Direct observation of NMR in a rotating coordinate system and suppression of nuclear dipole interactions in a solid

A. E. Mefed and V. A. Atsarkin

Institute of Radioengineering and Electronics, USSR Academy of Sciences
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A report is present of the first direct observation of NMR spectra in a rotating coordinate system (RCS), by registering the longitudinal component of the nuclear magnetization at the frequency of the Larmor precession in the effective field. The method makes it possible to increase by simple means the resolving power of NMR in solids.

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It is known that a nuclear spin system placed in a constant magnetic field $\mathbf{H}_0 \| z$ and in a high-frequency field $2H_1 \cos\omega t$ perpendicular to it ($\omega \approx \omega_0 = \gamma H_0$, where γ is the nuclear gyromagnetic ratio), in a coordinate system rotating about $\mathbf{H}_0$ with frequency ω (RCS), is acted upon by a static effective magnetic field $H_e = \sqrt{\Delta^2 + H_1}$, where $\Delta = (\omega - \omega_0)/\gamma$, making an angle $\theta = \tan^{-1}(H_1/\Delta)$ with the z axis (Fig. 1). Nuclear magnetic resonance at the Larmor precession frequency $\Omega_0 = \gamma H_e \ll \omega_0$ is possible in this field, but up to now this phenomenon was assessed only from indirect data, namely from various changes of the "ordinary" NMR signals at the frequency ω. [1,2] In view of the exceptional importance of experiments in RCS in modern NMR spectroscopy, we have attempted to observe NMR directly in a RCS, at its natural (low) frequency Ω_0.

For a direct observation of NMR in a RCS it is necessary to register the component $\mathbf{M}_\perp^{RCS}$ of the nuclear magnetization $\mathbf{M}$ perpendicular to $\mathbf{H}_e$ and rotating about $\mathbf{H}_e$ with frequency Ω_0 (Fig. 1). This rotation gives rise to an alternating component of the magnetization along the immobile axis z, $M_z = \tilde{M}_\perp^{RCS} \sin\theta \times \exp(i\Omega_0 t)$, which we in fact recorded with the aid of a special receiver coil tuned to the frequency Ω_0 and directed along $\mathbf{H}_0$ (the exciting coil that produced the field H_1 was oriented in the usual manner).

NMR can be directly observed in RCS both by stationary methods and in transient regimes (induction, echo, etc.). In the former case it is necessary to produce an additonal magnetic field $2H_2 \cos\Omega t (\Omega \approx \Omega_0)$, perpendicular to $\mathbf{H}_e$

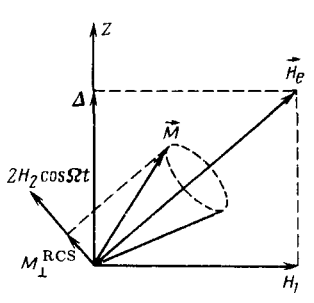

FIG. 1. Vector diagram of the magnetic field in a RCS.

(Fig. 1), and in the latter to use pulsed switching of the field H_2 or H_1 in accordance with the required program. We report below results of experiments of stationary type.

The experiments were performed on ^1H nuclei in water and ^{19}F nuclei in CaF_2 crystals and BaF_2 and CdF_2 powders at $H_0 \approx 3500$ Oe, $\omega/2\pi = 14$ MHz, $H_1 = 20.4$ Oe, $\Omega/2\pi = 100$ kHz, and temperatures 293 and 412 K. The condition $H_1 \gg H_L$, was satisfied in all cases, where H_L is the local magnetic field in the sample. The field $2H_2 \cos \Omega t$ was produced either by the receiving coil itself (in which case a Q meter was used to register the absorption and dispersion at the frequency Ω) or with the aid of frequency (or amplitude) modulation of the high-frequency field at a frequency Ω. In the second variant no voltage whatever is produced in the receiving system other than the NMR signal, and this variant is therefore preferable. The receiving coil had 1500 turns and $Q \approx 10$.

