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QUENCHING OF FLUORESCENCE BY CROSS RELAXATION IN $\text{LaF}_3:\text{Pr}^{3+}$

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Abstract - The temporal dependence of the fluorescence from the $^3\text{P}_0$ level in concentrated samples of $\text{LaF}_3:\text{Pr}^{3+}$ has been modeled in terms of cross relaxation processes due to either short range superexchange or long range electric dipole-electric dipole ion pair interactions. Both models can be fitted to the observed data, however, it is concluded that the picture of a single dominant microscopic interaction is not sufficient to completely describe the macroscopic properties of the emission.

I - INTRODUCTION

Energy transfer in luminescent materials has received renewed interest in recent years due to the development of the laser as a spectroscopic tool. A great deal of effort has been devoted to understanding the nature of the interaction of optically active ions doped in inorganic hosts /1/. In concentrated systems, these interactions can have various effects on the luminescence emitted from an excited set of donor ions. Such phenomena include the spectral migration of energy within an inhomogeneously broadened emission line, termed donor-donor transfer, as well as quenching of the fluorescence by transfer of the excitation to trapping centers, a process called donor-acceptor transfer. Trapping can be caused by optically active ions which are dissimilar to the donor ions or by cross relaxation when one excited donor ion can couple to an adjacent unexcited donor ion. In the latter instance the coupled pair acts as the acceptor. For a disordered system of optically active ions which are randomly distributed on the host's lattice, the temporal evolution of the fluorescence has been modeled by taking an ensemble average of the decay from all possible site configurations /2,3,4/. From this macroscopic treatment the nature and strength of the ion-ion interactions can be inferred. Both of the above mentioned phenomena have been observed in LaF_3 doped with Pr^{3+} and are deduced to be long range electric dipole-electric dipole in nature /2,5/. The intrinsic interaction between near neighbor (NN) Pr^{3+} pairs has also been studied in dilute $\text{LaF}_3:\text{Pr}^{3+}$ by selectively exciting and subsequently observing fluorescence from specific $^3\text{P}_0$ pair lines /6/. By comparing the interaction strength of various pairs it was concluded that the interaction was superexchange. Furthermore, by using these microscopic quenching parameters the macroscopic fluorescence observed by Hegarty et al. /5/ from the more concentrated system could be accurately predicted. In order to reconcile these conflicting results the $^3\text{P}_0$ fluorescence following

pulsed laser excitation of five samples of LaF_3 doped with various concentrations of Pr was studied and we sought a uniform description of the temporal behavior of the decay from all samples by either of the proposed interaction models.

II - EXPERIMENTAL DESIGN

Five single crystal samples of LaF_3 doped with Pr in nominal molar concentrations of 1%, 5%, 20%, 50% and 80% were obtained from Optovac and are referred to by these doping levels throughout this paper. The exact concentrations, as determined by electron microprobe analysis, are 1.5%, 5.2%, 16.8%, 49.1% and 76.3% and are used in the calculations. Using a minimum spot size of $3 \mu\text{m}$ the concentration was found to vary by less than 1% across the surface of the crystals.

A nitrogen pumped dye laser oscillator and amplifier were used to excite the $^3\text{P}_0$ level in each sample while immersed in a dewar of liquid helium below its λ point. The oscillator cavity consisted of an output coupler and diffraction grating in Littrow configuration tuned to the $^3\text{H}_4(1) - ^3\text{P}_0$ transition at 4777 Å. This transition is inhomogeneously strain broadened at these concentrations with linewidths of as much as 15 cm^{-1} . By using different grating orders we varied the bandwidth of the laser to be approximately twice the linewidth in each case, thus ensuring that a representative sample of Pr^{3+} ions was excited. The resulting strong $^3\text{P}_0 - ^3\text{H}_6(1)$ fluorescence at 5985 Å was selected by a Spex 0.85 m double monochromator and photoelectrically detected with an EMI 9659 photomultiplier tube. The spectrometer slit widths were adjusted to match the bandwidth of the fluorescence from each sample, ensuring that emissions from any spurious sites would not be recorded. The intensity of the laser beam was kept below 10 kW/cm^2 to reduce heating effects and to keep the density of excited Pr^{3+} ions low, thus minimizing non-linear processes such as stimulated emission [7]. The output from the P.M.T. was digitized and averaged by a DATA 6000 transient waveform analyzer which had a 5 ns minimum time resolution. The resulting averaged decay was plotted on an x-y recorder and the digitized data were analyzed by a DEC Micro-11 computer.

