High-T_c SQUIDs for Low-Field NMR and MRI of Room Temperature Samples

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***Abstract*—We have constructed a high-T_c SQUID spectrometer to detect NMR signals from samples at room temperature in magnetic fields up to 3 mT. The multiloop SQUID magnetometer has a system noise of about 30 fT/Hz$^{1/2}$ at the relevant frequencies of 2 to 100 kHz. The magnetometer is operated in vacuum at 77 K, and is separated from the sample, which is less than 1.5 mm away, by a sapphire window. In a magnetic field of 2 mT we can detect the proton spin echo at 86 kHz without signal averaging. This sensitivity enables us to obtain one-dimensional images. In addition, we present data on hyperpolarized ^{129}Xe, which has an optically pumped polarization of several percent.**

I. Introduction

Low transition temperature (low-T_c) superconducting quantum interference devices (SQUIDs) have been used in numerous experiments to detect nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) signals [1-10]. This approach has been especially successful in giving information related to structural [1], [2] and dynamic aspects [3] of materials through interactions with nuclear spins at zero and low magnetic fields. The feasibility of magnetic resonance imaging (MRI) with low-T_c SQUIDs at low fields has also been demonstrated [4], [8]. In low field NMR (typically $\leq$ 10 mT) the spin precesses at correspondingly low frequencies, typically below 500 kHz, around the field direction. In conventional NMR experiments, in which a resonant circuit is used to detect the precessing magnetization, the induced voltage signal, V, is proportional to the spin magnetization, M, and its rate of change, ω. Since the magnetization is also proportional to the frequency, V scales as ω^2. As a result, it is difficult to detect NMR signals at low fields with a conventional Faraday detector. In contrast, SQUIDs can be used to measure the magnetic flux directly, resulting in a much higher signal-to-noise (S/N) ratio at low frequencies. However, the samples were maintained at room temperature in only a few cases [7-11]. At liquid helium temperatures, there is a limited number of materials with sufficiently short spin-lattice relaxation times to allow one to signal average in pulsed experiments. Moreover, to investigate biological samples one requires room temperature access, and a large sample space is highly desirable for MRI. Kumar et al. [11] were the first to use a high-T_c SQUID to obtain NMR spectra from room temperature samples. In this paper we describe a newly constructed high-T_c SQUID spectrometer that detects NMR signals from samples at room temperature in magnetic fields up to 3 mT.

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II. Experimental Configuration

A. SQUID

The SQUID is operated in a flux locked loop. A block diagram of the SQUID electronics is shown in Fig. 1. The preamplifier that detects the voltage across the SQUID consists of four parallel AD 797 (Analog Devices) amplifiers with a measured spectral white noise level of 0.65 nV/Hz$^{1/2}$. After the second stage, which has variable gain, the signal passes through a single-pole integrator. The integrated voltage is fed back to the SQUID as a magnetic flux via a single-turn feedback coil made from copper wire. After being amplified and filtered the feedback voltages are stored in a computer.

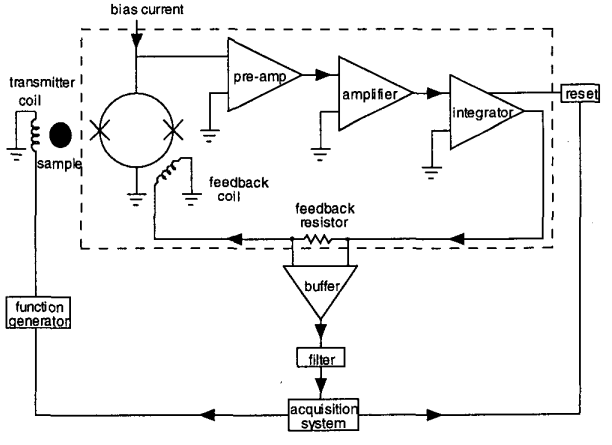

Fig. 1. Block diagram of the SQUID electronics. The dashed rectangle encloses the flux locked loop.

For the first tests we used a directly coupled magnetometer with a square washer pickup loop [12]. In the relevant frequency range the system magnetic flux noise was 56 $\mu\Phi_0/Hz^{1/2}$, where Φ_0 is the flux quantum, corresponding to a magnetic field noise of 390 $fT/Hz^{1/2}$.

In our recent measurements, we used a multiloop magnetometer [13] with a larger effective area (~1.8 mm^2). In this case, the system flux noise is 25 $\mu\Phi_0/Hz^{1/2}$, corresponding to a field noise of 30 $fT/Hz^{1/2}$. The bandwidth of the system with the multiloop magnetometer is 1.1 MHz.

