

trons in the tunneling process, but then one must deal with an impurity band.

Finally, the inclusion of nonmagnetic impurities inside the tunneling barrier, when perturbation theory is valid, cannot generally be detected except when they are in very small number and when they are concentrated in the vicinity of an edge of the barrier. Such conclusions lead us to presume that the giant anomalies are probably observed either in the limit of very high

concentrations (in which case the impurities are likely to be gathered in clusters of various sizes) or in the limit of low concentrations if the impurities are very attractive (positive ions for example).

ACKNOWLEDGMENTS

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Optical Detection of a Phonon Bottleneck in Nd-Doped Lanthanum Ethyl Sulfate†

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The spin-lattice relaxation times of Nd¹⁴² and natural Nd doped into lanthanum ethyl sulfate (LaES) have been measured by an optical technique as a function of crystal size, concentration, and temperature. The measurements were performed with a microwave pump frequency of about 23 GHz with the steady magnetic field parallel to the *c* axis of the crystals. A phonon bottleneck independent of crystal size was observed for the Nd¹⁴²-doped LaES. Holstein's theory of resonant trapping is reviewed and is shown to be inapplicable to the observed bottleneck. However, for rare-earth salts with direct-process relaxation times of approximately 10⁻⁵ sec or shorter, resonant trapping can appreciably lengthen the effective lifetime of the excited spin states. The observed bottleneck is explained with a simple kinetic theory and by assuming a large phonon reflection coefficient at the boundaries of the crystal. From this formulation, the lifetime of 23-GHz phonons in Nd-doped LaES is deduced to be 32 μsec at liquid-helium temperatures.

I. INTRODUCTION

THE rate equations for the spin-lattice relaxation of a two-state spin system tacitly imply that the phonon distribution either is an infinite heat sink or remains in equilibrium with an infinite heat sink, i.e., the helium bath. The direct and Orbach processes of relaxation create phonons whose bandwidth is approximately the same as that of the spin system. Since the number of phonon modes within this bandwidth is usually orders of magnitude smaller than the number of excited spins, the phonons must relax orders of magnitude faster than the spin system to remain in thermodynamic equilibrium. At low temperatures, where the Orbach and direct processes are dominant, the phonon relaxation time cannot always satisfy this condition. As a result, the phonon frequencies within the ESR linewidth have much greater occupation numbers during spin-lattice relaxation than their thermal equilibrium values. These excess phonons pump the spin system and prolong the spin-lattice relaxation time when the spin populations are not inverted. The phonons therefore "bottleneck" the transfer of energy from the spin system to the helium bath.

Van Vleck¹ first investigated this problem, and in recent years several experimenters have observed spin-lattice relaxation rates which were indicative of a phonon bottleneck.² Shiren³ has successfully detected the excess phonons directly, after inverting the population of the spin system. Scott and Jefferies,² using the formulation of Faughnan and Strandberg,⁴ have successfully explained the T^{-2} temperature dependence of the observed bottlenecked relaxation rates. From their measurements, the phonon relaxation time was deduced to be the time of flight to the sides of the crystal. Later measurements by Larson and Jefferies⁵ on bottlenecks in other rare-earth-doped crystals indicated that the phonon relaxation time was several times longer than the time of flight.

The purpose of this paper is (1) to point out the similarity of the results of Faughnan and Strandberg's formulation of the bottleneck to that of a phenomenon called resonant trapping, (2) to remove some of the

¹ J. H. Van Vleck, *Phys. Rev.* **59**, 724 (1941); **59**, 730 (1941).

² P. L. Scott and C. D. Jefferies, *Phys. Rev.* **127**, 32 (1962); J. A. Giordimaine, L. E. Alsop, F. R. Nash, and C. H. Townes, *ibid.* **109**, 302 (1958); R. H. Ruby, H. Benoit, and C. D. Jefferies, *ibid.* **127**, 51 (1962).

³ N. S. Shiren, *Phys. Rev. Letters* **17**, 958 (1966).

⁴ B. W. Faughnan and M. W. P. Strandberg, *Phys. Chem. Solids* **19**, 155 (1961).

⁵ G. H. Larson and C. D. Jefferies, *Phys. Rev.* **141**, 461 (1966).

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ambiguity of interpretation resulting from this similarity by indicating numerically when resonant trapping will be a factor in lengthening spin-lattice relaxation lifetimes, and (3) to report on an observed bottleneck in Nd¹⁴²-doped lanthanum ethyl sulfate (LaES) which is not due to resonant trapping but can be explained simply by means of kinetic theory.

II. CALCULATION OF PHONON ABSORPTION CROSS SECTION AND LIFETIME

Anderson⁶ has pointed out the analogy of the phonon bottleneck with the theory of trapped resonant radiation. The theory describes a gas emitting optical radiation and the subsequent transport of the radiation to the extremities by a series of absorptions and emissions. The resulting process of diffusion, termed imprisonment of resonant radiation, can lengthen the effective lifetime of the excited atoms by several orders of magnitude. The necessary condition for the occurrence of imprisonment is that the mean free path, calculated at the center of the absorption line, is much smaller than the sample dimensions. If this condition prevails, the radiation transport is diffusive and can no longer be described by an exponential attenuation.

Holstein⁷ has formulated a Boltzman-type integro-differential equation to solve this problem. By simply observing conservation of particles and translating Holstein's notation from excited atoms and photons to excited spins and phonons, one obtains the following expression for the phonon lifetime in a semi-infinite slab:

$$T_b = [T_1 N \sigma(\omega_0) l / 1.06] [\ln \frac{1}{2} N \sigma(\omega_0) l]^{1/2}, \quad (1)$$

where $\sigma(\omega_0)$ is the absorption cross section for phonons at the center frequency of the EPR line, l is the thickness of the slab, N is the number of spins per unit volume, and T_1 is the spin-lattice relaxation time.

It is emphasized here that the theory of trapped phonon radiation assumes that the major portion of phonons, generated during spin-lattice relaxation, escape from the solid by transport to the boundaries. If the phonons relax by some internal mechanism, the theory does not apply.

Al'tshuler⁸ and Orbach⁹ have computed the phonon cross section for the direct process. The cross section is computed here in a form more convenient for the subsequent analysis of the phonon bottleneck.

