High-field studies of spin-lattice relaxation processes in an optically excited Kramers doublet of LaF₃:Er³⁺

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Spin-lattice relaxation by the direct process and by the Orbach process has been studied for the lower Kramers doublet $S(1)$ of the optically excited $^4S_{3/2}$ quartet state of Er³⁺ ions in LaF₃ up to a magnetic field $B = 8$ T. The direct process dominates at a crystal temperature of 2 K; this is concluded from a B^5 dependence of the relaxation rate found for a very large range of the magnetic field. At 4.2 K, on the other hand, an Orbach process via the upper Kramers doublet $S(2)$, which is at zero field 30 cm⁻¹ above $S(1)$, gives a strong contribution to the relaxation rate. We found evidence that the Orbach relaxation rate increases with the magnetic field strength. This observation is explained by the magnetic field dependence of the energy separations between the $S(1)$ and $S(2)$ Zeeman levels.

I. INTRODUCTION

The spin-lattice relaxation (SLR) in the lowest Kramers doublet $S(1)$ of the metastable $^4S_{3/2}$ excited state of LaF₃:Er³⁺ has recently been the subject of several studies. It has been reported[1,2] by Broer and co-workers that SLR at magnetic fields B below 1 T and at low crystal temperature $(T < 2$ K) can be due to a cross-relaxation process caused by unknown impurities. Wolfrum et al.[3] have investigated SLR at magnetic fields $B > 1$ T and observed, at $T = 2$ K, a B^5 dependence for the SLR rate which shows that the SLR at high magnetic fields is dominated by a direct process. Furthermore, it has been found by Broer and co-workers[1,2] that, at temperatures above 3 K, SLR by an Orbach process occurs. In this process the second Kramers doublet $S(2)$ of the $^4S_{3/2}$ state of the Er³⁺ ion is involved. At zero magnetic field the $S(2)$ doublet is located about 30 cm⁻¹ above the $S(1)$ doublet.

In this paper we report an extended study in which we have determined SLR rates over a very large range of the magnetic field. We will show that in our crystal the SLR at $T \leq 2$ K, measured from 8 down to 0.5 T, is mainly due to the direct process and that no cross relaxation is observable. Our results obtained for crystal temperatures up to 4.2 K indicate that the SLR rate for the Orbach process increases with the magnetic field. This is to our knowledge the first experiment which shows a clear field dependence for the Orbach process.

We like to point out that these investigations are of interest not only because various SLR processes can be studied for the excited Er³⁺ ion in LaF₃, but

also because this system is of importance for other studies. Recently, it has been shown that the direct-process relaxation is responsible for the optical dephasing of the $^4S_{3/2}$ excitation at magnetic fields higher than 2 T.[4] The Kramers doublet $S(1)$ has a relatively large effective g value (5.3 for $B||c$, see also Table I) and therefore, the Zeeman splitting can reach large values at high magnetic fields. The doublet can therefore be used for the detection of high-frequency phonons up to 1 THz.[5] The system should also be suitable for tunable phonon generation: Sox et al.[6] reported evidence for stimulated phonon emission within the $S(1)$ Kramers doublet; it was found that the SLR rate at a magnetic field of 2 T becomes faster by a factor of 5 if the upper level of the doublet is optically pumped to a high population by strong laser-pulse excitation.[6]

II. EXPERIMENT

Our measurements were performed on crystals from Optovac, Inc. having a concentration of Er³⁺ ions of 0.3 mol%. We will compare the new results with those obtained in a previous experiment for a crystal containing 0.05 mol% Er³⁺ ions.[3] We have not determined the absolute concentration; however, by an absorption experiment with an optical spectrometer at a crystal temperature of 77 K we confirmed that the Er³⁺ concentration differs at least by a factor of 4.

