Long-Delayed Fluorescence of Nd^{3+} in Pure $LaCl_3$ and in $LaCl_3$ Containing Ce^{3+}†

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Fluorescence from the $^4F_{3/2}$ level of Nd^{3+} in pure $LaCl_3$ and in $LaCl_3$ containing Ce^{3+} was found to be delayed appreciably ($\sim$100 μsec) when levels above the $^4F_{3/2}$ level were selectively pumped with a pulse of light. Increasing the concentration of Nd^{3+} in $LaCl_3$ resulted in decreased delays; other evidence also suggests that cross relaxation between Nd^{3+} ions decreases the delay with increased concentration. Decreased delays in the Nd^{3+} fluorescence were obtained when the Ce^{3+} concentration was increased with the Nd^{3+} concentration fixed at 1%; however, when Ce^{3+} completely replaced the La^{3+}, the neodymium surprisingly exhibited long fluorescent delays and lifetimes. Delays and lifetimes of higher lying levels for two crystals were examined at 4.2°K, 77°K, and room temperature.

INTRODUCTION

THE observation of long-delayed fluorescence of Nd^{3+} in $LaCl_3$ was briefly reported previously.[1] Flourescence from the $^4F_{3/2}$ level of Nd^{3+} was found to be delayed appreciably when a level above that level was selectively pumped with light; for example, the peak of the fluorescence from the $^4F_{3/2}$ level occurred in 110 μsec when the D level, lying 6000 cm^{-1} above the $^4F_{3/2}$ level, was pumped with a 2 μsec pulse. Such long delays indicate weak coupling of the Nd^{3+} ion to energy sinks. The delays give a measure of the order of magnitude of the nonradiative coupling rates between the electronic states of the ion.

Additional measurements of delayed fluorescences of Nd^{3+} in $LaCl_3$ and of Nd^{3+} co-doped with Ce^{3+} in $LaCl_3$ were made for a variety of dopant concentrations. The crystals investigated were $LaCl_3$ crystals containing neodymium in the following percentages (where neodymium replaces lanthanum): 0.1%, 1%, 1.5%, 2%, 4%, 5%, 10%, 50%, 100%. Also investigated were $LaCl_3$ crystals double doped with 1% Nd and 0.1% Ce, 1% Nd and 1% Ce, 1% Nd and 99% Ce. The results are presented here.

In addition, the delayed fluorescence peaks and lifetimes of a number of higher lying fluorescing levels (above the $^4F_{3/2}$ level) were measured for the 0.1% and 1.5% concentration crystals for 4.2°K, 77°K, and room temperatures. It was generally found that the fluorescence delay decreased with increased concentration of neodymium ions. This has suggested that Nd^{3+} ions in high-lying states are cross relaxing with unexcited, neighboring Nd^{3+} ions. The cross-relaxation process undoubtedly requires phonon-assist in order to conserve energy.

The cross-relaxation process between neodymium and cerium, however, cannot describe the delay of fluorescence behavior of Nd^{3+} in $LaCl_3$ containing a second dopant, cerium; as the concentration of Ce^{3+} is increased from 0.1% to 99%, the delay first decreases with increasing concentration, and then actually *increases* at the highest concentration. This effect is not understood at present.

At low temperatures, very poor energy transfer from the higher lying levels to the $^4F_{3/2}$ level of Nd^{3+} in $LaCl_3$ was observed, particularly for the 0.1% Nd^{3+} sample. The low-energy transfer rate resulted in weak fluorescence of the crystals at low temperature, making it difficult to measure delayed fluorescence accurately.

The details of the experimental results are presented here, together with an evaluation of the results.

PREVIOUS RELATED STUDIES

The absorption and fluorescence spectra of Nd^{3+} in $LaCl_3$ were first observed and analyzed by Carlson[2] and Dieke.[3] Carlson observed fluorescence from most of the higher lying Stark manifolds of Nd^{3+} and reported more than 200 fluorescence lines at liquid helium temperature. Varsanyi and Dieke[4] observed the $^4I_{13/2}$ and $^4I_{15/2}$ manifolds in infrared absorption. Judd,[5] Carlson[2] and Dieke,[3] Wong,[6] and Eisenstein[7] have analyzed the data. The fluorescent lifetimes of some of the higher lying levels of 0.1% Nd^{3+} in $LaCl_3$ and of 1% Nd^{3+} in $LaCl_3$ were measured by Partlow and Carlson[8] and by Barasch and Dieke,[9] respectively.

Feofilov[10] has observed nonexponential decay of fluorescence of Tb^{3+} in CaF_2. Pollack[11] has also observed nonexponential decay of fluorescence of Er^{3+} in CaF_2 and has described the result in terms of multistage transitions.

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[2] E. H. Carlson, Johns Hopkins Spectroscopic Report No. 18, 1960 (unpublished).

[3] E. H. Carlson and G. H. Dieke, J. Chem. Phys. 34, 1602 (1961).

[4] F. Varsanyi and G. H. Dieke, J. Chem. Phys. 33, 1616 (1960).

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[7] J. C. Eisenstein, J. Chem. Phys. 39, 2134 (1963).

[8] W. D. Partlow and E. H. Carlson, J. Chem. Phys. 41, 3645 (1964).

[9] G. E. Barasch and G. H. Dieke, J. Chem. Phys. 43, 988 (1965).

[10] P. P. Feofilov, Opt. i Spektroskopiya 10, 142 (1960) [English transl.: Opt. Spectry. (USSR) 10, 70 (1961)].

[11] S. A. Pollack, J. Chem. Phys. 38, 2521 (1963).

EXPERIMENTAL APPARATUS

A xenon PEK XE9-1 flashlamp was used as the excitation source for the fluorescence delay measurements; in this specially designed lamp, the afterglow tail of the flash is rapidly quenched by wall collisions. The lamp was driven by a 0.1-μF, low-inductance coaxial Tobe Deutschbein capacitor charged to 18 kV. The pump light was passed through a $\frac{1}{4}$-m Bausch and Lomb monochromator before exciting the crystal sample. The fluorescent light from the sample was passed through a Jarrell-Ash $\frac{1}{4}$-m monochromator and detected with a cooled S-1 or S-20 photomultiplier tube; the photomultiplier output was displayed directly on an oscilloscope.

The absorption and fluorescence spectra were taken with a $\frac{1}{2}$-m scanning spectrometer, using a cooled S-20 photomultiplier. A 500-Hz lock-in system was used when necessary.

ABSORPTION AND FLUORESCENCE SPECTRA OF Nd^{3+} IN $LaCl_3$ AND $CeCl_3$

Portions of the absorption and fluorescence spectra of Nd^{3+} in $LaCl_3$ and $CeCl_3$ at 77°K are shown in Figs. 1(a), 1(b) and 2(a), 2(b). An interesting feature of these spectra is that there is virtually no shift of the neodymium lines when the lanthanum ions are completely replaced by cerium ions. However, the absorption lines appear to be considerably more broadened in $CeCl_3$ than in $LaCl_3$. On the other hand, the fluorescence spectra for both crystals appear remarkably similar in line positions, linewidths, and relative intensities.

