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Ion-Ion Interactions in Rare-Earth-Doped LaF₃

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A systematic study of quantum efficiencies and lifetimes has been carried out for the visible fluorescences of Pr^{3+} in single-crystal LaF₈. An analysis of the results as a function of Pr^{3+} concentration is given in terms of a two-site model in which a Pr³⁺ ion can either be in an isolated site or in a site where it is coupled to other impurity ions. This model leads to ion-ion interaction ranges varying from ~ 5 Å (nearest neighbor) to ~ 12 Å depending on the fluorescent level studied. Throughout this range of interaction lengths, Dexter's model of electrostatic ion-ion interaction shows that the dominant contribution comes from the quadrupole-quadrupole term. Temperature effects in the interaction are consistent with the lack of exact resonance between the electronic levels. It appears that the lattice can readily absorb excess energy up to $\sim 1000 \text{ cm}^{-1}$.

A set of samples doped with a second rare earth (Ce³⁺, Nd³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺) has demonstrated the existence of selection rules for ion-ion interaction in addition to energy-matching requirements. The system 0.5% Pr³⁺: x% Ce³⁺ has been studied in more detail.

INTRODUCTION

THE quenching of the fluorescence from rare-earth \mathbf{I} ions has been the subject of several investigations.¹⁻³ The bulk of these investigations have been concerned with the variation of either the quantum efficiencies or the lifetimes of the fluorescent levels as the concentration of the rare-earth ion was varied. We consider that both types of measurement are necessary for an adequate interpretation of the quenching processes.

Furthermore, there is great interest in the transfer of energy from one rare-earth ion to a neighbor and in the nature of this ion-ion interaction. This investigation is concerned with the quantum efficiency and lifetime measurements of the system Pr3+:M3+:LaF3 in which we believe ion-ion interaction is the dominant source of fluorescence quenching for M = Pr or Ce.

The study of fluorescence quenching of the singly doped (Pr³⁺) samples with concentration provides information on interaction between like ions. Interaction between unlike ions can be examined by doubly doped crystals. The choice of Ce³⁺ as the codopant with Pr³⁺ in LaF_3 came from an examination of the 10 doubly doped specimens, of general form 0.5% Pr³⁺:2% M³⁺: LaF₃. The main reasons for its selection may be summarized:

(i) Its ionic radius is very similar to that of La^{3+} and it fits substitutionally into the LaF3 lattice. Also, pure CeF₃ has the same crystal structure as LaF₃. Thus a range of crystals from 100% LaF₃ to 100% CeF₃ can readily be grown.

(ii) It has an extremely simple energy-level scheme of just two multiplets separated by 2200 cm^{-1} (Fig. 1), and

(iii) Experimentally it was found to have a large effect on fluorescence from the ${}^{3}P_{0}$ level of Pr^{3+} (Fig. 1) and this was thought to be due to ion-ion interaction.

It is also necessary to ensure that variations in the experimental results with dopant concentration are indeed dominantly due to ion-ion interaction; any complicating effects must be reduced to a minimum. These complications arise from two sources:

(i) The rare-earth ion itself. The complications may be reduced to a minimum by choosing a simple ion like Pr^{3+} whose fluorescing level, the ${}^{3}P_{0}$, introduces

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 ¹ L. G. Van Uitert, J. Electrochem. Soc. **107**, 803 (1960).
 ² L. G. Van Uitert, J. Chem. Phys. **37**, 981 (1962).
 ³ L. G. Van Uitert and S. Iida, J. Chem. Phys. **37**, 986 (1962).



FIG. 1. The energy-level schemes for Pr³⁺ and Ce³⁺ in LaF₃.

no multiplet structure ambiguities [only Pr³⁺ fluorescence has been studied in both the single-(Pr³⁺) and double-(Pr³⁺, Ce³⁺) doped samples], and

(ii) The substitution of the rare-earth ions into the host lattice. The complications here stem from two main sources:

(a) Any strain introduced into the lattice may produce changes in the site symmetry of the crystal field acting on the ion, and;

(b) Any tendency of the rare-earth ions to cluster which will invalidate interpretations based on a random distribution.

The experimental information which led us to conclude that these complicating factors are not present in the crystals studied in this work arise from an examination of the width and structure of the fluorescence spectra both as the Pr³⁺ concentration was raised to 100% in the mixed (La, Pr)F₃ crystal and as the concentration of Ce3+ was raised to 100% in the mixed Pr³⁺: (La, Ce) F₃ crystals.

This examination showed that below 50% Pr³⁺ or Ce³⁺ there was no variation in the relative linewidths outside a $\pm 20\%$ variation which occurred in a random manner. However, there was a progressive broadening of the absorption above 50% in the (La, Ce)F₃ mixture. Throughout the whole 0% to 100% range there was no change in the relative line structure or intensity. The typical linewidth of a sharp line at 4.2°K in the 20% Pr³⁺:LaF₃ samples was 3 to 6 cm^{-1.4} This linewidth indicates that all the ions are seeing the same crystalline field; that is, there can be little or no strain

⁴ E. Y. Wong, O. M. Stafsudd, and D. R. Johnston, J. Chem. Phys. **39**, 786 (1963).

or clustering along fault lines for both of these would give a large variation of the crystalline field.

