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Hyperfine Structure of the Electronic Ground States of Rb^{85} and Rb^{87}†

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A study has been made of the ground states of Rb^{85} and Rb^{87} with a high-resolution atomic beam magnetic resonance apparatus. The hfs interactions have been measured to give $\Delta\nu_{85}=3\,035\,732\,439\pm5$ cps, $\Delta\nu_{87}=6\,834\,682\,614\pm3$ cps. The nuclear magnetic moment μ_I for Rb^{85} has been measured independently of $\Delta\nu$ by observing the separation between components of the doublet $(3,-1)\leftrightarrow(2,-2)$ and $(3,-2)\leftrightarrow(2,-1)$ near the frequency minimum. This frequency is given by $\delta\nu=2g_I\mu_0H$. The value of μ_I is calculated to be 1.348 206(45) nm without diamagnetic correction or 1.352 70(25) nm with it.

The mean frequency of the doublet, 2 611 882 320±20 cps, agrees with that calculated by the Breit-Rabi equation to within one part in 10^8.

The value of the hfs anomaly, ${}_{85}\Delta_{87}$, is calculated to be 0.003 513 5(17).

INTRODUCTION

THE principal purposes of the experiments described herein are to determine with high precision the hyperfine-structure interaction constants for the ground state of the two stable Rb isotopes, Rb^{85} and Rb^{87}, and also to make a direct measurement of the nuclear magnetic moment of Rb^{85}.

The hyperfine structure separation $\Delta\nu$ for the ground state of Rb^{87} has been measured earlier by the optical pumping technique with an accuracy of ±7 cps,[1] and this transition has been used for the development of gas cell frequency standards. In view of the complex problem of correcting the frequencies measured by the optical pumping method for the several perturbing effects present, a value of comparable accuracy obtained by the atomic beam technique is highly desirable. The measurements made on $\Delta\nu_{85}$ and $\Delta\nu_{87}$ by the atomic beam resonance technique previously had uncertainties of 5 and 10 kc/sec and are thus inadequate for a comparison with optical pumping values.

While the nuclear resonance measurements of μ_I of Rb have been performed with high precision they are subject to molecular effects of second-order paramagnetism, which are extremely difficult to evaluate, and to atomic diamagnetism. The atomic beam data are subject only to the atomic diamagnetic correction which in the case of Rb amounts to about 0.0033 and is believed to be in error by less than 0.0002.[2]

The research described in this paper was performed on an apparatus essentially the same as that used in the previous paper.[3] A study of the stable Rb isotopes facilitated an evaluation of the limits of precision of our atomic beam apparatus.

† Work done at Brookhaven National Laboratory for the United States Atomic Energy Commission.

* On leave from the University of Heidelberg.

[1] P. L. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Letters **1**, 311 (1958).

[2] W. C. Dickinson, Phys. Rev. **80**, 587 (1950).

[3] V. W. Cohen, T. I. Moran, and S. Penselin, preceding paper [Phys. Rev. **127**, 517 (1962)].

Δν MEASUREMENTS

To determine the hyperfine structure separations of Rb^{85} $(I=5/2)$ and Rb^{87} $(I=3/2)$, the $\Delta F=\pm1$ transitions $m_F=0\leftrightarrow m_{F'}=0$ were measured with the Ramsey separated oscillating-field method at low field where they show a very small quadratic dependence on the external magnetic field. For inducing these $\Delta m=0$ transitions, we used rf loops producing the rf magnetic field at the position of the atomic beam parallel to the external magnetic field, as shown in Fig. 1. With this construction of the loop, the rf magnetic field falls off rapidly below the inner conductor. Only that portion of the beam within about 2 mm of the conductor experiences appreciable transition proba-

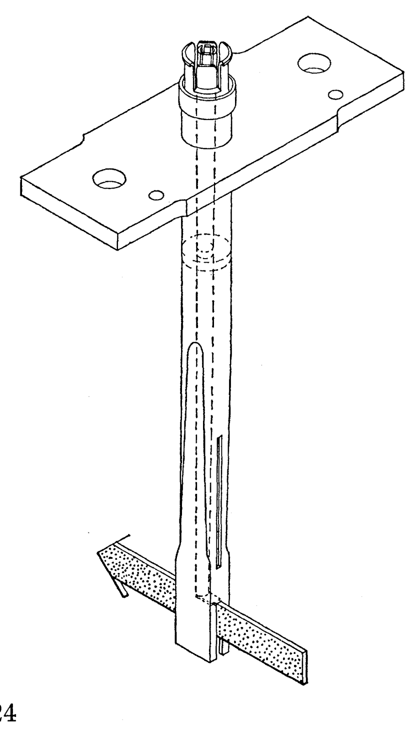

FIG. 1. Loop producing the oscillatory field parallel to the steady C field for inducing $\Delta F=0$ transitions. The principal conductor producing the fields is the termination between the lower end of the central conductor and the right-hand side of the outer conductor.

