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Temperature-Dependent Concentration Quenching of Fluorescence by Cross Relaxation of Nd^{3+} in LaF_3†

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The fluorescence lifetimes of the $^4F_{3/2}$ level of Nd^{3+} in LaF_3 and Nd^{3+} in $LaCl_3$ were measured for various concentrations of Nd^{3+} at 4.2, 77, and 300°K and intermediate temperatures. It is found that the lifetime-concentration curves differ greatly for the two crystals. The optical energy levels of Nd^{3+} in LaF_3 at various concentrations were examined and two sets of levels with precisely overlapping electric dipole transitions have been found; no such overlapping transitions were found for the $LaCl_3$ crystal, however. It is suggested that cross relaxation between these levels can account for the strong, temperature-dependent concentration quenching in the LaF_3 crystal. Using rate equations with cross relaxation terms, a one-parameter expression for fluorescence lifetime versus temperature was found which fitted experimental points for the 4.7 and 8.3% concentration crystals reasonably well. Since the overlap of transitions greatly affects cross relaxation rates, the linewidths and lineshifts were examined. Large heterogeneous linewidths and wavelength shifts were observed for the intermediate concentration crystals. The transitions were observed to sharpen in the low-dilution crystals and in the 100%-concentration crystals (NdF_3), but relative shifts in wavelengths are observed.

INTRODUCTION

OBSERVATION of quenching of fluorescence with concentration and temperature is not new. An example of previous studies of concentration effects is in an 1889 paper by Walter[1]; he suggested that concentration quenching is related to pair formation and higher aggregate formation. In 1904 Lenard and Klatt[2] showed that many substances which exhibit luminescence at room temperature do not luminesce at elevated temperatures, and in 1939 Randall[3] showed that some substances which are not luminescent at room temperature will luminesce at low temperatures. Extensive experimental investigation of concentration and temperature quenching of the fluorescence of rare-earth ions in crystalline hosts has been carried out by Botden[4] and recently by Van Uitert.[5] Our detailed investigation of the fluorescence behavior of the $^4F_{3/2}$ level of Nd^{3+} in LaF_3 indicates that the mechanism for concentration-temperature quenching of this material is a type of resonance transfer, known as cross relaxation, between certain specific levels of this crystal.

The theory of resonance transfer of electronic excitation energy in inorganic phosphors has been developed by Perrin,[6] Forster,[7] and Dexter.[8] It is found that transfer rates between centers separated by large distances (a few dozen angstroms) may be as much as 10^8 sec^{-1} when the emission and absorption bands overlap. The transfer mechanism is the overlapping of the electric dipole fields rather than the overlapping of the electronic wave functions of the two centers which occurs in exchange. The latter is effective only for relatively short distances.

A theory of concentration quenching in inorganic phosphors has been proposed by Dexter and Shulman.[9] The theory concerns the migration of the excitation energy from one activator center (the fluorescing center) to another and eventually to an imperfection which may act as an energy sink. Dexter and Shulman calculated the dependence of fluorescence yield on concentration; they showed that appreciable quenching occurs with concentrations of 10^{-3} to 10^{-2} when the transitions in the activator are electric dipole or electric quadrupole, and with concentrations of a few percent when the activator transitions are of the magnetic dipole type. It is concluded that the transfer rates for the excitation energy are so high in strongly absorbing crystals that the energy can readily migrate to only a few sinks dispersed throughout the crystal.

The above theory is concerned primarily with the resonance transfer of excitation energy among activator centers (until the energy is transferred to a sink). The rates of transfer of the excitation energy among the activators are determined as a function of the type of transitions (electric dipole–electric dipole, electric dipole–electric quadrupole, magnetic dipole–magnetic dipole, etc.). However, the nature of the sink and the mechanism for the transfer of energy from the activator to the sink are not described.

Cross relaxation was proposed by Bloembergen *et al.*[10] as the energy sink mechanism for describing the observed quenching of spin-lattice relaxation times of ions in crystals. The cross relaxation mechanism, together with precise magnetic resonance data, has been applied to explain the concentration quenching of spin-lattice

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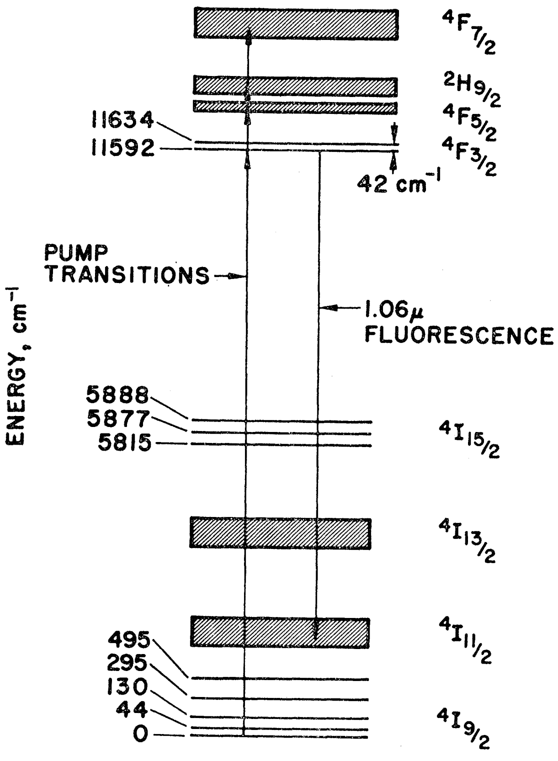

