

## Sample Spinning and Field Modulation Effects in Nuclear Magnetic Resonance\*

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Sideband resonances have been observed in high resolution nuclear magnetic resonance experiments in which a cylindrical sample is rotated in a magnetic field with a linear gradient. It is shown that these sidebands arise in a manner similar to the sidebands observed when the magnetic field is modulated by an external source. The general question of time dependent local magnetic fields is considered and the effects of coherent fluctuations are compared with those of random fluctuations for several simple models.

### 1. INTRODUCTION

THIS article is concerned primarily with the nuclear magnetic resonance absorption of a sample which is rotated under particular conditions in an inhomogeneous magnetic field,  $H$ . The case in question is not entirely new, inasmuch as it falls between two extremes whose features are quite well known. On the one hand, there are the narrowing effects of random lattice motions<sup>1-3</sup> upon the splitting of a nuclear resonance by local magnetic fields; and on the other, there are the sideband resonances produced by modulating  $H$  coherently and uniformly throughout the sample.<sup>4-7</sup>† However, the present case has some novel features, which warrant comparison with the related phenomena.

Consider an ensemble of  $N$ -identical nuclei in a homogeneous large static magnetic field  $H$  in the  $z$ -direction. In the most general case each of these nuclei will also be subject to local magnetic fields which broaden or split the resonance. These local fields may be time dependent and may have an arbitrary distribution over the ensemble; they are in addition to whatever rf field is applied coherently in the  $xy$  plane to observe the magnetic resonance. There are several types of local field: (a) the direct nuclear magnetic dipole fields<sup>1</sup>; (b) the chemical shifts which result from differences in the electronic shielding of the nuclei<sup>8</sup>; (c) the indirect spin-spin coupling<sup>2</sup> produced by the nuclear

dipolar polarization of the electrons; (d) inhomogeneities in the applied field  $H_a$ , to which the bulk magnetic susceptibilities and shape of the sample and container can contribute.<sup>9</sup>

Those instances where the local fields are influenced by a random dynamic process are characterized by a gradual averaging out of the local field effects as the average rate of the process increases. The first analysis of the problem was made by Bloembergen, Purcell, and Pound<sup>1</sup> who described the narrowing by random lattice motions of resonance lines broadened by the direct dipole interactions. This case is complicated by the continuous character of the broadening. However, if the local magnetic fields have a few discrete values instead of a continuous distribution, line shapes can be calculated readily as a function of the average lifetime  $\tau$  of a nucleus in each local field.<sup>2,3</sup> In liquids, resonances have been observed with resolved fine structure resulting from chemical shifts or the indirect spin-spin coupling and for which there are random natural processes such as chemical exchange or intramolecular reorientation changing the nuclei from one local field to another. For two local fields differing by  $\Delta H$  and equally populated, the doublet resonance gradually coalesces as  $\tau$  becomes shorter and only a single line occurs when  $1/\tau \geq \gamma \Delta H / 2\sqrt{2}$ .  $\gamma$  is the gyromagnetic ratio of the nuclei.

If the dynamic process influences the local magnetic fields at all of the nuclei in a coherent manner, the results differ significantly from those for random processes. The sideband resonances produced by modulating  $H$  uniformly over the sample are one case of this sort. Another instance is a double resonance experiment on two groups of nuclei coupled by the indirect spin-spin interactions. The coupling,  $\hbar A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$ , ordinarily splits each resonance into discrete components separated by  $\delta\nu = A_{ij}$ . However, the coupling depends upon the spin coordinates of the two groups of nuclei and the application of an rf field of amplitude  $H_{12}$  at  $\omega_2$  changes the spin coordinates of the 2-nuclei coherently with an angular frequency  $\gamma_2 H_{12}$ . The multiplet structure of the resonance at  $\omega_1$  is observed to coalesce when

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<sup>1</sup> Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

<sup>2</sup> Gutowsky, McCall, and Slichter, J. Chem. Phys. **21**, 279 (1953).