EXPERIMENTAL RESULTS AND DISCUSSION

Delayed Fluorescence Versus Concentration, Nd^{3+} in $LaCl_3$

The delayed fluorescence peaks and the lifetimes of the $^4F_{3/2}$ level of Nd^{3+} in $LaCl_3$ and in $LaCl_3$ containing Ce^{3+} are shown in Fig. 3 for several concentrations of dopants. The crystals were maintained at room temperature. The table shows, for example, that when the E level or the $^4G_{7/2}$ manifold is selectively excited by a short pulse of light (approximately 2 μsec) the fluorescence from the R level of the $^4F_{3/2}$ manifold is delayed, reaching a peak intensity in 85 μsec for the 1.5% Nd sample (see Fig. 4). When the same level is excited in the 4% Nd sample, the delay peak occurs in 25 μsec. The delay peak was not measurable in the 50% and 100% Nd samples; the nonradiative process rate for these samples exceeded that measurable with the present detection apparatus.

The entries in Fig. 3 show that the fluorescence delay decreases with increasing concentration. The decrease with concentration in the delay peak is appreciable when the higher lying levels (above 16 000 cm^{-1}) are pumped.

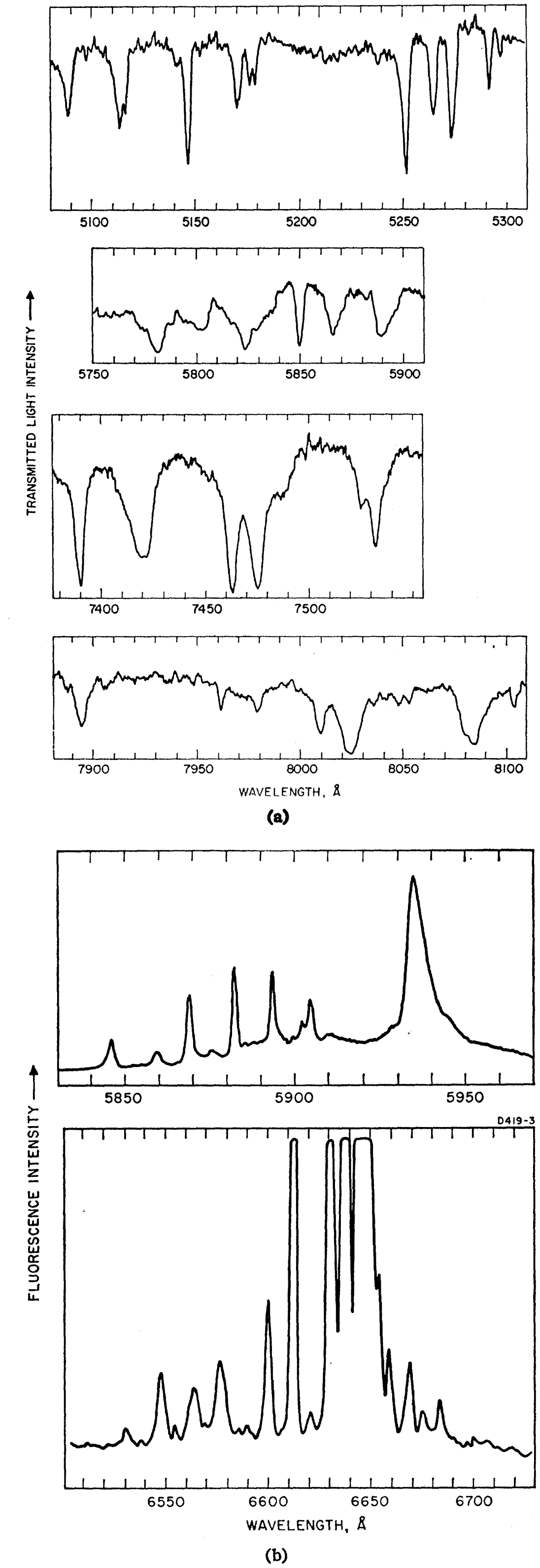

FIG. 1. Absorption and fluorescence spectra of 1.5% Nd^{3+} in $LaCl_3$ at 77°K. (a) Absorption spectrum. (b) Fluorescence spectrum. (Pump at 5200 Å; 200 Å wide.)

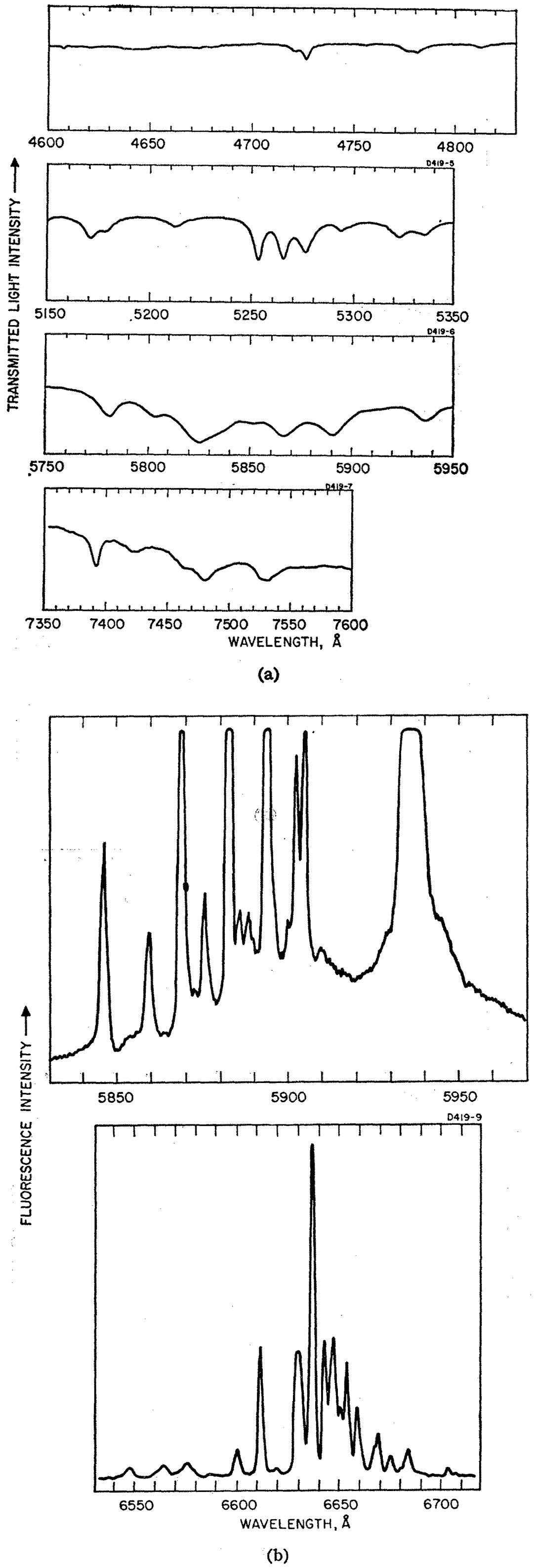

FIG. 2. Absorption and fluorescence spectra of 1% Nd^{3+} in $CeCl_3$ at 77°K. (a) Absorption spectrum. (b) Fluorescence spectrum. (Pump at 5200 Å; 200 Å wide.)

