Detection of nuclear magnetic resonance in the microtesla range using a high $T_c$ dc-SQUID

Ning Wang, Yirong Jin, Shao Li, Yufeng Ren, Ye Tian, Yingfei Chen, Jie Li, Genghua Chen, Dongning Zheng
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
Jyr-king@iphy.ac.cn

Abstract. We have detected the ultra-low field nuclear magnetic resonance signal from water samples using a high-$T_c$ dc-SQUID sensor. The measurements were carried out in a home-made magnetically shielded room. Resonance spectra of $^1$H from tap water and other substance samples were obtained in the field range from 7-110 μT, corresponding to resonance frequency 300-4.68kHz. Two kind of experimental systems were built, the first one is a directly coupled system, its signal to noise ratio in a single-shot measurement is around 4 for about 15 ml water. The second one used a Cu coil to transfer the flux to the SQUID sensor. Signal to noise ratio was improved to about 20 in a single-shot measurement for 5ml water, which benefits from the improvement of coupling efficiency. The effect of residual gradient in the magnetically shielded room was also investigated. J-coupling of 2,2,2-Trifluoroethyl alcohol was measured, the peaks are consistent with high field results.

1. Introduction

Nuclear magnetic resonance (NMR) is one of the most powerful tools used in determining molecular structures. It is widely used in scientific and industrial researches. In conventional induction detection method, the sensitivity of the pick-up coil is proportional to the square of magnetic field. Therefore, great effort has been made to develop NMR systems operating at higher and higher magnetic fields. However, NMR working with very low magnetic fields has constantly attracted substantial attention and been explored for various kinds of reasons [1]. Because of the rapid decrease of the signal sensitivity with decreasing magnetic field for conventional induction coil sensors, a number of alternative sensors have been investigated to record NMR signal at very low fields [2]. In recent years, ultra-low field (typically in the microtesla range) NMR and magnetic resonance imaging (MRI) using superconducting quantum device (SQUID) as signal detectors has been studied by a number of groups [3]-[8]. In the microtesla range, the absolute inhomogeneity of the measurement field is significantly reduced, leading to very narrow line width. The advantages of microtesla NMR and MRI include reduced line width and hence improved J-coupling resolution, minimized susceptibility artifacts, enhanced $T_1$ contrast, possibility of NMR measurements or imaging in the presence of metal. Also, the ultra-low field means the greatly simplified coil design and construction, and possibly simple, inexpensive, portable NMR or MRI systems. Here we present the results of NMR experiments in microtesla range using a high-$T_c$ dc SQUID as signal detector.
2. Experimental

The experiment was carried out in a moderately shielded space. The magnetically shielded room (MSR) used in this work consists of three layers. The inner layer is made of 1 mm thick μ-metal plates. The next layer is made of 4 mm thick copper that is placed next to the μ-metal plates. The outer layer is 10 mm thick soft iron. The inner dimension of the MSR is 2.4×2.4×2.4 m³. The residual field at the middle of the MSR is about 100 nT in the vertical direction.

Two kinds of experimental system setup have been used. In the first system, the measurement field \( B_0 \) was supplied by a pair of Helmholtz coil of 0.6 m diameter. The pre-polarization field \( B_p \) was generated in the direction perpendicular to \( B_0 \) by a solenoid wound with four layers of copper wire. Its length was 110 mm and the inner diameter was 24.5 mm. A dc-SQUID operating in a flux-locked loop was used to record the free-induction-decay (FID) signal from the sample. Sample was placed in the pre-polarization coil directly under the SQUID sensor. The distance between the sample upper surface and SQUID sensor was about 2.5 mm. A pair of Maxwell coil of 0.6 m diameter was used to generate the gradient field along the measurement filed \( (G_z) \). As the NMR signal was directly coupled to the SQUID sensor, we call this system directly detection system, or directly coupled system, which is shown in figure 1(a).

The white noise of the SQUID sensor was about 70 fT/Hz\(^{1/2}\) measured in the MSR. However, the noise level increased to about 150 fT/Hz\(^{1/2}\) after \( B_p \) being applied for a few times. This is attributed to the trapped flux lines in the pick-up loop of the SQUID sensor.

In the second system, the measurement field coils and the \( G_z \) field coils were the same as the first one, but the FID signal from the sample were coupled by a solenoid pick-up coil, and then transferred to an input coil closely beneath the SQUID sensor through twisted copper wire pair, similar to that reported in ref [9]. The SQUID sensor and the input coil are placed inside a 3-layer μ-metal shielded LN\(_2\) dewar. A capacitance was added in the loop to form a RLC circuit, which enhances the signal at the resonance frequency. The pre-polarization coil was a larger solenoid wound surrounding the pick-up coil. Two set of biplane coil pairs were also added to generate the gradient field on the two other directions \( (G_x \) and \( G_y) \). We call this system coil transformer coupled system, which is schematically shown in figure 1(b).

