Hyperfine Structure of Seven Low Atomic Levels in Co^{59}, and the Nuclear Electric-Quadrupole Moment*

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The hyperfine structure of the seven lowest atomic levels in Co^{59} has been examined with the atomic-beam magnetic-resonance technique. Quantitative agreement with earlier measurements is found for those states for which results have been published. All of the results are corrected for the effects of off-diagonal hyperfine interactions, and the effective-operator theory used for the interpretation also takes into account such effects as intermediate coupling, configuration interaction, and relativistic effects. The emphasis is on examining the consistency of the results from state to state. Although a very high degree of agreement between theory and experiment is found, some difficulty is encountered in understanding details of the quadrupole interaction. Values for the quadrupole moment of the Co^{59} nuclear ground state are determined in each of two electron configurations. The difference between the two values found is well outside experimental error and is presumably due to different Sternheimer shielding in the two configurations. The value found for Q is consistent with earlier determinations and with nuclear theory. Values are given for the electronic g factor in each state examined.

INTRODUCTION

DEDUCTION of the value of the electric-quadrupole moment Q of the nucleus from even high-precision hyperfine-structure (hfs) measurements on a single atomic level requires assumptions about the purity of the atomic state, the appropriate value of $\langle r^{-3}\rangle$ to use, etc. If measurements are available for several levels of a given electron configuration, some of these assumptions can be tested (i.e., the effective number of assumptions can be reduced). Unfortunately, however, such experiments do not measure the Sternheimer-shielding correction to the deduced value of Q, since this correction is expected theoretically to be the same for every level of a configuration. It is therefore desirable to make such measurements in several levels of at least two different electron configurations so that any differences in the shielding can be revealed. Clearly, as data become available for more and more levels of a particular atom, the theory can be put to an increasingly severe (and hence more interesting) test.

The number of atoms for which precision hyperfine-structure measurements are available for several atomic levels has increased substantially in recent years; but the results are in most cases limited to members of a single multiplet of one configuration. This experimental development has been accompanied by a considerable refinement in the theoretical techniques with which to analyze the experimental results.

Recently, a detailed investigation of the hfs of the $3d^34s^2\ ^4F_{9/2,7/2,5/2,3/2}$ and $3d^44s\ ^6D_{9/2,7/2,5/2,3/2,1/2}$ levels of V^{51} was published.[1] The theory was found to be substantially more successful in accounting for the dipole and quadrupole hfs effects in the $3d^34s^2$ multiplet than for the ^6D multiplet formed from nonequivalent electrons. Comparison of the results for V I with those for Co I, in which the lowest configuration ($3d^74s^2$) is conjugate to that ($3d^34s^2$) of V I, should be of interest. Precision hfs measurements have been published[2,3] for three members of the $3d^74s^2\ ^4F$ ground term of Co^{59}, but not for the fourth. In addition, no measurements were available for the competing $3d^84s$ configuration. It was decided to repeat the earlier work so that the effects of off-diagonal hyperfine mixing with nearby levels could be included in the analysis and, in addition, to study as many more Co^{59} levels as possible. Another reason for the interest in comparing the hfs of V^{51} and Co^{59} is that the principal difference, from the theoretical point of view, is the much greater departure of Co I from the LS limit. The increased importance of spin-orbit mixing can, in principle, be taken into account in the theoretical treatment; and it is of interest to see if the theory is, in fact, as successful for Co^{59} as for V^{51}.

From the analysis of the Co^{59} hyperfine interactions in the various levels studied, an accurate value for the electric-quadrupole moment of the nuclear ground state can be deduced from two different electron configurations. The difference between them is a measure of the difference in Sternheimer shielding in the configurations.

APPARATUS

The method used in the present investigation is the classic atomic-beam magnetic-resonance technique as devised by Rabi[4] and modified by Zacharias.[5] Cobalt metal (100% Co^{59}) was placed in a ZrO crucible equipped with a cap and having a vertical slit 0.010 in. wide cut in the upper portion of its side. The crucible was held in a tantalum holder which was heated by electron bombardment until the beam of neutral Co^{59}

* Work performed under the auspices of the U. S. Atomic Energy Commission.
[1] W. J. Childs and L. S. Goodman, Phys. Rev. **156**, 64 (1967); W. J. Childs, *ibid.* **156**, 71 (1967).
[2] D. von Ehrenstein, Ann. Physik **7**, 342 (1961).
[3] K. H. Channappa and J. M. Pendlebury, Proc. Phys. Soc. (London) **86**, 1145 (1965).
[4] I. I. Rabi, J. R. Zacharias, S. Millman, and P. Kusch, Phys. Rev. **53**, 318 (1938).
[5] J. R. Zacharias, Phys. Rev. **61**, 270 (1942).

atoms emerging from the oven slit was sufficiently intense. The collimated beam of neutral atoms is directed through two strong, inhomogeneous magnetic fields (with aligned gradients) which deflect it away from a central detector unless the effective magnetic moment of the atom is reversed in direction during the passage through the region between the deflecting fields. The reversal of the effective magnetic moment can be accomplished by inducing a transition between two appropriate hyperfine states separated by the energy difference $\Delta E=h\nu$. The change of state is effected by allowing the atomic beam to pass through an rf magnetic field of frequency ν in the presence of a homogeneous dc magnetic field H. Those atoms that interact with the rf field in such a way as to undergo a transition to the state with opposite effective magnetic moment are refocused through a detector slit and counted by the detector. The resonance frequency ν and the dc field H required for such a flop-in transition are measured, and an ensemble of such measurements over a range of H and ν normally leads to a quantitative evaluation of the hyperfine interaction constants A, B, and C, and the electronic g factor g_J.

The detector used to count the atoms that pass through the detector slit has been described previously.[6] The atomic beam is bombarded by an intense beam of electrons, and the ions that are produced are drawn off, accelerated, and passed through a magnetic mass spectrometer which rejects ions that do not have the proper mass. The ions are then further accelerated into a magnetic electron multiplier. The principal modification of the system since the description in Ref. 6 is in the method[7] of handling the counts from the multiplier. The rf power used to induce the atomic transitions is swept in steps of about 0.2 linewidth through the rf interval of interest; and each time the frequency is stepped, the counts are fed into a new channel of a multichannel scaler. The procedure is repeated over and over automatically until the signal-to-noise ratio appears sufficient. The homogeneous magnetic field, set by observing a resonance in an independent beam of K^{39}, is held constant during the collection of data.

Most of the required radiofrequencies below 1000 Mc/sec were obtained by sweeping a 0–50-Mc/sec Solartron model D0-1001 precision signal generator, and then multiplying and/or amplifying the output as required. Frequencies between 1 and 4 Gc/sec were obtained by phase-locking a klystron or voltage-tuned magnetron to a multiple of the Solartron reference frequency added to a swept 30-Mc/sec i.f. signal. The phase-locking was achieved with a Dymec model 2650A oscillator synchronizer. Frequencies in the range 4–8 Gc/sec were obtained from a Micro-Now Instrument Co. model No. 701 backward-wave oscillator, phase-locked as described above. An E-H Research Laboratories 1-W 4–8-Gc/sec microwave amplifier was a necessary adjunct. A Boonton Electronics Corp. model No. 41A microwattmeter, whose sensitivity through 7 Gc/sec was 0.001 μW, proved of great value for line tuning, and an Eldorado Electronics Model No. 946 frequency counter was used to measure directly all frequencies from dc to 4 Gc/sec. At higher frequencies, a transfer oscillator was required.

[6] W. J. Childs, L. S. Goodman, and D. von Ehrenstein, Phys. Rev. 132, 2128 (1963).
[7] W. J. Childs and L. S. Goodman, Phys. Rev. 148, 74 (1966).

THEORY OF THE EXPERIMENT

In the approximation that hyperfine and Zeeman interactions with different atomic states may be ignored as negligibly small, the observed hfs of a state $|\alpha SLJ\rangle$ may be described by the Hamiltonian[8]

$$\mathcal{H}_{\rm hfs}=A_J\mathbf{I}\cdot\mathbf{J}+B_JQ_{\rm op}+C_J\Omega_{\rm op}+g_J\mu_0H(J_z+\gamma I_z), \quad (1)$$

where $\mathbf{I}$ and $\mathbf{J}$ are the nuclear spin and total electronic angular momentum operators, respectively, A_J, B_J, and C_J are, respectively, the magnetic-dipole, electric-quadrupole, and magnetic-octupole hyperfine-interaction constants of the state J, g_J is the electronic g factor, μ_0 and H are, respectively, the Bohr magneton and the external magnetic field, and $\gamma=g_I/g_J$, where $g_I=-\mu_I/(\mu_0 I)$ is the nuclear g factor. It may be noted that this Hamiltonian says nothing about the hyperfine-interaction constants A_J, B_J, or C_J. The required matrix elements of the dipole and quadrupole operators are[9]

$$\langle FM|\mathbf{I}\cdot\mathbf{J}|FM\rangle=\tfrac{1}{2}[F(F+1)-I(I+1)-J(J+1)]\equiv\tfrac{1}{2}K \quad (2)$$

and

$$\langle FM|Q_{\rm op}|FM\rangle=[\tfrac{3}{4}K(K+1)-I(I+1)J(J+1)]/2I(2I-1)J(2J-1). \quad (3)$$

The corresponding expression for the octupole interaction is given on p. 277 of Ref. 8.

