

On the Hyperfine Structure of Gallium†

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The hyperfine structures of the ground $^2P_{1/2}$ and the metastable $^2P_{3/2}$ states of Ga⁶⁹ and Ga⁷¹ have been determined by the atomic beam magnetic resonance method. The h.f.s. levels for an atom whose nucleus has a magnetic dipole, electric quadrupole, and magnetic octupole moment are given by the formula $W = aC/2 + bC(C+1) + c(C^3 + 4C^2 + 4C/5)$, where $C = F(F+1) - I(I+1) - J(J+1)$. For the metastable state of gallium, with $I = J = 3/2$, there are four levels at zero external magnetic field, corresponding to $F = 3, 2, 1$, and 0. The determination of the separations of these levels permits the calculation of the constants a , b , and c in the equation above. It was found that only the first two terms are needed to explain the hyperfine splitting of each Ga isotope, within the precision of these measurements. An upper limit for the value of c is 3×10^{-9} cm⁻¹. Other results are:

$$a: 6.3644 \times 10^{-3} \text{ cm}^{-1} = 190.790 \times 10^6 \text{ sec.}^{-1}$$

$$b: 8.6894 \times 10^{-5} \text{ cm}^{-1} = 2.6049 \times 10^6 \text{ sec.}^{-1}$$

$$Q: 0.186 \times 10^{-24} \text{ cm}^2$$

Ga⁷¹

$$a: 8.0868 \times 10^{-3} \text{ cm}^{-1} = 242.424 \times 10^6 \text{ sec.}^{-1}$$

$$b: 5.4759 \times 10^{-5} \text{ cm}^{-1} = 1.6416 \times 10^6 \text{ sec.}^{-1}$$

$$Q: 0.117 \times 10^{-24} \text{ cm}^2$$

The $\Delta\nu$ of the normal state and the g_I of each isotope have been determined by the use of transitions in which $\Delta m_I = \pm 1$, $\Delta m_J = 0$ in the Paschen-Back region.

Ga⁶⁹

$$\Delta\nu: 0.089319 \text{ cm}^{-1} = 2677.56 \times 10^6 \text{ sec.}^{-1}$$

$$g_I: -.0007239$$

Ga⁷¹

$$\Delta\nu: 0.113488 \text{ cm}^{-1} = 3402.09 \times 10^6 \text{ sec.}^{-1}$$

$$g_I: -.0009218$$

The ratio $(\Delta\nu_{71}/\Delta\nu_{69}) = 1.27059$ is in good agreement with $(a_{71}/a_{69}) = 1.27063$.

1. INTRODUCTION

THE hyperfine splitting of an atomic energy level is caused chiefly by the interactions of the magnetic field and the gradient of the electric field of the electronic configuration with the nuclear magnetic dipole moment and electric quadrupole moment, respectively. There is also a possibility that higher order nuclear moments may produce measurable effects. Since the magnitude of these interactions depends on the angle between the angular momentum of the nucleus and that of the electrons, states with different values of the total angular momentum, F , will differ in energy.

As has been pointed out previously,¹ the atomic beam magnetic resonance method offers a direct means of determining the hyperfine structure of atomic energy levels. This method has a number of important advantages over optical methods and the atomic beam method of zero moments. The precision is very good because only the measurement of a radio frequency is involved. The resolution is high enough

to permit the observation of a clearly resolved Zeeman pattern of a hyperfine structure line in a magnetic field as low as 0.05 gauss. Lastly, the results are easier to interpret than those obtained by optical methods, since only one atomic energy level is involved.

This method has been applied^{1,2} to the ground states of a number of atoms. In all these cases, the electronic configuration in the ground state was spherically symmetrical. It is evident that any electrostatic interaction between a nucleus with a quadrupole moment and a spherically symmetrical electronic charge distribution cannot depend on the relative orientations of I and J , and thus on F ; therefore the hyperfine splitting is unaffected. The quadrupole interaction is thus zero and no information can be obtained as to the quadrupole moment of the nucleus.

It is possible to produce and detect atomic beams of gallium by the use of well developed experimental techniques.³ The investigation of the hyperfine structure of gallium is, then, not only possible but also of considerable interest. Gallium exists in two isotopic forms, Ga⁶⁹ (61.5

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¹ P. Kusch, S. Millman, and I. I. Rabi, Phys. Rev. **57**, 765 (1940). Hereinafter referred to as KMR.

² S. Millman and P. Kusch, Phys. Rev. **58**, 438 (1940).

