Direct observation of nuclear magnetic resonance in a rotating coordinate system

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A method for the direct observation of nuclear magnetic resonance in a rotating coordinate system is proposed and realized. The method is based on registering the longitudinal (relative to the constant magnetic field) component of the nuclear magnetization at the Larmor frequency of the spin precession in an effective magnetic field. It is shown that this method has sufficiently high sensitivity and can be used to improve the resolution and to measure NMR chemical shifts in solids, without the use of coherent pulse sequencing or Fourier transformation of the output signal. The spectra of the nuclear magnetic resonance in a rotating coordinate system are obtained from the $^{19}F$ nuclei in CaF$_2$ crystals, from the protons in water, and others. In CaF$_2$, under the conditions of the "magic" angle, a narrowing of the nuclear magnetic resonance line by a factor of 50 has been obtained, and the spin-temperature saturation theory has been confirmed. The chemical shifts were resolved for CaF$_2$, BaF$_2$, MgF$_2$, and CaF$_3$. Further possibilities of the method for the investigation of spin dynamics and structure analysis in solids are analyzed.

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1. PRINCIPLE OF DIRECT OBSERVATION OF NUCLEAR MAGNETIC RESONANCE IN A ROTATING COORDINATE SYSTEM

Considerable progress has been made recently in spectroscopy of nuclear magnetic resonance (NMR) in solids, as a result of investigations of the dynamics of nuclear spin systems in strong high-frequency magnetic fields. Thus, the sensitivity of NMR signal registration has been increased by several orders of magnitude, exceeding very slow atomic and molecular motions have been detected; methods have been developed for the suppression of nuclear dipole interactions, and high-resolution spectra were obtained from solids (see, e.g., [1-3]). In all these cases, the motion of the nuclear magnetic moments must be considered in the so-called rotating coordinate system (RCS) [4-9].

Let a solid sample containing nuclear spins $I$ be placed in a constant magnetic field $H_0$ directed along the z axis and in a high-frequency field $2\omega H_1 \cos \omega t$ perpendicular to it, with $\omega = \omega_n = \gamma H_0$, where $\gamma$ is the nuclear gyromagnetic ratio. In a coordinate system (RCS) that rotates about the z axis with frequency $\omega$, the spins are acted upon by a static effective magnetic field $H = (\Delta + H_1) I_z^{1/2}$, where $\Delta = H_0 - \omega / \gamma$, which is directed at an angle $\theta = \tan^{-1}(H_1 / \Delta)$ to the z axis (Fig. 1). At $H_1 = H_0$, where $H_0$ is the local magnetic field produced by the spin-spin interactions in the laboratory frame (l.a.), the quantization axis $Z$ in the RCS is directed along $H_0$, i.e., it makes an angle $\theta$ with the z axis. The effective spin Hamiltonian in this coordinate system is [10]

$$H = -I_z I_x + I_x H_1.$$  (1)

where $I_x$ denotes the $Z$ component of the total spin of the sample, while $H_1$ denotes the secular part of the nuclear dipole-dipole interactions in the RCS, and its value in first-order perturbation theory is

$$H_1 = \frac{3\gamma I_n}{2\gamma} (1 - 3 \cos^2 \theta),$$

with $\gamma = \gamma_i = \gamma_j = \gamma_k$. $r_{ij}$ is the radius vector joining the spins $I_i$ and $I_j$ and $\theta_{ij}$ is the angle between $r_{ij}$ and $H_0$.

The Hamiltonian (1) is analogous to the ordinary spin Hamiltonian

FIG. 1. Geometry of magnetic fields and principle of direct observation of NMR in a rotating coordinate system.
Hamiltonian in the l.s., except that $H_x$ is replaced by $H_y$ and the secular part $\mathcal{X}_{\mu}$ of the dipole interactions in the l.s. is replaced by $\mathcal{X}_{\mu}'$. Consequently, at the frequency $\omega_y - \omega_x$ of the Larmor precession of the spins in the field $H_y$ it is possible in principle to have NMR in the RCS, just as "ordinary" NMR at the frequency $\omega_x$ is produced in the l.s.

Notwithstanding a certain similarity between the NMR phenomena in the l.s. and in the RCS, there are also substantial differences between them:

1) The maximum values of $H_y$ attained in practice ($\sim 100$ Oe) are lower than $H_x$ by two or three orders of magnitude, so that the frequency $\omega_y$ does not exceed several hundred kilohertz (whereas usually $\omega_x \approx 10 - 100$ MHz).