The probability of phonon reabsorption per unit

time per spin is

$$\begin{aligned} \frac{dp}{dt} &= \frac{WN^-}{N}(n-n_0) - \frac{WN^+}{N}(n+1-n_0-1) \\ &= (n-n_0)W \frac{N^- - N^+}{N}, \quad (2) \end{aligned}$$

where n is the phonon occupation number, n_0 is the thermal equilibrium value of the occupation number, W is the transition probability, N^+ and N^- are the number of spins in the upper and lower states, respectively, and N is the total number of spins.

Using a Maxwell-Boltzman distribution for N^+ and N^- , and relating the transition probability to the phonon lifetime, we obtain from expression (2)

$$\frac{dp}{dt} = \frac{1}{T_{1d}(\omega)} \frac{n-n_0}{2n_0+1} \tanh \frac{\hbar\omega}{2kT_s}, \quad (3)$$

where ω is the angular frequency of the spin resonance, T_s is the spin temperature, and T_{1d} is the spin-lattice relaxation time due to the direct process. The phonon cross section using a Debye spectrum is found to be

$$\sigma(\omega) = \frac{2\pi v^2}{T_{1d}(\omega)} \tanh \frac{\hbar\omega}{2kT} \tanh \frac{\hbar\omega}{2kT_s} L(\omega-\omega_0) / 3\omega^2, \quad (4)$$

where v is the phonon velocity and $L(\omega-\omega_0)$ is the normalized spin-shape function.

If $2kT > \hbar\omega$ and $2kT_s > \hbar\omega$, then expression (4) simplifies to

$$\sigma(\omega_0) = \frac{\pi^2}{6} \frac{v^2 \hbar^2}{kT kT_s T_{1d}(\omega_0)} \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{1}{\Delta\omega}, \quad (5)$$

where the line-shape function has been taken as Gaussian and $\Delta\omega$ is its width at half-intensity.

It is pointed out here that $\sigma(\omega_0)$ is not a constant throughout the relaxation process, but is inversely proportional to the spin temperature. Physically, this dependence results from the pumping of the spin system by the phonons, which effectively reduces the number of absorbing spin states. Holstein's theory of resonant trapping was formulated assuming the number of excited atoms is small compared to the total number, and thus $\sigma(\omega_0)$ is taken to be constant. As a result, the theory of resonant trapping applies to phonons only when $T_s \cong T$. Thus if the spins are not pumped too far out of equilibrium, or if only the tail of the relaxation curve is observed, the phonon cross section is approximately a constant. Under these conditions, expression (1) is valid for the bottlenecked phonon lifetime. Substitution of the phonon cross section into this expression, with the approximation that the spin temperature is equal to the equilibrium lattice temperature,

⁶ P. W. Anderson, Phys. Rev. **114**, 1002 (1959).

⁷ T. Holstein, Phys. Rev. **72**, 1212 (1947); **83**, 1159 (1951).

⁸ S. A. Al'tshuler, Dokl. Akad. Nauk SSSR **85**, 1235 (1952); Zh. Eksperim. i Teor. Fiz. **28**, 38 (1955); **28**, 49 (1955) [English transl.: Soviet Phys.—JETP **1**, 29 (1955); **1**, 37 (1955)].

⁹ R. Orbach, dissertation, University of California at Berkeley, 1960 (unpublished).

results in the following expression for T_b :

$$T_b = 1.06 \left(\frac{\ln 2}{\pi} \right)^{1/2} N \left(\frac{\pi v \hbar}{kT} \right)^2 \frac{l}{\Delta\omega} \times \left\{ \ln \left[\frac{1}{12} \left(\frac{\ln 2}{\pi} \right)^{1/2} \left(\frac{\pi v \hbar}{kT} \right)^2 \frac{Nl}{T_{1d} \Delta\omega} \right] \right\}^{1/2}. \quad (6)$$

As stated previously, the criterion for the occurrence of resonant trapping is that the mean free path is much less than the sample dimensions. For the particular case of 3% Nd¹⁴²-doped LaES, the cross section $\sigma(\omega_0)$ at 2°K, with $v = 2 \times 10^5$ cm/sec, an applied field of 4660 G, and a linewidth of 100 G, is 3.2×10^3 b. The resulting mean free path is 6.6 cm, which is much larger than the thickness of samples used in the experiments reported on here. Hence resonant trapping will not provide a bottleneck mechanism. Also, no dependence of T_b on l was observed, which is consistent with this conclusion.

It is noted that some of the non-Kramer's rare-earth salts have much shorter direct-process relaxation times, which can provide the shorter mean free paths which are necessary for resonant trapping. For example, the direct-process lifetime of a Pr isotope in LaES at a microwave frequency of 23 GHz is estimated to be 10^4 times shorter than Nd in LaES. For 1% Pr doping and a linewidth of 100 G, the phonon cross section would be 10^7 b, resulting in a mean free path of 10^{-3} cm.

We would like to point out the similarity of the above expression for the effective lifetime to that obtained by the hot-phonon bottleneck theory of Faughnan and Strandberg.⁴ For most phonon bottlenecks, the square root of the logarithmic term in the resonant trapping lifetime is approximately a constant over the liquid-helium temperature interval and numerically is about 1. The expression for the hot-phonon lifetime is given by

$$T_b \cong T_1 + T_{ph} \pi^2 \hbar^2 v^3 N / 6 (kT)^2 \Delta\omega. \quad (7)$$

If T_{ph} is taken to be the time of flight to the sides of the crystal, and neglecting T_1 , the two lifetimes are almost identical except for the numerical factor $(\ln 2/\pi)^{1/2}$. The similarity introduces ambiguity in the interpretation of the phonon relaxation and transport.

The experimentally measured phonon lifetime in the case of a bottleneck is approximately the time for the created phonons to be removed from the bandwidth of the spin resonance. This process can take place directly by transport of the phonons out of the crystal, or indirectly through interaction with other modes of energy transport. In this sense, resonant trapping is a direct removal of phonons, and the lifetime can be interpreted to be approximately the average number of direct-process interactions as the phonons are diffusing to the sides of the crystal, multiplied by the capture time T_{1d} . This interpretation assumes that the time between phonon absorptions is much smaller than the capture time which has been explicitly assumed in the formulation of the resonant trapping theory.

The hot-phonon theory with the phonon lifetime equal to the time of flight applies only where the phonon mean free path is greater than the crystal size. Thus the ambiguity between the two formulations can be resolved by a simple computation of the phonon mean free path.

