a second-order process with respect to ion-ion interaction. For this reason, it is expected to be essentially due to strongly coupled Pr^{3+} triads.

In this paper we report the observation of both up-conversion processes in $CaF_2:Pr^{3+}$ after laser excitation of level $^1D_2$. The analysis of the emission arising from levels $^3P_0$ and $^1S_0$ allows the observation of multi-ion clusters. In contrast to previous results,[30] a large number of different impurity sites are observed. In addition, the observation of up-conversion associated with single-impurity clusters indicates the presence of intercluster interaction.

II. EXPERIMENTAL DETAILS

The sample used in this experiment was a 0.1-mol % Pr-doped CaF_2 crystal ($6 \times 6 \times 6$ mm^3) purchased from Optovac. The sample was not submitted to any thermal treatment after delivery from the manufacturer. All the experiments were done at a temperature of 18 K obtained with a closed-cycle helium refrigerator. The excitation laser pulses, with wavelength around the transition $^3H_4 \rightarrow {}^1D_2$, were obtained from a dye laser mounted in the grazing incidence configuration[38,39] and pumped by the second harmonic of a Nd:YAG (yttrium-aluminum-garnet) laser. The output of the dye laser was 20-kW peak power pulses of 5 ns duration and 0.2 cm^{-1} bandwidth. For some experiments a broad-band excitation was required. In those cases the tuning mirror of the laser cavity was blocked. The resulting output consisting of the single pass stimulated emission had the desired characteristics. Two dye solutions were used for this purpose, Kyton Red and 7D4M Coumarin. In the latter case a N_2 laser was used for pumping the dye. For some measurements, a cw argon laser was also used for exciting the fluorescence from level $^3P_0$. The laser beam was focused with a 68-mm focal length lens into the crystal. The fluorescence was collected at a right angle through uv transmitting optics. When broad-band fluorescence detection was necessary, a $\frac{1}{4}$-m spectrometer was used with 5-mm wide slits. Appropriate filters were used to avoid residual laser light. For an increased resolution a 1.4-m double spectrometer was used. For the infrared spectra the signal was collected by a C 31034 (GaAs photocathode) photomultiplier tube cooled to $-30\,^{\circ}$C. Visible and uv spectra were taken with the same or with an 1P28 photomultiplier tube. A boxcar averager (PAR 162) was used for the electronic signal treatment.

III. RESULTS

A. Overall fluorescence

Figure 1(a) shows the fluorescence spectrum of the up-converted blue light obtained after broad-band (585—595 nm) pulsed excitation of the $^1D_2$ level. This kind of excitation is not site selective and pairs of Pr ions having the same or different energy levels can contribute to the emission. The observed fluorescence corresponds to the $^3P_0 \rightarrow {}^3H_4$ transition. Figures 1(b) and 1(c) show the fluorescence arising from level $^3P_0$ after direct excitation with a broad-band laser pulse (450—475 nm) and with a

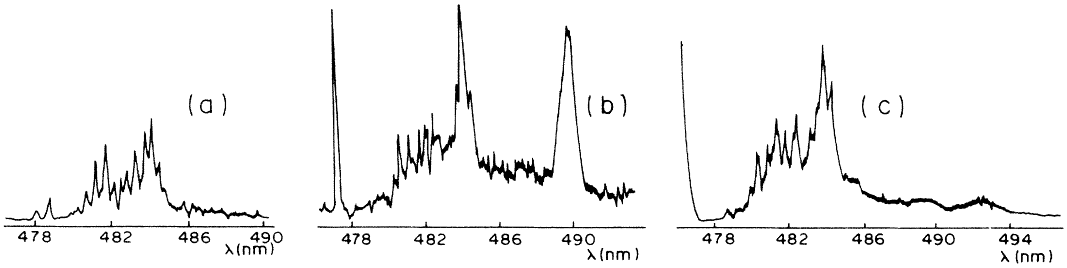

FIG. 1. Fluorescence spectra corresponding to the transition from level $^3P_0$ to level $^3H_4$ (a) after excitation with a broad-band laser pulse of 585—595-nm bandwidth, (b) after excitation with a 450—475-nm bandwidth laser pulse, and (c) after excitation with the 476.5-nm line from a cw argon laser. Intensity units are arbitrary and independent in each case.