Two types of computer programs are normally used[10] in the interpretation of atomic-beam magnetic-resonance observations. The first computes transition frequencies (energy differences between eigenvalues of $\mathcal{H}_{\rm hfs}$, characterized by the quantum numbers F and M). The second type accepts an ensemble of observations of this type at various values of H and varies some or all of the parameters A_J, B_J, C_J, g_J, and g_I to make a least-squares fit of the calculated transition frequencies to the observed ones. The best-fit values of the hyperfine-interaction constants and g factors are then printed out.

[8] N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), pp. 272–277.
[9] N. F. Ramsey, Ref. 8, pp. 73, 272.
[10] These programs are modifications of routines kindly sent by Professor H. A. Shugart of the University of California, Berkeley. Both assume explicitly that J is a good quantum number.

EXPERIMENTAL PROCEDURE

As was mentioned above, precision values for the hfs constants and electronic g factors for the $3d^74s^2\ {}^4F_{9/2,7/2,5/2}$ states have been published by other authors.[2,3] Calculations indicated, however, that a careful comparison of their results with the theory would be of much greater value if the effects of off-diagonal hyperfine interactions were taken into account. Corrections for such shifts in resonance frequency cannot be applied directly to the published hyperfine-interaction constants, but must be applied to the observed resonance frequencies (which were not available for several of the states in question). The desired remeasurement of the $\Delta F=\pm 1$ hyperfine intervals was not too difficult, however, since the hyperfine-interaction constants were known (subject only to the small corrections mentioned). Measurements of several $\Delta F=0$, $\Delta M_F=\pm 1$ transition frequencies were also made at fields up to 720 G to obtain accurate values of g_J. The effects of J mixing (within a SL multiplet) caused by both the hyperfine and Zeeman interactions were taken into account in the computer programs[11] used to extract the corrected value of the electronic g factor g_J for each state. In addition, hyperfine interaction with other nearby atomic states was allowed for in the extraction of the corrected values of the hyperfine-interaction constants A, B, and C for each state.

Atoms in the $3d^74s^2\ {}^4F_{3/2}$ state, in addition to being less abundant in the atomic beam as a result of the smaller Boltzmann factor, are also very difficult to deflect because the g factor is only about $\frac{2}{5}$. Preliminary results on this state were reported by Channappa and Pendlebury.[3] Although the intensity of transitions in this state could have been greatly enhanced by suitably altering the machine geometry, it was found unnecessary. The appearance of the $(5,-3\leftrightarrow 5,-4)$ transition at 1320 G is shown in Fig. 1. Several transitions of the type $(F=4, M\leftrightarrow F=3, M)$ are shown in Fig. 2, as observed at 0.568 G. The rf power was produced by a phase-locked, voltage-tuned magnetron, swept in 5-kc/sec steps. It is interesting to note that the center of this pattern (i.e., the $F=4\leftrightarrow 3$ zero-field hyperfine interval) may be predicted to within 0.9 Mc/sec at 4152 Mc/sec, i.e., to 0.02%, by the effective-operator theory and the observed hfs constants (suitably corrected for off-diagonal effects) of the other three members of the multiplet. In making the calculation, however, careful attention must be paid to the intermediate-coupling composition of all four members of the multiplet.

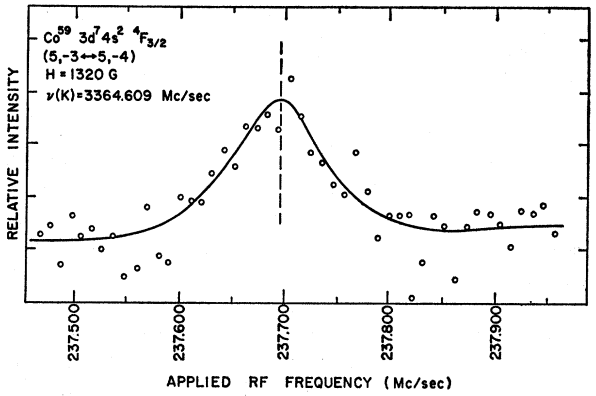

FIG. 1. The transition $(5,-3\leftrightarrow 5,-4)$ in the $3d^74s^2\ {}^4F_{3/2}$ state of Co^{59} as observed at 1320 G. The small value of the electronic g factor ($g_J\approx\frac{2}{5}$) is responsible for the relatively small transition frequency. The observed intensity for transitions in this state was reduced substantially below that expected by the Boltzmann factor because of the difficulty of deflecting atoms with such a small g factor.

For every transition $(F, M\leftrightarrow F', M')$ in a particular member J of the $3d^74s^2\ {}^4F$ ground multiplet, there is an analogous transition in the excited multiplet $3d^8(^3F)4s\ {}^4F$ since the quantum numbers (to the extent that they are pure) $SLJIFM$, $F'M'$ are identical. Indeed, the transition frequencies themselves are nearly identical (at modest values of H), and differ at very low field only because of slight differences in the electronic g factors. As H is increased, however, any difference between the hyperfine-interaction constants becomes more important, and the transition frequencies move apart. Figure 3 shows this effect for the transition $(6,-3\leftrightarrow 6,-4)$ in the $^4F_{5/2}$ states at 200 G. The dashed line at the left of the figure shows the known position of the transition in the $3d^74s^2$ configuration. The transition in $3d^84s$ is clearly shown in the center. It is expected to be about 12 times weaker in $3d^84s$ than in $3d^74s^2$ because of the smaller Boltzmann factor.

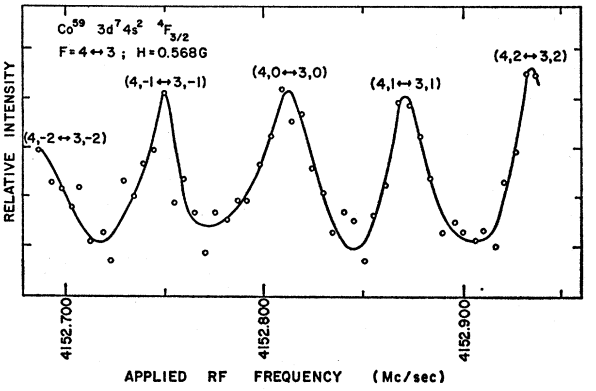

FIG. 2. Several transitions of the type $(4, M\leftrightarrow 3\ M)$ in the $3d^74s^2\ {}^4F_{3/2}$ state of Co^{59} as observed at $H=0.568$ G. The rf signal, produced by a phase-locked voltage-tuned magnetron, was repeatedly swept through the frequency interval shown.

[11] A program that sets up and diagonalizes the complete matrix of all J and F for a given M has been written. It works at arbitrary magnetic field H, and will do the calculation for any state of any configuration of the type l^N or l^Ns. It is presently limited to calculating the eigenvalues (and transition frequencies) in the LS limit and considers only the states of a single multiplet. Calculation of a single transition frequency in one of the ^4F levels of Co^{59} (for which the matrix size is about 25×25, depending on the values of M) requires about 2 min on the CDC-3600 computer. Publication of a detailed account of the program is planned.

Care had to be taken to distinguish between such $3d^84s$ transitions and poorly refocused and/or multiple-quantum transitions in $3d^74s^2$. For these reasons, $3d^84s$, $\Delta F=0$ resonances were not studied below about 100 G.

Figure 4 shows the appearance of the $(5, 0 \leftrightarrow 4, 0)$ transition in the $3d^84s\ ^4F_{9/2}$ state at 1 G. The sharp central minimum is due to the existence of two regions of rf field, out of phase by 180°. Such patterns have been observed before, and the cause of the line shape is understood.[12] The scatter of the points is representative of the data obtained for the excited ^4F multiplet.

From the results obtained for the $J=\frac{9}{2}, \frac{7}{2}, \frac{5}{2}$ members of the $3d^84s\ ^4F$ term, the electronic g factor and hyperfine-interaction constants of other states of the configuration can be predicted theoretically. The intensity of transitions in the $^4F_{3/2}$ state is expected to be anomalously low, however, just as was found for the $3d^74s^2\ ^4F_{3/2}$ state. Frequency scans of up to $1\frac{1}{2}$-h duration around the frequency predicted at $H=100$ G proved to be

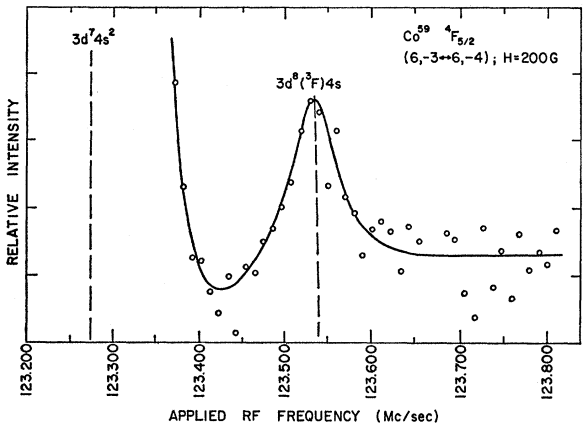

FIG. 3. The appearance of the transition $(6, -3 \leftrightarrow 6, -4)$ observed in both the $3d^74s^2\ ^4F_{5/2}$ and $3d^84s\ ^4F_{5/2}$ states at 200 G. The intensity of the second transition is expected to be only about $\frac{1}{12}$ that of the first because of its smaller Boltzmann factor in the atomic beam. Although the transition frequencies of the two resonances are nearly identical at small H, the separation increases with H as a result of a small difference in g_J and larger differences in the hyperfine-interaction constants.

inadequate to reveal a transition. It was disappointing because the theory cannot be properly tested unless the hfs of at least four states in the configuration is examined.

