Electron-Nuclear Double Resonance, Nuclear Moments, and $\langle r^{-3}\rangle$ of Neodymium-143 (III) and Neodymium-145 (III) in Lanthanum Trichloride*

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The electron-nuclear double resonance (ENDOR) spectra of dilute solutions of trivalent Nd^{143} and Nd^{145} ions occurring at the La^{+3} ion sites in the axially symmetric $LaCl_3$ structure have been measured at the temperature of boiling He. For laboratory fields of $\approx 10^3$ G the frequencies ν_n of the ENDOR transitions are in the range $10 \leq \nu_n \leq 1000$ Mc sec^{-1}. The experimental results for each nuclide have been summarized by giving values of the parameters in the spin Hamiltonian, $\mathcal{H}_s = |\beta|\mathbf{H}\cdot g\cdot\mathbf{S}+\mathbf{S}\cdot T'\cdot\mathbf{I}+P'[I_z^2-\frac{1}{3}I(I+1)]-\beta_n\mathbf{H}\cdot g_n'\cdot\mathbf{I}$, which produce a rigorous least-squares fit to the data for the two experimental conditions $\mathbf{H}\perp\mathbf{c}$ and $\mathbf{H}\|\mathbf{c}$, where $\mathbf{c}$ is a vector parallel to the hexagonal axis of symmetry of the $LaCl_3$ crystal. The frequencies were fitted with rms deviations of 0.08δ for $\mathbf{H}\|\mathbf{c}$ and 0.3δ for $\mathbf{H}\perp\mathbf{c}$, where δ is the average ENDOR line width, 3×10^5 cps. The g_n' factor in the spin Hamiltonian was found to be anisotropic, with $|g_{n\parallel}'/g_{n\perp}'| = 0.62$. A comprehensive theoretical interpretation of the spin Hamiltonian parameters using eigenvectors precisely calculated from the best available crystal field interaction parameters yielded $\mu(Nd^{143})/\mu(Nd^{145}) = +1.60883\pm0.00004$, $\mu(Nd^{143}) = -1.079\pm0.06$ nuclear magneton, $\mu(Nd^{145}) = -0.671\pm0.04$ nuclear magneton, $Q(Nd^{143})/Q(Nd^{145}) = +1.96\pm0.2$, $Q(Nd^{143}) = (+0.0206\pm0.003)\times10^{-24}$ cm^2, $Q(Nd^{145}) = (+0.0105\pm0.002)\times10^{-24}$ cm^2, $\langle r^{-3}(Nd^{+3},4f^3)\rangle = (36.9\pm4.5)\times10^{24}$ cm^{-3}. An upper limit of one part in two thousand was established for the contribution, if any, of a contact term to the hyperfine interaction. The errors quoted are estimated standard deviations of the mean based upon internal consistency. A discussion of the errors and their sources is given. In particular, the precision of the determination of the nuclear moments μ and Q, of $\langle r^{-3}\rangle$, and of the contact term was limited mainly by the inaccuracies of the best available values of the crystal field parameters $A_n{}^m\langle r^n\rangle$. Numerical values of the spin Hamiltonian parameters, crystal field eigenvectors, and relevant interaction multiplicative factors are tabulated.

I. INTRODUCTION

SEVERAL interesting and precise experimental observations and theoretical analyses have been reported for Nd^{+3} ions in the anhydrous $LaCl_3$ crystal structure. The structure of $LaCl_3$ is known,[1] and single crystals may be grown in which Nd^{+3} ions are substituted for La^{+3} ions.[2] The paramagnetic resonance (PMR) of the ground electronic doublet has been investigated by Hutchison and Wong[2] in crystals containing $\approx 0.2\%$ and $\approx 2\%$ Nd^{+3}. Using identical samples, Carlson and Dieke[3,4] have measured and analysed the optical absorption and fluorescence spectra and thereby have obtained most of the energy level splittings within the ground term ^4I. On the basis of the splittings within $^4I_{9/2}$ and $^4I_{11/2}$ and with consideration of the spin-orbit interaction,[5] Judd[6] has determined moderately reliable numerical values for the $A_n{}^m\langle r^n\rangle$ parameters in the crystal field interaction formalism developed by Stevens,[7] Elliott and Stevens,[8,9] Judd,[10] and Elliott, Judd, and Runciman.[11] Wong[12] has used Judd's values of the $A_n{}^m\langle r^n\rangle$ together with Wybourne's intermediate coupling eigenvectors[13] for Nd^{+3} to perform a rather complete analysis of the spectra obtained by Carlson and Dieke.

A convenient spin Hamiltonian formalism applicable to the ground electronic doublet has been developed by Abragam and Pryce,[14] Elliott and Stevens,[8] and Baker and Bleaney.[15] By an approximate fit of the spin Hamiltonian to their Nd^{+3} PMR data, Hutchison and Wong[2] were able to predict, *a posteriori*, line positions with a mean error of 1.8 G. In a similar study of Nd^{+3} in $La(C_2H_5SO_4)_3\cdot9H_2O$ Bleaney, Scovil, and Trenam[16] were able to fit the PMR lines found at strong magnetic fields to within the experimental error of 0.5 G. These PMR studies included Nd^{143} ($I=7/2$, 12% natural abundance), Nd^{145} ($I=7/2$, 8% natural abundance), and the even-even nuclides of Nd ($I=0$, 80% natural

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[1] W. H. Zachariasen, J. Chem. Phys. **16**, 254 (1958).

[2] C. A. Hutchison, Jr., and E. Wong, J. Chem. Phys. **29**, 754 (1958).

[3] E. Carlson and G. H. Dieke, J. Chem. Phys. **29**, 229 (1958).

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

[5] B. R. Judd and R. Louden, Proc. Roy. Soc. (London) **A251**, 127 (1959).

[6] B. R. Judd, Proc. Roy. Soc. (London) **A251**, 134 (1959).

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

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

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

[10] B. R. Judd, Proc. Roy. Soc. (London) **A227**, 552 (1955).

[11] J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957).

[12] E. Y. Wong, J. Chem. Phys. **34**, 1989 (1961).

[13] B. G. Wybourne, J. Chem. Phys. **34**, 279 (1961).

