Hyperfine structure of high-L states in ^{143,145}Nd I by atomic-beam laser-rf double resonance

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The atomic-beam laser-rf double-resonance technique has been used to study the hyperfine structure (hfs) of the metastable $^7L_{5-11}$ and $^7K_4$ states of the $4f^45d6s$ configuration in ^{143,145}Nd I. Four zero-field intervals were measured in each state and the results used to assign the conventional hfs constants A and B. Comparison of the results with predictions of the Sandars-Beck model allowed evaluation of the relevant single-electron radial hfs integrals. These are compared with earlier results from the Nd I atomic ground term and with extrapolations from other rare-earth elements. The unusually large orbital-angular-momentum values ($L=7$ and 8 for the states studied) do not appear to have introduced any anomalous effects. *Ab initio* calculations are not yet feasible for the complex $4f^45d6s$ levels studied.

I. INTRODUCTION

The ground multiplet of Nd I is the ^5I term of the $4f^46^2$ configuration [1]. The term extends over about 5000 cm^{-1}, and the ground state is $^5I_4$. The next series of even-parity states lie in the $4f^45d6s$ configuration, the lowest two terms being ^7L at 8400–14 300 cm^{-1} and ^7K at 9800–15 100 cm^{-1}; these are the subject of the present study. There are also many odd-parity levels beginning at about 6700 cm^{-1}.

The hyperfine structure (hfs) of the ^5I ground term was studied [2,3] in detail by atomic-beam magnetic resonance in 1963 and 1972. The present work extends the earlier studies to the metastable $4f^45d6s$ levels. These states are much more complex than the ground term since they are built from three open shells rather than one. The four $4f$ electrons couple to ^5I as in the ground term, but the contributions of the $5d$ and $6s$ electron are coupled to this core. An unusual feature of the particular levels studied is their extremely large orbital angular momentum ($L=7$ and 8), and it is of interest to see if this feature presents any problem for the theory. Because of the extreme complexity of the three-open-shell nature of the states, it is not now feasible [4] to make *ab initio* multiconfiguration Dirac-Fock (MCDF) hfs calculations; we must instead fall back on the semiempirical effective-operator approach of Sandars and Beck [5].

The atomic-beam laser-rf double-resonance method was used for the measurements. It allows measurement of the zero-field hfs intervals to a precision of a few kHz.

II. EXPERIMENTAL CONSIDERATIONS

The apparatus has been described before [6]. Neodymium metal is evaporated from a tantalum oven heated by electron bombardment, and collimated to form an atomic beam. A discharge struck in the beam populates the metastable levels to be studied. A single-mode cw ring dye laser is used to deplete the population of one hfs level of the metastable state to be studied. Light from the same laser is used downstream as a probe to determine if the population of the depleted level has been replenished by the action of an rf field located between the pump and probe regions. The replenishment, detected as a resonant increase in fluorescence induced by the probe beam, is due to an rf transition to the depleted level from an adjacent hfs level. The linewidth of such rf transitions is determined by the transit time of the atoms in the rf field, and is typically 10 kHz. A cooled photon-counting photomultiplier is used to detect the fluorescence. The laser is monitored by a 50-cm Fabry-Pérot interferometer (for incremental frequency measurement) and an air-track wavemeter. The radio frequency is generated by a computer-controlled synthesizer.

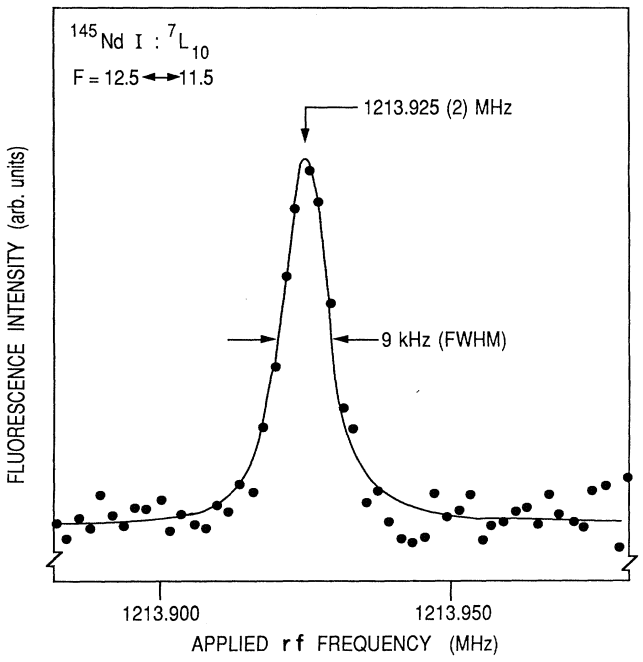

FIG. 1. A typical rf spectrum. The resonant increase in fluorescence intensity is shown as a function of the rf frequency applied. The particular curve shown is for the $F=12.5\leftrightarrow11.5$ interval in the $^7L_{10}$ state of ^{145}Nd.

