

## Spectroscopic Properties and Luminescence Concentration Quenching of the $\text{Pr}^{3+}$ Ion in $\text{La}_{1-x}\text{Pr}_x\text{OCl}$

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Luminescence spectra of  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$  ( $0.01 \leq x \leq 0.3$ ) were recorded at liquid helium and room temperature. From these spectra, the energy level diagram of  $\text{Pr}^{3+}$  in  $\text{LaOCl}$  was deduced. The decay times of the  $\text{Pr}^{3+}$  emission in  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$  were measured using a high-resolution dye laser system. The linear concentration quenching and exponential decay times are explained assuming cross relaxation and energy transfer between the  $\text{Pr}^{3+}$  ions. © 1987 Academic Press, Inc.

### I. Introduction

Recently the luminescence of the concentrated rare-earth system  $\text{EuOCl}$  (1) and  $\text{TbOCl}$  (2) was reported. In these systems there is luminescence concentration quenching due to energy migration over the rare-earth ions to quenching centers. In this paper we report on our investigations of the luminescence of  $\text{Pr}^{3+}$  in  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$  ( $0.01 \leq x \leq 0.3$ ) in order to elucidate the concentration quenching mechanism in this system. In addition to the possibility of energy migration to quenchers, there is in the case of  $\text{Pr}^{3+}$  the possibility of quenching by cross relaxation. The luminescence properties of  $\text{Pr}^{3+}$  ions in several host lattices were described in Refs. (3-8). Concentration quenching in  $\text{La}_{1-x}\text{Pr}_x\text{P}_5\text{O}_{14}$  (9, 10) and  $\text{LaF}_3:\text{Pr}^{3+}$  (11-13) were studied extensively during recent years. Quenching of the  $^3P_0$  emission of the  $\text{Pr}^{3+}$  ion can be due

to three different processes:

(i) Decay to the  $^1D_2$  level due to multiphonon emission, as observed for  $\text{PrP}_5\text{O}_{14}$  (7). This process is independent of the  $\text{Pr}^{3+}$  concentration.

(ii) Cross relaxation between pairs of  $\text{Pr}^{3+}$  ions as proposed for  $\text{La}_{1-x}\text{Pr}_x\text{F}_3$  (13).

(iii) Energy migration to a quencher (which might be a cross-relaxing  $\text{Pr}^{3+}$  pair) as proposed for  $\text{La}_{1-x}\text{Pr}_x\text{F}_3$  by Hegarty *et al.* (14).

In this paper we report on a spectroscopical investigation of  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$ . This system was chosen because the frequency of the lattice vibrations is so low that  $^3P_0 \rightarrow ^1D_2$  multiphonon emission may be expected to have a negligible rate. The examples of  $\text{EuOCl}$  and  $\text{TbOCl}$  have shown that the interaction between the rare-earth ions is relatively strong in this structure.

The crystal structures of  $\text{LaOCl}$  and  $\text{PrOCl}$  are isomorphous with that of  $\text{PbFCl}$  (15) and consist of alternating  $[\text{LaO}]_2^{2+}$  and  $\text{Cl}_2^-$  layers perpendicular to the *c*-axis.

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There is only one crystallographic site for the  $\text{La}^{3+}$  and  $\text{Pr}^{3+}$  ions. The rare-earth site symmetry is  $C_{4v}$ . The nearest-neighbor distance between  $\text{Pr}^{3+}$  ions in the layer is  $\approx 4.1 \text{ \AA}$ , and between  $\text{Pr}^{3+}$  ions in two different layers  $\approx 5.3 \text{ \AA}$ . From the data to be presented it can be deduced that cross-relaxation as well as excitation energy migration to quenching centers occurs in  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$  down to low temperatures.

