Hyperfine Structure and Quadrupole Moment of Lanthanum-139

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We have studied the hyperfine structure of La^{139} in the ground level $5d6s^2\,{}^2D$ by the atomic-beam magnetic resonance method. The beam of lanthanum atoms was detected by a hot tungsten filament operated at 2680±30°K. Of the eight hyperfine intervals resulting from the interaction of a nuclear spin of $\frac{7}{2}$, with the J values of the ground state, seven have been measured. They are, for $J=\frac{5}{2}$,

$$\nu_1=W(F=6)-W(F=5)=1120.902\pm0.005 \text{ Mc/sec},$$
$$\nu_2=W(F=5)-W(F=4)=912.793\pm0.005 \text{ Mc/sec},$$
$$\nu_3=W(F=4)-W(F=3)=716.288\pm0.003 \text{ Mc/sec},$$
$$\nu_4=W(F=3)-W(F=2)=529.090\pm0.010 \text{ Mc/sec},$$

and for $J=\frac{3}{2}$,

$$\nu_6=W(F=5)-W(F=4)=737.967\pm0.015 \text{ Mc/sec},$$
$$\nu_7=W(F=4)-W(F=3)=551.987\pm0.005 \text{ Mc/sec},$$
$$\nu_8=W(F=3)-W(F=2)=391.603\pm0.010 \text{ Mc/sec}.$$

From these values the magnetic dipole interaction constants are found to be $A'(J=\frac{5}{2})=182.1706\pm0.0006$ and $A''(J=\frac{3}{2})=141.1959\pm0.0016$ Mc/sec, the quadrupole interaction constants to be $B'=54.213\pm0.014$, and $B''=44.781\pm0.014$ Mc/sec, while the octupole interaction constants are zero within the accuracy of the present experiment. The unobserved line of the ${}^2D_{5/2}$ hyperfine multiplet is calculated to be $\nu_5=W(F=2)-W(F=1)=348.843\pm0.014$ Mc/sec. A serious discrepancy was noted between the observed A values, both relatively and absolutely, and those given by theory. The assumption of s-configuration mixing apparently resolved this difficulty. The values of the nuclear quadrupole moment calculated from B' and B'' are fairly consistent with each other. The average value, after application of the Sternheimer correction is $Q=(0.268\pm0.010)\times10^{-24}$ cm^2.

I. INTRODUCTION

THE nuclear spin and magnetic moment of $_{57}La^{139}$ were determined early in 1934 by optical studies[1] of hyperfine structure in the excited states. Later Dickinson[2] and Sheriff and Williams[3] made accurate measurements of the magnetic moment by the nuclear resonance technique. More recently and again by optical methods, Murakawa and Kamei[4] and Lührs[5] deduced approximate values for the quadrupole moment of the nucleus. Their optical data on hyperfine structure constants facilitated the search for resonances in the present atomic-beam experiment.

In applying the atomic-beam technique to the study of the hyperfine structure of La^{139}, there was at first considerable difficulty with the detection. After this difficulty was resolved, low-frequency transitions of $\Delta F=0$ were observed, both in the ground state ${}^2D_{\frac{3}{2}}$ and in the metastable state ${}^2D_{\frac{5}{2}}$. With a nuclear spin of $\frac{7}{2}$, there should be eight hyperfine intervals in these two states. Inasmuch as three intervals at least are needed to determine the electronic interaction with a nuclear magnetic octupole,[6] if it be nonzero, it was thought advantageous to measure as many intervals as possible among the eight. In this experiment seven have been measured, the unobserved one being in the ${}^2D_{\frac{5}{2}}$ hyperfine multiplet. For the interpretation of the observed intervals it was found sufficient to assume only a dipole and a quadrupole interaction. Any repulsion between hyperfine levels of the ground doublet,[7] for instance, turned out to be less than the experimental error.

The evaluation of the experimental results gave very accurate values for the magnetic dipole interaction constants A' and A''. However, the A constants do not bear the proper ratio to each other required by the theory of hyperfine structure,[8] and are incompatible with the known nuclear magnetic moment.[2,3] By assuming the mixing of a higher s configuration with the ground configuration $5d6s^2$, one may solve for corrected constants A_0' and A_0'' from the observed A values. The solution has been carried out. The resulting A_0' and A_0'' bear the proper theoretical ratio to each other, and are compatible with the known nuclear magnetic moment.

The experimental results gave less accurate values for the quadrupole interaction constants B' and B''. The quadrupole moments deduced from them are however fairly consistent with each other and are in good agreement with earlier optical data.[5] The results will be compared with theory.

Since the octupole interaction is small for D states, the corresponding interaction constants C are expected to be very small. The accuracy in the present work is not sufficient to place a close limit on the octupole moment.

II. THEORY

A. First-Order Energy Level Diagram

The first-order energy of the perturbation Hamiltonian arising from noncentral interactions between

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1 O. E. Anderson, Phys. Rev. **45**, 685 (1934); **46**, 473 (1934); M. F. Crawford, Phys. Rev. **47**, 768 (1935).
2 W. C. Dickinson, Phys. Rev. **76**, 1414 (1949).
3 R. E. Sheriff and D. Williams, Phys. Rev. **82**, 651 (1951).
4 K. Murakawa and T. Kamei, Phys. Rev. **92**, 325 (1953); K. Murakawa, Phys. Rev. **98**, 1285 (1955); J. Phys. Soc. Japan **10**, 927 (1955).
5 Gerold Lührs, Z. Physik **141**, 486 (1955).
6 Jaccarino, King, Satton, and Stroke, Phys. Rev. **94**, 1798 (1954); H. B. G. Casimir and Karreman, Physica **9**, 494 (1942).
7 H. G. B. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, Haarlem, 1936), p. 221.
8 C. Schwartz, Phys. Rev. **97**, 380 (1955).

electrons and the atomic nucleus is, up to and including the octupole term,

$$W_F=\tfrac{1}{2}AK+B\frac{\frac{3}{8}K(K+1)-\frac{1}{2}I(I+1)J(J+1)}{I(2I-1)J(2J-1)}+C\frac{20[K^3+4K^2+\frac{4}{5}K\{3+J(J+1)+I(I+1)-3I(I+1)J(J+1)\}-4I(I+1)J(J+1)]}{2I(2I-1)(2I-2)(2J)(2J-1)(2J-2)}. \quad (1)$$

