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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 sequences or Fourier transformation of the output signal. The spectra of the nuclear magnetic resonance in a rotating coordinate system are obtained from the ¹⁹F nuclei in CaF₂ crystals, from the protons in water, and others. In CaF₂, 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 CaF₂, BaF₂, MgF₂, and CdF₂. 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; exceedingly 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). [4-5]

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 $2H_1 \cos \omega t$ perpendicular to it, with $\omega \approx \omega_0 \equiv \gamma H_0$ where γ is the nuclear gyromagnetic ratio. In a coordinate system (RCS) that rotates about the z axis with frequency ω , the spins are acted upon by a static effective magnetic field $H_e = (\Delta^2 + H_1^2)^{1/2}$, 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 $H_1 \gg H_L$, where H_L is the local magnetic field produced by the spin-spin interactions in the laboratory frame (l.s.), the quantization axis Z in the RCS is directed along H_e , i.e., it makes an angle θ with the z axis. [1] The effective spin Hamiltonian in this coordinate system is [4]

$$\mathcal{H} = -h\gamma I_z + \tilde{\mathcal{H}}_{dip}^0, \quad (1)$$

where I_z denotes the Z component of the total spin of the sample, while $\tilde{\mathcal{H}}_{dip}^0$ denotes the secular part of the nuclear dipole-dipole interactions in the RCS, and its value in first-order perturbation theory is

$$\tilde{\mathcal{H}}_{dip}^0 = 1/2 (3 \cos^2 \theta - 1) \sum_{i < j} B_{ij} (I_{zi} I_{zj} - 1/3 I_i \cdot I_j), \quad (2)$$

with

$$B_{ij} = \frac{3\gamma^2 \hbar^2}{2r_{ij}^3} (1 - 3 \cos^2 \theta_{ij}),$$

r_{ij} is the radius vector joining the spins I_i and I_j ; θ_{ij} is the angle between r_{ij} and H_0 .

The Hamiltonian (1) is analogous to the ordinary spin

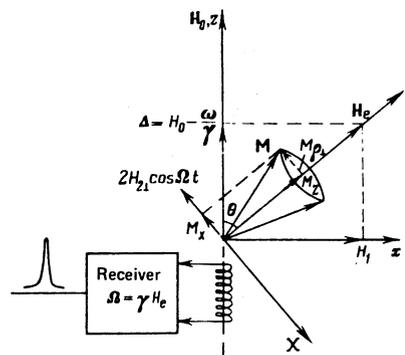


FIG. 1. Geometry of magnetic fields and principle of direct observation of NMR in a rotating coordinate system.

Hamiltonian in the l.s., except that H_0 is replaced by H_e and the secular part \mathcal{H}_d^0 of the dipole interactions in the l.s. is replaced by $\mathcal{H}_{d\rho}^0$. Consequently, at the frequency $\Omega_0 = \gamma H_e$ of the Larmor precession of the spins in the field H_e it is possible in principle to have NMR in the RCS, just as "ordinary" NMR at the frequency ω_0 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_e attained in practice (~100 Oe) are lower than H_0 by two or three orders of magnitude, so that the frequency Ω_0 does not exceed several hundred kilohertz (whereas usually $\omega_0 \sim 10 - 100$ MHz).

2) As seen from (2), at the so-called "magic angle" $\theta = \theta_M = \cos^{-1}(1/\sqrt{3})$, the term $\mathcal{H}_{d\rho}^0$ vanishes, so that the NMR line width in the RCS can be much smaller than in the l.s. [4-6]

So far, NMR in the RCS was observed only by indirect methods, in which the signal was registered at the high frequency ω_0 , and the NMR effect manifested itself in the RCS only as one change or another in this signal (the method of nonstationary nutations [7] the method of rotational saturation [4, 8]). It is curious that in Redfield's fundamental paper [4] the opinion is advanced that direct observation of NMR in the RCS at the frequency Ω_0 is not 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 $M_{\rho\perp}$ perpendicular to the field H_e , see Fig. 1. Since, however, the direction of H_e is not constant relative to the measuring instrument (i.e., in the l.s.) but precesses about the z axis with a frequency ω , direct registration of NMR in the RCS calls for the use not of the entire value of $M_{\rho\perp}$, but only its projection $M_z(t) = M_{\rho\perp} \sin\theta \exp(i\Omega_0 t)$ on the immobile axis z . This magnetization component, which oscillates at the frequency Ω_0 , can be measured with the aid of a receiving induction coil oriented along z and connected to a receiver operating at the frequency Ω_0 .