FIG. 1. Energy levels of Nd^{3+} in LaF_3 at 4.2°K. The $^4F_{3/2}$ levels were populated either by pumping directly into those levels or to the levels immediately above them. The lowest component of $^4I_{15/2}$ was found to be at almost midway between the lowest ground state and the upper component of $^4F_{3/2}$.

relaxation in the ground state of ruby.[11–14] This mechanism has also been suggested[15,16] for describing optical energy transfer and concentration quenching of optical fluorescence of Nd^{3+} in glass and the tungstates.

The enhancement or the quenching of fluorescence of Pr^{3+} in LaF_3 due to the presence of another rare-earth codopant has been reported by Wong *et al.*[17] and Brown *et al.*[18] The results indicate pair interaction for the transfer of energy; the latter authors suggest the existence of selection rules for ion-ion interaction.

We have examined the optical energy levels of Nd^{3+} in LaF_3 for various concentrations and find two sets of precisely overlapping electric dipole transitions which can account for strong, temperature-dependent optical concentration quenching by cross relaxation. Using rate equations, including cross relaxation terms, a one-parameter expression for fluorescence lifetime versus temperature is found, and reasonable fits to the experimental points are made for the 4.7% and 8.3% concentrations.

Since the overlapping transitions severely affect the cross relaxation rates, the transition linewidths were measured. Large, heterogeneous linewidths are observed in the intermediate concentration crystals, indicating direct overlap of transitions. The transitions were observed to sharpen at low dilutions and in the 100% (NdF_3) concentration crystals. In addition, the transitions were observed to shift toward shorter wavelengths with increasing concentration.

I. EXPERIMENTAL PROCEDURE

The $^4F_{3/2}$ levels of Nd^{3+} in LaF_3 were populated either directly by pumping into these levels, or indirectly by pumping into levels immediately above, as shown in Fig. 1. The positions of the $^4I_{9/2}$ and $^4I_{15/2}$ levels were given by Caspers *et al.*[19] A xenon flash source of 15-μsec duration and suitable interference filters were used for pumping. The 1.06-μ fluorescent light was passed through an interference filter to a silicon photodiode, and the lifetimes were measured directly on an oscilloscope. This technique was found to be adequate for high intensity fluorescence. Temperatures between 4.2 and 80°K were obtained by a liquid-helium heat-exchange apparatus which was inserted into existing spectroscopic-type Dewars.

The absorption spectrum was taken with a synchronous detection system. The light from a 650-W tungsten-iodine lamp was chopped at 100 cps before passing through the sample; the transmitted light was passed through a $\frac{1}{2}$-m scanning spectrometer and detected by an S-20 surface photomultiplier.

All of the crystals used in these experiments were grown by the modified Stockbarger method. La_2O_3 of 99.997% purity (Lindsay) was converted to lanthanum fluoride in a hydrogen fluoride atmosphere at 700°C. The product from this reaction was melted at 1500°C in a helium-hydrogen fluoride atmosphere and used as the starting material for crystal growth. NdF_3 was obtained from 99.9% Nd_2O_3 in the same manner.

Analysis of the crystals indicated that no Nd^{3+} was lost during growth; the boules were found to be homogeneous. In the discussion below, concentration is defined as the percentage of neodymium ions in the available sites, i.e.,

$$\frac{\text{number of Nd ions}}{(\text{number of Nd ions})+(\text{number of La ions})}\text{(in percent)}.$$

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II. EXPERIMENTAL RESULTS

A. Fluorescence Lifetimes Versus Concentration

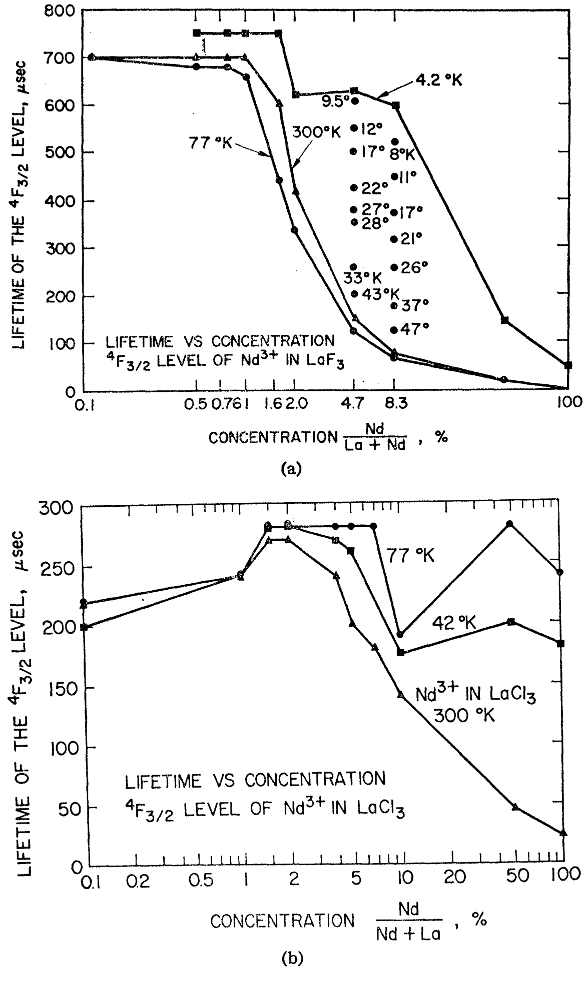
The fluorescence lifetimes versus concentration of Nd^{3+} in LaF_3 for the 4.2, 77, and 300°K temperatures are shown in Fig. 2(a). Two interesting features are to be noted in the figure: (1) in the 77 and 300°K crystals, there is a sharp decline in lifetime as the concentration increases beyond 1%, with the lifetimes for 77°K lying lower than the lifetimes for 300°K, and (2) the lifetimes for the 4.2°K temperatures remain high until much higher concentrations are reached. The 4.7% and 8.3% crystal lifetimes at temperatures between 4.2 and 80°K are also indicated in Fig. 2(a).

