# $M1$, $E2$, and $M3$ hyperfine structure and nuclear moment ratios for $^{151,153}$Eu

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The atomic-beam laser-rf double-resonance technique has been used to obtain precise values for the hyperfine structure (hfs) splittings in ten $4f^7 5d6s\ ^{10}D_J$ and $^8D_J$ levels of $^{151,153}$Eu I. Detailed studies of the second-order hfs lead to the isotopic ratios of the hfs constants, and reveal surprisingly strong hfs interactions between the two multiplets. The dipole ratios, when compared with the known ratio of the nuclear dipole moments, reveal striking $J$- and term-dependent hyperfine anomalies. The quadrupole ratios (after corrections for the second-order hfs) are consistent with the atomic ground-state value and self-consistent among the ten levels studied. The precision of the measurements allows evaluation of the ratio of the magnetic octupole hfs interaction constants between the two isotopes. The result, which is taken to be the ratio of the nuclear ground-state magnetic octupole moments $\Omega$, is found to be $\Omega(^{151}\text{Eu})/\Omega(^{153}\text{Eu})=0.87(6)$.

## I. INTRODUCTION

The only two stable europium isotopes are $^{151}$Eu and $^{153}$Eu, both with nuclear spin $I=\frac{5}{2}$. The atomic ground state is $4f^7 6s^2\ ^8S_{7/2}$, and there is a gap of about 12 000 cm$^{-1}$ above the ground state without other atomic levels. The lowest excited odd-parity levels are in the $4f^7 5d6s\ ^{10}D$ and $^8D$ multiplets; these ten levels are the subject of the present investigation. Numerous additional odd-parity levels lie above 19 000 cm$^{-1}$, and a host of even-parity levels occurs beginning at about 14 000 cm$^{-1}$. Although a great deal of optical spectroscopy has been done on the electronic level structure of Eu, as in the other rare earths, the work is far from complete [1].

High-precision hyperfine structure (hfs) studies have been made on the atomic ground state [2] in both isotopes with radio-frequency techniques, and the hfs of a number of levels in the excited $4f^7 5d6s$ configuration has been studied [3,4] with less precision by laser spectroscopy. The ground-state studies reveal electric quadrupole hfs even though the state is nominally an $S$ state (with $L=0$), and a value for the isotopic hfs electric quadrupole ratio $B(^{151}\text{Eu})/B(^{153}\text{Eu})$ has been obtained. The non-$S$ admixture arises through the spin-orbit interaction [5]. In addition to measuring the dipole and quadrupole hfs, the atomic-beam magnetic-resonance method has been used [5] to measure, independent of the hfs, the ratio of the nuclear magnetic dipole moments between the two isotopes. The laser spectroscopic work [3,4] on levels in the excited $4f^7 5d6s$ configuration has obtained values for the (a) magnetic dipole and (b) electric quadrupole hfs constants, although the precision for the quadrupole constants is rather limited. Some radio-frequency hfs work has also been done on low levels in Eu II [6]. In addition to the hyperfine-structure work, much work has been done on the isotope shift of optical europium lines [7].

The present work extends the high-precision radio-frequency studies of the ground state [2,5] to the excited $4f^7 5d6s\ ^{8,10}D$ levels to see what additional information a several-orders-of-magnitude increase in precision can yield. The atomic-beam laser-rf double-resonance technique [8] is used for the measurements. As will be shown, the ratio of the nuclear magnetic octupole moments between $^{151}$Eu and $^{153}$Eu can be obtained, as well as evaluation of the $J$ and term dependence of the (magnetic dipole) hyperfine anomaly. The surprising extent of hyperfine interactions between different multiplets of a single electronic configuration is also studied.

## II. EXPERIMENTAL DETAILS

The apparatus has been described previously [9]. A europium atomic beam is produced by electron-bombardment heating (to about 980 K) of a cylindrical tantalum oven (2.0 cm tall by 0.7 cm diameter with a 1.5-mm hole in the top) containing europium metal chips. The beam is collimated, and the fluorescence produced 47 cm downstream by a weak (typically 1–5 mW), orthogonal "probe" laser beam is collected by a polished ellipsoidal reflector and focused onto the dynode of a cooled, photon-counting photomultiplier. An interference filter, centered on the fluorescence wavelength with a bandwidth of 100 Å, is used to reduce background caused by scattered laser photons and/or light from the beam source. The laser is a single-mode cw dye laser pumped by an argon ion laser. Because of the orthogonality of the atomic and laser beams, the induced fluorescence spectra are nearly Doppler free. The observed linewidth of each hyperfine component of an optical line is typically 15 MHz.

