Correlation of the Orbach Relaxation Coefficient with Optical Linewidths: LaF_3:Er^{3+}†

W. M. Yen, W. C. Scott,* and P. L. Scott‡

Department of Physics, Stanford University, Stanford, California

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We have measured the lifetime of the first excited state of trivalent erbium in lanthanum fluoride, and find, for 0.05% erbium concentration, an inverse lifetime $W = (7.0\pm0.9)\times10^{10}$ sec^{-1}. For this salt, this value is observed to be *equal* to the Orbach coefficient occurring in the spin-lattice relaxation of the ground-state doublet, recently measured by M. Schulz using electron-spin-resonance techniques. The equality of the inverse lifetime and the Orbach coefficient is in agreement with existing theory. We have also observed concentration-dependent satellite structure in the ground state of trivalent erbium in lanthanum fluoride, which we tentatively attribute to exchange-coupled pairs. We have also observed concentration-dependent broadening in the optical transitions studied; this may be evidence of energy transfer between impurity ions.

I. INTRODUCTION

IT has been shown that lattice vibrations, or phonons, play a leading role in determing the widths of sharp optical transitions,[1] and in spin-lattice (T_1) relaxation processes[2] of rare-earth impurities in solids. It has also been pointed out that correlations exist and may be made between esr T_1 studies and optical linewidth measurements.[1]

In particular, the process proposed by Orbach[3,4] to account for the rapid exponential temperature dependence observed in T_1 relaxation times of certain rare earth impurities allows us such a direct correlation. Consider the energy level diagram shown in Fig. 1, drawn for the particular case of Er^{3+} in LaF_3.[5] The three levels shown in Fig. 1(a) are all Kramers doublets. The two optical transitions originating from the metastable ($^4S_{3/2}$) state may be observed in emission as shown. While both of the lines will be broadened by lattice strains, the 5402-Å line will have an *additional* broadening because of the short lifetimes of the states c and d. These lifetimes are determined by the probability for the spontaneous emission of a phonon of energy Δ, accompanied by the transition of the Er^{3+} ion to the ground state. This latter nonradiative process is represented by W in Fig. 1(a).

Figure 1(b) shows the lower two doublets when a magnetic field is applied, and shows separately all the possible nonradiative transitions involving a single phonon of energy $\approx\Delta$. In terms of these transition probabilities, the lifetimes of the states c and d may be

written as τ_c and τ_d, where

$$\tau_c^{-1} = W_{cb} + W_{ca},$$

and   (1)

$$\tau_d^{-1} = W_{db} + W_{da}.$$

For our samples, it may be shown[6] that $W_{ca} = W_{db} \equiv W_1$, and $W_{cb} = W_{da} \equiv W_2$, so that

$$\tau_c^{-1} = \tau_d^{-1} = W_1 + W_2 \equiv W \equiv \tau^{-1}.$$ (2)

In general, $W_1 \neq W_2$.

Among the many processes allowing electron spin-lattice relaxation between the two states a and b, the

FIG. 1. (a) Relevant optical transitions of LaF_3:Er^{3+}, showing crystal field state positions. All states represented are Kramers doublets. (b) The two lowest doublets in a magnetic field, showing all possible transitions of the type W.

* NSF Predoctoral Fellow, 1964–65.
‡ Alfred P. Sloan Fellow, 1964–65.
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[2] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962), and references therein.
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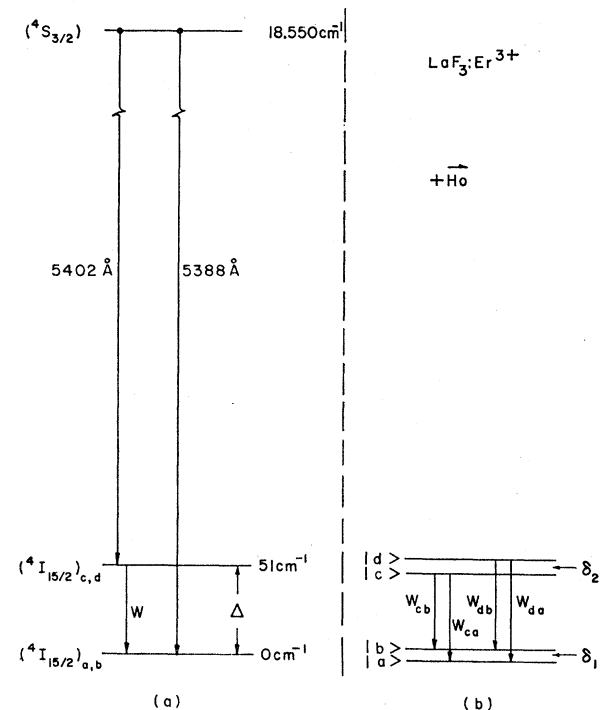[5] W. F. Krupke and J. B. Gruber, J. Chem. Phys. **39**, 1024 (1963).

