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Electron-Paramagnetic-Resonance Absorption by Trivalent Neodymium Ions in Single Crystals of Lanthanum Trichloride and Lanthanum Ethyl Sulphate in Zero Magnetic Field*

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Measurements of magnetic-dipole transition frequencies of $^{143,145}\mathrm{Nd}^{3+}$ occurring substitutionally for La^{3+} in LaCl_3 were made for the first time in the absence of an external magnetic field. The sensitive [10^{13} spins/(Mc/sec linewidth)], versatile, cavity-type, variable-frequency (1000-4600 Mc/sec) spectrometer developed for these experiments is described. Measurements of magnetic-dipole transition frequencies of $^{143,145}\mathrm{Nd}^{+3}$ in $\mathrm{La(C_2H_5SO_4)_3 \cdot 9H_2O}$ made at low field by Bleaney were repeated at zero magnetic field. The results are summarized in terms of a least-squares best fit of the spin Hamiltonian

$$H=AS_zI_z+B(S_xI_x+S_yI_y)+P[I_z^2-\tfrac{1}{3}I(I+1)]$$

to the data. The spin-Hamiltonian parameters are independent of temperature between 4° and 15°K. Theoretical interpretation of the spin-Hamiltonian parameters yielded $^{143}\mu_N/^{145}\mu_N=1.60892\pm0.00010$, $^{143}g_n\langle r^{-3}\rangle=(11.59\pm0.10)\times10^{24}$ cm^{-3}, and $^{143}\mu_N=(1.10\pm0.10)$ nm for the $\mathrm{LaCl_3}$ crystal; and $^{143}\mu_N/^{145}\mu_N=1.60886\pm0.00029$, $^{143}g_n\langle r^{-3}\rangle=(11.56\pm0.10)\times10^{24}$ cm^{-3} and $^{143}\mu_N=(1.10\pm0.10)$ nm for the $\mathrm{La(C_2H_5SO_4)_3 \cdot 9H_2O}$ crystal assuming $\langle r^{-3}\rangle=(36.9\pm4.5)\times10^{24}$ cm^{-3}. The close agreement of $g_n\langle r^{-3}\rangle$ for the two crystals implies that $\langle r^{-3}\rangle$ is independent of the host for these two crystals.

1. INTRODUCTION

1.1. General Remarks

MEASUREMENTS of magnetic dipole transition frequencies in the microwave region in the absence of an external magnetic field provide valuable information about the low-lying energy levels of many paramagnetic ions and molecules in crystals.[1–3] Examples of systems in which separations (zero-field splittings, ZFS) of energy levels in the absence of an external magnetic field are in this region of the radio-frequency spectrum and between which magnetic dipole transitions are allowed are (a) ions of some transition elements, rare earths, and actinides in diamagnetic crystal environments for which the separations of the lowest group of levels arise from the hyperfine interaction [e.g., $^{143,145}\mathrm{Nd}^{3+}$ or $^{233,235}\mathrm{U}^{3+}$ in [4–6]$\mathrm{LaCl_3}$, $^{143,145}\mathrm{Nd}^{3+}$ in $\mathrm{La(C_2H_5SO_4)_3 \cdot 9H_2O}$,[1] and Mn^{2+} in $\mathrm{K_4Fe(CN)_6 \cdot 3H_2O}$ [7]]; (b) S-state ions of transition elements, rare earths, and actinides in diamagnetic crystal environments where the ZFS is due to the combined effects of the spin-orbit and crystal-field interactions (e.g., Gd^{3+} in $\mathrm{La(C_2H_5SO_4)_3 \cdot 9H_2O}$,[1] Eu^{2+} in $\mathrm{CaF_2}$,[8,9] and Cm^{3+} in $\mathrm{LaCl_3}$ [10]); (c) diamagnetic molecules containing an atom with a large nuclear electric quadrupole moment, where the ZFS is due to the interaction of this quadrupole moment with the electric field gradient at this nucleus (e.g., $\mathrm{UO_2}$ in $\mathrm{UO_2Rb(NO_3)_3}$ single crystal[11]); and (d) organic molecules in triplet states in diamagnetic molecular crystal environments where the ZFS is due to the magnetic dipole-dipole interaction between the two unpaired electrons of the triplet molecule (e.g., naphthalene molecule in a triplet state in durene single crystals[2,3,12–14]).

Measurements of ZFS can, in some cases, yield more precise spin-Hamiltonian parameters than can conventional EPR measurements. The precision of a measurement of a ZFS is limited by the linewidth. At the temperatures normally used, the linewidths $\Delta\nu=\Delta E/h$, in almost all of the examples cited above, are due to the interactions of the paramagnetic ion with the magnetic fields (H_{local}) of the neighboring nuclei. In some cases, the separations of the energy levels at low magnetic fields may be given by

$$E=E_0+4\beta^2H^2/E_0,\quad \beta H\ll E_0/2, \tag{1}$$

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where β = Bohr magneton, h = Planck's constant, H = magnetic intensity (Oe), and at high magnetic fields by

$$E=E_0+2\beta H, \quad 2\beta H \gg E_0. \tag{2}$$

If, for example, one takes $H_{\text{local}}=5$ Oe, $E_0/h=2000$ Mc/sec, it can be seen that magnetic dipole linewidths in the absence of an external magnetic field are much smaller than are the magnetic dipole linewidths at high magnetic field.