## 2. Experimental

Seven powder samples of  $\text{LaOCl}$  doped with  $\text{Pr}^{3+}$  in nominal molar concentrations of 1, 2, 3, 6, 10, 20, and 30% were obtained by dissolving the rare-earth oxides (Highways International, 99.999%) in  $\text{HCl}$  (Baker), evaporating to dryness, and firing in air at  $700^\circ\text{C}$  for 5 hr. The resulting products had a pale-green color. The samples were checked by X-ray powder diffraction. According to diffuse reflectance spectroscopy the samples did not contain  $\text{Pr}^{4+}$ .

A number of general luminescence measurements were performed using a Perkin-Elmer spectrofluorometer MPF-44B. A nitrogen (Molelectron UV 14)-pumped dye laser (Molelectron DL-200) was used to excite the  $^3P_0$  level in each sample while im-

mersed in liquid helium. The laser generated a pulse with a peak power of  $30 \text{ kW/cm}^2$  and a width of 10 nsec. The temperature of the samples could be regulated between 4.2 K and room temperature using a temperature controller (Thor Cryogenics Model 3020 II). For all experiments the laser was adjusted to the  $^3H_4(1) \rightarrow ^3P_0$  absorption line (493.6 nm).

The population of the  $^3P_0$  level after pulse excitation was measured by monitoring the  $^3P_0 \rightarrow ^3H_6(1)$  transition at  $15,627 \text{ cm}^{-1}$  with a Spex 1704 X high-resolution monochromator. The output from the RCA-C31034A photomultiplier was digitized by a Tektronix 7912 D digital oscilloscope. The resulting decay was plotted on a printer and the digitized data were analyzed with a BBC microcomputer system.

## 3. Results

### a. Spectroscopic Properties of $\text{Pr}^{3+}$ in $\text{La}_{1-x}\text{Pr}_x\text{OCl}$

The LHeT emission spectrum of 10 mole%  $\text{Pr}^{3+}$  in  $\text{LaOCl}$ , excited at 493.6 nm, is shown in Fig. 1 as a representative example. The spectrum shown consists of several narrow peaks attributed to the  $^3P_0 \rightarrow$

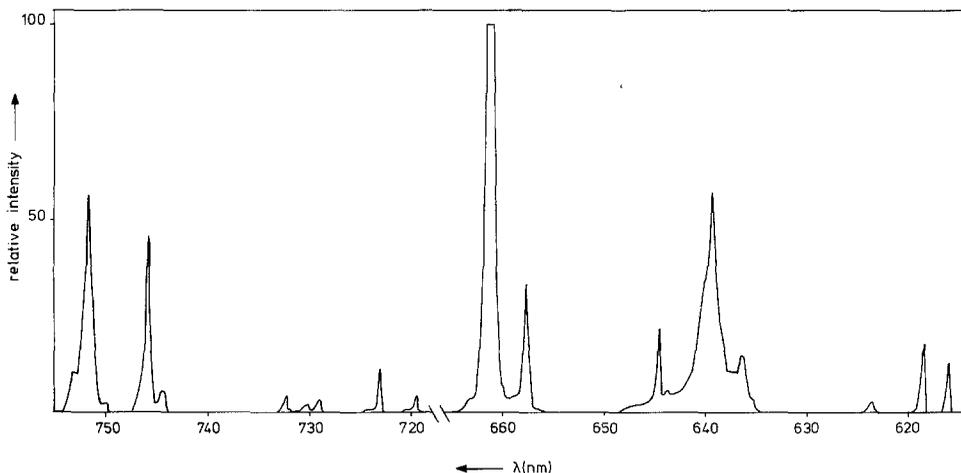


FIG. 1. The emission spectrum of the  $\text{Pr}^{3+}$  luminescence of  $\text{La}_{0.9}\text{Pr}_{0.1}\text{OCl}$  at LHeT ( $\lambda_{\text{exc}} = 493.6 \text{ nm}$ ).

