Multiphonon Relaxation in LaCl$_3$:Nd^{3+} †

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Lifetime and quantum-efficiency measurements were used to determine the transition rates between several adjacent groups of Stark levels lying above R of LaCl$_3$:Nd^{3+}. By choosing transitions for which the ion pair interaction could be excluded as a relaxation mechanism, the rate of energy transfer to the lattice by emission of several phonons was determined. The 4.2°K rates were found to be due to spontaneous emission, and for $C \rightarrow B$, $S \rightarrow R$, and $D \rightarrow C$ are $(2.23 \pm 0.38) \times 10^3$ sec^{-1}, $(4.59 \pm 0.64) \times 10^4$ sec^{-1}, and $(6.3 \pm 3.1) \times 10^3$ sec^{-1}, respectively. At higher temperatures increased rates due to emission stimulated by thermally populated phonon states were measured. Fitting the temperature dependences permitted estimates of the magnitude of the phonons involved, and determined their frequencies to be in the range of the optical branches of the LaCl$_3$ phonon spectrum. A technique for measuring quantum efficiencies is presented which does not require the use of a spectrometer which has been calibrated for transmission.

I. INTRODUCTION

PREVIOUS studies[1-3] have shown that there is a definite relationship between the energy difference to the next-lowest level and the fluorescence efficiency of a given rare-earth level. In general, fluorescence is not observed in LaCl$_3$ from states for which the energy gaps to the next-lowest state is less than 1000 cm^{-1}. The ion-ion interaction[4,5] as well as the ion-lattice interaction may serve as a quenching mechanism. A recent study of LaCl$_3$:Ho^{3+} indicates ion-pair interactions giving transition rates on the order of radiative rates for rare-earth concentration in LaCl$_3$ greater than 1%.[6] In the present study, both lifetime and quantum efficiency measurements were taken to directly determine transition rates between adjacent levels. Transitions were chosen for which the Nd^{3+}–Nd^{3+} ion-pair interaction could be confidently excluded as a competing process. Concentration dependences were measured to check these assumptions. Samples of high purity were used, and the resulting relaxation rates were attributed to phonon emission. The temperature behavior of these rates confirms the conclusions and permits estimates of the phonon energies.

II. SAMPLES

Both single crystals and polycrystalline samples of LaCl$_3$ doped with NdCl$_3$ were used. These samples were grown from chlorides which had been converted in this laboratory from the oxides. Starting materials were claimed by the manufacturer to be 99.999% pure with respect to other rare earths. An analysis of one of these samples indicated between 10 and 100 ppm of Gd, Tb, Pr, and Yb. None of these ions could serve as a competing ion-pair mechanism for the rates studied here, although it is possible that they could cause transitions to other final states. No evidence was found, however, to indicate that this was the case.

The samples were mounted in quartz tubes containing 0.5 atmospheres of helium gas in order to maintain thermal contact with the temperature baths.

III. TEMPERATURES

Baths of liquid helium, liquid nitrogen, and dry-ice–alcohol were used. Intermediate temperatures were obtained below 300°K by passing cooled nitrogen gas over the sample. Temperatures above 300°K were obtained using water bath heated by a resistor. The intermediate temperatures were measured with a copper-Constantan thermocouple referenced to the nearest standard bath. The difference between standard bath and sample was never more than 100°C, and these differences were measured to about 3%.

IV. LIFETIME MEASUREMENTS

Lifetimes were measured both by a stroboscopic technique which has been described previously[2,7] and by the use of a P.A.R. model T.D.H.-9 wave form eductor to monitor fluorescence decay after excitation with pulsed Edgerton, Germeshausen, and Grier FX-31 and FX-31B xenon flash lamps. Fluorescence was detected with EMI 9558 and RCA 7102 photomultipliers at the exit slit of scanning monochromators operated from 5 to 30 Å bandpass. 75-cm Ebert, 75-cm Czerny-Turner, and 100-cm Czerny-Turner spectrometers were used. The sensitivity of the apparatus was such that lifetimes of states with extremely low radiative quantum efficiencies could be determined in low-concentration samples. Excitation wavelengths were selected

[1] G. H. Dieke, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 2, p. 237.

