Decay of the free precession of nuclear spins in a solid in a rotating coordinate system under magic-angle conditions; three-spin interactions

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Experiments show that the signal representing the decay of the free precession of nuclear spins of ^{19}F in a CaF_2 crystal decreases in a monotonic fashion, without oscillations, in a rotating coordinate system under magic-angle conditions. The decrease is thus fundamentally different from that in the laboratory coordinate system. When a deviation from the magic angle is introduced, oscillations appear in the precession-decay signal. These oscillations are distinctive in that the signal does not reach zero at the first few minima. These features of the free-precession decay are explained on the basis that the nuclear dipole–dipole interactions in the rotating coordinate system under magic-angle conditions are fundamentally different from those in the laboratory system. Theoretical predictions agree qualitatively with the experimental results.

The shape of the NMR line in a solid is one of the most fundamental problems in spin dynamics. It has been the subject of active research for many years now. So far, however, only the ordinary dipole–dipole interactions between nuclear spins, whose Hamiltonian is determined by binary elementary processes, has been taken into consideration. The secular part of this Hamiltonian, $\hat{\mathcal{H}}_d^0$, in a magnetic field $H_0 \| z$, i.e., in the laboratory coordinate system, is[1]

$$\hat{\mathcal{H}}_d^0 = \sum_{i \neq j} b_{ij}(2\hat{I}_{iz}\hat{I}_{jz} - \hat{I}_{ix}\hat{I}_{jx} - \hat{I}_{iy}\hat{I}_{jy}), \tag{1}$$

where $\hat{I}_{ip}$ are the p components of the operator of the ith nuclear spin, $\hat{I}_i$ $(p = x,y,z)$, and b_{ij} are the known dipole coefficients.[1] It was established a long time ago that in this case, for a simple rigid cubic lattice (the spins of ^{19}F in a CaF_2 crystal are a typical example of this case), the signal representing the decay of the free precession (FPD) is a damped curve with clearly defined oscillations. The corresponding NMR line, which is related to the FPD by a Fourier transformation, has a shape which is a cross between a Gaussian and a square.[1,2] Many serious studies have been carried out to

theoretically derive the FPD in CaF_2. The results of these studies are in more or less satisfactory agreement with experiment (Refs. 3 and 4, for example).

There are, on the other hand, situations in which more than two spins are involved in the elementary interaction event. For example, this is true when the main secular dipole–dipole interactions, (1), are completely suppressed by a strong rf field. This effect is utilized in advanced methods for artificially narrowing NMR lines in solids.[5] In particular, when a strong, cw rf field $2H_1 \cos \omega t$, with a detuning $\Delta = H_0 - \omega/\gamma$ from the exact resonance, is applied to a spin system, the secular part which remains in the Hamiltonian of the dipole–dipole interactions, and which determines the shape of the NMR lines in the rotating coordinate system in the effective field $H_e = (\Delta^2 + H_1^2)^{1/2}$, becomes[6,7]

$$\hat{\mathcal{H}}_{d\rho}^{*} = \frac{1}{2}(3\cos^2\theta - 1)\hat{\mathcal{H}}_{d\rho}^{0} + \hat{\mathcal{H}}_{d\rho}^{00}. \tag{2}$$

Here $\theta = \arccos(\Delta/H_e)$ is the angle between the z and Z axes; Z is parallel to $\vec{H}_e$; and $Z \| \vec{H}_e$; $\mathcal{H}_{dp}^{0}$ differs from (1) only in that the indices x, y, z are replaced by X, Y, Z. In addition, we have

$$\hat{\mathcal{H}}_{d\rho}^{00} = \sum_{i \neq j \neq k} \{\beta_{ijk} I_{iZ} I_{jZ} I_{kZ} + \alpha_{ijk} I_{kZ}(I_{iX} I_{jX} + I_{iY} I_{jY})\}. \tag{3}$$

Explicit expressions for the coefficients β_{ijk} and α_{ijk} can be found in Refs. 8 and 9. At the "magic" angle $\theta = \theta_M = \arccos(1/\sqrt{3}) = 54°44'$, the first term in (2) is zero, and the dynamics of the spin system is determined exclusively by "three-spin" interaction (3). In the present letter we report an experimental observation and an analysis of the FPD signal under these fundamentally new conditions.