[14] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[15] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

[16] B. Bleaney, H. E. D. Scovil, and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

abundance).[17] Halford, Hutchison, and Llewellyn have observed[18] electron-nuclear double resonance (ENDOR) transitions in both Nd^{143} and Nd^{145} in $LaCl_3$. They pointed out that ENDOR measurements yield precise information on the nuclear moments and on $\langle r^{-3}\rangle$ of the f electrons in Nd^{+3}, and they predicted that the $-\beta_n g_n' \mathbf{H}\cdot\mathbf{I}$ term in the spin Hamiltonian would be anisotropic due to an anisotropic effect similar to the paramagnetic chemical shift of an ordinary nuclear resonance.

The present paper reports the continuation and completion of the ENDOR experiments begun by Halford, Hutchison, and Llewellyn[18] on Nd^{+3} in $LaCl_3$ and gives a comprehensive analysis of the results. The experiments are described in Sec. II. The capability of the spin Hamiltonian in summarizing the precise resonance data for both $\mathbf{H}\perp\mathbf{c}$ and $\mathbf{H}\|\mathbf{c}$ where $\mathbf{c}$ is a vector parallel to the hexagonal axis of the $LaCl_3$ structure is investigated in Sec. III. The interpretation of the spin Hamiltonian parameters required consideration of the mixing by the crystal field interaction of JM_J states. The complete crystal field and spin-orbit coupling energy matrix for the $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ manifolds was computed and diagonalized. The eigenvectors are given in Table II. A more detailed discussion of their derivation is given in Sec. IV. In Sec. V the sets of spin Hamiltonian parameters are used to deduce the nuclear moments and $\langle r^{-3}\rangle$ of Nd^{+3}. Some comments on the results and their reliability are made in Sec. VI.[19,20]

II. APPARATUS AND EXPERIMENTAL METHODS

The PMR measurements were made at $\nu\approx 9.2\times10^9$ cps using a $\nu_m=1.25\times10^5$ cps cavity loop modulation scheme of Llewellyn.[21] The resonant microwave transmission cavity was immersed in liquid He. It was evacuated. The magnetic field $\mathbf{H}$ could be rotated about the cavity in one plane while observing the PMR spectrum on an oscilloscope. The crystal was placed within the hairpin loop in the cavity[22] with its symmetry axis simultaneously (a) parallel to the plane of rotation of $\mathbf{H}$, (b) at $\pi/4$ to the microwave magnetic field vector, and (c) at $\pi/4$ to the plane of the loop. The ENDOR spectra for the two orientations (a) $\mathbf{H}\perp\mathbf{c}$ and (b) $\mathbf{H}\|\mathbf{c}$ were extensively studied; the anisotropy of the PMR spectrum was used to decide if either of the two orientations (a) and (b) had been attained. Details of the complete PMR apparatus have been given by Wong.[23]

The ENDOR transitions were detected in a modification of the PMR absorption experiment.[18] The magnetic field and the microwave frequency and power level in the cavity were adjusted to partially saturate any one of the PMR transitions. The 1.25×10^5 cps modulation current normally used in the hairpin loop for PMR detection was replaced with ≈0.1 A of current of frequency ν_n generated by a General Radio 1208-B or 1209-B Unit oscillator[24] with $65\leq\nu_n\leq900$ Mc sec^{-1}. The single tube unit oscillator was frequency modulated at $\nu_m=1.25\times10^5$ cps by means of a Varicap[25] voltage sensitive capacitor. The signal frequency of the ENDOR oscillator was slowly swept through the range in which the ENDOR transition(s) was expected. Low-frequency amplitude modulation components of the transmitted microwave signal were detected by a crystal diode. The component of frequency ν_m was analyzed for phase and amplitude by a tuned phase-sensitive detector (PSD). The output of the PSD was displayed on a recording potentiometer. A component of frequency ν_m was present only when the conditions for ENDOR were fulfilled.[26]

Switchable polystyrene capacitors in an integrating resistor-capacitor network in the dc amplifier of the PSD allowed use of various time constants of up to 30 sec in order to observe extremely weak ENDOR lines. The detection of each ENDOR transition predicted by the spin Hamiltonian (1) was attempted. Several lines expected in the $\mathbf{H}\|\mathbf{c}$ ENDOR spectra were apparently too weak to be observed in 2% crystals at 30 sec time constant.

The relative magnitudes H of the magnetic field at the sample were determined by measuring each corresponding frequency of the nuclear magnetic resonance (NMR) absorption of protons in a sample of H_2O placed near the cavity. The PMR absorption of $\approx10^{-3}$ gm of 1,1-diphenyl-2-picrylhydrazyl located on the

[17] B. Bleaney and H. E. D. Scovil, Proc. Phys. Soc. (London) **A63**, 1369 (1950).

[18] D. Halford, C. A. Hutchison, Jr., and P. M. Llewellyn, Phys. Rev. **110**, 284 (1958).

[19] A study of U^{235} in $LaCl_3$ by the method of ENDOR is the subject of a dissertation currently under preparation by Mrs. Narcinda R. Lerner. A detailed description of the ENDOR apparatus of this laboratory will be given in her dissertation.

[20] For an application of the ENDOR method to tetravalent Pa^{231} in Cs_2ZrCl_6 see J. D. Axe, H. J. Stapleton, and C. D. Jeffries, Phys. Rev. **121**, 1630 (1961). An application to Co^{+2} in MgO is reported by D. J. I. Fry and P. M. Llewellyn, Proc. Roy. Soc. (London) **A266**, 84 (1962).

[21] P. M. Llewellyn, J. Sci. Instr. **34**, 236 (1957). Dr. Llewellyn supervised the initial construction and installation in this laboratory of PMR apparatus using 1.25×10^5 cps magnetic field modulation.

[22] C. A. Hutchison, Jr., and B. W. Mangum, J. Chem. Phys. **34**, 908 (1961). The cavity shown in their Fig. 1 is similar in design except that it contains a quartz window.

[23] E. Y. Wong, thesis, University of Chicago, 1957 (unpublished).

[24] General Radio Company, West Concord, Massachusetts.

[25] Pacific Semiconductors, Inc., Hawthorne, California.

[26] The technique used for detection of ENDOR is due to Dr. P. M. Llewellyn. The reader may contrast it against the method used by G. Feher, Phys. Rev. **103**, 834 (1956). Experimental difficulties were encountered in the use of amplitude modulation of the ENDOR oscillator. The use of frequency modulation instead of amplitude modulation was due to the suggestion of Professor Hutchison.

TABLE I. Summary of experimental results on Nd^{+3} in $LaCl_3$.

