formulas coincide in term up to the first order in \hbar . Formulas (17a) and (17b) are once again used in this identification.

The spectral moments of the isotropic R and of the vibrational-rotational anisotropic R spectra are similar in many respects, to the corresponding ir spectra. It must be stressed, however, that the vibrational moments extracted from these three sorts of spectra are not necessarily identical. This only happens if M, α , β , and $V_S(r, t)$ are

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PHYSICAL REVIEW A

statistically independent. If they are not, definite although probably small differences exist.

A last comment may be of interest. Stochastic theories are often useful in describing irreversible processes, but they generally need justification in terms of intrinsically more complete thermodynamic theories.¹¹ It is therefore satisfactory that the spectral moments, when available, are found to be basically equivalent in the two theories under study.

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Reanalysis of the Hyperfine Structure of the $4f^{6}6s^{27}F$ Multiplet in 147,149 Sm, Including Measurements for the 7F_6 State*

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The hyperfine structure (hfs) of the J=6 member of the $4f^{6}6s^{27}F$ ground multiplet of 147,149 Sm has been measured by the atomic-beam magnetic-resonance technique, and that of the J=1-5 states has been remeasured. The magnetic-dipole and electric-quadrupole hyperfineinteraction constants obtained, after correction for second-order hfs, are found to be consistent to a very high order with the three-parameter formulation of the Sandars-Beck effectiveoperator theory of hfs and with the Conway-Wybourne eigenvectors for the J=1-6 ⁷F states of Sm. The earlier apparent failure of these eigenvectors to be consistent with the magnetic dipole hfs of the 7F states with J=1-5 is now resolved.

I. INTRODUCTION

The hyperfine structure (hfs) of the $4f^66s^{27}F$ ground term of the samarium atom has been investigated in detail by Woodgate¹ and by Robertson, Waddington, and Summers-Gill² with the atomicbeam magnetic resonance technique. The multiplet comprises seven states with J values of 0, 1,..., 6. The ${}^{7}F_{0}$ level lies lowest and is the atomic ground state; the excitation energy of the others increases with J, and the highest level (J=6) lies at 4021 cm⁻¹.³

Because samarium is relatively volatile,⁴ the highest usable temperature for an atomic beam from a normal oven is low, only about 850 °C. At this temperature, the Boltzmann factors for the states with J=4, 5, and 6 are extremely small, and the very small population of individual magnetic sublevels of these states makes observation

of transitions between them very difficult. In 1961, Pichanick and Woodgate⁵ measured the electron g factor g_J for all six $J \neq 0$ states by observing transitions in the abundant even-even isotopes (which have no hfs), and in 1966 Woodgate¹ was able to measure the hfs of ^{147,149}Sm in the states with J=1, 2, 3, and 4. Robertson *et al.*² in 1968 had sufficient sensitivity to extend the hfs work to the J=5 level but were unable to make the corresponding measurements for the final state, ${}^{7}F_{6}$.

The ^{7}F multiplet of Sm I has been studied theoretically by Judd and $Lindgren^{6}$ and by Conway and Wybourne.⁷ Both studies obtained eigenvectors for each of the states in terms of the appropriate Russell-Saunders basis states. In addition to vielding excellent fits to the known excitation energies, the eigenvectors (particularly the more recent ones of Conway and Wybourne) were remarkably consistent with the g_J values measured

by Woodgate.⁵

The classic 1965 paper of Sandars and Beck⁸ on the effective-operator approach to the relativistic hfs interaction was exploited by Woodgate¹ in his analysis of the hfs of the J=1, 2, 3, and 4 members of the ${}^{7}F_{J}$ multiplet of 147,149 Sm. Although his results were generally in good agreement with the three-parameter formulation of the Sandars-Beck theory and the Conway–Wybourne⁷ samarium eigenvectors, it was clearly desirable to increase the number of states used to five or six in order to determine the parameters and test the wave functions more closely.

When Robertson *et al.*² considered their hfs results for the J=5 state, they reanalyzed Woodgate's results¹ for J=1-4 and used the combined data in their analysis. They found that although the electric-quadrupole hfs constants *B* were well fitted with the Conway–Wybourne⁷ eigenvectors and the three-parameter theory, the magnetic-dipole hfs constants *A* were not. They attributed this to inaccuracies in the eigenvector components and pointed out that the dipole constants could be expected to be more sensitive to admixture than the quadrupole constants.

Preliminary experiments with a two-chamber atomic-beam oven indicated that it should be possible to populate the J=6 state sufficiently to complete the hfs measurements for the ⁷F multiplet. The present experiment was performed with the hope that the additional information thereby obtained would help to clear up some of the problems mentioned. It was felt that this was particularly desirable for the ⁷F multiplet of Sm since it is now widely regarded⁹ as a classic example of atomic hyperfine structure.

II. APPARATUS

The apparatus used for the present experiment is a conventional atomic-beam magnetic resonance machine equipped with an electron-bombardment universal detector; it has been described previously.^{10,11} Although surface ionization detection, as used by Robertson *et al.*,² is probably at least two orders of magnitude more efficient for Sm than the universal detector used here, the overall sensitivity of the present detection system (including the electronic data-handling system) is very high.¹¹ Using a single-chamber cylindrical Ta oven heated to about 850 °C by electron bombardment, it was found that transitions could be easily observed in all six $J \neq 0$ states in the eveneven isotopes but that observation of hfs transitions in the 7F_5 and 7F_6 states of 147,149 Sm was exceedingly difficult.

Except for differences in transition probability, the ease of seeing transitions between magnetic sublevels in a particular state 7F_J is proportional

to the Boltzmann factor for the state. Table I lists the excitation energies and Boltzmann factors for the maximum useful oven temperature of about 850 °C, at which the vapor pressure of samarium is 0.1 Torr. It was apparent from this that the population of the higher states had to be increased before hfs measurements could be made. One approach to this problem was to control the rate of vapor production and the final vapor pressure of atoms leaving the oven system independently by using a two-chamber oven.

The final design used is shown in Fig. 1. The entire assembly is rigidly mounted on a watercooled pneumatically driven piston compatible with the rapid-loading oven system previously described.¹⁰ The Sm metal is placed in a $\frac{1}{4}$ -in.-diam Ta oven held in a $\frac{1}{4}$ -in. -thick Cu block which butts against the water-cooled end of the piston. A hollow Ta tube connects this first oven chamber with a second chamber, a hollow $\frac{3}{8}$ -111. -W cube with a 0.5 mm slit. Two thin Ta heat shields are positioned between the two chambers, and the walls of the connecting tube are thin to minimize heat transfer between the two chambers. Heat is applied by electron bombardment of the W slit area from the extreme right of the figure, and the W slit chamber can be run very much hotter than the 850 °C required for the first chamber. The temperature differential between the two chambers clearly depends in detail on a number of adjustable parameters, and some experimentation was carried out. Calculations indicated that the number of beam atoms in the 7F_6 state could be increased nearly an order of magnitude; experimentally, a real increase was observed, and it made the experiment possible.