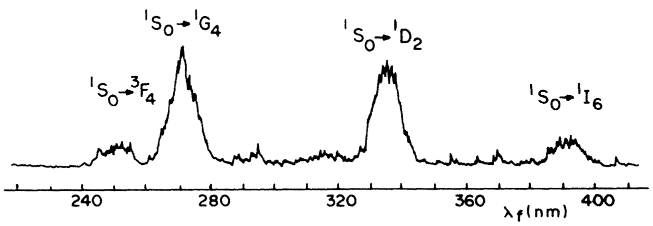

FIG. 2. Fluorescence spectrum of the uv emission observed after excitation of level $^1D_2$. The corresponding transitions are indicated.

476.5-nm argon cw laser, respectively. Most of the fluorescence lines are common to the three spectra. The main difference comes from the contribution of the lines at 477 and 490 nm. As shown below, these lines correspond to the emission from tetragonal sites. The contribution of these sites to the overall fluorescence spectrum [Fig. 1(a)] is very small. This can be attributed to the fact that the excitation frequencies of tetragonal sites lie on the side of the excitation pulse frequency distribution and to the fact that only pairs of interacting tetragonal Pr sites contribute to the emission. When the $^3P_0$ level is directly excited with the broad-band laser pulse which corresponds to the $^3H_4 \rightarrow {}^3P_1$ absorption frequencies [Fig. 1(b)], the contribution of tetragonal sites is predominant, in agreement with the well-accepted fact that this kind of site is the more abundant in this material at low dopant concentration.[1] In the spectrum of Fig. 1(c) the 477-nm line is hidden in the excitation laser line side. However, the line at 490 nm is clearly weaker than that of the spectrum in Fig. 1(b), suggesting that the Ar laser excitation, which could be site selective, discriminates against excitation of tetragonal sites.

By pumping the $^1D_2$ multiplet it was also possible to observe uv emission due to process (2). Figure 2 shows the fluorescence spectrum of the observed uv light. Transitions from $^1S_0$ to lower levels are indicated in agreement with previous observations.[40]

B. Excitation spectra

The excitation spectra of the blue up-converted emission were recorded, collecting the total fluorescence between 472 and 492 nm and scanning the excitation laser frequency (bandwidth 0.2 cm^{-1}) over the $^1D_2$ multiplet absorption band. Its time-integrated spectrum is shown in Fig. 3(b). One important characteristic of this spectrum as compared to the excitation spectrum obtained by monitoring the signal emitted directly from level $^1D_2$ to level $^3F_2$ [Fig. 3(a)] is its higher number of lines. According to the process described by (1), the observed lines correspond to the excitation frequencies of ions which interact with a neighbor impurity having the same excitation frequency. Ignoring accidental coincidences, the observed lines corre-

