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Off-Diagonal Hyperfine Structure in Sc^{45} †

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The *three* independent coefficients in the magnetic-dipole hyperfine Hamiltonian cannot be determined by measurements of the hfs constants of the *two* atomic states $3d4s^2\ ^2D_{3/2,5/2}$. However, the interaction between these states at a high magnetic field shifts the resonance frequencies for transitions between magnetic substates of either state, and the necessary additional information for evaluating the coefficients may be obtained by observing these frequency shifts. Such measurements, together with more accurate low-field determinations of the hfs constants, lead to ratios of the coefficients in the dipole hfs Hamiltonian in agreement with a recent theoretical prediction. More precise values for the electron g factors are also reported.

I. INTRODUCTION

The lowest term of the neutral scandium atom is ^2D, which arises from the $3d4s^2$ configuration. The atomic ground state is $^2D_{3/2}$, and the metastable $^2D_{5/2}$ state lies at an excitation[1] of 168.34 cm^{-1}. Both levels are rather pure LS states.

The atomic-beam magnetic-resonance technique was used by Fricke *et al.*[2] in 1959 to measure the hyperfine structure of both the $^2D_{3/2}$ and $^2D_{5/2}$ states in the only stable isotope (Sc^{45}, for which the nuclear spin is $I=\frac{7}{2}$). In these measurements, the magnetic-dipole and electric-quadrupole hyperfine-interaction constants A and B were measured in each state (diagonal hfs), but direct observation of hyperfine-structure effects due to interactions between the states (off-diagonal hfs) was not attempted. Similar measurements have been made[3] on a number of radioactive isotopes of scandium in order to measure the spin and moments of the nuclear ground states.

More recently it has been shown[4] that the magnetic-dipole hfs Hamiltonian consists of three parts, each with a different tensor character. Since the relative importance of these parts is influenced by such effects as configuration interaction, it is of interest to measure not only the total value of A but also the relative contributions of the three parts separately. Because diagonal hfs studies lead only to A values for the *two* states $^2D_{3/2}$ and $^2D_{5/2}$, they are not sufficient to identify the *three* contributions to the dipole hfs Hamiltonian separately. Several authors[5] have used off-diagonal hfs studies for such investigations in other

atoms, and Mme. Bauche-Arnoult[6] recently suggested the desirability of such measurements in Sc^{45}. The latter author's particular interest in Sc^{45} arose from her theoretical study of the effects of configuration interaction on the Sc^{45} hfs. It is also of interest to see how the different parameters in the dipole hfs Hamiltonian change as one progresses through the $3d^N4s^2$ transition elements[7] from Sc, for which $N=1$, to Cu for which $N=9$.

At zero magnetic field, the shift of a transition frequency in either of the ^2D states due to interaction with the other can arise only from the hyperfine interaction. Such shifts are normally not observable, since they have the effect of changing the apparent values of the hyperfine-interaction constants. At high field, however, the frequencies are also affected by the Zeeman interaction, which can act coherently with each term in the hfs operators. Observations of transitions at high field thus contain additional information and make it possible to evaluate each of the terms separately.

In connection with this study of the off-diagonal hfs effects, the zero-field hyperfine intervals were remeasured with higher precision than was previously possible. In addition, high-field measurements of $\Delta F=0$ transition frequencies yielded greatly improved values of the electron g factor g_J for each of the two states.

II. EXPERIMENTAL PROCEDURE

The general principles of the atomic-beam magnetic-resonance technique[8] and the details of the particular apparatus[9] used for the present experiment have both been described before. No important modifications were required. The beam was produced by electron-bombardment heating of a Ta oven containing a sharp-lipped Ta inner crucible loaded with Sc metal. The beam was detected by an electron-bombardment universal detector equipped with a mass spectrometer.

Although it would at first appear that very high fields would be most suitable for quantitative observation of the effects of off-diagonal interactions, this is not necessarily so. Because there is no high-precision g_J value available (and no even-even $I=0$ isotope of Sc in which to make such a measurement), calculated transition frequencies at high field will contain considerable uncertainty from this source. In addition, the linewidth for field-dependent transitions increases rapidly with field, and consequently it becomes increasingly difficult to measure small shifts from predicted frequencies.