III. PROCEDURE

The even-even isotopes ^{152,154}Sm were examined pilmarily as a quick means of checking the extent to which the ${}^{7}F_{6}$ state was being populated; accurate g_{J} values for all six $J \neq 0$ levels had already been obtained by Pichanick and Woodgate.⁵ Figure 2 shows a typical radio-frequency spectrum

TABLE I. Excitation energies ΔE and Boltzmann factors for the $4f^{6}6s^{2}$ ⁷F levels of Sm1 at 850 °C.

Atomic state	Excitation (cm ⁻¹)	$\exp(-\Delta E/kT)$
$\overline{\mathbf{F}_{0}}$	0	1.000
${}^{7}F_{1}$	293	0.686
7F_2	812	0.352
${}^{7}F_{3}$	1490	0.148
7F_A	2273	0.054
${}^{7}F_{5}$	3125	0.018
${}^{7}\boldsymbol{F}_{6}$	4021	0.006

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FIG. 1. Two-chamber oven designed to yield a samarium atomic beam with an enhanced population of the 7F_6 metastable atomic state. Samarium metal is vaporized in the cylindrical lower-temperature chamber, near the center of the figure. The vapor is then raised to a higher temperature in the W chamber at the right, which is heated by electron bombardment. The Cu block is in contact with the end of the water-cooled piston in order to hold down the temperature of the cylindrical oven chamber.

obtained at H = 200 G. The flop-out transitions shown are primarily of the type $(J; M_J = 0 - J; M_J)$ $=\pm 1$; they were obtained with the obstacle wire removed. The intensity of the transitions in the ${}^{7}F_{6}$ state is encouragingly strong. The splitting of the J=1 transition into two components arises from the Paschen-Back effect, which distinguishes between the transitions going to $M_J = +1$ and -1; the splitting was observed to be 58 kHz at 200 G, 240 kHz at 400 G, and about 998 kHz at 800 G. The splitting in the J=2 state, though much smaller, was observed to be about 84 kHz at 800 G. The observations, shown in Table II, are in good agreement with the theory of the Paschen-Back effect, and the g_x values deduced agree well with those found earlier by Pichanick and Woodgate.⁵ An improvement in precision was possible for the 7F_6 state.

Because of the very low intensity expected for hfs transitions in the ${}^{7}F_{6}$ state, it was clearly desirable to make some effort to optimize the datataking procedure. The first step was to observe a $\Delta F = 0$, $\Delta M_{F} = \pm 1$ transition at a very small field such as 2 G, for which any particular $\Delta F = 0$ transition in 147 Sm or 149 Sm would be at the same accurately predictable rf frequency; the mass resolution of the detector system was intentionally reduced for this measurement. The success of this run indicated that hfs transitions in the ${}^{7}F_{6}$ state could be observed.

With the equations given in Tables IV (a) and IV (b) of Robertson *et al.*² (which are based on the three-parameter Sandars-Beck theory⁸ and the Conway-Wybourne⁷ eigenvectors), it was possible to calculate both A and B for ^{147,149}Sm ⁷F₆ to within about



FIG. 2. Flop-out transitions of the type $(J; M_J = 0 \rightarrow J; M_J = \pm 1)$ in ^{152,154}Sm at 200 G. The population of the ⁷F₆ state relative to those of the lower states is enhanced by the two-chamber oven. Paschen-Back splitting of the J=1 transition is evident.

2%. With these numbers and the accurately known g_J value, it was then straightforward¹² to predict the resonance frequencies for all transitions of interest in the 7F_6 state of 147,149 Sm as a function of field. Because of the associated uncertainties, prediction of $\Delta F = \pm 1$ transition frequencies at all fields and of $\Delta F = 0$ transition frequencies at fields higher than about 50 G were characterized by unacceptably large uncertainties. Intense efforts at 50 G finally revealed three $\Delta F = 0$ transitions near the predicted frequencies for 147 Sm. A subsequent observation of an $F = \frac{19}{2}$ transition at 100 G then allowed the computer optimization program to calculate A and B for the 7F_6 state of 147 Sm with sufficiently small uncertainties that the resonance

TABLE II. Transitions observed in 152,154 Sm at 200 and 400 G. The appearance of the transitions listed for 200 G is shown in Fig. 2.

Atomic state	Transition $(J, M_J \rightarrow J, M'_J)$	Н (G)	Observed resonance frequency (MHz)
" <i>F</i> 1	$(1, 0 \rightarrow 1, 1)$	200	419.427(10)
- 1	,, _, _,	400	838,760(10)
	$(1, 0 \rightarrow 1, -1)$	200	419.487(10)
		400	839.020(10)
${}^{7}F_{2}$	$(2, 0 \rightarrow 2, \pm 1)$	200	419.292(10)
-		400	838.542(10)
${}^{7}F_{3}$	$(3, 0 \rightarrow 3, \pm 1)$	200	419.092(10)
Ū		400	838.132(15)
7F_4	$(4, 0 \rightarrow 4, \pm 1)$	200	418.862(10)
•		400	837.683(15)
${}^{7}F_{5}$	$(5, 0 \rightarrow 5, \pm 1)$	200	418.603(10)
Ū		400	837.163(15)
${}^{7}\boldsymbol{F}_{6}$	$(6, 0 \rightarrow 6, \pm 1)$	200	418.280(13)
Ŷ		400	836.528(15)

frequencies for the $\Delta F = \pm 1$ transitions could be closely predicted at small field. Six of these transitions were ultimately observed at 1 G in both ¹⁴⁷Sm and ¹⁴⁹Sm, although the signal-to-noise ratio was never good. One run through the $F = \frac{15}{2}$, M_F $= \frac{5}{2} \longrightarrow F = \frac{17}{2}$, $M_F = \frac{3}{2}$ transition in the 7F_6 state of ¹⁴⁷Sm is shown in Fig. 3. The value of g_J found by the computer fit to all the data for the 7F_6 state of ¹⁴⁷Sm is in good agreement with that measured for the even-even isotopes.

For the sake of consistency, most of the $\Delta F = \pm 1$ intervals were measured for the states ${}^7F_{1,2,3,4,5}$ in 147,149 Sm in addition. Relative to the previous work, 1,2 these results allowed some refinement of the extracted hfs information for the 7F_4 and 7F_5 levels. No attempt was made to compete with Woodgate's¹ more precise results for the ${}^7F_{1,2,3}$ states. The present experimental results for the ${}^7F_{1,2,3,4,5}$ levels, shown in Table III for 147 Sm and Table IV for 149 Sm, are consistent with the earlier results. 1,2 The residuals, given in the right-hand column of each table, include corrections for offdiagonal hyperfine and Zeeman interactions between 7F states of different J, as discussed in Sec. IV C.