<sup>3</sup> H. S. Gutowsky and C. H. Holm, J. Chem. Phys. (to be published).

<sup>4</sup> R. Karplus, Phys. Rev. **73**, 1027 (1948). This reference treats the effects of frequency modulation upon microwave spectra, but the approach is a general one which serves as a basis for the later discussions of magnetic field modulation effects in nuclear magnetic resonance.

<sup>5</sup> Smaller, Yasaitis, and Anderson, Phys. Rev. **81**, 896 (1951); B. Smaller, Phys. Rev. **83**, 812 (1951).

<sup>6</sup> J. H. Burgess and R. M. Brown, Rev. Sci. Instr. **23**, 334 (1952).

<sup>7</sup> W. A. Anderson, Ph.D. thesis, Stanford University, 1955 (unpublished); Phys. Rev. **102**, 151 (1956).

† Note added in proof.—This question has also been discussed by K. Halbach, Helv. Phys. Acta **29**, 37 (1956).

<sup>8</sup> N. F. Ramsey, Phys. Rev. **78**, 699 (1950); **86**, 243 (1952).

<sup>9</sup> Reilly, McConnell, and Meisenheimer, Phys. Rev. **98**, 264(A) (1955).

$\gamma_2 H_{12} > \delta\omega$  but sideband resonances appear in the intermediate stages.<sup>7,10</sup>

The source of the local magnetic field usually is unimportant in determining the effects of a given type of dynamic process. But it may prove difficult to obtain experimentally a particular type of dynamic process for all sources of local magnetic fields. Thus, it seems unlikely that conditions could be found under which a chemical shift would be averaged out by a coherent rather than by a random process.

## 2. MATHEMATICAL ANALYSIS

The nuclei are contained in a cylindrical sample mounted along the  $x$  axis and exposed to a radio-frequency field  $2H_1 \cos\omega t$ , in the  $x$  direction. We wish to know the effects of time dependent local magnetic fields  $H_i(t)$  which perturb the static field  $H$ . The Hamiltonian for the system is

$$\begin{aligned} \mathfrak{H} &= \sum_{i=1}^N -\gamma\hbar\mathbf{I}_i \cdot \{i2H_1 \cos\omega t + \hat{k}[H + H_{il}(t)]\} \\ &= \sum_{i=1}^N -\gamma\hbar\mathbf{I}_i \{2\mathbf{I}_{ix}H_1 \cos\omega t + \mathbf{I}_{iz}[H + H_{il}(t)]\}. \end{aligned} \quad (1)$$

It is convenient to rearrange Eq. (1) as follows:

$$\mathfrak{H} = \mathfrak{H}^{(0)} + \mathfrak{H}^{(1)},$$

where

$$\mathfrak{H}^{(0)} = \sum_{i=1}^N -\gamma\hbar\mathbf{I}_{iz}[H + H_{il}(t)], \quad (2)$$

$$\mathfrak{H}^{(1)} = \sum_{i=1}^N -2\gamma\hbar\mathbf{I}_{ix}H_1 \cos\omega t. \quad (3)$$

The frequency components of  $H_{il}(t)$  in question are in the audio range, much smaller than  $\gamma H$ , so it is proper to use the instantaneous total eigenfunctions of  $\mathfrak{H}^{(0)}$ . For a particular nucleus in a given state  $m$ , we have

$$\begin{aligned} \Phi_m(\phi, t) &= -\frac{1}{(2\pi)^{\frac{1}{2}}} e^{im\phi} e^{-im\gamma H t} \\ &\quad \times \exp\left(-im\gamma \int_{-\infty}^t H_i(t') dt'\right). \end{aligned} \quad (4)$$