It was decided instead to search for values of H for which particular transition frequencies are field independent ($\partial\nu/\partial H=0$). Observations under such conditions should show lines that are not broadened by field inhomogeneities and for which the observed resonance frequency contains no uncertainty arising from imprecision in setting the field or from lack of precise knowledge of g_J. Extensive calculations of resonance frequency as a function of field revealed a number of values of H for which $\partial\nu/\partial H$ vanishes for particular $\Delta F=1$ transitions, and none for $\Delta F=0$ transitions. The off-diagonal shift of each of these frequencies was then calculated at the particular field for which $\partial\nu/\partial H=0$. By the same procedure (discussed at the end of this section), the off-diagonal shifts for the $\Delta F=1$ transitions at zero field were also calculated for comparison. The calculated off-diagonal shift for the transition $(4, -2 \leftrightarrow 3, -1)$ at 553 G (for which $\partial\nu/\partial H=0$) in the $^2D_{3/2}$ state was found to differ from that calculated at zero field by more than the corresponding difference for any of the other transitions considered in either state. For a reasonable choice of the parameters in the dipole hfs Hamiltonian, it was predicted that the perturbation of the transition frequency would change from -2 kHz at $H=0$ to -12 kHz at 553 G. Thus, measurement of the transition frequency at each field to within about 2 kHz could be useful for specifica-

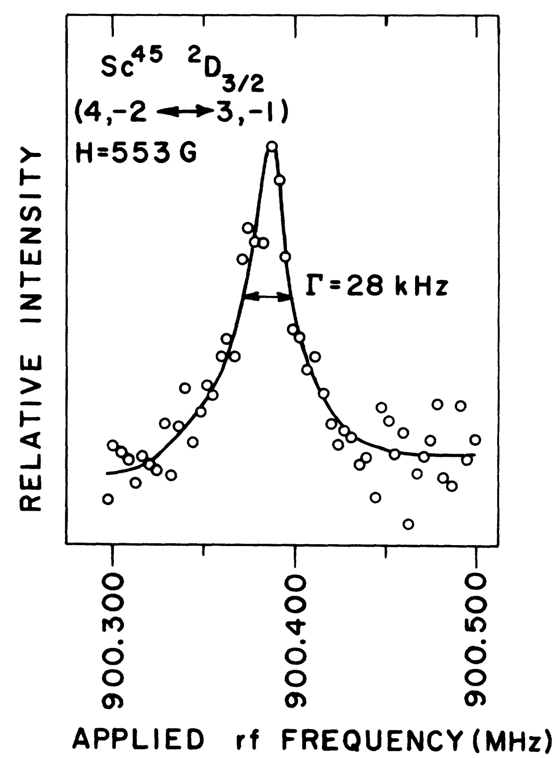

FIG. 1. Appearance of the $(4, -2 \leftrightarrow 3, -1)$ transition in the $^2D_{3/2}$ atomic ground state of Sc^{45} as observed at 553 G. The sharpness of the line is due to the fact that at this field the resonance frequency is field-independent. A number of runs were made at this field to determine the resonance frequency accurately.

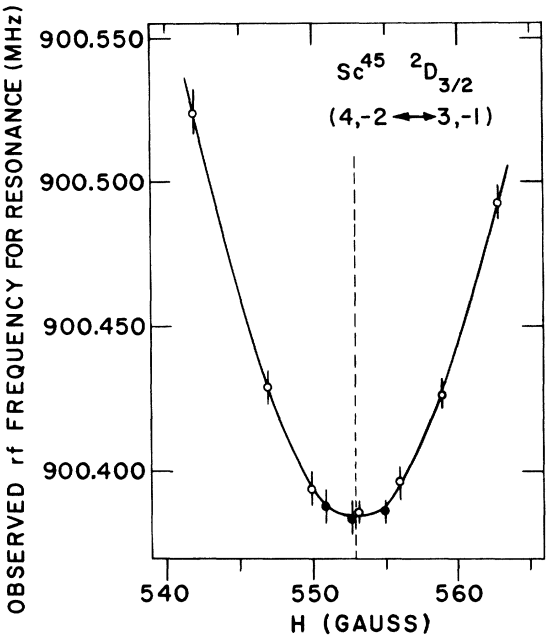

FIG. 2. Observed field dependence of the $(4,-2 \leftrightarrow 3,-1)$ transition frequency in the $^2D_{3/2}$ state of Sc^{45} in the vicinity of $H = 553$ G, for which $\partial\nu/\partial H = 0$. The field was set by a gaussmeter to within ±2 G for the solid circles. For the open circles, the field was set to within ±0.03 G by observation of a transition in the $^7S_3$ ground state of Cr^{52}. The chromium beam was produced by adding chromium metal to the Sc^{45} in the oven.