One possible explanation of this is that cross relaxation occurs between neighboring ions, a process in which a high-lying excited Nd^{3+} ion interchanges a part of its energy with a nearby unexcited Nd^{3+} ion. For example, an excited ion in the D state can go to level R while the neighboring ion can go from the Z level to the W level. The cross-relaxation process should be more effective as the concentration is increased. In order to conserve energy, the slight mismatch of transition energies can be taken up by the emission or absorption of lattice phonons.

An anomalous entry in the 1.5% Nd column is noted. The delay peak of the 1.06-μ fluorescence occurs in 115 μsec when the C group is excited; the value exceeds the 80-to-110-μsec delay peak values when levels above the C group are excited. This indicates that level C is partially bypassed in the energy cascade downward from higher lying levels.

Lifetime Versus Concentration, Nd^{3+} in $LaCl_3$

The measured lifetime of the $^4F_{3/2}$ level of Nd^{3+} in $LaCl_3$ is shown in the bottom row of Fig. 3. The lifetime was determined from the slope of the natural logarithm of the flourescence intensity versus time; the straight line portion of the tail of the curve was used to determine the lifetime. The lifetime for the most dilute sample was found to be shorter than that for the 1.5% concentration sample. As the concentration was increased to 100%, with neodymium completely replacing lanthanum, the lifetime of the level monotonically decreased to 20 μsec.

The increase in lifetime from 200 to 260 μsec at room temperature as the concentration increases from 0.1% to 1.5% is thought to be a result of self-absorption of resonance radiation, i.e., an emitted photon resulting from the transition from the $^4F_{3/2}$ level to the $^4I_{9/2}$ level of an excited ion traverses the crystal until an unexcited ion absorbs the radiation. The over-all effect is the extension of the measured lifetime.

As noted above, the lifetime decreased gradually as the concentration increases beyond 1.5%. The decrease of lifetimes of the $^4F_{3/2}$ level of Nd^{3+} with concentration in the $LaCl_3$ crystal is not as drastic as that observed for the LaF_3; in LaF_3, the behavior has been ascribed to cross relaxation between like neodymium ions.[12] However, in the chloride crystal no such cross relaxation is possible; there is no precise overlap of the two transitions $^4F_{3/2} \rightarrow {}^4I_{15/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$.

Two possible mechanisms for accounting for the decreased fluorescent lifetimes with increasing concentrations are mentioned here. In each case the relaxation rate increases with concentration because of decreased ion-ion distances.

The first mechanism is phonon-assisted cross relaxation. A large number of weak vibronic, or phonon-assisted lines occur in the spectra of rare-earth ions in

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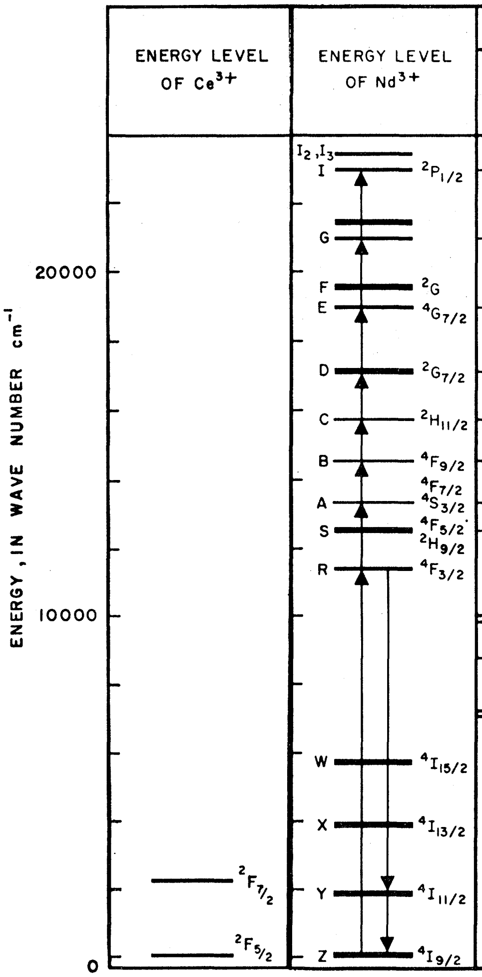
[12] C. K. Asawa and M. Robinson, Phys. Rev. 141, 251 (1966).



DELAY PEAK IN μsec
LaCl$_3$ CRYSTALS CONTAINING Nd OR Nd-Ce IMPURITIES. ROOM TEMP.

Level	0.1 % Nd	1 % Nd	1.5 % Nd	2 % Nd	4 % Nd	5 % Nd	10 % Nd	50 % Nd	100 % Nd	1 % Nd 0.1 % Ce	1 % Nd 1 % Ce	1 % Nd 99 % Ce
$^2P_{1/2}$			110	75	25	30		DELAY NOT MEASURABLE	DELAY NOT MEASURABLE			
G		110	90	65	25	25				120	50	175
$^4G_{7/2}$	170	110	85	60	25	25	15			110	50	140
$^2G_{7/2}$	150	110	80	60	25	25	15			110	40	125
$^2H_{11/2}$			115									
$^4F_{9/2}$		50	55	40	20	20				50		60
$^4F_{7/2}$, $^4S_{3/2}$	20	30	30	20	15	15				20	20	30
$^4F_{5/2}$, $^2H_{9/2}$	20	25	25	15	10	15	<10			30	15	25

LIFETIME OF THE $^4F_{3/2}$ LEVEL, μsec

	0.1 % Nd	1 % Nd	1.5 % Nd	2 % Nd	4 % Nd	5 % Nd	10 % Nd	50 % Nd	100 % Nd	1 % Nd 0.1 % Ce	1 % Nd 1 % Ce	1 % Nd 99 % Ce
τ =	200	220	260	250	200	180	140	40	20	240	120	240

FIG. 3. Delay of fluorescence peak and lifetime of the $^4F_{3/2}$ level of Nd^{3+} in LaCl$_3$ and in LaCl$_3$ containing Ce^{3+}.

crystals, occurring along the sides of the stronger pure electronic lines. These transitions encompass a wide spectral range (the phonon spectral width) and are available for matching pairs of cross-relaxation transitions even though the pairs of pure electronic transitions are somewhat mismatched. The phonon-assisted cross-relaxation process will be weaker than the process not requiring phonons. The cross relaxation rate depends upon the ion-ion separation; for example, for dipole-dipole transition for the ion-ion pair, the rate is inversely proportional to the sixth power of the ion-ion separation. Increased concentration will then result in increased relaxation rates and therefore decreased lifetimes.

