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Concentration dependence of residual spin-lattice relaxation in the $^4S_{3/2}$ state of Er^{3+}:LaF_3

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Spin-lattice relaxation in the lower doublet of the excited $^4S_{3/2}$ state of Er^{3+}:LaF_3 shows a weak temperature dependence for low magnetic fields and at temperatures below ≈ 2.5 K. Orbach relaxation is not yet effective in this temperature range and for magnetic fields $\lesssim 0.8$ T the residual relaxation process is field independent, which rules out the direct process as a relaxation mechanism. Er^{3+}-Er^{3+} cross relaxation can act as a relaxation process and depends on the Er^{3+} concentration. We measured the residual spin-lattice relaxation rates in the range 1.5–3 K for different Er^{3+} concentrations, using a laser spectroscopic method. No apparent correlation between the Er^{3+} concentration and the measured relaxation rates was observed. A model involving cross relaxation between Er^{3+} ions and impurities is used to fit the data.

I. INTRODUCTION

In an earlier paper[1] we reported on the spin-lattice relaxation (SLR) in the excited $^4S_{3/2}$ state of Er^{3+} in LaF_3. This state is split into two Kramers doublets separated by 31 cm^{-1}. The Kramers degeneracy is removed by an external magnetic field and SLR occurs between the two Zeeman-split levels of the lower doublet $^4S_{3/2}(1)$. It was observed[1] that for temperatures above ≈ 2.5 K the SLR time T_1 is strongly temperature dependent and the relaxation mechanism was identified as the Orbach process[2] through the upper doublet. Below 2.5 K the SLR rate weakly depends on the temperature and was fitted to the direct process.[2] However, the characteristic magnetic field dependence of the direct process was not observed for fields ≤ 0.8 T and it was concluded that there is a residual SLR process at these low fields and temperatures. In a more recent paper, Wolfrum *et al.*[3] repeated the experiment at stronger magnetic fields (> 1.3 T) and showed that the direct process dominates the relaxation within this doublet for these stronger fields. It was suggested[1] that the residual relaxation at low magnetic fields was caused by optical cross relaxation or energy transfer between the Er^{3+} ions. This suggestion was based on the observation of residual SLR rates in the $^4I_{15/2}(1)$ ground state by Schulz and Jeffries,[4] who showed that these results were consistent with single ion-pair cross relaxation.

The purpose of this investigation was to determine if the residual SLR is due to Er^{3+}-Er^{3+} interactions. Since such processes would be concentration dependent, we extended the initial T_1 measurements on a 0.3-mol% sample to different Er^{3+} concentrations. Although there is no apparent correlation between the residual relaxation rates and the concentration, the data can be fit to a two-spin-system cross-relaxation model in which the Er^{3+} ion presumably interacts with impurities.

SLR between Zeeman-split levels is normally observed by standard EPR methods.[4] Other methods, such as magnetic circular dichroic absorption (MCDA) or Faraday rotation,[5–8] involve optical means and probe ground-state SLR. Excited-state SLR has been studied with a combination of optical and microwave techniques.[9,10] With the advent of narrow-band, tunable, pulsed dye lasers it has become possible to study SLR in an excited state by purely optical means. Selective pulsed excitation creates a nonequilibrium population distribution in the Kramers doublet and the SLR is revealed by the time development of the fluorescence from the Zeeman components to the ground state. This method was used in previous work[1,3] and was used in this study.

II. EXPERIMENTAL DETAILS

The initial T_1 measurements[1] on a 0.3-mol% Er^{3+} sample were extended to concentrations of 0.05, 0.1, and 1.0 mole%. The relevant energy levels and the pumping scheme are shown in Fig. 1. The lower component of the $^4S_{3/2}(1)$ doublet was excited with a tunable, narrow-band, N_2 laser-pumped dye laser.[1] The thermalization of the doublet was measured by observing the rise in the fluorescence intensity from the other Zeeman component (line C in Fig. 1). The fluorescence was analyzed with a SPEX double monochromator and detected with an EMI 9658 photomultiplier tube. The time evolution of the fluorescence was observed with standard gated integrator techniques.[11] In the case of a weak signal (low-concentration samples), a photon-counting system was used, which stored the data in an on-line computer.

