PHYSICAL REVIEW B VOLUME 8, NUMBER 5 1 SEPTEMBER 1973

Electron-Paramagnetic Resonance of Photoexcited Trivalent Neodymium Ions in Lanthanum Trichloride Single Crystals*†‡§

Jan P. Hessler and Clyde A. Hutchison Jr.

The Department of Chemistry and The Enrico Fermi Institute, The University of Chicago, Chicago, Illinois, 60637

(Received 12 March 1973)

The electron-paramagnetic-resonance spectra of $^{143}\mathrm{Nd}^{+3}$ dilutely substituted for La^{+3} in LaCl_3 single crystals have been obtained for the lowest Kramers doublets of the photoexcited $^4I_{13/2}$ and $^4I_{15/2}$ states. The values of the parameters in the spin-Hamiltonian description of the EPR spectra of both $^{143}\mathrm{Nd}^{+3}$ and $^{145}\mathrm{Nd}^{+3}$ in these two photoexcited states, as well as in the ground $^4I_{9/2}$ state, have been summarized and compared.

I. INTRODUCTION

The electron-paramagnetic-resonance (EPR) spectra of $^{143}\mathrm{Nd}^{+3}$, $^{145}\mathrm{Nd}^{+3}$, and the even isotope Nd^{+3} species, each in the lowest Kramers doublet of the $^4I_{9/2}$ ground state and dilutely substituted for La^{+3} in LaCl_3 single crystals, were first investigated by Hutchison and Wong[1] in this laboratory. Subsequently, in this laboratory the Nd^{+3} electron-nuclear-double-resonance (ENDOR) spectra of these same systems were studied by Halford, Hutchison, and Llewellyn,[2] and by Halford,[3] and the zero-external-field magnetic-resonance spectra were investigated by Erickson.[4]

Recently, Clarke and Hutchison[5] gave a preliminary account of studies of these systems in photoexcited states. They gave EPR results for $^{145}\mathrm{Nd}^{+3}$ in LaCl_3 crystals. This last mentioned work and the investigation of the $^4S_{3/2}$ state of Er^{+3} in YCl_3 crystals by Fürrer, Pelzl, and Hüfner,[6] constitute the only studies to date, by EPR methods, of any photoexcited states of trivalent rare-earth ions. Several investigations of photoexcited states of divalent rare-earth ions have been referenced in the previous communication.[5]

In this paper we report the EPR results for $^{143}\mathrm{Nd}^{+3}$ in LaCl_3 in photoexcited $^4I_{13/2}$ and $^4I_{15/2}$ excited states and summarize all of the excited-state results for both $^{143}\mathrm{Nd}^{+3}$ and $^{145}\mathrm{Nd}^{+3}$. We also compare these results with our EPR and ENDOR[3] measurements for both Nd^{+3} species in the ground $^4I_{9/2}$ state.

II. EXPERIMENTAL PROCEDURES

Single crystals of LaCl_3, each containing both Nd^{+3} and U^{+3} dilutely substituted for La^{+3}, were prepared by the methods previously described.[1] The boule used for the measurements described in the previous paper[5] and the boule used for the measurements described in this paper were each grown from a melt which contained equal mole fractions of Nd^{+3} and U^{+3}. One boule was grown from a melt which contained 0.002 mole fraction of Nd^{+3} enriched in $^{145}\mathrm{Nd}$ and the EPR measurements on two crystals from that boule have been reported[5] and the experimental details have been described previously.[5] The other melt contained ~0.003 mole fraction of Nd^{+3} enriched in $^{143}\mathrm{Nd}$. The $^{143}\mathrm{Nd}$ measurements described below were made using six different single-crystal samples cleaved from this boule. These samples were approximately $0.1\times0.3\times0.4$ cm in linear dimensions. They possessed good cleavage surfaces.