SLR rates were determined using an optical method. Figure 1 gives the scheme of the relevant Er³⁺ energy levels. The crystals were oriented with the c axis parallel to the direction of the magnetic
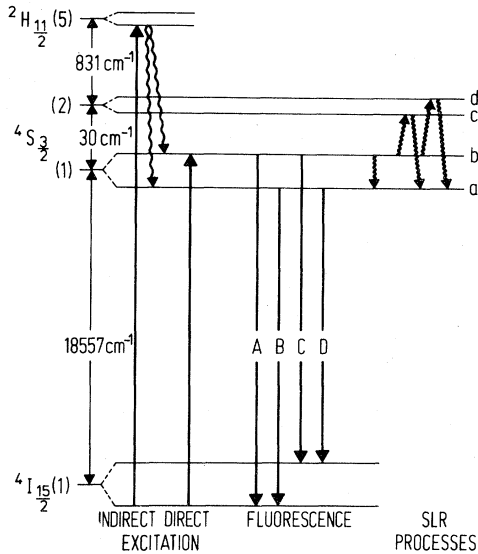

FIG. 1. Method for the measurement of spin-lattice relaxation rates in the $^4S_{3/2}(1)$ state of Er^{3+} ions in LaF_3 crystals. Level b is populated by excitation with radiation of a pulsed-dye laser either directly (through transition A) or indirectly (via the $^2H_{11/2}$ manifold). SLR is observed through the decay of the fluorescence on transition C.

TABLE I. Zeeman splitting (in cm^{-1}/T) of several Kramers doublets for $B||c$.

State	This work	Other values
$^4S_{3/2}(2)$	0.5 ± 0.2	0.6^a
$^4S_{3/2}(1)$	2.1 ± 0.2	2.5^a
$^4I_{15/2}(2)$	3.0 ± 0.2	
$^4I_{15/2}(1)$	3.5 ± 0.2	3.6^b
		4.4^a

^{a}From Ref. 2.
^{b}From Ref. 7.

field. In this orientation the six possible Er^{3+} positions in the crystal unit cell are magnetically equivalent.[7] Zeeman-splitting factors for several Kramers doublets were determined from excitation spectra and are shown in Table I, together with results from previous experiments.

SLR rates were obtained by monitoring the fluorescence decay of the upper Zeeman component of the $S(1)$ doublet after pulsed excitation with a nitrogen-laser-pumped dye laser. A nonequilibrium population of this Zeeman component was obtained either by indirect pumping via the $^2H_{11/2}$ manifold or by direct excitation via transition A, while the population decay was measured by observing fluorescence on line C (Fig. 1). From the decay time τ of the fluorescence on line C the SLR rate was determined. At high magnetic fields level b decays mainly by SLR and therefore τ is a direct measure of the SLR time. At low fields where the SLR is slow and comparable with the radiative decay of level b the situation is more complicated (see Sec. III).

With indirect excitation one takes advantage of the larger absorption cross section of some of the $^2H_{11/2}$ states compared to that of the $^4S_{3/2}(1)$ doublet.[8] The electronic transition from the $^2H_{11/2}$ states to the $^4S_{3/2}(1)$ doublet has been found to be fast enough (<30 ns) not to influence the observation of the SLR.[3] Since indirect excitation leads to approximately equal initial populations of both $S(1)$ Zee-

man components, the observation of SLR is limited to large Zeeman splittings for which the quasiequilibrium populations, established by the relaxation processes, differ significantly from equal populations. At small magnetic fields (below 1.3 T) the $S(1)$ doublet was directly excited into the upper Zeeman component. Using direct excitation we were able to measure SLR at $T=2$ K down to magnetic fields of about 0.5 T. At lower fields the lifetime of the $S(1)$ levels is mainly determined by radiative decay to the $^4I_{15/2}$ ground-state Zeeman levels. On the high-field side the observation of SLR rates was limited to about 8 T due to the time resolution (about 2×10^{-8} s) of our detection electronics, which consisted of a transient recorder (Biomation 6500) in combination with a signal averager (Ortec Ultima II).[3]

We like to mention here that we also performed measurements using the method of Broer et al.[1] in which the $S(1)$ doublet is optically pumped into the lower Zeeman level (line B) and the increase in fluorescence from the upper Zeeman level (line C) due to SLR is monitored. We found the same SLR rates as measured with the methods described above. We can therefore conclude that the experimental results do not depend on the techniques used in the different experiments.