Fit No.	Nuclide	I	H, c orientation	Method	Least-squares values of spin Hamiltonian parameters[a] A' (Mc sec^{-1})	$\lvert B\rvert$ (Mc sec^{-1})	P' (Mc sec^{-1})	g_n'	g	δ_{rmws}	χ^2	n number of transitions
1	Nd^{even}	0	$\parallel$	PMR	...	...	...	...	+3.9903±0.0005	0.6 G	1.2×10^{2}	12
2	Nd^{even}	0	$\perp$	PMR	...	...	...	...	1.7635±0.0012	7 G	1.2×10^{4}	9
3	Nd^{145}	7/2	$\parallel$	ENDOR	−790.736 ±0.016	310.682±0.14	+0.0427±0.0022	−0.347±0.018	(+3.9903)	0.031 Mc sec^{-1}	6.1×10^{1}	19
4	Nd^{145}	7/2	$\perp$	ENDOR	−790.810 ±0.30	310.540±0.048	+0.035 ±0.012	0.538±0.009	(1.7635)	0.12 Mc sec^{-1}	6.8×10^{2}	30
5	Nd^{143}	7/2	$\parallel$	ENDOR	−1272.1428±0.008	499.568±0.042	+0.0887±0.0010	−0.543±0.003	(+3.9903)	0.023 Mc sec^{-1}	1.3×10^{2}	38
6	Nd^{143}	7/2	$\perp$	ENDOR	−1273.036 ±0.24	499.532±0.040	+0.136 ±0.015	0.874±0.007	(1.7635)	0.088 Mc sec^{-1}	2.0×10^{3}	28
7	Nd^{143}	7/2	$\perp$	ENDOR	−1267.4 ±1.6	499.92 ±0.14	+0.066 ±0.010	0.865±0.015	1.754 ±0.001	0.065 Mc sec^{-1}	1.1×10^{3}	28
8	Nd^{143}	7/2	$\perp$	ENDOR	−1272.95 ±0.40	499.536±0.076	+0.176 ±0.025	0.897±0.014	(1.7635)	0.25 Mc sec^{-1}	2.7×10^{4}	53

[a] The errors are standard deviations of the mean based on external consistency.

sample was also observed. The value of the magnitude of H was computed by the method of Hutchison and Mangum.[22] The proton NMR and microwave PMR absorption signals could be individually or simultaneously displayed on a chopped-beam oscilloscope. The microwave frequency in each PMR experiment was measured with a cavity wavemeter calibrated with a digital frequency counter and transfer oscillator.[27] The frequency counter was also used to measure the NMR and ENDOR oscillator frequencies. It was continually calibrated against the standard 10^7 cps carrier broadcast by WWV.[28]

Nine single crystals were studied. They were selected from three different batches; each batch of crystals was grown from the melt by the method of Anderson and Hutchison[29] as modified by Hutchison and Wong.[2,23] The three melts were prepared with the stoichiometry $Nd_xLa_{1-x}Cl_3$ where (a) $x\approx0.02$, (b) $x\approx0.002$, (c) $x\approx0.002$ by (a) Wong,[2] (b) Wong,[2] and (c) the author, respectively. More than 200 measurements of ENDOR frequencies were made on the various crystals, of which 147 were obtained with sufficient[30] precision to warrant their use in the various data analyses described in the next section.

III. EXPERIMENTAL RESULTS

The results of the resonance experiments were summarized by obtaining values of the spin Hamiltonian parameters which produce a rigorous least-squares fit to the data. The spin Hamiltonian used in each case was

$$\begin{aligned}\mathcal{H}_s=&g_{11}|\beta|H_zS_z+g_1|\beta|(H_xS_x+H_yS_y)+hA'S_zI_z\\&+hB(S_xI_x+S_yI_y)+hP'[I_z^2-\tfrac{1}{3}I(I+1)]\\&-g_{n11}'\beta_nH_zI_z-g_{n1}'\beta_n(H_xI_x+H_yI_y),\\S=&\tfrac{1}{2}.\end{aligned}\tag{1}$$

For the condition $\mathbf{H}\parallel\mathbf{c}$ the matrix of the spin Hamiltonian (1) factors into 2 matrices of order one and $2I$ matrices of order two. For $\mathbf{H}\perp\mathbf{c}$ it factors into 2 matrices of order $2I+1$. For $I\neq0$ in the latter situation the ordinary perturbation theory expansions[31] for the eigenvalues of $\mathcal{H}_s$ do not converge rapidly enough to treat this problem.[16] In order to fit the spin Hamiltonian accurately to the data for Nd^{143} ($I=7/2$) and for Nd^{145} ($I=7/2$), a least-weighted squares fitting program, AMD132/ECOMP, which embodied exact nu-

[27] No. 524B, 525A, 525B, and 540A, Hewlett-Packard Company, Palo Alto, California.
[28] Operated by the Central Radio Propagation Laboratory, National Bureau of Standards, Washington, D. C.
[29] J. H. Anderson and C. A. Hutchison, Jr., Phys. Rev. **97**, 76 (1955).
[30] See Sec. III.
[31] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957), p. 30.

merical diagonalization of the factored matrices, was coded for Argonne National Laboratory's high-speed digital computer GEORGE.

The single intense PMR line observed on the oscilloscope due to the Nd even-even nuclides ($I=0$) was used to obtain values of $g_{\parallel}$ and $g_{\perp}$ in the spin Hamiltonian (1). The results quoted in rows 1 and 2 of Table I are the averages of measurements made on two 0.2% crystals and three 2% crystals. The $\mathbf{H}\perp\mathbf{c}$ measurements show an order of magnitude greater scatter in $H_{\text{resonance}}$ than do the $\mathbf{H}\|\mathbf{c}$ measurements. The random error inherent in each measurement of the magnetic field throughout the experiments was estimated to be ± 0.2 G. The value 3.9903 ± 0.0005 established for $g_{\parallel}$ in these experiments is in significant disagreement with the value 3.996 ± 0.001 reported by Hutchison and Wong.[2]

The AMD132/ECOMP program was used to fit the spin Hamiltonian to the observed ENDOR frequencies for Nd^{143} and Nd^{145} for each orientation of the magnetic field. The results of each of four computer runs in which A', B, P', and g_n' were simultaneously fitted are given in rows 3, 4, 5, and 6 of Table I. For these fits $g_{\parallel}$ and $g_{\perp}$ were constrained to have the values determined experimentally from PMR of the even-even nuclides. Each transition was weighted by the inverse of its estimated variance. In Table I, δ_{rmws} is the root mean weighted square of the difference between the position of a transition as computed from the spin Hamiltonian parameters and the position of the experimentally observed transition, that is

$$\delta_{\text{rmws}}=[\textstyle\sum_m w_m\delta_m{}^2]^{\frac{1}{2}}[\sum_m w_m]^{-\frac{1}{2}}.$$

χ^2 is the statistical measure of goodness of fit, that is,

$$\chi^2=\textstyle\sum_m w_m\delta_m{}^2.$$

The number of transitions used in each fit is denoted by n. Each of the two $\mathbf{H}\perp\mathbf{c}$ ENDOR fits (rows 4 and 6) shows four times greater scatter than does the corresponding $\mathbf{H}\|\mathbf{c}$ ENDOR fit (rows 3 and 5).