IV. ANALYSIS AND RESULTS

A. Introduction

The hyperfine and Zeeman Hamiltonians have been given many times for a free atom, and their properties and diagonalization have been extensively discussed.¹² Computer programs based on these Hamiltonians routinely vary the appropriate parameters (typically the magnetic-dipole, elec-



FIG. 3. Appearance of a $\Delta F = 1$ transition in the ${}^{7}F_{6}$ state of 147 Sm at 1 G. It was not possible to achieve a good signal-to-noise ratio, but such transitions were reproducible.

TABLE III. Observations in ¹⁴⁷Sm. The residuals in the right-hand column include corrections for secondorder hfs. That all residuals are zero for J=1, 2, and 3 is due to the fact that the number of parameters (hfs constants) varied is equal to the number of observations. For J=4, 5, and 6, the number of observations exceeds the number of parameters (hfs constants) varied.

Atomic state	Transition $(F, M \leftrightarrow F', M')$	Н (G)	Observed resonance frequency (MHz)	$\nu^{obs} - \nu^{calc}$ (kHz)
⁷ <i>F</i> ₁	$(\frac{7}{2}, \frac{7}{2} \leftrightarrow \frac{9}{2}, \frac{5}{2})$	1	206.706(5)	0
	$\left(\frac{5}{2}, \frac{3}{2} \leftrightarrow \frac{7}{2}, \frac{5}{2}\right)$	1	42.633(8)	0
⁷ F ₂	$(\frac{7}{2}, \frac{5}{2} \leftrightarrow \frac{9}{2}, \frac{3}{2})$	1	182.063(6)	0
	$(\frac{9}{2}, \frac{7}{2} \leftrightarrow \frac{11}{2}, \frac{5}{2})$	1	263.542(3)	0
${}^{7}F_{3}$	$(\frac{7}{2}, \frac{3}{2} \leftrightarrow \frac{9}{2}, \frac{1}{2})$	1	221,792(6)	0
	$(\frac{9}{2}, \frac{5}{2} \leftrightarrow \frac{11}{2}, \frac{3}{2})$	1	279.801(7)	0
	$(\frac{11}{2}, \frac{7}{2} \leftrightarrow \frac{13}{2}, \frac{5}{2})$	1	343.097(5)	0
${}^{7}F_{4}$	$(\frac{7}{2}, \frac{1}{2} \leftrightarrow \frac{9}{2}, -\frac{1}{2})$	1	273.612(8)	0
	$(\frac{9}{2}, \frac{3}{2} \leftrightarrow \frac{11}{2}, \frac{1}{2})$	1	331,138(7)	0
	$(\frac{11}{2}, \frac{5}{2} \leftrightarrow \frac{13}{2}, \frac{3}{2})$	1	386.862(6)	0
	$(\frac{13}{2}, \frac{7}{2} \rightarrow \frac{15}{2}, \frac{5}{2})$	1	440.478(6)	0
${}^7\boldsymbol{F}_5$	$(\frac{7}{2}, -\frac{1}{2} \leftrightarrow \frac{9}{2}, -\frac{3}{2})$	1	330.548(10)	-1
	$(\frac{9}{2}, \frac{1}{2} \leftrightarrow \frac{11}{2}, -\frac{1}{2})$	1	394.976(7)	0
	$(\frac{11}{2}, \frac{3}{2} \leftrightarrow \frac{13}{2}, \frac{1}{2})$	1	454.017(8)	1
	$(\frac{13}{2}, \frac{5}{2} \leftrightarrow \frac{15}{2}, \frac{3}{2})$	1	506.807(8)	-1
	$(\frac{15}{2}, \frac{7}{2} \leftrightarrow \frac{17}{2}, \frac{5}{2})$	1	552.425(5)	0
${}^{7}F_{6}$	$(\frac{7}{2},-\frac{3}{2}\leftrightarrow\frac{9}{2},-\frac{5}{2})$	1	390.485(10)	4
	$(\frac{9}{2}, -\frac{1}{2} \leftrightarrow \frac{11}{2}, -\frac{3}{2})$	1	465.305(16)	-10
	$(\frac{11}{2}, \frac{1}{2} \leftrightarrow \frac{13}{2}, -\frac{1}{2})$	1	532.525(20)	6
	$(\frac{13}{2}, \frac{3}{2} \leftrightarrow \frac{15}{2}, \frac{1}{2})$	1	591.026(10)	-7
	$(\frac{15}{2}, \frac{5}{2} \leftrightarrow \frac{17}{2}, \frac{3}{2})$	1	639,616(7)	6
	$(\frac{17}{2}, \frac{7}{2} \rightarrow \frac{19}{2}, \frac{5}{2})$	1	676.952(10)	-2
	$(\frac{11}{2}, \frac{1}{2} \leftrightarrow \frac{11}{2}, -\frac{3}{2})$	50	182.649(20) ^a	19
	$(\frac{9}{2}, -\frac{1}{2} \leftrightarrow \frac{9}{2}, -\frac{5}{2})$	50	210.650(10) ^a	- 6
	$(\frac{17}{2}, \frac{7}{2} \leftrightarrow \frac{17}{2}, \frac{3}{2})$	50	141,890(30) ^a	4
	$(\frac{19}{2}, \frac{9}{2} \leftrightarrow \frac{19}{2}, \frac{5}{2})$	100	276.816(20) ^a	44

^aThe values at H = 50 and 100 G are $\Delta E/h = 2\nu^{obs}$.

tric-quadrupole, and magnetic-octupole hfs constants A, B, and C, respectively, and the electron g factor g_J) to obtain a least-squares fit to the observed resonance frequencies. The nuclear spins and dipole moments are known^{1,13} for ^{147,149}Sm. The fits are typically of high quality, and close limits can thereby be set on the parameters varied. The problem that remains is to understand these and other observable properties of the atomic states in terms of (a) a consistent set of eigenvectors and (b) modern self-consistent calculations of the relevant radial expectation values.

B. g_J Values and Eigenvectors

The present values of g_J were deduced from observations in ^{152,154}Sm, as discussed in Sec. III.

TABLE IV. Observations in ¹⁴⁹Sm. The residuals in the right-hand column include corrections for secondorder hfs. The residuals given for J=2 and 3 are zero because the number of parameters (hfs constants) varied is equal to the number of observations. For J=1,4,5, and 6, the number of observations exceeds the number of parameters (hfs constants) varied.