III - RESULTS AND DISCUSSION

$^3\text{P}_0 - ^3\text{H}_6(1)$ fluorescence decay, after pulsed excitation, observed from all five samples at 2 K is reported in figure 1. The temporal dependence of the emission was non-exponential at early times for the 1%, 5% and 20% samples; however, the decay rates asymptotically approached that of the isolated ion ($51 \mu\text{s}$). A similar but much weaker behavior was observed for the 50% Pr sample; however, the signal to noise ratio was poor. The fluorescence decay of the 80% sample was almost exponential for the first few μs and the decay rate increased gradually at later times before the signal disappeared into the noise. The observed fluorescence decay rate at $t = 0$ for each sample, listed in table I column 2, increased gradually from twice the isolated ion decay rate for the

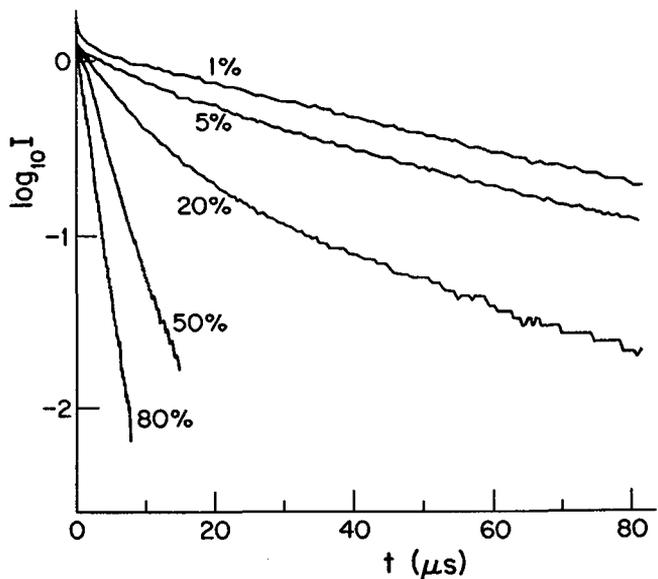


Fig. 1 - $\text{LaF}_3:\text{Pr}^{3+}$ fluorescence decay at 5985 Å following pulsed excitation of the $^3\text{P}_0$ level of samples for different dopant concentrations ($T = 2 \text{ K}$).

1% sample to half the decay rate of PrF_3 for the 80% sample.

The phenomenon of fluorescence from donor atoms in the presence of traps for a randomly disordered system has been treated by Huber /4/. From fluorescence line narrowing studies on $\text{LaF}_3:\text{Pr}^{3+}$ the $^3\text{P}_0$ donor-donor transfer rate at 2 K is calculated to be $\sim 1000 \text{ s}^{-1} / 2/$ and can be ignored. Thus, at these temperatures the only decay mechanism for a $^3\text{P}_0$ excited ion is fluorescence or cross relaxation with a nearby unexcited Pr^{3+} ion. The temporal evolution of the fluorescence following pulsed excitation of a representative sample of ions is predicted by taking an ensemble average of the decay mechanisms for all possible Pr^{3+} site arrangements /3/ and yields,

$$I(t) = I_0 e^{-\frac{\gamma_r t}{n}} \prod (1 - c + ce^{-W_{\text{on}} t}) \quad (1)$$

In this equation γ_r is the isolated ion decay rate, c is the Pr concentration and W_{on} is the cross relaxation rate between an excited ion at site "o" and an unexcited ion at site "n", separated by a distance R_{on} . For long range multipolar interactions,

$$W_{\text{on}} = \left(\frac{R_0}{R_{\text{on}}}\right)^s W_0 \quad (2)$$

Here W_0 is the nearest neighbor cross relaxation rate for ions separated by a distance R_0 . For ion pair coupling by the electric dipole-electric dipole, electric dipole-electric quadrupole or electric quadrupole-electric quadrupole interaction the exponents will have a value of 6, 8 or 10, respectively. The infinite product in equation (1) is approximated in the continuum limit by the model of Inokuti and Hirayama /8/,

$$\ln(I/I_0) + t/\tau_0 \approx -\frac{4\pi}{3} c R_0^3 (W_0 t)^{3/s} \Gamma(1 - 3/s) \quad (3)$$

Here $\tau_0 (=1/\gamma_r)$ represents the lifetime of the isolated ion and Γ is the gamma function. For cross relaxation by a specific multipolar interaction, a plot of $\ln(I/I_0) + t/\tau_0$ vs. $t^{3/s}$ yields a straight line for only one value of s , which identifies the nature of the interaction. Furthermore, the slope of the line gives the NN transfer rate, W_0 , provided R_0 and c are known. The initial fluorescence decay rate may be obtained by differentiating equation (1) and substituting from equation (2),

$$\frac{d}{dt} \ln(I/I_0) = -\gamma_r - c W_0 \sum_n \left(\frac{R_0}{R_{\text{on}}}\right)^s \quad (4)$$