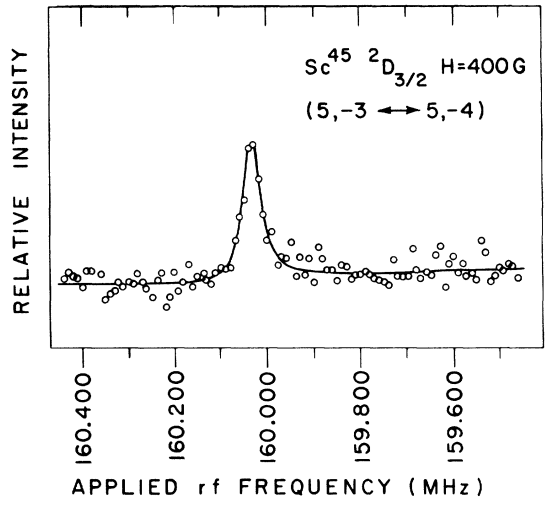

FIG. 3. Appearance of the $(5,-3 \leftrightarrow 5,-4)$ transition in the $^2D_{3/2}$ ground state of Sc^{45} at 400 G. Observations of this type were used to determine the value of g_J for each state.

tion of the dipole Hamiltonian.

The homogeneous "C" field was than set to 553 G by means of a rotating-coil gaussmeter, and the $(4, -2 \leftrightarrow 3, -1)$ transition was observed. As shown in Fig. 1, the resonance was found to be sharp – as expected for a field-independent transition. To establish the field-independence of the line frequency, the measurements were then repeated for gaussmeter readings of 551 and 555 G, as shown by the three solid circles on Fig. 2. Because the calibration of the gaussmeter itself was open to question, however, some chromium (for which the vapor pressure[10] at the oven temperature should be nearly identical to that of Sc) was added to the oven charge. The Zeeman transition in the $^7S_3$ atomic ground state of Cr^{52}, for which g_J has

TABLE I. Summary of observations in the $^2D_{3/2}$ atomic ground state. The first column of residuals results when the theoretical frequencies are calculated from Eq. (1), and the second when the off-diagonal effects of Eq. (11) are properly taken into account.

H (G)	δH (G)	Transition $(F, M \leftrightarrow F', M')$	Observed resonance frequency (MHz)	$\nu^{obs} - \nu^{calc}$ Uncorrected (kHz)	Corrected (kHz)
1.000	0.100	$4,0 \leftrightarrow 3,0$	1085.761(3)	8	1
1.100	0.100	$4,0 \leftrightarrow 3,0$	1085.763(3)	10	3
0.500	0.010	$4,0 \leftrightarrow 3,0$	1085.759(3)	6	0
0.857	0.050	$4,0 \leftrightarrow 3,0$	1085.760(7)	7	1
553.000	2.000	$4,-2 \leftrightarrow 3,-1$	900.384(6)	−6	−2
553.000	0.010	$4,-2 \leftrightarrow 3,-1$	900.386(2)	−4	0
553.000	0.030	$4,-2 \leftrightarrow 3,-1$	900.385(2)	−5	−1
553.000	0.030	$4,-2 \leftrightarrow 3,-1$	900.385(3)	−5	−1
1.000	0.012	$5,-2 \leftrightarrow 4,-3$	1328.962(9)	0	1
1.000	0.012	$5,2 \leftrightarrow 4,3$	1328.962(9)	−2	−1
2.004	0.008	$5,2 \leftrightarrow 4,3$	1328.962(7)	−5	−3
2.004	0.008	$5,-2 \leftrightarrow 4,-3$	1328.962(7)	0	1
1.020	0.012	$5,-3 \leftrightarrow 4,-3$	1328.614(9)	−7	−5
2.015	0.008	$5,-3 \leftrightarrow 4,-3$	1328.289(8)	2	4
400.009	0.007	$5,-3 \leftrightarrow 5,-4$	160.032(8)	−4	−1
400.009	0.007	$4,-2 \leftrightarrow 4,-3$	129.922(8)	3	1

been measured[11] to be 2.00183(3), was then used to set the field precisely, and the data shown by the open circles in Fig. 2 were obtained. This curve shows that the transition frequency does indeed pass through a minimum near 553 G, and the resonance frequency at this field was then remeasurable several times to reduce the uncertainty.

Most of the observable $\Delta F = 1$ transitions in the $^2D_{3/2,\,5/2}$ states were then observed at several small values of H. Measurements were also made of a number of the $\Delta F = 0$ transitions at 400 G in order to reduce the uncertainty in g_J for the two states. One of these observations, the (5, −3 ⟷ 5, −4) transition in the $^2D_{3/2}$ state at 400 G, is shown in Fig. 3. The frequency was swept downward for the scan. Except for the measurements at 553 G described above, the field was set in each case by use of an auxiliary beam of K^{39} from a separate oven. The measurements on the $^2D_{3/2}$ and $^2D_{5/2}$ states are summarized in Tables I and II, respectively.