Another complete set of computer runs was made in which g, A', B, P', and g_n' were simultaneously fitted to the data. The results obtained were essentially the same as the results of the previous fits except for Nd^{143} with $\mathbf{H}\perp\mathbf{c}$ for which the results are listed in row 7 of Table I.

All measured ENDOR frequencies which were assigned weights greater than $(0.1\times 10^6 \text{ cps})^{-2}$ were used[32] in fits 3, 4, 5, 6, and 7 except for 33 lines of the $\mathbf{H}\perp\mathbf{c}$ spectrum of Nd^{143}. One of the latter, at 226.266 Mc sec^{-1} in a field of 3301.3 G, could not be assigned to any transition in the theoretical energy-level scheme. The other 32 lines which were discarded had widths greater than 0.5×10^6 cps measured between points of maximum slope. Many were highly distorted from the symmetric S-shaped first derivative curve observed for all other ENDOR lines. The average width of the lines involved in the fits listed in rows 3 to 7 was 0.3×10^6 cps measured between points of maximum slope. An AMD132/ECOMP run on the Nd^{143} $\mathbf{H}\perp\mathbf{c}$ ENDOR data with inclusion of the broad lines gave $\delta_{\text{rmws}}=0.24$ Mc sec^{-1} for the least-squares fit. The results of the fit are given in row 8 of Table I.[33]

IV. THEORY

Spin Hamiltonian Parameters

The parameters of the spin Hamiltonian $\mathcal{H}_s$ were interpreted in the same manner as by Elliott and Stevens[8,9] but with the following exceptions: (a) Second-order corrections were made to the equations for the A, P, and g_n parameters as discussed by Baker and Bleaney,[15,18] (b) the Landé values for the factors $\langle J'\|\Lambda\|J\rangle$ were replaced by values which included the effects of intermediate coupling and the Schwinger correction to the gyromagnetic ratio for the electron spin, (c) the contact term for s electrons in the hyperfine interaction was considered, and (d) the two fictitious-spin states and the two crystal field eigenstates comprising the ground Kramers doublet were assigned the particular one-to-one correspondence[34]

$$\begin{aligned}&|S=\tfrac{1}{2},M_s=\pm\tfrac{1}{2}\rangle\approx|\pm\rangle,\\ &|\pm\rangle\equiv\textstyle\sum_J[(\pm 1)^{J+7/2}n_J|J,M_J=\pm 7/2\rangle\\ &\qquad+(\pm 1)^{J-5/2}n_J'|J,M_J=\mp 5/2\rangle.\end{aligned}\quad(2)$$

The resulting equations are

$$g_{\parallel}=+2\langle+|L_z+2.00232S_z|+\rangle,\quad(3)$$

$$|g_{\perp}|=2|\langle-|L_x+2.00232S_x|+\rangle|,\quad(4)$$

$$A'=+4|\beta|\beta_n g_n\langle r^{-3}\rangle\langle+|N_z|+\rangle h^{-1}+C+\Delta A,\quad(5)$$

$$|B|=|4\beta\beta_n g_n\langle r^{-3}\rangle\langle-|N_x|+\rangle h^{-1}+C|,\quad(6)$$

$$P'\approx-[9e^2Q/4I(2I-1)]\langle r^{-3}\rangle\langle+|M|+\rangle h^{-1}+\Delta P,\quad(7)$$

$$g_{n\parallel}'=+g_n+\Delta g_{n\parallel}',\quad(8)$$

$$|g_{n\perp}'|=|g_n+\Delta g_{n\perp}'|,\quad(9)$$

where

[32] Seven of the 147 frequencies were obtained in the $\mathbf{H}\perp\mathbf{c}$ spectrum of Nd^{143} in the preliminary experiments of Halford, Hutchison, and Llewellyn (reference 18).

[33] The seven frequencies mentioned in footnote 32 were omitted from this fit.

[34] M. H. L. Pryce, Phys. Rev. Letters **3**, 375 (1959).

TABLE II. Eigenvectors and energies of Nd^{+3} in $LaCl_3$.

Type[a]	Eigenvectors: Normalized coefficients of basis vectors $\|J,M_J\rangle$						Energy/hc (cm^{-1}) Calc[b]	Exptl[c]
	$J=9/2$ $M_J=\mp1/2$	11/2 $\pm11/2$	11/2 $\mp1/2$	13/2 $\pm11/2$	13/2 $\mp1/2$	13/2 $\mp13/2$		
^6X	+0.015842	±0.009580	−0.005904	±0.110705	−0.448642	±0.886616	4028.63	4031.86
^5X	+0.009390	±0.023066	+0.039539	±0.309860	−0.831116	∓0.459402	4004.16	3998.89
^4X	+0.010578	±0.039495	+0.028536	±0.942314	+0.327547	±0.047658	3925.71	3931.84
^3X	+0.043600	∓0.656188	+0.753109	±0.000159	+0.009314	±0.016019	2044.48	2044.19
^2X	+0.008603	∓0.752366	−0.655471	±0.059545	−0.021609	∓0.014758	2013.58	2012.58
^1X	+0.998786	±0.034329	−0.027824	∓0.015172	+0.011306	∓0.010742	114.20	115.39
	$J=9/2$ $M_J=\pm9/2$	9/2 $\mp3/2$	11/2 $\pm9/2$	11/2 $\mp3/2$	13/2 $\pm9/2$	13/2 $\mp3/2$		
^6Y	+0.013266	∓0.007099	+0.008970	∓0.059858	−0.533069	±0.843770	4047.35	4042.08
^5Y	+0.014847	∓0.016558	+0.059425	∓0.016219	−0.842626	∓0.534502	3975.20	3974.88
^4Y	+0.034334	±0.055827	−0.264002	±0.959900	−0.058910	±0.033616	2051.27	2051.60
^3Y	+0.042870	±0.036216	−0.960040	∓0.268943	−0.040423	∓0.034780	1972.36	1973.85
^2Y	+0.565186	∓0.824110	−0.013986	±0.025291	+0.023903	±0.001224	247.84	249.35
^1Y	+0.822892	±0.562219	+0.069419	∓0.042152	+0.011944	∓0.004391	125.88	123.21
	$J=9/2$ $M_J=\pm7/2$	9/2 $\mp5/2$	11/2 $\pm7/2$	11/2 $\mp5/2$	13/2 $\pm7/2$	13/2 $\mp5/2$		
^6Z	+0.001901	∓0.004469	−0.002533	±0.039505	+0.684268	∓0.728139	4080.89	4083.0
^5Z	+0.009941	±0.021519	−0.056086	±0.023679	+0.726477	±0.684079	4013.55	4012.92
^4Z	+0.004102	±0.005077	−0.418623	±0.906260	−0.058208	∓0.004096	2058.40	2058.90
^3Z	+0.080839	∓0.057707	+0.901924	±0.418038	+0.019987	±0.038891	2027.96	2026.90
^2Z	+0.307713	∓0.947934	−0.074945	∓0.030165	+0.007494	±0.012288	242.42	244.40
^1Z	+0.947976	±0.312382	−0.050180	∓0.030106	+0.012876	∓0.013001	1.99	0.00