2) As seen from (2), at the so-called "magic angle" $\theta = \theta_y = \cos(\pi/\sqrt{3})$, the term $\mathcal{X}_{\mu}'$ vanishes, so that the NMR line width in the RCS can be much smaller than in the l.s.

So far, NMR in the RCS was observed only by indirect methods, in which the signal was registered at the high frequency $\omega_y$, and the NMR effect manifested itself in the RCS only as one change or another in this signal (the method of nonstationary nutation\(^{11,12}\) the method of rotational saturation\(^{11,13}\)). It is curious that in Redfield's fundamental paper\(^{11}\) the opinion is advanced that direct observation of NMR in the RCS at the frequency $\omega_y$ is impossible at all because of the small value of the absorption at low frequencies. However, as will be shown below, the NMR signals in the RCS turned out to be quite observable directly and were even comparable in magnitude with the ordinary NMR signals in the RCS.

According to the general principle of observation of magnetic resonance, to register NMR directly in a RCS it is necessary to excite and measure the rotating nuclear-magnetization component perpendicular to the static magnetic field, in our case the component $M_x$ perpendicular to the field $H_y$, see Fig. 1. Since, however, the direction of $H_y$ is not constant relative to the measuring instrument (i.e., in the l.s.) but precesses about the z axis with a frequency $\omega$, direct registration of NMR in the RCS calls for the use not of the entire value of $M_x$, but only its projection $M_x(z) = M_x \sin(\theta_0)$ on the immobile axis $z$. This magnetization component, which oscillates at the frequency $\omega_0$, can be measured with the aid of a receiving induction coil oriented along $z$ and connected to a receiver operating at the frequency $\omega_0$.

Thus, the proposed method differs from the usual one also in that it measures the longitudinal rather than the transverse (relative to $H_y$) component of the nuclear magnetization. As to the actual schemes for observing NMR in RCS, it is possible to use here any of the known NMR spectroscopy devices, such as measurement of absorption or dispersion, the methods of induction, of echo, and of nonstationary nutations, and others. If it is possible at the same time to preserve during the measurement time the large magnetization stored by the nuclei in the field $H_y$, the decrease of the sensitivity compared with the ordinary NMR (owing to the decrease of the frequency by a factor $\omega_0/\omega_x$) can be compensated for by a considerable degree by increasing the number of turns in the low-frequency receiving coil, even if we ignore the increased NMR signal in the RCS as a result of the narrowing of the line near the magic angle.

To register NMR in a RCS directly by a quasistationary method, it is necessary to apply to the sample an additional weak alternating field $H_2(t) = 2 \omega_0 \sin(\omega t)$, perpendicular to the $Z$ axis (see Fig. 1), with frequency $\omega_0 = \omega_0$ and pass smoothly through the resonance region by varying one of the parameters ($\omega_0$, $H_y$, or $\omega$), which affects the satisfaction of the resonance condition

$$\omega = \omega_0.$$

In this case the receiver will register the spectrum of the resonant absorption or dispersion in the RCS.

To produce the field $H_2(t)$ we can apply an additional alternating field of frequency $\omega$ along the $z$ axis (for example, by applying a suitable voltage on the receiving coil, thus obtaining the well-known "$\Omega$"-meter" system (see, e.g., \(^{11,12}\)). It is more convenient, however, to use shallow modulation of the frequency $\omega_0$ or of the amplitude $H_y$ of the high-frequency field at a frequency $\Omega$, which also leads, as seen from Fig. 1, to the appearance in the RCS of an alternating magnetic field having an $X$-axis component (in the former case $2H_x \sin(\omega_0 t)$, in the latter $2H_x \sin(\omega t)$, where $\omega_0$ and $\omega$ are the depths of the corresponding modulation). In this case no additional voltage of frequency $\Omega$ is produced in the receiving coil, other than the NMR signal, so that this method is analogous to the operation of an induction spectrometer with crossed coils.

We note that in all these methods there appears also a component $H_z(t) = H_0 \cos(\omega_0 t)$ parallel to $H_y$. As shown theoretically in\(^{11}\), this component can lead to the appearance of multiple and parametric resonances but under our conditions ($H_y = H_{\text{res}}$, $H_0$) its influence can be neglected.