The second mechanism for accounting for the weak lifetime-concentration behavior is described here. The increase in neodymium ions also tends to increase the concentration of trace impurities, such as other rare-earth ions. Certain impurities can act as sinks for the neodymium ions in the $^4F_{3/2}$ state. Close proximity of all of the neodymium ions to the impurity ion is not necessary, since the excitation energy can readily

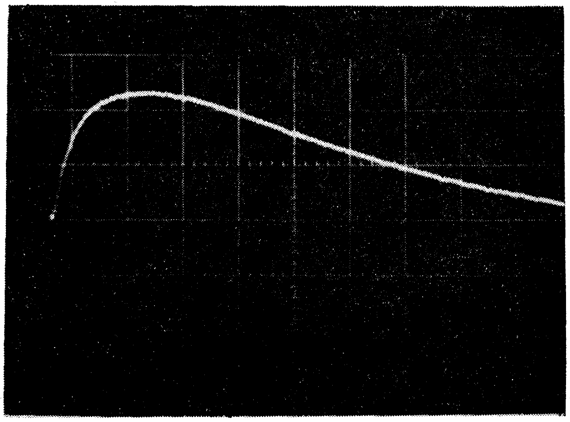


FIG. 4. Oscilloscope trace of the fluorescence at 1.06 μ ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) of 1.5% Nd^{3+} in LaCl$_3$ at room temperature. E and F groups pumped with light centered at 5200 Å (200 Å wide). Abscissa scale: 50 μsec/large division.

migrate nonradiatively[13,14] from neodymium ion to neodymium ion until the sink ion is approached. This nonradiative resonant transfer process is distinct from the process of self-absorption of radiation which was invoked to describe the extension of lifetime for the lower concentrations. The nonradiative migration process arises from the electrostatic interaction between the ions[13]; the rate of this process is determined by the distances between pairs of the neodymium ions or between the neodymium ion and the impurity ion. Since distances between ions decrease with increasing concentration, shortening of lifetime with concentration can be expected by this process. However, the nonradiative rate tending to decrease the lifetime must dominate the resonance radiation self-absorption rate which tends to increase the lifetime with increasing concentration. Further evaluation of these processes is necessary.

The possibility that the oscillator strength of the electric dipolar transitions increase markedly with concentration, thereby resulting in shorter lifetimes, is not indicated by absorption measurements. No large variation in absorption cross section (the absorption coefficient per ion) with concentration was observed for the transition between the ground $^4I_{9/2}$ state and the $^4F_{3/2}$ level.

Delayed Fluorescence and Lifetime of Nd^{3+} in $LaCl_3$ Which Contains Ce^{3+}

Entries in the last three columns of Fig. 3 are the delayed fluorescence peaks and the lifetimes for 1% Nd^{3+} in $LaCl_3$ when 0.1%, 1%, and 99% Ce^{3+} are also incorporated into the crystal. (The 99% cerium crystal contains no lanthanum ions.)

The remarkable result here is that the delayed fluorescence peak and the lifetime of the $^4F_{3/2}$ level do not decrease *monotonically* with cerium concentration. The delay and lifetime of the Nd^{3+} ion decrease with increasing cerium concentration until 99% cerium is reached; the delay of fluorescence of the 99% cerium sample exceeds that of the 0.1% cerium sample (for example, 140 versus 110 μsec). It was noted that the neodymium fluorescence efficiency was just as high in $CeCl_3$ as in $LaCl_3$.

The basic mechanism for this concentration behavior is not clear at this time. Figure 3 shows the 2200 cm^{-1} separation between the $^2F_{5/2}$ and the $^2F_{7/2}$ levels of Ce^{3+} (these are the only levels of Ce^{3+} within the $4f$ configuration). There are several pairs of levels above the $^4F_{3/2}$ level of Nd^{3+} with separations of this size. By cross relaxation with the neighboring Ce^{3+} ions, the delay of Nd^{3+} fluorescence can be decreased. With increased cerium concentration, the neodymium-cerium interaction should be increased, resulting in decreased delays. However, the experimental data show large Nd delays for the 99% $CeCl_3$ crystal, contrary to what would be expected with the above model. The result is not understood. Similarly the variation in lifetime with concentration is not understood at this time.

Lifetimes and Fluorescence Delays of Levels above the $^4F_{3/2}$ Level of Nd^{3+} Temperature Variations

In order to determine whether the delay of fluorescence from the $^4F_{3/2}$ level can be accounted for by sequential cascade of the energy down the ladder of levels, the lifetimes of the upper levels were measured.

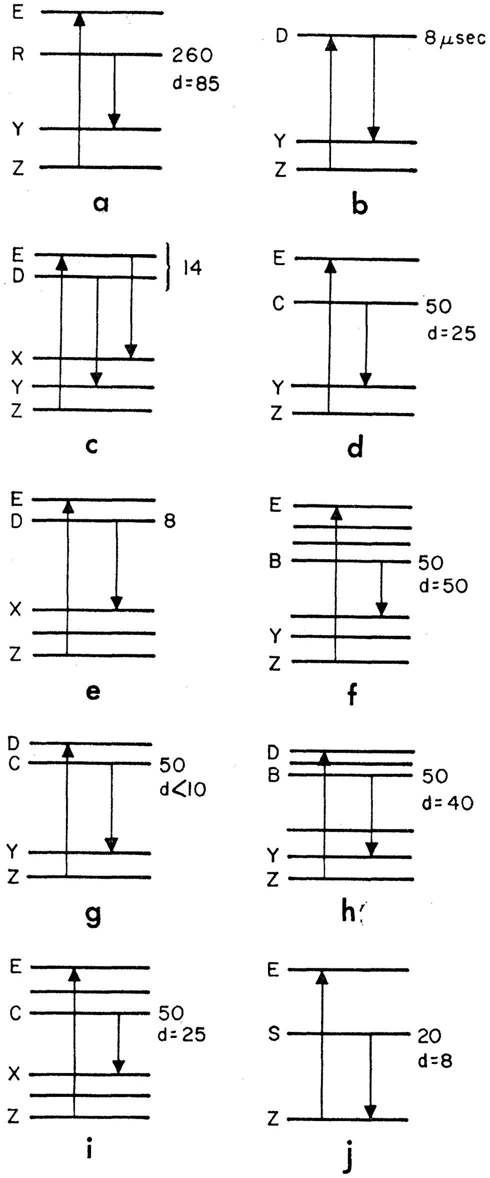


FIG. 5. Flourescence delays and lifetimes of levels above $^4F_{3/2}$ level of Nd^{3+}. For $LaCl_3$ containing 1.5% Nd, room temperature. Time is in μsec.

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[13] D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

[14] D. L. Dexter and H. H. Shulman, J. Chem. Phys. 22, 1063 (1954).

