THE
PHYSICAL REVIEW
A Journal of Experimental and Theoretical Physics Established by E. L. Nichols in 1893
VOL. 57, No. 9 MAY 1, 1940 SECOND SERIES

The Electric Quadrupole Moments of Ga^{69} and Ga^{71}

An Atomic Beam Study of the Hyperfine Structures of the $^2P_{1/2}$ and $^2P_{3/2}$ States of Ga^{69} and Ga^{71} *

NICHOLAS AUGUSTUS RENZETTI
Columbia University, New York, New York
(Received February 23, 1940)

An investigation of the hyperfine structures of the ground $^2P_{\frac{1}{2}}$ state, and the metastable $^2P_{3/2}$ state of the two isotopes 69 and 71 of gallium has been made with the zero-moment method of atomic beams. Six zero-moment peaks, three for each isotope, of the metastable state and two, one for each isotope, of the ground state have been observed. It has been found that the h.f.s. energy levels for the higher state can be described by an equation of the form $E=aC/2+bC(C+1)$, where "a" and "b" are the interval rule and quadrupole interaction constants, respectively.

Ga^{69}: $b/a=0.0136\pm0.0004$, $b=(8.69\pm0.43)\times10^{-5}$ cm^{-1}, $a=(6.39\pm0.12)\times10^{-3}$ cm^{-1}

Ga^{71}: $b/a=0.0068\pm0.0004$, $b=(5.51\pm0.39)\times10^{-5}$ cm^{-1}, $a=(8.11\pm0.11)\times10^{-3}$ cm^{-1}.

From these the h.f.s. separations are

Ga^{69}: $\Delta\nu=(0.0362\pm0.0007)$ cm^{-1}; Ga^{71}: $\Delta\nu=(0.0474\pm0.0007)$ cm^{-1}

and the quadrupole moments are

$Q^{69}=0.20\times10^{-24}$ cm^2; $Q^{71}=0.13\times10^{-24}$ cm^2.

The nuclear spins are verified to be $\frac{3}{2}$. From the zero-moment peaks of the normal state we obtain $\mu_{71}/\mu_{69}=\Delta\nu_{71}/\Delta\nu_{69}=1.270\pm0.006$ and these separations are

Ga^{69}: $\Delta\nu=(0.0897\pm0.0011)$ cm^{-1}; Ga^{71}: $\Delta\nu=(0.1139\pm0.0019)$ cm^{-1}

and from these the nuclear moments are

$\mu_{69}=2.11$; $\mu_{71}=2.69$.

INTRODUCTION

THE nuclear properties of the two isotopes of gallium ($_{31}Ga^{69}$ and $_{31}Ga^{71}$) have been measured by various experimenters. Jackson[1] worked with the GaI spectrum and found the value $\frac{3}{2}$ for each of the spins. Campbell,[2] working with the GaII spectrum, substantiated these values and found the ratio of the nuclear moments to be 1.27. Schüler and Korsching[3] studied the GaII spectrum and in addition to obtaining agreement with the above measurements ob-

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.
[1] D. A. Jackson, Zeits. f. Physik **75**, 229 (1932).
[2] J. S. Campbell, Nature **131**, 204 (1933).
[3] H. Schüler and Korsching, Zeits. f. Physik **103**, 434 (1936).

served that the hyperfine structure separations of various P states did not follow the interval rule. From this they concluded that the gallium nuclei possessed electrical quadrupole moments and obtained the values $Q^{69}=1\times10^{-24}$ cm^2 and $Q^{71}=0\pm0.5\times10^{-24}$ cm^2. Because of the large uncertainty in these numbers, it was thought interesting to check the quadrupole hypothesis by a study of some other state with the atomic beam method of zero-moments.

Gallium possesses many features which make it suitable for investigation by this method. Its ionization potential is not too high for the surface ionization method used in detecting atomic beams of the nongaseous elements and its boiling point is low enough to get appreciable beam intensities at reasonable temperatures (1400°K–1600°K). Furthermore, as a consequence of the relatively small doublet fine structure, there are present in the beam atoms in the metastable $^2P_{3/2}$ state as well as those in the ground $^2P_{1/2}$ state. The separation of these states is 826.0 cm^{-1} and the ratio of the number of atoms in the higher state to those in the ground state is given by the Boltzman factor multiplied by the ratio of the statistical weights, i.e., $2\cdot e^{-hc\Delta\nu/kT}$. At an absolute temperature of 1600°, since the excitation of the other states is negligible, the abundance of atoms in the upper state is 50 percent. This circumstance gives the opportunity for studying the quadrupole moment of gallium since in the higher P state, with $J=\frac{3}{2}$, one can seek deviations from the interval rule produced by the interaction of the electrons with a quadrupole. S states and $P_{1/2}$ states, because they possess spherically symmetrical electronic charge distributions show no effect of quadrupole moment in their h.f.s. even though the nucleus may have a nonspherical charge density.

Method

The atomic beam method of zero-moments[4] is based upon the behavior of the atomic energy states in a magnetic field. If one considers the progress of the energies of the states into which the h.f.s. levels split on applying a magnetic field, H, then for certain states there will be a value of $H=H^\circ$ (different for different states) at which the energy is a maximum or a minimum, i.e., $dE/dH=0$. An atom for which dE/dH is zero experiences no net translational force at a point in an inhomogenous field for which $H=H^\circ$. If a beam of atoms is made to traverse this field and the intensity at the position of zero deflection is observed as a function of H, "peaks" are found at the zero-moment fields of the various states. Actually the occurrence of such peaks is brought about by the progressive reorientation of J, the electronic angular momentum, by the external field, H. As the field is strengthened there is a decoupling of I, the nuclear angular momentum, and J, and during that process there may be some value of H such that the time average direction of J is perpendicular to H. The strength of the field necessary to bring this about is proportional to the strength of the interaction of the electrons and the nuclear magnetic dipole moment if one neglects the quadrupole interaction. If now the nucleus has a quadrupole moment, another torque in addition to that exerted by the nuclear magnetic moment acts upon J with a different dependence on the relative orientations of I and J. As a result, the value of the field necessary for the reorientation is greater or less depending upon whether or not the process has been hindered or helped by the added torque. Thus a measurement of the relative values of the fields at which the zero-moment peaks occur determines the relative strengths of the magnetic dipole and electric quadrupole interactions. The real advantage of the zero-moment method lies in the fact that the peaks are indeed shifted by large amounts (from 10 percent to 50 percent in the present experiment). On the other hand, the optical spectroscopist relies on the small differences between the wave-lengths of the components of a well-resolved spectral line. The calculation of Q is based upon the deviation of these differences from the interval rule and in many cases these deviations are not much larger than the limit of the experimental method.