For the laser-rf double-resonance measurements reported here, most of the dye-laser power is used to form a second, "pump," laser beam (50–100 mW) that intersects the atomic beam close to its source. When the laser wavelength coincides with that of a hyperfine component of an optical line, the population of the lower hyperfine level is strongly depleted by the pump beam and relatively little fluorescence is induced by the probe beam downstream. If the depleted level is refilled by driving a radio-frequency transition from an adjacent hfs level, however,

 

a strong resonant increase in fluorescence is induced by the probe beam. The linewidth of such a radio-frequency transition is determined by the flight time of the atoms through the rf region, and is typically 7–15 kHz. (Shielding is used to eliminate broadening due to the Zeeman effect of the Earth's magnetic field.) The method can therefore be used to measure the zero-field hfs intervals of any atomic state present in the beam with a precision of a few kHz. The state must live sufficiently long to survive transiting the apparatus (about 1 ms), and must be produced with sufficient probability in the source. For the highly excited states investigated here, the Boltzmann factor is nearly zero and the states are populated by a discharge struck in the atomic beam by the electrons heating the oven.

The laser wavelength is determined by a Hall-Lee [10] -type wavemeter, and marker fringes, spaced 150 Mhz apart, are obtained by passing some of the laser light through a 50-cm confocal Fabry-Pérot interferometer. The fringes are valuable for use in deducing rough (0.1%) values of the hfs splittings prior to making precise measurements with the double-resonance method. The rf signals were computer controlled and generated by a modified Systron-Donner Model No. 1702 0–1-Ghz synthesizer, successively doubled to yield higher frequencies where necessary.

The procedure was to select an optical line that connects the metastable state to be studied with a much higher-lying level and then to use laser-rf double resonance to study the hfs splittings of the lower level. It was first necessary to understand the complex pattern of the optical hyperfine structure for each line so that the laser could be held on the appropriate hfs component while the rf was scanned. The interpretation of the optical hfs is in principle straightforward, but can be tedious since something like 30 components (not always fully resolved) must be understood in detail. Since "rough" values for the zero-field hyperfine intervals of the relevant states in $^{151,153}$Eu can be deduced from the published [3,4] hfs constants, rf scans of 5 MHz were usually sufficient to locate the resonance frequencies, and then longer, much narrower sweeps could be made to obtain the values more precisely. Figure 1 shows a typical radio-frequency scan. The resonance is that due to the $F=6\leftrightarrow F=5$ hfs interval in the $4f^7 5d6s\ ^{10}D_{7/2}$ state of $^{153}$Eu I. Two or three such scans were made through each hfs interval to be measured.

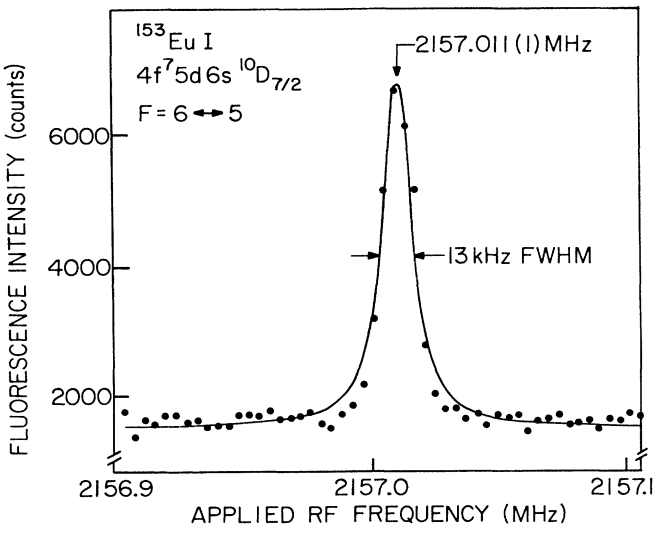


FIG. 1. Change in fluorescence intensity, using the atomic-beam laser-rf double-resonance technique, when the applied rf frequency is swept through the frequency corresponding to the $F=6\leftrightarrow5$ hfs interval in the $^{10}D_{7/2}$ (13 048.90 cm$^{-1}$) level of $^{153}$Eu I.

## III. RESULTS AND ANALYSIS

Table I lists the present values of the zero-field hfs intervals in the $4f^7 5d6s\ ^{10}D$ and $^8$D levels in $^{151,153}$Eu I. The uncertainty in each frequency $\Delta\nu$ is $\pm\Delta\nu/10^6$, i.e., 1–7 kHz. The excitation energies [1] of the states are given in cm$^{-1}$ to aid in identification. Comparisons of the new values with those calculated from the published [3,4] hfs constants shows that the precision of the earlier values is remarkable considering that they were deduced from measured separations of hfs peaks in optical spectra. The present $10^3$-fold improvement in precision is made possible by the double-resonance technique. Although the average error in the earlier $\Delta\nu$ values for $^{151}$Eu is only about 500 kHz, the resulting errors in the electric quadrupole $B$ values are, for some states, as large as 10 MHz, which is reflected in the published uncertainties. The situation is particularly severe for the $^{10}D_{11/2}$ state, for which the earlier $B$ values [3,4] is given as

$$B(^{10}D_{11/2}) = +1.0 \pm 1.5 \text{ MHz} .$$

Because the $^{10}D_{11/2}$ state has such a small $B$ value (the $B$'s for the other states range from 30 to 300 MHz), it can provide an especially sensitive test of the theory.

