NUCLEAR MAGNETIC RESONANCE WITH DC SQUID PREAMPLIFIERS

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Abstract

Sensitive radio-frequency (rf) amplifiers based on dc Superconducting QUantum Interference Devices (SQUIDs) are available for frequencies up to 200 MHz. At 4.2 K, the gain and noise temperature of a typical tuned amplifier are 18.6 ± 0.5 dB and 1.7 ± 0.5 K at 93 MHz. These amplifiers are being applied to a series of novel experiments on nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR). The high sensitivity of these amplifiers was demonstrated in the observation of "nuclear spin noise", the emission of photons by ^{35}Cl nuclei in a state of zero polarization. In the more conventional experiments in which one applies a large rf pulse to the spins, a Q-spoiler, consisting of a series array of Josephson junctions, is used to reduce the Q of the input circuit to a very low value during the pulse. The Q-spoiler enables the circuit to recover quickly after the pulse, and has been used in an NQR experiment to achieve a sensitivity of about 2×10^{16} nuclear Bohr magnetons in a single free precession signal with a bandwidth of 10 kHz. In a third experiment, a sample containing ^{35}Cl nuclei was placed in a capacitor and the signal detected electrically using a tuned SQUID amplifier and Q-spoiler. In this way, the electrical polarization induced by the precessing Cl nuclear quadrupole moments was detected: this is the inverse of the Stark effect in NQR. Two experiments involving NMR have been carried out. In the first, the 30 MHz resonance in ^{119}Sn nuclei is detected with a tuned amplifier and Q-spoiler, and a single pulse resolution of 10^{18} nuclear Bohr magnetons in a bandwidth of 25 kHz has been achieved. For the second, a low frequency NMR system has been developed that uses an untuned input circuit coupled to the SQUID. The resonance in ^{195}Pt nuclei has been observed at 55 kHz in a field of 60 gauss.

Introduction

Superconducting QUantum Interference Devices (SQUIDs) have been used for two decades for the detection of magnetic resonance[1-11]. Most[2-11] of this work has involved SQUIDs as magnetometers in the audio frequency range, and has been restricted to the study of magnetic resonance at low frequency[10-12] or to changes in the static susceptibility of a sample induced by magnetic resonance at high frequencies[2-9]. However, the development of low noise radio-frequency (rf) amplifiers based on dc SQUIDs[13] enables one to detect the magnetic resonance directly at frequencies up to about 200 MHz.

Two broad classes of amplifiers have been developed, with untuned and tuned input circuits[13], both involving thin film, planar SQUIDs with spiral input coils. The SQUID is current and flux biased in the vicinity of its point of maximum gain, and the output is coupled to a room temperature rf amplifier via an appropriate impedance matching network. The SQUID is not operated in a flux-locked loop. In the untuned amplifier, one connects the signal source across a resistor and the input coil in series, thereby obtaining a broad frequency response that may extend up to 200 MHz or more. The upper frequency limit is usually determined by the parasitic capacitance. In a typical amplifier designed to optimize the noise temperature, the power gain was 16.5 ± 0.5 dB and the noise temperature, T_N, 3.8 ± 0.9 K at 100 MHz for a bath temperature T of 4.2 K. These results were in good agreement with theory: in particular, T_N scaled as ωT, where ω is the signal frequency.

To make a tuned amplifier, one connects a capacitor C_i in series with the input coil, L_i, chosen so that the series L_iC_i resonant frequency corresponds to the signal frequency. At 4.2 K and 93 MHz, the measured gain and noise temperature of a particular amplifier were 18.6 ± 0.5 dB and 1.7 ± 0.5 K, again in fair agreement with theoretical predictions. Both the untuned and tuned amplifiers have the lowest noise temperatures of any available at frequencies up to a few hundred megahertz; at higher frequencies, cooled GaAs-FET amplifiers become very competitive.

We have used the SQUID-based amplifiers in a series of NMR and NQR experiments, five of which are briefly reviewed in this paper: (i) We have been able to observe "nuclear spin noise", that is, the spontaneous emission of photons from an ensemble of ^{35}Cl nuclei in the zero polarization state[14]. (ii) We describe the use of the "Q-spoiler" in conventional NQR and NMR measurements in which one applies a large rf pulse to the nuclei to make them precess. We first illustrate the use of this switch in an NQR experiment[15,16]. (iii) We also used the Q-spoiler in an experiment to detect the oscillating electric polarization induced by ^{35}Cl nuclear quadrupole moments[17]. The sample is placed between the plates of a capacitor that is part of the tuned input circuit of the amplifier. (iv) We have extended the use of the Q-spoiler and SQUID amplifier to NMR, detecting the signal from ^{119}Sn nuclei at 30 MHz. (v) Finally, we describe the use of a SQUID amplifier with an untuned input circuit to detect the low frequency NMR signal at 55 kHz from ^{195}Pt nuclei in an applied field of 60 gauss.