All T_1 measurements were carried out with a magnetic field of 0.8 T applied along the *c* axis of the samples. The resulting four lines *A*, *B*, *C*, *D* in Fig. 1 were easily resolved with this field. The sample was mounted in an immersion cryostat, in which the temperature was varied between 1.5 and 3 K. In this temperature region the Orbach process does not dominate the thermalization process and the residual relaxation can be studied in detail.

III. THEORETICAL REVIEW

A. Single-ion SLR

Pumping into level *a* of the $^4S_{3/2}(1)$ doublet and subsequent thermalization causes the population of level *b* to increase (Fig. 1). The fluorescence intensity from level *b* is proportional to the population of level $b(n_b)$ where[1]

$$n_b = A\exp(-t/\tau_R)[1-\exp(-t/T_1)] \ , \qquad (1)$$

with τ_R the radiative lifetime, T_1 the SLR time, and *A* a constant. One can therefore determine T_1 by measuring the time evolution of the fluorescence from level *b*; τ_R is known from the decay of the luminescence from level *a* (lines *B* and *D* in Fig. 1). The relevant SLR processes in this case are the direct and the Orbach process.[2] For the direct process the relaxation rate is given by

$$T_1^{-1} \sim B^5 \coth(\delta/2kT) \ , \qquad (2)$$

where *B* is the applied magnetic field and $\delta = g\mu_B B$ is the splitting of the $^4S_{3/2}(1)$ doublet. This relaxation process involves the absorption (or emission) of a single phonon of energy δ. For the Orbach process,

$$T_1^{-1} \sim \exp(-\Delta/kT) \ , \qquad (3)$$

where Δ (31 cm^{-1}) is the crystal-field splitting between the $^4S_{3/2}(1)$ and $^4S_{3/2}(2)$ doublets. In this process absorption of a phonon raises the ion from level *a* to level *c* and a phonon is emitted, which takes the ion to level *b*.

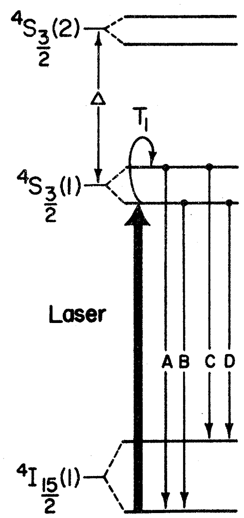

FIG. 1. Spin-lattice relaxation in the Zeeman-split $^4S_{3/2}(1)$ state. Level *a* is excited with a narrow-band laser and thermalization is observed through the rise in fluorescence from the conjugate component (lines *A* and *C*). The other Stark component of the $^4S_{3/2}$ manifold is at an energy Δ above the $^4S_{3/2}(1)$ level.

B. Cross relaxation

At low temperatures where the Orbach process is not yet effective, one expects the relaxation of the $^4S_{3/2}(1)$ doublet to be caused by the direct process. As can be seen from Eq. (2), this process has a weak temperature dependence. Although in the 0.3-mol% sample the residual relaxation data were fitted to a $\coth(\delta/2kT)$ curve,[1] the strong magnetic field dependence was not observed. This field dependence is a much stronger test for the direct process[7,12] and it is therefore ruled out that in our low-field experiment ($B = 0.8$ T) the residual relaxation in the 0.3-mol% sample was caused by the direct process. Such anomalous behavior at low fields is not unusual; Panepucci and Mollenauer[6] observed this phenomenon in *F* centers in alkali halides, as did Sabisky and Anderson[7] in Tm^{2+}: $\mathrm{SrF_2}$. Schulz and Jeffries[4] measured residual SLR rates in the $^4I_{15/2}(1)$ (ground) state of Er^{3+}:$\mathrm{LaF_3}$ which were strongly dependent on the concentration. These effects are ascribed to cross relaxation between the single ion and pairs or clusters of Er^{3+} ions or impurities. We will use the notation of Larson and Jeffries[13] to describe this cross-relaxation model.