$$(\Delta\nu)_{\text{zero field}}=0.1\ \text{Mc/sec},$$

$$(\Delta\nu)_{\text{high field}}=30\ \text{Mc/sec}.$$

Specific examples of this phenomenon are: (a) the transition in $^{145}\text{Nd}^{3+}$ in LaCl_3 single crystal (this work) for which the projection of the total angular momentum ($k=S_z+I_z$) on the crystallographic axis of symmetry is unchanged and equal to zero, where

$$(\Delta\nu)_{\text{zero field}}=1\ \text{Mc/sec}$$

and

$$(\Delta\nu)_{\text{high field}}=50\ \text{Mc/sec};$$

and (b) all magnetic dipole transitions in the naphthalene molecule in its lowest triplet state in durene single crystal,[15] where

$$(\Delta\nu)_{\text{zero field}}=0.25\ \text{Mc/sec}$$

and

$$(\Delta\nu)_{\text{high field}}=20\ \text{Mc/sec}.$$

It follows that measurements of the magnetic dipole transition frequencies in the absence of an external field can yield far more precise spin-Hamiltonian parameters than can be obtained by measurements at high magnetic field. Therefore, it becomes possible to study such examples as the small, but significant, effects that the intermolecular forces have on the spin-Hamiltonian parameters of the paramagnetic molecules in diamagnetic molecular crystals. An estimate of the magnitude of the changes in the spin-Hamiltonian parameters due to the intermolecular forces may be made from the differences between the spin-Hamiltonian parameters for a given paramagnetic molecule in two different diamagnetic crystals. The largest known differences are approximately ten times the standard deviations of high-field results.[2] Since the very small effects of temperature and pressure on the spin-Hamiltonian parameters should yield important information on the nature of the intermolecular forces, it should be useful to have spin-Hamiltonian parameters which are more precise than can be obtained by conventional EPR techniques. Similarly, in experimental investigations of the transfer of energy in mixed molecular crystals, it is of interest to measure changes, if any, of the ZFS as the concentrations of the paramagnetic (guest) molecules in the diamagnetic (host) molecular crystal, to prove the absence of aggregation of the various guest molecules. This must be established before it can be concluded that the excitation is transferred from one guest molecule to another via the host crystal. The magnitude of the changes in the spin-Hamiltonian parameters on substitution of deuterons for protons of the paramagnetic molecule in the diamagnetic crystal are known to be approximately one-tenth the magnitude of the changes due to the intermolecular forces.[16] Detailed investigation of the deuteration effects on the spin-Hamiltonian parameters requires measurements of the ZFS at least as precise as those which may be obtained by direct measurements of the ZFS.

There are other examples of information which may be obtained only at zero field. For example, measurements of the pure quadrupole spectrum of $^{233,235}\text{UO}_2$ should yield precise values of the quadrupole coupling constants for the two isotopes and a value of the ratio of the quadrupole moments far more precise than is known at present (1%).[4,17] The knowledge of the quadrupole coupling constants is of great importance in the analysis of the measurements of the anisotropy of decay of $^{233,235}\text{UO}_2$.[11]

In the presence of an external magnetic field, the energy-level separations are a function of the direction of the magnetic field for systems with nonzero ZFS. If the magnetic field is removed, this anisotropy disappears (except for the polarization of the magnetic dipole transitions). Therefore, it is possible to directly measure the ZFS in randomly oriented systems (polycrystals or glasses).

Since it is difficult to construct a variable-frequency spectrometer in the microwave region, conventional EPR experiments are done at fixed frequency. The necessary perturbation of the energy levels to obtain energy-level separations of one fixed microwave quantum is very conveniently done using a magnetic field. Typically, this resonance condition may be satisfied for a free electron at 10 000 Mc/sec with an easily obtainable 3500-G magnetic field. If the ZFS is larger than the energy of one microwave quantum, a very large magnetic field may be required to bring the energy levels close enough together to satisfy the resonance condition.

However, the use of this convenient variable introduces some complication in the interpretation of the experimental data. In ions of rare earths and actinides, second-order interactions between the Zeeman operator $\mathbf{Z}=\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})$ and the hyperfine operator

$$\mathbf{N}=\sum_i \mathbf{l}_i-\mathbf{s}_i+\frac{3(\mathbf{r}_i\cdot\mathbf{s}_i)\mathbf{r}_i}{\mathbf{r}_i{}^2},$$

one of the form[18,19]

$$2\sum_j \frac{\langle\phi_0|\mathbf{Z}|\phi_j\rangle\langle\phi_j|\mathbf{N}|\phi_0\rangle}{W_0-W_j},$$

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where W_0 = energy of the ground state ϕ_0, W_j = energy of the excited state ϕ_j, produce large anisotropic shifts in the observed nuclear g factor (50% in $^{143}Nd^{3+}$ in $LaCl_3$ [6]). The necessity of making such large theoretical corrections severely limits the precision of experiments at high magnetic field. It follows that, if any of the interactions which complicate the interpretation of the experimental data can be removed (e.g., by turning off the magnetic field), it would be useful to remove them before making the measurements, thereby simplifying the analysis.

It becomes possible to determine the signs of the ratios of some of the spin-Hamiltonian parameters when the external magnetic field is removed. The sign of the ratio P/A is determined by observation of the relative intensities of some of the magnetic dipole transitions. (See Sec. 1.2.1.)

Some experiments have been done at low magnetic field at fixed microwave frequency.[1,2,13,20,21] However, in every case, detailed knowledge of the spectrum was available to enable the experimenter to carefully choose frequencies near the magnetic dipole transition frequency in the absence of an external magnetic field. Fixed-frequency low-field experiments are too difficult to enable the experimenter with little or no previous knowledge of the spectrum to gain new information in a reasonable period of time. If the energy-level separation is described by Eq. (1), at the lowest usable magnetic field (one linewidth in the magnetic variable), the linewidth $\Delta\nu$ for the example given is fifteen times the zero-field linewidth. Consequently, low-field measurements of magnetic dipole transition frequencies, in some cases, give less precise spin-Hamiltonian parameters than measurements at zero magnetic field.

Several direct investigations of ZFS have been made in widely separated regions of the radio-frequency spectrum. Bogle,[22,23] using an insensitive spectrometer (10^{17} spins at 77°K), has studied the crystal-field spectrum of Fe^{3+} ion in methyl amine alum in the region from 7800 Mc/sec to 26 000 Mc/sec. Cole[24] has observed some magnetic dipole transitions in the absence of an external magnetic field of Cr^{3+} in MgO and of several free radicals in the region from 10 to 100 Mc/sec.