In order to compute the absorption spectrum we require the time dependence of the coefficient of the eigenfunction. For simplicity we assume that  $I$  is  $\frac{1}{2}$ ; and for an initial state  $m = +\frac{1}{2} \rightarrow m = -\frac{1}{2}$ , the coefficient  $a_{+\frac{1}{2}}(t)$  is given by ordinary first-order time-dependent

perturbation theory to be

$$\begin{aligned} a_{+\frac{1}{2}}(t) &= -\frac{i}{\hbar} \int_{-\infty}^t \int_0^{2\pi} \Phi_{+\frac{1}{2}}^{*(1)} \mathfrak{H}^{(1)} \Phi_{-\frac{1}{2}} dt d\phi \\ &= i\gamma H_1 \int_{-\infty}^t \cos\omega t e^{i\gamma H t} \exp\left(i\gamma \int_{-\infty}^t H_i(t') dt'\right) dt \\ &= \frac{i\gamma H_1}{2} \int_{-\infty}^t (e^{i\omega t} + e^{-i\omega t}) e^{i\gamma H t} \\ &\quad \times \exp\left(i\gamma \int_{-\infty}^t H_i(t') dt'\right) dt. \end{aligned} \quad (5)$$

Further analysis requires a specific choice of  $H_i(t)$ .

### External Modulation of $H$

One of the simplest cases is to modulate  $H$  at an audio frequency uniformly throughout the sample. Some but not all features of this case have been described<sup>5-7</sup>; a more complete analysis facilitates discussion of the spinning sample. For a cosine wave form of angular frequency  $\omega_a$ , we have

$$H_i(t) = H_i^0 \cos(\omega_a t + \phi), \quad (6)$$

where  $\phi$  is a phase angle, and Eq. (5) becomes

$$\begin{aligned} a_{+\frac{1}{2}}(t) &= \frac{i\gamma H_1}{2} \int_{-\infty}^t (e^{i\omega t} + e^{-i\omega t}) e^{i\gamma H t} \\ &\quad \times \exp\left(\frac{i\gamma H_i^0}{\omega_a} \sin(\omega_a t + \phi)\right) dt. \end{aligned} \quad (7)$$

Introduction of the Bessel functions of the first kind by the relation<sup>11</sup>

$$e^{iz \sin\theta} = \sum_{n=-\infty}^{\infty} e^{in\theta} J_n(z)$$

converts Eq. (5), upon integration, to

$$\begin{aligned} a_{+\frac{1}{2}}(t) &= \frac{\gamma H_1}{2} \sum_{n=-\infty}^{\infty} e^{in\phi} \\ &\quad \times J_n\left(\frac{\gamma H_i^0}{\omega_a}\right) \left\{ \frac{e^{i(\gamma H + n\omega_a + \omega)t} - 1}{\gamma H + n\omega_a + \omega} \right. \\ &\quad \left. + \frac{e^{i(\gamma H + n\omega_a - \omega)t} - 1}{\gamma H + n\omega_a - \omega} \right\}. \end{aligned} \quad (8)$$

The second term in the parantheses in Eq. (8) corresponds to absorption, for which the transition proba-

<sup>11</sup> P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), pp. 619, 1322.

<sup>10</sup> A. L. Bloom and J. N. Shoolery, *Phys. Rev.* **97**, 1261 (1955).

bility is given by

$$a_{+\frac{1}{2}}^*(t)a_{+\frac{1}{2}}(t) = \frac{\gamma^2 H_1^2}{4} \sum_{n=-\infty}^{\infty} \sum_{n'=-\infty}^{\infty} e^{i(n'-n)\phi} \times J_n(k)J_{n'}(k) \left\{ \frac{e^{-i(\gamma H+n\omega_a-\omega)t}-1}{\gamma H+n\omega_a-\omega} \right\} \times \left\{ \frac{e^{i(\gamma H+n'\omega_a-\omega)t}-1}{\gamma H+n'\omega_a-\omega} \right\}, \quad (9)$$

where  $k = \gamma H l^0 / \omega_a$ .