The results indicate that the energy transfer process is not a simple energy cascade downward but that it is complicated by cross relaxation transfer through large energy gaps.

$LaCl_3$ Containing 1.5% Nd^{3+}, Room Temperature

The measured values of lifetimes of the various levels are shown in Fig. 5. The delay of the fluorescence peak of some of the levels above the $^4F_{3/2}$ level, where higher levels are excited, is also shown. Figure 5(a) shows that the lifetime of the *R*, or $^4F_{3/2}$, level is 260 μsec and that the delay *d* of the peak is 85-μsec when level *E* is excited. If the delay is due to the downward cascade of energy from the excitation level *E* through the intermediate levels, the 85 μsec delay should be manifested in the cumulative delays to intermediate levels and the lifetime of the intermediate levels. This appears to be so for levels *B* and *C*; the delay peaks to level *B* and *C* are 50 and 25 μsec, respectively, and the lifetime of each level is 50 μsec. These values appear to be approximately correct in accounting for the delay of 85 μsec for the $^4F_{3/2}$ level.

However, the diagram in Fig. 5(j) is not consistent with an assumed process of sequential cascade downward. When the *E* level is excited, fluorescence for the *S* level (just above the $^4F_{3/2}$ level) has a relatively short delay peak of 8 μsec. The *S* level must be populated by a different process from that which populates the *B* and *C* levels. One possibility is that an ion in level *E* cross relaxes with a neighboring ion in the ground state, the process being $E \rightarrow S$ in the excited ion and $Z \rightarrow W$ in the unexcited neighboring ion. This cross-relaxation process completes with the processes which populate the other intermediate levels, *A* to *D*, after level *E* is excited.

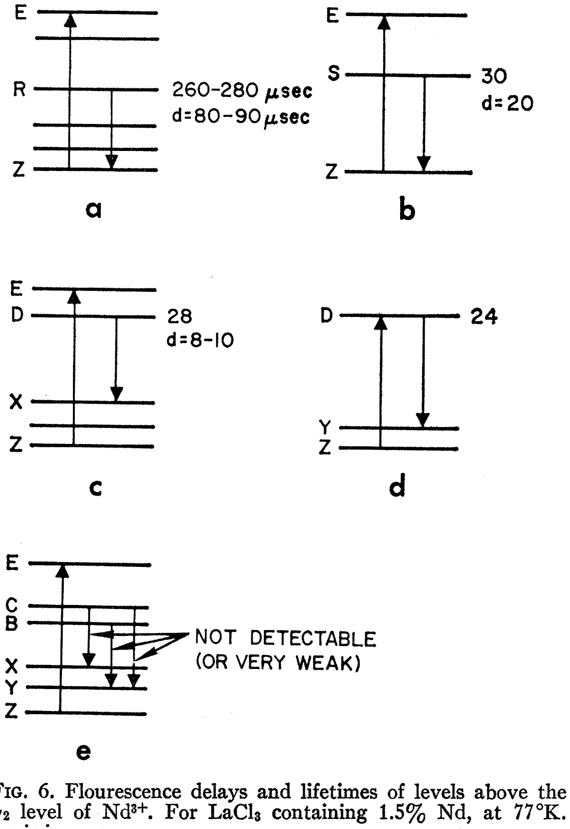

FIG. 6. Flourescence delays and lifetimes of levels above the $^4F_{3/2}$ level of Nd^{3+}. For $LaCl_3$ containing 1.5% Nd, at 77°K. Time is in μsec.

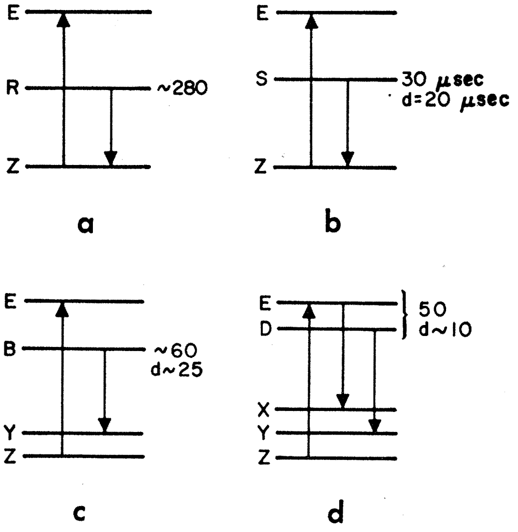

FIG. 7. Flourescence delays and lifetimes of levels above the $^4F_{3/2}$ level of Nd^{3+}. For $LaCl_3$ containing 1.5% Nd, at 4.2°K. Time is in μsec.

$LaCl_3$ Containing 1.5% Nd^{3+}, 77 and 4.2°K

Similar measurements for the 77 and 4.2°K crystals are shown in Figs. 6 and 7. However, the fluorescence from the *B* and *C* levels was quite weak and the delay and lifetime were unmeasurable when the *E* level was excited in the 77°K crystal. It was not determined whether this is a result of absorption of less pump light arising from the narrowing or the absorption lines, or of less efficient transfer from the *E* level to the *C* and *D* level. The delay and lifetime for the *D* level when the *E* level was excited are indicated in Fig. 6(c) for the 77°K crystal.

Lowering the temperature did not substantially change the values of lifetime or delay peak of most of the levels, except that the lifetime of the combined *D* and *E* levels increased from 14 μsec to about 50 μsec when the temperature was reduced from room temperature to 4.2°K.

$LaCl_3$ Containing 0.1% Nd^{3+}, 77 and 4.2°K

Attempts were made to measure the delayed fluorescence peaks and lifetimes of the levels of 0.1% Nd^{3+} in $LaCl_3$ at 77 and 4.2°K (Figs. 8 and 9, respectively). Weak fluorescence, often barely discernible with the present apparatus, resulted from the smaller amount

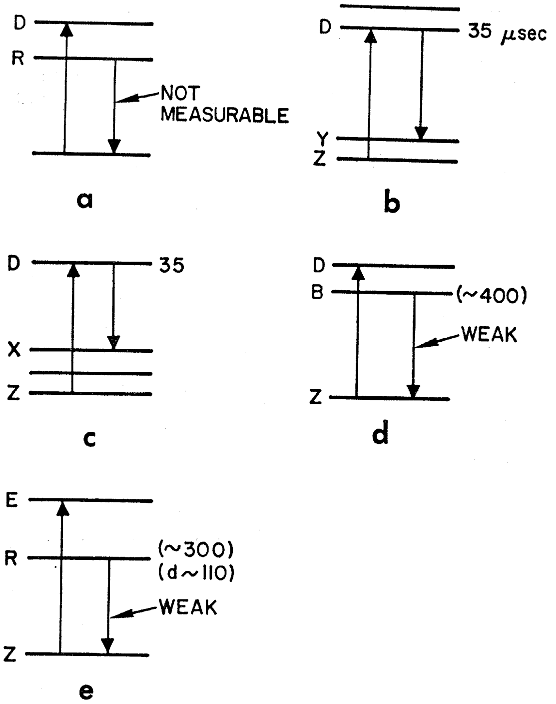

FIG. 8. Flourescence delays and lifetimes of levels above the $^4F_{3/2}$ level of Nd^{3+}. For $LaCl_3$ containing 0.1% Nd, at 77°K. (The numbers in parentheses are not reliable due to the low signal-to-noise ratios.) Time is in μsec.

of neodymium ion in this crystal than in the other samples; however, the weak fluorescence also appeared to result from very poor energy transfer. For example, when the D level was pumped in the 77°K crystal, the fluorescence from the R, or $^4F_{3/2}$ level, was barely discernible, and the delay peak and lifetime were unmeasurable (Fig. 8). However, the fluorescence transition from the D level to the X and Y levels was measurable [Fig. 8(b) and 8(c)]; the D level appears to be depopulated mainly by *radiative* emission.