1.2. Specific Systems Studied

In order to investigate the ZFS of $^{143,145}Nd^{3+}$ in $LaCl_3$ and in $La(C_2H_5SO_4)_3 \cdot 9H_2O$, a versatile, sensitive, variable-frequency, electron-paramagnetic-absorption spectrometer was developed which operated from 1000 to 4600 Mc/sec. The instrument was capable of detecting 10^{13} spins/(Mc/sec linewidth) at 77°K. The zero-field splittings of $^{143,145}Nd^{3+}$ in $LaCl_3$ were investigated at approximately 14°K and at approximately 4°K. In addition the ZFS of $^{143,145}Nd^{3+}$ in $La(C_2H_5SO_4)_3 \cdot 9H_2O$ obtained by Bleaney[1] by extrapolation of low-magnetic-field data to zero magnetic field, were remeasured in the absence of a magnetic field at approximately 4°K.

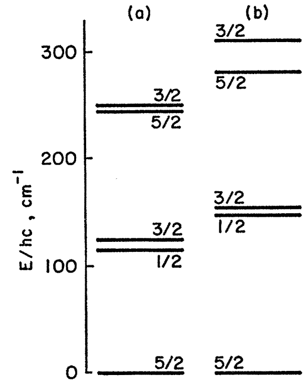

FIG. 1. Crystal-field energy-level diagram for Nd^{3+} in (a) $LaCl_3$[26] and (b) $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$[28]. The levels are labeled by crystal quantum numbers.

1.2.1. $^{143,145}Nd^{3+}$, f^3 in $LaCl_3$ Single Crystal

The Nd^{3+} ion occurs substitutionally for the La^{3+} ion in the $LaCl_3$ crystal[25]; consequently, its environment consists of nine almost equidistant nearest-neighbor Cl^- ions. The point symmetry at the location of the Nd^{+3} is C_{3h}. The Hund ground level $^4I_{9/2}$ is split under the action of the crystal electric field into 5 Kramers doublets as shown in Fig. 1. The lowest Kramers doublet may be described approximately as

$$\begin{aligned} |\pm\rangle = n_1 |J=\tfrac{9}{2}, J_z=\pm\tfrac{7}{2}\rangle \\ +(1-n_1^2)^{1/2}|J=\tfrac{9}{2}, J_z=\mp\tfrac{5}{2}\rangle, \end{aligned} \quad (3)$$

where $n_1 = 0.940$. (This approximation ignores mixing of $|J, J_z=\pm\frac{7}{2}\rangle$ and $|J, J_z=\mp\frac{5}{2}\rangle$ into the ground doublet where $J = 11/2$, 13/2, and 15/2.)

The hyperfine interaction in the ground Kramers doublet is best treated in terms of a spin Hamiltonian[1,19]

$$H = AS_zI_z + B(S_xI_x + S_yI_y) + P(I_z^2 - \tfrac{1}{3}I(I+1)), \quad (4)$$

where $2S+1=2$ is the degeneracy of the lowest crystal-field state in the absence of Zeeman and hyperfine interactions. The nuclear spin I is $\frac{7}{2}$. The z axis is the hexagonal axis of the crystal which is also the axis of the C_{3h} symmetry about the Nd^{3+} ion. When this matrix is diagonalized within the manifold of states $|S=\frac{1}{2}, M_s; I, M_I\rangle$, one obtains for the energy levels[1]

$$\begin{aligned} W = -A/4 + P(k^2 + \tfrac{1}{4} - \tfrac{1}{3}I(I+1)) \\ \pm\tfrac{1}{2}[(A-2P)^2k^2 + B^2(I(I+1) + \tfrac{1}{4} - k^2)]^{1/2}, \end{aligned} \quad (5)$$

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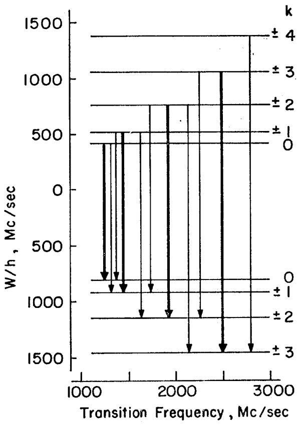

FIG. 2. Hyperfine structure in the ground Kramers doublet of ^{145}Nd^{+3} in LaCl$_3$. The heavy lines indicate the $\Delta k=0$ transitions. The separation of the $\Delta k=1$ transitions (light lines) is exaggerated for clarity.

where $k=M_s+M_I$. k takes the values ±4, ±3, ±2, ±1, and 0. For $k=\pm4$, only the positive sign is taken before the radical if A is positive and the negative sign if A is negative. (See Fig. 2). Measurements of the allowed magnetic dipole transition frequencies ($\Delta k=0$, $\Delta k=1$) yield $|A-2P|$, $|B|$, P where the sign of P/A may be determined. $|B|$ and P may be determined more precisely by a zero-field experiment than by a conventional high-magnetic-field EPR experiment.[1]

The optical spectrum of Nd^{3+} in LaCl$_3$ has been measured by Carlson and Dieke[26] and has been analyzed by Judd.[27] EPR spectra have been obtained by Hutchison and Wong[5] at high magnetic field. Electron nuclear double-resonance (ENDOR) spectra have been obtained by Halford[6] at high magnetic field.

1.2.2. ^{143,145}Nd^{3+}, f^3 in La(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O Single Crystal

The Nd^{3+} ion occurs in the La(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O crystal substitutionally for the La^{3+} ion. The point symmetry at the location of the Nd^{3+} ion is C_{3h}. The Hund ground level $^4I_{9/2}$ is split under the action of the crystal field into five Kramers doublets as shown in Fig. 1. The lowest Kramers doublet is given by Eq. (3) with $n_1=0.911$. The hyperfine interaction may be described by Eqs. (4) and (5). A, B, and P take values which are different from those for the LaCl$_3$.