The experiments were carried out on the nuclear spins of ^{19}F in a CaF_2 crystal at room temperature. We used a time-dependent version of the method of directly detecting the NMR in a rotating coordinate system. In this method, the FPD signal in the field H_e is detected at the frequency $\Omega_e = \gamma H_e$ with the help of an inductance coil oriented parallel to $\vec{H}_0$ (Refs. 7, 10, and 11). The experiments were carried out at $H_0 = 0.94$ T, $H_e = 2.5$ mT, and $\Omega_e/2\pi = 100$ kHz. We used amplitude detection of the signal. The variations in the field H_e over the volume of the sample (0.07 cm^3) were less than 0.15%. The decay of this field over the duration of the experiment (< 10 ms) was less than 0.1%. Experimental details on the excitation and detection of the FPD in the rotating coordinate system can be found in Refs. 10 and 11.

Figure 1a shows an FPD curve recorded at $\theta = \theta_M$ in the crystal orientation $[100] \| \vec{H}_0$. We see a monotonic decrease, without oscillations of any sort. This behavior is radically different from the ordinary FPD signals in the laboratory coordinate system.[1,2] The initial stage of the decrease (to the level $\simeq 50\%$) corresponds approximately to a Gaussian curve, while the tail of this decrease corresponds to a simple exponential function. The meaning here is that the shape of the NMR line in the frequency domain is nearly Lorentzian at its center and nearly Gaussian in its wings, in agreement with a preliminary qualitative conclusion.[7]

The other curves in Fig. 1 correspond to an increasing deviation from the magic angle. We see that progressively sharper oscillations arise, evidently because of an

