estimated the ground-state configuration coordinate frequency to be 1.7×10^{12} cps or about one-fifth the longitudinal optical mode frequency. In CsBr the corresponding ground-state frequency (0.77×10^{12} sec^{-1}) is about one-fifth the longitudinal optical mode frequency (4.1×10^{12} sec^{-1}) which is much lower in CsBr than in NaCl.

The appropriate model for the M center appears to be two F centers.[19] It is surprising that the M band in CsBr, if it too arises from two adjacent F centers, does not exhibit the structure of the F band. Other aggregate bands, especially the R, do not develop to a great extent in CsBr; the bands located between the F and M bands are weak at all times. No "negative absorption"[3] occurred in the region between the F and M bands. Irradiation seems necessary in order for luminescence to be stimulated in this wavelength region.

ACKNOWLEDGMENTS

The author wishes to thank R. W. Major who aided in the early stages of the experimental work and Dr. Ronald Fuchs for several helpful discussions.

---

[19] C. Z. van Doorn and Y. Haven, Philips Research Repts. **11**, 479 (1956), and C. Z. van Dorn, Philips Research Repts. **12**, 309 (1957).

PHYSICAL REVIEW VOLUME 127, NUMBER 5 SEPTEMBER 1, 1962

Direct Optical Detection of the Ground-State Population Changes of Neodymium in Ethylsulfate Crystals*

C. K. Asawa†
Hughes Research Laboratories, Malibu, California

AND

R. A. Satten‡
Department of Physics, University of California, Los Angeles, California

(Received April 16, 1962)

A method is described for optically detecting population changes in paramagnetic salts and applied to the ground state of neodymium ethylsulfate and neodymium in lanthanum ethylsulfate. By observing the transmitted right or left circularly polarized light, the population of *one* of the ground Zeeman levels is selectively monitored. The ground-state population is changed by paramagnetic resonance and thermal relaxation processes. Knowing the ground state, the circular polarization of the light, and the selection rules, information about the excited states can be obtained. The spin-lattice relaxation time between Zeeman sublevels of the ground state is also obtained. After pulsing the microwave resonance transition, the decay of the transmitted light is observed; the decay curve is related to the spin-lattice relaxation curve. Relaxation-time measurements in the temperature range of 1.87 to 2.16°K were made in both the pure and dilute salt. The values ranged from 17 msec for the lower temperature to 11 msec for the higher temperature. The slope of the relaxation time versus the temperature T indicates a temperature dependence for the relaxation time of $T^{-2.5}$ in this temperature range for the 3% neodymium in lanthanum ethylsulfate and $T^{-1.7}$ for the neodymium ethylsulfate crystal. The crystal c axis was oriented parallel to the magnetic field of 4780 Oe; the microwave frequency was 23.6×10^{9} cps.

INTRODUCTION

A VARIETY of experiments have been discussed or performed whose purpose has been to measure optically population changes or spin relaxation between ground Zeeman sublevels.

Wesemeyer and Daniels[1,2] have examined the effect of paramagnetic resonance saturation on the Faraday effect in neodymium ethylsulfate. They examined the spectral region about 200 Å away from strong absorption lines using the 5461 Å line of mercury as did Becquerel, DeHaas, and van den Handel[3] in their work on the Faraday rotation of neodymium ethylsulfate. Daniels and Wesenmeyer found that when the crystal absorbed microwave energy in paramagnetic resonance and the microwave power was sufficient to cause appreciable saturation, the magnetic moment and the Faraday rotation were reduced, as predicted by Kastler.[4]

More recently, Daniels and Rieckhoff[5] have utilized

---

* The research reported herein was supported in part by the Army Research Office, Durham, North Carolina.

† This paper forms a part of the dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics at the University of California, Los Angeles, California, January, 1962.

‡ On leave as Fulbright Research Scholar (1961–62) at the Institut de Physique, Université de Strasbourg, Strasbourg, France.

[1] H. Wesemeyer and J. M. Daniels, Z. Physik **152**, 591 (1958).

[2] J. M. Daniels and H. Wesemeyer, Can. J. Phys. **36**, 405 (1958).

[3] J. Becquerel, W. J. DeHaas, and J. van den Handel, Physica **5**, 753 (1938).

[4] A. Kastler, Compt. rend. **232**, 953 (1951).

[5] J. M. Daniels and K. E. Rieckhoff, Can. J. Phys. **38**, 604 (1960).

the Faraday rotation to measure instantaneous populations in the ground doublet. The populations were disturbed by pulses of microwave power, and the approach to equilibrium was studied. The relaxation times for neodymium ethylsulfate were measured for the temperatures between 1.3 and 4.2°K and for magnetic fields between 80 and 6000 Oe. *X*-band equipment was used. The 5461 Å line of mercury was used for the study. Daniels and Rieckhoff found that the relaxation time decreased with magnetic field and varied with temperature approximately as $1/T^3$.