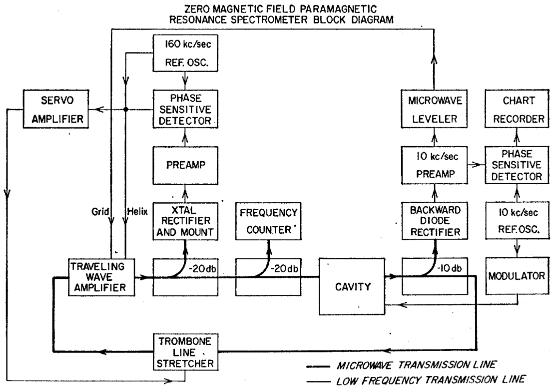

FIG. 3. Block diagram of the apparatus.

The optical spectrum of pure Nd(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O has been obtained by Gruber and Satten.[28] EPR spectra have been obtained by Bleaney, Scovil, and Trenam.[1]

2. EXPERIMENTAL PROCEDURE

The measurements of the magnetic dipole transition frequencies were made using a cavity-type variable-frequency spectrometer. A block diagram of the apparatus is shown in Fig. 3. The cavity, traveling-wave amplifier, and slide-trombone line stretcher were used as a regenerative microwave oscillator. The microwave frequency was varied by varying the resonant frequency of the cavity (Fig. 4) by moving the upper wall of the cavity with a clock motor. The traveling-wave amplifier and the feedback loop were about forty wavelengths long. The length of the feedback loop was varied by a servo-controlled trombone line stretcher to maintain maximum amplitude of the microwave oscillation as the microwave frequency was changed. This was accomplished by phase modulation (electrical length) of the traveling wave tube (TWT) at 160 kc/sec. The signal to control the servo-operated line stretcher was obtained

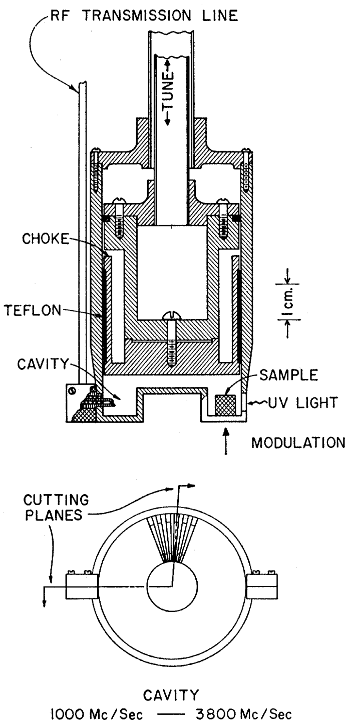

FIG. 4. Microwave cavity. This cavity was used from 1000 Mc/sec to 3800 Mc/sec. The choke makes a sliding fit in the cavity body.

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

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[28] J. B. Gruber, and R. A. Satten, J. Chem. Phys. 39, 1455 (1963).

by phase-sensitive detection of the 160-kc/sec amplitude modulation of the microwaves.

The microwave amplitude was regulated by control of the gain and saturation power output of the TWT through action of its control grid. The rectified current from the backward diode detector (Fig. 3) was used to obtain a control voltage.

One of the two re-entrant cavities used is shown in Fig. 4. The sample was placed in the cavity in a region of strong microwave magnetic field. The cavity was slotted radially to allow the magnetic modulation field to enter the cavity.[29] The loaded Q of the cavity was about 1000. The cavity was surrounded by a fused silica tube and the entire assembly was placed in a cryostat, as shown in Fig. 5.

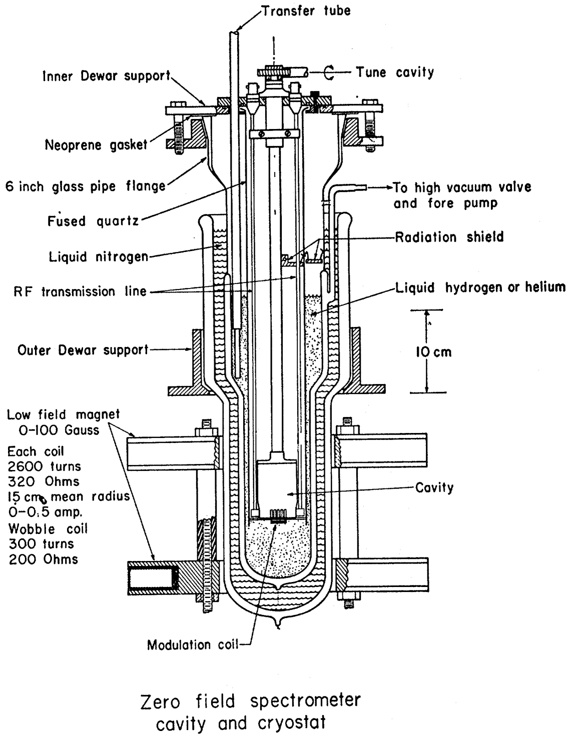

FIG. 5. Schematic diagram of the cavity and cryostat assembly.

The cavity when dielectrically loaded with polystyrene was used from 1000 to 3800 Mc/sec. Another cavity, one-half as large, was used from 3000 to 4600 Mc/sec with no dielectric load.

The sample was modulated by a magnetic field with time dependence shown in Fig. 6. The magnetic field was produced by a 300-mA current in a 500-turn, 1.5-cm-diam coil placed immediately below the cavity.

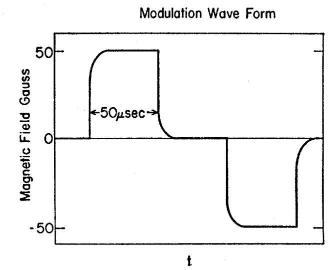

FIG. 6. Magnetic modulation field waveform.

The EPR signal was detected by tuned amplification of the 10 kc/sec component of the rectified current from the backward diode detector. The detection system bandwidth of 0.05 sec^{-1} was obtained by phase-sensitive detection of the output of the tuned amplifier. The signal was recorded on a recording potentiometer.