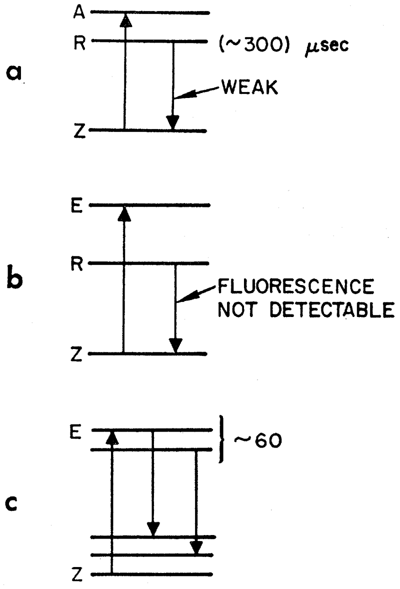

FIG. 9. Flourescence delays and lifetimes of levels above the $^4F_{3/2}$ level of Nd^{3+}. For $LaCl_3$ containing 0.1% Nd, at 4.2°K. (The numbers in parentheses are not reliable due to the low signal-to-noise ratios.) Time is in μsec.

This result has suggested that efficient populating of the R level must arise from cross-relaxation transfer in the higher concentration crystals; as the concentration is increased so that ion pair interaction is increased, the $^4F_{3/2}$ level can be populated by pumping into the D level.

On the other hand, when the E or $^4G_{7/2}$ level is excited, a slightly stronger fluorescence from the $^4F_{3/2}$ level is observed [Fig. 8(e)]. (The estimated values of 110 μsec for the delay peak and 300 μsec for the lifetime are not completely reliable.) Pumping into the E level appears to be more efficient for populating the $^4F_{3/2}$ level than pumping into the D level in the 0.1% Nd sample. The reason for this is not clearly understood at this time, but it evidently is not caused by a greater absorption of pump light by the E level. (The result may result from a weak cross transfer from level E: $E \rightarrow S$ and $Z \rightarrow W$ as suggested earlier for the 1.5% Nd sample at room temperature—and then from $S \rightarrow R$.)

Analysis of an Idealized Model

In order to gain some insight into the problem, a simple idealized model was analyzed.

Let levels 1 and 2 represent two Stark manifolds in this idealized case, with level 2 lying adjacent and above level 1. The dominant terms in the rate equations for levels 1 and 2 are

$$\frac{dn_2}{dt} = -\left(\frac{1}{\tau_2}+\omega_{21}+\sum_{i\neq 1}\omega_{2i}\right)n_2+\omega_{12}n_1+\sum_{i\neq 1}\omega_{i2}n_i \qquad (1)$$

$$\frac{dn_1}{dt} = -\left(\frac{1}{\tau_1}+\omega_{12}+\sum_{i\neq 2}\omega_{1i}\right)n_1+\omega_{21}n_2+\sum_{i\neq 2}\omega_{i1}n_i, \qquad (2)$$

where

$n_i \equiv$ population of level i,
$t \equiv$ time,
$\omega_{ij} \equiv$ thermal, or lattice, relaxation from level i to level j,
$\tau_i \equiv$ natural lifetime of level i.

Cross relaxation and energy transfer to other ions are neglected.

In Eqs. (1) and (2) the terms containing ω_{12}, ω_{i2}, and ω_{i1} can be neglected when the energy separation between levels 1 and 2 and between levels 1 or 2 and lower-lying levels is much greater than the effective temperature. Equations (1) and (2) then become

$$\frac{dn_2}{dt}+\frac{1}{t_2}n_2=0, \qquad (3)$$

where

$$\frac{1}{t_2}=\left(\frac{1}{\tau_2}+\omega_{21}+\sum_{i\neq 1}\omega_{2i}\right), \qquad (4)$$

and

$$\frac{dn_1}{dt}+\frac{1}{t_1}n_1=\omega_{21}n_2, \qquad (5)$$

where

$$\frac{1}{t_1}=\left(\frac{1}{\tau_1}+\sum_{i\neq 2}\omega_{1i}\right). \qquad (6)$$

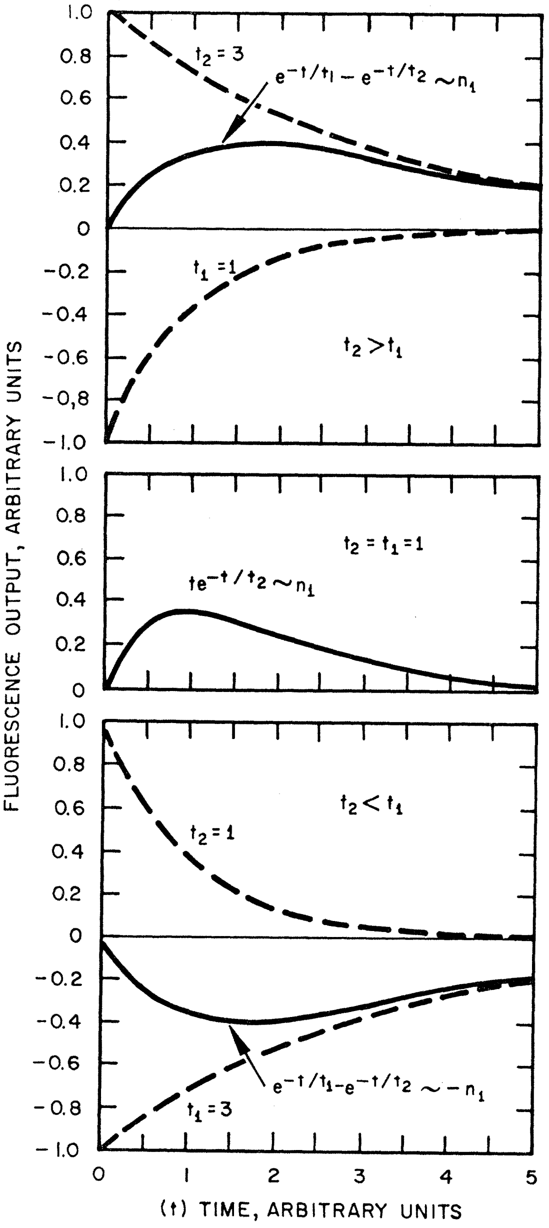

FIG. 10. Population of level 1 after exciting level 2 with pulse.

