MAGNETIC RESONANCE IMAGING AND SPECTROSCOPY USING SQUID DETECTION

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INTRODUCTION

Magnetic Resonance Imaging (MRI), with its unique capability to image soft tissues, has become one of the most powerful nondestructive diagnostic tools in medicine. MRI is still a developing methodology in non-medical nondestructive evaluation (NDE); this is because solids with their broader nuclear magnetic resonance (NMR) linewidths are more difficult to image than biological tissue. However, recently MRI has been attracting increasing interest in a number of areas where the NMR linewidth is not as serious a problem. These include fluid flow determination in materials including porous media [1], detecting defects in ceramics still in the green (unfired) state [2], and the evaluation of polymers such as rubber and other elastomers [3].

Superconducting Quantum Interference Devices, or SQUIDs, with their great sensitivity and broad bandwidth have the potential to enhance MRI in both medical and non-medical applications.

In medicine, the high cost of MRI severely restricts its availability. This cost can be reduced significantly by using lower magnetic fields. Low-field MRI (generally defined to be below 0.1 tesla) also has important ancillary benefits such as, greater safety, being more adaptable to open magnet geometries (thereby reducing the discomfort of patients who must spend long periods within the magnet), minimizing radiofrequency (rf) power dissipation in the patient, and providing improved image contrast for certain tissues. However, low-field MRI systems cannot realize their full potential unless they approach the intrinsic sensitivity limits defined by the magnetic noise of the patient’s body. Existing low-field instruments cannot reach this limit because conventional magnetic resonance detectors, based on the induced voltage in a copper pickup coil, are intrinsically noisy at low frequencies.

This sensitivity problem can be solved using SQUIDs. SQUIDs are the most sensitive magnetic-field detectors known and, unlike conventional detection coils, they maintain their sensitivity as the frequency decreases. SQUID detectors can be operated to have noise floors below body noise over the full range of frequencies of interest in low-field MRI. Even SQUIDs based on high-temperature superconductors (HTS) can operate below the body-noise limit.

Furthermore, SQUID detectors make it possible to increase the bandwidth of the detection circuit without sacrificing sensitivity. In contrast, conventional detectors...
require resonant input circuits with very high Qs. At low fields, the narrow frequency response of high-Q detectors can restrict the signal bandwidth available for image encoding. SQUID detectors alleviate such bandwidth restrictions.

These issues of bandwidth and low-frequency sensitivity are also important in NDE applications. The available bandwidth is especially important for materials NDE because, typically, due to their larger proton NMR linewidths, the solid samples require larger imaging gradient fields than biological tissue. The larger gradient results in a greater spread of NMR frequencies in the imaged sample necessitating larger detection bandwidth.

The ability to obtain good images at low fields will also be important in NDE. This is due to the fact that many practical applications in materials NDE will require a single-sided imaging system (where the sample does not have to be enclosed by the magnet and the detector). It is, however, difficult to project large homogeneous fields into the sample in a single-sided geometry. A single-sided system is best operated at low fields. Consequently, SQUIDs with their sensitivity and bandwidth at low fields may turn out to be ideal for single-sided imaging.

In addition to the broad bandwidth and the sensitivity at low fields, the SQUID's sensitivity is independent of frequency. Generally non-hydrogen nuclei have NMR frequencies which are lower than that of hydrogen at a given magnetic field. A conventional detector's sensitivity decreases with field; consequently this is disadvantageous for non-hydrogen NMR. On the other hand the SQUID does not suffer from this disadvantage. Non-hydrogen nuclei of interest include, for example, include sodium, nitrogen, carbon-13, and phosphorous. Moreover, the broadband nature of the SQUID will allow the simultaneous detection of different NMR-sensitive nuclei in a given sample.

In this paper, we present a number of experimental results which illustrate the unique broadband, low-frequency capabilities of SQUIDs as detectors for NMR.

**SQUID NMR EXPERIMENTS**

Our experiments have shown that SQUIDs can operate well with the sample subjected to rf magnetic fields. To enable this, standard commercial SQUID electronics was modified to be able to measure rf signals with the SQUID operated in the flux-lock mode [4]. Importantly this high frequency SQUID electronics is designed to permit one to effectively isolate it from the fields generated by the rf pulses which are applied to the sample; the electronics is then able to recover in 1-2 microseconds to detect the NMR signal. This allows the SQUID electronics to be relatively unperturbed during the application of the rf pulse. To do MRI, suitable gradients will have to be applied to the sample in addition to rf pulse sequences. The SQUID electronics be similarly isolated as the MRI gradients are being switched.

We have obtained transverse NMR signals from a number of room-temperature samples using a broadband SQUID detector. The samples include biologically relevant materials such as salt water and animal tissue. The magnetic fields in which the experiments were performed range from about 0.0006 to 0.01 tesla. We have also obtained sodium and, possibly, phosphorous NMR signals. Details of our experiments are presented elsewhere [5]. To the best of our knowledge, our experiments are the first NMR experiments on room temperature samples which have used the SQUID as
an untuned broadband detector. Previous SQUID NMR experiments on room temperature samples have used the SQUID as a tuned detector [6], or have measured the dc shift in the longitudinal magnetization at resonance [7,8]. A representative example of our SQUID NMR data is shown in Figure 1 which is a pulse-NMR spectrum obtained from a sample consisting of about 0.5 cc each of hexafluorobenzene and water. The larger proton NMR peak is at about 302 kHz whereas the smaller fluorine peak appears at about 284 kHz. The fluorine peak is smaller primarily because there are much less fluorine atoms in the hexafluorobenzene than there are hydrogen atoms in the water.