The microwave frequency was measured by a frequency counter below 3000 Mc/sec. At higher frequencies, a harmonic of a transfer oscillator was phase-locked to the microwave frequency. The frequency of the transfer oscillator was measured using a frequency counter.[30] The short-term drift of the microwave oscillator was less than 20 kc/sec during one-minute intervals. The frequency modulation of the microwaves was less than 20 kc/sec peak-to-peak. Approximately 5 kc/sec peak-to-peak of this FM was due to 160-kc/sec phase modulation of the TWT used for control of the trombone line stretcher.

The earth's magnetic field was cancelled to within 10 mG using an orthogonal pair of Helmholtz coils of radius 0.5 m and 0.3 m. A rotating coil magnetometer was used.

The Nd^{3+} in $LaCl_3$ crystals were prepared from La_2O_3 containing 0.1 mole% Nd_2O_3 by a method of Hutchison

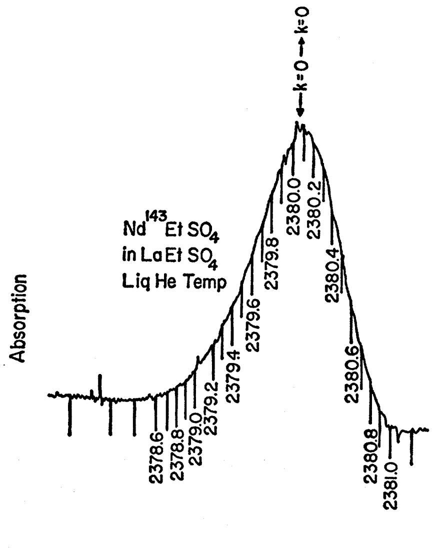

FIG. 7. Electron-paramagnetic-resonance absorption peak $k=0 \rightarrow k=0$ of $^{143}Nd^{+3}$ in $La(C_2H_5SO_4)_3 \cdot 9H_2O$ at 4°K.

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[29] The slots may also be used as a window for uv irradiation of the sample in other experiments.

[30] A Hewlett Packard 5245L, 5253B, and 5254A frequency counter and 2590A transfer oscillator were used.

Table I. Summary of results for Nd^{3+} in $LaCl_3$ at approximately 4.2°K.

	$^{145}Nd^{3+}$			$^{143}Nd^{3+}$		
1 Transition $k \rightarrow k'$	2 Measured transition frequency ν_M (Mc/sec)	3 Calculated[a] transition frequency ν_{MC} (Mc/sec)	4 $\sigma\{\nu_{MC}\}$[b] (Mc/sec)	5 Measured transition frequency ν_M (Mc/sec)	6 Calculated[a] transition frequency ν_{MC} (Mc/sec)	7 $\sigma\{\nu_{MC}\}$[b] (Mc/sec)
4 3	2840.6	2839.8	0.63	4563.7	4566.9	0.62
3 3	2511.3	2510.5	1.2	4040.2	4039.9	0.84
3 2	2213.5	2213.7	0.21	3560.4	3560.1	0.43
2 2	1912.5	1912.6	0.68	3078.7	3077.6	0.49
2 1	1675.7	1677.2	0.29	2698.8	2697.4	0.26
1 1	1434.7	1439.2	0.24	2315.0	2315.6	0.17
1 0	1340.8	1341.1	0.14	2156.3	2157.1	0.10
0 0	1241.93	1241.90	0.08	1998.02	1998.00	0.04

[a] The calculated transition frequencies were obtained from Eq. (5) and the least-squares best-fit spin-Hamiltonian parameters.
[b] The standard deviations of the transition frequencies (calculated).

Table II. Summary of results for Nd^{3+} in $LaCl_3$ at approximately 1.4°K.

	$^{145}Nd^{3+}$			$^{143}Nd^{3+}$		
1 Transition $k \rightarrow k'$	2 Measured transition frequency ν_M (Mc/sec)	3 Calculated[a] transition frequency ν_{MC} (Mc/sec)	4 $\sigma\{\nu_{MC}\}$ (Mc/sec)	5 Measured transition frequency ν_M (Mc/sec)	6 Calculated[a] transition frequency ν_{MC} (Mc/sec)	7 $\sigma\{\nu_{MC}\}$ (Mc/sec)
4 3	2839.6	2839.0	0.43	4565.8	4565.3	0.54
3 3	2512.3	2511.3	0.65	4040.0	4040.8	0.64
3 2	2213.2	2213.0	0.33	3559.8	3558.8	0.38
2 2	1911.6	1913.0	0.38	3077.8	3078.1	0.38
2 1	1674.4	1676.6	0.20	2696.0	2696.5	0.23
1 1	1434.8	1439.1	0.14	2316.1	2315.6	0.13
1 0	1340.8	1340.6	0.09	2156.2	2156.6	0.09
0 0	1241.67	1241.70	0.07	1997.81	1997.80	0.05

[a] See footnote a, Table I.

Table III. Least-squares best-fit spin-Hamiltonian parameters for Nd^{3+} in $LaCl_3$.

	Approximately 4.2°K		Approximately 1.4°K	
	$^{145}Nd^{3+}$ (Mc/sec)	$^{143}Nd^{3+}$ (Mc/sec)	$^{145}Nd^{3+}$ (Mc/sec)	$^{143}Nd^{3+}$ (Mc/sec)
$\lvert A-2P\rvert/h$	790.75 ± 0.41	1272.55 ± 0.30	791.06 ± 0.23	1272.90 ± 0.23
$\lvert B\rvert/h$	310.475 ± 0.020	499.506 ± 0.010	310.412 ± 0.017	499.454 ± 0.012
P/h[a]	$+0.43 \pm 0.21$	$+0.26 \pm 0.15$	$+0.18 \pm 0.12$	-0.12 ± 0.12
$^{143}A/^{145}A$	1.6104 ± 0.0013		1.6081 ± 0.00081	
$^{143}B/^{145}B$	1.60884 ± 0.00011		1.60900 ± 0.00010	