The measurements of Refs. [3] and [4] are more than adequate to allow dependable evaluation of the single-electron hfs parameters $a_{nl}$ and $b_{nl}$ for the shells involved in the $4f^7 5d6s\ ^{8,10}D_J$ states. The states were represented in intermediate coupling (they are in fact surprisingly near the $LS$ limit) and their $A$ and $B$ values were expressed in terms of the relevant single-electron hfs parameters. Least-squares fits to their observations then led to evaluation of the parameters. The present data do not lead to any significant change in their conclusions. The much greater precision of the double-resonance method does, however, make possible detailed comparisons between the ratios of hfs constants and nuclear moments between the two isotopes $^{151}$Eu and $^{153}$Eu, and this is the focus of the present work.

Earlier measurements [2,6] in other atomic states have shown that the isotopic electric quadrupole hfs ratio $B(^{151}\text{Eu})/B(^{153}\text{Eu})$ is about 0.393. The ratio $Q(^{151}\text{Eu})/Q(^{153}\text{Eu})$ of the nuclear ground-state electric quadrupole moments is conventionally taken to be the same, since the quadrupole moments cannot be directly measured like the dipole moments. If the standard two-parameter hfs theory [11] [i.e., the first-order theory al-

lowing for magnetic dipole ($A$) and electric quadrupole ($B$) hfs interactions] is fitted to the observed hfs intervals listed in Table I for the $^{10}D_{11/2}$ state, the results $^{151}B = 3.193(60)$ MHz and $^{153}B = 4.040(60)$ MHz are obtained. We thus find the ratio $^{151}B/^{153}B = 0.790(20)$, completely inconsistent with the anticipated result, 0.393. The discrepancy cannot arise from imperfect knowledge of admixtures which would alter the $B$ value for each isotope by the same factor and therefore leave the ratio unchanged. It must instead arise from second-order hfs, which can perturb hfs splittings by hfs interactions between the $^{10}D_{11/2}$ level and other atomic states. By far, the dominant term in the perturbation is the magnetic dipole term due to the 6$s$ electron, $a_{6s}$ $\mathbf{s}\cdot\mathbf{I}$. This is due to

TABLE I. Observed values of the zero-field hyperfine splittings $\Delta\nu$ in ten metastable atomic levels of $^{151,153}$Eu I. The uncertainty in each interval is $\pm\Delta\nu/10^6$.

| Atomic state | Excitation energy ($cm^{-1}$) | $F \leftrightarrow F'$ | $\Delta\nu$ (MHz) $^{151}$Eu | $^{153}$Eu |
|---|---|---|---|---|
| $4f^7 5d6s\ ^{10}D_{5/2}$ | 12 923.72 | 5↔4 | 6075.812 | 2837.911 |
| | | 4↔3 | 4800.986 | 2121.688 |
| | | 3↔2 | 3565.984 | 1504.609 |
| | | 2↔1 | 2360.785 | 961.821 |
| | | 1↔0 | 1175.436 | 468.537 |
| $4f^7 5d6s\ ^{10}D_{7/2}$ | 13 048.90 | 6↔5 | 5334.089 | 2157.011 |
| | | 5↔4 | 4522.375 | 1995.420 |
| | | 4↔3 | 3668.385 | 1725.722 |
| | | 3↔2 | 2780.684 | 1369.716 |
| | | 2↔1 | 1867.771 | 949.049 |
| $4f^7 5d6s\ ^{10}D_{9/2}$ | 13 222.04 | 7↔6 | 5306.284 | 2175.070 |
| | | 6↔5 | 4608.228 | 2018.222 |
| | | 5↔4 | 3882.471 | 1790.341 |
| | | 4↔3 | 3133.641 | 1503.271 |
| | | 3↔2 | 2366.363 | 1168.860 |
| $4f^7 5d6s\ ^{10}D_{11/2}$ | 13 457.21 | 8↔7 | 5561.459 | 2471.759 |
| | | 7↔6 | 4865.333 | 2161.607 |
| | | 6↔5 | 4169.609 | 1851.947 |
| | | 5↔4 | 3474.206 | 1542.695 |
| | | 4↔3 | 2779.069 | 1233.774 |
| $4f^7 5d6s\ ^{10}D_{13/2}$ | 13 778.68 | 9↔8 | 5919.624 | 2878.256 |
| | | 8↔7 | 5186.847 | 2368.549 |
| | | 7↔6 | 4480.582 | 1925.887 |
| | | 6↔5 | 3797.496 | 1541.884 |
| | | 5↔4 | 3134.271 | 1208.147 |
| $4f^7 5d6s\ ^{8}D_{3/2}$ | 15 137.72 | 4↔3 | −7250.964 | −3113.563 |
| | | 3↔2 | −5505.551 | −2504.188 |
| | | 2↔1 | −3702.533 | −1750.074 |
| $4f^7 5d6s\ ^{8}D_{5/2}$ | 15 248.76 | 5↔4 | −4911.320 | −2429.759 |
| | | 4↔3 | −3820.588 | −1672.778 |
| | | 3↔2 | −2801.864 | −1096.170 |
| | | 2↔1 | −1837.524 | −655.204 |
| | | 1↔0 | −909.622 | −304.899 |
| $4f^7 5d6s\ ^{8}D_{7/2}$ | 15 421.25 | 6↔5 | −4107.208 | −1998.908 |
| | | 5↔4 | −3358.150 | −1504.860 |
| | | 4↔3 | −2644.287 | −1098.567 |
| | | 3↔2 | −1958.583 | −762.492 |
| | | 2↔1 | −1293.991 | −479.082 |
| $4f^7 5d6s\ ^{8}D_{9/2}$ | 15 680.28 | 7↔6 | −3755.521 | −1640.475 |
| | | 6↔5 | −3227.607 | −1430.543 |
| | | 5↔4 | −2695.778 | −1209.400 |
| | | 4↔3 | −2160.646 | −978.864 |
| | | 3↔2 | −1622.842 | −740.780 |
| $4f^7 5d6s\ ^{8}D_{11/2}$ | 16 079.76 | 8↔7 | −3510.679 | −1289.233 |
| | | 7↔6 | −3155.677 | −1343.924 |
| | | 6↔5 | −2767.171 | −1312.318 |
| | | 5↔4 | −2349.930 | −1206.708 |
| | | 4↔3 | −1908.720 | −1039.409 |