Wybourne[13] has shown, however, that the parameters required for the effective-operator theory do not depend, in lowest order, on the particular multiplet of the configuration considered. Attempts were therefore

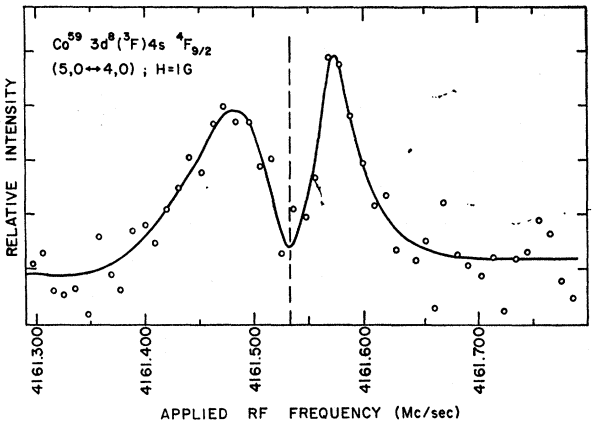

FIG. 4. The $(5, 0 \leftrightarrow 4, 0)$ transition in the $3d^84s\ ^4F_{9/2}$ state of Co^{59} at about 1 G. The unusual pattern results from the presence of two nearby regions of rf field, 180° out of phase.

made to observe transitions in the $3d^84s\ ^2F_{7/2}$ state at 7442 cm^{-1}. Although resonances were observed and followed with H from 10 to 60 G, the time required for data collection was felt to be unreasonable in relation to the possible benefits. It was shown, however, that the magnetic-dipole hyperfine-interaction constant A and electronic g factor g_J are consistent with the values predicted theoretically.

The observations of $\Delta F=0$ and $\Delta F=\pm 1$ transitions are summarized in Tables I and II, respectively. Table III gives the convention used for labeling the $\Delta F=0$ transitions.

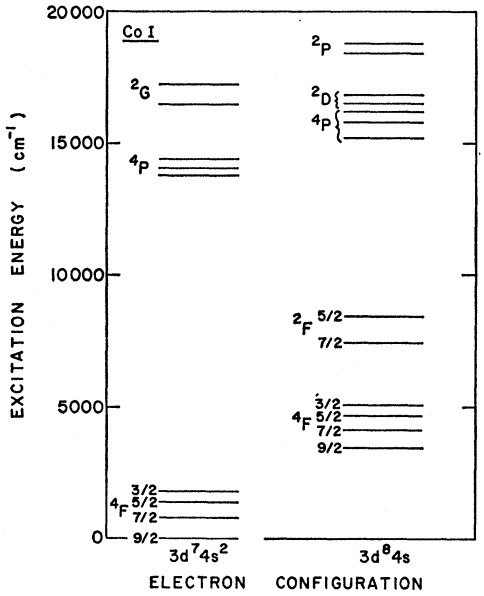

FIG. 5. Energy levels of Co I below 20 000 cm^{-1}. The large degree of spin-orbit mixing in each configuration is evident from the spread of each multiplet. Since the lowest term of both the $3d^74s^2$ and the $3d^84s$ configurations is ^4F, and since these two terms lie close together, some configuration interaction may be expected as well.

[12] Such patterns have been observed by many people. See, for example, W. J. Childs, L. S. Goodman, and L. J. Kieffer, Phys. Rev. **122**, 891 (1961). The theory of the line shape is given by N. F. Ramsey, Ref. 8, p. 124.

[13] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience Publishers, Inc., New York, 1965), pp. 148–150.

COMPARISON OF THEORY WITH EXPERIMENT

The low even-parity atomic levels of Co I are shown in Fig. 5. All of the known levels of the three lowest configurations, $3d^74s^2$, $3d^84s$, and $3d^9$, lie below about 28 000 cm^{-1}. It can be seen immediately from the considerable spread of each multiplet that the spin-orbit interaction is substantial, and that the consequent mixing of states of the same J will be appreciable within each configuration. In addition, the large energy span for which several configurations overlap would lead one to expect some configuration interaction, particularly between corresponding members of the ^4F terms in $3d^74s^2$ and $3d^84s$.

Correction of $\Delta F=\pm1$ Intervals for Hyperfine Mixing with Other Atomic States

Many of the $\Delta F=\pm1$ energy intervals were measured at small values of H for the $3d^74s^2\,{}^4F_{9/2,7/2,5/2,3/2}$ and $3d^84s\,{}^4F_{9/2,7/2,5/2}$ states. These energy intervals, however, are slightly altered even at zero field by hyperfine interactions with nearby atomic states. Values of the hyperfine-interaction constants extracted by use of Eq. (1) from the observed spacings will be referred to as uncorrected experimental values. When the observed spacings have been corrected for interactions with other atomic states, the corrected experimental values of the interaction constants may be determined. The corrections are thus not calculated directly, but are the differences between the corrected and uncorrected experimental values. The results are summarized in Table IV.[14]

Shifts in the zero-field hyperfine intervals of a state $3d^74s^2\,{}^4F_J$ may arise from hyperfine interactions (a) with other members of the ^4F multiplet, (b) with higher terms of $3d^74s^2$, or (c) with terms of $3d^84s$, particularly the nearby $3d^84s\,{}^4F$ term. Because of the very large separation between the $3d^74s^2\,{}^4F$ term and all other terms of its own configuration, the effects of type-(b) interactions should be negligible. Shifts of types (a) and (c) were calculated explicitly, except that no terms of $3d^84s$ higher than ^4F were considered. Thus, the energy shift in the $3d^74s^2\,{}^4F_{J,F}$ level was computed from the relation

$$\delta E(3d^74s^2\,{}^4F_{J,F})=\sum_{J'\neq J}\frac{|\langle 3d^74s^2\,{}^4F_{J,F}|\mathcal{H}_{\rm hfs}|3d^74s^2\,{}^4F_{J',F}\rangle|^2}{E(3d^74s^2\,{}^4F_J)-E(3d^74s^2\,{}^4F_{J'})}+\sum_{J'}\frac{|\langle 3d^74s^2\,{}^4F_{J,F}|\mathcal{H}_{\rm hfs}|3d^84s\,{}^4F_{J',F}\rangle|^2}{E(3d^74s^2\,{}^4F_J)-E(3d^84s\,{}^4F_{J'})}. \quad (4)$$

Both magnetic-dipole and electric-quadrupole hyperfine interactions were included. Expressions for the matrix elements required for the first term have been given by Childs.[15] The value used for $\langle 3d^74s^2\,{}^4F|r^{-3}|3d^84s\,{}^4F\rangle$ is not critical because the second term is very much smaller than the first. Because of the small size of this interconfiguration term, details of the calculation will not be given.

The zero-field hyperfine intervals of the $3d^84s\,{}^4F_J$ states are shifted by hyperfine interactions with $3d^74s^2\,{}^4F$ and $3d^84s\,{}^2F$ states as well as with the $3d^84s\,{}^4F_{J'}$ states. These shifts were calculated explicitly by use of the expression

$$\delta E(3d^84s\,{}^4F_{J,F})=\sum_{J'\neq J}\frac{|\langle 3d^84s\,{}^4F_{J,F}|\mathcal{H}_{\rm hfs}|3d^84s\,{}^4F_{J',F}\rangle|^2}{E(3d^84s\,{}^4F_J)-E(3d^84s\,{}^4F_{J'})}+\sum_{J'}\frac{|\langle 3d^84s\,{}^4F_{J,F}|\mathcal{H}_{\rm hfs}|3d^84s\,{}^2F_{J',F}\rangle|^2}{E(3d^84s\,{}^4F_J)-E(3d^84s\,{}^2F_{J'})}$$
$$+\sum_{J'}\frac{|\langle 3d^84s\,{}^4F_{J,F}|\mathcal{H}_{\rm hfs}|3d^74s^2\,{}^4F_{J',F}\rangle|^2}{E(3d^84s\,{}^4F_J)-E(3d^74s^2\,{}^4F_{J'})}. \quad (5)$$

Although the energy denominator of the second term is about six times that of the first, the matrix elements are correspondingly larger and the $^4F\leftrightarrow{}^2F$ hyperfine interaction is comparable to the $^4F\leftrightarrow{}^4F$ $(J'\neq J)$ interaction. For this reason, large uncertainties were arbitrarily assigned to the corrected experimental values of the hyperfine-interaction constants for the $3d^84s\,{}^4F$ states to allow for the effects of hyperfine interactions with states of $3d^84s$ still higher than ^2F. The interaction with $3d^74s^2\,{}^4F$ is very small in comparison. The expression for the matrix elements appearing in the first two terms is given in Ref. 15, except that because of the substantial departure of Co I from the LS limit, an additional term with a new parameter $a_l(s)$ should be added to the right-hand side of Eq. (A14) of Ref. 15 to characterize the contact magnetic-dipole hfs of the l^N core. The required term is

$$(-1)^{J'+I+F}\begin{Bmatrix}J & J' & 1\\ I & I & F\end{Bmatrix}[I(I+1)(2I+1)(2J+1)(2J'+1)]^{1/2}\delta(L,L')\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')(-1)^{S+L+J'+S_1+S'+\frac{1}{2}}$$
$$\times[(2S+1)(2S'+1)]^{1/2}\begin{Bmatrix}J & J' & 1\\ S' & S & L\end{Bmatrix}[S_1(S_1+1)(2S_1+1)]^{1/2}\begin{Bmatrix}S & S' & 1\\ S_1 & S_1 & \frac{1}{2}\end{Bmatrix}a_l(s). \quad (6)$$

[14] *Note added in proof.* Some of the results of Table IV differ from those published [W. J. Childs and L. S. Goodman, Bull. Am. Phys. Soc. **12**, 1046 (1967)] because the second term of Eq. (5) was not considered in the preliminary evaluation.

