

Electron paramagnetic resonance and electron-nuclear double-resonance of $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ in yttrium-trichloride single crystals

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The electron-paramagnetic-resonance and electron-nuclear double-resonance spectra of $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ dilutely substituted at Y^{3+} sites in YCl_3 single crystals have been obtained. The values of the spin-Hamiltonian parameters which describe these spectra are reported. These values and the ratios of the values for the two nuclides are discussed and compared with the results previously obtained for Nd^{3+} in other host crystals.

I. INTRODUCTION

The magnetic properties of Nd^{3+} ions in various host crystals have been extensively investigated. EPR (electron paramagnetic resonance) spectroscopy has been employed in other laboratories to study the Nd^{3+} ion in $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$,¹⁻³ $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$,⁴⁻⁶ $\text{Y}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$,⁷⁻⁹ $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$,¹⁰⁻¹² $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$,¹³ $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$,¹⁴ CaF_2 ,^{15,16} SrF_2 ,¹⁵ YCl_3 ,¹⁷ europium gallium garnet,¹⁸ frozen aqueous solutions,¹⁹ and intermetallic compounds.²⁰

In our laboratory EPR²¹⁻²⁴ and ENDOR^{25,26} (electron-nuclear double-resonance) spectroscopy have been used to study the Nd^{3+} ion in its lowest-energy Kramers doublet state in LaCl_3 . We have also used EPR and ENDOR techniques for investigations of photoexcited states²⁷⁻²⁹ of Nd^{3+} in LaCl_3 .

In this paper we report EPR and ENDOR studies of Nd^{3+} ions dilutely substituted for Y^{3+} ions in YCl_3 single crystals. Both $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ have been investigated. Both ions have nuclear spin, $I = \frac{7}{2}$, and the electron configuration is well described as $4f^3$ outside closed shells. In the YCl_3 crystal the tenfold degenerate $^4I_{9/2}$ ground state splits into five Kramers doublets. In our present EPR and ENDOR studies we have examined the ions in their lowest-energy doublet state.

The results of our experiments will be parametrized by means of the conventional spin Hamiltonian,

$$\mathcal{H}_S = |\mu_B| \vec{B}_0 \cdot \vec{g}_e \cdot \vec{S} + \vec{S} \cdot \vec{A} \cdot \vec{I} + \vec{I} \cdot \vec{Q} \cdot \vec{I} - |\mu_n| \vec{B}_0 \cdot \vec{g}_n \cdot \vec{I}; \quad (1)$$

$$S = 1/2, \quad I = 7/2.$$

II. CRYSTAL STRUCTURE OF YCl_3

The crystal structure of YCl_3 is known from x-ray diffraction studies.³⁰ The crystal is monoclinic and the structure has space group symmetry, $C2/m$. The point symmetry at the Y^{3+} site is C_2 . There are four YCl_3 's in the unit cell. The Cl^- ions are arranged approximately as cubically close-packed spheres. The Y^{3+} ions are located in the octahedral interstices between alternate pairs of close-packed layers of Cl^- ions. The six nearest Cl^- ions form an approximately regular octahedron centered on the Y^{3+} ion. All the Y^{3+} ions are related by the elements of the space group. The crystal cleavage is observed to be parallel to the (001) plane in agreement with expectations on the basis of the layered structure.

III. EXPERIMENTAL PROCEDURES

Crystal boules were grown from melts by previously described methods.²¹ The melts were prepared by dissolving Nd_2O_3 and Y_2O_3 in HCl solutions with subsequent dehydration by heating in vacuum followed by distillation at $\sim 1000^\circ\text{C}$ into the crystal growing tubes.

The crystal samples were cleaved from the boules and cut to form rectangular parallelepipeds $\sim 0.5 \times 0.3 \times 0.2 \text{ cm}^3$ in size. A crystal sample was held and rotated inside the cavity of the X-band EPR-ENDOR spectrometer (similar to one previously described³¹) by means of an epoxy rod. A plane surface was machined parallel to the rod axis and the crystal was mounted with its cleavage plane in contact with that surface. The brass rectangular parallelepipedal cavity with length, $\sim 6.0 \text{ cm}$, and $\sim 1.8 \times \sim 1.0\text{-cm}^2$ cross section, was operated in the TE 102 mode.