Atomic state		$\rightarrow F'M'$)	Н ((G)	Observed resonance frequency (MHz)	$\nu^{obs} - \nu^{calc}$ (kHz)
⁷ <i>F</i> ₁	$(\frac{7}{2}, \frac{7}{2})$	$\rightarrow \frac{9}{2}$,	<u>5</u>)	1	107.262(5)	- 3
	$(\frac{5}{2}, \frac{3}{2})$	$\frac{1}{2}$,	<u>5</u>)	1	116.578(5)	4
	$(\frac{7}{2}, \frac{7}{2})$	$\rightarrow \frac{9}{2}$,	<u>5</u>)	9.995	103.070(4)	2
	$(\frac{5}{2}, \frac{3}{2})$	$\frac{1}{2}$,	<u>5</u>)	9.995	107.234(4)	0
	$(\frac{5}{2}, \frac{3}{2})$	$\frac{1}{2}$,	52) 2	9.995	107.229(6)	- 5
${}^{7}F_{2}$	$(\frac{7}{2}, \frac{5}{2})$	$\rightarrow \frac{9}{2}$,	3 <u>2</u>)	1	153.808(6)	0
	$(\frac{9}{2}, \frac{7}{2})$	$\rightarrow \frac{11}{2}$,	<u>5</u>)	1	176.483(3)	0
${}^{7}F_{3}$	$(\frac{7}{2}, \frac{3}{2})$	$\leftrightarrow \frac{9}{2}$,	$\frac{1}{2}$)	1	188.596(7)	0
	$(\frac{9}{2}, \frac{5}{2})$	$\frac{11}{2}$,	<u>3</u> 2)	1	227.857(5)	0
	$(\frac{11}{2}, \frac{7}{2})$	$\rightarrow \frac{13}{2}$,	5 2)	1	265.576(6)	0
${}^{7}F_{4}$	$(\frac{7}{2}, \frac{1}{2})$	<u>→ ⅔</u> , –	$\frac{1}{2}$)	1	221.718(9)	2
	$(\frac{9}{2}, \frac{3}{2})$	$\rightarrow \frac{11}{2}$,	<u>1</u>)	1	271.538(9)	-5
	$(\frac{11}{2}, \frac{5}{2})$	$\leftrightarrow \frac{13}{2}$,	<u>공</u>)	1	321.875(5)	2
	$(\frac{13}{2}, \frac{7}{2})$	$\rightarrow \frac{15}{2}$,	5 <u>2</u>)	1	372.828(6)	0
${}^{7}F_{5}$	$(\frac{7}{2}, -\frac{1}{2})$	$\rightarrow \frac{9}{2}, -$	<u>3</u>)	1	252.765(10)	5
	$(\frac{9}{2}, \frac{1}{2})$	<u>11</u> , -	1 <u>2</u>)	1	311.209(10)	- 5
	$(\frac{11}{2}, \frac{3}{2})$	$\rightarrow \frac{13}{2}$,	1 <u>2</u>)	1	371,071(7)	-4
	$(\frac{13}{2}, \frac{5}{2})$	$\leftrightarrow \frac{15}{2}$,	3)	1	432,721(7)	5
	$(\frac{15}{2}, \frac{7}{2})$	$\rightarrow \frac{17}{2}$,	<u>5</u>)	1	496.446(8)	-2
${}^{7}\boldsymbol{F}_{6}$	$(\frac{7}{2}, -\frac{3}{2})$	$\leftrightarrow \frac{9}{2}, -$	5 <u>2</u>)	1	281.312(10)	-1
	$(\frac{9}{2}, -\frac{1}{2})$	$\rightarrow \frac{11}{2}, -$	3) 2)	1	347.487(10)	0
	$(\frac{11}{2}, \frac{1}{2})$	↔ <u>13</u> , -	1 <u>2</u>)	1	415.398(20)	4
	$(\frac{13}{2}, \frac{3}{2})$	$\leftrightarrow \frac{15}{2}$,	<u>1</u>)	1	485.680(20)	2
	$(\frac{15}{2}, \frac{5}{2})$	$\rightarrow \frac{17}{2}$,	3 <u>2</u>)	1	558.798(8)	-2
	$(\frac{17}{2}, \frac{7}{2})$	$\leftrightarrow \frac{19}{2}$,	5 2)	1	635.168(10)	1

The results, given in the third column of Table V, are seen to be in excellent agreement with the earlier results (column 2) of Pichanick and Woodgate.⁵ The weighted average of the two determinations (column 4) will be referred to as the experimental values.

Calculation of theoretical g_J values requires detailed specification of the states, usually by giving an eigenvector or listing of the amplitudes and phases of the various Russell-Saunders basis states included in the superposition for each real state of the atom. The most successful such set for Sm was published by Conway and Wybourne⁷ in 1963, although the eigenvectors given therein unfortunately contain a number of typographical errors. These errors have been corrected in the eigenvector sets listed by Woodgate¹ (J=1-4), Robertson *et al.*² (J=5,6), and Armstrong⁹ (J=1-5); these three tabulations are consistent where they overlap and will be referred to as the Conway-Wy-bourne eigenvectors. That the set is consistent with Pichanick and Woodgate's⁵ g_J values to a very high order was shown in Conway and Wybourne's⁷ publication.

Because of the difficulties Robertson *et al.*² had in understanding the hfs of the ${}^{7}F_{1,2,3,4,5}$ states of 147 Sm with this eigenvector set, the authors asked for and obtained from Conway¹⁴ a new set of Sm I eigenvectors; they will be called the Conway eigenvectors. The new set was intended to reproduce the computer printout of the original set (now lost), but has been found to be (a) slightly different in some details and (b) slightly superior in fitting the hfs. The differences are due to slight differences in the electrostatic and spin-orbit integrals used.

Although each of the new Conway eigenvectors is normalized to a nominal 100.00%, the round-off error is not negligible compared to the uncertainties in the experimental values of g_{J} . Because all six $J \neq 0$ ⁷*F* states are so close to the *LS* limit, this is of importance only for the principal $({}^{7}F)$ component. If the eigenvectors are normalized exactly to unity, and if the relativistic and diamagnetic corrections calculated by Judd and Lindgren⁶ are then applied, the calculated g_J values listed in Table V are obtained. That they are consistent with experiment for every value of J is indeed remarkable, and would seem to justify still greater experimental precision. The larger components of these new eigenvectors are given in Table VI as received from Conway¹⁴; no renormalization has been applied. It is seen that inclusion of these 17 basis terms retains at least 99.97% of each state for ${}^7F_{0,1,2,3,4,5,6}$.

C. Hyperfine-Interaction Constants

Least-squares computer fits of the hfs and Zeeman Hamiltonians to the observed hfs transition frequencies in 147,149 Sm were described in Sec. IV A. The values found for the hfs interaction constants A, B, and C for 147 Sm and 149 Sm from these fits

TABLE V. Summary of g_J values. The agreement between theory and experiment is to within experimental error for every J.

		Experime	ntal value of	g j	
J	Pichanick and Woodgate	Present	Weighted average	Calculated g _J	$g_J^{obs} - g_J^{calc}$
1	1.49840(5)	1.49838(3)	1.49839(3)	1.49838	0.00001(3)
2	1.49779(3)	1.49778(5)	1.49779(3)	1.49779	0.00000(3)
3	1.49707(3)	1.497 06(5)	1.49707(3)	1,49707	0,00000(3)
4	1.49625(4)	1.49625(4)	1.49625(3)	1.49628	-0.00003(3)
5	1.49533(6)	1.49532(5)	1.49532(4)	1.49533	-0.00001(4)
6	1.49419(10)	1.49417(4)	1.49417(4)	1,49414	0.00003(4)

are listed in the "Present results—uncorrected" column in Tables VII and VIII, respectively. Since J=1 for the ${}^{7}F_{1}$ state, C must be exactly zero. For the ${}^{7}F_{2}$ state, only two $\Delta F=1$ hfs intervals were measured, and the three hfs constants A, B, and C could not be uniquely determined. The octupole constant C is always very nearly zero, however, and A and B were determined by requiring C=0 for the fit. Observation of three or more $\Delta F=1$ intervals for each of the remaining states ${}^{7}F_{3,4,5,6}$ permitted evaluation of all three constants, although the values found for C are all consistent with zero.