The interaction constants A, B, and C as separated from the geometric coefficients K, etc., represent, respectively, the effect of the magnetic dipole, electric quadrupole, and magnetic octupole moments. The explicit forms[8] of A, B, and C are, for one electron outside closed shells or subshells,

$$A=g_I\frac{\beta_e\beta_N}{h\times10^6}\left(\frac{2l(l+1)}{J(J+1)}\right)\left[F\left\langle\frac{1}{r_e^3}\right\rangle\right]_J \text{ Mc/sec}, \quad (2a)$$

$$B=\frac{e^2Q}{h\times10^6}\left(\frac{2J-1}{2J+2}\right)\left[R\left\langle\frac{1}{r_e^3}\right\rangle\right]_J \text{ Mc/sec}, \quad (2b)$$

$$C=\Omega\left[\frac{Z\delta T}{H}\frac{\beta_e\beta_N}{2.911h\times10^3a_0^5}\right]\times\left[\frac{80l(l+1)}{2l+1\pm3}\frac{(2l-2)!}{(2l+3)!}\frac{4J^2-1}{(2J+4)(2J+2)}\right] \text{ kc/sec}, \quad (2c)$$

where the signs ($\pm$) are for $J=l\pm\frac{1}{2}$. In Eq. (2), δ is the fine-structure doublet splitting in cm^{-1}, Z the effective nuclear charge, a_0 the Bohr radius; β_e and β_N are, respectively, the Bohr magneton and the nuclear magneton; Ω is the octupole moment in units of nuclear magneton cm^2; and F, R, T, and H are relativity correction factors. The mean value $\langle 1/r_e^3\rangle$ is usually determined from the fine-structure doublet formula:

$$\delta=2.911HZ(2l+1)\langle a_0^3/r_e^3\rangle \text{ cm}^{-1}. \quad (2d)$$

These formulas for A, B, and C take into account only the part of interaction potential external to the nuclear volume, and hence do not include nuclear structure effects.[9]

In the presence of an external magnetic field $\mathbf{H}$, the interaction Hamiltonian has the additional terms

$$g_J\beta_e\mathbf{J}\cdot\mathbf{H}-g_I\beta_N\mathbf{I}\cdot\mathbf{H} \quad (3)$$

which removes the degeneracy of W_F with respect to M_F. The hyperfine intervals observed at weak fields can be easily corrected to zero field by standard formulas of perturbation theory. The numerical results of such corrections expressed in powers of the field-calibration frequency will be given in Sec. IIID. For the case of La^{139}, $I=\frac{7}{2}$, $J=\frac{3}{2}, \frac{5}{2}$, the qualitative variation of the energy levels as a function of the external field is shown in Fig. 1. In calculating the variation, only the magnetic dipole interaction is taken into account and perturbation methods are used in the limiting regions of very weak fields and very strong fields. The high-frequency lines ($\Delta F=\pm1$) chosen for the measure-

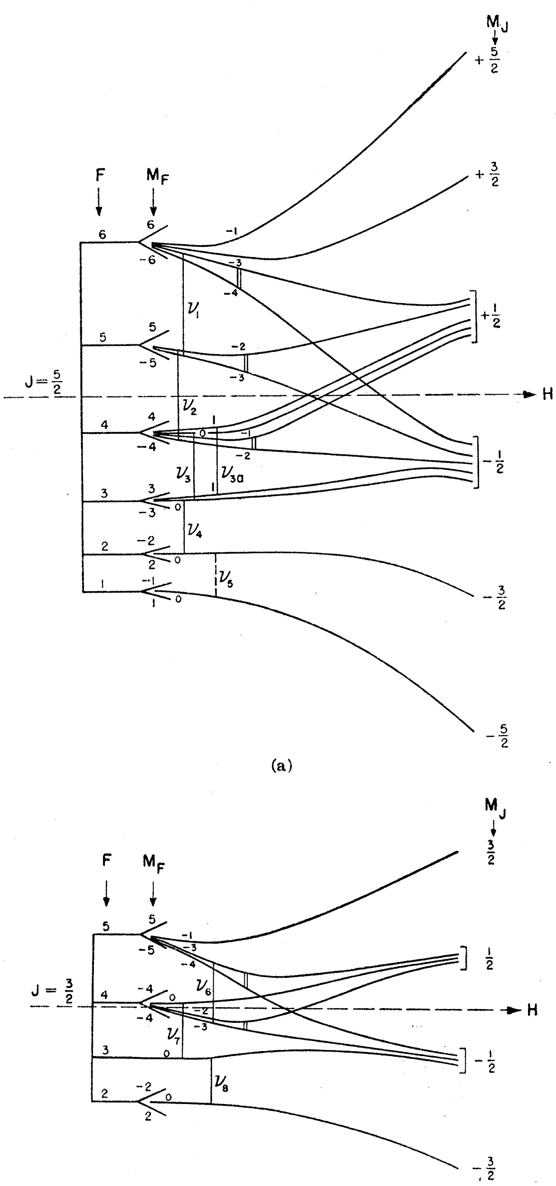

FIG. 1.(a) Energy levels for the case $J=\frac{5}{2}$, $I=\frac{7}{2}$. (b) Energy levels for the case $J=\frac{3}{2}$, $I=\frac{7}{2}$.

[9] A. Bohr and V. F. Weisskopf, Phys. Rev. 77, 94 (1950).

ment of hyperfine intervals are labeled by $\nu_1, \nu_2, \cdots \nu_8$. The low-frequency lines ($\Delta F=0$) are indicated by double vertical bars.

B. Second-Order Perturbation Energy

In a systematic review of this problem recently given by Schwartz,[8] the noncentral interaction Hamiltonian was expanded in the form of tensor products,

$$H_1=\sum_{k>0} T_e^{(k)}\cdot T_n^{(k)}. \qquad (4)$$

The rank $k=1, 2, 3, \cdots$ corresponds to the order of multipole interaction, and subscripts e and n indicate, respectively, the space of electronic and nuclear coordinates in which the tensor $T^{(k)}$ operates. The invariance of the scalar products in the combined space of **J** and **I** is borne out by the fact that the general matrix of H_1 in the I, J, F representation must be diagonal in F. Hence the second or higher order perturbation energy of H_1 arises from off-diagonal elements in J only. For a doublet level, the second-order perturbation energy of H_1 is, up to the octupole interaction, [Eq. (42) of Schwartz[8]]

$$W_F^{(2)}=\pm\frac{1}{\delta}|\langle I,J,F|\sum_{k=1,2} T_e^{(k)}\cdot T_n^{(k)}|I,J-1,F\rangle|^2$$
$$=\pm\frac{1}{30\,000\delta}(I+J-F)(J-I+F)(I-J+F+1)$$
$$\times(I+J+F+1)\left[-\frac{J+1}{2(2J-1)(2J+1)}\xi A-\frac{3[F(F+1)-I(I+1)-J^2+1]}{2J(2J-1)(2J-2)2I(2I-1)}\eta B\right]^2 \text{Mc/sec.} \qquad (5)$$

Here the signs ($\pm$) are for the two levels $J=l+\frac{1}{2}$ and $J=l-\frac{1}{2}$, respectively, ξ and η are proportionality factors not far from unity, A and B are in Mc/sec, and δ is in cm^{-1}. If in the final interpretation we are interested only in the quadrupole interaction constant, the off-diagonal elements of the quadrupole term in (5) may be dropped,

$$W_F^{(2)}=\pm\epsilon'(I+J-F)(J-I+F)(I-J+F+1)\times(I+J+F+1), \qquad (5a)$$

ϵ' being a constant proportional to A^2/δ. This is the same as the result given by Casimir.[7]