Apparatus and Procedure

The high resolution apparatus used in this experiment is essentially the same as that in the experiment of Hamilton.[5] A schematic top view

[4] V. W. Cohen, Phys. Rev. **46**, 713 (1934).

[5] D. R. Hamilton, Phys. Rev. **56**, 30 (1939).

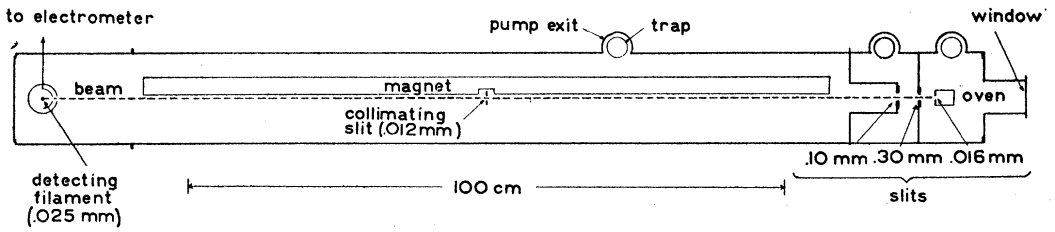

FIG. 1. Schematic top view of the apparatus.

is shown in Fig. 1. It consists of a brass can 6″ o.d., $5\frac{3}{4}$″ i.d. separated into three chambers which are pumped out in parallel. The high temperatures necessary for an appreciable intensity of gallium atoms require good separation and high pumping speeds. With this arrangement it is possible to maintain a pressure of better than 10^{-6} mm of Hg in the main chamber with a pressure of 5×10^{-5} in the oven chamber.

A preliminary investigation was made to determine whether gallium could be detected with an oxide-coated filament (tungsten). This experiment consisted of evaporating the gallium from a tungsten coil about 10 cm from the detector. A continual stream of oxygen was played upon the detector in a manner first developed by Manley and Millman[6] to raise the work function of the tungsten surface to that of the ionization potential of the atom which makes the detection possible. For gallium this potential has a value 5.97, and is 0.27 volt higher than the highest previously detected by this means. Another feature of this experiment was the use of a graphite oven in which the gallium was placed. Attempts to use other materials all met with failure. At first we utilized a molybdenum block as in the experiment of Millman, Rabi and Zacharias[7] on indium. Slit jaws both of molybdenum and tantalum were used. However, in each case, the gallium combined with the molybdenum to give an extremely hard compound which a surface grinder had difficulty in removing. A beam of molecules was observed for a short time. Tantalum was used in the form of a rod with a hole drilled into it and inserted diagonally down in the molybdenum and also as material for the slits. In this case the liquid gallium crept up on to the slits giving a broad beam for a short time. Ovens made completely of iron and nickel gave no beam at all; the gallium combined with the material of the oven and closed the slit jaws. A complete graphite oven gave considerable difficulty by a continual evolution of gas. The oven ultimately used had a graphite rod with a hole drilled into it and inserted diagonally into a molybdenum block and graphite slits. The heating coils (in the molybdenum) with the aid of 1-mil molybdenum sheets wrapped around the oven acting as a radiation shield gave temperatures of the order of 1600°K.

Figure 2 shows a cross section of the deflecting magnet at right angles to the plane of the beam. It consists of two copper tubes 0.144″ o.d. and 0.066″ i.d. each set in the face of a Duralumin block 3.5 by 5 by 115 cm. The tubes are insulated from each other and the block by mica sheets and carry the same current in opposite directions and are water cooled. This two-wire type of field[8] without iron has the advantage of having no magnetization difficulties. After placing the wires in the block, we found the average deviation of the surface tangent to the wires to the mean tangent plane to be about 0.007 mm. The current supply (at times as high as 1500 amperes) for this magnet was furnished by a bank of six-volt storage batteries which had a normal capacity of 3500 ampere-hours. A Leeds and Northrup Type K potentiometer across a 50-millivolt, 1500-ampere shunt was used to measure the current. The calibration of the field at the position of the beam is made with the aid of a beam of caesium atoms in the manner described below.

The requirements of high resolution are met by making the beam long and narrow. The total

[6] J. H. Manley and S. Millman, Phys. Rev. **51**, 19 (1937).
[7] S. Millman, I. I. Rabi and J. R. Zacharias, Phys. Rev. **53**, 384 (1938).
[8] I. I. Rabi, M. J. B. Kellogg and J. R. Zacharias, Phys. Rev. **46**, 157 (1934).

beam length is 165 cm; the oven and collimating slit (the latter at the center of the beam path) which define the beam are set at about 0.01 mm, and the path in the deflecting region is 115 cm. This symmetrical arrangement has the advantage of making the results independent of the parallelism of the beam plane to the surface of the field wires within wide limits. The slits and the detector (0.025 mm in diameter) are movable under vacuum so that the beam could be put at any desired distance from the field wires. For this purpose the oven is seated on three tungsten pegs set in a dovetail slide operated from outside the can by an Invar screw and the collimating slit and the detector are mounted eccentrically on ground joints. All the runs were made with the beam 0.1 mm inside the surface tangent to the wires.

It is important (see next section) that the detecting filament be accurately centered with respect to the beam. This is done by placing the filament midway between two points of equal intensity on the sides of the beam. During the course of the experiment, the position of the beam at zero field is recorded before and after two or three peaks are observed. The position of the filament, given by a microscope, and thus the relative position of the beam could be observed to 0.0005 mm. Ordinarily, the average shift of the beam was 0.001 mm or less and corrections for this are negligible.

Experimental Data

Figure 3 shows the beam intensity as a function of the magnet current. The $^2P_{3/2}$ peaks are superimposed upon a sloping background which is made up of the undeflected atoms in the ground state. The atoms in this latter state have an over-all magnetic moment of $\frac{1}{3}$ Bohr magneton as compared with 2 Bohr magnetons for the atoms in the $^2P_{3/2}$ state and therefore higher fields are required to sweep them out of the beam. To locate the exact positions of these peaks this background is represented by an empirically drawn smooth curve which is then subtracted from the total intensity. The results of this last operation are given in Fig. 4 which shows the intensity of the atoms in the $^2P_{3/2}$ state alone.

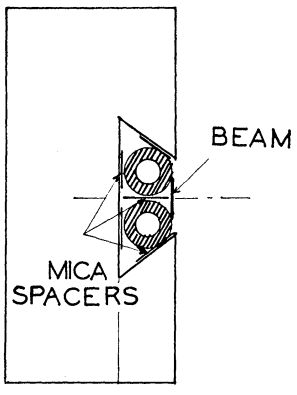

FIG. 2. Cross section of the deflecting magnet. Field wires enlarged relative to the Duralumin block. The direction of the beam is perpendicular to the plane of the paper.