The optical spectrum obtained by scanning the laser wavelength through a line displays the various hfs components, each with a nearly-Doppler-free linewidth of 15 MHz. Because there are two odd Nd isotopes (^{143}Nd and ^{145}Nd) each with nuclear spin $I=\frac{7}{2}$, and five even-even isotopes with spin zero, the spectrum of a typical optical line is usually complex and in some cases not all of the 40–50 components of a line are cleanly resolved. For the double-resonance measurements, the laser is set on one hfs component of a suitable optical line connecting the metastable level to be studied with a highly excited level. The rf is then scanned to search for the resonant fluorescence increase due to a lower-state hfs interval. Although four (of the seven possible for $I=\frac{7}{2}$) hfs intervals are measured for each electronic state studied the four selected vary from state to state because of the congestion in the optical spectrum. No confusion is possible since any four intervals over determine [7] the two hfs constants A and B. Figure 1 shows a typical double-resonance spectrum; it displays the resonant increase in fluorescence caused by the probe laser beam when the radio frequency is swept through the lower-state hfs interval, thereby repopulating the state depleted by the pump laser beam. The particular curve shown is for the $F=12.5\leftrightarrow F=11.5$ interval in the $^7L_{10}$ state of ^{145}Nd.

III. RESULTS AND ANALYSIS

Table I lists the zero-field hfs intervals measured by double resonance in the $4f^45d6s$ ^7L and ^7K levels of ^{143,145}Nd I. The excitation energies are listed in column 2.

TABLE I. Zero-field hyperfine intervals measured for the $4f^45d6s$ $^7L_{5-11}$ and $^7K_4$ states of ^{143,145}Nd I. The experimental uncertainty in each measurement is ±2 kHz. The negative signs follow from analysis of the ordering of the optical hfs components; the rf spectra are insensitive to the ordering of the F levels.

State	Excitation energy (cm^{-1})	$F\leftrightarrow F'$	$\Delta\nu$ (MHz) ^{143}Nd	^{145}Nd
$^7L_5$	8475.355	8.5↔7.5	−482.551	−300.073
		7.5↔6.5	−418.867	−261.122
		6.5↔5.5	−357.778	
		5.5↔4.5	−298.935	−187.143
		4.5↔3.5		−151.749
$^7L_6$	9115.092	9.5↔8.5	−1463.710	−908.509
		8.5↔7.5	−1303.188	−809.486
		7.5↔6.5	−1144.816	−711.595
		6.5↔5.5	−988.342	−614.695
$^7L_7$	9939.704	10.5↔9.5	−1782.343	−1106.083
		9.5↔8.5	−1606.504	−997.526
		8.5↔7.5	−1432.489	
		7.5↔6.5	−1260.119	−783.211
		6.5↔5.5		−677.243
$^7L_8$	10 897.998	11.5↔10.5	−1934.146	−1200.238
		10.5↔9.5	−1760.280	−1092.868
		9.5↔8.5	−1587.959	−986.321
		8.5↔7.5	−1417.042	−880.514
$^7L_9$	11 959.761	12.5↔11.5	−2032.277	−1261.195
		11.5↔10.5	−1864.625	−1157.621
		10.5↔9.5	−1698.237	−1054.717
		9.5↔8.5	−1533.006	−952.426
$^7L_{10}$	13 101.411	13.5↔12.5	−2116.251	−1313.462
		12.5↔11.5	−1955.246	−1213.925
		11.5↔10.5	−1795.217	−1114.905
		10.5↔9.5	−1636.093	−1016.362
$^7L_{11}$	14 304.110	14.5↔13.5	−2201.876	−1366.841
		13.5↔12.5	−2046.806	−1270.878
		12.5↔11.5		−1175.278
		11.5↔10.5		
		10.5↔9.5		−985.064
		9.5↔8.5	−1432.916	
		8.5↔7.5	−1280.781	
$^7K_4$	9814.683	7.5↔6.5	−307.914	−196.939
		6.5↔5.5	−291.773	−183.812
		5.5↔4.5	−264.956	−165.055
		4.5↔3.5	−229.099	−141.538

2. The uncertainty in each measurement is ±2 kHz. The negative sign (which indicates that the level with larger F lies lower) for each interval follows from analysis of the optical hfs pattern; the rf-measurement procedure is insensitive to the level ordering. Table II lists the magnetic-dipole hfs constant A and electric-quadrupole constant B determined for each state by fitting the standard two-parameter first-order hfs theory [5, 7] to the observed hfs intervals. The statistical uncertainty in each A value is less than 1 kHz and in each B value less than 10 kHz. The hfs constants in Table II have not been corrected for any second-order hfs effects [7], however. This would be difficult to do with precision because of the complexity of the structure.