III. KINETIC FORMULATION OF PHONON BOTTLENECK

It is well known that there exists a large acoustic impedance mismatch between the ethyl sulfates and liquid helium. The acoustic-energy transmission coefficient for normal incidence is given by $T_a = 4A/(1+A)^2$, where

$$A = \frac{\rho_{He} v_{He}}{\rho_{ES} v_{ES}} = \frac{(0.125 \text{ g/cm}^3) \times (2.4 \times 10^4 \text{ cm/sec})}{(1.8^3 \text{ g/cm}^3) \times (2.0 \times 10^5 \text{ cm/sec})} \cong 8.3 \times 10^{-3}. \quad (8)$$

Assuming specular-type reflection, the lifetime of the phonon in the crystal due to this attenuation process alone is approximately 1.5×10^{-5} sec for a crystal thickness of 1.0 mm. The phonon flux makes 30 passes through a 1-mm crystal before it is attenuated by one exponential. Acoustic measurements for quartz immersed in liquid He verify the use of expression (8) for the transmission coefficient.¹⁰

A theory is proposed for these cases, which possess in combination a phonon reflection coefficient and mean free path such that the phonon flux, generated by spin-lattice relaxation, is constant throughout the crystal. As a consequence, the spin temperature is also constant throughout the crystal. The flux acts as a pumping term for the spin system and inhibits the relaxation if the spin population is not inverted.

The rate equations for the spin system and the phonon flux are

$$\frac{d\Delta N^+}{dt} = -\frac{\Delta N^+}{T_1} + N \bar{\sigma} \Phi, \quad (9)$$

$$\frac{d\Phi}{dt} = -v \frac{d\Delta N^+}{dt} - \frac{\Phi}{T_{ph}}, \quad (10)$$

where Φ is the phonon flux, $\bar{\sigma}$ is the average cross section for the flux, T_{ph} is the lifetime of the flux, and $\Delta N^+ = N^+ - N_0^+$ (N_0^+ is the static equilibrium density of the spins). The equations will be solved assuming $\bar{\sigma}$ is a constant, or $T_s \cong T$. This is equivalent to assuming $|\Delta N^+| \ll N_0^- - N_0^+$.

The initial conditions $\Phi(t=0) = 0$ and $\Delta N^+(t=0) = \Delta N^+(0)$ are assumed. The solution is given by

$$\Delta N^+(t) = \frac{\Delta N^+(0) (N \sigma v + 1/T_{ph})}{b-a} (e^{-at} - e^{-bt}) + \frac{\Delta N^+(0)}{a-b} (ae^{-at} - be^{-bt}), \quad (11)$$

¹⁰ B. E. Keen, P. W. Matthews, and J. K. Wilks, Phys. Letters 5, 5 (1963).

where

$$a = \frac{1}{2} \left\{ 1/T_1 + 1/T_{ph} + vN\bar{\sigma} + \left[(1/T_1 + 1/T_{ph} + vN\bar{\sigma})^2 - 4/T_1 T_{ph} \right]^{1/2} \right\},$$

$$b = \frac{1}{2} \left\{ 1/T_1 + 1/T_{ph} + vN\bar{\sigma} - \left[(1/T_1 + 1/T_{ph} + vN\bar{\sigma})^2 - 4/T_1 T_{ph} \right]^{1/2} \right\}.$$

For the experimental results reported on here, $T_1 \gg T_{ph}$, and hence we have

$$(1/T_1 + 1/T_{ph} + vN\bar{\sigma})^2 > 4/T_1 T_{ph}.$$

Therefore, we have

$$a \cong 1/T_1 + 1/T_{ph} + vN\bar{\sigma}, \quad b \cong 1/(T_1 + T_{ph} + T_1 T_{ph} v \bar{\sigma}).$$

Now $a \gg b$, and Eq. (11) reduces to

$$\Delta N^+(t) = \Delta N^+(0) e^{-bt}. \quad (12)$$

The decay constant $1/b$ is the bottleneck relaxation time T_b :

$$T_b = T_1 (1 + T_{ph} v \bar{\sigma}) + T_{ph}. \quad (13)$$

The cross section, given in Eq. (5), averaged over a Gaussian line is $\sigma(\omega_0)/\sqrt{2}$. Substitution of this result into (13) yields

$$T_b = T_1 + T_{ph} + \frac{1}{2} (\pi^2 \ln 2)^{1/2} (\hbar/kT)^2 v^3 (N/\Delta\omega) T_{ph}. \quad (14)$$

It is worthwhile pointing out two cases of interest when $\bar{\sigma}$ is not a constant during the relaxation. When T_s is infinite, at the beginning of the relaxation, the absorption cross section is zero. The spin system will initially relax at the true spin-lattice rate. If T_s is negative, the cross section becomes negative, signifying induced emission, and the spin system relaxes at a rate exceeding the true spin-lattice relaxation time. This effect was observed by Brya and Wagner.¹¹ In each of these cases, $T_s = \infty$, and $T_s < 0$, the subsequent relaxation of the spin system will be nonlinear.

The bottleneck relaxation time calculated here is almost identical, except for a numerical factor, to that computed by Scott and Jefferies.² However, the physical models used to derive the results are quite different. The model used here depends upon a large phonon reflection coefficient at the surface. As a result, there is no spatial dependence of the spin temperature. The equations can thus be applied to those physical situations where the spin temperature and phonon flux are spatially independent regardless of the cause. This fact is the reason for the agreement with the results of the equations used by Scott and Jefferies.

The equations derived here predict that a bottlenecked condition will exist, with the restriction $T \cong T_s$, when

$$T_{ph} \geq L/v,$$

where L is the mean free path and v is the group velocity of the phonons.

¹¹ W. J. Brya and P. E. Wagner, Phys. Rev. Letters 14, 431 (1965).

In contrast to the above results, the condition necessary for a bottleneck due to resonant trapping of phonons is $l > L$, where l is the sample thickness. This condition again points out that resonant trapping does not account for phonon relaxation processes within the crystal.

