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RECENT ADVANCES IN SQUID NMR TECHNIQUES

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RECENT ADVANCES IN SQUID NMR TECHNIQUES*

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ABSTRACT

A discussion of the techniques used for performing a variety of magnetic resonance experiments using a SQUID is presented. In particular, measurements of the nuclear magnetism of liquid ^3He in the temperature range 1.2 K to 2 mK in magnetic fields of 3.7 to 309 Oe using pulsed NMR, cw NMR, adiabatic fast passage and static susceptibility using the same detection system will be discussed.

INTRODUCTION

In the last ten years a great deal of progress has been made in the experimental understanding of superconducting devices based on the Josephson effect.¹ This in turn has led to a wide variety of applications, primarily in the measurement of weak magnetic phenomena. One area of importance that has not received a great deal of attention is in the use of a SQUID for the detection of nuclear magnetic resonance (NMR) signals. The ability to isolate and study a single nuclear spin species combined with the sensitivity of the SQUID should allow new and interesting magnetic phenomena to be investigated under experimental conditions that previously made a conventional NMR experiment impossible.

In this paper a discussion is presented of the techniques used for performing pulsed NMR, cw NMR, adiabatic fast passage as well as static susceptibility measurements using the same SQUID based detection system in magnetic fields as low as 3.7 Oe in the temperature range 4.2 to 0.002 K. SQUID NMR is not new. One of the first NMR uses of a superconducting weak link was by Silver et al.² who observed the rf absorption in the ^{59}Co nuclear spin system. Both the adiabatic fast passage and cw NMR measurements reported to date^{3,4} used a SQUID to detect the change in the average value of the z-component of magnetization as the frequency of a transverse H_1 field was swept through resonance. Only recently have experiments using pulsed SQUID NMR been reported^{5,6} even though the advantage of this technique over conventional methods is the most apparent. Following a single rf pulse, both a complete record of the relaxation process and the value of susceptibility are obtained, independent of dephasing times. A detailed description of SQUID NMR techniques can be found elsewhere.⁷

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APPARATUS

The measurements were made in an adiabatic demagnetization cell using Cerous Magnesium Nitrate (CMN) as the low temperature refrigerant. This cell is shown schematically in fig. 1. It was

Fig. 1. Schematic drawing of the demagnetization cell used in this work.

ments^{5,6} the H_1 field was shielded from the SQUID detection coils by a thin, high conductivity metallic shield. The disadvantage of this technique is that the pickup coil must be located outside the eddy current shield and results in a lower detection sensitivity. Also the L/R time constant of the shield may severely limit the frequency response of the system. Furthermore, the Johnson noise in this shield will increase the background noise of the system, and the magnetic impurities in the shield may interfere with the static susceptibility measurements. For ultra-low temperature use, there is an additional problem of eddy current heating. The technique employed in this work was to install a small 1 Ω resistor, constructed from manganin wire, in parallel with the superconducting pickup coil and SQUID input coil.

thermally connected to the mixing chamber of a dilution refrigerator via a Zn heat switch. The ^3He measured was contained in a 3 mm i.d. tower located above the main CMN. The static field H_0 , parallel to the axis of the tower, was trapped in a 10.9 mm i.d. Nb tube. A 42-turn rf saddle coil, wound on a diameter of 5 mm using 0.076 mm Nb wire, provided the transverse rf field, H_1 . The change in the ^3He magnetization was sensed by a 3 mm long Nb pickup coil wound astatically on a 4.3 mm diameter. The pickup coil was connected to the superconducting input coil of a two-hole symmetric SQUID operated in the flux-locked loop⁸ configuration. Temperatures were determined, with the aid of a second SQUID, by 17 Hz mutual inductance measurements⁸ on 10 mg of CMN located in a second magnetically shielded tower.

In order to achieve the optimum signal-to-noise ratio, the H_1 field must be kept from coupling to the SQUID.

In the earlier SQUID NMR experi-

This resistor was thermally grounded to the mixing chamber of the dilution refrigerator. Thus the Johnson noise temperature could be minimized and actually contributed a negligible amount of noise at 10 mK when compared to the intrinsic noise of the SQUID and associated electronics.⁸ The value of the time constant was chosen carefully so as not to distort any signal within the full bandwidth of the flux-locked loop and was calculated to be 2.6×10^{-6} sec.

A block diagram of the measuring system used in this work is shown in Fig. 2. The SQUID measures the change in the average

Fig. 2. Block diagram of the measuring system.

value of the z-component of the magnetization, either as the frequency of the rf field is swept through resonance or after the application of an rf pulse. For either the cw NMR measurements or the adiabatic fast passage measurements, the output of the flux-locked loop was fed to the vertical channel of an x-y recorder while the horizontal channel was driven by a voltage proportional to the frequency of the H_1 field. The output of the generator was fed through a large resistor to the H_1 coil. For pulsed work the generator was operated in the gated mode with the pulse

width determined by a pulse generator. The output of the flux-locked loop was then recorded on either a strip-chart recorder or an oscilloscope. In low static fields it was expected that the effectiveness of the 1Ω resistor in keeping the rf field away from the SQUID would be reduced. Consequently, a small nulling mutual inductor with a superconducting secondary was placed in series with the pickup-coil and input-coil to the SQUID. Its purpose was to cancel most of the rf current in the superconducting input circuit. The rf null electronics was to provide both the in-phase and out-of-phase signal fed to the nulling mutual inductor. However, even in 3.7 gauss this null scheme proved unnecessary and was not used.