The first-order energy expectation values of H_1 are the same as in Eq. (1), but may be written in a more concise form:

$$W_F^{(1)}=\sum_{k>0} M(I,J,F;k)A_k. \qquad (6)$$

The physical factors A_k are given by

$$A_k=\langle T_n^{(k)}\rangle_{m_I=I}\cdot\langle T_e^{(k)}\rangle_{m_J=J}, \qquad (6a)$$

and are related to the more familiar constants A, B, C through

$$A_1=IJA,\quad A_2=B/4,\quad \text{and}\quad A_3=C. \qquad (6b)$$

The coefficients $M(I,J,F;k)$ are expressible in terms of Racah coefficients. When the hyperfine intervals are measured, one may (i) solve simultaneous equations deduced from formula (1) to determine A_k, or (ii) obtain A_k directly from the relation given by Schwartz [his Eq. (8)]:

$$A_k=a_k\sum_F(2F+1)M(I,J,F;k)W_F,$$
$$a_k=(2k+1)\times\frac{[(2I)!(2J)!]^2}{(2I-k)!(2J-k)!(2I+k+1)!(2J+k+1)!}. \qquad (7)$$

The effect of second-order perturbation may be included in method (i) by assuming a repulsion parameter, or in method (ii) by computing the corrections to A_k:

$$\Delta A_k=-a_k\sum_F(2F+1)M(I,J,F;k)W_F^{(2)}. \qquad (7a)$$

C. Effects of Configuration Interaction

Besides the second-order perturbation which affects the evaluation of all interaction constants, the mixing of a higher configuration such as $5d6s7s$ with the ground configuration $5d6s^2$ will have a direct effect on the dipole interaction constant. The effect may be considerable even though the percentage of mixing is small because s electrons contribute to the hyperfine energy more efficiently than the d electron (the two s electrons in the ground configuration being in a closed subshell). If in the relation

$$A_1=\langle T_n^{(1)}\rangle_{m_I=I}\cdot\langle T_e^{(1)}\rangle_{m_J=J}=\mu_I\frac{(2J)!}{[(2J-1)!(2J+2)!]^{\frac{1}{2}}}(J\|T_e^{(1)}\|J), \qquad (8)$$

one writes the total dipole operator $T_e^{(1)}$ as a sum of an operator $T_{5d}^{(1)}$ acting on the $5d$ electron and another $T_s^{(1)}$ acting on the s electrons, one gets an expression of the form:

$$A=A_1/IJ=\frac{\mu_I}{IJ}\frac{(2J)!}{[(2J-1)!(2J+2)!]^{\frac{1}{2}}}\{(J\|T_{5d}^{(1)}\|J)+(J\|T_s^{(1)}\|J)\}=A_0+\delta_{JJ}, \qquad (9)$$

where A_0 and δ_{JJ} are defined by the relation. Thus A_0 is the first-order dipole interaction energy due to the $5d$ electron in the absence of configuration interaction and δ_{JJ} is the correction due to the s electrons. This δ_{JJ} is equal to Schwartz's Δ_{JJ} multiplied by the coefficient of the term in curly brackets in (9). If the dipole interaction constants A' and A'' of both states of the doublet $J=\frac{5}{2}, \frac{3}{2}$, respectively, are measured, one may write simultaneous expressions of the form (9) for the two states and, using theoretical relations given by Schwartz between A_0' and A_0'' and between $\delta_{\frac{5}{2}\frac{5}{2}}$ and $\delta_{\frac{3}{2}\frac{3}{2}}$, solve for A_0' and A_0''. In fact, the theoretical relations which will be used are

$$A_0'/A_0''=3\theta/7 \quad \text{and} \quad \delta_{\frac{5}{2}\frac{5}{2}}=-\delta_{\frac{3}{2}\frac{3}{2}},$$

where θ is a relativistic factor of the order of unity.

Similarly, the change in the off-diagonal elements of the dipole interaction may be inserted into the dipole term ξA of Eq. (5),

$$\zeta=1+\frac{\Delta_{JJ-1}}{(lJ\|T_{5d}{}^{(1)}\|lJ)} =1+\frac{1}{\xi}\frac{[(J-1)/(J+1)]A''-\theta A'}{A'+A''}\left(\frac{4J^2-1}{J-1}\right). \tag{9a}$$

In Eq. (9a), $J=l+\frac{1}{2}$, $\theta=(F''/F)|\mathcal{C}''|^2/|\mathcal{C}'|^2$, $\mathcal{C}'$ and $\mathcal{C}''$ are normalization constants. Thus, configuration mixing affects the quadrupole interaction constant, and, more seriously, the octupole interaction constant, through second-order perturbation of the dipole interaction.

III. EXPERIMENT

The atomic-beam apparatus of this laboratory has been described in a paper[10] by Lew. Reference may be made to this paper for details concerning the various components discussed below.

A. Preliminary Studies

(*i*) *Oven material*.—The oven is essentially a tubular resistance with a narrow slit in the middle. The axis of the tube and the slit are vertical. When lanthanum is heated in such an oven in vacuum to above the melting point (826°C) it usually permeates the oven walls. After several trials it was found that tantalum was a suitable oven material, permitting stable operation for nearly 20 hours at an operating temperature of 1500°C. In each refilling, the oven cap had to be replaced because it was invariably sealed to the oven proper by molten lanthanum. Often the oven as a whole became bent or contracted after long heating, and had to be replaced.

(*ii*) *Detector*.—The electron bombardment ionizer[11] was first tried as the detector. There was a very large background from the detector in the range of heavy masses. Under optimum conditions we found a "zero-field flop" but did not observe any low-frequency ($\Delta F=0$) transitions.

We then tried a tungsten ribbon as a surface-ionization detector. The ribbon was $1\frac{1}{2}$ inches long, 0.002 inch thick, and 0.010 inch wide and usually carried a current of 0.8 to 1.7 amperes. The background was very low. However, there was a few seconds delay in the appearance of ions after the lanthanum beam was turned on and a very long persistence after it was turned off. Apparently lanthanum atoms accumulated on the hot wire during the exposure to the beam. At a filament current of 2.7 amperes, the delay of ion evaporation at the onset of incidence became unnoticeable but the persistence after the beam was turned off was still several minutes. At a still higher current of 3.0 amperes, the detector response followed incidence almost instantaneously, and a 10-cycle beam chopper worked satisfactorily. There remained frequent bursts of ion current far above the normal response, presumably arising from lanthanum atoms on the cooler parts of the hot wire. By covering up the wire length near its two ends, and leaving only a $\frac{3}{8}$-inch opening at the center to receive the incident beam, the bursts became much less frequent. Further increase of the filament current again caused erratic counts.