IV. DESCRIPTION OF OPTICAL METHOD

The method of optical detection of spin-lattice relaxation to be described here was first performed by Asawa and Satten.¹² The method is based on the fact that the excited states $|4f)^{x-1}$, $|5d\rangle$ of opposite parity to the ground state $|4f)^x$ are far removed in energy, owing to the free-ion Hamiltonian. This is the reason for neglecting the terms of odd parity in the static and dynamic crystalline field terms. It is just these odd-parity terms that cause a very small amount of wave-function mixing between opposite parity states; and, as a result, weak optical electric dipole transitions are allowed between the $|4f)^x$ states. The selection rules are no longer determined by the spherical symmetry of the free ion but, rather, by the symmetry of the nearest neighbors surrounding the rare-earth ion. For certain point symmetry groups, circularly polarized light will selectively monitor one of the states comprising the ground-state doublet.

In the above discussion, it has been presumed that the light is traversing the crystal along the major symmetry axis. If the light traverses the crystal along a different axis, then the states of the crystal must be rotated to this new axis. The optical selection rules are determined by both the ground and optically excited states, so that a rotation must be performed for both. In addition to the wave-function mixing, the optical activity along the new axis may change the light polarization. Both effects will cause the incident circularly polarized light to monitor both states of the ground doublet instead of a single spin state. The signals from the $|+\rangle$, $|-\rangle$ ground states are opposite in polarization, and there is a loss of signal when the light monitors both states. For this reason, the light and magnetic field are along the c axis of the rare-earth ES crystals used in the experiments reported on here.

The word monitor is emphasized here, because the transitions are weak (oscillator strength about 10^{-6}),¹³ and only a small fraction of the atoms are pumped by normal optical light sources. For the odd-electron rare-earth ions, C_{3h} symmetry generates selection rules that allow selective monitoring of the ground-state doublet.

The spin-lattice relaxation is measured in the following manner. The population of the ground-state spin system is pulsed out of equilibrium by microwave radiation at the Larmor frequency. The change in population of either the $|+\rangle$ or $|-\rangle$ states comprising the ground doublet is monitored by the right- or left-circularly

¹² C. K. Asawa and R. A. Satten, Phys. Rev. 127, 1542 (1962).

¹³ R. A. Satten (private communication).

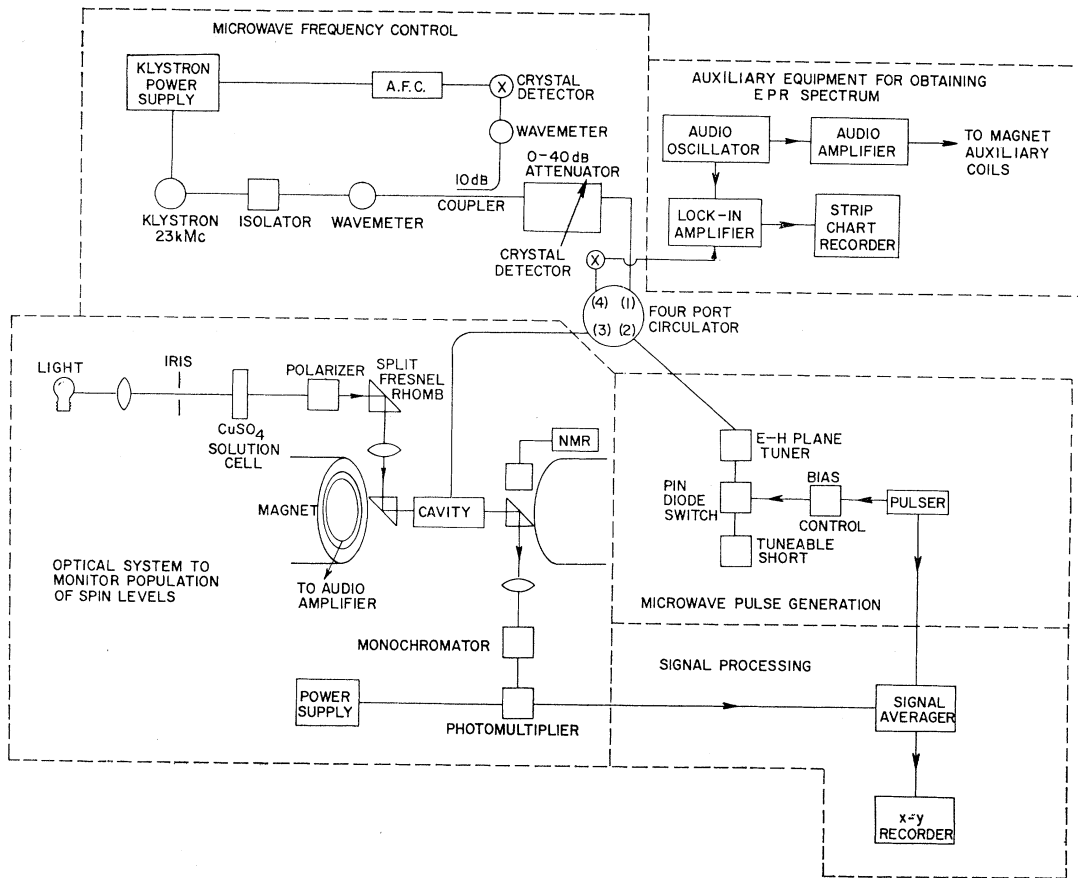


FIG. 1. Block diagram of microwave optical detection system.

polarized light. A block diagram of the optical and microwave equipment is shown in Fig. 1. The selection rules for absorption to the optically excited state will determine which mode of circularly polarized light will monitor the $|+\rangle$ or the $|-\rangle$ state. The strength of the absorption is related to the number of spins in the state being monitored.

The monochromator used in this experiment was a Jarrell-Ash $\frac{1}{2}$ -m Fastie modified Ebert mount with proving ring slits for better light-gathering power. The instrument used a 30 000-line/in. grating (2×2 in.) blazed at 7500 \AA . The resolution of the instrument in first order was at best 0.3 \AA , with the minimum slit width of 5μ .

The slit width was variable from 5 to 100μ . Because of the broad optical line utilized, the monochromator was operated with the maximum slit width of 100μ . The dispersion of the instrument at the exit slit is 16 \AA/mm . The bandwidth of the instrument is given by

$$\Delta\nu = (c/\lambda^2)\Delta\lambda = (c/\lambda^2)sd, \quad (15)$$

where s is the operating slit width and d is the dispersion.