<sup>3</sup>F<sub>2,3,4</sub>, <sup>3</sup>H<sub>6</sub> and to the <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> transitions. The intensity of the <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> emission is relatively weak compared to the <sup>3</sup>P<sub>0</sub> → <sup>3</sup>F<sub>2,3,4</sub> luminescence intensity. The luminescence of the Pr<sup>3+</sup> ion in the system La<sub>1-x</sub>Pr<sub>x</sub>OCl is observed up to  $x \approx 0.3$ . For  $x > 0.3$  this luminescence is quenched (see also Fig. 2). The number of emission lines observed for the separate transitions is equal to or less than the number of lines expected for the Stark splitting in a single site with symmetry C<sub>4v</sub>. The derived energy level diagram for La<sub>1-x</sub>Pr<sub>x</sub>OCl at LHeT is given in Fig. 3. It is constructed using the emission lines listed in Table I. Note that for concentrations of Pr<sup>3+</sup>  $x > 0.1$ , there is a complete absence of emission originating from the <sup>1</sup>D<sub>2</sub> level. Although the energy level scheme is not complete, it can be deduced that the energy mismatch for the cross-relaxation process <sup>3</sup>P<sub>0</sub> + <sup>3</sup>H<sub>4</sub> → <sup>1</sup>D<sub>2</sub> + <sup>3</sup>H<sub>6</sub> is about 500 cm<sup>-1</sup>. The data do not allow a determination of the energy mismatch for the cross-relaxation process which quenches the <sup>1</sup>D<sub>2</sub> emission. The general observation is that the latter mismatch is much smaller than

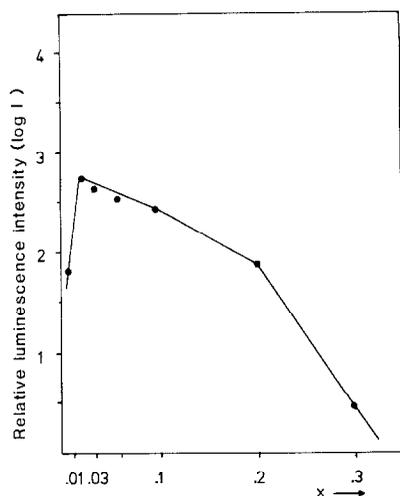


FIG. 2. Concentration dependence of the relative emission intensity of the luminescence from the <sup>3</sup>P<sub>0</sub> level at room temperature in La<sub>1-x</sub>Pr<sub>x</sub>OCl for 0.01 ≤  $x$  ≤ 0.30.

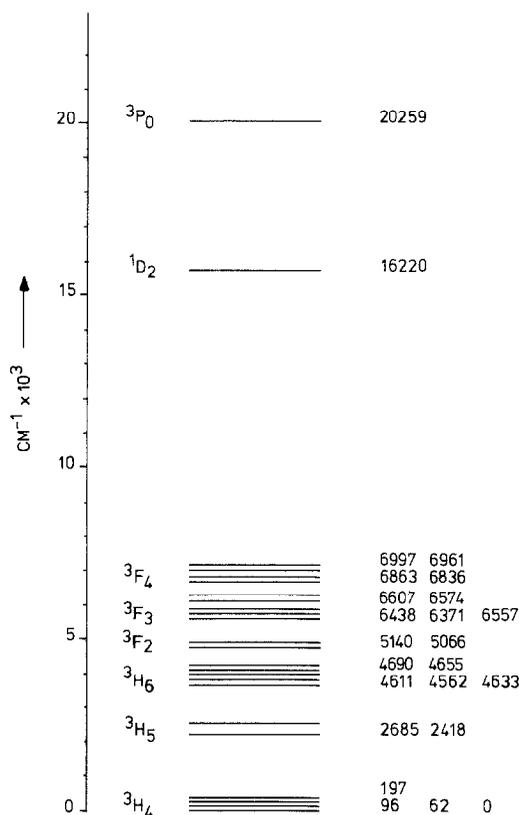


FIG. 3. The energy level diagram of the Pr<sup>3+</sup> ion in LaOCl as deduced from the emission spectra.

the former (16). For Pr<sup>3+</sup> in the LaF<sub>3</sub> the former amounts to 190 cm<sup>-1</sup> (14).