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Orbach relaxation process[3] is one involving the excited states c and d, in which phonons of approximate energy Δ are absorbed and emitted. This spin-lattice relaxation process may be written[2]

$$T_1^{-1} = [4W_1W_2/(W_1+W_2)]e^{-\Delta/kT}, \qquad (3)$$

where T_1 is the spin-lattice relaxation time, and W_1 and W_2 are as defined in the preceding paragraph. If $W_1 = W_2$, then the relaxation rate becomes $T_1^{-1} = We^{-\Delta/kT}$, and the excited state inverse lifetime is $\tau^{-1} = W$. In general, however, we note that since $4W_1W_2/(W_1+W_2) \leq (W_1+W_2)$, a measurement of the Orbach relaxation coefficient gives only an upper bound on the lifetime of the excited state. In the following paragraphs, we give experimental data showing that the nonradiative lifetime gotten by comparing optical linewidths is essentially equal to the Orbach coefficient, thus implying that for our sample, $W_1 \approx W_2$. From the theoretical standpoint, we expect that $W_1 \approx W_2$. Each of these transition probabilities will be proportional to the square of a matrix element of the dynamic crystal field. Because of the large value of J for the ground multiplet, and the low crystal symmetry, there may be as many as thirteen dynamic crystal field parameters, and the wave functions a, b, c, and d will each contain many different J_z states. Hence, each of the transition probabilities will be a sum of twenty or thirty similar terms, and it is not likely that the two sums will be very different from each other. Put in another way, we say that rigorous selection rules are not likely to hold when the crystal symmetry is very low.

We have also done some preliminary studies on the concentration dependence of some spectral lines of $LaF_3:Er^{3+}$. We find a number of satellite levels accompanying the ground state of Er^{3+} which we attribute to ion pairs.[7] Some concentration broadening of the lines studied is also observed and may be an indication that energy transfer processes between impurity ions are occurring.[8]

II. EXPERIMENTAL DETAILS

Unoriented single crystals of LaF_3 doped with various concentrations (0.05% to 1%) of trivalent erbium were grown by H. Muir of Varian Associates using a Bridgman technique.

Optical linewidths were studied both in absorption and fluorescence using a high resolution 1.8-m Jarrell-Ash Ebert scanning spectrometer. Detailed accounts of experimental procedures are given elsewhere and will not be repeated here.[1,9,10]

The Er^{3+} impurity site in LaF_3 has C_{2v} symmetry[11,12]; the optical spectrum of $LaF_3:Er^{3+}$ has also been published recently.[5] It is easily shown that in this crystal configuration, all degeneracy, except the Kramers degeneracy due to time reversal symmetry, is lifted in the weak crystal field J states of the Er^{3+} ion.[13] All states of a given J manifold are thus doubly degenerate and esr T_1 measurements may be made on the ground doublet of Er^{3+} in this coordination. Such measurements have recently been made by Schulz.[14]

To obtain correlation with the Orbach coefficient the optical transitions of interest are those shown in Fig. 1(a).

At 4.2°K, the fluorescence transition at 5288 Å reabsorbs heavily and produces considerable artificial weakening and broadening[15] of the 5388-Å line even at low Er^{3+} concentrations. To circumvent this difficulty, it was necessary to study the widths of this line in absorption. The widths of the 5402-Å line were, on the other hand, studied in emission, since the $(^4I_{15/2})_{c,d}$ state, lying 51 cm^{-1} above the ground state, is essentially unpopulated at 4.2°K.