III. SLR BY THE DIRECT PROCESS

Experimental results of SLR measurements at $T=2$ K are shown in Fig. 2. For fields larger than 2 T the SLR rate w_1 is directly given by the fluorescence decay rate τ^{-1}. For smaller fields a correction was made taking into account the finite radiative lifetime $\tau_R=(1.30\pm0.05)\times10^{-3}$ s of the $^4S_{3/2}$ levels. Below 2 T w_1 is determined from the relation

$$w_1=\tau^{-1}-\tau_R^{-1} . \qquad (1)$$

Equation (1) does not account for the optical decay of the lower Zeeman level. It can be shown, however, that within our experimental errors Eq. (1) can be
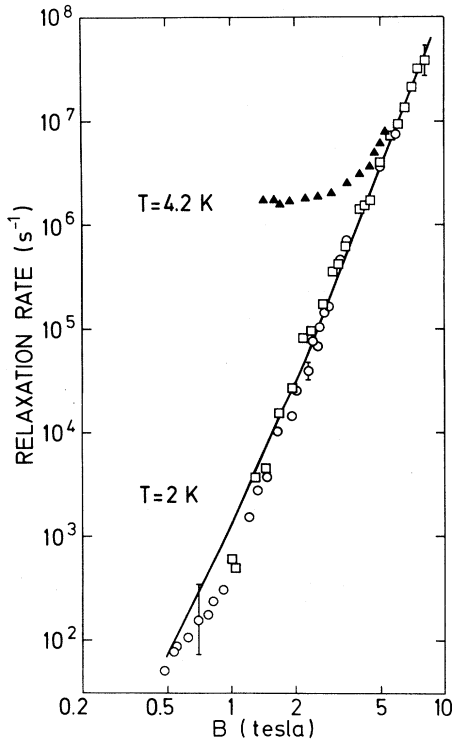
FIG. 2. SLR rates at crystal temperatures of 2 K (lower curve) and 4.2 K (upper curve, triangles). The SLR rates at 2 K are obtained by direct excitation (circles) or by indirect excitation (squares), respectively (see text). The solid line corresponds to the magnetic field dependence for the direct-process relaxation according to Eq. (2). The strong increase of the SLR rates between 2 and 4.2 K is due to an Orbach relaxation process.

used down to fields of 0.5 T.

We find that the experimental SLR rate w_1 at 2 K can be described in the whole region of the magnetic field by the expression

$$w_1 = AB^5 \coth\left[\frac{\delta_1}{2kT}\right] . \tag{2}$$

This dependence is characteristic for the direct-process relaxation in a Kramers doublet,[9] where $w_1^{-1} = T_1$ is the lifetime for SLR by the direct process. In Eq. (2) A is a constant, $\delta_1 = g\mu_B B$ is the Zeeman splitting of the $S(1)$ doublet, g is the effective g value for $B||c$, and μ_B is the Bohr magneton.

The solid line in Fig. 2 gives the theoretical slope according to Eq. (2). The good agreement with the experimental values, over a range of almost six decades, gives clear evidence that the SLR at 2 K and below is mainly determined by the direct process. We note that in our field range the acoustic phonons emitted (and absorbed) in the direct-process relaxation have frequencies ranging from 30 to 500 GHz.