In the case of a near-neighbor only cross relaxation process (as for superexchange), equation (1) reduces to the simpler form,

$$I(t) = I_0 e^{-\frac{\gamma_r t}{\alpha}} \prod_{\alpha} (1 - c + ce^{-W_{\alpha} t})^{N_{\alpha}} \quad (5)$$

where the product is over only the near-neighbor sites, and N_{α} is the number of similar ion sites making up a class of pairs of type α with the excited ion. Again the initial fluorescence decay rate is obtained by differentiating equation (5).

$$\frac{d}{dt} \ln(I/I_0) = -\gamma_r - c \sum_{\alpha} N_{\alpha} W_{\alpha} \quad (6)$$

Equations (3 - 6) were fitted to the data in figure 1 to determine if either model gives a consistent set of results for all five samples. Hegarty et al. /5/ have successfully fitted equation (3) to their data for a sample of 20% Pr in LaF_3 by observing that an exponential component of the fluorescence, with the isolated ion lifetime of 51 μs , must first be deconvoluted from the signal. We also observed this asymptotic behavior in the fluorescence signal from the 5%, 20% and 50% samples and this contribution was subtracted in each case. Equation (3) was subsequently fitted to the resultant data yielding values for W_0 which appear in table I column 6. The nearest neighbor rare earth inter-ion distance for LaF_3 , $R_0 = 4.148 \text{ \AA}$, was used for all dopant concentrations. In each case the best fit was obtained for $s = 6$, which suggests that cross relaxation is induced by the electric dipole-electric dipole interaction for all dopant concentrations. No value of W_0 is reported for the 1% sample as the deviation of the fluorescence decay from a single

c	INITIAL DECAY RATES ($\times 10^4$ s $^{-1}$)				CROSS RELAXATION RATES		
	Observed	Short Range Predicted	Long Range Predicted Measured		$(\times 10^4$ s $^{-1})$ W ₀ W _F W _a		
~0%	1.96	1.96			9.5	9.7	2.5
1%	3.9	2.6	3.8	18			
5%	4.0	5.1	8.1	8.1	3.4	5.7	5.2
20%	11	13	23	12	9.3	8.3	4.1
50%	32	36	62	29	11	9.5	2.8
80%	65	54	95	65	10	12	2.5
100%	130	70.0			10.6		

Table I - Observed and calculated fluorescence decay rates at $t = 0$ and cross relaxation rates in LaF₃ doped with c% Pr. Column 2 lists the observed fluorescence decay rates at $t = 0$. The initial decay rates predicted by the short range model, equation (6), and the long range model, equation (4), are listed in columns 3 and 4. The measured initial decay rates when the asymptotic exponential component at 51 μ s is deconvoluted from the data are listed in column 5. Columns 6 - 8 contain the nearest neighbor cross relaxation rates obtained by fitting equation (3) (long range model) and equation (6) (short range model) to the data. The ~0% and 100% values in column 6 are calculated using 760 ns as the 3P_0 lifetime in PrF₃.

exponential at 51 μ s was quite small. The transfer rate obtained for the 5% Pr sample is about one third of the value obtained for the three other samples. In these latter cases the results are consistent with the values predicted for PrF₃ and a dilute sample of LaF₃:Pr³⁺. The value predicted for PrF₃ is obtained using equation (1) with $c = 1$ and $\tau = 750$ ns. The smaller value in the dilute sample is due to an R^{-6} decrease in W_0 with increasing lattice size from 4.085 Å to 4.148 Å. It should be noted that the calculated value of W_0 in table I column 6 does not increase uniformly with increasing Pr concentration as expected for a shrinking lattice size. The initial decay rate of the residual data was compared with that predicted from equation (4) using $s = 6$ and $W_0 = 9.7 \times 10^4$ s $^{-1}$. A lattice sum for LaF₃ yields $R_0^6/R_{on}^6 = 12.6$. The results shown in Table I columns 4 and 5, do not agree well with each other in this case.