Thus, the proposed method differs from the usual one also in that it measures the longitudinal rather than the transverse (relative to H_0) 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_0 , the decrease of the sensitivity compared with the ordinary NMR (owing to the decrease of the frequency by a factor ω_0/Ω_0) can be compensated for to 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 $H_X(t) = 2H_{2\perp} \cos\Omega t$ perpendicular to the Z axis (see Fig. 1), with frequency $\Omega \approx \Omega_0$, and pass smoothly through the resonance region by varying one of the parameters (H_0 , ω , H_1 , or Ω), which affect the satisfaction of the resonance condition

$$\Omega = \gamma H_e. \quad (3)$$

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

To produce the field $H_X(t)$ we can apply an additional alternating field of frequency Ω along the z axis (for example, by applying a suitable voltage on the receiving coil, thus obtaining the well known "Q-meter" system (see, e.g., [11, 12]). It is more convenient, however, to use shallow modulation of the frequency ω or of the amplitude H_1 of the high-frequency field at a frequency Ω , 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 $2H_{2\perp} = (\delta\omega \sin\theta)/\gamma$, in the latter $2H_{2\perp} = \delta H_1 \cos\theta$, where $\delta\omega$ and δH_1 are the depths of the corresponding modulation). In this case no additional voltage of frequency Ω 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 $H_z(t) = H_{2\parallel} \cos\Omega t$ parallel to H_e . As shown theoretically in [13], this component can lead to the appearance of multiple and parametric resonances but under our conditions ($H_e \gg H_{2\perp}$, $H_{2\parallel}$) 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 $H_1 = \text{const} \gg H_1$), or else by adiabatically tuning on H_1 (at $\Delta = \text{const} \gg H_1$). In this case almost the entire equilibrium magnetization M_0 stored in the field H_0 is established along H_e [3, 5] and the smooth variation of Δ or H_1 can be simultaneously used for the passage through the NMR line in the RCS. On the other hand, if the field H_e is turned on abruptly, the Z component of the magnetization (M_z) amounts to only $M_0 \cos\theta$, and to pass through resonance in the RCS it becomes necessary to sweep the frequency Ω or Δ . 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 $T_{1\rho}$ and T_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-notation 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 CdF_2 powders, and also on the nuclei ^1H in water at $H_0 = 3500$ Oe, $\omega/2\pi = 14\text{MHz}$, and temperatures $T_0 = 293$, 78 , and 4.2°K . In all the experiments except those described in Sec. 4, the condition $H_1 \gg H_L$ 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 Ω and ω , and their Q values at room temperature were 10 and 100, the receiving coil having 1500 turns. The inhomogeneity of the field H_1 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 $H_{2\perp}$ in the RCS was produced by frequency or amplitude modulation of the high-frequency field $2H_1 \cos \omega t$ with frequency Ω fixed. The receiver (a resonant amplifier tuned to the frequency Ω) was connected to the receiving coil through a low-pass filter that blocked the exciting signal of frequency ω and passed the useful signal of frequency Ω . The absorption and dispersion signals $v_\rho(\Omega)$ and $u_\rho(\Omega)$, 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 Ω . Their time constant was 3–5 msec.

The exciting field $2H_1 \cos \omega t$ was turned on after the sample magnetization reached its equilibrium value M_0 in the field H_0 , and at that instant the absolute magnitude of the detuning exceeded the value

$$\Delta_0 = [(\Omega/\gamma)^2 - H_1^2]^{1/2},$$

corresponding to the condition (3) for resonance in the RCS. This was immediately followed by the start of 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 ($T_1^{-1}, T_2^{-1} \ll H_1^{-1} dH_0/dt \ll \gamma H_1$),^[5] thus ensuring a sufficiently high magnetization directed along H_e . 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_e but also in the angle θ . Therefore to observe NMR in RCS under conditions of the magic angle the values of H_1 and Ω were chosen beforehand such that the conditions $\Delta = \Delta_0$ and $\theta = \theta_M$ were realized during the sweep simultaneously. It is easily seen that this is attained at $3H_1^2 = 2\Omega^2/\gamma^2$, i.e.,

for example, for the nuclei ^{19}F ($\gamma/2\pi = 4007\text{Hz/Oe}$) and $\Omega/2\pi = 100$ we chose $H_1 = 20.38$ Oe. The ultimate fine setting of H_1 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_e varies in the general case nonlinearly. In a small vicinity of a certain value of θ , however, the increments dH_e and dH_0 can be regarded as proportional, so that if H_1 is constant then $|dH_e| = dH_0 |\cos \theta|$. This was taken into consideration in the calibration of the sweep, which is given throughout, unless otherwise stipulated, in units of H_e .