The noise performance and bandwidth could be further improved with the use of additional positive feedback (APF) [14]. This would eliminiate the noise contribution from the preamplifier, reducing the system noise by about a factor two.

B. Dewar and NMR Coils

A simplified sketch of the dewar and coils is shown in Fig. 2. The SQUID magnetometer is operated in vacuum, separated from the sample, which is less than 1.5 mm away, by a sapphire window. Efficient cooling is provided by a 10 cm long sapphire rod, thermally anchored to the liquid nitrogen reservoir. The dewar is similar to that described in detail in [15].

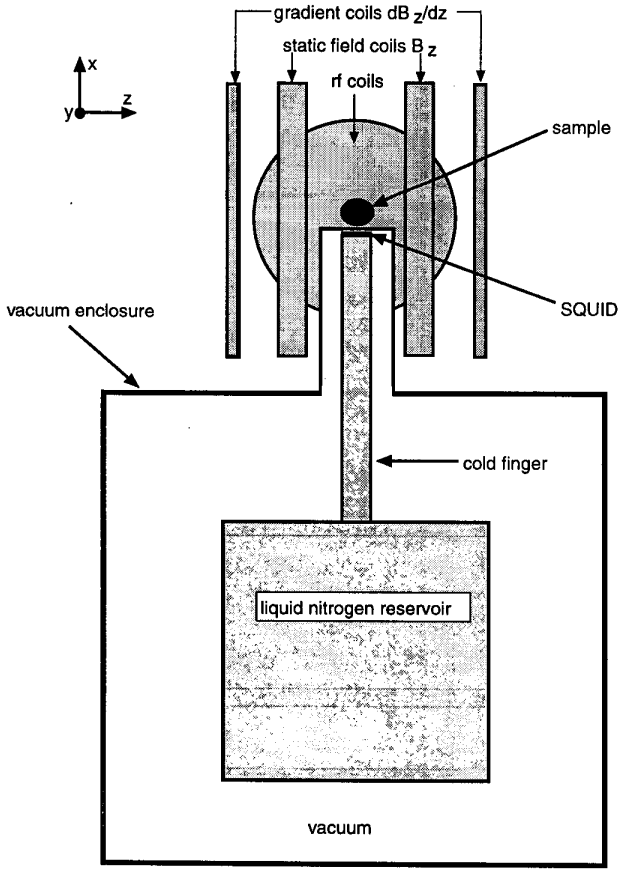

Fig. 2. Configuration of NMR system, including liquid nitrogen dewar, SQUID, and coils.

The static magnetic field B_z in the z-direction is produced by a Helmholtz pair of coils each with a diameter of 11.7 cm and 1,300 turns. The calculated field homogeneity in the center of the coils is better than 0.07 % (0.7 %) in a cubic volume of 1 cm^3 (8 cm^3). External fields are attenuated by a three-layer mumetal shield enclosing the whole apparatus. For the pulsed NMR experiments an alternating magnetic field B_y is applied in the y-direction by the transmitter coils, in this case, a Helmholtz pair perpendicular to the static field coils. Each transmitter coil has a diameter of 8.6 cm and 20 turns. The calculated field homogeneity in the center of these coils is better than 0.12 % (1.2 %) in a cubic volume of 1 cm^3 (8 cm^3). For our one-dimensional imaging experiments an additional gradient field dB_z/dz was applied by a Maxwell pair of coils parallel to the static field coils. Each coil has a diameter of 12.2 cm and 50 turns. The linearity of the field gradient is better than 0.3 % (1.0 %) in a cubic volume of 1 cm^3 (8 cm^3) around the center. All three coils were wound from insulated copper wire and mounted on a common frame made from G-10 fiberglass and plexiglass. To avoid accoustic resonances in the coils, this frame was designed to be extremely rigid.

C. Spectrometer

The pulsed NMR experiments are computer controlled. We describe a typical sequence for a proton spin echo experiment in a field of 2.03 mT. In order to prevent the integrator from being saturated, the feedback loop is switched off during the excitation pulses. The sequence starts with a 90° pulse generated by applying a 793 μs long 86.6 kHz signal to the transmitter coil. The amplitude is adjusted to produce a field of 14.8 μT. After a few milliseconds a 180° pulse with the same field amplitude and frequency but with double the pulse length is applied. Subsequently, because of ringing in the coils caused by the impedance mismatch between the coils and the signal generator, the system is paused for about 100 μs before the feedback loop is switched on. Data acquisition starts 10 μs later. To allow the spins to relax completely, the repetition rate is low, 2.5 Hz. The experiment is performed in an electromagnetically screened room.