[a] The sign of P/A is given.

and Anderson.[31,32] The Nd^{3+} in $La(C_2H_5SO_4)_3 \cdot 9H_2O$ crystals were grown by slow evaporation at room temperature of a solution prepared by heating 10 mg Nd_2O_3, 11 g La_2O_3, 50 ml $(C_2H_5)_2SO_4$, and 50 ml H_2O to 95°C.[33]

3. EXPERIMENTAL RESULTS

The measured zero-magnetic-field transition frequencies and the transition frequencies calculated from Eq. (5) and the least-squares best-fit spin-Hamiltonian parameters for Nd^{3+} in $LaCl_3$ are given in Tables I and II. The least-squares best-fit spin-Hamiltonian parameters are given in Table III. The measured transition frequencies and the calculated transition frequencies for Nd^{3+} in $La(C_2H_5SO_4)_3 \cdot 9H_2O$ are given in Table IV. The

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[31] Johnson Matthey and Company "Specpure" Nd_2O_3, and Lindsay La_2O_3 were used as starting materials.

[32] J. H. Anderson, and C. A. Hutchison, Jr., J. Chem. Phys. **97**, 76 (1955).

[33] Johnson Matthey "Specpure" Nd_2O_3, Research Chemicals La_2O_3, and Fisher $(C_2H_5)_2SO_4$ were used.

TABLE IV. Summary of results for Nd^{3+} in $La(C_2H_5SO_4)_3\cdot 9H_2O$ at approximately 4.2°K.

			$^{145}Nd^{3+}$			$^{143}Nd^{3+}$	
1		2	3	4	5	6	7
Transition $k \rightarrow k'$		Measured transition frequency ν_M (Mc/sec)	Calculated[a] transition frequency ν_{MC} (Mc/sec)	$\sigma\{\nu_{MC}\}$ (Mc/sec)	Measured transition frequency ν_M (Mc/sec)	Calculated[a] transition frequency ν_{MC} (Mc/sec)	$\sigma\{\nu_{MC}\}$ (Mc/sec)
4	3		2573.4	4.0	4164.4	4160.9	2.3
3	3	2327.5	2335.8	2.2	3774.5	3753.7	1.2
3	2	2127.0	2115.9	2.8	3415.1	3419.4	1.5
2	3	2140.5	2128.0	3.3	3400.1	3401.7	1.1
2	2	1910.0	1908.8	1.2	3078.3	3067.5	0.6
2	1	1749.7	1749.1	1.4	2821.4	2823.7	0.8
1	2	1760.3	1756.4	1.6			
1	1	1601.5	1597.4	0.4	2569.5	2569.2	0.2
1	0	1537.2	1537.2	0.5	2477.5	2476.4	0.3
0	1	1540.1	1539.6	0.5	2474.0	2472.9	0.2
0	0	1479.32	1479.39	0.2	2380.02	2380.11	0.2

[a] See footnote a, Table I.

least-squares best-fit spin-Hamiltonian parameters are given in Table V. Typical observed electron resonance peaks are shown in Figs. 7–9. The separation of the transitions $k=1\rightarrow k=0$ and $k=0\rightarrow k=1$ is equal to $2P$. The sign of P/A is positive if the higher frequency transition is more intense. These transitions could not be resolved in the $LaCl_3$ single crystals.

The theory of Elliott and Stevens[34–37] was used to relate the spin-Hamiltonian parameters and the nuclear magnetic dipole moment. Eigenfunctions for the ground Kramers doublet were constructed from the following equations:

$$|\pm\rangle = n_1|J=\tfrac{9}{2}, J_z=\pm\tfrac{7}{2}\rangle + n_2|J=\tfrac{9}{2}, J_z=\mp\tfrac{5}{2}\rangle$$

$$\pm n_3|J=11/2, J_z=\pm\tfrac{7}{2}\rangle \pm n_4|J=11/2, J_z=\mp\tfrac{5}{2}\rangle,$$

$$n_1^2+n_2^2+n_3^2+n_4^2=1,$$

$$\frac{\langle+|(\mathbf{L}+2\mathbf{S})_z|+\rangle}{\langle-|(\mathbf{L}+2\mathbf{S})_x|+\rangle} = \begin{bmatrix} g_{\parallel} \\ \overline{g_{\perp}} \end{bmatrix}_{\text{expt}}, \quad \frac{\langle+|\mathbf{N}_z|+\rangle}{\langle-|\mathbf{N}_x|+\rangle} = \begin{bmatrix} A \\ \overline{B} \end{bmatrix}_{\text{expt}}.$$

The experimental values of $g_{\parallel}$ and $g_{\perp}$ were obtained from Halford[6] and Bleaney.[1] The operator equivalent factors not including the intermediate coupling corrections and the Schwinger corrections used were obtained from Halford.[6]

The value of n_3/n_4 was fixed at the value given by second-order perturbation theory.[26–28,37] The calculated $g_{\parallel}$ values were 1.5% high for the $LaCl_3$ crystals and 2.5% high for the $La(C_2H_5SO_4)_3\cdot 9H_2O$ crystals. A 10% variation in n_3/n_4 resulted in a variation of 0.02% in $g_{\parallel}$ and 0.1% in N_z for the $LaCl_3$ crystals and a variation of 0.02% in $g_{\parallel}$ and 0.03% in N_z for the $La(C_2H_5SO_4)_3$

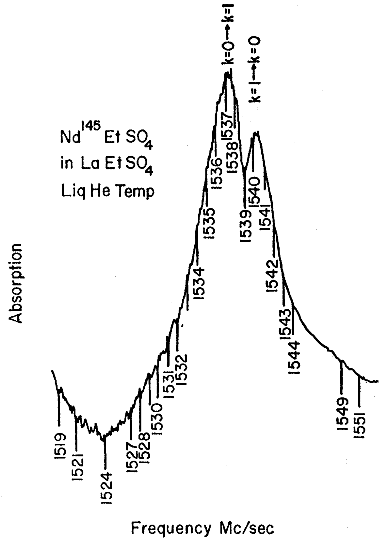

FIG. 8. Electron paramagnetic resonance absorption peaks $k=1\rightarrow k=0$ and $k=0\rightarrow k=1$ of $^{145}Nd^{+3}$ in $La(C_2H_5SO_4)_3\cdot 9H_2O$ at 4°K. The separation of the two peaks is equal to $2P$.