It is well known, however, that both the hyperfine and Zeeman Hamiltonians can connect ${}^{7}F$ states of different J and that this perturbs the observed resonance frequencies for transitions. Corrections for these second-order (off-diagonal) perturbations were applied to the calculated transition frequencies (obtained in the usual way¹² with J assumed to be a good quantum number) before the latter were compared with experiment. As discussed by Childs, ¹² each magnetic sublevel $E(\mathfrak{F}, M)$ of the state Ψ at field H is perturbed by the amount

 $\delta E(\Psi, I\mathcal{F}M)$

$$= \sum_{\Psi' \neq \Psi} \sum_{F'} \frac{|\langle \Psi, I \mathcal{F} M | \mathcal{K}_{hfs} + \mathcal{K}_{a}^{e1} | \Psi', IF' M \rangle|^{2}}{E(\Psi) - E(\Psi')} , \quad (1)$$

where \mathfrak{F}, M is the particular linear combination of zero-field sublevels F, M required at the field H. For the present case, the states Ψ' are other members of the ⁷F term so that this sum runs over J. The nuclear spin I is $\frac{7}{2}$ for ^{147,149}Sm, ¹³ \mathscr{K}_{hfs} is the sum of the magnetic-dipole and electric-quadrupole hfs Hamiltonians, and \mathscr{K}_{z}^{e1} is the electronic part of the Zeeman operator. ¹² These corrections were smaller than the experimental uncertainties for all states except ⁷F_{1,2}. The present technique for calculating the second-order corrections takes explicit account of the departure of the states from the LS limit by using the Conway–Wybourne⁷ eigenvectors for Ψ and Ψ' in Eq. (1). Though different in detail, it is entirely equivalent to the procedure used by Woodgate¹ and by Robertson *et al.*²

After all the calculated transition frequencies have been corrected for the second-order perturbations, new least-squares fits to the observed resonance frequencies are made. The resulting "final" values of the hfs constants are listed in column 4 of Tables VII and VIII, where they may be compared with the corrected results of Woodgate¹ (column 6) and of Robertson *et al.*² (column 5). It should be noted that the results given by Woodgate¹ and by Robertson *et al.*² for the states with J=1-4 are based on the same data (that of Woodgate¹) but the second-order corrections were made slightly differently. Robertson *et al.*² felt that their corrections were more realistic than those previously applied by Woodgate.¹

It is seen in Tables VII and VIII that the present results are in good agreement with the earlier values. Though of less precision for J=1, 2, and 3, they are of higher precision for J=4 and 5 and are the only data for J=6.

TABLE VI. The new eigenvector set of Conway, after truncation to the 17 terms listed. They have not been renormalized. The subscripts in column 1 follow the convention of Nielson and Koster.^a

			Eige	nvector compone	ent $\alpha_i(J)$		
Term	J = 0	J = 1	J = 2	J = 3	J = 4	J = 5	J = 6
^{7}F	0,9710	0.9764	0,9832	0.9884	0.9904	0.9889	0.9837
${}^{5}D_{1}$	-0.1736	-0.1578	-0.1308	-0.0967	-0.0575	0	0
${}^{5}D_{3}$	0.1584	0.1408	0.1117	0.0771	0.0418	0	0
${}^{5}F_{2}$	0	0.0257	0.0447	0,0615	0.0723	0.0694	0
${}^{5}G_{1}$	0	0	0,0150	0.0332	0.0568	0.0853	0.1178
${}^{5}G_{2}$	0	0	-0.0049	-0.0115	-0.0222	-0.0393	-0.0659
${}^{5}G_{3}$	0	0	-0.0139	-0.0310	-0.0535	-0.0816	-0.1159
${}^{3}P_{1}$	-0.0216	-0.0153	-0.0077	0	0	0	0
${}^{3}P_{3}$	0.0237	0.0158	0.0067	0	0	0	0
${}^{3}P_{6}$	0.0290	0.0201	0.0097	0	0	0	0
${}^{5}D_{2}$	0.0021	0.0055	0.0102	0.0134	0.0120	0	0
${}^{5}F_{1}$	0	0.0159	0.0274	0.0370	0.0420	0.0378	0
$5p^{-1}$	0	-0.0026	-0.0040	-0.0037	0	0	0
${}^{5}H_{1}$	0	0	0	0.0014	0.0034	0.0063	0.0092
${}^{5}I_{2}$	0	0	0	0	-0.0004	-0.0010	-0.0015
${}^{5}H_{2}$	0	0	0	0.0022	0.0051	0.0083	0.0102
${}^{3}H_{3}$	0	0	0	0	0.0017	0.0051	0.0124
$\sum_{i} (\alpha_{i})^{2}$	0.99994	0.99992	0.99978	0.99978	0.99970	0.99978	0.99966

^aC. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations (MIT Press, Cambridge, Mass., 1963).

6

2017

		¹⁴⁷ Sm hyp	¹⁴⁷ Sm hyperfine-interaction constants (MHz)				
Atomic	hfs	Present		Robertson			
state	constant	Uncorrected	Final	et al.	Woodgate		
⁷ <i>F</i> ₁	A	-33.497(2)	-33.493(2)	- 33. 4932(1)	- 33, 4936(1)		
-	В	- 58, 756 (6)	- 58.688(6)	-58.6848(8)	- 58. 6920(8)		
${}^{7}F_{2}$	A	-41.188(2)	-41.186(2)	-41.1839(7)	- 41.1845(2)		
4	В	-62.258(13)	-62.229(13)	-62.218(6)	-62.226(3)		
${}^{7}F_{3}$	A	-50.244(2)	- 50, 243(2)	- 50, 2396(4)	- 50, 2401(1)		
5	В	-33.692(40)	-33.668(40)	-33.678(4)	-33.681(2)		
	С	-0.001(3)	-0.002(3)				
${}^{7}F_{4}$	A	- 59.708(1)	-59.707(1)	- 59. 707(2)	- 59.707(2)		
*	В	21.221(36)	21.241(36)	21.234(72)	21.230(72)		
	С	0.000(3)	0,000(3)				
${}^{7}F_{5}$	A	-69.136(1)	-69.136(1)	-69.1354(13)			
U U	В	100.590(33)	100,608(33)	100.579(52)			
	С	-0.002(4)	-0.002(4)				
${}^{7}F_{6}$	A	-78.360(1)	-78.360(1)				
v	В	203,409(32)	203.432(32)				
	C	0.002(4)	0.002(4)				

TABLE VII. Hyperfine-structure constants for the ${}^{7}F$ states of ${}^{147}Sm$. The present results are seen to be in good agreement with those of Woodgate (Ref. 1) and Robertson *et al.* (Ref. 2).

