Optical detection of cross relaxation between rare-earth ions in lanthanum trichloride crystals

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The dynamics of relaxation and interionic energy-transfer processes for Nd^{3+} and Er^{3+} ions, dilutely cosubstituted at La^{3+} sites in $LaCl_3$ single crystals, have been investigated in a series of optical-magnetic double-resonance experiments. These processes have been studied by measuring the effects of electron-paramagnetic-resonance absorption at microwave frequencies on the fluorescence radiation emitted during continuous Ar-ion-laser irradiation. In cases for which the ratio of the magnetic field energy splitting of the ground Kramers doublet of Er^{3+} to that of Nd^{3+} had values relatively close to $\frac{1}{2}$, 1, 2, 3, or 4, the time for regaining steady-state-level populations after termination of microwave irradiation was markedly reduced compared with other ratios and was minimum at those particular values. This observation is interpreted as due to energy-conserving cross-relaxation processes involving several Nd^{3+} and Er^{3+} ions simultaneously.

I. INTRODUCTION

The study of relaxation processes in spin systems was initiated by the classic paper of Waller[1] in 1932. Subsequently the development of resonance techniques for their study made possible the direct observation of transient behavior of spin systems. It became clear that not only the coupling of the spins to the phonons in a crystal, but also the exchange of energy between spins, permitting the spin system to come to thermal equilibrium, decoupled from the crystal structure to various extents, was an important consideration in such studies. This cross relaxation was discussed by Bloembergen *et al.*[2] in 1958. Since then there has been extensive study of mechanisms that account for the transfer of energy from excited ions to their neighbors in crystals. It has been established that interactions important to such transfer include magnetic dipole-dipole, electric multipole, and superexchange interactions.[3] There have been many studies of these interactions by magnetic resonance methods.[4–10]

The EPR (electron-paramagnetic-resonance) spectra of Nd^{3+} ions in their lowest Kramers doublet state in the $LaCl_3$ crystal were first studied in this laboratory.[11] Subsequently we have also studied the ENDOR (electron-nuclear-double-resonance) spectra of the ground state and both EPR and ENDOR spectra for a number of photoexcited states including photoexcited nearest-neighbor pairs of ions.[12–16] Among all the rare-earth ion systems that have been studied, Nd^{3+} in $LaCl_3$ stands out as the only system for which parallel investigations by both EPR and ENDOR have been made for both ground and electronically excited states in single crystals.

Later optical-magnetic double-resonance experiments[17,18] in our laboratory on $LaCl_3$ crystals containing both Nd^{3+} and Er^{3+}, described in Sec. III A of this article, have shown the possibilities of studies of processes of energy transfer between rare-earth ions in the $LaCl_3$ crystal by EPR, ENDOR, and various types of optical-magnetic double-resonance experiments. Similar studies of cross relaxation between rare-earth ions in ethylsulfate crystals have been reported by Moore *et al.*[19]

In this article we present the results of studies of the dynamics of cross relaxation and energy transfer between Nd^{3+} and Er^{3+} ions in $LaCl_3$ single crystals.

II. THE CRYSTAL SYSTEM

A. $LaCl_3$ crystal structure

The $LaCl_3$ crystal structure is hexagonal with space group $P6_3/m$ and with two La^{3+} ions per unit cell.[20,21] The lattice parameters are

$$|a| = |b| = 7.478 \pm 0.001 \text{ Å}$$

and

$$|c| = 4.375 \pm 0.001 \text{ Å} .$$

The point symmetry at the La^{3+} site is C_{3h}. A La^{3+} ion has two nearest cation neighbors which lie

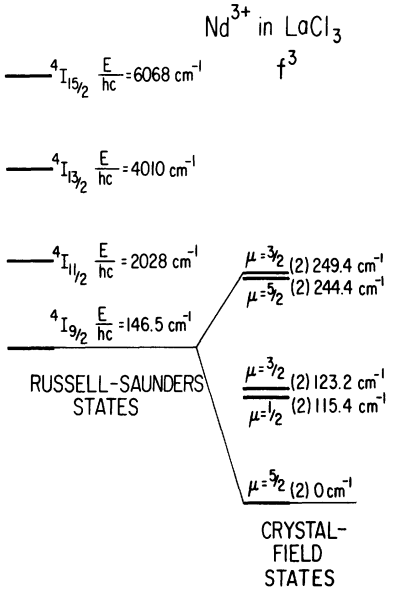

FIG. 1. Energy levels of Nd^{3+} in $LaCl_3$ crystal.

above and below the mirror plane along the c axis at the distance 4.375 Å. The second-nearest cation neighbor is 4.80 Å away and the line between the two ions of this $2n$ pair makes an angle 0.35π (63.1°), with respect to the c axis. There are six second-nearest cation neighbors which are related by the threefold axis and the mirror plane.

The coordination sphere for the La^{3+} ion consists of nine nearly equidistant Cl^- ions. Three Cl^- ions lie in the mirror plane at a distance 2.97 Å from the La^{3+} ion. The remaining six Cl^- ions lie three each in the planes parallel to the mirror plane at $\pm\frac{1}{2}|c|$. The La^{3+}–Cl^- distance for these six Cl^- ions is 2.99 Å.