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Nuclear Spin Noise

The ^{35}Cl nucleus with I=3/2 exhibits nuclear quadrupole resonance (in zero external magnetic field) between two doubly degenerate energy levels separated by a frequency $\omega_s/2\pi$ = 30.6857 MHz. The transverse relaxation time is T_2 = 240 μs, corresponding to a linewidth $\Delta f_s = 1/\pi T_2$ = 1.3 kHz. In the experiment,[14] a sample of $NaClO_3$ or $KClO_3$ is placed in an inductor connected to a tuned SQUID amplifier, as indicated in Fig. 1. One uses the SQUID to measure the modification of the Nyquist noise current in the resonant circuit introduced by the presence of the sample; in the absence of the sample, the spectral density of this current would be a Lorentzian. One can treat this situation by representing the sample as an additional resistance $R_s(\omega)$ and inductance $L_s(\omega)$ in the tuned circuit. We actually performed two different experiments using this system. In the first, the sample was in thermal equilibrium, with the population of the spin states given by the Boltzmann factor. The principal effect of the sample was to induce a spin resistance into the tuned circuit, thereby producing a dip at frequency $\omega_s/2\pi$ with a width Δf_s. This effect arises from the absorption of power from the tuned circuit by the spins.

In the second experiment, one applies an rf pulse to the sample at frequency $\omega_s/2\pi$, thereby equalizing the populations of the two levels (corresponding to an infinite spin temperature, T_s). After the pulse is turned off, the spin population relaxes very slowly, over a period of days. The spectral density of the Nyquist noise is given by [14]

$$S_I(\omega)|_{T_s=\infty} = \frac{(2/\pi)\, k_B\, [\, R_i\, T + R_s(\omega)\, T_s]}{R_i^2 + [\, \omega(L_i + L_p) - 1/\omega C_i]^2} \quad . \quad (1)$$

In Eq. (1), $R_s(\omega) \rightarrow 0$ and $T_s \rightarrow \infty$ in such a way that $R_s(\omega)T_s$ is a constant: thus, one expects to observe a "bump" in the spectral density due to this term. This bump is shown in Fig. 2, and is in good agreement with theoretical predictions. The bump arises from the spontaneous emission of photons into the tuned circuit as the spins decay towards the equilibrium state. We note that the system has sufficient sensitivity to detect this process even though the spontaneous emission rate for one spin is extremely low, A = 2×10^{-16} sec^{-1} (about 1 flip in 10^6 centuries!). Since the number of nuclei, N, is about 2×10^{21}, the total emission rate is NA/2 = 2×10^5 sec^{-1}, corresponding to a total emissive power of 5×10^{-21} W.

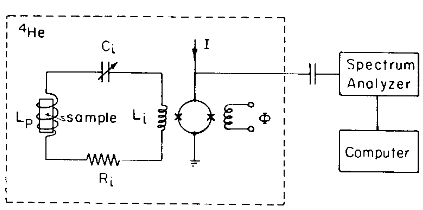

Figure 1. Experimental configuration of experiment to observe nuclear spin noise. Components in dashed box are immersed in liquid ^{4}He.

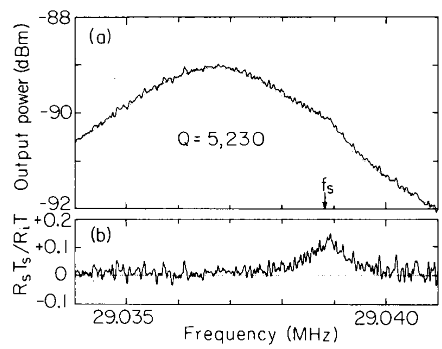

Figure 2. Results of nuclear spin noise experiment: spectral density of (a) noise current for a $KClO_3$ sample with saturated spins ($T_s = \infty$), and (b) nuclear spin noise of sample obtained from (a).