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

[3] M. J. Weber, in *Proceedings of the Conference on the Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., New York, 1966), p. 350.

[4] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).

[5] M. R. Brown, J. S. S. Whiting, and W. A. Shand, J. Chem. Phys. **43**, 1 (1965).

[6] J. F. Porter, Jr., and H. W. Moos, Phys. Rev. (to be published).

[7] C. F. Hendee and W. B. Brown, Philips Tech. Rev. **19**, 50 (1957).

TABLE I. Lifetimes of lower optical states of $LaCl_3:Nd^{3+}$. Lifetimes are given in msec.

Level	T (°K)	0.1% NdCl₃ in LaCl₃	1.0% NdCl₃ in LaCl₃	10% NdCl₃ in LaCl₃	100% NdCl₃
R	4.2	206 (5)[a]	196 (5)	209 (5)	
R	77	190 (5)	223 (5)	246 (5)	242 (5)
R	201	162 (5)	230 (5)	212 (5)	
R	295[b]	165 (5)	225 (5)	171 (5)	21.2 (10)
S	4.2	19.3 (10)	19.8 (5)	13.6 (10)	
S	77	22.0 (5)	21.8 (5)	12.0 (5)	
S	120		18.8 (5)		
S	168		14.0 (5)		
S	201		11.4 (5)		
S	240		9.9 (5)		
S	279		7.9 ([c]6.9)		
S	295[b]		8.1 ([c]7.5)	7.0 ([c]6.0)	
S	322		7.0 ([c]6.0)		
S	335		7.0 ([c]6.0)		
S	345		6.6 ([c]5.6)		
S	367		less than 5.4		
B	4.2	106 (5)	74.2 (5)	12.8 (10)	
B	77	114 (5)	81.4 (5)	16.7 (10)	
B	201	66.7 (10)	61.1 (10)		
B	295[b]	25.5 (10)	24.3 (10)	15.2 (10)	
C	4.2	366 (5)	344 (5)	269 (8)	
C	77	458 (5)	433 (5)	331 (5)	
C	151	261 (4)			
C	201	152 (5)	153 (5)	129 (5)	
C	247	84.0 (3)			
C	295[b]	53.3 (5)	53.5 (5)	48.5 (5)	
C	296	51.0 (2.5)			
C	339	34.2 (2)			
C	369	26.1 (2)			
D	4.2	29.7 (5)	30.4 (5)	11.9 (5)	
D	77	31.3 (5)	33.2 (5)	6.3 (10)	
D	201		20.1 (5)		
D	295[b]	15.1 (7)	12.3 (10)		

[a] Parenthesis includes percent accuracy of the measurement.
[b] Approximate temperature (room temperature).
[c] The reciprocal lifetime is near the initial decay rate of the flash. Here the value given is that representing the maximum negative slope on the decay curve and the value in parentheses is an estimate of a lower limit of the lifetime, considering the shape of the flash.

with a 10-cm Ebert $f/1.4$ monochromator or with monochromatic interference filters. A No. 60 set of Optics Technology variable bandpass interference filters and various Corning filters were employed to reduce scattered pump light. In most cases, the fluorescing level was pumped resonantly; however, in certain cases it was necessary to pump the higher adjacent level in order to observe fluorescence. In such cases the lifetime of the upper level was also measured, and the resulting rise times were accounted for in the data processing. The lifetimes of the levels of interest are presented in Table I. All fluorescence decay curves were observed to be single exponentials except for S (Fig. 1)[8] at high temperatures. Here, when S is pumped it decays according to a linear combination of two exponentials.[9]

The lifetime of S is much shorter than R, so the decay curve represents the two states attaining temporary thermal equilibrium with each other in times characteristic of the lifetime of S, then decaying together at approximately the decay rate of R.[10]

V. QUANTUM EFFICIENCIES

Consider two levels A and B, A lying above B by an amount of energy much greater than kT. When B is pumped, the quantum yield of an arbitrary fluorescence transition L originating at B is given by

$$Q_{LB} = (P_B/\nu_B)\eta_L,$$

where η_L is the quantum efficiency of this particular transition, P_B is the power absorbed by B from the

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

[9] Here we have a case where the up-rate W_{RS} cannot be neglected. The radiative rates of R and S are about equal: $W_{Ri} = W_{Si} = W_i$. The solution of the rate equations for the population of S is a linear combination of two exponentials whose "lifetimes" are W_i^{-1} and $(W_{SR}+W_{RS}+W_i)^{-1}$.