B. Nd^{3+} in $LaCl_3$

Nd^{3+} substitutes for La^{3+} at the La^{3+} ion sites in $LaCl_3$. Its ground-state electronic configuration is well described as f^3 and its lowest-energy Russell-Saunders term as $^4I_{9/2}$. Our knowledge of its excited electronic states is derived mainly from the optical studies of Dieke[22] and his colleagues and his measurements for the ^4I manifold are summarized in Fig. 1. In the absence of an external magnetic field the $LaCl_3$ crystal field splits the $^4I_{9/2}$ tenfold degenerate term of this Kramers ion into five twofold degenerate states with wave numbers given in Fig. 1. The lowest-energy crystal field state is described by the crystal field quantum number $\mu=\frac{5}{2}$.

The Zeeman interaction of Nd^{3+} ions with zero nuclear spin in the $\mu=\frac{5}{2}$ ground state was first investigated by microwave EPR spectroscopy by Hutchison and Wong.[11] The interaction is described by the spin Hamiltonian[13]

$$\mathcal{H}_s = +|\mu_B|\vec{B}_0\cdot\underline{g}\cdot\vec{s}\ ,\quad S=\tfrac{1}{2}\ ,$$
$$g_{||}=3.994\,58\ (2)\ , \tag{1}$$
$$g_{\perp}=1.761\,33\ (14)\ .$$

Nd^{3+} ions in $LaCl_3$ crystals exhibit intense and narrow absorption and fluorescence lines in the visible region of the optical spectrum. One very intense optical absorption results from the transition from the $^4I_{9/2}$ ground state to the $^2G_{9/2}$ state. This optical excitation is followed by radiationless transitions to the $^4G_{7/2}$ and $^4G_{5/2}$ states. Intense fluorescence emission then follows due to transitions to the lower energy states, $J=\frac{15}{2}$, $\frac{13}{2}$, $\frac{11}{2}$, and $\frac{9}{2}$, of the ^4I manifold. One selected path of this optical absorption-emission pumping cycle is shown in Fig. 2.

The $1/e$ times, τ, for Nd^{3+} in the lowest crystal field Kramers doublet states of excited terms mentioned above have been found to be[23]

$$\tau\,(^2G_{9/2}\,,\mu=\tfrac{1}{2})=28\ \mu\text{s}\ ,$$
$$\tau\,(^4G_{7/2}\,,\mu=\tfrac{3}{2})=50\ \mu\text{s}\ ,$$
$$\tau(^4I_{15/2},\mu=\tfrac{1}{2})=15.7(1.1)\ \text{ms}\ ,$$
$$\tau\,(^4I_{13/2},\mu=\tfrac{1}{2})=22.3(1.6)\ \text{ms}\ ,$$
$$\tau\,(^4I_{11/2},\mu=\tfrac{3}{2})=89(30)\ \text{ms}\ .$$

The spin-lattice relaxation time for the ground-state Kramers doublet of Nd^{3+} at superfluid helium temperatures is of the order of one second.[24]

The lifetimes of the $^4I_{15/2}$ and $^4I_{13/2}$ Kramers doublets of lowest energy are long enough that optical pumping of the type described in Fig. 2 for the $^4I_{11/2}$ doublet provides populations sufficient to permit normal cw microwave EPR spectroscopy of

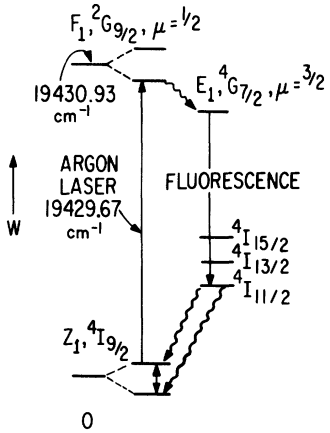

FIG. 2. Optical pumping cycle, Nd^{3+} in $LaCl_3$ crystal.

Nd^{3+} in those states, particularly when U^{3+} ions, which serve efficiently to absorb and transfer energy to the Nd^{3+}, are incorporated in the same crystal.

The Zeeman interaction for Nd^{3+} in the ${}^2G_{9/2},\mu=\frac{1}{2}$ state is described by Eq. (1) with $g_{||}=0.64$ and $g_{\perp}=5.01$.

C. Er^{3+} in $LaCl_3$

Er^{3+} substitutes for La^{3+} at the La^{3+} ion sites in the $LaCl_3$ crystal. Its ground electronic state configuration is well described as f^{11} and its lowest-energy Russell-Saunders term as ${}^4I_{15/2}$. The EPR spectrum of Er^{3+} with zero nuclear spin in its lowest-energy crystal field state, ${}^4I_{15/2},\mu=\frac{5}{2}$, is described by Eq. (1) with $g_{||}=1.989$ (1) and $g_{\perp}=8.757$ (2).[11]