TABLE I. Experimental data for the determination of $\Delta\nu$ of Rb^{87}.

Run	Measured frequency (cps)	Magnetic field correction (cps)	Reference crystal correction (cps)	$\Delta\nu_{87}$ (cps) without phase correction	$\Delta\nu_{87}$ (cps) averaged for phase shift	Loop-system orientation	Frequency standard	Frequency synthesizer
1	6 834 682 666	−9.5	+3.7	6 834 682 660.2	6 834 682 660.2	0°	Atomichron	Ft. Monmouth
2	666	−9.5	+3.7	660.2		180°	Atomichron	Ft. Monmouth
3	666	−9.0	+3.7	660.7	663.5	0°	Atomichron	Ft. Monmouth
4	672	−9.5	+3.7	666.2		180°	Atomichron	Ft. Monmouth
5	684	−8.5	+3.7	679.2	669.2	0°	Atomichron	Ft. Monmouth
6	670	−14.5	+3.7	659.2		180°	Atomichron	Ft. Monmouth
7	685	−14.5	+3.7	674.2	664.2	0°	Atomichron	Ft. Monmouth
8	668	−17.5	+3.7	654.2		180°	Atomichron	Ft. Monmouth
9	683	−11.1	+7.2	679.1	665.2	0°	crystal	Schomandl
10	653	−9.0	+7.2	651.2		180°	crystal	Schomandl
11	668	−10.1	−3.8	654.1	668.9	180°	crystal	Schomandl
12	697	−17.1	+3.7	683.6		0°	Atomichron	Ft. Monmouth
13	663	−13.5	+3.7	653.2	668.0	180°	Atomichron	Ft. Monmouth
14	697	−17.9	+3.7	682.8		0°	Atomichron	Ft. Monmouth
				Average	6 834 682 665.6			

bility. Figure 2 shows a typical "Ramsey" pattern of such a transition recorded with a time constant of about 0.5 sec. The loop system was tuned in this case for a phase difference of 180° between the two loops, while all further measurements were made with the rf in-phase in the two loops giving a Ramsey pattern with a central maximum. The high signal-to-noise ratio made it possible to measure the center of the central peak with an uncertainty of approximately one thousandth of its width by averaging the frequencies of points of equal intensity on each side of the central peak. This was done in each case for about five different intensities. The averages as thus measured for the different intensities were consistent within about one cycle. Using loops 1 and 5 with a separation of 195 mm between them, the central peak had a width of about 1.3 kc/sec. Table I shows the measurements of Rb^{87} together with the special conditions, under which they were made and which will be discussed in detail below. The statistical error of the measured frequencies in Table I was in most cases smaller than 1 cps. In view of this small statistical error, attempts were made to reduce all instrumental errors to nearly the same figure.

Possible Errors and Corrections

Rf *phase difference between the loops.* The most likely reason for a distortion of the Ramsey pattern is a phase difference between the oscillatory fields in the two loops which may be produced for example by a slight propagation asymmetry in the loop system. To make the phases as nearly equal and constant as possible, the two loops were firmly attached to a very rigid coaxial system outside of the vacuum chamber. A schematic drawing of the system, which was mounted on a Plexiglas plate 1 in. thick, is shown in Fig. 3. The system is loosely coupled to the klystron and tuned in length by the two line stretchers. Minimum reflection as measured by the directional coupler serves as a tuning indicator. The upper part of the line has a slotted section through which a magnetic coupling loop is inserted. This line can be used in both the in-phase or 180° out-of-phase modes of oscillation by suitable adjustment of total length and position of the coupling

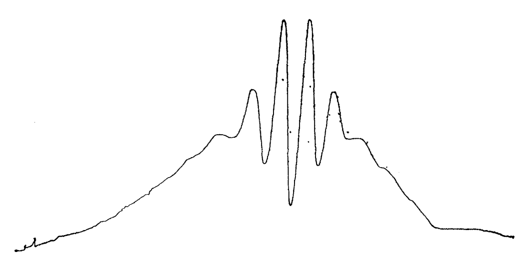

FIG. 2. A typical "Ramsey" pattern of the $\Delta F=\pm 1$ field-independent transition with 180° phase difference between loops. The frequency difference between the two maxima is about 2.6 kc/sec.