TABLE V. Least-squares best-fit spin-Hamiltonian parameters for Nd^{3+} in $La(C_2H_zSO_4)_3\cdot 9H_2O$ at approximately 4.2°K.

	$^{145}Nd^{3+}$ (Mc/sec)		$^{143}Nd^{3+}$ (Mc/sec)
$\|A-2P\|/h$	706.99	±0.80	1135.87±0.44
$\|B\|/h$	369.85	±0.06	595.03±0.05
P/h[a]	1.21	±0.40	1.76±0.59
$\|A-2P\|/h$[b]	704.7		1139.4
$^{143}A/^{145}A$	1.6172 ±0.0031		
$^{143}B/^{145}B$	1.60886±0.00029		

[a] The sign of P/A is given.

[b] This value was obtained from a least-squares fit of the $\Delta k=0$ data only. The value of B from this fit is the same as the value listed in the table for the least-squares best-fit parameters obtained from all of the data.

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[34] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[35] R. J. Elliott, and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952).

[36] R. J. Elliott, and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

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

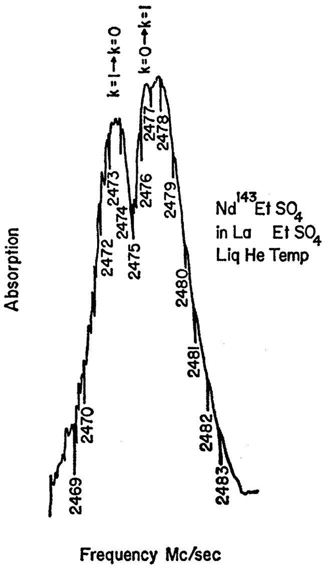

FIG. 9. Electron paramagnetic resonance absorption peaks $k=1\rightarrow k=0$ and $k=0\rightarrow k=1$ of $^{143}Nd^{3+}$ in $La(C_2H_5SO_4)_3\cdot 9H_2O$ at 4°K. The separation of the peaks is equal to $2P$.

$\cdot 9H_2O$ crystals. The calculations may be improved by addition of $J=13/2$ and $J=15/2$ states and by considerations of intermediate coupling to the operator-equivalent factors $\mathbf{L}+2\mathbf{S}$ and $\mathbf{N}$. However, in view of the incomplete nature of the spectral data and of the calculated intermediate coupling corrections, further refinement was considered unjustified at present.

The values of $g_n\langle r^{-3}\rangle$ obtained from the calculated values N_z, N_x, and the experimental values A and B are given in Table VI. The values of the nuclear dipole moments were calculated using Halford's measured value of $\langle r^{-3}\rangle$.

TABLE VI. Summary of calculations.

	Nd^{3+} in	
Quantity	$LaCl_3$	$La(C_2H_5SO_4)_3\cdot 9H_2O$
n_1[a]	+0.947277	+0.920990
n_2	+0.315033	+0.385790
n_3	−0.052307	−0.042998
n_4	−0.026153	−0.033075
$g_\parallel$	4.05206	3.62740
$g_\perp$	1.79077	2.12625
N_z	3.88436	3.48540
N_x	1.52455	1.82017
	$g_n\langle r^{-3}\rangle\times 10^{-24}$	
	(cm^{-3})	(cm^{-3})
$^{143}Nd^{+3}$ [b]	11.587	11.561
$^{143}Nd^{+3}$ [c]	11.586	
$^{145}Nd^{+3}$ [b]	7.202	7.186
$^{145}Nd^{+3}$ [c]	7.201	
	nm	nm
$^{143}\mu_N$	1.099	1.097
$^{145}\mu_N$	0.683	0.682

[a] $1+\rangle=n_1|J=9/2,\ J_z=7/2\rangle+n_2|9/2,\ -5/2\rangle+n_3|11/2,\ 7/2\rangle+n_4|11/2,\ -5/2\rangle$.
[b] Temperature approximately 4.2°K.
[c] Temperature approximately 14°K.

4. DISCUSSION

4.1. Spin Hamiltonian

The rms deviations of the measured transition frequencies from the calculated transition frequencies for $^{143,145}Nd^{3+}$ in $LaCl_3$ were between 0.84 and 1.9 Mc/sec. The total number of measured transition frequencies was 146. The values of $^{143}A/^{145}A=1.6104\pm0.0013$, 1.6081 ± 0.00081; and $^{143}B/^{145}B=1.60884\pm0.00011$, 1.60900 ± 0.00010, agree within experimental error with Halford's[6] value of the ratio of the nuclear magnetic moments $^{143}\mu_N/^{145}\mu_N=1.60883\pm0.00004$. (The estimated errors are the standard deviations calculated from the least-squares best-fit spin-Hamiltonian parameters.) The values of P (Table III) are zero within experimental value for both isotopes. The spin-Hamiltonian parameters are independent of temperature from approximately 4° to 14°K.