To illustrate the uniqueness of the lifetime-concentration characteristics of Nd^{3+} in LaF_3, the behavior of Nd^{3+} in $LaCl_3$ is shown in Fig. 2(b). The lifetime of the $^4F_{3/2}$ level for the latter material at 77°K is longer than at the other temperatures; this behavior is exactly opposite that of the LaF_3 crystals. It is noted that the quenching of fluorescence at the 300°K temperature occurs at a higher concentration in the chloride crystals than in the fluoride crystals. We have examined the energy levels of Nd^{3+} in $LaCl_3$ at 4.2°K and have found no possible matching pairs of transitions; concentration quenching by cross relaxation is unlikely unless a higher order process occurs, i.e., a simultaneous emission or absorption of phonons or a higher order cross relaxation involving several impurity ions.

The contrasting behavior of lifetime quenching of the $^4F_{3/2}$ level of Nd^{3+} in two different crystalline hosts at lower temperatures strongly suggests that the quenching mechanism varies from material to material. The actual mechanism appears to depend upon the details of the electronic energy levels, the lattice phonon structure, the electron-lattice interaction, and the interaction between impurity ions. In the case of Nd^{3+} in LaF_3, the accidental matching of transitions and the strong quenching at low concentrations imply that pair cross relaxation may be the dominant relaxation mechanism as concentration exceeds 1%. This is discussed further below.

B. Heterogeneous Linewidths and Lineshifts Versus Concentration

The absorption spectra of LaF_3 crystals doped with Nd^{3+} at concentrations corresponding to 0.5%, 2%, 8.3%, and 100% NdF_3 were examined. The transitions from the lowest component of the ground state $^4I_{9/2}$ to the $^4F_{3/2}$ and to the $^4F_{5/2}$ multiplets showed significant changes as a function of concentration. The transition to the lower component R_1 of the $^4F_{3/2}$ level appears to reach its maximum width of 12 cm^{-1} as the concentration is increased to 8.3%, while the width is 9 cm^{-1} in the 100% crystal [Fig. 3(a)]. The wavelength shift at the peak of absorption is about 3 cm^{-1} between 8.3 and 100% crystal; the shift between the 0.5 and the 8.3% crystals is small. The transition to the upper component R_2 of the $^4F_{3/2}$ level reaches a width of 26 cm^{-1} for both the 8.3 and the 100% crystals; however, there is a shift of the transition toward shorter wavelengths in the 100% crystal.

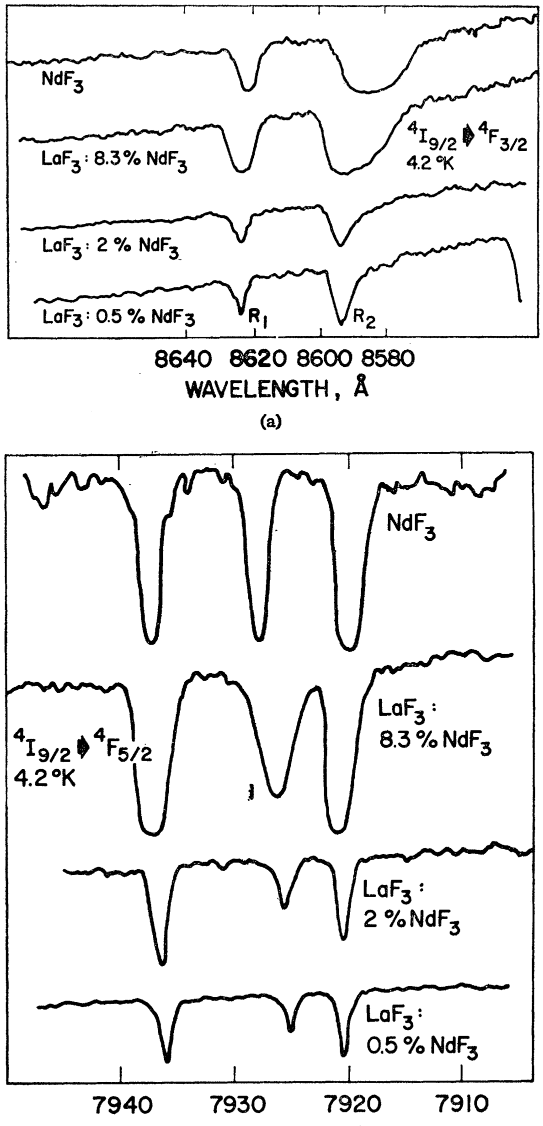


(a)