the fact that the perturbation is proportional to the square of the off-diagonal matrix element, and thus to $(a_{6s})^2$; previous work [3,4] has shown that $a_{6s}$ is about 40 times larger than the single-electron parameters for the $5d$ or $4f$ electrons. The off-diagonal effects of the electric quadrupole interaction should be much smaller still. To evaluate the necessary off-diagonal hfs matrix elements, we represent the $^{8,10}D_J$ states as

$$|\Psi_1 S_1 L_1, 6s; \Psi\rangle ,$$

where

$$\Psi_1 = |4f^7(^8S)5d; {}^9D\rangle .$$

We then evaluate

$$\langle \Psi_1 S_1 L_1, 6s; SLJIFM | a_{6s}\mathbf{s}\cdot\mathbf{I} | \Psi_1 S_1 L_1, 6s; S'L'J'IFM\rangle , \tag{1}$$

and find that, for the $^{8,10}D$ states of interest, this becomes

$$(-1)^{F+1\frac{3}{2}}[35(2J+1)(2J'+1)(2S+1)(2S'+1)]^{1/2} \times \begin{Bmatrix} J & J' & 1 \\ \frac{5}{2} & \frac{5}{2} & F \end{Bmatrix} \begin{Bmatrix} J & J' & 1 \\ S' & S & 2 \end{Bmatrix} \begin{Bmatrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & 4 \end{Bmatrix} a_{6s} . \tag{2}$$

In evaluating the second-order corrections to the various hyperfine levels $F$ of the ten $^{8,10}D_J$ levels, we use for $a_{6s}$ the values [4] 9100 MHz for $^{151}$Eu and $(^{153}\mu/^{151}\mu)9100 = 4018$ MHz for $^{153}$Eu and proceed in the normal way. Each $F$ level of a given $J$ value is perturbed by the levels of the same $F$ in the states with $J+1$ and $J-1$. After making the corrections to all the $F$ levels of every $J$ within each multiplet (but omitting, at this point, hfs interactions between the $^8D$ and $^{10}D$ terms), we find the hfs intervals altered typically by several MHz. At this point, the two-parameter hfs theory can again be applied yielding "corrected" values for the $A$ and $B$ factors of each state. The point of greatest interest is that the quadrupole ratio $^{151}B/^{153}B$ for the $^{10}D_{11/2}$ state has changed from 0.790 by about the amount expected, but in the wrong direction, i.e., the corrected value is 1.100 while the true value must be near 0.393, as discussed above. The conclusion is that the corrections made do not include all of the important perturbations.

While corrections for second-order hfs effects are almost always dominated by interactions within a given $SL$ term, interactions between different terms are in principle allowed; thus, an hfs level $F$ within the state $\alpha SLJ$ can be perturbed by levels of the same $F$ in a state $\alpha' S'L'J'$ of a different multiplet. Perturbations between the $^8D$ and $^{10}D$ terms were therefore evaluated using Eq. (1). It was found that although the energy denominators are about seven times larger for the $^8D$-$^{10}D$ interactions, the corresponding matrix elements are in many cases as large as or even larger than for the diagonal interactions. The effects of including the cross-term interactions were comparable to those arising within each term. After including these additional corrections, the $^{10}D_{11/2}$ quadrupole ratio became 0.476(80), virtually consistent with the expected value of 0.393. This result is felt to be as close to the anticipated value as can be expected (a) considering the approximations made in evaluating the perturbations and (b) ignoring states still more removed from the $^{10}D_{11/2}$ state.