III. EXPERIMENTS

A. Introduction

The Ar^+ laser emission at 19 429.67 cm^{-1} lies close in energy to the previously mentioned

$${}^4I_{9/2},\mu=\tfrac{5}{2}\rightarrow{}^2G_{9/2},\mu=\tfrac{1}{2}$$

intense absorption at 19 430.93 cm^{-1}. By application of an external magnetic field $\vec{B}_0$, Zeeman components of this absorption can be shifted into resonance with the Ar^+ laser emission. Because the wave number of the laser emission is smaller by 1.26 cm^{-1} than that of the

$${}^4I_{9/2},\mu=\tfrac{5}{2}\rightarrow{}^2G_{9/2},\mu=\tfrac{1}{2}$$

level separation, and because $\underline{g}$ has the principal values given previously, the optical resonance occurs, for $\vec{B}_0\perp c$, at a field magnitude given by

$$|\vec{B}_0|=1.26\frac{hc}{|\mu_B|}(2/|5.01\pm1.76|), \qquad (2)$$

i.e., at 7.97 kG corresponding to the sum of the two g values and at $\sim$16.6 kG corresponding to the difference. Hutchison and Liu[17] and Hutchison, Clemens, Hessler, and Liu[18] have observed the maximum in fluorescence at $\sim$7.97 kG when $|\vec{B}_0|$ is varied at constant laser intensity with $\vec{B}_0\perp c$, due to the maximum in the efficiency of the pumping cycle shown in Fig. 2.

For values of $|\vec{B}_0|$ in the vicinity of the

$$g_{\perp}({}^2G_{9/2})+g_{\perp}({}^4I_{9/2})$$

and other optical resonances, the intensity of the fluorescence depends upon the Ar^+ laser intensity, the value of $|\vec{B}_0|$, and the population of the higher-energy Zeeman level of the ground-state Kramers doublet. Therefore, the introduction, in the resonant cavity of an EPR spectrometer, of microwave radiation of frequency such as to induce paramagnetic-resonance absorption by the ground doublet, will produce an enhancement of the fluorescence by increasing the population of the ground doublet's upper level that is involved in the optical pumping cycle. This phenomenon has been reported by Hutchison and Liu[17] and by Hutchison, Clemens, Hessler, and Liu.[18] The latter have also reported observation of the expected deenhancement of fluorescence produced by Nd^{3+} ground-state microwave EPR absorption for values of $|\vec{B}_0|$ in the vicinity of the

$$g_{\perp}({}^4I_{9/2})\rightarrow g_{\perp}({}^2G_{9/2})$$

optical resonance with $\vec{B}_0\perp c$, due to depopulation of the lower level of the optical resonance. The marked changes in fluorescence intensity just described afford a convenient means for ODMR (optical detection of magnetic resonance) in this crystal system. Both EPR and ENDOR spectra have been so obtained and investigated.[18]

Hutchison and Liu[17] and Hutchison, Clemens, Hessler, and Liu,[18] have reported an enhancement of the

$${}^4G_{7/2},\mu=\tfrac{3}{2}\rightarrow{}^4I_{11/2},\mu=\tfrac{3}{2}$$

fluorescence of Nd^{3+} produced by ground-state EPR absorption of Er^{3+} in a $LaCl_3$ crystal containing both Nd^{3+} and Er^{3+} ions, when the crystal was being irradiated with the single 19 429.67 cm^{-1} line in an EPR spectrometer with $|\vec{B}_0|$ in the vicinity of the

$$g_{\perp}({}^2G_{9/2})+g_{\perp}({}^4I_{9/2})$$

resonance and for $\vec{B}_0$ in various directions with respect to c. It is to be carefully noted that there is no Er^{3+} optical transition that will permit any absorption of either the laser emission or any of the Nd^{3+} fluorescence emissions.[22]

This observation demonstrates the existence of communication between Nd^{3+} and Er^{3+}, in the $LaCl_3$ crystal, of such a nature that the EPR-induced population changes in the Er^{3+} ground-state Kramers doublet components produce a similar population change in the Nd^{3+} ground-state components. Moreover, these workers observed that as angle θ between $\vec{B}_0$ and the c axis was varied, for values of θ such that the ratio of the Er^{3+} ground-state doublet splitting to the Nd^{3+} ground-state doublet splitting had values $\frac{1}{2}$, 1 or 2, the enhancement of the Nd^{3+} fluorescence emission to the ${}^4I_{11/2}$ state produced by Er^{3+} EPR passed through a relatively sharp maximum. These conditions are described by the relation

$$\theta=\tan^{-1}\left[\frac{Rg^2(\mathrm{Nd})-g^2(\mathrm{Er})}{Rg^2(\mathrm{Nd})-g^2(\mathrm{Er})}\right]^{1/2}, \quad (3)$$

in which $R=\frac{1}{2}$, 1, or 2. Substitution into Eq. (3) of the g values given above yields the θ values

$6.6\times10^{-3}\pi$ (1.2°),

0.122π (22.0°),

0.244π (44.0°),

0.330π (59.4°),

and

0.399π (71.8°),

corresponding, respectively, to R values $\frac{1}{2}$, 1, 2, 3, and 4. The first three of these values are the angles at which the enhancement was observed to have maxima. It was in this way demonstrated that when the ground-state Kramers doublet Zeeman quantum for Er^{3+} was equal to the ground-state Kramers doublet Zeeman quantum for Nd^{3+}, or was $\frac{1}{2}$ or 2 times it, the communication between the Nd^{3+} and Er^{3+} was greatly facilitated. These experiments indicate that energy-conserving exchanges of ground-state Zeeman quanta between Nd^{3+} and Er^{3+} are involved in the communication between these ions in $LaCl_3$. It is also clear that not only flip-flop processes involving just two ions are involved in the energy transfer but that three-ion flip-flip-flops and flip-flop-flops may participate.