³ N. A. Renzetti, Phys. Rev. **57**, 753 (1940).

percent) and Ga^{71} (38.5 percent). In addition, it exists in the ground ($^2P_{3/2}$) state and in the metastable ($^2P_{1/2}$) state, 826 cm^{-1} above the ground state. At the oven temperatures at which beams are produced ($\sim 1600^\circ\text{K}$) approximately 50 percent of the atoms occur in the metastable state. The lifetime of the state is sufficiently great to permit the propagation of atoms in this state through the length of a molecular beam apparatus. Thus it is possible to determine the quadrupole interaction in the $^2P_{3/2}$ state for each of the two isotopes. A very precise determination of the ratio of the two quadrupole moments is possible, even though the value of neither can be determined with precision from experimental data.

It has been pointed out in earlier papers that the ratio of the $\Delta\nu$'s of two isotopes of an atomic species should be directly determinable from the ratio of the nuclear moments of the two isotopes

if only electromagnetic interactions exist between nucleus and electrons. Earlier data indicated that the ratios did, indeed, agree as anticipated. However, the experimental uncertainties were rather large, because of the considerable uncertainty in the determination of nuclear g values from the observations of molecular spectra by the molecular beam magnetic resonance method. In the present case the determination for each of two isotopes and for each of two atomic states of the constants which describe the interaction of the nuclear magnetic dipole moment with the electronic configuration will serve to give a very accurate check of the assumption that electromagnetic interaction alone can account for h.f.s. patterns. This results from the very great precision with which atomic spectra may be observed as compared to unresolved molecular spectra.

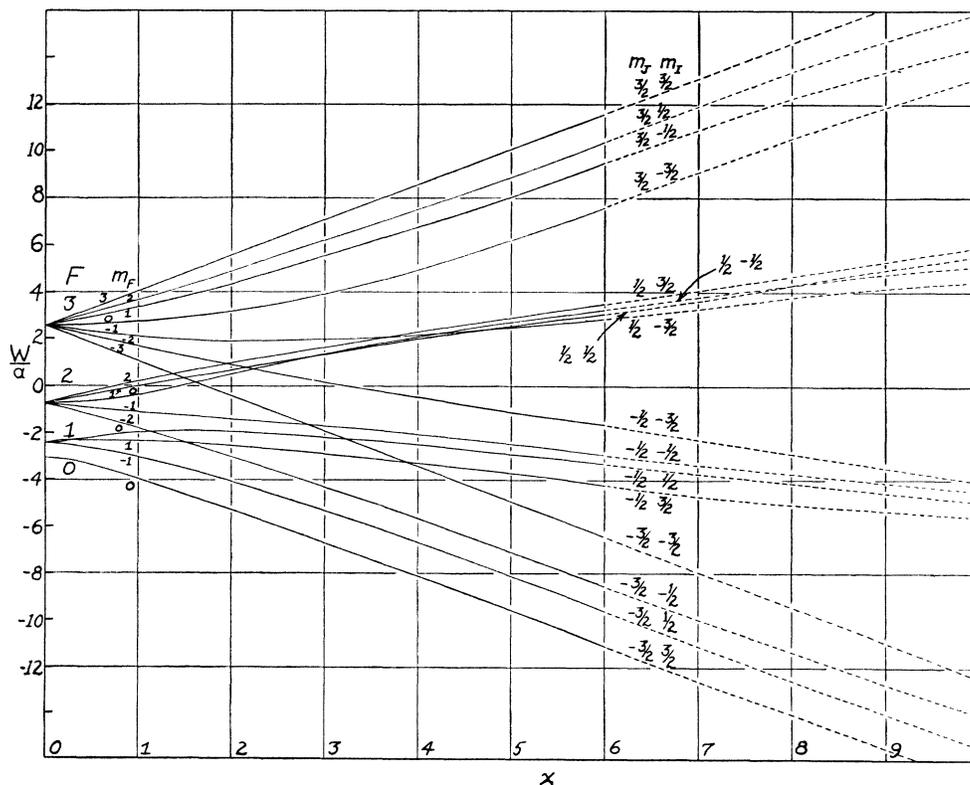


FIG. 1. The variation with magnetic field of the energy levels for Ga^{69} in the $^2P_{3/2}$ state. For values of $x = g_I \mu_0 H/a$ from 0 to 6, the levels have been computed with a Hamiltonian including the magnetic dipole and electric quadrupole interactions. Numerical values for b/a and g_I were taken from Renzetti. At $x=10$, the calculation was made for a high field approximation, and the dotted curves join the two solutions smoothly.