In the final measurements, for greater strength, the filament was changed to one of 0.015-inch width and 0.002-inch thickness, carrying a correspondingly higher current of 4.1 amperes. It sustained normal use for two to three weeks, during which time the filament current was gradually lowered from 4.1 to 3.8 amperes to maintain the same operating temperature. The apparent temperature observed with a 0.65-micron optical pyrometer was approximately 2080°C. This corresponds to 2600°K after emissivity correction.[12] In view of the difficulty of comparing filament brightness with a dot in the pyrometer a subsequent determination[13] of the temperature was made by comparing the brightness of the ribbon with the brightness of a tungsten wire of round cross section mounted closely parallel to it. The temperature of the wire was then computed with the aid of the tables of Jones and Langmuir.[14] The operating temperature of the ribbon in the present experiment was thereby found to be 2680±30°K.

B. The rf System

According to the optical data,[5] the frequencies of hyperfine transitions ($\Delta F=0,\pm1$) within the ground level ^2D should be less than 1500 Mc/sec. To cover this range, four oscillators were employed. In Fig. 2, oscillator A was the General Radio 1209A butterfly oscillator incorporated with a 50 to 1 worm-gear drive for slow-frequency sweep and powered by a highly stabilized external power supply. Oscillator B consisted of a Sylvania 5837 klystron and a tunable external cavity immersed in oil. Small adjustments of the

[10] H. Lew, Phys. Rev. **91**, 619 (1953).

[11] G. Wessel and H. Lew, Phys. Rev. **92**, 641 (1952).

[12] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1955), thirty-seventh edition, p. 2489.

[13] This determination was made by Dr. H. Lew after the author had left the laboratory.

[14] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 312 (1927).

reflector voltage of the klystron permitted a very fine frequency sweep. Oscillator C was a type 124A oscillator of the Airborne Instruments Laboratory which utilized a 2C39A light-house tube and a tunable external cavity. Its wide frequency range and fine tuning facilitated the searching of high-frequency ($\Delta F \pm 1$) lines. The filaments of all three oscillators were battery operated. Their frequencies were measured by comparison with the harmonics of a 1-Mc/sec secondary standard in the usual manner (Fig. 2). The 1-Mc/sec standard was known to be 2 parts in 10^7 beneath its nominal value and was checked at its 25th harmonic on the Hewlett-Packard 524B electronic counter, which, in turn, was driven by a 100-kc/sec primary standard. The electronic counter also read the frequency of oscillator D. The latter was a General Radio 1001 signal generator employed for measuring low-frequency transitions ($\Delta F=0$, $\Delta M_F=\pm 1$) in both lanthanum and caesium atoms. It served also as a monitor on the stability of the lanthanum beam and the constancy of the C field.

C. Operating Conditions

The lanthanum metal, being readily oxidized, was preserved in oil before use. Each charge weighed about 0.3 gram and usually outlasted the oven tube. The charged oven was gently heated for about 10 hours in vacuum, mainly to outgas the tantalum tube and cap, and then raised to 1300°C to generate the beam. The ionized atoms coming off the detector (Sec. IIIA) were focused onto an electron multiplier by an accelerator voltage of 550 volts and a mass-spectrometer field of 3.1 kilogauss. The amplification and recording system following the electron multiplier was approximately the same as described in a previous paper[15] on copper. Because of the smallness of the atomic g factors of lanthanum in comparison with copper, the deflection fields A and B were raised to 7 kilogauss, while the slit widths were reduced to 0.006 inch at the oven, 0.007 inch at the collimator, and 0.015 inch at the detector.

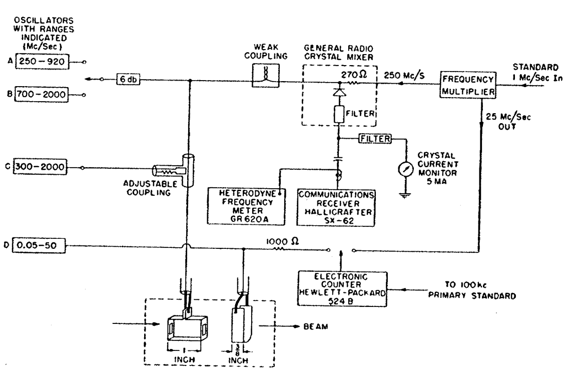

FIG. 2. The rf system.

[15] Yu Ting and Hin Lew, Phys. Rev. **105**, 581 (1957).

TABLE I. Corrections to the observed frequencies to yield field-free intervals. ν_{3a} and ν_{Cs} are the field calibration frequencies.

J	$F, M_F \to F', M_F'$	$\delta^{(1)}\nu/\delta^{(1)}\nu_{3a}$	$\delta^{(2)}\nu/\nu_{Cs}^2$ (Mc/sec)$^{-1}$
$\frac{5}{2}$	ν_1: $6,-3\to 5,-3$	$-6/7$	1.03×10^{-3}
	ν_2: $5,-2\to 4,-2$	-1	0.246
	ν_3: $4,0 \to 3,0$	0	-9.85
	ν_{3a}: $4,1 \to 3,1$		-5.24
	ν_4: $3,0 \to 2,0$	0	-15.24
	(ν_5: $2,0 \to 1,0$)	0	202
$\frac{3}{2}$	ν_6: $5,-3\to 4,-3$	$-12/7$	2.63
	ν_7: $4,0 \to 3,0$	0	2.05
	ν_8: $3,0 \to 2,0$	0	32.76

During the first few hours of heating a new charge, the "straight beam," i.e., the portion which remained undeflected, was not noticeably weaker than the total beam. Barium impurity was suspected, which has zero atomic magnetic moment and has its most abundant isotope 138 right next to La^{139} in the mass spectrum. Heating the oven at 1100°C (the boiling point of barium being 1140°C) for 12 to 16 hours reduced the straight beam to about 5% of the total.

After the above operations the oven temperature was raised to 1500°C. The background arising from the "straight beam" in the presence of the deflection fields gave a count of about 2600 per second, while the observed resonance signals gave about 6000 counts per second. A biasing device in the amplification system permitted only the fluctuations above the average background to be amplified and recorded. Typical ratios of the signal to the partially suppressed background was 16 to 1 for a "zero-field flop" and 3 or 4 to 1 for a low-frequency ($\Delta F=0$) resonance. When these values were realized, high-frequency lines ($\Delta F=\pm 1$) could be satisfactorily measured.

The vacuum of the beam apparatus was maintained at $(2\text{–}7)\times 10^{-7}$ mm Hg during measurement.