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION³⁾

A. Absorption and dispersion signals

Fig. 2 shows oscillograms of the absorption and dispersion signals v_ρ and u_ρ , obtained in the RCS with a CaF_2 crystal at $H_0 \parallel [111]$, $T_0 = 78^\circ\text{K}$ and at different amplitudes $H_{2\perp}$. All the signals were obtained at $\theta = \theta_M$.

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 $H_{2\perp}$ the signal v_ρ is symmetrical, and u_ρ is antisymmetrical. With increasing $H_{2\perp}$, 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,^[18, 3] when applied to the RCS at $\theta = \theta_M$,^[19] with Fig. 2a corresponding to the absence of saturation, Fig. 2b to intermediate saturation, and Fig. 2c to strong saturation of the NMR in the RCS.

This conclusion is confirmed by examination of Fig. 3,

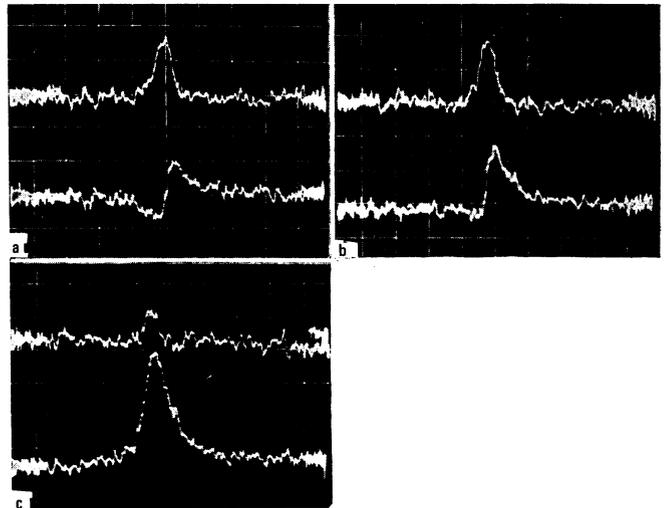


FIG. 2. Oscillograms of NMR in RCS at the frequency $\Omega/2\pi = 100$ kHz from ^{19}F nuclei in a CaF_2 crystal under conditions of the magic angle (top—absorption, bottom—dispersion) at amplitudes of the recording field $H_{2\perp}$: a—3.8 mOe, b—6.0 mOe, c—12.0 mOe. One horizontal division is equal to 0.16 Oe.

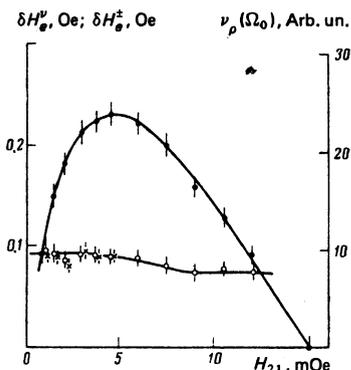


FIG. 3. Width δH_e^v of absorption signal (light points), width δH_e^z of dispersion signal (crosses) at amplitude $\nu_\rho(\Omega_0)$ of absorption signal (dark points) of NMR in the RCS for the ^{19}F nuclei in CaF_2 at $\theta = \theta_M$ as a function of the amplitude $H_{2\perp}$ of the recording field.

which shows the values of the width δH_e^v of the absorption line of NMR in the RCS at half height, its amplitude $\nu_\rho(\Omega_0)$, and also the widths of the antisymmetrical dispersion signal between its positive and negative maxima (δH_e^z) as functions of the field amplitude $H_{2\perp}$. It is seen that in the region of the intermediate saturation ($4\text{mOe} \lesssim H_{2\perp} \lesssim 10\text{mOe}$) the quantity $\nu_\rho(\Omega_0)$ passes through a maximum, and δH_e^v decreases somewhat, in full agreement with Provotorov's theory.^[18]

The strong-saturation region, judging from Figs. 2 and 3, corresponds to values $H_{2\perp} \gtrsim 10\text{mOe}$. This is confirmed also by a numerical estimate of the saturation factor

$$s_\rho = 1/2 \gamma^2 H_{2\perp}^2 g_\rho(\Omega_0) t_{\text{pass}},$$

where $g_\rho(\Omega)$ is the form factor of the NMR line in the RCS, and t_{pass} is the line passage time. In our case $t \approx 20\text{msec}$, so that $s_\rho > 1$ at $H_{2\perp} > 9\text{mOe}$.