![Figure 1](image)

**Figure 1.** (a) Directly detection system. (b) Schematic of coil transformer coupled system.

During the measurement, a 10-20 mT pre-polarization field was applied for 8-10 s before being switched off within ~25 μs. The FID signal was recorded a few milliseconds later. The signal from the SQUID electronics was then collected by a data acquisition device (DAQ) with a sample rate of 40 Kbit/s. The spectrum was obtained from FID or spin echo data by Fast-Fourier-Transformation (FFT).

3. Results and Discussion

Figure 2(a, b) shows the NMR spectra of \(^1H\) obtained from the directly detection system described above. Two tap water samples with different volume (15 ml and 3 ml) were used. The pre-polarization time was 10 seconds and the measure time was 1 second. The signal has been averaged for 100 times. For the sample with larger volume, the resonance peak can be seen in a single-shot measurement with signal-to-noise ratio (SNR) ~4. Samples of de-ionized water have also been measured and the similar results were obtained. The magnitude of the resonance peak can be estimated using the formula,
M=ρ\gamma^2h^2B_p/4k_BT, where ρ=6.7×10^{28} m^{-3} is the spin density and \gamma is the magnetogyric ratio of proton. The value is about 2.1 pT that is comparable but slightly larger than the value we obtained. We suggest that the lower than expected resonance peak is probably due to the inhomogeneity and time variation of the field B_0. In figure 2(c), the spectra for 15 ml water sample were shown. The two peaks correspond to the measurements with B_0 applied in opposite directions. From the peak difference, the residual field in the B_0 direction was estimated to be 34 nT. This value is consistent with that measured by a fluxgate magnetometer.

![Figure 2](image)

Figure 2. NMR spectrum of 15 ml (a) and 3 ml water (b) for B_p=10 mT and B_0=9.51 μT (100 times averaging). (c) measurement results for B_0 applied in opposite directions, where B_0 = 19.31 μT.

In the coil transformer coupled system, the NMR spectra of ^1H were also obtained, with much better SNR to ~20 for 5 ml water in a single-shot measurement (figure 3(a)). The pre-polarization field was enhanced to about 16 mT and the measurement field was about 110 μT. The improvement of the SNR can be mainly attributed to the improvement of the coupling efficiency. Although the coil transformer (includes the pick-up coil, input coil and the connection wires) itself will bring additional Johnson noise, we can control it less than or comparable with the noise of the SQUID sensor. As a result, the total noise level raises only a little and decreases the SNR no more than a factor or 2. The spin echo signal was also observed, which is shown in figure 3(b).

![Figure 3](image)

Figure 3. (a) NMR spectrum of 5 ml water measured by the coil transformer coupled system for B_p=16 mT and B_0=110 μT (10 times averaging). (b) The spin echo signal measured by the coil transformer coupled system.

We noticed that residual gradients still exist in the MSR. In addition, the measurement field applied by Helmholtz coil pair may also have a gradient due to a tiny asymmetry for the installation of the coil pair. The residual gradients will decrease T_2^∗, so as the SNR of spectra. As a result, we tried to compensate the magnetic field by using the three sets of gradient coils. Figure 4 shows the comparison before and after add gradient compensation in three directions. Better SNR was achieved by the gradient compensation, and the peak width was also narrowed. The compensation gradients are G_x = 70nT/cm, G_y = 4.7nT/cm and G_z = 0.

The J-coupling spectrum of 2,2,2-Trifluoroethyl alcohol was also measured (figure 5). The spectrum shows 3 peaks around ^19F nuclei and 5 peaks around ^1H nuclei due to the interaction between them. The peaks are consistent with high field results.
4. Conclusion
We have built two experimental systems for ultra-low field NMR spectrum measurement based on HTS dc-SQUID. The NMR spectra of $^1$H in water samples were obtained in both systems. For the directly detection system, SNR was about 4 in a single-shot measurement of 15 ml water. For the coil transformer coupled system, SNR was improved to about 20 in a single-shot measurement of 5 ml water. We consider the improvement of SNR mainly comes from the improvement of the coupling efficiency. Gradient compensation in three directions was done by using the three sets of gradient coils. The J-coupling spectrum of 2,2,2-Trifluoroethyl alcohol was also measured.

5. Acknowledgements
This work is supported by the National Basic Research Program of China (973 Program) (No. 2011CBA00106 and No. 2009CB929102), as well as by National Natural Science Foundation of China (No. 11104333 and No. 10974243).

References
[1] Greenberg Y S, Rev. Mod. Phys. 70, 175 (1998).
[2] Goodson B, "Mobilizing magnetic resonance", Physics World, p.28 (2006).
[3] McDermott R et al, Science 295, 2247 -2249 (2002).
[4] McDermott R, Kelso N and Lee S et al, J. Low Temp. Phys. 135, 793(2004).
[5] Seton H C, Hutchison J M S and Bussell D M, Meas. Sci. Technol. 8 198(1997).
[6] Yang H C, Liao S H, Horng H E et al, Appl. Phys. Lett. 88, 252505 (2006).
[7] Qiu L Q, Zhang Y, Hans-Joachim Krause et al, Appl. Phys. Lett. 91, 072505 (2007).
[8] Zotev V S et al, Journal of Magnetic Resonance 194, 115 (2008).
[9] Shu-Hsien Liao et al. Supercond. Sci. Technol. 22 045008(2009).