The EPR measurements were made with the crystals in contact with superfluid He at approximately 1.8 °K as determined by measurement of the He vapor pressure. The crystals were irradiated with the light from a 1000-W Hg-Xe arc filtered through a 10-cm path length of $\mathrm{H_2O}$. The crystals were held in rotatable fused-silica cylinders with open ends for He contact. The desired relative orientation of the laboratory magnetic field, $\vec{\mathrm{H}}_0$, and the $\hat{c}$ axis of the crystal, was obtained by rotating $\vec{\mathrm{H}}_0$ and the crystal while observing the oscilloscope display of the EPR spectrum.

The measurements were made by superheterodyne detection with magnetic field modulation at frequency 1.25×10^5 Hz. The EPR spectral line positions were measured by displaying the lines on an oscilloscope together with the proton fluxmeter signal, by use of a 60-Hz sweep field of ~2-G amplitude. Values of field at the sample were determined by previously described methods.[7] The microwave carrier frequencies were in the range $\sim2.39-\sim2.44\times10^{10}$ Hz for the measurements of five of the crystal fragments, and was $\sim9.38\times10^9$ Hz for the other fragment. The microwave magnetic field amplitude at the crystal was $\sim3\times10^{-2}$ G. The spectrometers were the same as those used for previous experiments.[5]

III. EXPERIMENTS

The EPR experiments on $^{143}\mathrm{Nd}^{+3}$ are listed in Table I. We observed, just as in the previous work,[5] the spectra of the $^4I_{13/2}$, $2\mu=1$, and $^4I_{15/2}$, $2\mu=1$ states, which lie 3932 and 5869 cm^{-1},[8–10] re-

TABLE I. Summary of EPR experiments on $^{143}\mathrm{Nd}^{+3}$ in LaCl_3 at ~1.8 °K and microwave frequency ν_M.

Crystal sample No.	$\nu_M \times 10^{-10}$ (Hz)	J	Orientation	Number of lines measured for $^{143}\mathrm{Nd}^{+3}$
1	~2.40	$\frac{9}{2}$	$\vec{H}_0 \perp \hat{c}$	8
		$\frac{13}{2}$	$\vec{H}_0 \parallel \hat{c}$	5
		$\frac{15}{2}$	$\vec{H}_0 \parallel \hat{c}$	6
		$\frac{15}{2}$	$\vec{H}_0 \perp \hat{c}$	8
2	~0.94	$\frac{9}{2}$	$\vec{H}_0 \perp \hat{c}$	7
		$\frac{13}{2}$	$\vec{H}_0 \perp \hat{c}$	4
3	~2.41	$\frac{13}{2}$	$\vec{H}_0 \parallel \hat{c}$	7
		$\frac{15}{2}$	$\vec{H}_0 \parallel \hat{c}$	4
		$\frac{15}{2}$	$\vec{H}_0 \perp \hat{c}$	8
4	~2.44	$\frac{13}{2}$	$\vec{H}_0 \perp \hat{c}$	7
		$\frac{15}{2}$	$\vec{H}_0 \perp \hat{c}$	8
5	~2.39	$\frac{9}{2}$	$\vec{H}_0 \parallel \hat{c}$	8
6	~2.44	$\frac{13}{2}$	$\vec{H}_0 \parallel \hat{c}$	5
		$\frac{15}{2}$	$\vec{H}_0 \parallel \hat{c}$	5

spectively, above the ground $^4I_{9/2}$, $2\mu = 5$ state. μ is the crystal quantum number.[10] These are in each case the lowest energy crystal-field states of their J manifold.[8–10] The $J=\frac{11}{2}$ state was not observed and would not be expected to be as a result of the fact that its lowest crystal-field component has $2\mu = 3$,[8–10] which implies that this Kramer's doublet does not satisfy the $\Delta M_j = \pm 1$ condition necessary for magnetic dipole transitions. The character and quality of the spectra were similar to those previously described and pictured.[5] Precise measurements of some lines were prevented by overlapping of spectra and those lines are not listed in Table I. During each set of measurements except the single set for sample No. 4, $J=\frac{13}{2}$, the line for the Nd^{+3} species with nuclear spin I equal to zero ($I=0$) was also measured and is not listed in Table I.