In attempting to understand the J dependence of the hfs constants in the ^7L term we first note that the purity of the ^7L states is reported as varying from 93% to 100%. While such small departures from the LS limit may appear unimportant, experience has shown that they can lead to significant distortions of the hfs constants. Although one would like to take the admixtures due to intermediate coupling into account explicitly, the fact that the ^7L states are built up from three open shells (one of which is $4f^4$) makes this unfeasible at present. We can reduce the effects of such distortions on the analysis to a large extent by concentrating on the states reported to be closest to the LS limit. The four purest states, with their purities, are [1] $^7L_{11}$ (100%), $^7L_5$ (99%), $^7L_{10}$ (97%), and $^7K_4$ (98%).

LS-limit expressions have been given [6] for the hfs constants of atomic states built from three open electron shells. Before we can apply these expressions to the Nd levels $|4f^4(^5I)5d6s(^3D)^{2S+1}L_J\rangle$ we must interchange the ordering of the $4f^4$ and the $5d6s$ parts to be consistent with the published expressions, writing the state as

$$|5d6s(^3D)4f^4(^5I)^{2S+1}L_J\rangle ,$$

where $S=3$, and $L=8$ for the ^7L states and $L=7$ for the ^7K state. Since we are concerned only with diagonal matrix elements, phase changes that might arise from the interchange can have no effect on the present analysis. (Clearly, we are assuming no configuration interaction as well as no intermediate coupling.) On applying the published expression for the A value of such a state we obtain for the ^7L states

$$A(^7L_J)=[J(J+1)(2J+1)]^{-1/2}\left\{(-1)^J(2J+1)\begin{Bmatrix}J&J&1\\8&8&3\end{Bmatrix}3\sqrt{17/2}(a^{01}_{5d}+3a^{01}_{4f})\right.$$
$$+(-1)^J(2J+1)\begin{Bmatrix}J&J&1\\3&3&8\end{Bmatrix}\sqrt{7/3}(a^{10}_{6s}+a^{10}_{5d}+4a^{10}_{4f})$$
$$\left.+(2J+1)\begin{Bmatrix}3&3&1\\8&8&2\\J&J&1\end{Bmatrix}\sqrt{969/7}(a^{12}_{5d}-\tfrac{7}{15}a^{12}_{4f})\right\} ,$$

where the quantities a are the standard single-electron radial integrals of the theory [5,7]. In the nonrelativistic limit we may assume [7] $a^{12}=a^{01}$ for both the $4f$ and $5d$ shells separately. If we write

$$A^{10}=a^{10}_{6s}+a^{10}_{5d}+4a^{10}_{4f} ,$$

we note that in the same limit $A^{10}=a_{6s}$. We can thus express the expected LS-limit A value for each state as a linear combination of the parameters a_{6s}, a_{5d}, and a_{4f}. The procedure also leads to an expression for $A(^7K_4)$. The corresponding expressions for the electric-quadrupole constants B are (again, in the nonrelativistic limit) linear in the standard hfs parameters b_{5d} and b_{4f}.

When we make a least-squares fit of the three-parameter theoretical expressions [5, 7] to the measured ^{143}Nd A values (for the four purest states, as discussed

TABLE II. Hfs constants A and B deduced from the hfs intervals listed in Table I. The uncertainty in each A value is less than 1 kHz and in each B value less than 10 kHz.

	hfs constants (MHz)			
State	$A(^{143}\text{Nd})$	$B(^{143}\text{Nd})$	$A(^{145}\text{Nd})$	$B(^{145}\text{Nd})$
$^7L_5$	−55.216	−36.285	−34.482	−19.152
$^7L_6$	−152.684	−38.931	−94.901	−20.480
$^7L_7$	−168.496	−40.847	−104.682	−21.541
$^7L_8$	−167.080	−41.323	−103.784	−21.795
$^7L_9$	−161.645	−39.370	−100.401	−20.781
$^7L_{10}$	−156.014	−34.764	−96.900	−18.366
$^7L_{11}$	−151.318	−27.494	−93.982	−14.533
$^7K_4$	−46.805	107.319	−29.289	56.561

above), we find the fit is to the order of 4% (the rms residual is 3.8 MHz), and the single-electron radial integrals take the values

$$a_{5d} = -61.5 \text{ MHz} ,$$

$$a_{4f} = -140.7 \text{ MHz} ,$$

$$a_{6s} = -1504 \text{ MHz} .$$

The corresponding fit for the ^{143}Nd B values has rms residual of 5.5 MHz, and gives the parameter values