III. Experimental Results

For our first test we used samples with either a high density of protons or an optically enhanced polarization (^{129}Xe). For the proton samples we chose mineral oil because of its relatively short spin-lattice relaxation time T_1 and relatively long spin-spin relaxation time T_2. This allows us to exploit the advantage of pulsed NMR experiments and to improve the S/N ratio by signal averaging. The ^{129}Xe was polarized far above its equilibrium value by means of optical pumping as described elsewhere [6], [18].

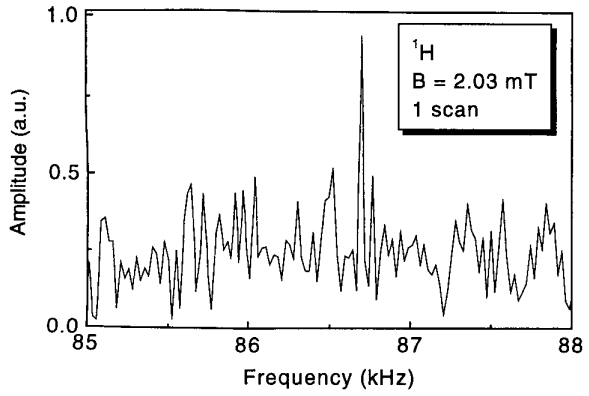

Fig. 3. Single shot proton NMR signal from mineral oil in a magnetic field of 2.03 mT.

A. Mineral Oil

Most of our experiments were performed in magnetic fields between 1 mT and 2 mT; depending on the nucleus the frequencies were between 10 kHz and 90 kHz. In a magnetic field of 2.03 mT we can detect the proton spin echo signal at 86.67 kHz without signal averaging. The corresponding spectrum after Fourier transformation is shown in Fig. 3.

In order to achieve a higher S/N ratio we averaged 1,000 times. The spin echo is shown in Fig. 4(a), and its Fourier transform in Fig. 4(b). The S/N ratio for this proton signal is 44.

In a field of 0.059 mT, which is comparable to the earth's magnetic field, we can resolve the proton spin echo produced by 1 ml of mineral oil at 2.5 kHz after 2,000 averages even though the equilibrium proton polarization is only 2×10^{-10}. The results obtained in this ultralow field will be published elsewhere [16].

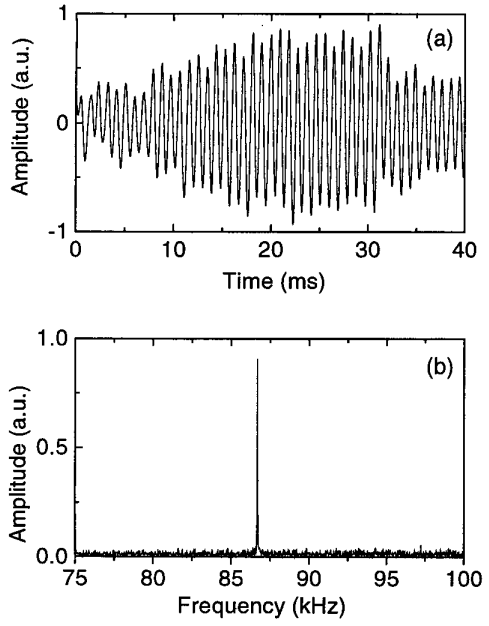

Fig. 4. Proton NMR signal from mineral oil in a magnetic field of 2.03 mT after 1,000 signal averages: (a) spin echo, after the real time signal has been demodulated with 85.6 kHz and filtered, (b) Fourier transform.

B. One-dimensional Imaging

The S/N ratio obtained in fields of 2 mT enables us to obtain one-dimensional images by detecting proton NMR signals. Our SQUID magnetometer does not enclose the sample, but acts as the surface coil used in conventional NMR [17]. The intensity of an NMR signal from a given part of the sample depends on its position with respect to the magnetometer. Thus, for images in one-dimension, besides frequency encoding we also have position encoding. To obtain the images we calculate the correction function

$$\Phi(z) = \int\int \phi(x, y, z)dxdy, \tag{1}$$

where $\phi(x,y,z)$ describes the contribution of an ensemble of dipoles, localized at the coordinates (x,y,z), to the total magnetic flux Φ_{tot} through the magnetometer. The center of the magnetometer defines the origin in space (0,0,0). In our case, on resonance and with the gradient $G = dB_z/dz$ along the direction of the static magnetic field B_z, the signal is given by

