Paramagnetic Resonance Absorption in Uranium (III) Chloride and the Nuclear Spin, Magnetic Dipole Moment, and Electric Quadrupole Moment of Uranium-233†

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Paramagnetic resonance absorption in single crystals of $U^{233}Cl_3$ diluted with $LaCl_3$ has been investigated. The values of the parameters in the appropriate Hamiltonian are given. The values of the nuclear spin, magnetic dipole moment, and electric quadrupole moment obtained from these studies are discussed. The ratios of the moments of U^{235} and U^{233}, which can be obtained with much higher accuracy than the individual moments, are given.

INTRODUCTION

PARAMAGNETIC resonance absorption in single crystals of UCl_3 diluted with $LaCl_3$ and containing U^{235} in its normal abundance has been examined recently by Hutchison, Llewellyn, Wong, and Dorain.[1] Crystals of $LaCl_3$ containing UCl_3 enriched in U^{235} have also been investigated by Bleaney, Hutchison, Llewellyn, and Pope,[2] and this has permitted a study of the $\Delta m=\pm1$, ±2 transitions as well as of the $\Delta m=0$ hyperfine lines. In the present paper we report similar results obtained for U^{233} in the same system, and also the ratios of the values of the nuclear dipole and quadrupole moments for the two isotopes which can be determined with more certainty than can the individual values.

EXPERIMENTAL PROCEDURE

$U^{233}Cl_3$ was prepared in a single quartz microflask of about 2 cm³ volume from the hydrated nitrate. Either the nitrate or UO_3 prepared from it reacted with hexachloropropene[3] to form UCl_4 and the liquid reaction products and excess hexachloropropene were removed. Then Zn metal was added and after evacuation the flask was sealed and heated; reduction to UCl_3 took place and excess reagents and reaction products, apart from the UCl_3, sublimed to a cool portion of the neck of the flask.[4] The portion of the flask containing the pure UCl_3 was sealed and removed to a dry box where it was added to $LaCl_3$ prepared by the method described by Anderson and Hutchison.[5] Crystals were prepared as described previously.[1]

The resonance experiments were performed at a frequency of 2.32×10^{10} cy sec^{-1} and at 4.2°K. The crystals contained approximately 0.01 mole percent U^{233} in La.

EXPERIMENTAL RESULTS

The magnetic resonance spectrum in the position in which the c-axis of the crystal is parallel to $\mathbf{H}$ consists of six nearly equally spaced lines and the spin of U^{233} is clearly 5/2. This is in agreement with the results of optical studies.[6]

The nature of the ground state of U^{3+} in the $LaCl_3$ structure has been discussed previously.[1] Taking $S=1/2$ and $I=5/2$ the spectrum has been analyzed using the spin Hamiltonian

$$\mathcal{H}=\beta\{g_{\parallel}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)\}+hcAS_zI_z +hcB(S_xI_x+S_yI_y)+hcP\{I_z^2-\tfrac{1}{3}I(I+1)\} -g_N\beta_N\mathbf{H}\cdot\mathbf{I}, \quad (1)$$

with $g_{\parallel}=4.153$ and $g_{\perp}=1.520$ as given previously.[1]

The theory of this Hamiltonian with special reference to nuclear effects has been given by Bleaney.[7] When the c axis of the crystal is parallel to $\mathbf{H}$ only the $2I+1$ transitions for $\Delta m=0$ are observed (m is the nuclear quantum number). As the crystal is rotated the transitions for $\Delta m=\pm1$ appear, two lines between each hyperfine pair as shown in Fig. 1. In the orientation in which the c axis is perpendicular to $\mathbf{H}$, the intensity of the $\Delta m=\pm1$ lines has fallen to zero and only the $\Delta m=\pm2$ lines, which appear near this angle, remain in addition to the $\Delta m=0$ lines. This situation is shown in Fig. 2.

In the analysis of the present data, we have treated the off-diagonal elements of $AS_zI_z+B(S_xI_x+S_yI_y)$ by perturbation theory and have inserted the calculated second-order hyperfine energies as diagonal terms in the matrix of the quadrupole interaction. Then to the approximation of second-order perturbation theory and omitting terms of order higher than P^3/B^2, we find that in the perpendicular orientation the following relations are valid.