The influence of strain was also assessed by comparing first a crystal of low strain (optic axis perpendicular to growth axis) with one of high strain (optic axis at 10° to 15° to growth axis) and secondly a crystal cooled normally (15-20 h) with one quenched from 1250° C in $1\frac{1}{2}$ h. In both cases the change in quantum efficiency between specimens was less than 10% while the linewidth changed by a factor of 3. This shows that a 20% variation in the linewidth from strain effects would not be expected to affect the quantum efficiency significantly.

A random distribution of the Pr³⁺ and Ce³⁺ ions in LaF₃ could be expected if the ions were completely interchangeable in the lattice. The evidence that they are in fact interchangeable is common to both ions in that both fit substitutionally into the lattice (the ionic radii of Pr³⁺ is 1.10 Å as compared with 1.00 Å for La^{3+}) and both are hard to remove from the lattice by zone refining and similar purification methods.

EXPERIMENTAL

Preparation and Analysis

The fluoride crystals used in this work were all grown in a vacuum furnace substantially of the type designed by Stockbarger.⁵

The starting material in each case was the fluoride of 99.9% purity, which had been purified to remove any oxide present. The mixed-fluoride charge was loaded into a graphite crucible with CdF_2 as a scavenger. This was then lowered at a rate of 1.2 mm/h in an atmosphere of dry nitrogen at 10 mm pressure. The crystals used were grown with the optic axis approximately perpendicular to the direction of growth as this minimized the induced strains.

The analysis of the rare-earth dopings was performed in two ways; by the strength of the absorption lines and by spectrochemical techniques. These methods always gave results in agreement to $\pm 10\%$. The main rare-earth impurities in the LaF₃ were Ce and Nd both of which were present to about 100 ppm, other impurities being present to less than 100 ppm.

Lifetimes

The lifetimes of the fluorescent levels were measured by a stroboscopic method originally developed by Hendee and Brown.6

The basis of the stroboscopic method is that the sample is illuminated by a series of light pulses of duration short compared with the fluorescent decay time. The excited fluorescent light is sampled at a known time after the exciting pulse by a gated detector and the output integrated as the variable delay is

⁵ D. C. Stockbarger, Discussions Faraday Soc. **5**, 299 (1949). ⁶ C. F. Hendee and W. B. Brown, Philips Tech. Rev. **19**, 50 (1957).

swept through at a slow rate. The details of the apparatus have been given previously.⁷ The $1-\mu$ sec time resolution of the equipment is set by the width of the exciting pulse.

Quantum Efficiency

The absorption and fluorescence spectra were recorded on a Perkin-Elmer 13.U spectrometer whose resolution is roughly 1 in 5000 when a dense flint prism is used in the monochromator section.

To measure the quantum efficiencies of a group of crystals it is sufficient to measure the relative efficiencies of the spectrum and then determine the absolute efficiencies of a selected few.

The absolute quantum efficiency was measured by recording the output from a xenon lamp and narrowband filter combination, the absorption of the metastable level and the total fluorescence excited by this light. An integration of the source combination's output over the absorption line gave a measure of the number of ions excited into the metastable level. The fluorescence intensity was a measure of the fraction of these ions that decay by the radiative transitions. This fraction is the absolute quantum efficiency for that level.

The relative quantum efficiencies were measured by taking the ratio between the fluorescent outputs (under constant pump power) and the relative absorption strengths of the different samples in the one group.



FIG. 2. The quantum efficiencies of the ${}^{3}P_{0}$ level of Pr^{3+} as a function of Pr^{3+} concentration and temperature.

⁷ M. R. Brown, W. A. Shand, and J. S. S. Whiting, "Some Aspects of Infrared Quantum Counter Action in Er Doped $SrF_{2,7}$ " Brit. J. Appl. Phys. (to be published).



FIG. 3. The lifetimes of the ${}^{3}P_{0}$ level of Pr^{3+} as a function of Pr^{3+} concentration and temperature.

RESULTS

Pr³⁺:LaF₃

The quantum efficiency and lifetimes of the two states ${}^{8}P_{0}$ and ${}^{1}D_{2}$ are shown in Figs. 2, 3, and 4 as a function of the Pr^{3+} concentration at the three temperatures 290°, 77°, and 4.2°K.

It should be noted that the only measurements possible for Pr^{3+} concentrations greater than 20% were the ${}^{3}P_{0}$ quantum efficiencies at 77° and 4°K (see Fig. 2). Furthermore, pumping the ${}^{3}P$ multiplet did not excite any ${}^{1}D_{2}$ fluorescence. Only room-temperature measurements are given for the ${}^{1}D_{2}$ level (Fig. 4) as no temperature dependence was found for this level. This figure also shows a few points for Pr^{3+} in CeF₃ with the 0.5% Pr^{3+} results normalized to the curve for Pr^{3+} in LaF₃. It is clear that the same concentration dependence holds for both lattices.

