Pulsed Fourier-Transform NQR of ^{14}N with a dc SQUID

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The zero-field free induction decay of solid ammonium perchlorate at 1.5 K has been directly detected with a dc superconducting quantum interference device. The Fourier-transform spectrum consists of three sharp lines at 17.4, 38.8, and 56.2 kHz arising from pure ^{14}N nuclear quadrupole resonance transitions. The absence of splittings and resonance transitions from dipolar-coupled proton spins is attributed to reorientation of the ammonium groups by quantum tunneling in combination with motional averaging in the three proton levels characterized by the irreducible representation T. The measured ^{14}N spin-spin relaxation time is 22 ± 2 ms and the spin-lattice relaxation time is 63 ± 6 ms.

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Although nuclear magnetic dipole-dipole and electric quadrupole interactions in nuclear magnetic resonance (NMR) can provide valuable information about interatomic distances and local electric field gradients in solids [1-3], the random orientations of molecules with respect to the applied field in polycrystalline or disordered materials give rise to a "powder pattern" in which structural information is often obscured. It is well known, however, that in the absence of an applied magnetic field (which imposes a preferred direction in space), for example, in nuclear quadrupole resonance (NQR) [4] or zero-field NMR [5], all crystallites or equivalent sites have the same resonance frequencies, allowing the possibility of sharp, "crystal-like" spectra. Unfortunately, in many instances, for example, zero-field NMR of pure nuclear spin dipole-dipole interactions or NQR with weak quadrupole couplings, the frequencies are low (below about 200 kHz) leading to weak signals and making it necessary to resort to magnetic field cycling [6] or synchronized sample spinning and radio-frequency pulse sequences in high field [7].

An alternative approach is to detect the low-frequency signal directly by means of a dc superconducting quantum interference device (SQUID) configured as a low noise amplifier [8] in either continuous-wave [9] or pulsed mode [10]. The direct detection of pulsed low-frequency NQR or zero-field NMR is particularly advantageous in that it can yield the full free induction signal in a single measurement, thereby increasing the speed of data acquisition and making it possible to implement coherent pulsed experiments such as spin echoes [11] and multidimensional spectroscopy [12]. In this Letter we report the first detection of pulsed zero-field and spin-echo NQR of ^{14}N in solid ammonium perchlorate; the Fourier-transform spectrum shows the lowest ^{14}N transition frequencies yet observed.

A schematic diagram of the spectrometer [10] is shown in Fig. 1. The sample is placed inside one half of the turns of the superconducting pickup loop L_p, wound in a gradient configuration. This coil is connected to an input coil L_i to form a superconducting flux transformer that couples the signal from the sample into the SQUID. Precessing magnetization of the sample is induced by magnetic rf pulses from the transmitter solenoid, which is wound coaxially around the sample and pickup coil. The SQUID, its input circuit, and the sample are all immersed in liquid ^{4}He. The dc SQUID is operated in a flux-locked mode with a flux modulation frequency of 500 kHz. During the application of the rf pulse, the feedback loop is opened; after the pulse is turned off the integrator is reset to zero before data acquisition begins [10]. It is important to note that, in contrast to standard high-field NMR, the input circuit is untuned. This has two advantages: First, the bandwidth of the spectrometer is not limited by the input circuit, but only by the bandwidth of the feedback electronics (200 kHz in our case). Second, at the measurement frequency the input circuit is lossless and does not produce Johnson noise. As a result, the noise of the spectrometer is determined by the SQUID

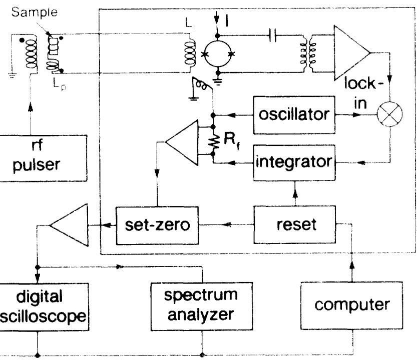

FIG. 1. Schematic circuit of a NQR Fourier-transform spectrometer based on a dc SQUID amplifier.

noise. The flux noise of the SQUID is typically $6\mu\Phi_0$ $\mathrm{Hz}^{-1/2}$ ($\Phi_0 = h/2e$ is the flux quantum) leading to an effective noise temperature [10] for the spectrometer of approximately 1 mK, 3 orders of magnitude below the bath temperature.