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[4] See reference 3, pp. 450–452.

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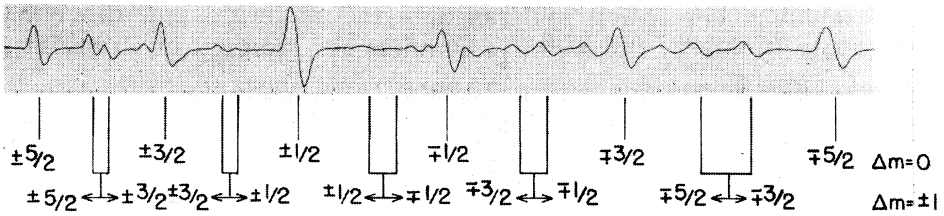

FIG. 1. Recorder chart showing derivative of absorption *versus* magnetic field strength. The angle between the c axis and **H** is 91.9°. (Field strength increasing to the right. The $\Delta m=\pm 2$ transitions are not labeled although they appear in the photograph.) The recorder curves were inked for reproduction purposes with a line whose width was equal to the noise height.

(i) The magnitude of the separation between the outermost peaks of the spectrum ($\Delta m=0$ for these) is

$$\left|5B+\frac{10P^2B}{B^2-9P^2}\right|.$$

(ii) The magnitude of the separation between the next two outermost peaks is

$$\left|3B+\frac{18P^2B}{B^2-P^2}\right|.$$

(iii) The magnitude of the mean of the two intervals (a) between the line $(+1/2, +5/2)\leftrightarrow(-1/2, +1/2)$ and the line $(+1/2, +1/2)\leftrightarrow(-1/2, +5/2)$ and (b) between the line $(+1/2, -5/2)\leftrightarrow(-1/2, -1/2)$ and the line $(+1/2, -1/2)\leftrightarrow(-1/2, -5/2)$ is

$$\left|6P-\frac{30P^3}{B^2-9P^2}-\frac{9P^3}{B^2-P^2}\right|.$$

(iv) The magnitude of the similar mean involving the $m=\pm 3/2$ and $m=\mp 1/2$ levels is

$$\left|2P-\frac{18P^3}{B^2-P^2}-\frac{15P^3}{B^2-9P^2}\right|.$$

(v) At other angles the formulas of Bleaney[7] give for the magnitude of the mean of the two intervals (a) between the line $(+1/2, +5/2)\leftrightarrow(-1/2, +3/2)$ and the line $(+1/2, +3/2)\leftrightarrow(-1/2, +5/2)$ and (b) between the line $(+1/2, -5/2)\leftrightarrow(-1/2, -3/2)$ and the line $(+1/2, -3/2)\leftrightarrow(-1/2, -5/2)$ the value

$$\left|4P\frac{3A^2g_{\parallel}^2}{K^2g^2}(\cos^2\theta-1)\right|,$$

where $K^2g^2=A^2g_{\parallel}^2\cos^2\theta+B^2g_{\perp}^2\sin^2\theta$ and terms of the order P^3/B^2 are omitted.

When one uses these formulas, the best values obtained for the parameters in (1) are

$$I=5/2,$$
$$|A|=(378.6\pm 1.2)\times 10^{-4}\ \text{cm}^{-1},$$
$$|B|=(123.6\pm 1.0)\times 10^{-4}\ \text{cm}^{-1},$$
$$|P|=(9.9\pm 1.0)\times 10^{-4}\ \text{cm}^{-1}.$$

The value of $|A|$ was obtained by use of the relation

$$|A|=|\Delta H|\,\tilde{\nu}_0/5H_0,$$

where $|\Delta H|$ is the interval in the parallel orientation between the transitions $(+1/2, +5/2)\leftrightarrow(-1/2, +5/2)$ and $(+1/2, -5/2)\leftrightarrow(-1/2, -5/2)$, $\tilde{\nu}_0$ is the wave number corresponding to the microwave frequency, and H_0 is the quantity appearing in the expression