As already noted, to attain high sensitivity the nuclear magnetization must be as large as possible during the time of the measurements. This can be achieved, for example, by adiabatically decreasing the detuning $|\Delta|$ from large values, i.e., from the far wing of the NMR in the l.s., to the required value (at $H_y = \text{const}$ $\gg H_0$), or else by adiabatically turning on $H_y$ at $\Delta = \text{const} \gg H_0$. In this case almost the entire equilibrium magnetization $M_0$ stored in the field $H_y$ is established along $H_y$ (\(^{11,12}\)) and the smooth variation of $\Delta$ or $H_0$ can be simultaneously used for the passage through the NMR line in the RCS. On the other hand, if the field $H_y$ is turned on abruptly, the $Z$ component of the magnetization $M_0$ amounts to only $M_0 \cos \theta_0$, and to pass through resonance in the RCS it becomes necessary to sweep the frequency $\Omega$ or $\Delta$. It is clear that in either case the entire experiment is best carried out in a time shorter than the respective spin-lattice relaxation times $\tau_{1/2}$ and $\tau_1$ in the RCS and in the l.s.
Direct observation of NMR in the RCS is possible also by nonstationary methods with registration of the free-induction, echo, or nonstationary-notification signals. The prospects for their utilization will be discussed in Sec. 5.

2. APPARATUS, PROCEDURE, AND EXPERIMENTAL CONDITIONS

The experiments were performed on $^{19}$F nuclei in CaF$_2$, BaF$_2$, and MgF$_2$ single crystals and in BaF$_2$ and CaF$_2$ powders, and also on the nuclei $^3$He in water at $H_s = 3650$ Oe, $\omega/2\pi = 14\text{MHz}$, and temperatures $T_s = 293$, 78, and 4.2° K. In all the experiments except those described in Sec. 4, the condition $H_s \gg H_H$ was satisfied.

The NMR was observed in the RCS by the quasistationary method at $\Omega/2\pi = 100$ kHz. The receiving (low-frequency) and exciting (high-frequency) coils were oriented parallel and perpendicular to $H_0$, respectively, were tuned to the frequencies $\Omega$ and $\omega$, and their $Q$ values at room temperature were 10 and 100, the receiving coil having 1500 turns. The inhomogeneity of the field $H$, in the volume of the sample (cylinder 3 mm in diameter and 5 mm long) were determined by measuring in the RCS the line width of the NMR of the protons of water and amounted to 0.12%. (See Sec. 4A).

The field $H_{s0}$ in the RCS was produced by frequency or amplitude modulation of the high-frequency field $2H_0 \cos \omega t$ with frequency $\Omega$ fixed. The receiver (a resonant amplifier tuned to the frequency $\Omega$) was connected to the receiving coil through a low-pass filter that blocked the exciting signal of frequency $\omega$ and passed the useful signal of frequency $\Omega$. The absorption and dispersion signals $S_+(\Omega)$ and $S_-(\Omega)$, proportional respectively to the imaginary and real parts of the transverse magnetic susceptibility in the RCS, were separated by two orthogonal phase detectors controlled by a reference voltage of frequency $\Omega$. Their time constant was 3–5 msec.

The exciting field $2H_0 \cos \omega t$ was turned on after the sample magnetization reached its equilibrium value $M_s$ in the field $H_0$, and at that instant the absolute magnitude of the detuning exceeded the value

$$\Delta = \left| \left( \Omega/\omega \right|^2 - 1 \right|$$

corresponding to the condition (3) for resonance in the RCS. This was immediately followed by the start a smooth decrease of $\Delta$ (by sweeping the field $H_0$), which terminated after passage through $\Delta = \Delta_0$. The duration of one sweep was 1 sec, and its rate satisfied the condition of adiabatic fast passage in the RCS ($\dot{\Delta} \geq \Delta_0/\tau_1 = \Delta_0/\tau_2 = \Delta_0/\tau_3$, $\tau_1 = 56$), thus ensuring a sufficiently high magnetization directed along $H_0$. The NMR and RCS signals were observed on an oscilloscope whose sweep was synchronized with variation of $H_0$.

It is clear that in this procedure changes take place in the time of passage not only in $H_0$, but also in the angle $\theta$. Therefore to observe NMR in RCS under conditions of the magic angle the values of $\Delta_0$ and $\theta_0$ were chosen beforehand such that the conditions $\Delta = \Delta_0$ and $\theta = \theta_0$ were realized during the sweep simultaneously. It is easily seen that this is attained at $2\Delta_0\Omega/2\pi = 3\Omega^2/t$, i.e., for example, for the nuclei $^{19}$F ($\Omega/2\pi = 400\text{kHz/Oe}$) and $\Omega/2\pi = 100$ we chose $\theta_0 = 20.38$°. The ultimate fine setting of $H_0$ was my minimizing the width of the NMR signal in the RCS.

