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Operation of a 500 MHz high temperature superconducting NMR: Towards an NMR spectrometer operating beyond 1 GHz

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ABSTRACT

We have begun a project to develop an NMR spectrometer that operates at frequencies beyond 1 GHz (magnetic field strength in excess of 23.5 T) using a high temperature superconductor (HTS) innermost coil. As the first step, we developed a 500 MHz NMR with a Bi-2223 HTS innermost coil, which was operated in external current mode. The temporal magnetic field change of the NMR magnet after the coil charge was dominated by (i) the field fluctuation due to a DC power supply and (ii) relaxation in the screening current in the HTS tape conductor; effect (i) was stabilized by the ^{2}H field-frequency lock system, while effect (ii) decreased with time due to relaxation of the screening current induced in the HTS coil and reached 10^{-8}(0.01 ppm)/h on the 20th day after the coil charge, which was as small as the persistent current mode of the NMR magnet. The 1D ^{1}H NMR spectra obtained by the 500 MHz LTS/HTS magnet were nearly equivalent to those obtained by the LTS NMR magnet. The 2D-NOESY, 3D-HNCO and 3D-HNCACB spectra were achieved for ubiquitin by the 500 MHz LTS/HTS magnet; their quality was closely equivalent to that achieved by a conventional LTS NMR. Based on the results of numerical simulation, the effects of screening current-induced magnetic field changes are predicted to be harmless for the 1.03 GHz NMR magnet system.

1. Introduction

Nuclear magnetic resonance (NMR) is widely used in biology, organic chemistry, and material science [1]. As both the NMR sensitivity and the NMR signal resolution improve with increasing magnetic field strength, NMR spectroscopists pursue higher magnetic fields for NMR spectrometers [2,3]. A field of 23.5 T, allowing NMR operation at 1 GHz, has already been achieved by using low temperature superconductors (LTS) such as NbTi and Nb_3Sn [4]. However, the critical current density for Nb_3Sn decreases steeply as the magnetic field strength exceeds 23 T, and therefore it is improbable that LTS NMR magnet operation can substantially exceed 1 GHz, although fields allowing operation at slightly >1 GHz are likely to be feasible if we could take advantage of a re-stacked rod process (RRP) Nb_3Sn or Nb_3Al [5,6]. On the contrary, if we use magnets of high temperature superconductor (HTS) such as $Bi_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) [7], $Bi_2Sr_2CaCu_2O_x$ [8] and $YBa_2Cu_3O_x$ [9], sufficiently high current density is available above 1 GHz (23.5 T), enabling an NMR to substantially exceed 1 GHz (23.5 T), such as 1.3 GHz (30.53 T), by using HTS materials.

Thus, we have started a project to develop an NMR spectrometer that may be operated at frequencies of 1.03 GHz (magnetic field strength 24.2 T) by using an innermost coil made of the Bi-2223 HTS coil [10,11]; this is a first step towards an NMR spectrometer operated at substantially beyond 1 GHz. The project consists of two programs. The first program is to develop a LTS/HTS 500 MHz NMR spectrometer to investigate the basic behavior of the LTS/HTS NMR spectrometer; the LTS/HTS NMR coil consists of a low-field LTS coil and a high-field HTS coil. The second program has the goal of developing a LTS/HTS 1.03 GHz NMR spectrometer. The purpose of this paper is to describe the experimental results from the first program.

The LTS NMR magnet is usually operated in persistent current mode with a decay rate of $<10^{-8}$ (10 ppb)/h. It is stabilized to 10^{-10} (0.1 ppb) by an internal ^{2}H field-frequency lock system

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installed in the NMR spectrometer [11]. Due to the low *n*-index value of the Bi-2223 HTS tape conductor [12] and the difficulty in guaranteeing a superconducting joint, a Bi-2223 HTS coil is unlikely to provide a persistent current sufficient for NMR measurement. Therefore, the LTS/HTS NMR magnet is driven by an external DC power supply. The current fluctuation of the DC power supply causes a field fluctuation, generating noticeable sidebands on the NMR spectrum and a deviation in peak frequency [11]. We have demonstrated that the ^{2}H field-frequency lock system stabilizes the magnetic field fluctuation, if the peak–peak amplitude of the fluctuation is <3×10^{-6} (±1.5 ppm) [11]. Thus, we have developed an ultra-stabilized DC power supply with a current stability of <10^{-6} (1 ppm), so that the field fluctuation caused by the power supply is stabilized by the ^{2}H field-frequency lock system [13]. The effects of the power supply on the spectra are described in this paper.

When the Bi-2223 magnet is charged, a screening current is induced in the Bi-2223 tape conductor, generating an additional central magnetic field as shown by Hahn et al. [14]. Its relaxation results in the positive drift of the central magnetic field with time, after the magnet is charged to the operation current [15]. If the temporal change in the screening current-induced magnetic field exceeds 3×10^{-6} (±1.5 ppm), the field-frequency lock system loses operation and it is impossible to achieve a high resolution NMR spectrum. Thus the effect of screening current-induced magnetic field on the magnetic field stability for the LST/HTS NMR is investigated in this paper and the results will be discussed based on a numerical simulation study.