Passage through the resonance region in the RCS was by sweeping the field H_0 (i.e., by varying Δ) in the fast adiabatic passage regime. This made it possible to direct along $\mathbf{H}_e$ almost the entire equilibrium magnetization M_0 attained in the field $\mathbf{H}_0$, and by the same token obtain the maximum NMR and RCS signals. We note that in the same manner we can turn any of the quantities (ω, Ω, H_1) that affect that fulfillment of the resonance condition $\Omega = \gamma H_e$.

Several oscillograms of the NMR spectra in RCS, obtained by the method described above, are shown in Fig. 2. All correspond to the "magic" value of the angle $\theta = \theta_M = \arccos(1/\sqrt{3})$. It is known[2,3] that in this case the secular part of the nuclear dipole interactions in solids vanishes, and this explains the abrupt decrease of the line width for CaF_2 samples (a, c, d) in comparions with the "usual" value of approximately 20 kHz in the chosen orientation $\mathbf{H}_0 \parallel [111]$. This makes it possible, in particular, to resolve the structure produced in the NMR spectra by chemical shifts, as was done by us for a mixture of BaF_2 and CdF_2 powders.

The "residual" line width at $\theta = \theta_M$ (approximately 500 Hz) is due here to the inhomogeneity of the field H_1, as is clear from a comparions of the signals from CaF_2 (a, d) and water (b). The line width increases with increasing amplitude of

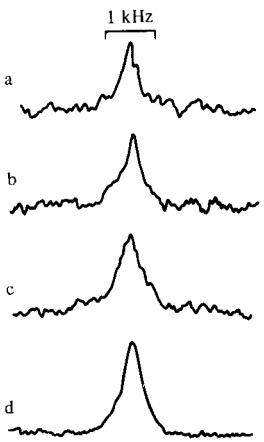

FIG. 2. Oscillograms of NMR signals in RCS: a—CaF_2, 293K, $H_2 = 0.015$ Oe; b—H_2O, 293K, $H_2 = 0.015$ Oe; c—CaF_2, $H_2 = 0.03$ Oe; d—CaF_2, 4.2K, $H_2 = 0.006$ Oe. Sample volume (a—c) 50 mm^3; (d) 10 mm^3. Oscillograms (c) and (d) are shown with the vertical scales reduced in a ratio 1 : 1.5 and 1 : 4, respectively.

H_2, and the NMR signal increases simultaneously (c). We note that NMR line shape in the RCS is close to Lorentzian.

The signals shown in Fig. 2 were obtained by single passage, with a detecting system having a time constant 5 msec. It is clear that signal accumulation via multiple passage through the resonance region, as well as an increase of M_0 by increasing the field H_0, will greatly increase the sensitivity of the method.

Let us list some possibilities uncovered by direct registration of NMR in a RCS.

1. It becomes possible to obtain NMR spectra of increased resolution and to measure chemical and other shifts of the NMR frequencies in solids without the use of Fourier transformation of the output signal and without complicated coherent pulsed apparatus (see[4]).

2. The registration of the signal at a low frequency Ω_0 can be used in conjunction with the known methods of pulsed NMR spectra.[4,5] This makes it possible, in particular, to avoid turning off the field H_1 when the signal is registered, and by the same token get rid of the restrictions imposed by finite intervals between the pulses.[4]

3. By using pulsed switching of the field H_2, it is possible to reproduce in the RCS (at the frequency Ω_0) various experiments of the spin-echo type. This results in new methods of measuring the relaxation time in the RCS and makes it possible to eliminate the influence of the inhomogeneity of the field H_1 on the resolution.

4. It becomes possible to study NMR and nuclear magnetic relaxation in a coordinate system with double rotation (the second rotation is about H_e with frequency Ω), thus adding to the information that can be obtained in NMR spectroscopy.

The described method of direct observation of NMR in RCS was described by us in[6]. Preliminary results were reported in[7].

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