Consider first the diagonal terms,  $n = n'$ , in the double sum. Upon rearrangement these are

$$\frac{\gamma^2 H_1^2}{4} \sum_{n=-\infty}^{\infty} J_n^2(k) \frac{4 \sin^2[\frac{1}{2}(\gamma H+n\omega_a-\omega)t]}{(\gamma H+n\omega_a-\omega)^2}. \quad (10)$$

One of these terms can be large and absorption can occur whenever  $\gamma H + n\omega_a = \omega$ , where  $n = 0, \pm 1, \dots$ . This condition can be met by adjusting either  $\omega$  or  $H$ . For constant field,  $H = H_0$ , the resonance absorption observed as a function of  $\omega$  would consist of the fundamental at  $\omega = \gamma H_0$  with sidebands spaced in frequency by  $\omega_a$ ; while in our experiments at constant radio-frequency,  $\omega = \omega_0$ , the fundamental occurs at a field  $H = \omega_0 / \gamma$  with sidebands spaced in field by  $\omega_a / \gamma$ .

The intensity of absorption is proportional to the transition probability per unit time and this may be calculated for a given term in Eq. (10) by integrating the term over a small region of magnetic field about the value  $\gamma H = (\omega_0 - n\omega_a) / \gamma$ . The function is sharply peaked so the integration limits may be taken as  $\pm \infty$  without significant error, and this gives

$$I[(\omega_0 - n\omega_a) / \gamma]_{n=n'} = \left[ \frac{a^* a}{t} \right]_{n=n'} = \frac{\pi \gamma^2 H_1^2}{2} J_n^2(k) \rho(\gamma H). \quad (11)$$

The total absorption for the sample has been obtained by multiplying Eq. (11) by  $\rho(\gamma H)$ , a line shape function describing the density of states in the absence of the local fields. It is assumed that  $H_1$  is sufficiently small that saturation does not occur and  $\rho(\gamma H)$  thus is not perturbed by the experiment. Equation (11) shows that, except for any effects from the cross terms, the intensities of the resonance components at  $\gamma H = \omega_0 - n\omega_a$  go as  $J_n^2(\gamma H l^0 / \omega_a)$ .

The cross terms in Eq. (9) contain frequency components at  $(n' - n)\omega_a$  which produce an amplitude modulation of the resonance sidebands and fundamental. The effects of the components oscillating at

$\omega_a$  have been described by Smaller<sup>5</sup> and by Brown.<sup>6</sup> They are not of immediate importance here.

The over-all effects of magnetic field modulation are the same as those predicted<sup>4</sup> for the case in which the rf source is frequency modulated. Similar results are obtained if the rf source is amplitude modulated<sup>12</sup>; however, if the rf source is modulated and the spectrum is observed by changing  $H$ , then the receiver must also be adjusted to each sideband. The effects of other types of modulation wave forms can be obtained by replacing Eq. (6) with the Fourier transform of the wave form and carrying through the analysis in a manner similar to that given for the cosine form.

### Modulation of $H$ by Sample Spinning

If the sample is rotated mechanically without turbulence in an inhomogeneous field,  $H_{il}$  undergoes a cyclical change. For a field homogeneous except for a linear gradient in the  $z$  direction, the amplitude of  $H_{il}$  is a function  $H_{il}^0(r_i)$  of the distance  $r_i$  between a nucleus and the axis of rotation. Defining the cylinder radius to be  $R$  and setting  $H_{il}^0(0) = 0$ ,  $H_{il}^0(R) = H_{il}^0$ , we have  $H_{il}^0 = H_{il}^0 r_i / R$  and for a sample spinning at a constant angular frequency  $\omega_s$ ,

$$H_{il}(t) = H_{il}^0 \frac{r_i}{R} \cos(\omega_s t + \phi_i). \quad (12)$$

$\phi_i$  describes the relative angular positions of the nuclei about the axis of spin. Equation (12) leads to a result identical with Eq. (9) for the external modulation of  $H$  except that  $H_{il}^0$  is replaced by the  $H_{il}^0 r_i / R$  of Eq. (12). At this point the analysis must be modified because the spectrum of the spinning sample includes different contributions from nuclei at different  $r$ .