The data in Tables I and II may be analyzed with the aid of the usual Hamiltonian for an atom in an atomic state with a definite angular momentum J (diagonal hfs), namely,

$$\mathcal{H} = A(\vec{I}\cdot\vec{J}) + B\left[\frac{\frac{3}{8}K(K+1) - \frac{1}{2}I(I+1)J(J+1)}{I(2I-1)J(2J-1)}\right] + C\,f(I,J,F) + g_J\mu_B H\left(J_z + \frac{g_I}{g_J}I_z\right), \quad (1)$$

where

$$K = F(F+1) - I(I+1) - J(J+1) = 2\langle FM|\vec{I}\cdot\vec{J}\,|FM\rangle\,. \quad (2)$$

In these expressions, A, B, and C are the magnetic-dipole, electric-quadrupole, and magnetic-octupole hyperfine-interaction constants; $\vec{I}$ and $\vec{J}$ are the nuclear and electronic angular momentum operators and I_z and J_z are their projections on the field axis; F is the quantum number for the total angular momentum of the atom; g_J and g_I are the electron and nuclear g factors; μ_B is the Bohr magneton, and H is the magnetic field. The octupole function f, although well known, is not given explicitly above, because C is found to be near zero in the present experiment.

The data of Tables I and II were computer-fitted with this Hamiltonian by holding g_I to the NMR value[12] and allowing A, B, C, and g_J to vary freely until the best fit was obtained. The residuals for

TABLE II. Summary of observations in the $^2D_{5/2}$ atomic state. The first column of residuals results when the theoretical frequencies are calculated from Eq. (1), and the second when the off-diagonal effects are properly taken into account by the analog of Eq. (11).

H (G)	δH (G)	Transition ($F, M \longleftrightarrow F', M'$)	Observed resonance frequency (MHz)	$\nu^{obs} - \nu^{calc}$ Uncorrected (kHz)	Corrected (kHz)
1.000	0.005	6, −3 ⟷ 5, −3	634.805(10)	−1	−1
1.000	0.005	6, −3 ⟷ 5, −3	634.806(13)	0	0
2.000	0.005	6, −3 ⟷ 5, −3	634.640(10)	1	1
1.000	0.005	5, −2 ⟷ 4, −2	543.628(8)	5	5
1.000	0.005	5, −2 ⟷ 4, −2	543.620(11)	−3	−3
1.000	0.005	5, −2 ⟷ 4, −2	543.622(8)	−1	−1
1.116	0.020	4, 2 ⟷ 3, 3	444.738(12)	7	7
1.109	0.020	4, 2 ⟷ 3, 3	444.728(12)	−2	−2
3.000	0.005	4, 2 ⟷ 3, 3	444.875(18)	−2	−2
1.116	0.020	4, 1 ⟷ 3, 2	444.500(18)	−5	−5
1.109	0.020	4, 1 ⟷ 3, 2	444.505(15)	−1	−1
3.000	0.005	4, 1 ⟷ 3, 2	444.240(14)	−2	−2
3.000	0.005	4, 1 ⟷ 3, 2	444.240(14)	−2	−2
1.116	0.020	4, 1 ⟷ 3, 1	444.875(15)	−15	−15
1.109	0.020	4, 1 ⟷ 3, 1	444.877(14)	−12	−12
1.116	0.020	4, 0 ⟷ 3, 0	444.676(12)	6	6
1.109	0.020	4, 0 ⟷ 3, 0	444.677(12)	7	7
3.000	0.005	4, 0 ⟷ 3, 0	444.655(8)	−2	−2
3.000	0.005	4, 0 ⟷ 3, 0	444.655(6)	−2	−2
5.000	0.005	4, 0 ⟷ 3, 0	444.635(6)	4	4
400.009	0.007	6, −3 ⟷ 6, −4	400.455(15)	20	11
400.009	0.007	5, −2 ⟷ 5, −3	461.050(12)	2	1
400.009	0.007	4, −1 ⟷ 4, −2	573.204(14)	10	−25
400.000	0.007	4, −1 ⟷ 4, −2	573.149(14)	−29	14

these fits are given in the next-to-the-last column of Tables I and II. The best-fit values found for A, B, C, and g_J will be discussed in Sec. III, as will the significance of the other column of residuals.

III. INTERPRETATION AND RESULTS

The low even-parity configurations in Sc I are relatively well separated[1]: States of $3d4s^2$ lie at 0–168 cm^{-1}, those of $3d^24s$ at 11 500–21 500 cm^{-1}, and those of $3d^3$ above 33 700 cm^{-1}. Wilson[13] has investigated the mixing of levels within the $3d^24s$ configuration in Sc I, and has shown that in La I (which has the same structure except for a larger principal quantum number) there is a great deal of mixing between the ds^2 and d^2s configurations.