Consider the two-spin systems shown in Fig. 2. The *a* spins represent the $^4S_{3/2}(1)$ doublet and the *b* spins represent a doublet of some impurity or pair, either in the ground state or in an excited state at an energy $\Delta' \gtrsim kT$ above the ground state. The splitting of the two doublets is the same, so that energy is conserved when both carry out a spin flip. The rate equations for the two-spin system are[4,13,14]

$$\frac{dn_a}{dt} = \omega(-N_b n_a + N_a n_b) - (n_a - n_{a0})/T_{1a} \ , \qquad (4)$$

$$\frac{dn_b}{dt} = \omega(-N_a n_b + N_b n_a) - (n_b - n_{b0})/T_{1b} \ , \qquad (5)$$

where T_{1a} and T_{1b} are the T_1 times of the *a* and *b* spins, respectively, ω is the sum over the probabilities of mutual spin flips between the *a* and *b* spins; n_{a0} and n_{b0} are equilibrium population differences, and N_a and N_b are the total number of

a and b spins.[13] Solving these equations[14] in the approximation $N_a \gg N_b$ yields the relevant time constant λ^- for the rise in the luminescence from level b:

$$\lambda^- \approx \frac{1}{T_{1a}} + \frac{\frac{1}{T_{12}}\left(\frac{1}{T_{1b}} - \frac{1}{T_{1a}}\right)}{\frac{1}{T_{12}} + \frac{1}{T_{1b}} - \frac{1}{T_{1a}}} \frac{N_b}{N_a} , \tag{6}$$

where T_{12} is the cross-relaxation time which is related to ω. This decay rate can be simplified in the following cases.

(i) Strong cross relaxation between the two spin systems[4]:

$$\lambda^- \approx \frac{N_b}{N_a} \frac{1}{T_{1b}} . \tag{7}$$

Schulz and Jeffries considered the N_b population to be the excited-state doublet at an energy Δ' above the ground state. Hence N_b in the above expression should be replaced by $N_b/[1+\exp(\Delta'/kT)]$, where N_b is now the total concentration of b spins. If the b-spin doublet relaxes by the "inverse" Orbach process,[15]

$$T_{1b}^{-1} \sim [1-\exp(-\Delta'/kT)]^{-1} , \tag{8}$$

the expression for λ^- [Eq. (7)] becomes

$$\lambda^- \sim \operatorname{csch}(\Delta'/kT) . \tag{9}$$

(ii) Strong SLR of the excited state b spins:

$$\lambda^- \approx \frac{N_b}{N_a} \frac{1}{T_{12}} . \tag{10}$$

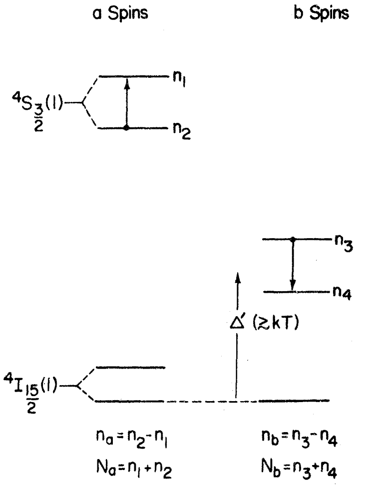

FIG. 2. Cross relaxation between ions in the $^4S_{3/2}(1)$ doublet (a spins) and impurity ions or clusters in an excited state (b spins); n_a and n_b represent population differences between the two components in each doublet. N_a and N_b are the total populations in each doublet.

Here N_b has again to be replaced by $N_b/[1+\exp(\Delta'/kT)]$. For a temperature-independent T_{12}, the time constant becomes

$$\lambda^- \sim [1+\exp(\Delta'/kT)]^{-1} . \tag{11}$$

If the b spins represent a ground-state doublet, Eq. (10) becomes temperature independent, since in that case N_b becomes the *total* concentration of impurities, pairs, or clusters. Equations (9)–(11) describe the temperature dependence of the cross-relaxation processes in the various regimes and will be used to fit the residual SLR rates.