The two-parameter theory can also be applied to the $\Delta\nu$'s of all the other $^8D$ and $^{10}D$ states, suitably corrected for off-diagonal hfs both within and between the two multiplets. When this is done, "corrected" values are obtained for the $A$ and $B$ values of these states. These results are not tabulated here, since the exact values obtained depend in detail on all the assumptions and approximations made in applying the corrections. [The uncorrected hfs intervals (i.e., the observations) are atomic constants and are listed in Table I, however.] The isotopic ratios of the hfs constants are much less sensitive to details of the corrections applied (except for the unusual case of the $^{10}D_{11/2}$ state for which the observed $B$ values are so small as to be comparable to the corrections themselves). Table II lists the values of $^{151}A/^{153}A$ and $^{151}B/^{153}B$ for each state, including all corrections. The uncertainties assigned are about one-fourth of the size of the second-order corrections, and are consequently much larger than experimental error for the quadrupole ratios. It is seen that all of the $B$-value ratios are consistent with the $4f^76s^2\,{}^8S_{7/2}$ atomic ground-state result and with recent measurements [6] for the $4f^75d\,{}^9D_{2\text{-}5}$ term in Eu II. It is impressive that for every one of the ten levels studied, the corrected value of the isotopic quadrupole ratio $^{151}B/^{153}B$ is closer to the ground-state value [5] than the uncorrected (observed) value, i.e., in every case the correction has been in the right direction and of about the right magnitude. (In contrast, we note that if the cross-term corrections are ignored, the corrections are in the wrong direction for four of the ten levels investigated.) The surprising importance of second-order hfs interactions between two terms is thereby clearly demonstrated.

Column 3 of Table II lists the isotopic ratios of the $A$ values $^{151}A/^{153}A$ for each of the states studied as well as for the Eu I atomic ground state [2,5] and four levels [6] in Eu II. All of the $^{8,10}D$ values differ from the ground-state value, and a striking $J$ dependence is observed within each term. There is also an $SL$ or term dependence, the $J$ dependence being in opposite directions in the $^8D$ and $^{10}D$ terms. Traditionally, any difference between the dipole hfs ratio and the corresponding ratio of the nuclear magnetic dipole moments $[\mu(^{151}\text{Eu})/\mu(^{153}\text{Eu})$ has the measured ratio value [5] of 2.265 05(42)] is expressed as a hyperfine anomaly $^{151}\Delta^{153}$ by the relation

$$^{151}\Delta^{153} = [(^{151}A/^{153}A)/(^{151}\mu/^{153}\mu)] - 1 . \tag{3}$$

Table II also lists the calculated hyperfine anomalies; they are calculated using the corrected "$A$" ratios, but the results using the uncorrected $A$'s are only marginally different. The precision in the anomalies is limited by that of the dipole moment ratios of the dipole moment ratio [5]. It should be noted that the anomaly in the atomic ground state is consistent with zero. Figure 2 displays the anomaly information graphically. The figure shows the opposite signs of the $J$ dependence for the $^8D$ and $^{10}D$ states, as well as the much stronger $J$ dependence of the anomaly for the $4f^75d\,{}^9D$ term of Eu II. The apparent in-

TABLE II. Isotopic ratios for the (a) magnetic dipole and (b) electric quadrupole hfs interaction constants. The large uncertainties given for the quadrupole ratios result from uncertainties in the second-order hfs corrections applied to the observed hfs intervals; the uncertainties due to experiment alone are much smaller. Values for the hfs anomaly show both a $J$ and a term dependence. The anomaly values for the $^8S_{7/2}$ atomic ground state and for some Eu II levels are given for comparison.

| Atomic states | $^{151}A/^{153}A$ | $^{151}\Delta^{153}$ | $^{151}B/^{153}B$ | Source |
|---|---|---|---|---|
| Eu I | | | | |
| $4f^7 5d6s\ ^{10}D_{5/2}$ | 2.248 45(5) | −0.007 33(18) | 0.386(6) | a |
| $4f^7 5d6s\ ^{10}D_{7/2}$ | 2.249 85(5) | −0.006 71(18) | 0.390(6) | a |
| $4f^7 5d6s\ ^{10}D_{9/2}$ | 2.250 65(5) | −0.006 36(18) | 0.390(6) | a |
| $4f^7 5d6s\ ^{10}D_{11/2}$ | 2.251 04(5) | −0.006 19(18) | 0.476(80) | a |
| $4f^7 5d6s\ ^{10}D_{13/2}$ | 2.251 08(5) | −0.006 17(18) | 0.392(6) | a |
| Eu I | | | | |
| $4f^7 5d6s\ ^{8}D_{3/2}$ | 2.252 09(5) | −0.005 72(18) | 0.395(6) | a |
| $4f^7 5d6s\ ^{8}D_{5/2}$ | 2.250 60(5) | −0.006 38(18) | 0.393(6) | a |
| $4f^7 5d6s\ ^{8}D_{7/2}$ | 2.249 41(5) | −0.006 90(18) | 0.393(6) | a |
| $4f^7 5d6s\ ^{8}D_{9/2}$ | 2.248 70(5) | −0.007 22(18) | 0.390(6) | a |
| $4f^7 5d6s\ ^{8}D_{11/2}$ | 2.248 58(5) | −0.007 27(18) | 0.392(6) | a |
| Eu I | | | | |
| $4f^7 6s^2\ ^{8}S_{7/2}$ | 2.264 98(8) | −0.000 03(19) | 0.3928(20) | b |
| Eu II | | | | |
| $4f^7 5d\ ^{9}D_2$ | 2.2565(1) | −0.003 77(19) | 0.3920 | c |
| $4f^7 5d\ ^{9}D_3$ | 2.2520(1) | −0.005 76(21) | 0.3919 | c |
| $4f^7 5d\ ^{9}D_4$ | 2.2445(1) | −0.009 07(19) | 0.3919 | c |
| $4f^7 5d\ ^{9}D_5$ | 2.2365(1) | −0.012 60(21) | 0.3908 | c |