For reasons to be mentioned shortly, it was also found necessary to observe the changes in the pattern produced when the detector is shifted slightly away from its position of zero deflection, i.e., away from the "beam plane" or plane defined by the source and collimating slits. In these observations, complete curves were obtained as in Fig. 3 and the resulting positions of the peaks as a function of the position of the detector are shown in Fig. 5. It should be noted that the maximum lateral displacement given to the detector was only 0.04 mm. The reason for the shifts in the peak positions is given in the following discussion. As explained previously,[5] any zero-moment peak may be classified as a "focusing" or a "nonfocusing" peak, according to whether d^2E/dH^2 is positive or negative at $H°$. In the former, or focusing case, the atoms of the state in question are attracted toward that region of the field where $H=H°$, and hence travel along a potential valley whose center is the so-called "zero-moment plane," the locus of points for which $H=H°$. Correspondingly, the atoms of a nonfocusing state are repelled from the zero-moment plane and travel along a potential ridge with its center at the zero-moment plane. As the exciting current in the magnet is increased, the zero-moment plane for a given state moves away from the deflecting magnet; i.e., the center of the potential ridge or valley moves toward the beam plane. When the zero-moment plane of a given state and the beam plane coincide, atoms in that state are not deflected and a zero-moment peak is observed. Considering the atoms in a nonfocusing state, we see that when the field at the beam plane has a value less than the zero-moment value, i.e., the

zero-moment plane has not yet reached the beam plane, the atoms are deflected from the beam plane in a direction away from the magnet; this deflection decreases as the zero-moment plane approaches the beam plane. If the detecting filament is laterally displaced from the beam plane in a direction away from the deflecting magnet, the atoms will reach the detector at smaller magnet currents, i.e., the peak will appear to have been shifted to lower current

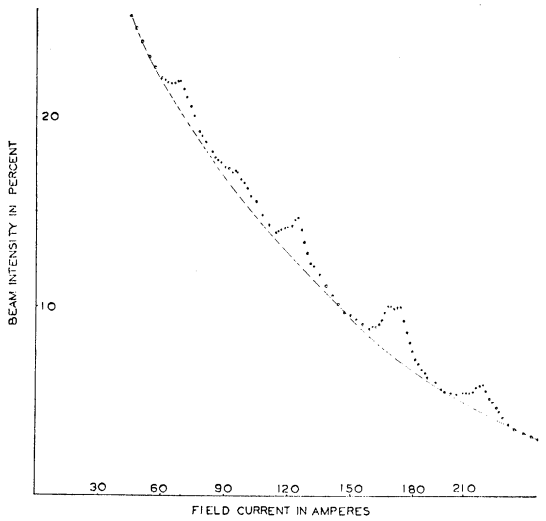

FIG. 3. Beam intensity at the position of zero deflection as a function of the current in the field wires. Background of the $^2P_{\frac{1}{2}}$ atoms is included.

values. A similar argument shows that the focusing peaks are displaced toward higher current values. This last statement is true even when the sides of the potential valley are so steep that the atom may pass from one side of the zero-moment plane to the other several times in the course of its passage through the deflecting field.

The advantage of these considerations is brought out in the case of the fourth and fifth peaks, which as Fig. 4 shows, are quite close together and therefore difficult to locate exactly. However, the procedure described above disclosed that the fourth is a nonfocusing and the fifth a focusing peak and therefore a shift of the detector away from the magnet separates these two peaks. By observing the separation for a number of positions of the detector, an extrapolation back to zero displacement may be made with considerable accuracy. (See Fig. 5.)

The second use of the data shown in Fig. 5 is as an aid to later identification of the experimental peaks. From the criterion given above and the data of the figure, it is known which of the peaks are focusing and which are nonfocusing. (An upward slant to the right in Fig. 5 indicates a focusing peak.) Likewise one can determine from the calculations described later whether d^2E/dH^2 is positive or negative for each of the theoretically predicted peaks. Then any fit of the two sets of peaks must identify a "focusing" experimental peak with a "focusing" theoretical peak.

The procedure which was followed in interpreting the data obtained from the various runs consisted of locating for each run a most probable position of each of the observed peaks, using the

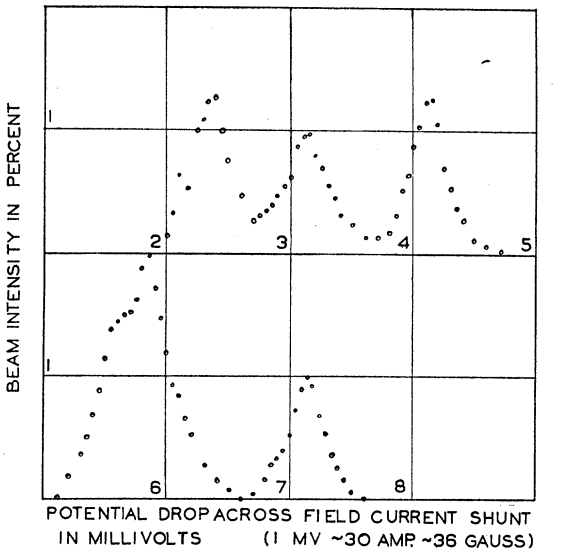

FIG. 4. Beam intensity, at the position of zero deflection, of the $^2P_{3/2}$ atoms alone.

methods described above. From the identification of the peaks and the theoretical interpretation of their positions (to be discussed in the next section) values of the desired h.f.s. constants were obtained; the numerical values will be discussed following the presentation of the method by which they were calculated.

Zero-moment peaks arising from atoms in the ground state are also observed. These are shown in Fig. 6. For the large values of the field here

involved, the peaks occur without any background. There are no peaks of either state in the region between 7.5 and 35 millivolts. The theory involved in the interpretation of their positions and the information to be derived therein are discussed in the section devoted to the $^2P_{1/2}$ state. The data are summarized in Table I.

Finally, the ratio of the zero-moment peaks arising from the atoms in the ground states of

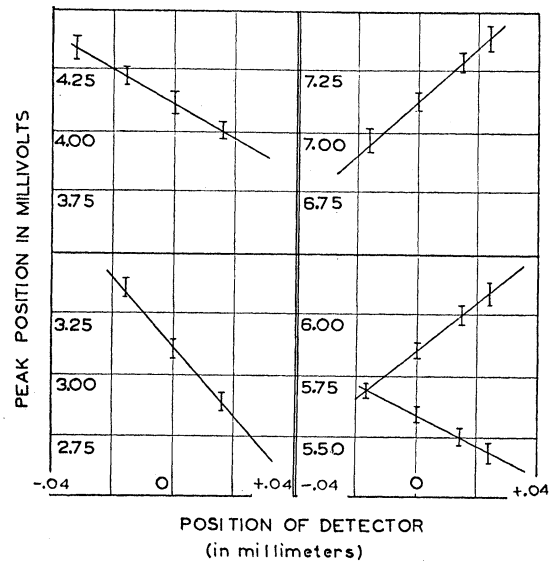

FIG. 5. Peak position as a function of the position of the detector. The positive numbers indicate that the detector was moved away from the magnet.

sodium and lithium was measured as a check on the accuracy of the apparatus. This ratio is very accurately known from the ratio of the h.f.s. $\Delta\nu$'s measured by the new magnetic resonance method by Kusch, Millman, and Rabi.