IV. RESULTS

A. Residual relaxation versus direct process

As mentioned before, the relaxation rate of the 0.3-mol% sample did not show the magnetic field dependence of the direct process over the temperature range 1.5–2.5 K. Wolfrum[3] *et al.* measured in a 0.05-mol% sample at 1.8 K a direct relaxation rate of 2.8×10^3 s^{-1} at a field of 1.3 T. Writing the direct process rate as

$$W = A_1 B^5 \coth(\delta/2kT) ,$$

we find, using the above numbers, the constant $A_1 \approx 655$ T^{-5} s^{-1}. Assuming this value for A_1, the direct relaxation rate at $B=0.8$ T becomes $W_{0.8\,\mathrm{T}} \approx 240$ s^{-1}. At 1.95 K and $B=0.8$ T a rate of $\approx 2.8\times10^3$ s^{-1} was observed in the 0.3-mol% sample.[1] This means that for lower-field values, the direct process is obscured by the "residual" process. Therefore, the anomalous behavior of the 0.3-mol% sample is not inconsistent with the observation of the direct process by Wolfrum[3] *et al.* This is confirmed by the rate $T_1^{-1} \approx 1.5\times10^3$ s^{-1} at 1.86 K and 0.8 T for our 0.05-mol% samples. This value is still larger than the direct process would be expected to exhibit at 0.8 T if we use Wolfrum's numbers.

B. Concentration dependence

We measured the T_1 times for the 0.05-, 0.1-, and 1.0-mol% sample at $B=0.8$ T and over the temperature range 1.5 K $< T <$ 3 K. The results, including previously[1] taken data for the 0.3-mol% concentration, are shown in Fig. 3. There is no apparent correlation between the Er^{3+} concentration and the observed rates. We checked, therefore, the concentrations of the samples by a measurement of the integrated absorption spectrum.[16] We found that the relative concentrations of the 0.05-, 0.1-, 0.3-, and 1.0-mol% samples were actually 0.02, 0.03, 0.07, and 0.42 mole%. All four concentrations show an Orbach process which begins to dominate at ≈ 2.5 K. This Orbach pro-

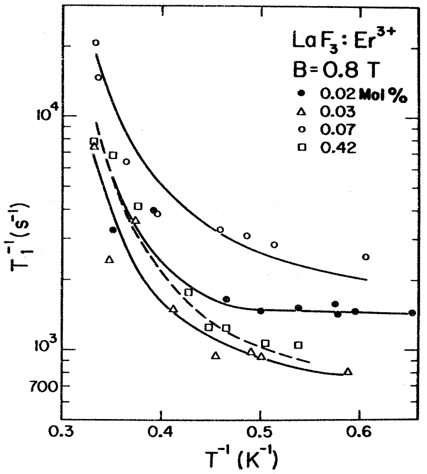

FIG. 3. Measured values of $1/T_1$ as a function of temperature for four Er^{3+} concentrations. The bottom solid line is a fit to the 0.03-mol% data, the dashed line to the 0.42-mol% data, and the two upper solid lines are the fit to, respectively, the 0.07-mol% and the 0.02-mol% data.

cess is, within the variation of the data points, independent of the concentration. This is to be expected,[2] since this relaxation mechanism is a single-ion process and this was also observed in ground-state SLR of Er^{3+}:LaF_3.[4] An attempt was made to fit the data to expressions consisting of a combination of Eqs. (9) and (11). These represent, respectively, strong cross relaxation between Er^{3+} ions and some impurity or Er^{3+} ion pairs or clusters, as well as strong SLR of the impurity. A combination of these processes was observed in ground-state SLR in Yb^{3+}:LaF_3.[4] A temperature-independent term for the case of strong SLR of an impurity ion in its ground state [Eq. (10)] can also be included. No direct-process term $\sim\coth(\delta/2kT)$ was used in the curve fitting since it was shown that at this magnetic field ($B=0.8$ T), the direct process rate is negligible compared to the observed rates.