In the region of strong saturation, the dispersion signal is symmetrical (Fig. 2c) and it can be characterized by a width δH_e^u at half-height. The dependence of δH_e^u on $H_{2\perp}$ is shown in Fig. 4 together with the data obtained for protons of water at $T_0 = 293^\circ\text{K}$ on a sample of the same volume as the CaF_2 crystal. The results shown in this figure correspond in fact to the regime of adiabatic fast passage through resonance in the RCS (the isolation from the lattice during the time t_{pass} is confirmed, in particular, by the symmetrical shape of the u_ρ signal). In such a passage, the magnetization M follows the direction of the new effective field

$$H_e' = [(H_e - \Omega/\gamma)^2 + H_{2\perp}^2]^{1/2},$$

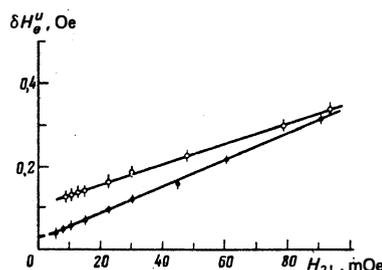


FIG. 4. Width δH_e^u of dispersion signal in adiabatic fast passage through the NMR in the RCS at $\theta = \theta_M$, as a function of the amplitude $H_{2\perp}$ of the recording field: light points— ^{19}F nuclei in CaF_2 , dark points—protons of water.

which acts in a doubly rotating coordinate system—DRCS (the second rotation is around H_e with frequency Ω), and after the passage of the resonance it turns out to be rotated 180° relative to H_e (compare with the analogous passage in the l.s.^[3,5]).

From the conservation of the entropy in the DRCS (at $H_{2\perp} \approx H_{L\rho}$ where H_L is the local

$$\frac{1}{T_e'} [(H_e')^2 + H_{L\rho}^2]^{1/2} = \text{const},$$

where T_e' is the single spin temperature in the DRCS. From this we can obtain for the dispersion signal at the frequency

$$u_\rho = \text{const} \cdot \frac{M_0 H_1}{H_e} \frac{H_{2\perp}}{[(H_e')^2 + H_{L\rho}^2]^{1/2}},$$

and for the width of the signal u_ρ at half height, as measured by us,

$$\delta H_e^u = 2[(3H_{2\perp}^2 + H_{L\rho}^2)]^{1/2} \quad (4)$$

(at $\delta H_e^u \ll H_e$, which is satisfied in our case).

The dependence of δH_e^u on $H_{2\perp}$, which follows from (4), agrees satisfactorily with Fig. 4 and makes it possible to obtain the value of $H_{L\rho}$ at $\theta = \theta_M$, a value which will be discussed in the next section. We note that in the case of strong saturation, but when still $H_{2\perp} \ll H_{L\rho}$, we have according to^[18,19] $\delta H_e^v = 2H_{L\rho}$, i.e., the ratio $\delta H_e^u / \delta H_e^v = \sqrt{3}$, 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 $\theta = \theta_M$ agrees with the temperature theory developed for ordinary NMR,^[4,18,3] and registration of u_ρ under conditions of adiabatic fast passage in RCS makes it possible to determine $H_{L\rho}$ directly.

TABLE I. Parameters of NMR line of ^{19}F in CaF_2 in the laboratory frame and in a rotating coordinate frame at the magic angle.

| Crystal orientation in field H_0 | Laboratory frame | | | Rotating coordinate system*, $\theta = \theta_M$ | | | | |
|------------------------------------|---------------------------------|----------------------------------------|--------------------------------|--------------------------------------------------|------------------------|--------------------------------|----------------------------------|--------------------------|
| | $\delta H_e, \text{Oe}$ [21] | $\sqrt{M_{2\perp}}, \text{Oe}$ [22] | $H_{L\rho}, \text{Oe}$ [22] | Experiment | | Theory | | |
| | | | | $(\delta H_e^u)_0, \text{Oe}$ | $H_{L\rho}, \text{Oe}$ | $\delta H_e^v, \text{Oe}^{**}$ | $\sqrt{M_{2\perp}^0}, \text{Oe}$ | $H_{L\rho}^0, \text{Oe}$ |
| [100] | 9.24 | 3.60 | 2.08 | 0.34 ± 0.02 | 0.099 ± 0.004 | — | 0.210 | 0.107 |
| [110] | 5.38 | 2.19 | 1.26 | 0.18 ± 0.02 | 0.053 ± 0.004 | — | 0.078 | 0.040 |
| [111] | 3.80 | 1.51 | 0.87 | 0.11 ± 0.02 | 0.031 ± 0.004 | 0.092 ± 0.007 | 0.041 | 0.029 |

*Present work.