NQR and the Q-Spoiler

Our system to detect NQR in $NaClO_3$ is shown in Figure 3. The sample is inserted into a coil connected in series with an identical, oppositely wound coil, adjusted mechanically to minimize pick-up from the transmitter coil. These coils, in turn, are connected in series with a tuning capacitor, C_i, the input coil of the SQUID, L_i, and an array of 20 Josephson tunnel junctions.[15] When the rf pulse is applied to the transmitter coil, the relatively large pulse induced in the input circuit causes this array to switch very rapidly to the resistive state with a total resistance of about 1 kΩ. Thus, the array acts as a Q-spoiler[16], reducing the Q of the tuned circuit to the order of unity, and minimizing the signal passed onto the SQUID. After the rf pulse is turned off, the current induced in the tuned circuit decays very rapidly, and the junctions revert to the zero resistance state, thereby restoring the Q to a large value, typically 2000-5000. In this state, the tuned amplifier is very sensitive, with a noise temperature of about 1 K, and can detect the NQR signal from the precessing spins. The amplified signal is mixed down by a mixer referenced to the rf generator, and, after filtering, observed on an oscilloscope and recorded for further analysis.

Figure 4 illustrates the effect of the Q-spoiler in reducing the amplitude of the rf pulse applied to the SQUID. In each figure, the upper trace is the input pulse, and the lower is the mixed-down output signal. Figure 4(a) shows the response to an rf pulse corresponding to a peak-to-peak magnetic field of ~50 mgauss at the sample, in the absence of the Q-spoiler. The oscillations arise from the fact that the SQUID has been driven through many flux quanta, and the recovery time after the pulse is turned off is about 250 μs or 10τ, where τ is the ring-down time of the tuned circuit. By contrast, Fig. 3(b) shows the response to the same rf pulse with the Q-spoiler in place. The recovery time has been reduced to ~ 50 μs (2τ); this recovery time can be maintained even for much larger pulses.

The combination of the low noise of the SQUID amplifier and the Q-spoiler, which enables one to use much higher values of Q than would otherwise be the case, yields very high sensitivity for the detection of NQR and, as we shall see, NMR. We estimate that the system can detect 2×10^{16} nuclear Bohr magnetons after a single pulse in a bandwidth of 10 kHz.

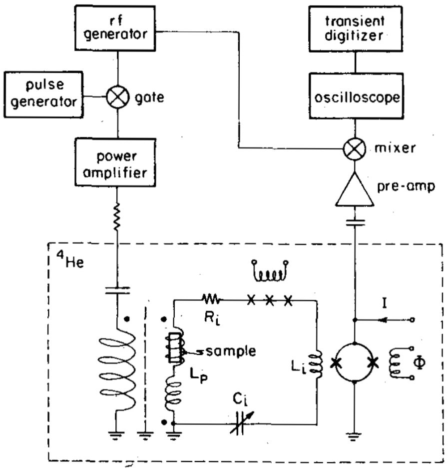

Figure 3. Schematic layout for SQUID-based detection of NQR.

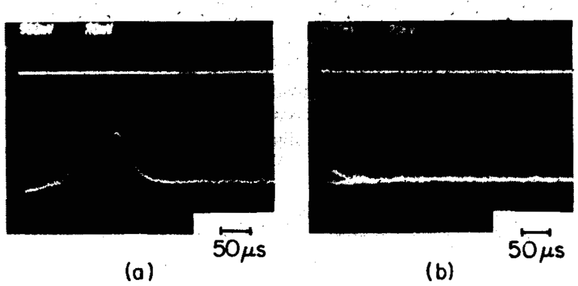

Figure 4. Demonstration of the effect of the Q-spoiler in a circuit with no NQR sample. Oscilloscope traces show the ring-down of tuned circuit (lower traces) following the rf pulse (upper traces), with Q=2,500: (a) without Q-spoiler; (b) with Q-spoiler.