The SQUID-based spectrometer was used to study the zero-field resonance of ammonium perchlorate (NH_4ClO_4) at helium temperature. This molecular solid has been the subject of extensive investigations, including high-field NMR experiments on single crystals between room temperature and 150 K [13], because the ammonium ions have an unusually low barrier for reorientation; values as low as 2.5 kJ/mole have been quoted in the literature [14]. Neutron diffraction measurements [15] at temperatures between 10 and 298 K indicate an orthorhombic crystal structure with space group P_{nma}. The nitrogen and chlorine atoms lie on planes with mirror symmetry. The low reorientational barrier of the ammonium group leads to quantum tunneling of the four protons which removes the degeneracy of the librational ground state. The resulting tunneling splittings have been measured by inelastic neutron scattering by Prager and Press [16] and are between 45 MHz and 1.7 GHz. The spatial and spin wave function of each level can be characterized by one of the three irreducible representations of the tetrahedral group T, labeled A, E, or T. The total wave function of the proton must be antisymmetric under any interchange of two protons and therefore symmetric under any tetrahedral reorientation. This leads to a correlation between the symmetry of the spatial and spin parts of the proton wave function. The proton wave function with spatial symmetry A is associated with spin symmetry A and total proton spin $S=2$, the level with spatial symmetry E is associated with spin symmetry E and $S=0$, and the three levels with spatial symmetry T have spin symmetry T and $S=1$.

The sample consisted of 0.5 g of powdered reagent grade ammonium perchlorate in an open 8-mm-diam NMR tube. Figure 2(a) shows the zero-field signal excited by a two-pulse sequence at a temperature of 1.5 K. The pulses consisted of a single rf cycle each at 45 kHz, the first pulse with an amplitude of 3.8 mT followed 5 ms later by the second pulse with an amplitude of 6.5 mT. The signal, a sum of 16000 accumulations with a recycle rate of 3 Hz, shows a free induction decay after the second pulse and the formation of a spin echo after 5 ms. For the purpose of display, the signal was demodulated with a frequency of 35 kHz. Figure 2(b) shows the Fourier transform of an echo obtained with the same pulse parameters as in Fig. 2(a), except that the pulse spacing was reduced to 4 ms. The spectrum consists of three sharp peaks at 17.4, 38.8, and 56.2 kHz. Note that the frequencies of the lower two peaks add up to the highest frequency, indicating that we are exciting and observing simultaneously the three transitions of a three-level system. The peak at 10.6 kHz arises from a magnetoacoustic resonance of the input circuit.

