The Nuclear Magnetic Moments of N^{14}, Na^{23}, K^{39} and Cs^{133} *

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(Received May 1, 1939)

The nuclear gyromagnetic ratios of N^{14}, Na^{23}, K^{39} and Cs^{133} have been measured by the molecular beam magnetic resonance method. The values of the nuclear magnetic moments, obtained from these measurements and the known spins, are 0.402, 2.216, 0.391 and 2.572 nuclear magnetons for N^{14}, Na^{23}, K^{39} and Cs^{133}, respectively. The shape of the resonance curves in some cases indicates a type of interaction of the nucleus with the rest of the molecule which may arise from the nuclear electric quadrupole moment. It is of interest to note that for the case of the alkali nuclei the magnetic moments calculated from the observed hyperfine splitting of atomic energy states by use of the Goudsmit, Fermi-Segrè formula agree fairly well with the results here given.

INTRODUCTION

BRIEF preliminary reports on the application of the molecular beam magnetic resonance method to the determination of the nuclear magnetic moments of N^{14}, Na^{23}, K^{39} and Cs^{133} have already been published.[1] In the present paper we will give a more complete report of the work on these nuclei.

The method, which has been described in a recent paper,[2] measures the Larmor precession frequency, ν, in a known magnetic field, H, of a nucleus which possesses spin, I, (in units of $h/2\pi$) and magnetic moment, μ. These quantities are related by the formula, $\nu = \mu H/hI$. A knowledge of the precession frequency and the magnetic field permits an immediate evaluation of the ratio of nuclear magnetic moment to nuclear spin. The determination of the magnetic moment is then possible for all cases for which the spin is known.

Apart from the high precision of which it is capable, a most important advantage of this method lies in the fact that the moment is obtained from experimental data directly by means of the simplest physical concepts. The values of the nuclear moments which we obtain are interesting not only for nuclear physics but also for a discussion of the large body of experimental and theoretical work which concerns the measurement and evaluation of the hyperfine structure of atomic energy levels.

In a recent paper Millman[3] has pointed out that it is possible to determine the sign of nuclear moments by taking advantage of certain asymmetries in the resonance curves introduced by the end effects of currents in the wires which produce the oscillating magnetic field.

The N^{14} nucleus belongs to the group of stable nuclei characterized by an odd atomic number and even mass number, and whose other members are the nuclei $_1D^2$, $_3Li^6$ and $_5B^{10}$. These nuclei should, on the basis of simple models,[4] have the same spin and the same magnetic moment. In fact $_1D^2$ and $_3Li^6$, both of which have a spin of 1, have moments of 0.853 and 0.820 nuclear magneton, respectively,[2, 5] in first-order agreement with these predictions. The nuclear spin of N^{14} is known[6] to be 1 from observations on the alternation of intensities in the band spectrum of the N_2 molecule but Bacher[7] who attempted to observe the h.f.s. of N^{14} concluded from its nonappearance that the moment is less than 0.2 nuclear magneton.

The hyperfine splitting of the atomic energy states of Na^{23}, K^{39} and Cs^{133} has been studied extensively[8] both by spectroscopic means and by the use of atomic beam methods, from which the spins are known to be 3/2, 3/2 and 7/2, respectively.[9] The h.f.s. of the ground states of these

[1] S. Millman, P. Kusch and I. I. Rabi, Phys. Rev. **54**, 968 (1938); P. Kusch and S. Millman, Phys. Rev. **55**, 596 (1939).

[2] I. I. Rabi, S. Millman, P. Kusch and J. R. Zacharias, Phys. Rev. **55**, 526 (1939).

[3] S. Millman, Phys. Rev. **55**, 628 (1939).

[4] M. E. Rose and H. A. Bethe, Phys. Rev. **51**, 205 (1937).

[5] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr. and J. R. Zacharias, Phys. Rev. **55**, 595 (1939).