CALIBRATIONS

The absolute calibration of the SQUID magnetometer was performed in the temperature range 0.3 to 1.2 K using three different techniques. The first was to measure the change in flux coupled to the SQUID, in a field H_0 , as the liquid ^3He sample slowly filled the region containing the detection coils. The change in flux $\Delta\phi$ coupled to the SQUID is equal to

$$\Delta\phi/\phi_0 = \lambda(X_p + X_D) \quad (1)$$

where X_p and X_D are the paramagnetic and diamagnetic susceptibilities of ^3He respectively, and λ is the calibration constant in the field H_0 . Using the known value for X_p ⁹ and from measurements of $\Delta\phi$ obtained at many different temperatures it was determined that $\lambda = (6.38 \pm 0.15) \times 10^7$ and $X_D (V/N) = -2.08 \pm 0.05 \times 10^{-6} \text{ cm}^3/\text{mole}$, where V/N is the molar volume of ^3He . A check on the value of λ was made by performing both adiabatic fast passage and 180° pulse NMR measurements in the same temperature range. For these two cases the change in SQUID output should be $\Delta\phi/\phi_0 = 2\lambda X_p$, remembering that the diamagnetic susceptibility is not coupled to in a NMR experiment. Using the known value of X_p , the value of λ determined using these two techniques agreed with the static value to within $\pm 1.5\%$.

PULSED NMR

Figure 3 shows a tracing of a typical response of the ^3He sample following a 91° rf pulse in a magnetic field of

Fig. 3. Response of SQUID magnetometer following a 91° rf pulse.

309 gauss at a temperature of 15 mK. The rf pulse width was 25 μsec . At the end of the rf pulse the magnetization vector has been rotated by 91° , but this initial change was faster than the flux-locked loop could respond and it momentarily lost lock. The new lock point is in general not simply related to the old one and cannot be used for the baseline determination.

However, shortly after the magnetization change has occurred, the SQUID can continually track the recovery of the magnetization back toward equilibrium. The baseline is determined by a straight line extrapolation of the end of the recovery process back to the beginning of the trace. The absolute value of the magnetization change can be determined by an extrapolation of the recovery curve back to the time of the end of the rf pulse.

The calibration of the current into the rf coil necessary to produce a known rotation of the magnetization vector is determined by measuring the change in magnetization obtained for a number of different currents. A typical calibration is shown in Fig. 4, where the extrapolated flux change immediately following a 24.5 μsec rf pulse is plotted as a function of the voltage applied to the superconducting rf coil. The impedance, z ,

Fig. 4. Maximum change in flux coupled to the SQUID as a function of the applied rf voltage to the H_1 coil for a time $\tau = 24.5 \mu\text{sec}$.

Fig. 5. Four examples of recovery of the magnetization of superfluid ^3He obtained at 2 mK in a 180 gauss field. The time scale for the 90° and 120° data is 0.5 msec/cm and 2.0 msec/cm for the 150° and 180° data.

of this coil was about 500Ω in this field. The solid curve is a fit to the data using $M = M_N(1 - \cos\theta)$. The value of M_N was determined using the calibration constant λ . The relationship between the magnitude of the H_1 field and the rotation angle is $H_1\tau = \theta\pi/180^\circ$, where τ is the pulse width. The maximum pulse width is determined by the inhomogeneity in H_0 over the sample region and must be kept short enough so as to completely couple to all the sample spins in the detection region. An example of the real advantage of SQUID pulsed NMR is shown in Fig. 5 where four typical traces of the recovery of the magnetization in superfluid $^3\text{He-B}$ are shown¹⁰ at a temperature of 2 mK for four different rotation angles. Relaxations that have exponential, linear and square-root time dependences are observed and easily studied using a single rf pulse.

CW NMR

A typical cw NMR trace obtained in 309 gauss at 15 mK is shown in Fig. 6. This trace was obtained by sweeping the frequency of the H_1 field through resonance in the time shown. The two peak resonance curve is due to the gradient in magnetic field over the sample and will be discussed below. The direction of the sweep was from low frequencies to high frequencies. The high-frequency tail on the resonance curve is due to the fact that the sweep rate was slightly faster than the rate required to establish equilibrium conditions at each

Fig. 6. tracing of a typical cw NMR experiment.