Nuclear Electric Quadrupole Induction of Atomic Polarization

This is a new resonance response mechanism, in which precessing nuclear quadrupole moments induce electric dipole moments in neighboring atoms.[17] This effect, which is the inverse of the Stark effect in NQR,[18] occurs only in noncentrosymmetric crystals containing nuclear quadrupole moments. The ^{35}Cl nuclei have both a magnetic dipole moment and an electric quadrupole moment, and the electric field gradient from the other atoms in $NaClO_3$ produces two, doubly degenerate levels separated by about 30 MHz. The application of a small, static magnetic field H_0 removes the degeneracies, producing 4 distinct levels. When an rf magnetic pulse is applied, the ^{35}Cl nuclei tip and precess, producing oscillating magnetic and electric fields; the former provides the signal in the NQR experiment described in the previous section. The oscillating electric fields induce an electric polarization in neighboring atoms. For certain orientations of the single crystal, one finds a net electric polarization on summing these atomic polarizations over all the atoms in the unit cell, provided that $H_0 \neq 0$.

The experimental configuration is shown in Fig. 5. An oriented $NaClO_3$ crystal is placed between the plates of a capacitor C_p that forms a part of a high-Q resonant circuit coupled to a SQUID; the circuit contains a Q-spoiler. With H_0=0, we applied rf pulses at the NQR frequency and observed the magnetic resonance that was coupled to the amplifier via stray inductance [Fig. 6(a)]. We minimized this unwanted signal by adjusting L_c mechanically. We then set H_0 = 8.8 gauss, and observed the electric polarization shown in Fig. 6(b).

We have made a detailed analysis of this effect and shown that the signal provides information on the local polarizability and positions of near-neighbor atoms of the active nucleus. It is particularly sensitive to bond angles. Since the effect depends on the number of polarizable charges in the immediate neighborhood of the nuclear quadrupole moments, the signal could be used to monitor local atomic re-arrangements and fluctuations, for example, those associated with phase transitions or charge density waves.

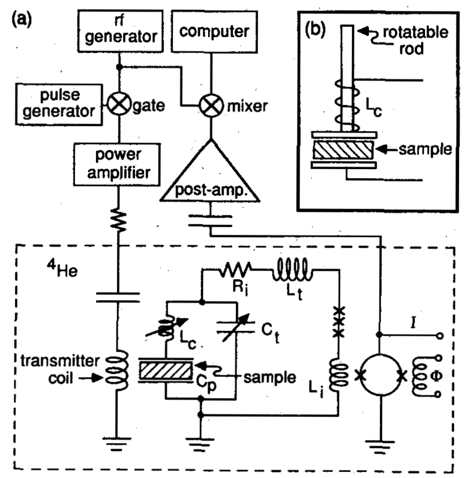

Figure 5. (a) Experimental configuration for electric quadrupole induction of atomic polarization. (b) Geometry of sample capacitor and cancellation coil.

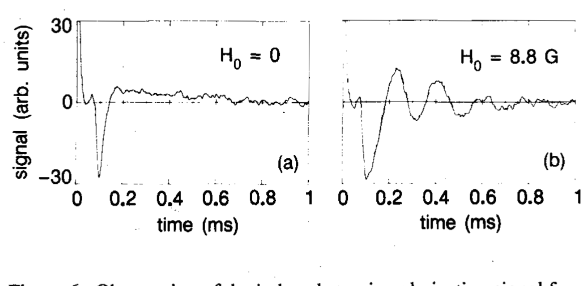

Figure 6. Observation of the induced atomic polarization signal for $NaClO_3$ (a) with H_0 = 0 and (b) with H_0 = 8.8 gauss.

High Field NMR

The widespread application of high field NMR to the study of solids has motivated us to extend the use of the radio-frequency amplifier and Q-spoiler to the detection of high field NMR signals. The unprecedented sensitivity achieved by the SQUID amplifier should enable one to apply solid state NMR techniques to a wide range of low signal systems, for example, impurities and single-crystal surfaces. These systems have remained largely inaccessible to NMR because of a lack of sensitivity.

The sensitivity of typical high field spectrometers is limited by the Nyquist noise in the receiver coil at room temperature or by the first stage amplifier noise if the probe is cooled. Thus, a typical optimized NMR spectrometer operating at frequencies above 10 MHz has an amplifier noise temperature of 80 to 100 K. Cooled FET amplifiers have obtained noise temperatures as low as 7 K[19]. Other important considerations include the quality factor of the tuned receiver circuit and, in pulsed NMR, the recovery time of the system after the rf pulse. Our SQUID-based amplifier used in the high field NMR probe described here has obtained an amplifier noise temperature of 3 K, a figure actually limited by the noise contribution of the second stage amplifier rather than the SQUID itself. With the aid of the Q-spoiler, the system recovers from the rf pulse in 50 μsec.