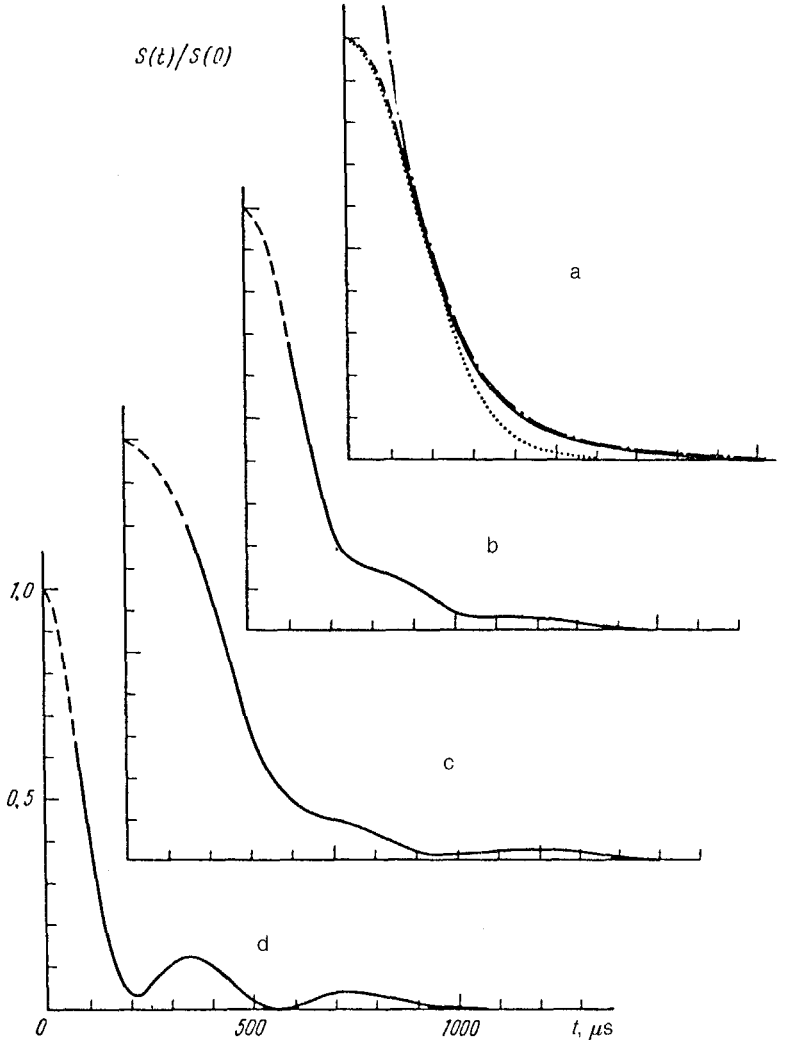

FIG. 1. Experimental signals representing the decay of the free precession in a rotating coordinate system, obtained from the nuclear spins of ^{19}F in a CaF_2 crystal at room temperature. a: $[100]||H_0$, $\theta = \theta_M = 54.73°$. Dotted line—Gaussian, $1.0 \cdot \exp\{-[t/(230\ \mu s)]^2\}$; dot-dashed line—exponential, $2.04 \cdot \exp[-t/(135\ \mu s)]$. b: $[100]||H_0$, $\theta \simeq 52.8°$. c: $[111]||H_0$, $\theta \simeq 52°$. d: $[110]||H_0$, $\theta \simeq 41.3°$. The dashed lines are the initial parts of the signals, reconstructed by eyeball.

increasing contribution of the "binary" Hamiltonian $\hat{\mathcal{H}}^0_{dp}$ in (2). We also see that the signal does not reach zero at the first few minima of the oscillations. The apparent reason is the contribution of the "three-spin" Hamiltonian $\hat{\mathcal{H}}^{00}_{dp}$.

Curves *a* ($[100]\|\vec{H}_0$, $\theta = \theta_M$) and *b* ($[111]\|\vec{H}_0$, $\theta \neq \theta_M$) in Fig. 1 decrease at about the same rate, but their shapes are qualitatively different. This behavior suggests

that the disappearance of the oscillations at $\theta = \theta_M$ is not due to variations in the field H_e.

In some similar experiments carried out on samples with an intense molecular motion (solid benzene[10] and a fluoroplastic), monotonic FPD curves (without oscillations) were observed at arbitary values of the angle θ.

Developing a theoretical interpretation of these results requires calculating the correlation function $M_{\rho\perp}(t)$ for the component of the nuclear magnetization of the sample which is transverse with respect to the field $\vec{H}_e$. This component is proportional to the FPD signal. However, it is essentially impossible to carry out an accurate direct calculation of $M_{\rho\perp}(t)$, so we will restrict the discussion here to an approximate analysis based on the memory-function method.[12] In that method, the function $M_{\rho\perp}(t)$ is determined by the equation

$$\frac{d}{dt}M_{\rho\perp}(t) = -\int_0^t G_\rho(t-t_1)M_{\rho\perp}(t_1)dt_1 + i\int_0^t R_\rho(t-t_1)M_{\rho\perp}(t_1)dt_1. \qquad (4)$$

The complexities which arise rule out a rigorous direct calculation of the memory function $G_\rho(t) - iR_\rho(t)$. However, we know[13] from the ordinary NMR in the laboratory coordinate system (at $\theta = 0$ in our case) that a qualitatively correct description of the FPD can be derived by taking the memory function to be a Gaussian or exponential function with characteristic parameter values determined by several lowest moments $M_{n\rho}(\theta)$ of the function $M_{\rho\perp}(t)$. We chose the two parts of the memory function to be

$$G_\rho(t) = M_{2\rho}(\theta)\exp\{-A(\theta)t\}; \quad R_\rho(t) = tM_{3\rho}(\theta)\exp\{-A(\theta)t\}, \qquad (5)$$

where $A(\theta) = 0.77[M_{2\rho}(\theta)]^{1/2}(\mu - 1)$, and $\mu \equiv M_{4\rho}(\theta)[M_{2\rho}(\theta)]^{-2}$. A rigorous expression for the second moment, $M_{2\rho}(\theta)$, is known from Ref. 9. We have derived expressions for the third moment $M_{3\rho}(\theta)$ and the fourth moment $M_{4\rho}(\theta)$ in the approximation of large-dimension lattices.[14] The curve of $|M_{\rho\perp}(t)|$, detected experimentally, was calculated for the orientation $[100]||\vec{H}_0$ of the CaF_2 crystal for angles θ of 54.73°, 45°, 25°, and 0°. The coefficient of 0.77 in the expression for $A(\theta)$ was determined for $\theta = 0$ by requiring that the oscillation damping times which we calculated be the same as those found in previous experiments on FPD in the laboratory coordinate system.[2] The calculated values of the parameters $M_{2\rho}(\theta)/4\pi^2$, $M_{3\rho}(\theta)/8\pi^3$, and $\mu(\theta)$ are, respectively, 0.71 kHz^2, 0.51 kHz^3, and 4.11 for $\theta = \theta_M$; 13.99 kHz^2, 37.15 kHz^3, and 2.98 for $\theta = 45°$; 111.89 kHz^2, 177.54 kHz^3, and 2.37 for $\theta = 25°$; and 208.09 kHz^2, 0.00 kHz^3, and 2.33 for $\theta = 0$.