[6] L. S. Ornstein and W. R. Van Wijk, Zeits. f. Physik **49**, 315 (1928).

[7] R. F. Bacher, Phys. Rev. **43**, 1001 (1933).

[8] References to the work on these nuclei are given in the article on nuclear moments by H. A. Bethe and R. F. Bacher, Rev. Mod. Phys, **8**, 82 (1936).

[9] I. I. Rabi and V. W. Cohen, Phys. Rev. **46**, 707 (1934); S. Millman, Phys. Rev. **47**, 739 (1935); V. W. Cohen, Phys. Rev. **46**, 713 (1934).

TABLE I. *The values of g here given are defined by the ratio of the magnetic moment, μ, of the nucleus in units of $eh/4\pi M_p c$ to the nuclear spin, I, in units of $h/2\pi$, or by μ/I. The diamagnetic correction A is calculated from a simple electron precession model using appropriate screening constants. The correction B is calculated from the Fermi-Thomas model. The values for the magnetic moments from h.f.s. data have been calculated from the ground state with the formula of Fermi and Segrè.*

NUCLEUS	I	g OBS.	μ OBS.	DIAGMAGNETIC CORRECTION A (%)	B (%)	CORRECTED μ	MOMENTS FROM H.F.S.
N^{14}	1	0.402	0.402	0.03	0.04	0.402	$\mu < 0.2$*
Na^{23}	3/2	1.476	2.214	0.08	0.08	2.216	2.01
K^{39}	3/2	0.260	0.390	0.13	0.16	0.391	0.374
Cs^{133}	7/2	0.730	2.555	0.57	0.67	2.572	2,53

* Absence of h.f.s.

alkali atoms as determined by the two methods are in excellent agreement. Data for the splitting of excited energy levels are available only from spectroscopic investigations. Our results indicate, as seen from Table I, that with the exception of N^{14} the nuclear moments which were obtained from h.f.s. with the use of the Goudsmit, Fermi-Segrè formula[10] were accurate to within a few percent. The values of nuclear magnetic moments as obtained from the h.f.s. of different levels and as obtained by different methods of calculation applied to a single level disagree between themselves far beyond the limits of error of the experimental data.[8] The results of the present method furnish a criterion by means of which the validity of various methods of analysis of h.f.s. data may be tested and can thus lead to a deeper insight into the nature of atomic energy levels.

EXPERIMENTAL

The apparatus and experimental procedure used in this work have been described elsewhere.[2] We shall merely discuss the molecular compounds used in these determinations. A nucleus whose magnetic moment is to be determined by means of the present apparatus must occur in a molecule having several special properties. The molecule must contain an alkali atom, since the detector is of the surface ionization type and can detect only substances whose ionization potential is less than the work function of the tungsten filament. The molecule must be sufficiently stable so that it will not decompose to any large degree at temperatures at which its vapor pressure is sufficiently high (about 1 mm of Hg) to produce an intense beam. Finally the molecule

[10] S. Goudsmit, Phys. Rev. 43, 636 (1933); E. Fermi and E. Segrè, Zeits, f. Physik 82, 729 (1933).

must be in such a state that no appreciable magnetic moment is contributed by the electronic structure of the molecule, in order that the deflections in the inhomogeneous magnetic fields arise chiefly from the nuclear moments. In practice the last requirement introduces no difficulty since the ground states of most molecules are characterized by the absence of resultant electronic moment.

The molecules NaCN, KCN and RbCN were used for the work on N^{14}. At temperatures of about 1000°K, to which these compounds had to be raised in order to obtain a sufficiently intense beam, considerable dissociation occurred. In the absence of any fields the alkali atoms constituted about 50 percent of the beam intensity. However, when the inhomogeneous fields were turned on, the atomic portion of the beam, possessing large extranuclear moment, was deflected onto the pole faces of the magnets producing the fields and was thus lost. The free atoms, then, interfered in no way with a study of the nuclear moments of the atoms in the molecule. An attempt was made to observe the N^{14} resonance minimum in molecules other than the cyanides. The two compounds, $NaNO_3$ and $NaNH_2$, decomposed to such a degree that the observed molecular beam was of insufficient intensity and altogether too unsteady to permit of the observation of resonance curves.