Because the spectra for $^{143}\mathrm{Nd}^{+3}$ and $^{145}\mathrm{Nd}^{+3}$ in the ground $J=\frac{9}{2}$ state were very accurately known from the previous ENDOR studies,[3] they were also measured during these EPR experiments for better assessment of the errors and reliability of the present measurements on these same ions in their photoexcited states.

IV. TREATMENT OF DATA

The parameters, $g_\parallel$, $g_\perp$, A, B, in the spin Hamiltonian,

$$\mathcal{H} = |\mu_B| \left[g_\parallel H_z S_z + g_\perp (H_x S_x + H_y S_y) \right] + A S_z I_z + B(S_x I_x + S_y I_y) ,$$
$$S=\tfrac{1}{2}, \quad I=\tfrac{7}{2} , \tag{1}$$

were adjusted to give an approximate least-squares best fit to the measurements summarized in Table I. Other parameters (P, g_n) in the spin Hamiltonian used previously[3] in this laboratory for fitting the ENDOR measurements on $^{143}\mathrm{Nd}^{+3}$ in the $J=\frac{9}{2}$ state had, for the present case, values small enough that they could not be determined with sufficient accuracy to merit their consideration in a discussion of these EPR results.

For the adjustment procedure used to obtain values of A and B the sets of data for $\vec{H}_0 \parallel \hat{c}$ and $\vec{H}_0 \perp \hat{c}$ obtained in the experiments summarized in Table I were paired as indicated in the second and third columns of Table II. Initial approximations to values of A and B were obtained from these pairs of data sets by use of perturbation theory formulas[11] for line positions and by averaging the values of A and B so obtained from all the measured lines of the two sets. Then an adjustment of the value of B was made in the formula[11]

$$h\nu_M(m_I) \cong g_\perp \mu_B |\vec{H}_0(m_I)| + m_I B + \frac{A^2+B^2}{g\mu_B|\vec{H}_0(m_I)|}\left(\frac{63}{16} - \frac{m_I^2}{4}\right) , \tag{2}$$

in which $\nu_M(m_I)$ is the microwave frequency and $|\vec{H}_0(m_I)|$ is the applied field at which the EPR line for m_I was observed, to give a least-squares best fit to the ν_M values obtained in the data set with $\vec{H}_0 \perp \hat{c}$. A was kept fixed during this adjustment at the approximate value mentioned above, and $g_\perp$ was kept fixed at the value measured for the $I=0$ species and is given in Table II. The values of B so obtained, together with their standard deviations, are listed in Table II. Then an adjustment of the value of A was made in the exact expressions[11] for ν_M as a function of $|\vec{H}_0(m_I)|$, obtained from Eq. (1) for $\vec{H}_0 \parallel \hat{c}$, to give a least-squares best fit to the ν_M values obtained in the data set with $\vec{H}_0 \parallel \hat{c}$. B was kept fixed during this adjustment at the value listed in Table II and $g_\parallel$ was kept fixed at the value measured for the $I=0$ species and is given in Table II. The values of A so obtained, together with their standard deviations, are listed in Table II. Further iteration of the steps of this process produced no further changes in A and B values to the precision to which they are given in Table II.