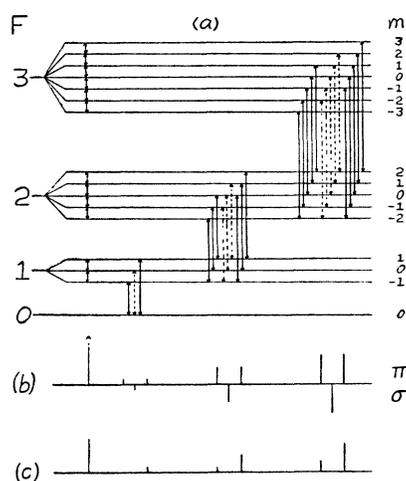


FIG. 2a. A schematic diagram showing the magnetic levels at low field of the hyperfine structure multiplet of a $^2P_{3/2}$ state for a nuclear spin of $3/2$, and the allowed transitions between these levels. This diagram shows correctly the relative spacing of the levels for each F -value, but the intervals between F -levels are not drawn to scale. (b) The spectrum resulting from the transitions shown in (a). Again, the diagram shows correctly only the relative spacings of lines for a given transition for which $\Delta F = \pm 1$ or $\Delta F = 0$. (c) The spectrum actually observed with the experimental arrangement described in this paper.

The interaction constants of gallium have been measured earlier both by use of optical methods⁴ and the atomic beam zero moment method.³ This present experiment was undertaken to determine these quantities more precisely and to investigate the possibility of the presence of higher order nuclear moments. Theoretical considerations indicate⁵ that the ratio between octupole and dipole interactions should be of the order of magnitude (nuclear radius/atomic radius),² which would make any octupole effects extremely difficult to measure. However, for the case of iodine, Tolansky⁶ reports that a term such as would be produced by an octupole moment is needed for an explanation of the hyperfine structure.

2. THEORY

Aside from constant terms which are independent of F and which, therefore, do not affect the hyperfine splitting, the energy levels of a

⁴ H. Schuler and H. Korsching, *Zeits. f. Physik* **103**, 434 (1936).

⁵ H. B. G. Casimir and G. Karreman, *Physica* **9**, 494 (1942).

⁶ S. Tolansky, *Proc. Roy. Soc. A* **170**, 205 (1939).

hyperfine structure multiplet at zero magnetic field are given by the expression^{5,7}

$$W = aC/2 + bC(C+1) + c(C^3 + 4C^2 + 4C/5), \quad (1)$$

where $C = F(F+1) - I(I+1) - J(J+1)$. The three terms in (1) arise from the interaction of the nuclear magnetic dipole moment, nuclear electric quadrupole moment, and nuclear magnetic octupole moment, respectively, with the orbital electrons.

In order to study the behavior of the energy levels in a magnetic field, the octupole interaction will be neglected. The Hamiltonian for the interactions becomes

$$\mathcal{H} = \mu_0 H (g_J J_z + g_I I_z) + a \mathbf{I} \cdot \mathbf{J} + b 2\mathbf{I} \cdot \mathbf{J} (2\mathbf{I} \cdot \mathbf{J} + 1), \quad (2)$$

where the first two terms on the right are the interaction of the external field, taken in the z -direction, with the electrons and the nucleus. Substitution in the secular equation gives linear, quadratic, cubic, and quartic equations which may be solved for the energies of the states in terms of a , b , g_J , g_I , and H . With Renzetti's⁸ values for b/a and g_I , the energy levels are plotted as a function of $x = g_J \mu_0 H / a$ in Fig. 1.

There are four levels at zero external field, corresponding to the four possible values of $F = 3, 2, 1, \text{ and } 0$. If C is evaluated for each F and substituted in (1), there will result an expression for the energy of each F -level in terms of the constants a , b , and c . The frequencies corresponding to the energy differences between these levels are,

$$W_4 - W_3: f_3 = 3a + 24b + 171.3c$$

$$W_3 - W_2: f_2 = 2a - 24b + 54.2c$$

$$W_2 - W_1: f_1 = a - 24b + 153.1c$$

where a , b , and c are expressed in frequency units. These frequencies for the $^2P_{3/2}$ state of Ga all lie in the range of $100\text{--}800 \times 10^6 \text{ sec.}^{-1}$

At very low external magnetic field, the splitting of each F level into $(2F+1)$ levels is adequately described by the Zeeman approximation.

$$W_{(F,m)} = W_F + m\mu H = W_F + m g_F \mu_0 H. \quad (4)$$

⁷ H. B. G. Vasimir, *Interaction between atomic nuclei and electrons* (Verh. Teyler's 2e Genootschap, Haarlem, 1937); also: *Arch. du Musée Teyler*, **III**, 8, 201.