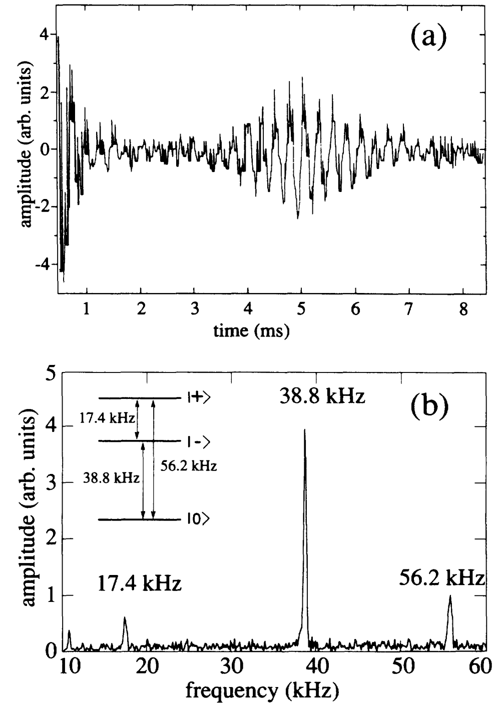

FIG. 2. (a) Free induction decay after second pulse and spin echo of NH_4ClO_4 at $T=1.5$ K. For the purpose of display, the real-time signal has been demodulated with 35 kHz. (b) Fourier transform of spin echo. The three resonant peaks are due to transitions between energy levels (shown inset) of ^{14}N nuclei in the presence of electric field gradient in NH_4ClO_4 (see text). In the inset, $|0\rangle = |10\rangle$ and $|\pm\rangle = (|11\rangle \pm |1-1\rangle)/\sqrt{2}$ where $|I,m\rangle$ is the eigenstate of the ^{14}N nucleus ($I=1$) with $I_z = m$.

Unlike high-field NMR, zero-field NMR is not isotope selective and it is instructive to identify the nuclei responsible for the signal. Likely candidates are the proton spins in a T manifold with $S=1$ or ^{14}N nuclei in a small electric field gradient. In a separate measurement, we recorded the amplitude of the free induction decay after the application of a soft rf pulse of known variable amplitude that excited only a single transition (at 38.8 kHz). As shown in Fig. 3, the measured signal amplitude A versus tipping angle θ could be well described by

$$A(\theta) = A_0(\cos\theta/\theta - \sin\theta/\theta^2), \tag{1}$$

where $\theta = \gamma B_1 \tau$; B_1 is the amplitude of the applied magnetic rf pulse, τ is the duration of the pulse, and $\gamma = (1.9 \pm 0.2)\times 10^7$ Hz/T is the fitted magnetogyric ratio. The experimental uncertainty in γ is due predominantly to the uncertainties in the calibration of B_1. Equation (1) describes the expected dependence of the free induction decay (FID) amplitude on the tipping angle for a spin-1 nucleus in an asymmetric field gradient after taking the powder average. The fitted value for γ

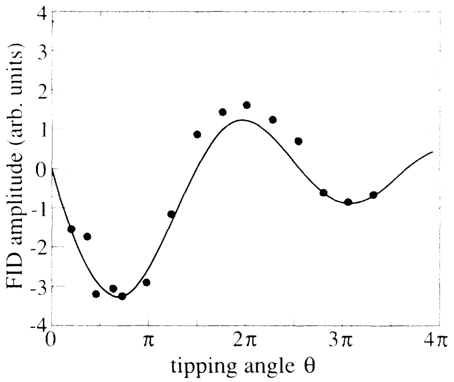

FIG. 3. FID amplitude vs tipping angle. Solid circles are experimental data, and solid line is a fit by Eq. (1).

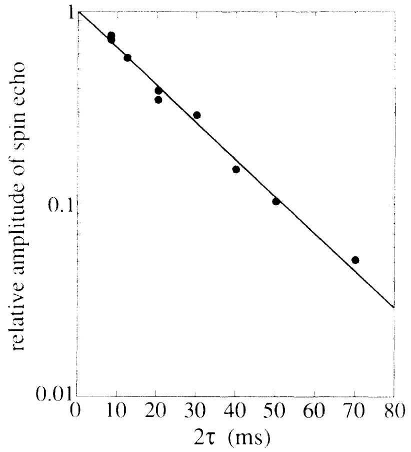

FIG. 4. Spin-echo amplitude vs 2τ for the transition at 38.8 kHz (τ is delay time between pulses). Solid circles are experimental data, and solid line is a fit by an exponential decay with $T_2=22$ ms.