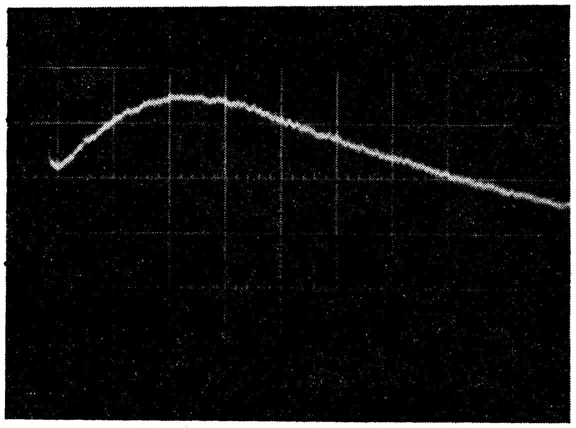

FIG. 11. Oscilloscope trace of the fluorescence at 1.06 μ of 1% Nd^{3+} in $CeCl_3$ at room temperature. *E* and *F* groups pumped with light centered at 5200 Å (200 Å wide). Abscissa scale: 50 μsec/large division.

After level 2 is populated with a Dirac δ function pulse, the population of level 1 is found to be

$$n_1=\frac{n_2^0\omega_{21}}{(1/t_2)-(1/t_1)}\left(e^{-(t/t_1)}-e^{-(t/t_2)}\right), \qquad (7)$$

where n_2^0 is the population of level 2 at $t=0+$.

This equation is shown graphically in Fig. 10 for three cases: (a) $t_2>t_1$, (b) $t_2=t_1$, and (*c*) $t_2<t_1$. Note that the population n_1 is symmetrical in t_1 and t_2; that is, the delayed fluorescence output from level 1 remains unchanged when the lifetimes of levels 1 and 2 are interchanged. Case (b) arises when n_2 is an exponential $\exp(-t/t_2)$ and t_1 is replaced by t_2 in Eq. (5); the solution of Eq. (5) for n_1 is then

$$n_1=n_0^2\omega_{21}te^{-t/t_2}.$$

The expression is also obtainable from Eq. (7) as $t_1\rightarrow t_2$.

The fluorescence trace of Fig. 11 was fitted to expression (7); the fluorescence arises for the $^4F_{3/2}$ level of 1% Nd^{3+} in $CeCl_3$ when the *D* level is pumped. An idealized two level system was assumed, although a number of levels actually exist between the excited *D* level and the $^4F_{3/2}$ fluorescent level. The fluorescent lifetime of 240 μsec of the lower level was measured from the tail of the trace. The delay peak was measured to be 125 μsec. The effective fluorescence lifetime of the upper level was then calculated to be 71 μsec. Using this value, the expression is graphed and compared with the actual trace (see Fig. 12). The fit is surprisingly close.

The lifetimes of the excited levels of 1% Nd^{3+} in $CeCl_3$ are given in Table I. It is clear that if most of the excited ions cascaded downward sequentially, the cumulative effect of the lifetimes would greatly exceed the $t_2=71$ μsec calculated for the simple two-level system. This suggests that the main energy cascade is via selected intermediate levels only. Further experi-

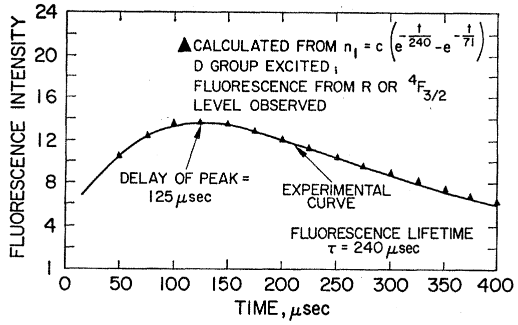

FIG. 12. Oscilloscope trace of fluorescence rise and decay (1% Nd^{3+} in $CeCl_3$, at room temperature.) Comparison of experimental trace and calculated points.

mental study is necessary in order to determine the precise branching of energies.

Upper Bound for the Nonradiative Rates

The lifetime t_2 of level 2 was deduced from the delayed fluorescence peak and the lifetime of level 1. We note that t_2 is related to the nonradiative rate by Eq. (4):

$$\frac{1}{t_2}=\left(\frac{1}{\tau_2}+\omega_{21}+\sum_{i\neq 1}\omega_{2i}\right).$$

We have tacitly assumed no cross-relaxation transfer in this simplified case; however, for weak optical pumping rates for the excitation pulse, the cross-relaxation coefficient can be incorporated into the ω_{2i}'s as an added term.

The lattice relaxation downward from level 2 to level i ($i\neq 1$) should be small compared with that from level 2 to level 1. Hence, $\sum_{i\neq 1}\omega_{2i}$ can be neglected in comparison with ω_{21}

$$\frac{1}{t_2}=\left(\frac{1}{\tau_2}+\omega_{21}\right).$$

It is not possible to determine the relative values of $1/\tau_2$ and ω_{21} without making further measurements, such as quantum efficiency measurements, or by calculating $1/\tau_2$ under several approximations.

However, the upper limit for ω_{21} is determinable in some cases. For example, consider the 0.1% Nd^{3+} in $LaCl_3$ crystal at 77°K [Fig. 8(a)]. The transfer of energy from level D to R is so weak that the fluorescence from the R, or $^4F_{3/2}$, level is barely discernible when D is pumped. On the other hand, the fluorescence from level D is strong and has a lifetime $t_2=35$ μsec. Therefore,

$$\frac{1}{35\times 10^{-6}\ \text{sec}}=\frac{1}{t_2}\sim\frac{1}{\tau_2},$$

or ω_{21} is much less than $(1/35)\times 10^{+6}$ sec^{-1}.

TABLE I. Lifetime of the excited levels of 1% Nd^{3+} in $CeCl_3$.

Level	Lifetime, μsec
D	30
C	35
B	38
A	40
S	90
R	240

SUMMARY AND CONCLUSIONS

The long delayed fluorescence of Nd^{3+} in $LaCl_3$ and $LaCl_3$ containing Ce^{3+} indicates weak coupling of the Nd^{3+} ion to the vibrations of the crystals or weak cross-relaxation interaction. The delays give a measure of the order of magnitude, or the upper bound, of the nonradiative coupling rates.

The determination of the nonradiative rates via the lattice alone is complicated by the effect of nonradiative cross relaxation of ion energy. This latter effect manifests itself when the concentration of Nd^{3+} ions exceeds about 0.1% in the $LaCl_3$ crystal.