The lines will therefore be found at frequencies

$$\nu = (W_F - W_{F-1})/h + (m_F - m_{F-1})g_F\mu_0 H/h, \quad (5)$$

where

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} + g_I \frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)}.$$

If the term in g_I is neglected, g_F has the value $\frac{2}{3}$ for the $^2P_{\frac{1}{2}}$ state for all values of F . This means that the $(2F+1)$ levels for each F are separated from each other by a constant amount. Figure 2a is a schematic diagram showing the Zeeman splitting in low magnetic field. Figure 2b shows the line pattern derived from an application of the selection rules for magnetic dipole radiation, $\Delta F=0, \pm 1$; $\Delta m=0, \pm 1$. The π lines, for which $\Delta m = \pm 1$, represent transitions caused by the component of the oscillating magnetic field perpendicular to the constant field, H , and the σ lines, for which $\Delta m=0$, arise from the component parallel to H . Note that in low magnetic field all transitions for which $\Delta F=0$ have the same frequency, and that this frequency goes to zero as the magnetic field goes to zero. Moreover, this frequency gives the difference between the frequency of a π line at field H and its frequency at field zero. Note also that the average of the two π lines for a transition $\Delta F = \pm 1$ gives directly the frequency at zero field. (If the σ lines were observable, they also would give the frequencies at zero field.) Thus there is a check on the determination of each f for which both π lines are observable. The validity of Eq. (4) as a description for the Zeeman splitting at field strengths actually used in this experiment could be tested simply by using several different field strengths and verifying that the splitting did have the predicted symmetry.

For the normal state, it was found convenient to determine the $\Delta\nu$ by use of a method described in *KMR*, which involves the measurement of the frequencies of the lines resulting from a change in the nuclear magnetic quantum number, m_I , in strong magnetic field. It has been shown that this method yields the value of $\Delta\nu$ with accuracy as good as is obtained by work in

TABLE I. The lines in the spectrum of *Ga* in the $^2P_{\frac{1}{2}}$ state resulting from the transitions $\Delta m_I = \pm 1, \Delta m_J = 0$.

| Transitions | Expressions for the frequencies |
|-----------------------------------|--|
| $(2, 2) \leftrightarrow (2, 1)$ | $\frac{1}{2}\Delta\nu[(1+x) - (1+x+x^2)^{\frac{1}{2}}] + g_I\mu_0 H/h$ |
| $(2, 1) \leftrightarrow (2, 0)$ | $\frac{1}{2}\Delta\nu[(1+x+x^2)^{\frac{1}{2}} - (1+x^2)^{\frac{1}{2}}] + g_I\mu_0 H/h$ |
| $(1, 1) \leftrightarrow (1, 0)$ | $\frac{1}{2}\Delta\nu[(1+x+x^2)^{\frac{1}{2}} - (1+x^2)^{\frac{1}{2}}] - g_I\mu_0 H/h$ |
| $(2, 0) \leftrightarrow (2, -1)$ | $\frac{1}{2}\Delta\nu[(1+x^2)^{\frac{1}{2}} - (1-x+x^2)^{\frac{1}{2}}] + g_I\mu_0 H/h$ |
| $(1, 0) \leftrightarrow (1, -1)$ | $\frac{1}{2}\Delta\nu[(1+x^2)^{\frac{1}{2}} - (1-x+x^2)^{\frac{1}{2}}] - g_I\mu_0 H/h$ |
| $(2, -2) \leftrightarrow (2, -1)$ | $\frac{1}{2}\Delta\nu[(1-x) + (1-x+x^2)^{\frac{1}{2}}] - g_I\mu_0 H/h$ |

low fields. It has the advantage that the frequencies are lower, approaching the value $\Delta\nu/(2I+1)$. This may be seen from the expression⁸ for the energies of the states in the Paschen-Back region:

$$W_{m_I m_J} = m_I g_I \mu_0 H + m_J g_J \mu_0 H + [\Delta W / (I + \frac{1}{2})] m_I m_J \quad (6)$$

where $\Delta W = h\Delta\nu$. From this equation, with $m_J = \pm \frac{1}{2}$, it is clear that transitions for which $\Delta m_I = \pm 1, \Delta m_J = 0$ give rise to lines whose frequencies approach the limiting value $\Delta\nu/(2I+1)$, since the term $m_I g_I \mu_0 H$ is still relatively small in comparison with the term $[\Delta W / (I + \frac{1}{2})] m_I m_J$ for the highest fields used in this experiment.

The exact expression for the energy of the states of a level with $J = \frac{1}{2}$ is given by the Breit-Rabi formula⁹

$$W_{F, m} = -\frac{\Delta W}{2(2I+1)} + g_I m \mu_0 H \pm \frac{\Delta W}{2} \left(1 + \frac{4m}{2I+1} x + x^2 \right)^{\frac{1}{2}} \quad (7)$$

where $x = (g_J - g_I)\mu_0 H / \Delta W$. The frequencies for the $\Delta m_I = \pm 1$ transitions as found from Eq. (7) are listed in Table I.

The determination of these frequencies at constant magnetic field yields the values of $\Delta\nu$, g_I , and H . Furthermore, the field needs to be only approximately constant because the frequencies depend very little on the field in the Paschen-Back region. This is shown in Fig. 3,

⁸ E. Back and S. Goudsmit, *Zeits. f. Physik* **47**, 174 (1928).