Although the present g_J values are in agreement with the best previous values,[14] the uncertainties are an order of magnitude smaller. Table III compares the experimental g_J values for the $^2D_{3/2,\,5/2}$ states of ds^2 in both Sc I and La I[15] with the LS-limit values. It is seen that while the differences for La I are substantial (reflecting the considerable configuration interaction found by Wilson[13] and by Stein[16]), the differences for Sc I are about an order of magnitude smaller. The remaining discrepancies may well arise from failure to take relativistic and diamagnetic corrections into account in calculating the theoretical g values, rather than from configuration interaction. Thus the ^2D states of Sc I appear relatively free from configuration interaction when viewed through the Zeeman interaction.

It has been shown by Sandars and Beck[4] that the magnetic-dipole hyperfine structure for a state in which only one electron shell $(nl)^N$ is open may be described by the Hamiltonian

$$\mathcal{H}_{\rm hfs}(M-1)=\sum_{i=1}^{N}[a(l)\vec{l}_i-\sqrt{10}\,a(sC^2)(\vec{s}\times\vec{C}^{(2)})_i^{(1)} +a(s)\vec{s}_i]\cdot\vec{I}\,, \qquad (3)$$

in which $\vec{C}^{(2)}$ is the spherical tensor operator proportional to the spherical harmonic of order 2. For the particularly simple case of Sc I, we have $N=1$, and the summation sign may be omitted. The interaction thus contains three terms, and the relative importance of each is given by the size of the three coefficients $a(l)$, $a(sC^2)$, and $a(s)$. Although the values of the coefficients are affected both by relativity and by configuration interaction, it can be shown that relativistic effects for the $3d$ shell of the light scandium atom are very small and may be ignored. [If the relativistic contributions are evaluated by the Sandars-Beck theory[4] using Casimir factors[17] for the relativistic radial integrals, it is found that $a(sC^2)/a(l)=1.002$ and $a(s)/a(l)=0.0007$. These values may be compared with the corresponding nonrelativistic values 1 and 0.] Configuration interaction, on the other hand, is expected to distort the values of these ratios noticeably, and the observation of these distortions is the principal object of the present experiment.

If one takes matrix elements of this Hamiltonian within a state $|l^N\alpha SLJ\rangle$, the first term of Eq. (1) is recovered, i.e.,

$$\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(M-1)\,|\,l^N\alpha SLJIFM\rangle =\langle FM|\vec{I}\cdot\vec{J}\,|FM\rangle A\,, \qquad (4)$$

and it follows in addition that

$$A=(2-g_J^*)a(l)+\left[\frac{30(2J+1)l(l+1)(2l+1)}{J(J+1)(2l-1)(2l+3)}\right]^{1/2} \times\langle l^N\alpha SL\,\|\,V^{(12)}\,\|\,l^N\alpha SL\rangle \begin{Bmatrix} S & S & 1\\ L & L & 2\\ J & J & 1\end{Bmatrix} a(sC^2) +(g_J^*-1)a(s)\,, \qquad (5)$$

in which g_J^* is the Lande value of the g factor. In particular, for the $3d4s^2\ ^2D_{3/2,\,5/2}$ states of Sc^{45}, we have from Eq. (5) that

$$A(^2D_{3/2})=\tfrac{6}{5}a(l)+\tfrac{2}{5}a(sC^2)-\tfrac{1}{5}a(s)=269.556(1)\ \text{MHz}\,, \qquad (6)$$

$$A(^2D_{5/2})=\tfrac{4}{5}a(l)-\tfrac{4}{35}a(sC^2)+\tfrac{1}{5}a(s)=109.032(1)\ \text{MHz}\,,$$

in which the numerical values on the right-hand side result from fitting Eq. (1) to the data of Tables I and II without applying corrections for off-diagonal effects. The experimental values are given in the "uncorrected" column of Table IV. They are in good agreement with the results of Ref. 2, but the uncertainty is an order of magnitude smaller. The three coefficients $a(l)$, $a(sC^2)$, and $a(s)$ cannot be evaluated separately until additional (off-diagonal) information is available.

Expressions for the electric-quadrupole hyperfine Hamiltonian and for its matrix elements – the analogs of Eq. (3) and of Eqs. (4) and (5), respec-

TABLE III. Comparison of the g_J values for the ds^2 $^2D_{3/2,\,5/2}$ states of Sc^{45} and La^{139} with the LS-limit values. The much smaller departures of the Sc values from the LS limit is evidence of the much smaller degree of configuration interaction in Sc.