Na_2, K_2 and Cs_2 were the simplest molecules used in the study of the nuclear moments of Na^{23}, K^{39} and Cs^{133}. These molecules were produced by heating the metallic element in an oven. The beam observed in the absence of magnetic field consisted for the most part of atoms. The molecular content was less than 1 percent of the total beam for K_2 and Cs_2 and about 1.5 percent
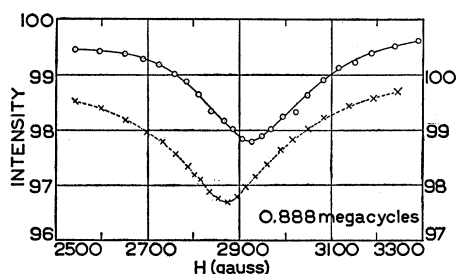
FIG. 1. Resonance curves for N^{14} observed in NaCN. An oscillating current of about 40 amperes produced a field of amplitude of the order of 100 gauss. The length of the oscillating field was about 7 cm.

for Na_2. It depended upon a number of factors such as the slit width of the oven and the temperature. When the inhomogeneous magnetic fields were turned on, the atomic content, as in the case of the cyanides, was removed from the beam. In spite of the low molecular content of the original beam the molecular beam so obtained was very steady and could be maintained at sufficient intensity to study the resonance minima. Other sources yielding resonance curves were: for Na^{23}, the molecules NaF, $Na_2B_4O_7$ and NaCN; for K^{39}, the molecule KCN; and for Cs^{133}, the molecules CsF and CsCl.

Resonance curves for each nucleus were observed for a wide range of values of the homogeneous magnetic field for each of the molecules used. The resonance curves were taken alternately with the homogeneous field in one direction and with the field direction reversed. This procedure permits the determination of the signs of the nuclear moments and leads to more accurate measurements of magnetic moments than would otherwise be possible.[3]

RESULTS

Resonance curves in which the beam intensity is plotted as a function of the magnetic field for a fixed frequency of the oscillating field are shown in Figs. 1, 2, 3 and 4 for the nuclei N^{14}, Na^{23}, K^{39} and Cs^{133}, respectively. The two curves in Fig. 1 were observed for N^{14} in NaCN under identical conditions except that the homogeneous field in one curve was opposite in direction to that for the other curve. The shift in the apparent minimum is due to end effects in the oscillating field and a determination of the sign of the nuclear moment may be made from an observa-

tion of the direction of shift on reversal of field.[3] Figs. 2 and 3 show the resonance curves of Na^{23} and K^{39} observed for the molecules Na_2 and K_2. The central minimum in each curve corresponds to the resonance minimum due to the nuclear magnetic moment as can be determined by comparison with the resonance minima observed for other molecules. Additional evidence on this point is the fact that the central minimum is the only one for which the ratio of the frequency to
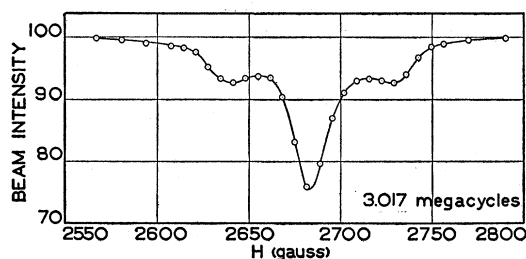

FIG. 2. Resonance curve for Na^{23} observed in Na_2 with an oscillating current of about 3 amperes.

the applied magnetic field, f/H, is independent of field. The structure observed on both sides of these minima will be discussed in a following section. No appreciable shift of the minima occurred due to field reversal in the resonance curves for Na^{23} and Cs^{133} shown in Figs. 2 and 4, because of the small amplitude of the oscillating magnetic field. The observation of the shift of the minimum for the determination of the sign of the moment was made when larger amplitudes of oscillating field were used. A small shift was observed for the case of K^{39} shown in Fig. 3.