THEORY AND EVALUATION OF THE EXPERIMENTAL RESULTS—$^2P_{3/2}$ STATE

In this section we shall first discuss the effect of a quadrupole moment on the h.f.s. energy levels. Then we shall describe the behavior of these levels in a magnetic field and discuss the calculations necessary for the evaluation of the h.f.s. constants. Finally, we shall show how the experimental peaks are fitted to the theoretical curves and give the numerical results.

In the presence of an interaction with a quadrupole moment the h.f.s. energy levels are described by the equation

$$E=aC/2+bC(C+1) \qquad (1)$$

where $C=F(F+1)-I(I+1)-J(J+1)$ and F is the total angular momentum, nuclear plus electronic. The first term in this equation gives the interval rule which arises from the cosine interaction of the nuclear magnetic dipole and the field at the nucleus produced by the electrons. The second term gives the quadrupole interaction with[9]

$$b=-\left\langle\left[\frac{3\cos^2\theta-1}{r^3}\right]_{JJ}\right\rangle_{Av} \times\frac{\frac{3}{8}Q}{ij(2i-1)(2j-1)}2R\alpha^4\ \text{cm}^{-1}. \qquad (2)$$

The expression in the brackets is the average value for the electronic state $M_j=J$; the mean value of $(3\cos^2\theta-1)$ is a measure of the deviation from spherical symmetry of the charge density of the electrons. Q itself is defined as the average of $(3z^2-r^2)$ over the nuclear charge density for the state $M_i=I$, i.e.,

$$eQ=\int\rho(3z^2-r^2)d\tau$$

where $\int\rho d\tau=Ze$. Thus Q is a measure of the quadrupole moment of the nuclear charge distribution and leads to a cosine squared interaction with the electrons.

In order to obtain the positions of the zero-moment peaks arising from the atoms in the $^2P_{3/2}$ state and their dependence on Q, one must study the behavior of the energy levels in a magnetic field. To do this, one first obtains the Hamiltonian for the interactions and puts it into the secular equation for the energy. If we take the direction of the field as z, and omit constant terms independent of F, this Hamiltonian is given by[9]

$$\mathcal{H}=\mu_0H(g_jJ_z+g_iI_z)+a\mathbf{I}\cdot\mathbf{J} +b2\mathbf{I}\cdot\mathbf{J}(2\mathbf{I}\cdot\mathbf{J}+1). \qquad (3)$$

The terms are, in order, the interaction of the

[9] H. B. G. Casimir, "On the interaction between atomic nuclei and electrons," Prize Essay published by Teyler's Tweede Genootschap (1936).

external field with the electrons and with the nucleus; the electron-nuclear interaction due to the nuclear magnetic dipole and due to the nuclear electric quadrupole. The h.f.s. energy levels in zero field are specified by the F values 3, 2, 1, and 0, since $I=\frac{3}{2}$ and $J=\frac{3}{2}$ and $F=I+J$, $I+J-1$, $\cdots I-J$. In a magnetic field each F state splits into $2F+1$ states, a total of 16 in all. Thus we must solve a 16-rowed determinant for the energies. However, in the (M_f, F) representation $\mathfrak{H}$ is diagonal in $M(\equiv M_f)$, the z component of the total angular momentum and since at most 4 states have the same M, the determinant, which reads as follows

$$|(F'M|\mathfrak{H}|F''M)-\delta(F', F'')E|=0 \qquad (4)$$

factors into 4 smaller determinants. In addition, in this representation, the last two terms of Eq. (2) are diagonal with matrix elements given by $aC/2+bC(C+1)$ from which Eq. (1) arises. In the calculations it is found convenient to express energies in terms of "a." Therefore we define

$$x=g_j\mu_0 H/a \qquad (5)$$

and Eq. (3) now becomes

$$\mathfrak{H}/a=x(J_z+I_z g_i/g_j)+\mathbf{I}\cdot\mathbf{J} +b/a2\mathbf{I}\cdot\mathbf{J}(2\mathbf{I}\cdot\mathbf{J}+1). \qquad (6)$$

The matrix elements of I and J are well known and are given by Condon and Shortley.[10] After the numerical values of the elements involving the angular momenta are calculated, the equations to be solved for the energies contain as parameters x, g_i/g_j, and b/a. Given any particular state, one desires the value of x, say x_0, at which $\delta E/\delta x=0$ (provided x_0 exists). x_0 will depend on the values of g_i/g_j and b/a; numerical calculation of this dependence is necessary—i.e., one assumes values for g_i/g_j and b/a, calculates $\delta E/\delta x$ for several values of x, and interpolates to find x_0. This process must be repeated to obtain x_0 for as many values of g_i/g_j and b/a as are necessary.

TABLE I. *Final determination of peak positions.*

Peak (M,F)		$^2P_{3/2}$ Peak Position millivolts	$^2P_{1/2}$ Peak Position millivolts
Ga^{71}	$(-1, 3)$	7.12±0.01	
	$(0, 1)$	5.57±0.02	47.20±0.10
	$(+1, 1)$	3.12±0.03	
Ga^{69}	$(-1, 3)$	5.84±0.02	
	$(0, 1)$	4.12±0.02	37.14±0.03
	$(+1, 1)$	2.27±0.03	

The effect of g_i/g_j is actually so small in this case that the theoretical calculations were made with the g_i's set equal to zero. The effect of the approximately known values of g_i^{69} and g_i^{71} is discussed later. The results of the calculations are shown in Figs. 7 and 8. To take care of the fact that perturbations might reduce the value of "a," the pattern was calculated for values of b/a from minus infinity to plus infinity.

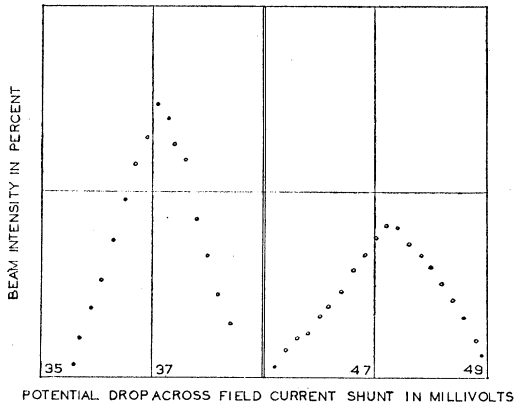

FIG. 6. Beam intensity, at the position of zero deflection, of the $^2P_{\frac{1}{2}}$ atoms.