**For unsaturated signal.

B. Suppression of nuclear dipole-dipole interactions

As already noted, at $\theta = \theta_M$ one should expect a strong narrowing of the NMR in the RCS.^[4-6] This is confirmed by the experimental dependence of the NMR line width in the RCS on the amplitude H_1 (at $\Omega_0 = \text{const}$), obtained at three orientations of the CaF_2 crystal relative to H_0 (Fig. 5). It is seen that the minimal value of δH_e^u is indeed reached at $\theta = \theta_M$. 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 δH_e^u the part of the line width which is independent of $H_{2\perp}$:

$$(\delta H_e^u)_0 = [(\delta H_e^u)^2 - 12H_{2\perp}^2]^{1/2}, \quad (5)$$

as well as to find $H_{L\rho} = (\delta H_e^u)_0 / 2\sqrt{3}$. It turns out that at $\theta = \theta_M$ the values of $(\delta H_e^u)_0$ and $H_{L\rho}$ depend strongly on the crystal orientation, and a distinct correlation with the orientation dependence of the width δH of the NMR line in the l.s. is observed (see the table). This indicates that even at $\theta = \theta_M$ 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.^[6]

Eliminating from the Hamiltonian the terms that lead in the indicated approximation to a small shift $M_{1\rho}$ of the resonant frequency, it is possible to use the known prescription^[6, 19] to calculate the local field $H_{L\rho}^0$ and the second moment $M_{2\rho}^0$ of the unsaturated NMR line in the RCS relative to its center at $\theta = \theta_M$. The calculation yields

$$(H_{L\rho}^0)^2 = \frac{1}{\hbar^4 \gamma^4 H_e^2 N} \left[\frac{I(I+1)^2}{729} \left(\frac{17}{4} \sum_{i \neq j \neq k} B_{ij}^2 B_{ik}^2 + 4 \sum_{i \neq j \neq k} B_{ij} B_{ik} B_{jk}^2 \right) + \frac{I(I+1)(2I-1)(2I+3)}{720} \sum_{i \neq j} B_{ij}^4 \right], \quad (6)$$

$$M_{2\rho}^0 = \frac{1}{\hbar^4 \gamma^4 H_e^2 N} \left[\frac{I(I+1)^2}{486} \left(11 \sum_{i \neq j \neq k} B_{ij}^2 B_{ik}^2 + 19 \sum_{i \neq j \neq k} B_{ij} B_{ik} B_{jk}^2 \right) + \frac{5}{1296} I(I+1)(2I-1)(2I+3) \sum_{i \neq j} B_{ij}^4 \right], \quad (7)$$

where N is the number of nuclei in the sample.

For a primitive cubic lattice and $I = \frac{1}{2}$ (for example, for the nuclei ^{19}F in CaF_2) the values of $H_{L\rho}^0$ and $M_{2\rho}^0$

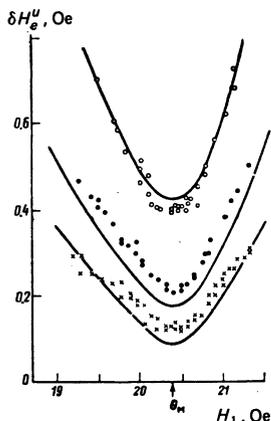


FIG. 5. Width δH_e^u of NMR signal in RCS for ^{19}F nuclei in CaF_2 crystal as a function of the amplitude H_1 for the high-frequency field at $\Omega_0 = \text{const} = 2\pi \cdot 100$ kHz near the magic angle (indicated by the arrow), for different orientations of the crystal: light points— $H_0 \parallel [100]$, $H_{2\perp} = 60$ mOe; dark points— $H_0 \parallel [110]$, $H_{2\perp} = 30$ mOe; crosses— $H_0 \parallel [111]$, $H_{2\perp} = 15$ mOe, curves—theory.