Pr³⁺:M³⁺:LaF₃

The results for the 10 double-doped crystals of composition 0.5% $Pr^{3+}:LaF_3:2\%$ M³⁺ are given in Fig. 5.

Pr³⁺: (La, Ce)F₃

The results of the measurement of quantum efficiency and lifetime of the ${}^{3}P_{0}$ (0.5% Pr³⁺) level at 290°K are given in Fig. 6 as a function of the fractional concentration of Ce³⁺. The quantum-efficiency measurements could be carried out to 100% Ce³⁺, but signal weakness limited lifetime studies to 35% Ce³⁺. Once again, no temperature dependence was found.



FIG. 4. The quantum efficiencies and lifetimes of the ${}^{1}D_{2}$ level of Pr^{3+} as a function of Pr^{3+} concentration for the temperatures 290°, 77°, and 4°K. Points marked \square are for Pr^{3+} in CeF₂.

Measurements were also made of the quantum efficiency of the ${}^{1}D_{2}$ level when pumping into the ${}^{3}P$ multiplet (i.e., the variation of the ${}^{3}P_{0}$ to ${}^{1}D_{2}$ drain mechanism) and these are given in Fig. 7. Figure 7 also shows the quantum efficiency of the ${}^{1}D_{2}$ level when resonance pumping for comparison.

The lifetime measurements of the ${}^{1}D_{2}$ as given in Fig. 8, are for ${}^{3}P_{0}$ pumping, since it is easier to measure the lifetime of the ${}^{1}D_{2}$ level when pumping into the ${}^{3}P_{0}$ level because of scattered-light problems. It was found



FIG. 5. The quantum efficiencies and lifetimes of the 3P_0 level of Pr^{3+} for the series of crystals 0.5% Pr^{3+} 2% $\mathrm{M}^{3+}.$

during these measurements that the decay for the ${}^{1}D_{2}$ level was nonexponential even at 4°K, decaying initially at 50 to 70 µsec and ending at 300 µsec. Some indication of this nonexponential behavior has also been observed in Pr^{s+} : LaF₃ samples but was difficult to show conclusively because of the necessity of resonance pumping. The values given in Fig. 8 are the long-lifetime part of the decay. The quantum efficiency of the ${}^{1}D_{2}$ for resonance pumping is also shown in Fig. 8.

It was also noted during these measurements that the build-up time of the ${}^{1}D_{2}$ fluorescence when pumping into the ${}^{3}P_{0}$ level was less than 1 µsec while the decay of the ${}^{3}P_{0}$ fluorescence was around 20 µsec (see Fig. 6).

Measurements were also made on a limited number of 2.5% Pr^{3+} : (La, Ce) F_3 and it was found that these



FIG. 6. The quantum efficiencies and lifetimes of the ${}^{3}P_{0}$ level of 0.5% Pr³⁺ as a function of Ce³⁺ concentration.

had the same behavior relative to the 2.5% Pr^{3+} :LaF₃ sample as did the 0.5% Pr^{3+} samples relative to the 0.5% Pr^{3+} :LaF₃ sample.

All the above measurements of quantum efficiency and lifetime were found to be independent of crystal shape and size. Thus, reabsorption of the fluorescence is negligible.

DISCUSSION

The model used to interpret the experimental work is set up by taking a single paramagnetic ion (Pr^{3+}) in the ionic-host lattice (LaF_3) as the unperturbed system. A perturbation is introduced by replacing a number of the La^{3+} ions by M^{3+} ions where M=Pror Ce.

In the unperturbed system the decay of a fluorescing level can be divided into two parts: (i) σ_r —radiative decay rate and (ii) σ_{nr} —nonradiative decay rate, where σ_r is due to the sum of all the decay rates for spontaneous emission of electromagnetic radiation from the fluorescing level and σ_{nr} is due to the interaction of the fluorescing ion with its surrounding in the LaF₃ lattice.

The two experimentally measured quantities are the quantum efficiency and the lifetime of the fluorescing level. These can be defined as follows:

quantum efficiency $\eta = \sigma_r / (\sigma_r + \sigma_{nr})$,and lifetime $\tau = 1 / (\sigma_r + \sigma_{nr})$.

When the perturbation is added to the system it can either affect all the Pr^{3+} ions equally or only affect those ions in its immediate vicinity; that is the ionion interactions can be either long or short range.

If the perturbation affects all the ions equally then any observed variation in quantum efficiency and lifetime must be due to either a variation in σ_r or σ_{nr} or both. If the variation was purely due to a change in σ_{nr} then both η and τ would vary in the same manner. A study of Figs. 2–7 show, however, that in general this is not the case. Thus, in order to explain the results in terms of long-range interactions one would have to postulate a variation in σ_r . However, since it has been found that the matrix element in absorption is independent of concentration, it seems reasonable to assume that the matrix element involved in fluorescence behaves in the same way. This means that σ_r is independent of the perturbation and thereby rules out the possibility of long-range interactions.