The observations described above were made with $LaCl_3$ crystals in which ~0.002 of the La^{3+} sites were occupied by Nd^{3+} ions and the same number of sites by Er^{3+} with a mean interionic separation ~35 Å, between neighboring paramagnetic ions.

In the work reported in this article we have investigated the dynamics of the exchange of ground-state Zeeman energy between Nd^{3+} and Er^{3+} and of the optical pumping cycle described in Fig. 2. This system is particularly convenient for studying such processes inasmuch as optical resonance can be obtained simply by scanning magnetic field strength $|\vec{B}_0|$ with no need for a tunable laser or other tunable light source, and various magnetic energy conserving conditions can be established simply by changing direction of $\vec{B}_0$ in the $LaCl_3$ crystal.

B. Crystals

Single crystals of $LaCl_3$ with Nd^{3+} and Er^{3+} of normal isotopic abundance dilutely substituted for La^{3+}, were prepared from the melt by the method of Anderson and Hutchison.[25] The fraction of La^{3+} ions replaced by Er^{3+} and by Nd^{3+} in the $LaCl_3$ melt was ~0.0020 in both cases. The crystals cleaved easily along the $\hat{a}\,\hat{c}$ and $\hat{b}\hat{c}$ planes and the interaction of two such planes clearly defined the c axis.

C. Apparatus and procedures

The light source for our experiments was a 3-W argon-ion laser with a single line,

$$19431\ \mathrm{cm}^{-1}\ (\lambda=5147\ \text{Å}),$$

1-W output power. The light was directed parallel to $\vec{B}_0$ through a hole drilled along the axis of the 12-in.-diameter magnet pole, to the $LaCl_3$ crystal in the microwave resonant cavity of the EPR spectrometer. The fluorescence emission passed through a similar hole in the opposite pole and was focused on the entrance slit of a Spex 1000 3/4-m Czerny-Turner monochromator which was tuned to the $^4G_{7/2}\rightarrow{}^4I_{11/2}$ emission at

$$\sim1.696\ \mathrm{cm}^{-1}\ (\lambda=5894\ \text{Å}).$$

An EMI photomultiplier with S-20 cathode, cooled to ~270 K, was used to monitor the emission intensity. The photomultiplier signal was fed through an analog-to-digital converter to a multichannel analyzer and data averaging system, and subsequently recorded.

The EPR spectrometer operated at carrier frequency ~24–25 GHz, and employed a conventional klystron microwave source with output power ~200 mW. The right circular cylindrical microwave resonant cavity had a slotted wall which permitted light to enter and leave. It was operated in the TE011 mode. The cavity was submerged in liquid helium at temperatures in the range 1.3 to 4.2 K, and with the $LaCl_3$ crystal in direct contact with the helium. Normal microwave absorption EPR spectra were obtained by use of a homodyne microwave bridge and phase-sensitive detection. ODMR spectra were obtained by sweeping $|\vec{B}_0|$ and recording the photomultiplier signal as described previously. The values of $|\vec{B}_0|$ required for EPR were measured by means of a proton fluxmeter. The liquid-helium crysotat was provided with fused silica windows for passage of light. A ferrite microwave switch was used to switch on and off the microwave field at the $LaCl_3$ crystal. The rise and fall times for this switch were ~20 μs. The optical detection channel was fast compared with this time. Thus we were able to measure the time dependence of the fluorescence intensity changes produced by the switching with uncertainty ~20 μs.

The $LaCl_3$ crystals containing Nd^{3+} and Er^{3+} were mounted on an epoxy sample holder at the midpoint on the axis of the crylindrical cavity. The

sample holder could be rotated about an axis parallel to both the cavity axis and the microwave magnetic field and perpendicular to $\vec{B}_0$, through known angles, by means of a control external to the cryostat. Details of this procedure have been described elsewhere.[26] The $LaCl_3$ crystals were mounted on the crystal holder in a manner such that the c axis could be rotated in a plane containing $\vec{B}_0$. The microwave magnetic field remained fixed $\perp\vec{B}_0$. Rotation of the $LaCl_3$ crystal thus scanned all angles between $\vec{B}_0$ and c from $\vec{B}_0 \| c$ to $\vec{B}_0 \perp c$ for both Nd^{3+} and Er^{3+}. It is to be noted that the previously given g values show that as the crystal is rotated from a position such that $\vec{B}_0 \| c$ to one in which $\vec{B}_0 \perp c$, the Zeeman splitting of the Nd^{3+} ground-state Kramers doublet is decreasing and at the same time is increasing for the Er^{3+} doublet. Thus the scanning of angle provided a range of values of the R that appears in Eq. (3). The proper orientation of the $LaCl_3$ crystal on the holder was verified by measurement of the maximum and minimum values of the ratio ν_M/ν_P of the microwave frequency to the proton fluxmeter frequency for Nd^{3+} EPR, as the angle variable was scanned over a range π (180°). Comparison with the g values given previously revealed any deviations from the desired orientation. In all cases reported here, desired orientations within ~ 0.011 (2°) were achieved.