With the exception of the transmitter and receiver coils, the configuration of the NMR system (Fig. 7) is the same as that used for the detection of NQR. The solenoid magnet geometry requires us to use a Helmholtz pair as a transmitter and an orthogonal solenoidal receiver, instead of the series counterwound receiver coils and solenoidal transmitter shown in Fig 3. The configuration of Fig. 7 is similar to that used by Freeman et al.[12] to detect NMR in thin films of He^3 at 2 MHz. The SQUID input coil is in series with the receiver tank circuit and two arrays of 20 Josephson junctions which act as the Q-spoiler. Since solid state NMR requires the application of high peak power rf pulses (over 1 kW is required to produce a 90° pulse using the Helmholtz-coil transmitter), the junctions are essential to avoid flux trapping in the SQUID and to enable it to return to its correct flux bias point after the pulse has been turned off. The SQUID and series junctions are enclosed in a Nb shield placed 0.15 m from the receiver coil, well outside the 30 kgauss static field. As a result of the long leads between the tank circuit and the SQUID, the isolation between the receiver and transmitter networks is limited to about 60 dB. Parasitic loses in these leads limit the Q to a maximum of 300.

We measured the system noise temperature by first calibrating the gains of the SQUID and postamplifiers, and then measuring the noise power at the output of the amplifier chain with a spectrum analyzer. The output noise consisted of a white noise background and a noise peak at the resonant frequency of the tuned circuit that comes from Nyquist noise. We estimated the noise temperature of the SQUID-postamplifier chain (with the Nyquist noise subtracted out) to be 7 K. Most of this noise was attributable to the postamplifier.

We have made preliminary tests of the spectrometer by observing the NMR signal from metal powders and thin films at 30 MHz. We choose metals because of their short relaxation times at low temperatures (typically, $T_1 = 50$ ms). Figure 8 shows the signal from a 16 mm^3 sample of copper powder. The NMR signal is large enough to produce several flux quanta in the SQUID, so that the initial output from the SQUID is approximately a Bessel function. After decaying about $5T_2$, the signal amplitude enters the linear region of the flux-to-voltage transfer function and the free induction decay is undistorted. We attempted to calibrate the absolute sensitivity of the spectrometer by using a thin film of Sn. Figure 9 shows the NMR signal from a 70 mm^2 x 4 μm film of Sn containing 8 x 10^{17} ^{119}Sn spins. Since the skin depth at 30 MHz is > 4 μm, the film should be uniformly penetrated by the rf fields. In this example, the spins were tipped by about 13° from equilibrium with a 15 μs transmitter pulse. Larger pulses produced intermittent loss of the optimum flux bias point, probably because of the rearrangement of flux in the SQUID.

From these measurements, we estimate the minimum number of ^{119}Sn nuclei observable (signal-to-noise of unity) from a single free precession decay following a 13° pulse to be about $N_{min} \sim 10^{18}$ in a 25 kHz bandwidth. This corresponds to $\sim 10^{18}$ nuclear Bohr magnetons. For comparison, we can estimate N_{min} theoretically by calculating the signal power, P_s, and the noise power, P_n, and setting $P_s = P_n$. The signal power is

$$P_s = \frac{V_s^2}{R_i} = \frac{2\pi\omega M_o^2 Q}{V_c} \sin^2\theta \ \exp(-2t_d/T_2) . \quad (2)$$

Here, M_o is the total equilibrium nuclear magnetization, V_c is the

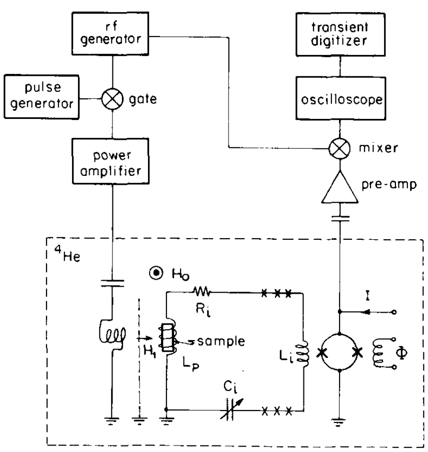

Figure 7. Experimental configuration for the SQUID-based detection of high field NMR.