If the interactions are short range then the behavior of the ion will be determined by the number of M^{3+} ions near it. This will mean that all the ions are not in equivalent sites and, indeed, that there exists a number of different types of sites. This idea is supported experimentally by two facts:

(i) that the fluorescent decay from the ${}^{3}P_{0}$ and ${}^{1}D_{2}$ levels of the Pr^{3+} ion were found to be nonexponential, and

(ii) that the decay of the ${}^{3}P_{0}$ to the ${}^{1}D_{2}$, in the case of 0.5% Pr³⁺: (La, Ce) F₃, was less than 1 μ sec while



FIG. 7. The quantum efficiencies of the ${}^{1}D_{2}$ level of 0.5% Pr³⁺ as a function of Ce³⁺ concentration when pumping into the ${}^{3}P_{0}$ level (lower curve) and when resonance pumping (upper curve).



FIG. 8. The quantum efficiencies and lifetimes of the ${}^{1}D_{2}$ level of 0.5% Pr³⁺ as a function of Ce³⁺ concentration.

the decay of the ${}^{3}P_{0}$ fluorescence was of the order 20 μ sec. This strongly suggests that Pr^{3+} ions which decay to the ${}^{1}D_{2}$ did not show up in the fluorescent decay.

It should be noted that no observable changes have been found in the absorption and fluorescence spectra arising from different sites to within the resolving power of the spectrometer (1 in 5000).

Hence, in a typical crystal containing Pr^{3+} (say 1%) one would expect to find a range of types of ions depending on the number of perturbing ions in the neighborhood of any particular Pr³⁺ ion. In order to simplify the picture it will be assumed that (i) if one of the ions which is in an excited state loses all its energy of excitation to another ion thus raising it to the equivalent excited state, the system is unchanged and there is no contribution to σ_{nr} ; that is there is no energy transport, and (ii) all the types can be divided into only two groups (a) isolated Pr^{3+} ions and (b) Pr^{3+} ions coupled to other M³⁺ ions. This assumption suggests that every Pr³⁺ ion has a sphere of influence into which the M³⁺ ion must come before interaction takes place. The two conditions that are imposed by this model are: (i) that the ion-ion interaction is of limited range, and (ii) that this interaction has a relatively strong dependence on distance within this range.

In order to change a Pr^{3+} ion from Type (a) to Type (b), at least one M^{3+} ion must fall within the sphere of influence of the Pr^{3+} ion. In Type (b) there will be a large variety of types of ions depending on the strength of the $Pr^{3+}:M^{3+}$ interaction. More than one M^{3+} may interact with any one Pr^{3+} ion in this group. The size of the sphere of influence of the Pr^{3+} ion will depend on the type of $Pr^{3+}:M^{3+}$ interaction and also on the type of M^{3+} ion. If there are S possible sites, within the sphere of influence, into which an M^{3+} ion can fall, then the number of isolated ions [Type (a)] is given by:

$$N^{(a)} = N(1-C)^{s},$$
 (1)



FIG. 9. Plot of log (η/τ) against $[1+\log_{10}(1-C)]$ for the ${}^{3}P_{0}$ level. C is the concentration of Pr^{3+} .

where C is the concentration of Pr^{3+} ions and N is the total number of Pr^{3+} ions.

In this two-site model one has the following decay rates: σ_r —radiative decay rate for Type (a) and Type (b) (this assumption is discussed below).

 $\sigma_{nr}^{(a)}$ —nonradiative decay rate for Type (a), $\sigma_{nr}^{(b)}$ —nonradiative decay rate for Type (b) (average value).

The quantum efficiency of the fluorescing level in the two types of ions are as follows:

Type (a)
$$\eta^{(a)} = \sigma_r / [\sigma_r + \sigma_{nr}^{(a)}],$$

Type (b)
$$\eta^{(b)} = \sigma_r / [\sigma_r + \sigma_{nr}^{(b)}].$$
(2)

Similarly the lifetimes are

Type (a)
$$\tau^{(a)} = 1/[\sigma_r + \sigma_{nr}^{(a)}],$$

Type (b)
$$\tau^{(b)} = 1/[\sigma_r + \sigma_{nr}^{(b)}].$$
(3)

If there are $N^{(a)}$ ions of Type (a) and $N^{(b)}$ ions of Type (b) then the experimentally measured quantum efficiency will be

$$\boldsymbol{\eta} = (1/N) \left[N^{(a)} \boldsymbol{\eta}^{(a)} + N^{(b)} \boldsymbol{\eta}^{(b)} \right], \tag{4}$$

and the measured decay will be

$$dN/dt = \eta^{(a)} N^{(a)} \exp(-t/\tau^{(a)}) + \eta^{(b)} N^{(b)} \exp(-t/\tau^{(b)}),$$
(5)

where $N = N^{(a)} + N^{(b)}$, the total number of ions.