Dehmelt[6] has observed the spin relaxation of optically polarized sodium atoms by examining the transmitted light. In the initial experiments microwave radiation was not used. Dehmelt[7] has suggested that a weak light beam at a right angle to the main polarizing beam will be modulated at radio frequencies. Bell and Bloom[8] have extended this discussion and have observed this effect. Recently, Bloembergen, Pershan, and Wilcox[9] suggested the application of Dehmelt's method to the modulation of light at radio frequencies using paramagnetic solids. Optical detection of paramagnetic resonance in ruby has been reported by Wieder.[10] The optical detection of paramagnetic resonance in the ground state of ruby using circularly polarized light has been suggested as an experiment by Brossel, Geschwind, and Schawlow.[11]

The following three topics are discussed in this paper: (1) the optical detection of ground-state population changes utilizing the absorption of circularly polarized light; (2) utilization of the technique to obtain information about the excited states; (3) direct, instantaneous measurement of the spin-lattice relaxation time in the ground state. The population changes in the ground state are induced by microwave paramagnetic resonance absorption and spin-lattice relaxation processes. The use of circularly polarized light permits the observation of the population change of *one* of the ground Zeeman levels.

Broad-spectrum, circularly polarized light is transmitted through the crystal containing the paramagnetic ion. The transmitted light is examined at the absorption lines with a medium-resolution spectrometer.

The neodymium ion satisfies the requirements for the experimental method of this report. The ion not only shows strong paramagnetic resonance absorption but shows sharp optical absorption lines which lie within the spectral range of high-brightness sources and sensitive photodetectors. In recent years, knowledge about the ion and its crystalline hosts has been greatly expanded. The identification of many of the energy levels serves as a guide for developing the techniques of this experiment.

DISCUSSION OF THE EXPERIMENT

Neodymium

The ground configuration of the triply ionized neodymium ion is $4f^3$ and its nuclear charge is $Z=60$; the ground state of the ion is given by Hund's rule as $^4I_{9/2}$. The degenerate J levels of the free ion are split by the host crystalline electric fields. Since triply ionized neodymium has an odd number of electrons, its energy levels will have an even degeneracy in any crystalline electric field (Kramer's theorem). Since the site symmetry of the neodymium ion in the ethylsulfate crystal is C_{3h} with nearest-neighbor symmetry D_{3h}, the normal degeneracy of the levels in this environment is twofold. This simplifies the analysis of our experiment somewhat. A number of workers have contributed to the interpretation of neodymium ion spectra which has lead to our present state of knowledge of this ion. However, it seems inappropriate to enumerate them all here. Rather we shall mention only one, the work of Carlson and Dieke,[12] as illustrative. From paramagnetic resonance data for neodymium ethylsulfate, Elliott and Stevens[13] calculated the crystal field splittings of the ground $^4I_{9/2}$ manifold and determined the states and energy levels as

State	Energy (cm^{-1})
$0.92\|\pm7/2\rangle+0.38\|\mp5/2\rangle$	0
$\|\pm1/2\rangle$	130
$0.75\|\pm9/2\rangle+0.66\|\mp3/2\rangle$	170
$0.38\|\pm7/2\rangle-0.92\|\mp5/2\rangle$	340
$0.66\|\pm9/2\rangle-0.75\|\mp3/2\rangle$	350

Selection Rules—Electric Dipole Transitions for Circularly Polarized Light

In agreement with the convention used by Born and Wolf,[14] "we say that the polarization is *right-handed* when to an observer looking in the direction from which the light is coming, the end point of the electric vector would appear to describe the ellipse in the clockwise sense." With *left-handed* polarization, counter-clockwise rotation would be observed. The conservation of angular momentum or the semiclassical treatment of the interaction of radiation and matter shows that σ_R corresponds to the operator $\sigma^-=x-iy$, and σ_L corresponds to the operator $\sigma^+=x+iy$, by which we imply that σ^- lowers M_J by one and σ^+ increases M_J by one in absorption. However, one must not suppose that the M_J states for transitions within the f^n configuration will necessarily follow such a rule.

---

[6] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957).

[7] H. G. Dehmelt, Phys. Rev. **105**, 1924 (1957).

[8] W. E. Bell and A. L. Bloom, Phys. Rev. **107**, 1559 (1957).

[9] N. Bloembergen, P. S. Pershan, and L. R. Wilcox, Phys. Rev. **120**, 2014 (1960).

[10] I. Wieder, Phys. Rev. Letters **3**, 468 (1959).

[11] J. Brossel, S. Geschwind, and A. L. Schawlow, Phys. Rev. Letters **3**, 548 (1959).