$$s(k) = \int\int\int \phi(x, y, z)\rho(x, y, z)\exp(i2\pi kz)dxdydz, \tag{2}$$

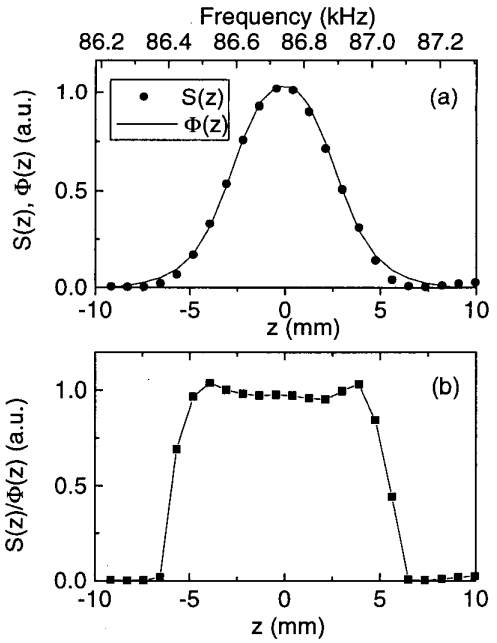

Fig. 5. One-dimensional image of a 11 mm wide container obtained by averaging 10,000 proton NMR signals from mineral oil in a magnetic field of 2.03 mT. (a) Spectrum S(z) and the calculated correction function $\Phi(z)$; the position z and frequency f are connected via $z=2\pi(f-f_{res})/\gamma G$, where f_{res} is the resonance frequency. (b) Corrected image (see text) with a solid line to guide the eye.

where $\rho(x,y,z)$ is the spin density and $k=\gamma Gt/2\pi$; γ is the gyromagnetic ratio. We measured s(k) from a sample consisting of 2.2 ml mineral oil in a rectangular phantom of 11 mm x 11 mm cross sectional area and 18 mm height. The static magnetic field gradient was about 1.32 mT/m. Figure 5(a) shows a plot of S(z), the Fourier transform of s(k), and a plot of the correction function $\Phi(z)$. Figure 5(b) shows a profile image obtained by dividing S(z) by $\Phi(z)$. We consider this correction reasonable for values of S(z) with S/N ratio greater than 2.

C. Hyperpolarized ^{129}Xe

In addition to protons in mineral oil we have also performed experiments on hyperpolarized ^{129}Xe, which has a pumped polarization of 2-3 %. Without optical pumping the equilibrium polarization in a field of 1.3 mT would be only 1.2×10^{-9} at room temperature. We have measured the free induction decay (FID) of ^{129}Xe with the directly coupled magnetometer after a single 90° pulse. The sample tube was 14 mm long and had an inner diameter of 5 mm. The spectrum, shown in Fig. 6, has a S/N ratio of 15 for the FID signal at 14.89 kHz. We plan to measure the NMR signal of hyperpolarized ^{129}Xe with the multiloop magnetometer. We expect the higher sensistivity and larger effective area to improve the S/N ratio by a factor 15 to a value greater than 200 without signal averaging.

IV. Concluding Remarks

We plan further experiments to obtain two-dimensional images of proton samples using the projection-reconstruction method [4]. We also plan to extend our experiments by using three-dimensional pulsed gradients for improved two-dimensional imaging. In the case of ^{129}Xe we will add a self-contained gas flow system to allow continous optical pumping. Finally, as noted earlier, we expect to improve the noise level of the magnetometer by a factor of 2 by using APF.

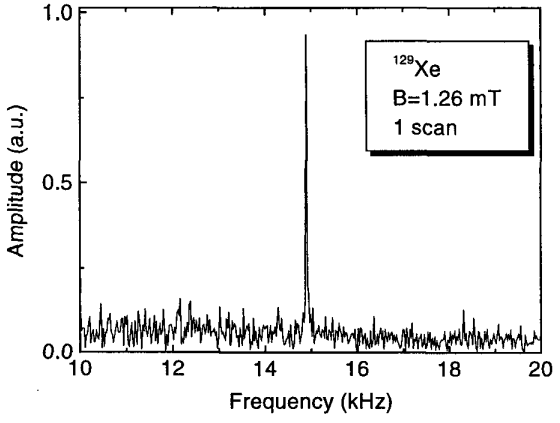

Fig. 6. Single-shot ^{129}Xe NMR signal from hyperpolarized gas in a magnetic field of 1.26 mT.