The microwave frequency was ~ 9.38 GHz. One end of the cavity was iris coupled to the bottom of a vertical microwave transmission line of sufficient length to support the cavity vertically, immersed in superfluid He at ~ 1.5 °K at the bottom of the cryostat. The epoxy rod with crystal sample was inserted horizontally through holes in the cavity walls, which served to support it midway along the length of the cavity with its axis parallel to the ~ 1.8 cm dimension and bisecting the ~ 1.0 cm dimension. Thus the axis of rotation of the rod and crystal sample was horizontal and parallel to the microwave \vec{B}_1 field at a position of its maximum intensity. One end of the epoxy rod protruded from the cavity and was attached to a brass gear which in turn meshed with a gear at the bottom end of a vertical rod. The top end of this vertical rod protruded from the top of the cryostat and permitted the rotation of the sample through known angles while the cavity assembly was immersed in superfluid He at ~ 1.5 °K. The static magnetic field \vec{B}_0 was horizontal and could be rotated through known angles about a vertical axis which was perpendicular to the axis of rotation of the epoxy rod and crystal sample. In this way \vec{B}_0 could be put in any direction in an axis system fixed in the crystal sample. All angles (of crystal sample rotation and \vec{B}_0 rotation) were measured with calibrated dials. A 125-kHz amplitude modulation of \vec{B}_0 was provided by means of two wires parallel to the epoxy rod, one just above and the other just below the rod in the vertical midplane of the cavity. The rf field for ENDOR was supplied by two wires on either side of the epoxy rod in the horizontal midplane of the cavity. The EPR spectrum was obtained by crystal detection and phase sensitive amplification at 125 kHz. To obtain the ENDOR spectrum the rf field was swept from 8 to 32 times over the region in which the resonances occurred, and the resulting changes in amplitude of the EPR signal were averaged and recorded.

The temperature of the He bath was determined by the measurement of the helium vapor pressure. Magnetic field strengths were measured by previously described methods.³²

We determined three pairs of dial readings (each pair consisting of one reading for the sample rotator and one for the magnetic field rotation) for which \vec{B}_0 was parallel to the three principal axes, \hat{u}_1 , \hat{u}_2 , \hat{u}_3 , of \vec{g}_e in Eq. (1), by making measurements of $|\vec{B}_0|$ as a function of sample rotation and magnet rotation. With this information we could then determine the direction cosines of \vec{B}_0 in the basis, $(\hat{u}_1\hat{u}_2\hat{u}_3)$ for any arbitrary pair of dial readings.

The C_2 axis (\hat{b} axis) of the crystal must be a principal axis of each of the matrixes, \vec{g}_e , \vec{A} , \vec{Q} , and \vec{g}_n . This axis was \hat{u}_2 . The other two principal axes must be in the mirror plane (\hat{a} - \hat{c} plane) perpendicular to the \hat{u}_2 axis.

Subsequent to the determination of the directions

of the \hat{u}_1 , \hat{u}_2 , and \hat{u}_3 axes the EPR and ENDOR spectra were obtained for various directions of \vec{B}_0 in the three principal planes, i.e., the \hat{u}_1 - \hat{u}_2 , \hat{u}_2 - \hat{u}_3 , and \hat{u}_3 - \hat{u}_1 planes. Data were obtained at intervals 0.100π (18.0°), in the direction of \vec{B}_0 in the three principal planes.

IV. EXPERIMENTS

Two single crystals were used in this research. Both came from boules grown from a melt containing 0.010 mole fraction NdCl_3 . The NdCl_3 in one boule was enriched in ^{143}Nd and the other in ^{145}Nd . Both boules contained trace amounts of spinless Nd nuclei. The compositions of the melts are shown in Table I.

One hundred and ninety EPR spectra and 250 ENDOR spectra were obtained for $^{143}\text{Nd}^{3+}$, and 180 EPR spectra and 226 ENDOR spectra for $^{145}\text{Nd}^{3+}$, including many repetitions for the various orientations of B_0 .

The EPR linewidth between maximum slope points was ~ 7 G for $\vec{B}_0 \parallel \hat{u}_3$ and ~ 50 G in the \hat{u}_1 - \hat{u}_2 plane.

V. DATA

From the study of the angular variations of the EPR and ENDOR spectra of $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ in

TABLE I. Isotopic compositions of YCl_3 crystals in which the fraction, 0.010, of the Y^{3+} sites contain Nd^{3+} . The ratio of the amount of each Nd nuclide to the total amount of Nd is listed. (Standard deviations are given in parentheses.)