V. DISCUSSION OF RESULTS

In Table III we have summarized our EPR results for the $J=\frac{13}{2}$ and $\frac{15}{2}$ states of $^{143}\mathrm{Nd}^{+3}$ and the $I=0$ species, together with the previously obtained EPR results for $^{145}\mathrm{Nd}^{+3}$. We have also included the present EPR measurements and the previous

TABLE II. Summary of values of parameters in the spin Hamiltonian, Eq. (1), which give approximate least-squares best fits of measurements of EPR spectra of $^{143}Nd^{+3}$ in $LaCl_3$. [The pairs of sample numbers in a given row denote the sets of $\vec{H}_0 \parallel \hat{c}$ and $\vec{H}_0 \perp \hat{c}$ data used in the manner described in the text for the estimation of A and B. The numbers in parentheses for best values of $g_\parallel$ and $g_\perp$ are standard deviations of the means of the individual measurements. The numbers in parentheses for the best values of A and B are the standard deviations of the means of the weighted averages of the individual measurements, the weights being inversely proportional to the squares of the standard deviations of the individual measurements which are given in parentheses below each individual value. $\sigma_\parallel$ and $\sigma_\perp$ are the standard deviations of data from the values given by the spin Hamiltonian (1) with the given parameter values.]

J	Crystal sample No. (Table I) $\parallel$	$\perp$	$g_\parallel$	$g_\perp$	$\|A\|/h$ (MHz)	$\|B\|/h$ (MHz)	$\sigma_\parallel$ (MHz)	$\sigma_\perp$ (MHz)
$\frac{9}{2}$	5	1	3.99456	1.76144	1273.42 (0.86)	499.36 (0.44)	5.5	2.9
	···	2	···	1.76138	··· ···	498.8 (~8.0)	··· ···	4.0 ···
	3	3	3.99459	1.76117	···	···	···	···
	Best values		3.99458 (2)	1.76133 (14)	1273.42 (0.86)	499.36 (0.44)	···	···
$\frac{13}{2}$	3	4	10.1937	···	1345.28 (0.78)	184.2 (4.3)	4.7	21.7
	1	···	10.1842	···	1340.2 (6.5)	Ref. a	29.8	···
	6	···	10.1897	···	1339.9 (2.5)	Ref. a	9.6	···
	···	2	···	1.3447	···	only 4 lines	···	···
	Best values		10.1892 (47)	1.3447	1344.7 (4.0)	184.2 (4.3)	···	···
$\frac{15}{2}$	1	1	9.5569	5.1223	1001.7 (2.2)	535.4 (0.7)	13.7	4.8
	3	3	9.5238	5.1213	993.7 (1.6)	535.6 (0.3)	7.9	2.2
	6	4	9.5618	5.1201	998.1 (3.5)	536.1 (2.2)	20.3	14.6
	Best values		9.5475 (207)	5.1212 (11)	996.6 (2.6)	535.6 (1.4)	···	···

[a] B/h is assumed to equal 184.2 MHz to calculate A/h.

ENDOR[3] results for the $J=\frac{9}{2}$ state. Also in Table III, the following are given for comparison: (a) the values of $g_\parallel$ calculated by Eisenstein[12] for the $J=\frac{13}{2}$ and $\frac{15}{2}$ states; (b) the values calculated previously[5] for $g_\perp$ for the $J=\frac{13}{2}$ and $\frac{15}{2}$ states; and (c) the values of $g_\parallel$ and $g_\perp$ calculated by Halford[3] for the $J=\frac{9}{2}$ state. The calculations of $g_\parallel$ by Eisenstein[12] included the Coulomb, spin-orbit, and crystal-field interactions within the f^3 configuration. The previous calculation of $g_\perp$ for the $J=\frac{13}{2}$ state employed the eigenvectors of the crystal field given by Halford[3] within the manifold described by $J=\frac{9}{2}$, $\frac{11}{2}$, and $\frac{13}{2}$ only. The previous calculation[5] of $g_\perp$ for the $\frac{15}{2}$ state was very crude, neglecting interactions with other J states.