D. Measurements

1. The Nd^{3+} ODMR spectrum

In our studies of this spectrum with the $LaCl_3$ crystal containing both Nd^{3+} and Er^{3+} the 19431 cm^{-1} Ar^+ laser line was used for optical excitation of the Nd^{3+} only. We confirmed that we could identify all observed fluorescence lines as Nd^{3+} lines by comparison with the wavelength tables of Dieke.[22] If the only optical cycles operative in our system were the ones of the type depicted in Fig. 2, the intensities of all the lines of the fluorescence spectrum should depend on the population of the upper Zeeman level of the Nd^{3+} ground-state Kramers doublet. Thus, for example, all these lines should increase in intensity upon the inducing of Nd^{3+} ground-state EPR, especially for values of $|\vec{B}_0|$ in the vicinity of the

$$g_\perp(^2G_{9/2},\mu=\tfrac{1}{2})+g_\perp(^4I_{9/2},\mu=\tfrac{5}{2})$$

optical resonance. This we showed to be the case by modulating microwave power at a frequency of a few Hz and detection of the photomultiplier signal by phase-sensitive detection at that modulation frequency. In this way one detects only light emission that is sensitive to EPR. Indeed the spectral lines

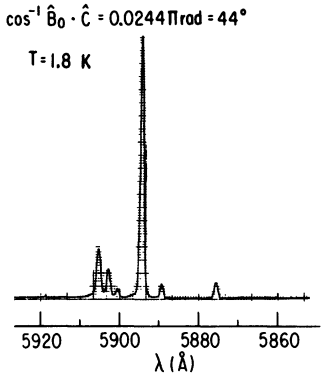

FIG. 3. $^4G_{7/2} \rightarrow {}^4I_{11/2}$ fluorescence spectrum of Nd^{3+} in $LaCl_3$ crystal.

observed in this ODMR experiment coincided with the fluorescence lines observed as described previously in the absence of EPR thus confirming that optical cycles of the type represented in Fig. 2 predominated in our experiments.

The group of fluorescence lines originating with the $^4G_{7/2} \rightarrow {}^4I_{11/2}$ transition are the most intense of the emissions. Our observations of these lines are described in Fig. 3. All of our measurements on the spin system dynamics and cross relaxation were made with the monochromator tuned to the strongest line at

$$1.6966 \times 10^4 \text{ cm}^{-1} \text{ (5894 Å)}.$$

This fluorescence is very intense and easily detected.

2. The effect of Nd^{3+} ground-state EPR on Nd^{3+} fluorescence

In Sec. II B we listed the lifetimes of the excited states involved in the optical pumping cycle described in Fig. 2. Because these times are all so very short relative to the $\sim$1-second spin-lattice relaxation time[24] of the Nd^{3+} ground-state Kramers doublet that is involved in the microwave EPR absorption, any alteration of rates of change of ground-state populations, due to spin dynamics, after termination of microwave irradiation, was seen immediately as an alteration of the fluorescence intensity. Thus the optical cycle that predominated in our experiments was well suited for the detection of cross relaxation between the Er^{3+} and Nd^{3+} systems through the effects of Er^{3+}-Nd^{3+} interactions on changes in the population recovery of the components of ground-state Kramers doublets following microwave saturation.

We performed a series of experiments as follows. The crystal was irradiated continuously with 19430.93 cm^{-1} Ar^+ laser emission of fixed intensity during these experiments. For a succession of angles θ between $\vec{B}_0$ and c for the $LaCl_3$ crystal con-

taining both Nd^{3+} and Er^{3+}, the value of $|\vec{B}_0|$ was in each case adjusted to the value for Nd^{3+} ground-state Kramers doublet EPR. The angle was varied from 0 to $\pi/2$ (90°). For our fixed value 24.670 GHz, of microwave frequency ν_M, these values of $|\vec{B}_0|$ were in the vicinity of those required for optical resonance of the 19430.93 cm^{-1} laser line with the transition from the upper level of the ground-state Kramers doublet to the lower level of the upper $^2G_{9/2}$ Kramers doublet as shown in Fig. 2. During the variations of the angle between $\vec{B}_0$ and c, the ground-state doublet separation remained constant but the varying value of $|\vec{B}_0|$ required for Nd^{3+} ground-state EPR resulted in a varying value of the excited-state Zeeman splitting. Thus the deviation from the optical resonance condition varied. The mismatch Δ between the Ar^+ laser wave number and the wave-number separation of the lower-energy component of the $^2G_{9/2}, \mu=\frac{1}{2}$ doublet and the higher-energy level of $^4I_{9/2}, \mu=\frac{5}{2}$ doublet is given by the expression

$$\Delta(\mathrm{cm}^{-1})=1.26-\frac{\nu_M}{2c}\left[1+\frac{g_{\parallel}^2(^2G_{9/2})\cos^2\theta+g_{\perp}^2(^2G_{9/2})\sin^2\theta}{g_{\parallel}^2(^4I_{9/2})\cos^2\theta+g_{\perp}^2(^4I_{9/2})\sin^2\theta}\right]^{1/2}, \tag{4}$$