Atomic state	Atom	g_J value Observed	LS-limit	Difference (obs.$-LS$)
$^2D_{3/2}$	Sc^{45}	0.79933(3)	0.79954	−0.00021(3)
$^2D_{3/2}$	La^{139}	0.79755(3)	0.79954	−0.00199(3)
$^2D_{5/2}$	Sc^{45}	1.20029(2)	1.20046	−0.00017(2)
$^2D_{5/2}$	La^{139}	1.19907(4)	1.20046	−0.00139(4)

TABLE IV. Best-fit values of the hyperfine-interaction constants A, B, and C, and the g factor g_J for the $^2D_{3/2,5/2}$ states, together with the χ^2 values for the fits. For the first fit, off-diagonal effects were ignored in calculating the theoretical transition frequencies. For the second, the off-diagonal effects were computed with $\alpha = 1.1$.

Atomic state	Quantity	Uncorrected value, with experimental uncertainty	Corrected value, with total uncertainty
$^2D_{3/2}$	A	269.556(1)	269.558(1)
	B	−26.346(4)	−26.360(8)
	C	...	...
	g_J	0.79935(3)	0.79933(3)
	χ^2	41.1	3.0
$^2D_{5/2}$	A	109.032(1)	109.033(1)
	B	−37.387(12)	−37.373(15)
	C	0.0017(10)	0.0015(12)
	g_J	1.20028(2)	1.20029(2)
	χ^2	7.7	6.5

tively – have been given[18]; but because the quadrupole interaction plays only a minor role in the Sc^{45} off-diagonal hfs observed, they will not be repeated here. (In the computer calculation of the off-diagonal shifts, full account of the quadrupole effects is taken.) For the present purpose we may use the classic result,[19]

$$B(^2D_J) = [(2J-1)/2(J+1)]\, b_{nl}\,, \tag{7}$$

in which

$$b_{nl} = e^2 Q' \langle r^{-3} \rangle_{nl}\,. \tag{8}$$

In Eq. (8), Q' is the apparent value of the electric-quadrupole moment of the nuclear ground state (before application of the Sternheimer[20] shielding correction). For the $^2D_{3/2,5/2}$ states of Sc^{45}, we have from Eq. (7) that

$$\begin{aligned} B(^2D_{3/2}) &= \tfrac{2}{5} b_{3d} = -26.346(4)\ \text{MHz}\,, \\ B(^2D_{5/2}) &= \tfrac{4}{7} b_{3d} = -37.387(12)\ \text{MHz}\,, \end{aligned} \tag{9}$$

in which the numerical values on the right are again the result of fitting Eq. (1) to the data of Tables I and II without taking account of off-diagonal effects. The new values are again consistent with those of Fricke *et al.*,[2] but with uncertainties an order of magnitude smaller.

Equations (9) can be solved for b_{3d} for each of the two states, the results being

$$\begin{aligned} b_{3d}(^2D_{3/2}) &= -65.865(10)\ \text{MHz}\,, \\ b_{3d}(^2D_{5/2}) &= -65.427(21)\ \text{MHz}\,. \end{aligned} \tag{10}$$

These two values, though not the same to within experimental uncertainty, differ by less than 0.7% and may confidently be substituted into Eq. (8) to extract Q'.

For a particular transition, calculation of the resonance-frequency shift due to off-diagonal interactions involves calculating the shift for the upper and lower levels of the transition separately and then combining the results. The shift for any level $\mathfrak{F}, M$ of the $^2D_{3/2}$ state may, for example, be expressed[21] at field H by

$$\delta E(^2D_{3/2}, \mathfrak{F}M) = -[1/E(^2D_{5/2})] \times \sum_{F'} \left| \langle {}^2D_{3/2}, \tfrac{7}{2}\, \mathfrak{F}M | \mathcal{H}_{\text{hfs}} + \mathcal{H}_z | {}^2D_{5/2}, \tfrac{7}{2} F'M \rangle \right|^2, \tag{11}$$

in which $\mathfrak{F}M$ represents the particular combination of zero-field FM basis states for the level at field H. The fact[12] that $I(Sc^{45}) = \frac{7}{2}$ has been used in Eq. (11). The operator in Eq. (11) contains the dipole, Eq. (3), and quadrupole hfs operators and the Zeeman term $\mu_B(\vec{L} + 2\vec{S}) \cdot \vec{H}$ coherently. Its matrix elements, and the resulting frequency shifts, depend on the relative sizes of $a(l)$, $a(sC^2)$, and $a(s)$ in a complex way. Because of Eqs. (6), however, specification of any one of the three dipole coefficients (or any ratio between them) specifies $\mathcal{H}_{\text{hfs}}$ and therefore completely determines all off-diagonal shifts of resonance frequencies. The shift in frequency for each observed transition in the $^2D_{3/2}$ state was calculated as a function of the quantity