The constant A in Eq. (1) is determined by $A = 860 \pm 100$ s^{-1}T^{-5}. In our earlier experiment[3] with a weakly doped crystal A was 900 ± 100 s^{-1}T^{-5}, which shows that there exists no concentration dependence of the direct-process relaxation for crystals containing less than 0.5 mol% Er^{3+} ions. We found no indication of cross-relaxation processes in our crystals. These processes, which have been found to be responsible for weakly field-dependent relaxation rates in the order of 10^3 s^{-1} for the crystals investigated by Broer and co-workers,[1,2] should be easily detectable in our experiment as we can follow the direct process down to relaxation rates below 10^2 s^{-1} (Fig. 2). Therefore, our experiment gives additional evidence that cross relaxation observed by Broer et al. does not occur between Er^{3+} ions, but, is rather due to (unknown) impurities, as already discussed by Broer et al. We conclude that the concentration of such impurities in our crystals is very small.

IV. SLR BY THE ORBACH PROCESS

In the preceding section we discussed the SLR at 2 K. In this section we present results of experiments at higher crystal temperatures. SLR rates measured at 4.2 K using direct excitation via transition A (Fig. 1) are shown by the triangles in Fig. 2. At a magnetic field of 2 T, for instance, an increase in the crystal temperature by only 2 K leads to an increase of the SLR rate by 2 orders of magnitude. The temperature-dependent portion of the SLR rate is attributed to an Orbach relaxation process.[1,2] Figure 3 shows in a semilogarithmic plot the additional SLR rate w_0 vs $1/T$ at a constant magnetic field of
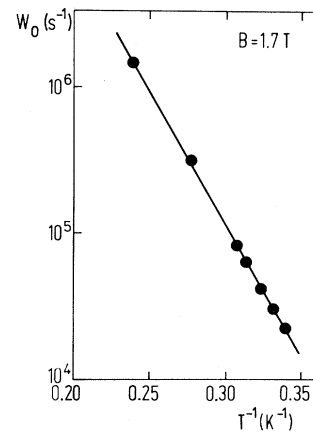

FIG. 3. Temperature-dependent portion w_0 of the SLR rate measured at a magnetic field of 1.7 T. The rate w_0 varies as expected for an Orbach process according to Eq. (3).

1.7 T. The experimental data can be described by the expression

$$w_0 = C \exp\left[-\frac{\Delta}{kT}\right], \qquad (3)$$

which is expected for an Orbach relaxation process.[9] From Fig. 3 we obtain $\Delta = 29.5 \pm 1$ cm^{-1} which is in good agreement with the optically observed energy splitting between the two Kramers doublets $S(1)$ and $S(2)$ of the $^4S_{3/2}$ state (Fig. 1). Our experiment therefore confirms the results of Broer *et al.*[1] that the Orbach SLR process occurs via the upper Kramers doublet $S(2)$. The constant C is determined from Fig. 3 to be 3.6×10^{10} s^{-1}. From previous experiments by Broer and Yen[2] C has been found to lie in the range 1.4×10^{10} to 4.2×10^{10} s^{-1}.

We were able to determine the Orbach relaxation rate up to fields of 5.4 T. In this high-field range the Zeeman splittings δ_1 and δ_2 are no longer negligible compared to, respectively, the crystal-field splitting between $S(1)$ and $S(2)$, and the value of kT. Therefore, the Orbach SLR rate can become dependent on the strength of the magnetic field.

In the following we will discuss this question in more detail. The relaxation pathway is illustrated in Fig. 4. From level b to a the relaxation occurs in two subsequent steps: from level b to either c or d by the absorption of a resonant phonon and from there to a by phonon emission. For the backward transition a to b the step sequence is reversed. For our experimental conditions ($\Delta \gg kT$, populations $N_c, N_d \ll N_a, N_b$) the Orbach relaxation process can be described by a single exponential decay[10] with a rate w_0 given by

$$w_0 = \frac{w_{bc}w_{ca} + w_{ac}w_{cb}}{w_{cb} + w_{ca}} + \frac{w_{bd}w_{da} + w_{ad}w_{db}}{w_{db} + w_{da}}, \qquad (4)$$

with w_{ij} describing the one-phonon SLR rates between the levels i and j, given by

$$w_{ij} = M_{ij}E_{ij}^3\bar{n}_{ij}$$

and $\qquad (5)$

$$w_{ji} = M_{ij}E_{ij}^3(\bar{n}_{ij} + 1) .$$

M_{ij} is a measure of the matrix element for the transition from i to j, E_{ij} is the energy separation between the levels i and j, and $\bar{n}_{ij}$ is the thermal phonon occupation number for phonons of energy E_{ij}, where i represents the levels a and b and j the levels c and d, respectively.