[15] William J. Childs, Phys. Rev. **156**, 71 (1967).

TABLE I. Summary of the observations of $\Delta F=0$ transitions in Co^{59}. The key to the labeling of the transitions is given in Table III. Two differences between observed and calculated values are given in the last two columns. The differences labeled "Uncorrected" result when the transition frequencies are calculated without taking account of hyperfine and Zeeman interactions with nearby atomic states. Those labeled "Corrected" result when such effects are explicitly included in the calculation. Although the χ^2 for the corrected set is lower than that for the uncorrected set for every state studied, the effect is most pronounced for the states $3d^74s^2\ {}^4F_{5/2,3/2}$. The residuals listed are for fits to all the observed transitions ($\Delta F=\pm1$ as well as $\Delta F=0$) for each state, and the parameters A, B, C, and g_J were varied simultaneously. (The value of g_I was considered known from high-precision nuclear-magnetic-resonance work.) The g values obtained from the uncorrected and corrected fits are given in Table IV in columns 3 and 5, respectively.

Configuration	State	H (G)	Transition	Observed frequency (Mc/sec)	$(\nu_{obs}-\nu_{calc})$ in kc/sec Uncorrected	Corrected
$3d^74s^2$	$^4F_{9/2}$	80	α	84.620(10)	−1	0
		100	α	105.993(9)	−4	−3
		200	α	214.209(12)	−5	−3
		200	γ	233.559(12)	7	5
		400	α	437.470(14)	−13	−9
		400	β	457.106(15)	3	3
		400	γ	484.027(15)	10	6
	$^4F_{7/2}$	100	β	88.241(11)	4	5
		100	α	87.737(8)	−4	−1
		100	δ	88.341(11)	5	2
		200	α	177.817(8)	0	5
		400	α	365.043(15)	−22	−12
		400	β	373.447(13)	10	11
		400	γ	383.004(15)	−5	−10
		400	δ	383.097(15)	12	−1
	$^4F_{5/2}$	400	α	253.478(14)	−23	−8
		400	β	242.013(15)	7	2
		400	γ	216.337(13)	13	−5
		720	α	476.557(15)	−45	−18
		720	β	468.054(20)	11	3
		720	γ	436.857(20)	65	38
	$^4F_{3/2}$	100	α	16.788(20)	3	−1
		400	β	46.851(10)	−22	0
		400	α	68.334(10)	16	−2
		1320	α	237.697(16)	83	3
		1320	β	174.208(12)	−59	−1
$3d^84s$	$^4F_{9/2}$	80	α	84.336(14)	−3	−5
		100	α	105.545(12)	−1	−3
		130	α	137.452(11)	4	1
		200	α	212.327(12)	10	7
		200	γ	230.218(13)	8	8
		400	β	445.847(15)	−4	−8
		400	γ	468.398(20)	−14	−14
		400	δ	499.129(15)	−1	1
		400	ϵ	533.619(14)	0	5
	$^4F_{7/2}$	200	α	176.438(15)	−19	−24
		200	γ	179.229(25)	20	21
		270	α	239.887(20)	22	15
		270	γ	244.950(20)	−11	−9
		270	δ	243.087(15)	−7	−2
		400	β	365.590(18)	6	3
		400	α	359.918(20)	9	−1
		400	γ	371.573(14)	4	8
		400	δ	368.608(20)	−13	−5
	$^4F_{5/2}$	200	α	123.534(11)	21	16
		200	γ	101.321(18)	17	24
		400	α	254.741(17)	9	−1
		400	β	243.549(16)	6	9
		400	γ	218.064(14)	−3	7
		720	α	481.068(20)	−14	−23
		720	β	473.865(25)	7	12
		720	γ	445.343(25)	−28	−23

TABLE II. Summary of the observations of $\Delta F=\pm 1$ transitions in Co^{59}. Although the residuals given in the last column are for calculations which include off-diagonal hyperfine effects, the *quality* of the fit to the $\Delta F=\pm 1$ observations is not markedly influenced by such corrections. The extent to which the *values* found for A, B, and C for each state depend on these corrections is indicated in Table IV.

Configuration	State	H (G)	Transition $(F, M \leftrightarrow F', M')$	Observed frequency (Mc/sec)	$(\nu_{obs}-\nu_{calc})$ (kc/sec)
$3d^74s^2$	$^4F_{9/2}$	0.962	(8, −3 ↔ 7, −3)	3655.596(25)	2
		1.000	(7, −2 ↔ 6, −2)	3169.558(15)	−3
		1.000	(6, −1 ↔ 5, −1)	2695.147(8)	1
		1.000	(5, 0 ↔ 4, 0)	2230.651(8)	2
		0.133	(5, 0 ↔ 4, 0)	2230.649(8)	−1
		0.133	(5, 0 ↔ 4, −1)	2230.827(6)	−2
		1.000	(4, 1 ↔ 3, 1)	1774.266(8)	0
	$^4F_{7/2}$	0.962	(7, −3 ↔ 6, −3)	3474.824(25)	2
		1.000	(6, −2 ↔ 5, −2)	2953.177(13)	−2
		1.000	(5, −1 ↔ 4, −1)	2443.193(15)	4
		1.000	(4, 2 ↔ 3, 2)	1942.912(10)	−1
	$^4F_{5/2}$	1.000	(4, 1 ↔ 3, 1)	2438.075(13)	1
		1.000	(5, −1 ↔ 4, −2)	3069.697(8)	0
		0.962	(6, −3 ↔ 5, −3)	3715.213(25)	0
	$^4F_{3/2}$	0.570	(4, −1 ↔ 3, −1)	4152.749(6)	3
		0.570	(4, 0 ↔ 3, 0)	4152.813(6)	3
		0.570	(4, 1 ↔ 3, 1)	4152.871(6)	−2
		1.000	(4, −2 ↔ 3, −2)	4152.586(6)	0
		1.000	(4, −1 ↔ 3, −1)	4152.692(6)	−6
		1.000	(4, 0 ↔ 3, 0)	4152.809(6)	−1
		1.000	(4, 1 ↔ 3, 1)	4152.922(10)	0
		1.000	(4, 2 ↔ 3, 2)	4153.037(6)	3
		1.000	(4, 3 ↔ 3, 3)	4153.151(6)	5
		1.000	(4, 4 ↔ 3, 3)	4153.248(6)	−9
		1.000	(5, −3 ↔ 4, −3)	5262.915(10)	0
$3d^84s$	$^4F_{9/2}$	1.000	(4, 3 ↔ 3, 2)	3338.442(12)	7
		1.000	(4, 4 ↔ 3, 3)	3338.158(13)	3
		1.000	(4, 2 ↔ 3, 1)	3338.715(25)	1
		0.500	(4, 4 ↔ 3, 3)	3337.895(15)	−4
		0.962	(4, 2 ↔ 3, 1)	3338.662(20)	−12
		0.986	(5, 0 ↔ 4, 0)	4161.528(20)	−14
		1.000	(6, −1 ↔ 5, −1)	4978.526(13)	4
		1.000	(7, −2 ↔ 6, −2)	5787.046(14)	0
		1.000	(8, −3 ↔ 7, −3)	6585.762(13)	0
	$^4F_{7/2}$	0.963	(4, 3 ↔ 3, 2)	2692.760(20)	21
		0.963	(4, 2 ↔ 3, 2)	2691.910(15)	3
		1.000	(5, −1 ↔ 4, −1)	3352.734(22)	−7
		0.500	(5, −1 ↔ 4, −1)	3352.719(15)	−22
		1.000	(6, −2 ↔ 5, −2)	4005.518(15)	18
		1.000	(7, −3 ↔ 6, −3)	4648.584(13)	−3
	$^4F_{5/2}$	5.000	(4, −1 ↔ 3, −1)	2260.524(30)	4
		5.000	(4, 1 ↔ 3, 2)	2260.722(18)	3
		1.000	(4, 1 ↔ 3, 1)	2261.530(20)	0
		1.000	(4, −1 ↔ 3, 0)	2260.883(20)	−12
		1.000	(4, 0 ↔ 3, 1)	2261.072(25)	9
		1.000	(6, −3 ↔ 5, −3)	3344.840(10)	0

The values used for the parameters are those obtained below from fitting the theoretical expressions for the interaction constants to the observed values.

For both the magnetic-dipole and electric-quadrupole hyperfine-interaction constants, the corrections caused by off-diagonal hfs interactions are seen to be larger than experimental error in almost every case, particularly in the case of the electric-quadrupole constants. Because of lack of precision in the measurements of the octupole interaction constants, little can be said about the relative size of the corrections to them; but the corrections could well be comparable to the values of the constants.

Table IV also gives the experimental results for the electronic g factors of the states studied. At nonzero values of the magnetic field H, transition frequencies

can be altered by both Zeeman and hyperfine interactions with nearby atomic states; and in fact, interference terms between the off-diagonal hfs and Zeeman interactions are important. Within an LS multiplet, these frequency shifts (which must be evaluated to obtain the corrected experimental values of g_J) can be calculated with Eq. (17) of Ref. 15 (perturbation theory). Since the computer program mentioned above (which diagonalizes the complete matrix of all J and F within a multiplet) is valid at arbitrary field, it was used instead to calculate the frequency shifts. Since the Zeeman operator does not connect states of $3d^74s^2$ with those of $3d^84s$, or those of $3d^84s\ ^4F$ with $3d^84s\ ^2F$, such interactions play no role.