It must be recognized that when the field $H_0$ is swept the value of $H_0$ varies in the general case nonlinearly. In a small vicinity of a certain value of $\theta$, however, the increments $dH_0$ and $d\Delta_0$ can be regarded as proportional, so that if $H_0$ is constant then $|dH_0| = |d\Delta_0| \cos \theta_0$. This was taken into consideration in the calibration of the sweep, which is given throughout, unless otherwise stipulated, in units of $H_0$.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

A. Absorption and dispersion signals

Fig. 2 shows oscillograms of the absorption and dispersion signals $S_+$ and $S_-$, obtained in the RCS with a CaF$_2$ crystal at $H_H = [111]$, $T_s = 78$°K and at different amplitudes $H_{ss}$. All the signals were obtained at $\theta = \theta_0$.

The most characteristic feature of these signals—their abrupt narrowing in comparison with the NMR in the RCS—will be discussed in Sec. 3B. We shall dwell here on the shapes and amplitudes of the absorption and dispersion lines. As seen from Fig. 2a, at small field amplitudes $H_{ss}$, the signal $S_+$ is symmetrical, and $S_-$ is asymmetrical. With increasing $H_{ss}$, the amplitude of the absorption line first increases (Fig. 2b) and then decreases abruptly (Fig. 2c), while the dispersion signal becomes first asymmetrical and then symmetrical increasing at all time in amplitude. This picture agrees qualitatively with the temperature-dependent theory of saturation of NMR in solids, when applied to the RCS at $\theta = \theta_0$.

This conclusion is confirmed by examination of Fig. 3.

FIG. 2. Oscillograms of NMR in RCS at the frequency $\Omega/2\pi = 100$ kHz from $^{19}$F nuclei in a CaF$_2$ crystal under conditions of the magic angle ($\theta = \text{absorption, bottom—dispersion}$) at amplitudes of the recording field $H_{ss}$: $a - 3.8$ Oe, $b - 6.0$ Oe, $c - 12.0$ Oe. One horizontal division is equal to 6.16 Oe.

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which shows the values of the width $\Delta H_2$ of the absorption signal (dark points) of NMR in the RCS for the $^{19}$F nuclei in CaF$_2$ at $\theta = \theta_p$, as a function of the amplitude $H_{1p}$ of the recording field.

which acts in a doubly rotating coordinate system—DRCS (the second rotation is around $H_2$ with frequency $\Omega$), and after the passage of the resonance it turns out to be rotated $180^\circ$ relative to $H_2$ (compare with the analogous passage in the l.s.\cite{4}).

From the conservation of the entropy in the DRCS (at $H_{1p} \neq H_{1s}$, where $H_{1s}$ is the local

The dependence of $\delta H$ on $H_{1s}$, which follows from (4), agrees satisfactorily with Fig. 4 and makes it possible to obtain in the value of $H_{1s}$ at $\theta = \theta_p$, a value which will be discussed in the next section. We note that in the case of strong saturation, but when still $H_{1s} = H_{1c}$, we have according to $^{18,19} \delta H^2 = 2H_{1c}$, i.e., the ratio $\delta H^2/H_{1c}^2 \approx 1/3$, in good agreement with the experimental value 1.75 ± 0.10 (cf. Figs. 3 and 4).

Thus, saturation of the NMR signal in the RCS at $\theta = \theta_p$ agrees with the temperature theory developed for ordinary NMR, $^{18,19}$ and registration of $\delta H_p$ under conditions of adiabatic fast passage in RCS makes it possible to determine $H_{1s}$ directly.

### Table 1. Parameters of NMR line of $^{19}$F in CaF$_2$ in the laboratory frame and in a rotating coordinate frame at the magic angle.

<table>
<thead>
<tr>
<th>Crystal orientation</th>
<th>$H_{1s}$ (Oe)</th>
<th>$H_{1c}$ (Oe)</th>
<th>$H_{1p}$ (Oe)</th>
<th>$\delta H$ (Oe)</th>
<th>$\delta H_p$ (Oe)</th>
<th>$\delta H_p^2$ (Oe$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}$F</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0001</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>3.1</td>
<td>2.7</td>
<td>2.2</td>
<td>0.001</td>
<td>0.0001</td>
<td>0.000001</td>
</tr>
</tbody>
</table>

*Present work.