in which 1.26 cm^{-1} is the zero-field mismatch. Thus the value of Δ decreases from 0.78 cm^{-1} for $\theta=0$ to 0.00 for $\theta=0.37\pi$ (67°) and rises again to 0.32 cm^{-1} for $\theta=\pi/2$ (90°). For each of the angles between $\vec{B}_0$ and c the ferrite switch was used to initiate and terminate the microwave magnetic field at the $LaCl_3$ crystal, while keeping the laser intensity constant. The variation of the fluorescence intensity I_{fl} with time t, during initiation and termination of microwave irradiation, is shown in Fig. 4. The decay of the fluorescence was well described by the relation

$$I_{fl}(t)\propto I_{fl}(0)e^{-t/\tau}. \tag{5}$$

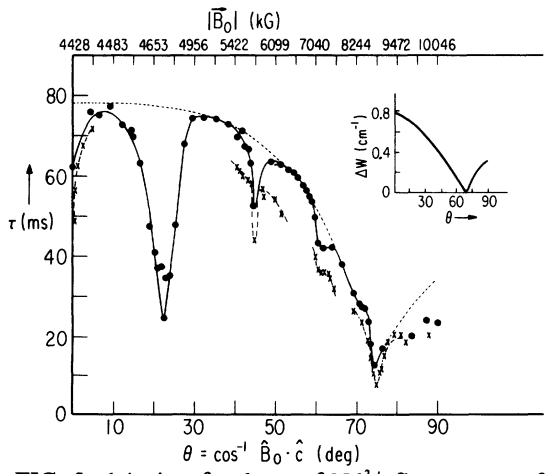

FIG. 5. $1/e$ time for decay of Nd^{3+} fluorescence after termination of microwave irradiation vs $\theta=\cos^{-1}\hat{B}_0\cdot\hat{c}$; Nd^{3+} and Er^{3+} in $LaCl_3$ crystal.

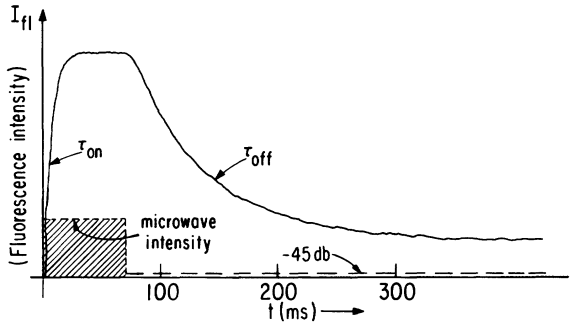

FIG. 4. Nd^{3+} fluorescence intensity I_{fl}, versus time t during initiation and termination of microwave irradiation; Nd^{3+} and Er^{3+} in $LaCl_3$ crystal.

In Fig. 5 are plotted the values of τ in Eq. (5) as a function of θ. The points connected by the dashed broken line are the results of an experiment at appreciably higher laser power than the one for which the points are connected by the solid line. Two features of this plot are to be noted. First, there is a general decrease in the value of τ as θ increases, indicated by the dotted line in the figure. Second, there are superimposed on this general trend marked, relatively sharp, dips at angles very nearly equal to those listed in Sec. III A as satisfying Eq. (3) for $R=\frac{1}{2}$, 1, 2, 3, and 4, i.e., at angles at which one or more ground-state Zeeman quanta can be exchanged between Nd^{3+} and Er^+ with conservation of energy. The value of Δ computed from Eq. (4) is plotted vs θ in the inset in Fig. 5.

For

$$\theta=0.244\pi\ (44.0°),\quad R=2,$$

we measured as a function of $|\vec{B}_0|$ the $1/e$ times, τ, for both the increase of Nd^{3+} fluorescence upon initiation of microwave radiation and the decrease upon termination. The results are shown in Fig. 6 and the $1/e$ times are referred to as τ_{on} and τ_{off}, respectively. The decrease in τ_{on} and the increase in τ_{off} changed to $\frac{1}{2}$ their maximum magnitudes as the value of $|\vec{B}_0|$ was increased or decreased by $\frac{55}{2}G$ from its value for maximum magnitude of change.

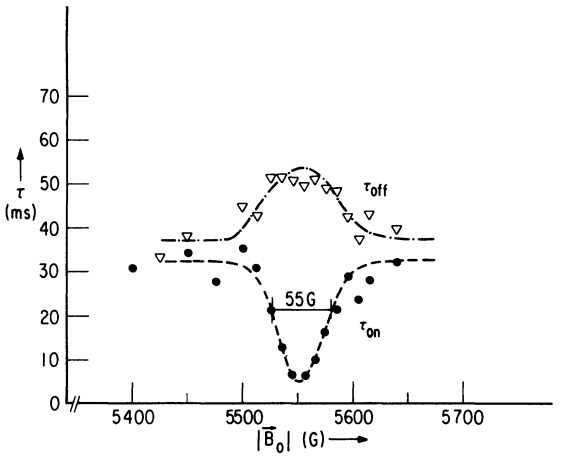

FIG. 6. τ_{on} and τ_{off} for Nd^{3+} fluorescence vs $|\vec{B}_0|$ in vicinity of $\theta=\cos^{-1}\hat{B}_0\cdot\hat{c}=0.244\pi$ (44.0°); Nd^{3+} and Er^{3+} in $LaCl_3$ crystal.