$$H_0-\frac{hc}{g_{\parallel}\beta}Am-a\{I(I+1)-m^2\}$$

for the field at which the $\Delta m=0$ transitions occur in the parallel orientation at fixed frequency.[7] The constant, H_0, was evaluated empirically from the hyperfine peak positions. $|P|$ was calculated by using the formulas of (iii), (iv), and (v), the last at two angles, 100° and 98°, between the c axis and **H**. The values 10.30, 13.0, 8.93, and 10.60×10^{-4} cm^{-1}, respectively, were obtained. The value 13.0 was discarded because of large uncertainty in this case, the lines for one of the intervals being unresolved. In the calculation of P by the formulas of (iii) and (iv), the value obtained is not sensitive to the value taken for $|B|$ and 1/5 the total spread of the spectrum in the perpendicular orientation was used. The better value of $|B|$ was then obtained from the formulas of (i) and (ii).

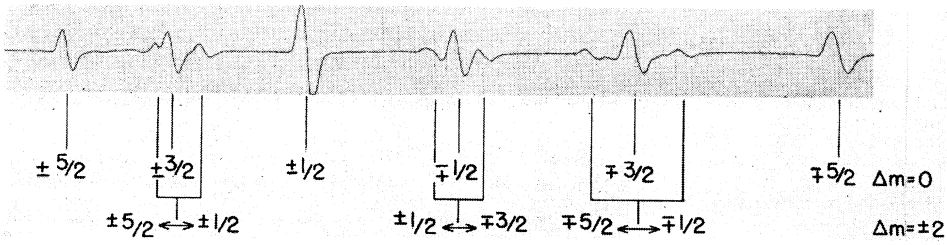

FIG. 2. Recorder chart showing derivative of absorption *versus* magnetic field strength. The angle between the c axis and **H** is 90.0°. The recorder curves were inked for reproduction purposes with a line whose width was equal to the noise height.

When H_0 for the parallel orientation (calculated as described above) and H_0 for the perpendicular orientation (calculated using the extension of Bleaney's relations[7] which was described above) are used to calculate g's, one obtains

$$g_{\parallel}=4.149, \quad g_{\perp}=1.520,$$

the values previously given[1] on the basis of measurements on U^{238} being

$$g_{\parallel}=4.153\pm0.005, \quad g_{\perp}=1.520\pm0.002.$$

The origin of the unlabeled lines in the spectrum of Fig. 2 is unknown.

DISCUSSION

Using the values of the parameters given above, one obtains

$$(g_{\parallel}A)/(g_{\perp}B)=1.12,$$

in close agreement with the value 1.10 which is obtained using the parameters for U^{235} given in the previous paper.[2] The significance of this value has been discussed.[1] The relation

$$\left(\frac{|A|}{|B|}\right)_{235}\Big/\left(\frac{|A|}{|B|}\right)_{233}=1.019$$

is found to hold. This ratio must theoretically be unity to a very high degree of approximation and the largest uncertainty in its experimental value arises from the determination of $|B|$.

The nuclear magnetic dipole moment may be calculated by employing the formula

$$\mu_N=\frac{I}{2\beta\beta_N\langle r^{-3}\rangle}\frac{\langle J\|\Lambda\|J\rangle}{\langle J\|N\|J\rangle}\{hc|A|/g_{\parallel},hc|B|/g_{\perp}\} \quad (2)$$

given by Elliott and Stevens[8] and the values of the multiplicative factors obtained from their tables. The large uncertainty in this calculation lies in the value used for $\langle r^{-3}\rangle$. Taking the value 50 A^{-3} obtained as described in the previous papers[1,2] one finds the values of the moment given in Table I. The ratio of the moments for the two isotopes may be given with much greater accuracy since the large uncertainty in $\langle r^{-3}\rangle$ is not involved. One finds the values given in Table I. The value in the left-hand column was calculated from the expression

$$|\mu_N{}^{235}|/|\mu_N{}^{233}|=|\Delta H^{235}|/|\Delta H^{233}|,$$

where the definition of ΔH for U^{235} is the same as that previously given for U^{233} except that 7/2 is substituted for 5/2. The value in the right-hand column is just the ratio of the μ_N's calculated from the formula (2).

[8] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

TABLE I. Numerical values.