[a] Notation of Judd. See reference 6.
[b] The center of gravity of each level ^4I_J has been adjusted to give a best fit to the crystal field splitting within the level. All entries are positive in sign.
[c] Determined by Carlson and Dieke, reference 4.

$$\Delta A = -2(2\beta\beta_n g_n\langle r^{-3}\rangle)^2\hbar^{-1}\sum_j \frac{\langle\phi_j|N_x|+\rangle\langle\phi_j|iN_y|+\rangle}{-\Delta_j}, \tag{10}$$

$$\Delta P = +(2\beta\beta_n g_n\langle r^{-3}\rangle)^2\hbar^{-1}\sum_j \frac{|\langle\phi_j|N_z|+\rangle|^2-|\langle\phi_j|N_x|+\rangle|^2}{-\Delta_j}, \tag{11}$$

$$\Delta g_{n\parallel}' = -4\beta^2 g_n\langle r^{-3}\rangle\sum_j \frac{\langle\phi_j|L_z+2.002\,32S_z|+\rangle\langle\phi_j|N_z|+\rangle}{-\Delta_j}, \tag{12}$$

$$\Delta g_{n\perp}' = -4\beta^2 g_n\langle r^{-3}\rangle\sum_j \frac{\langle\phi_j|L_x+2.002\,32S_z|+\rangle\langle\phi_j|N_x|+\rangle}{-\Delta_j} \tag{13}$$

are the second-order corrections. In the notation of Elliott and Stevens[35]

$$\langle+|M|+\rangle=\textstyle\sum_J\langle J\|\alpha\|J\rangle\langle+|J_z^2-\frac{1}{3}J(J+1)|+\rangle.$$

In these equations $\langle r^{-3}\rangle$ refers to the electrons of the $4f^3$ configuration of Nd^{+3}. g_n and Q are the nuclear g factor and the nuclear electric quadrupole moment, respectively. C is an isotropic contribution to the hyperfine interaction arising from the contact term for s electrons, if any. All other second-order corrections and all higher-order terms were found to be negligible. The $|\phi_j\rangle$ refer to all electronic eigenstates other than the pair $|+\rangle$ and $|-\rangle$ making up the ground Kramers doublet. Δ_j is the energy separation of the $|\phi_j\rangle$ from the ground energy level.

It is possible to deduce the relative signs of $g_{\parallel}$ and $g_{n\parallel}'$ and also the relative signs of A' and P' from the ENDOR experiments. Equations (8) and (12) may be

[35] Reference 8, p. 563, Eqs. (6.9) and (6.10). In the present problem all matrix elements of the quadrupole interaction between basis states of different J_z vanish. The matrix elements which are nondiagonal in J are neglected; this approximation is indicated by the symbol ≈ in Eq. (7) of this paper.

used to determine the sign of g_n relative to $g_{n\parallel}'$. Equation (5) may be used to determine the sign of A' relative to g_r. Equation (3) predicts both the magnitude and sign of $g_{\parallel}$. The signs of $g_\perp$, B, and $g_{n\perp}'$ are physical nonobservables.

Crystal Field Eigenstates

The crystal field eigenstates of the levels $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ were obtained through numerical diagonalization of the matrix of the Hamiltonian,

$$\begin{aligned}\mathcal{H}_e&=\mathcal{H}_{\text{crystal field}}+\mathcal{H}_{\text{spin orbit}}+\mathcal{H}_f\\&=hcA_2^0\langle r^2\rangle P_2^0(\cos\theta)+hcA_4^0\langle r^4\rangle P_4^0(\cos\theta)\\&\quad+hcA_6^0\langle r^6\rangle P_6^0(\cos\theta)+hcA_6^6\langle r^6\rangle P_6^6(\cos\theta)e^{i6\phi}\\&\quad+hcA_6^{-6}\langle r^6\rangle P_6^{-6}(\cos\theta)e^{-i6\phi}+\mathcal{H}_{\text{spin orbit}}+\mathcal{H}_f,\end{aligned}\tag{14}$$

taken within the manifold described by $J=9/2$, $11/2$, and $13/2$. The system of coordinates is chosen so that A_6^{-6} vanishes. $\mathcal{H}_f$ is that part of the Hamiltonian of the free ion which depends only upon the configurational variables of the electrons. It can be neglected here as a constant, additive term. The experimental values[4] of the splittings in ^4I of the different J levels were used for the nonzero matrix elements of $\mathcal{H}_{\text{spin orbit}}$.