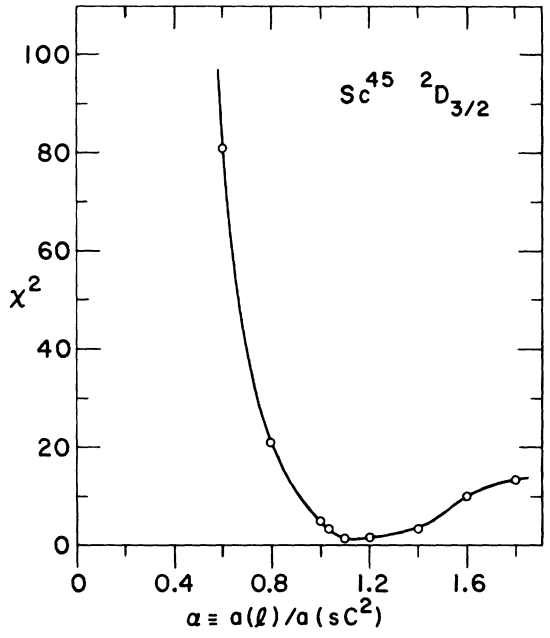

FIG. 4. Value of χ^2 for fitting the calculated transition frequencies to the data, plotted as a function of the value of $\alpha = a(l)/a(sC^2)$ used in computing the off-diagonal corrections to the computed frequencies. The value $\chi^2 = 43$ is obtained if corrections for off-diagonal effects are ignored.

$$\alpha = a(l)/a(sC^2)\,. \tag{12}$$

For each value of α considered, these corrections to the calculated transition frequencies were then included in a new fit to the data. In Fig. 4 the χ^2 achieved in the $^2D_{3/2}$ fits[22] is plotted as a function of α. Comparison between the residuals and the experimental uncertainties suggests that for a reasonable fit we should require $\chi^2 \lesssim 3.5$. In contrast, the value for the entirely unsatisfactory fit in which off-diagonal effects are ignored[22] is $\chi^2 = 43$. From Fig. 4 it is concluded that the value of the ratio $a(l)/a(sC^2)$ for an acceptable fit is

$$\alpha = 1.13^{+0.27}_{-0.10}\,. \tag{13}$$

When the corrected theoretical frequencies for the particular choice $\alpha = 1.1$ are fitted to the $^2D_{3/2}$ data (and a similar fit is made to the $^2D_{5/2}$ data), the residuals are as given in the right-hand columns of Tables I and II, and the values found for A, B, C, g_J, and χ^2 are as given at the right in Table IV. Because the values found for A and B are so nearly the same as for the uncorrected fits, substitution of the new values for A and B into Eqs. (6) and (9) does not affect the conclusions drawn from them.

The result given in Eq. (13) may be compared with the theoretical prediction of Bauche-Arnoult,[6] who used second-order perturbation theory to study the extent to which configuration-interaction distorts the values of the dipole coefficients. She concluded that the value of α for Sc I should be nearly equal to that for Ti I, for which it has been found[7] to be

$$\alpha(\text{Ti I}) = 1.03\,. \tag{14}$$

The present result that $\alpha = 1.13$ for Sc^{45}, though not a high-precision determination, is consistent with her prediction.

The value of α for Sc I can also be inferred by comparison of the Sc^{45} hfs with that of other $3d^N4s^2$ atoms. From Fig. 1 of Ref. 7, it would appear by extrapolation that we must have

$$-25 \lesssim \frac{a(s)}{|\mu_I/I|} \lesssim -10\,\frac{\text{MHz}}{\mu_N} \tag{15}$$

for Sc^{45}, and closer limits could probably be used with safety. From Eq. (15) and the known[12] values of μ_I and I, we find

$$-34.0 \lesssim a(s) \lesssim -13.6\ \text{MHz}\,. \tag{16}$$

From this, using Eq. (6), we have

$$0.95 \lesssim \alpha \lesssim 1.07\,, \tag{17}$$

in agreement with Eq. (13). It should be emphasized, however, that the value given by Eq. (17) results not from measurements on Sc but from extrapolation from the properties of other atoms of the same series.