**For unsaturated signal.
B. Suppression of nuclear dipole-dipole interactions

As already noted, at \( \theta = \phi_0 \) one should expect a strong narrowing of the NMR in the RCS. This is confirmed by the experimental dependence of the NMR line width in the RCS on the amplitude \( H_1 \) (at \( \phi = \text{const} \)), obtained at three orientations of the CaF\(_2\) crystal relative to \( H_1 \) (Fig. 5). It is seen that the minimal value of \( \Delta \omega \) is indeed reached at \( \theta = \phi_0 \). Since these data were obtained under conditions of adiabatic fast passage of NMR in the RCS (see Sec. 3A), formula (4) is applicable to them. With the aid of this formula it is possible to separate from \( \Delta \omega \) the part of the line width which is independent of \( H_1 \),

\[
(\Delta \omega)^2 = (\Delta \omega_0)^2 + 12\Delta \omega_0 \Delta \omega_1,
\]

(5)

as well as to find \( H_1 = (\Delta \omega_0)^2 / 2 \Delta \omega_1 \). It turns out that at \( \theta = \phi_0 \) the values of \( \Delta \omega_0 \) and \( \Delta \omega_1 \) depend strongly on the crystal orientation, and a distinct correlation with the orientation dependence of the width of the NMR line in the RCS is observed (see the table). This indicates that even at \( \theta = \phi_0 \) the observed width of the NMR line in the RCS is determined by nuclear dipole interactions whose secular part differs from zero under these conditions only in second-order perturbation theory.\(^{14}\)

Eliminating from the Hamiltonian the terms that lead in the indicated approximation to a small shift \( M_{ls} \) of the resonant frequency, it is possible to use the known prescription\(^{10-14}\) to calculate the local field \( H_{ls} \) and the second moment \( M_{ls} \) of the unsaturated NMR line in the RCS relative to its center at \( \theta = \phi_0 \). The calculation yields

\[
(H_{ls})^2 = \frac{1}{N} \sum_{j=1}^{N} \left( \frac{P(z)}{z^2} \sum_{j_1=1}^{N} \sum_{j_2=1}^{N} B_{j_1} B_{j_2} B_{j_3} \right.
\]

\[
+ \frac{1}{N^2} \sum_{j=1}^{N} \sum_{j_1=1}^{N} \sum_{j_2=1}^{N} B_{j_1} B_{j_2} B_{j_3},
\]

\[
-19 \sum_{j=1}^{N} B_{j_1} B_{j_2} B_{j_3} + \frac{5}{19} \sum_{j=1}^{N} \sum_{j_1=1}^{N} \sum_{j_2=1}^{N} B_{j_1} B_{j_2} B_{j_3},
\]

(6)

where \( N \) is the number of nuclei in the sample. For a primitive cubic lattice and \( 1 = \frac{1}{2} \) (for example, for the nuclei \(^{19}\)F in CaF\(_2\)) the values of \( H_{ls} \) and \( M_{ls} \) can be set in correspondence with the second moment of the NMR in the l.s.

\[
M_{ls} = \frac{(1/10)}{3N^2} \sum_{j=1}^{N} \delta j.
\]

Thus, for the orientations \( H_1 || [100], [110] \) and \([111]\) we obtain, respectively\(^{14}\)

\[
M_{ls} = \begin{cases} 0.320 & \text{for } (100); \\ 0.230 & \text{for } (110); \\ 0.461 & \text{for } (111). 
\end{cases}
\]

We note also that at any orientation we have \( M_{ls} \) \( M_{ls} \), the numerical values of \( M_{ls} \) and \( M_{ls} \) are given in the table (in the column "Theory") for \( H_1 = 25 \) Oe.

To compare these data with experiment we have used for \( H_{ls} \), formula (6) and for \( (\Delta \omega_0)^2 \) formula (4), in which we substitute the theoretical value

\[
H_{ls} = \frac{(3\cos^2 \theta - 1)\gamma H_1 \Delta \omega_0^2}{4 \Delta \omega_1},
\]

(7)

which follows directly from (2) and (6). The corresponding curves are shown in Fig. 5. It is seen that the theory agrees satisfactorily with experiment, although there are some quantitative deviations at the orientations \([100] \) and \([111]\). It is natural to attribute them to the additional line broadening due to the inhomogeneity of the field \( H_1 \) in the interior of the sample, as seen from the data in Fig. 4 for \( \Delta \omega_0 \) in water (as \( H_1 = 0 \)), this broadening amounts to approximately 0.035 Oe.

If we exclude this inhomogeneous part from the value of \( \Delta \omega_1 \) observed in the absence of saturation at \( H_1 || [111] \) (see the table), then the remainder \( (\Delta \omega_0) \) ranges from 0.06 to 0.01 to 0.08 to 0.01 Oe (depending on the assumption made concerning the line shape). The ratio \( (\Delta \omega_1)(3\cos^2 \theta - 1)\gamma H_1 \) is at any rate not larger than 1.0 or 0.1, i.e., it is smaller than in the l.s., where at the same orientation we have \( \Delta \omega_1/2\Delta \omega_1 = 1.26 \). This indicates that the shapes of NMR lines are different in the l.s. and the RCS (at \( \theta = \phi_0 \)), this broadening amounts to approximately 0.035 Oe.