[10] C. K. Asawa and M. Robinson, Phys. Rev. **141**, 251 (1966). These authors have also reported lifetimes of R of Nd^{3+} in $LaCl_3$. Our results are essentially in agreement with these measurements.
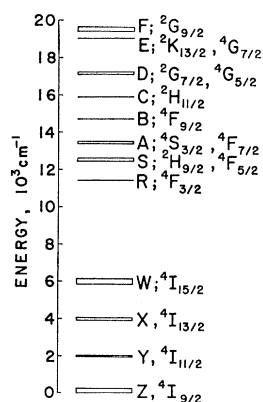
FIG. 1. Energy levels of LaCl$_3$: Nd^{3+}.

Energy levels (ENERGY, 10^3 cm^{-1}):

F; $^2G_{9/2}$
E; $^2K_{13/2}$, $^4G_{7/2}$
D; $^2G_{7/2}$, $^4G_{5/2}$
C; $^2H_{11/2}$
B; $^4F_{9/2}$
A; $^4S_{3/2}$, $^4F_{7/2}$
S; $^2H_{9/2}$, $^4F_{5/2}$
R; $^4F_{3/2}$
W; $^4I_{15/2}$
X, $^4I_{13/2}$
Y, $^4I_{11/2}$
Z, $^4I_{9/2}$

pump beam, and ν_B is the frequency of the absorption. The quantum yield of L when A is pumped is

$$Q_{LA} = (P_A/\nu_A)\eta_{AB}\eta_L.$$

η_{AB} is the quantum efficiency of the $A \to B$ process. Dividing the two expressions and solving for η_{AB},

$$\eta_{AB} = \frac{\nu_A}{\nu_B} \frac{P_B}{P_A} \frac{Q_{LA}}{Q_{LB}}. \tag{1}$$

These ratios may be obtained by using the same monochromatic source to sweep both the excitation spectrum of L and the absorption spectrum of A and B. A Bausch and Lomb 50-cm scanning monochromator with a 650-W tungsten-iodine lamp was used as the source. The absorptions were measured by monitoring the trnsmitted light from the source with an Amperex 150 CVP photomultiplier whose spectral sensitivity was calibrated against a C. M. Reeder thermopile. The fluorescence was detected with the 75-cm Czerny–Turner spectrometer.

The quantum efficiency η_{AB} is

$$\eta_{AB} = W_{AB} / \sum_i W_{Ai},$$

where W_{AB} is the transition rate from A to B and W_{Ai} are the transition rates from A to all other levels to which it decays. Knowing the lifetime

$$\tau_A = 1 / \sum_i W_{Ai},$$

W_{AB} may be determined by

$$W_{AB} = \eta_{AB}/\tau_A.$$

This technique for quantum-efficiency measurements is especially convenient since a spectrally calibrated spectrometer is not required. The rates which are obtained by measuring both lifetimes and quantum efficiencies are not subject to error due to resonance radiation trapping or ion-pair processes which are not in direct competition with the measured rate.

The quantum efficiencies are given in Table II. The C absorption from the ground state is very weak,

and quantum efficiencies for transitions involving C could be made only in the 10% sample. η_{AR} is presented but will not be discussed further.