Hahn et al. [14] achieved a ^{1}H NMR spectrum with an LTS/HTS 700 MHz NMR magnet driven by an external DC power supply. They used neither room temperature shims nor a field-frequency lock system and therefore the half-height line width of the spectrum was as large as ~kHz. The present 500 MHz LTS/HTS NMR spectrometer uses both these features and therefore the resolution and the sensitivity are several orders of magnitude better than those reported by Hahn et al. [14]. The magnetic field stability, line shape, NMR sensitivity and 1D, 2D and 3D NMR spectra on proteins will be used to demonstrate NMR operation in this paper.

2. Experimental procedure

2.1. The Bi-2223 HTS innermost coil

The multi-filamentary Bi-2223 HTS tape used for the innermost coil of the LTS/HTS NMR magnet was 4.55 mm in width and 0.36 mm in thickness, reinforced by copper-alloy tapes soldered on both sides. It was wrapped with Kapton tape for electrical insulation. The Bi-2223 HTS tape was developed by Sumitomo Electric Industries, Ltd. Two winding methods, i.e. double-pancake winding and solenoid winding, may be used for HTS coil fabrication. The double-pancake coil consists of a number of pancakes, each of which resembles a tape recorder spool. From the viewpoint of coil fabrication, the double-pancake method is desirable for a tape of Bi-2223. On the other hand, a solenoid method is preferable from the perspective of magnetic field homogeneity as the coil is tightly wound by the conductor; however, winding a solenoid with Bi-2223 tape is rather difficult as the aspect ratio of the tape is as large as 13. After testing several Bi-2223 model coils, wound by both methods, we decided to employ solenoid winding for the Bi-2223 innermost coil.

The Bi-2223 innermost coil was 81.2 mm in inner diameter, 121 mm in outer diameter, and 375 mm in length. An Nb_3Sn innermost coil from a conventional 600 MHz NMR magnet made by JASTEC was replaced by the Bi-2223 innermost coil. The Bi-2223 HTS coil was designed to generate 1.797 T, while the LTS was capable of 9.947 T at the operation current of 144 A (11.743 T). More details of the design and fabrication of the Bi-2223 coil will be found elsewhere [16].

2.2. Highly stabilized DC power supply

The Bi-2223 HTS coil was connected in series to the LTS backup coil and charged simultaneously by an ultra-stabilized external DC power supply. As described above, the ^{2}H field-frequency lock system stabilized the magnetic field fluctuation with a peak–peak amplitude <3×10^{-6} (±1.5 ppm). We developed a highly stabilized external DC power supply, assisted by Danfysik [17]; its long-term current stability over 8 h was <10^{-6} (1 ppm) with short-term current stability achieving <5×10^{-7} (0.5 ppm). The field fluctuation provided by the DC power supply was therefore assumed to be fully stabilized by the ^{2}H field-frequency lock [11,13].

2.3. Cryostat

The LTS/HTS NMR magnet was operated in liquid helium at 4.2 K. In the external current mode of the NMR magnet, both heat conduction and Joule heating on the current leads increase liquid helium consumption [18]. Thus, an HTS single-crystal bulk rod, with high thermal resistivity, was used as a part of the current lead so that heat leak to the helium bath was suppressed. Secondly, a two stage cryocooler, i.e. a small refrigerator with two cold stages, was installed on top of the cryostat; vaporized helium gas was reliquefied by the second stage of the cryocooler¸ running at 4 K. The high temperature end of the HTS bulk rod was anchored to the first stage of the cryocooler, at a temperature of 50 K.

Two kinds of cryocooler were employed for the NMR magnet, a Gifford–McMahon (GM) cycle cryocooler and a pulse-tube cryocooler. The advantage of the GM cryocooler is its large cooling capacity, typically 1 W, while it has the disadvantage of inducing mechanical vibration on the magnet due to reciprocating movement of the displacer inside the cryocooler. The pulse-tube cryocooler on the other hand has low levels of mechanical vibration, but offers lower cooling power (0.5 W). Long-term NMR experiments over two months were conducted using each type of cryocooler. Temperatures of the LTS coil, a radiation shield, and the cold stages of the cryocooler were continuously measured over the experiment interval.

2.4. NMR probe and spectrometer

The LTS NMR magnet was originally manufactured for a 600 MHz NMR spectrometer, although we operated it at 500 MHz in this experiment. A commercial 600 MHz triple resonance probe (Bruker) was used for the NMR measurement; its resonance frequency was changed from 600 to 500 MHz. The 500 MHz NMR spectrometer (DMX 500 by Bruker Biospin) was used for NMR measurements; a ^{2}H field-frequency lock system built into the spectrometer was used to stabilize the magnetic field fluctuation caused by the DC power supply, as described below.

3. Experimental results

3.1. Initial change in the magnetic field after charging the NMR magnet

The NMR magnet was charged to 145.000 A (a magnetic field of 11.846 T, corresponding to an operating frequency of 504.352 MHz), and was operated in external current mode. Fig. 1 (black-solid line) shows the initial change in the magnetic field intensity with time measured by an NMR meter (Model PT 2025, Metrolab