From the diffuse reflectance spectra it becomes clear that in the LaOCl lattice the transition  $4f^2 \rightarrow 4f5d$  of the Pr<sup>3+</sup> ion lies at an energy of approximately 40,000 cm<sup>-1</sup>. For Tb<sup>3+</sup> and Ce<sup>3+</sup> in LaOCl the energy of this  $4f \rightarrow 5d$  transition is 44,000 cm<sup>-1</sup> (17) and 33,000 cm<sup>-1</sup> (18), respectively. Hoefdraad and Blasse (19) have established that in CaZrO<sub>3</sub>:Pr<sup>3+</sup> the position of the  $4f \rightarrow 5d$  band is at 41,000 cm<sup>-1</sup>, and that this energy level feeds only the <sup>3</sup>P<sub>2,1,0</sub> levels. Thus only <sup>3</sup>P<sub>0</sub> emission is observed for CaZrO<sub>3</sub>:Pr<sup>3+</sup> upon UV excitation. This is also the case in LaOCl:Pr<sup>3+</sup>. A relaxation process <sup>3</sup>P<sub>0</sub> → <sup>1</sup>D<sub>2</sub> via the  $4f5d$  configuration seems rather improbable.

TABLE I  
POSITION AND RELATIVE INTENSITY OF THE EMISSION LINES OF Pr<sup>3+</sup> IN La<sub>1-x</sub>Pr<sub>x</sub>OCl

Transition	$\lambda$ (nm)	$\sigma$ (cm <sup>-1</sup> )	Relative intensities					
			$x = 0.01$	$x = 0.02$	$x = 0.03$	$x = 0.10$	$x = 0.20$	$x = 0.30$
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> H <sub>5</sub>	560.5	17 841	13	16	—	7	—	—
	569.0	17 574	31	18	—	14	—	—
<sup>1</sup> D <sub>2</sub> → <sup>3</sup> H <sub>4</sub>	616.5	16 220	—	—	95	31	—	—
	618.9	16 158	—	—	140	42	—	—
	620.2	16 124	—	—	29	8	—	—
	624.1	16 023	25	—	58	14	—	—
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> H <sub>6</sub>	637.0	15 698	34	98	80	36	2	0.5
	639.0	15 649	300	480	350	146	10	2
	639.9	15 627	150	245	170	72	5	1
	640.8	15 605	70	120	55	30	2	—
	642.3	15 569	15	20	10	6	0.5	—
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> F <sub>2</sub>	658.2	15 193	170	650	500	80	20	1
	661.4	15 119	1000	4000	3300	560	150	14
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> F <sub>3</sub>	720.0	13 888	20	95	89	11	—	—
	723.5	13 821	70	250	200	28	—	—
	729.8	13 702	—	400	—	70	11	—
	730.7	13 685	—	—	—	50	—	—
	732.5	13 652	—	—	—	34	—	—
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> F <sub>4</sub>	745.0	13 423	25	100	80	14	3	—
	746.5	13 396	238	660	530	118	30	1
	752.0	13 298	431	1150	920	150	35	3
	754.0	13 262	25	56	44	11	2	—

### b. The Luminescence Decay Measurements

At LHeT the measured luminescence decay time of the <sup>3</sup>P<sub>0</sub> emission in La<sub>0.99</sub>Pr<sub>0.01</sub>OCl is 6.9  $\mu$ sec. The decay curve is exponential. In view of the small amount of <sup>1</sup>D<sub>2</sub> emission for this concentration, the decay is assumed to correspond in good approximation to a radiative decay. This shows the inefficiency of <sup>3</sup>P<sub>0</sub> → <sup>1</sup>D<sub>2</sub> multiphonon emission. For Pr<sup>3+</sup> in LaF<sub>3</sub> the radiative decay time is 51  $\mu$ sec (14). The shorter time in our case is easily related to the lower position of the 5d level in oxides and chlorides relative to fluorides, but the site symmetry may also have some influence.