VI. EXPECTED TEMPERATURE DEPENDENCE

The temperature dependence of a transition rate involving the emission of p_i phonons is expected to be given by

$$W = W_i^0 (\bar{n}_i + 1)^{p_i}, \tag{2}$$

where W_i is the spontaneous rate, containing the atomic matrix elements of the ion-lattice interaction[11] Hamiltonian and the density of states. The quantity $\bar{n}_i$ is the average occupation number of the ith vibrational mode and is given by

$$\bar{n}_i = [\exp(h\nu_i/kT) - 1]^{-1}, \tag{3}$$

ν_i being the frequency of this mode. Conservation of energy requires that $p_i h\nu_i = \Delta$, the amount of energy transferred from the atomic system to the lattice. In the above equation only "direct" processes involving phonons of a single frequency were considered. More general types of processes are possible: Consider the case where p_1 phonons of mode 1 and p_2 of mode 2 are involved, such that

$$p_1 h\nu_1 \pm p_2 h\nu_2 = \Delta. \tag{4}$$

The temperature dependence in such a case would be given by

$$W = W_{12}^0 (\bar{n}_1 + 1)^{p_1} (\bar{n}_2 + b)^{p_2}. \tag{5}$$

In the case where the p_2 phonons were emitted, the quantity b would be unity and the plus sign in Eq. (4) would be correct. For absorption, $b = 0$ and the negative sign would be used. Sufficient evidence is not available to indicate that the latter processes are of primary importance in optical relaxation, and the data were fitted to Eq. (2).

TABLE II. Quantum efficiencies of $C \to B$, $S \to R$, $A \to R$, and $D \to C$ transitions. Values in parentheses are estimates of the experimental accuracy in percent.

Transition	Temperature °K	Quantum efficiency 1.0% NdCl$_3$ in LaCl$_3$	Quantum efficiency 10% NdCl$_3$ in LaCl$_3$
$C \to B$	77		0.55 (20)
$C \to B$	295		1.2 (20)
$S \to R$	4.2	0.90 (10)	0.66 (10)
$S \to R$	77	0.87 (10)	0.53 (10)
$S \to R$	295	0.98 (10	0.93 (10)
$A \to R$	4.2	0.77 (10)	0.59 (10)
$A \to R$	77	0.87 (10)	0.66 (10)
$A \to R$	295	0.98 (10)	0.92 (10)
$D \to C$	77		0.034 (10)

[11] J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

When an initial state consists of a number of levels which attain thermal equilibrium in times short compared to the decay time of the total multiplet, the total transition rate from this state is given by

$$W_T = \frac{\sum_j W_j \exp(-\Delta_j/kT)}{\sum_j \exp(-\Delta_j/kT)}, \qquad (6)$$

where Δ_j is the energy difference between the jth level and the lowest level of the multiplet. This approximation is generally valid in rare earths,[12] whose free-ion levels are split by the crystal-field interaction.

VII. TRANSITION RATES

A. *C-B* Relaxation

The concentration dependence of the C lifetime is shown in Fig. 2 and indicates that concentration-dependent quenching is negligible at 0.1% concentration. The $C{\rightarrow}B$ quantum efficiency was measured at
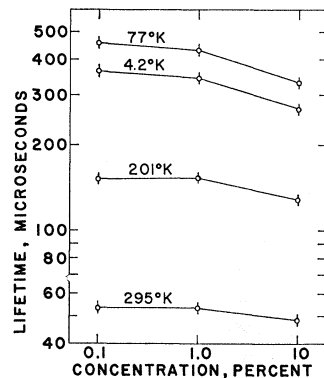
FIG. 2. Concentration dependence of C lifetimes for several temperatures.

77°K in the 10% sample and this, along with the lifetime of C under the same conditions, yields a $C{\rightarrow}B$ transition rate of $(1.68\pm0.42)\times10^3$ sec^{-1} at 77°K. Contributions to the $C{\rightarrow}B$ rate due to Nd^{3+} ion-pair relaxation are negligible, since such a process would be nonresonant and would require the absorption of about 800 cm^{-1} of energy from the lattice, so the concentration quenching must be due to a rate other than $C{\rightarrow}B$. Since radiative rates for energy gaps of this size are orders of magnitude smaller than the measured $C{\rightarrow}B$ rate, it is attributed to phonon emission,[13] which is also expected to be independent of concentration. The measured $C{\rightarrow}B$ rate is subtracted from the reciprocal lifetime of C in the 0.1% sample at 77°K to determine the radiative rate of C. This quantity is $(0.50\pm0.38)\times 10^3$ sec^{-1}. The radiative rate should be independent of temperature, so the $C{\rightarrow}B$ rate at other temperatures may be obtained by subtracting it from the reciprocal