It is seen that the corrections to the g_J values are not appreciably larger than experimental error in any case except for the $3d^74s^2\ ^4F_{3/2}$ state. Judd[16] has given the relation

$$(J+1)g_J-(J-1)g_{J-1}=aJ^2+b \qquad (7)$$

to be satisfied by the g factors of the members of an LS multiplet. Measurement of g_J in three states thus permits evaluation of the constants a and b, and leads

TABLE III. Convention for labeling the $\Delta F=0$ transitions observed. The labeling is the same for each of the two multiplets studied.

J	Transition $(F, M \leftrightarrow F', M')$	Label
$\frac{9}{2}$	$(8, -3 \leftrightarrow 8, -4)$	α
	$(7, -2 \leftrightarrow 7, -3)$	β
	$(6, -1 \leftrightarrow 6, -2)$	γ
	$(5, \ 0 \leftrightarrow 5, -1)$	δ
	$(4, \ 1 \leftrightarrow 4, \ 0)$	ϵ
$\frac{7}{2}$	$(7, -3 \leftrightarrow 7, -4)$	α
	$(6, -2 \leftrightarrow 6, -3)$	β
	$(5, -1 \leftrightarrow 5, -2)$	γ
	$(4, \ 0 \leftrightarrow 4, -1)$	δ
$\frac{5}{2}$	$(6, -3 \leftrightarrow 6, -4)$	α
	$(5, -2 \leftrightarrow 5, -3)$	β
	$(4, -1 \leftrightarrow 4, -2)$	γ
$\frac{3}{2}$	$(5, -3 \leftrightarrow 5, -4)$	α
	$(4, -2 \leftrightarrow 4, -3)$	β

TABLE IV. Summary of the experimental values of the hyperfine-interaction constants A, B, and C, and electronic g factor g_J for each state studied. The values in the third column are those obtained if the theory used for fitting the data takes no account of interactions (both hyperfine and Zeeman) between states of different SLJ. If such off-diagonal effects are allowed for explicitly, the values in the last column are found. They are to be considered the final, corrected values. The difference between the corrected and uncorrected values is listed in column 4. The corrections to both the magnetic-dipole and electric-quadrupole hyperfine-interaction constants are larger than experimental error in nearly every case. The corrections to the g factors are small except for the $3d^74s^2\ ^4F_{3/2}$ state.

State	Quantity measured	Observed (uncorrected) value (Mc/sec)	Correction (Mc/sec)	Corrected experimental value (Mc/sec)
$3d^74s^2\ ^4F_{9/2}$	A	450.287(1)	−0.004	450.283(1)
	B	139.655(30)	−0.425	139.230(30)
	C	0.001(3)	−0.001	0.000(3)
	g_J	1.33291(2)	−0.00002	1.33289(2)
$3d^74s^2\ ^4F_{7/2}$	A	490.580(2)	−0.013	490.567(2)
	B	95.099(36)	−0.598	94.501(36)
	C	0.002(4)	−0.002	0.000(4)
	g_J	1.23781(2)	−0.00003	1.23778(2)
$3d^74s^2\ ^4F_{5/2}$	A	613.376(3)	−0.027	613.349(3)
	B	68.232(43)	−0.691	67.541(50)
	C	0.001(3)	−0.003	−0.002(3)
	g_J	1.02827(2)	−0.00001	1.02826(2)
$3d^74s^2\ ^4F_{3/2}$	A	1043.007(1)	−0.026	1042.981(1)
	B	67.266(12)	+0.352	67.618(20)
	C	(Assumed to be 0; only two hyperfine intervals measured)		
	g_J	0.39911(2)	+0.00029	0.39940(2)
$3d^8(^3F)4s\ ^4F_{9/2}$	A	828.808(1)	−0.009	828.799(4)
	B	−117.633(25)	−1.118	−118.751(300)
	C	0.004(3)	−0.002	0.002(4)
	g_J	1.33340(2)	+0.00003	1.33343(4)
$3d^8(^3F)4s\ ^4F_{7/2}$	A	668.933(1)	−0.014	668.919(3)
	B	−79.248(38)	+0.027	−79.221(200)
	C	0.005(4)	−0.001	0.004(4)
	g_J	1.23658(2)	+0.00003	1.23661(4)
$3d^8(^3F)4s\ ^4F_{5/2}$	A	562.203(2)	−0.020	562.183(3)
	B	−54.902(21)	+0.096	−54.806(250)
	C	(Assumed to be 0; only two hyperfine intervals measured)		
	g_J	1.02708(2)	+0.00001	1.02709(4)

[16] B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

TABLE V. Values of the electronic g factors g_J for each state studied. The calculated values result from a least-squares fit to all the known optical levels of the three competing low, even-parity configurations $3d^74s^2$, $3d^84s$, and $3d^9$. The rms fit to all the levels is good to 15 cm^{-1}. The calculated values take explicit account of the Schwinger corrections, intermediate coupling, and the most important configuration-interaction effects; but small relativistic and diamagnetic corrections have not been included and they are felt to contribute the bulk of the small differences in column 4. For comparison, the last column gives the departure of the experimental values from the LS limit.

State	g_J (calc)	g_J (expt)	g_J(expt)$-g_J$(calc)	g_J(expt)$-g_J{}^{LS}$
$3d^74s^2\ {}^4F_{9/2}$	1.33355	1.33289(2)	−0.00066	−0.00122
${}^4F_{7/2}$	1.23842	1.23778(2)	−0.00064	−0.00087
${}^4F_{5/2}$	1.02884	1.02826(2)	−0.00058	−0.00038
${}^4F_{3/2}$	0.39970	0.39940(2)	−0.00030	+0.00079
$3d^84s\ {}^4F_{9/2}$	1.33398	1.33343(2)	−0.00055	−0.00068
${}^4F_{7/2}$	1.23706	1.23661(2)	−0.00045	−0.00204
${}^4F_{5/2}$	1.02759	1.02709(2)	−0.00050	−0.00155

to a prediction for the g factors of any remaining members of the multiplet. The expression, in addition to satisfying the Landé formula with the Schwinger correction, also takes account of spin-orbit mixing through second order and of relativistic and diamagnetic corrections to the g factors. Although it disregards the effects of configuration interaction, in lowest order (at least) such effects contribute nothing to the values of the g factor. If one evaluates a and b for the $3d^74s^2\ {}^4F$ term from the corrected g values of the $J=\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ states, one can predict the g factor of the ${}^4F_{9/2}$ state to be 1.33291(8), which is consistent with the (corrected) experimental value.

Development of Intermediate-Coupling Eigenvectors

Once the experimental values of the hyperfine-interaction constants have been corrected for the effects of hfs interactions with other atomic states as described above, the corrected values are available for testing the theory. The procedure will be (1) to develop intermediate-coupling wave functions in the LS basis for the states of interest, (2) to postulate the effective hyperfine Hamiltonians, (3) to work out the matrix elements of these operators between the LS basis states, (4) from these matrix elements and the wave functions, to develop expressions for the hfs interaction constants, and finally (5) to least-squares fit the theoretical expressions to the corrected experimental values of the hfs constants by varying the parameters that occur in the effective Hamiltonians. Comparison of the calculated g_J values with theory requires only step (1), since the operator which characterizes the g factor is diagonal in the LS scheme, and the g factor of each such basis state is well known.

The eigenvectors were calculated by Dr. M. S. Fred at Argonne National Laboratory on the CDC-3600 computer. All states of $3d^74s^2$, $3d^84s$, and $3d^9$ were considered simultaneously, and the appropriate parameters were varied to produce a best fit to all the known optical levels associated with these configurations. Configuration interaction between the three configurations mentioned was included explicitly, and interaction with higher configurations was taken into account by the techniques discussed by Rajnak and Wybourne.[17] A total of 17 parameters was varied to fit the 32 known levels; the rms error was 15 cm^{-1}. Table V compares the corrected experimental g_J values with the calculated values and with the LS limit. The remaining discrepancies are relatively independent of the state or configuration and are thought to be due to relativistic and diamagnetic corrections[16] which have not yet been applied to the theoretical values.

The eigenvectors produced by the computer program and used in the calculation of the g factors, while apparently of considerable accuracy, are not immediately suitable for use in predicting the hfs constants since they include states of three configurations. The hfs effective-operator theory refers explicitly to states of one configuration, and allows for configuration interaction by permitting the parameters in the hfs operators to vary freely. While the hfs interactions between states of different configurations can be worked out explicitly, additional radial parameters are required, and the amount of available data does not permit evaluation of them. For these reasons, it was decided to truncate (and, of course, renormalize) the eigenvectors to states of a single configuration.

Several methods for achieving such truncated eigenvectors are possible. The most straightforward is simply to make a least-squares fit, as described above, to the levels of only one configuration by varying the parameters associated with that configuration. Aside from its failure to make use of the more sophisticated wave functions already calculated, this approach has one principal disadvantage. It explicitly ignores configuration interaction and consequently the parameter values must change to fit the observed levels (whose energies are influenced strongly by configuration interaction). The eigenvectors will thus contain inaccuracies caused by these changes.