[12] E. H. Carlson and G. H. Dieke, J. Chem. Phys. **34**, 1602 (1961).

[13] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

[14] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, New York, 1959), p. 27.

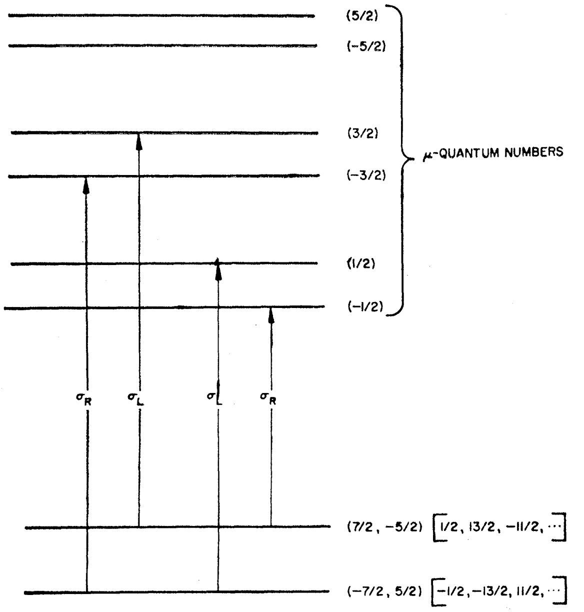

FIG. 1. Electric dipole selection rules for circularly polarized light in neodymium ethylsulfate. The 5211 and 5795 Å absorption lines arise from transitions to the ($\pm 1/2$) states while the 5099, 5227, and 5751 Å lines arise from transitions to the ($\pm 3/2$) states. See Table I.

Such a rule *does* permit the determination of selection rules if applied to opposite parity parts of the lower and upper states of a transition, as illustrated below.

The electric dipole transitions observed in the absorption spectra of the rare-earth ions in crystals whose electric fields are of trigonal symmetry arise from weak mixing of the higher configurations of opposite parity into the ground f^n configuration, the mixing is a result of the odd-parity part of the crystal field. Although in the crystalline-field energy calculations the odd-parity portion of the field plays no part, it is of primary importance in permitting the observed electric dipole transitions. The expansion of the crystalline-field potential V_c in terms of the spherical harmonics in the coordinates of the $4f$ electrons about the nucleus as origin is given as

$$V_c=\sum_{l=0}^{\infty}\sum_{m=0}^{l} A_l^m r^l[Y_l^m(\theta,\phi)+(-1)^m Y_l^{-m}(\theta,\phi)] + iB_l^m r^l[Y_l^m(\theta,\phi)-(-1)^m Y_l^{-m}(\theta,\phi)],$$

summed over all the electrons. For either D_{3h} or C_{3h} symmetry,

$$A_l^m=0,$$

unless

$$m=6n \text{ for } l \text{ even}, \quad m=6n+3 \text{ for } l \text{ odd},$$

for $n=0, 1, 2, \cdots$. For C_{3h} symmetry, the condition on the B_l^m coefficients is the same; for D_{3h}, the $B_l^m=0$. The odd-l terms with $m=3, 9, 15, \cdots$ form the odd-parity part of the crystal field; these are the terms which mix the opposite-parity configurations and permit the observed electric dipole transitions.

The selection rules for neodymium ethylsulfate are now considered. At liquid-helium temperatures only the lowest doublet $(0.92|\pm 7/2\rangle+0.38|\mp 5/2\rangle)$ is appreciably populated. With the application of a magnetic field along the c-axis, the $(0.92|+7/2\rangle+0.38|-5/2\rangle)$ state is found to be the upper state and $(0.92|-7/2\rangle+0.38|+5/2\rangle)$ is the lower state. Positive $g_{\|}$ value is assumed here (this sign gives results consistent with the σ and π spectra).

The odd-parity part of the crystalline field, noted previously, mixes opposite-parity configurations and appends to the ground states (in parentheses) small amounts of opposite-parity M_J wavefunctions (in brackets):

$$(7/2, -5/2), \quad [1/2, 13/2, -11/2]\cdots$$
$$(-7/2, 5/2), \quad [-1/2, -13/2, 11/2]\cdots.$$

The appended wavefunctions permit the electric dipole transitions to the excited states. The diagram of Fig. 1 shows the permitted electric dipole transitions from the ground states. The excited states ($\pm 1/2$), ($\pm 3/2$), and ($\pm 5/2$) arising from the ground configuration are shown. Only the μ-crystal quantum numbers,[15] denoting the residue class $M_J\equiv\mu$ (mod 6), are shown for the excited states; the ground state is indicated as above. No opposite-parity parts for the excited states are shown, since they yield redundant information for determining electric dipole transitions. No physical significance is attached to the order of labeling nor to the spacings of the magnetically split excited levels in the diagram.