D. Measurement of the Hyperfine Intervals

All the high-frequency lines ($\Delta F=\pm 1$) that have been measured are of the $\Delta M_F=0$ type. They were observed by means of the one-inch long σ loop shown in Fig. 2. The lines designated by the various ν's in the discussion below are identified in Fig. 1 and in Table I. The settings of the C field were very low so that perturbations due to the magnetic field [Eq. (3)] need be calculated at most to the second order. The magnitude of the C field was measured either by means of the line ν_{3a} of La or by means of the line ($F=4$, $M_F=-3\to -4$) $\equiv \nu_{Cs}$ of Cs^{133}. The corrections to be deducted from the observed frequencies to obtain field-free intervals are also listed in Table I. The first-order corrections were derived by comparison with the ν_{3a} line, also measured by means of the σ loop. Since ν_{3a} converges to ν_3 at zero field, its first-order field correction is

$$\delta^{(1)}\nu_{3a}=(\nu_{3a}-\delta^{(2)}\nu_{3a})-(\nu_3-\delta^{(2)}\nu_3). \qquad (10)$$

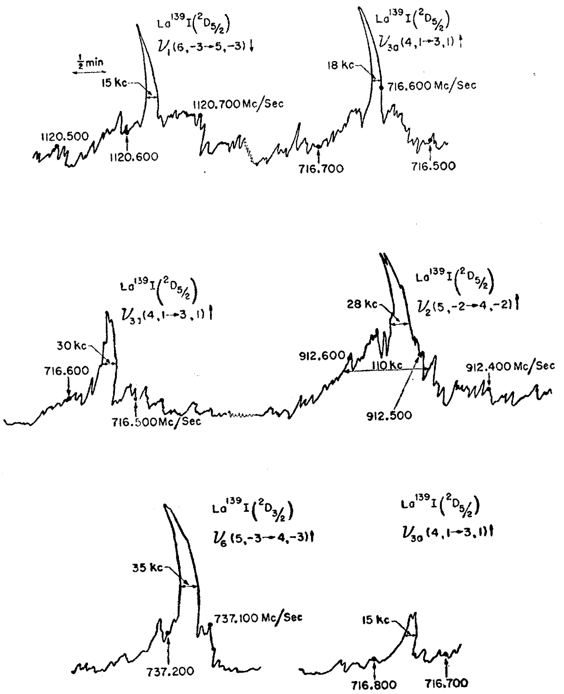

FIG. 3. Typical tracings of ν_1, ν_2, and ν_6, each with an accompanying field-calibration line ν_{3a}. The arrows (↑↓) beside the line identifications indicate the direction of the frequency sweep (increasing or decreasing).

The ratio $\delta^{(1)}\nu_6/\delta^{(1)}\nu_{3a}$ was computed with the help of Landé g_J factors for LS coupling which proved later to be very close to the observed values. The second-order field corrections were expressed in terms of $\nu_{Cs}{}^2$. Where ν_{3a} was measured for field calibration, ν_{Cs} in Table I was replaced by $\delta^{(1)}\nu_{3a}\times(g_{Cs}/g_{3a})$.

According to Table I, the lines may be collected into two groups.

(i) Lines which are field dependent to the first order: ν_1, ν_2, and ν_6. The transitions were all excited by oscillator C while the field-calibration line ν_{3a} was excited by oscillator B. Typical traces of ν_1, ν_2, and ν_6 with the accompanying ν_{3a} line are shown in Fig. 3. The up and down arrows indicate the direction of frequency sweep in tracing a line from right to left. The rate of sweep was about 1 to 3 kc/sec per second. On account of the finite time constant of the amplification and recording system, corrections amounting to a few kc/sec were applied to the observed line frequency. The accuracy of line ν_6 was not good and, unfortunately, further measurements were not made.

(ii) Lines which are field dependent only in the second order: ν_3, ν_4, ν_7, and ν_8. Typical traces of the four lines, each taken at several settings of the C-field, are shown in Fig. 4. Lines ν_3, and ν_7, were excited by oscillator B and C, respectively. The two lines and the three in group (i) were all measured by the "flop-in" method. In this method, only atoms that underwent a transition from the $M_J=\pm\frac{1}{2}$ state to the $M_J=\mp\frac{1}{2}$ state were refocused on the detector. The two possibilities corresponded to stimulated emission and absorption. By moving a 0.007-inch diameter wire to one side of the 0.020-inch diameter stop-wire which intercepted the "straight beam," the emission or absorption component can be blocked. To observe line ν_4, oscillator B was set at the peak of line ν_3 ($F, M_4=4,0\rightarrow3,0$), and the "emission" beam was blocked. The intensity observed then depended on the population in the lower level ($F, M_F=3,0$). A second oscillator (oscillator C), which was connected in parallel with the first with adequate rf attenuation in between, was swept through the expected region of ν_4. When simultaneous resonance of ν_3 and ν_4 occurred, the lower level ($F, M_F=3,0$) was depopulated because atoms having $M_J=-\frac{3}{2}$ (Fig. 1) in the A- or B-field region

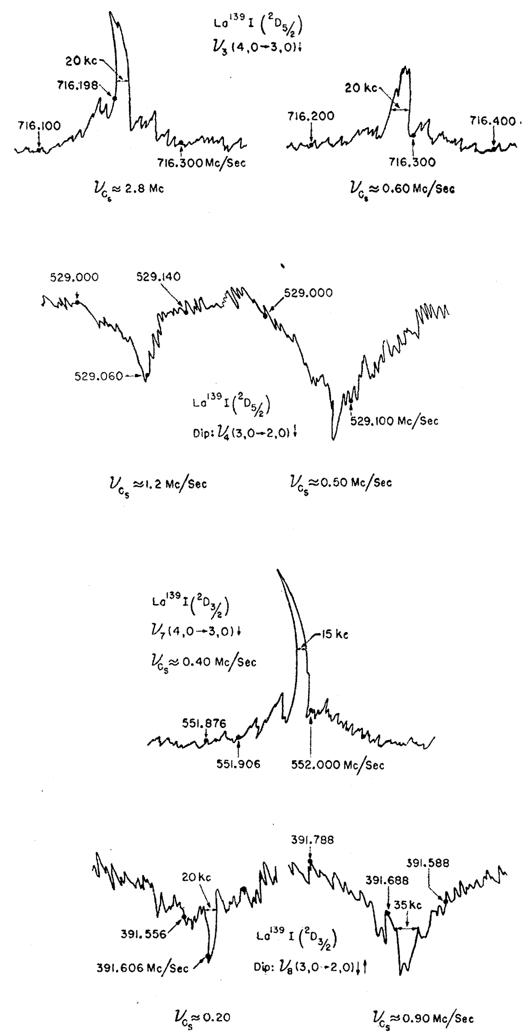

FIG. 4. Typical tracings of ν_3, ν_4, ν_7, and ν_8. The lines ν_4 and ν_8 appear as single dips on top of ν_3 and ν_7 respectively (see text). The field monitoring frequency ν_{Cs} which was induced by a π loop has been corrected for field inhomogeneities to the position of the σ loop.

were not refocused. Thus a dip corresponding to the line ν_4 was observed on top of the ν_3 line.[16] Similarly line ν_8 was measured by observing the absorption component of ν_7 with oscillator A and sweeping oscillator C through the expected region of ν_8.

The results for the two groups of lines (i) and (ii) are listed in Table II. In part (i) of Table II both second-order and first-order field corrections were evaluated from ν_{3a}, while in part (ii) second-order corrections were evaluated from ν_{Cs}.