For low concentration, where $N^{(a)}\eta^{(a)} \gg N^{(b)}\eta^{(b)}$ the measured lifetime approximates to

$$\tau = \tau^{(a)} = 1/[\sigma_r + \sigma_{nr}^{(a)}], \qquad (6)$$

and the measured quantum efficiency to

$$\boldsymbol{\eta} = (1/N) N^{(a)} \boldsymbol{\eta}^{(a)} = [N^{(a)}/N] \boldsymbol{\sigma}_r / [\boldsymbol{\sigma}_r + \boldsymbol{\sigma}_{nr}^{(a)}]. \quad (7)$$

Thus,

$$\eta/\tau = [N^{(a)}/N]\sigma_r^{(a)}, \qquad (8)$$

and hence from (1) η/τ should be of the form

$$\eta/\tau = \sigma_r^{(a)} (1 - C)^S. \tag{9}$$

This equation is used to analyze both the Pr³⁺:Pr³⁺ interaction and the Pr³⁺:Ce³⁺ interaction in the following four sections:

(1) $3P_0$ level under $Pr^{3+}:Pr^{3+}$ interaction. The plot of Eq. (9), that is, $\log(\eta/\tau)$ against $\log(1-C)$ should yield a straight line of slope S for low concentrations. Fig. 9 is such a plot for Pr^{3+} concentrations up to 2.5% at 290°, 77°, and 4°K. In fact these plots are not straight lines suggesting that for the concentration range >2.5% the approximation $\eta^{(a)}N^{(a)} \gg \eta^{(b)}N^{(b)}$ does not hold. As the approximation breaks down one would expect each plot to curve away from the straight line as, indeed, is the case. The values of S obtained from the slopes of the tangents to the beginning of each curve are given in Table I, together with the radius of a sphere which would contain this number of sites.

(2) ${}^{1}D_{2}$ level under Pr^{3+} : Pr^{3+} interaction. The plot of Eq. (9) is shown in Fig. 10. Once again there is a deviation from the straight-line relation. The value of S obtained by drawing a tangent is 320 ± 30 . This means a sphere of 320 ion sites which corresponds to a distance of 16 Å.

(3) ${}^{3}P_{0}$ level under $\operatorname{Pr}^{3+}:\operatorname{Ce}^{3+}$ interaction. The plot of $\log(\eta/\tau)$ against $\log(1-C)$ out to 20% Ce³⁺ is shown in Fig. 11. In this case the plot is a good straight line of slope 9, that is, the approximation $\eta^{(a)}N^{(a)} \gg \eta^{(b)}N^{(b)}$ is good out to 20% Ce³⁺. The slope indicates a sphere of influence of nine sites which is equivalent to only nearest-neighbor interactions at 5 Å.

(4) ${}^{1}D_{2}$ level under Pr^{3+} : Ce^{3+} interaction. In this case no effect was observed at all, giving S=0, that is, there was no significant interaction.

The low-concentration analysis on the above model involves only parameters describing the (a) sites which, by definition, are independent of concentration. The departure of the curves from a straight line as the concentration of Pr^{3+} or Ce^{3+} is increased is consistent with the quantum efficiency of both sites being positive and that of the (b) sites being less than that of the (a)sites. In general, there will be a range of values for η and τ describing (b) sites since this category contains all ions subject to ion-ion interaction and these will not, in general, be equivalent sites. This is most clearly

TABLE I. S values and interaction ranges for the ${}^{3}P_{0}$ level under Pr^{3+} : Pr^{3+} interaction for different temperatures.

 T(°K)	S	Distance (Å)	
 300 77 4	160 ± 40 100 ± 10 90 ± 20	13 11 11	

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brought out experimentally by the nonexponential decay of the fluorescence at high concentration.

The decrease in η may result from a decrease in σ_r or an increase in σ_{nr} , or both. First, consider σ_r , the fluorescent radiative relaxation rate. If σ_r decreases with concentration, then the fluorescent lifetime, $\tau =$ $1/(\sigma_r + \sigma_{nr})$ should increase. This is not so experimentally, hence either σ_r does not increase or σ_{nr} increases more rapidly than σ_r decreases. In fact, present evidence suggests that σ_r is independent of concentration. It has already been noted that the absorption transition probability to the fluorescent level is independent of concentration. However, this does not imply unequivocably that σ_r is also independent of concentration because of the Frank-Condon principle, that is because of a rearrangement of the lattice when an ion is excited into another energy level. Nevertheless, it seems unlikely that such an effect is significantly concentration dependent in the present work because the good fit and nearly equal masses of the impurity and host-lattice ions imply small changes in lattice behavior with concentration. This is borne out experimentally by (i) the Stokes shifts are beyond the resolving power of the spectrometer, that is, less than 3 cm⁻¹ for all concentrations, and (ii) vibronic structure observed on the wings of some fluorescent lines is independent of concentration. Thus it seems likely that σ_r has the same value for both (a) and (b) sites (justifying this initial assumption) and that concentration quenching effects are dominantly contained within an increase in σ_{nr} .

