Development of Cryogenic Probe system for high-sensitive NMR Spectroscopy

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Abstract. Utilizing a cryogenic probe system is a promising approach to improve signal-to-noise-ratio (SNR) in the nuclear magnetic resonance (NMR) spectrometer. We have been developing an NMR spectrometer based on a superconducting-split-pair magnet. This unique structure of the magnet allows using solenoid-shaped antenna coil, which ensures about 2 times higher sensitivity than the conventional saddle-shaped antenna coil. The goal of the present study is to realize higher sensitivity by implementing the superconducting-split-pair magnet and solenoidal-shaped antenna coil. Our immediate objective is to establish the cryogenic probe system for the superconducting-split-pair magnet. In this paper, the basic idea and design of the system and some preliminary results are described.

1. Introduction

Improvement of measurement sensitivity is the most important task for nuclear magnetic resonance (NMR) spectroscopy. In fact, much effort has been made for the difficult problem. Up to now, main trend is to build an NMR system with higher magnetic field [1]. This is because that there exists relationship between the signal-to-noise ratio (SNR) and the strength of the magnetic field. That is, the resonant frequency ($\omega_0$) of the nuclear-spin is proportional to the strength of magnetic field ($B_0$). Moreover, SNR has a relationship to resonant frequency as ($SNR$) $\sim \omega_0^\alpha$ ($\alpha=7/4$). In addition, cryogenic probe is an efficient manner to induce SNR, since low temperature environment suppresses the loss due to the resistance of an antenna coil and enhances the performance of low-noise-amplifier (LNA).

In the present study, we are taking another challenge to improve the SNR in the NMR spectroscopy. Firstly, we have been developing split-pair superconducting magnet system [2-3]. Based on the structure, there is no restriction for the shape of an RF antenna. Namely, a solenoidal-shaped antenna
coil can be easily utilized in the system. The advantage of the solenoidal-shaped antenna coil is better performance of sensitivity. In fact, it was pointed out that the solenoidal-shaped antenna coil improves SNR by a factor of 2-3 comparing with saddle-shaped antenna [4].

The goal of the present study is to achieve higher SNR than ordinary NMR facility by using a split-pair superconducting magnet and a cryogenic probe system which includes a solenoidal-shaped antenna coil. Our immediate objective is to complete a proper design of the cryogenic probe system and basic investigation of each part. In this paper, design and specification of the cryogenic probe is given; design issues and related specification of cooling system, LNA and the antenna are explained. In particular, characterization of antenna coil which is made of superconducting thin film (MgB$_2$) is shown [5-11]. Finally, preliminary result of NMR measurement with a cooled normal metal antenna coil is described.

2. Design and Specification
In figure 1, a schematic of cryogenic probe system in the present study is shown. Main features of the system are as follows. Firstly, we introduced a peculiar cooling system with a double Gifford-MacMahon (G-M) cryo-cooler. Based on the cryo-cooler, target temperature of the antenna coil was set to 5 K. Second feature is operation of LNA at low temperature. Since the cryogenic probe system reduces equivalent-thermal-noise, the performance of LNA can be easily improved. As a result, one can expect effective enhancement of SNR. In this sense, design of LNA is quite important issue. Finally, for the antenna coil, we investigated the implementation of superconducting magnesium diboride (MgB$_2$) thin film [5-11]. For the characterization of the antenna coil, the value of quality factor was evaluated. Results are compared with those of normal metal antenna coil. In the following sub-section, brief descriptions of features are given.

2.1. Cooling System
Cooling technology is a key issue for the cryogenic probe system, since its efficiency determines the performance of the system. In particular, operation temperature for the antenna coil and LNA are quite important specification. In this study, we are aiming to implement an antenna coil made of superconductive thin film. Hence, lower temperature would increase the operation margin of the antenna coil. Therefore, we set the target temperature of the antenna coil to 5 K. The operation temperature of LNA was set to 40 K, as well. To reach the target temperature, cryo-cooling system was designed and constructed.

In figure 2, a schematic of the cryogenic probe system is depicted. The system consists of circular cooling unit, transfer tube and probe unit. The circular cooling unit includes double G-M cryo-coolers. The antenna coil and LNA were mounted and attached to corresponding cold stage. After the 12 hours drive of the system, resulting temperature of cold stage for antenna coil and LNA were about 5.3 K and 40 K. The description of the present cryo-cooling system in detail would be reported in elsewhere [12].

Figure 1. A schematic of cryogenic probe system.