The SLR data are best fitted by

$$T_1^{-1}=A[1+\exp(\Delta/T)]^{-1}+B\,\mathrm{csch}(\Delta'/T)+C\exp(-44.6/T)+D\ , \qquad (12)$$

where the values of the parameters A, B, C, D, Δ, and Δ' for the four concentrations are shown in Table I. Due to the scatter in the data points, one must be careful in interpreting these results in terms of the responsible cross-relaxation mechanism. The 0.02-mol%-sample data can equally well be fitted to a term $A\,\mathrm{csch}(5.5/T)+B+C\exp(-44.6/T)$ where A, B, and C are constants and the 0.03-mol% data can be fitted to a term $\sim\mathrm{csch}(3.5/T)$. In the latter case this would mean that strong cross relaxation to an impurity or a pair of Er^{3+} ions causes the residual relaxation process, rather than strong SLR of the impurity or the pair in an excited state 3.5 K above the ground state. Similar problems were encountered by Schulz and Jeffries[4] in fitting ground-state SLR data in Er^{3+}:LaF_3. The static and dynamical spectral properties of the main ${}^4S_{3/2}(1)\rightarrow{}^4I_{15/2}(1)$ line were examined for the presence of exchange-coupled Er^{3+} pairs or clusters, which may cross relax with the single ions. An excitation scan of the 0.07-mol% sample showed the main line to be inhomogeneously broadened with a Gaussian profile (full width at half maximum $\approx 0.17\ \mathrm{cm}^{-1}$). No asymmetries were found in the line shape, which may be caused by satellites, as was found[17] in Pr^{3+}:LaF_3. Only the 0.42-mol% sample had a strong satellite structure around the main transition, which may indicate the existence of Er^{3+} pairs. Hence, we have no evidence of coupled Er^{3+}-Er^{3+} pairs for the used concentrations, as was observed by Yen[18] *et al.*

Ion-ion interaction in the form of self quenching may result at these low temperatures in a nonexponential fluorescence decay[19] due to cross relaxation between an excited and an unexcited ion. This was not observed in any concentration and the radiative lifetime is the same for all concentrations. These results suggest strongly that the Er^{3+} ion-ion interaction (in the form of energy transfer or cross relaxation) is negligible in these low concentrations. Consequently, there is no indication of pairs or clusters of Er^{3+} ions with which the single ions may cross relax in the SLR process. It is reasonable then to explain the residual relaxation by cross relaxation between

TABLE I. Measured parameters A, B, C, D, Δ, Δ' in the SLR rate $T_1^{-1}=A[1+\exp(\Delta/T)]^{-1}+B\,\mathrm{csch}(\Delta'/T)+C\exp(-44.6/T)+D$ for different Er^{3+} concentrations in LaF_3:Er^{3+}.

Concentration (%)	A ($10^4\ s^{-1}$)	B ($10^4\ s^{-1}$)	C ($10^{11}\ s^{-1}$)	D (s^{-1})	Δ (K)	Δ' (K)
0.02	0.21		0.24	860	1.6	
0.03	0.63		0.14		3.3	
0.07	1.50		0.42		3.0	
0.42		0.53	0.24			3.3

Er^{3+} ions and impurities, either in the ground or in an excited state and not to Er^{3+} ion-ion interactions. The absence of a correlation between the Er^{3+} concentration and the observed rates can be attributed to a varying concentration of these impurities in the samples.

V. CONCLUSION

The process responsible for the thermalization within the $^4S_{3/2}(1)$ doublet is a concentration-independent Orbach relaxation through the upper doublet of the $^4S_{3/2}$ manifold above 2.5–3 K. At lower temperatures and at high magnetic fields (1.3–7.6 T) Wolfrum[3] *et al.* demonstrated the characteristic field dependence of the direct process. Using their rate values we showed that the direct process, at $B = 0.8$ T, is about 10 times slower than the observed residual relaxation rate. Although there is no correlation between the Er^{3+} concentration and the residual relaxation rates, the data were fit to a cross-relaxation model. The insensitivity of the data to the different fitting functions makes an interpretation of the exact nature of the responsible interaction difficult. There is no evidence for the existence of Er^{3+} pairs or clusters, which may cross relax with the single ions and cause the residual SLR. The anomalous behavior of the SLR rate at low magnetic fields (where the direct process is not effective) is therefore not due to an Er^{3+}-Er^{3+} ion interaction, but is apparently caused by cross relaxation between an Er^{3+} ion and impurities in the samples.

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