Optical Detection of Paramagnetic Resonance

In this experiment a measured change in the optical absorption indicates that a change in the population of the Zeeman-split ground doublet has occurred. The latter change is brought about by the absorption of microwave energy.

Again consider the example of neodymium ethylsulfate in Fig. 1. The c axis of the crystal is aligned along the magnetic field. In thermal equilibrium the population of the upper $(7/2, -5/2)$ state is less than the population of the $(-7/2, 5/2)$ state by the Boltzmann factor $\exp(-\Delta E/kT)$, where ΔE is the splitting of the levels. Microwave resonance between the levels is permitted if $\Delta M_J=\pm 1$; the oscillating, microwave magnetic field is aligned perpendicular to the dc magnetic field. On the application to the crystal of sufficient microwave power of frequency $\nu=\Delta E/h$, the populations tend to equalize.

The average optical absorption coefficient α over some fraction of the linewidth is proportional to the difference in populations of the initial and final states.

---

[15] K. H. Hellwege, Ann. Physik 4, 95 (1948).

If light of intensity I_0 enters a crystal, light of intensity $I_0 \exp(-\alpha l)$ leaves the crystal, where l is the path length in the crystal. Thus, a change in the transmitted light will indicate that changes have occurred in α or in the populations of the initial and final levels. In most cases where the optical radiation intensity is low, the population of the final or excited level is safely assumed to be negligible.

Referring to Fig. 1, the initial states are the magnetically split ground states $(\pm 7/2, \mp 5/2)$. The final states are indicated by $(\pm 1/2)$, $(\pm 3/2)$, $(\pm 5/2)$ (μ-crystal quantum numbers). Consider the transition to the $(\pm 1/2)$ levels. Transitions with right circularly polarized light σ_R can occur from the $(7/2, -5/2)$ state to the $(-1/2)$ state. Left circularly polarized light σ_L will induce transitions from the $(-7/2, 5/2)$ state to the $(1/2)$ state. When the populations of the $(\pm 7/2, \mp 5/2)$ states are equalized by microwave absorption, the population of the $(7/2, -5/2)$ state is *increased* by one-half the difference of the initial equilibrium populations, and the population of the $(-7/2, 5/2)$ state is *decreased* by the same amount. The σ_R transitions for right circularly polarized light will be increased, i.e., the optical absorption coefficient for right circularly polarized light will be increased by a quantity $\Delta\alpha$. Similarly, the optical absorption coefficient for left circularly polarized light will be decreased by the same amount $\Delta\alpha$. The transmitted σ_R light will be decreased; the transmitted σ_L light will be increased.

The Excited States

The use of circularly polarized light in this experiment will yield information about the excited state. By noting the sign of the change in the transmitted light intensity as a result of microwave saturation, one can determine whether the excited-state doublet is a $(\pm 1/2)$ doublet or a $(\pm 3/2)$ doublet. Consider the transitions from the ground doublet to the $(\pm 1/2)$ doublet; the intensity of σ_R light transmitted through the sample will decrease when microwave power is applied, and the intensity of the transmitted σ_L light will increase. For the transitions to the $(\pm 3/2)$ levels the transmitted σ_R light intensity will increase, and the transmitted σ_L light intensity will decrease.

Relaxation-Time Measurement

The population of the lower or upper of the ground Zeeman levels is selectively monitored with the transmitted light. Equations (1) and (2) give the relationship between the transmitted light intensity and the change $\Delta\alpha$ of the absorption coefficient. Since α is proportional to the ground-state population, the change of the transmitted light intensity gives a measure of the change in the ground-state population. The lower and upper levels are labeled 1 and 2, respectively. The changes in intensities are given by

$$I_1' - I_1 = I_1[\exp(\Delta\alpha l) - 1], \tag{1}$$

$$I_2' - I_2 = I_2[\exp(-\Delta\alpha l) - 1]. \tag{2}$$

The unprimed I's are the transmitted intensities at thermal equilibrium; the primed I's are the intensities at nonequilibrium.

If $\Delta\alpha l$ is much less than unity, the above can be written as

$$I_1' - I_1 = I_1 \Delta\alpha l \tag{3}$$

and

$$I_2' - I_2 = -I_2 \Delta\alpha l. \tag{4}$$

The population change is given directly by the change in the transmitted light. If the populations of the two levels are equalized by a pulse of microwave radiation, the decay of the populations toward the equilibrium value can be directly observed. If $\Delta\alpha l$ is large, the decay is determined with Eqs. (1) and (2). The characteristic decay time is interpreted as the spin-lattice relaxation time.