D. Ratios of Hyperfine Constants

For a particular atomic state, the ratio of the magnetic-dipole hyperfine interaction constant measured for one isotope to that for another should be the same as the ratio of the nuclear g factors g_I , subject to a small correction for a possible hyperfine anomaly. Any anomaly would arise from

 $s_{1/2}$ and $p_{1/2}$ electrons, however, and the $4f^{N}6s^{2}$ configurations of the neutral rare-earth atoms contain little core polarization^{12,15} so that the anomaly can be expected to be extremely small for Sm. For this reason, the ratios $A^{147}(J)/A^{149}(J)$ should be virtually independent of J and, because the nuclear spins of ¹⁴⁷Sm and ¹⁴⁹Sm are the same $(I=\frac{T}{2})$, should be equal to the ratio of the nuclear

TABLE VIII. hfs constants for the ${}^{7}F$ states of 149 Sm. The present results are seen to be in good agreement with those of Woodgate (Ref. 1) and Robertson *et al.* (Ref. 2).

	¹⁴⁹ Sm hyperfine interaction constants (MHz)							
Atomic	hfs	Present	results	Robertson				
state	constant	Uncorrected	Final	et al.	Woodgate			
⁷ <i>F</i> ₁	A	- 27.613(1)	- 27.610(1)	-27.6107(1)	-27.6109(1)			
1	В	16.916(3)	16.963(3)	16.9668(4)	16,9624(4)			
${}^{7}F_{2}$	A	- 33,953(2)	- 33,952(2)	- 33, 9508(3)	- 33.9508(2)			
2	В	17.963(13)	17.990(13)	17.988(3)	17.987(3)			
${}^{7}F_{3}$	A	-41.419(2)	-41.418(2)	- 41. 4177(4)	-41.4176(4)			
- 3	B	9.727(40)	9.746(40)	9,748(6)	9.749(6)			
	C	-0.001(3)	-0.001(3)					
${}^{7}F_{4}$	A	-49,222(1)	-49.222(1)	- 49.218(3)	-49.218(3)			
4	В	-6.119(38)	-6.102(38)	-6.194(80)	-6.161(80)			
	С	-0.003(3)	-0.003(3)					
${}^{7}F_{5}$	Α	- 56.994(1)	- 56.994(1)	- 56.992(2)				
v	В	- 29.048(34)	- 29.033(34)	- 29.031 (92)				
	С	-0.004(4)	-0.004(4)					
${}^{7}F_{6}$	A	- 64.598(1)	- 64.598(1)					
v	В	- 58.763(30)	- 58,746(30)					
	C	-0.001(4)	-0.001(4)					

dipole moments μ_I of the two isotopes.

The values of this ratio are listed in Table IX, where the present values found from the entries in Tables VII and VIII are compared with the corresponding values found by Woodgate¹ and by Robertson *et al.*² The agreement with the earlier work is good, and the value found is indeed independent of J as expected. The weighted average of the result for all six states gives

$$A^{147}/A^{149} = 1.21305(2) . (2)$$

While this ratio is nominally the same as μ_I^{147}/μ_I^{149} , the uncertainty in the latter ratio must include a contribution due to the possibility of a small hyper-fine anomaly.

Similarly, the ratio $B^{147}(J)/B^{149}(J)$ should be independent of J. The present values found for this ratio are also compared with the earlier results^{1,2} in Table IX. The value found for this ratio agrees well with the earlier results, and is independent of J to within experimental error. The results are illustrated in Fig. 4. The larger uncertainties for J=3 and 4 arise from the difficulty of obtaining small relative uncertainties for the B values of these states. The weighted average

$$B^{147}/B^{149} = -3.4601(6) \tag{3}$$

is nominally the same as the ratio of the nuclear electric-quadrupole moments Q^{147}/Q^{149} . It is unfortunately not possible to obtain an accurate independent ratio of the quadrupole moments themselves.

E. Consistency of Final hfs Constants

Sandars and Beck⁸ have shown how the A and B values for any atomic state arising from a configuration of the type nl^N can be expressed as a linear combination of three radial integrals. While the principal portion of these integrals, including relativistic contributions, can often be calculated in detail, the contributions of configuration interaction cannot and it is therefore sometimes convenient to regard the integrals as adjustable parameters.



FIG. 4. Value of the ratio of the electric-quadrupole hfs constants B of 147 Sm and 149 Sm, as observed for each $J \neq 0$ atomic state of 7F . The final value is indicated by the dashed line.

The parameters are then evaluated from leastsquares fits of the theoretical expressions to the measured hfs constants, and the values found can then be compared with those predicted from the relativistic Hartree-Fock-Slater theory.

Such calculations depend in detail on the eigenvectors used for the states. We shall distinguish between three sets of theoretical expressions for the *A* and *B* values. Set I is that contained in Tables IV(a) and IV(b) of Robertson *et al.*,² except for differences of notation; his $A_1(J)$ is IJ times our A(J), and his $A_2(J)$ is $\frac{1}{4}$ of our B(J). Set I was calculated, as discussed in detail by Robertson *et al.*, from the Conway–Wybourne⁷ eigenvectors discussed in Sec. III B. Set II is also based on the Conway–Wybourne eigenvectors, ¹⁶ and was

TABLE IX. Values of the ratios A^{147}/A^{149} and B^{147}/B^{149} as a function of J. There is good consistency between the ratios for different values of J and good agreement with the earlier results.

	Valu	ues of the ratio A^{147}	/A ¹⁴⁹	Values of the ratio B^{147}/B^{149}			
Atomic		Robertson			Robertson		
state	Present	et al.	Woodgate	Present	et al.	Woodgate	
${}^{7}F_{1}$	1.21310(6)	1.21305(1)	1.21305(1)	-3.4597(7)	-3.4588(1)	- 3.4601(1)	
$^{7}F_{2}$	1.213 07(6)	1.21305(2)	1.21306(1)	- 3,4591 (25)	-3.4588(8)	- 3.4595(8)	
${}^{7}F_{3}$	1.21306(6)	1.213 00(2)	1.21301(2)	- 3,455(15)	-3.4548(24)	- 3.4549(24)	
${}^{7}F_{4}$	1.21303(3)	1,21311(11)	1,21312(11)	-3.481(22)	-3.428(55)	-3.446(55)	
${}^{7}F_{5}$	1.21304(3)	1,21306(5)	• • •	-3.4654(42)	-3.465(10)	•••	
${}^{7}F_{6}$	1,21305(2)	• • •	• • •	-3.4629(19)	•••	•••	
Weighted							
average	1.21305(2)	1.21304(2)	1.21305(2)	-3.4601(6)	-3.4588(1)	-3.4601(3)	

2019

derived according to the procedures discussed by Childs.¹² The procedures used for sets I and II should be equivalent, and the resulting equation sets should be equivalent (except for the definition of the three parameters), but they are not. Set II was obtained only after the failure of set I to fit the hfs constants of the ${}^{7}F_{1,2,3,4,5,6}$ states suggested the possibility of numerical errors in set I.