The dependence of σ_{nr} on concentration may arise from (i) ion-ion interaction or (ii) changes in coupling of the ion to the lattice due to the introduction of localized modes of vibration. However, the negligible Stokes shift and the concentration-independent vibronic



FIG. 10. Plot of log (η/τ) against $[1+\log_{10}(1-C)]$ for the ${}^{1}D_{2}$ level. C is the concentration of Pr^{3+} .



FIG. 11. Plot of log (η/τ) against $[1+\log_{10}(1-C)]$ for the ${}^{3}P_{0}$ level of 0.5% Pr³⁺. C is the concentration of Ce³⁺.

structure indicate that the coupling to the lattice is most likely independent of concentration. Dexter⁸ has considered the problem of ion-ion interaction theoretically for the simplest case of only two ions interacting and for which the initial and final states of the coupled system are directly linked by an interaction Hamiltonian. Obviously, more complex interaction involving intermediary states and multi-ion interactions can be envisaged. However, we do not have sufficient information to handle these interactions. We confine ourselves, therefore to a naive interpretation on the Dexter model. In this model the interaction Hamiltonian is taken to be an electrostatic potential expanded into a multipole series. Dexter has further made the approximation that the wavefunction, describing the coupled ions, can be written as products of single-ion wavefunctions. Following Axe and Weller⁹ the ratio of transition probabilities for interaction arising from different terms in the electrostatic potential series can be obtained from Eq. (17) of Dexter's paper, whence

$$P_{dq}/P_{dd} \approx (f_{A}^{(q)}/f_{A}^{(d)}) (\bar{\nu}_{AB}{}^{2}R_{AB}{}^{2})^{-1},$$

$$P_{aa}/P_{dd} \approx (f_{A}^{(q)}f_{B}^{(q)}/f_{A}^{(d)}f_{B}^{(d)}) (\bar{\nu}_{AB}{}^{4}R_{AB}{}^{4})^{-1}, \quad (10)$$

where $f^{(d)}$ is the electric dipole oscillator strength, $f^{(q)}$ is the electric quadrupole oscillator strength, R_{AB} is the separation between Ion A and Ion B and $\bar{\nu}_{AB}$ is the energy (in wavenumbers) of the transition for either ion. Any energy mismatch in the electronic system must be transferred to the lattice, but will be approximately the same for the different multipole interactions.

Pr³⁺: Pr³⁺ Interaction

The results of the analysis obtained from Eq. (9) can be interpreted in terms of the Dexter model by

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⁸ D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

⁹ J. D. Axe and P. F. Weller, J. Chem. Phys. 40, 3066 (1964).

TABLE II. Ratio of P_{dq} to P_{dd} and of P_{qq} to P_{dd} for the ${}^{3}P_{0}$ and ${}^{1}D_{2}$ levels under Pr^{3+} : Pr^{3+} interaction.

Level	Temperature (°K)	R	P_{dq}/P_{dd}	P_{qq}/P_{dd}
³ P ₀	300 77 and 4	13 11	60 80	3500 7000
${}^{1}D_{2}$	300 to 4	16	40	1500

setting $\bar{\nu}_{AB} \sim 10^4 \text{ cm}^{-1}$, $f^{(d)} \sim 10^{-5}$ (forced electric dipole) and $f^{(q)} \sim 10^{-9}$ in Eqs. (10) and (11) (Axe and Weller⁹). These are set out in Table II from which it appears that quadrupole–quadrupole interaction is much stronger than either dipole–dipole or dipole–quadrupole interactions.

³P₀ Level

Three of the possible mechanisms which can contribute to $\sigma_{nr}^{(b)}$ and for which the mean energy mismatch is less than 1500 cm⁻¹ are summarized in Table III. In this Table $|A, B\rangle$ represents the state of Ion 1 in Level A and Ion 2 in Level B for the pair system. The error in the energy arises from allowing for the multiplet structure of the levels. The third column indicates whether the energy mismatch has to be emitted to or absorbed from the lattice.

The relative importance of these mechanisms is best compared with experiment in the two temperature regions, room temperature to 77° K and 77° to 4° K.

We first consider the region 77° to 4°K which is characterized experimentally by the temperature-independent ion-ion interaction range. Group (2) of Table III can be eliminated as the dominant processes in this region because absorption of energy 600 cm⁻¹ as phonons would lead to a marked temperature dependence in the interaction strength and therefore in the range. Group (3) has been included for the ${}^{3}P_{0}$ level, as an appreciable thermal population of the ${}^{3}P_{1}$ has been observed at room temperature. However, this group cannot dominate in this region since it would again give a marked temperature dependence from the variation in population of the ${}^{3}P_{1}$ level associated with the excitation energy of 600 cm⁻¹. Hence Group (1) probably accounts for the ion-ion interaction since emission of phonons of energy 875±900 cm⁻¹ would only have a very weak temperature dependence.