⁹ S. Millman, I. I. Rabi, and J. R. Zacharias, *Phys. Rev.* **53**, 384 (1938).

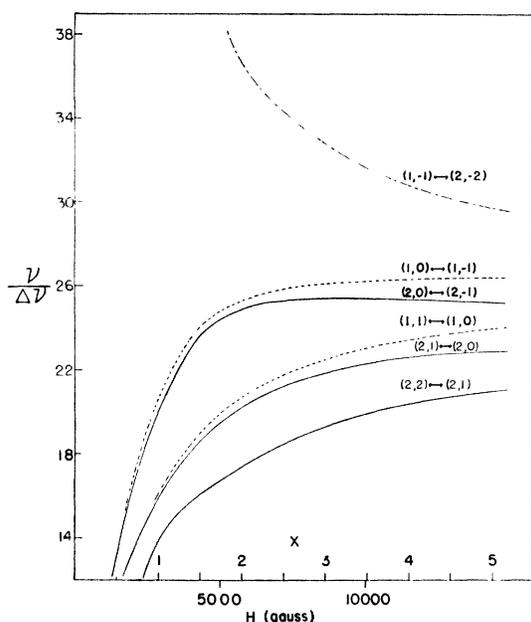


FIG. 3. The field dependence of the frequencies of the lines of Ga^{69} in the $2P_{1/2}$ state resulting from the transitions $\Delta m_I = \pm 1$, $\Delta m_J = 0$.

a plot of frequency *versus* magnetic field for the transitions $\Delta m_I = \pm 1$, $\Delta m_J = 0$.

3. METHOD

In the magnetic resonance method, the atoms in a beam are first deflected in an inhomogeneous magnetic field, then pass through a homogeneous magnetic field with a weak superimposed radio-frequency oscillating field, and finally are de-

flected in the opposite direction by a second inhomogeneous field to strike the detecting filament. The net deflection is zero only when the component of the magnetic moment of the atom in the direction of the field is the same in the two deflecting fields. If the frequency of the oscillating field corresponds to the energy difference between two levels in the atom, transitions which are consistent with selection rules will occur. If such a transition produces a change in the magnetic moment of the atom larger than the minimum observable moment change, there will be a drop in the intensity of the beam at the detector. The radiofrequency spectrum of an atom in a given magnetic field is observed simply by the measurement of the intensity of the beam as a function of the applied frequency.

The magnitude of the inhomogeneous fields is, in general, not critical, but the order of magnitude is dictated by the type of transition being studied and by the dimensions of the apparatus. For a transition for which $\Delta m_I = \pm 1$, the magnetic moment in high fields remains practically unchanged because m_J , and therefore the electronic moment, is the same in both states. Thus, if strong inhomogeneous fields were used in this case, the transition would not be detected. However, if the deflecting field is small ($x < 1$), the difference in magnetic moment between the two states is appreciable, and the atoms will miss the detector provided that the deflecting power is great enough for this value of x . This last requirement determines the necessary length and the ratio of gradient to field of the inhomogeneous magnets.

For many of the low field transitions for which $\Delta F = \pm 1$ or $\Delta m = \pm 1$, the change in magnetic moment is appreciable at high fields ($x > 1$). Thus, the deflecting fields may be made large, which means that the gradient will be large; in fact, large differential deflections become possible over a large range of x , and the particular values chosen depend on instrumental details. For some of the transitions just mentioned, however, the moment change is not large at large x . The effective magnetic moment in a given state is determined by the slope of the curves in Fig. 1, since $\mu = -\partial W / \partial H$. As an example, reference to Fig. 1 shows that for the transition $(3, -3) \leftrightarrow (2, -2)$, the moment change

TABLE II.*

| Observed frequencies | Mean f_2 | Observed f_0 | f_2 |
|----------------------|------------|----------------|--------------------|
| 445.321 445.563 | 445.442 | 0.105 | 445.426 445.458 |
| 445.341 445.558 | 445.450 | 0.105 | 445.446 445.453 |
| 445.177 445.726 | 445.452 | 0.275 | 445.452 445.451 |
| 445.138 445.774 | 445.456 | 0.325 | 445.463 445.449 |
| Mean | 445.450 | | |

* Column one gives the observed frequencies of the lines for the transition $(F=2) \leftrightarrow (F=1)$ for the $2P_{1/2}$ state of Ga^{69} . Column two gives the means of the pairs of π lines for each trial. Column three lists the observed frequencies for the transitions for which $\Delta F = 0$, $\Delta m = \pm 1$. Column four gives the values of f_2 found by combining the values of f_0 with the frequencies in column one. The frequencies are in mc/sec.

at values of $x > 1$ is very small. For the $^2P_{1/2}$ state H is about 115 gauss for $x=1$. If the moment change be made large by reducing the inhomogeneous field to this value, the gradient of the field becomes low, and in the apparatus used in this work, the transition is still not observable. With magnets of fixed length and ratio of gradient to field, no point can be found where the product of moment change and gradient is sufficient to permit observation of these lines. With this factor taken into account, the line pattern with the expected relative intensities is given in Fig. 2c. The σ lines, which are produced by the component of the oscillating field parallel to the homogeneous field, are not observed, because the oscillating field is designed to be perpendicular to the homogeneous field.