can be set in correspondence with the second moment of the NMR in the l.s.,

$$M_2 = \frac{I(I+1)}{3\hbar^2 \gamma^2 N} \sum_{i \neq j} B_{ij}^2.$$

Thus, for the orientations $H_0 \parallel [100]$, $[110]$ and $[111]$ we obtain, respectively^[4]

$$H_{L\rho}^0/M_2 = 0.207/H_e; 0.222/H_e; 0.230/H_e; \\ \sqrt{M_{2\rho}^0}/M_2 = 0.407/H_e; 0.442/H_e; 0.454/H_e.$$

We note also that at any orientation we have $M_{1\rho} = M_2/6H_e$.^[6] The numerical values of $H_{L\rho}^0$ and $M_{2\rho}^0$ are given in the table (in the column "Theory") for $H_e = 25$ Oe.

To compare these data with experiment we have used for $H_{L\rho}^0$ formula (6) and for δH_e^u formula (4), in which we substitute the theoretical value

$$H_{L\rho}^2 = 1/4 (3 \cos^2 \theta - 1)^2 H_L^2 + (H_{L\rho}^0)^2, \quad (8)$$

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 $[110]$ 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 δH_e^u in water (as $H_{2\perp} \rightarrow 0$), this broadening amounts to approximately 0.035 Oe.

If we exclude this inhomogeneous part from the value of δH_e^u observed in the absence of saturation at $H_0 \parallel [111]$ (see the table), then the remainder $(\delta H_e^u)_0$ ranges from 0.06 ± 0.01 to 0.08 ± 0.01 Oe (depending on the assumption made concerning the line shape). The ratio $(\delta H_e^u)_0 / 2\sqrt{M_{2\rho}^0}$ is at any rate not larger than 1.0 ± 0.1 , i.e., it is smaller than in the l.s., where at the same orientation we have $\delta H / 2\sqrt{M_2} = 1.26$. This indicates that the shapes of NMR lines are different in the l.s. and the RCS (at $\theta = \theta_M$).

We note that for unsaturated signals the ratio is $\delta H_e^u / \delta H_e^s \approx 1$ (Fig. 3). This ratio, however, is not very sensitive to the line shape and therefore cannot yield substantial information concerning this shape.^[23]

It is useful to note that for NMR in the RCS at $\theta = \theta_M$ there exists no universal relation between $M_{2\rho}^0$ and $H_{L\rho}^0$ (it is known^[3, 5] that in the l.s. $M_2 = 3H_L^2$ for dipole interactions). This means that a measurement of $H_{L\rho}^0$, 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 (δH_e^u at $H_0 \parallel [111]$, Fig. 3), amount to 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 $\theta = \theta_M$, as is well known, can be used to increase the resolution in NMR spectroscopy of solids and, in particular, to mea-

sure the chemical shift of the NMR frequency.

In the hitherto employed method^[2,3] 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 Ω_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 an oscillogram of the NMR spectrum of ^{19}F in the RCS at $\theta = \theta_M$, for CaF_2 and BaF_2 crystals placed simultaneously in the spectrometer pickup ($H_0 \parallel [111]$, $T_0 = 78^\circ\text{K}$). The horizontal scale is graduated here in terms of the mismatch Δ (i.e., the field H_0), which is related near $\theta = \theta_M$ to the scale of the field H_z like $1/\cos\theta_M = \sqrt{3}$ (see Sec. 2). Inasmuch as the z -component σ_{zz} of the chemical-shift tensor is decreased by a factor $1/\cos\theta$ on going to the RCS,^[1] 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.^[24] The relative chemical shift for the nuclei ^{19}F were also resolved in the crystals BaF_2 and CdF_2 powders.

We emphasize that the frequency $\omega_0 = 14$ MHz (and correspondingly the field $H_0 = 3.5$ kOe) used in these experiments is much lower than customary in typical measurements of chemical shifts. It is clear that the increase ω_0 and H_0 leads to an improvement of the resolution.