For higher Pr<sup>3+</sup> concentrations the decay

time decreases to 0.72  $\mu$ sec for La<sub>0.7</sub>Pr<sub>0.3</sub>OCl. From the above data we conclude that concentration quenching of the <sup>3</sup>P<sub>0</sub> emission occurs in this system. This quenching does not result in a build-up of the <sup>1</sup>D<sub>2</sub> emission. Figure 4 summarizes the concentration dependence ( $x$ ) of the quenching rate  $q(x) = \tau^{-1} - \tau_0^{-1}$  in La<sub>1-x</sub>Pr<sub>x</sub>OCl at LHeT and RT. Here  $\tau$  presents the exponential decay time and  $\tau_0$  the radiative decay time, i.e., the value observed for La<sub>0.99</sub>Pr<sub>0.01</sub>OCl.

### 4. Discussion

The luminescence of the Pr<sup>3+</sup> ion in LaOCl shows a pronounced concentration quenching above 2% Pr<sup>3+</sup>. Here we wish to

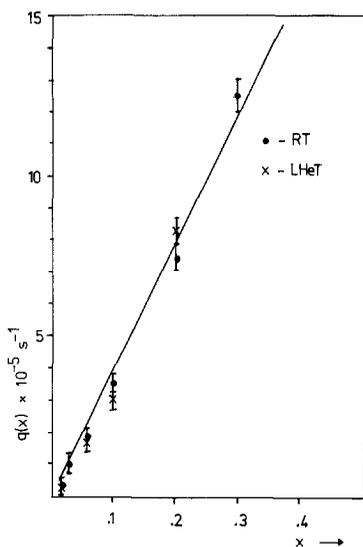


FIG. 4. The quenching rate  $q(x) = \tau^{-1} - \tau_0^{-1}$  as a function of the concentration  $x$  in La<sub>1-x</sub>Pr<sub>x</sub>OCl.

consider the question of whether this quenching is due to cross-relaxation between pairs of Pr<sup>3+</sup> ions or to energy migration among Pr<sup>3+</sup> ions to quenching centers.

The concentration dependence of the measured <sup>3</sup>P<sub>0</sub> decay rate  $\tau^{-1}(x)$  originates from a concentration-dependent quenching rate  $q(x)$  as expressed

$$1/\tau(x) = 1/\tau_0 + q(x). \quad (1)$$

The intrinsic decay rate may primarily be due to a multiphonon relaxation process (<sup>3</sup>P<sub>0</sub> → <sup>1</sup>D<sub>2</sub>,  $\Delta E \sim 4000$  cm<sup>-1</sup>). It is well known that the multiphonon relaxation ( $W_{\text{MPR}}$ ) rates in 4*f*-4*f* transitions of all rare-earth ions in one host obey the exponential energy-gap law,

$$W_{\text{MPR}} = \beta \exp[-\alpha \Delta E], \quad (2)$$

where  $\alpha$  and  $\beta$  are constants for a given host lattice and  $\Delta E$  gives the energy gap. The equation was modified by Van Dijk and Schuurmans (20) as follows:

$$W_{\text{MPR}} = \beta_{e1} \exp[-(\Delta E - 2h\omega_{\text{max}})\alpha], \quad (3)$$

which is now valid for all host lattices. We have  $\alpha \approx 5 \times 10^{-3}$  cm and  $\beta_{e1} \approx 5.10^7$  sec<sup>-1</sup>.

The maximum energy of phonons in the case of LaOCl is 600 cm<sup>-1</sup>, as derived by us from infrared spectra. In this way Eq. (3) yields  $W_{\text{MPR}} \sim 40$  sec<sup>-1</sup>. Although this value gives only an order of magnitude of the process, it shows clearly that multiphonon emission for the <sup>3</sup>P<sub>0</sub> level can be neglected in our case, as was expected.

Let us now return to Eq. (1). We note that the quenching rate  $q(x)$  in the system La<sub>1-x</sub>Pr<sub>x</sub>OCl depends linearly on  $x$  (see Fig. 4) and is not strongly dependent on temperature. All decay curves were linear within experimental accuracy.