It is found that for $b/a=0$, i.e., for zero quadrupole, the states $M=0$, $F=1$; $M=+1$, $F=1$; and $M=-1$, $F=3$ have zero moments at different values of the field. As b/a assumes values different from zero, some states which at first had no zero-moment now do, and, in some cases, (i.e., the closed curves in Fig. 7) one state has zero-moments for two different values of x. This situation is explained with the aid of Figs. 9 and 10. In the first of these the relative positions of the field free energy levels are plotted as a function of b/a. These curves are a plot of Eq. (1) (it must be noted, however, that actually the center of gravity of the fine structure level (n, j) is not altered by the quadrupole interaction). It is observed that the interval rule pattern is completely disrupted with the F levels freely exchanging their order. As the levels

[10] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935).

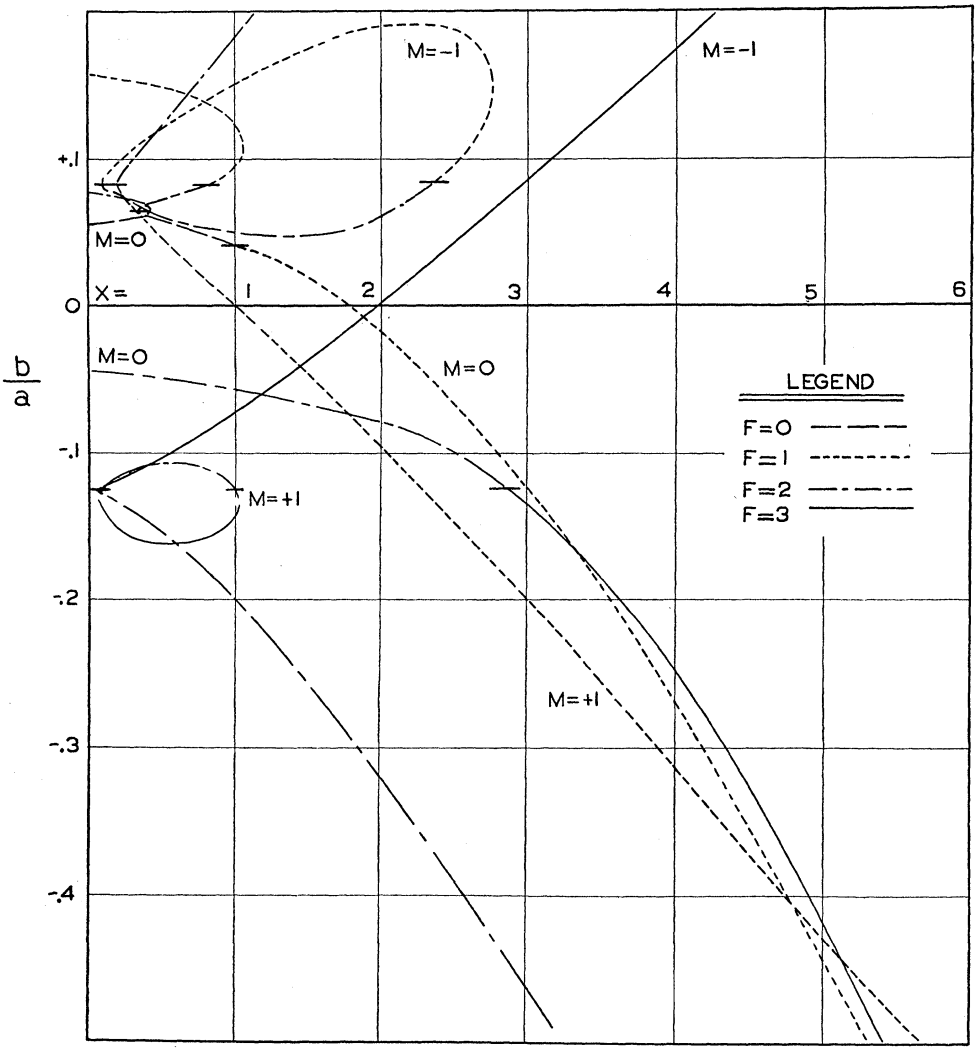

FIG. 7. Theoretical peak position in x as a function of the quadrupole interaction constant where $x \sim 7 \times 10^{-3} H$. Peaks are denoted by their (M,F) values and the short heavy horizontal lines indicate that at this point of the curve there is a transition of the F state involved. These transitions occur where the F states cross in Fig. 9.

$F=1$ and $F=2$ approach each other at $b/a=1/12$, their behavior in the field changes considerably. This is shown in Fig. 10. In this diagram the slope of the energy curve as a function of x is plotted against x for each of the two states for various values of b/a. Plotted in this way, i.e., the effective moment against x, the effect is brought out more strikingly. As the states approach each other, the repulsion between them becomes large compared with the interactions with the field and the upper of the two moment curves is pushed up toward smaller values. As the transition point ($b/a=0.0825$) is reached, the upper curve is pushed up more sharply until it crosses the zero line. In this region the state in question shows zero-moment values corresponding to a minimum and a maximum in the energy curve. This phenomenon continues after the states have crossed and are still close to each other. Once we get past $b/a=0.2$ the mutual interaction becomes small and no zero-moments occur. In each case there is included in the diagram the corresponding curve of the $M=-1$, $F=3$ state which has the property that it crosses

the zero line at higher values of x as b/a is increased. The states $M=+1$, $F=1$, 2 and the $M=-1$, $F=2$, 3 are expected to show the phenomenon of zero-moment since they start out with moments of one sign in the Zeeman region and finish with moments of the opposite sign in the Paschen-Back region. All the other zero-moments occur as a result of considerations similar to the above. The numerical calculations, which involved quartic equations for $M=0$ and cubic for $|M|=1$, were made for values of b/a differing by 0.01 in the region $+0.2>b/a>-0.3$ and at more widely separated values in the remaining regions.

Evaluation of b/a

To identify the peaks one has to begin with the data of Fig. 7 (replotted with the same ordinates but with abscissae corresponding to ratios of lower theoretical peaks to highest peak). One then plots the experimentally known peaks to the same scale and records all those values of b/a, within or nearly within the experimental error, for which there is a coincidence of the two sets of peaks. These correspond to a number of tentative classifications of two or more peaks as belonging to a given isotope. Furthermore, an analysis of the half-widths of the theoretically predicted peaks indicates that none of the peaks should be unobservable unless, of course, two peaks nearly coincide and appear as one. This possibility is taken into consideration. In no instance is it found possible to assign more than three peaks to a given isotope.

As shown in reference 5, the various zero-moment peaks for a given isotope may have considerable differences in maximum intensity or in area under a peak, although the states which give rise to the various peaks are equally populated for a given isotope. Because of this variation in intensity among the peaks of a given isotope, and because the isotopes are present to the same order of magnitude (i.e., to the ratio of 3 : 2), it is impossible to distinguish between peaks by intensity considerations alone. Thus three peaks might belong to each isotope, or the division might be 1 and 5.