For these reasons, the procedure actually followed was to assume that the parameter values found above (with configuration interaction explicitly considered)

[17] B. G. Wybourne, Ref. 13, pp. 69–75; K. Rajnak and B. G. Wybourne, Phys. Rev. **132**, 280 (1963); G. Racah and J. Stein, *ibid.* **156**, 58 (1967).

are sufficiently good so that they should not be varied further. The configuration-interaction parameters were set equal to zero, and the eigenvectors were recalculated with no further parameter variation permitted. The result is that the eigenvector found for each state is artificially truncated (and renormalized) to a single configuration. The resulting set of truncated eigenvectors is undoubtedly subject to improvement, but works remarkably well for the $3d^74s^2$ configuration. A good test for the $3d^84s$ eigenvectors could not be made since insufficient data were available, as discussed below.

The (truncated) eigenvector of the $3d^74s^2\ {}^4F_{3/2}$ state in intermediate coupling is found to be

$$|{}^4F_{3/2}'\rangle=0.998671|{}^4F_{3/2}\rangle-0.043119|{}_3{}^2D_{3/2}\rangle+0.028074|{}_1{}^2D_{3/2}\rangle+0.003073|{}^2P_{3/2}\rangle+0.000492|{}^4P_{3/2}\rangle, \quad (8)$$

for example. All of the states involved are in the $3d^74s^2$ configuration. The lower-left subscript on the $^2D_{3/2}$ states refers to the seniority. While the $^4F_{3/2}'$ state is 99.7% pure, and 0.3% impurity can produce disproportionately large changes in the expectation values of operators that are not diagonal in the LS basis states. For example, if the matrix element of a hyperfine operator between the states $|{}^4F_{3/2}\rangle$ and $|{}_3{}^2D_{3/2}\rangle$ is comparable to the diagonal element, as is typically the case, a 9% change is produced by this portion of the 0.3% impurity. Clearly, a quantitative understanding of quantities measured as precisely as hyperfine-interaction constants requires that careful attention be paid to even very small impurities in the wave function.

Effective Hamiltonian and Its Matrix Elements between LS Basis States

Once one obtains the eigenvectors for all the states on which observations were made, the next step is to postulate the hfs Hamiltonians. For configurations of the type l^Ns, the effective Hamiltonian for the magnetic-dipole hyperfine interaction is taken to be

$$\mathcal{H}_{\rm hfs}(M1)=\sum_{i=1}^{N}[a(l)\mathbf{l}_i-(10)^{1/2}a(sC^2)(\mathbf{sC}^{(2)})_i{}^{(1)}+a_l(s)\mathbf{s}_i]\cdot\mathbf{I}+a_s(s)\mathbf{s}_{N+1}\cdot\mathbf{I}, \quad (9)$$

where the four quantities $a(l)$, $a(sC^2)$, $a_l(s)$, and $a_s(s)$ are to be treated as free parameters. For configurations l^N of equivalent electrons, the final term in Eq. (9) is, of course, dropped. This Hamiltonian, with varying nomenclature, has been discussed by several authors.[13,15,18] Near the LS limit, the effects of the two contact terms are indistinguishable. Sandars and Beck[18] have shown that such a Hamiltonian allows for the presence of relativistic effects, and Wybourne[13] has shown that in first order the effects of configuration interaction are absorbed by the parameters. Wybourne's analysis also shows that in first approximation the values of the parameters are independent of the particular state of the configuration considered. In the nonrelativistic limit and in the absence of configuration interaction, it can be shown that

$$a(l)=a(sC^2)=a_{nl}\equiv 2\beta\beta_N(\mu_I/I)\langle r^{-3}\rangle_{nl}, \qquad a_l(s)=0, \quad (10)$$

and that $a_s(s)=a_{ns}(s)$ is just the A factor of the unpaired s electron.

Matrix elements of this effective Hamiltonian are given by Eq. (A10) of Ref. 15, except that an additional term must be added because of the new term

$$\sum a_l(s)\mathbf{s}_i\cdot\mathbf{I} \quad \text{in} \quad \mathcal{H}.$$

The new term in the matrix element is given by Eq. (6) with J' replaced by J.

The effective operator for the electric-quadrupole hyperfine interaction is taken from Ref. 18 and for either l^N of l^Ns configurations may be expressed as

$$\mathcal{H}_{\rm hfs}(E2)=\mathbf{T}_n{}^{(2)}\cdot\sum_{i=1}^{N}\{P^{02}\mathbf{U}_i{}^{(02)2}+P^{13}\mathbf{U}_i{}^{(13)2}+P^{11}\mathbf{U}_i{}^{(11)2}\}, \quad (11)$$

where

$$\langle II|\mathbf{T}_n{}^{(2)}|II\rangle=\tfrac{1}{2}eQ \quad (12)$$

and P^{02}, P^{13}, and P^{11} are to be treated as parameters. The properties of the mixed unit tensor operators $\mathbf{U}^{(k_s,k_l)K}$ are discussed by Sandars[18] and by Judd.[19] Sandars[18] has shown that all three of these interactions are necessary to account for relativistic effects. However, Wybourne[13] shows that in lowest order the presence of configuration interaction does not require the operators $\mathbf{U}^{(13)2}$ or $\mathbf{U}^{(11)2}$, but simply multiplies the

TABLE VI. The result of a least-squares fit of the three-parameter theoretical expressions (in intermediate coupling) to the four corrected experimental values of the $3d^74s^2\ {}^4F$ magnetic-dipole hyperfine-interaction constants A_J. All of the A factors are fitted to within 0.0026% with the parameter values listed. Nevertheless, it is clear that the fit is not within experimental error. It is likely that very slight inaccuracies in the intermediate-coupling wave functions used give rise to the small discrepancies. Such a critical test of the theory and of the eigenvectors is possible only because of the extreme precision obtainable in measuring hyperfine-interaction constants. Parameter values: $a(l)=692.316$ Mc/sec; $a(sC^2)=749.239$ Mc/sec; and $a(s)=-86.014$ Mc/sec.

State	$A_{\rm calc}$ (Mc/sec)	$A_{\rm expt}$ (Mc/sec)	$A_{\rm expt}-A_{\rm calc}$ (Mc/sec)
$^4F_{9/2}$	450.289	450.283(1)	−0.006(1)
$^4F_{7/2}$	490.554	490.567(2)	+0.013(2)
$^4F_{5/2}$	613.358	613.349(3)	−0.009(3)
$^4F_{3/2}$	1042.980	1042.981(1)	+0.001(1)

[18] P. G. H. Sandars and J. Beck, Proc. Roy. Soc. (London) A289, 97 (1965).

[19] B. R. Judd, J. Math. Phys. 3, 557 (1962); B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Co., New York, 1963).

matrix element of the first operator $\mathbf{U}^{(02)2}$ by a constant which is independent of the state of the configuration. Thus Sandars takes any interaction of the other two types as evidence of a relativistic effect.

The matrix element of this Hamiltonian, between states of the same J, may be written

$$\langle l^N\alpha_1S_1L,s;\,SLJIFM\,|\,\mathcal{H}_{\rm hfs}(E2)\,|\,l^N\alpha_1'S_1'L',s;\,S'L'JIFM\rangle=\langle FM\,|\,Q_{\rm op}\,|\,FM\rangle\left\{\frac{4J(2J+1)(2J-1)}{(J+1)(2J+3)}\right\}^{1/2}$$

$$\times\Bigg\{(-1)^{S+L'+J}\delta(S,S')\begin{Bmatrix}J & J & 2\\ L' & L & S\end{Bmatrix}\langle l^N\alpha_1S_1L\|U^{(2)}\|l^N\alpha_1'S_1'L'\rangle\left\{\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right\}^{1/2}b_{02}$$

$$+\begin{Bmatrix}S & S' & 1\\ L & L' & 3\\ J & J & 2\end{Bmatrix}\langle l^N\alpha_1S_1L\|V^{(13)}\|l^N\alpha_1'S_1'L'\rangle\left[(-1)^{S_1+S'-\frac{1}{2}}\begin{Bmatrix}S & S' & 1\\ S_1' & S_1 & \frac{1}{2}\end{Bmatrix}\{(2S+1)(2S'+1)\}^{1/2}\right]b_{13}+\begin{Bmatrix}S & S' & 1\\ L & L' & 1\\ J & J & 2\end{Bmatrix}$$

$$\times\langle l^N\alpha_1S_1L\|V^{(11)}\|l^N\alpha_1'S_1'L'\rangle\left[(-1)^{S_1+S'-\frac{1}{2}}\begin{Bmatrix}S & S' & 1\\ S_1' & S_1 & \frac{1}{2}\end{Bmatrix}\{(2S+1)(2S'+1)\}^{1/2}\right]b_{11}\Bigg\} \quad (13)$$

for l^Ns. For l^N, the left-hand side becomes

$$\langle l^N\alpha SLJIFM\,|\,\mathcal{H}_{\rm hfs}(E2)\,|\,l^N\alpha'S'L'JIFM\rangle.$$

On the right-hand side, α_1 and S_1 are replaced by α and S, respectively, α_1' and S_1' by α' and S', and the square brackets become unity. The three parameters b_{k_s,k_l} are proportional to the parameters P^{k_s,k_l} appearing in the Hamiltonian. Thus we have

$$b_{02}=\left\{\frac{b_{nl}}{e}\left[\frac{(2l-1)(2l+3)}{2l(l+1)(2l+1)}\right]^{1/2}\frac{1}{\langle r^{-3}\rangle_{nl}}\right\}P^{02},$$

$$\begin{pmatrix}b_{13}\\ b_{11}\end{pmatrix}=\left\{\frac{b_{nl}}{3e}[2\cdot3\cdot5]^{1/2}\right\}\frac{1}{\langle r^{-3}\rangle_{nl}}\begin{pmatrix}P^{13}\\ P^{11}\end{pmatrix}. \quad (14)$$