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References

[1] C. Hilbert, J. Clarke, T. Sleator, and E. Hahn, "Nuclear quadrupole resonance detected at 30 MHz with a dc superconducting quantum interference device", Appl. Phys. Lett., vol. 47, pp. 637-639, September 1985.

[2] N. Q. Fan and John Clarke, "Low-frequency nuclear magnetic resonance and nuclear quadrupole resonance spectrometer based on a dc superconducting quantum interference device", Rev. Sci. Instrum., vol. 62, pp. 1453-1459, June 1991.

[3] B. Black, G. Majer and A. Pines, "SQUID-NMR study of methyl quantum tunneling in a series of carboxylic acids", Chem. Phys. Lett., vol. 201, pp. 550-554, January 1993.

[4] M. P. Augustine, A. Wong-Foy, J. L. Yarger, M. Tomaselli, A. Pines, Dinh M. TonThat, and John Clarke, "Low field magnetic resonance images of polarized noble gases obtained with a dc superconducting quantum interference device", Appl. Phys. Lett., vol. 72, pp. 1908-1910, April 1998.

[5] Dinh M. TonThat and John Clarke, "Direct current superconducting quantum interference device spectrometer for pulsed nuclear magnetic resonance and nuclear quadrupole resonance at frequencies up to 5 MHz", Rev. Sci. Instrum., vol. 67, pp. 2890-2893, August 1996.

[6] Dinh M. TonThat, M. Ziegeweid, Y.-Q. Song, E. J. Munson, S. Appelt, A. Pines, and John Clarke, "SQUID detected NMR of laser-polarized xenon at 4.2 K and at frequencies down to 200 Hz", Chem. Phys. Lett., vol. 272, pp. 245-249, June 1997.

[7] H. C. Seton, D. M. Bussell, J. M. S. Hutchison, I. Nicholson, and D. J. Lurie, "DC SQUID-based NMR detection from room temperature samples", Phys. Med. Biol., vol. 37, 2133, 1992.

[8] H. C. Seton, J. M. S. Hutchison, and D. M. Bussell, "A Tuned SQUID Amplifier for MRI Based on a DOIT Flux Locked Loop", IEEE Trans. on Appl. Supercond., vol. 7, pp. 3213-3216, June 1997.

[9] S. Kumar, B. D. Thorson, and W. F. Avrin, "Broadband SQUID NMR with Room-Temperature Samples", J. Magn. Reson., Series B, vol. 107, pp. 252-259, 1995.

[10] S. Kumar, W. F. Avrin, and B.R. Whitecotton, "NMR of Room Temperature Samples with a Flux-Locked dc SQUID", IEEE Trans. Magnetics, vol. 32, pp. 5261-5264, November 1996.

[11] S. Kumar, R. Matthews, S. G. Haupt, D.K. Lathrop, M. Takigawa, J. R. Rozen, S. L. Brown, and R. H. Koch, "Nuclear magnetic resonance using a high temperature superconducting quantum interference device", Appl. Phys. Lett., vol. 70, pp.1037-1039, February 1997.

[12] E. Dantsker, "High Transition-Temperature SQUID Magnetometers and Practical Applications", PhD thesis, University of California, Berkeley, May 1997.

[13] F. Ludwig, E. Dantsker, R. Kleiner, D. Koelle, John Clarke, S. Knappe, D. Drung, H. Koch, Neil McN. Alford, and Tim W. Button, "Integrated high-T_c multiloop magnetometer", Appl. Phys. Lett., vol. 66, pp. 1418-1420, March 1995.

[14] D. Drung, E. Dantsker, F. Ludwig, H. Koch, R. Kleiner, John Clarke, S. Krey, D. Reimer, B. David, and O. Doessel, "Low noise $YBa_2Cu_3O_{7-x}$ SQUID magnetometers operated with additional positive feedback", Appl. Phys. Lett., vol. 68, pp. 1856-1858, March 1996.

[15] T. S. Lee, E. Dantsker, and John Clarke, "High-transition temperature superconducting quantum interference device microscope", Rev. Sci. Instrum., vol. 67, pp. 4208-4215, December 1996.

[16] K. Schlenga, R. E. de Souza, A. Wong-Foy, A. Pines, J. Clarke, unpublished.

[17] M. D. Harten, "Sample noise with circular surface coils", Med. Phys., vol. 14, 616, 1987.

[18] T.G. Walker and W. Happer, "Spin-exchange optical pumping of noble-gas nuclei", Rev. Mod. Phys., vol. 60, pp. 629-642, April 1997.