The region room temperature to 77°K is characterized by a temperature dependence of the interaction range. Clearly, Group (1) will still be active in this region and could lead to a suitable temperature dependence through stimulated phonon emission. However, it should be noted that in the case of $Pr^{3+}:Ce^{3+}$ interaction, a transfer process involving an energy excess mismatch of 1700 cm⁻¹ exhibits no temperature dependence. Group (2) involving the ${}^{1}D_{2}$ level could become important in this region. The lack of ${}^{1}D_{2}$ fluorescence is not conclusive evidence against this form of transfer since the ion left in the ${}^{1}D_{2}$ level would be in a (b) site $[S({}^{1}D_{2}) > S({}^{8}P_{0})]$ which has a lower quantum efficiency. The thermal population of the ${}^{3}P_{1}$ level is about $\frac{1}{20}$ of that of the ${}^{3}P_{0}$ level at room temperature. Hence if $\sigma_{nr}^{(b)}$ for the ${}^{3}P_{1}$ level is $> 20\sigma_{nr}^{(b)}$ for the ${}^{3}P_{0}$ level, then the effective interaction range as determined by monitoring the ${}^{3}P_{0}$ fluorescence could be modified, that is, an ion in the ${}^{3}P_{0}$ could be excited thermally to the ${}^{3}P_{1}$ level and ion-ion interaction occur through this level [Group (3)]. Now, on Dexter's model $\sigma_{nr}^{(b)} \propto [\sigma_{r}^{(x)}]_{A}[\sigma_{r}^{(y)}]_{B}$ where x and y may be d (dipole moment) or q (quadrupole moment). Fluorescence and absorption data for the ${}^{3}P_{0}$ and ${}^{3}P_{1}$ levels give

$$\sigma_r^{(d)}({}^{3}P_1 \rightarrow {}^{3}H_6) \sigma_r^{(d)}({}^{3}H_4 \rightarrow {}^{1}D_2) \sim 30 \lceil \sigma_r^{(d)}({}^{3}P_0 \rightarrow {}^{1}G_4) \sigma_r^{(d)}({}^{3}H_4 - {}^{1}G_4) \rceil,$$

which is one of the possible sets of transitions in the ion-ion interaction. While no definite estimate can be given of the ratio of quadrupole radiative rates, it could be comparable to the ratio of the dipole moments. Thus $\sigma_{nr}^{(b)}({}^{3}P_{1}, {}^{3}H_{4} \rightarrow {}^{3}H_{6}, {}^{1}D_{2}) \gtrsim 20\sigma_{nr}^{(b)}({}^{3}P_{0}, {}^{3}H_{4} \rightarrow {}^{1}G_{4}, {}^{1}G_{4})$ is not unreasonable, though the different energy matches for the ${}^{3}P_{0}$ and ${}^{3}P_{1}$ interactions may alter the ratio significantly.

$^{1}D_{2}$ Level

Within the same energy matching condition as used before, the group of mechanisms can be typically represented by the transition

$$| {}^{1}D_{2} {}^{3}H_{4} \rangle$$
 to $| {}^{1}G_{4} {}^{3}F_{4} \rangle$ or $| {}^{3}F_{4} {}^{1}G_{4} \rangle$.

The energy match in this case is such that either the absorption or emission of phonons could take place $(50\pm60 \text{ cm}^{-1})$. Hence this could give a very weak or negligible temperature dependence in agreement with experiment.

Pr³⁺: Ce³⁺ Interaction

$^{3}P_{0}$ Level

In this case S=9, that is nearest-neighbor interactions which corresponds to a distance of just less than 5 Å. This gives the ratio $P_{dq}/P_{dd} \sim 400$ and

TABLE III. Ion-ion interaction schemes for the ${}^{3}P_{0}$ level under Pr^{3+} : Pr^{3+} interaction together with their energy mismatches.

Group	Transition	Energy mismatch (cm ⁻¹)	
1	$ {}^{3}P_{0}, {}^{3}H_{4}\rangle \rightarrow {}^{1}G_{4}, {}^{1}G_{4}\rangle$	875±900	emission
2	$ \begin{array}{l} {}^{3}P_{0}, {}^{3}H_{4}\rangle \rightarrow {}^{1}D_{2}, {}^{3}H_{6}\rangle \\ {}^{8}P_{0}, {}^{3}H_{4}\rangle \rightarrow {}^{3}H_{6}, {}^{1}D_{z}\rangle \end{array} $	605 ± 450 595 ± 450	absorption
3	$\begin{array}{l} {}^{3}P_{1}, {}^{3}H_{4}\rangle \rightarrow {}^{1}G_{4}, {}^{1}G_{4}\rangle \\ {}^{3}P_{1}, {}^{3}H_{4}\rangle \rightarrow {}^{3}H_{6}, {}^{1}D_{2}\rangle \end{array}$	$1480 \pm 900 \\ 50 \pm 400$	emission emission/ absorption

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 $P_{qq}/P_{dd} \sim 16 \times 10^4$. Thus once again the quadrupole interaction is the dominant component.