The assignment of an observed resonance minimum to a nuclear moment may be made unambiguously in the case of each of the three alkali atoms, since only one common resonance minimum occurs for a wide variety of molecular compounds. The case of the nitrogen moment presents a somewhat more difficult problem because of the similarity of all the molecules for which the resonance minimum was observed. A resonance minimum characterized by a constant f/H was observed for the molecules NaCN and KCN. The same resonance minimum was observed for RbCN although in this case the insufficient beam intensity prevented an accurate test of the constancy of f/H. The question occurs as to whether this observed resonance minimum

is due to N^{14} or to some other moment common to the molecules. The minimum cannot be due to C^{12} since the nucleus possesses no magnetic moment. The observed effect is much too large to be due to C^{13} which has an abundance of only about 1 percent. It seems unlikely that the observed moment is due to a rotation of the molecule as a whole because of the fact that the three cyanide molecules will have different moments of inertia and hence probably different gyromagnetic ratios. The assumption that the rotation of the CN group, as such, which might be common to the three molecules studied, has a moment which is the cause of the observed resonance, is ruled out by the fact that f/H is constant. This means complete decoupling of the hypothetical rotation from the rotation of the molecule as a whole which seems absurd at the low magnetic fields used in this work. (H varied from 1000 to 5000 gauss.)

An approximate estimate of the over-all magnetic moment of a molecule may be made by observing the deflection of a molecular beam in a single inhomogeneous magnetic field. In this way the average over-all magnetic moment of the KCN molecule was found to be about one nuclear magneton. The smallest moment of inertia which the cyanides may have is that of the CN group about its center of gravity. The separation of the carbon and nitrogen atom is known[11] to be 1.15×10^{-8} cm in the HCN molecule and this value probably is not very different from that of
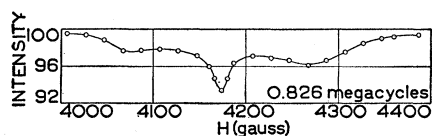

FIG. 3. Resonance curve for K^{39} observed in K_2 with an oscillating current of about 30 amperes.

the corresponding value in KCN. With this value the moment of inertia of the CN group becomes $I=14.2\times10^{-40}$ g cm². The most probable rotational angular momentum at the temperature of the oven (about 1000°K) can be found from $Jh/2\pi=(2IkT)^{\frac{1}{2}}$ and is about $19h/2\pi$. Since the observed g is 0.402, this would result in a magnetic moment of $19\times0.4\sim8$ nuclear magnetons. Any larger moment of inertia, such as that of

[11] H. Sponer, *Molekulspektren* (J. Springer, 1935).

the molecule rotating as a whole, would give rise to a still larger magnetic moment. These magnetic moments do not occur and the observed gyromagnetic ratio cannot, therefore, be assigned to the rotation of the molecule or any part of it. It seems certain that the common minimum observed for the cyanides can only be due to the nuclear magnetic moment of nitrogen.

No resonance minimum was observed which could be attributed to K^{41}. The low abundance of this isotope is not the only reason why it is unobserved in our apparatus. A nucleus with a small g value is subject to a small deflecting force in the inhomogeneous magnetic fields. If the deflection is small compared with the width of the beam, the change in orientation, which occurs in the homogeneous field, produces only a small change in the beam intensity at the detector.

It is noteworthy that the depths of the resonance minima vary widely for the same nucleus in different molecules. For example, the maximum observed drop in intensity at the minimum of Na^{23} was 4 percent in NaF, 9 percent in NaCN and 50 percent in Na_2. Similar effects are observed in the other cases. The specific nature of this effect, which probably depends on the interaction of the nuclear spin with the molecule, is not yet understood. Fortunately this effect does not interfere with the measurement of nuclear magnetic moment, because the results for the same nucleus in different molecules, yielding resonance curves of widely varying depths and widths, are in excellent agreement.