If quenching occurred mainly by cross-relaxation, we would expect nonlinear decay curves as described by Inokuti and Hirayama (21). These have been observed for LaF<sub>3</sub>:Pr<sup>3+</sup> at low temperatures (14). The present results seem to exclude such an interpretation. Also, such a process seems to have a low probability at low temperatures in view of the energy mismatch. Since a phonon has to be absorbed, the rate expression carries a term  $\exp(-\Delta/kT)$  if the mismatch  $\Delta$  ( $\approx 500$  cm<sup>-1</sup>) is large compared to  $kT$ . Also this temperature dependence was not observed.

An interesting way to explain the occurrence of exponential decay and a linear quenching rate has been proposed by Broer *et al.* (22, 23). They showed that the decay of the donor for small trapping rates (weak quenching) and in the absence of donor-donor transfer can be given by  $N_D(t) = N_D(0)\exp(-t/\tau_0) \cdot f(t)$ , where  $N_D$  is the number of Pr<sup>3+</sup> ions in the <sup>3</sup>P<sub>0</sub> level and

$$f(t) \approx \exp(-tx \sum_1 X_{01}). \quad (4)$$

Here  $X_{01}$  is the quenching rate between a donor at site 0 and an acceptor at site 1. This results in an exponential decay rate  $\tau^{-1}$  given by

$$\tau^{-1} = \tau_0^{-1} + x \sum_1 X_{01}. \quad (5)$$

This equation shows a linear dependence on the concentration  $x$ . Equation (4) was derived for the condition  $\tau_0 \approx X_{01}^{-1}$ . Since the quenching (i.e., cross-relaxation) rate is low (see above), this condition might well be fulfilled. Interestingly enough, Eq. (4) also describes the high-temperature decay when rapid donor–donor transfer occurs (22).

This model explains our experimental observations rather well (Fig. 4). From the slope of the linear curve of  $q(x)$  vs  $x$ , we derive for  $\Sigma_1 X_{01}$  a value of about  $4 \times 10^6 \text{ sec}^{-1}$ . This is of the same order of magnitude as  $\tau_0^{-1}$  ( $1.5 \times 10^5 \text{ sec}^{-1}$ ), but larger, which shows that effectively we are just outside the region for which Eqs. (4) and (5) are valid. Probably our measurements are not accurate enough to make a deviation from these equations visible in the experimental results. From the fact that the cross-relaxation, invoked to explain the quenching in the system  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$ , does not result in a corresponding amount of  $^1D_2$  emission, we conclude that the  $^1D_2$  emission is more rapidly quenched than the  $^3P_0$  emission. This has also been observed for the system  $\text{La}_{1-x}\text{Pr}_x\text{P}_5\text{O}_{14}$  (16) and may be related to the smaller energy mismatch for cross-relaxation in the case of the  $^1D_2$  quenching.

The rapid increase of the donor–donor transfer rate, inherent to the model used, can easily be understood from existing theories on phonon-assisted energy transfer (24). We note that the situation in the present system is very similar to that in the system  $\text{La}_{1-x}\text{Nd}_x\text{P}_5\text{O}_{14}$  (22). Also, there the cross-relaxation rate is low and temperature independent, due to a large energy mismatch ( $1000 \text{ cm}^{-1}$ ).

There are two other possibilities to explain the linear quenching, viz., donor–donor transfer not important at LHeT and RT and rapid donor–donor transfer at LHeT and RT. Both are considered to be unlikely (25): the former because the donor–donor

transfer rate is expected to increase rapidly with increasing temperature, the latter because the donor–donor transfer rate is expected to be slow at LHeT.

Unfortunately the weakness of the luminescence involved and the restrictions of the instrumentation used prevent a more detailed analysis of the present data. The results suggest, however, that in  $\text{La}_{1-x}\text{Pr}_x\text{OCl}$  energy migration occurs as a temperature-dependent process next to a slow, temperature-independent trapping process. We plan to investigate these phenomena further when a better instrument has become available.

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