4. RESONANCE AND RELAXATION SIGNALS IN WEAK EFFECTIVE FIELDS

In the experiments described above, the ratio H_0/H_L reached 10–20. With decreasing H_1 , the suppression of the dipole-dipole interactions at $\theta = \theta_M$, in accordance with (5), becomes less effective (NMR oscillograms in the RCS are shown in Fig. 7 for $H_1 = 3$ Oe and $\Omega/2\pi = 14.7$ kHz), while at $H_1 \lesssim H_L$ the registered v_p and u_p signals lose their resonant character completely. Under these conditions, an essential role is assumed by the nonsecular part of the dipole interactions (in the

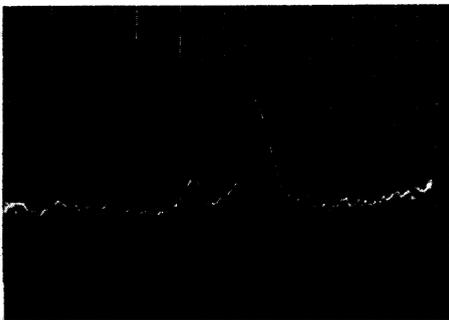


FIG. 6. Oscillogram of RCS spectrum of NMR of ^{19}F nuclei in the crystals CaF_2 (right-hand signal) and BaF_2 (left-hand signal) at $\theta = \theta_M$. One horizontal division is equal to 0.13 Oe in the scale of the sweep of the field H_0 .

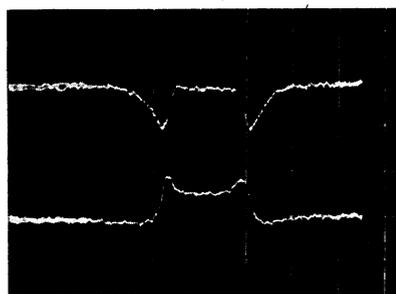


FIG. 7. Oscillograms of RCS NMR signals from the ^{19}F nuclei in CaF_2 at $\Omega/2\pi = 14.7$ kHz and $H_1 = 3.0$ Oe. Top—absorption, bottom—dispersion. The right-hand and left-hand signals correspond to $\Delta > 0$ and $\Delta < 0$ at $\theta = \theta_M$. One horizontal division is equal to 2.4 Oe.

RCS), which leads to energy exchange between the Zeeman (in the field H_0) and dipole-dipole pools and to establishment of a unified spin temperature T_S in the RCS.^[3,5] This process corresponds to a relaxation longitudinal magnetic susceptibility $\chi_{zz} = dM_z/dH_z$, so that now, besides the transverse component of the alternating field $H_x(t)$, the observed signals contain also contribution from the longitudinal component $H_z(t) = H_{2\parallel} \cos \Omega t$,

If the alternating fields $H_x(t)$ and $H_z(t)$ are produced by modulation of the detuning Δ at a frequency Ω , then the receiving coil oriented along the z axis will register signals proportional to

$$\chi_{zz}(\Omega) = \chi_{zz} \cos^2 \theta + \chi_{xx} \sin^2 \theta,$$

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

$$\chi_{xz}(\Omega) = \frac{dM_x}{dH_z} = \frac{dM_x}{dH_1} = (\chi_{zz} - \chi_{xx}) \sin \theta \cos \theta$$

(the x axis is directed along the field H_1 in the RCS, see Fig. 1). χ_{xz} can be measured amplitude-modulating the field H_1 at the frequency Ω .

The situation becomes much simpler at $H_1 \ll H_L$, when it can be assumed that $Z \parallel z$ and $\chi_{ZZ} = \chi_{zz}$. In this case, in analogy with the so-called adiabatic susceptibility measured in the l.s., in weak fields H_0 ,^[25] the quantity χ_{zz} is equal to^[26]

$$\chi_{zz} = \chi_{zz}' - i\chi_{zz}'' = \chi_0 \frac{T_0}{T_S} \frac{H_L^2}{(H_0^2 + H_L^2)} \frac{1}{(1 + i\Omega\tau_S)} \quad (9)$$

where χ_0 is the static nuclear magnetic susceptibility and τ_S is the time of establishment of a single temperature in the RCS and is determined by the relation (see, e.g.,^[3]):

$$\tau_S^{-1} = 1/2 (\gamma H_1)^2 g(\Delta) (1 + \Delta^2/H_L^2), \quad (10)$$

where $g(\Delta)$ is the foreign factor of the NMR line in the l.s.^[5]

It follows from (9) and (10) that the maximal signals

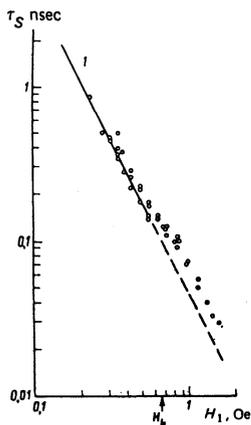


FIG. 8. Time τ_S of establishment of a single spin temperature in the RCS as a function of the amplitude H_1 of the high-frequency field (CaF_2 , $H_0 \parallel [111]$). The points were obtained from the experimental data in accordance with formula (11); 1—theory.