Nuclide	$^{143}\text{Nd}^{3+}$ in YCl_3	$^{145}\text{Nd}^{3+}$ in YCl_3
142	0.0241 (0.0005)	0.0125 (0.0002)
143	0.9106 (0.0010)	0.0078 (0.0001)
144	0.0443 (0.0005)	0.0362 (0.0003)
145	0.0039 (0.0003)	0.8967 (0.0005)
146	0.0150 (0.0005)	0.0431 (0.0003)
148	0.0014 (0.0003)	0.0026 (0.0001)
150	0.0009 (0.0003)	0.0012 (0.0001)
Other	<0.002	<0.002

the three principal planes of \vec{g}_e , it was found that the extrema of the ENDOR frequencies, with respect to magnet angle in the crystal, occurred when \vec{B}_0 was precisely parallel to the principal axes of \vec{g}_e . The largest term in Eq. (1) is the one linear in \vec{B}_0 and \vec{S} , and the one linear in \vec{J} and \vec{I} is next largest. The remaining terms are expected to be $\sim 10^{-4}$ times as large as the two larger ones. These EPR and ENDOR results make it clear that the principal axes of \vec{g}_e and \vec{A} are parallel, and the principal axes for \vec{Q} and \vec{g}_n in the smaller terms were assumed to be parallel to those for the larger terms.

The spin-Hamiltonian parameters g_r , $r = 1, 2, 3$, in the $(\hat{u}_1\hat{u}_2\hat{u}_3)$ diagonalizing basis, were adjusted to give the least-squares best fit to 18 EPR measure-

ments for the $I = 0$ line in the $^{143}\text{Nd}^{3+}$, and 14 measurements in the $^{145}\text{Nd}^{3+}$ case. Having thus fixed the g values, the values of the other spin-Hamiltonian parameters, A_{rr} , g_{rr} , $P = \frac{1}{2}3Q_{33}$, and $\eta = (Q_{11} - Q_{22})/Q_{33}$, were adjusted to give a least-squares best fit to the EPR and ENDOR data. The best-fit values are listed in Table II. Sixty four ENDOR frequencies were employed for the least-squares fit in the $^{143}\text{Nd}^{3+}$ case and 38 for the $^{145}\text{Nd}^{3+}$. The best-fit values of the parameters were used to calculate ENDOR frequencies for comparison with all of the measured values. The root mean-square deviation of calculated from measured values was 0.4 MHz. The observed ENDOR linewidths were ~ 0.5 MHz.

TABLE II. Spin-Hamiltonian parameters. (Standard deviations are given in parentheses.)

Crystal	$^{143}\text{Nd}^{3+}$ in YCl_3	$^{145}\text{Nd}^{3+}$ in YCl_3
$\left \frac{A_{11}}{h} \right $	420.10 MHz (0.16)	260.3 MHz (3.0)
$\left \frac{A_{22}}{h} \right $	571.40 MHz (0.18)	355.79 MHz (0.34)
$\left \frac{A_{33}}{h} \right $	816.93 MHz (0.10)	507.77 MHz (0.25)
$ g_{11} $	1.1729 (0.0035)	1.1633 (0.0074)
$ g_{22} $	1.6517 (0.0043)	1.6540 (0.0053)
$ g_{33} $	2.6359 (0.0036)	2.6328 (0.0029)
$\frac{P}{h}$	+1.634 MHz (0.014)	+0.905 MHz (0.021)
η	+0.111 (0.021)	+0.062 (0.026)
$ g_{n11} $	2.477 (0.022)	1.56 (0.035)
$ g_{n22} $	2.346 (0.032)	1.426 (0.061)
$ g_{n33} $	0.581 (0.029)	0.397 (0.066)

VI. DISCUSSION

No optical absorption or fluorescence data are available for Nd^{3+} ions dilutely substituted for Y^{3+} in the YCl_3 crystal and no crystal-field parameters have been reported in the literature. In previous work in our laboratory, e.g., in experimental studies^{26,33} of Nd^{3+} and Sm^{3+} in LaCl_3 similar to those reported here for Nd^{3+} in YCl_3 , it was possible, because of the availability of the optical information, to deduce values for nuclear moments and other fundamental physical properties from the determined values of the spin-Hamiltonian parameters. In the present case the possibilities for such analyses are limited.

It was first pointed out by Elliott and Stevens^{34,35} that within a given J manifold there is a linear rela-

TABLE III. Ratios of spin-Hamiltonian parameters. (Standard deviations are given in parentheses.)