(b)

FIG. 2. Fluorescence lifetime of the $^4F_{3/2}$ level of Nd^{3+} in LaF_3 and $LaCl_3$ versus concentration at 4.2, 77, and 300°K. (a) Nd^{3+} in LaF_3. Two features characterize this graph: (1) The sharp dropoff for the 77 and 300°K lifetimes as the concentrations exceed 1%; (2) the 77°K lifetimes lie lower than the 300°K lifetimes. (b) Nd^{3+} in $LaCl_3$. It is noted that the lifetime dropoff for the 300°K crystals occurs at higher concentrations than for the LaF_3. The 77°K lifetimes are longer than the 300 or 4.2°K values.

The transition to the $^4F_{5/2}$ state also exhibits an apparent change in the crystalline field parameters as the concentration is increased [Fig. 3(b)]. Three transitions to these multiplets are observed at 4.2°K—7920.2, 7925.5, and 7936.0 Å (±0.5 Å) in the 0.5%, 2.0%, and 8.3% crystals (the wavelengths denote the peaks of the lines). The wavelengths for the 100% crystal are 7919.4, 7927.1, and 7936.9 Å. A marked wavelength shift with concentration of the middle component relative to the outer two components is observed. The linewidths for the 8.3% crystal are larger than those for the more



(a)

(b)

FIG. 3. Part of the Nd^{3+} in LaF$_3$ absorption spectrum for four different concentrations at 4.2°K. (a) $^4I_{9/2} \to {}^4F_{3/2}$. The shift in wavelengths between the 0.5% and the 100% (NdF$_3$) crystals is noted. The 8.3% crystal exhibits broadened lines, due to heterogeneity of the crystalline field. (b) $^4I_{9/2} \to {}^4F_{5/2}$. The middle component shifts considerably relative to the other two components with increasing concentration.

dilute crystals or for the 100% crystal. It is noted that the two outer components of the 8.3% concentration are overabsorbed and hence appear to have larger linewidths than actually exist. However, the middle component is not overabsorbed and clearly exhibits a greater linewidth than the middle component of the 100% crystal. The results again indicate that the Nd^{3+} ions in the 8.3% concentrations experience a relatively heterogeneous crystalline field compared with the more lightly doped crystals or the 100% crystal.

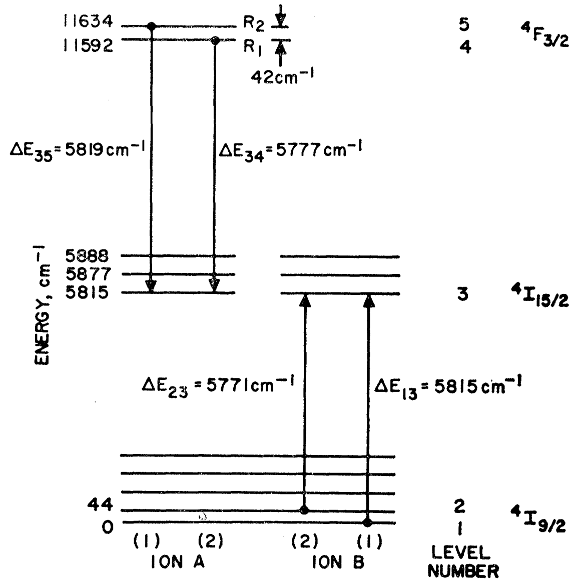


FIG. 4. The two cross relaxation transitions are denoted by (1) and (2). It is noted that as the temperature is lowered, levels 2 and 5 become depopulated so that cross relaxation effectively ceases.

III. DISCUSSION OF RESULTS

A. Cross Relaxation

The absorption and fluorescence spectra show two pairs of possible cross-relaxation dipolar transitions as indicated in Fig. 4:

1. the transition from the upper component R_2 of the $^4F_{3/2}$ levels to the lowest component of $^4I_{15/2}$ of ion A and the simultaneous companion transition from the lowest ground state to the same component of $^4I_{15/2}$ of ion B.
2. the transition from the lowest component R_1 of $^4F_{3/2}$ to the lowest component of $^4I_{15/2}$ of ion A and the simultaneous transitions from the second level of the ground $^4I_{9/2}$ level to the same lowest component of $^4I_{15/2}$ of ion B.