	Value calculated from $\|A\|$, $g_{\parallel}$	Value calculated from $\|B\|$, $g_{\perp}$
$\|\mu_N{}^{233}\|$	0.54 nm	0.48 nm
$\|Q^{233}\|$	3.5×10^{-24} cm^2	3.3×10^{-24} cm^2
$\|\mu_N{}^{233}\|/\|Q^{233}\|$	$(1.52\pm0.15)\times10^{23}$ nm cm^{-2}	$(1.44\pm0.15)\times10^{23}$ nm cm^{-2}
$\|\mu_N{}^{235}\|$	0.35 nm	0.32 nm
$\|Q^{235}\|$	4.1×10^{-24} cm^2	3.9×10^{-24} cm^2
$\|\mu_N{}^{235}\|/\|Q^{235}\|$	$(0.85\pm0.08)\times10^{23}$ nm cm^{-2}	$(0.82\pm0.08)\times10^{23}$ nm cm^{-2}
$\|\mu_N{}^{235}\|/\|\mu_N{}^{233}\|$	0.651 ± 0.002	0.663 ± 0.012
$\|Q^{235}\|/\|Q^{233}\|$	1.17 ± 0.20	

The electric quadrupole moment may be calculated from the formula,

$$|Q|=\frac{4hc|P|I(2I-1)}{-9e^2\langle r^{-3}\rangle\langle J\|\alpha\|J\rangle\langle+|J_z{}^2-\frac{1}{3}J(J+1)|+\rangle},$$

given by Elliott and Stevens[8] and the multiplicative constant obtained from their tables. The value of the matrix element is somewhat different depending upon whether the coefficients of $\pm7/2$ and $\mp5/2$ in the ground state are computed from $g_{\parallel}$ or from $g_{\perp}$. The values using $\langle r^{-3}\rangle=50$ A^{-3} are given in Table I.

The ratio of the magnetic moment to the electric moment of the same isotope may be given with much less uncertainty than either individual moment because they both depend in the same way on $\langle r^{-3}\rangle$, the uncertain quantity in these calculations. There still remains an uncertainty of some 10% arising from mixing with J values other than those mentioned above which renders the formulas used inaccurate to that extent. One finds the values given in Table I.

The ratio of the quadrupole moments may likewise be found with relatively high accuracy, from the data of this and the preceding paper,[2] and are given in Table I. This ratio was calculated from the expression

$$|Q^{235}|/|Q^{233}|=(21/10)|P^{235}|/|P^{233}|.$$

The value of $\langle r^{-3}\rangle$ used in this paper probably represents something close to the upper limit for this quantity and it would not be too unlikely for it to be smaller by a factor of two. The values given here for $|\mu_N|$ and $|Q|$ are therefore probably close to their lower limits.

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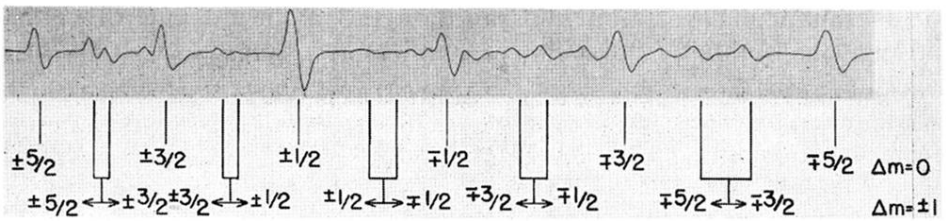

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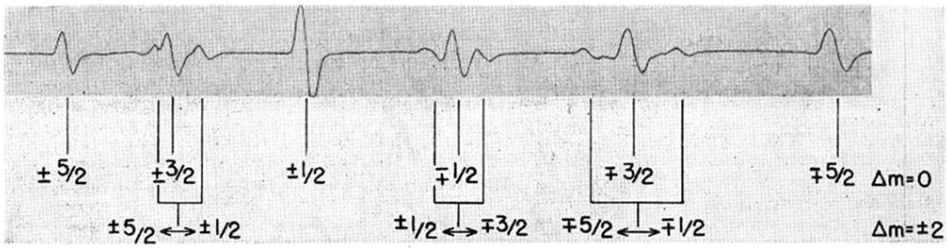

FIG. 2. Recorder chart showing derivative of absorption *versus* magnetic field strength. The angle between the c axis and **H** is 90.0°. The recorder curves were inked for reproduction purposes with a line whose width was equal to the noise height.