The bandwidth above corresponds to a magnetic field width of

$$\Delta H = (h/g\beta)csd/\lambda^2. \quad (16)$$

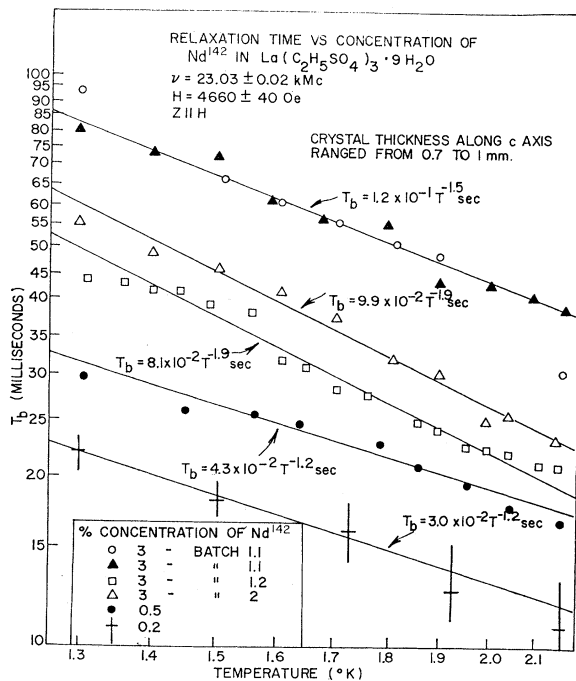


FIG. 2. Relaxation time versus concentration of Nd^{142} in LaES.

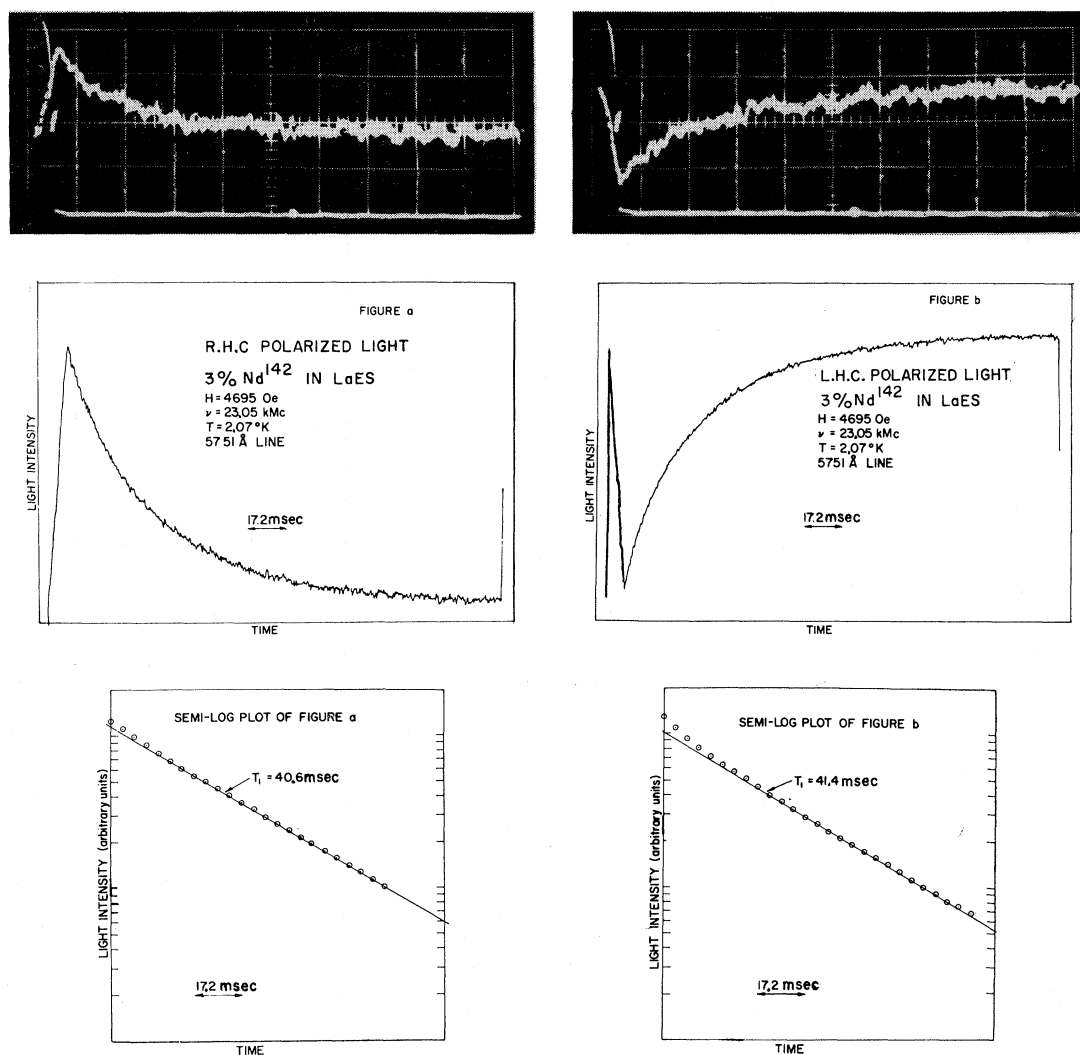


Fig. 3. Spin-lattice relaxation monitored by left- and right-circularly polarized light.

For a $100\text{-}\mu$ slit, and taking $\lambda = 5000 \text{ \AA}$ and $g = 3.54$,

$$\Delta H = 3.9 \times 10^4 \text{ Oe.}$$

Therefore, the optical method for detection of spin-lattice relaxation monitors not only the EPR line that is being saturated by microwave power, but also all other components of the line due to dipolar, hyperfine, etc., interactions.

It is instructive at this point to compute the linewidth monitored by the usual microwave method of detection of spin-lattice relaxation:

$$\Delta H = (\hbar/g\beta)\Delta\nu,$$

where $\Delta\nu$ is the bandwidth of the klystron power spectrum. Using the same g value as in the optical case, and estimating the bandwidth of the klystron radiation to be $\Delta\nu \cong 0.1 \text{ MHz}$, we obtain

$$\Delta H \cong 0.02 \text{ Oe.}$$

It is concluded that the optical method of measuring spin-lattice relaxation is not affected by spin diffusion within the ESR linewidth or cross relaxation to hyperfine components within 10^4 G of the line being measured. The microwave method must ensure that the entire linewidth is saturated; otherwise spin diffusion to the wings of the line will cause an apparent shortening of the spin-lattice relaxation time.¹⁴

V. DISCUSSION OF EXPERIMENTAL RESULTS FOR Nd^{142} LaES

The spin-lattice relaxation times were measured in Nd^{142} LaES and natural-Nd LaES within the temperature range $1.29\text{--}2.15^\circ\text{K}$. The magnetic field was parallel to the c axis, and the microwave frequency was approximately 23 GHz . The resonant frequency varied

¹⁴ C. F. Davis, Jr., M. W. P. Strandberg, and R. L. Kyhl, Phys. Rev. **111**, 1268 (1958).