Although the peaks of the transitions do not match, the transitions overlap considerably. The transition from the lowest component of the $^4I_{9/2}$ state to the lowest component state of $^4I_{15/2}$ is more than 5 cm^{-1} wide, whereas the transitions to the R_1 and R_2 levels of $^4F_{3/2}$ are 12 and 26 cm^{-1} for the 8.3% concentration. The latter transitions are shown in Fig. 3(a). It should be noted that the width of an optical transition from a component of the $^4F_{3/2}$ level to the lowest component of the $^4I_{15/2}$ level is not necessarily the sum of the widths of the transitions from the ground state to the two components. The actual width of the former transition may be smaller than either of the latter transitions; this was not determined experimentally.

Even for high concentrations of rare-earth ions, the ions can be treated essentially as independent systems which are perturbed only slightly by neighboring interaction. The evidence for this is the fact that the optical spectra change only slightly with concentration. Thus, in the crystal field representation, the ion-ion interaction leads to small off-diagonal terms, and the use of rate equations for just a single species of ions appears to be valid.

The rate equations are given for levels 4 and 5 of Fig. 4.

$$\begin{aligned} dn_5/dt &= -\omega_{54}n_5+\omega_{45}n_4-\textstyle\sum_{i\neq4}(\omega_{5i}+A_{5i})n_5 \\ &\quad -\omega_{51,33}N^{-1}(n_5n_1-n_3n_3)\,, \\ dn_4/dt &= \omega_{54}n_5-\omega_{45}n_4-\textstyle\sum_{i\neq5}(\omega_{4i}+A_{4i})n_4 \\ &\quad -\omega_{42,33}N^{-1}(n_4n_2-n_3n_3)\,, \end{aligned} \tag{1}$$

where

$n_i\equiv$population of the ith level,
$N\equiv$total number of Nd ions,
$\omega_{ij}\equiv$relaxation transition probability per unit time from level i to level j via the lattice (the reverse process is neglected),
$A_{ij}\equiv$spontaneous radiation emission transition probability per unit time from level i to level j,
$\omega_{ij,kl}\equiv$cross relaxation transition probability per unit time, levels $i\rightarrow k$, $j\rightarrow l$.

The steady-state terms are neglected in the above rate equations. $\omega_{51,33}$ and $\omega_{42,33}$ are the cross relaxation rates for processes 1 and 2, respectively, as described above. For low radiation field, n_3, n_4, and n_5 are much less than n_1 or n_2; then n_5n_1 is much greater than $n_3{}^2$ and n_4n_2 much greater than $n_3{}^2$. Hence, if $n_3{}^2$ is neglected, levels 4 and 5 are coupled only with themselves. The $\omega_{54}=\omega_{45}e^{-1.44(42/T)}$ rates of 10^{10} to 10^{13} sec^{-1} for Stark splittings of 10 to 100 cm^{-1} are much larger than the other rates. Hence, levels 4 and 5 (relative to each other) assume the lattice temperature before emission. The lifetimes of the levels are then

$$\tau=\frac{1}{\sum_{i\neq5}(\omega_{4i}+A_{4i})}(1+e^{-T_{45}/T})\left(1+\frac{\sum_{i\neq4}(\omega_{5i}+A_{5i})e^{-T_{45}/T}+(\omega_{42,33}e^{-T_{12}/T}+\omega_{51,33}e^{-T_{45}/T})/Q(T)}{\sum_{i\neq5}(\omega_{4i}+A_{4i})}\right)^{-1}, \tag{2}$$

where $T\equiv$temperature (°K), $T_{ij}\equiv$energy difference between levels i and j in Boltzmann temperature, and Q is the partition function [$Q=1+\exp(-T_{12}/T)+\cdots+\exp(-T_{1i}/T)+\cdots$, where i runs through all levels; all levels are doubly degenerate so that the degeneracy factor of two is ignored]. If we place $T_{12}=T_{45}$ and assume that the cross relaxation rates are much greater than the spontaneous or lattice relaxation rates for level 5, a one-parameter expression for τ is obtained:

$$\tau=\tau_0\frac{1+e^{-T_{45}/T}}{1+Ae^{-T_{45}/T}/Q(T)}\,, \tag{3}$$

where

$$\tau_0=1/\textstyle\sum_{i\neq5}(\omega_{4i}+A_{4i})\,,$$

$$A=(\omega_{42,33}+\omega_{51,33})/\textstyle\sum_{i\neq5}(\omega_{4i}+A_{4i})\,.$$

The assumption that

$$\textstyle\sum_{i\neq4}(\omega_{5i}+A_{5i})$$

is much less than the cross relaxation rate for intermediate concentrations appears correct for two reasons: (1) At low concentrations (less than 1%) where cross relaxation rates are negligible there is only a relatively small change in lifetimes between 4.2 and 300°K; this indicates that

$$\textstyle\sum_{i\neq4}(\omega_{5i}+A_{5i})<0.10\sum_{i\neq5}(\omega_{4i}+A_{4i})\,.$$

(2) The experimentally determined A coefficient lies between 14 and 36. Hence, the ratio

$$\textstyle\sum_{i\neq4}(\omega_{5i}+A_{5i})/\sum_{i\neq5}(\omega_{4i}+A_{4i})$$

is much less than

$$(\omega_{42,33}+\omega_{51,33})/\textstyle\sum_{i\neq5}(\omega_{4i}+A_{4i})\,,$$

so that the former term may be neglected.