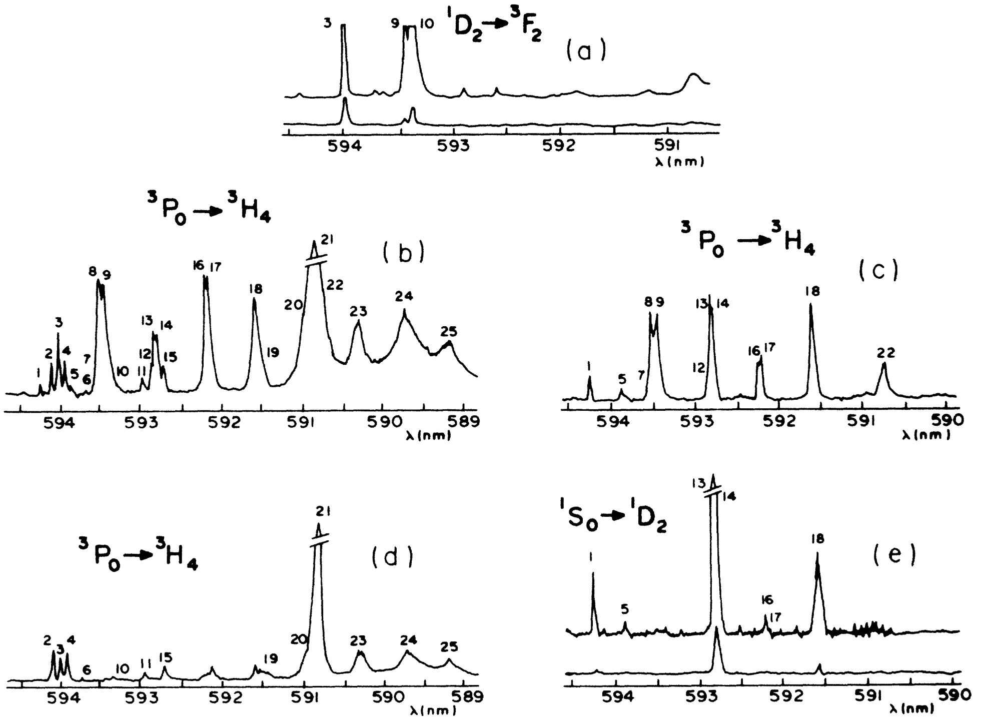

FIG. 3. Excitation spectra of the observed emissions following excitation of level $^1D_2$. (a) Excitation spectrum of the $^1D_2$ to $^3F_2$ transition. (b) Time-integrated excitation spectrum of the $^3P_0$ to $^3H_4$ transition. (c) and (d) Excitation spectra of the $^3P_0$ to $^3H_4$ transition using an integration gate of 5 μs positioned immediately after the laser excitation and an integration gate of 50 μs positioned 50 μs after excitation, respectively. (e) Excitation spectrum of the $^1S_0$ to $^1D_2$ transition. Intensity units are arbitrary and independent in each case.

spond to pairs of equivalent or quasiequivalent ions, in the sense that the Stark energy levels must differ in less than the laser bandwidth. In particular, the technique is suitable for observing clusters containing more than two Pr ions and presenting some symmetry element transforming one impurity into another (if we assume that the dynamic coupling between $4f$ states of the two symmetric impurities is weak enough to maintain the degeneracy of the pair states). As a result of these observations, we conclude that pairs of Pr ions can exist in sites which differ from the sites previously identified by observation of the direct fluorescence.[30] Peaks 3, 9, 10, and 13 are present in both, the blue up-conversion and the direct fluorescence excitation spectra, but their relative intensities are completely modified.

The temporal evolution of the up-converted emission is dramatically different from that of the direct emission. In the latter case all the observed line intensities decrease with time constants of the order of several hundreds of microseconds,[30] while in the former the characteristic evolution times range from 1 to 240 μs. Figure 3(c) shows the excitation spectrum recorded with an integration gate of 5 μs positioned immediately after the excitation pulse, and Fig. 3(d) shows the spectrum obtained with a 50-μs integration gate placed 50 μs after the excitation. Based on their appearance in these spectra the observed lines can be classified into "fast" and "slow" lines. As will be discussed later, a physical meaning can be given to this classification.

An interesting feature appearing in Figs. 3(c) and 3(d) concerns the structure corresponding to a wavelength shorter than 591 nm. This structure has already been observed in the direct-emission excitation spectrum[30] and has been attributed to a vibronic side band involving all site symmetries. When observing this structure via up-conversion, it appears that it is only associated with sites giving a slow emission. As shown below, a limited number of sites can account for this structure, suggesting that a new interpretation should be necessary.

Figure 3(e) shows the uv excitation spectrum. As discussed previously, this technique allows the observation of strongly interacting clusters containing three or more ions. The observed uv emission has a transient decay time of the order of 1 μs. A clear correlation exists between the peaks appearing in this spectrum and those of Fig. 3(c), with the exception of peaks 8, 9, and 22. This observation indicates that part of the blue emission, corresponding to the fast lines, is associated with clusters containing more than two strongly coupled Pr ions. Peaks 8, 9, and 22 are probably due to a cluster with two Pr ions.

In addition to the spectral lines appearing in the previous spectra, blue emission evolving in less than 1 μs is present in all the observed spectral region. This fast background has a characteristic fluorescence spectrum different to that of the observed excitation lines [Fig. 4(k)]. No systematic study of the origin of this background was intended.

C. Fluorescence spectrum and site classification

In order to associate the observed excitation frequencies with the corresponding sites, we have recorded the fluorescence spectra of all the lines presented in Fig. 3(b). The lines presenting the same fluorescence spectrum were assumed to correspond to different Stark levels from a single site. Following this procedure we have identified ten different sites. The results are summarized in Table I. After identification of the characteristic fluorescence of each site it was generally possible to select fluorescence lines arising from a single site and to record single-site excitation spectra. These characteristic emissions were also used to measure the temporal evolution of the fluorescence signal, reducing in this way the distortion due to the fast nonresonant background already mentioned.