The simple criterion of consistency removes many of the possible values of b/a; i.e., a classification of the first, fifth and sixth peaks as belonging to one isotope must be false unless there is a corresponding tentative identification of the second, third and fourth as belonging to the other. A further criterion is provided by the experimental classification (see Fig. 5), previously discussed, of all except the first peak as focusing or nonfocusing peaks. Thus any value of b/a which is associated with the coincidence of a focusing and a nonfocusing peak is discarded.

In this manner all but two of the possible assignments are removed. For each of the remaining, the values of "a" for the two isotopes are calculated. A ratio of the "a's" of the two isotopes is obtained for each of the assignments; this ratio should be the same as the ratio of the magnetic moments of the two isotopes. Since the spins are the same, and any perturbations arising from an electronic source must be the

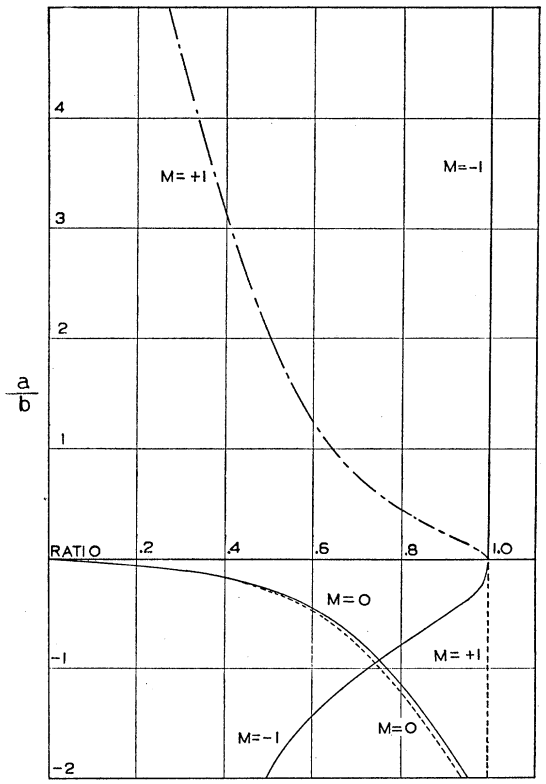

FIG. 8. Theoretical peak position as a function of the reciprocal of the quadrupole interaction constant plotted as ratios, taking the ratio of each peak in x to the highest peak. This was also done for Fig. 7 in obtaining the final results and together with 7 cover the entire range of b/a from minus infinity to plus infinity. The same notation indicates the F states involved.

same for the two isotopes, the ratio of the moments is equal to the ratio of the magnetic dipole interaction constants. The two ratios thus calculated are 1.020 and 1.268. As mentioned above, the true value of this ratio is 1.270 both from spectroscopic data[2,3] and measurements with the present apparatus (see the results for the $^2P_{1/2}$ state). There is thus no doubt that only one assignment of the peaks to the two isotopes is possible and the values of b/a obtained are unique. These are

$$\mathrm{Ga}^{71}: \ b/a=0.0068\pm0.0004;$$
$$\mathrm{Ga}^{69}: \ b/a=0.0136\pm0.0004.$$

It is to be emphasized that the method of determining b/a makes these ratios independent of an absolute measurement of the magnetic field.

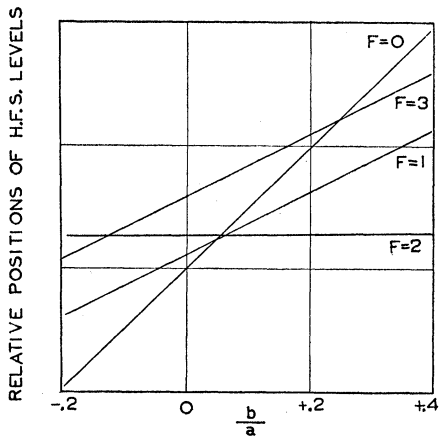

FIG. 9. This is a plot of the equation $E/a=C/2+b/a\ C(C+1)$. It is understood that actually the center of gravity of the h.f.s. levels is not altered by this type of interaction, i.e., $\Sigma_f(2f+1)\Delta_f\nu=0$. Ordinates correspond to energy in units of "A."

The hyperfine structure separations

Knowing b/a, we may now determine from the calculations upon which Figs. 7 and 8 are based the value of x at which any given peak occurs. A measure of the value of the field at this peak then gives a/g_j directly, by Eq. (5). As mentioned above, the most accurate way of calibrating the field is to run another element whose peaks occur at known fields. In this case a beam of caesium atoms is used. For practical purposes it was found necessary to make a caesium run between two gallium runs. The $\Delta\nu$ of the $^2S_{1/2}$ ground state of caesium has been measured spectroscopically.[11] A value of 0.3067 ± 0.0004 cm^{-1} was obtained. Millman and Fox,[12] using atomic beam methods, found a value of 0.307 ± 0.003 cm^{-1} for the $\Delta\nu$ and a value of 7/2 for the nuclear spin. With this information the field at any zero-moment peak is known. If we follow exactly the same procedure used in evaluating the results for the ground state of gallium (see later), we see that the first peak of caesium occurs at a field, $H'=0.3067hc/8\mu_0$ (since $y=-2M/2i+1=1/4$ for $M=-1$, $i=7/2$ and $y=g_j\mu_0H'/hc\Delta\nu$). The most accurately reproducible gallium peak is the $M=-1$, $F=3$, for which the above assignment of b/a gives an x value of 2.075 ± 0.010 belonging to the isotope 71. From Eq. (5) the field at this peak $H''=2.075a_{71}hc/g_j\mu_0$. Experimentally the ratio of H'' to H' is 0.3294 ± 0.0012. From these numbers one obtains $a_{71}/g_j=(6.086\pm0.062)\times10^{-3}$ cm^{-1}. If one assumes this state is a pure one, then $g_j=4/3$ and $a_{71}=(8.11\pm0.082)\times10^{-3}$ cm^{-1}. However, because of the possible influence of perturbations on g_j (see later), we increase the limits of error and take $a_{71}=(8.11\pm0.11)\times10^{-3}$ cm^{-1}. From the discussion given above $a_{71}/a_{69}=1.270\pm0.006$. Therefore,

$$a_{69}=(6.39\pm0.12)\times10^{-3}\ \mathrm{cm}^{-1}.$$

If there were no quadrupole moments, the h.f.s. separations would be

$$\Delta\nu_{71}'=6a_{71}=0.0487\pm0.0007\ \mathrm{cm}^{-1};$$
$$\Delta\nu_{69}'=6a_{69}=0.0383\pm0.0007\ \mathrm{cm}^{-1}.$$

However, its presence shifts the top and bottom levels by different amounts so that making use of the values $b_{71}=(5.51\pm0.39)\times10^{-5}$ cm^{-1} and $b_{69}=(8.69\pm0.43)\times10^{-5}$ cm^{-1}, the true separations are

$$\Delta\nu_{71}=0.0474\pm0.0007\ \mathrm{cm}^{-1};$$
$$\Delta\nu_{69}=0.0362\pm0.0007\ \mathrm{cm}^{-1}.$$

Nuclear spin and nuclear g factors

The previously measured[1,2] values of the spins for each isotope (3/2) are used in the theoretical

[11] L. P. Granath and R. K. Stranathan, Phys. Rev. **48**, 725 (1935).
[12] S. Millman and M. Fox, Phys. Rev. **50**, 220 (1936).