4. APPARATUS

For reasons of intensity and ease of line-up, it is, in general, desirable to have the apparatus as short as possible. The length is determined chiefly by the deflecting power required. As is clear from the discussion in the last section, the deflecting fields for the experiment with the metastable state can be relatively short. The apparatus is modified from that described by Zacharias¹⁰ in his work on K⁴⁰. The deflecting power of the apparatus has been increased. The present lengths of A and B fields are 10.4 and 16.4 cm, respectively, and the ratio of gradient to field is 3.2. The apparatus functions as described by KMR, that is, the two gradients are oppositely directed and no stop is interposed in the path of the beam. In Zacharias' work, the gradients were in the same direction and refocusing occurred around a stop in the path of the undeflected beam. The oscillating field was produced by the passage of the oscillating current through a $\frac{1}{2}$ by $\frac{1}{8}$ -inch copper sheet bent into the form of a vertical hairpin, with a one millimeter gap for the passage of the beam. The oscillating field thus produced was perpendicular to the homogeneous C field. No doubt there was also a small component parallel to the field, but it was not large enough to produce any observable transitions.

The same apparatus would be suited for ex-

TABLE III. Final mean values of the frequencies of the transitions for which $\Delta F = \pm 1$ at zero external field for the metastable state of Ga⁶⁹ and Ga⁷¹. The frequencies are given in mc/sec.

| | Ga ⁶⁹ | Ga ⁷¹ |
|------------------------------------|---------------------|---------------------|
| $f_3: (F=3) \leftrightarrow (F=2)$ | 634.890 ± 0.020 | 766.673 ± 0.020 |
| $f_2: (F=2) \leftrightarrow (F=1)$ | 319.062 ± 0.010 | 455.450 ± 0.010 |
| $f_1: (F=1) \leftrightarrow (F=0)$ | 128.274 ± 0.010 | 203.028 ± 0.010 |

periments with the normal $^2P_{1/2}$ state if transitions for which $\Delta F = \pm 1$ in low magnetic field were observed. The frequencies required for this are inconveniently high, however, and it was decided to observe the high-field $\Delta m_I = \pm 1$ transitions instead. To meet the demands for increased deflecting power, it was necessary to use another apparatus which was designed primarily for work with molecules. Each magnet was 50 cm in length, and the ratio of gradient to field was 8.

The oven design and the temperature of operation were the same as described by Renzetti.³

The required frequencies were produced by simple tuned-lines oscillators using WE 316A and 368A tubes. Frequency measurements were made by use of a General Radio heterodyne frequency meter, Type 620A. No attempt was made to determine the shapes of the resonance lines, but the continuously variable oscillator was set at the frequency producing the peak deflection, and the frequency meter was simultaneously tuned to zero beat. The precision for a single setting was about one part in 20,000. The frequency of the quartz crystal against which the wave meter was calibrated was in turn calibrated against a signal from WWV to within one part in a hundred thousand, and therefore introduces no error within the precision of our measurements.

TABLE IV. Values of the interaction constants a and b for the $^2P_{3/2}$ states of Ga⁶⁹ and Ga⁷¹, expressed in sec.⁻¹.

| | Ga ⁶⁹ | Ga ⁷¹ |
|---------------------------|--|--|
| $a = f_2 - f_1$: | $190.788 \pm 0.014 \times 10^6$ | $242.422 \pm 0.014 \times 10^6$ |
| $a = (f_2 + f_3)/5$: | 190.790 ± 0.005 | 242.425 ± 0.005 |
| $a = (f_1 + f_3)/4$: | 190.791 ± 0.006 | 242.425 ± 0.006 |
| $b = (2f_2 - 3f_3)/120$: | $2.6050 \pm 0.0004 \times 10^6$ | $1.6416 \pm 0.0004 \times 10^6$ |
| $b = (f_2 - 3f_1)/96$: | 2.6049 ± 0.0004 | 1.6416 ± 0.0004 |
| $b = (f_2 - 2f_1)/24$: | 2.6048 ± 0.001 | 1.6414 ± 0.001 |
| Final values a : | $190.790 \pm 0.005 \times 10^6 \text{ sec.}^{-1}$ | $242.424 \pm 0.005 \times 10^6 \text{ sec.}^{-1}$ |
| | $6.3644 \pm 0.0002 \times 10^{-9} \text{ cm}^{-1}$ | $8.0868 \pm 0.0002 \times 10^{-9} \text{ cm}^{-1}$ |
| b : | $2.6049 \pm 0.0004 \times 10^6 \text{ sec.}^{-1}$ | $1.6416 \pm 0.0004 \times 10^6 \text{ sec.}^{-1}$ |
| | $8.6894 \pm 0.0013 \times 10^{-9} \text{ cm}^{-1}$ | $5.4759 \pm 0.0013 \times 10^{-9} \text{ cm}^{-1}$ |