We will again give only the analysis of the diagonal terms, which for the nuclei at a given  $r$  are the same as those in Eq. (11) except that the deviation ratio of the

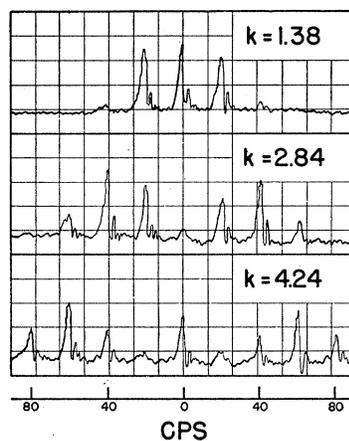


FIG. 1. Proton magnetic resonance spectra of a water sample showing the effects of external audiomodulation at 20 cps of the magnetic field for various modulation indices,  $k = \gamma H l^0 / \omega_a$ . The spectra were recorded at a fixed radio-frequency of 17.735 Mc/sec; the magnetic field sweep was 43 milligauss and the sweep time, 13 sec.

<sup>12</sup> H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. **19**, 1259 (1951).

Bessel function is  $\gamma H l^{00} r / \omega_s R$ . The spectrum of the diagonal terms is obtained by multiplying the modified Eq. (11) by the fraction of nuclei at a given  $r$  and integrating. This yields

$$I[(\omega_0 - n\omega_a) / \gamma]_{n=n'} = \frac{\pi \gamma^2 H_1^2 \rho(\gamma H)}{4\pi R^2} \times \int_0^R J_n^2\left(\frac{\gamma H l^{00} r}{\omega_s R}\right) 2\pi r dr. \quad (13)$$

The integral can be evaluated by introducing the general formula<sup>11</sup> relating Bessel functions,

$$\int z J_n^2(\alpha z) dz = \frac{1}{2} z^2 [J_n^2(\alpha z) - J_{n-1}(\alpha z) J_{n+1}(\alpha z)]. \quad (14)$$

With this substitution, we find

$$I[(\omega_0 - n\omega_s) / \gamma]_{n=n'} = \frac{\pi \gamma^2 H_1^2}{2} \rho(\gamma H) \times [J_n^2(k) - J_{n-1}(k) J_{n+1}(k)], \quad (15)$$

where  $k$  is now  $\gamma H l^{00} / \omega_s$ . More complicated distributions of field inhomogeneities can be treated by replacing Eq. (12) with a Fourier series and using the appropriate distribution function in Eq. (13). Sidebands will still occur at  $n\omega_s$ , but their relative intensities will no longer be given by expressions as simple as Eq. (15).

In the above analyses, we have not considered the sawtooth sweep in  $H$  which is used to scan the resonance in the experiments. Strictly speaking, this contributes a term  $2H_s(t-t_0) \equiv 2H_s T$  to  $H_l(t)$  in Eqs. (6) and (12). However, for slow sweeps, the effects are negligible for reasons analogous to those given by Karplus<sup>4</sup> for frequency sweeps.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

The proton resonance in water was observed at room temperature with a high-resolution nuclear magnetic resonance (nmr) spectrometer.<sup>3,13</sup> Figure 1 illustrates the resonance sidebands produced by external audio-modulation of  $H$  at a frequency  $\nu_a$  of 20 cps. In this experiment, the effects of the oscillating terms not included in our analyses were rejected by the narrow band pass (1 cps) of the rf receiver, dc amplifier and recording system. The three spectra correspond to modulation amplitudes,  $H l^0$ , of about 6.5, 13, and 20 milligauss. The relative intensities of the components of the resonances, averaged over several recordings, are in good agreement with the ratios of  $J_n^2(\gamma H l^0 / \omega_a)$ , as predicted by Eq. (11).

The line shapes of the fundamental and sidebands are the same, as is expected from Eq. (11) providing the various components do not overlap. However, satura-

<sup>13</sup> Gutowsky, Meyer, and McClure, Rev. Sci. Instr. **24**, 644 (1953).