χ'_{zz} and χ''_{zz} will be observed at the frequencies $\Omega \approx \tau_S^{-1}$, corresponding to the acoustic band $10^3 - 10^{12}$ Hz. On the other hand, since the ratio $|T_0/T_S|$ can be easily increased to values $10^3 - 10^4$, the value of χ_{zz} can exceed χ_0 by two or three orders of magnitude.^[26]

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

$$\tau_S = \frac{1}{\Omega} \frac{\chi_{zz}''}{\chi_{zz}'}, \quad (11)$$

which was used by us for an experimental determination of the time τ_S in the crystal CaF_2 at 4.2°K, $H_0 \parallel [111]$, and $0.2 \lesssim H_1 \lesssim 2.0$ Oe, see Fig. 8.

In these experiments (see also^[16]), the frequency $\Omega/2\pi$ was only 1.16 kHz; the corresponding receiving coil had 6,000 turns and its Q was approximately 15, while the sample volume was 0.4 cm³. The absorption and dispersion signal at the frequency Ω were observed in adiabatic fast passage of the field H_0 through the NMR line in the l.s. and were bell-shaped with a maximum at $\Delta = 0$. The waveform of these signals (see^[10]) agreed satisfactorily with relations (9) and (10), with allowance for the variation of T_S in the adiabatic passage^[3, 5]:

$$T_S(\Delta) = \text{const} \cdot (H_e^2 + H_L^2)^{1/2}.$$

The data of Fig. 8 corresponds to $\Delta = 0$. It is seen that at $H_1 \lesssim 0.6$ Oe the experimental points agree well with the theoretical dependence (10), calculated with $z(0) = 70 \mu\text{sec}$;^[21, 22] it is interesting that the extrapolation of (10) into the region $H_1 \gtrsim H_L$, 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_0 or by signal accumulation.

In the quasistationary regime, direct observation of

the NMR signals in the RCS yields the NMR frequency spectrum in the field H_e 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_1 .

To increase further the resolving power we can use nonstationary methods. Thus, the free-induction and echo signals in the RCS at the frequency Ω_0 can be obtained by pulsed applications of the field $H_{2\perp}$ in accordance with a definite program, in analogy with the pulses of the field H_1 used in similar experiments in the l.s.^[28] It is thus possible, in particular, to exclude the influence of the inhomogeneity of the field H_1 .

Signals of the induction and echo type in RCS can be produced also by a jumpwise application of the field H_1 followed by variation of its phase in (or frequency); in this case we must have $H_{2\perp} = 0$.^[1, 28-30] Since the field H_1 can be turned on in such experiments continuously, such experiments are free also of the shortcomings 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.^[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.^[1]

The low sensitivity of the low-frequency receiver relative to turning the field $H_{2\perp}$ 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 Ω_0 , 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.^[5]). These moments, just as the quantity $H_{L\rho}^0$ measured in the quasistationary experiments (see Sec. 3B), can yield additional information on the structure of a solid.

New possibilities may be uncovered by registration of nonstationary nutations in the case of jumpwise applications of the field H_2 . Just as observation of nonstationary nutations in jumpwise application of the field H_1 has made it possible to study NMR in the RCS,^[7, 29] the proposed method makes it possible to investigate NMR and relaxation phenomena in an effective field H_e' 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 $T_{1\rho}$, the transverse-relaxation time $T_{2\rho}$ 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

particular, the possibility of rapid measurement (within the time of one experiment) of these relaxation times.

In conclusion, the authors thank M. I. Rodak for interest in the work and for a discussion of the results, and V. M. Buznik for supplying the BaF₂ and MgF₂ crystals for the investigations.

- ¹The abbreviation RCS will henceforth pertain throughout to this inclined rotating coordinate system.
- ²Magnetic resonance in RCS was observed also on electron spins in gases by an optical registration method.^[9,10]
- ³Preliminary results were reported at the Fifth All-Union School and Symposium on Magnetic Resonance,^[14] at the Second Specialized AMPERE Colloquium,^[15] and at the All-Union Conference on Magnetic-Resonance Problems (Donetsk, 1976), and reported also in^[16,17].
- ⁴In formula (74), given in^[6], for the second moment in the RCS, the coefficient preceding the term

$$\sum_{i \neq j \neq k} B_{ij}^2 B_{ik}^2$$

is incorrect. In addition, the ratio M_{2p}^0/M_{2p}^2 in Table I of that reference is half the correct value.

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