The transitions between a and d and between b and c involve a larger spin flip ($\Delta m = 2$ transition)
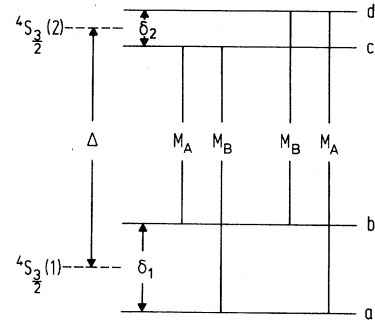

FIG. 4. Schematics of the Orbach relaxation pathway within the Kramers doublets of the $^4S_{3/2}$ excited state. Δ is approximately 30 cm^{-1}. δ_1 and δ_2 are the Zeeman splittings of the $S(1)$ and $S(2)$ doublet, respectively. M_A and M_B refer to matrix elements for phonon emission from $S(2)$ to $S(1)$ with small spin change ($\Delta m = 1$) and large spin change ($\Delta m = 2$), respectively.

than the transitions between a and c or b and d ($\Delta m = 1$ transition). It is reasonable to assume[1] that

$$M_{ad} = M_{bc} = M_A \quad \text{and} \quad M_{ac} = M_{bd} = M_B .$$

With the approximations

$$\frac{\bar{n}_{ij}}{\bar{n}_{ij} + 1} \approx \bar{n}_{ij} \quad \text{for } \bar{n}_{ij} \ll 1$$

and

$$E_{ij}^3 \approx \Delta^3 \left[1 \pm \frac{3(\delta_1 \pm \delta_2)}{2\Delta}\right],$$

it follows from Eq. (4) for the Orbach SLR rate that

$$w_0 = \alpha(\beta, T)\frac{4M_A M_B}{M_A + M_B}\Delta^3 \exp\left[-\frac{\Delta}{kT}\right] \qquad (6)$$

with

$$\alpha(B, T) = \left[\left[\cosh\frac{\delta_2}{2kT}\right] - \frac{3}{2\Delta}\left[\delta_2 + \delta_1\frac{M_B - M_A}{M_B + M_A}\right]\right.$$

$$\left. \times \sinh\frac{\delta_2}{2kT}\right]\cosh\frac{\delta_1}{2kT} .$$

$$(7)$$

The variation of w_0 with the magnetic field is given by the factor $\alpha(B, T)$. For small magnetic fields, i.e., for Zeeman splittings $\delta_1, \delta_2 \ll kT$, $\alpha(B, T)$ becomes equal to unity leading to an Orbach relaxa-

tion rate which is independent of the field strength. For Zeeman splittings comparable to kT, however, $\alpha(B,T)$ will increase leading to an increase of w_0 at large magnetic fields.

From Eq. (7) it can be seen that $\alpha(B,T)$ changes when M_A and M_B are exchanged. Broer et al.[1] found that M_A and M_B differ by about an order of magnitude. They determined the homogeneous optical linewidth of the $^4I_{15/2}(1) \rightarrow {}^4S_{3/2}(2)$ transition and obtained from the linewidth a $S(2) \rightarrow S(1)$ relaxation rate of 1.2×10^{11} s^{-1}. This value is determined by the larger matrix element, either M_A or M_B, while the Orbach relaxation rate is determined by the smaller matrix element. Comparing the $S(2)$ decay rate with the Orbach relaxation rate we find from Eqs. (3) and (6) that M_A and M_B differ by a factor of 12. It is not clear, however, whether M_A is larger than M_B or vice versa. Since according to Eq. (7) one expects different magnetic field dependences of w_0 in case of $M_A \gg M_B$ than in case of $M_A \ll M_B$, a measurement of $w_0(B)$ could allow us to distinguish between the two cases.