Site A has two excitation lines (3 and 10) in the observed region which are also the principal lines of the excitation spectrum of the $^1D_2 \rightarrow {}^3F_2$ transition. Their

TABLE I. Classification of the observed impurity sites. Line numbers refer to Fig. 3(b). The wavelengths are in nanometers. T_1, T_2, and T_3 are the observed exponential decay times (in microseconds) of the blue up-converted emission, the direct fluorescence from state $^1D_2$, and the direct fluorescence from state $^3P_0$, respectively.

Site	Lines	Wavelength	T_1	T_2	T_3
A	3, 10	594.0, 593.4	240±10	480±20	95±5
B	4, 15, 21 23, 25	593.9, 592.7, 590.9 590.3, 589.2	80±5		
C	2, 19	594.1, 591.5	60±4		
D	11	593.0	35±3		
E	24	589.7	23±3		
F	6, 7, 16, 17	593.7, 593.54, 592.2 592.1	12±2		13±2
G	8, 9, 22	593.51, 593.46, 590.7	1.8 ±0.3		2 ±0.3
H	12, 13, 14	592.9, 592.83, 592.80	1.1 ±0.3		
I	18	591.55	1.8 ±0.3		
J	1	594.3	1.5 ±0.3		

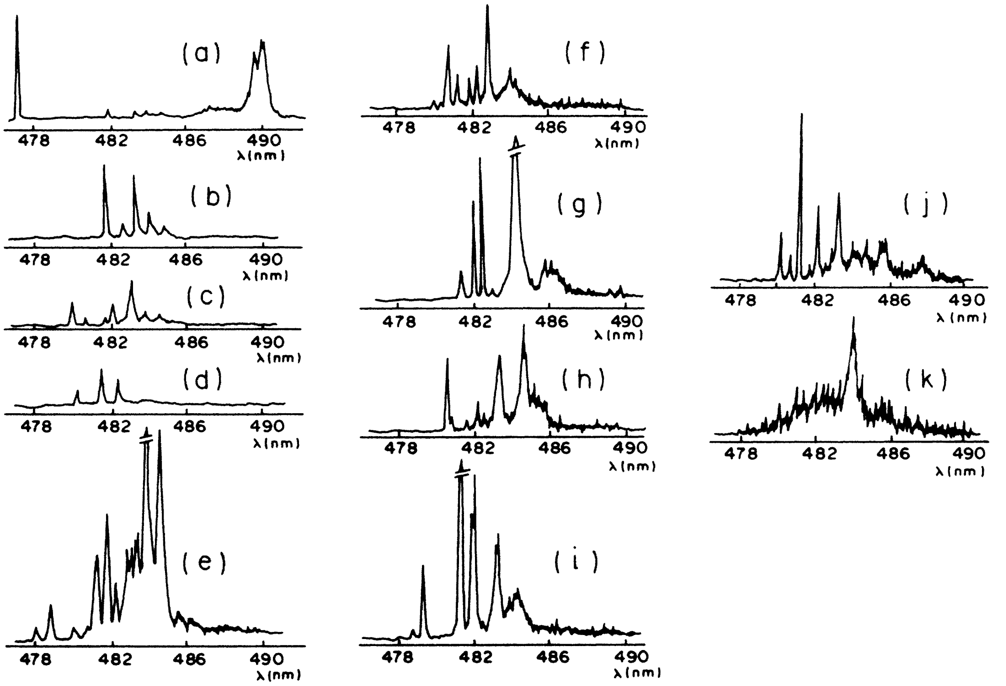

FIG. 4. Fluorescence spectra of the $^3P_0$ to $^3H_4$ transition corresponding to the different sites listed in Table I. The letters refer to the corresponding sites [(a) to A, (b) to B, etc.]. Spectrum (k) corresponds to the fast background (see text).