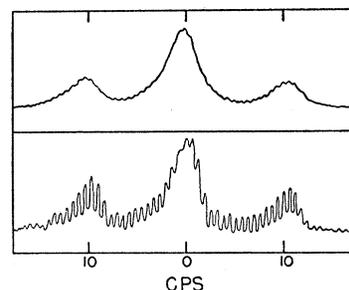
tion effects are discernible at higher rf levels if the sweep rate and  $\omega_a$  are such that the components are spaced in time by intervals less than or comparable to the spin-lattice relaxation time  $T_1$ . This is indicated by spectra in Fig. 1 where components in the right half of the sweep are less intense than their counterpart in the first half. Another effect which can be important at high rf levels is the perturbation of the sideband separations as  $\gamma H_1 \rightarrow \omega_a$ . Anderson<sup>7</sup> has shown that the separation  $\delta\omega$  between fundamental and the first sideband is given by  $\delta\omega^2 = \omega_a^2 + (\gamma H_1)^2$ , which provides a good method for measuring  $H_1$ .

The effects of the oscillating components are illustrated by the two spectra in Fig. 2. For this experiment, the band pass of the spectrometer was adjusted first to be less than the audiomodulation frequency  $\nu_a$  and then to lie between  $\nu_a$  and  $2\nu_a$ . The spectrum for the first case is similar to those in Fig. 1. The second, however, shows an amplitude modulation at  $\nu_a$  of the resonance components. The limited band pass rejects terms other than those for which  $\Delta n = \pm 1$ ; the higher terms are generally less important in any event. The earliest observations of sideband effects produced by external modulation of  $H$  were made<sup>5</sup> with a broadband rf receiver using a phase sensitive audioamplifier sharply tuned to  $\nu_a$ . In this event only the oscillating components are observed.

The various phenomena are of interest in themselves; in addition they can serve as a convenient method for calibrating magnetic field<sup>14</sup> or radio-frequency sweeps. Also, a direct measurement<sup>15</sup> can be made of the separation of two resonance lines by adjusting  $\nu_a$  until the first sideband from each resonance coincides with the fundamental of the other resonance. However, for small splittings the audiomodulation effects will interfere unless the band pass of the system is correspondingly small.

<sup>14</sup> J. T. Arnold and M. E. Packard, J. Chem. Phys. **19**, 1608 (1951).

<sup>15</sup> Huggins, Pimentel, and Shoolery, J. Chem. Phys. **23**, 1244 (1955).



The resonance sidebands produced by mechanically spinning the sample in a magnetic field with a linear inhomogeneity are exhibited by the spectra in Fig. 3. In these experiments the band pass of the spectrometer was reduced below the spinning frequency  $\nu_s$  so that the amplitude modulation of the sidebands does not appear. The relative intensities of the components should be given by Eq. (15). For convenience, this function has been calculated from the Bessel functions<sup>16</sup> and is plotted in Fig. 4 for the fundamental and first four sidebands.

Comparison of the experimental with the calculated intensities was complicated by difficulties experienced in obtaining independent measurements of the field gradient. The field gradients were generated by passing a dc current in the same directions through what were effectively two long parallel wires mounted symmetrically on either side of the sample.<sup>17</sup> Actually each conductor was a semicircular coil of 20 turns. In principle, the gradients may be calculated from the current and the geometry of the system, but in order that inhomogeneities of the magnet itself would not influence the results, the sample was located in the most homogeneous spot in the magnetic field. This spot was not centrally located, which complicates the correction for the image currents in the magnet pole faces.