This "linewidth" has the same size as has the Nd^{3+} ODMR line.

3. *The effect of Er^{3+} ground-state EPR on Nd^{3+} fluorescence*

We repeated the experiments of Hutchison and Liu,[17] and of Hutchison, Clemens, Hessler, and Liu,[18] described in Sec. III A, in which Er^{3+} EPR was detected by Nd^{3+} fluorescence enhancement. In addition we made measurements, in this case, of τ_{on} and τ_{off}, for the fluorescence enhancement of the type just described in Sec. III D 2. These measurements were made with

$$\theta=0.244\pi\ (44°)\quad R=2\ .$$

Within our experimental accuracy we found that

$$\tau_{on}=\tau_{off}=30(5)\text{ms}\ .$$

IV. DISCUSSION OF RESULTS

It is clear from the experimental results summarized in Fig. 5 that there are two important influences on the Nd^{3+} fluorescence decay times τ when microwave irradiation at the Nd^{3+} ground-state EPR frequency is terminated and the laser radiation is maintained at constant intensity.

The first of these influences is the rate of laser photon absorption by the Nd^{3+} ions. An increase in this rate of absorption results in a decrease in the magnitude of τ. This effect is manifested in two ways by the experimental results summarized in Fig. 5. The first is the parallelism between (a) the decrease in mismatch of the laser wave number and the optical absorption wave number for the Nd^{3+} as the value of θ is increased from 0 to 0.37 π (67°) (see inset in Fig. 5), and (b) the general decrease in the value of τ over that same range of angle as indicated by the dotted line in Fig. 5. The second is the decrease in the value of τ for all values of θ, when the value at which the laser intensity is maintained during the experiment is increased. This effect is shown by the results for the experiments at higher laser power, summarized by the broken line in Fig. 5. Our interpretation of the effect of rate of laser light absorption, as shown in both of these ways, is as follows. Consideration of the optical pumping cycle depicted in Fig. 2 reveals that this cycle carries Nd^{3+} ion population from the upper to the lower ground-state Kramers doublet energy levels. This results from the radiationless transitions from the optically populated $^4I_{11/2}$ state to both of the ground-state ($\mu=\frac{5}{2}$) doublet energy levels as indicated by the two wavy lines in Fig. 2. A complete discussion of the changes, produced by optical pumping, in relative populations of the two components of the ground-state doublet is quite complicated and must include other pumping cycles in which the $^4I_{15/2}$ and $^4I_{13/2}$ states, shown in Fig. 2, are involved, as well as cross-relaxation effects. For a quantitative discussion there is required a number of transition probabilities and branching ratios whose values are unknown. Nevertheless, the situation is qualitatively represented by the highly schematic diagram shown in Fig. 7. It is clear that in addition to the normal spin-lattice relaxation, represented by $^{Nd}w_1$ in the figure, there are the various optically driven radiative and nonradiative processes indicated there, which combine to produce the redistribution of populations indicated by the wide cross-hatched arrow labeled w_{opt}. Both $^{Nd}w_1$ and w_{opt} are responsible for the distribution of populations within the Nd^{3+} ground-state doublet. However, for values of θ off from those at which the sharp dips occur in the curves of Fig. 5, i.e., for values of θ for which cross relaxation with Er^{3+}

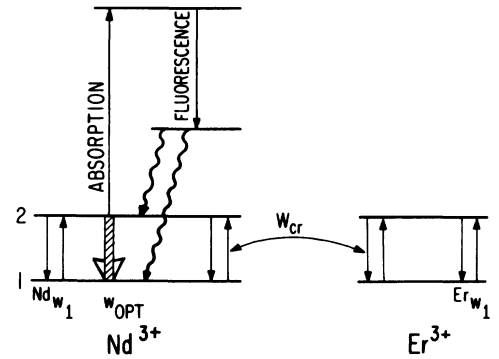

FIG. 7. Schematic diagram of relaxation processes; Nd^{3+} and Er^{3+} in $LaCl_3$ crystal.

does not conserve individual ion ground-state Zeeman energies, the rate at which final population values are attained is determined mainly by w_{opt} because of the relatively very long spin lattice relaxation time ~ 1 s. Thus the optical pumping carries the doublet's population ratio to one in which the lower level has a larger value than that corresponding to a Boltzmann distribution at the lattice temperature. The resulting upper-state population determines the final value of the pumping rate and hence of the fluorescence intensity. Equilibrium ground-state populations are more quickly attained the greater the optical pumping rate and thus τ becomes smaller as mismatch of laser and Nd^{3+} absorption wave numbers becomes less or as laser power becomes greater.

The redistribution of the populations of the Nd^{3+} ground-state doublet components produced by the optical pumping thus accounts for (a) the very rapid relaxation of the ODMR signal (seen in Figs. 4 and 5) relative to the spin-lattice relaxation time, (b) the general decrease in value of τ as θ increases from zero, shown by the dotted curve in Fig. 5, and (c) the decrease in value of τ at all values of θ when laser intensity is increased as shown by the dashed curve in Fig. 5.