[a]Present work. [b]References [2] and [5]. [c]Reference [6].

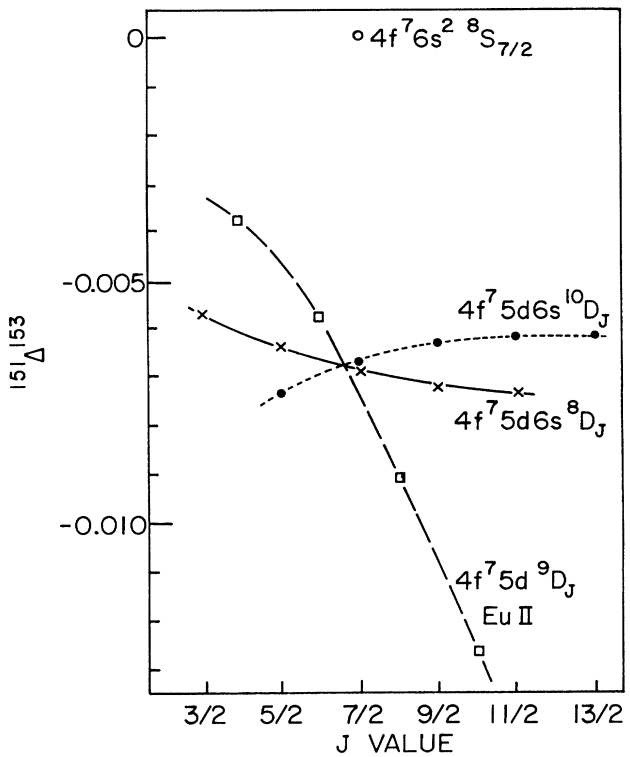


FIG. 2. Hyperfine anomaly values determined from the magnetic dipole hfs constants measured for the $4f^7 5d6s\ ^{8,10}D$ levels of $^{151,153}$Eu I. Previously measured values for the $4f^7 5d\ ^9D$ levels of Eu II are also shown. The anomaly for the $4f^7 6s^2\ ^8S_{7/2}$ atomic ground state is consistent with zero; it appears at the top of the figure.

tersection of the three anomaly curves for $J = \frac{7}{2}$ may be accidental.

The origin of a hyperfine anomaly has been studied theoretically by several workers [12], although any $J$ dependence for the states of an atomic multiplet has received little attention. Our discussion closely follows that of Sorensen [12], though in greatly abbreviated form. Although nuclear dipole moments are measured in a uniform magnetic field, the dipole hfs occurs in the nonuniform field of the electrons, and the anomaly arises from this different environment. It is therefore dependent on the volume distribution of the nuclear magnetism. The magnetic field **B** (from the electrons) at the nucleus arises, for the excited $4f^7 5d6s\ ^{8,10}D$ states of Eu, from the $6s$ electron, which has only a spin. (Core polarization could also play a role, but for the Eu levels considered the contribution of the unpaired $6s$ electron should be much larger.) The theory takes account of the volume distribution of magnetization from the neutron and proton spin moments, and the system of currents due to the orbiting protons. Since each atomic state can be represented as a linear combination of well-defined $LS$ basis states, it is clear that there will be differences, however small, in the importance of the $6s$ electron between the states of different $J$ within a multiplet. These differences will result in slight differences in the resulting nonuniform magnetic field **B** with which the spatially extended magnetic nucleus interacts, and these will manifest themselves in slight differences in the observed hyperfine anomaly. Thus, while a small $J$ dependence is qualitatively to be expected, it is clear that a quantitative theoretical treatment would be of value.