We note that for unsaturated signals the ratio is \( \Delta \omega_1/2\Delta \omega_1 = 1 \) (Fig. 3). This ratio, however, is not very sensitive to the line shape and therefore cannot yield substantial information concerning this shape.\(^{15}\)

It is useful to note that for NMR in the RCS at \( \theta = \phi_0 \) there exists no universal relation between \( M_{ls} \) and \( H_{ls} \) (it is known\(^{14}\) that in the l.s. \( M_{ls} \approx 3\Delta \omega_1 \) for dipole interactions). This means that a measurement of \( M_{ls} \) similar to that performed in the present study, yields independent on the lattice sums that enter in (6), i.e., on the structure of the crystal.

We note in conclusion that the minimal energy of the NMR line in the RCS, obtained in our experiments (\( M_{ls} \) at \( H_1 || [111] \), Fig. 3) is somewhat lower than 0.075 Oe, i.e., 300 Hz, corresponding to a fiftyfold narrowing in comparison with the l.s.

C. RESOLUTION OF CHEMICAL SHIFT IN SOLIDS

The suppression of dipole interactions at \( \theta = \phi_0 \), as well known, can be used to increase the resolution in NMR spectroscopy of solids and, in particular, to measure...
sure the chemical shift of the NMR frequency.

In the hitherto employed method\(^{3,4}\) this result was achieved with definite sequences of coherent high-frequency pulses, and the observed signal had to be decoded with the aid of a Fourier transformation. It is clear that the method described above of observing NMR in a RCS at a low frequency \(H_0\) can also be used for this purpose, and requires neither a complicated coherent pulse technique nor a Fourier transformation of the output signal.

An example of the resolution of chemical shifts is seen in Fig. 6, which shows oscillograms of the NMR spectrum of \(^{19}\)F in the RCS at \(B = \theta_s\), for CaF\(_2\) and BaF\(_2\) crystals placed simultaneously in the spectrometer pickup (11 kHz, \(T_2 = 2\) s). The horizontal scale is graduated here in terms of the mismatch \(\delta\), i.e., the field \(H_\theta\), which is related near \(\theta = \theta_s\) to the scale of the field \(H_\theta\) like \(1/(\cos \theta_s \sqrt{\delta})\) (see Sec. 3). Inasmuch as the \(x\)-component \(\psi_x\) of the chemical-shift tensor is decreased by a factor \(1/(\cos \theta_s)\) on going to the RCS,\(^{1,11}\) this decrease is exactly offset by the indicated change of the sweep scale. Thus, the distance between the lines on Fig. 6 (approximately 0.39 Oe, i.e., 1.56 kHz) yields the true difference between the chemical shifts of \(^{19}\)F in CaF\(_2\) and BaF\(_2\), which agrees with the known data.\(^{1,4}\)

The relative chemical shift for the nuclei \(^{19}\)F were also resolved in the crystals BaF\(_2\) and CaF\(_2\) powders.

We emphasize that the frequency \(\omega_s = 14\) MHz (and correspondingly the field \(H_\theta = 3.5\) kOe) used in these experiments is much lower than customary in typical measurements of chemical shifts. It is clear that the increase \(\omega_s\) and \(H_\theta\) leads to an improvement of the resolution.

4. RESONANCE AND RELAXATION SIGNALS IN WEAK EFFECTIVE FIELDS

In the experiments described above, the ratio \(H_s/H_\theta\) reached 10–20. With decreasing \(H_\theta\), the suppression of the dipole-dipole interactions at \(\delta = \theta_s\), in accordance with (5), becomes less effective (NMR oscillograms in the RCS are shown in Fig. 7 for \(H_s = 3\) Oe and 1:27 \(\pm 14\) kHz). Then at \(H_s = \theta_s\), the registered \(\omega_s\) and \(H_\theta\) signals lose their resonant character completely. Under these conditions, an essential role is assumed by the nonsecular part of the dipole interactions (in the

![Image](image_url)

FIG. 6. Oscillogram of RCS NMR spectrum of \(^{19}\)F nuclei in the crystals CaF\(_2\) (right-hand signal) and BaF\(_2\) (left-hand signal) at \(\theta = \theta_s\). One horizontal division is equal to 0.13 Oe in the scale of the sweep of the field \(H_\theta\).