By the cross relaxation process described above, the Nd^{3+} ions are "pumped" from the $^4F_{3/2}$ and $^4I_{9/2}$ levels to the lowest component of the $^4I_{15/2}$ level. Attempts to observe the fluorescence transitions from the latter component to the lower lying $^4I_{9/2}$ and $^4I_{11/2}$ levels were not successful. This leads to the conclusion that nonradiative relaxation rates (multiple phonon process or higher order cross relaxation process) from the $^4I_{15/2}$ level to lower levels are much greater than the radiative rate.

B. Lifetime-Temperature Curves

Experimental values of fluorescence lifetime versus temperature for the 8.3% and 4.7% crystals are shown in Fig. 5(a) and (b), respectively. The one-parameter expression (3) for τ was fitted to two experimental points. The lower curves of Fig. 5(a) and (b) are the curves fitted to the experimental values at 4.2 and 80°K. These curves account quantitatively for the rise in the lifetimes as the temperature exceeds 80 to 100°K. It is noted that the rise is due to the $Q(T)$ factor. However, in the region between 10 and 80°K, the curves lie lower than the experimental point.

When the curves are fitted to a pair of lower temperatures (4.2 and 40°K) the variations between theoretical and experimental values occur at the higher temperature. The values on the curves lie higher than the

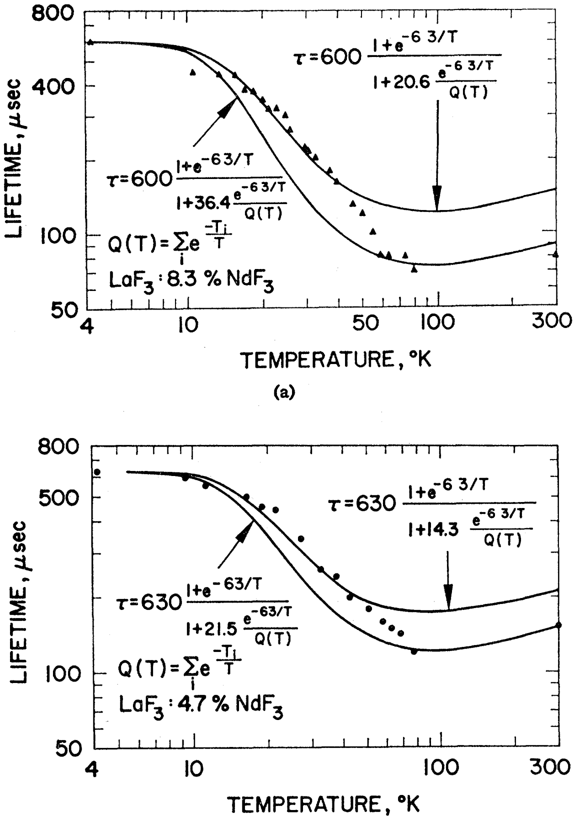


FIG. 5. Lifetime of the $^4F_{3/2}$ level of Nd^{3+} in LaF_3 versus temperature for the 4.7 and 8.3% concentrations. Equation (3) was fitted to two pairs of points: 4.2 and 80°K, lower curve; 4.2 and 40°K upper curve. The deviation between theoretical and experimental values arise from assuming a constant value for the A parameter over the entire temperature interval. (a) 8.3% concentration. (b) 4.7% concentration.

experimental points at temperatures above 60°K [upper curves of Fig. 5(a) and (b)]. This is not particularly surprising, since the cross relaxation rates $\omega_{51,33}$ and $\omega_{42,33}$ depend on the overlapping of a pair of transitions. In the theoretical expression, the cross relaxation rate is assumed to be constant with temperature; the calculated lifetime is dependent upon the temperature only as it arises from the Boltzmann population of the electronic levels. It is well known that as temperatures increase, the linewidths increase and the lines shift toward longer wavelengths. It is important to note that as temperature increases, the lines are homogeneously broadened by thermal phonons so that greater overlap is more easily attained. This would mean greater cross relaxation rates would occur at the higher temperatures, resulting in further shortening of fluorescence lifetimes. It thus appears that when expression (3) is fitted to experimental points at lower temperatures and A is then increased with temperature, precise fits to the experimental points are possible.

C. Interaction Energy and Cross Relaxation Transition Rates

The Coulombic interaction between the electrons and cores of ion A and ion B gives rise to the dominant cross relaxation processes. The interaction energy H_I can be expanded in reciprocal powers of the internuclear distances. This results in the familiar electric dipole-dipole, dipole-quadrupole, and higher multiple-multiple operator terms.[8] Then H_I is written as the dipole-dipole term plus higher order terms:

$$H_I(\mathbf{R})=(e^2/\kappa R^3)[\mathbf{r}_A\cdot\mathbf{r}_B-3(\mathbf{r}_A\cdot\mathbf{R})(\mathbf{r}_B\cdot\mathbf{R})R^2]+\text{higher order terms},\qquad(4)$$

where

$R\equiv$ internuclear distance,

$\mathbf{r}_A=\sum_i \mathbf{r}_{Ai}$, where $\mathbf{r}_{Ai}$ is the vector from the nucleus to the electron i of ion A. $\mathbf{r}_B$ is defined similarly,

$e\equiv$ magnitude of electronic charge,

$\kappa\equiv$ dielectric constant of the medium.