III. RESULTS

At sufficiently low temperatures, the linewidths of optical transitions show the effects of random crystal imperfections and any other, radiative or nonradiative, lifetime-limiting mechanisms affecting the interacting states.[1,9] At 4.2°K, for the 0.05% $LaF_3:Er^{3+}$ sample, we find that

$$\Delta\bar\nu_{5388} = (0.24 \pm 0.02)\text{cm}^{-1},$$

$$\Delta\bar\nu_{5402} = (0.50 \pm 0.50)\text{cm}^{-1},$$

where the measured widths are the half-widths at half-maximum.

Radiative lifetimes are normally too long to produce an observable optical breadth; thus, in our case, at 4.2°K, the optical widths of the lines studied may be written[1]

$$\Delta\bar\nu_{5388} = \Delta\bar\nu_{\text{strain}},$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (4)$

$$\Delta\bar\nu_{5402} = \Delta\bar\nu_{\text{strain}} \pm (W/2\pi c),$$

where $\Delta\bar\nu$ represent widths in energy units (cm^{-1}), and W is as defined by Eq. (2). We now make two remarks: First, we assume that lattice strains contribute equally to both lines. While it may be possible to verify this assumption by observing the static shifts of these lines under the application of a uniaxial stress, such measure-

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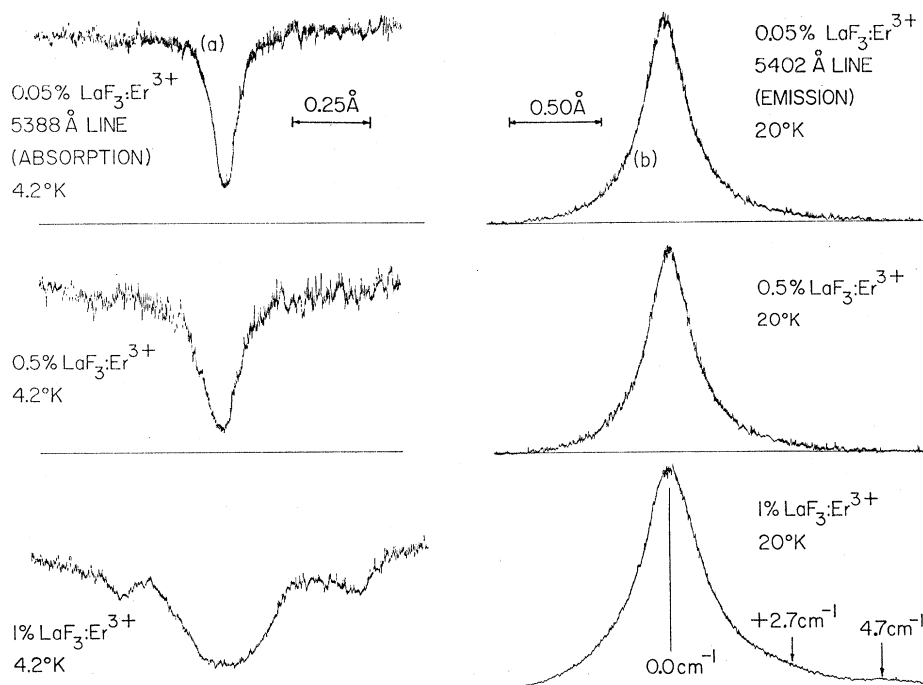[15] A. L. Schawlow, J. Appl. Phys. **33**, 395 (1962).

FIG. 2. Concentration dependence of the Er^{3+} (a) 5388-Å line in absorption and (b) 5402-Å line in emission. The 5388-Å line shows concentration broadening and some satellite structure. Asymmetries of the 5402-Å line are indicated by arrows in (b). Baselines are denoted by black lines.

ments have proved difficult, as the crystals tend to shatter rather easily. Second, we note that the second of Eqs. (4) is not strictly correct, as the strain broadening is expected to give a Gaussian line shape, while the lifetime broadening is expected to give a Lorentzian line shape. Our observations show that the 5388-Å line *is* Gaussian near the line center, but approaches a Lorentzian shape in the wings, while the 5402-Å line follows a Lorentzian shape rather closely. As the best approximation, we assume that the 5388-Å line is purely Gaussian, and use a numerical method to obtain the proper linewidth subtraction in order to obtain a value for W.[9,16] We find

$$W/2\pi c = (0.37 \pm 0.05)\text{cm}^{-1},$$

or   (5)