The observed values of the gyromagnetic ratio, the known spins and the resultant magnetic moments are listed in Table I. The values given refer to the value of the nuclear moment of Li^7 ($\mu_{Li^7}=3.250$). The corrections listed in columns 5 and 6 arise from the diamagnetism of the
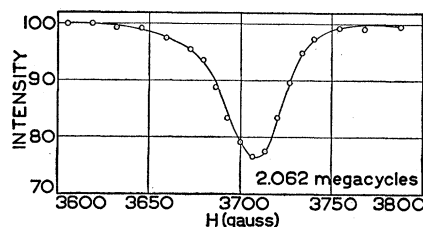

FIG. 4. Resonance curve for Cs^{133} observed in Cs_2 with an oscillating current of about 2 amperes.

atoms and tend to raise the value of the nuclear moment. The evaluation of these corrections is discussed in a later section. The corrected values of the nuclear moments are given in column 7. As was pointed out in an earlier paper, all magnetic moment measurements on the present apparatus are in doubt by about 0.5 percent because of an uncertainty in the calibration of the magnetic fields. From the point of view of the internal consistency of the data alone the relative values of the nuclear moments of N^{14}, Na^{23}, K^{39} and Cs^{133} referred to that of Li^7 have a precision of about 0.4, 0.1, 0.3 and 0.2 percent, respectively. Since the curves for the three alkali atoms are very narrow (in all cases the half-width is of the order of 1 percent), it seems unlikely that any interaction not contemplated by the simple theory could shift the minimum from its ideal position by an amount great enough to affect seriously these precision values. In the case of the N^{14} nucleus, however, the resonance curves were obtained for large amplitudes of oscillating field in order to give an observable effect. The observed resonance curves were broad (the half-widths were of the order of 5 to 10 percent) and it is possible that asymmetries in the structure of the curve, not corrected for, may shift the minimum in some systematic way so as to introduce an additional error. It is to be expected that this error will be no greater than 0.5 percent.

The signs of all nuclear moments here reported were found to be positive. No previous determinations are available for the sign of the moment of N^{14}. The results for the alkali nuclei are in agreement with those obtained from h.f.s. and atomic beam methods.[8, 12]

DISCUSSION

It will be observed (Figs. 2 and 3) that the resonance minima for both sodium and potassium are accompanied by subsidiary minima on both sides of the principal minimum. For all values of the applied frequency these subsidiary minima occur at values of the magnetic field which differ from that at which the principal minima occur by a constant amount. The principal minimum, however, always occurs at the same value of f/H.

12 H. C. Torrey, Phys. Rev. 51, 501 (1937); S. Millman and J. R. Zacharias, Phys. Rev. 51, 1049 (1937).

These facts imply the existence of some form of interaction between the nuclear spin and the rest of the molecular structure. Such an interaction, in sufficiently high external magnetic fields, will no longer depend on the applied field but will be given by some terms such as Am_Im_J as in the Paschen-Back effect. There may possibly be a nuclear quadrupole interaction with the rest of the molecule which will also give a term independent of field. It is evident that such an interaction will give a group of lines rather than a single line because of the many values which may be assumed by the rotational quantum numbers J and m_J. Such a group of lines, probably overlapping, when combined with the appropriate statistical weights, may result in a simple broadening of the resonance minimum or even the appearance of wings. However, these perturbation effects must be symmetrical about the principal energy value which corresponds to the precession of the nucleus in the external field and the central minimum is, therefore, the appropriate point from which to evaluate the nuclear moment. This is confirmed by the fact that only the central minimum has the constant value of f/H.