Figure 2 shows the results of a numerical solution of (4) with memory functions (5). We see that these results agree with the experimental data in terms of the most important points. There are absolutely no oscillations in the FPD at the magic angle, and oscillations grow gradually as θ deviates from θ_M. The formal explanation for the disappearance of the oscillations at $\theta = \theta_M$ is that as θ approaches θ_M, the rate of decrease of the memory function increases sharply in comparison with the FPD, as is shown by the increase in the parameter μ from 2.33 at $\theta = 0$ to 4.11 at $\theta = \theta_M$.

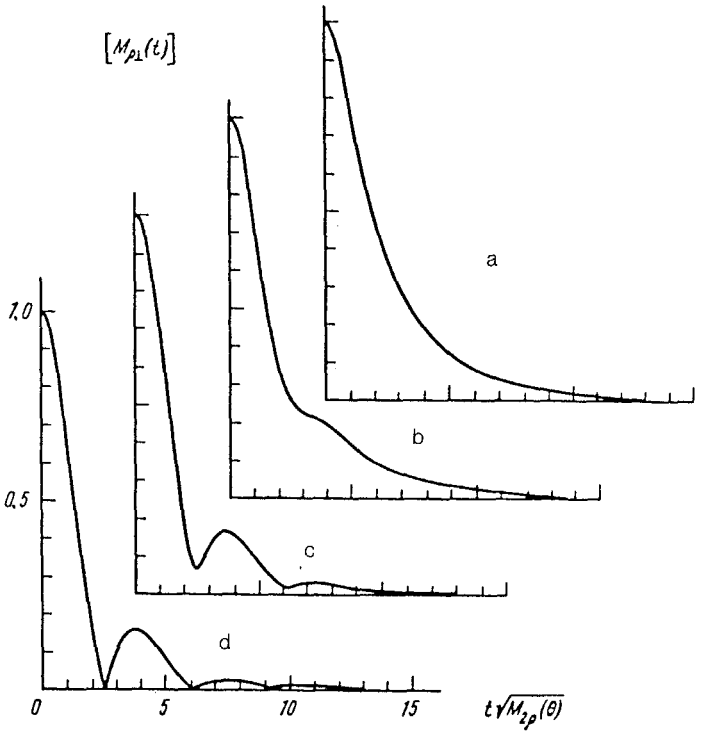

FIG. 2. Theoretical time evolution of the absolute value of the correlation function, $|M_{\rho\perp}(t)|$, calculated for the $[100]||H_0$ orientation of CaF_2 crystal. a—$\theta = 54.73°$; b—$\theta = 45°$; c—$\theta = 25°$; d—$\theta = 0°$.

Another feature is also reproduced in Fig. 2: The FPD signal does not reach zero at the minima of the oscillations. The explanation here is that the function $M_{\rho\perp}(t)$ has an imaginary part, which does not vanish at the same time as the real part. This result means in turn that the phase of the magnetization precession changes in the course of the FPD.[15]

While the theoretical results on the FPD agree qualitatively with the experimental data, they differ substantially from the latter in the quantitative sense. In particular, the FPD curve in Fig. 2a is damped more slowly than the curve in Fig. 1a by a factor of nearly 2. The derivation of a rigorous theory is a task for the future.

In summary, the signal representing the free-precession decay in the rotating coordinate system under magic-angle conditions has a shape qualitatively different from that of the corresponding signal in the laboratory coordinate system. This signal could be utilized to obtain independent information on the structure of a solid. Measurements of the moments of this signal, combined with the moments of the FPD signal in the laboratory system, can add substantially to the capabilities of the NMR method in structural studies of matter in the solid state. The FPD signal in the rotating coordinate system can also serve as an additional test for selecting successful

theoretical approaches to the problem of the NMR lineshape in solids.

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