The cross relaxation transition probability per unit time ω is

$$\omega_{ij,kl}=(2\pi/\hbar)|\langle kl|H_I|ij\rangle|^2 g,\qquad(5)$$

where $\langle kl|H_I|ij\rangle$ is the matrix element of the interaction energy H_I between the initial and final states of the interacting ions and where g is a function of the overlap of the two transitions.

D. Inhomogeneous Line

Inhomogeneous broadening of the optical absorption lines for the intermediate concentration crystals shown in Fig. 3 arises from the inhomogeneous crystalline fields to which the neodymium ions are subjected. Whether the nearest anion neighbors of the neodymium ion are all neodymium ions, lanthanum ions, or a mixture of both, they apparently affect the physical configuration of the fluorine cations forming the local crystal field of the neodymium ion. The over-all effect is the inhomogeneous broadening of the line; however, large portions of the inhomogeneous lines are presumed to be homogeneous as a result of indeterminacy broadening by phonon relaxation[20] between the Stark components.

Since the overlap of transitions determines the g factor, the inhomogeneous nature of the transitions may greatly affect the cross relaxation rate $\omega_{ij,kl}$. The question arises as to whether the homogeneous components within the inhomogeneous lines relax individually or cross relax together. In order to answer this question, it is necessary to know the rate for the diffusion process of homogeneous components across the inhomogeneous line. If the diffusion rate is slow, the situation becomes complex: homogeneous components within the inhomo-

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[20] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).

geneous line relax individually with the homogeneous components of the companion inhomogeneous line.

Experimental evidence points toward homogeneous relaxation of the fluorescent level; fluorescence decay curves were found to have only a single lifetime τ, within experimental errors. This means that the diffusion rate across the inhomogeneous line is much greater than the fluorescence lifetime.

E. LaF_3 Crystal Symmetries and Dipolar Selection Rules

The cross relaxation rate is proportional to the square of the matrix element of the interaction H_1 between initial and final electronic states. The states are, in zero order, antisymmetrized product wave functions of the individual ions A and B. For calculation purposes the $\mathbf{r}_A$ and $\mathbf{r}_B$ quantities of the interaction energy must be resolved into components along axes chosen for the individual wave functions. In addition, the interaction H_1 must be summed over all possible pairs of interacting ions; the value of the coefficient for the dipole-dipole term can be determined in principle, but in practice it is difficult to determine unless isotropic systems and averages are assumed. However, selection rules can be determined precisely when the crystal symmetries are well defined.

Electric dipole-electric dipole transitions have been assumed to be the dominant cross relaxation process in our case because quenching begins at low concentrations and the absorption spectra exhibit possible overlapping transitions. Current progress toward determining the crystalline symmetry of LaF_3 and the site symmetry of the lanthanum ion is briefly reviewed here. Knowledge of the crystalline symmetry is required for the analysis of the lattice vibration (the phonon spectrum) and knowledge of the site symmetry is necessary for determining selection rules.

It is well known that electric dipole transitions are observed within the apparent $4f^n$ configuration of a rare-earth ion when the ion is placed in a crystalline site without inversion symmetry; the electric dipole transitions are permitted by the mixing of the excited $4f^{n-1}5d$ configuration with the $4f^n$ configuration by the odd part of the crystal field. The selection rules for the dipolar transitions depend upon the site symmetry of the rare-earth ion.

1. *LaF_3 crystal symmetries.* The x-ray investigation of the LaF_3 crystal of Oftedal[21] in 1929 indicated a hexamolecular unit cell with $D_{6h}{}^3(P6_3/mcm)$ symmetry. The site symmetry of the lanthanum ion is given as C_{2v}. However, Schlyter[22] re-examined the crystal; his data indicated a bimolecular hexagonal cell with $D_{6h}{}^4(P6_3/mmc)$ symmetry. The paramagnetic-resonance data of Baker and Rubins[23] on rare-earth-doped LaF_3 suggest the hexamolecular cell. The optical absorption spectrum of Nd^{3+} in LaF_3 taken by Wong *et al.*,[24] is polarized in contradiction to the selection rules for C_{2v} site symmetry. Krupke and Gruber[25] suggested that the polarization spectrum of Er^{3+} in LaF_3 could be described by a slight trigonal D_{3h} distortion. Finally, the infrared (evaporated LaF_3 film) and Raman studies at room temperature of the lattice vibrations by Caspers *et al.*,[26] favor the bimolecular unit cell.

In summary, the above mentioned investigations have not led to definitive crystalline symmetries for the rare-earth-doped LaF_3. Further studies in this area are evidently necessary.