The matrix elements of $\mathcal{H}_{\text{crystal field}}$ were computed from equations published by Judd.[10] The values of the $A_n{}^m\langle r^n\rangle$ parameters used were those obtained by Judd.[6] They are

$$\begin{aligned}&A_2^0\langle r^2\rangle=+103.7\text{ cm}^{-1},\quad A_4^0\langle r^4\rangle=-36.0\text{ cm}^{-1},\\&A_6^0\langle r^6\rangle=-44.5\text{ cm}^{-1},\quad |A_6^6\langle r^6\rangle|=426.2\text{ cm}^{-1}.\end{aligned}\tag{15}$$

The interaction multiplicative factors $\langle J\|\theta_n\|J\rangle$, where $\langle J\|\theta_2\|J\rangle=\langle J\|\alpha\|J\rangle$, $\langle J\|\theta_4\|J\rangle=\langle J\|\beta\|J\rangle$, and $\langle J\|\theta_6\|J\rangle=\langle J\|\gamma\|J\rangle$,[7,8] have been tabulated by Judd[6] with corrections for intermediate coupling. The values of $\langle J'\|\theta_n\|J\rangle$ for $J'\neq J$ were obtained from unpublished calculations by Judd, and they were not corrected for intermediate coupling. Some of these factors have been given previously by Elliott and Stevens.[8] The $\langle J'\|\theta_n\|J\rangle$ factors used are tabulated in Table III. The eigenvectors appear in Table II.

Exclusion of $^4I_{15/2}$ from these calculations has negligible effect on the eigenvectors derived from $^4I_{9/2}$ while the correspondingly larger errors introduced into the

TABLE III. Some interaction multiplicative factors for Nd^{+3} ground term ^4I.[a]

	$\langle J'\|\theta_2\|J\rangle$		
J' \ J	9/2	11/2	13/2
9/2	[−7/1089]0.954		
11/2	[+2(14)$^{\frac{1}{2}}$/1573]	[−136/33 033]0.983	
13/2	[+(55)$^{\frac{1}{2}}$/7865]	[−106(770)$^{\frac{1}{2}}$/825 825]	[−1/325]1.014
	$\langle J'\|\theta_4\|J\rangle$		
J' \ J	9/2	11/2	13/2
9/2	[−136/467 181]0.958		
11/2	[+544(14)$^{\frac{1}{2}}$/3 270 267]	[−1598/16 351 335]0.974	
13/2	[+34(55)$^{\frac{1}{2}}$/2 335 905]	[−184(770)$^{\frac{1}{2}}$/16 351 335]	[−4/70 785]1.002
	$\langle J'\|\theta_6\|J\rangle$		
J' \ J	9/2	11/2	13/2
9/2	[−1615/42 513 471]0.965		
11/2	[+190(14)$^{\frac{1}{2}}$/4 723 719]	[−380/127 540 413]0.972	
13/2	[+95(55)$^{\frac{1}{2}}$/18 220 059]	[−10(770)$^{\frac{1}{2}}$/6 073 353]	[−1/552 123]0.992
	$\langle J'\|\Lambda\|J\rangle$		
J' \ J	9/2	11/2	13/2
9/2	[+8/11]1.0073		
11/2	[+(14)$^{\frac{1}{2}}$/22]0.9844	[+138/143]1.0013	
13/2	0	[+(770)$^{\frac{1}{2}}$/182]0.9943	[+72/65]0.9995
	$\langle J'\|N\|J\rangle$		
J' \ J	9/2	11/2	13/2
9/2	[+476/363]		
11/2	[−193(14)$^{\frac{1}{2}}$/4356]	[+14 920/14 157]	
13/2	0	[−941(770)$^{\frac{1}{2}}$/180 180]	[+2612/2925]

[a] For each entry the bracketed fraction is the value for pure Russell-Saunders coupling. See reference 8. Some entries are followed by a correction factor in the form of a decimal fraction. The correction factors are discussed in the text.

TABLE IV. Constants derived from g_n' parameters of spin Hamiltonian.

Nuclide	μ (nm)	g_n	$\langle r^{-3}\rangle$ (cm^{-3})	$g_n\langle r^{-3}\rangle$ (cm^{-3})	$\Delta g_{n\parallel}'$	$\Delta g_{n\perp}'$
Nd^{143}	-1.079 ± 0.06	-0.308 ± 0.018	$(36.9\pm4.5)\times10^{24}$	$(-11.4\pm1.5)\times10^{24}$	-0.235 ± 0.018	-0.564 ± 0.018
Nd^{145} [a]	-0.671 ± 0.04	-0.192 ± 0.011		$(-7.1\pm1.0)\times10^{24}$	-0.146 ± 0.011	-0.350 ± 0.011

[a] Computed from values for Nd^{143} and $g_n(Nd^{143})/g_n(Nd^{145})=+1.60883$.

eigenvectors for the higher energy states have negligible effect on the interpretation of the current ENDOR measurements. The splittings predicted by this calculation agree with the crystal field splittings[4] of the first two levels $^4I_{9/2}$ and $^4I_{11/2}$ to within ±2.5 and ±1.2 cm^{-1}, respectively. These results for the splittings are comparable to those obtained by Judd[6] using a second-order perturbation treatment rather than rigorous diagonalization. The splitting between the highest and the lowest energy levels in $^4I_{9/2}$ is 249.35 cm^{-1}; hence it is plausible to regard the eigenvectors obtained for $^4I_{9/2}$ to be uncertain by about 1%. Another test of the eigenvectors is to compare the experimental values of $g_\parallel$ and $g_\perp$ with the values computed from $|+\rangle$ and $|-\rangle$ by means of Eqs. (3) and (4). This test is made and discussed in Sec. V.

The matrix elements required in Eqs. (3) to (13) were evaluated using the eigenvectors in Table II. The corrected values of the interaction multiplicative factors $\langle J'\|\Lambda\|J\rangle$ were used. The $\langle J'\|N\|J\rangle$ values were computed by the method of Elliott and Stevens.[8] The $\langle J'\|\Lambda\|J\rangle$ and $\langle J'\|N\|J\rangle$ factors are tabulated with the $\langle J'\|\theta_n\|J\rangle$ factors in Table III. They are followed by a correction factor if one was used. Many of the $\langle J'\|\Lambda\|J\rangle$ and $\langle J'\|N\|J\rangle$ values have been given previously by Elliott and Stevens.[8] The results were

$$\langle+|L_z+2.00232S_z|+\rangle = \sum_J(\langle J\|\Lambda\|J\rangle[n_J^2(+7/2)+n_J'^2(-5/2)] +\langle J+1\|\Lambda\|J\rangle\{2n_{J+1}n_J[(J+1)^2-(7/2)^2]^{\frac{1}{2}} -2n_J'n_{J+1}'[(J+1)^2-(5/2)^2]^{\frac{1}{2}}\})=+2.05080, \quad (16)$$