![Image](image_url)

FIG. 7. Oscillograms of RCS NMR signals from the \(^{19}\)F nuclei in CaF\(_2\) at 1/27 \(\pm 14.7\) kHz and \(H_s = 3\) Oe. Top—absorption, bottom—dispersion. The right-hand and left-hand signals correspond to \(\Delta > 0\) and \(\Delta < 0\) at \(\theta = \theta_s\). One horizontal division is equal to 3.4 Oe.

RCS, which leads to energy exchange between the Zeeman (in the field \(H_s\) and dipole-dipole pools and to establishment of a unified spin temperature \(T_s\) in the RCS.\(^{1,11}\)

This process corresponds to a relaxation longitudinal magnetic susceptibility \(\chi_{xx} = dM_x/dH_s\), so that now, besides the transverse component of the alternating field \(H_\theta\), the observed signals also contain contribution from the longitudinal component \(H_s(1) - H_s(0)\cos \theta_s\).

If the alternating fields \(H_s(1)\) and \(H_s(0)\) are produced by modulation of the detuning \(\Delta\) at a frequency \(\Omega\), then the receiving coil oriented along the \(x\) axis will register signals proportional to

\[\chi_{xx}(\theta_s) = \chi_{xx} \cos \theta + x_{xx} \sin \theta,\]

where \(\chi_{xx} = dM_x/dH_s\) is the transverse susceptibility, which contributes to the NMR signals (in the RCS) described in the preceding sections. Thus, \(\chi_{xx}(\theta_s)\) is a mixture of two components which can be separated by additionally measuring the quantity

\[\chi_{xx}(\theta_s) = \frac{dM_x}{dH_s} \frac{dH_s}{dH_s},\]

where \(\chi_{xx} = \chi_{xx} \sin \theta + x_{xx} \cos \theta_s\). In this case, in analogy with the so-called adiabatic susceptibility measured in the i.a., in weak fields \(H_s^{1,11}\), the quantity \(\chi_{xx}\) is equal to

\[
\chi_{xx} = \frac{\Delta(\Delta - \omega_s^2) - \omega_s^2}{\omega_s^2 + (\Delta - \omega_s^2)^2} \exp \left( - \frac{T_s}{\Delta - \omega_s^2} \right),
\]

(9)

where \(\chi_{xx}\) is the static nuclear magnetic susceptibility and \(T_s\) is the time of establishment of a single temperature in the RCS and is determined by the relation (see, e.g.,

\[
\chi_{xx} = \frac{1}{\phi(\Delta - \omega_s^2) \exp \left( - \frac{T_s}{\Delta - \omega_s^2} \right)},
\]

(10)

where \(\phi(\Delta)\) is the Fourier factor of the NMR line in the i.a.\(^{11}\)

It follows from (9) and (10) that the maximal signals
The NMR signals in the RCS yields the NMR frequency spectrum in the field \( H_z \), directly in finite form, without the need for a Fourier transformation. This uncovers a simple method of increasing the resolution of NMR and of measuring chemical shifts of solids (experiments at the magic angle). The resolution is limited so far by dipole interactions of second order and by the inhomogeneity of the field \( H_z \).

To increase further the resolving power we can use nonstationary methods. Thus, the free-induction and echo signals in the RCS at the frequency \( f_0 \) can be obtained by pulsed applications of the field \( H_z \), in accordance with a definite program, in analogy with the pulses of the field \( H_z \) used in similar experiments in the L.A.\cite{18} It is thus possible, in particular, to exclude the influence of the inhomogeneity of the field \( H_z \).

Signals of the induction and echo type in RCS can be produced also by a jumpwise application of the field \( H_z \), followed by variation of its phase in (or frequency); in this case we must have \( H_z \geq 0.1 \text{mT} \). Since the field \( H_z \) can be turned on in such experiments continuously, such experiments are free also of the shortcoming of ordinary pulsed methods, such as phase transients at the instant when the high-frequency field is turned on and off, and the large duration of the cycles, which is determined mainly by the time of registration of the signal in the intervals between the pulses.\cite{30,31} In this connection, the proposed method can turn out to be more effective than the known pulsed methods of suppressing the nuclear dipole interactions.\cite{13}

The low sensitivity of the low-frequency receiver relative to turning the field \( H_z \) on and off, and also to changes of the phase and frequency of the high-frequency field, permit, in principle, continuous registration of the NMR signal at the frequency \( \Omega_n \), and this offers definite advantages over nonstationary experiments of the usual type. In particular, this permits a more accurate measurement of the initial section of the free-induction signal, a necessary requirement for the determination of the moments of the NMR line in the RCS (see, e.g.\cite{13}). These moments, just as the quantity \( H_1^{\alpha} \) measured in the quasistationary experiments (see Sec. 3c), can yield additional information on the structure of a solid.