2. *Dipolar selection rules.* If the site symmetry of the Nd^{3+} ion is low and contains odd components, the electronic states are well mixed so that large numbers of electric dipole transitions are possible. This situation would enhance cross relaxation when appropriate transitions match since the probability per unit time for electric dipole-electric dipole transitions far exceeds that for transitions containing higher multipoles or magnetic dipoles.[8] When the symmetry is higher, such as in C_{3h}, D_{3h}, or O, the higher electric multipole or magnetic dipole transitions may be necessary for matching transitions. As an *example*, the selection rules for electric dipolar transitions of Nd^{3+} for C_{3h} and D_{3h} symmetries and the forbidden transitions for dipolar cross relaxation are tabulated below:

C_{3h}, D_{3h}	$\pm\frac{1}{2}$	$\pm\frac{3}{2}$	$\pm\frac{5}{2}$
$\pm\frac{1}{2}$		σ	σ, π
$\pm\frac{3}{2}$	σ	π	σ
$\pm\frac{5}{2}$	σ, π	σ	

The electronic states are categorized by the μ quantum numbers where μ denotes the residue class of all m_j, the magnetic quantum numbers for the electronic states, satisfying $m_j \equiv \mu$ (mod 3). As an example of a forbidden dipolar cross relaxation process, consider the potential cross relaxation situation in Fig. 6(a), (b), and (c). Assume that the two energy gaps are equal. When the electronic states are as indicated in Fig. 6(a), electric dipolar transitions between the upper two levels are forbidden, although electric dipole transitions to both levels from the ground are permitted. In Fig. 6(b) and 6(c), possible cross relaxation transitions occur. In Fig. 6, the angular momentum of the ion system is not conserved; the balance of angular momentum must be transferred to the lattice and appears as a rotation of the whole crystal.[10]

IV. CONCLUSIONS

There are undoubtedly several different mechanisms which give rise to the concentration quenching of

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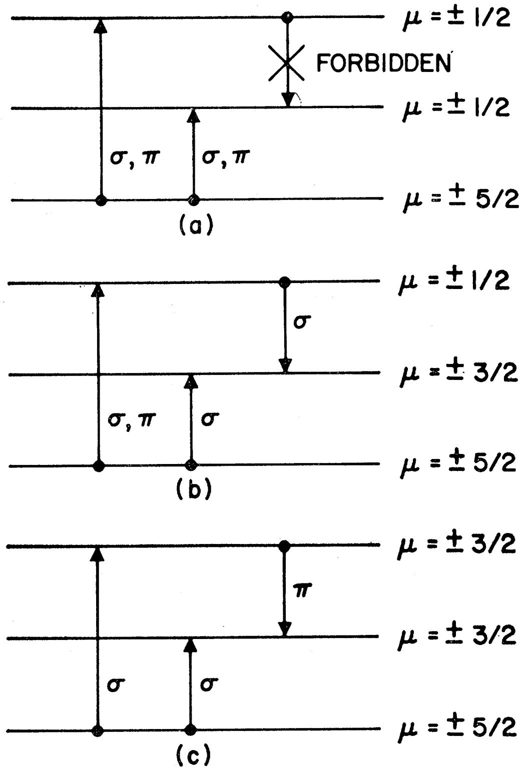

FIG. 6. Examples of forbidden and permitted electric dipole-dipole cross relaxation transitions. Nd^{3+} in crystal fields of C_{3h} or D_{3h} symmetries. The angular momentum of ion system is not conserved but that of the ion-lattice system is conserved. (a) Forbidden electric dipolar cross relaxation transitions. (b) Electric dipolar cross relaxation permitted. (c) Electric dipolar cross relaxation permitted.

fluorescence. To delineate the dominant mechanism, a detailed study of the spectra of the impurity ion in the crystalline lattice and of the crystalline lattice must be made; a detailed study of temperature effects is also desirable. Then a model for concentration quenching can be more readily formulated.

The present study of the quenching with higher concentrations of the fluorescence lifetime of the $^4F_{3/2}$ level of Nd^{3+} in LaF_3 indicates that cross relaxation between certain specific levels of Nd^{3+} occurs. Theoretical considerations, which include this cross relaxation process, lead to a one-parameter, temperature-dependent expression for the lifetime; the temperature dependence arises from the Boltzmann population of the cross relaxing levels. Reasonably good fit to the experimental points for the 4.2 to 50°K temperature interval is obtained. If the parameter of the theory (the ratio of the cross relaxation rate to the other rates from the fluorescing level) is varied over other temperature intervals, a precise fit to experimental values is possible; this can occur since the overlapping of transitions changes with temperature.

The contrasting behavior of the lifetime concentration curves of Nd^{3+} in $LaCl_3$ suggest that one cannot categorically state that "cross relaxation" describes concentration quenching for Nd^{3+} in all host lattices. Indeed, the spectrum of Nd^{3+} in $LaCl_3$ indicates no matching electric dipolar transition and hence no strong concentration quenching.

Several higher order processes can act as sinks for the excitation energy in concentration quenching. For example, the coupling of three or more ions can lead to a higher order cross relaxation process. Another example is a phonon-assisted cross relaxation, where a phonon is emitted or absorbed simultaneously during two electronic transitions (in order to conserve energy for mismatched pure electronic transitions). These higher order processes should be weaker and manifest themselves only at the higher concentrations.

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