An approximate calibration of the field gradient coils was made by moving the sample in steps of one mm and measuring the shift in resonance position produced by a given current. The accuracy of this procedure is not great because of the magnet inhomogeneities; the calibration obtained in this manner was  $(\gamma/2\pi) dH/dr = 44.5$  cps/mm amp. A number of spectra were recorded for different spinning frequencies and different currents. The spinning frequencies were determined from the separation of the sidebands under calibrated field sweep conditions. Deviation ratios,  $k_e = \gamma H_i^{00}/\omega_s$ ,

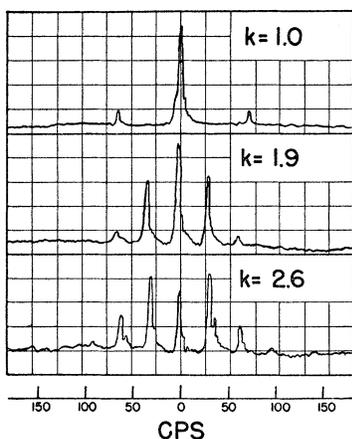


FIG. 3. Sideband resonances produced in proton spectra by spinning a cylindrical sample in an artificially produced linear gradient in the magnetic field. The modulation indices,  $k$ , are those calculated from the relative intensities.

were calculated from these data and the diameter of the sample (1.27 mm). In addition, deviation ratios  $k_i$  were read off the graphs in Fig. 4 using the intensities observed for the sidebands. The results for ten different sets of experimental conditions are summarized in Table I. The values  $k_i$  obtained via the intensities differ by a constant ratio of 1.32 from  $k_e$ , those calculated via the approximate calibration of the field gradient coils. It appears reasonable to conclude that the spinning sidebands originate as described and that 59 cps/mm amp is the proper calibration figure for the field gradient coils.

Sample rotation<sup>18,19</sup> is one of the more successful methods of the many which have been proposed for improving the effective homogeneity of the static magnetic field in high-resolution nmr studies. The present experiments show that the motion of the sample is coherent when a cylindrical container is rotated about one axis at a constant angular velocity. In this event,  $z$  inhomogeneities along the axis of spin are unaffected

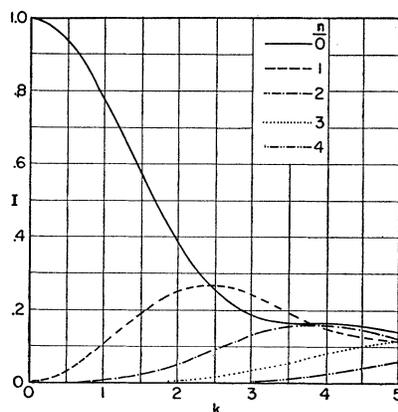


FIG. 4. The relative intensities of the resonance sidebands for a cylindrical sample spinning coherently in a magnetic field with a linear gradient as a function of the modulation index given in Eq. (15). The fundamental ( $n=0$ ) and first four sidebands are plotted.

by the spinning, which suggests that oval-shaped pole caps could be a more efficient magnet design for high resolution. The frequency required for coherent spinning to average out a given inhomogeneity is somewhat different from that stated by Bloch,<sup>19</sup> who considered only the case of random motions.

A comparison of the effects of the two types of motion can be made quite readily for local fields such that the resonance in the absence of a perturbing dynamic process consists of two identical sharp components separated by  $2\gamma H_i^0$ . For a random process transferring nuclei between these two local fields, we noted in the introduction that the "average" frequency  $\nu_s$  required to coalesce the two components is  $\nu_s \geq \gamma H_i^0/2\sqrt{2}$  cps. If the local fields are inhomogeneities in which the sample is spun coherently, sidebands are formed which

<sup>16</sup> G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1944).

<sup>17</sup> H. Y. Carr and E. M. Purcell, *Phys. Rev.* **94**, 630 (1954).

<sup>18</sup> The earliest experiment using spinning sample techniques appears to be that described by H. Y. Carr, Ph.D. thesis, Harvard University, 1952 (unpublished).

<sup>19</sup> Bloch, Anderson, and Arnold, *Phys. Rev.* **94**, 496, 497 (1954).

move out and decrease in intensity as the spinning frequency is increased and the two main components coalesce. An experiment approximating this uses two liquids with different bulk magnetic susceptibilities, a small cylinder of one inside a larger cylinder of the other. This assembly gives U-shaped resonances with splittings related to the differences in bulk susceptibility.<sup>9</sup> Upon spinning the assembly, the doublets are averaged out and the arrangement is useful in comparing the resonance positions of nuclei in the two samples.