One can show there is an optimum value of αl for best signal-to-noise ratio, if one takes the noise in the photomultiplier to be proportional to the square root of the photocurrent (hence square root of the intensity of light). Using Eqs. (1) and (2), one finds the optimum value

$$\alpha_1 l = 2/(1-\gamma) \ln[(3-\gamma)/(1+\gamma)],$$

for which the relative intensity change is

$$(I_1' - I_1)/I_1 = 2(1-\gamma)/(1+\gamma),$$

where γ is the Boltzmann factor, $\gamma = \exp(-1.44\nu/T)$; here ν is the Zeeman splitting in wave numbers, and T is the temperature. For $T = 2°\text{K}$, $\gamma = 0.56$ and the optimum transmission is seven percent of the incident light. Likewise the optimum for $\alpha_2 l$ is

$$\alpha_2 l = -2\gamma/(1-\gamma) \ln\gamma,$$

for which

$$(I_2' - I_2)/I_2 = (1-\gamma)/\gamma.$$

For the higher Zeeman level the optimum transmitted light is 23%, when $\gamma = 0.56$.

EXPERIMENTAL APPARATUS

A simple microwave assembly was used. A Varian reflex klystron 2K96, which nominally delivered 15 mW of microwave power, was used as the microwave source. A rectangular microwave cavity was made to operate in the TE_{102} mode. The size of the coupling iris overcoupled the cavity so that at resonance a matched condition was approached. The optical holes at the sides of the cavity lowered the Q of the cavity; with the sample in the cavity the Q was found usually to be about 1500.

The arrangement of the optical system is shown schematically in Fig. 2. A 300-W Sylvania zirconium arc lamp was used as the illumination source. Since a magnet with a hole along the axis was not readily available, a unique method was devised for obtaining circularly polarized light and transmitting it through the sample along the magnet axis. A "split" Fresnel rhomb was used. The rhomb is found to be superior to a quarter-wave plate in that the former has a broad optical range, whereas the latter is good for only a narrow optical range. The first part of the split Fresnel rhomb was designed as a right-angle glass prism with a refractive index of 1.548 for the sodium line. The glass right-angle prism at the entrance optical hole of the microwave cavity constituted the second part of the split Fresnel rhomb; the refractive index of the glass was 1.596 for the sodium line. The difference in indices of refraction of the two prisms arises from the fact that the interface of the first prism, where total internal reflection occurs, is glass to air, whereas that of the second prism is glass to liquid helium at 2°K (index of refraction, 1.028). The spectrometer was a Jarrell-Ash 1/2-meter Fastie-modified Ebert mount with curved slits for high resolution. A 30 000 lines/in. grating (2×2 in.) blazed for 5000 Å was used. The resolution was about 0.3 Å in the first order in the visible range.

DISCUSSION OF RESULTS

Optical Detection of Microwave Paramagnetic Resonance Absorption

Figures 3(a) and 3(b) illustrate the effect of paramagnetic resonance on the circularly polarized light that is transmitted through the sample; the spectrometer was set on the 5751 and 5211 Å absorption lines, respectively.

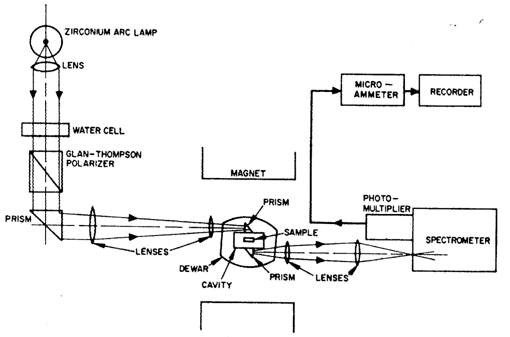

FIG. 2. Schematic of the optical system.