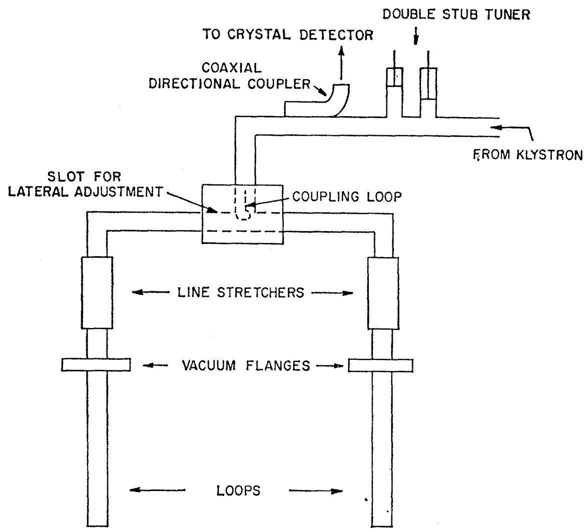

FIG. 3. Schematic arrangement of tuned line for feeding the rf loops and the adjustable components for tuning the input.

loop. The horizontal slide adjustment also permitted optimum coupling between the resonant loop system and the source of rf power. After tuning, the system can be fixed rigidly in its position. While the line was designed to be as nearly symmetrical as possible, some slight residual phase shift remained. After each set of measurements the entire loop system was removed from the apparatus, rotated 180° and replaced. By averaging the two sets of measurements, we assume that the residual phase-shift effects are eliminated. The two positions of the loop-system are marked in Table I by 0° and 180°.

For the first four measurements only the relative position has been recorded. As can be seen from the table, for the measurements 5–14 the difference of the frequency pairs for the two position is 20···30 cps, and the maximum spread of the average frequencies of the pairs is 5 cps. A reason for the slight deviation of the first four measurements from the mean value of the other measurements may possibly be that, during these measurements, there was a brass shim, 5 mils thick, bent around the two broader sides of the loops and the open end at the bottom of the loops to give them a snug fit between the pole faces of the C magnet. These grass spacers were not rigidly attached to the loops and in moving might have introduced a very slight uncontrolled phase shift. They were removed after measurements No. 4.

Purity of the rf *spectrum*. In the case of Rb^{87}, we used for the generation of the rf of about 6834 Mc/sec two completely different systems. One[4] of the systems was a klystron 2K44 phase locked to the sum of a multiple of the 5 Mc/sec-output of an Atomichron[4] and a variable frequency of 0–30 Mc/sec, produced by a Rohde and Schwarz frequency synthesizer XUA. The other system consisted of a Sanders klystron oscillator type CLC4-8 phase locked by a Schomandl Syncriminator FDS3 to the sum of the 10th harmonic of a 680-Mc/sec signal, derived from a Schomandl frequency synthesizer FD3, plus the variable frequency from the Rohde and Schwarz frequency synthesizer XUA. The Schomandl synthesizer was fed by a 10-Mc/sec signal derived from the 100-kc/sec output of the Atomichron by multiplication in a General Radio Standard frequency multiplier type 1112. The purity of both systems could be checked directly by a Stalo tester No. 392 made by Airborne Instruments Co.

In typical operation it appeared that the residual frequency modulation had peak values of not over 10 cps in a period of about 0.01 sec. Whether this apparent modulation was in the klystron or the Stalo tester could not be determined. The fact that there is no systematic difference in the values for $\Delta\nu$ derived with the two different frequency systems, as can be seen from Table I, makes it very unlikely that there is any apparent shift in the frequencies caused by frequency impurities.

Frequency standards. As a frequency standard we used an Atomichron Model NC 1001, Serial No. 119, which was compared with a $133\frac{1}{3}$-kc/sec standard frequency transmitted by the station A5XA at Fort Monmouth, which is accurate to better than 1 part in 10^{10}. The frequency of the Atomichron 119 was consistently higher than the A5XA frequency by (4 ± 2) parts in 10^{10}. For the runs 9, 10, and 11 we used as a standard a 1-Mc/sec quartz crystal oscillator FS 1100* (James Knights Co.), which was calibrated against the Atomichron. All frequencies in Table I are given in the time system upon which the Atomichron is based, which defines the second by setting

$$\Delta\nu(Cs^{133}) = 9\,192\,631\,840 \text{ cps.}$$

The correction due to the standard given in Table I corrects for (a) the deviation of the Atomichron from the frequency of the station A5XA, (b) for the magnetic field correction of the Atomichron, and (c) in the runs 9–11, for the difference between the quartz crystal and the Atomichron.