Attempts to measure ν_5 ($J=\frac{5}{2}$, F, $M_F=2, 0\rightarrow 1, 0$) by observing a triple resonance of ν_3, ν_4, and ν_5 failed. An attempt to observe ν_5 by the "flop-out" method with the B-field gradient reversed was also unsuccessful. The attempt was abbreviated by the failure of one of the diffusion pumps of the beam apparatus. When the trouble was finally corrected time precluded a resumption of the search for this line.

Among the lines measured, ν_3 ($J=\frac{5}{2}$, F, $M_F=4, 0\rightarrow 3, 0$) was the first to be studied. Figure 5 shows two typical tracings of ν_3 with two satellites in a preliminary series of measurements. Each line showed some structure, although the position of the central peak agreed with that of later measurements. After careful adjustments of the beam intensity and reduction of rf power, the line structure was simplified. Final measurements were taken on these purified lines (Figs. 3, 4). In general they appeared as a single peak on top of a broad hump. Considering the rf distribution around the one-inch long σ probe (Fig. 2), one would expect the rf fields to be nearly constant along the probe length and pass over to negative values just beyond the two ends. This would give rise to the line shape observed. At an oven temperature of 1500°C, the average velocity of the atoms was $v=(2kT/M)^{\frac{1}{2}}\approx 4.7\times 10^4$ cm/sec. According to the uncertainty principle, the line width should have been of the order of $\Delta\nu = v/\text{probe length} = (4.7/2.54)\times 10^4 \approx 20$ kc/sec. Actually the thick stop-wire (0.020-inch diameter) slightly cut into the transition beam, and hence allowed only the low-velocity atoms to pass. This should have resulted in a further narrowing of the line. The observed width ranged from 15 to 35 kc/sec, as shown in Figs. 3 and 4. The apparent half-width was slightly less than the real value because the biasing device in the amplification and recording system cut off the background as well as part of the signal.

There was one series of measurements on ν_8 in which a doublet presistently appeared. The reason was not understood. The beam intensity used was higher than in another series of measurements in which only a single "dip" of ν_8 was observed. The doublet splitting was very small and the midpoint was closely equal to the central frequency of a single dip. Figure 6 shows a typical tracing of the doublet.

[16] A similar technique was applied by J. G. King and V. Jaccarino, Phys. Rev. **94**, 1610 (1954), where two rf sources were fed to two separate probes.

TABLE II. Observed high-frequency transitions and the hyperfine intervals at zero field.

(i) Lines ν_1, ν_2, ν_6, and ν_{3a}. The listed values are ν_1-1120, ν_2-912, ν_6-737, $\nu_{3a}-716$ and ν_{Cs}, all in Mc/sec. The column "Average observed frequency," except ν_{Cs}, include second-order field correction and the time-constant correction for up and down frequency sweep. Both first- and second-order field corrections are computed from ν_{3a}.

Average observed frequency	Hfs interval	Average observed frequency	Hfs interval	Average observed frequency	Hfs interval
Cs 0.735		Cs 0.71		Cs 0.775	
3*a* 0.618		2 0.521		3*a* 0.608	
1 0.620	0.896	3*a* 0.549	0.790	6 0.432	0.971
3*a* 0.610		2 0.537		3*a* 0.595	
Cs 0.725		3*a* 0.534		6 0.471	0.978
		2 0.548	0.790	3*a* 0.571	
Cs 1.30		3*a* 0.526		6 0.480	0.956
3*a* 0.901		Cs 0.60		3*a* 0.560	
1 0.387	0.907				
3*a* 0.889		Cs 1.045		Cs 1.070	
Cs 1.20		3*a* 0.781		3*a* 0.807	
1 0.399	0.904	2 0.312	0.801	6 0.136	0.984
3*a* 0.866		Cs 1.035		3*a* 0.760	
				6 0.156	0.946
$\nu_1=1120.902\pm0.005$		$\nu_2=912.793\pm0.005$		3*a* 0.741	
				$\nu_6=737.967\pm0.015$	

(ii) Lines ν_3, ν_4, ν_7, and ν_8. The frequency ν_{Cs} was observed at the π probe and corrected to the σ probe. The error in this correction was added to the statistical error in taking the average. The arrows (↑↓) indicate direction of frequency sweep (increasing and decreasing frequency) in tracing a line.

	Frequency observed in Mc/sec	Corrected ν_{Cs}	Hfs interval		Frequency observed in Mc/sec	Corrected ν_{Cs}	Hfs interval
ν_3	716.285↑			ν_7	551.990↑		
	716.286↑	0.60	716.288		551.984↑	0.38	551.984
	716.282↓				551.981↓		
	716.211↑				551.983↓		
		2.80	716.287			0.42	551.987
	716.209↓				551.990↑		
	Av=716.288±0.003				551.996↑		
					551.994↑	0.97	551.991
ν_4	529.091↑				551.995↑		
		0.36	529.090		Av=551.987±0.003		
	529.085↓						
	529.090↑			ν_8	391.604↑		
		0.43	529.089		391.601↓	0.20	391.601
	529.085↓				391.601↑		
	529.081↓				391.608↑		
	529.083↓	0.52	529.090			0.23	391.606
	529.086↑				391.608↓		
	529.075↓				391.623↓		
		0.79	529.091			0.90	391.603
	529.077↑				391.638↑		
	529.060↑	1.22	529.085		Av=391.603±0.010		
	Av=529.090±0.010						

E. Determination of Approximate g_J-Values

The five low-frequency lines ($\Delta F=0$, $\Delta M_F=\pm 1$) marked by double bars in Fig. 1 were measured against a caesium line ($F=4$, $M_F=-3\rightarrow -4$) at the same π loop. They are, for $J=\frac{5}{2}$, ν_A ($F=6$, $M_F=-3\rightarrow -4$), ν_B ($F=5$, $M_F=-2\rightarrow -3$), ν_C ($F=4$, $M_F=-1\rightarrow -2$), and for $J=\frac{3}{2}$, ν_D ($F=5$, $M_F=-3\rightarrow -4$), ν_E ($F=4$, $M_F=-2\rightarrow -3$). The lines were swept manually and the frequencies at peak intensity as monitored by earphones were directly measured on the electronic counter Hewlett-Packard 524*B* in Fig. 2. The field corrections up to the third order were computed for the five lanthanum lines and the caesium line. The measure-