[12] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).
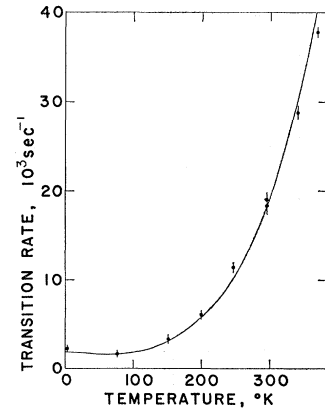[13] A. Kiel, Ph.D. thesis, The Johns Hopkins University, 1962 (unpublished).

FIG. 3. $C{\rightarrow}B$ transition rate versus temperature. The solid curve represents a six-phonon process from a level which is thermally depopulated to another lying 50 cm^{-1} above it.

lifetimes of C in the 0.1% sample. The values for the $C{\rightarrow}B$ rate thus obtained are displayed in Fig. 3. Comparison of the experiment points to Eq. (2) leads to identification of the flat portion of the curve at low temperatures as being due to spontaneous emission of phonons and the high-temperature rate increase as being due to induced emission. Using the measured value of the spontaneous rate, however, it is not possible to fit the data to Eq. (2). The data vary too strongly with temperature for a five-phonon process and too weakly for a six-phonon process. The level C, however, consists of six crystal-field components distributed over a range of about 50 cm^{-1}, all of which are appreciably populated in the range of temperatures studied. Equation (6) was used to compensate for this population by replacing all of the upper levels of C by an effective level at energy Δ_2 and with zero spontaneous rate. The result is the two-parameter expression

$$W = W_0\left[\frac{\exp(\Delta_1/kT)}{\exp(\Delta_1/kT)-1}\right]^p\left[\exp\left(-\frac{\Delta_2}{kT}\right)+1\right]^{-1}. \qquad (7)$$

The total energy gap being known, the order of the process may be varied in integral steps. Selection of p
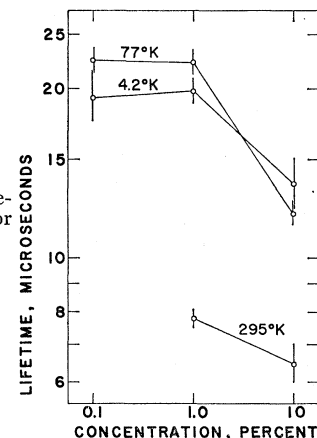
FIG. 4. Concentration dependence of S lifetimes for several temperatures.
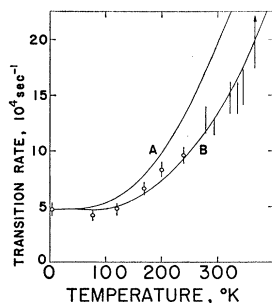
FIG. 5. $S \rightarrow R$ transition rate. Curve A represents a pure four-phonon process. Curve B represents a four-phonon process from a level thermally depopulated by another lying 150 cm^{-1} above it.

determines Δ_1, the phonon energy, since the conservation of energy demands that

$$p\Delta_1 = \Delta.$$

The solid curve in Fig. 3 represents Eq. (7) with $p=6$ and $\Delta_2=50$ cm^{-1} and using the approximate $C \rightarrow B$ energy gap of 1200 cm^{-1}; or a phonon energy of 200 cm^{-1}. Systematic deviations of the curve from the experimental points may be easily seen. However, the gross features of the temperature dependence are described by this function, and the phonon energy determined in this manner represents a good estimate, and certainly an upper limit if the phonons are of equal energy.