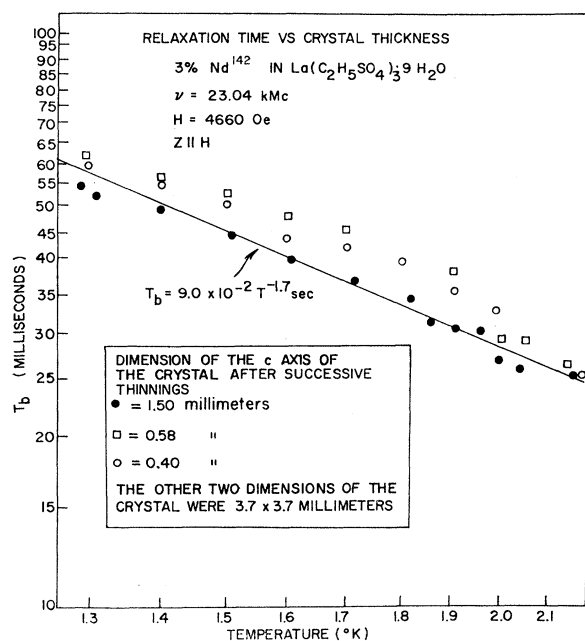


FIG. 4. Relaxation time versus crystal thickness.

slightly with temperature and sample size. The natural-Nd concentration in LaES ranged from 0.5 to 100% by weight. The Nd^{142} concentration was varied from 0.2 to 3% by weight.

From Gruber and Satten's¹⁵ crystal field parameters for NdES, it has been calculated that the direct process should be the dominant mechanism of relaxation within the temperature range of the measurements. The calculated relaxation time for the direct process is given by

$$T_1(\text{predicted}) = (7.3 \times 10^{-3} \text{ sec})/T,$$

with T in degrees Kelvin. If the Scott-Jefferies (SJ) experimental results (Fig. 16 of Ref. 2) for the relaxation of 0.5% Nd^{142} LaES are extrapolated by the $1/\omega^4$ dependence of the direct process, the following is obtained:

$$T_1 = (1.0 \times 10^{-2} \text{ sec})/T.$$

For the extrapolation, the SJ value of $T_1 = 2.7 \times 10^{-1}$ sec at 9.36 GHz with \mathbf{H} parallel to the c axis and $T = 1.4^\circ\text{K}$ has been used.

Figure 2 shows the relaxation time for various Nd^{142} concentrations. The data for the 0.2% concentration determine $T_b = 3.0 \times 10^{-2} T^{-1.2}$ and demonstrate that the relaxation is proceeding at almost the rate determined by the extrapolated result. As SJ have confirmed, and as is also confirmed here, the theoretically predicted relaxation rate is in surprisingly good agreement with the observed rate, considering the approximations that have

¹⁵ J. B. Gruber and R. A. Satten, *J. Chem. Phys.* **39**, 1455 (1963).

been used. The relaxation rate measured here also confirms the $1/\omega^4$ dependence of the direct process.

As the concentration is increased, the data clearly indicate an increase in the relaxation times and a temperature dependence approaching T^{-2} . Figure 3 displays the relaxation rate for a 3% Nd^{142} sample monitored by both left- and right-circularly polarized light. Figures 3(a) and 3(b) are the sums of approximately 500 signals which were stored in the memory of the Fabritek noise averager. At the beginning of the relaxation, the rate is several times faster than the rate at the tail of the curve. The faster relaxation rate agrees well with the rate measured for the 0.2% concentration at this temperature. This indicates that the spin system starts to relax by the direct process, and then the rate of relaxation is impaired by the phonon flux that has been created. The fast recovery at the beginning of the relaxation became more apparent for the higher concentrations. The two rates were clearly apparent in about 60% of the data for concentrations equal to or greater than 3% Nd.

A 3% sample was thinned along the c axis, and the relaxation times were measured for a thickness ranging from 1.5 to 0.40 mm. The data for this sample are displayed in Fig. 4. The relaxation times increased very slightly with the thinning. This result establishes that the observed bottleneck relaxation time does not arise from a process which is dependent on the actual crystal thickness. The following processes are then eliminated.

(1) *Phonon transport described by classical diffusion equation.* Giordimaine *et al.*² have computed a diffusion constant for $\hbar\omega \gg kT$ and $\hbar\omega \ll kT$. They obtain

$$D_S = 48\pi^2\omega^2/N \quad \text{and} \quad D_S = 24(kT)^2/N\hbar^2,$$

respectively. For a rectangular plate, infinite in the y and z directions, the simplest eigenfunction solution of the diffusion equation ($\text{sink}x$) fixes $T_{\text{ph}} = l^2/D_S\pi^2$, where l is the thickness of the plate.

(2) *Resonant phonon trapping.* As previously discussed, this process yields a $T_b \propto l(\ln Al)^{1/2}$ and does not depend on T_{ph} .

(3) *Transmission of phonons through crystal walls.* For specular reflection and perpendicular incidence, we have

$$\frac{d\Phi}{dt} = -T_a \frac{\Phi}{l}.$$

Then $T_{\text{ph}} = l/vT_a$, where v is the phonon velocity, Φ is the phonon flux, and T_a is the acoustic transmission coefficient.

For specular reflection not at perpendicular incidence, and for diffuse reflection, l will have a numerical coefficient in front of it which accounts for the different phonon path lengths through the crystal.

(4) *Inelastic scattering at crystal wall.* This case is the same as (3) except that T_a is replaced by the proba-

bility of phonon inelastic scattering upon collision with the walls.