fluorescence spectrum is shown in Fig. 4(a). The fluorescence line at 477 nm is the shortest wavelength of the whole spectrum and is clearly recognizable in the directly excited $^3P_0$ fluorescence spectrum of Fig. 1(b) and in the Ar-laser excited spectrum of Fig. 1(c). This line is also observable, as an isolated one, in the absorption spectrum.[30] This site has been studied by different authors,[26,28,30] and it has been accepted that it corresponds to ions in the simplest charge-compensated cluster configuration which has a C_{4v} symmetry. It has recently been shown[33] that the ground-state wave function of this site is A_1 and that the lower $^1D_2$-state wave function is E. Our observations are consistent with these assignments, considering that two of the four expected excitation frequencies probably lie out of the observed spectral region.[33] The time evolution of the up-converted blue emission from this site is shown in Fig. 5(a). The exponential decay time is 240±10 μs and is the longest observed. As the 477-nm fluorescence line is easily selected with a spectrometer, we have recorded the temporal evolution of this emission when directly excited by a broad-band blue laser pulse. The observed exponential decay time in this case is 95±5 μs. In addition, the decay time of the emission directly arising from state $^1D_2$ has been measured to be 480±20 μs.

Site B presents five excitation lines (4, 15, 21, 23, and 25) and the corresponding fluorescence spectrum is shown in Fig. 4(b). Peaks 23 and 25 from this site are situated in the frequency region which was previously identified as a vibronic band.[30] The shape of these lines, along with the fact that they are associated specifically to this site, suggest that they are in fact Stark levels of the $^1D_2$ multiplet which are strongly broadened by spontaneous phonon emission. The observed linewidth corresponds to phonon emission rates of the order of 10^{11} s^{-1}. Similar linewidths are observable in LaF$_2$:R^{3+} for the higher Stark levels of several multiplets.[41] Additional information including the temperature dependence would be necessary to check this hypothesis. The temporal evolution of the blue up-conversion emission arising from this site is shown in Fig. 5(b).

Site C (lines 2 and 19) shows the fluorescence spectrum of Fig. 4(c) and the temporal evolution presented in Fig. 5(c). Only one excitation line (11) associated with site D was detected. The corresponding fluorescence spectrum and temporal evolution are shown in Figs. 4(d) and 5(d), respectively.

Site E (line 24) presents an unique situation, as no sharp excitation line could be associated with it. The fluorescence spectrum arising from excitation at line 24 is shown in Fig. 4(e), and its temporal evolution in Fig. 5(e). This line corresponds presumably to an accidental coincidence between broad Stark levels of nonequivalent ions.

The remaining sites, listed below, are all characterized by a rapid temporal evolution. In all cases the rise time of the blue up-converted fluorescence is less than 0.5 μs.

The site F (lines 6, 7, 16, and 17) fluorescence spectrum is presented in Fig. 4(f). The exponential decay time of this fluorescence is 12±2 μs.

Site G (lines 8, 9, and 22) presents the fluorescence spectrum shown in Fig. 4(g). Its fluorescence intensity decays with an exponential decay time of 1.8 μs. Line 9 has

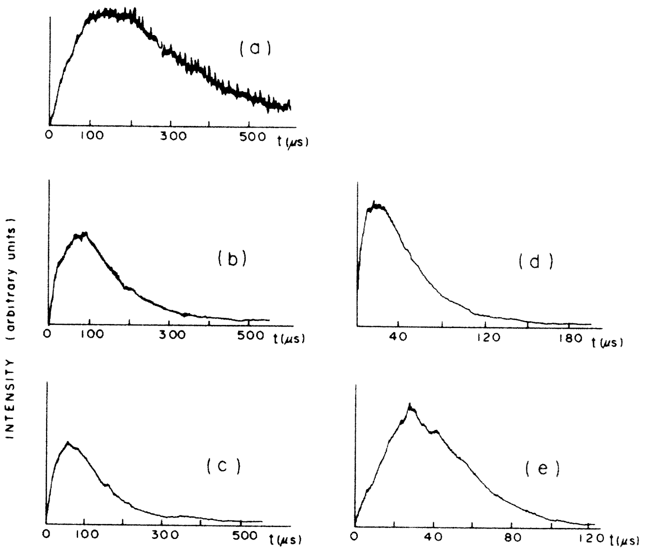

FIG. 5. Temporal evolution of the fluorescence corresponding to the ${}^3P_0$ to ${}^3H_4$ transition for sites A to E. Intensity units are arbitrary and independent in each case.

the same position as a strong line appearing in the excitation spectrum of the direct emission from ${}^1D_2$. However, line 8 is absent in this spectrum and line 22 appears only as a small bump. This could suggest that line 9 belongs to a different site than lines 8 and 22. All attempts to distinguish between the fluorescence arising from line 9 and that of lines 8 and 22 had failed, although we cannot exclude the possibility that this may be due to the large overlap between lines 8 and 9. The luminescence from ${}^1D_2$ excited at line 9 has been attributed to sites having O_h and C_{3v} symmetries and presenting energy transfer between them.[30] Our observations are compatible with a C_{3v} symmetry, and no evidence for cubic sites is observed.