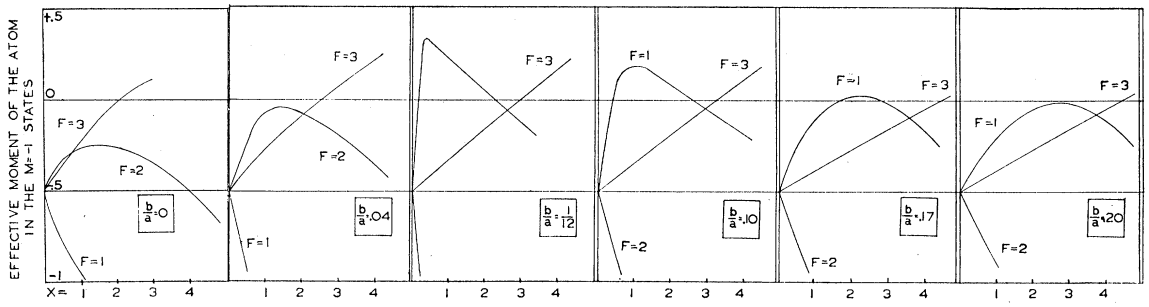

FIG. 10. The slope of the energy curve (i.e., effective moment), dE/dx, as a function of x for various values of b/a on either side of the transition $F=1$, $F=2$ at $b/a=1/12$. All the curves correspond to $M=-1$ states.

calculations upon which Figs. 7 and 8 are based. The fact that we can make the above unambiguous identifications is a verification of these values.

The nuclear g factors as calculated from the hyperfine structure separations of the ground state are more accurate than from the $^2P_{3/2}$ state. The effect of g_i/g_j on the relative positions of the peaks is indeed very slight. The theoretical calculations were made with the g_i's set equal to zero. If we take $g_i=-0.000907$ for Ga^{71} and $g_i=-0.000725$ for Ga^{69} corresponding to $\mu_{71}=2.5$ and $\mu_{69}=2.0$ nuclear magnetons, the resulting changes in the values of b/a are 1.4 percent and 0.7 percent, respectively. The basis for the calculation of these effects is given in reference 5. These results are utilized in the final determination of b/a.

The quadrupole moments

The relation between Q and "b" for the $^2P_{3/2}$ state is given by[9,5]

$$Q=b\frac{i(2i-1)Z_iHC}{\delta R'}\frac{60}{e^2}\mu_0^2.$$

In this expression δ is the doublet separation, 826.0 cm^{-1}. It occurs because it is proportional to $\langle r^{-3}\rangle_{Av}$ of Eq. (2). H, R' and C are relativistic correction factors which enter because of the use of δ to give $\langle r^{-3}\rangle_{Av}$. Calculations of these quantities have been made by Casimir, from whose tables we obtain $H=1.018$ and $R'=1.028$. C is a correction for the fact that in calculating H and R' the difference in the normalization integrals of the $^2P_{1/2}$ and $^2P_{3/2}$ states, caused by the difference in the energies of these states, was neglected. Casimir gives an analytic expression for this effect from which we obtain $C=1.013$. Z_i is the effective nuclear charge. On the basis of the relativistic wave functions from which H, R', and C are calculated, Casimir obtains an expression for δ which depends on Z_i. From the doublet separations and the term values of the series $4s^2np$, a value of Z_i may be obtained for $n=5$, 6, and 7. We find as the average $Z_i=26.4=Z-4.6$, with an average deviation of 0.4. Finally in the calculation of μ_0/e, in which μ_0 and e are the Bohr magneton and the electronic charge, respectively, we have taken $h/e=1.3759\times10^{-7}$ e.s.u. and $e/m=1.7591\times10^7$ e.m.u. "b" is in cm^{-1}. Substitution of these numerical values gives

$$Q^{71}=+0.13\times10^{-24}\ cm^2;$$
$$Q^{69}=+0.20\times10^{-24}\ cm^2.$$

In assigning the deviations from the interval rule to the effect of a quadrupole moment of the nucleus, one must consider the effect of perturbations on this term. In view of the large fine structure separation, the deviations arising from a second-order effect in the magnetic interaction are very small. Casimir has shown that the order of magnitude of these deviations is given by the hyperfine structure splitting squared divided by the fine structure separation.

However, in the consideration of the magnitude of "b," one must study the effect on the $4s^24p\ ^2P_{3/2}$ state in question, of the electrostatic coupling with the states of the same total angular momentum in higher configurations, notably the states with $J=\frac{3}{2}$ in the $4s4p5s$ configuration. From the discussion on the closely

analogous cases of thallium[13] and indium,[5] it is concluded that although the perturbation on $\Delta\nu$ is large, it is only of the order of 1 percent on Q. The latter occurs because in both configurations it is only the $4p$ electron which gives quadrupole contributions to the energy levels; the s electrons, having spherically symmetric wave functions, do not. As concerns g_j, the same considerations show that it might be increased by 0.3 percent.

Theory and Evaluation of Experimental Results—$^2P_{1/2}$ State

The positions of the zero-moment peaks arising from the atoms in the $^2P_{1/2}$ state are described by the Breit-Rabi formula[14] which is valid for the case where either I or $J=\frac{1}{2}$. Since $J=\frac{1}{2}$, there is no quadrupole effect in this term. One gets that the magnetic moment of an atom with $J=\frac{1}{2}$, nuclear spin "I," and positive nuclear moment, in a magnetic field H is, in units of the Bohr magneton μ_0

$$\mu_M=\mp\frac{y+(2M/2I+1)}{2[1+(4M/2I+1)y+y^2]^{\frac{1}{2}}}g_J.$$

In this formula M is the total magnetic quantum number as above and y is defined by the equation

$$y=g_j\mu_0 H/hc\Delta\nu \qquad (7)$$

where $\Delta\nu$ is the separation in wave numbers between the hyperfine levels $F=I+\frac{1}{2}$ and $F=I-\frac{1}{2}$. In this approximation ($g_i=0$), it is seen that, for negative values of M, there are certain values of y for which $\mu_M=0$ in two of the $2(2I+1)$ levels. These come at $y=-2M/2I+1$, $M=-\frac{1}{2}$, $-\frac{3}{2}\cdots(I-\frac{1}{2})$ if the spin is integral, and -1, -2, $\cdots-(I-\frac{1}{2})$ if the spin is a half-integer. Since the spin of each isotope is known to be $\frac{3}{2}$, there is one zero-moment peak for each. These have the same $y(\frac{1}{2})$, but because the $\Delta\nu$'s are the different, the peaks occur at different values of the magnetic field.