Simultaneous with the calculation of set II, a new set of Sm eigenvectors (the "Conway" set, as described above) was obtained,¹⁴ and equation set III was obtained from them in exactly the same fashion that set II had been obtained from the Conway-Wybourne⁷ eigenvectors. It follows directly from the eigenvectors of Table VI.

The three radial integrals, or parameters, needed to describe the dipole hfs constants A(J)are a^{01} , a^{12} , and a^{10} , in which the first and second numbers in the superscripts are the ranks k_s and k_l of the associated tensor operator in spin and orbital space, respectively. For the quadrupole constants B(J), the Sandars-Beck⁸ theory shows that three parameters are again required; they may be written as b^{02} , b^{13} , and b^{11} , with the same notation. It should be noted that only the first, b^{02} , is required by the nonrelativistic theory. For set III, for example, the theoretical expressions for the A and B values are

```
\begin{array}{l} A(1)=0.\ 501323a^{01}-0.\ 242788a^{12}+0.\ 498597a^{10}=-33.\ 4932\ {\rm MHz},\\ A(2)=0.\ 501773a^{01}-0.\ 189481a^{12}+0.\ 498003a^{10}=-41.\ 1839\ {\rm MHz},\\ A(3)=0.\ 502461a^{01}-0.\ 126257a^{12}+0.\ 497315a^{10}=-50.\ 2396\ {\rm MHz},\\ A(4)=0.\ 503228a^{01}-0.\ 060407a^{12}+0.\ 496474a^{10}=-59.\ 707\ {\rm MHz},\\ A(5)=0.\ 504184a^{01}+0.\ 004686a^{12}+0.\ 495599a^{10}=-69.\ 136\ {\rm MHz},\\ A(6)=0.\ 505213a^{01}+0.\ 068465a^{12}+0.\ 494450a^{10}=-78.\ 360\ {\rm MHz},\\ B(1)=0.\ 196140b^{02}-0.\ 026000b^{13}+0.\ 019994b^{11}=-58.\ 6848\ {\rm MHz},\\ B(2)=0.\ 206695b^{02}-0.\ 003178b^{13}+0.\ 065613b^{11}=-33.\ 678\ {\rm MHz},\\ B(3)=0.\ 110648b^{02}+0.\ 032412b^{13}+0.\ 065513b^{11}=21.\ 241\ {\rm MHz},\\ B(4)=-0.\ 070842b^{02}+0.\ 031267b^{13}+0.\ 129006b^{11}=100.\ 608\ {\rm MHz},\\ B(5)=-0.\ 329290b^{02}-0.\ 049772b^{13}+0.\ 166474b^{11}=203.\ 432\ {\rm MHz},\\ B(6)=-0.\ 659506b^{02}-0.\ 049772b^{13}+0.\ 166474b^{11}=203.\ 432\ {\rm MHz},\\ \end{array}
```

where the best corrected experimental values for 147 Sm are given on the right-hand side. For each particular value of J, the fact that the sum of the coefficients of a^{01} and a^{10} is slightly less than unity (the sum rule limit¹²) is due to the slight truncation of the Conway eigenvectors shown in Table VI.

The corresponding expressions for sets I and II differ only in detail. Although the six equations for the *B* values may be immediately least-squares fitted to the six measured values, a complication arises for the fit to the dipole constants. As pointed out by Woodgate¹ and by Robertson *et al.*,² for terms that have S = L and in addition lie very close to the *LS* limit (e.g., the ⁷F state of Sm), it is extremely difficult to distinguish between the parameters a^{01} and a^{10} , and it is only the very slight departure of the Sm states from the *LS* limit which makes it possible in principle. However, Woodgate¹ was able to show from high-field observations that for ¹⁴⁷Sm

$$a^{01} - a^{10} = -145.23(50) \text{ MHz}$$
 (5)

For the fits to the A values discussed below, this condition (the Woodgate constraint) is used, and the dipole fits are in effect two-parameter fits. It has been established² that the quality of the dipole fits is not affected by substantial changes in

this constraint. The fits to the quadrupole constants B are three-parameter fits.

The degree to which each of the three sets of equations is consistent with the known A and B values of ¹⁴⁷Sm is summarized in Table X, which gives the rms difference between the measured values (including the second-order corrections) and those calculated from the fits. It is seen that when set I is used to fit the hfs constants of the states with J=1-4 only, rather good fits result as reported by Woodgate.¹ Similarly, set I fits the B values of the states with J=1-5 remarkably well

TABLE X. Root-mean-square differences (kHz) between the experimental values of A and B and the calculated values obtained when each of the three sets of theoretical expressions for the hfs constants was least-squares fitted to the observed values. Equation sets II and III are seen to be much superior to set I.

				en experi onstant (I		
J's	Se	et I	Se	et II	Se	et III
used	A	В	A	В	A	В
1-4	0.036	0.003	0.037	0.007	0.018	0.003
1-5	0.383	0.003	0.034	0.009	0.018	0.009
1-6	0.461	0,176	0.032	0.013	0.017	0.017

(4)

(in fact, the rms error is *much* smaller than typical experimental uncertainties) but, as found by Robertson *et al.*,² it fails badly in accounting for the five A values. Curiously, set I will fit the A values for J=1-4, and J=6, but not J=5.

When the data for J=6 became available, it was found that $B(^{147}\text{Sm}, {}^{7}F_{6})$ differs by more than 1 MHz from that predicted on the basis of the extremely good fit of set I to the first five B values. Set I was not capable of fitting either the A's or B's of all six states. Because the Conway–Wybourne⁷ eigenvectors for Sm fitted the excitation energies considerably better than did the corresponding eigenvectors⁷ for the ground term of Nd I, it seemed curious that the eigenvectors for Nd should be in substantially better agreement with the observed hfs¹⁷ than were those for Sm.

The equations of set II are in very much better agreement with experiment than are those of set I. In fact, when it is recalled that the eigenvectors are specified only to four decimals, that configuration interaction is ignored, that the eigenvectors are not exactly normalized, etc., one has no right to expect better agreement. At this point in the analysis, however, the new Conway¹⁴ eigenvectors became available, and the resulting equations (set III) were found to fit the dipole hfs constants even better than set II. The actual leastsquares fits for set III are shown in Table XI. It is not known whether the apparent improvement over set II is meaningful or not.

It may be noted that if the Woodgate¹ constraint relating a^{01} and a^{10} is relaxed and a three-parameter fit is made to the six known A values, the value of a^{10} found with set I is + 363 MHz with a large uncertainty. The corresponding results for sets II and III (-8±60 and + 22±60 MHz, respectively) are much closer to the correct value (+5 MHz) found with the Woodgate constraint.