It is of interest to examine the residuals ($\Delta\nu_{obs}-\Delta\nu_{calc}$) resulting from the two-parameter fits to the observed zero-field hfs intervals (after correction for second-order hfs effects). For two states ($^{10}D_{7/2}$ and $^{8}D_{5/2}$), they are found to be 50–100 times larger than the experimental uncertainties, and strongly suggest the presence of a physical effect not included in the two-parameter ($A$ and $B$) model used in the fits. The extent to which the residuals exceed experimental error for the other eight states is much less, and is essentially zero for the $^{8}D_{7/2}$ level. Table III lists in column 3 the residuals for the two-parameter fits to the intervals of $^{151}$Eu in its $^{8}D_{5/2}$ and $^{8}D_{7/2}$ states. It can be seen that the fit for the former state results in residuals much greater than the experimental uncertainties of 1–5 kHz while the fit for the $^{8}D_{7/2}$ level is to within the experimental error. The two most likely reasons for large residuals are (1) higher-order hyperfine interactions (i.e., magnetic octupole, electric $2^4$ pole, etc.) and (2) inadequacy of the second-order corrections. The latter might include neglect of other terms in the off-diagonal hfs Hamiltonian, use of poor values for the radial integrals in the interaction, the effects of any admixtures on the corrections, the choice of perturbing states selected, etc. As will be shown, higher-order hfs interactions, and not shortcomings of the second-order corrections, are the dominant source of the large residuals in the two-parameter fits to the states mentioned.

If the expected $F$ dependence of the magnetic octupole and electric $2^4$ pole interactions is worked out [13] for the $\Delta\nu$'s of the ten states, it is found that the residuals in the two-parameter fits, which neglect these effects, are closely proportional to the expected octupole dependence and not at all to the expected $2^4$-pole dependence. Using standard nomenclature, we call the magnetic octupole and electric $2^4$ pole hfs interaction constants for a state $C$ and $D$, analogous to $A$ and $B$ for the magnetic dipole and electric quadrupole. When three-parameter fits ($A$, $B$, and $C$) are made to the $\Delta\nu$'s of the $^{10}D_{7/2}$ and $^{8}D_{5/2}$ states (i.e., those with the largest residuals), the residuals drop to a few kHz (i.e., to within experimental error), as is shown (for the $^{8}D_{5/2}$ level) in the final column of Table III. Fitting with the four parameters $A$, $B$, $C$, and $D$ cannot improve this further, but it should be noted that an attempted fit using $A$, $B$, and $D$ is totally unsatisfactory. This is extremely strong evidence that the measurements are revealing magnetic octupole effects in the zero-field hfs spacings.

Three-parameter ($A$, $B$, and $C$) hfs fits were made to the five $\Delta\nu$'s of each of the 10 states for both $^{151}$Eu and $^{153}$Eu, and the residuals were found to be at the level of experimental error for each of the 20 fits. While the values of all the $A$'s and $B$'s are slightly different than for the corresponding two-parameter fits, the changes in the ratios $^{151}A/^{153}A$ and $^{151}B/^{153}B$ (given for the two-parameter fits in Table II) were hardly perceptible.

As expected, the $C$ values found from the three-parameter fits are very much smaller than the $A$ or $B$ values. It is interesting to note that the $C$ values obtained for all the states are the same (to within the relatively large experimental uncertainties) whether obtained from the raw data or the corrected $\Delta\nu$'s, again indicating that the effect is real and not an artifact introduced by the second-order corrections. The ratios $C(^{151}\text{Eu})/C(^{153}\text{Eu})$ are listed in Table IV. The uncertainty for the two states with the largest residuals ($^{10}D_{7/2}$ and $^{8}D_{5/2}$) is about 0.06, while that for the others is best indicated by the scatter. The residuals for the $^{8}D_{7/2}$ state are too small to allow evaluation of the ratio. In calculating a weighted average of the octupole hfs constant ratio, it is probably best to give less weight to the measurement in the $^{10}D_{11/2}$ state because of the anomalously small electric quadrupole interaction. The final value is

$$C(^{151}\text{Eu})/C(^{153}\text{Eu})=0.87(6)\ .$$

It is assumed that the corresponding isotopic ratio of the nuclear ground-state magnetic octupole moments has the same value. Evaluation of the nuclear octupole moment for either $^{151}$Eu or $^{153}$Eu alone is much more difficult,

TABLE III. Residuals from two-parameter ($A$ and $B$) hfs fits for two of the ten $^{151}$Eu I levels studied. The fit for the $^{8}D_{5/2}$ state reveals residuals (due to the magnetic octupole hfs interaction) up to 100 times experimental error. The fit to the $^{8}D_{7/2}$ state, on the other hand, is virtually consistent with experimental error, implying a very small octupole interaction.

| | | Residuals[a] (MHz) | |
|---|---|---|---|
| Atomic state | $F\leftrightarrow F'$ | Two-parameter fit ($A,B$) | Three-parameter fit ($A,B,C$) |
| $^{8}D_{5/2}$ | 5↔4 | 0.110 | 0.000 |
| | 4↔3 | −0.219 | 0.001 |
| | 3↔2 | −0.037 | 0.000 |
| | 2↔1 | 0.145 | −0.001 |
| | 1↔0 | 0.148 | 0.002 |
| $^{8}D_{7/2}$ | 6↔5 | 0.000 | 0.000 |
| | 5↔4 | −0.003 | −0.003 |
| | 4↔3 | 0.004 | 0.004 |
| | 3↔2 | −0.002 | −0.002 |
| | 2↔1 | −0.001 | 0.000 |

[a]Observed values minus calculated values.