Site H (lines 12, 13, and 14) shows the fluorescence spectrum of Fig. 4(h) and an exponential decay time of 1.1 μs. One of these lines (13) corresponds to a weak line of the ${}^1D_2$ direct emission excitation spectrum attributed to C_s symmetry. As for the case of lines 16 and 17 of site F and 8 and 9 of site G, it can be argued that these groups of close lines are inhomogeneous structures of single Stark levels rather than different Stark levels. In the former case a small difference in the fluorescence spectrum could be expected. No such difference was detected.

Site I (line 18) presents the fluorescence spectrum shown in Fig. 4(i). Its decay time is 1.8 μs.

Line 1 arises from site J and presents a fluorescence spectrum shown in Fig. 4(j). Its fluorescence intensity decreases with a time constant of 1.5 μs. The spectra obtained after excitation at line 5 were strongly contaminated by other lines, preventing an unambiguous characterization of the corresponding site.

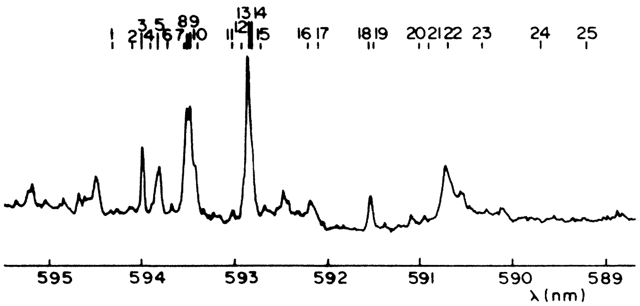

FIG. 6. Absorption spectrum at 20 K of 0.1 mol% $CaF_2:Pr^{3+}$. The positions of the excitation spectrum lines appearing in Fig. 3 are indicated.

IV. DISCUSSION

Although the observation of up-converted emission only gives information related to pairs of equivalent (or quasiequivalent) ions, the results summarized in Table I show that Pr ions exist in at least ten different sites. As can be seen in Fig. 6, the absorption spectrum of our sample around the ${}^3H_4 \rightarrow {}^1D_2$ transition shows several lines corresponding to the excitation frequencies of many of the sites listed above. This is a clear indication that the sites detected by the up-conversion technique are not minor sites but are present in concentrations comparable to those of the single-ion sites. We must then consider two questions. Firstly, which are the characteristics of the actual sites, and secondly, whether the ions participating in the up-conversion process belong to a single cluster or to different interacting clusters (considering as a cluster a group of strongly coupled Pr ions and their charge-compensating F^- ions).

Our technique has proved to be more suitable for answering the second question than the first. As an attempt to characterize the observed sites, a group-theory calculation of the allowed electric dipole transitions (at low temperature) from level ${}^3H_4$ to level ${}^1D_2$ and from ${}^3P_0$ to ${}^3H_4$ has been performed. However, unless otherwise indicated in the preceding section, unambiguous identification of the site symmetry was not possibly by simply counting the observed excitation and fluorescence lines. One possible explanation for this difficulty is the possible contribution of thermally populated lines. In addition, the difference in strength between the allowed lines can be such that some of them are hidden by the noise background. Also, the number of expected excitation lines depends on the knowledge of the ground-state wave function, which is only available in a few cases.[17,28]

The main information for the discussion of the second question comes from the temporal behavior of the up-converted fluorescence. This temporal behavior, for the process described by (1), has been discussed in Ref. 42. As shown there, the main parameter governing the time evolution of the fluorescence is the up-conversion transfer rate W_t. These authors also show that dramatic variations of this rate can take place when the distance between interacting ions varies. For long distances, the transfer rate is observed to vary roughly as $1/R^6$, as expected for dipole-dipole coupling. However, for short interionic distances, the transfer rate increases by two orders of magnitude suggesting the existence of a short-range interaction, namely, the superexchange interaction.[43] As no charge compensation exists in $LaF_3:Pr^{3+}$, the superexchange takes place via the crystal lattice F^- anions. In $CaF_2:Pr^{3+}$, multi-ion clusters form dense structures with interstitial fluorines[9] presumably favoring superexchange coupling.