The rms deviations of the measured transition frequencies from the calculated transition frequencies for $^{143,145}Nd^{3+}$ in $La(C_2H_5SO_4)_3\cdot 9H_2O$ were 4.1 and 4.5 Mc/sec, respectively. The total number of transition frequencies measured was 82. The value of $^{143}A/^{145}A=1.6172\pm0.0031$ is in poor agreement with the value of $^{143}B/^{145}B=1.60886\pm0.00029$ and Halford's published value of $^{143}\mu_N/^{145}\mu_N$. The value of $^{143}P/^{145}P=-1.45\pm0.65$ disagrees in sign with the published values of $^{143}Q/^{145}Q=1.96\pm0.2$ (ENDOR)[6] and 1.89 ± 0.02 (atomic beam).[38]

The lack of agreement between the measured transition frequencies and the calculated transition frequencies (using Eq. (5) and the best-fit spin-Hamiltonian parameters) for $^{143,145}Nd^{3+}$ in $La(C_2H_5SO_4)_3\cdot 9H_2O$ first reported by Bleaney[1] was observed. These results agree with those of Bleaney.[1] The rms deviations of measured frequencies from calculated frequencies were three times as large as those for the $LaCl_3$ crystals. For example, the calculated $k=3\rightarrow k=3$ transition frequency (see Table IV) is higher for $^{145}Nd^{3+}$ and lower for $^{143}Nd^{3+}$ than the measured frequency. The sign of the deviation corresponds to the sign of P. The absence of this type of anomaly in the $LaCl_3$ crystal may be related to the small value of P for both isotopes.

4.2. Nuclear Magnetic Dipole Moments

The values of $g_n\langle r^{-3}\rangle$ obtained for the $LaCl_3$ crystals and the $La(C_2H_5SO_4)_3\cdot 9H_2O$ crystals are the same well within the estimated accuracy (2%) of the calculated values of N_z and N_x. (The deviations of the calculated values of N_z and N_x from the true values are assumed to be about the same as the deviations of the calculated values of $g_\parallel$ and $g_\perp$ from the measured values. The devia-

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[38] B. Bleaney, in *Proceedings of the International Conference on Quantum Electronics, Paris, 1963* (Columbia University Press, New York, 1964), Vol. I, p. 595.

tion of the calculated ratio $(g_{\|\mathrm{LaCl_3}}/g_{\|\mathrm{La(C_2H_5SO_4)_3\cdot 9H_2O}})$ from the experimental ratio is 1.1%.) The values of the nuclear magnetic moments, 1.097±0.11 and 0.682±0.07 agree with the values of Halford[6] (1.079±0.06, and 0.671±0.04) and with those of Unsworth[38] (1.0644 ±0.0040 and 0.6534±0.0040).

4.3. Additional Comments

The measured ratios of the magnetic dipole moments of the two isotopes is essentially determined by the ratio of the two transition frequencies $k=0\rightarrow k=0$ because of the small line width of these transitions (1 Mc/sec). This provides a simple method of determining the ratio of the magnetic dipole moments of two isotopes. (The ratio is independent of the salt in which the measurement is made and independent of the temperature of the salt from 4° to 14°K for $\mathrm{Nd^{3+}}$.)

Further investigation of $\mathrm{Nd^{3+}}$ in $\mathrm{La(C_2H_5SO_4)_3\cdot 9H_2O}$ is required to elucidate the nature of the anomalous behavior at zero magnetic field. ENDOR studies at zero magnetic field and at high magnetic field should be undertaken.

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Longitudinal Plasma Oscillations near Electron Cyclotron Harmonics

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A theory is developed for longitudinal plasma oscillations (normal modes) which are excited in a warm plasma column at microwave frequencies in the presence of a strong magnetic field. The oscillations manifest themselves as a set of absorption peaks near the harmonics of the electron cyclotron frequency. Good agreement is found between the observed positions of the peaks and a model calculation. The important property of the oscillations is that they are confined to a region near the axis of the plasma column, and are "quantized" by the shape of the electron density distribution.

I. INTRODUCTION

A CAREFULLY obtained microwave absorption spectrum of a plasma column in the presence of a longitudinal magnetic field exhibits considerable structure near the electron cyclotron harmonics (Fig. 1). The structure contains many lines (denoted a, b, c, d . . . in Fig. 1) at magnetic fields somewhat larger than the cyclotron harmonic fields $B=m\omega/en$, superimposed on a background absorption which is only a weak function of magnetic field. Here n is an integer and ω the microwave frequency. The structure is most prominent near the second harmonic, but it has been clearly discerned, albeit with diminishing amplitude, near the third, fourth and fifth harmonics. To observe such absorption either microwave cavities or waveguides can be used, but the modes must be such that the electric field of the wave is polarized at right angles to the static magnetic field, that is, the electromagnetic field must have, at least in part, the polarization of an extraordinary wave. It is well known[1] that such a wave, when it propagates nearly at right angles in a cold plasma, possesses a (hybrid) resonance at $\omega^2=\omega_p^2+\omega_b^2$, where ω_p and ω_b are the electron plasma and cyclotron frequencies, respectively. Indeed, the background absorption in Fig. 1 results from the absorption caused by the hybrid resonance.[2]

The line spectrum was first observed in emission by Mitani, Kubo and Tanaka,[3] and probably even earlier by Ishii.[4] It has since been studied in absorption by us,[5] by Crawford, Kino, and Weiss, by Harp,[6] and by Schmitt, Meltz, and Freyheit.[7] Schmitt reports as many as 30 lines near the second harmonic which he observed in an afterglow plasma using strip-line techniques

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[1] W. P. Allis, S. J. Buchsbaum, and A. Bers, *Waves in Anisotropic Plasmas* (MIT Press, Cambridge, Massachusetts, 1963), p. 30.

[2] S. J. Buchsbaum, Bull. Am. Phys. Soc. **7**, 151 (1962); G. Bekefi, J. D. Coccoli, E. B. Hooper, and S. J. Buchsbaum, Phys. Rev. Letters **9**, 6 (1962).

[3] K. Mitani, H. Kubo, and S. Tanaka, J. Phys. Soc. Japan **19**, 211 (1964).

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[5] S. J. Buchsbaum and A. Hasegawa, Phys. Rev. Letters **12**, 685 (1964).

[6] F. W. Crawford, G. S. Kino, and H. H. Weiss, Phys. Rev. Letters **13**, 229 (1964). R. S. Harp, Appl. Phys. Letters **6**, 51 (1965).

[7] H. J. Schmitt, G. Meltz, and P. J. Freyheit, Phys. Rev. **139**, A1432 (1965).