Fig. 7. Maximum change in magnetization occurring during a NMR experiment as a function of H_1^2 .

over the sample and is the major disadvantage of SQUID NMR. The Nb shield traps an integral number of flux lines, and the field H_0 at any cross section of the tower should be $H_0 = d\phi/dA_{\text{eff}}$, where ϕ is the total flux threading the cylinder and A_{eff} is the cross sectional area of the Nb shield minus the area of any superconducting material in the cross section considered. The superconducting pickup coil has finite length but is also sensitive to magnetization changes occurring outside the coil. It is expected that a two peak resonance curve should be observed because of the nearly discontinuous change in H_0 on going from the region just outside the coil to the region just inside the coil. The field change is calculated to be $H = 0.013 H_0$ for the present experiment, while the measured peak separation is $H = (0.016 \pm 0.0005) H_0$.

point on the curve. The baseline shows a slight upward drift due to the temperature-dependent paramagnetic background and imperfect temperature control of the cell. The maximum change in magnetization for a number of different H_1 fields is shown in fig. 7 as a function of the square of the H_1 field. The behavior of the z-component of magnetization as a function of the H_1 field is given by

$$\frac{\Delta M_z}{M_N} = \frac{(\gamma H_1)^2 T_1 T_2}{1 + (\gamma H_1)^2 T_1 T_2} \quad (2)$$

The solid curve drawn through the data is a fit that uses Eq. (2) with only T_2 , the spin-spin relaxation time, as a free parameter. T_1 was measured using pulsed NMR and M_N was determined using the calibration constant. The value of T_2 used in the fit was $T_2 = 3.3 \times 10^{-5}$ sec and is in agreement with the estimate of T_2 one can make from the observed width of the curve displayed in Fig. 6.

The linewidth observed in this experiment is completely due to the inhomogeneity in H_0

ADIABATIC FAST PASSAGE

Adiabatic fast passage is a cw technique used to invert the magnetization vector by applying a large H_1 field and quickly sweeping the frequency of the rf field through resonance. The conditions for an adiabatic fast passage in a SQUID NMR experiment are^{3,7}

$$|\gamma H_1|^2 \gg \frac{d\omega}{dt} \gg \frac{\gamma \Delta H}{T_1} \quad (3)$$

Fig. 8. Tracing of a typical adiabatic fast passage experiment obtained on He^3 .

where ΔH is the inhomogeneity in H_0 and T_1 is the spin lattice relaxation time. The first part of the inequality insures that the magnetization vector will be reversed adiabatically,¹¹ and the second part insures that the resonance curve is traversed in a time short compared to T_1 . A typical adiabatic fast passage experiment on He^3 at 15 mK is shown in Fig. 8. Only the passage through resonance is shown and not the recovery of the magnetization back toward equilibrium. The experimental conditions under which this trace was obtained are

$$|\gamma H_1|^2 = 2.2 \times 10^6 \gg \frac{d\omega}{dt} = 6 \times 10^5 \gg \frac{\gamma \Delta H}{T_1} = 8 \times 10^3 \quad (4)$$

Fig. 9. Tracing of a pulsed NMR experiment in 3.7 gauss.

where the value of ΔH used was the full experimental linewidth. After the rf field has been swept through resonance the spin lattice relaxation time as well as the value of the susceptibility the sample can be obtained.

FUTURE OF SQUID NMR

An example of the extreme sensitivity of the SQUID for the detection of nuclear magnetism is shown in Fig. 9. A tracing is shown of a pulsed NMR experiment performed in 3.7 gauss at a temperature of 12 mK following a nominal 180° pulse. The H_1 field was 0.154 gauss, and the pulse width was 1×10^{-3} sec. The change in susceptibility,

ΔX , is shown on the right-hand vertical scale. The signal-to-noise ratio for this trace was better than 100/1, and the bandwidth was 10 Hz. This trace demonstrates that zero field NMR is possible on some solids, using only the local field of the atoms for orientation. Although SQUID NMR is more sensitive than conventional NMR at low fields, in very large magnetic fields conventional NMR should in general be more sensitive because the detection sensitivity⁷ is proportional to $\omega_0^{3/2}$ as compared to ω_0 for SQUID NMR.

The major technological problem that must be solved is that of the inhomogeneity in the static field over the sample region. I believe that for a small sample, the use of a split-Helmholtz design for the SQUID pick up coil, with the ends of the coil kept away from the sample, can easily result in a homogeneity in H_0 on the order of 1×10^{-4} . For the case of a long sample the inhomogeneity problem is more severe. The use of superconducting shims or some other suitable technique may be required to cancel most of the change in the effective area occurring near the ends of the detection coil.

Fig. 10. Schematic drawing of a 1.2 K to 400 K variable temperature SQUID NMR magnetometer.

The use of SQUID NMR will not be restricted to the temperature range below 4.2 K. In the near future we can expect that commercial variable temperature SQUID NMR magnetometers will be available that operate in the temperature range 1.2 K to 400 K. Figure 10 shows a schematic diagram of such a proposed variable temperature SQUID NMR magnetometer. If the frequency response of the system can be increased to 0.1 to 1 μ sec, this type of instrument may prove to be even more useful than conventional NMR spectrometers because of the low field and static susceptibility measuring capability.

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