Crystals	$^{143}\text{Nd}^{3+}$ in YCl_3	$^{145}\text{Nd}^{3+}$ in YCl_3
$\frac{A_{11}g_{33}}{A_{33}g_{11}}$	1.1557 (0.0038)	1.160 (0.015)
$\frac{A_{22}g_{33}}{A_{33}g_{22}}$	1.1162 (0.0033)	1.1153 (0.0040)
$\frac{A_{11}g_{22}}{A_{22}g_{11}}$	1.0354 (0.0041)	1.040 (0.014)
Crystals	$^{143}\text{Nd}^{3+}$ in LaCl_3^a	$^{145}\text{Nd}^{3+}$ in LaCl_3^a
$\frac{A_{\parallel}g_{\perp}}{A_{\perp}g_{\parallel}}$	1.12541 (0.00078)	1.12483 (0.00093)

^aReference 26.

tion between the nuclear hyperfine interaction and the electron Zeeman interaction and thus a value, unity, for the ratios, $A_{rr}g_{qq}/A_{qq}g_{rr}$, in which $r, q = 1, 2, 3$. Thus a crystal-field interaction size comparable with the separation of the higher energy J manifolds from the ground state, with consequent mixing of the higher J states with the ground, may produce appreciable departures of these ratios from unity. Thus their values afford some measure of the relative size of the crystal-field interaction.

In Table III we have summarized the values of these ratios calculated from the values of the spin-Hamiltonian parameters listed in Table II. We have also listed the values of the ratios obtained previously²⁶ in this laboratory for $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ in LaCl_3 for comparison with the YCl_3 values. For the previous LaCl_3 case, for which the higher states were known from optical spectroscopy, the normalized ground doublet state contained an admixture of the higher states such that the sum of the squares of

TABLE IV. Ratios of spin-Hamiltonian parameters for $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ in YCl_3 . (Standard deviations are given in parentheses.)

Nd^{3+} in YCl_3		Nd^{3+} in LaCl_3 (Ref. 26)	
$\left \frac{A_{11}(^{143}\text{Nd})}{h} \right \left/ \left \frac{A_{11}(^{145}\text{Nd})}{h} \right = 1.614 \right.$	(0.019)	$\left \frac{A_{\perp}(^{143}\text{Nd})}{h} \right \left/ \left \frac{A_{\perp}(^{145}\text{Nd})}{h} \right = 1.6080 \right.$	(0.0007)
$\left \frac{A_{22}(^{143}\text{Nd})}{h} \right \left/ \left \frac{A_{22}(^{145}\text{Nd})}{h} \right = 1.6060 \right.$	(0.0016)	$\frac{A_{\parallel}(^{143}\text{Nd})}{h} \left/ \frac{A_{\parallel}(^{145}\text{Nd})}{h} = 1.60881 \right.$	(0.00003)
$\left \frac{A_{33}(^{143}\text{Nd})}{h} \right \left/ \left \frac{A_{33}(^{145}\text{Nd})}{h} \right = 1.60886 \right.$	(0.00082)	$g_{n\perp}(^{143}\text{Nd})/g_{n\perp}(^{145}\text{Nd}) = 1.625$	(0.030)
$g_{n11}(^{143}\text{Nd})/g_{n11}(^{145}\text{Nd}) = 1.59$	(0.36)	$g_{n\parallel}(^{143}\text{Nd})/g_{n\parallel}(^{145}\text{Nd}) = 1.565$	(0.082)
$g_{n22}(^{143}\text{Nd})/g_{n22}(^{145}\text{Nd}) = 1.645$	(0.074)	$g_n(^{143}\text{Nd})/g_n(^{145}\text{Nd}) = 1.60883$	EPR & ENDOR (Ref. 26)
$g_{n33}(^{143}\text{Nd})/g_{n33}(^{145}\text{Nd}) = 1.46$	(0.25)	$g_n(^{143}\text{Nd})/g_n(^{145}\text{Nd}) = 1.625$	Atomic Beam (Ref. 39)
$g_n(^{143}\text{Nd}) = -0.308$	(0.018)	$g_n(^{143}\text{Nd})/g_n(^{145}\text{Nd}) = 1.690$	Calculated (Refs. 40,41)
$g_n(^{145}\text{Nd}) = -0.192$	(0.011)	$\frac{P(^{143}\text{Nd})}{h} \left/ \frac{P(^{145}\text{Nd})}{h} = 1.806 \right.$	(0.045)
$g_n(^{143}\text{Nd}) = -0.304$	(0.005)	$\frac{P(^{143}\text{Nd})}{h} \left/ \frac{P(^{145}\text{Nd})}{h} = 2.08 \right.$	(0.11)
$g_n(^{145}\text{Nd}) = -0.187$	(0.004)		
$g_n(^{143}\text{Nd}) = -0.503$	(0.004)		
$g_n(^{145}\text{Nd}) = -0.298$	(0.004)		
		or	
$Q(^{143}\text{Nd})/Q(^{145}\text{Nd}) = 1.96$	EPR & ENDOR (Ref. 26)	$Q(^{143}\text{Nd})/Q(^{145}\text{Nd}) = 1.91$	Atomic Beam (Ref. 39)
(0.20)		(0.11)	

their coefficients in the mixture was $\sim 3.8 \times 10^{-3}$.