New possibilities may be uncovered by registration of nonstationary mutations in the case of jumpwise applications of the field \( H_z \). Just as observation of nonstationary mutations in jumpwise application of the field \( H_z \) has made it possible to study NMR in the RCS\cite{15,19} the proposed method makes it possible to investigate NMR and relaxation phenomena in an effective field \( H_z \) in DRCS and to increase the amount of information available by NMR spectroscopy.

Finally, we point out the possibility of using direct registration of NMR in the RCS for the measurement of \( T_1 \), the transverse-relaxation time \( T_2 \) in the RCS, and also the time of the spin-lattice relaxation of the dipole-dipole pool in the RCS. For these measurements one can propose a number of procedures (both quasistationary and nonstationary), the advantage of which is, in

\[ x^{'*} \text{ and } x^{*} \text{ will be observed at the frequencies } \Delta \leq T_2^{-1} \text{, corresponding to the acoustic band } 10^4 \text{ to } 10^5 \text{ Hz. On the other hand, since the ratio } T_2/T_3 \text{ can be easily increased to values } 10^3 \text{ to } 10^4 \text{, the value of } x^{'*} \text{ can exceed } x^{*} \text{ by two or three orders of magnitude.} \]

As seen from (9) and (10), measurement of the relaxation longitudinal susceptibility in the RCS can yield significant information on the temperature \( T_0 \), the time \( T_2 \), and the value of \( H_z \). In particular, (9) leads to the simple formula

\[ x^{'*} = \frac{1}{Q} \left( \frac{\Delta}{\omega} \right)^2 \]  

which was used by us for an experimental determination of the time \( T_2 \) in the crystal CaF\(_2\) at 4.2 K, \( H_z \)\(\text{[11]}, \text{ and } 0.2 < H_z < 2 \text{ Oe}, \text{ see Fig. 8.} \)

In these experiments (see also\cite{12}), the frequency \( \Delta/2\pi \text{ was only } 1.16 \text{ kHz; the corresponding receiving coil had } 6,000 \text{ turns and its } Q \text{ was approximately } 15, \text{ while the sample volume was } 0.4 \text{ cm}^3. \text{ The absorption and dispersion signal at the frequency } \Delta \text{ were observed in adiabatic fast passage of the field } H_z \text{ through the NMR line in the L.A. and were bell-shaped with a maximum at } \Delta = 0. \text{ The waveform of these signals (see}\text{[13]) agreed satisfactorily with relations (9) and (10), with allowance for the variation of } T_2 \text{ in the adiabatic passage}\text{[13].}

\[ T_2(\Delta) = \text{const} \left( \frac{\Delta^2}{\omega^2} \right)^{\gamma} \]

The data of Fig. 8 corresponds to \( \Delta = 0. \text{ It is seen that at } H_z < 0.6 \text{ Oe the experimental points agree well with the theoretical dependence (10), calculated with (9) } \Delta = 70 \mu\text{sec} \text{.} \text{[13,16]} \text{ It is interesting that the extrapolation of (10) into the region } H_z < H_{\text{cr}} \text{, where this formula is in general incorrect, differs from the experimental values by only 30%.} \]

5. CONCLUSIONS AND PROSPECTS

Our experiments have shown that direct observation of NMR in the RCS is perfectly realizable and requires no exotic technology whatever. Despite the considerable decrease of the resonant frequency, this method has quite satisfactory sensitivity which, just as in ordinary NMR, can be increased by increasing \( H_z \) or by signal accumulation.

In the quasistationary regime, direct observation of

\[ 384 \text{ Sov. Phys. JETP 47(2), Feb. 1978} \quad \text{A. E. Medved and V. A. Atarkin} \quad 384 \]
particularly, the possibility of rapid measurement (within the time of one experiment) of these relaxation times.

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1) The abbreviation RCS will henceforth pertain throughout to this inclined rotating coordinate system.

2) Magnetic resonance in RCS was observed also on electron spins in gases by an optical registration method. (2, 3)

3) Preliminary results were reported at the Fifth All-Union School and Symposium on Magnetic Resonance, at the Second Specialized AMPERE Colloquium, (3) and at the All-Union Conference on Magnetic-Resonance Problems (Konevka, 1976), and reported also in (19, 20).

4) In formulas (3.4), given in (17), for the second moment in the RCS, the coefficient preceding the term

\[ \sum \frac{b_i^2}{N_i} \]

is incorrect. In addition, the ratio \[ \frac{M_2}{M_0} \] in Table I of that reference is half the correct value.

References:


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