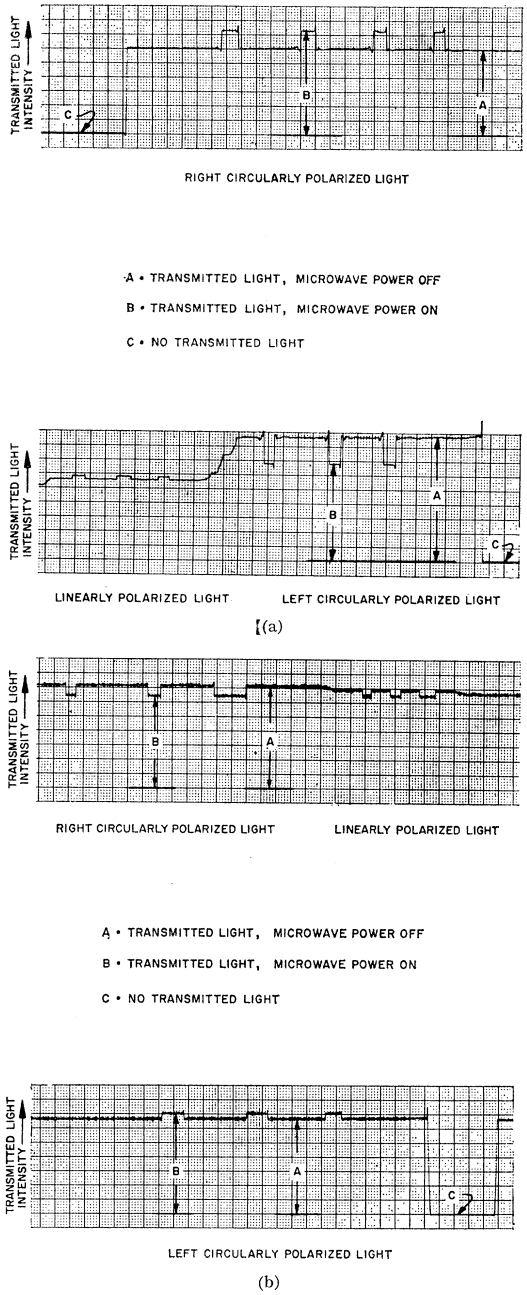

FIG. 3. (a) 5751 Å line, 3% neodymium in lanthanum ethylsulfate, 2.03°K. (b) 5211 Å line, 3% neodymium in lanthanum ethylsulfate, 1.97°K.

The sample was always mounted in the cavity with the *c* axis parallel to the magnetic field. The klystron and power supply were adjusted for continuous radiation at the cavity frequency, 23.6×10^9 cps. The magnetic field was adjusted so that the sample absorbed the microwave power. A manual waveguide switch permitted microwave power to be turned on and off. The Keithley microammeter and the recorder recorded the change in transmitted light as the microwave power was switched on and off. A 3% concentration of neodymium in lanthanum ethylsulfate was used for this study. The absorption lines at the following wavelengths were investigated: 5099, 5211, 5227, 5751, and 5795 Å. In all cases, on changing from right to left circularly polarized light, the sign of the output also changed.

When the incident light is plane (linearly) polarized or even unpolarized, it is found that microwave radiation affects the transmitted light intensities, as seen in Figs. 3(a) and 3(b). This occurs since plane polarized

TABLE I. The excited state.

Wavelength λ (Å)	Transmitted σ_R light	Excited state μ values From experiment	 From σ, π spectra
5099	Decrease	($\pm 3/2$)	($\pm 3/2$)
5211	Increase	($\pm 1/2$)	($\pm 1/2$)
5227	Decrease	($\pm 3/2$)	($\pm 3/2$)
5751	Decrease	($\pm 3/2$)	($\pm 3/2$)
5795	Increase	($\pm 1/2$)	($\pm 1/2$)

and unpolarized light contain both circular components at each frequency. Consider the transitions to the ($\pm 1/2$) levels in Fig. 1. The transition to the ($+1/2$) level occurs with the absorption of σ_L light of a certain frequency; the σ_R component at the same frequency will pass through the crystal without absorption. The transition to the ($-1/2$) level occurs with the absorption of σ_R light of a different frequency; the σ_L component is not absorbed. When the two frequencies corresponding to the transitions to the ($+1/2$) and ($-1/2$) levels are not resolvable by the spectrometer (resolution of approximately 0.3 Å), a change in the intensity of the transmitted light will occur upon the application of microwave power. The change is given by the sum of the right sides of Eqs. (1) and (2). The transmitted light should *decrease* with the application of microwave power regardless of whether the excited levels are ($\pm 1/2$) or ($\pm 3/2$). However, it was noticed that the opposite behavior occurred for some absorption lines, i.e., the ($\pm 3/2$) levels in Fig. 3(a). There are two possible explanations for this result: (1) The excited state splitting may have been large enough and in the appropriate direction so that the transitions to the excited Zeeman doublet were resolvable. Then possibly the spectrometer may have been set closer to one of the transition frequencies. (2) The incident light may have been elliptically polarized to a slight extent.

The Excited States

Again referring to Fig. 1, σ_R light is absorbed for the transition from the upper ground state to the excited level ($-1/2$) and from the lower ground state to the excited level ($-3/2$). These transitions are resolvable in the optical absorption spectra. With microwave saturation the σ_R transition to the excited level ($-1/2$) increases, thereby decreasing the transmitted σ_R light. The σ_R transition to the excited level ($-3/2$) decreases, thereby increasing the transmitted light. The *decrease* or *increase* of the transmitted σ_R light indicates whether the excited level is ($-1/2$) or ($-3/2$), respectively. The σ_L transitions yield just the opposite behavior. Since the optical transitions from the ground doublet to an excited doublet are not optically resolvable, the excited levels are labeled ($\pm 1/2$) and ($\pm 3/2$). In Table I are listed the absorption lines that were investigated, the increase or decrease of the transmitted σ_R light, and the labeling of the excited levels. The result obtained with σ_L light is redundant and hence is not listed in the table.