$$b_{5d} = -302 \text{ MHz} ,$$

$$b_{4f} = -512 \text{ MHz} .$$

The value found for a_{4f} is virtually identical to the -140.6 MHz found [3] earlier from studies of the hfs of the $4f^4 6s^2\,{}^5I$ levels in the ground term of ^{143,145}Nd, while the present b_{4f} value is about 8% smaller than the earlier ground term value. The ratio a_{4f}/a_{5d} is found to be 2.3, and the ratio b_{4f}/b_{5d} is 1.7. Since both of these should (nonrelativistically) be equal to $\langle r^{-3}\rangle_{4f}/\langle r^{-3}\rangle_{5d}$, the difference between the two can be taken to indicate the level of validity of the assumptions and approximations mentioned above. If the experimental data set to be fitted by the theory is expanded to include all of the ^7L and ^7K states studied (rather than just the four purest ones), the parameter values for the $5d$ and $4f$ electron shells are severely distorted and take on unphysical values.

The values found for the single-electron parameters can also be compared with those deduced from hfs studies of similar electron configurations in neighboring rare-earth-element atoms. Dipole constants a_{nl} must first be divided by the nuclear g factor $g_I = \mu_I/I$, and quadrupole constants b_{nl} by the nuclear quadrupole moment Q to eliminate dependence on specifically nuclear effects. The procedure can only give meaningful results for the dipole case, through, because of uncertainties arising from Sternheimer [8] shielding effects. When this is done, the ^{143}Nd results rae found to lie relatively smoothly between those for lighter and heavier rare-earth elements studied [9] earlier; the procedure is of course not expected to be precise.

The isotopic ratio of the electric-quadrupole B values $B(^{143}\text{Nd})/B(^{145}\text{Nd})$ should be equal to the ratio of the electric-quadrupole moments $Q(^{143}\text{Nd})/Q(^{145}\text{Nd})$, and therefore independent of the atomic state in which it is measured. For the seven states in which measurements were made, the ratio of the B values was (a) extremely constant, namely 1.896 ± 0.005, and (b) virtually identical to the value 1.897 found earlier [3] in studies of the $4f^4 6s^2\,{}^5I$ ground term of Nd I. The excellent agreement of the isotopic quadrupole hfs ratio with the ground-term value and the lack of any J dependence both suggest that any second-order hfs effects (which have been omitted from the treatment) are rather small. The corresponding dipole ratio, $A(^{143}\text{Nd})/A(^{145}\text{Nd})$, is found to have a slight J dependence as observed recently [6, 10] in several other rare-earth-element multiplets, and is indicative of a J-dependent hyperfine anomaly.

IV. CONCLUSIONS

In summary, the zero-field hyperfine intervals in eight $4f^4 5d6s\,{}^7L$ and ^7K metastable levels in ^{143,145}Nd I have been measured precisely, and the corresponding values of the magnetic-dipole and electric-quadrupole hfs constants A and B determined by least-squares fits of the first-order theory to the observations. Values of the single-electron radial hfs integrals were then determined by comparing the deduced A and B values with those expected from the semiempirical theory. The results are consistent with earlier hfs studies in the ground term of Nd I, but we extend them to more complex, highly excited levels. The new results are also qualitatively consistent with expected hfs behavior based on extrapolations to both lighter and heavier rare-earth-element atoms. The observed isotopic hfs ratios $A(^{143}\text{Nd})/A(^{145}\text{Nd})$ and $B(^{143}\text{Nd})/B(^{145}\text{Nd})$ suggest that second-order hfs effects and any hyperfine anomaly are relatively small.

The unusually large orbital angular momentum in the states studied ($L = 7$ and 8) does not appear to lead to any anomalous results. It is unfortunate that the very complex $4f^4 5d6s$ three-open-shell nature of the states studied makes *ab initio* hfs calculations unfeasible [4] at present; it is hoped that such calculations may become possible within a few years.

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[1] The energy-level structure of Nd I is summarized in *Atomic Energy Levles, the Rare Earth Elements,* Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 60, edited by W. C. Martin, R.Zalubas, and L. Hagen (U.S. GPO, Washington, DC, 1978).

[2] I. J. Spalding, Proc. Phys. Soc. London **81**, 156 (1963).

[3] W. J. Childs and L. S. Goodman, Phys. Rev. A **6**, 1772 (1972).

[4] U. Nielsen (private communication).

[5] P. G. H. Sandars and J. Beck, Proc. R. Soc. London Ser. A **289**, 97 (1965).

[6] W. J. Childs, Phys. Rev. A **39**, 4956 (1989).

[7] See, for example, W. J. Childs, Case Stud. At. Phys. **3**, 215 (1973).

[8] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966); **164**, 10 (1967).

[9] The earlier results are summarized in a review paper by V. Pfeufer, Z. Phys. D **4**, 351 (1987).

[10] W. J. Childs, Phys. Rev. A (to be published).