The limiting cases can be considered. If W_t is small, the up-converted signal rises with a rise time of the order of the lifetime of state $^3P_0$ and decreases exponentially with a time constant which is half the lifetime of state $^1D_2$. On the other hand, if W_t is large, the rise time is of the order of W_t^{-1} and the decay time corresponds to the lifetime of state $^3P_0$.

The two situations were identified in the present experiments. Site A is an example of the first case. For this site all the concerned lifetimes are available and the observed temporal evolution is in agreement with the previous description. Consequently, in this case the up-conversion process is due to a weak long-range interaction. This is consistent with the previous[30] identification of this site as a cluster formed by a single Pr ion with a single charge compensator. For such a cluster to participate in the up-conversion process, it has to interact with another similar cluster. This can take place via dipole-dipole interaction and is favored by the large number of such clusters in the crystal. This is, to our knowledge, the first indication of intercluster interaction in this material. Although the lifetimes of levels $^1D_2$ and $^3P_0$ are not available for sites B, C, D, and E, we believe, due to their long decay and rise times, that the previous description applies to them as well. Consequently, what we have called "slow lines" corresponds to single-ion clusters with intercluster interaction.

Site F is an example of the opposite situation. In this case the lifetime of state $^3P_0$ can be measured by monitoring the fluorescence at 482.7 nm [see Figs. 4(f) and 1(b)]. The measured lifetime was 13 ± 2 μs, in good agreement with the decay time observed for this site. A similar result was obtained for site G. In this case the monitored fluorescence line was that at 484.2 nm and the observed lifetime of level $^3P_0$ was 2 μs. The rapid rise time observed for all the "fast lines" indicates a strong ion-ion coupling. This fact, along with the already mentioned correspondence between the fast blue and the uv excitation spectrum (which is sensitive to strong coupled triads) indicate that in this case the up-conversion takes place via a strong short-range interaction. Thus, the up-conversion fluorescence arising from sites F to J has to be attributed to strong intracluster interaction.

V. CONCLUSIONS

We have observed, in $CaF_2:Pr^{3+}$, up-conversion from state $^1D_2$ to states $^3P_0$ and $^1S_0$ via pair and triad interaction, respectively. The analysis of the blue emission arising from level $^3P_0$ allows the observation of ten different impurity ion sites, including single impurity, pair and more than two-ion clusters, indicating, that as in BaF_2,[44] the site distribution in rare-earth doped CaF_2 cannot be complete without the inclusion of cluster sites. The temporal evolution of the fluorescence generated by up-conversion provides an indication of both intercluster and intracluster ionic coupling.

ACKNOWLEDGMENTS

We would like to thank J. R. Rios Leite for very stimulating discussions. Thanks are also due to E. A. de Almeida and F. Aguiar for sharing the N_2 and argon lasers used in the experiments. This work was supported by FINEP (Financiadora Nacional de Estudos e Projetos), CAPES (Coordenacão de Aperfeicoamento de Pessoal de Ensino Superior), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), and FIPEC (Fundo de Incentivo à Pesquisa Técnico-Científica do Banco do Brasil), all of which are Brazilian agencies.