Table III shows that the departures of the values of the $A_{rr}g_{qq}/A_{qq}g_{rr}$ ratios from unity are approximately the same for YCl_3 as for LaCl_3 . Dieke *et al.*³⁶ have obtained and interpreted optical spectra of Nd^{3+} in LaCl_3 , Er^{3+} in LaCl_3 , and Er^{3+} in YCl_3 and the crystal-field parameters are known for these other systems. Er^{3+} has configuration, $4f^{11}$, outside closed shells, and thus is well described by the same term designations as for the Nd^{3+} ion. Rakestraw and Dieke³⁷ compared the energy separations of the various J manifolds for Er^{3+} in LaCl_3 and YCl_3 , and found that the crystal-field splittings are appreciably larger for YCl_3 than for LaCl_3 . They attributed this to a stronger crystal field at the ion site in YCl_3 because of the fact that the Cl^- ions are much closer to the rare-earth ion in that case. In the YCl_3 crystal there are two ions at each of the distances 2.53, 2.63, and 2.69 Å whereas in LaCl_3 the three nearest ions are at distance 2.98 Å with next nearest at 3.02 Å. However, because of the lower site symmetry, C_2 in the present case than C_{3h} , in the case of our previous work^{25,26} on Nd^{3+} in LaCl_3 , there is a larger number of higher states admixed in the present case and comparisons of the $A_{rr}g_{qq}/A_{qq}g_{rr}$ ratios in terms of state admixtures is difficult and must await the availability of optical data.

Under the assumption of identical wave functions for $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ the ratios $A_{11}(^{143}\text{Nd})/A_{11}(^{145}\text{Nd})$, $A_{22}(^{143}\text{Nd})/A_{22}(^{145}\text{Nd})$, $g_{n11}(^{143}\text{Nd})/g_{n11}(^{145}\text{Nd})$, and $g_{n22}(^{143}\text{Nd})/g_{n22}(^{145}\text{Nd})$ must all be equal to the true nuclear g -value ratio,^{34,35} $g_n(^{143}\text{Nd})/g_n(^{145}\text{Nd})$. Moreover, if the second-order correction terms^{26,35,38} are neglected,

the ratio $A_{33}(^{143}\text{Nd})/A_{33}(^{145}\text{Nd})$ must be equal to the nuclear g -value ratio, $g_n(^{143}\text{Nd})/g_n(^{145}\text{Nd})$ and the ratio, $P(^{143}\text{Nd})/P(^{145}\text{Nd})$ must equal the nuclear-quadrupole-moment ratio,^{34,35} $Q(^{143}\text{Nd})/Q(^{145}\text{Nd})$.

The various ratios of the spin-Hamiltonian parameters which we have determined in the present work are listed in Table IV together with numerical values for the LaCl_3 case.^{25,26} It will be seen from this table that the values of the ratios $|A_{rr}(^{143}\text{Nd})/h|/|A_{rr}(^{145}\text{Nd})/h|$ and $g_{nrr}(^{143}\text{Nd})/g_{nrr}(^{145}\text{Nd})$ for the YCl_3 case are in agreement with the values of these ratios for the LaCl_3 case and with the value of the ratio, $g_n(^{143}\text{Nd})/g_n(^{145}\text{Nd})$, within the standard deviations of the measurements. This agreement for $r=3$ indicates the relatively small size of the second-order corrections to A_{33} in the YCl_3 crystal as was also the case for LaCl_3 .²⁶ For both YCl_3 and LaCl_3 the values of $[P(^{143}\text{Nd})/h]/[P(^{145}\text{Nd})/h]$ deviate markedly from the values of $Q(^{143}\text{Nd})/Q(^{145}\text{Nd})$. The second-order corrections to P are evidently appreciable in the YCl_3 case, as was found for the LaCl_3 crystal.²⁶ It should also be noted that in the YCl_3 case the measured values of g_{n11} and g_{n22} for both $^{143}\text{Nd}^{3+}$ and $^{145}\text{Nd}^{3+}$ are ~ 8 times larger than the value of g_n , indicating a much larger pseudonuclear Zeeman effect for the YCl_3 crystal. Konstantinov *et al.*^{40,41} have calculated the magnetic moments of ^{143}Nd and ^{145}Nd nuclei using the Bohr and Mottelson⁴² nuclear model. Their calculated values are also listed in Table IV.

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