$$|\langle-|L_x+2.00232S_x|+\rangle| = |\sum_J(\langle J\|\Lambda\|J\rangle n_Jn_J'[(J+7/2)(J-5/2)]^{\frac{1}{2}} -\langle J+1\|\Lambda\|J\rangle\{n_{J+1}n_J'[(J+7/2)(J+9/2)]^{\frac{1}{2}} +n_Jn_{J+1}'[(J-5/2)(J-3/2)]^{\frac{1}{2}}\})|=0.89623, \quad (17)$$

$$\langle+|N_z|+\rangle=+3.89205, \quad (18)$$

$$|\langle-|N_x|+\rangle|=1.51142, \quad (19)$$

$$\langle+|M|+\rangle=\sum_J\langle J\|\alpha\|J\rangle\{n_J^2[(7/2)^2-\tfrac{1}{3}J(J+1)] +n_J'^2[(5/2)^2-\tfrac{1}{3}J(J+1)]\} =-0.020822, \quad (20)$$

$$\Delta A=-2(2\beta\beta_n g_n\langle r^{-3}\rangle)^2h^{-1}(-0.018639\ \text{cm}/hc), \quad (21)$$

$$\Delta P=+(2\beta\beta_n g_n\langle r^{-3}\rangle)^2h^{-1}(+0.032100\ \text{cm}/hc), \quad (22)$$

$$\Delta g_{n\parallel}'=-4\beta^2g_n\langle r^{-3}\rangle(-0.011901\ \text{cm}/hc), \quad (23)$$

$$\Delta g_{n\perp}'=-4\beta^2g_n\langle r^{-3}\rangle(-0.028636\ \text{cm}/hc). \quad (24)$$

V. ANALYSIS OF THE SPIN HAMILTONIAN PARAMETERS

$g_{n\parallel}'$ and $g_{n\perp}'$

Values of $g_n(Nd^{143})$ and $\langle r^{-3}\rangle$ were obtained by a weighted least-squares fit to the four independently determined values of g_n' listed in rows 3, 4, 5, and 6 of Table I. For this calculation Eqs. (8) and (9) were used together with Eqs. (12), (13), (23), and (24) and with the constraint $g_n(Nd^{143})/g_n(Nd^{145})=+1.60883$. The results appear in Table IV. The product $g_n\langle r^{-3}\rangle$ is also tabulated. It is in excellent agreement with the more precise value independently obtained from the hyperfine interaction. The second-order contributions to the g_n' factors are given in the last two columns of Table IV.

$g_\parallel$ and $g_\perp$

Equations (3) and (4) yielded the theoretical values $g_\parallel=+4.1016$ and $|g_\perp|=1.7925$ which are 2.8% and 1.6% higher, respectively, than the experimental values. Since the eigenvectors were determined by fitting them within $\approx\pm1$% accuracy to the crystal field splittings, they may be expected to be in error by greater than ±1% for other applications. The discrepancies between the theoretical and the experimental values of the g factors may be assumed to be due entirely to the approximate nature of the $A_n^m\langle r^n\rangle$ parameters of Eqs. (15). By using this assumption the values of the integrals $\langle+|N_z|+\rangle$ and $\langle-|N_x|+\rangle$ may be significantly corrected by multiplying them by the factors

$$g_{\parallel\text{experiment}}/(2\langle+|L_z+2.00232S_z|+\rangle)=+0.97286$$

and

$$|g_{\perp\text{experiment}}/(2\langle-|L_x+2.00232S_x|+\rangle)|=0.98384,$$

respectively. This adjustment is not applicable to the remaining integrals of interest.

TABLE V. Constants derived from A' and B parameters of spin Hamiltonian.

Nuclide	$\langle+\|N_z\|+\rangle$	$\left\|\frac{\langle-\|N_x\|+\rangle}{\langle+\|N_z\|+\rangle}\right\|$	ΔA (Mc sec^{-1})	C (Mc sec^{-1})	$g_n\langle r^{-3}\rangle$ (cm^{-3})	$\mu(\mathrm{Nd}^{143})/\mu(\mathrm{Nd}^{145})$
Nd^{143}	+3.78642	0.392718	+0.0351±0.0010	+0.09±0.6	$(-11.884\pm0.12)\times10^{24}$	+1.60883±0.00004
Nd^{145} [a]			+0.0136±0.0004	+0.06±0.4	$(-7.387\pm0.07)\times10^{24}$	

[a] Computed from values for Nd^{143} and $g_n(Nd^{143})/g_n(Nd^{145}) = +1.60883$.

A' and $|B|$

The magnitudes of A' and B cannot be used individually to evaluate the contact term C because of their dependence upon g_n and $\langle r^{-3}\rangle$. However, the ratio of $A'-\Delta A$ to B is independent of g_n and $\langle r^{-3}\rangle$, and Eqs. (5) and (6) may be solved for

$$C=(A'-\Delta A)\times\frac{[|B/(A'-\Delta A)|-|\langle-|N_x|+\rangle/\langle+|N_z|+\rangle|]}{[1-|\langle-|N_x|+\rangle/\langle+|N_z|+\rangle|]}. \quad (25)$$

The second-order term ΔA is expected to be very small, in which case

$$\Delta A\approx-2[(A'-C)/(2\langle+|N_z|+\rangle)]^2h(-0.018639\text{ cm}/hc). \quad (26)$$

Equations (25) and (26) were solved simultaneously for ΔA and C using the $\langle+|N_z|+\rangle$ and $\langle-|N_x|+\rangle$ integrals adjusted as described in the discussion of g factors. The values for ΔA and C so obtained are listed in Table V. Note that the value obtained for C does not differ significantly from zero. Equation (5) was solved for the product

$$g_n\langle r^{-3}\rangle=h(A'-C-\Delta A)(4|\beta|\beta_n\langle+|N_z|+\rangle)^{-1}. \quad (27)$$

The values of $g_n\langle r^{-3}\rangle$ listed in Table V were computed with Eq. (27) using the values given for C, ΔA, and $\langle+|N_z|+\rangle$.