TABLE IV. Values of the hfs octupole ratio $^{151}C/^{153}C$ obtained for ten atomic states from three-parameter ($A$, $B$, and $C$) fits to the hfs intervals, after correction for second-order hfs effects.

| Atomic state | $^{151}C/^{153}C$ |
|---|---|
| $^{10}D_{5/2}$ | 0.9 |
| $^{10}D_{7/2}$ | 0.84 |
| $^{10}D_{9/2}$ | 1.0 |
| $^{10}D_{11/2}$ | 1.1 |
| $^{10}D_{13/2}$ | 0.9 |
| $^{8}D_{3/2}$ | 0.8 |
| $^{8}D_{5/2}$ | 0.90 |
| $^{8}D_{7/2}$ | |
| $^{8}D_{9/2}$ | 0.8 |
| $^{8}D_{11/2}$ | 0.9 |

since it depends not only on uncertainties in the second-order hfs corrections, but also [14] on the effective value of $\langle r^{-5}\rangle_{5d}$, which can be perturbed very strongly by octupole shielding or antishielding analogous to the well-known Sternheimer shielding [15] for the quadrupole interaction. Such effects could easily be (relatively) much larger than for the quadrupole interaction. That the octupole interaction arises primarily from the $5d$ electron is due to the $L=0$ character of the $6s$ and $4f^7$ ($^8S$) electron shells.

It is felt that the arguments presented give extremely strong evidence that the magnetic octupole hfs interaction is indeed being observed. It is only fair to say, however, that if one works out [16] the expected $J$ dependence of the $C$ values from the $LS$ limit model (which predicts the $A$ and $B$ values in good agreement with experiment), the results are not consistent with the observed $J$ dependence. One may note, however, that the predicted value of $B(^{10}D_{11/2})$, which happens to be two orders of magnitude smaller than the $B$ values for the other states, is not well predicted by the model either. The $C$ values are an additional two to three orders of magnitude smaller still, and a large number of very small perturbations could certainly distort the hfs intervals enough to drive the $C$ values from their expected $J$ dependence. The critical point to be emphasized is that these tiny effects are virtually identical for $^{151}$Eu and $^{153}$Eu within any particular atomic state, and this is why the ratio $^{151}C/^{153}C$ is observed to be state independent (within experimental error) even though the $J$ dependence of $C$ for either isotope alone is hard to account for. Previous studies [17] of the (atomic) state dependence of the magnetic octupole hfs interaction in $^{51}$V and $^{197}$Au have also been found to be inconsistent with predictions of the $LS$ limit model. Even if one ignores the problem of evaluating the "octupole Sternheimer shielding" effects, the uncertainty in attempting to derive an experimental value for a nuclear magnetic octupole moment from hfs observations is clear.

## IV. CONCLUSIONS

Precise values for the zero-field hfs splitting have been given for ten excited levels in two terms of the $4f^7 5d\,6s$ electron configuration in $^{151,153}$Eu I. In order to compare the hfs constants $A$, $B$, and $C$ determined from fits to these intervals with a theoretical model, corrections for second-order hfs interactions have been carried out. These calculations include hfs perturbation effects between the two terms as well as the usual ones within each term. The surprising importance of the cross-term perturbations is demonstrated. The importance of including the second-order corrections is shown by the requirement that the isotopic quadrupole hfs ratio $^{151}B/^{153}B$ be state independent. The corresponding magnetic dipole ratio $^{151}A/^{153}A$ is evaluated and reveals both a $J$ dependence and a term dependence. These effects are reflected in the hyperfine anomaly values presented.

Study of the details of the two-parameter ($A$ and $B$) fits to the corrected hfs intervals reveals residuals that (1) range up to 100 times experimental error and (2) exhibit the $F$ dependence predicted for a magnetic octupole hfs interaction. When such an interaction is allowed, all residuals drop to the level of experimental error. The isotopic magnetic octupole hfs ratio $^{151}C/^{153}C$ is evaluated and found to be the same to within experimental error for all of the atomic states studied; it is assumed to be the same as the ratio of the magnetic octupole moments within the $^{151,153}$Eu nuclear ground states. No theoretical estimate of this ratio is known to the author, but an effort is now being made by Chasman [18] to predict the ratio on the basis of current nuclear models.

Determination of the nuclear octupole moment for either isotope alone is at present unfeasible due to (a) the difficulties of evaluating possibly large, Sternheimer-like octupole shielding effects (i.e., evaluating $\langle r^{-5}\rangle_{5d}$) reliably and (b) the difficulty of understanding the observed $J$ dependence of the hfs octupole interaction.

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