For a large acoustic impedance mismatch, we have

$$T_b \cong T_1 + (T_{ph}/T^2)_{1/2} (\pi^3 2 \ln 2)^{1/2} (\hbar/K)^2 v^3 N / \Delta\omega.$$

In the expression above, T_{ph} has been deleted, since $T_1 \gg T_{ph}$. For 3% doping of Nd^{142} , the linewidth was measured to be 100 Oe. Inserting the numerical factors in the above expression, we determine the relation

$$T_b = 1.0 \times 10^{-2} / T + 2.5 \times 10^3 (T_{ph}/T^2) \text{ sec},$$

where T has units of °K and T_{ph} has units of sec. (The extrapolated result of SJ has been used for T_1 .) The above expression is then compared with the following experimental results from Fig. 2:

$$T_b = 8.1 \times 10^{-2} / T^{1.9} \cong 8.1 \times 10^{-2} / T^2 = 2.5 \times 10^3 T_{ph} / T^2, \\ T_{ph} = 3.2 \times 10^{-5} \text{ sec}.$$

For the other 3% sample in Fig. 2, with $T_b = 9.9 \times 10^{-2} T^{-1.9}$, and the progressively thinned sample in Fig. 3, with $T_b = 9.0 \times 10^{-2} T^{-1.7}$, T_{ph} equals 39 and 36 μ sec, respectively. The same assumptions have been made here as in the previous calculation.

It is noted that the times for T_{ph} are approximately 70 times greater than the time of flight to the sides of the crystal, which confirms that the relaxation is not the time of flight to the sides. The measurements indicate that T_{ph} does not vary with temperature, and hence the relaxation cannot be due to phonon-phonon collision, which Klemens¹⁶ has computed to have a T^{-4} dependence. Also, the experimental T_{ph} is about a factor of 2 longer than the predicted lifetime due to specular reflection. This indicates that the impedance mismatch at the liquid-helium-crystal interface is larger than that computed by Eq. (8).

By comparing the direct and bottleneck rates, and assuming T_{ph} is temperature-independent, we predict that the relaxation will not be bottlenecked for $T > 9^\circ\text{K}$. The product of T_{1d} and the phonon absorption cross section becomes too small at higher temperatures to influence the relaxation. However, the above transition would not be observed in this instance, since the Raman process becomes dominant at these higher temperatures, and thereby dissolves the bottleneck.

The relaxation times for several crystals with 3% concentration of Nd^{142} were measured, because of a disagreement in the results obtained for the first two samples. One batch of crystals (denoted as 1.1 in Fig. 2) yielded longer relaxation times and a $T^{-1.5}$ temperature dependence.

Another batch of crystals was grown from a beaker of prepared solution from which the solution for batch 1.1 had been taken. These new crystals (labeled 1.2) yielded shorter relaxation times and a $T^{-1.9}$ temperature dependence which has already been discussed. A com-

¹⁶ P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. VII, p. 1.

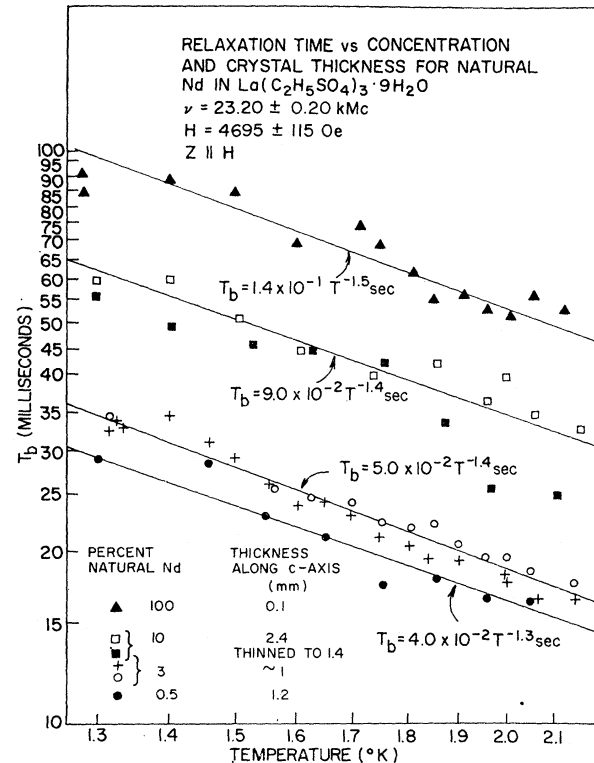


Fig. 5. Relaxation time versus concentration and crystal thickness for natural Nd in LaES.

pletely new solution was prepared, and the results from this batch (designated batch 2) were in good agreement with the results of batch 1.2.

It is presumed that the results for batch 1.1 differed from the results for the other 3% crystals because of a longer T_{ph} and, possibly, a longer T_1 associated with it.¹⁷ Batch 1.1 yielded crystals of unusually good quality. The crystals were very clear, well-shaped hexagonal plates and rods of jewel-grade quality.

If the curves for batch 1.1 were fitted to a T^{-2} dependence, T_{ph} would be approximately 1.4 times larger than the average of the three values already computed.

VI. DISCUSSION OF EXPERIMENTAL RESULTS FOR NATURAL Nd IN LaES

On comparing the data for natural Nd (Fig. 5) and Nd^{142} (Fig. 2). We conclude that the results are in fair agreement for the 0.5% concentrations. For the higher concentrations of natural Nd, the relaxation time increases, but more slowly than that of Nd^{142} . Also, the temperature dependence does not approach T^2 as the Nd^{142} does.

The part of T_b which has a $1/T^2$ dependence is proportional to $N/\Delta\omega$. The linewidths at 3 and 100% are estimated to be 100 and 400 Oe, respectively. Therefore,

¹⁷ D. R. Mason and J. S. Thorp, *Phys. Rev.* **157**, 191 (1967).

the ratio of $N/\Delta\omega$ at 3% to that at 100% is 8.3. The relaxation times observed at 100 and 3% are given by

$$T_b(100\%) = 1.4 \times 10^{-1} T^{-1.5} \text{ sec},$$

$$T_b(3\%) = 5.0 \times 10^{-2} T^{-1.4} \text{ sec}.$$

If their temperature dependence is taken to be approximately equal, then we have

$$T_b(100\%)/T_b(3\%) = 2.8.$$

It is concluded that the bottlenecked relaxation rate is increasing at less than the rate predicted by the $N/\Delta\omega$ dependence. These facts could indicate that the hyperfine components associated with the natural Nd are effective in relieving the bottleneck. Approximately 20.5% of the isotopes included in the natural Nd have a nuclear moment.