Magnetic field correction. The magnetic field between the two rf loops was measured by the $\Delta F=0$ transition in Rb^{85} in the loops 2, 3, and 4 before and after each of the 14 runs. The frequency of the transition was about 60 kc/sec, equivalent to about 0.130 G. At this field the $\Delta F=0$ transition in Rb^{87} has a frequency of 90 kc/sec. The linewidth of the $\Delta F=0$ transitions was 40 kc/sec, so that the transitions are not completely separated at this field. A correction of one cycle for the shift of the Rb^{85} line by the Rb^{87} line was taken into account. The field corrections finally applied to the frequencies are given in Table I. Because the field

[4] This equipment was kindly loaned to us by the U. S. Army Signal Corps Research and Development Laboratory, Fort Monmouth, New Jersey.

TABLE II. Experimental data for the determination of $\Delta\nu$ of Rb^{85}.

Run No.	Orientation	Measured ν (cps) 3 035 732+	H (cps) correction	Frequency corrected for H (cps) 3 035 732+	Average for 0° and 180° $\Delta\nu_{85}$ (cps)
1	0°	482.5	−24	458.5	460.8
2	180°	486.1	−23	463.1	
3	0°	482.8	−26	456.8	461.6
4	180°	494.5	−28	466.5	
5	0°	480.4	−26	454.4	456.8
6	180°	487.2	−28	459.2	
7	0°	478	−26	452	456.4
8	180°	487.9	−27	460.9	
				Average	458.9

could not be measured in loops 1 and 5, immediately before and after each run, the accuracy of the field correction is limited to ±2 cps.

Results

The final result for $\Delta\nu_{87}$ is obtained by averaging the values in Table I averaged for the phase shift and adding to the statistical error the additional error of the magnetic field correction. This yields

$$\Delta\nu_{87}=6\ 834\ 682\ 665\pm3 \text{ cps}.$$

The measurement of $\Delta\nu$ for Rb^{85} was essentially similar to that of Rb^{87}. The field dependence of the frequency in Rb^{85} is appreciably greater than that in Rb^{87}, and hence the error in evaluating the field correction amounts to about ±3 cps. The phase-shift error is less than in Rb^{87} due to the lower operating frequency.

Table II summarizes the Rb^{85} data with the result that $\Delta\nu_{85}=3\ 035\ 732\ 462\pm5$ cps. Since the various errors are not all random, the error given is a conservative estimate based upon the individual errors.

As mentioned before, the results are given in the atomic time system, in which $\Delta\nu(Cs^{133})=9\ 192\ 631\ 840$ cps. In the more generally accepted atomic time system, in which $\Delta\nu(Cs^{133})$ defines the frequency 9 192 631 770 cps and which is in best agreement with Ephemeris time,[5] our results are

$$\Delta\nu_{85}=3\ 035\ 732\ 439\pm5 \text{ cps},$$

$$\Delta\nu_{87}=6\ 834\ 682\ 614\pm3 \text{ cps}.$$

The result for $\Delta\nu_{87}$ is in agreement with the atomic beam value, measured by Essen *et al.*,[6] of 6 834 682 614±1 cps, and the optical pumping value, measured by Bender *et al.*,[1] of 6 834 682 608±7 cps.

MEASUREMENT OF μ_I OF Rb^{85}

In order to measure the magnetic moment μ_I of Rb^{85}, we measured the two transitions $\nu_I=(3,-1)\leftrightarrow(2,-2)$ and $\nu_{II}=(3,-2)\leftrightarrow(2,-1)$ using the method previously described.[2] The measurements were made using loops 2 and 4 for the separated oscillating fields at a C field of about 560 G, where both transitions pass through a frequency minimum. At this field $\delta\nu=\nu_I-\nu_{II}$ was of the order of 463 kc/sec, and the average frequency of the two transitions was 2 611 882 312 cps. The field was measured by the $\Delta F=0$, $(3,-2)\leftrightarrow(3,-3)$ transition in Rb^{85} in the loops 2, 3, and 4 before and after each measurement of a pair of $\Delta F=1$ transitions. Table III shows the measured frequencies. Because the field measurement depends on g_J(Rb), the actual quantity measured is g_I^{85}/g_J(Rb), and the result was

$$g_I^{85}/g_J(\text{Rb})=-1.466\ 764(30)\times10^{-4},$$

TABLE III. Measured frequencies for the determination of $\mu_I(Rb^{85})$.