The experimental result for the magnetic field dependence of w_0 obtained at 4.2 K is shown in Fig. 5. Between 2 and 5.4 T w_0 increases by more than a factor of 2. We have performed a numerical calculation of w_0 at $T = 4.2$ K using Eq. (4). According to the experimental results we have chosen the energy splitting at zero magnetic field $\Delta = 29.5$ cm^{-1}, and the Zeeman splittings 2.0 cm^{-1}/T for the $S(1)$ state and 0.5 cm^{-1}/T for the $S(2)$ state. M_A and M_A/M_B are adjustable parameters. In Fig. 5 two calculations are shown for $M_A = M_B/12$ and $M_A = 12M_B$, respectively.

The calculated curve for $M_A \ll M_B$ can reasonably describe the experimental result. The curve for $M_A \gg M_B$ is just outside the region of the experimental data points. Our analysis gives, therefore,
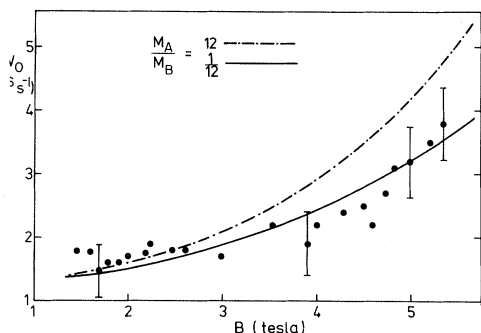

FIG. 5. Magnetic field dependence of the rate w_0 for the Orbach relaxation process at a temperature of 4.2 K. The curves are obtained from Eq. (4) for $M_A/M_B = \frac{1}{12}$ (solid line) and $M_A/M_B = 12$ (dashed line).

evidence that the relaxation between the $S(2)$ and $S(1)$ doublets of the $^4S_{3/2}$ excited state of Er^{3+} occurs with a higher probability by small spin-flip $(\Delta m = 1)$ transitions than by larger spin-flip transitions $(\Delta m = 2)$. We point out that the observed SLR processes in LaF$_3$:Er^{3+} are due to spin-orbit interaction mechanisms in the Er^{3+} ion. Our result gives, therefore, experimental evidence that the relaxation which is caused by spin-orbit interaction behaves differently than that caused by spin-spin interaction: It has been found that in triplet states of organic molecular crystals, where spin-spin interaction dominates, the matrix elements for $\Delta m = 1$ and 2 SLR transitions have comparable magnitude (at equal energy separation),[11] which is different from our result for LaF$_3$:Er^{3+}.

V. CONCLUSION

With the use of an optical method, spin-lattice relaxation has been studied for the Kramers doublet $S(1)$ of the $^4S_{3/2}$ quartet state of excited Er^{3+} ions in LaF$_3$. While Broer and co-workers[1,2] have found that the spin-lattice relaxation at 2 K and at magnetic fields below 1 T is due to a cross-relaxation process in which unknown impurities are involved, we have found that this cross relaxation does not occur in our crystals. Therefore, it was possible to observe the direct-process relaxation and the Orbach relaxation processes over a very large range of magnetic fields.

Within the range of fields in our experiment (0.5–8 T) we found that the relaxation rate at 2 K increases by 6 orders of magnitude and that the rate is proportional to B^5 as expected from theory for a direct-process relaxation in a Kramers doublet. Furthermore, we found by SLR measurements at 4.2 K that the rate for the Orbach relaxation, which occurs via the $S(2)$ Kramers doublet, depends on the magnetic field strength. The observed dependence can be explained by the change of the energy separations between the $S(1)$ levels and the $S(2)$ levels due to the large Zeeman splitting of these levels at high magnetic fields. From the field dependence we obtain information about transition probabilities for small $(\Delta m = 1)$ spin-flip and large $(\Delta m = 2)$ spin-flip transitions.

ACKNOWLEDGMENTS

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