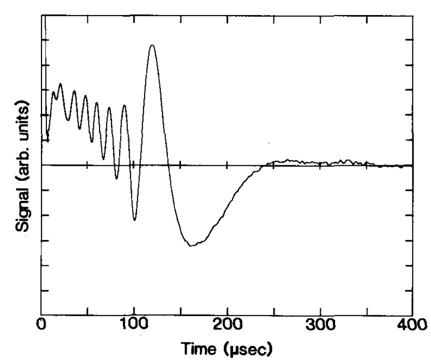

Figure 8. The free induction decay of ^{63}Cu in a large powder sample. The initial oscillations result from the Bessel function response of the SQUID to large signals. The undistorted free induction decay envelope is visible after about 200 μs. T_2 is about 40μs.

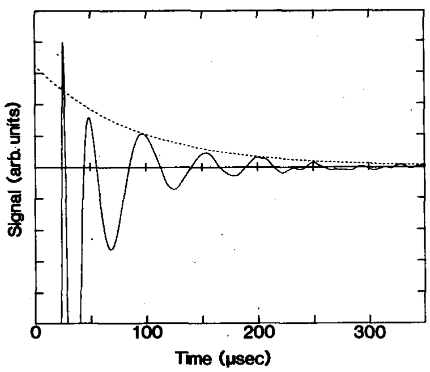

Figure 9. The free induction decay of Sn in a thin film containing 8×10^{17} ^{119}Sn nuclei. The magnetization was tipped 13° from equilibrium by a 15 μs pulse 20 kHz off resonance. The signal was mixed down with the oscillator, and observed in a 25 kHz bandwidth. The trace is the result of 4900 averages.

coil volume (600 mm^3), θ is the tipping angle, and t_d is the dead time, that is, the time required for the system to recover from the overload produced by the rf pulse. The noise power in a bandwidth B is $4k_BT_NB$, where T_N is the sum of the amplifier noise temperature and the bath temperature. Thus, the minimum number of detectable spins, N_{min} , is

$$N_{min} = \frac{4k_BT_s}{\gamma\hbar^2\omega}\left(\frac{2k_BT_NV_C\,B}{\pi\,\omega\,Q}\right)^{\frac{1}{2}}\frac{(\exp t_d/T_2)}{\sin\theta} \quad . \qquad (3)$$

Using the parameters from the experiment with $T_s = 4.2$ K and $T_N = 11$ K, we find $N_{min} \approx 10^{17}$ ^{119}Sn spins, an order of magnitude better than the measured resolution. We are presently investigating the reason for this discrepancy, and hope to make a more accurate measurement of the sensitivity in the near future.

In conclusion, we have developed a SQUID-based system for the detection of weak NMR signals obtained from samples in high magnetic fields. We expect to make several improvements to our spectrometer. We should be able to reduce the noise power in the system by a factor of 4 by replacing the second stage amplifier by a cooled FET and reducing the bath temperature to 1 K. We can enhance the signal by increasing the Q of the tank circuit and increasing the isolation of the transmitter and receiver circuit so that we can employ a 90° tipping angle. We also plan to increase the signal by operating the spectrometer at higher frequencies. With these improvements, we hope to detect 10^{16} nuclear Bohr magnetons in a single observation. One remaining problem is the fact that many materials have long relaxation times (T_1), at 4 K so that one has to wait an inordinately long time between pulses. We hope to overcome this difficulty by means of a cryostat that will allow us to maintain the sample at any temperature between 4 K and 300 K where T_1 has a reasonable value, while keeping the SQUID-based receiver at 4.2 K.

Low Field NMR in Pt

We describe a low-field NMR experiment as a first step in developing a zero-field NMR spectrometer for frequencies below 250 kHz to study amorphous and polycrystalline materials. It is well known that high field NMR has a very high resolution, of the order of 1 Hz, for liquid samples, but suffers a substantial linewidth broadening, as large as 100 kHz, for solid powders because of the magnetic dipole interaction between spins. One can achieve high resolution in a solid by performing NMR in zero external magnetic field.[20] However, the resonant frequency of the zero field NMR is typically under 250 kHz, so that the energy levels are very nearly equally populated at any reasonably accessible temperature. As a result, it is very difficult to detect the signal directly with a conventional semiconductor preamplifier. Fortunately, the development of a low noise SQUID magnetometer with a large flux-locked bandwidth by Wellstood et al.[21] has made it possible to achieve a zero field NMR system with the desired bandwidth and sensitivity. In this section, we describe a Fourier transform spectrometer for low field pulsed NMR based on a dc SQUID, and the successful observation of the NMR signal from ^{195}Pt at 4.2 K. This pulsed NMR system is able to detect signals at frequencies up to 250 kHz, and enables one to observe an NMR signal from a solid with a resonant frequency that can be as low as 30 kHz at 4.2 K. This observation has previously been very difficult because the NMR signal is proportional to $Q\omega_s^3T_2/T^2$: Thus, for solids with low values of T_2 (<1 ms) and $\omega_s/2\pi$ (~30 kHz) at a relatively high temperature T (4.2 K), the NMR signal is extremely small. However, our low field NMR observation indicates that our system has sufficient sensitivity and bandwidth to perform zero field NMR.