The contact term C in Eq. (5) is linear in g_n while the ΔA term is not. Since both Nd^{143} and Nd^{145} have the same spin the ratio of their nuclear magnetic moments is given by

$$\frac{\mu(\mathrm{Nd}^{143})}{\mu(\mathrm{Nd}^{145})}=\frac{g_n(\mathrm{Nd}^{143})}{g_n(\mathrm{Nd}^{143})}=\frac{A'(\mathrm{Nd}^{143})-\Delta A(\mathrm{Nd}^{143})}{A'(\mathrm{Nd}^{145})-\Delta A(\mathrm{Nd}^{145})}=+1.60883\pm0.00004. \quad (28)$$

Weighted means of the A' and $|B|$ parameters obtained in the $\mathbf{H}\|\mathbf{c}$ and $\mathbf{H}\perp\mathbf{c}$ fits were used in the calculations. An analysis of the hyperfine interaction done without adjustment of the $\langle+|N_z|+\rangle$ and $\langle-|N_x|+\rangle$ integrals gave the following results for Nd^{143}:

$$C=-9\pm20\text{ Mc sec}^{-1},\quad \Delta A=+0.033\pm0.002\text{ Mc sec}^{-1},$$
$$g_n\langle r^{-3}\rangle=(-11.5\pm0.4)\times10^{24}\text{ cm}^{-3}.$$

These values are consistent with the more precisely determined values given in Table V.

P'

The ΔP term was computed from Eq. (22) using the value of $g_n\langle r^{-3}\rangle$ obtained in the analysis of the hyperfine interaction. Equation (7) was solved for

$$Q\approx-h(P'-\Delta P)(4I)(2I-1)(9e^2\langle r^{-3}\rangle\langle+|M|+\rangle)^{-1}. \quad (29)$$

The Q values were computed from Eq. (29) using the values of $\langle+|M|+\rangle$ of Eq. (20) and the value of $\langle r^{-3}\rangle$ obtained from the analysis of the g_n' parameters. Equation (29) was applied to both nuclides to obtain

$$\frac{Q(\mathrm{Nd}^{143})}{Q(\mathrm{Nd}^{145})}=\frac{P'(\mathrm{Nd}^{143})-\Delta P(\mathrm{Nd}^{143})}{P'(\mathrm{Nd}^{145})-\Delta P(\mathrm{Nd}^{145})}=+1.96\pm0.2. \quad (30)$$

The values obtained are listed in Table VI. Weighted means of the P' parameters were used.

VI. DISCUSSION

Each uncertainty quoted in Table I for the spin Hamiltonian parameters is the standard deviation of the mean based upon external consistency. All other errors quoted are based upon internal consistency. The latter are propagated in the calculations and arise from (a) an assumed ±2% uncertainty in the values used for $\langle+|N_z|+\rangle$, $\langle-|N_x|+\rangle$, $\langle+|M|+\rangle$, and the sums of integrals appearing in the second order correction terms, (b) an assumed ±1% uncertainty in the value of the $\langle 9/2\|N\|9/2\rangle$ factor used, and (c) the quoted standard deviations of the spin Hamiltonian parameters. Source (c) was important only in the ratios of nuclear moments μ^{143}/μ^{145} and Q^{143}/Q^{145}. Source (b) could have been eliminated by taking into account the effect of intermediate coupling on the $\langle J'\|N\|J\rangle$ factors. Carlson and Dieke[4] quoted errors ranging from ±(0.1 cm^{-1})hc to

$\pm(1\ \text{cm}^{-1})hc$ in their determinations of the crystal field energy splittings within the $^4I_{9/2}$ and $^4I_{11/2}$ levels; the usual error was $\pm(0.2\ \text{cm}^{-1})hc$. A more precise interpretation of the current ENDOR results would be possible if values of the $A_n{}^m\langle r^n\rangle$ parameters which produce a least-squares fit to the data of Carlson and Dieke were available. In such a fit a tenfold improvement over the fit obtained by Judd[6] might be obtained.

The result $\langle r^{-3}\rangle=(36.9\pm4.5)\times10^{24}\ \text{cm}^{-3}$ lies between the values $(42\pm2)\times10^{24}\ \text{cm}^{-3}$ obtained by Bleaney[36] and $(32.7\pm1.5)\times10^{24}\ \text{cm}^{-3}$ calculated by Judd and Lindgren.[37] The close agreement of the product $g_n\langle r^{-3}\rangle$ obtained from the anisotropy of the g_n' factor and the value independently obtained from the hyperfine interaction indicates that the results reported here for $\langle r^{-3}\rangle$ and g_n may be of greater import than is indicated by their assigned errors.

Wong[38] has pointed out that appreciable mixing into the ground states $4f^3$, ^4I of other ^4I states of configurations having at least one unpaired s electron is unlikely. Only admixtures of ^4I states are expected.[6] This is consistent with the null result for a contact term in the hyperfine interaction obtained in the present study.

The magnitudes and the ratio of the nuclear magnetic moments of Nd^{143} and Nd^{145} determined in this study agree with the less precise results reported by Bleaney, Scovil, and Trenam[16] as analyzed by Elliott and Stevens,[9] within their stated errors. The signs of the nuclear magnetic moments agree with the signs obtained by Murakawa and Ross[39] from optical measurements of Nd^{+1}. No independent determinations of the nuclear electric quadrupole moments of neodymium have been reported, although Elliott and Stevens[9] have set upper limits of $|Q|\approx1\times10^{-24}\ \text{cm}^2$ for both nuclides.

TABLE VI. Constants derived from P' parameter of spin Hamiltonian.

Nuclide	ΔP (Mc sec^{-1})	Q (cm^2)	$Q(\text{Nd}^{143})/Q(\text{Nd}^{145})$
Nd^{143}	$+0.0302\pm0.0008$	$(+0.0206\pm0.003)\times10^{-24}$	$+1.96\pm0.2$
Nd^{145}	$+0.0117\pm0.0003$	$(+0.0105\pm0.002)\times10^{-24}$	

The value of $|\mu(\text{Nd}^{147})|=0.56\pm0.06$ nuclear magneton obtained by Kedzie, Abraham, and Jeffries[40] can be recalculated from their experimental determination of $|B(\text{Nd}^{143})/B(\text{Nd}^{147})|=1.317\pm0.002$ and the value for $\mu(\text{Nd}^{143})$ obtained in this research. The result is $|\mu(\text{Nd}^{147})|=0.585\pm0.03$ nuclear magneton.

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[36] B. Bleaney, Proc. Phys. Soc. (London) **A68**, 937 (1955).
[37] B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).
[38] E. Y. Wong (private communication).
[39] K. Murakawa and J. S. Ross, Phys. Rev. **82**, 967 (1951).
[40] R. W. Kedzie, M. Abraham, and C. D. Jeffries, Phys. Rev. **108**, 54 (1957).