In their study of pair line emission from dilute LaF₃:Pr³⁺ samples, Vial and Buisson /6/ conclude that the cross relaxation process is due to a superexchange interaction and that only two classes of ion pairs are sufficiently coupled to contribute to fluorescence quenching. They propose that there are six ion pairs of a class which they label "f" and four pairs labeled "a". Class "f" consists of all the 1st and 2nd NN pairs, while class "a" is composed of the 4th NN pairs. From the fluorescence lifetime of the pair lines they estimate that $W_f = 9.7 \times 10^4$ s $^{-1}$ and $W_a = 2.5 \times 10^4$ s $^{-1}$. Using this model, equation (5) was fitted to the data in figure 1 by varying W_a and W_f with $N_a = 4$ and $N_f = 6$. The values which give the best fit are shown in table I columns 7 and 8. Again, since the fluorescence decay of the 1% Pr sample is almost exponential it was ignored. Results for the other samples are in reasonable agreement with the intrinsic values quoted above. The values obtained for W_f increase and for W_a decrease with increasing Pr concentration, suggesting that the 1st and 2nd NN pair separations decrease while the 4th NN pair distances increase as the lattice contracts. The model was also tested by comparing the observed initial fluorescence decay rate with that calculated from equation (6) using the intrinsic quenching rates measured by Vial and Buisson. The agreement is good for all samples studied (table I column 3), however, the model underestimates the decay rate in PrF₃ by a factor of two.

Although either model provides a reasonable description of the observed fluorescence decay from the samples there are drawbacks associated with both. In the short range model Vial and Buisson argue that the two 3rd NN ion pairs are prevented from contributing to cross relaxation due to symmetry constraints, thus N_a is 4 not 6.

Due to the difference in La^{3+} and Pr^{3+} ionic radii this symmetry restriction could be relaxed by concentration induced microscopic strains. This effect would be most pronounced in the 50% sample and yet the data fits the microscopic transfer parameters best here. In addition, the model fails to predict the decay rate for PrF_3 , as indicated in table I columns 2 and 3; the calculated value is only half of that observed. Perhaps the variation in W_a and W_f with contracting lattice size as the concentration increases is sufficient to account for this difference. However, the data in Table I is not sufficiently exact to accurately predict W_a and W_f for PrF_3 . Nonetheless, if we assume that $W_a \approx 2 \times 10^4 \text{ s}^{-1}$ for $c = 100\%$, $N_a = 4$ and $N_f = 6$ and use the observed decay rate for PrF_3 we can estimate from equation (5) that $W_f = 20 \times 10^4 \text{ s}^{-1}$. Such a value is not totally unreasonable as superexchange interactions are known to change rapidly with varying inter-ion distances. However, it seems likely that in more concentrated samples additional cross relaxation processes will occur. For example, superexchange interactions in the other near neighbor pairs could be significant at shorter inter ion distances. In addition, there is a greater likelihood for small clusters of Pr^{3+} ions to occur so that multi-ion interactions could also quench the 3P_0 emission. The major drawback of the long range interaction model lies in the need to subtract from the fluorescence decay a contribution due to ions which do not participate in the cross relaxation process. Non-participation in cross relaxation processes may indicate large clustering of Pr^{3+} ions or the presence of spurious sites; however, electron microprobe analysis did not detect concentration gradients in any of these samples.

IV - CONCLUSIONS

We have attempted to reconcile two different experimental observations of energy trapping in $\text{LaF}_3:\text{Pr}^{3+}$. In the first, the intrinsic interaction between selectively excited ion pairs in dilute systems was studied and the observed cross relaxation parameter used to predict the macroscopic fluorescence properties of concentrated systems. In the second experiment, the macroscopic fluorescence behavior was used to identify the intrinsic ion pair interactions. The models used to relate the intrinsic interactions to the macroscopic fluorescence properties assumed that only one type of ion pair coupling is prevalent in the cross relaxation process regardless of the dopant concentration. Both the short range superexchange and the long range electric dipole-electric dipole interactions have been used to describe the temporal decay of the fluorescence and have yielded similar values for the nearest neighbor cross relaxation rates. This suggests that both processes may contribute significantly to the quenching process and thus the use of only one interaction model is not sufficient to describe the quenching of fluorescence from the 3P_0 level in concentrated samples of $\text{LaF}_3:\text{Pr}^{3+}$.

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REFERENCES

- /1/ Laser Spectroscopy of Solids, edited by Yen, W.M. and Selzer P.M. (Springer Verlag, Berlin) 1981.
- /2/ Huber, D.L., Hamilton, D.S. and Barnett B., Phys. Rev. B16 (1977) 4642.
- /3/ Golubov, S.I. and Konobeev, Y.V., Fiz. Tverd. Tela. 13 (1981) 3185 Sov. Phys. Solid State, 13 (1972) 2679 .
- /4/ Huber, D.L., Phys. Rev. B20 (1979) 2307.
- /5/ Hegarty, J., Huber, D.L. and Yen, W.M., Phys. Rev. B25 (1982) 5638.
- /6/ Vial J.C. and Buisson, R., J. Physique-Lett. 43 (1982) L745.
- /7/ Hegarty, J. and Yen, W.M., J. Appl. Phys. 51 (1980) 3545.
- /8/ Inokuti M. and Hirayama, F., J. Chem. Phys. 43 (1965) 1978.