As shown in Fig. 10, the magnetic field and transmitter and receiving coils are in the standard configuration. The external static magnetic field in the z-direction is produced by a persistent current in a superconducting solenoid. We can easily change the current in the solenoid by means of the superconducting thermal switch connected across it. The transmitter coil consists of a pair of saddle coils producing a rf magnetic field in the x-direction. These coils are connected to the rf pulse circuitry via several passive and active blocking components (not shown) to prevent noise from being transmitted into the SQUID. The receiver consists of a pair of saddle coils, which are superconducting and pick up the magnetic field along the y-direction. These coils are connected to the SQUID input coil with superconducting joints to produce a superconducting magnetic flux transformer. The inductance of the pick-up coil Lp is designed to be equal to that of the SQUID input coil to maximize the signal energy transferred into the SQUID. The resistor $R_i = 100\ \Omega$ in parallel with the coil forms a low pass filter to prevent high frequency interference from being coupled into the SQUID. The fact that the circuit is untuned means that one loses the signal enhancement factor Q. However,

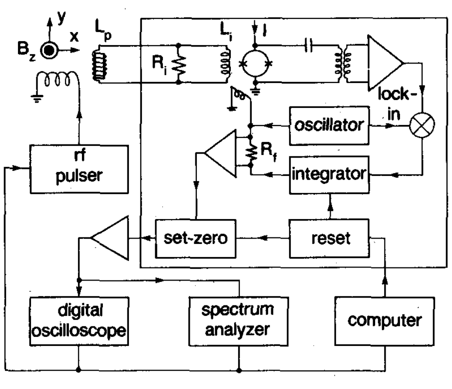

Figure 10. Experimental configuration of low field NMR spectrometer.

this loss is more than offset by the fact that the sensitivity is not limited by the thermal noise generated in the input circuit, so that one can take advantage of the low effective noise temperature of the SQUID (<< 4.2 K) achievable at these low frequencies.

The sample is packed in a 5 mm diameter NMR tube, which can be lowered into the pick-up coils from the top of the cryostat. This feature greatly facilitates the changing of samples. To detect the NMR signal, we apply an rf pulse at the Larmor frequency to the transmitter coil, thus inducing a magnetization M precessing about the static field B_z. The y-component of this magnetization produces an oscillating magnetic field $B_y = 4\pi M_y$ that in turn induces an oscillating flux in the pick-up coil. This signal is coupled into the flux-locked SQUID via the superconducting transformer. The signal from the feedback circuit is filtered, amplified, and transmitted to the digital oscilloscope for time-domain analysis and the spectrum analyzer for frequency-domain analysis. The entire system is computer controlled.

The most crucial elements in the system are the SQUID and the fast recovery feedback electronics, which is based on an earlier design.[21] The SQUID is modulated with a 500 kHz square wave, and the voltage across the SQUID is amplified and lock-in detected. The output from the lock-in detector is integrated and fed back to a coil coupled to the SQUID to obtain a flux-locked loop. This circuit can track signals at frequencies up to 250 kHz. To make the system suitable for pulsed NMR, we have incorporated a reset and a set-zero circuit , as shown in Fig. 10. After the rf pulse in the transmitter coil is turned off, the integrator is enabled by the reset circuit. To prevent the generation of a large voltage step across the feedback resistor, R_f, the set-zero circuit holds this voltage at zero until the feedback circuit has stabilized. Both the reset and the set-zero circuit are controlled by the computer, with appropriate time delays provided by a timing circuit (not shown in the figure). The computer is connected to this circuit via an optical coupler to eliminate noise from the computer.