¹⁰ J. R. Zacharias, Phys. Rev. **61**, 270 (1942).

5. RESULTS

 ${}^2P_{3/2}$

The pattern of resonance lines shown in Fig. 2c was observed for both isotopes at values of the homogeneous magnetic field from 0.1 gauss to 0.35 gauss. These values of the field are calculated from the separation of the pairs of π lines for a given $\Delta F = \pm 1$ transition. From the simple theory of the Zeeman pattern given earlier, it may be calculated that each π line moves from the zero-field frequency 0.93 mc/sec. gauss. The zero-field frequency may be determined either by averaging the two π lines, where there are two observed, or by adding to or subtracting from the π lines the frequency for the transition $\Delta F = 0, \Delta m = \pm 1$. This latter line was used as a kind of calibration line for the homogeneous field. A representative example of the frequency measurements taken is given in Table II for the $(F=2) \leftrightarrow (F=1)$ transition for Ga⁷¹. The observations recorded were taken on several separate days, and at least two different harmonics of the wave-meter were used. For the transitions $(F=1) \leftrightarrow (F=0)$, for which only one π line could be observed, about twice the number of separate observations were made to get a better average value. The estimate of the probable limit of error is increased for this line because of the lack of a check. Table III gives the final values of the zero-field frequencies for each isotope.

Assuming $c=0$, f_1 may be calculated from f_2 and f_3 to be 128.272 and 203.025 mc/sec. These values lie well within the limits of error of the observed f_1 . If these frequencies are substituted

TABLE V. A series of observations of frequencies of lines of the ${}^2P_{3/2}$ state of Ga⁷¹ resulting from transitions for which $\Delta m_I = \pm 1, \Delta m_J = 0$.*

| (1, 0) ↔ (1, -1) | (2, 0) ↔ (2, -1) | (2, 2) ↔ (2, 1) |
|------------------|------------------|-----------------|
| 808.724 | 795.539 | 524.183 |
| 808.679 | 795.580 | 524.174 |
| 808.741 | 795.543 | 524.204 |
| Mean 808.715 | 795.554 | 524.187 |

* The sequence of observations is in the order in which the lines are tabulated. The transitions are labelled as in Table I. Frequencies are in mc/sec.

in Eq. (3), the values of c are $c_{69} = c_{71} = 6 \times 10^{-10}$ cm⁻¹. Since these are less than the probable limit of error, 3×10^{-9} cm⁻¹, the value of c is taken to be zero, and the values of a and b thus found are listed in Table IV.

The relation between b and the nuclear quadrupole moment Q as given by Casimir⁷ is

$$b = -\frac{e^2}{hc} \left(\left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle \right)_{JJ} \times \frac{\frac{3}{8} Q}{IJ(2I-1)(2J-1)} \text{ cm}^{-1}, \quad (8)$$

with Q in cm² and r in cm. Q is defined as the average of $(3z^2 - r^2)$ over the nuclear charge density for the state $m_I = I$. Thus, $eQ = \int \rho(3z^2 - r^2) d\tau$, where $\int \rho d\tau = Ze$. The quantity $[(3 \cos^2 \theta - 1)/r^3]$ is averaged over the electronic state $m_J = J$.

For the ${}^2P_{3/2}$ state, $\langle (3 \cos^2 \theta - 1) \rangle = -\frac{2}{5}$, and $\langle (1/r^3) \rangle = [R'Chc\delta/HZ_i\mu_0^2(2I+1)]$ cm⁻³. δ is the doublet separation, 826.0 cm⁻¹; R', C , and H are small relativistic correction factors here taken to be 1.028, 1.013, and 1.018, respectively; Z_i is the effective nuclear charge, taken to be 26.4. These are the same numbers used by Renzetti,³ and discussed in more detail by him. The equation for Q becomes

$$Q = \frac{bZ_iHC\mu_0^2}{R'\delta e^2} \times 180 \quad (9)$$

and the quadrupole moments are

$$Q^{69} = +0.186 \times 10^{-24} \text{ cm}^2$$

$$Q^{71} = +0.117 \times 10^{-24} \text{ cm}^2.$$

The fact that the values of b calculated from three pairs of frequencies are in good agreement is strong evidence that the departure from the interval rule is due to a nuclear quadrupole moment, and not to some kind of perturbation. Renzetti³ has given a brief discussion showing that any perturbations from the other term of the fine structure doublet or from states of the same total angular momentum in higher configurations would not be expected to have any appreciable effect on the value of Q .