Figure 2. A block diagram of cryo-cooling system with double G-M cooler.
2.2. Low Noise Amplifier

Figure 3 is a block diagram of receiver circuit in the cryogenic probe system. Cryogenic receiver circuit consists of a single pole double throw (SPDT) switch and LNA, and both circuits were cooled.

In the present study, HEMT was chosen for amplifying device. Generally, HEMT is used for applications with the band width of GHz. In our case, 600 MHz (i.e. $B_0=14$ T) is assumed, thus, one has to pay peculiar attention for the design of LNA. Namely, in the band width of several hundred MHz, gain of the HEMT increases which might disturbs the stability of the LNA. Moreover, operation at low temperature would result similar concern; at the low temperature, value of resistance in the cryogenic receiver circuit decreases and this situation might induce unstable state of the circuit.

The circuit parameters were carefully determined using the numerical simulation. Based on the initial design, test circuits were fabricated and measured. Stability of the circuit was measured by network analyzer and noise-figure (NF) was measured by an NF meter. At first, measurements and adjustment of the fabricated circuit were repeated at room temperature. After this optimization procedure, we characterized the performance of receiver circuit in the low temperature (77 K and 50 K). In figure 4, dependencies of NF and gain of receiver circuit on temperature are depicted. Objective specification of NF is less than 0.5 dB at operation temperature (40 K). In the present results (Fig. 4), we have successfully cleared the condition. In the actual test of NMR measurement, the fabricated circuits (SPDT switch and LNA) circuit were implemented in the cryogenic probe system.

![Figure 3. A block diagram of receiver circuit.](image1)

![Figure 4. Dependency of gain and NF of fabricated switch and LNA on temperature.](image2)

2.3. Antenna Coil

Superconducting thin film is a promising candidate for the antenna coil due to its low surface resistance. From the viewpoint of margin of operation temperature, oxide high-$T_c$ superconductor is proper material [13-16]. On the other hand, magnesium diboride (MgB$_2$) is proper candidate, as well [5-11]. Since the material is intermetallic compound, one can expect easier fabrication and post processing, i.e. wiring and packaging.

We fabricated and tested a solenoidal-shaped antenna coil using MgB$_2$ thin film. The thin film of was deposited by means of molecular beam epitaxy (MBE). Each thin film was patterned in loop shape to be a single turn element. These single turn elements were wired by Cu tape and stacked to form a 2-turn solenoidal-shaped antenna coil. Characterization of the antenna coil was obtained by measurement of quality factor. Descriptions of fabrication and characterization are reported in elsewhere [17].

In figure 5, typical result of resonant curve, i.e. dependency of impedance on frequency is shown. The evaluated quality factor ($Q_{\text{MGB}_2}$) was 7880; the impedance was matched to 50 $\Omega$ at the center frequency of 400 MHz. To compare the efficiency of cryogenic antenna coil made of normal metal, similar tests were performed. Two kinds of antenna coil made of Cu were prepared; one is the same dimension antenna expect film thickness and the other is made of Cu wire ($\phi 1.0$). The evaluated quality factor of antenna coil made of MgB$_2$ was $Q_{\text{MGB}_2}=6550–10640$ in the frequency range of
300-500 MHz. These values are 2–11 times higher than those of antenna coil made of Cu. The present results indicate that superconducting thin film antenna take great advantage to those of normal metal one. Unfortunately, we have not tested NMR measurement using superconducting antenna yet. Presumably, some preliminary results based on the superconducting antenna will be reported in the near future.

3. Preliminary Result of NMR spectroscopy based on the cryogenic probe
Using the cryogenic probe system, test measurements of NMR spectroscopy were performed. The strength of the magnetic field was 14 T (600 MHz for the proton nuclei resonance). The standard sample (0.1 % ethyl benzene) was measured and obtained SNR was 4523. As mentioned above, an antenna coil made of normal metal (Cu) was used in the present measurement. At the present, we guess that there should be some points of improvement. Introducing superconducting antenna coil is quite important approach. Moreover, further advance of uniformity of static magnetic field should be a critical issue. By fixing all concern and revision, we believe that SNR over than 8000 would be realized in our developing NMR facility, split-pair magnet and cryogenic probe with solenoidal-shaped antenna coil.

4. Summary
In this paper, development of cryogenic probe with split-pair magnet and solenoidal-shaped antenna coil is described. Features of the present cryogenic probe systems are summarized as follows;
1) Cryo-cooling system with double G-M coolers which achieves 5 K cooling for the antenna coil.
2) Design of low-noise-amplifier for low temperature operation.
3) Introducing superconducting thin film (MgB₂) antenna to gain SNR.
Preliminary test result of NMR measurement proves the efficiency of the cryogenic probe and further improvement of SNR.

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