The thin film dc SQUID is coupled to a 20-turn input coil with a self-inductance $L_i = 120$ nH via a mutual inductance $M_i = 6$ nH. Each of the two saddle-shaped pickup coils has an area of about 50 mm^2 and 2 turns. The measured flux transfer coefficient from input coil to the SQUID is about 0.06. The system flux noise referred to the SQUID is $6\mu\Phi_0/\sqrt{Hz}$ for the present SQUID. We note that the noise immediately after the rf pulse has been turned off is no higher, indicating the blocking components in the transmitter line are adequate. The recovery time of the system is less than 40 μs.

In our preliminary experiments, we used ^{195}Pt powder. The platinum nucleus has spin 1/2 and a gyromagnetic ratio γ = 0.92 kHz/gauss. Compared with other solids at 4.2 K, it has a relatively long T_2 (1.1 ms), because of spin exchange, and a short T_1 (10 ms), because of free electron assisted relaxation.[22] The sample is in powder form to allow the rf field to penetrate uniformly.

We carried out the NMR experiments with several values of the static field, ranging from 30 gauss to 200 gauss. Every 0.5 sec, a rf pulse is applied to initiate a free induction decay (FID). The free induction signal is averaged to enhance the signal-to-noise ratio. Typically, the rf pulse applied to the sample is about 2 gauss peak-to-peak, and 0.4 ms long. Experimental results with a static field of about 60 gauss are shown in Fig. 11. Figure 11(a) is the real time trace of the average of 256 FID signals, while fig. 11(b) is the Fourier transform of the average of 40 FID signals. The measured resonant frequency is 54.75 kHz.

In conclusion, we have observed the NMR signal from ^{195}Pt at low fields with our Fourier transform pulsed NMR spectrometer based on a SQUID preamplifier. After further refinement and calibration of the system, we intend to use it to study zero field NMR, which is the main goal of this work. We note, however, that the results on ^{195}Pt may have immediate application to thermometry in the millikelvin temperature range, since this technique combines the advantages of the traditional pulsed NMR thermometry with the low noise presently offered by SQUIDs in cw-NMR thermometry.[23]

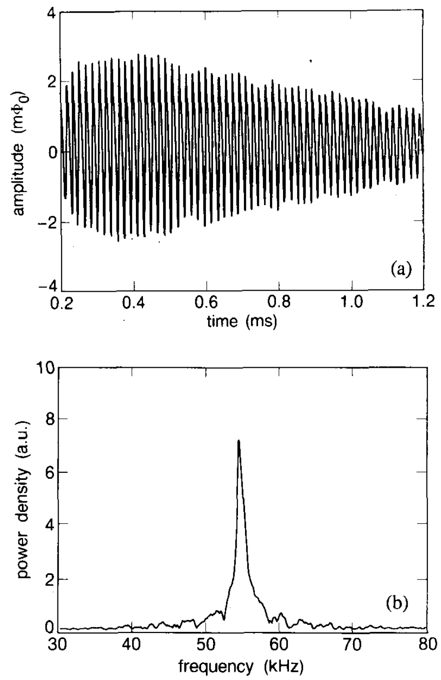

Figure 11. Observation of low field NMR: (a) The free induction decay of ^{195}Pt powder at 60 gauss. The amplitude is the flux signal in the SQUID. (b) The Fourier transform of the free induction decay.

Concluding Remarks

We have presented a series of experiments illustrating the application of dc SQUID amplifiers to magnetic resonance experiments. Two of the experiments, the observation of nuclear spin noise and the nuclear electric quadrupole induction of atomic polarization, are novel manifestations of NQR made possible by the high sensitivity of the amplifier coupled with the very high Q input circuit and, in the second case, the Q-spoiler. The experiments on the detection of NQR and NMR are conventional in concept, but offer higher sensitivity than is possible with room temperature electronics. It is the combination of the low-noise amplifier and high Q circuit together with the Q-spoiler that enables us to obtain the high sensitivity in the NQR experiment. The Q-spoiler is essential to reduce the ring-down time of the tuned circuit to an acceptable level and has allowed high Q (>1000) circuits to be applied to the detection of pulsed magnetic resonance signals from typical solids. We have not yet been able to achieve high values of Q in the high field NMR experiment, and its sensitivity has suffered accordingly.

Finally, we described a preliminary experiment in which we observe NMR in ^{195}Pt at 55 kHz. In this experiment, the input circuit is untuned, so that thermal noise in the input circuit does not limit the sensitivity. This experiment implies that one should be able to make a direct detection of the zero field NMR signal from amorphous and polycrystalline materials.

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