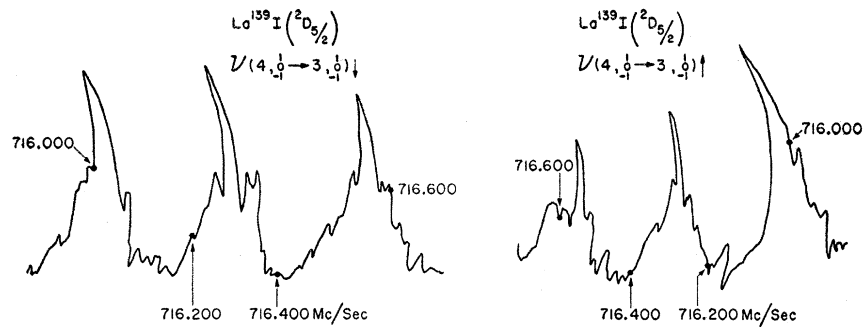

FIG. 5. Typical tracings of ν_3 and two satellites in a preliminary series of measurements.

ments gave

$$g(^2D_{\frac{5}{2}})=1.201\pm0.002,\quad g(^2D_{\frac{3}{2}})=0.7988\pm0.0005. \tag{11}$$

The accuracy was not very high because a double peak structure appeared in some of these low-frequency lines. Their closeness to the Landé g factors, 1.2 and 0.8, respectively, substantiates the LS coupling scheme. Earlier spectroscopic data[17] gave $g_{\frac{5}{2}}=1.203$ and $g_{\frac{3}{2}}=0.790$.

IV. EVALUATION. DISCUSSION OF RESULTS

A. Interaction Constants

The constants A', B', C', of the $^2D_{\frac{5}{2}}$ state and A'', B'', C'', of the $^2D_{\frac{3}{2}}$ state may be derived from the observed frequencies by means of formula (6) or more directly by means of formula (7). The coefficients $M(I,J,F;k)$ in both formulas are listed in Table III.

Method (i).—Assuming that the main contributions to the second-order perturbation of the hyperfine levels are from the off-diagonal elements of the magnetic dipole interaction within the ground level ^2D and taking the positive repulsion parameter ϵ' in Eq. (5a) to be $\epsilon/12$, one may determine the seven constants A', B', C', A'', B'', C'', and ϵ from the seven measured intervals. The solution of the simultaneous equations as derived from formula (6) gives $\epsilon=-0.0010\pm0.0015$ Mc/sec. Since the ϵ value is smaller than the experimental error and takes a negative mean value in contradiction to the assumption of a positive repulsion, we put it equal to zero. The remaining six constants are then found to be closely equal to the results obtained by method (ii), the difference being well within the assigned errors.

Method (ii).—Substitution of ν_6, ν_7, and ν_8 of Table II into formula (7) gives

$$^2D_{\frac{3}{2}}:\begin{cases}A''=141.1959\pm0.0016\text{ Mc/sec},\\ B''=44.781\pm0.014\text{ Mc/sec},\\ C''=0.15\pm0.44\text{ kc/sec}.\end{cases} \tag{12}$$

Similarly, the data on ν_1, ν_2, ν_3, and ν_4 in Table II leads to

$$^2D_{\frac{5}{2}}:\begin{cases}A'=176.8311\pm0.0005+(3/196)\nu_5,\\ B'=209.947_3\pm0.012-(25/56)\nu_5,\\ C'=-18.1695\pm0.0007+(5/96)\nu_5.\end{cases} \tag{13}$$

The remaining unknown ν_5 is determined by substituting Eq. (13) into formula (6). There are five solutions for ν_5, corresponding to the five intervals in $^2D_{\frac{5}{2}}$. Taking the statistical weight of each solution in inverse proportion to its error, we obtain an average value,

$$\nu_5=348.843\pm0.014\text{ Mc/sec}, \tag{14}$$

TABLE III. Coefficients $M(I,J,F;k)$ for $I=\frac{7}{2}$.

F	$7M(1)^a$ $J=5/2$	$J=3/2$	$7M(2)^a$ 5/2	3/2	$7M(3)^a$ 5/2	3/2
6	7		7		7	
5	2.2	7	−7.4	7	−21.8	7
4	−1.8	1/3	−8.4	−13	9.2	−33
3	−5.0	−5.0	−2.0	−5	22.0	55
2	−7.4	−9.0	7.0	15	2.2	−33
1	−9.0		15.0		−33.0	

[a] Number in parenthesis after M is value of k.

in which the assumed error is twice the root-mean-square value. Substitution of (14) into (13) gives

$$^2D_{\frac{5}{2}}:\begin{cases}A'=182.1706\pm0.0006\text{ Mc/sec},\\ B'=54.213\pm0.014\text{ Mc/sec},\\ C'=-0.6\pm1.0\text{ kc/sec}.\end{cases} \tag{15}$$

The present values may be compared with Lührs' optical values,[5] $A''=139.5\pm2.4$, $B''=43.5\pm15.0$, and $A'=180\pm9$ Mc/sec.

B. A Values and the Nuclear Magnetic Moment

In Sec. IIA, Eq. (2a) indicates that aside from a factor θ which is close to unity, the A values of a doublet should be inversely proportional to $J(J+1)$. Hence

$$A_0'/A_0''=3\times5/5\times7=3/7.$$

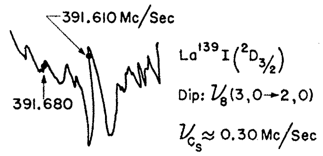

FIG. 6. Typical tracings of ν_8 in one series of measurements. The doublet dips are within 15 kc/sec of the central peak.

[17] H. N. Russell and W. F. Meggers, J. Research Natl. Bur. Standards 9, 625 (1932).

The ratio of observed A values is

$$A'/A'' \approx 9/7,$$

that is, three times too large. Moreover, if one evaluates the nuclear magnetic moment from either A' or A'' with the help of formulas (2a) and (2d), in which $\delta = 1053.20\ \text{cm}^{-1}$, the result deviates far from the nuclear resonance value,[2,3] $\mu_I = 2.778$ nuclear magnetons.

Second-order perturbation within the ground manifold of $J=\frac{3}{2}, \frac{5}{2}$ contributes very little to the constants A' and A''. The atomic g factors, as mentioned before, are closely equal to the LS-coupling values. The perturbation between the ground level $^2D_{\frac{3}{2}}$ and the higher level $^4F_{\frac{3}{2}}$ is probably very small, according to Ufford's calculation.[18] Moreover, the observed B values are fairly consistent with what is expected according to Eq. (2b).

These considerations suggest that configuration mixing of the sort discussed in Sec. IIB may be present. This mixing is known to affect the dipole constants directly and change the quadrupole constants only slightly via second-order perturbation. According to Eq. (9) we may write

$$\begin{aligned} A_0' + \delta_{\frac{3}{2}\frac{5}{2}} &= 182.17\ \text{Mc/sec}, \\ A_0'' + \delta_{\frac{5}{2}\frac{3}{2}} &= 141.20\ \text{Mc/sec}, \end{aligned} \tag{16}$$

Substituting $3A_0'' = 7\theta A_0'$, $\delta_{\frac{3}{2}\frac{5}{2}} = -\delta_{\frac{5}{2}\frac{3}{2}}$, $\theta = 1.06$, we find $A_0' = 93.0$ Mc/sec and $A_0'' = 230$ Mc/sec. If the effective nuclear charge is taken to be $57-11=46$, the evaluated magnetic moment will be within 15% of the nuclear resonance value. This is not considered to be a serious disagreement. Recently Murakawa[4] studied the Z_{eff} values of a series of elements and concluded from hfs in excited states that the most probable value for lanthanum was 39.7. If this new value is adopted, the magnetic moment evaluated from A_0' and A_0'' agrees completely with the nuclear resonance value.