One may treat the quantities b_{k_s,k_l} as independent parameters, to be evaluated by fits to the observed B factors. Alternatively, if configuration interaction is ignored, Sandars[18] has shown that the b_{k_s,k_l} may be evaluated in terms of certain integrals of the relativistic radial wave functions. If such integrals (or wave functions) are not available, the Casimir factors tabulated by Kopfermann[20] for l^N configurations may be used, subject to their known deficiencies. With this approximation, for l^N configurations, the three parameters are given by

$$b_{02}=\frac{b_{nl}}{(2l+1)^2}[(l+2)(2l-1)R_r(l+\tfrac{1}{2},Z_i)+(l-1)(2l+3)R_r(l-\tfrac{1}{2},Z_i)+6S_r(l,Z_i)]\approx b_{nl},$$

$$b_{13}=-\frac{2}{5}\frac{b_{nl}}{(2l+1)}\left\{\frac{105(l+2)(l-1)l(l+1)}{(2l+3)(2l+1)(2l-1)}\right\}^{1/2}\times[(2l-1)R_r(l+\tfrac{1}{2},Z_i)-(2l+3)R_r(l-\tfrac{1}{2},Z_i)+4S_r(l,Z_i)]\approx0,$$

$$b_{11}=-\frac{2}{5}\frac{b_{nl}}{(2l+1)}\left\{\frac{30l(l+1)}{2l+1}\right\}^{1/2}[-(l+2)R_r(l+\tfrac{1}{2},Z_i)+(l-1)R_r(l-\tfrac{1}{2},Z_i)+3S_r(l,Z_i)]\approx0, \quad (15)$$

where Z_i is taken to be about $Z-11$ for d electrons ($l=2$). Note that in the absence of relativity and configuration interaction $b_{13}=b_{11}=0$, and b_{02} approaches the value

$$b_{nl}=e^2Q\langle r^{-3}\rangle_{nl}. \quad (16)$$

The reduced matrix elements $\langle l^N\alpha_1S_1L\|U^{(2)}\|l^N\alpha_1'S_1'L'\rangle$ and $\langle l^N\alpha_1S_1L\|V^{(11)}\|l^N\alpha_1'S_1'L'\rangle$ are tabulated for $l\leqslant3$ by Nielson and Koster.[21] Values of

$$\langle l^N\alpha_1S_1L\|V^{(13)}\|l^N\alpha_1'S_1'L'\rangle$$

may be worked out[22] from Eq. (2-101) of Ref. 13 by using the coefficients of fractional parentage given in Ref. 21. Equations (15) will not be as good an approximation for l^Ns configurations since the radial wave functions may be different from those for l^N.

[20] H. Kopfermann, *Nuclear Moments*, translated by E. E. Schneider (Academic Press Inc., New York, 1958), pp. 445–449.

[21] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (The MIT Press, Cambridge, Mass., 1963).

[22] Values of $\langle l^N\alpha SL\|V^{(1x)}\|l^N\alpha'S'L'\rangle$ may also be obtained from R. I. Karaziya, Ya. I. Vibraraite, Z. B. Rudsikas, and A. P. Yutsis, *Tables for the Calculation of Matrix Elements of Atomic Operators* (in Russian) (Akademiya Nauk SSSR, Moscow, 1967). In taking values of $\langle l^N\alpha SL\|U^{(1x)}\|l^N\alpha'S'L'\rangle$ from the table, however, note that the quantity they define is $(2S+1)^{1/2}$ times the one defined in Refs. 13 and 21, for example.

Intermediate-Coupling Expressions for the Hyperfine-Interaction Constants

The procedure for obtaining the required eigenvectors in the LS scheme has been described, and expressions for the matrix elements between such basis states (only elements diagonal in J are required) have been given or referred to. Comparison of these expressions with Eqs. (1)–(3) makes it possible to separate the F-dependent parts from the remainder in the conventional way. The remainder is thus seen to be the parametrized theoretical expression for the A or B factor between the bra and ket appearing in the particular matrix element evaluated. With this procedure and the eigenvectors already found, expressions for the A and B factors for the real states in intermediate coupling are readily obtainable. The expression for the magnetic-dipole hyperfine-interaction constant for the $3d^8(^3F)4s\ ^4F_{5/2}$ state in intermediate coupling is found to be

$$A(3d^8 4s;\ ^4F_{5/2}') = 0.972467a(l) + 0.050186a(sC^2) + 0.046724a_l(s) - 0.019191a_s(s), \quad (17)$$

for example. [A sum rule stating that the coefficients of $a(l)$, $a_l(s)$, and $a_s(s)$ must add up to unity for each state, regardless of the degree of intermediate coupling, is readily established for $l^N s$ configurations and constitutes a useful check on such calculations. For l^N configurations, the sum of the coefficients of $a(l)$ and $a_l(s)$ must be unity.] It is instructive to compare this expression with the corresponding one obtained in the LS limit, namely,

$$A(3d^8 4s;\ ^4F_{5/2}) = 0.971428a(l) + 0.066939a(sC^2) + 0.019048a_l(s) + 0.009524a_s(s). \quad (18)$$

Although the effect of extremely small admixtures in the eigenvector [a typical eigenvector is given in Eq. (8)] on the coefficient of $a(l)$ is small, the effect on the coefficients of the other parameters may be relatively very large. For example, the coefficient of $a_s(s)$ in the example above has changed sign in the transition to intermediate coupling. This emphasizes the importance of retaining both contact terms in $\mathcal{H}_{\rm hfs}(M1)$ when the degree of intermediate coupling is substantial.

Similar expressions are obtained for the electric-quadrupole hyperfine-interaction constants. The expression for the $3d^7 4s^2\ ^4F_{7/2}$ state in intermediate coupling is

$$B(3d^7 4s^2;\ ^4F_{7/2}') = 0.190125b_{02} + 0.036360b_{13} - 0.129610b_{11}, \quad (19)$$

for example.

Comparison of the Effective-Operator Theory with Experiment

Once expressions are obtained in intermediate coupling for the hyperfine-interaction constants of the states in question, they may be fitted to the corrected experimental values of the constants by varying the parameters involved. It should be noted that while the relative signs of A, B, and C were measured for each state, the absolute signs were not. That they are as indicated is inferred from the known sign of μ_I and from the very-high order of agreement between the experimental values (with the signs as indicated) and the theory. Table VI shows the results of such a fit to the magnetic-dipole hyperfine-interaction constants of the states $3d^7 4s^2\ ^4F_{9/2,7/2,5/2,3/2}$. The measured values of A_J for the four states are fitted by the three-parameter theoretical expressions to 0.013 Mc/sec out of 490 Mc/sec, i.e., to 0.0026%. It may be noted that the χ^2 for fitting the same data with three-parameter theoretical expressions calculated for the LS limit is 14 000 times larger. The importance of very slight admixtures is thus apparent. In spite of the extremely high quality of the fit obtained, however, it is not within experimental error. It is likely that the remaining discrepancy is mostly attributable to very slight inaccuracies in the intermediate-coupling wave functions used. Higher order configuration-interaction effects could also be responsible.

The values found for the parameters are given in the table. The ratio $a(sC^2)/a(l)$, which is unity in the absence of configuration interaction and in the nonrelativistic limit, is seen to be 1.082. If configuration interaction is ignored, expressions analogous to Eqs. (15) (with Casimir factors) predict a ratio of 1.006 relativistically. That the value of this ratio departs from unity by more than 10 times the amount predicted by the relativistic theory indicates strongly that the effect is due primarily to configuration interaction. Another indication of this is in the fact that the value found for $a_l(s)$ is more than 50 times the value calculated from the relativistic theory in the absence of configuration interaction. The large contact term is interpreted as arising primarily from so-called core polarization, which may be viewed as configuration interaction with states of the type $nsn's(^1S_0)3d^7\ ^4F_J$. The extreme closeness of the terms $3d^7 4s^2\ ^4F$ and $3d^8(^3F)4s\ ^4F$ presumably also leads to a strong Coulomb mixing with resultant effects on the values of the parameters required for a best fit to the data.

Table VII presents the results obtained when the theoretical expressions for the electric-quadrupole hyperfine-interaction constants B_J for the states $3d^7 4s^2\ ^4F_J$ were fitted to the corrected experimental values. The one-parameter fit given in the third column is for a relativistic calculation in which the quantities b_{02}, b_{13}, and b_{11} are evaluated in terms of the single parameter b_{3d} by means of Eqs. (15). Although the J dependence of the B factors is fitted to within 0.6%, the calculated values depart from the measured values by much more than the probable error in every case. Column 4 gives the results of a similar 3-parameter

TABLE VII. The results of two least-squares fits of the theoretical expressions for the electric-quadrupole hyperfine-interaction constants B_J to the corrected experimental values for the $3d^74s^2\,{}^4F$ multiplet of Co^{59}. Both fits are in intermediate coupling. The one-parameter fit explicitly includes relativistic effects by the use of Casimir factors. The three-parameter fit again includes all three types of tensor interaction, but allows the relative amount of each to be characterized by a separate parameter. The three-parameter fit is consistent with the experimental results while the one-parameter fit is not.