The EPR values of $g_\parallel$ and $g_\perp$ given in Table III represent the best determinations of these quantities. The present value, 3.9946, for $g_\parallel$ is in considerably better agreement with the early value,[1] 3.996 with standard deviation $\sigma = 0.001$, than with the value 3.9903 with $\sigma = 0.0005$ given by the EPR measurements of Halford.[3] The present value 1.7613 with $\sigma = 0.0001$ for $g_\perp$ is in reasonably good agreement with both the early value[1] 1.763 with $\sigma = 0.001$ and the value 1.7635 with $\sigma = 0.0012$, given by Halford.[3]

We have given in Table IV some comparisons of spin-Hamiltonian parameters for the two isotopes and for the $\vec{H}_0 \parallel \hat{c}$ and $\vec{H}_0 \perp \hat{c}$ orientations of the external field. It is to be noted that the value of the ratio A/B of the hyperfine interactions for the parallel and perpendicular orientations approaches the

TABLE III. Summary of best values of parameters in the spin Hamiltonian, Eq. (1), for ^{143}Nd^{+3} and ^{145}Nd^{+3} in LaCl$_3$ single crystals, from the present and previous[a,b] work, and some calculated[b,c] g values. (Experimental values for $|g_\parallel|$, $|g_\perp|$, and $|A|/h$, $|B|/h$ for ^{143}Nd^{+3} are taken from Table II. The numbers in parentheses are the standard deviations taken from Table II or appropriate references, except for the case of $J=\frac{9}{2}$, $g_\parallel$, in which case the number was estimated from *a priori* consideration of the magnetic field measurement method.)

		$I={}^0$Nd^{+3}		^{143}Nd^{+3}		^{145}Nd^{+3}	
J	Method	$\lvert g_\parallel\rvert$	$\lvert g_\perp\rvert$	$\lvert A\rvert/h$ (MHz)	$\lvert B\rvert/h$ (MHz)	$\lvert A\rvert/h$ (MHz)	$\lvert B\rvert/h$ (MHz)
$\frac{13}{2}$	EPR	10.1892 (47)	1.3447 ...	1344.7 (4.0)	184.2 (4.3)	828.1[b] (5.0)	111.3[b] (2.0)
$\frac{13}{2}$	Calc.	10.26[c]	1.196[b]	...	...	...	...
$\frac{15}{2}$	EPR	9.548 (21)	5.1212 (11)	996.6 (2.6)	535.6 (1.4)	620.9[b] (4.0)	335.3[b] (2.0)
$\frac{15}{2}$	Calc.	9.67[c]	4.426[b]	...	...	...	...
$\frac{9}{2}$	EPR	3.9946 (2)	1.7613 (1)	1273.4 (0.9)	499.4 (0.4)	...	...
$\frac{9}{2}$	ENDOR	...	...	1272.143[a] (0.008)	499.532[a] (0.040)	790.736[a] (0.016)	310.540[a] (0.048)
$\frac{9}{2}$	Calc.	4.1016	1.7925	...	...	...	...

[a] Reference 3. [b] Reference 5. [c] Reference 12.

value of the ratio $g_\parallel/g_\perp$ of the g factors more closely as J increases. As first pointed out by Elliott and Stevens,[13] the departure from unity of the ratio of these two ratios implies that the eigenstates are not eigenstates of J. The admixture of the different J states can be produced only by the crystal field and cannot result from breakdown of Russell-Saunders coupling or from configuration interaction. The three energy separations of the adjacent J levels of the ^4I manifold are almost equal.[8-10] Thus the change in the departure of this ratio from unity from 0.12 for $J=\frac{9}{2}$ to <0.01 for $J=\frac{15}{2}$ indicates a reduction in the admixture of different J states with increasing J value.

The fact that there are no second-order corrections[3,14] to the parameter $|B|$ in the spin Hamiltonian (1) leads to the conclusion that the ratio of the values of $|B|$ for ^{143}Nd^{+3} and ^{145}Nd^{+3} is equal to the ratio of the nuclear magnetic dipole moments for the two nuclear species. The constancy of the value of this ratio for the $J=\frac{9}{2}$, $\frac{13}{2}$, and $\frac{15}{2}$ states thus again confirms the consistency of all of the measurements for the three J states.