From Eqs. (6) and (13), it follows that

$$a(l) = 168.0^{+3.7}_{-1.8}\ \text{MHz}\,. \tag{18}$$

The value of $a(l)$ is relatively insensitive to the extent of configuration interaction (its indicated value changes only 1.4% if configuration interaction is ignored) and may be taken to be

$$a(l) = 2\mu_B\mu_N(\mu_I/I)\langle r^{-3}\rangle_{nl}\,, \tag{19}$$

the value given by the nonrelativistic theory if configuration-interaction effects are ignored. By eliminating $\langle r^{-3}\rangle_{nl}$ between Eqs. (8) and (19) and solving for Q', the apparent electric-quadrupole moment of the nuclear ground state of Sc^{45} is found to be

$$Q' = \frac{2}{e^2}\,\mu_B\mu_N\frac{\mu_I}{I}\,\frac{b_{3d}}{a(l)}\,. \tag{20}$$

If the numerical value of b_{3d} is taken to be the average of Eqs. (10), that of $a(l)$ from Eq. (18), and that of μ_I/I from Ref. 12, it is found that

$$Q' = -0.216\ \text{b}\,, \tag{21}$$

in agreement with Ref. 2. The uncertainty arises mainly from Eq. (18) and the assumption of Eq. (19), and is less than 4%. In Sternheimer's notation,[20] the true quadrupole moment Q is obtained from the apparent value Q' by the relation

$$Q = Q'/(1 - R_{3d})\,. \tag{22}$$

Although the correction factor $1/(1 - R_{3d})$ has been calculated[20] to be 1.217 for $Cu(3d^94s^2)$, its value for Sc (at the other end of the $3d$ shell) is unknown.

IV. CONCLUSIONS

The principal result of the present experiment is to confirm Mme. Bauche-Arnoult's theoretical prediction for the ratio $\alpha = a(l)/a(sC^2)$ between coefficients which occur in the Sc^{45} magnetic-dipole hfs Hamiltonian. The agreement gives increased confidence in the treatment of configuration-interaction effects by second-order perturbation theory. In addition, the new experimental values for the hfs constants and g_J values of the $3d4s^2\ ^2D_{3/2,\,5/2}$ states of Sc^{45} are an order of magnitude more precise than those previously available. The value found for the electric-quadrupole moment of the Sc^{45} nuclear ground state is in agreement with the previous result.

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[21]This is a special case of Eq. (10) in Ref. 15.
[22]There are two minor differences between the fitting procedures used for the $^2D_{3/2}$ fit of Tables I and IV and for the fits summarized in Fig. 4. Because a different χ^2 minimization routine was used for the latter fits, a slightly different value of χ^2 results for fitting the same data. In addition, the two $\Delta F = 0$ observations at 400 G were omitted from the fits of Fig. 4; these data had not yet been obtained when the curve was drawn. The shape of the χ^2 vs α curve would not have been altered if these data had been included.

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Perturbation Treatment of the Hartree-Fock-Slater ($X\alpha$) Equations*

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The α-parametrized Hartree-Fock-Slater ($X\alpha$) equations are solved in the framework of Z^{-1} expansion theory for the two- and four-electron ions in their ground-state configurations ($1s^2$) and ($1s^2 2s^2$), respectively. The first two terms in the Z^{-1} expansion of α are given when α is determined by various criteria.

I. INTRODUCTION

The Slater[1] (S) and the Gaspar[2]-Kohn-Sham[3] (GKS) local approximations to the exchange term V_{ex} in the Hartree-Fock (HF) equations differ only by a multiplicative constant, α. The former corresponds to the α value 1, and the latter to $\frac{2}{3}$, in the expression[4]

$$V_{X\alpha} = -\tfrac{2}{3}\alpha\,[(3/\pi)\,\rho(\vec{r})]^{1/3}, \tag{1}$$

where $\rho(\vec{r})$ is the charge density at r.

Investigation for atomic systems of the orbital solutions $u(\vec{r})$ of the self-consistent-field (SCF) equations

$$(-\tfrac{1}{2}\nabla^2 - Z/r + V_{ee} + V_{ex})\,u(\vec{r}) = \epsilon\, u(\vec{r}) \tag{2}$$

(where V_{ee} and V_{ex} are the Coulomb and exchange terms, respectively), with each of these local exchange potentials, yielded results[5-8] for various physical properties which were significantly different from those obtained with the HF exchange potential. The S potential overestimates, while the GKS potential underestimates, exchange.

For this reason, there has been extensive interest, in recent years,[9] in employing a value of α intermediate between 1 and $\frac{2}{3}$ in order to retain the calculational advantages of the local exchange but obtain a closer approximation to the HF exchange and its effects.

We thus have the problem of the choice of the optimum α. Probably the earliest suggested criterion[10] (hereafter called criterion A) was to construct a *normalized* Slater determinant $\Phi(\alpha)$ from the