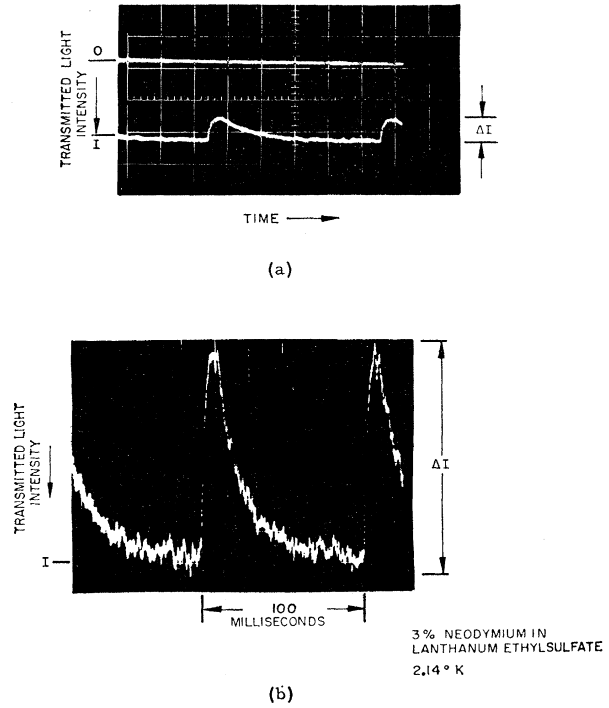

FIG. 4. Oscilloscope traces. Relaxation-time measurements. 3% neodymium in lanthanum ethylsulfate, 2.14°K. (a) Measurement of $\Delta I/I$. (b) Expanded vertical scale.

The information about the excited states can be obtained, of course, by taking σ and π absorption spectra; the transitions to the ($\pm 1/2$) states occur in both σ and π spectra, while the transitions to the ($\pm 3/2$) states occur only in the σ spectrum. The σ and π spectra were taken; the results of Table I were confirmed. The 5751 Å line is broad, however; the excited level appears to contain a small amount of the ($\pm 1/2$) states.

The sign of the $g_{\parallel}$ value was taken as positive for calculating the upper and lower states of the ground Zeeman doublet. If the sign of the g value is unknown, the σ and π spectra and the method of this experiment will determine the sign.

Relaxation-Time Measurements

Measurements of relaxation time were made. A pulse generator modulated the reflector voltage of the klystron at 10 cps, turning the klystron on the resonance frequency for 10 msec and off the resonance frequency for 90 msec. The photomultiplier output at the spectrometer was connected directly to an oscilloscope. The pulse generator also triggered the sweep of the oscilloscope. The oscilloscope traces were photographed with a polaroid camera. The oscilloscope trace showed the decay curve of the transmitted light. The decay curve for the neodymium ethylsulfate sample is similar to the

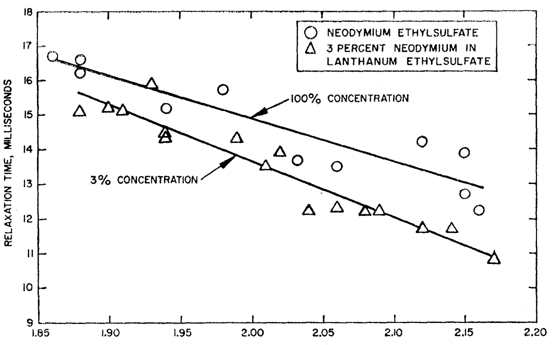

FIG. 5. Relaxation time versus temperature. Magnetic field, 4780 Oe c axis$\|H$. Microwave frequency 23.6×10^9 cps.

traces for the sample containing 3% neodymium in lanthanum ethylsulfate. For a small variation of the transmitted light the trace directly indicated the population change of the ground state versus time. Figure 4 shows the change in transmitted light ΔI (the decay curve) and the transmitted light I at equilibrium. The maximum ratio $\Delta I/I$ is 0.28. The logarithm of the decay curve will give the time variation of $\Delta\alpha l$. It was found that the logarithm of the decay curve is an exact fit to an exponential curve. The interpretation of the decay curve of the transmitted light as the relaxation curve in this case will give an error of less than five percent. To eliminate some of the shot noise of the photomultiplier tube, a 1000-$\mu\mu$F capacitor shunted the 1-MΩ input impedance of the oscilloscope. The 1-msec time constant was accounted for in the measurement of the relaxation time.