The study of the fluorescence delay versus neodymium concentration in the $LaCl_3$ crystal has suggested that cross-relaxation between neighboring neodymium ions plays a part in populating levels below the optically pumped level; as the neodymium concentration was increased, the delay in populating the levels below the pumped level decreased rapidly.

The lifetime of the $^4F_{3/2}$ level of Nd^{3+} in the $LaCl_3$ at room temperature was found to increase with concentration until the 1.5% concentration was reached. Thereafter, the lifetime was found to decrease with concentration.

The effect on the fluorescence of Nd^{3+} when Ce^{3+} was also incorporated in the $LaCl_3$ crystal was examined. The delay of the fluorescence and the lifetime of the $^4F_{3/2}$ state of Nd^{3+} was found to decrease with increasing concentration of cerium ions. However, when cerium ions completely displaced the lanthanum ions, the delay and lifetime reached their maximum values. The results cannot be explained by cross relaxation.

The measurement of the lifetimes and the delay of fluorescence of some of the levels above the $^4F_{3/2}$ level was made for two concentrations of neodymium in $LaCl_3$ at various temperatures. The results show that branching of energy from the pumped level to the $^4F_{3/2}$ level is complex, i.e., it is not a sequential cascade down the ladder of the energy levels.

Further detailed examination of these crystals obviously is necessary to clarify the nonradiative processes, some of which were mentioned above. The anhydrous chloride crystals containing rare-earth ions are excellent hosts for examining these processes, since their rate is small in these crystals and fluorescence from most of the levels of the rare-earth ions results.

It must be determined why the coupling of the rare-earth ion to the energy sink is weak in the chloride crystal; it must be decided whether this is caused by the high symmetry of the crystal (resulting in fewer lattice vibrations), the weak coupling of the ion to the lattice vibrations, or other factors.

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Lifetime of Positrons in an Electron Gas*

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New estimates of the lifetime of a positron in an electron gas are presented. The discussion is based on a modified ladder-type approximation to the electron-positron Green's function chosen so that the displaced-charge sum rule is identically satisfied. This constitutes a refinement of the simple ladder sum used by Kahana which leads to a large unphysical accumulation of charge about the positron. While this violation of the displaced-charge sum rule is, to say the least, annoying, reasons are given why it may not be very serious if one is concerned only with the computation of annihilation rates. We find, in fact, that the rates obtained in the more consistent modified ladder scheme are not very different from those quoted by Kahana although they represent a distinct improvement.

I. INTRODUCTION

When a positron enters an electron gas, it faces the hazard of annihilation against one of the electrons with subsequent emission of two gamma rays. In this paper we present new estimates of the lifetime of a positron immersed in an interacting system of conduction electrons. The calculations are based on the Bethe-Goldstone approach first introduced by Kahana[1] and a modification suggested by Bergersen.[2] If one considers the problem of a low-energy (nonrelativistic) electron-positron pair annihilating in free space from a scattering state, one finds that the annihilation cross section is completely determined by solving the Schrödinger equation for the wave function of the pair coupled through their Coulomb field.[3] In fact, the annihilation cross section depends only on the square of this wave function at $\mathbf{x}_e=\mathbf{x}_p$ where $\mathbf{x}_e(\mathbf{x}_p)$ is the electron (positron) coordinate—a result which is eminently sensible.

In the present work we are of course concerned with annihilation in the medium of all the other metallic electrons which do not participate directly in the annihilation process but are nevertheless around and capable of influencing this process in a profound way. Even in this case, however, one may well attempt as a first approximation to remain within the framework of writing down a Schrödinger-type equation for the annihilating pair, trying at the same time to incorporate within this framework as much of the presence of the other electrons as is possible.

The first modification that seems essential is to change the bare Coulomb force to a more appropriate screened Coulomb force. This accounts for the polarization of the surrounding medium by the annihilating pair. Further, it is important to recognize that in an electron gas the Pauli exclusion principle plays an essential role. Because of the existence of an electron sea, all the plane-wave states below the Fermi surface are occupied and therefore cannot be employed in building up the electron part of the effective-pair wave function.

When these changes are made in the original Schrödinger equation it becomes a Bethe-Goldstone equation. The solution of this latter equation using a suitable effective force yields rates in fair agreement with experiment for a large number of metals. This is a striking improvement over the Sommerfeld model which fails completely to account even qualitatively for the observed rates.

The failure of the Sommerfeld model is easily understood. If one goes back to quantum electrodynamics and derives an expression for the total rate R for a many-body system of low-energy electrons and a positron, one finds that R is proportional to the *electronic density* at *the positron* averaged over all positron positions.[4] This result is general and includes interactions. But the Sommerfeld model corresponds to ignoring all Coulomb forces so that the electronic density at the positron comes out to be the average density in the system. This

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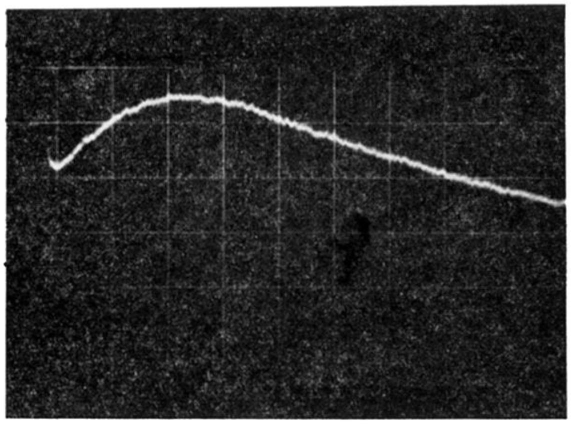

FIG. 11. Oscilloscope trace of the fluorescence at 1.06 μ of 1% Nd^{3+} in $CeCl_3$ at room temperature. *E* and *F* groups pumped with light centered at 5200 Å (200 Å wide). Abscissa scale: 50 μsec/large division.

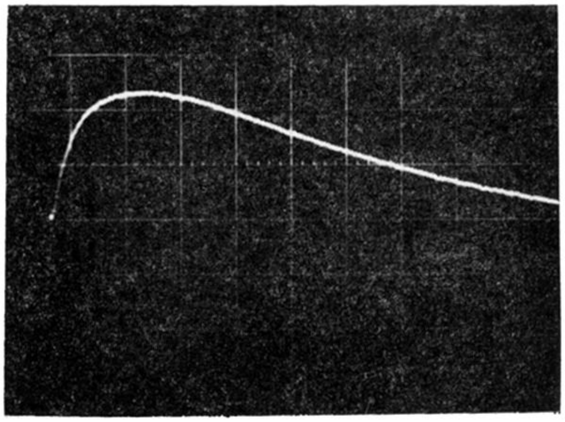

FIG. 4. Oscilloscope trace of the fluorescence at 1.06 μ ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) of 1.5% Nd^{3+} in $LaCl_3$ at room temperature. E and F groups pumped with light centered at 5200 Å (200 Å wide). Abscissa scale: 50 μsec/large division.