B. $S \rightarrow R$ Relaxation

From the quantum-efficiency and lifetime data, the $S \rightarrow R$ transition rate at 4.2°K was found to be $(4.59 \pm 0.64) \times 10^4$ sec^{-1} and $(4.91 \pm 1.10) \times 10^4$ sec^{-1} in the 1 and 10% samples, respectively. The respective results at 77°K are $(4.03 \pm 0.62) \times 10^4$ sec^{-1} and $(4.45 \pm 0.64) \times 10^4$ sec^{-1}. These rates are attributed to phonon emission for the same reasons as were the $C \rightarrow B$ rates. It may be seen from Fig. 4 that S becomes quenched at 10% concentration; the measured $S \rightarrow R$ rates, however, are independent of concentration within experimental error, and the concentration quenching is attributed to a Nd^{3+} pair process involving W, for which a near resonance exists.[14] Figure 4 also shows the S lifetimes to be independent of concentration below 1%, and the radiative rate from S is found by subtracting the $S \rightarrow R$ rates from the reciprocal lifetimes in the 1% sample. This quantity is found to be $(0.53 \pm 0.50) \times 10^4$ sec^{-1}, and is used to obtain the $S \rightarrow R$ rates from the lifetimes at other temperatures in this sample. These results are displayed in Fig. 5. Although the experimental uncertainty in the S lifetimes is large, the data clearly indicate that the $S \rightarrow R$ rate is varying more slowly with temperature than the

most slowly varying process which is possibly consistent with the phonon spectrum[15,16] of LaCl$_3$, namely, the four-phonon process involving phonons of 250 cm^{-1}. The minimum energy difference for $S \rightarrow R$ is 1004 cm^{-1}. In this case, thermal population of upper levels of S is the only reasonable explanation for this behavior. The upper levels of S possibly extend over a 200 cm^{-1} range. Equation (7) with $p=4$ and $\Delta_2=150$ cm^{-1} gives an approximate reproduction of this behavior, although the extended structure of S would predict a much more complicated temperature dependence than can be accounted for by Eq. (7).

C. Other Rates

The $D \rightarrow C$ transition rate was measured in the 10% sample at 77°K and found to be $(5.51 \pm 1.1) \times 10^3$ sec^{-1}. Taking the radiative rate of D at 0.1% concentration to be independent of temperature, the $D \rightarrow C$ spontaneous rate of $(6.3 \pm 3.1) \times 10^3$ sec^{-1} is obtained.

The concentration dependence of B lifetimes indicates that it is relaxed by a phonon process which is approximately equal to the $C \rightarrow B$ rate. The terminal state A for this process relaxes to S with a rate of the order of magnitude of 10^6 sec^{-1} or more. This, complicated by the fact that B relaxes directly to S by an ion-pair process makes it impossible to obtain the $B \rightarrow A$ spontaneous rate with the present experimental apparatus.

VIII. CONCLUSION

It has been possible to obtain multiphonon relaxation rates with no radiative or ion pair contributions. The phonon relaxation rates are comparable to radiative rates in at least sixth-order processes. It also has been possible to distinguish between the spontaneous and stimulated temperature regions and consequently to estimate the energies of the phonons involved. The Debye temperature of LaCl$_3$ is 150°K,[17] corresponding to maximum-energy acoustical phonons of 104 cm^{-1}. In addition, the acoustical part of the vibronic sidebands of LaCl$_3$:Nd^{3+} are observed to decrease at about 80 cm^{-1}.[16] Therefore, the energies of the phonons participating in the two processes studied fall in the region of the optical modes, which extend out to about 250 cm^{-1}.

In order to obtain more accurate estimates of the phonon energies or information of a more detailed nature about the process, it would be necessary to study relaxation of states with fewer and more closely spaced crystal-field components.

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[14] A recent experiment in this laboratory performed by L. A. Riseberg confirms this conclusion. Fluorescence from W to Z is observed at 4.2°K in the 10% sample when pumping S but not when pumping R. The ratio of the number of photons emitted in the $W \rightarrow Z$ fluorescence to the number emitted in $S \rightarrow W$ fluorescence is about 20.

[15] Isaac Richman, Robert A. Satten, and Eugene Y. Wong, J. Chem. Phys. 39, 1833 (1963).

[16] E. Cohen and H. W. Moos, Bull. Am. Phys. Soc. 11, 813 (1966).

[17] F. Varsanyi and J. P. Maita, Bull. Am. Phys. Soc. 10, 609 (1965).