The observed field difference between the central minimum and either of the satellites in Na_2 is 47 gauss and in the case of K_2 is about 100 gauss. These results may be expressed in wave numbers by the use of the expression, $\Delta\nu(\text{cm}^{-1}) = 2.54\times10^{-8}g\Delta H$. The separations are 1.76×10^{-6} cm^{-1} and 0.66×10^{-6} cm^{-1} for Na_2 and K_2, respectively. These intervals, though apparently small, are, from the point of view of our experiments, very large as may be seen from an inspection of the resonance curves.

As a model, merely to fix orders of magnitude, consider the field due to a unit charge rotating about the nucleus in question at a distance equal to the internuclear distance. This distance is 3.07×10^{-8} cm for Na_2 and 3.91×10^{-8} cm for K_2. A simple calculation shows that this extra field, in gauss, is $J/33$ for Na_2 and $J/117$ for K_2, where J is the rotational angular momentum quantum number. At the oven temperatures we use, the most probable value of J is about 55 for Na_2 and about 80 for K_2. The field at the nucleus due to the rotation is of the order of 1 gauss. The magnetic dipole interaction of the two nuclei

gives a field of the order of μ/r^3 where μ is the nuclear moment and r the internuclear distance. The fields due to the dipole interaction are 0.4 and 0.03 gauss for Na_2 and K_2, respectively. It is apparent that we have to deal with effects of a much higher order of magnitude to account for the observed separations of 47 gauss for Na_2 and 100 gauss for K_2.

It appears likely to us that these large effects may be due, in part, to the presence of a quadrupole electrical moment in the nucleus which interacts electrostatically with the rest of the molecule. Our knowledge of the molecules concerned is, at present, too meager to test this hypothesis.

Finally we must consider an effect arising from the diamagnetic susceptibility of the atom which introduces a small correction in the evaluation of the magnetic moment of the heavier nuclei with the molecular beam magnetic resonance method. The Larmor rotation of the electrons in the molecule produces a magnetic field at the nucleus which opposes the external field. The real field acting on the nucleus is less than the applied field, so that the value of f/H which we take from the observed resonance minima is too small. The correction serves to increase the value of the moment. For the purposes of this evaluation we may neglect the influence of the molecular forces on the atom of the nucleus in question since the contribution to the local field by an inner electron is greater than that by an outer electron, in contradistinction to their contributions to the diamagnetic moment. Consider the field produced by the Larmor rotation of a ring-shaped element of charge rotating about the z axis, which coincides with the direction of the applied field. Every point of this element has polar coordinates r and θ. The field $d\bar{H}$ in the z direction at the origin due to this element of charge is $2\pi\rho\omega r \sin^3\theta drd\theta$ where ρ is the charge density and ω is the Larmor frequency $eH/2mc$. For a single electron the integral of the charge density over an infinite volume is e/c. The value of the integral $\bar{H}$ for a single electron then becomes $e^2H/3mc^2\bar{r}$. If the electron has a quantum number n, $1/\bar{r}=Z/a_0n^2$ where Z is the atomic number and a_0 the Bohr radius. Since there are $2n^2$ electrons for each quantum number n, the contribution to the field at the nucleus by the electrons is $2Ze^2H/3mc^2a_0\times$(number of electron shells), if penetration and screening are neglected. The correction to the field is therefore $\bar{H}/H=2Ze^2/3mc^2a_0$ for each electron shell. The inclusion of screening constants lowers this value. The corrections obtained from this formula by the use of screening constants given by Slater[18] are tabulated in column 5 of Table I. A calculation by Dr. W. E. Lamb, Jr. of the Columbia University Physics Department with the use of the Fermi-Thomas atom model yields the more convenient expression, $\bar{H}/H=CZ^{4/3}$, where $C=0.320\times10^{-4}$. The corrections obtained from this formula are listed in column 6 of Table I. It is seen that they are in substantial agreement with the corrections obtained from the simple electron precession model. It is evident that the correction is of importance only for atoms of high atomic number; the corrections may almost be neglected for K and Na.

[18] J. C. Slater, Phys. Rev. **36**, 57 (1930).