Figure 5 is a graph of relaxation time versus temperature for the neodymium crystals. The temperature range is 1.86 to 2.17°K. The magnetic field was 4780 Oe. The 5109 Å absorption line was examined. Each point on the graph represents the average of three independent measurements of relaxation time for each photographed decay curve. It is estimated that individual points may be in error as much as ten percent due to the residual photomultiplier noise. A straight line was fitted visually to each set of points. The graph shows that both samples have approximately the same relaxation times. The 3% sample shows lower relaxation times and a slightly greater slope for the fitted line than the 100% sample; however, due to the possible measurement errors, this distinction may not be significant. Figure 6 is a plot of the same data as Fig. 5, but with logarithmic axes. Straight lines were fitted through the points by least squares. From the slopes the temperature dependence for the relaxation time is found to be $T^{-2.5}$ for the 3% neodymium in lanthanum ethylsulfate and $T^{-1.7}$ for the neodymium ethylsulfate.

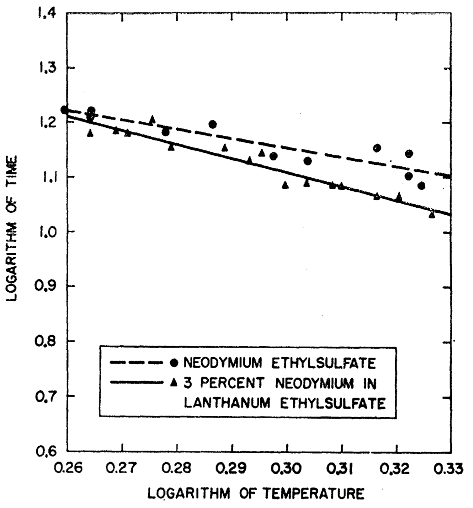

FIG. 6. Relaxation time vs temperature on log-log scale. Straight lines are fitted by least squares. Magnetic field, 4780 Oe c axis$\|H$. Microwave frequency 23.6×10^9 cps.

In this experiment the lower limit of temperature was imposed by the capacity of the vacuum pump and the large heat leak of the special dewar. The upper limit was the λ point of liquid helium. Above the λ point the transmitted light varied appreciably and randomly as a result of the bubbling of the liquid helium, so that the decay curve could not be resolved on the oscilloscope trace.

Daniels and Rieckhoff[5] measured the spin-lattice relaxation time by their Faraday effect method for neodymium ethylsulfate throughout a range of magnetic-field values. At 2.06°K, for example, they found that with a magnetic field of 1290 Oe the relaxation time was 72 msec; with a field of 2540 Oe the relaxation time was measured as 61 msec. Their results for this temperature show very little field dependence for the relaxation time. Our measurement for the relaxation time at 2.06°K with a field H of 4780 Oe is about 14 msec; this value is in agreement with a recent result.[16]

Spin-lattice relaxation times of Nd in La ethylsulfate have recently been measured by Scott and Jeffries.[17] Their results show a direct plus a Raman process: $T_1^{-1}=AT+BT^9$.

ACKNOWLEDGMENTS

One of the authors (C. K. A.) is greatly indebted to I. J. D'Haenens for many helpful discussions. The use of the facilities of the Hughes Research Laboratories for a part of this work is gratefully acknowledged.

---

[16] C. J. Gorter (private communication through Professor K. H. Hellwege).

[17] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

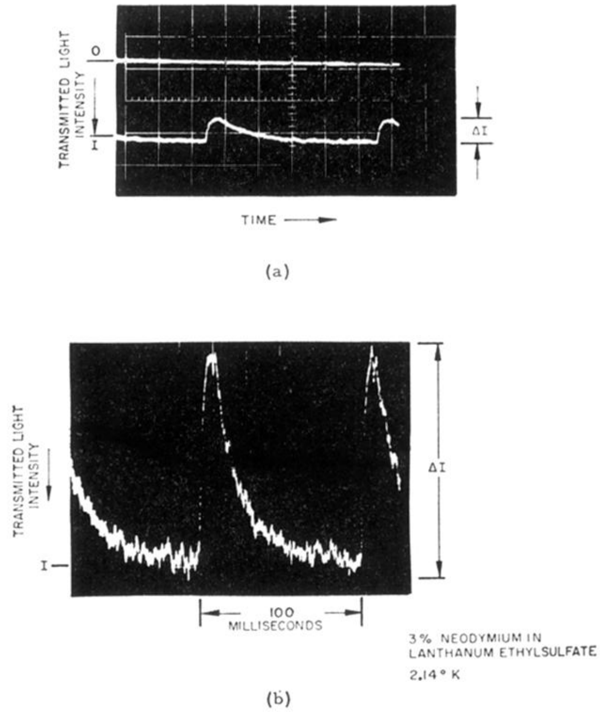

FIG. 4. Oscilloscope traces. Relaxation-time measurements. 3% neodymium in lanthanum ethylsulfate, 2.14°K. (a) Measurement of $\Delta I/I$. (b) Expanded vertical scale.