$$W = \tau^{-1} = (7.0 \pm 0.9) \times 10^{10} \text{ sec}^{-1}.$$

Using electron spin resonance techniques, Schulz has measured the value of the Orbach coefficient $4W_1W_2/(W_1+W_2)$ for four different crystals; he finds

$$\frac{4W_1W_2}{W_1+W_2}$$

$$= (6.8 \pm 0.2) \times 10^{10} \text{ sec}^{-1}, \quad 0.05\% \quad LaF_3:Er^{3+}$$

$$= (6.73 \pm 0.2) \times 10^{10} \text{ sec}^{-1}, \quad 0.1\%$$

$$= (6.8 \pm 0.2) \times 10^{10} \text{ sec}^{-1}, \quad 0.2\%$$

$$= (7.5 \pm 0.3) \times 10^{10} \text{ sec}^{-1}, \quad 0.5\%. \qquad (6)$$

The first and third samples listed in Eq. (6) were two of those on which our optical measurements were made. From the above data we conclude that, within the experimental error, for this sample, the Orbach coefficient is equal to the inverse lifetime of the excited state, thus implying that $W_1 \approx W_2$.

Optical measurements are made difficult at higher concentrations by concentration broadening and other effects which are dealt with below. No correlation was possible in the higher doped samples.

Even at the lowest concentrations of Er^{3+}, considerable satellite structure appears accompanying the 5388-Å line [Figs. 2(a) and 3]. No such structure accompanies the 5402-Å line, even though at higher
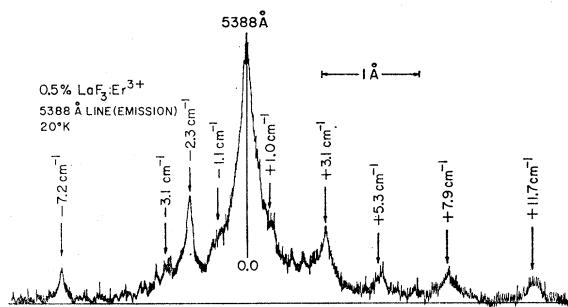

FIG. 3. The 5388-Å line of Er^{3+} shown in emission along with its satellites. Satellite positions are marked with respect to the central transition. Reabsorption broadening occurs in all lines.

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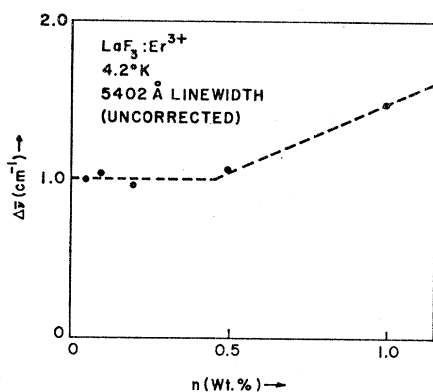17 L. F. Mollenauer and A. L. Schawlow (to be published).

FIG. 4. Uncorrected full widths of the 4.2°K 5402-Å transition plotted against nominal concentration. Broadening appears to occur at concentrations larger than 0.5% Er^{3+}.

concentrations the line becomes slightly asymmetric [Fig. 2(b)]; thus, the structure must be connected with the $(^4I_{15/2})_{a,b}$ ground state. Since the relative intensity of the 5388-Å satellites compared to the intensity of the central transition increases roughly as the square of the Er^{3+} concentration, we conclude that the structure is caused by exchange coupled pairs of Er^{3+} ions, much in the same sense as some of the satellite lines observed in Cr^{3+} in AlO_3 and MgO.[7,17,18]

The structure of the 5388-Å line is best seen in fluorescence (even though reabsorption broadening occurs)

and is shown in Fig. 3 along with the splittings from the center transition.

We find some concentration broadening of the lines studied; this can be seen in Fig. 2. The strain-uncorrected widths of the 5402-Å line as a function of concentration are plotted in Fig. 4. We believe that at higher concentrations, the broadening may be caused by resonant energy transfer between adjacent impurity ions via a multipolar interaction.[8] It is also possible that the concentration broadening may be due to local lattice strains caused by the presence of nearby impurities. Detailed studies of resonant, as well as non-resonant,[19] energy transfer processes could be carried out by considering optical linewidths, since Dexter has shown that multipolar transfer interactions yield transition probabilities which lead to observable optical broadenings.[8] Such studies are now being conducted in this laboratory.

ACKNOWLEDGMENTS

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