State	B_{expt} (Mc/sec)	One-parameter fit $B_{\text{expt}}-B_{\text{calc}}$ (Mc/sec)	Three-parameter fit $B_{\text{expt}}-B_{\text{calc}}$ (Mc/sec)
$3d^74s^2\,{}^4F_{9/2}$	139.230(30)	−0.330(30)	+0.005(30)
${}^4F_{7/2}$	94.501(36)	+0.400(36)	−0.048(36)
${}^4F_{5/2}$	67.541(50)	+0.418(50)	+0.063(50)
${}^4F_{3/2}$	67.618(20)	−0.288(20)	−0.018(20)

fit in which b_{02}, b_{13}, and b_{11} are simply treated as free parameters. The calculated values are now seen to be consistent with the measured values to within the $\sim 0.06\%$ probable errors. The values of the parameters found in the two fits will be discussed below after giving similar results for the $3d^84s\,{}^4F$ multiplet.

It may be noted from Eq. (9) that four parameters will be required to fit the magnetic-dipole hfs of states of the $3d^84s$ configuration in intermediate coupling. Since the A factors were measured for only three states, no test of the theory can be made, nor, in fact, can the parameters be evaluated uniquely. If it is arbitrarily assumed that the ratio $a(sC^2)/a(l)$ is unity to within 20%, as is found[23] for all known cases of $3d^N4s^2$ atoms, then tentative limits may be placed on the values of the other parameters. In this way it is inferred that $a(l)=636\pm4$ Mc/sec, $a(sC^2)=636\pm125$ Mc/sec, $a_l(s)=-175\pm17$ Mc/sec, and $a_s(s)=4200\pm85$ Mc/sec. To the extent that the spin-orbit parameter ζ_{3d} is regarded as being proportional to $\langle r^{-3}\rangle_{3d}$, one can estimate the value of $a(l)$ for $3d^84s$ from the value of $a(l)$ found for $3d^74s^2$ and the values found for ζ_{3d} in the two configurations. The value 622 Mc/sec is obtained in this way. The 2% difference is very small considering the uncertainties. The value 4200 ± 85 Mc/sec found for $a_s(s)$ is within 20% of the 5100 Mc/sec expected for a_{4s} from the known value of g_I and the optical energies of the levels $3d^8({}^3F)ns\,({}^4F_J)$ with $n=4$, 5 according to the theory summarized by Wybourne.[24]

For the electric-quadrupole hyperfine interaction in $3d^84s\,{}^4F$, the $4s$ electron plays no role and we have three parameters as before, and three measured values of the interaction constant. Thus although no test of the theory can be made, the three parameters can be evaluated. Table VIII gives the values found for the parameters for both multiplets. It is seen that for both configurations, the value of b_{02}, which approaches $b_{3d}\equiv e^2Q\langle r^{-3}\rangle_{3d}$ in the nonrelativistic limit, is much larger than that of b_{13} or b_{11} which both approach zero in the same limit. If relativistic effects alone are responsible for the nonzero values of b_{13} and b_{11}, their expected values may be calculated. If (in the absence of relativistic radial wave functions) the same Casimir factors are used in Eq. (15) for $3d^74s^2$ and $3d^84s$, one predicts $b_{13}=13.6$ Mc/sec, $b_{11}=-2.3$ Mc/sec for $3d^74s^2\,{}^4F_J$, and with less accuracy, $b_{13}\approx 11$ Mc/sec and $b_{11}\approx -2$ Mc/sec for the same term of $3d^84s$. There appears to be definite inconsistency between the values required to fit the B factors for the $3d^74s^2\,{}^4F$ term and the values predicted by use of Casimir factors, even if the value of the effective charge Z_i (on which the Casimir factors depend) is allowed to vary. For the $3d^84s$ configuration, the disagreement is not conclusive because of the much larger uncertainties in the corrected experimental values (for reasons discussed above), and the less accurate knowledge of the integrals of the radial wave functions for $3d^84s$. Two conclusions may be drawn: (1) all three of the tensor interactions in the effective quadrupole Hamiltonian, Eq. (11), are required to fit the $3d^74s^2\,{}^4F$ data, and (2) the values found for the parameters characterizing the operators $\mathbf{U}^{(11)2}$ and $\mathbf{U}^{(13)2}$ cannot be understood on the basis of the Casimir factors. Possible sources of the discrepancy are (a) substantial inaccuracies in the Casimir factors, and (b) higher-order effects of configuration interaction (with intermediate coupling).

Nuclear Electric-Quadrupole Moment

Since $b_{02}=b_{3d}$ to within 1%, the apparent value of the electric-quadrupole moment can be obtained readily by Eq. (16) from the value found for b_{02}. The value obtained for the quadrupole moment is quite insensitive to the uncertainties in the magnitudes of b_{13} and b_{11} discussed above. The constant of proportionality relating b_{02} and b_{3d} is given by Eq. (15) and is so near unity that any uncertainty in this factor is completely overshadowed by uncertainties in Sternheimer shielding.[25] The value of $\langle r^{-3}\rangle_{3d}$ may be obtained, for each configuration, from Eq. (10) and the experimental values of $a(l)$. Thus,

$$Q=\frac{2\beta\beta_N}{e^2}\left(\frac{\mu_I}{I}\right)\frac{b_{3d}}{a_{3d}}, \tag{20}$$

and we obtain the values

$$\begin{aligned} Q(\mathrm{Co}^{59},3d^74s^2;{}^4F)&=+0.380b,\\ Q(\mathrm{Co}^{59},3d^84s;{}^4F)&=+0.345b. \end{aligned} \tag{21}$$

The ratio of these numbers is

$$\frac{Q(\mathrm{Co}^{59},3d^74s^2;{}^4F)}{Q(\mathrm{Co}^{59},3d^84s;{}^4F)}=\left(\frac{b_{3d}}{a_{3d}}\right)_{3d^74s^2}\Big/\left(\frac{b_{3d}}{a_{3d}}\right)_{3d^84s}$$
$$=1.10\pm0.02, \tag{22}$$

[23] W. J. Childs, Phys. Rev. 160, 9 (1967).
[24] B. G. Wybourne, Ref. 13, pp. 130–131.
[25] R. M. Sternheimer, Phys. Rev. 146, 140 (1966). References to earlier work are included.

where the 2% uncertainty arises from uncertainty in the values of b_{3d} and a_{3d} for the $3d^84s$ configuration. The 2% error limit may be too small if $a(sC^2)/a(l)$ differs from unity by substantially more than 20% for the $3d^84s$ configuration.

It has been mentioned that the degree of Sternheimer shielding[25] is uncertain and that such shielding could cause a substantial difference between the true quadrupole moment and the value obtained from either configuration. In lowest order, such shielding causes the same shift in the apparent value of b_{02} (and hence Q) for every state of a given configuration; and consequently this shift cannot be determined in the present experiment. If one arbitrarily takes the mean of the two measured values, and assigns a 20% error to cover shielding uncertainties, the value

$$Q(\mathrm{Co}^{59}) = +0.36(7)b \qquad (23)$$

is obtained. This is consistent with the value obtained by von Ehrenstein[2] and also with earlier optical values.

CONCLUSIONS

It has been shown that the effective-operator theory of Sandars and Beck is capable of accounting for the hfs of an unclosed electron shell l^N to an extremely high accuracy, even in the presence of substantial spin-orbit mixing and some configuration interaction. The small difference between theory and experiment for the $3d^74s^2$ configuration of Co^{59} is probably due to very small inaccuracies in the intermediate-coupling wave functions used.

It was not possible to test the theory as carefully for the $3d^84s$ configuration because sufficient data were not obtainable.

While all three of the second-rank tensor interactions expected in the Sandars-Beck theory for the electric-quadrupole interaction are required to fit the data, the relative magnitudes found for the interactions are not understood for either the $3d^74s^2$ or $3d^84s$ configurations. It is possible that the use of true relativistic radial wave functions (when available) rather than the (approximate) Casimir factors would lead to better agreement between the relativistic theory and the experimental results. It is likely that higher-order configuration-interaction effects are also playing a role. The next step might be to increase the set of basis states to include all states of the three configurations $3d^74s^2$, $3d^84s$, and $3d^9$ explicitly.

TABLE VIII. Values of the effective-operator parameters required to fit the corrected experimental values of the electric-quadrupole hyperfine-interaction constants B for two multiplets in Co^{59}. The parameters b_{11} and b_{13}, which approach zero in the nonrelativistic limit, are seen to be much smaller than b_{02}, which approaches the value $b_{3d} \equiv e^2Q\langle r^{-3}\rangle_{3d}$ in the same limit. The relativistic theory predicts values of b_{11} and b_{13} that are much smaller than the values required to fit the $3d^74s^2\ {}^4F$ data. The reason for the failure of the theory in this respect is not understood, although inaccuracies in the Casimir factors, and higher order configuration-interaction effects (in the presence of intermediate coupling) very likely play a role.

Parameter	$3d^74s^2\ {}^4F$ (Mc/sec)	$3d^84s\ {}^4F$ (Mc/sec)
b_{02}	+487.698±5.6	+406.717± 8.1
b_{11}	−7.181±0.9	+9.859±11.1
b_{13}	+24.582±1.2	+12.943± 5.0

A value for the electric-quadrupole moment Q of the Co^{59} nuclear ground state is obtained independently from measurements in two electron configurations. The difference between the values obtained is well outside experimental error and is presumably due to different Sternheimer shielding in the two configurations. The final value obtained for Q is consistent with earlier determinations, and is not unreasonable for a nucleus with a single proton hole in the $f_{7/2}$ shell.

The experimental values obtained for the electronic g factors of the states examined differ from the theoretical values by an amount which is small and roughly the same for each state examined. It is felt that the small differences are due to failure to make appropriate relativistic and diamagnetic corrections to the theoretical g values before comparison with experiment. The discrepancies are of the right sign and approximate magnitude to be understood in this way.

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