The frequency-independent sensitivity of the SQUID enables it to sensitively detect signals at frequencies down to dc. This allows the SQUID to detect both the precessing magnetization in the plane transverse to the static field direction (i.e. transverse NMR) and the change in magnetization in the direction parallel to the static field (i.e. longitudinal NMR). Longitudinal NMR cannot be performed by a conventional faraday coil system; only a SQUID with its sensitivity at dc can be used for this measurement [7,8].

An advantage of longitudinal NMR is that its sensitivity is not dependent on the transverse spin-relaxation time $T_2$ as is the case with transverse NMR. This is an advantage for short-$T_2$ materials. In substance detection and NDE, many materials of interest are solids, for which the transverse spin-relaxation time, $T_2$, is much shorter than the longitudinal relaxation time, $T_1$. Because of this unfavorable $T_2/T_1$ ratio, the time available for observing the nuclear precession is much shorter than the time spent allowing the nuclei to polarize along the applied magnetic field. This low duty cycle adversely affects the sensitivity of the measurement in transverse NMR. Longitudinal NMR, on the other hand, is not limited by the lifetime of the precessing signal in the transverse plane. The signal lifetime in longitudinal NMR is governed by the longitudinal relaxation time $T_1$. Since the signal does not depend on $T_2$, longitudinal NMR can also tolerate more nonuniformities in the applied field than can transverse NMR.

We have performed longitudinal SQUID NMR experiments to discriminate between substances on the basis of their $T_1$ properties [9]. Our experiments were done by applying a given static magnetic field to the sample and sweeping the frequency of the rf field through resonance. Information about $T_1$ was derived from the amplitude of the longitudinal SQUID NMR signal as a function of the repetition rate of the frequency sweep.

Figure 2 shows the longitudinal SQUID NMR signal from nylon, a representative solid with a $T_1$ in the neighborhood of 0.1 sec. For this short-$T_1$ substance, the longitudinal spin relaxation occurs in a time comparable to the sweep rate of the rf frequency through the NMR line.

Some substances have highly field-dependent $T_1$s, which arise from a resonant interaction between the hydrogen and nitrogen nuclei within the molecule. This field-dependent $T_1$ provides a unique identifying signature for these substances. One such substance is hexamethylene tetraamine or HMT. At most magnetic fields, the hydrogen $T_1$ in HMT is very long, indicating an inefficient transfer of energy between the hydrogen nuclei and the surrounding material. However, the nitrogen nuclei are strongly coupled to the surrounding material through the interaction of their electric quadrupole moments with the electric field gradients within the molecule.
Figure 1. Transverse NMR spectrum from hexafluorobenzene and water at about 0.007 tesla.
Figure 2. Longitudinal NMR signals from nylon at 0.077 tesla (top) and at 0.085 tesla (bottom). The rf frequency is swept back and forth through resonance resulting in the resonance peak appearing twice in each figure. The x-axis gives the sweep time.
Figure 3. Longitudinal NMR signals from HMT at 0.077 tesla (top) and at 0.085 tesla (bottom).
At certain magnetic fields, the Larmor precession frequency of the hydrogen nuclei coincides with the nuclear quadrupole resonance of the nitrogens. This coincidence of frequencies, called a level crossing, creates an efficient, resonant energy transfer between the hydrogen and nitrogen nuclei, through the mutual interaction of the nuclear magnetic moments. Since the nitrogen nuclei are well coupled to the environment, this hydrogen-nitrogen coupling opens up a new, indirect path for thermal energy exchange between the hydrogen nuclei and the surrounding material. This enhanced energy transfer substantially reduces the hydrogen $T_1$ at the hydrogen-nitrogen level crossing [10,11].

Figure 3 shows the level-crossing effect in HMT. Figures 2 and 3 compare the spin-depolarization signals of HMT and nylon at two magnetic fields near the hydrogen-nitrogen level crossing of HMT. Nylon, like most materials, has a $T_1$ that varies only gradually with magnetic field. Its NMR signal increases gradually with magnetic field, reflecting the field dependence of the equilibrium nuclear polarization. As a result, the nylon NMR signal is slightly greater at 0.085 tesla than at 0.077 tesla (Figure 2). In contrast, HMT's SQUID NMR signal varies markedly with small changes in the magnetic field. At the level crossing (0.077 tesla), HMT has a short $T_1$ (roughly 60 msec [10]) and produces a strong SQUID NMR signal. However, at a field just above the level crossing (0.085 tesla), $T_1$ is much longer than the period of the RF frequency sweep, and the SQUID NMR signal is very weak. This weak signal occurs because, with their long $T_1$, the nuclear spins do not have time to recover their magnetization between rf sweeps.

CONCLUSION

Our experiments involving both transverse and longitudinal SQUID NMR have demonstrated the potential of using SQUIDs for MRI in medicine and in materials NDE, for low-field NMR spectroscopy, and for substance detection. In the past, the application of SQUIDs outside the laboratory has been impeded by the need for liquid helium. However, with the steady advances in HTS SQUID technology, it may be possible in the near future to develop very compact, self-contained SQUID systems using reliable, inexpensive miniature closed-cycle refrigerators. Reliable, reasonably priced refrigerators are now available even for SQUIDs based on low-temperature superconductors (LTS). SQUID detectors will require much less cooling power, and smaller cryogenic dewars, than superconducting MRI magnets. A low-field MRI system using a compact SQUID detector with a room-temperature magnet will be much simpler and less expensive than existing high-field MRI systems.

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