B. B Values and the Quadrupole Moment

In Sec. IIA, Eqs. (2a), (2b), and (2d) may be combined to yield the quadrupole moment either from B/δ or from B/A_0.

(i) From (2b) and (2d),

$$Q = \frac{B}{\delta} Z \left[2.911 a_0^3 \frac{h \times 10^6}{e^2} \right] (2l+1) \left(\frac{2J+2}{2J-1} \right) \frac{H}{R}.$$

With $Z=39.7$, $H=1.01$, $R'=1.028$, $R''=1.095$ (reference 7), we have

$$Q\begin{pmatrix} ^2D_{\frac{3}{2}} \\ ^2D_{\frac{5}{2}} \end{pmatrix} = \begin{pmatrix} 0.217 \\ 0.241 \end{pmatrix} \times 10^{-24}\ \text{cm}^2.$$

(ii) From (2a) and (2b),

$$\begin{aligned} Q\begin{pmatrix} ^2D_{\frac{3}{2}} \\ ^2D_{\frac{5}{2}} \end{pmatrix} &= \left(\frac{B}{A_0}\right)\left(\frac{F}{R}\right)\left(\frac{g_I\beta_e}{e^2}\right)\left(\frac{2J+2}{2J-1}\right)\left(\frac{2l(l+1)}{J(J+1)}\right) \\ &= 0.161 \times 10^{-24} \begin{pmatrix} 2.4F'B'/R'A_0' \\ 8.0F''B''/R''A_0'' \end{pmatrix} \\ &= \begin{pmatrix} 0.221 \\ 0.237 \end{pmatrix} \times 10^{-24}\ \text{cm}^2. \end{aligned}$$

The close agreement between (i) and (ii) is of course to be expected from the theory and the aforementioned consistency between $A_0 Z_{\text{eff}}$ and μ_I. A rounded-off value $Q = (0.230 \pm 0.010) \times 10^{-24}\ \text{cm}^2$ will be taken as observed. Since the quadrupole moment of a nucleus may induce a charge distribution in the atom that results in a compensating quadrupole potential,[19] the observed interaction energy is less than if there were no such effect. The correction factor for lanthanum is, according to Sternheimer, 1.614, which leads to

$$Q = (0.268 \pm 0.010) \times 10^{-24}\ \text{cm}^2.$$

The second-order perturbation, even when configuration mixing is considered, is too small to affect the Q value.

The quadrupole moment may be calculated from simple shell theory. Since in the $_{57}La^{139}$ nucleus the outermost shell is just one proton short of being a completed $5g_{7/2}$ shell,

$$\begin{aligned} Q &= +\langle r_n^2 \rangle (2I-1)/(2I+2) \\ &= 0.8 \times 139^{\frac{2}{3}} \times (1.35 \times 10^{-13})^2 \times 6/9 \\ &= 0.27 \times 10^{-24}\ \text{cm}^2. \end{aligned}$$

In the above calculation, the mean square radius of the nucleus is taken to be midway between the value of a surface charge distribution and that of a uniform volume distribution. The Q value is in excellent agreement with the present experimental result. Calculation for a spheroidal nucleus[20] gives $Q = +1.3 \times 10^{-24}\ \text{cm}^2$, which is five times too large.

D. C Values and the Octupole Moment

The second-order perturbation energy of the noncentral interaction between atomic electrons and the nucleus has been found to contribute very little to the octupole constants of lanthanum. From formula (5), the corrections to the C values are

$$\begin{aligned} \Delta C' &= \frac{\eta B'}{20\delta}\left[\frac{\xi}{4} IJA + \frac{B'}{28}\right] \cong 0.034\xi\eta\ \text{kc/sec}, \\ \Delta C'' &= \frac{\eta B'}{200\delta}\left[-\frac{\xi}{4} IJA + \frac{9}{28}\eta B'\right] \cong -\frac{\Delta C'}{10}, \end{aligned} \tag{17}$$

[18] C. W. Ufford, Phys. Rev. 44, 732 (1933).

[19] R. Sternheimer, Phys. Rev. 86, 316 (1952); 84, 244 (1951); 80, 102 (1950).

[20] R. Van Wageningen and J. de Boer, Physica 18, 369 (1952).

where the factors ξ, $\eta=1.01$. If the aforementioned configuration mixing is assumed, formula (7a) gives a very large correction factor $\zeta=-5.52$ to the dipole term of Eq. (17). This is expected in view of the serious deviation of A''/A' from the theoretical value. The C values become

$$C'=-0.6\pm0.7+0.034\zeta=-0.8\pm1.0 \text{ kc/sec},$$
$$C''=+0.15\pm0.44-0.003\zeta=+0.17\pm0.44 \text{ kc/sec}.$$

Thus, even with the above correction, the C values are smaller than the experimental error. From theory we expect the octupole interaction to be small in D states. Formula (2c) gives

$$\begin{pmatrix} C' \\ C'' \end{pmatrix}=\Omega\left[Z\delta\frac{T/H}{1708}\times10^{24}\right]\begin{pmatrix} 4/441 \\ 16/735 \end{pmatrix}$$
$$=\Omega\times10^{24}\begin{pmatrix} 0.2 \\ 0.5 \end{pmatrix} \text{ kc/sec},$$

in which $\Omega\times10^{24}$ is of the order of 0.1 nuclear magneton cm^2. Assuming the shell assignment of $(5g_{7/2})^{-1}$ for the ${}_{57}La^{139}$ nucleus, one may estimate the octupole moment by a formula of Schwartz's.[8] It is of the order $(0.04 \text{ to } 0.28)\times10^{-24}$ nuclear magneton cm^2, depending on the choice of the g_s factor for the proton hole. Hence the C values, after second-order correction, are most likely within the range 0.01 to 0.1 kc/sec. The accuracy in the present experimental work, and in the theoretical calculation, would have to be considerably improved in order to observe the octupole moment of lanthanum.

V. CONCLUSION

It has been shown that the observed hyperfine structure of La^{139} can be understood in terms of current theories of hyperfine structure provided it is assumed that the ds^2 ground configuration contains an admixture of a dss' configuration. It would be desirable, however, to obtain the wave functions of the ground state to check on this assumption and to determine the degree of admixture, if any. With a knowledge of the wave functions, one can, of course, compute a better value for the nuclear quadrupole moment and obtain a closer limit on the octupole moment. It is of interest to note that the simple single-particle model of the nucleus gives a theoretical value for the quadrupole moment which is in close agreement with the experimental. The agreement with respect to the magnetic dipole moment is not as good.

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