The fact that the second-order corrections to A for the $J=\frac{9}{2}$ state are relatively small[3] results in the experimentally observed fact that $^{143}A/^{145}A$ is equal to the ratio of nuclear magnetic dipole moments and to $^{143}B/^{145}B$ to less than the standard deviations of the measurements. We expect and find a similar situation for the $J=\frac{13}{2}$ and $\frac{15}{2}$ states as summarized in the fifth and sixth columns of Table IV.

The comparisons of spin-Hamiltonian parameters, including P and g_n, for the $J=\frac{13}{2}$ and $\frac{15}{2}$ states with more detailed calculations of crystal-field eigenstates and with ENDOR determined values of nuclear moments and moment ratios for the ground $J=\frac{9}{2}$ state must await the outcome of ENDOR measurements on the excited states.

The lifetimes of the excited states and the energy

TABLE IV. Summary of comparisons of spin-Hamiltonian parameters which fit EPR measurements for ^{143}Nd^{+3} and ^{145}Nd^{+3}in LaCl$_3$ single crystals and for $\vec{H}_0 \parallel \hat{c}$ and $\vec{H}_0 \perp \hat{c}$. (Numbers in parentheses are standard deviations computed from the standard deviations given in Table III for the factors in the numerators and denominators.)

J	Species	$\left\lvert\frac{Ag_\perp}{Bg_\parallel}\right\rvert$	$\frac{\lvert ^{143}B\rvert}{\lvert ^{145}B\rvert}$	$\frac{\lvert ^{143}A\rvert}{\lvert ^{145}A\rvert}$	$\frac{\lvert ^{143}A\,^{145}B\rvert}{\lvert ^{143}B\,^{145}A\rvert}$
$\frac{9}{2}$	143	1.12288 (12)	1.60859 (28)	1.608809 (34)	1.00014 (18)
$\frac{9}{2}$	145	1.12273 (20)			
$\frac{13}{2}$	143	0.963 (22)	1.655 (49)	1.623 (11)	0.981 (30)
$\frac{13}{2}$	145	0.982 (19)			
$\frac{15}{2}$	143	0.9980 (43)	1.597 (10)	1.605 (11)	1.0048 (93)
$\frac{15}{2}$	145	0.9932 (90)			

transfer properties of the cosubstituted U^{+3} ions are consistent with those previously[5] reported and discussed. Further discussion of these effects must await the results of studies designed to elucidate more details of these phenomena.

ACKNOWLEDGMENTS

We thank Bilin Tsai and Sharon Bellard for growing the crystals used in these experiments. We acknowledge the assistance of Clark E. Davoust and Karolis Avizienis in the construction of the equipment used for these measurements.

---

[*] Research supported by the National Science Foundation.

[†] Research supported by the U. S. Atomic Energy Commission.

[‡] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[§] We would like to acknowledge the general support of the Materials Research Laboratory by the National Science Foundation.

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

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

[3] D. Halford, Phys. Rev. 127, 1940 (1962).

[4] L. E. Erickson, Phys. Rev. 143, 295 (1966).

[5] R. H. Clarke and C. A. Hutchison Jr., Phys. Rev. Lett. 27, 638 (1971).

[6] R. Fürrer, J. Pelzl, and S. Hüfner, Z. Phys. 247, 267 (1971).

[7] C. A. Hutchison Jr. and B. W. Mangum, J. Chem. Phys. 34, 908 (1961)

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

[9] F. Varsanyi and G. H. Dieke, J. Chem. Phys. 33, 1616 (1960).

[10] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, edited by H. M. Crosswhite and Hannah Crosswhite (Interscience, New York, 1968).

[11] B. Bleaney, Philos. Mag. 42, 441 (1951).

[12] J. C. Eisenstein, J. Chem. Phys. 39, 2134 (1963).

[13] R. J. Elliott and K. W. H. Stevens, Proc. R. Soc. A 218, 564 (1953).

[14] I. Y. Chan and C. A. Hutchison Jr., Phys. Rev. B 5, 3387 (1972).