The second influence on the Nd^{3+} fluorescence decay time τ when microwave radiation is terminated, is the cross relaxation and energy transfer between Nd^{3+} and Er^{3+}. This influence is evidenced by the relatively sharp dips in the plots of

$$\tau \text{ vs } \theta = \cos^{-1}\hat{B}_0 \cdot \hat{c}$$

shown in Fig. 5. These occur at some values of θ which Eq. (3) specifies for conservation of the Zeeman energy where exchange occurs between a small number of Nd^{3+} and Er^{3+} ions. The set of values found for R indicates that energy-conserving exchanges involving as many as five ions are occurring. In the schematic diagram shown in Fig. 7, such processes are indicated by the arrows labeled w_{cr}. The consideration of theories of cross relaxations of this type was initiated by Bloembergen and his co-workers.[2] These authors developed a description of the exchange of Zeeman quanta between spin systems by flip-flop processes which conserved Zeeman energy. The quantitative description of the rate of transfer depended upon the overlap of magnetic-resonance line-shape functions for the two energy-exchanging spin systems with small mismatches in magnetic energy quanta taken up by the entire magnetic dipole-dipole reservoir. The facts that the marked dips in τ values occur at special values of θ required by energy-matching conditions plus the fact that the widths of these dips is about the same as the ODMR resonances shows that a theory of this type is applicable to our results.

The results of our experiments show that the relatively rapid communication between the Nd^{3+} and Er^{3+} spin systems that is made possible at those values of θ corresponding to $R = \frac{1}{2}$, 1, 2, 3, and 4 in Eq. (3) opens new channels for spin relaxation for the Nd^{3+} system. Following a treatment of such processes, such as that given by Moore and Satten[19] leads to a set of coupled differential equations whose solution depends upon values of transition rates and branching ratios whose measurement requires further experimentation.

Studies of cross-relaxation effects between different rare-earth ions have been performed by Moore and Satten[19] for systems with much higher paramagnetic ion concentrations. Cross relaxations similar to those corresponding in our case to values of R not equal to 1 in Eq. (2) have been observed in nickel-doped rubies in zero external magnetic field and found to involve as many as five spins.[27] Cross-relaxation processes for ground-state quartets involving more than two spins have been reported.[28] Various optical methods of detecting such cross relaxations have been described in the literature.[29,30] However, direct observation of effective spin communication involving more than two spins in strong magnetic fields has not been previously reported.

We now consider the results of the measurements of τ_{on} and τ_{off}, as a function of $|\vec{B}_0|$, that were discussed at the end of Sec. III D 2 and described in Fig. 6. The $1/e$ time for the increase of Nd^{3+} fluorescence intensity after microwave irradiation is initiated, as described by the solid circles in the figure, depends upon the rate of microwave pumping of the ground doublet. Thus moving $|\vec{B}_0|$ off the center value 5550 G for EPR has the effect of reducing this rate and so increases the value of θ_{on}, whether or not there are energy exchanging couplings to another spin system. On the other hand, however, after the microwave irradiation is terminated, if there were no communication of the Nd^{3+} spin system with another spin system, there should be no change of τ_{off} as $|\vec{B}_0|$ moves off the EPR value because τ_{off} would depend only upon relaxation processes internal to the Nd^{3+} spin systems (spin-lattice relaxation time is very long relative to the τ_{off} times) which would be negligibly affected by the effects of a few gauss changes in $|\vec{B}_0|$ on energy levels. The very clear existence of a dependence of τ_{off} on the relatively small shifts of $|\vec{B}_0|$ away from the EPR value (which in this experiment has just the value required for Zeeman energy conservation between the Nd^{3+} system and the Er^{3+} system with $R = 2$) is another indication of the existence of the resonant energy communication between the two spin systems, which, as we have seen

above, opens new channels for redistribution of populations of the Nd^{3+} ground-state doublet components. The extent of occurrence of such cross relaxation has been shown by our experiments to be strongly affected by small shifts in $|\vec{B}_0|$.

We lastly consider the experiments described in Sec. III D 3 on the effect of Er^{3+} ground-state Kramers doublet EPR on Nd^{3+} fluorescence. The value of θ in these experiments was 0.244π (44°) corresponding to $R=2$ in Eq. (3). Thus $|\vec{B}_0|$ required for Er^{3+} EPR was $\frac{1}{2}$ that required for Nd^{3+} EPR, and the mismatch between the Nd^{3+} optical absorption wave number and the laser emission wave number was large (see Fig. 5). Because the conditions in this experiment were far from those required for the optical resonance there was little optical pumping of the Nd^{3+} system and the ground-state doublet population redistribution produced by the optical pumping was enormously reduced from its value at optical resonance. In other words, the rate of the process indicated by w_{opt} in Fig. 7 was relatively very small and the Nd^{3+} ground-state doublet population redistribution time was probably no less than 100 ms. The fact that we found that $\tau_{on}=\tau_{off}=30$ ms in this experiment thus indicates that in this case cross relaxation was the dynamic bottleneck that accounted for the measured rates for the Er^{3+} ODMR signal. Thus 30 ms may be taken as our estimate of the value of the cross-relaxation time.

Further experiments for the purpose of measuring the rates of various processes, whose values are needed for a quantitative discussion of the results reported here, are in progress in our laboratory.

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