---

[1] W. J. Weber and R. W. Bierig, Phys. Rev. **134**, A1492 (1964).
[2] U. Ranon and W. Low, Phys. Rev. **112**, 1609 (1963).
[3] J. Short and R. Roy, J. Phys. Chem. **67**, 1860 (1963).
[4] J. B. Fenn, Jr., J. C. Wright, and F. Fong, J. Chem. Phys. **59**, 5591 (1973).
[5] R. H. Heist and F. K. Fong, Phys. Rev. B **1**, 2970 (1969).
[6] V. V. Osiko, Fiz. Tverd. Tela **7**, 1294 (1965) [Sov. Phys.—Solid State **7**, 1047 (1965)].
[7] S. L. Naberhuis and F. K. Fong, J. Chem. Phys. **56**, 1174 (1972).
[8] C. R. A. Catlow, J. Phys. C **9**, 1859 (1976).
[9] P. J. Bendall, C. R. A. Catlow, J. Corish, and P. W. M. Jacobs, J. Solid State Chem. **51**, 159 (1984).
[10] J. Corish, C. R. A. Catlow, P. W. M. Jacobs, and S. H. Ong, Phys. Rev. B **25**, 6425 (1982).
[11] C. R. A. Catlow, A. V. Chadwick, G. N. Greaves, and L. M. Moroney, Nature **312**, 601 (1984).
[12] J. L. Merz and P. S. Pershan, Phys. Rev. **162**, 235 (1967).
[13] C. G. Andeen, J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, R. J. Kimble, Jr., and G. E. Mattheus, Jr., J. Phys. C. **14**, 3557 (1981).
[14] Z. C. Nauta Leeffers and H. W. Hartog, Phys. Rev. B **19**, 4162 (1979).
[15] J. M. Baker, E. R. Davies, and J. P. Hurrel, Proc. R. Soc. London, Ser. A **308**, 403 (1968).
[16] S. D. McLaughlan, Phys. Rev. **150**, 118 (1966).
[17] R. M. Macfarlane, D. P. Burum, and R. M. Shelby, Phys. Rev. Lett. **49**, 636 (1982).
[18] Yu. K. Voron'ko, V. V. Osiko, and I. A. Scherakov, Zh. Eksp. Teor. Fiz. **56**, 151 (1969) [Soviet Phys.—JETP **29**, 86 (1969)].
[19] D. R. Tallant and J. C. Wright, J. Chem. Phys. **63**, 2074 (1975).
[20] D. R. Tallant, M. P. Miller, and J. C. Wright, J. Chem. Phys. **65**, 510 (1976).
[21] D. R. Tallant, D. S. Moore, and J. C. Wright, J. Chem. Phys. **67**, 2897 (1977).
[22] M. P. Miller and J. C. Wright, J. Chem. Phys. **71**, 324 (1979).
[23] D. S. Moore and J. C. Wright, J. Chem. Phys. **74**, 1626 (1981).
[24] M. B. Seelbinder and J. C. Wright, J. Chem. Phys. **75**, 5070 (1981).
[25] R. J. Hamers, J. R. Wietfeldt, and J. C. Wright, J. Chem. Phys. **77**, 683 (1982).

[26] W. A. Hargreaves, Phys. Rev. B **6**, 3417 (1972).

[27] V. P. Bhola, J. Lumin. **10**, 185 (1975).

[28] V. P. Bhola, Phys. Status Solidi B **68**, 667 (1975).

[29] J. Chrysochoos, P. W. Jacobs, and M. J. Stillman, J. Lumin. **28**, 177 (1983).

[30] J. Kliava, P. Evesque, and J. Duran, J. Phys. C **11**, 3357 (1978).

[31] P. Evesque, J. Kliava, and J. Duran, J. Lumin. **18-19**, 646 (1979).

[32] R. H. Petit, P. Evesque, and J. Duran, J. Phys. C **14**, 5081 (1981).

[33] R. M. Macfarlane, D. P. Burum, and R. M. Shelby, Phys. Rev. B **29**, 2390 (1984).

[34] M. R. Brown, J. S. S. Whiting, and W. A. Shand, J. Chem. Phys. **43**, 1 (1965).

[35] L. D. Livanova, I. G. Staitkulov, and A. L. Stolov, Fiz. Tverd. Tela **11**, 918 (1969) [Sov. Phys.—Solid State **11**, 750 (1969)].

[36] J. C. Vial, R. Buisson, F. Madeore, and M. Poirier, J. Phys. (Paris) **40**, 913 (1979).

[37] A. Lezama, M. Oriá, J. R. Rios Leite, and Cid B. de Araujo, Phys. Rev. B **32**, 7139 (1985).

[38] I. Shoshan, N. N. Danon, and U. P. Oppenheim, J. Appl. Phys. **48**, 4495 (1977).

[39] M. G. Littman and H. J. Metcalf, Appl. Opt. **17**, 2224 (1978).

[40] C. G. Levey, Ph.D. thesis, University of Wisconsin, Madison, 1984.

[41] See, for example, the Nd^{3+}:LaF_3 spectra reported in W. T. Carnall, Hannah Crosswhite, H. M. Crosswhite, Argonne National Laboratory Report (unpublished).

[42] R. Buisson and J. C. Vial, J. Phys. (Paris) Lett. **42**, L115 (1981).

[43] J. C. Vial and R. Buisson, J. Phys. (Paris) Lett. **43**, L339 (1982).

[44] M. P. Miller and J. C. Wright, Phys. Rev. B **18**, 3753 (1977).