Finally, as mentioned by Robertson *et al.*² for the states with J=1-5, attempts to fit the *B* values with one-parameter (i. e., with nonrelativistic) expressions fail badly. The one-parameter fit to the six *B* values has an rms error of about 1 MHz. This failure is conclusive evidence of the presence and importance of relativistic effects in the quadrupole hfs of Sm.

The least-squares fits to the ¹⁴⁹Sm hfs are entirely analogous to those for ¹⁴⁷Sm and need not be discussed separately.

F. Parameter Values Obtained

For the unweighted least-squares fits (Table XI) to the observed A and B values, the parameter values obtained are

$$a^{01} = -140.469 \text{ MHz}, \quad b^{02} = -303.654 \text{ MHz}, \\ a^{12} = -142.276 \text{ MHz}, \quad b^{13} = -25.877 \text{ MHz}, \quad (6) \\ a^{10} = 4.761 \text{ MHz}, \quad b^{11} = 11.243 \text{ MHz}.$$

These parameters are defined by the hyperfine Hamiltonians¹² in which they occur. Expressed in terms of the effective value of the expectation value $\langle r^{-3} \rangle$ and the nuclear g factor μ_I/I , the magnetic-dipole parameters are¹²

$$a^{k_{s}k_{I}} = 2\mu_{B}\mu_{N}(\mu_{I}/I) \left\langle \gamma^{-3} \right\rangle_{k_{s}k_{I}}$$
(7)

The electric-quadrupole parameters contain the nuclear electric-quadrupole moment and are proportional to the constants $P^{k_s k_l}$ defined by Sandars and Beck.⁸ The relationships¹⁸ are

$$\frac{eQ^{147}}{2h}P^{02} = \frac{1}{2} \left(\frac{2l(l+1)(2l+1)}{(2l+3)(2l-1)} \right)^{1/2} b^{02} ,$$

$$(eQ^{147}/2h)P^{13} = \frac{1}{2}\sqrt{\frac{3}{10}}b^{13} , \qquad (8)$$

$$(eQ^{147}/2h)P^{11} = \frac{1}{2}\sqrt{\frac{3}{10}}b^{11} ,$$

where l is the orbital angular momentum of each electron in the unfilled shell nl^N . For the $4f^{6}6s^{27}F$ multiplet of Sm, l=3 and the top equation of (8) becomes

$$(eQ^{147}/2h)P^{02} = \sqrt{\frac{14}{15}}b^{02}$$
 (9)

In Table XII, the values of $\langle r^{-3} \rangle_{k_s k_l}$ obtained from Eq. (7) by use of the magnetic-dipole parameters from Eq. (6) and Woodgate's¹ accurate triple-resonance value for μ_I are compared with those obtained by Robertson *et al.*² and by Wood-

TABLE XI. Details of least-squares fits to the hfs constants of all six $J \neq 0$ ⁷ F states by use of the theoretical expressions (set III) that result from the new Conway eigenvectors.

Atomic state	Observed (MHz)	Values of A Calculated (MHz)	$A^{obs} - A^{calc}$ (MHz)	Observed (MHz)	Values of <i>B</i> Calculated (MHz)	B ^{obs} – B ^{calc} (MHz)
${}^{7}F_{1}$	- 33.4932(1)	-33,504	0.011	- 58.6848(8)	- 58.661	-0.024
${}^{7}F_{2}$	-41.1839(7)	-41.154	-0.030	-62.218(6)	-62.226	0.008
${}^{7}F_{3}$	- 50.2396(4)	- 50.249	0.009	-33.678(4)	-33.700	0.022
${}^{7}F_{4}$	- 59.707(1)	- 59.730	0.023	21.241 (36)	21.241	0.000
${}^{7}F_{5}$	- 69.136(1)	-69.129	-0.007	100.608(33)	100.632	-0.024
${}^{7}F_{6}$	- 78.360(1)	-78.354	-0.006	203,432(32)	203.421	0.011

Quantity	Ex. Present	Experimental values Robertson Present <i>et al</i> . Woodgate				
$\langle \gamma^{-3} \rangle_{01}$	6.377(5)	6.382(7)	6.390(6)	6,225		
$\langle \gamma^{-3} \rangle_{12}$	6.459(5)	6.461(11)	6.513(12)	6.709		
$\langle \gamma^{-3} \rangle_{10}$	-0.216(5)	-0.217(5)	-0.208(6)	-0.230		
$(eQ^{147}/2h)P^{02}$	- 293.36(5)	- 293,17(6)				
$(eQ^{147}/2h)P^{13}$	-7.09(9)	-6.86(8)				
$(eQ^{147}/2h)P^{11}$	3.08(6)	3.04(7)				
P^{13}/P^{02}	0.024	0.023		0.030		
P^{11}/P^{02}	-0.010	-0.010		-0.014		

gate.¹ The agreement is generally good. Also listed are the results of the relativistic Hartree– Fock–Slater calculations of Rosen,¹⁹ in which he used a parametrized exchange potential. The agreement between the relativistic expectation values and experiment is seen to be rather good, and has been commented on by Rosen¹⁹ and by Armstrong.⁹

The extremely good agreement between the calculated and measured value of the contact dipole parameter a^{10} is particularly noteworthy. It is clear that virtually all of this term is relativistic

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in origin, and hence not truly contact in nature. For this reason, there should be virtually no hyperfine anomaly—and this prediction is borne out by the ratios given in Table IX.

V. CONCLUSIONS

The apparent inconsistency between the Conway-Wybourne⁷ eigenvector set and the observed hfs of the ${}^{7}F$ multiplet of Sm for J = 1-5 has been resolved. Both the Conway–Wybourne and the new Conway¹⁴ eigenvector sets are shown to be remarkably consistent with the observed excitation energies,³ the g_J values, the magnetic-dipole hfs constants A, and the electric-quadrupole hfs constants B for all six $J \neq 0$ states of the multiplet. The relativistic Hartree-Fock-Slater calculations of Rosen¹⁹ are in good agreement with the measurements and give $\langle r^{-3} \rangle_{01}$ to within 2.4% of experiment. That the calculated relativistic contactlike term is within 7% of the small observed contact term indicates that there is very little core polarization or hyperfine anomaly.

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¹²See, for example, W. J. Childs, *Case Studies in Atomic Physics* (North-Holland, Amsterdam, to be published).

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¹⁶The eigenvectors used for set II differ from those used for set I only in that set II omits the single basis state $\Phi \equiv |f^6 v WUSLJM\rangle \equiv |f^6 6(221)(31)^3H; JM\rangle$. This state occurs only for ⁷F₄ and only as a 0.0005% impurity. Because $\langle {}^7F \parallel U^{(2)} \parallel \Phi \rangle$ and $\langle {}^7F \parallel V^{(1x)} \parallel \Phi \rangle$ both vanish ($\Delta S = 2$), omission of Φ has virtually no effect on the equations for A and B.

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