The value of  $\nu_s$  required to average out the two local fields depends on how weak one wishes the sidebands to be. The problem can be treated as a "double" square wave modulation of  $H$  with the result that if the first sideband is to be less than 1% of the intensity of the coalesced fundamental, the spinning frequency is  $\nu_s \geq 5\sqrt{2}\gamma H l^2/\pi^2$ . Random processes thus appear to be about twice as effective as coherent processes in reducing local field effects. This apparent difference in the effectiveness of the two types of motion arises mainly from the continuous distribution of frequencies for the random motions in combination with the nonlinear relation<sup>3</sup> between frequency and extent of averaging.

Another situation of interest concerns the effect upon a resonance line of a random modulation of  $H$

TABLE I. Deviation ratios for a cylindrical sample rotating in a magnetic field with a linear gradient.  $k_c$  is the value calculated from an approximate calibration of the field gradient coil;  $k_i$ , that inferred from the relative intensities of the fundamental and sideband resonances.

Coil current	$\frac{\omega_s}{2\pi}$	$k_c$	$k_i$	$k_i/k_c$
0.25 amp	32.5 cps	0.48	0.60	1.25
0.50	32.5	0.94	1.19	1.27
0.50	64.7	0.48	0.60	1.25
0.75	32.2	1.43	1.9	1.33
0.75	66.8	0.69	0.92	1.33
1.00	31.6	1.95	2.6	1.33
1.00	32.0	1.93	2.6	1.35
1.00	36.2	1.70	2.3	1.36
1.00	39.8	1.54	2.1	1.36
1.00	59.0	1.00	1.4	1.40

uniformly throughout the sample, arising say from fluctuations in the current of an electromagnet or in the field sweep system. Of course, if the fluctuations  $\Delta H$  are of small amplitude and fast enough, they average out, the criterion being  $\nu_f \geq \gamma \Delta H/\sqrt{2}$ . If the frequencies are too low or the amplitudes too great the resonance is broadened by the fluctuations, depending on how long a time is taken to scan the resonance. It is apparent that sample spinning will not average out these local fields because it produces no change in them.

## Magnetic Moment of the Neutron\*

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An experiment has been performed to measure the magnetic moment of the neutron to a greater precision than has heretofore been obtained. The method is somewhat similar to that of atomic-beam magnetic resonance using separated oscillating fields. A beam of slow neutrons is polarized by reflection from a magnetized cobalt mirror and then reflected again from a similar mirror used as an analyzer. Between the two mirrors the neutrons pass through a region of uniform magnetic field where they may become depolarized by a resonant rf magnetic field. This results in a drop in intensity of neutrons reflected from the second mirror. The resonance frequency for depolarization is compared with the proton moment resonance frequency in the same transition region. In order to achieve high resolution of the neutron resonance, the path length of the neutrons in the uniform magnetic field was 110 cm. The measured ratio of resonant frequencies  $\nu_n/\nu_p = 0.685057 \pm 0.000017$ . This corresponds to a value of  $\mu_n = -1.913148 \pm 0.000066$  nm.

### INTRODUCTION

OF the simpler nuclei and nucleons, the one whose magnetic moment has been measured with the least precision is the neutron. Although the previously determined values of the neutron magnetic moment are of sufficient accuracy to point out the deficiencies of

present-day nucleon theory, it is to be hoped that more precise data will be of eventual value in view of the fundamental character of the nucleon.

The magnetic moment of the neutron has been measured in the past with various degrees of precision by Alvarez and Bloch,<sup>1</sup> Arnold and Roberts,<sup>2</sup> and Bloch,

<sup>1</sup> L. W. Alvarez and F. Bloch, *Phys. Rev.* **67**, 111 (1940).

<sup>2</sup> W. R. Arnold and A. Roberts, *Phys. Rev.* **71** 878 (1947); **70**, 766 (1940).

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