The ratio of the quadrupole moments is the ratio of the b 's and $b^{69}/b^{71} = Q^{69}/Q^{71} = 1.5868 \pm 0.0004$.

$^2P_{1/2}$

As was shown in an earlier section (Table I), there are six resonance lines to be expected for the transitions $\Delta m_I = \pm 1$, $\Delta m_J = 0$. In this experiment, for reasons of convenience, only five of these lines were observed for Ga^{69} , and only three for Ga^{71} . The data for one run with Ga^{71} are shown in Table V. These lines were observed at a field of about 5000 gauss. Figure 3 shows that the lines are field dependent in this region, but the data in Table V show that there was no significant drift in the homogeneous field during the series of measurements.

These lines were sufficient to permit calculation of the desired constants by use of the equations in Table I. The sets of equations are most simply solved by numerical methods. Since these equations are not linear in x , more than one mathematical solution is possible. However, an approximate knowledge of the field, H , eliminates all but the one correct physical solution. It should be noted that $\Delta\nu$ and x are determined in such a way that the value of $\Delta\nu$ does not depend on an assumed value of g_J . Results are given in Table VI. The values of μ are found by use of the relation $\mu = -I g_I (1836.6)$ nuclear magnetons. The low precision attached to the value of g_I as compared to that attached to $\Delta\nu$ arises from the fact that the determination of g_I depends on the observation of a small frequency difference between two lines of high frequency.

According to present theory, the $\Delta\nu$ -values of the ground states and the a -values determined from experiments with the metastable states depend only on the interaction of the nuclear magnetic dipole moment with the external electrons. Therefore, the ratio of the $\Delta\nu$ -values for the two isotopes should be equal to the ratio of the a -values, since the electronic wave functions are the same for both isotopes. Also, these ratios should equal the ratio of the g -factors, since the g -factor is proportional to the nuclear magnetic moment, and the nuclear spins for both isotopes are the same. From Tables IV and VI, these

TABLE VI. Constants derived from the data for the experiments with the ground $^2P_{1/2}$ state of Ga^{69} and Ga^{71} .

| | Ga^{69} | Ga^{71} |
|--------------|--|--|
| $\Delta\nu$ | $2677.56 \pm 0.10 \times 10^6 \text{ sec.}^{-1}$ | $3402.09 \pm 0.20 \times 10^6 \text{ sec.}^{-1}$ |
| ϵI | $0.089319 \pm 0.000003 \text{ cm}^{-1}$ | $0.113488 \pm 0.000006 \text{ cm}^{-1}$ |
| μ | -0.0007239 ± 0.0000015 | -0.0009218 ± 0.0000015 |
| μ | 1.994 ± 0.005 | 2.540 ± 0.005 |

ratios are $(a_{71}/a_{69}) = 1.27063 \pm 0.00006$; $(\Delta\nu_{71}/\Delta\nu_{69}) = 1.27059 \pm 0.00008$; $(g_{71}/g_{69}) = 1.273 \pm 0.05$. The first two ratios are in even better agreement than could have been expected in view of the uncertainties in the values of $\Delta\nu$ and a . The discrepancy in the third ratio is not significant, as it can be explained by the uncertainties in the g -factors. It is probable that the ratios are more accurate than the individual values, because of cancellation of any systematic errors which may be present.

It may be of interest to note the values of the nuclear magnetic moments obtained by use of the Goudsmit¹¹-Fermi-Segrè¹² formula for a p -electron:

$$\mu_I = \frac{aIZ_i(l + \frac{1}{2})J(J+1)1836.6\lambda}{\delta l(l+1)x} N.M. \quad (10)$$

λ and x are relativistic correction factors, and the other symbols have the same meaning as above. With the value of $(\Delta\nu/2)$ for the $^2P_{1/2}$ states substituted for a in (10), the moments are $\mu_{69} = 2.09$ and $\mu_{71} = 2.65$. These agree with the values given in Table VI within 5 percent. The values of a from the metastable states give values of μ equal to 1.56 and 1.99, which are too low by about 22 percent. This large discrepancy may be due to a perturbation by a higher configuration with the same value of J , as was discussed by Fermi and Segrè¹² for the case of Thallium.

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¹¹ S. Goudsmit, Phys. Rev. **43**, 636 (1933).

¹² E. Fermi and E. Segrè, Zeits. f. Physik **82**, 729 (1933)