coincides with the known value for ^{14}N ($\gamma=1.9325\times10^7$ Hz/T), and we extract a ^{14}N quadrupole coupling constant $|e^2qQ/h|=63.3$ kHz and an asymmetry parameter $\eta=0.550$. To our knowledge, the resonance at 17.4 kHz is the lowest directly detected ^{14}N NQR frequency. The line assignments were verified in two subsequent measurements. In a sample of NH_4ClO_4 enriched with ^{15}N, no signal was detected. We also performed a conventional pulsed high-field NMR measurement in a field of 5.75 T at a temperature of 4.2 K. The Fourier-transform powder pattern of the quadrupole echo showed the expected singularities at $\pm\frac{1}{2}(f_2-f_1)$, $\pm\frac{1}{2}(f_1+f_3)$, and $\pm\frac{1}{2}(f_2+f_3)$, where f_i ($i=1,2,3$) are the observed zero-field resonance frequencies. Of course, the determination of the parameters from the powder spectrum is considerably less certain than our conclusions from the sharp zero-field lines. Compared with single-crystal data at room temperature [13], our value for the quadrupole coupling constant at 1.5 K is 18% larger and that for the asymmetry parameter 4.3 times larger.

No proton zero-field NMR lines and no splittings of the ^{14}N NQR lines due to the protons were found. It is well known [17] that the dipole-dipole couplings between integer spins and nonresonant spins are quenched in first order. A group theoretical calculation [18] also shows that the dipolar interactions between the protons in states characterized by the irreducible representations A and E do not split the levels of the proton ground state and no zero-field proton resonance should be detected. For the T representation, however, a calculation of the expected proton resonance frequencies to first order using the overlap matrix elements from Ref. [16] and neglecting dipolar interactions with the nitrogen predicts nine lines at frequencies below 43 kHz. The absence of all these lines in the experimental results suggests a motional averaging by transitions between levels of the T manifold.

An unexpected result was the short spin-lattice relaxation time T_1 of the ^{14}N NQR lines. At 1.5 K, we measured $T_1=63\pm6$ ms for the central transition. The question arises whether this fast relaxation rate is caused by quadrupolar relaxation or is induced by dipolar interactions with the surrounding protons, inducing rapid transitions between the T levels. In the simplest theory, we model the proton interaction by fluctuating isotropic magnetic fields. In this case, we predict $T_2=2T_1=126\pm12$ ms for ^{14}N. As shown in Fig. 4, however, the relaxation time $T_2=22\pm2$ ms, as measured by the dependence of the spin echo amplitude on the time τ between pulses, is much shorter. Furthermore, with a magnetic dipolar relaxation process we expect that only the ^{14}N nuclei surrounded by protons in T states will be relaxed rapidly. To rule out this hypothesis, we compared the initial FID amplitude of NH_4ClO_4 with that of partially deuterated samples, keeping the recycle rate of 3 Hz constant. Deuteration changes the symmetry of the local environment and should strongly affect the fraction of ^{14}N nuclei that can be magnetically relaxed by the protons. However, within experimental uncertainty, we did not detect any dependence of the initial FID amplitude on deuteration. This indicates that the dominant ^{14}N relaxation at 1.5 K is caused by fluctuating electric field gradients and not by dipolar interactions with the protons.

In summary, we have described the direct detection of pulsed ^{14}N quadrupole resonance at a frequency as low as 17.4 kHz by means of a dc SQUID amplifier. The fact that the input circuit is broad band rather than tuned enabled us to excite and observe the three transitions of the three-level system simultaneously. Using spin echoes, we were able to make the first direct measurements of T_1 and T_2 in ^{14}N in a polycrystalline solid at a frequency below 1 MHz. The sensitivity, resolution, and broad bandwidth of the Fourier transform spectra, as well as the possibility of pulsed spin echo, relaxation, and multidimensional experiments, make the technique attractive for low-frequency NQR and NMR studies of a wide range of solids, particularly in the polycrystalline or amorphous state.

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