The hyperfine structure separations

It is seen from Eq. (7) that if we know the field at the peak arising from this state, the h.f.s. $\Delta\nu$ is known because there $y=-2M/2I+1$. Since $y=\frac{1}{2}$ for each isotope, the ratio of the fields at the peaks gives directly the ratio of the $\Delta\nu$'s. This number is equal to 1.270 ± 0.006 and is of course independent of any measurement of the absolute value of the field. Moreover, the $\Delta\nu$ is due only to the magnetic dipole interaction and therefore the ratio of the $\Delta\nu$'s gives directly the ratio of the nuclear moments. To obtain the absolute values of the $\Delta\nu$'s, the field was determined in the same manner as described in the results for the $^2P_{3/2}$ state. From that discussion we saw that the field at the caesium peak is given by $H'=0.3067hc/8\mu_0$ and the field at the first gallium peak which is due to Ga^{69} is $H''=\Delta\nu hc/2g_j\mu_0$. Experimentally this ratio is $H''/H'=1.754\pm0.012$. From these numbers

$$\Delta\nu_{69}/g_j=(0.1345\pm0.0016)\ \text{cm}^{-1}.$$

If this state is pure, $g_j=\frac{2}{3}$ and, therefore,

$$\Delta\nu_{69}=(0.0897\pm0.0011)\ \text{cm}^{-1};$$
$$\Delta\nu_{71}=(0.1139\pm0.0019)\ \text{cm}^{-1}.$$

The nuclear moments

With the information given above and the assistance of the Goudsmit[15] and Fermi-Segrè[13] formulae which relate the magnetic moment to the $\Delta\nu$ we are able to calculate these moments. We obtain as a consequence that

$$\mu_{69}=2.11;\quad \mu_{71}=2.69$$

in nuclear magnetons.

Discussion

Schüler and Korsching, who worked on the $^3P_{2,1,0}$ states of GaII obtained values of $Q^{69}=1.0\times10^{-24}$ cm^2; $Q^{71}=(0\pm0.5)\times10^{-24}$ cm^2. Because they observed deviations from the interval rule of the order of 0.001 cm^{-1} for an S state where there should be none, these authors set this number as the limit of error of the experimental method for well resolved lines. If one applies this criterion to their observations, the values of "b" and therefore Q are changed by factors ranging from 1.5 to 9. In the light of these observations one can say there is no real disagreement.

From the hyperfine separations of various levels these authors conclude that the ratio of the nuclear moments is $\mu_{71}/\mu_{69}=1.269$ and that

[13] E. Fermi and E. Segrè, Zeits. f. Physik **82**, 729 (1933).
[14] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).
[15] S. Goudsmit, Phys. Rev. **43**, 636 (1933).

these moments are $\mu_{71}=2.5$ and $\mu_{69}=2.0$. The agreement in the ratios is excellent and the values of the moments agree as well as this method of calculation allows. The values of the moments one gets from the $^2P_{3/2}$ $\Delta\nu$'s are too small by a factor 1.36. This number is obtained by taking the ratio of the expected $\Delta\nu$'s from the Goudsmit formula and comparing it with the experimental results. However, from the considerations given above, the diminished $\Delta\nu$ may be due to the effect of a perturbation by a higher configuration.

The experiment on gallium depended, as was seen, very critically on the ratios of the zero-moment peaks. We had occasion on this same apparatus to measure the ratio of the sodium and lithium hyperfine $\Delta\nu$'s given directly by the ratio of the zero-moment peaks. We obtained for this ratio $\Delta\nu_{Na}/\Delta\nu_{Li}=2.2098\pm0.0035$. Millman, Kusch and Rabi,[16] using the new and very accurate molecular beam resonance method, obtained the value $\Delta\nu_{Na}/\Delta\nu_{Li}=2.2052\pm0.0002$. The discrepancy of $\frac{1}{5}$ of 1 percent implies a systematic error of this magnitude in the zero-moment experiments. We believe, therefore, that this gives a good indication of the precision of the apparatus in locating zero-moment peaks.

The author wishes to thank Professor I. I. Rabi for suggesting this application of atomic beams to the measurement of quadrupole moments. He also wishes to express his great indebtedness to Mr. D. R. Hamilton for his continuously invaluable assistance during the course of the research. The other members of the molecular beam laboratory were generous in making available their valuable experience.

[16] The author is indebted to these authors for the communication of this result before its publication.

MAY 1, 1940 PHYSICAL REVIEW VOLUME 57

The Radiofrequency Spectra of Atoms

Hyperfine Structure and Zeeman Effect in the Ground State of Li^6, Li^7, K^{39} and K^{41} *

P. KUSCH, S. MILLMAN AND I. I. RABI
Columbia University, New York, New York

(Received February 26, 1940)

The molecular beam magnetic resonance method previously used for the study of molecules has been extended to the study of atoms. Transitions between the members of hyperfine structure multiplets of the ground state of atoms have been observed directly. In this way the hyperfine structure intervals of the normal states of Li^6, Li^7, K^{39} and K^{41} have been measured. Since the measurement of frequency alone is involved, the results are of very high precision. These spectra have been observed in external magnetic fields varying from 0.05 to 4000 gauss, i.e., from the ordinary Zeeman to the complete Paschen-Back region. The lines in the pattern are completely resolved even at the low fields. The h.f.s. separations derived from measurements at different fields are in excellent agreement. Comparison is made between the ratio of the nuclear moments of Li^7 and Li^6 as derived from the h.f.s. measurements with the directly measured ratio. The two ratios are 3.9610 and 3.9601, respectively. They agree within the experimental error of 0.04 percent. The h.f.s. separations are given both in absolute frequency units and in wave numbers.

	$sec.^{-1}\times10^{-6}$	cm^{-1}
Li^6	228.22	0.007613
Li^7	803.54	0.026805
K^{39}	461.75	0.015403
K^{41}	254.02	0.008474

INTRODUCTION

BECAUSE of the existence of nuclear spin the ground states of many atoms consist of a set of closely spaced energy levels. Each level of this hyperfine structure multiplet corresponds to a value of the total angular momentum of the atom. The spacings are caused chiefly by the feeble interactions of the magnetic and electric fields of the electrons with the nuclear magnetic moment and the electrical quadrupole moments,

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.