ν_I (Mc/sec)	ν_{II} (Mc/sec)	$\delta\nu$ (Mc/sec)	Field calibrating line averaged over loops 2, 3, 4 (Mc/sec)
2612.113 609	2611.651 023	0.462 586	423.645
2612.113 628	2611.651 026	0.462 602	423.659
2612.113 612	2611.651 023	0.462 589	423.657
2612.113 607	2611.651 034	0.462 573	423.651

[5] W. Markowitz, R. Glenn Hall, L. Essen, and J. V. L. Parry, Phys. Rev. Letters **1**, 105 (1958).

[6] During our investigation this new atomic beam value of high precision for $\Delta\nu_{87}$ has been published by L. Essen, E. G. Hope, and D. Sutcliffe, Nature **189**, 298 (1961).

where $g_I = -\mu_I/I\mu_0$ (μ_0 = Bohr magneton). The error is mainly due to fluctuations of the field and to the uncertainty in its measurement.

Using[7] $g_J(\text{Rb}) = 2.002\,409(27)$ and[8] $\mu_0/\mu_N = 1836.13(4)$ (μ_N = nuclear magneton), we get for the magnetic moment of Rb^{85} without shielding correction

$$\mu_I{}^{85} = 1.348\,206(45)\mu_N.$$

Applying the diamagnetic shielding correction of $\sigma = 0.0033$,[2] which is believed to be accurate to about 0.0002, gives

$$\mu_{85} = 1.352\,70(25).$$

Since the ratio μ_{87}/μ_{85} as measured by nuclear resonance[9] is not subject to chemical effects, one may use it to compute the value of μ_{87} from our value of μ_{85}, giving $\mu_{87} = 2.750\,5(5)$ nm.

MEASUREMENT OF $g_J{}^{85}/g_J{}^{87}$

Recently Conrad[10] concluded on the basis of paramagnetic resonance experiments, that g_J factors for Rb^{85} and Rb^{87} differed by one part in 10^4. We therefore undertook to measure the ratio $g_J{}^{85}/g_J{}^{87}$ by observing the frequencies of the transitions $(3,-2)\leftrightarrow(3,-3)$ in Rb^{85} and $(2,-1)\leftrightarrow(2,-2)$ in Rb^{87} in nearly identical fields in the neighborhood of 564 G. The frequencies were approximately 427 and 473 Mc/sec, respectively. The lines were approximately 45-kc wide and could be measured to a precision of about 2 kc. The ratio $g_J{}^{85}/g_J{}^{87}$ could be calculated from the Breit-Rabi formula. Eighteen resonances were observed alternating Rb^{85} and Rb^{87} in order to average out slight drift of the magnetic field with time. The ratio $g_J{}^{85}/g_J{}^{87}$ derived from these measurements was 1.000 002(4).[11]

TEST OF BREIT-RABI FORMULA

One can get an upper limit for possible deviations between the transition frequencies in Rb^{85} as calculated from the Breit-Rabi formula[12] and the actual frequencies as found in the experiment by comparing the average frequency of the doublet, which was measured for the determination of μ_{I85} at about 560 G, with the value for this frequency calculated using the measured value of $\Delta\nu_{85}$. The average frequency of the doublet was in our case 2611.882 320 Mc/sec. For these measurements we did not use the rigid loop system, which could be rotated to eliminate the phase shift of the rf between the two loops, but used a less rigid system which could not be rotated. A possible phase shift would have no influence on the doublet separation $\nu_{\text{I}}-\nu_{\text{II}}$, but the average frequency has an uncertainty due to the phase shift of about ± 20 cps. The average frequency as calculated from the Breit-Rabi formula is 2 611 882 312 cps, giving agreement between the measured and calculated frequencies with a difference of less than one part in 10^8.

Hfs—ANOMALY

The hyperfine-structure anomaly, ${}_1\Delta_2$, of two isotopes 1 and 2 is defined by

$${}_1\Delta_2 = [\Delta\nu_1(2I_2+1)/\Delta\nu_2(2I_1+1)]\,[g_{I(2)}/g_{I(1)}]-1.$$

With the ratio of the g_I's for Rb^{85} and Rb^{87} as measured recently by Blumberg, Eisinger, and Klein,[8] $g_I{}^{85}/g_I{}^{87} = 0.295\,973\,8(5)$ and our values for $\Delta\nu_{85}$ and $\Delta\nu_{87}$ we get the following value for the anomaly between Rb^{85} and Rb^{87}

$${}_{85}\Delta_{87} = 0.003\,513\,5(17),$$

which is consistent with and more accurate than an earlier measurement.[13] There is so far no theory to predict hfs anomalies with such accuracy.

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[10] D. Conrad, Z. Physik **162**, 160 (1961).
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[12] P. Kusch, S. Millman, and I. I. Rabi, Phys. Rev. **57**, 765 (1940), added the g_I terms to the formula first shown by G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).
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