The principal effect of the Ce³⁺ interaction with the Pr^{3+} is a strongly enhanced decay of the ${}^{3}P_{0}$ level to ${}^{1}D_{2}$ (see Fig. 7). The energy gap of this transition is \sim 3900 cm⁻¹ and close energy matching with the Ce³⁺ spectrum (Fig. 1) can only be obtained if a pair of Ce³⁺ ions are involved in the quenching of a single Pr^{3+} ion; that is, two Ce^{3+} ions are excited to the ${}^{2}F_{7/2}$ level for one Pr^{3+} ion going from ${}^{3}P_{0}$ to ${}^{1}D_{2}$. In this case there is an energy deficiency of 500 ± 300 cm⁻¹ which must be supplied from the lattice vibrations. Since this is comparable with thermal energy at room temperature ($\sim 200 \text{ cm}^{-1}$) one would expect a marked temperature dependence of the quenching. Experimentally, no temperature dependence is found. Thus it is likely that only single Ce3+: Pr3+ interactions are important, the excess energy of 1700 ± 250 cm⁻¹ being emitted as phonons (multiphonon processes may well be important as a decay mechanism¹⁰). One would expect a detectable temperature dependence in contradiction to the experimental results. Such a discrepancy could be explained by the fact that this is a very shortrange interaction and that the number of sites within the sphere of influence is not a sensitive measure of the strength of interaction. This is in contrast to the longer-range interaction found in the $Pr^{3+}: Pr^{3+} * P_0$ case where the number of sites can change markedly for a small change in interaction strength. Thus for a given change in interaction strength, R may change by, for example 1 Å at short range (~ 5 Å) whereas R would change by 2 Å at longer ranges (~ 10 Å). The former case would correspond to no increase in the number of lattice sites contained within the range while a change ~ 50 lattice site would be expected in the latter case. This just reflects the discrete nature of the lattice in that it is not a continuum of sites with R.

$^{1}D_{2}$ Level

The lack of any effect (S=0) on the ${}^{1}D_{2}$ level by the addition of Ce³⁺ may be due to the poor energy match between Pr³⁺ ion falling from ${}^{1}D_{2}$ to ${}^{1}G_{4}$ (7000 cm⁻¹) and a Ce³⁺ ion being raised from ${}^{2}F_{5/2}$ to ${}^{2}F_{7/2}$ (2200 cm⁻¹).

We have only considered energy matches as a guide to the strength of the various interaction schemes in the above discussions. This is certainly not the whole story since Fig. 5 suggests the operation of certain selection rules in addition to the energy-matching requirements. Thus, a drain mechanism from the ${}^{3}P_{0}$ to ${}^{1}D_{2}$ levels of Pr^{3+} appeared when the codopant was either Ce³⁺, Eu³⁺, Tb³⁺, or Yb³⁺ but for no other rare earth. These four ions have one feature in common, namely that their ground states possess the same orbital angular momentum of L=3, that is, an F state. This suggests that the interaction of the excited Pr^{3+} ions with these four ions is through the ground state of these ions and, therefore, dependent on the L value. However, the four ions were not equally effective in causing this drain mechanism. Yb³⁺ was the least effective, being 10⁻² down on the other three ions. This could well be due to the poor energy match (out by 6000 cm⁻¹).

Unfortunately it was not possible to monitor changes in excitation of the Ce³⁺ ions due to interaction with the Pr³⁺ ions because of the restricted level scheme of the Ce³⁺. However, unequivocal evidence for ion-ion interaction is provided by the large energy transfer between the Tm³⁺ ions and the Pr³⁺ ions. Evidence of this transfer was given by the appearance of the $Pr^{3+3}P_0$ fluorescence when the crystal was pumped in the region of the $Tm^{3+} D_2$ absorption. This is probably due to energy transfer from the ${}^{1}G_{4}$ of the Tm³⁺ at 21 300 cm⁻¹ to the ${}^{3}P$ multiplet of the Pr^{3+} because of the good energy match (to within 400 cm⁻¹). This transfer could not however be studied since TmF₃ is of a different crystal structure to LaF3 and if the concentration of Tm³⁺ was raised much above 1% the crystal shattered due to strain.

SUMMARY

A study of ion-ion interactions requires a knowledge of both quantum efficiencies and lifetimes of the interacting states. Such information has been obtained for Pr^{3+} in LaF₃ as a function of concentration and temperature. A simple two-site model in which a single ion is either isolated or coupled to its neighbors has been used to interpret the experimental data. The interaction sphere of influence has been found to extend from nearest-neighbor sites out to about 300 lattice sites depending on the interacting levels. An interpretation on Dexter's model of electrostatic coupling shows that quadrupole-quadrupole interaction predominates in all cases. The lack of exact resonance between the sets of electronic states is not inconsistent with the observed temperature effects.

The effect of other rare-earth codopants has shown that there are selection rules in addition to energymatching requirements.

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¹⁰ A. Kiel, Qu. Elec. Conf. Paris, 1963, 765 (1963).