A crystal of 10% natural-Nd LaES was thinned to one-half its original size. The data points (Fig. 5) obtained for both the thinned and unthinned crystals have considerably more scatter than the analogous data for the 3% Nd¹⁴². However, it is concluded that there is no appreciable difference in the relaxation between the thick and thin 10% crystals.

Since the optical method monitors the hyperfine structure along with the spins in the primary EPR line, cross relaxation *per se* will not affect the measured spin-lattice relaxation time. Upon relaxation, the hyperfine structure will emit phonons that are not resonant with the spins in the main EPR line. The phonons have a smaller probability for reabsorption because of the smaller number of spins associated with the particular hyperfine component. As a consequence, the cross relaxation effectively reduces the average phonon reabsorption probability.

VII. SUMMARY AND CONCLUSIONS

The lifetime due to resonant trapping via the direct process has been computed for phonons. It is concluded that resonant trapping can create a bottleneck only if the phonon mean free path is much less than the crystal dimensions. This requirement restricts resonant trapping to paramagnetic ions with short direct- or Orbach-process lifetimes and large paramagnetic ion concentrations.

The cross section for reabsorption by the direct process has been calculated and can be used to deter-

mine whether a phonon bottleneck due to resonant trapping is possible.

Also, if resonant trapping is the mechanism responsible for the bottleneck, then the phonon lifetime cannot be the time of flight to the sides of the crystal.

A bottlenecked relaxation rate has been observed for Nd¹⁴² concentrations of 3% in LaES. The calculated mean free path of the phonons is much greater than the sample size, and it is postulated that the bottleneck is a consequence of the large acoustic impedance mismatch at the crystal-liquid-helium interface. Since variation of the crystal thickness did not affect the bottleneck rate, it was concluded that the phonon relaxation is the result of an interaction process within the crystal. The average value of T_{ph} obtained from the 3% Nd¹⁴² samples is 36×10^{-6} sec. The diverse data for the various batches of 3% Nd¹⁴² crystals suggest that the phonon relaxation could be attributed to some type of crystal imperfection. The phonon could relax by exciting local phonon modes associated with the imperfection.

The data taken at a microwave frequency of 23 kMc for the 0.2% Nd¹⁴² agree well with the extrapolated results at 9.3 kMc of SJ for the same salt. The data are also in good agreement with the relaxation rates theoretically predicted by the phenomenological description of the direct process. The 0.2% results verify the $1/\omega^4$ dependence of the direct process, and demonstrate that the bottleneck has been averted by an order-of-magnitude reduction of the paramagnetic ion concentration. The reduction has two effects that quench the bottleneck. First, the phonon flux generated by the direct process is reduced; second, the macroscopic phonon absorption cross section ($N\sigma$) is also reduced. From Eq. (9) it is readily seen that a change in concentration leaves the equation invariant except for the pump term $N\sigma\Phi$, which is directly proportional to the change. Thus, with reduced concentration, the phonons become progressively ineffective as a pump on the spin system.

The results for natural Nd suggest that the T^2 dependence of the phonon bottleneck is modified by cross relaxation to the hyperfine components. Since the optical method monitors the main EPR line and the hyperfine components, cross relaxation *per se* has no observable effect on the relaxation. The spins within the hyperfine lines probably relax with an unbottlenecked rate, and one should not expect the observed relaxation times to agree with the time predicted by the usual formulation of the phonon bottleneck.

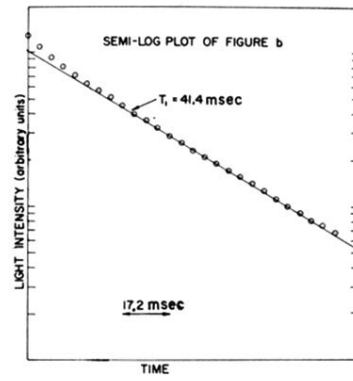
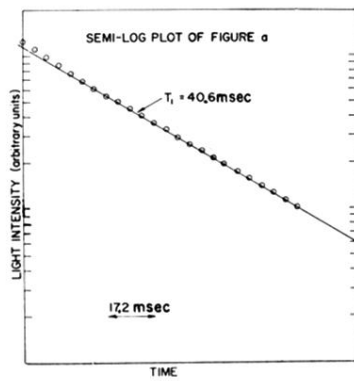
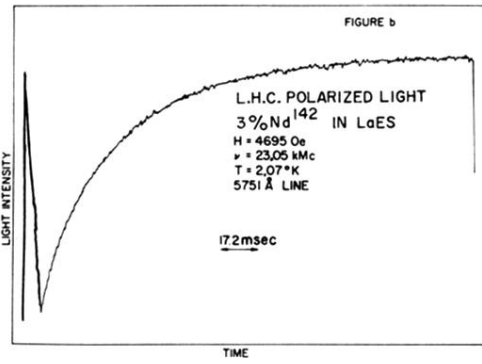
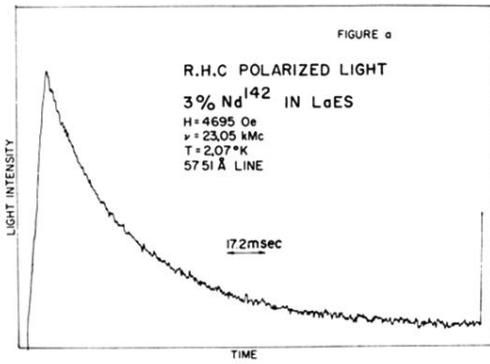
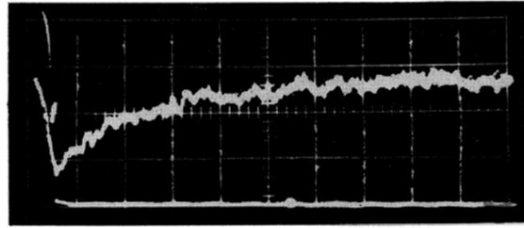
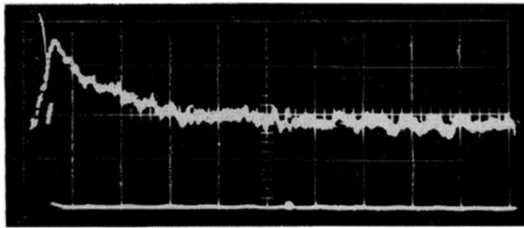


FIG. 3. Spin-lattice relaxation monitored by left- and right-circularly polarized light.